THE EMISSION OF GASES AND AEROSOLS FROM MOUNT EREBUS VOLCANO, ANTARCTICA

by

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Submitted in Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Geochemistry

New Mexico Institute of Mining and Technology
Socorro, New Mexico

October 1988

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ACKNOWLEDGMENTS

Many thanks to Dr. Philip Kyle for being a patient advisor and a guiding force of ideas and support. Ray Chuan was very helpful in the collection, analysis and interpretation of the QCM data. I thank Dr. Dave Norman and Dr. Dave Finnegan for their critical analysis of the paper.

I owe a great deal to several people at Los Alamos National Lab. Dr. Dave Finnegan guided me in every aspect of filter analysis and interpretation, and provided constant support. The staff at the Omega West Reactor site, particularly Sam Garcia provided tremendous help with neutron activation analysis. I thank Fraser Goff for his critical analysis and cheerleading. Marcia Jones played a key role in the final hours with her word processing skills and I greatly appreciate her help.

COSPEC measurements in 1987 were made by P.R. Kyle and members of his field party. I thank him for allowing me to use these data. Field work at Erebus was a collective effort of Bill McIntosh, Nelia Dunbar, Bob Andres and Dave Caldwell.

Finally, thanks to Eric Prestbo, Theresa Miller and Pud Fransblau for their critiques, ideas and sense of humor.

This thesis was supported by the National Science Foundation Grant DPP-8519122 to P.R. Kyle, Los Alamos National Lab and Associated Western Universities.

ABSTRACT

Measurements of aerosols and gases were made from the active lava lake at Mount Erebus volcano, Antarctica. SO_2 flux was measured with a correlation spectrometer (COSPEC). Particle emissions were measured by quartz crystal microbalance (QCM) and their morphology and chemistry were examined by scanning electron microscope. Acidic volatiles and trace metals were collected by using particle and base treated filters.

COSPEC data revealed an increase in SO_2 emissions from 16 to 51 tonnes/day between 1985 and 1987. Short term variations in SO_2 flux showed a subtle periodicity of about two hours possibly paralleling convection of less degassed magma to the surface of the lava lake. SO_2 flux actually decreased during an eruption indicating that exsolution and bubble growth at depth were not determined by sulfur solubility.

QCM data revealed a difference between particle sizes and chemistry at the crater rim and in the upper plume suggesting that fractionation was occurring in the plume as a function of formation conditions, chemical reactivity and residence times. Both Au and Au-Cl compounds were noted on QCM stages along with other metals indicating that these metals were volatilized possibly as Cl compounds.

Data from particle and base treated filters gave further evidence for vapor phase transport of metals. Cl in aerosols was enriched with respect to Erebus phonolite by five orders of magnitude. Other elements including F, As, S, Se, Zn, Sb, Hg and

In were also highly enriched. Erebus shows a uniquely high and variable Cl/S ratio (8-60). Other metals show varying enrichment with time. The lower EF's may indicate movement of less degassed magma to the surface. It also reflects the different solubilities of Cl and S which cause varying amounts of Cl and S to degas. Both COSPEC data and Cl/S ratios indicate that S is degassing at a very shallow depth in the lava lake.

Elemental fluxes to the atmosphere were determined using the average SO_2 flux for 1986. The Cl flux was conservatively estimated at an average of 100 tonnes/day however this flux could be greater by an order of magnitude, particularly during strong volcanic activity. Erebus' contribution of Cl to the atmosphere could be significant, varying seasonally and as a function of volcanic activity, however the residence time for HCl in the lower atmosphere is less than five days

1. INTRODUCTION

The study of volatile flux and speciation from volcanoes has become a valuable tool for monitoring the physical and chemical processes occurring in magmatic systems and for predictive models in volcanic hazards. Volcanic emissions of aerosols and gases to the atmosphere are probably minor compared to anthropogenic emissions, however, these emissions play an important role in the global atmospheric budget.

Mt. Erebus, Antarctica contains an active lava lake which directly emits gases and aerosols (solid and liquid particles) to the atmosphere. To date, little is known about the contribution of Erebus emissions to the Antarctic atmosphere or if there is a unique signature to Erebus emissions which could be recognized in snow and ice core and/or polar aerosols.

Acidic gases have been measured directly in volcanic fumaroles (Giggenbach, 1975), however, direct collection from active volcanoes is seldom possible and other techniques have been developed to monitor both volatile flux and speciation. It is not possible to collect samples directly from the lava lake at Erebus hence three techniques were used to measure emissions. SO_2 emission rates were measured by remote correlation spectrometer (COSPEC). Particle flux and aerosol morphology and chemistry were examined using a quartz crystal microbalance (QCM) and acidic volatiles and trace elements were collected with treated and particle filters. The major objectives of this study were to determine the emission rates of SO_2, halides, acidic volatiles, trace elements and particles from Mt. Erebus into the atmosphere. The purpose of these measurements were

1.) to look at long (years) and short (minutes) term variations in SO_2 emissions and relate these to volcanic activity and changes in the lava lake.

2.) study relative emission rates of particles and volatile species (acids and trace metals), characterize the composition of the material and study possible speciation and processes for transport of volatiles out of the magma; and

3.) define a chemical signature characteristic of Erebus emissions, compare this to signatures of other less alkaline and more basic volcanoes and evaluate the impact of Erebus emissions on the Antarctic atmosphere.

2. GEOLOGY AND ERUPTIVE HISTORY OF MT. EREBUS, ANTARCTICA

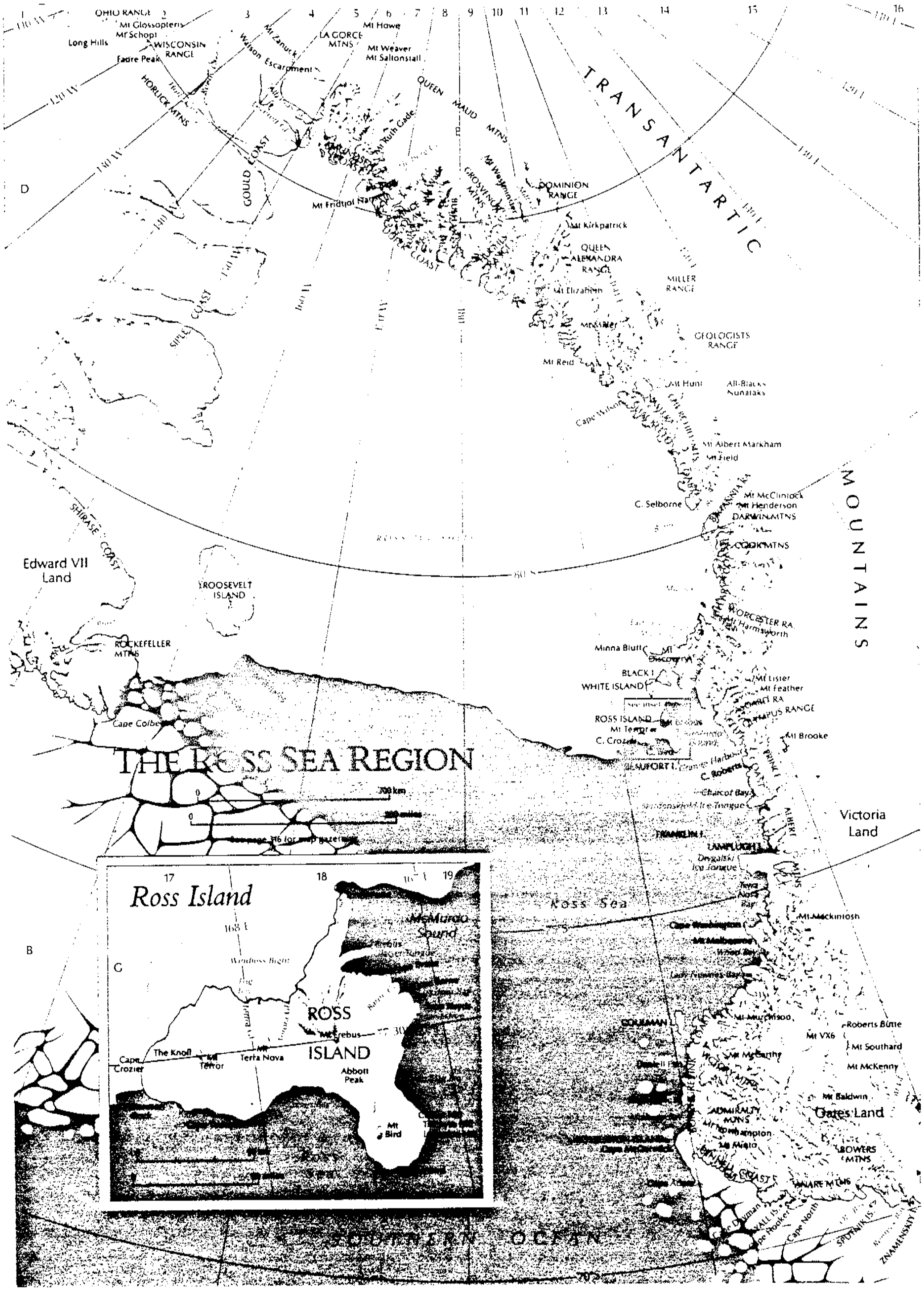
Physiography

Mt. Erebus is an active stratovolcano rising 3794 meters above sea level and situated at 77.53 S, 167.15 E on Ross Island near the western shore of the Ross Sea (Figure 2.1). It is radially surrounded by inactive vents: Mt. Terror, Mt. Bird and Hut Point Peninsula. Mt. Erebus contains an active convecting lava lake of anorthoclase phonolite magma which is believed to be connected at depth to a major magma chamber (Kyle et al., 1982).

Geologic and Tectonic Setting

The McMurdo Volcanic Group consists of mainly undersaturated alkaline volcanics of which the Erebus volcanic province is a part (Kyle and Cole, 1974). Mt. Erebus lies at the southern end of the Terror Rift within the Victoria Land Basin (VLB) (Cooper et al., 1982). The adjacent Transantarctic Mountains (TAM) consist of a basement complex of Proterozoic and Early Paleozoic metamorphic and silicic intrusive rocks overlain by sub-horizontal Devonian to Triassic shallow-water sedimentary rocks (the Beacon Supergroup). Tholeiitic sills, dikes and lavas (Ferrar Supergroup) were formed in mid-Jurassic time followed by a hiatus of 160 million years. Eruption of the alkaline lavas of the McMurdo Volcanic Group in the western Ross Sea commenced about 35 m.y. ago (Kyle et al., in press)

Figure 2.1: Map of Antarctica showing Mount Erebus and Ross Island. (Capricorn Press Pty Ltd, eds., 1975)


THE ROSS SEA REGION
TRANSANTARTIC MOUNTAINS
OHIO RANGE
Mt Glossopteris
Mt Schopf
Long Hills
WISCONSIN RANGE
Faure Peak
HORLICK MTNS
Watson Escarpment
Mt Zanuck
LA GORCE MTNS
Mt Howe
Mt Weaver
Mt Saltonstall
QUEEN MAUD MTNS
GOULD COAST
Mt Fridtjof Nansen
GROSVENOR MTNS
DOMINION RANGE
Mt Kirkpatrick
QUEEN ALEXANDRA RANGE
Mt Elizabeth
MILLER RANGE
GEOLOGISTS RANGE
Mt Reid
Mt Hunt
All-Blacks Nunataks
Cape Wilson
Mt Albert Markham
Mt Field
C. Selborne
Mt McClintock
Mt Henderson
DARWIN MTNS
COOK MTNS
WORCESTER RA
Mt Harmsworth
SIPLE COAST
SHIRASE COAST
Edward VII Land
ROOSEVELT ISLAND
ROCKEFELLER MTNS
Cape Colbeck
Minna Bluff
Mt Discovery
BLACK I.
WHITE ISLAND
ROSS ISLAND
Mt Erebus
Mt Terror
C. Crozier
Mt Lister
Mt Feather
OLYMPUS RANGE
Mt Brooke
BEAUFORT I.
C. Roberts
Charcot Bay
Victoria Land
FRANKLIN I.
Drygalski Ice Tongue
Terra Nova Bay
Ross Sea
Mt Mackintosh
Cape Washington
Mt Murchison
COULMAN I.
Mt VX6
Roberts Butte
Mt Southard
Mt McKenny
Mt Baldwin
Oates Land
ADMIRALTY MTNS
Mt Minto
BOWERS MTNS
SOUTHERN OCEAN
Cape Hallett
Cape North
ZNAMENSKIY
MOUNTAINS
See page 116 for map gazetteer
Ross Island
McMurdo Sound
Windless Bight
ROSS ISLAND
Mt Erebus
Cape Crozier
The Knoll
Mt Terror
Mt Terra Nova
Abbott Peak
Mt Bird

The 40 km thick crust beneath the TAM precludes uplift accompanied by thrusting and folding. Both uplift in the TAM and subsidence in the Ross Embayment (Fitzgerald et al., 1987; Gleadow and Fitzgerald, 1987) may be controlled by a shallow westerly dipping detachment fault zone which extends under the TAM.

Petrogenesis

The Mt. Erebus lavas define a broad basanite to phonolite association known as the Erebus lineage (EL). This undersaturated, sodic differentiation trend consists of basanite, Ne-hawaiite, Ne-mugearite, Ne-benmoreite and anorthoclase phonolite (Kyle et al., in press). The oldest K/Ar determinations from a phonolite flow at Cape Barne show the center to be at least 1 Ma old (Armstrong, 1978).

The dominant rock type on Mt. Erebus is a porphyritic anorthoclase phonolite with phenocrysts of anorthoclase, olivine, opaque oxides, clinopyroxene, apatite and rare nepheline. The monotonous composition of mafic phenocrysts suggests fairly constant temperature and oxygen fugacity during evolution of the EL (Kyle et al., in press).

Systematic trends of major and trace elements indicate that the EL evolved by fractional crystallization from a parental basanite magma derived from a heterogeneous mantle (Sun and Hanson, 1975). Lavas from volcanic vents surrounding Erebus are dominantly basanite and define the DVDP lineage (Kyle, 1981). The chemistry of this group indicates independent evolution from a lower temperature, more hydrous mineral assemblage than the EL.

The radial symmetry of vents surrounding Erebus may result from crustal fractures above a rising mantle diapir. EL lavas evolved in a large, high temperature magma chamber fed by basanite parental magma that formed by small degrees of partial melting of mantle peridotite in the center of the diapir. Basanite from the edges of the diapir provided the source for the DVDP lineage which evolved under lower temperature and higher water contents. Local patches of alkali basalt may have formed by higher degrees of partial melting in the mantle diapir (P. Kyle, pers. comm., 1987).

Eruptive History

The eruptive history of Mt. Erebus has been monitored intermittently since Sir James Ross first observed an eruption in 1841 (Ross, 1847). In 1972 the presence of a lava lake in the central crater was confirmed (Giggenbach et al., 1973). The evolution of the lake, its convective flow pattern and its ejecta were monitored through 1984 (Kyle et al., 1982; Kyle, 1977; Kyle and McIntosh, 1978) while parallel studies resulted from a seismic network established on Ross Island in 1983 (Nagata, 1983; Dibble et al., 1984; Shibuya et al., 1983)

A dramatic change occurred in the Erebus magmatic system in September 1984 (Figure 2.2). It is believed that a new batch of volatile rich magma was injected into the magma chamber and this resulted in violent explosions during which time the surface of the lake was buried in ejecta (P. Kyle, pers. comm., 1985). During the most violent eruptions bombs as large as ten meters were thrown 1.5 km from the crater. COSPEC measurements made later in 1984 revealed a drop in SO_2 from 230 to 25 tonnes/day.

As the former lake is slowly exhumed (Figure 2.3), SO_2 emissions have gradually increased. Strombolian eruptions are mild and infrequent (3-5/day), often related to large bubble activity in the lake. During strombolian eruptions, large gas bubbles rise to the surface of the lake, burst, and throw ash and ejecta over a small area. All eruptions recorded during the 1986/87 field season are presented in Table 1.1. A video camera and seismic monitoring station set up on the crater rim in 1986-87 (Dibble and Barrett, 1987) recorded the correlation between bubble growth, eruptions and seismicity. In December 1986 Mt. Erebus was emitting an average of 20 tonnes SO_2/day and contained a lava lake with a diameter of 20 meters and several fumarolic vents.

Figure 2.2 (overleaf) Diagram of the inner crater in January 1984 and November 1984 following increased eruptive activity, courtesy of P. Kyle.

Figure 2.3 (overleaf) Diagram inner crater and lava lake in December 1987, courtesy of P. Kyle.

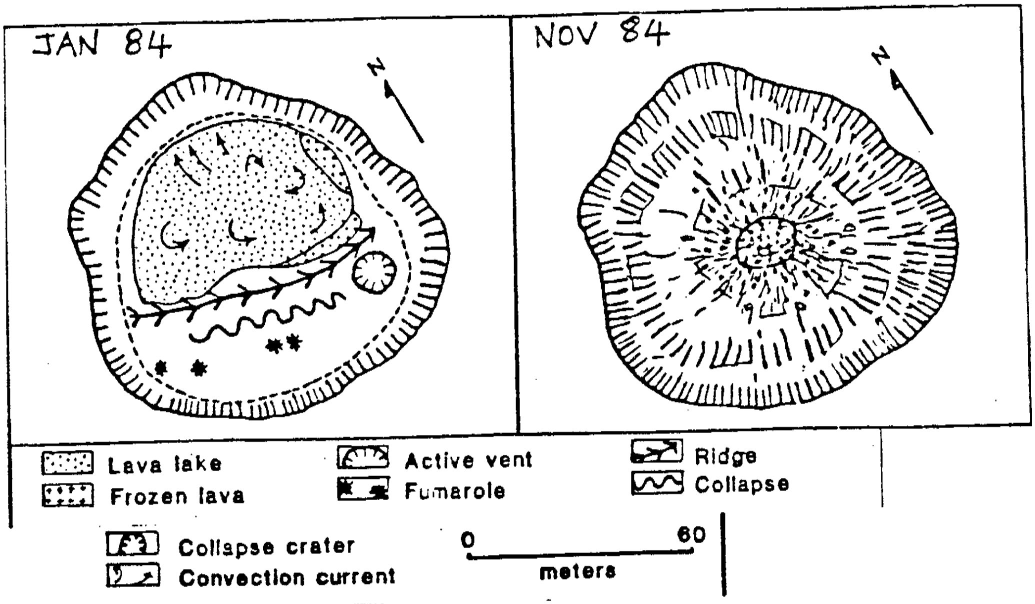


Figure 2.2

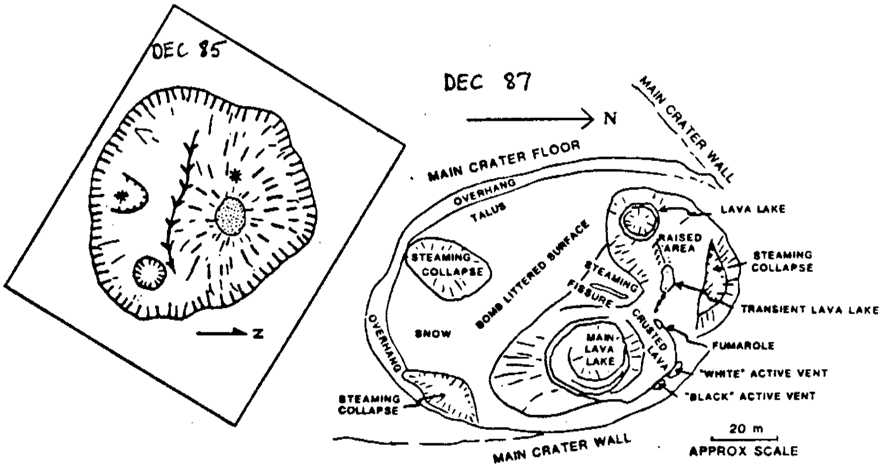


Figure 2.3

Table 2.1 Erebus eruptions observed during the 1986/87 field season.

Mount Erebus Eruptions
1986/87 Field Season

Date	Time	Duration	Comments
11-DEC-86	18:57:00	4 sec	bombs, ash plume
14-DEC-86	11:16:00	2 sec	plume >1000m
15-DEC-86	03:30:00	1 sec	no plume
15-DEC-86	19:59:00	1 sec	plume >150m, bombs over
15-DEC-86	18:59:00	1 sec	no plume, no bombs
19-DEC-86	18:39:00	1 sec	no bombs
21-DEC-86	18:46:00	1 sec	no bombs
22-DEC-86	11:21:00	1 sec	slight tremor at hut
25-DEC-86	19:01:00	1-2 sec	slight ash plume

3. SO_2 EMISSION RATES FROM MOUNT EREBUS

Introduction

SO_2 emission rates have been measured from volcanoes since 1972 (Moffat et al., 1971) by correlation spectrometer (COSPEC). The COSPEC was designed by Barringer Research, Toronto, Canada, primarily for environmental SO_2 monitoring (Millan et al., 1976) and later adapted for volcanic plumes (Stoiber et al., 1983). The principles of operation are reviewed in Appendix A-1. Briefly the COSPEC measures the pathlength concentration or burden (ppm.m) of SO_2 in a cross-section of a volcanic plume by analyzing incident ultra-violet radiation that has been attenuated by SO_2.

The COSPEC has been used to examine SO_2 from volcanic systems in various tectonic environments such as plate margin volcanism in Central America (Casadevall et al., 1984). Data from the COSPEC have been used to estimate global SO_2 concentrations from volcanoes (as addressed in chapter 5), to forecast volcanic events at Mt. Etna, Italy and Mt. St. Helens, Washington (Malinconico, 1979,1987; Casadevall et al., 1981), and to monitor magmatic activity at Kilauea, Hawaii (Greenland et al., 1985; Casadevall et al., 1987; Chartier et al., 1988). SO_2 and particle flux have been used to monitor activity on a yearly basis at White Island, N.Z. (Rose et al., 1986). Most studies have examined long term variations and average emission rates. A few studies have looked at short term periodicities. Chartier et al. (1988) made 38 COSPEC observations per day at Kilauea volcano.

The first (non-COSPEC) estimates of SO_2 emissions from Erebus varied from 3 tonnes/day (Polian and Lambert, 1979) to 35 tonnes/day (Radke, 1982). The first COSPEC measurements were made by Rose et al. (1986) using an aircraft survey method (Casadevall et al., 1981). They found an emission rate of 230 ± 90 tonnes/day which was considered to be a more accurate representation of Erebus emissions between 1972 and 1984.

In September, 1984, Erebus began to exhibit much more explosive and prolific activity during which time the lava lake was buried and decreased in size from 60m to about 10m in diameter (P. Kyle, pers. comm, 1987). Correspondingly, SO_2 emissions dropped to 25 tonnes/day in December 1984 (Symonds et al., 1985), indicating that variations in SO_2 flux might be correlated with the surface area of the lava lake.

Procedure

COSPEC measurements made during the Antarctic summers of 1985,1986 and 1987 involved a stationary technique in which the COSPEC was mounted on a tripod (Figure 3.1) about 2 km from the vertically rising plume. The COSPEC was tilted at 12 degrees and scanned horizontally through the width of a vertically rising plume. Measurements were usually made every 4 to 6 minutes for periods of up to five hours. On December 8 and 23, 1986, vertical scans were made through a horizontal plume.

Vertical windspeed, or rate of plume rise, was determined on the plume by sighting on a distinctive puff and timing its rise through a measured vertical angle. The plume rise rate was determined from the average of five measurements.

The SO_2 flux was calculated by using:

$$\text{Flux} = (B) * (PW) * (WS) \tag{1}$$

in which the burden (B) or concentration pathlength product (ppm.m) output by the COSPEC was multiplied by the width of the plume cross-section (PW) (m). This produced an SO_2 cross-section (ppm.m^2) which was multiplied by the rise rate or windspeed (WS) (m/sec) at which the plume crossed this two-dimensional area. The resulting flux (ppm.m3/sec) was converted to metric tonnes/day.

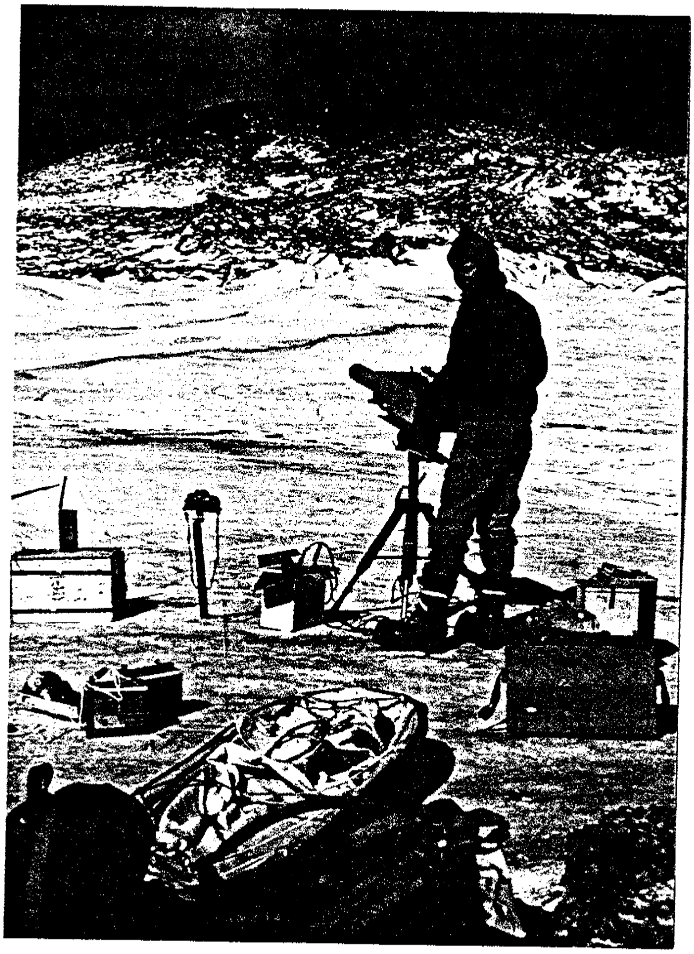


Figure 3.1 The COSPEC mounted on a tripod about 2 km from the crater rim of Mount Erebus.

Uncertainty in COSPEC Measurements

Uncertainties in COSPEC measurements are presented in Table 3.1 (Stoiber *et al.*, 1983). Each factor in equation (1); burden, plume width and windspeed can be a source of error.

The estimation of plume width of a vertical or horizontal plume contains inherent uncertainties. This estimate is directly proportional to the distance between the COSPEC and the plume. This distance varies when the plume is sheared by winds or sinks and flows down the side of the mountain. It is particularly difficult to estimate distance in a horizontal plume downwind from the crater.

Windspeed calculations can have the greatest uncertainty (10%-40%) and windspeed is the most difficult to measure due to its variability. Windspeed was estimated at Erebus by measuring the vertical plume rise rate and, based on five windspeed estimates per sampling period, the uncertainty was less than 10%.

Table 3.1: Estimation of errors in COSPEC calculations from Stoiber et al. (1983).

LIMITATIONS OF THE COSPEC CALCULATIONS		
Data :		
Calibration Cell Concentrations	: 425 ± 12 ppm.m	= ± 3 %
Chart Record Reading Error	: ± 0.5 mm	
(0.5 mm = 6 ppm.m)		
For an average deflection of 100 ppm.m		= ± 6 %
Distance Determination Error		= ± 5 % to ± 10 %
Windspeed determination		
(generally)		= ±10 % to ± 20 %
(worst case)		= ± 40 %
Total Error : (square root of the sum of the squares)		
Generally :		= ±13 % to ± 23 %
Worst Case :		= ± 42 %

Results

The average, maximum and minimum SO_2 emission rates for each sampling period during 1985, 1986 and for one continuous period in 1987 are presented in Table 3.2. In Appendix A-2 data for each day during these periods are presented in tables and plotted graphically as a function of time. All scans were horizontal through a vertically rising plume except for two days (12/8/86 and 12/23/86) when vertical scans were taken through horizontal plumes about 2 km downwind from the crater. Data collected from these horizontal plumes yield fluxes which are approximately one quarter the value of horizontal scans. It is likely that the plume was partly obscured and drifting across the ground.

The average of daily fluxes collected during the Antarctic summer each year calculated from horizontal scans show a trend which increases from 16.4 to 51.3 tonnes/day SO_2. The average SO_2 flux for 1986 was 20 tonnes/day. Therefore, the average sulfur flux of 10 tonnes/day was used to determine chlorine, fluorine and trace metal emissions during the 1986 field season (see chapter 5).

In an attempt to monitor SO_2 during an eruption, all eruptions were recorded and are presented in Table 2.1. Only one SO_2 measurement, taken on December 21, 1986, was obtained during an eruption. Immediately following the eruption, SO_2 flux fell from 18 to 5 tonnes/day.

Table 3.2: The average, maximum and minimum SO_2 fluxes for each sampling period used in this study during 1985, 1986 and 1987.

SO2 Emission Rates from Mount Erebus 1985-1987
SO2 Flux (tonnes/day)

Date	Scans No.	Average	Std Dev	Max	Min	Remarks
16-DEC-85	14	20	8	40	10	
17-DEC-85	48	13	6	35	3	
Average		16	7	37	7	
08-DEC-86	9	5	3	13	3	vertical scan
10-DEC-86	51	18	10	42	4	
11-DEC-86	68	21	12	61	5	
21-DEC-86	76	22	12	67	2	
23-DEC-86	40	6	3	14	3	vertical scan
Average		20	11	57	4	horizontal scan only
08-DEC-87	216	51	23	126	1	

Discussion

Sulfur Emissions from Erebus to the Atmosphere

Erebus SO_2 emissions to the atmosphere since 1984 have increased from 16 to 51 tonnes/day. This maximum value is significantly less than other volcanoes even during quiescent periods (White Island, 350 tonnes/day, Kilauea, 260 tonnes/day; Etna, 160 tonnes/day) (Rose et al., 1986; Casadevall et al., 1987; Malinconico, 1987) and less than 0.1% of the global estimates of active volcanoes by Stoiber et al. (1987).

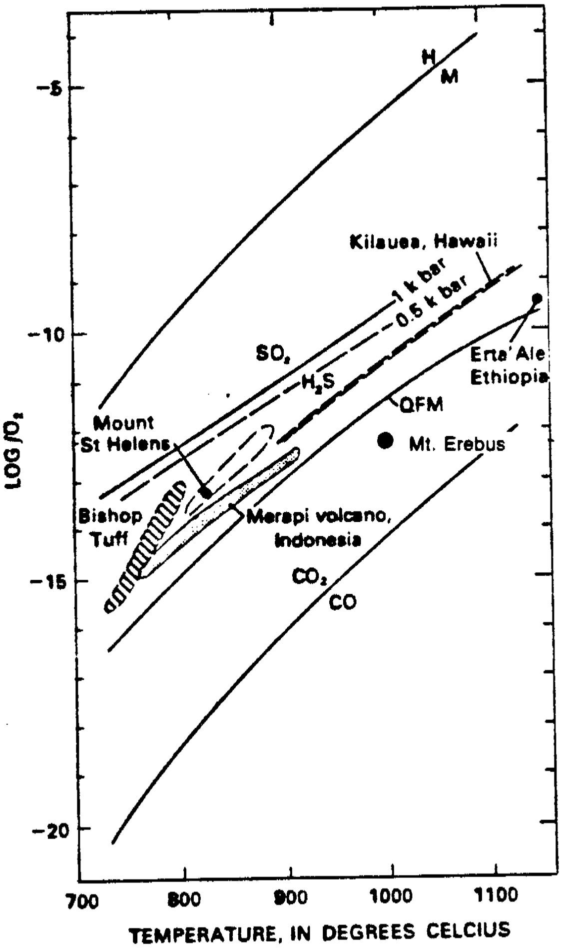
The average concentration of sulfur in the Erebus plume above the crater, based on COSPEC and plume width measurements, is .12 ppmV (ppm-volume). Maenhaut et al. (1979) measured a concentration of 4×10^{-5} ppmV sulfur on the polar plateau. This concentration of sulfur (measured as sulfate) could not be accounted for by oceanic sulfate, and may have been contributed to by Erebus particularly during active periods.

As a rule, COSPEC estimates assume that SO_2 quantitatively represents the sulfur emitted from a volcano. The low SO_2 emission rates from Erebus may indicate that the COSPEC is not measuring the total sulfur released from the melt. Sulfur species that may not have been measured include H_2SO_4 and H_2S.

Figure 3.2 shows oxygen fugacity and temperature for various volcanic melts including Mt. St. Helens with a data point for Erebus superimposed. As can be seen from Figure 3.2, at total pressures < 0.5 Kbar, one would expect H_2S to be the dominant sulfur gas released from the Erebus melt.

Mount St. Helens magma also falls in the H_2S field but Casadevall and Greenland (1985) found very low concentrations of H_2S in the plume in contrast to high concentrations in high temperature fumaroles. They deduced that H_2S was efficiently oxidized to SO_2 in high temperature cracks in and adjacent to the dome prior to incorporation in the plume. Rose et al. (1986) similarly concluded that H_2S was oxidized to SO_2 within several meters of the vent at White Island.

To date no H_2S measurements have been made in the Erebus plume and little is known about oxidation mechanisms of H_2S in the Antarctic atmosphere. However, the lack of a distinct H_2S odor makes it unlikely that H_2S is a dominant sulfur species at the crater rim.



—Log f_{O_2} versus temperature diagram for selected volcanic systems. Mount St. Helens oxygen fugacity calculated from ratio of CO_2 to CO. Hematite-magnetite (H/M) buffer and quartz-fayalite-magnetite (QFM) buffers shown for reference; CO_2/CO equal-concentration boundary calculated from thermodynamic data in Robie and others (1978); SO_2/H_2S equal-concentration boundary summarized from Ohmoto and Rye (1979) at the condition of $P_{H_2O} \cong 0.5$ kbar and 1 kbar, and $X_{H_2O} \cong 1.0$. f_{O_2} versus temperature conditions for the Pleistocene Bishop Tuff, California, from Hildreth (1979); Erta'Ale volcano, Ethiopia, data from Gerlach (1980); Kilauea volcano, Hawaii, data from Sato and Wright (1966); Merapi volcano, Indonesia, data from LeGuern and Gerlach (1979).

Figure 3.2: Log fO_2 versus temperature diagram presented by Casadevall and Greenland (1985). The fO_2 and temperature of Erebus magma (Kyle, 1977) are superimposed.

Homogeneous and heterogeneous conversion of SO_2 to sulfate can occur in a volcanic plume and SO_2 conversion rates to sulfate have been observed to vary from 0.5 to 30% h^{-1} (Finlaysson-Pitts and Pitts, 1986). However, water droplets provide a major pathway for the oxidation of SO_2 (Calvert and Stockwell, 1984) as do ash particles, both of which may be lower than normal for Erebus compared to most volcanoes. Second, QCM analyses have revealed the paucity of H_2SO_4 on QCM stages indicating that only minor oxidation of SO_2 to H_2SO_4 is occurring in the lower plume where COSPEC measurements are determined. Hence there is no conclusive evidence for H_2SO_4 or H_2S in the lower plume and the consistency of SO_2 measurements over time, regardless of sampling conditions, further confirm that SO_2 emissions from Erebus represent total sulfur.

Long Term Variations in SO_2 Emissions

Erebus has responded to long term changes in activity with long term variations in SO_2 emission rates. Yearly average SO_2 fluxes from Erebus between 1983 and 1987 are listed in Table 3.3. Included in this table are yearly estimates of the lava lake surface area. The increase in the flux of SO_2 since 1983 correlates with the increasing surface area of the lava lake which has slowly been exhumed since 1984. Kyle (pers. comm, 1987) proposes that this correlation reflects near surface exsolution of sulfur in a magma with a low sulfur content.

To date, little is known about sulfur exsolution but Moore and Fabbi (1971) have demonstrated that sulfur exsolution is insignificant at depths greater than 500 m in submarine lavas. Exsolution curves produced by Gerlach (1986) further indicate that most sulfur exsolution occurs below 2 MPa ($<$ 100m lithostatic, $<$ 200m hydrostatic).

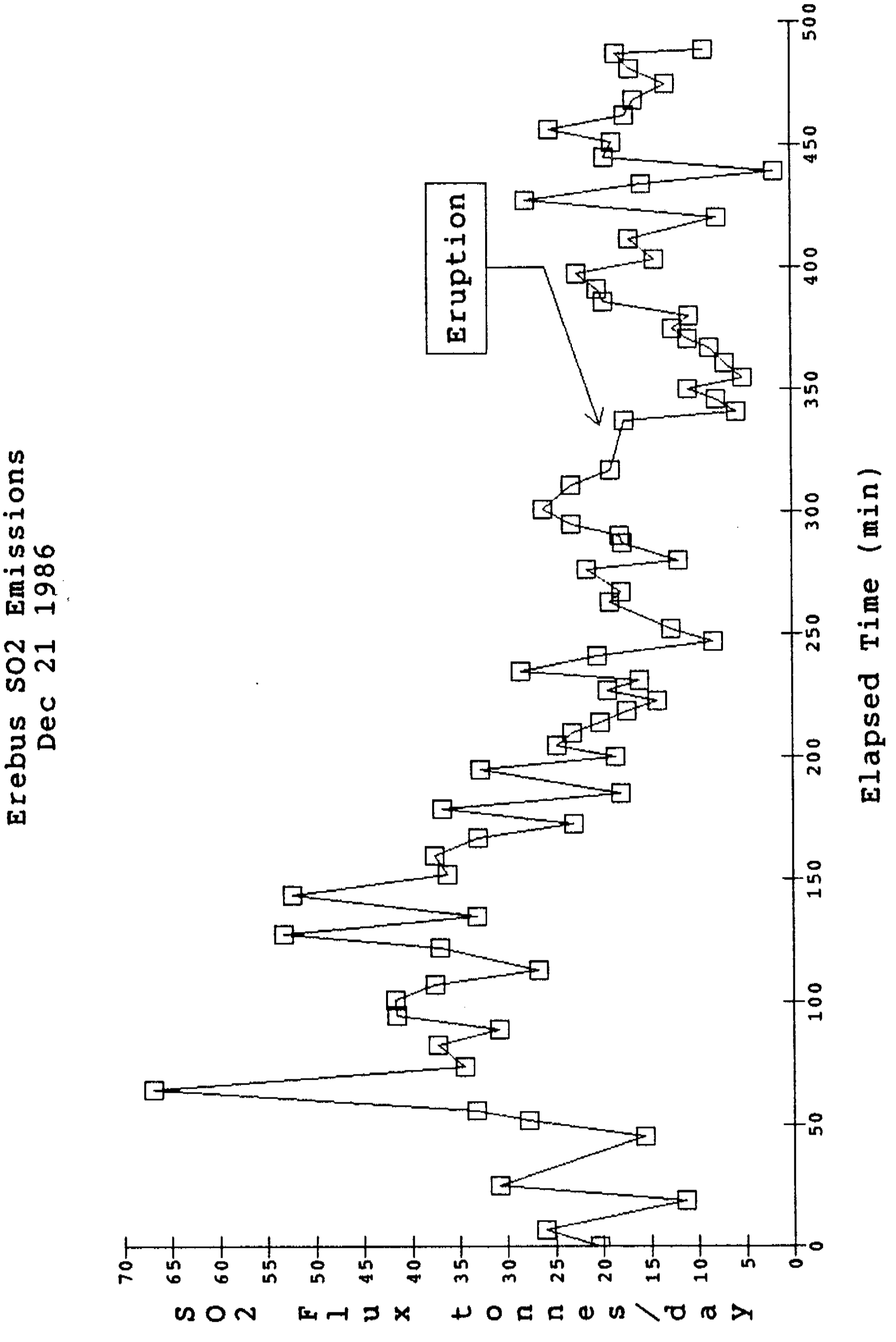
Table 3.3 Annual estimates of SO_2 flux based on COSPEC measurements made during Antarctic summer field seasons compared to lava lake diameter.

Average SO2 Emissions and Lake Surface Diameter
Mount Erebus

Year	SO2 Flux tonnes/day	Lake Diam. (m)	References
1983	260	60	Rose et al., 1983
1984	25	10	Symonds et al., 1985
1985	16	16	This study
1986	20	20	This study
1987	51	30	This study

To further understand sulfur exsolution in the Erebus system, an attempt was made to measure SO_2 during an eruption. Only one eruption occurred during continuous SO_2 monitoring (Figure 3.3, Table 2.1). Though the SO_2 flux increases slightly prior to the eruption, the flux actually decreases immediately after the eruption indicating that the explosive release of gas did not include additional SO_2 and hence, that these gas bubbles do not carry exsolved sulfur from depth. Therefore the data collected between 1985 and 1987 do not refute the hypothesis that sulfur exsolution occurs at shallow depths.

Figure 3.3 (overleaf) SO_2 flux measured during an eruption at Mount Erebus on December 21, 1986.


Erebus SO2 Emissions
Dec 21 1986
Eruption
SO2 Flux tonnes/day
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
Elapsed Time (min)
0
50
100
150
200
250
300
350
400
450
500

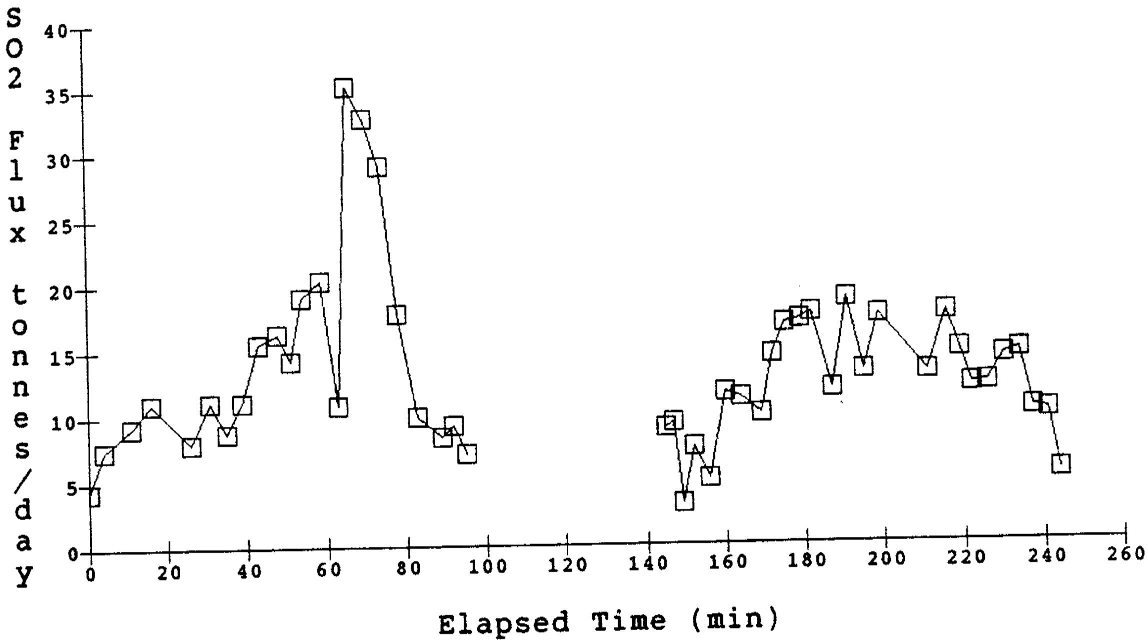
Short Term Variations in SO_2 Flux

Short term variations in SO_2 flux seem to reflect two phenomena. A very short term variation (on the order of minutes) reflects a puffing of the plume. These puffs occur on the average 3-4 times an hour but can be integrated over long sampling periods hence eliminating the possibility of skewing the data.

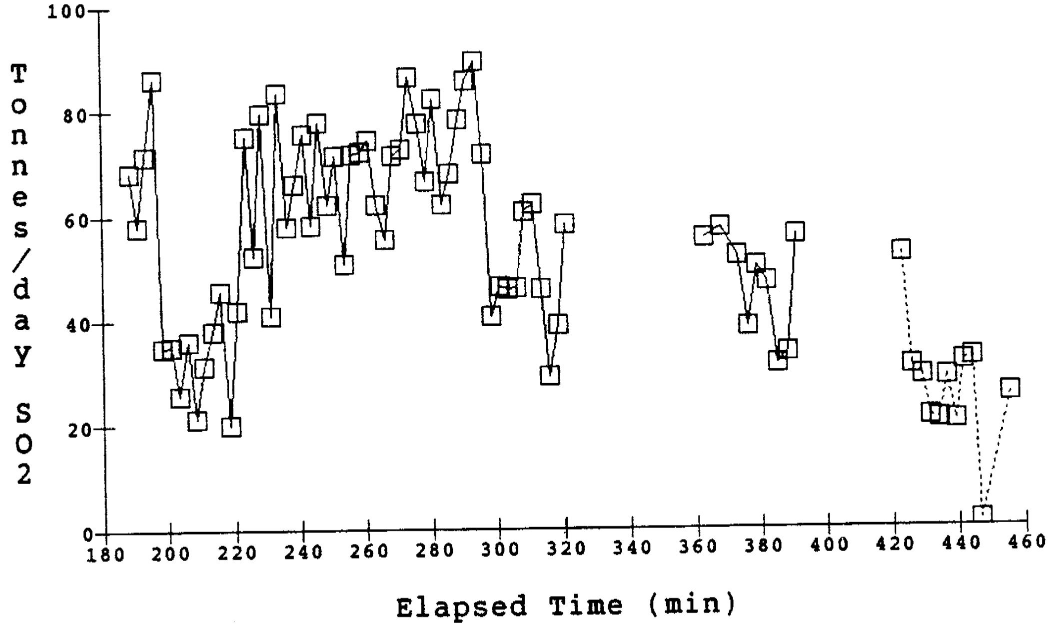
A longer term periodicity, of around two hours is observed particularly on December 17, 1985 (Figure 3.4a). Similarly, more subtle cycles of increased SO_2 flux over 2-3 hours are seen on December 23, 1986 and on December 8, 1987 (Figure 3.4b). Convective patterns have been observed in the lava lake and convection rates seem to vary as the lava lake crusts over or becomes more incandescent. However these occasional cycles of SO_2 flux may reflect the time necessary for the convection of new less degassed magma to arrive at the surface of the lava lake.

In summary, continuous monitoring of SO_2 flux has brought into focus several areas of study. Long term variations of SO_2 have been associated with the surface area of the lava lake thereby indicating that sulfur exsolution may be occurring near the surface of the lake and not continuously at greater depths. Continuous monitoring at less than 5 minute intervals have highlighted periodicities which may reflect possible convection of fresh magma within the lava lake.

Figure 3.4 (overleaf) SO_2 flux measured on Dec. 17, 1985 and Dec. 8, 1987 shows a cycle of about 2 hours.



Erebus SO2 Emissions
Dec 17 1985



SO2 Emissions from Erebus
Dec 8, 1987

4. PARTICLE EMISSIONS FROM MT. EREBUS

Introduction

Emission of particles and soluble aerosols is an important process during volcanic degassing. Volcanic aerosols can remain in suspension for periods of hours to years and can significantly impact the climate. Estimations of size distributions, compositions and fluxes are necessary to understand the total volcanic contribution throughout the world. Aerosols can also reveal information about the state of the magma and about physical and chemical processes occurring in the plume. Finally, aerosols and gases may provide information about magmatic vapor transport of metals in the evolution of ore deposits.

The quartz crystal microbalance (QCM) cascade impactor gives real-time estimates of particle size distribution in a volcanic plume and retains particles for later examination and chemical analysis by energy dispersive X-ray analysis (EDXRA) and scanning electron microscope (SEM) (Chuan, 1975).

The particle size distribution may be indicative of volcanic eruptive behavior (Casadevall et al., 1984; Rose et al., 1980; Woods and Chuan, 1982). For instance, a distinct bimodality in the particle size of aerosols emitted by some Central American volcanoes lead Rose et al. (1980) to suggest that a high percentage of submicron size particles could indicate an anomalously high gas to ash ratio caused by gas enrichment prior to an eruption. The Mt. St. Helens plume had the characteristics of an active cloud (abundant particles of magma and lithic material) prior to an eruption in August 1980 (Rose et al., 1982).

Actual size distribution in the sample varies depending on the sample location. Vertical size fractionation has been noted in the plume of White Island volcano in New Zealand (Rose et al., 1986). Monitoring particle flux (Rose et al., 1986, Chuan et al., 1986) is important in studying the contribution of both quiescent and active volcanoes to the ambient atmosphere.

The chemistry and morphology of volcanic aerosols can be compared with ambient aerosols to study environmental impact of volcanism. The QCM has been successful in segregating different chemical phases by size (Chuan et al., 1986). Dilute acid droplets are commonly seen in the submicron size range or as thin coatings on the silicates (Rose et al., 1980, Casadevall et al., 1984, Chuan et al., 1981, Rose et al., 1986, Woods and Chuan, 1982). H_2SO_4 and HCl emissions can be significant and a cause of concern in populated areas.

Chemical species are also indicative of both magmatic processes and atmospheric physico-chemical processes. In the 1-2 micron size range, reaction products and agglomerates are often seen. Ca-sulfate laths observed at El Chichon Volcano in Mexico (Woods and Chuan, 1982; MacKinnon et al., 1984) and at Central American volcanoes (Rose et al., 1980) have been attributed to ash reactions with moderate concentrations of H_2SO_4. Other salts (KCl, NaCl and possibly $FeCl_3$ and $AlCl_3$) are seen as coatings or as submicron size condensates (Rose, 1987).

Mount Erebus emanates a persistent low ash volcanic plume and is ideal for the study of submicron aerosols. The QCM has been used together with the COSPEC to determine particle flux and size distribution (Chuan _et al._, 1986). The main objectives of this study are to examine particle morphology and chemistry and compare this to chemical analyses of the plume, examine metals and try to better understand the processes by which they are vaporized and transported in the plume, study how aerosols in the plume vary with distance from the lava lake, and estimate the size distribution of particles emanating from Mount Erebus and their contribution to the Antarctic atmosphere.

Sampling and Analysis Methods

In order to obtain samples from three different environments during the 1986/87 and 1987/88 austral summer field seasons, QCM measurements were made from the plume at the crater rim, from the upper plume during airborne traverses and from the ambient air during routine flights to the south pole. The QCM (Figure 4.1) obtains samples at a rate of three liters per minute and separates particles according to their "effective size" through the process of inertial impaction. When a particle laden gas stream is forced by a boundary to change direction, the lighter particles will adjust to the new trajectory while the heavier particles will slip out of the trajectory and impact on the boundary surface (Chuan, 1975).

A four stage QCM was used during 1986/87 and for crater rim samples in 1987/88 with stage 1 through 4 containing the following geometric mean sizes: > 2.0, 0.9, 0.3 and 0.1 microns. A five stage QCM was used for airborne plume and ambient air samples in 1987/88, with the geometric mean sizes decreasing from >12, 6.2, 1.6, 0.4 and 0.1 microns. On Dec. 21, 1986 several consecutive plume measurements were made from the crater rim. On January 5, 1987, airborne plume samples were collected by flying through the plume about 700 m above the crater rim. Size distribution of the particles were not obtained in the airborne plume samples due to an electronic malfunction of the QCM.

During the 1987/88 field season simultaneous crater rim and airborne plume measurements were made on 5 December 1987. These were compared to ambient air measurements made during a routine South Pole flight on 3 December 1987.

The stages and trapped particles were retained and analyzed by SEM and EDXRA for identification of elements with atomic number (Z) of 11 or higher. In some cases, Auger-electron spectroscopy (AES) was used for elements such as C, N and F with atomic number lower than 11. A total of five samples were analyzed representing crater rim and airborne plume aerosols for each field season and representative ambient air samples for 1987/88.

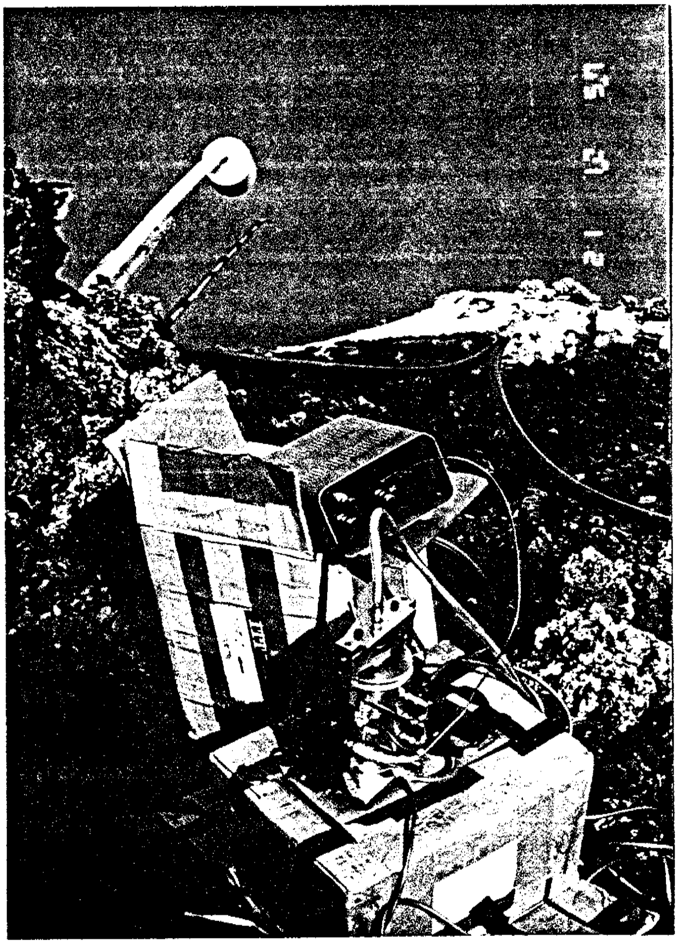


Figure 4.1 The QCM samples volumes of air at a rate of 3 l/min and separates particles into four size ranges.

Presentation of Data

Particle Size Distribution:

Particle size distributions and concentrations in µg/m3 for the 1986/87 and 1987/88 field seasons are presented in Table 4.1 and 4.2. No data are available for 1986/87 airborne plume samples.

The particle size distribution in the 1986/87 crater rim samples is consistently monomodal (Figure 4.2) except for an increase of intermediate size particles (0.3-0.9 µm) seen in samples 5 and 7 and probably associated with lower concentration and the waning stages of the plume. The majority of the particles average 0.1 microns.

The 1987/88 crater rim samples are bimodally distributed (Figure 4.3) with the 0.1 micron range again dominant. However, unlike the previous season a moderate percentage of crater rim particles are found in the intermediate to large size ranges. This may reflect the lower overall concentrations of particles in these samples.

Particle size distributions measured in a single airborne plume sample during the 1987/88 field season are compared with crater rim particle size distributions in Figure 4.3 and 4.4. The airborne plume measurements are compared with ambient air measurements made during the same period in 1987/88. The monomodal distribution of <0.1 um particles found in 1986 crater rim samples (Figure 4.3) is distinct from the bimodal distribution and lower concentration of particles in the airborne plume samples in 1987

(Figure 4.4). The 1987/88 crater rim sample is also slightly bimodal. During 1987/88 sampling periods, the plume emitted much lower concentrations of particles and this may be the reason for the different size distributions between the two seasons. Most of the airborne plume particles average around 1.6 microns. The ambient air sample is dominated by larger (>6.2 μm) particles although the > 6.2 μm particle concentration is still much higher in the airborne plume samples.

Table 4.1: Particle size distribution shown by concentration in μg/m3 for aerosols collected during the 1986/87 field season.

Erebus Particle Size Distribution
1986/87 Crater Rim
Sample #

Size (um)	#1	#2	#3	#4 (ug/m3)	#5	#6	#7	#8
0.1	103	153	197	97.40	111	32.60	47.50	106
0.3	10.10	7.80	7.60	1.71	67.10	0.00	19.90	16.30
0.9	1.70	0.87	0.00	0.29	14.80	2.30	7.80	3.70
2.0	5.60	2.40	11.50	0.00	0.00	3.50	1.70	3.50
				Percent				
0.1	86.00	93.00	91.00	98.00	58.00	85.00	62.00	82.00
0.3	8.00	5.00	4.00	2.00	35.00	0.00	26.00	13.00
0.9	1.00	1.00	0.00	0.03	8.00	6.00	10.00	3.00
2.0	5.00	1.00	5.00	0.00	0.00	9.00	2.00	3.00

Table 4.2: Particle size distribution and concentration in μg/m3 for aerosols collected during the 1987/88 field season.

A. Erebus Particle Size Distribution
1987/88 Airborne Plume

Size (um)	ug/m3	Percent
0.1	2.21	24
0.4	1.01	11
1.6	3.04	33
6.2	1.75	19
12.0	1.10	12

B. Erebus Particle Size Distribution
1987/88 Crater Rim
Sample #

Size (um)	#1 (ug/m3)	Percent	#2 (ug/m3)	Percent	#3 (ug/m3)	Percent
0.10	17.40	41	19.40	51	19.00	54
0.30	15.70	37	10.20	27	8.50	24
0.90	1.70	4	1.70	4	1.60	5
2.00	8.10	19	7.00	18	6.40	18

C. Erebus Particle Size Distribution
1987/88 Ambient Air Sample
South Polar Flight

Size (um)	S-bound ug/m3	Percent	N-bound ug/m3	Percent	Percent (average)
0.1	0.05	10	0.03	10	11
0.4	0.10	19	0.08	28	23
1.6	0.06	12	0.03	10	11
6.2	0.10	19	0.05	17	18
12.0	0.21	40	0.10	34	38

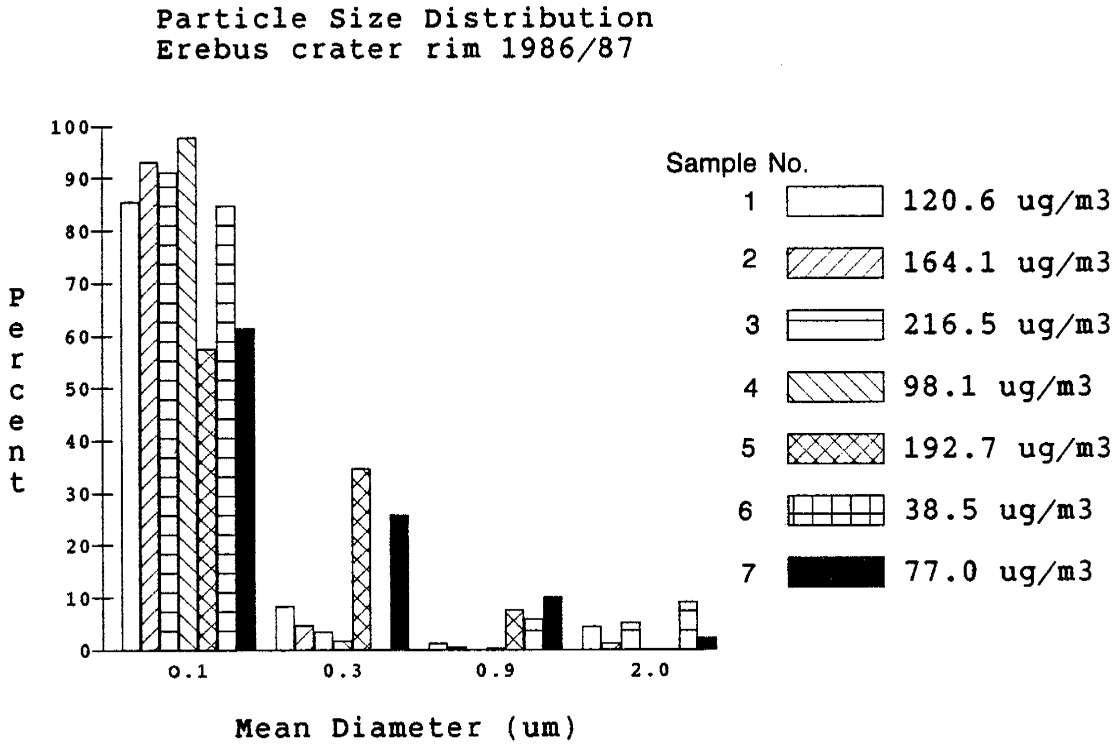


Figure 4.2 Particle size distribution for seven sampling periods from the Erebus crater rim during the 1986/87 field season. Total concentration in $\mu g/m3$ is included in the key.

Figure 4.3 (overleaf) Cumulative particle distribution for three sampling periods from the Erebus crater rim during the 1987/88 field season. Total concentration in $\mu g/m3$ is included in the key.

Figure 4.4 (overleaf) Cumulative particle distribution for airborne Erebus plume sample (Dec. 3, 1987) versus ambient air sample (collected enroute to the South Pole on Dec. 5, 1987).

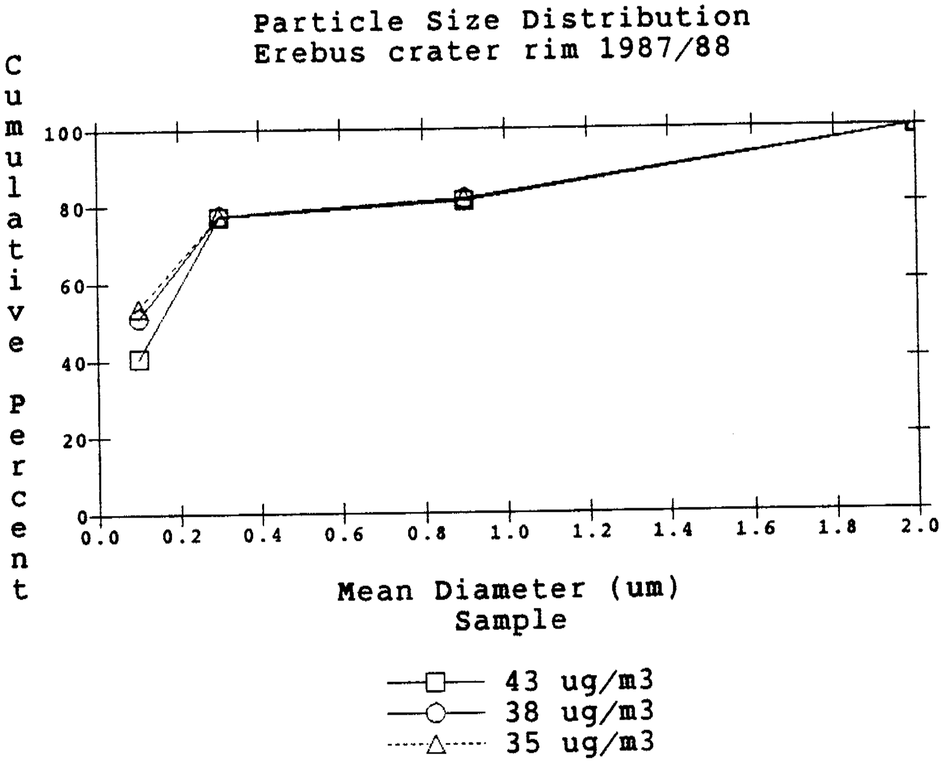


Figure 4.3

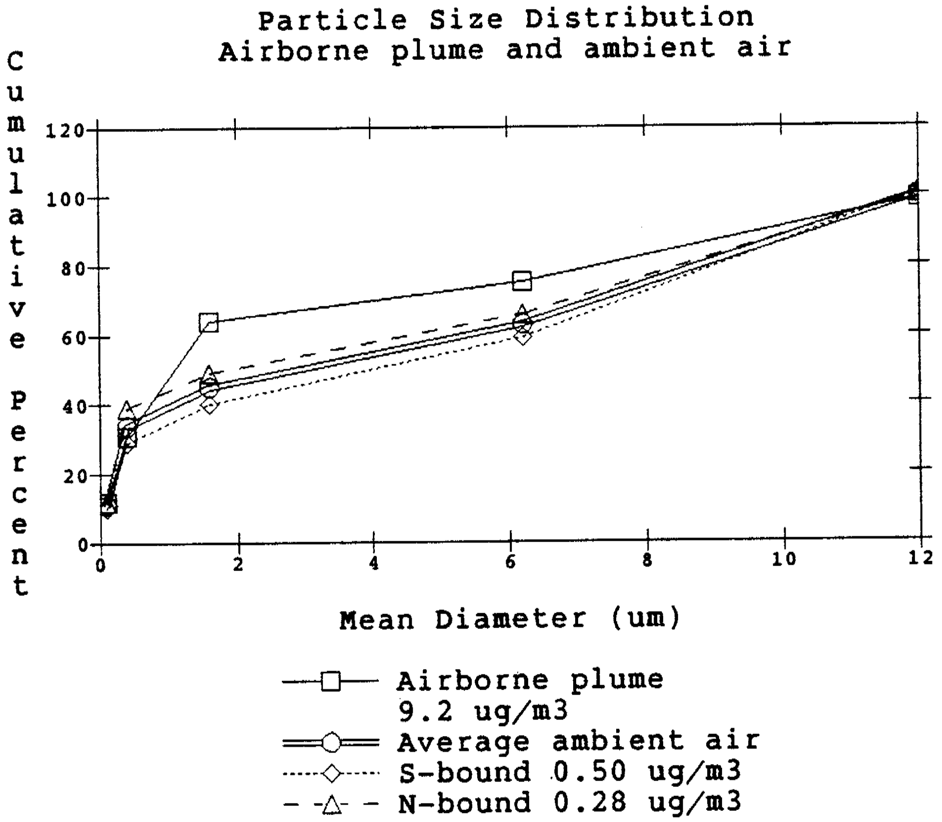


Figure 4.4

Morphology and Chemical Composition:

The morphology and composition of particles collected by the QCM were analyzed using the EDXRA and SEM. The number of particles analyzed for each stage are presented in Table 4.3. Appendix A-3 summarizes the observations made for each stage in each sample.

The morphology and composition of elements seen on the various stages during both seasons vary with particle size. Overall, the compounds are fairly simple and resemble some of the salts found on the Erebus crater rim (Keys, 1981). There is strong evidence for the compounds Na_2SO_4 (thenardite) and K_2SO_4 (arcantite), and possible evidence for $KAl_3(SO_4)_2(OH)$ (alunite) and $Al(SO_4)_3 \bullet nH_2O$ (alunogenite) and $CaSO_4.(H_2O)n$ (gypsum).

The particles can be grouped into large (>2.0 microns), intermediate (0.3-2.0 microns) and small (<0.3 micron) size ranges. SEM photos of characteristic particles are presented in Figures 4.5-4.10. The character of the large particles is least consistent although glass, olivine, pyroxene and other aluminosilicates characteristic of the magma are usually >2.0 microns. Gold is also seen in this range. Elemental gold (Figure 4.5) occurs as spongy to botriodal aggregates. Gold associated with chlorine (Figure 4.6) occurs as delicate platelets and may be a sublimate of $AuCl_3$.

Intermediate sized particles consist of volatile metals such as Au, Zn, Cu and Pb. These are often associated with Cl and/or S and oxides. In general more metals are seen in 1986/87 samples.

Of these, Au and Zn are predominant. Iron, Mg, Sn, Pb, Ce, Cr and Ti (usually associated with ash) have also been seen in this range. In 1987/88 elemental sulfur precipitated and formed crystals on the intermediate stages as well as on smaller stages (Figure 4.7). In places where acid had etched away the substrate, sulfur reacted with the Ag substrate to form AgS.

The small particles are mainly characterized by salts (KCl and NaCl) (Figure 4.8) though sometimes interspersed with sulfates (probably K_2SO_4 and Na_2SO_4) and (particularly in 1987/88) elemental sulfur (Figure 4.9). Amorphous silica and a low Z flocculent element (possibly carbon or fluorine) are also found in this range. H_2SO_4 and HCl droplets are conspicuously absent in both 1986/87 and 1987/88 samples, though acidic activity is inferred by wet spots and etched areas around precipitates on the stage.

Table 4.3 Number of particles analyzed on each stage of the QCM by EDXRA and SEM during the 1986/87 and 1987/88 field seasons.

Number of Particles analyzed by EDXRA and SEM

Four Stage QCM		1986/87		1987/88
Stage	Size (um)	Crater Rim	Airborne Plume	Crater Rim
1	>2.0	5	no particles	5
2	0.9	7	8	2
3	0.3	6	16	5
4	0.1	2	5	5

Ten Stage QCM		1986/87	1987/88
Stage	Size (um)	Airborne Plume*	Ambient Air**
2	>12	no particles	4
4	6.2	no particles	7
6	1.6	1	3
8	0.4	1	7
10	0.1	3	no particles

* Erebus plume flight - averaged 4 passes

** Ambient flight to South Pole, 26,000 to 28,000 ft. average time 90 minutes

Figure 4.5: Elemental gold from Erebus summit, 1986/87. Spongy aggregates reveal a semi-columnar cross-section.

Figure 4.6: Au-Cl sublimate (?) from Erebus plume, 1986/87. This delicate, platey Au-Cl compound was much less pervasive than elemental Au.

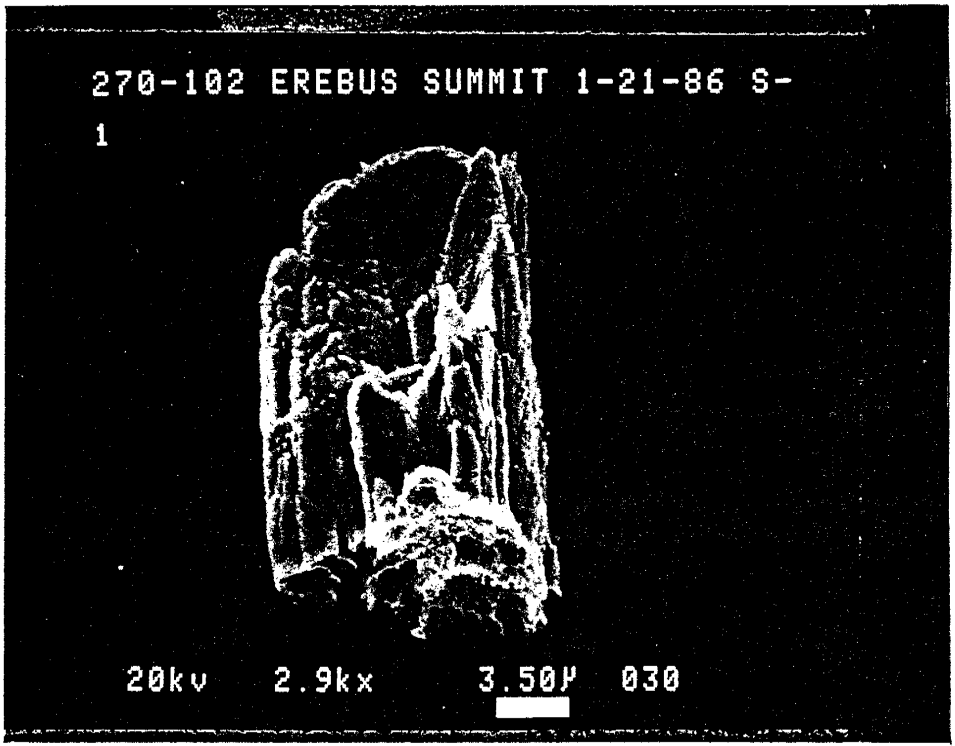


Figure 4.5

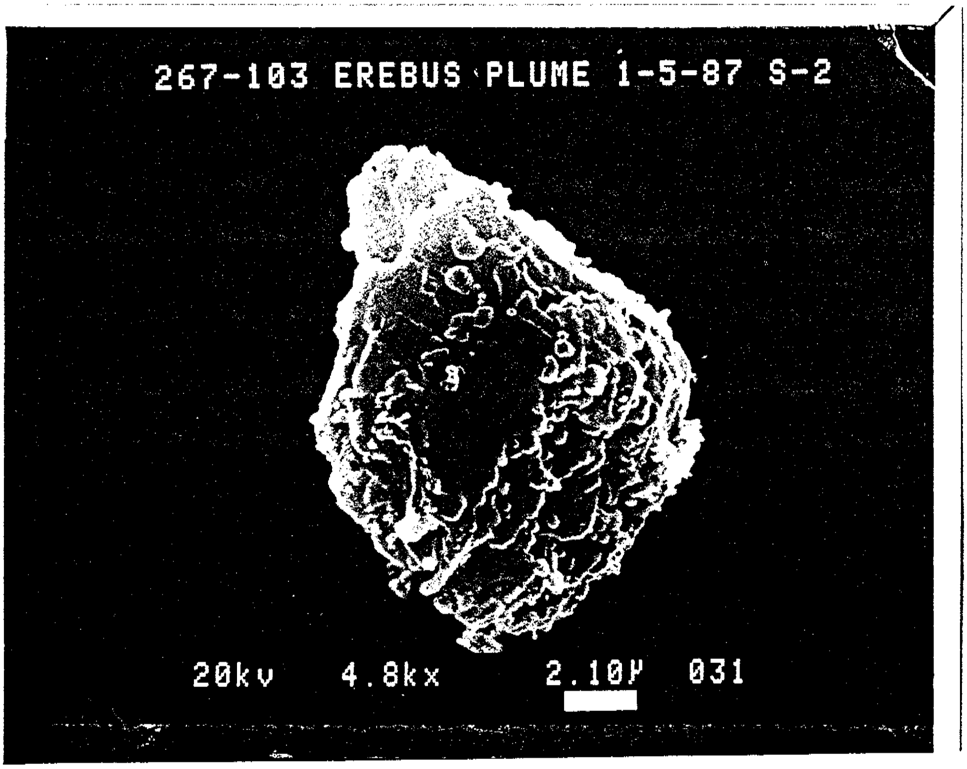


Figure 4.6

Figure 4.7: Large aggregate of elemental sulfur and silver sulfide (AgS) (isolated on right) formed by reaction of H_2SO_4 with the Ag substrate on the stage.

Figure 4.8: Coagulated salts, probably KCl and NaCl, dominate the smallest particle range. Collected on the Erebus summit, 1986/87.

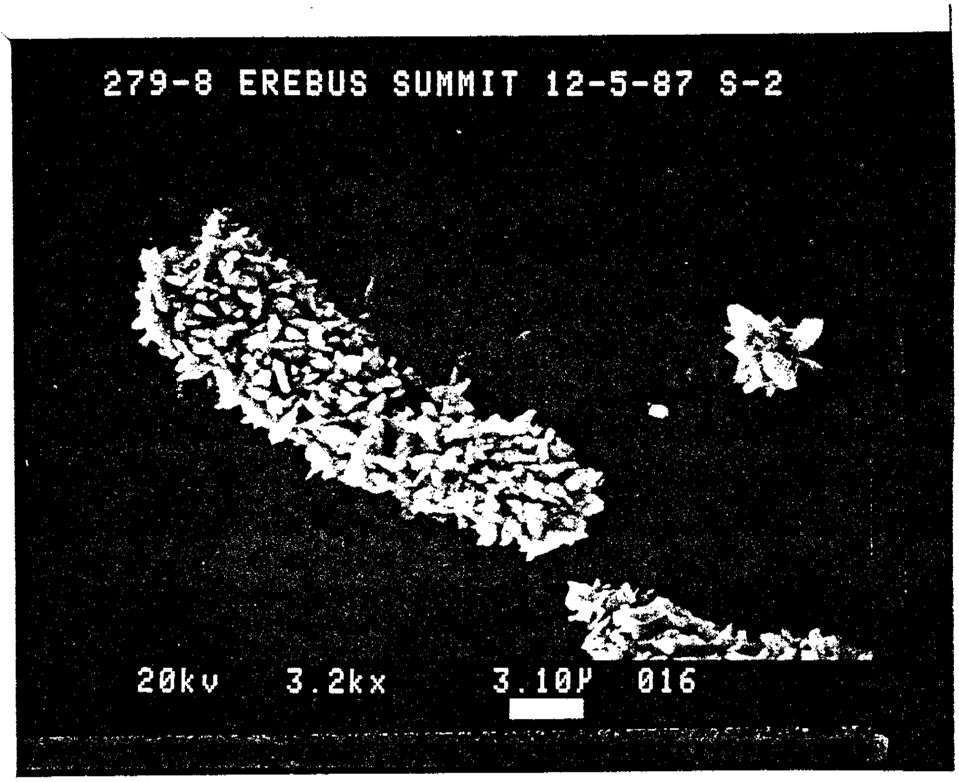


Figure 4.7

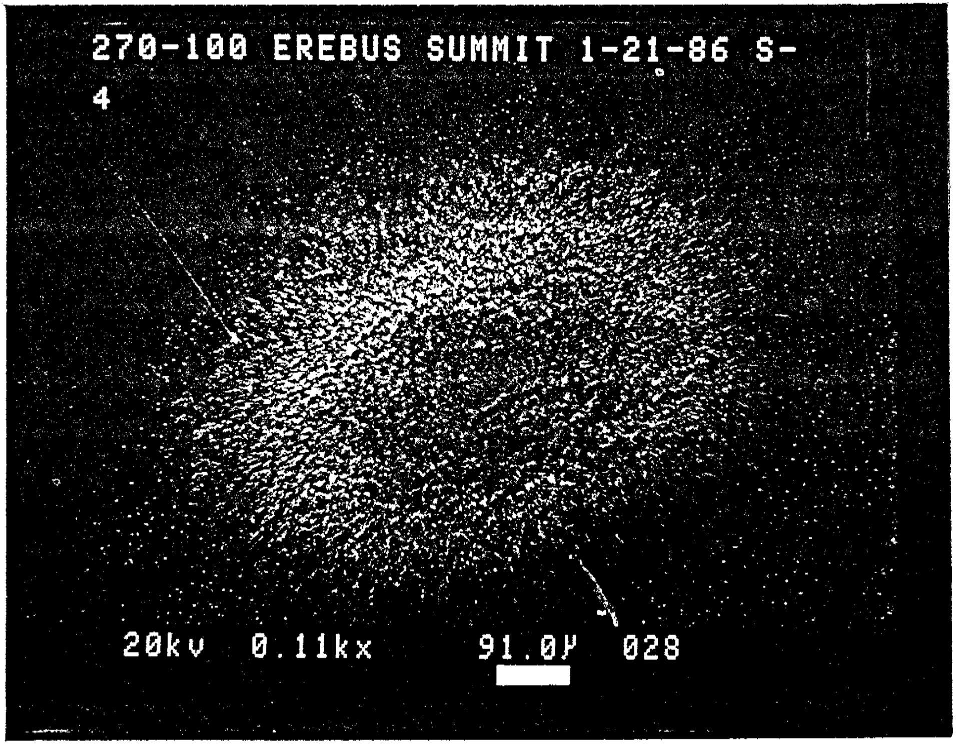


Figure 4.8

Figure 4.9: Aggregates of elemental sulfur, KCl, NaCl and amorphous masses of K and Na compounds, possibly hydrated sulfates from Erebus summit, 1987/88.

Figure 4.10: K, Ca, Al, Cl, S semi-amorphous particle which may be a reaction product or overgrowth on an ash particle. It is possibly Ca or Al sulfates and KCl overgrowth.

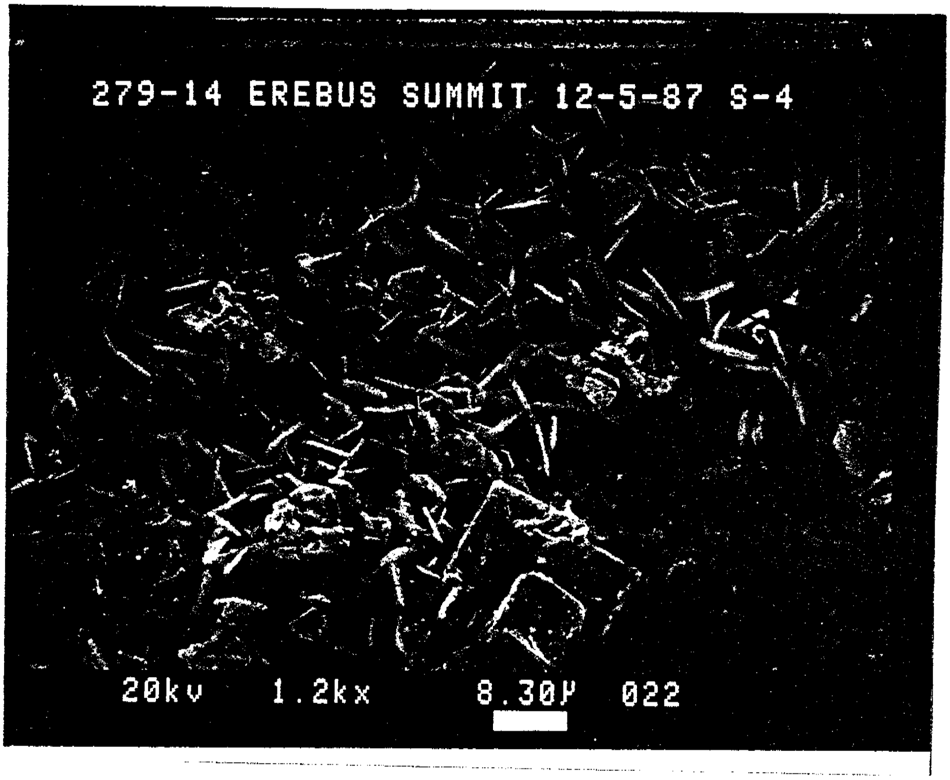


Figure 4.9

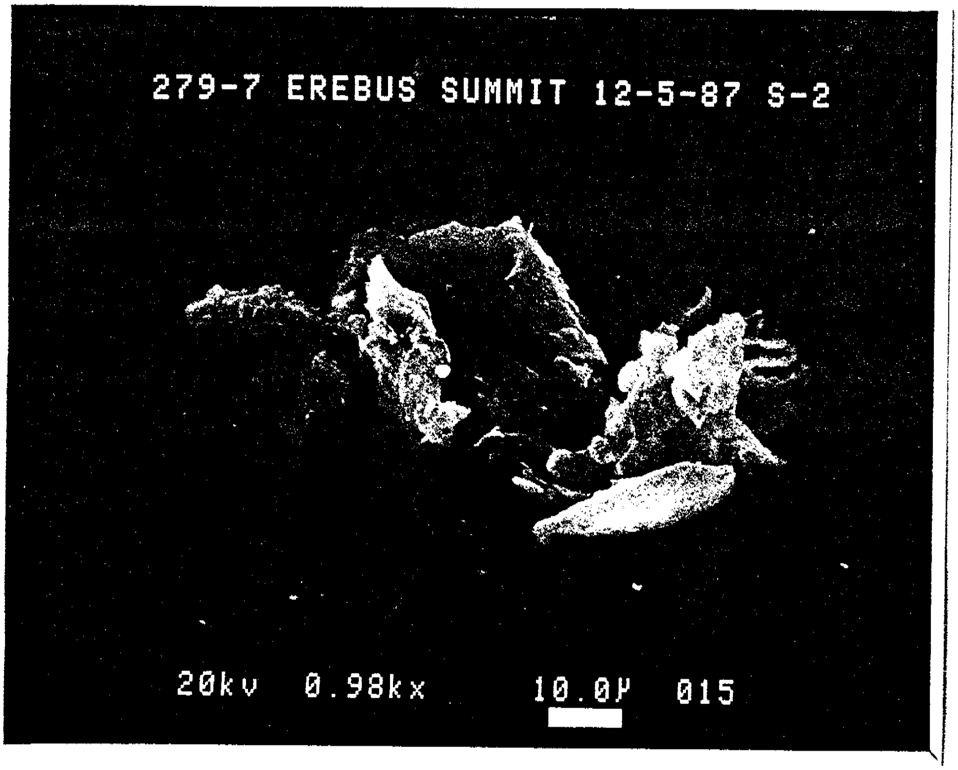


Figure 4.10

Discussion

The variation between airborne plume and crater rim samples, and between 1986/87 and 1987/88 samples may be indicative of a dynamic, changing system. Certain characteristics, such as the paucity of H_2SO_4 and HCl droplets, are consistent however and distinguish Erebus from other volcanoes. Spacial and temporal studies of plume particles during the 1986/87 and 1987/88 seasons indicate that 1.) both chemical and physical fractionation are occurring in the plume and 2.) that metals may be volatilized in a process that involves halides and possibly sulfur. Of these metals, gold is most consistently observed.

Chemical and Physical Fractionation in the Plume:

Particle size distribution and chemistry are inherently connected in that fractionation occurring in the plume is a function of formation conditions, chemical reactivity and the resulting residence times of different particles within the plume and surrounding atmosphere.

In 1987/88, simultaneous measurements at the crater rim and airborne in the plume revealed that 77% of particles at the crater were <0.3 microns (Figure 4.3) compared to only 31% of the airborne plume particles (Figure 4.4). In 1986, >90% of the particles collected on the crater rim were in the 0.1 micron range (Figure 4.2) whereas SEM analysis revealed no particles in this range in airborne plume samples. Agglomeration, scavenging, reaction, dilution and eventual dry or wet sedimentation in the cooler outer plume probably cause the variations seen between samples.

The lower particle concentration and dominance of larger particles in the outer plume during both seasons and the monomodal character of the 1986/87 crater rim plume indicate that the Erebus plume is behaving like the trimodal model described by Vie le Sage (1983) (Figure 4.11) in which nucleation of average 0.1 μm particles by homogeneous gas-particle conversion close to the vent proceeds accumulation by agglomeration and growth of the later particles (0.1-2 μm). This model suggests that particles >2.0 μm are mechanically generated. Analysis of Erebus particles has shown a low percentage of ash, reflecting a low energy plume.

A chemical fractionation may be occurring as a result of changing temperature and oxidizing conditions in the outer plume. The salts NaCl and KCl dominate stage 4 (0.1 μm) of the crater rim samples indicating that they form by gas-particle conversion and are replaced by sulfates (K_2SO_4 and Na_2SO_4) with distance from the vent. Flocculent aggregates, possibly Cu, Zn and Sn oxides, are also seen in the airborne plume samples.

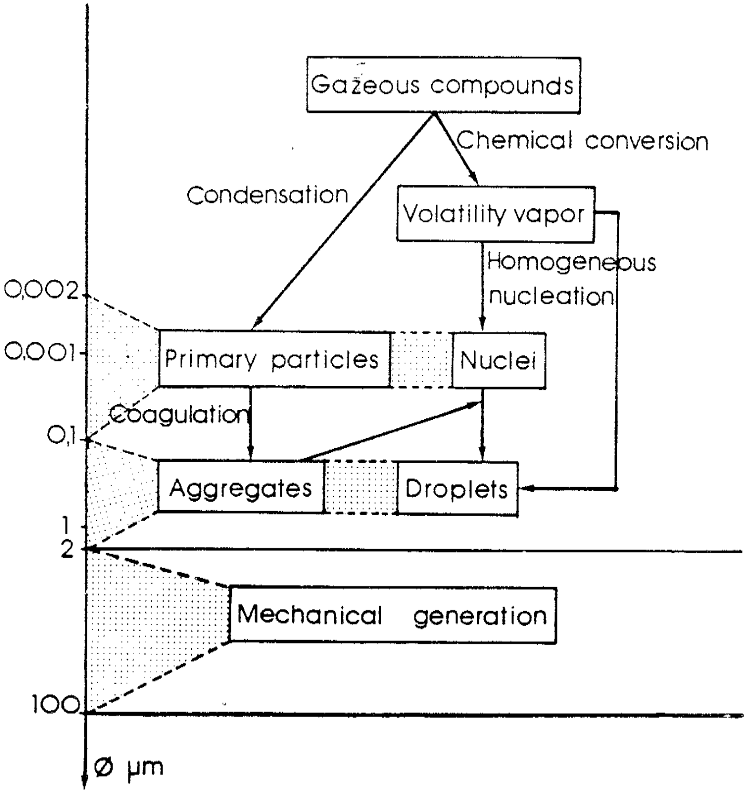


Figure 4.11 The trimodal model of Whitby (1978) which relates particle size and mode of generation in the atmosphere. (From Vie le Sage, 1983)

A hypothetical plume described by Oskarsson (1980) (Figure 4.12) is analogous to the Erebus plume particularly in 1986/87. Aerosol salts such as the KCl and NaCl seen in the crater rim samples (Figure 4.8) are formed at temperatures close to magmatic near the vent. At intermediate temperatures (below 700°C) halogen gases react with solidified material (ash) by surface adsorption. This middle zone is not clearly distinguished at Erebus due to the low ash content of the plume though the occasional silicates show overgrowths of salts and/or sulfates (Figure 4.10).

Further from the vent at lower temperatures and oxidizing conditions (Woods and Chuan, 1982; Naughton <u>et al.</u> 1974), as exhibited by particles in the airborne plume, sulfates replace salts in reactions such as :

(1) $2NaCl + H_2SO_4$ -----> $2HCl + Na_2SO_4$

Iron, zinc and copper oxides also form from halides at low temperature and oxidizing conditions. Cu_2SO_4 is an unstable intermediary (Naughton, 1974) and explains why CuO is the more common species in Erebus aerosols.

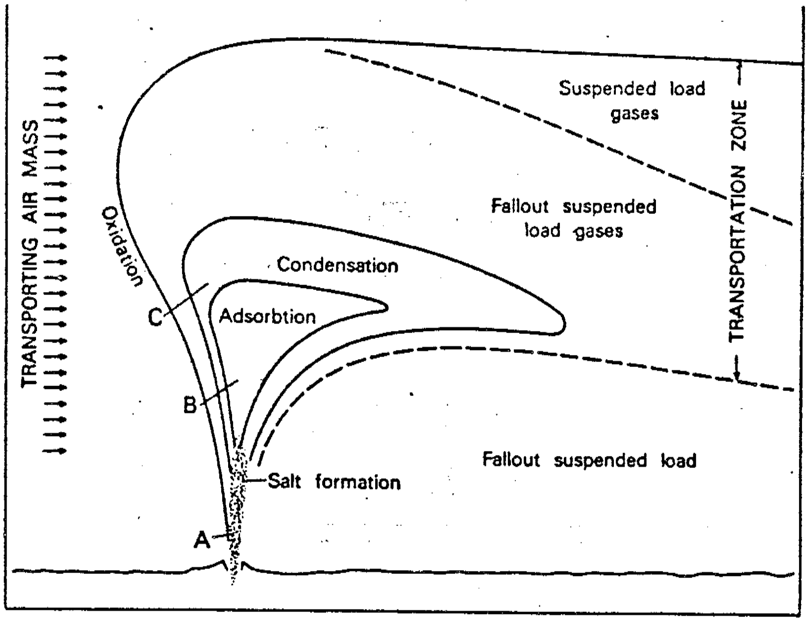


Figure 4.12 Hypothetical plume described by Oskarsson (1980) describing temperature dependent processes of particle generation.

Sulfuric acid normally condenses at lower temperatures but H_2SO_4 droplets are uncommon in the Erebus plume, seen only during occasional eruptions (Chuan _et al._, 1986). However, etched areas on the stages 3 and 4 demonstrate that at least some acidic material is passing through the QCM. The paucity of H_2SO_4 and HCl as droplets or mantling on particles from Erebus is unusual and not well understood. It may be due to the low sulfur content in the magma and the paucity of oxidizing agents such as silicates and Fe oxides or it may reflect the low water content of the Erebus plume. Erebus SO_2 emissions are relatively low (10-50 tonnes/day) explaining low H_2SO_4, but the abundance of Cl at Erebus is well known (Bigelow, 1985, this study). Chloride seems to be an agent in many reactions perhaps due to the low SO_2 emissions, and this may prevent free emission and condensation of HCl.

Vapor Transport of Metals and Other Compounds

The presence of metals and alkali salts as particles and precipitates on the QCM stage infers that these elements are transported out of the magma in a vapor phase. Halides play a prominent role in the vaporization process of metal compounds from the magma (Krauskopf, 1964), and Cl is more concentrated than S in the Erebus magma, so one would expect the Erebus plume to be dominated by compounds containing halides over sulfur. Matrix glass from recent bombs show an average of 1527 ppm and 2162 ppm (Bigelow, 1985) for Cl and F respectively in comparison to 260 ppm for sulfur.

The prevalence of metals on the QCM stages and on base treated filters, specifically Au, Zn, Cu, Sn, Pb and Ce infer that halide vaporization is occurring. The ubiquitous presence of submicron NaCl, KCl and amorphous silica is further evidence for halide transport. Gold, because of its unique morphology and economic significance will be addressed separately.

Gold:

Economically significant concentrations of gold have long been associated with fossilized volcanic systems. Therefore, Erebus presents an opportunity to study vapor transport of gold in an active volcano. Gold has been observed in QCM crater rim, airborne plume and ambient air samples as well as in Antarctic ice cores up to 5 km from the summit (J. Palais, pers. comm. to P. Kyle, 1987). It has also been analyzed on treated filters, conclusive evidence that gold is volatilized and dispersed within the Erebus plume.

Gold enrichment in volcanic aerosols has also been documented at Kilauea (Crowe et al., 1987, Zoller et al., 1983), Mt. St. Helens (Phelan et al., 1982), Etna (Buat-Menard et al., 1978) and Mt. Augustine (Lepel et al., 1978). At Kilauea, it is found on base-treated filters but most commonly collects on particle filters (T. Miller, pers. comm., 1988; this study).

Volcanic discharges of gold and other metals could be analogous to a magmatic vapor plume evolved in the generation of porphyry deposits. In a model derived by Henley and McNabb (1973), a low density "magmatic" vapor phase bounded by the system $NaCl-H_2O-CO_2$ transports Cu, Mo, Au, S and other ore components in a H_2O-HCl rich mixture as complex halide-hydroxyl species at temperatures in excess of $500^{\circ}C$. Theoretically, water and metals are derived from the convecting magma column and are subsequently exsolved as a free fluid phase.

In porphyry deposits (Henley and McNabb, 1973) a buoyant magmatic vapor thermal plume is established which permeates the country rock. A saline liquid condenses with cooling and often penetrates pre-existing ground water. Metal precipitation occurs in response to decreasing temperature and salinity as well as induced fO_2, pH and fH_2S variations. The magmatic input of such systems is often obscured (Gustafson and Hunt, 1975) by the ground water component.

During active volcanism exsolved vapor is expelled directly via the magma column to the surface. Hence the main mechanisms for deposition are probably variations in temperature, fO_2 and/or fH_2S. Krauskopf (1964) suggested that direct condensation of gold from hydrothermal vapor might result in gold dispersal through the plume, but generation of free gold in the plume would require a high vaporization temperature (2600°C).

Gold is most readily transported by complexes (Seward, 1984) involving Cl^- and S donor ligands such as HS^- and $S^=$. Furthermore, Fyfe and Henley (1973) showed that solubility of gold in Cl solutions increases from 10 ppm at 300°C to 1000 ppm at 510°C. Henley (1973) has shown that at high temperatures (500°C), gold forms solvation compounds such as $Au_2Cl_6.6HCl.nH_2O$. The low sulfur concentration in the Erebus plume and the presence of AuyClx species in QCM samples indicates that gold is probably concentrated and transported in the magmatic gas as chloride vapors but is reduced to the more stable elemental Au within the plume and after/during deposition.

Deposition of gold as particles in the plume and/or precipitates on the QCM stage is more difficult to explain. The Au_yCl_x species observed may be a direct sublimate of $AuCl_3$. However $AuCl_3$ disproportionates readily in water and HCl solutions in which $AuCl^-$ is formed (Cotton and Wilkinson, 1980). Gold compounds such as chloroauric acid $(H_3O)^+ (AuCl_4)^- \bullet 3H_2O$ can be precipitated out of solution along with other water-soluble salts ($KAuCl$ and $NaAuCl_4 \bullet 2H_2O$) but these species were not observed.

The unique spongy morphology (Figure 4.5) exhibited by the elemental gold has rarely been described in the literature (DiLabio et al., 1988) and could be interpreted as a chemical precipitate produced by adsorption (on to the stage or another particle) and reduction. Jean and Bancroft (1985) deduced that a sulfide surface was the most effective to initiate reduction of gold, two likely reactions being:

$$8AuCl^{-}_{4} + 2S^{=} + 12H_{2}O \dashrightarrow 8Au(o) + 3SO_{4}^{=} + 24H^{+} + 32Cl^{-} \qquad (2)$$

$$2AuCl^{-}_{4} + 3S^{=} \dashrightarrow 2Au(o) + 3S(o) + 8Cl^{-} \qquad (3)$$

The sulfide ZnS noted on QCM samples could be a potential reducing agent and the common occurrence of elemental sulfur may be evidence that reaction 3 is occurring. Gold has also been shown to adsorb on natural silicates and iron hydroxides (Krendelov et al., 1978), although the mechanisms are unknown.

Therefore, the presence of both Au-Cl species and elemental gold indicate the Au is transported as chloride species perhaps in a magmatic vapor phase. Metal precipitation is probably in response to decreasing temperature and changing fO_2 in the plume.

Transport of other metals:

Other compounds noted on the stage appear as sulfides, sulfates or oxides. The naturally formed sulfide ZnS was tentatively identified. Zn is partitioned strongly from the melt into a halide rich gas (Holland, 1972). The volatile species of

Zn are $ZnCl_2$ and $ZnBr_2$. Sphalerite is uncommon in fumarole deposits but has been observed at Merapi (Symonds, 1987) and could be formed from the reaction:

$$ZnCl_2(g) + H_2S(g) \text{ ----> } ZnS + 2HCl(g) \qquad (4)$$

The components K, Ca, Al, Fe, Si and Ce observed as salts, sulfates and oxides in the plume are generally less volatile. Symonds (1987) attributes their presence in fumaroles to fluorometasomatism during wallrock/particle interaction. Varekamp et al. (1986) propose vapor transport and eventual precipitation of Al and Si by the reactions:

$$2AlF_3(g) + 3H_2SO_4(aq) \text{ ----> } Al_2SO_4(s) + 6HF(g) \qquad (5)$$

$$SiF_4(g) + 2H_2O(aq) \text{ ----> } SiO_2(s) + 4HF(aq) \qquad (6)$$

Aluminum salts are abundant on the slopes of Erebus (Keys, 1980) and in plume samples along with abundant cristobalite (SiO_2) indicating that vapor fluoride transport might be important. Anomalous Ce was noted in Erebus aerosol by Germani (1980) and may also be transported as a fluorine compound (Varekamp et al., 1986), though these associations can not be verified by EDXRA.

Comparison of 1986/87 and 1987/88 QCM Samples

The main differences between 1986/87 and 1987/88 are the decrease in overall metal content and increase in elemental sulfur in 1987/88. These differences are briefly summarized in Table 4.4. Possibly lowered HCl activity may have reduced the metal carrying capacity of the plume, though this can not be verified since no treated filter samples were collected during the 1987/88 field season. The Erebus magma falls close to the QFM boundary (Chapter 3), and perhaps H_2S plays a more active role in the plume during cooler, low discharge periods. This could promote the formation of elemental sulfur (Chuan et al., 1986) by the spontaneous reaction:

$$2H_2S + SO_2 \text{ ---> } 3S + 2H_2O \qquad (7)$$

However, other factors to be considered are sampling conditions, sample location with respect to the central plume, and temperature gradient in the plume and the resulting affect on condensation reactions. The 1987/88 plume samples in particular may be less representative due to a sparse and dispersed plume.

Table 4.4: Summary of components seen in QCM samples during the 1986/87 and 1987/88 field seasons. Blank areas indicate that the component was not seen.

Mt Erebus QCM data
Components seen on QCM stages during 1986/87 and 1987/88

		1986/87	:	1987/88	
Species	crater	plume	:crater	plume	ambient
H2SO4	*	*	:*	*	*
HCl	*	*	:*		
ash	x	x	:*	*	
Low Z/C?	x	xx	:*	xx	xx
elem. S	*	*	:xx	*	*
SiO2/amorphous	xx	x	:*	*	*
Zn/ZnS	xx	x	:		
Au/AuCl	xx	x	:*		*
Cu/CuO	*	x	:	*	*
Sn/SnO		x	:		
Ce/CeO2		x	:		
Pb		*	:		
KCl	xx	*	:xx		
NaCl	xx	*	:x		
K/Na SO4	*	x	:x		
Al SO4	*	*	:x		
Ca SO4/Ca-rich			:x	x	xx
Al/AlCl/Al ox			:*		x
Fe/oxide		*	:*	*	x
Mn/oxide		*	:		
Cr/oxide			:		x
Co/oxide			:		*
Ti/oxide			:*		

Key

*	very rare
x	common
xx	abundant

Atmospheric Contribution of Erebus Particles

A brief analysis of ambient air QCM samples revealed a dominance of a low atomic number (possibly carbon) flocculent material, the origin of which is presently unknown. This flocculent material is also very common in the Erebus plume. A second dominating particle is $CaSO_4$ of probable marine origin. Other particles included an Al-Cl species and Fe, Mn and Cr oxides. H_2SO_4 was rarely seen, although a textured appearance on the 0.4 μm stage may be indicative of H_2SO_4 which could be from Erebus.

The Erebus plume contained only rare $CaSO_4$ and some Fe, Mn and Cr oxides. These oxides represent typical rock forming minerals and could be derived from anywhere along the route to the South Pole. Chuan (pers. comm, 1988) has noted a distinct increase in particle concentration over the Transantarctic Mountains indicating that they may be a source for a high percentage of the ambient particles. The textured appearance seen in ambient air samples is not similarly seen in Erebus plume samples suggesting that SO_2 is the dominant sulfur phase near the volcano. However, the H_2SO_4 in ambient samples could be partially derived from Erebus.

Summary

In summary, chemical and physical fractionation is apparently occurring in the Erebus plume defined by size and chemical variation between the crater rim and airborne plume samples. The presence of metals, particularly gold indicates that metal transport in a chlorine rich vapor phase may be the modern equivalent of the process involved in the evolution of porphyry deposits. This warrants further study of active volcanic emissions and fumaroles to elucidate on the processes controlling concentration, transport and deposition of precious metals.

Comparison of Erebus and ambient air QCM samples indicates that Erebus is not a significant contributor of particles to the Antarctic environment relative to marine and terrestrial input. However monitoring particles following active periods such as that in 1984, and perhaps during the winter months might show a greater contribution.

5. ELEMENT ENRICHMENT IN VOLCANIC EMISSIONS

Introduction

The measurement of elemental components in volcanic aerosols has been used to study volcanic contributions of heavy metals to the atmosphere and as indicators of volcanic activity. The low concentrations of most trace metals in volcanic emissions require sensitive analytical methods, however, to date over forty elements have been detected.

Absolute values of species vary and depend on the nature of the collecting site, the type of volcanic activity, and position with respect to the magma source. Distance from the magma source is particularly critical due to effects such as dilution, sedimentation, precipitation, reactivity and gas to particle conversion (Vie le Sage, 1983; Quisefit _et al._, 1987).

Because it is difficult to measure absolute concentrations, it is more reliable to study the relative element enrichment in volcanic emissions with respect to whole rock concentrations. Enrichment Factors (EF) are calculated using the following equation:

$$EF = \frac{X_{gas} / Y_{gas}}{X_{magma} / Y_{magma}}$$

where X is the element of interest and Y is a reference element chosen for normalization (Vie le Sage, 1983).

EF's normalized to an ash constituent (Sc or Al) are minimum values in an ashy plume because ash particles inflate Al with respect to the other volatile elements thereby lowering the EF. Bromine normalization was used at Kilauea, Hawaii by Crowe et al. (1987). EF's were multiplied by 10^5 which approximates the degree of enrichment of Br in the gas phase thereby adjusting the EF's for the nonenriched ash elements to unity.

Several techniques are used to examine trace element contents in volcanic fumes. Analysis of condensates (Stoiber and Rose, 1970; Gemmell, 1987), sublimates and incrustations (Stoiber and Rose, 1974; Naughton, 1974; Naughton et al., 1975; Oskarsson, 1981) provide information on volatilization, transport and deposition of volatile elements. Symonds et al. (1987) examined zoning in all three mediums at Merapi, Indonesia and compared these to a thermodynamic model.

Cadle (1973) pioneered research on volcanic aerosols at Kilauea by studying the potential hazards of toxic elements emitted by volcanoes and examined their role as catalysts for chemical reactions occurring in the regional atmosphere. Using a portable pump and filters, he measured SO_4^{2-}, NH_4^+, Cl, K, Na, Mg, Ca, and Si in the volcanic aerosol. He also noted that most of the sulfur in the plume was in the form of sulfur dioxide, sulfuric acid droplets and various sulfates.

Buat-Menard and Arnold (1978) established that Cu, Pb, Zn, Sb, As, Ag, Cd, Au, Hg, and Se were enriched by factors of greater than 100. They estimated the emission rates of the elements by normalizing the element/S ratio to the known emission rate of SO_2 in tonnes/day, and found the flux of Cd, Hg, Cu and Zn comparable to anthropogenic fluxes whereas Se was distinctly a volcanic contribution. Similar studies determined elemental fluxes at Mt. St. Helens and Poas volcanoes (Phelan et al., 1982, Finnegan, 1984).

Elemental analysis of aerosols has been used to fingerprint magma source and evolution. Lepel (1978) attributed anomalously enriched elements (AEE's) in the atmosphere to high temperature processes at Mt. Augustine, Alaska. The varying elemental ratio in aerosols emitted from separate eruptions at Augustine implied a fractionation of the magma possibly due to partial crystallization and preferential removal of some elements.

Often the volatile compounds have evolved since the initial degassing of the magma due to changing temperatures and chemical reaction with other materials. The molecular character of volatile elements can often be inferred. Finnegan (1984) determined the most likely forms by looking at the boiling point of elemental compounds and assuming most to be released as fluorides and chlorides. The alkali metals (Na, K, Rb, Cs) showed increasing enrichment with increasing molecular weight which also correlated with boiling point (Olmez et al., 1986; Finnegan, 1984).

Element enrichment can be an indicator of a particular phase in an eruption cycle. The May 18, 1980 eruption of Mt. St. Helens consisted of primarily juvenile material (Hobbs et al., 1982).

Vossler et al. (1981) noted that elements normally volatile were not significantly enriched in the plume on May 18. This was in contrast to other volcanoes and suggested that the plume was mainly airborne ash and not magmatic gases. Pronounced enrichments of halogens, W, In, Zn, S, Cd, Se, Sb, Hg, As and Au relative to ash were detected in a quiescent plume at Mt. St. Helens in September 1980 indicating a more volatile rich, higher temperature phase (Phelan et al., 1982). Hence aerosol emission was closely related to the phase (as described by Hobbs et al., 1982) of the mountain's eruptive history.

Kilauea has provided a perfect environment for constant monitoring of trace elements in volcanic gases. Past studies at Kilauea have shown significant iridium enrichment and high F/Cl ratios (0.1-0.5) (Olmez, 1986; Finnegan, 1984; Zoller, 1983; Naughton, 1974) implying a deep seated mantle derived magma source.

Recent studies at Kilauea have attempted to monitor changes in element composition of gases through different stages of episodic fountaining. Crowe et al. (1987) collected samples during active (fountaining) and repose periods during the episodic eruptions of the Pu'u O'o vent on the east rift zone of Kilauea. The EF's for several trace elements in the Pu'u O'o fume varied with temperature and eruptive phase. A distinct bivariance was noted between samples collected during eruptive activity versus during repose periods. A general pattern emerged in which trace metals with higher EF's occurred in the fountaining (active) stage of the eruptive cycle. The anomaly was significant enough to suggest that monitoring trace metal ratios in volcanic plumes may be a tool for predicting eruptions.

Analytical Method

Field collection

Nine sets of aerosol filters were collected on the Mt. Erebus crater rim during the 1986-87 field season. Samples were collected by pumping 10-30 l/min of air through 110 mm diameter filters packs with a portable battery powered pump. The filter pack consists of four ^{7}LiOH treated filters and a Fluoropore teflon filter for particles and condensed phases that exceed .01 microns (Finnegan, 1984, Crowe et al., 1987). Location, time and pump volume are included in Table 5.1. Estimates of pump volume may be in error up to 50% due to the lack of a flow meter. Two filters sets were exposed to ambient air about 2000 meters up wind of the plume to provide blanks.

Table 5.1: Date, time, location and pump capacity for all samples collected during December 1986.

Sample Number	Location	Date	Time (min)	Pump Vol. (l/min)	Volume (m3)
1	S. of Observ. Pt.	19-DEC-86	46	30	1.38
2	S. of Observ. Pt.	19-DEC-86	248	20	4.96
3	Observ. Pt.	20-DEC-86	105	30	3.15
4	Observ. Pt.	20-DEC-86	210	10	2.1
5	N. of Observ. Pt.	21-DEC-86	190	20	3.8
6	Observ. Pt.	22-DEC-86	432	10	4.32
7	Shackleton's C.	23-DEC-86	90	20	1.8
8	Battery site	24-DEC-86	37	30	1.11
9	N. of Observ. Pt.	24-DEC-86	169	20	5.07

Sample preparation and analytical procedure

The filters were cut into quarters, packaged in 4 cm^3 polyethylene vials and analyzed by instrumental neutron activation analysis (INAA). In INAA the nucleus of a stable isotope becomes radioactive by neutron capture. The unstable nucleus emits characteristic gamma rays from which the element present in the sample can be quantified. The length of irradiation needed depends mainly on the half-life of the isotope of interest and, in the case of short lived isotopes, on the chlorine concentrations on the filters. This is due to the high gamma-ray activity of chlorine.

All samples were irradiated in the graphite thermal column of the Omega West Reactor (OWR) at Los Alamos National Lab under the conditions specified in Table 5.2. Three separate irradiations were made, based on the half-life of the isotope, and are specified as I, II, and III in the table. Standards of known concentration were used for calibration. Isotopes with short half-lives (11 seconds to 38 minutes) were analyzed using an automated pneumatic INAA system (Minor et al., 1982). Neutron flux was monitored with a fission ion chamber in the automated system (Minor et al., 1982) and by cobalt flux monitors in the long irradiations.

After the short irradiations samples were counted using four Ge(Li) detectors. Gamma ray data were reduced using a software program RAYGUN (Minor et al., 1982). Sulfur requires a more sensitive technique, so a quarter of each treated filter was later analyzed by ion chromatography. All samples were blank corrected.

Field and analytical error

Field conditions often make it difficult to accurately sample volcanic plumes. Wind direction, degree of mixing in the atmosphere, temperature, and collection site relative to the plume caused significant variability in the data. To minimize these effects samples were taken up wind and as close to the plume as possible.

Errors in determining the concentration on the filter can be minimized by carefully changing, packaging and quartering filters to avoid contamination.

Analytical errors for each element are included in Table 5.2. The major sources of error during analysis were due to inaccurate standards and high dead-time of the Cl-rich samples. Neutron flux can vary slightly which may affect the analysis. A prior knowledge of high Cl samples is helpful in establishing the counting geometry to prevent these high dead times. Accurate sulfur analysis by ion chromatography was difficult due to the high pH of the LiOH treated filters and the low sulfur concentrations on the filters. The sulfur data contain errors between 10 and 20 percent.

Table 5.2: Procedures for neutron activation analysis of elements collected on filter samples.

Neutron Activation Analysis Procedures

Isotope	Half-life	Irrad*	Decay/Count**	Standard	% Error		Key
F-20	11s	I	10s/30s	fluorine	14	:	*Irradiations
Na-24	15.0h	II	10■/5■	BC,UP	4	:	I 30 second irradiat
Al-28	2.3■	II	20■/20■	UP,FA	5	:	TNF = 6.5 X 10E12 neut./c■2/sec
S-37	5.1■	II	10■/5■	sulfur		:	II 5 ■inute irradiati
Cl-39	55.5■	I,II	2■/2■, 10■/5■	chlorine	15	:	TNF = 6.5 X 10E12 neut./c■2/sec
K-42	12.4h	II	10■/10■	BC	16	:	III 4 hour irradiation
Ca-49	8.7■	II	10■/10■	UP,FA	18	:	TNF = 8-9 X 10E12 neut./c■2/sec
Sc-46	83.8d	III	30d/8h	FA	21	:	or 7 hour irradiation
Ti-51	5.8■	II	10■/5■	UP,FA	20	:	TNF = 1.5 X 10E12 neut./c■2/sec
V-52	3.77■	II	10■/5■	UP,FA	11	:	** Decay/Count
Cr-51	27.8d	III	30d/8h	BC,FA	11	:	Decay - decay period following
Mn-56	2.58h	II	10■/10■	UP,FA	22	:	irradiation
Fe-59	45d	III	30d/8h	FA	23	:	Count- Counting period
Co-60	5.27y	III	30d/8h	BC,FA	21	:	TNF - ther■al neutron flux
Cu-66	5.1■	II	10■/10■	UP	27	:	Standards:
Zn-65	245d	III	30d/8h	BC	12	:	BC-Bitu■inous Coal NBS SRM 1632
As-76	26.5h	III	3d/4h	BC	8	:	UP-Urban Particulate
Se-75	120d	III	30d/8h	BC,FA	20	:	FA-Fly Ash NBS SRM 1633a
Br-82	35.7h	III	3d/4h	BC	3	:	
Rb-86	18.77d	III	30d/8h	FA	17	:	
Mo-99	66h	III	3d/4h	BC	21	:	
Cd-115	2.3d	III	3d/4h	BC	19	:	
In-116	14s	I	10■/10■	UP	15	:	
Sn-113	118d	III	30d/8h	BC	18	:	
Sb-122	2.8d	III	30d/8h	BC,FA	13	:	
Cs-134	2.19y	III	30d/8h	BC	15	:	
La-140	40.2h	III	3d/4h	BC	16	:	
Ce-141	32.5d	III	30d/8h	BC,FA	8	:	
Nd-147	11.1d	III	30d/8h	BC,FA	11	:	
S■-153	47.1h	III	3d/4h	BC	7	:	
Eu-152	13y	III	30d/8h	BC,FA	17	:	
Yb-175	4.2d	III	30d/8h	BC,FA	13	:	
Hf-181	44.6d	III	30d/8h	BC,FA	13	:	
Ta-182	115d	III	30d/8h	FA	24	:	
W-187	24h	III	3d/4h	BC	9	:	
Au-198	64.8h	III	3d/4h	BC	13	:	
Hg-203	47d	III	3d/4h	BC,FA	17	:	

Results

Element Concentration and Flux of Erebus Emissions

Analysis of nine samples expressed as µg/m3 are given in Table 5.3, along with the percent of concentration on the particle filter. Saturation of the treated filters did not occur as shown by Figures 5.1 to 5.3. Bromine and some metals show more random distribution on the filters possibly due to their remobilization on the particle filter by HCl, H_2SO_4 and SO_2. The remobilized or evaporated HBr and other volatile halides, was then collected on the treated filter (Mingxing and Winchester, 1982).

Particle filters ideally collect ash constituents or trace metals which condense or precipitate onto the ash, whereas the LiOH treated filters collect acidic volatiles. At Erebus, most ash constituents (La, Sm, Fe, Co, Ca, V, Mn, Hf) are collected on the particulate filter. Some ash components (Ce, Eu, Yb, Sc, Cr, Ta) are seen on both particle and treated filters although these are probably contaminants, i.e. small particles which passed through the particulate filter. The volatile metals Sb, Hg, Na, K, Rb, Cs, and In are greater than 80% particulate but some metals (W, Au, Mo, Zn, Cu) appear on both particle and treated filters. Eighty percent of the volatile halides, As and Se are found on the treated filters whereas bromine is variable.

Table 5.3 Elemental concentrations on each of nine samples taken during the 1986/87 field season at Erebus, in μg/m3 unless otherwise specified. The percent of concentration collected on the particle filter is tabulated in parentheses.

Elemental Concentrations

Sample	1	2	3	4	5	6	7	8	9
Date	12/19/87	12/19/86	12/20/86	12/20/86	12/21/86	12/22/86	12/23/86	12/24/86	12/24/86
F	183 (nd)	166 (nd)	806 (nd)	649 (nd)	658 (nd)	228 (nd)	936 (nd)	455 (nd)	258 (nd)
Na	27.6 (94)	34.1 (100)	126 (100)	128 (97)	132 (100)	30.9 (92)	52.9 (84)	63.7 (83)	64.3 (100)
Al	3.5 (88)	7.2 (54)	5.1 (83)	19.2 (93)	7.05 (97)	5.0 (96)	20.1 (100)	16.8 (90)	70.5 (100)
S	13.3 (nd)	5.5 (nd)	149 (nd)	180 (nd)	171 (nd)	62.7 (nd)	10.9 (nd)	31.7 (nd)	10.2 (nd)
Cl	399 (7)	334 (13)	1830 (9)	1588 (9)	1784 (8)	664 (5)	670 (3)	444 (13)	448 (8)
K	26.1 (100)	25.9 (100)	113 (100)	79.1 (100)	134 (100)	26.1 (100)	39.0 (100)	43.8 (100)	29.2 (100)
Ca	nd	nd	14 (100)	23.0 (100)	nd	7.3 (100)	18.6 (100)	35.5 (100)	20.9 (100)
Sc*	1.0 (0)	.68 (63)	0.85 (37)	3.0 (48)	nd	0.77 (32)	2.3 (54)	2.8 (39)	7.5 (4)
Ti	nd	nd	nd	nd	nd	nd	nd	nd	
V	.02 (63)	nd	0.02 (96)	0.005 (100)	nd	nd	0.03 (85)	0.03 (100)	nd
Cr	1.2 (89)	0.09 (52)	0.05 (10)	0.10 (100)	0.16 (0)	0.01 (0)	0.18 (37)	0.11 (99)	0.40 (98)
Mn	.08 (100)	.40 (25)	0.55 (100)	0.86 (99)	0.34 (43)	0.13 (100)	0.45 (100)	0.52 (100)	1.6 (100)
Fe	19.9 (46)	14.0 (52)	7.4 (100)	18.9 (100)	9.1 (83)	6.8 (76)	20.6 (85)	26.2 (58)	42.2 (92)
Co	.18 (9.5)	nd	nd	nd	nd	0.004 (100)	0.01 (100)	0.57 (10)	0.001 (0)
Cu	.02 (0)	nd	3.8 (96)	4.9 (100)	nd	0.84 (0)	nd	0.008 (100)	nd
Zn	1.1 (0)	1.2 (84)	4.0 (78)	2.1 (0)	3.0 (95)	2.5 (34)	4.8 (21)	3.5 (43)	2.6 (73)
As	.06 (45)*	.50 (98)	2.0 (91)	2.0 (83)	1.5 (96)	0.36 (90)	0.54 (88)	0.51 (84)	0.48 (83)
Se	.08 (0)	.01 (0)	0.05 (49)	.03 (0)	0.04 (53)	0.05 (100)	nd	nd	0.03 (100)
Br	1.8 (1.2)	1.0 (37)	2.8 (78)	3.1 (68)	4.8 (2)	1.6 (9)	2.2 (4)	1.3 (25)	0.9 (44)
Rb	nd	.23 (100)	0.72 (100)	0.68 (100)	0.81 (100)	0.16 (100)	nd	0.32 (100)	nd
Mo	nd	nd	nd	nd	0.02 (0)	0.07 (0)	0.90 (87)	5.4 (2)	0.04 (0)
In	0.06 (66)	.05 (96)	0.19 (100)	0.17 (100)	0.20 (100)	0.04 (100)	0.04 (100)	0.04 (100)	0.03 (100)
Sn	nd	nd	nd						
Sb	.005 (0)	.01 (100)	0.06 (58)	0.08 (80)	0.03 (100)	0.007(100)	0.026(92)	0.04 (43)	0.04 (79)
Cs	.005 (0)	.01 (100)	0.02 (100)	0.02 (100)	0.04(67)	0.007(100)	0.015(100)	0.01 (100)	nd
La	0.004 (100)	.05 (0)	0.02 (100)	0.04 (92)	0.02 (100)	0.011(100)	0.046(91)	0.06 (58)	0.14 (100)
Ce	nd	.09 (21)	0.03 (100)	0.07 (100)	0.03 (100)	0.046(53)	0.154(47)	nd	0.27 (100)
Sm	nd	.01 (20)	nd	nd	0.004 (74)	0.001(100)	0.005(100)	0.006 (56)	0.02 (96)
Eu	nd	0.002 (0)	0.015 (22)	0.01 (0)	nd	0.001(88)	nd	nd	0.002 (89)
Yb	.02 (31)	0.006 (0)	0.008 (0)	0.01 (59)	0.01 (20)	0.023(21)	0.098(32)	0.2 (28)	0.08 (19)
Hf	.02 (26)	0.003 (75)	nd	0.006 (100)	0.008 (2)	0.055(3)	0.008(100)	0.01 (100)	0.02 (100)
Ta	0.03 (0)	0.006 (0)	0.002 (42)	0.04 (73)	0.01 (63)	nd	nd	nd	0.009 (100)
W	0.015 (0)	0.01 (9)	0.08 (0)	0.006 (0)	nd	0.01(100)	nd	0.004 (0)	nd
Au*	nd	0.52 (100)	nd	0.62 (71)	nd	1.31(0)	0.122(0)	0.58 (0)	0.75 (44)
Hg	nd	0.006 (100)	nd	nd	0.003 (100)	0.005(100)	nd	0.03 (0)	nd

* ng/m3
nd - not detected

Figure 5.1 Distribution of chlorine on filters. A is a particle filter. Filters B through E are LiOH treated filters.

Figure 5.2 Distribution of fluorine on filters. It is not possible to analyze for particulate F on fluoropore filters. Filters B through E are LiOH treated filters.

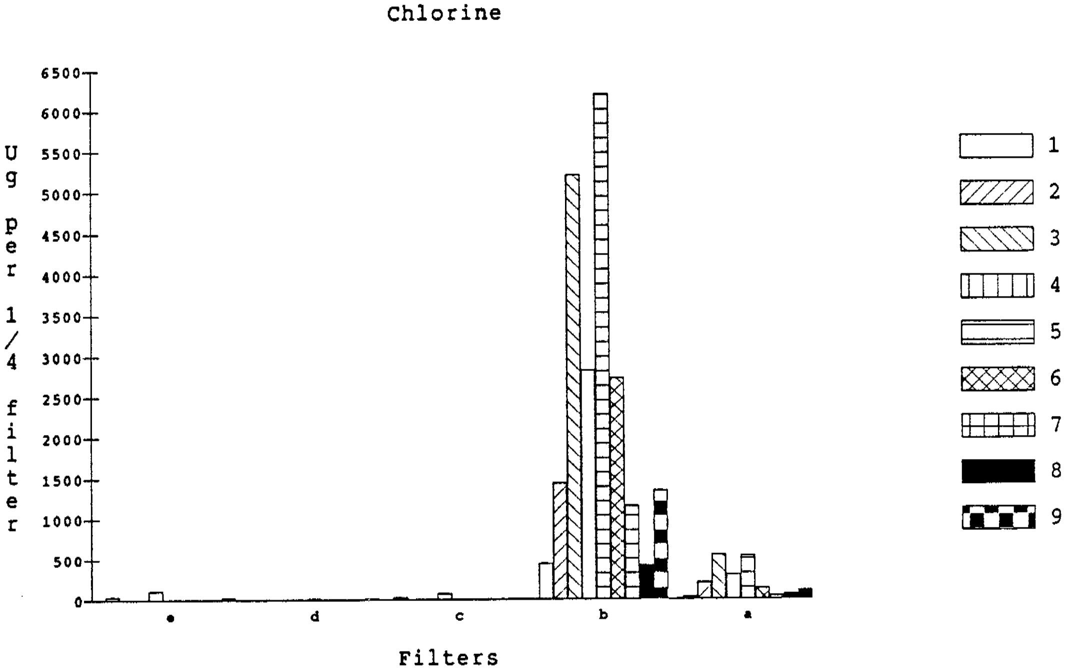


Figure 5.1

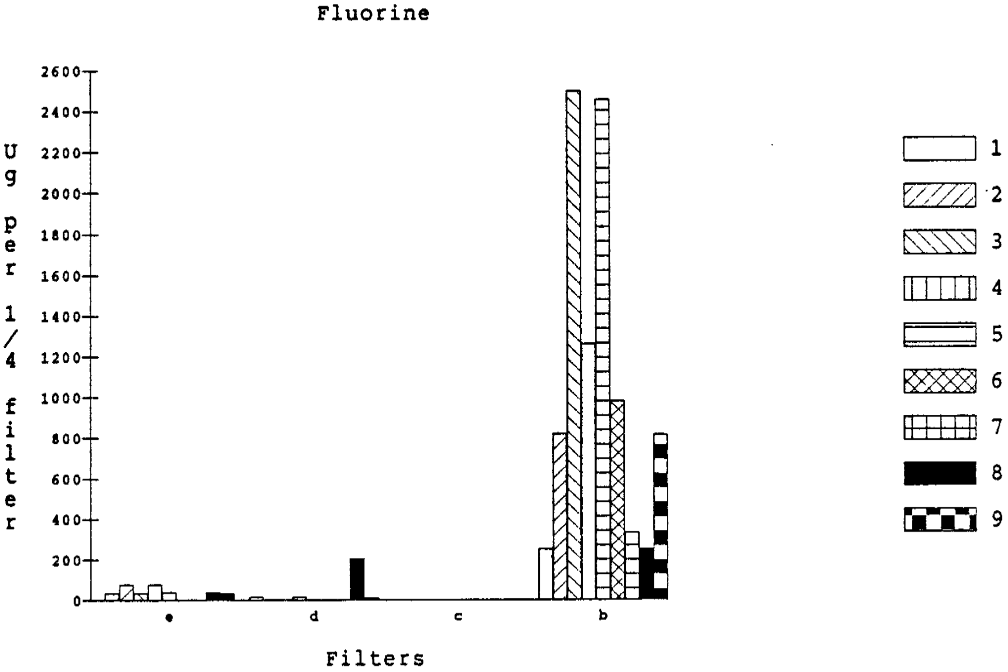


Figure 5.2

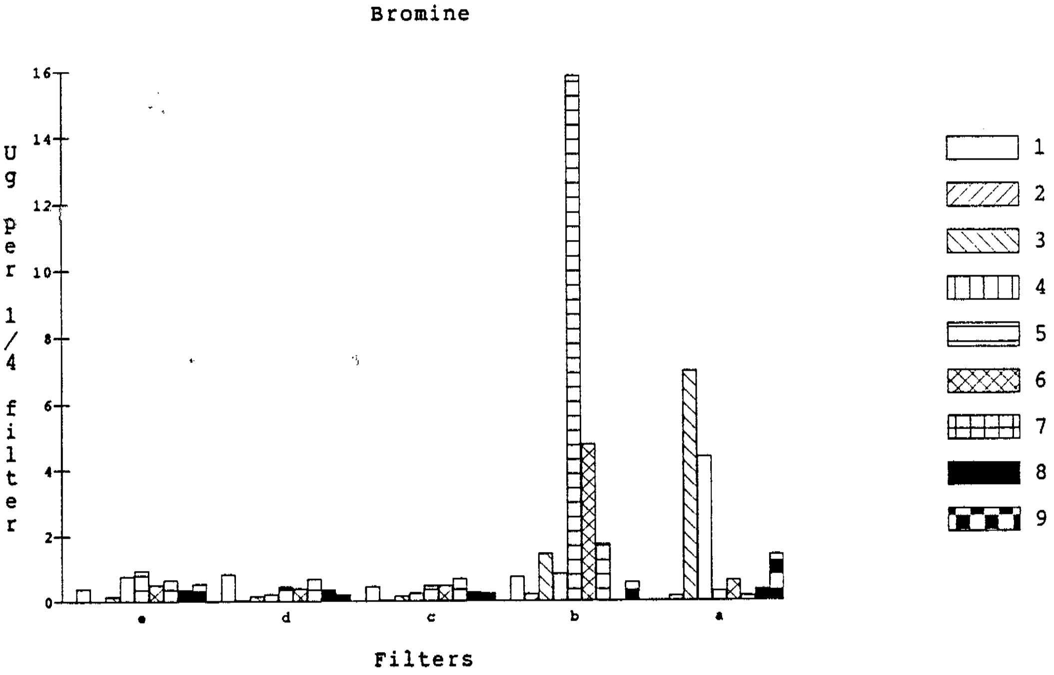


Figure 5.3: Distribution of bromine on filters. A is a particle filter. Filters B through E are LiOH treated filters.

Flux to the atmosphere was calculated for each element by multiplying the element/sulfur ratio by the average discharge of sulfur in tonnes/day (Table 5.4). SO_2 discharge, as measured by the COSPEC is assumed to represent minimum estimates of sulfur emission from Erebus (Chapter 3).

Table 5.4: Flux of volatile elements in tonnes/day unless indicated otherwise during December 20-23. This is based on an average SO_2 flux of 20 tonnes/day. Error in the ion chromatograph analysis of sulfur from filter packs varied between 10 and 20 percent on Dec 20,21 and 22.

Volatile Element Flux from Erebus

Element	Dec 20	Dec 21	Dec 22	Average	Std Dev
F	44.300	38.500	36.30	39.70	4.10
Na	7.700	7.700	4.90	6.80	1.60
Cl	104.000	104.000	105.00	104.00	0.70
K	5.800	7.800	4.20	5.90	1.80
Cu	0.260		0.13	0.20	0.09
Zn	0.185	0.175	0.40	0.25	0.12
As	0.122	0.090	0.06	0.09	0.03
Se*	2.000	2.000	8.00	4.00	3.00
Br	0.180	0.280	0.26	0.24	0.05
Rb	0.042	0.050	0.03	0.04	0.01
Mo*		1.000	10.00	5.00	6.00
In*	11.000	10.000	6.00	9.00	3.00
Sb*	4.300	2.000	1.00	2.00	2.00
Cs*	1.000	2.000	1.00	1.00	0.70
Ce*	5.000	2.000	7.00	5.00	2.00
Eu*	0.800		0.20	0.60	0.40
W*	3.000		2.00	2.00	1.00
Au*	0.040		0.20	0.10	0.10
Hg*		0.200	0.80	0.50	0.40

* kg/day

Enrichment Factors

Enrichment factors were calculated for each sample using the μg/filter data listed in Appendix A-4, and are presented in Table 5.5. Enrichments were calculated with respect to Erebus phonolite magma or crustal averages where analytical data on the phonolite were lacking (Table 5.6). The use of average crustal values may slightly skew EF's.

The influence of ash on the EF's was examined by comparing Al versus Br normalized values on two days. December 20 is more representative of Erebus aerosols and is low in ash, whereas December 24 is relatively ash rich (Figure 5.4). On December 24, EF's normalized to Al are lower than those normalized to Br by several orders of magnitude whereas on December 20 the difference between Br and Al normalized EF's is less than 1 order of magnitude. EF's calculated using Al normalization are minimized in ashier samples (December 24) so Br normalization is necessary for some volcanoes where ash is predominant. Erebus has sufficiently low ash emissions on most days to consider normalizing EF's to Al.

Table 5.5 Enrichment Factors (EF's) tabulated for nine samples. EF's are calculated by normalizing elements to the reference element bromine and the source rocks presented in Table 5.6.

Enrichment Factors
Bromine normalized EF's * 10^5

Element	1	2	3	4	5	6	7	8	9	Geom. Mean	Std. Dev
F	17000	28169	47411	35089	23063	24172	71151	59360	47757	35501	18322
Na	86.7	196	249	234	156	111	136	281	403	185	98
Al	6.61	24.3	6.1	21	5	10.6	30.9	44.2	264	19	78
S	10190	7705	72290	80020	49320	45700	6855	34040	15520	24921	26384
Cl	56619	86518	164507	131172	95532	107528	77919	88549	126825	99433	30685
K	137	247	375	241	264	156	167	322	305	233	76
Ca			95.8	140		88.1	159	522	435	187	188
Sc	59.2	70.3	30.3	97.4		49.6	108	220	847	103	273
V	32.7	0.806	15.7	4.7			31.8	70.2		69	137
Cr	2336	324.9	60.4	115	119	22.9	301	311	1601	1276	4412
Mn	1.68	14.3	6.8	9.8	2.5	2.9	7.3	14.5	64.4	8	18
Fe	136	174	32	75.3	23.5	53	115	252	575	102	162
Co	15361					383.2	912	67456	222	2405	29004
Cu	80.3		8740	10315		3467		39.3		4218	20321
Zn	3155	6347	7266	3495	3182	8168	11185	13977	14771	4130	4242
As	3495	50237	68552	63253	30982	22962	24564	39386	52444	31133	19879
Se	234	34	95.8	49.3	45	162			145	88	74
Rb		780	833	722	558	329		823		643	196
Mo					78.8	931	8888	91423	1010	2269	39827
In	119898	175233	234375	196461	149321	81223	68602	112736	137441	132364	53739
Sb	2079	9070	15104	19211	5057	3130	8368	20057	32197	9190	9856
Cs	531	1289	1570	1390	1587	789	1217	1962		1206	456
La	4.1	84.3	10	24.2	8.3	11.9	36.2	77.6	262	26	82
Ce		595	64.2	151	42.6	181	436		1861	232	643
Sm		98.6			10.5	11.8	28.8	67.2	249	43	91
Eu		326	784	661		69.7			395	341	282
Yb	671	392	192	220	136	984	3035	10625	5988	870	3617
Hf	122	46.1		23.9	22.7	454	47.7	101	328	83	160
Ta	334	118	10.9	234	43.3				191	97	122
W	1924	3089	6503	450		1455		728		1625	2237
Au		8257		3105		12916	867	7015	12944	5445	4961
Hg		26413			2756	15391		112449		18840	49746

Table 5.6 Concentrations of elements in Erebus phonolite lava and glass, source rock for aerosol enrichment values. Crustal average concentrations are used where phonolite data is lacking.

Sources for EF(magma) Values

Element	ppm	Source	:Key
F	2140	Bg	:Bg = Erebus glass (Bigelow, 1984)
Na	63275	Bwr	:Mg = Erebus glass (Meeker, this study)
Al	106000	Bwr	:Bwr = Erebus whole rock and lava (Bigelow, 1984)
S	260	Bwr	;Mwr = Erebus whole rock and lava (Moore, 1986)
Cl	1400	Bg	;Tc = crustal average (Taylor, 1964)
K	37935	Bwr	:Gg = Erebus glass (Germani, 1980)
Ca	19011	Bwr	:
Sc	3.52	Bg	:
V	25	Mwr	:
Cr	14	Mrw	:
Mn	10068	Bwr	:
Fe	29099	Bwr	:
Co	2.36	Mg	:
Cu	13	Mwr	:
Zn	115	Mwr	:
As	3.6	Mg	:
Se	1.4	Gg	:
Br	3.57	Mg	:
Rb	109	Bwr	:
Mo	16.2	Kg	:
In	0.1	Tc	:
Sb	0.5	Bg	:
Cs	2	Mg	:
La	207.6	Mg	:
Ce	57.3	Mg	:
Sm	26	Mg	:
Eu	2.4	Mg	:
Yb	5.25	Mg	:
Hf	27.4	Mg	:
Ta	18.1	Mg	:
W	1.5	Tc	:
Au	0.023	Mg	:
Hg	0.08	Tc	:

Figure 5.4 Comparison of bromine versus aluminum normalized EF's on December 20 (a) and December 24 (b). The sample on December 24 was the was the only sample with significant ash.

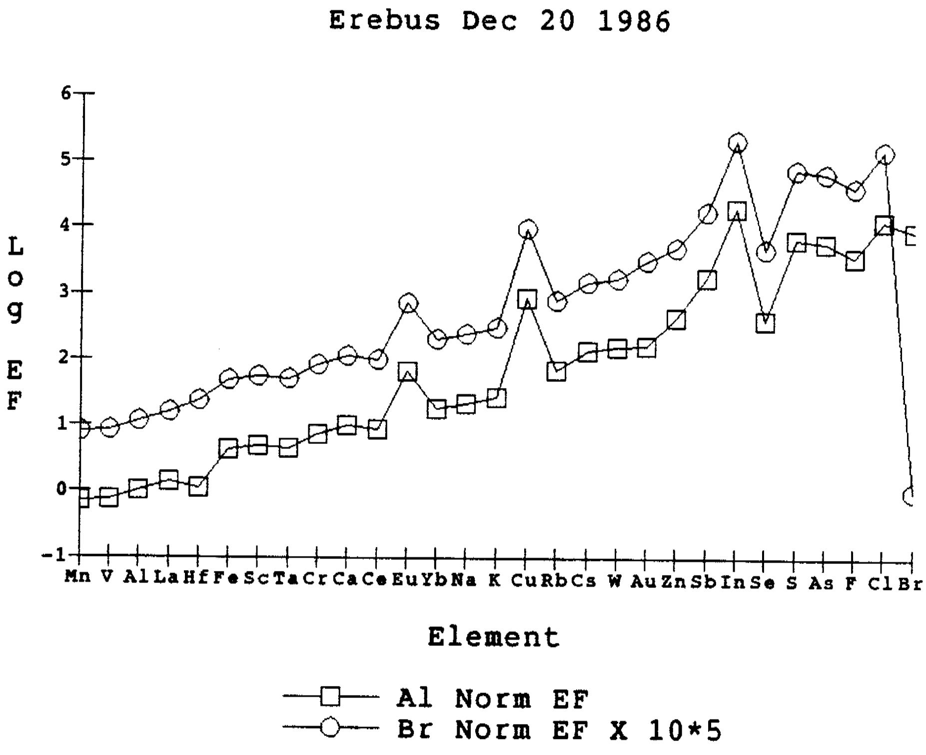


Figure 5.4a

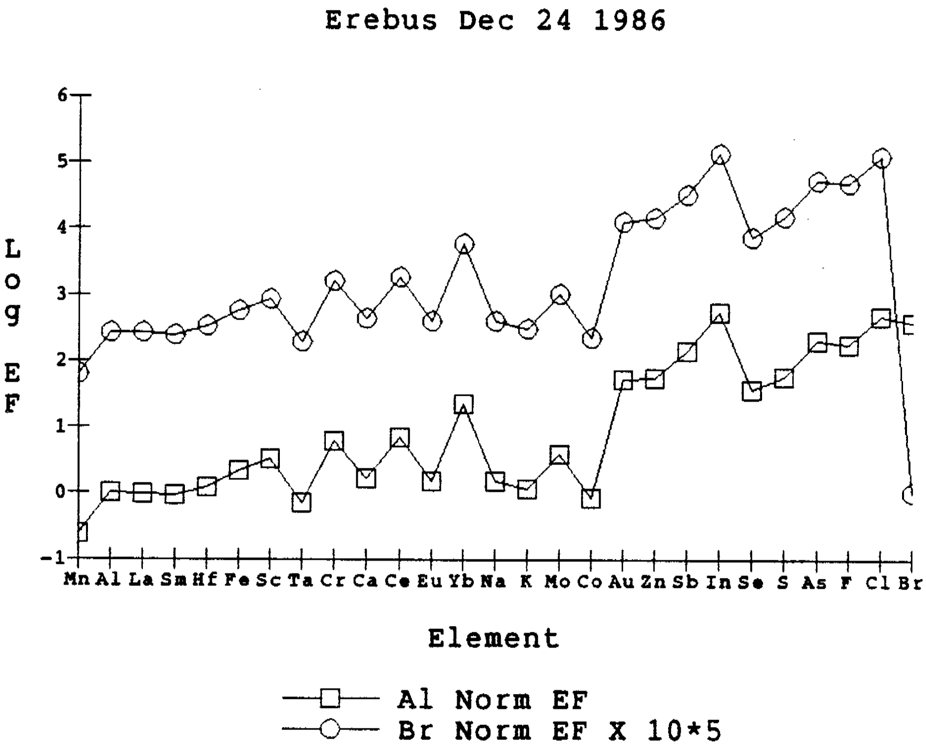


Figure 5.4b

Discussion

Particulate versus gaseous deposition

Erebus shows some unexpected variations in the percentage of ash constituents and volatiles on the particle versus treated filters (Table 5.3). The variable percentage of some less volatile elements on particle filters is best explained by contamination or variability of the blank filters. There is evidence from volcanic plume studies for volatization of Eu, Ce and Yb (Germani, 1980; Varekamp et al., 1986), and Cr and Co (Buat-Menard and Arnold, 1978; Zoller et al., 1984), however these elements were all collected on particle filters.

Gold, Zn, Se, W and Mo appear on both particle and treated filters. On days with consecutive short and long sampling periods (Dec 19,20,24), the particulate percentage increases for some metals and decreases for others. There are also large variations in the concentration per volume for some elements (Se, S, Au) which is in part due to variable plume density. Several things may cause the variable concentrations on treated vs particle filters. Over periods of 3-5 hours the LiOH treated filters may become neutralized and lose efficiency for collecting the less acidic species. If this occurred, the particle filter may have become preferentially enriched in the components relative to the treated filters. It is also possible for acid gases to scavenge elements which coat particles on the particle filter and deposit them onto the treated filter. This would effectively lower the percentage of an element on the particle filter relative to the treated filters.

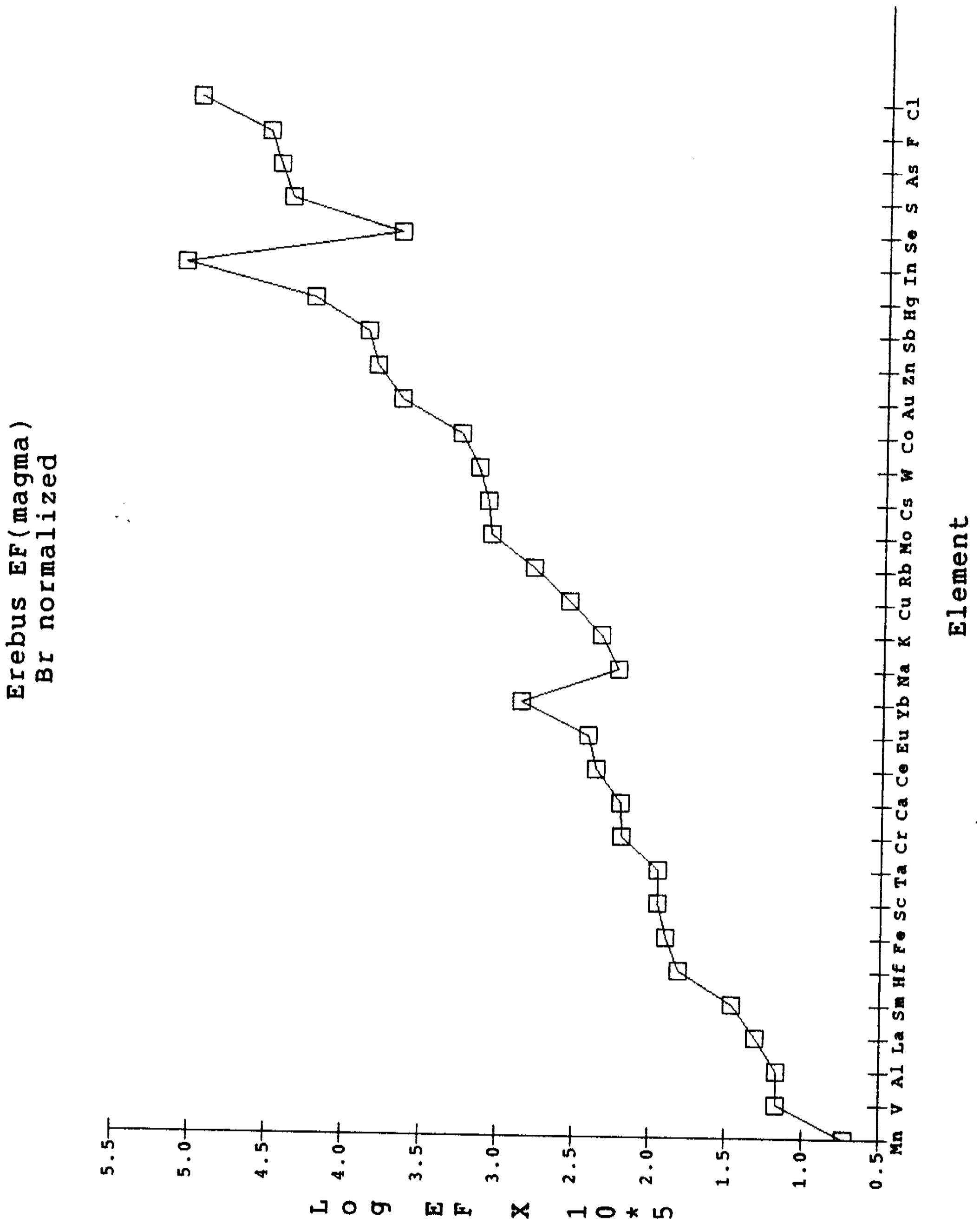
Enrichment Factors

The geometric mean of the nine determined enrichment factors (EF's) are plotted in Figure 5.5. Enrichment of F, Cl, Na, K, Rb, Cs, As, In, Hg, Sb, Zn, Au, Mo, W and Cu has been seen previously at Erebus (Germani, 1980) and in many other volcanic systems (Buat-Menard and Arnold, 1978; Finnegan, 1984; Olmez et al.,1986; Lepel et al., 1978) consistent with the theory that volatilization as halides and possibly sulfur compounds and elemental phases is occurring. Exact speciation of these compounds remains unclear.

Erebus gases in particular are enriched in In, Cl, F, Na, K (varying between 10^2 and 10^5) and possibly some rare earth elements. The anomalous REE EF's partly reflect the high concentration of these elements in the highly evolved Erebus magma. Similarly, emissions show abnormally low enrichment in S and Se consistent with the low emission rates of SO_2.

Correlation matrices and scatter plots clearly differentiate between ash constituents and volatiles. In Figure 5.6 it is clear that the EF of most ash constituents vary systematically as a function of time and ash in the plume. Aluminum is a common ash component but could be volatilized as fluoride (AlF_3) or chloride ($AlCl_3$) compounds (Varekamp, 1986; Rose, 1987) and Al is associated with fluoro-salts along the Erebus crater rim (Keys, 1980). Statistical studies however (Bergametti et al., 1983; Quisefit et al., 1987) indicate that Al, Si,Fe,Ca and Ti enrichment in the plume result from ash or wall rock interaction

Figure 5.5 Geometric mean of bromine normalized EF's to Erebus magma, calculated from data collected at Erebus on nine filter sets during December, 1986.

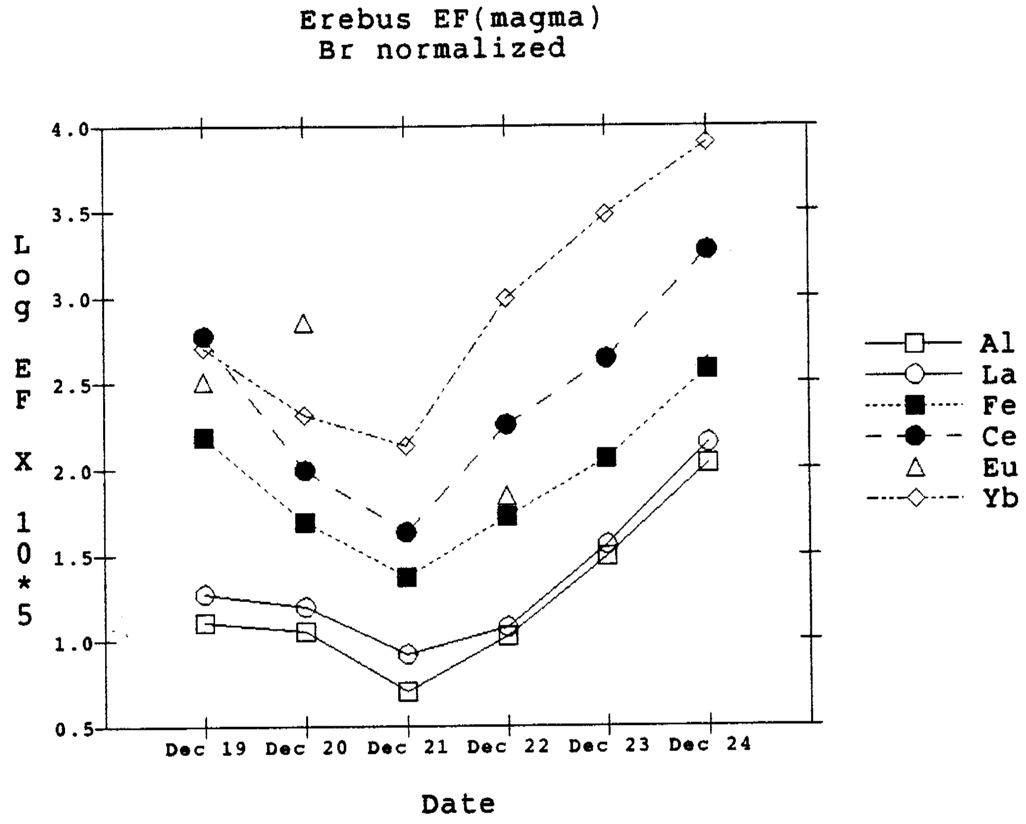


rather than from high temperature gas-gas processes. Thermodynamic models (Symonds et al., 1987) also indicate that particle-gas rather than gas-gas reactions are responsible for Al-rich salts.

The Erebus data show no evidence for Al volatilization. Aluminum shows no linear correlation on scatter plots with volatile halides. The average Al EF is close to unity (Figure 5.5) indicating that it is not varying greatly from the magma. Volatile AlF_3 may be partially responsible for Al-F salts formed close to the lava lake but salts collected on the crater rim and particles in the upper plume are probably the result of fluoro-metasomatism due to the interaction of a F-rich gas with the wallrock and ash.

Some filter samples show an apparent enrichment of the rare earth element Eu (Figure 5.6). Volatile enrichment of REE's is rarely identified in volcanic systems (Germani, 1980, Varekamp et al., 1986). Germani (1980) attributed Ce volatilization at Erebus to specific fluoride ($CeF_4 \bullet H_2O$, M.P.= 650°C) or chloride ($CeCl_3$. M.P.= 848°C) compounds both of which could be volatilized at the temperature of the lava lake (1000°C). However as Germani used crust to calculate the EF, it may simply reflect the enriched nature of the magma, relative to average crust. Anorthoclase feldspars are typically enriched in Eu over other REE's and the Erebus feldspars show similar Eu enrichment (Kyle, 1977). Therefore relict feldspars on the filters could account for high Eu EF's in some samples.

Figure 5.6 Variation of ash EF's with time. Al varies similarly with other ash constituents indicating that it is not being volatilized.



Alkali enrichments increase with increasing molecular weight and decreasing boiling point consistent with observations made by Finnegan (1984) and Olmez _et al._ (1986). At Erebus, alkalies correlate (R> 0.9) with most volatile metals and halides. The EF's for Cs, K and Na in particular increase with increased chlorine EF's on December 20 (Figure 5.7) suggesting they are scavenged out of the magma by Cl-rich gases.

The average Na/K ratio (1.36) of the plume is less than in Erebus magma (1.67). This may indicate that K is more readily vaporized from the magma. However, Na is more soluble in the vapor phase than K (Sakuyama and Kushiro, 1979) and in fact the Na/K ratio increases slightly on December 20 in conjunction with increased Cl, S and volatile metals (Figure 5.8). Perhaps some K enrichment can be attributed to fluoro-metasomatism and leaching of K from the wall rock.

Figure 5.7 Variation of Na, K, Rb and Cs EF's over time compared to Cl EF's.

Figure 5.8 Variation of Na/K ratio over time.

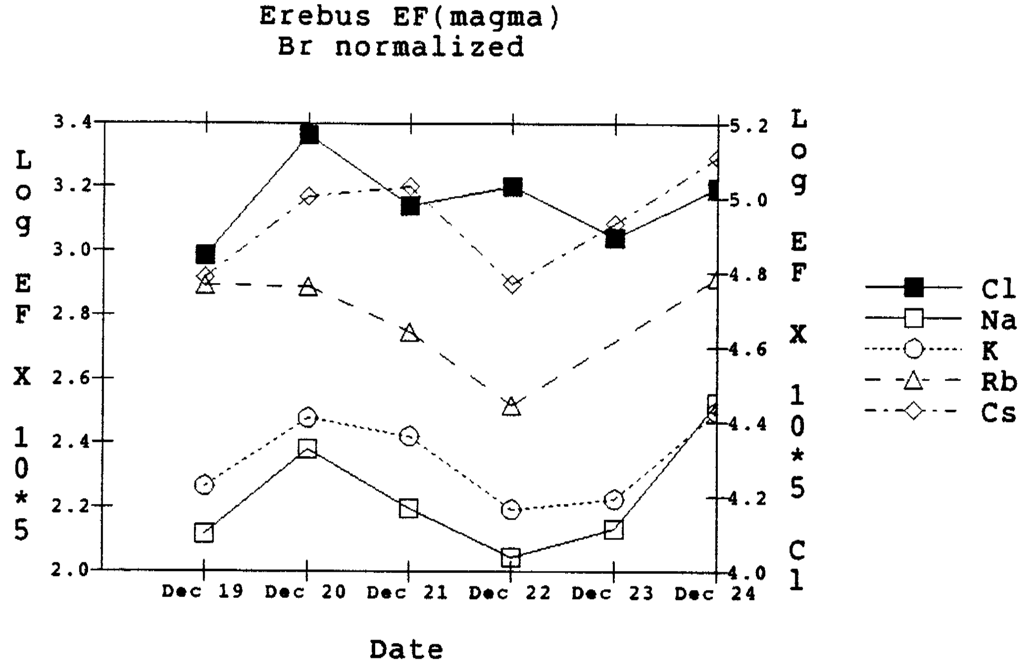


Figure 5.7

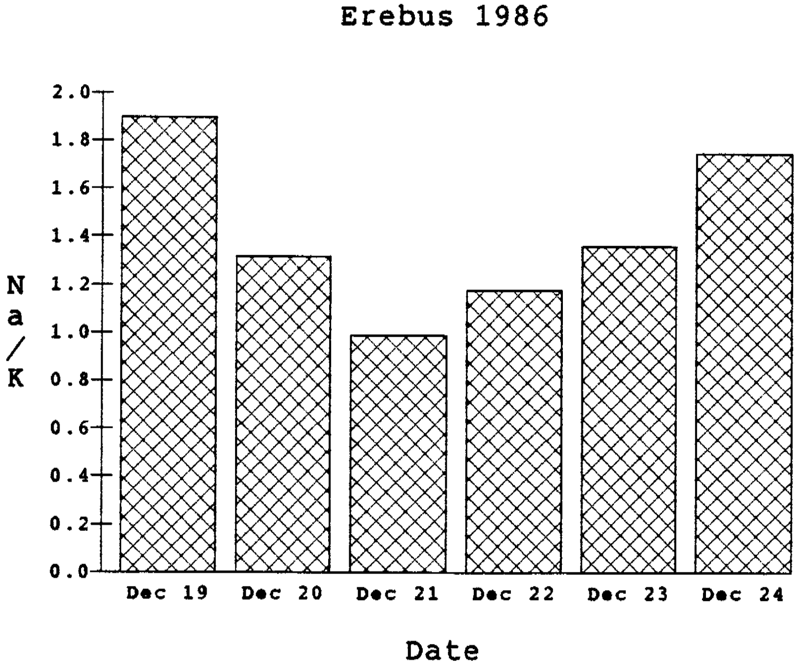


Figure 5.8

Metal Transport from the Magma

Associations between metals and acidic gases were determined by correlation diagrams in order to study possible transporting agents. In general, the halides, particularly Cl and Br correlate (R>0.8) with As, In, alkalies and possibly Eu. They correlate less well (R>0.7) with Sb, Zn and S. These metal-halide associations are consistent with studies by Krauskopf (1964) Naughton (1974) and Gemmell (1987) which attribute metal transport to halides particularly Cl and Br.

The remarkably high In EF in Figure 5.5 is difficult to explain at this time since no In was detected in the Erebus phonolite. Indium is certainly enriched with respect to average crust, and variations with time of In EF's closely parallel those for As and Cl (Figure 5.9). The vaporization temperature of $InCl_2$ (560^oC) is relatively low ($ZnCl_2$ vaporizes at 732^oC), good evidence that In is probably transported out of the magma as a halide.

A second association between Au and Cl was noted on QCM samples but was not confirmed by filter analysis. In fact Au showed no systematic trends except for a moderate correlation with Se, S and Zn. On time variation diagrams (Figure 5.10), the EF's for these elements are compared and one can see that Au parallels most closely with Se. Au was observed to be similarly random at Kilauea (T. Miller, pers. comm., 1988).

Zinc was commonly associated with sulfur on QCM samples and likewise Zn is the least well correlated with Cl. In Figure 5.10 it parallels Se indicating that it may be associated with S and Se. Mizutani (1970) suggested that vaporization of Zn chlorides was followed by a reaction with H_2S to form sulfides. This may explain why Zn is only moderately correlated with both S and Cl on the filter packs.

Figure 5.9 (overleaf) Variation of Zn, Sb, In, As Cl and F EF's over time.

Figure 5.10 (overleaf) Variation of Au, S, Se, Cl and Zn EF's over time. Au and Se are below detection limits on Dec 21 and Dec 23 respectively.

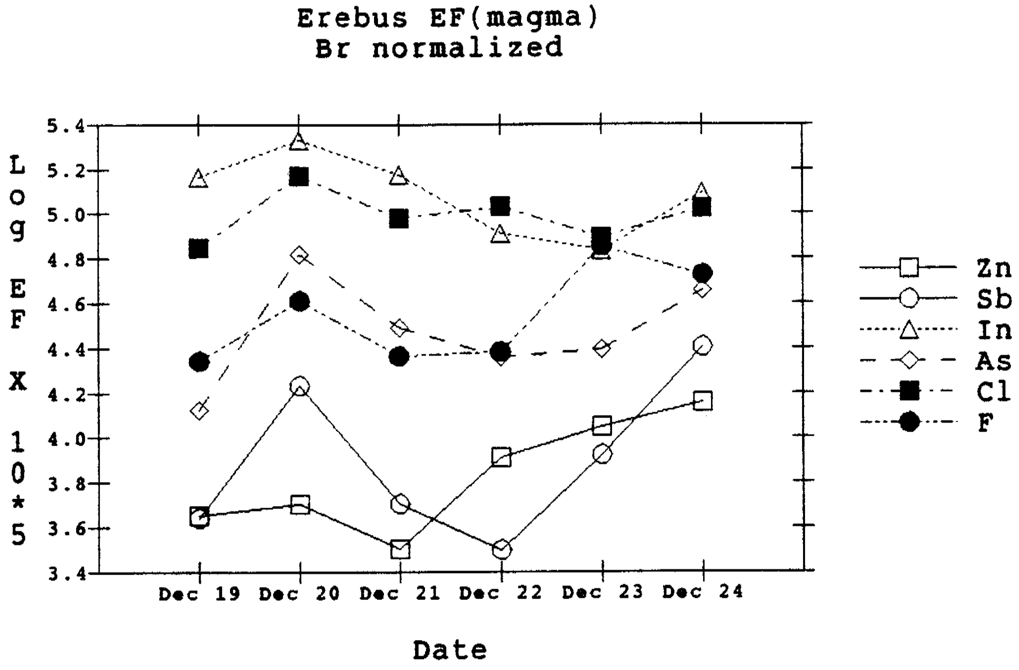


Figure 5.9

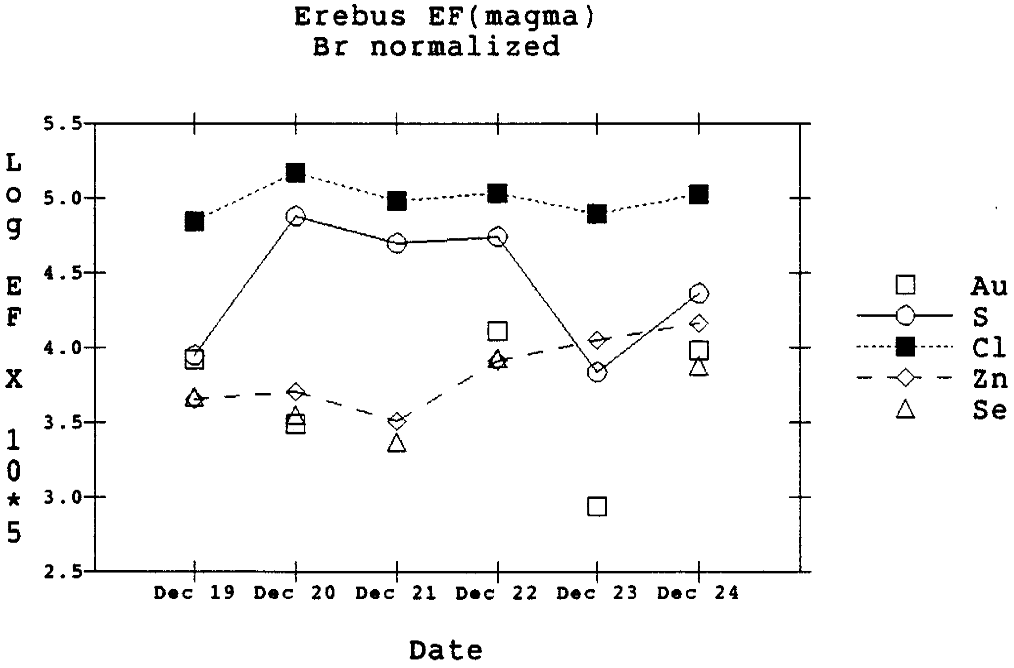


Figure 5.10

Trends in Halogen and Sulfur Ratios

F/Cl and S/Cl ratios have been used to fingerprint magma sources and to monitor magma activity. Fluorine concentrations are lower limits because F was not analyzed on the particle filter. Based on the average particulate Cl we assumed particulate F to be less than 10 percent. The F/Cl ratio at Erebus varies from 0.34 to 1.40 with an average of 0.61. This is less than the average F/Cl in Erebus magma (1.53) and is probably due to fluorine's smaller anionic size which more readily partitions into silicate melts (Holloway, 1981) and is less readily exsolved from the magma than Cl and S.

Erebus's F/Cl ratio is in contrast to the Central American volcanoes (Stoiber and Rose, 1973,1974) and Mount St. Helens, El Chichon and Poas volcanoes (Finnegan, 1984) where the F/Cl ratio is 0.01-0.05. Schilling et al. (1980) suggest that a F/Cl ratio greater than 1 is associated with a deep seated mantle derived magma. A high concentration of the less compatible F is also indicative of a highly evolved magma. The high F/Cl ratio at Erebus compares well with high fluorine systems such as Kilauea (Olmez et al., 1978; Zoller et al., 1983, Crowe et al., 1987) and Heimay Iceland (Mroz and Zoller, 1975; Oskarsson, 1980,81) and is further evidence that the anorthoclase phonolite has evolved from a mantle derived basanite parental magma (Kyle et al., in press).

The F/Cl ratio (Figure 5.11) averages about 0.45 until December 23 when it increases sharply to 1.4. The only metal that shows a similar rise on this date is Zn (Figure 5.10, 5.11). Both

Zn and F seem to be precusors of the general increase in volatile activity which occurs on December 23 and 24. Thomas et al. (1982) suggest that volatilization of Zn may be a precursor to eruptive activity at Mt. St. Helens and perhaps increased F and Zn EF's at Erebus similarly signal renewed activity. F-rich spikes in enrichment data are also seen at Kilauea (B. Crowe, pers. comm., 1988) and likewise seem to reflect slight inhomogeneities or pockets of volatiles in the magma.

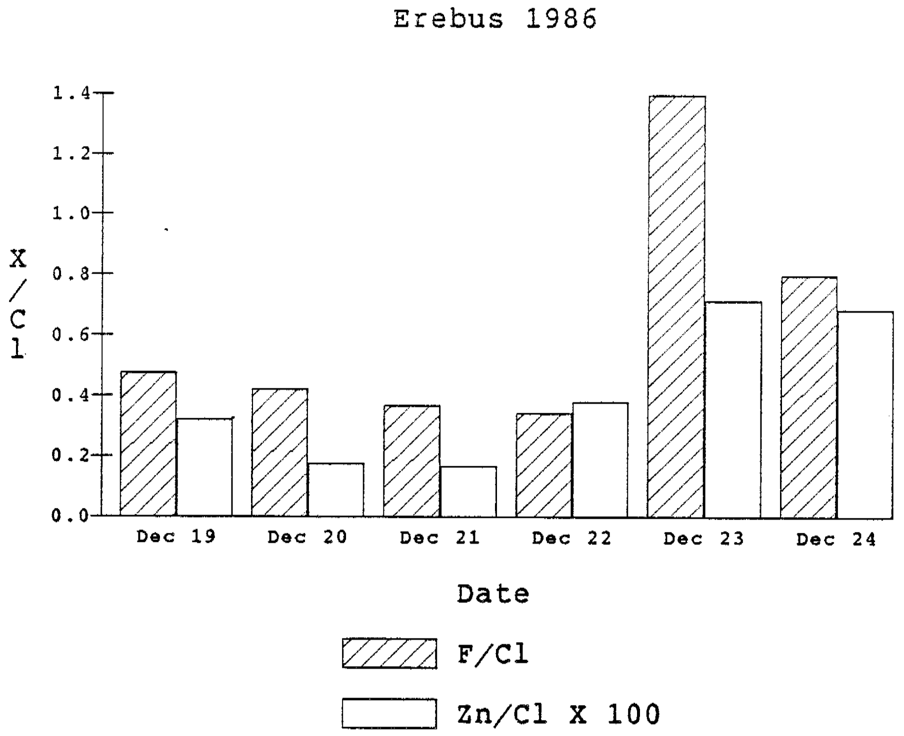


Figure 5.11 Variations in the Zn/Cl vs F/Cl ratio between December 19 and 24.

The S/Cl ratio varies from .016 to .11 with an average of .037 (Figure 5.12). These ratios are much lower than Kilauea S/Cl ratios (3-125) (Crowe et al., 1987), being more equivalent to S/Cl ratios found in Central American gases which vary around one (Stoiber and Rose, 1970). Unlike Central America however, Erebus ratios reflect the low S content of the magma.

An abrupt increase in the S/Cl ratio beginning Dec 20 parallels an increase in Cl, F, As and metal activity on the same day. Plotting these elements with respect to Br (Figure 5.13, 5.14), it is evident that S remains high until Dec 22 whereas Cl drops perceptively but remains fairly constant after Dec 20. Fluorine, Sb, As and In appear to decrease and increase again by Dec 24. Though quite subtle and possibly variable within the error, there is certainly a trend which may indicate two pulses of activity, one around Dec 20, the other around Dec 24.

Figure 5.12: (overleaf) Variations in the S/Cl ratio between Dec 19 and 24.

Figure 5.13: (overleaf) Variations in F/Br, Cl/Br and S/Br between December 19 and 24.

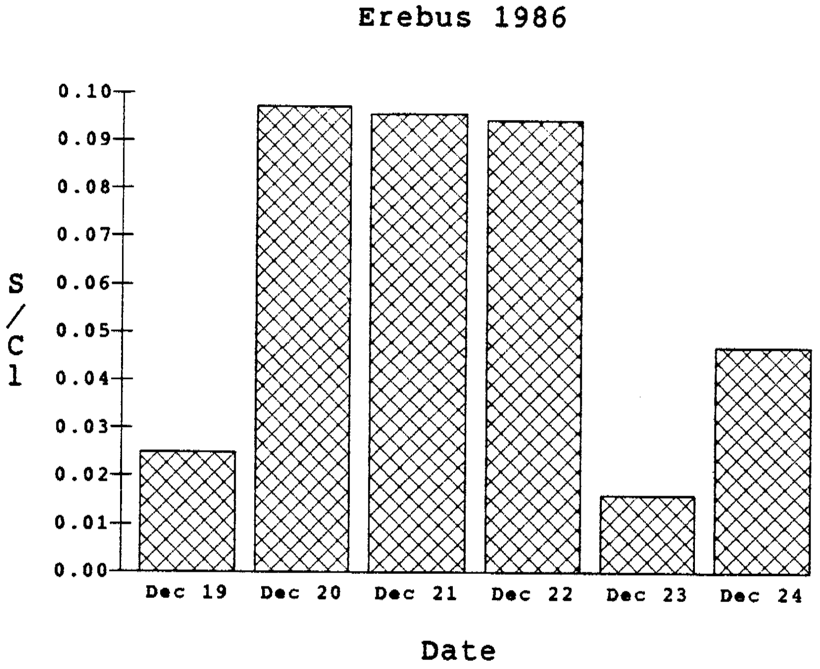


Figure 5.12

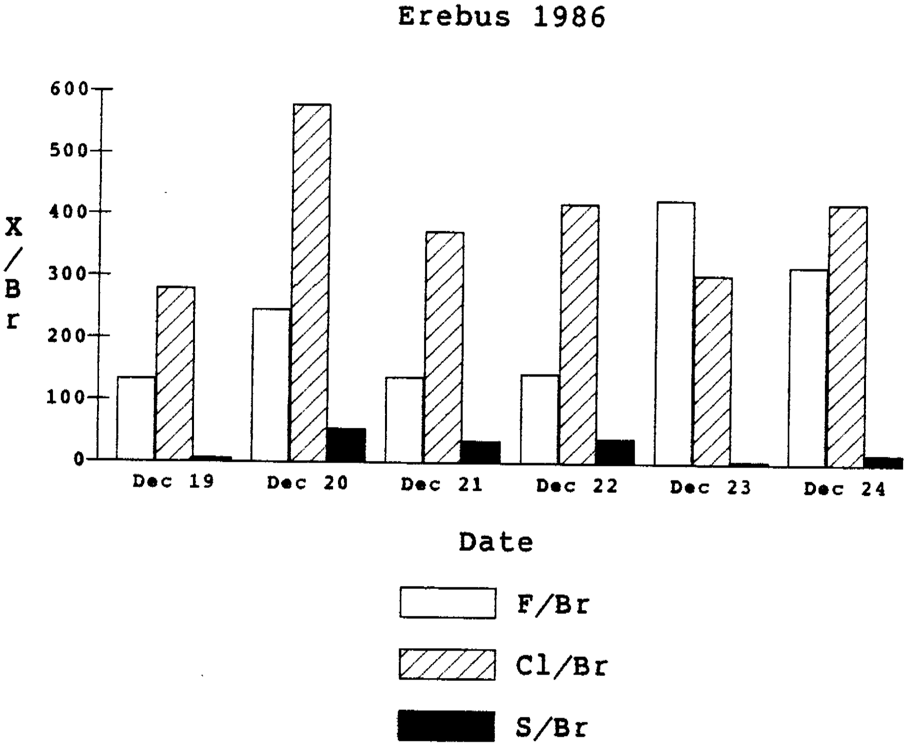


Figure 5.13

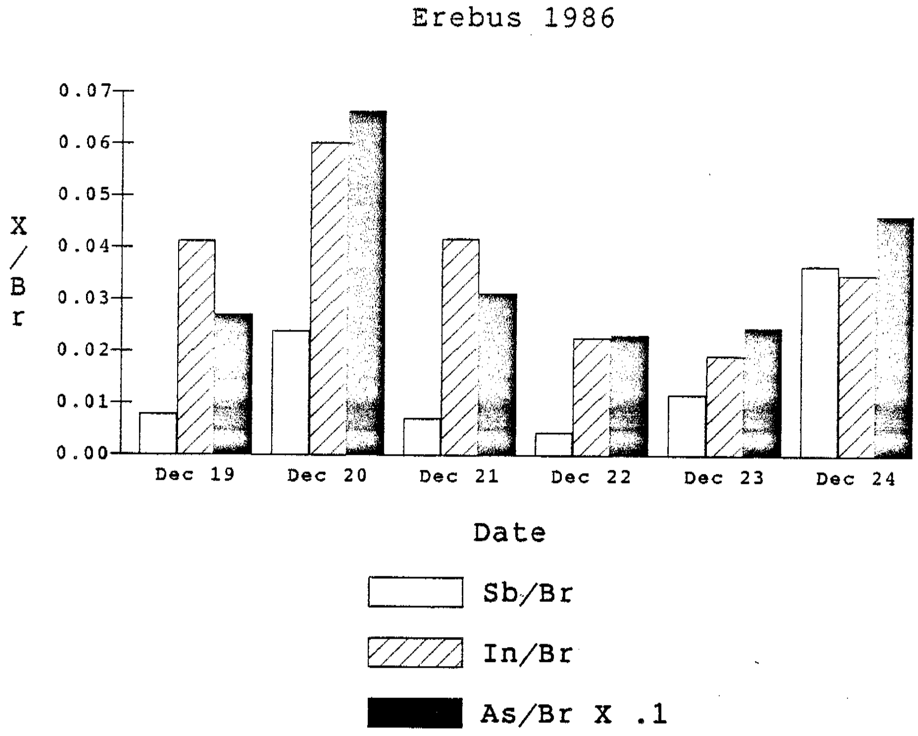


Figure 5.14: Variations in Sb/Br, In/Br and As/Br (normalized by .1) between December 19 and 24.

The S/Cl ratio is an interesting chemical signature of volcanic activity but clearly should be used in conjunction with other elements to monitor a degassing magma. Increases in S/Cl have been associated with increased volcanic activity at Kamchatka, USSR (Menyailov, 1976), Central American volcanoes (Stoiber and Rose, 1974,75; Rose, 1977) and White Island, N.Z. (Giggenbach, 1976) whereas decreases in the ratio have been used to signal eruptions at Sakurajima volcano (Hirabayashi et al., 1986) and Kilauea (Naughton et al., 1975). In addition, Stoiber and Williams (1986) noted that the S/Cl ratio increased downwind from the vent indicating that Cl was precipitated more readily out of the plume than S. Clearly, the ratio is a function of sampling location and varies from volcano to volcano, however, the sampling location at Erebus, directly above the lava lake on the crater rim, is probably a good representation of the degassing magma.

There are two possible explanations for varying S/Cl ratios in emissions from a convecting lava lake. The first involves the continuous fractionation during progressive convective overturn of a discrete volume of magma due to different saturation depths of Cl versus S. S and Cl exsolution as a function of P, T, fO_2 and crystallization are complex (Haughton et al., 1974) and beyond the scope of this paper. However exsolution curves derived by Gerlach (1986) and COSPEC data from this study indicate that S is saturated at shallow depths (< 500m) and in fact sulfur exsolution may be surficial in the Erebus lava lake. With the rise of a new batch of magma, S is saturated at a shallow depth.

Chloride, due to its different properties and higher concentration in the magma, may be saturated at a greater depth. Thus a greater volume of magma is degassed in Cl than S. Hence the Cl to S ratio is changing with each overturn and causing inhomogeneities in the magma. It is also possible that the greater Cl content in the Erebus magma makes it less affected by small perturbations in the lava lake. Cl degassing may occur at a constant rate relative to S, causing the S/Cl ratio to vary over time.

A second explanation is based on the assumption that Erebus is not a closed system. The magma volume may be continuously fed by a deeper source. Injection of volatile-rich (less degassed) magma may cause inhomogeneities in the convecting magma chamber. This along with the differential solubilities of Cl, S and F may cause varying degrees of enrichment over time in the aerosols.

In summary the volatile rich pulse seen on Dec 20 may have been caused by convection to the surface of less degassed magma. For two days sulfur, halides and metals showed increased degassing. A sharp increase in F in particular seems to correspond with the waning stage of the first influx and perhaps signals a new influx on December 23 or 24. These variations seem to reflect inhomogeneities in the magma. Smaller variations within this period may reflect the different transport mechanisms and vapor pressures of the metal-halides compounds, as well as reflect analytical errors and inconsistency in sampling.

EF(crust) of Different Volcanic Systems

Relative abundance of anomalously enriched elements (AEE's) can be a signature of magma composition. Mt. Erebus (this study); Mt. Etna, Italy (Andres, 1988); Kilauea, Hawaii (Crowe et al., 1987); Heimay, Iceland (Mroz and Zoller, 1975) and Mt. Augustine, Alaska (Lepel et al., 1978) show different enrichment patterns when normalized to average crustal values (Figure 4.15). Though Kilauea lacks some trace element data, some general trends can be seen.

Kilauea, Heimay, Etna, Augustine and Erebus define a trend from least (Kilauea tholeiitic to alkalic basalt) to most (Erebus phonolite) evolved magmas. Kilauea (Wright and Helz, 1987), Etna (Cristofolini and Romano, 1982) and Erebus (Kyle et al., in press) have evolved from mantle material with minimal crustal interaction. Heimay is generally considered to have had little crustal interaction. Augustine magmas (due to their andesitic composition) (Fisher and Schmincke, 1984) magmas may have evolved through some crustal interaction.

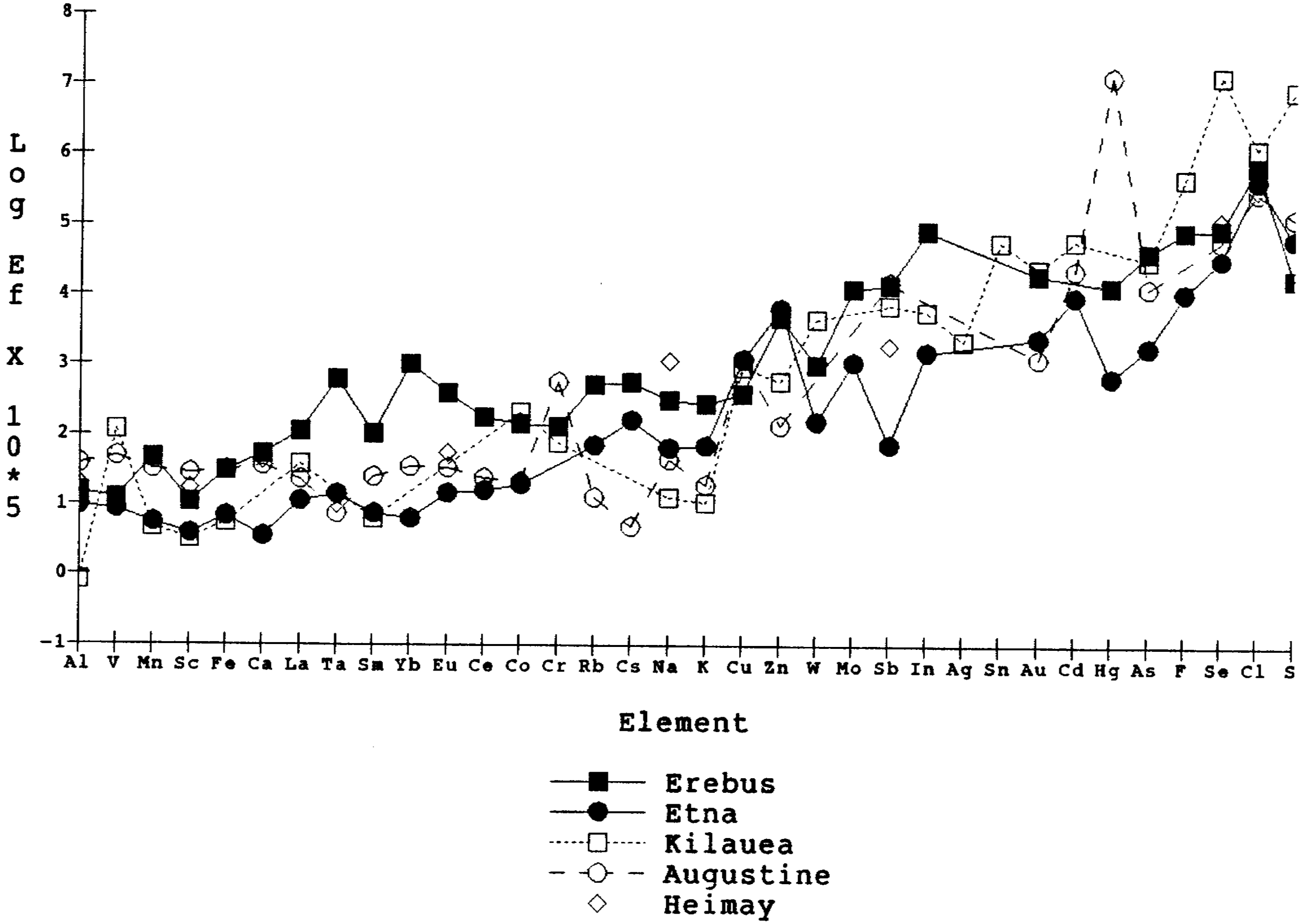
Figure 5.15 indicates that most ash constituents are close to unity except for Erebus which shows anomalously high REE's. Alkalies in general increase from Hawaii, Augustine, Etna, Erebus and Heimay respectively. Volatile metals Zn,Cu,Au and Se show no systematic trends as a function of magma evolution reiterating the idea that their enrichment reflects a complex set of parameters and consistent with Vie le Sage's (1983) observations of these elements for many volcanic systems.

Oskarsson (1981) suggests that volatilization of metal halides may be partly controlled by the Cl/F ratio of the magma. Erebus is highly evolved and shows high EF's for W and Mo. However, Kilauea which is obviously not evolved shows the second highest EF's for these elements indicating that the low Cl/F ratio for Kilauea magma may be conducive to transport of the less compatible elements.

Kilauea shows the highest S and Se consistent with its basaltic composition but it is also most enriched in other volatiles. Platinum group elements Re, Ir and Os which are enriched at Kilauea have been associated with deep seated mantle derived lavas (Zoller et al., 1983) and indicate that Kilauea magma is the least evolved and closest equivalent to mantle sources.

Figure 5.15 (overleaf) Comparison of EF's for five different volcanic systems; Erebus (this study), Mt. Etna (Andres, 1988), Kilauea (Crowe et al., 1987), Augustine (Lepel et al., 1978) and Heimay (Mroz and Zoller, 1975). All elements are normalized to Br and Taylor's (1964) crustal average.

EF(crust for Different Volcanoes
Br normalized



6. ATMOSPHERIC IMPACT OF EREBUS EMISSIONS

Introduction

Volcanic emissions can play an important role in the chemistry of the stratosphere and troposphere. Sulfur is a relatively abundant element which until recently has play an essential and balanced role in the environmental cycle (Kellog et al., 1972; Cullis and Hirschler, 1980). Increasing amounts of anthropogenic sulfur have shifted this balance point and inspired more research to try to quantify natural versus man-made sources. Various estimates of volcanic SO_2 emissions, summarized in Table 5.1, have been made since a global SO_2 flux evaluation was first attempted by Kellog et al. (1972). His estimate of 0.75×10^6 was based on the estimated volume of emitted lavas. With non-eruptive SO_2 measurements the estimates have risen by 1-2 orders of magnitude (Berresheim and Jaeschke, 1983; Rose et al., 1983).

Volcanic halide contributions (Cl, F, Br) are less easily monitored. The rising concern with ozone depletion in the atmosphere has directed research toward studying the role of volcanic halogens in both the troposphere and stratosphere. Fluorine and chlorine emissions vary greatly depending on the volcanic system and eruptive activity. Estimates of global volcanic HCl and HF emissions are included in Table 6.2 along with some estimates of trace element emissions from volcanoes. Included in Table 6.3 are Erebus fluxes for these elements and their percent of total volcanic emissions.

Table 6.1: Annual volcanic SO_2 emissions to the atmosphere.

Annual Volcanic SO2 Emissions to the Atmosphere

Reference	SO2 tonnes/year
Kellog et al., 1972	7.5e+05
Bartels, 1972	3.4e+07
Stoiber and Jepson, 1973	7.0e+06
Naughton et al., 1975	4.7e+07
Cadle, 1975	7.5e+06
Friend et al., 1982	4.0e+06
Le Guern, 1982	1.0e+07
Berresheim and Jaeschke,	1.5e+07
Stiber et al., 1987	1.8e+07
Lambert et al., 1988	5.0e+07

Table 6.2: Annual volcanic trace element emissions to the atmosphere.

Annual Volcanic Trace Element Emissions to the Atmosphere

Element	Reference	Global Flux tonnes/year
Cu	Nriagu, 1979	3.6e+03
	Lambert et al., 1988	1.5e+04
Zn	Nriagu, 1979	7.0e+03
	Lambert et al., 1988	5.0e+03
Na	Lambert et al., 1988	1.9e+05
K	Lambert et al., 1988	2.5e+05
As	Walsh et al., 1979	7.0e+03
Hg	Varekamp/Buseck, 1986	8.3e+02
	Olafsson, 1975	3.6e+00
HCl	Anderson, 1975	3.0e+06
	Cadle, 1975	7.8e+05
HF	Cadle, 1975	4.0e+04

Table 6.3 Comparison of Erebus trace element flux to estimates of volcanic global flux. Erebus flux is tabulated as a percent of the global flux.

Erebus Flux to Atmosphere

Element	Tonnes/ year	% Volcanic Global Flux	Remarks
Cu	7.3e+01	2.0	Nriagu, 1979
		0.5	Lambert et al., 1988
Zn	9.1e+01	1.3	Nriagu, 1979
		1.8	Lambert et al., 1988
Na	2.5e+03	1.3	Lambert et al., 1988
K	2.2e+03	0.9	Lambert et al., 1988
As	3.3e+01	0.5	Walsh et al., 1979
Hg	1.8e-01	0.0	Varekamp and Buseck, 1986
		5.0	Olafsson, 1975
Cl	3.8e+04	1.3	Anderson, 1975
		5.0	Cadle, 1975
F	1.4e+04	37.0	Cadle, 1975

Trace Element Flux from Erebus

From Figure 6.1 it is obvious that halogens are the most significant contribution from Erebus to the atmosphere. However, Cl emissions from Erebus are only 1/3 that emitted by Etna (Figure 6.2) and Etna emits 42 times more S than Erebus. Likewise, other volatile emissions from Erebus are less by factors of 5 to 24. Only As is comparable (Figure 6.3, 6.4). The difference in Au emissions is curious since Au was not observed on QCM samples at Mt. Etna (Andres, 1988). This may indicate that Au is collected as an acidic species at Etna and predominantly as elemental Au at Erebus.

Erebus annual emissions of Cu, Zn, Na, K, As and Cl are 1-2 percent of total global volcanic emissions (Table 6.3). Cl from Erebus is 5% of the global flux estimated by Cadle (1975). However Cadle's estimates are based on the assumption that all volcanic eruption gases contain 1 wt % of HCl and 0.05 wt % HF. Anderson's (1974) estimate of 3.0×10^9 kg/yr Cl for andesite volcanoes is probably closer to reality. If the trace elements from Erebus are 2% of the estimates for global volcanic flux, then only 50 active volcanoes equivalent to Erebus could exceed the global estimates. It is clear that these estimates should be recalculated.

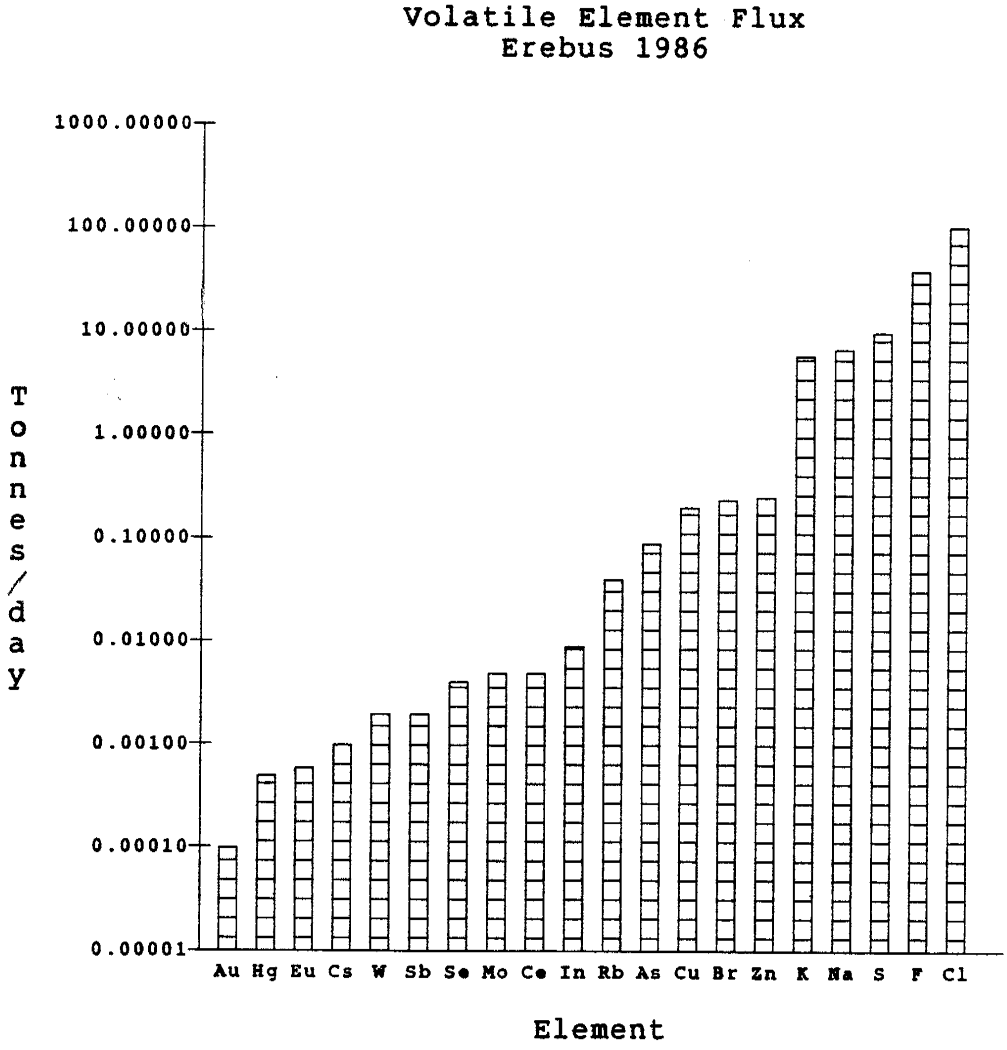


Figure 6.1 Estimated flux for volatile elements from Mount Erebus tabulated as log of tonnes/day.

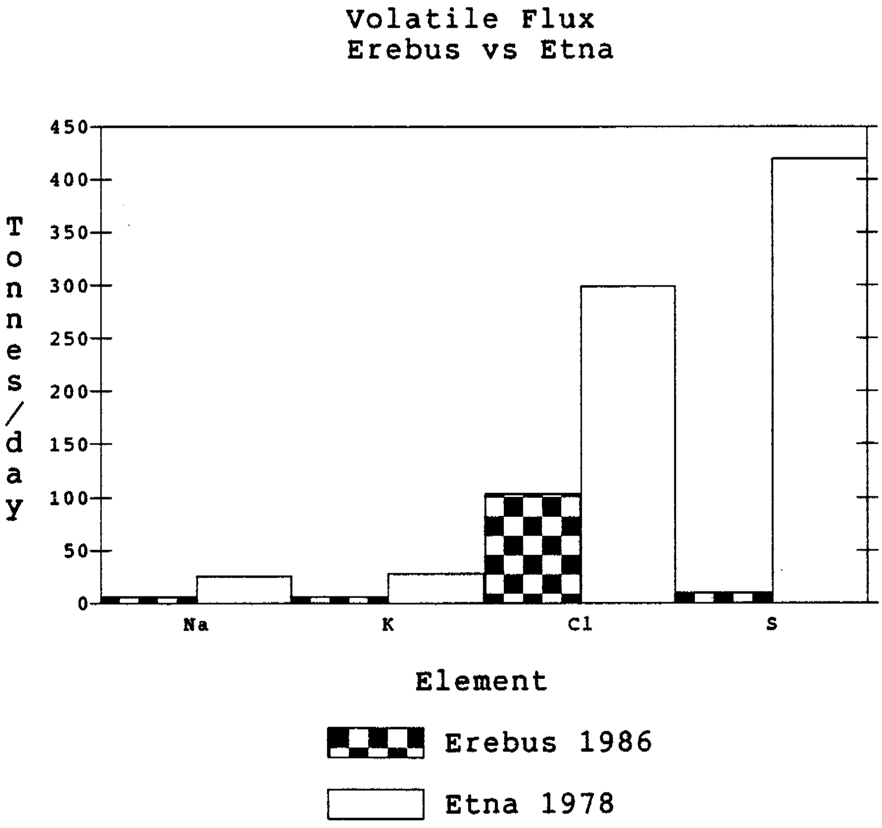


Figure 6.2 Comparison of flux from Erebus and Etna (Buat-Menard and Arnold, 1978) for Na, K, Cl and S.

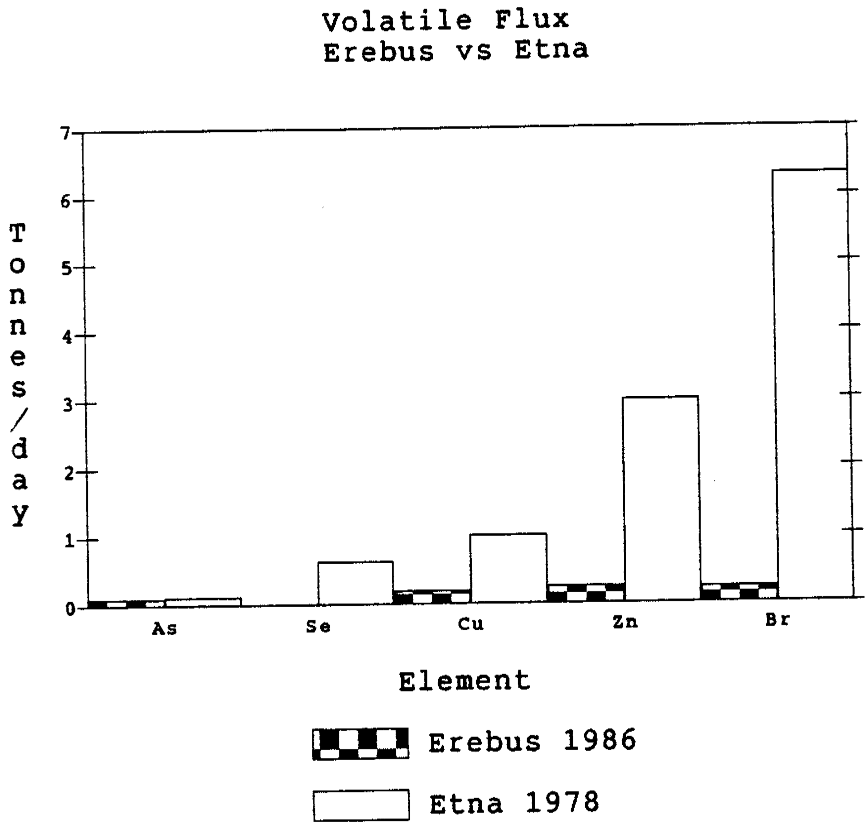


Figure 6.3 Comparison of flux from Erebus and Etna (Buat-Menard and Arnold, 1978) for As, Se, Cu, Zn and Br.

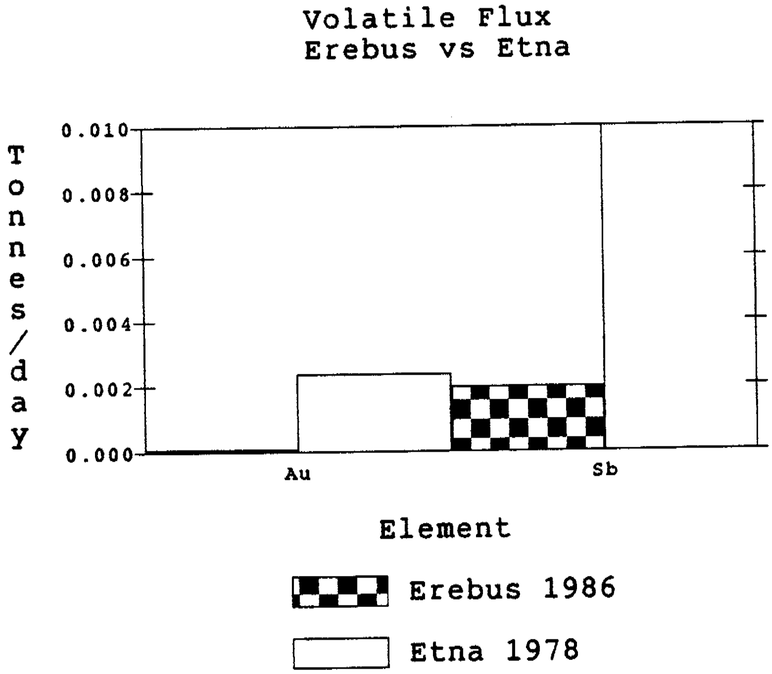


Figure 6.4 Comparison of flux from Erebus and Etna (Buat-Menard and Arnold, 1978) for Au and Sb.

Volcanic Aerosol Distribution in the Antarctic

Erebus's impact on the Antarctic region can be inferred by examining aerosols at the South Pole. (Zoller et al., 1974; Maenhaut et al., 1979). Erebus crustal EF values are plotted with respect to Al to differentiate between crustal weathering sources and actual volatile enrichment, and are compared with crustal EF values from South Pole aerosols (Figure 6.5). Na and K enrichment factors from South Pole aerosols (after correction for the oceanic components) indicate that Erebus does not contribute Na and K to the polar atmosphere. Other alkalies and Eu show similarly low values suggesting that their sources are crustal weathering.

Enrichment in Cl and Br at the South Pole are more difficult to explain. Cl has not been ocean corrected but is already lower than expected for combined oceanic and volcanic contributions. The Cl/Na ratio at the pole is about one half that of seawater consistent with Cl's shorter residence time in the atmosphere (Maenhaut et al., 1979). Br is anomalously high even after correction. Studies by Duce et al. (1973) showed that Br was enriched in South Pole aerosols about 10 fold over the concentration expected from bulk Br/Cl in sea-salt aerosols. The Br/Cl ratio in South Pole aerosols is 700 times that seen in Erebus particles. This suggests that Erebus is not a significant source for Br. Duce et al. (1973) suggested that the Br/Cl ratio approximated Br/Cl ratios seen in the stratosphere and that Br and S could be of stratospheric origin due to subsidence of the tropopause.

Of the trace elements (As, Zn,Sb, Au, Cu, In) enriched in South Pole aerosols, In is uniquely low. Maenhaut et al. (1979) suggest that these elements are evenly distributed around the globe. Erebus emits sufficiently high In to be a source for In at South Pole and perhaps Erebus is the main source. The high EF's for other elements may reflect several sources including Erebus.

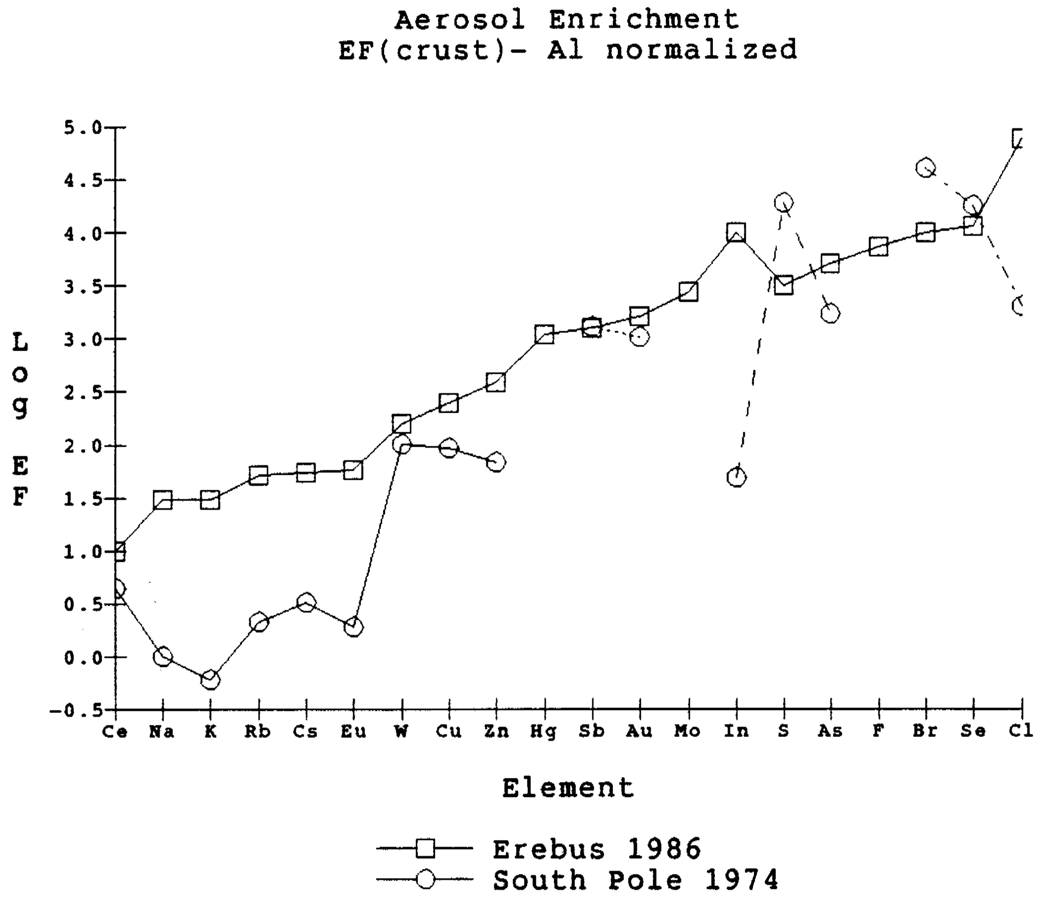


Figure 6.5 Erebus EF's vs aerosol EF's at the South Pole (Maenhaut et al., 1979). All samples are normalized to Al and crustal averages (Taylor, 1964).

The impact of volcanic HCl on the Antarctic atmosphere

The volcanic contribution of HCl to the stratosphere and its significance with respect to ozone depletion has been studied at explosive eruptions such as Mt. Augustine (Johnston, 1980) and others (Lazrus *et al.*, 1979; Cadle, 1980)). A significant downward trend in the antarctic ozone since 1979 (McCormick and Trepte, 1986) has been the subject of much debate. The overriding theory at present is that stratospheric Cl is a possible sink for ozone. Chemical/photochemical reactions involving catalytic cycles with halogen containing free radicals are primarily responsible for its destruction.

Hydrogen chloride (HCl) is the only significant chloride species emitted by volcanoes (Symonds *et al.*, 1988) HCl recycles the catalytically active Cl atom via the reaction (Finlayson-Pitts and Pitts, 1986):

$$HCl + OH \longrightarrow H_2O + Cl$$

The Cl radical initiates a chain of reactions the simplest of which is:

$$Cl + O_3 \longrightarrow ClO + O_2$$

$$ClO + O \longrightarrow Cl + O_2$$

A complete review of these processes is given by Rowland and Molina (1975) and Stolarski and Cicerone (1974). The limiting factor in HCl catalyzed destruction of the ozone is the residence time of HCl in the atmosphere and the necessity of it reaching the stratosphere. Explosive eruptions in which the plume penetrates the tropopause eliminate the need for HCl to diffuse into the stratosphere.

The average contribution of chlorine from Erebus (using an average of 10 tonnes/day S) is 104 tonnes/day, five times more than the average of 20 tonnes/day SO_2. This is a conservative estimate since it does not account for periods with high Cl/S and/or high SO_2 emissions such as Dec 23 when at least 3 times the average Cl was emitted. Assuming no change in the Cl/S ratio, Cl emissions from Erebus could easily reach 700-1000 tonnes/day during periods of stronger volcanic activity. This large deviation over time makes Erebus difficult to compare with other volcanoes such as Santiago Crater, Nicaragua which averages 830 tonnes/day (Stoiber and Williams, 1986) and is to date the largest recorded non-eruptive sustained release of HCl in the world.

Assuming that Na and K are major sinks for Cl in the plume and that Cl does not erupt as NaCl(v), an ion balance was calculated between Na, K and Cl for Dec 21 and for average emissions between Dec 20 and 23. On Dec 21, only 18 % of the Cl could be removed by reaction with Na and K. On average, Na and K could account for 30% of Cl. Even accounting for other metals, at least 50 to 70% of the Cl must be removed as HCl. HCl droplets are rarely seen on the QCM stage from samples collected at the crater rim inferring that HCl remains in the gaseous stage (or $<$ 0.07 size aerosols) at least beyond the crater rim.

In general HCl is not a great concern in the lower atmosphere because of its short residence time, though it is possible that HCl residence time is extended in the antarctic atmosphere. HCl is 300 times more soluble in water than SO_2. A typical lifetime for HCl in the troposphere is 83 hours versus the 1.3×10^3 hours for organic chlorine (Levine, 1985) explaining why anthropogenic chlorofluorocarbons are so much more destructive to the ozone.

This short residence time makes it unlikely that HCl will rise the several kilometers necessary to breach the tropopause. The Erebus plume seldom reaches beyond 2000 m above the rim and is often sheared by winds. Even during the winter with stratospheric subsidence, mixing along the boundary occurs downward due to the inversions created by higher temperatures in the stratosphere. The short life of HCl is further confirmed by polar measurements (Zoller _et al._, 1974; Maenhaut _et al._, 1979) which show that only a fraction of marine and volcanic Cl reaches the South Pole.

However HCl emissions from Erebus are significant and it is possible that during active periods HCl emissions could have a considerable impact on the atmosphere and perhaps effect ozone depletion in the stratosphere. For instance, using the average Cl/S ratio of 10 (± 20%), and the 230 tonnes/day SO_2 emitted in 1983, one could calculate an HCl flux of 900-1400 tonnes/day. At the maximum ratio of about 60, the flux increases to almost 7000 tonnes/day HCl. Obviously, it is unlikely for both the Cl/S and SO_2 emissions to be high, and more measurements are needed to better understand this relationship.

In conclusion, one can not eliminate the possibility that Erebus is playing a role in depletion of the Antarctic ozone. HCl emissions from Erebus should be continuously monitored along with more studies on HCl transport in the Antarctic.

7. CONCLUSIONS

Several important conclusions have been made in this study of volcanic emissions from Mount Erebus. These concern SO_2 emissions over time, volatile transport and enrichment with respect to the magma, and aerosol distribution and impact on the Antarctic atmosphere.

By using the COSPEC to measure short and long term variations in SO_2 flux, we have obtained a reliable and fairly consistent data set over four years. The volcano has emitted 10 to 50 tonnes/day SO_2 since 1984 and is uniquely low in sulfur compared to other volcanic systems for which measurements are available. SO_2 emissions have increased in direct relationship to increased surface area of the lava lake as it is exhumed following the abnormally explosive activity in 1984. The SO_2 flux has displayed subtle two hour periodicities which may reflect the time necessary for convection of new less degassed magma to the surface of the lava lake. SO_2 emissions did not increase during an eruption in 1986 indicating that exsolution and bubble growth from depth did not involve sulfur. The above evidence substantiates the hypothesis (P. Kyle, pers. comm., 1987) that the relationship between surface area and SO_2 emissions reflects a very shallow (almost surficial) exsolution curve (Gerlach, 1986) and a low concentration of sulfur in the magma.

QCM studies along with analyses of particle and treated filters lead to conclusions about vapor transport of trace elements and eventual dispersion within the plume. Enrichment with respect to the magma was seen for the following elements in decreasing order: Cl, In, F, As, S, Hg, Sb, Zn, Au, Se, Co, W, Cs, Mo, Rb, Cu, K and Na. The rare earths Ce and Eu also appear to be slightly enriched.

The high EF of Cl and the high aerosol Cl/S ratio sets Erebus apart from other volcanoes. Cl is strongly correlated with increased enrichment for most metals indicating that it is the major agent in their vapor phase transport. Gold in particular was associated with Cl in QCM samples but was more commonly seen in elemental form. Au is probably transported in a Cl rich magmatic vapor phase and may be adsorbed onto a sulfide and/or silicate phase and reduced to elemental Au within the plume and after/during deposition. Volcanic discharges of Au and other metals could be analogous to a magmatic vapor plume evolved in the generation of porphyry deposits.

Subtle but cyclic variations in aerosol EF's and halogen ratios (S/Cl and F/Cl) over time may represent convection to the surface of more volatile rich magma. Variations in the S/Cl ratio may be further evidence for differential solubilities for S and Cl. These variations also enhance the idea that Erebus is an open system subject to new batches of volatile rich magma.

Once transported out of the magma aerosols are subjected to physical and chemical processes in the plume. Particle size distribution and chemical variation between crater rim and airborne plume samples indicate that fractionation is occurring in the plume based on changing temperature and oxidizing conditions.

Knowing the average SO_2 flux from Erebus and average element/S ratios, we have determined the flux of some trace elements to the atmosphere. Erebus contributes an average of 100 tonnes/day Cl but could easily discharge 1000 tonnes/day and this is 1-5% of estimates for annual global volcanic contributions to the atmosphere. Sulfur represents <0.1% of global volcanic sulfur (Stoiber _et al._, 1987) and <5% of the total sulfur transported by the air mass over the Antarctic ice sheet (Delmas _et al._, 1982).

HCl is potentially the most significant contribution from Erebus and could have regional impacts. The Cl EF in South Pole aerosols is lower than expected for volcanic and oceanic contributions (Manhaut _et al._, 1979). However, studies of seasonal aerosol distribution (Mroz, 1984) show that though overall aerosol concentration decreases in the winter, stratospheric contributions decrease and oceanic NaCl actually increases at the South Pole indicating that air masses are moving inland. Erebus Cl and SO_4 therefore may have a greater impact during the winter months. Although HCl is an important link in the chain of ozone destruction in the stratosphere, the short residence time of HCl in the lower atmosphere relative to the time necessary to penetrate the tropopause make Erebus an unlikely contributor to Antarctica's ozone problem.

8. SUGGESTIONS FOR FUTURE WORK

In certain respects, Mount Erebus provides an ideal environment for the measurement of volcanic gases and aerosols. This thesis has been in part an experiment in methodology for measuring low level volcanic emissions in polar conditions over confined periods of time. Several improvements can be made, but more important continuous monitoring using combined techniques is necessary to confirm the preliminary results and to monitor how Erebus is evolving since the activity in 1984.

The low levels of SO_2 discharged from Erebus provide an interesting problem in estimating S flux from the magma. To ensure that SO_2 is representative of sulfur emissions, a system to monitor H_2S is being developed (R. Chuan, pers comm., 1988). Further studies are also necessary to determine the rate of conversion to H_2SO_4. Further airborne plume studies using the COSPEC and QCM simultaneously may differentiate the species of S which evolve after release from the lava lake.

Continuous monitoring over 10 to 12 hours and 4 minute intervals may provide more evidence for periodicity in SO_2 fluxes. Use of Fourier Transforms may determine some underlying cycles in the data. Measurement through eruptions is also necessary to better understand the relationship between bubble growth and sulfur emissions.

To better determine the chemical composition of particles released from Erebus, it is necessary to confirm the existence of low atomic number elements such as F, C, N, etc. More QCM samples from 1986 and 1987 should be analyzed to confirm the presence or absence of HCl and H_2SO_4 mantling and droplets. Further study of Au morphology and speciation is also necessary. Use of the QCM at Kilauea where Au is collected on filter packs may provide some insight into the speciation of Au in different volcanic systems. Finally, simultaneous QCM and filter pack measurements may show the different phases of a volatile once it is released from the magma. Simultaneous COSPEC and QCM sampling during high and low sulfur discharge periods may provide answers to the various species of S (elemental vs H_2SO_4 vs sulfides) which occur in the aerosols.

The filter pack should also be run simultaneously (perhaps in an airborne survey) with COSPEC measurements to obtain more accurate element flux determinations. Simultaneous airborne measurements might remove the error caused by fractionation and dispersal of particles in the plume. The S/Cl ratio should be compared with SO_2 flux over a 24 hour period (1 hour intervals) and over several weeks. Filter pack samples could be collected every 1-2 hours to determine how these ratios and EF's would vary over short time periods. This would confirm whether variations seen over several days are real or within analytical error. The treated filters should be run for a maximum time as well to obtain detectable amounts of S and to study the efficiency of the treated filters at different molalities of LiOH.

To study fractionation of aerosols in the plume and the relationship to salts on the crater rim, aerosols could be collected along directional axes away from the crater rim. This would also help define the prevailing wind directions which carry aerosols from Erebus to the regional atmosphere.

A recent set of South Pole data is necessary to study the impact of Erebus contributions. Airborne QCM studies along the route to the South Pole would be enhanced by QCM and filter pack samples from the South Pole. Summer and winter samples would be helpful to study seasonal variation.

Analyses of filter packs would be greatly improved by a representative sample of phonolite lava which would be used for all aerosol studies. The low sulfur concentration on the filters require analysis by ion chromatography. Using treated filters with a lower concentration of LiOH may facilitate IC determinations.

9. APPENDIX

Introduction

The following appendices contain the principle of operation of the COSPEC and a presentation of data collected by the COSPEC, QCM and filter packs.

APPENDIX A-1

Remote Sensing Correlation Spectrometer (COSPEC)

A. Theory of Operation

The COSPEC measures SO_2 by measuring the difference between absorption of scattered sunlight due to SO_2 molecules and non-absorbed radiation. Typical wavelengths in the troposphere are in the visible range between 290 and 700 nm and the COSPEC takes advantage of the several strong absorption peaks of SO_2 around 300nm.

The theory behind the COSPEC is Beer's Law:

$$\frac{I}{I_o} = \alpha l \, C$$

when I_o = spectral irradiance of a light source

I = spectral radiance of the light after transmission through an absorbing gas

α = the absorption cross-section of the target gas (cm^2/molecule)

C = average concentration of target gas

l = absorption path length of the absorbing gas.

The amount of light of a given wavelength that passes through a gas is dependent upon the initial amount of light available and a constant, peculiar to that gas and wavelength under consideration, times the average concentration and pathlength. Thus, the COSPEC measures burden, which is the product of 1*C.

B. Instrument Design

The COSPEC is an absorption spectrometer which gathers light by a Cassegrain-type telescope (Figure A.1). The light is focused on a diffraction grating which separates radiation into individual wavelengths so it arrives properly focused on a rotating correlation disc.

As the disc rotates it serves to chop the spectrum between absorption and non-absorption wavelengths. This difference in light intensity is processed in a photomultiplier tube which changes it into a current which is then processed into voltage and sent to a strip chart recorder. Two built-in silica cells with known amounts of SO_2 of 180 and 380 ppm.m (provided by the manufacturer) are used to calibrate the concentration of atmospheric SO_2. These are periodically inserted in front of the light beam to calibrate before each measurement.

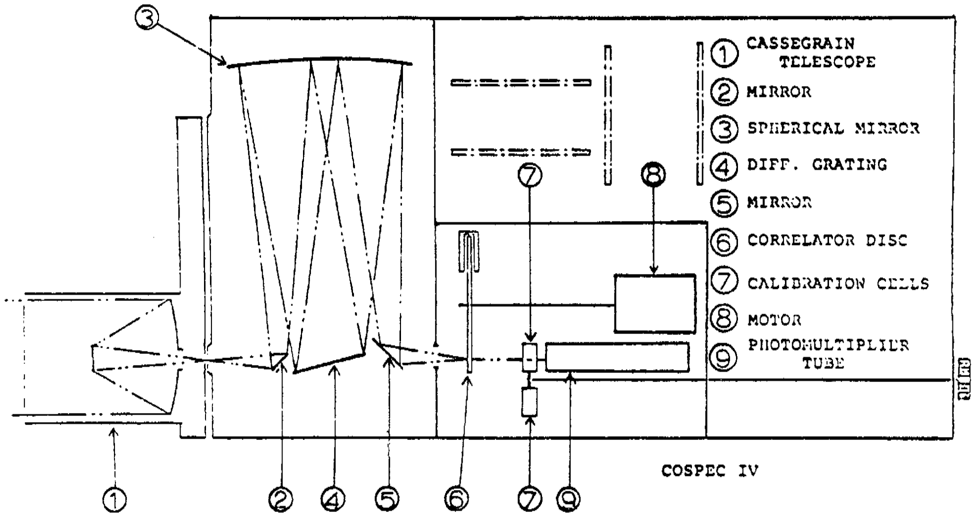
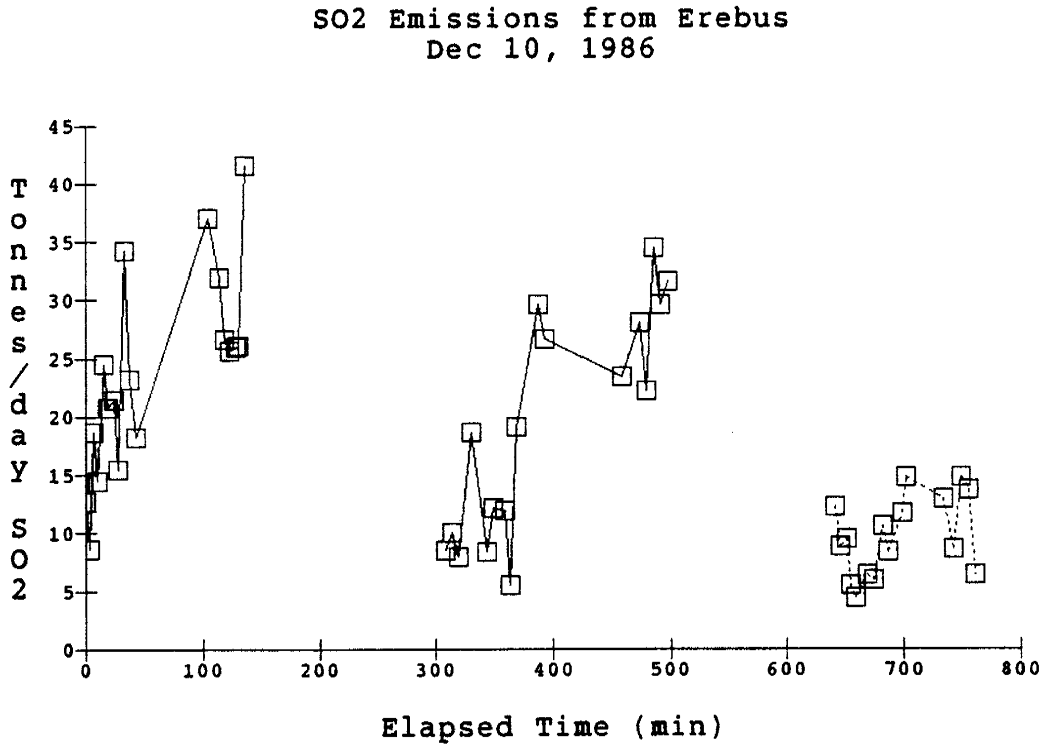


Figure A.1:

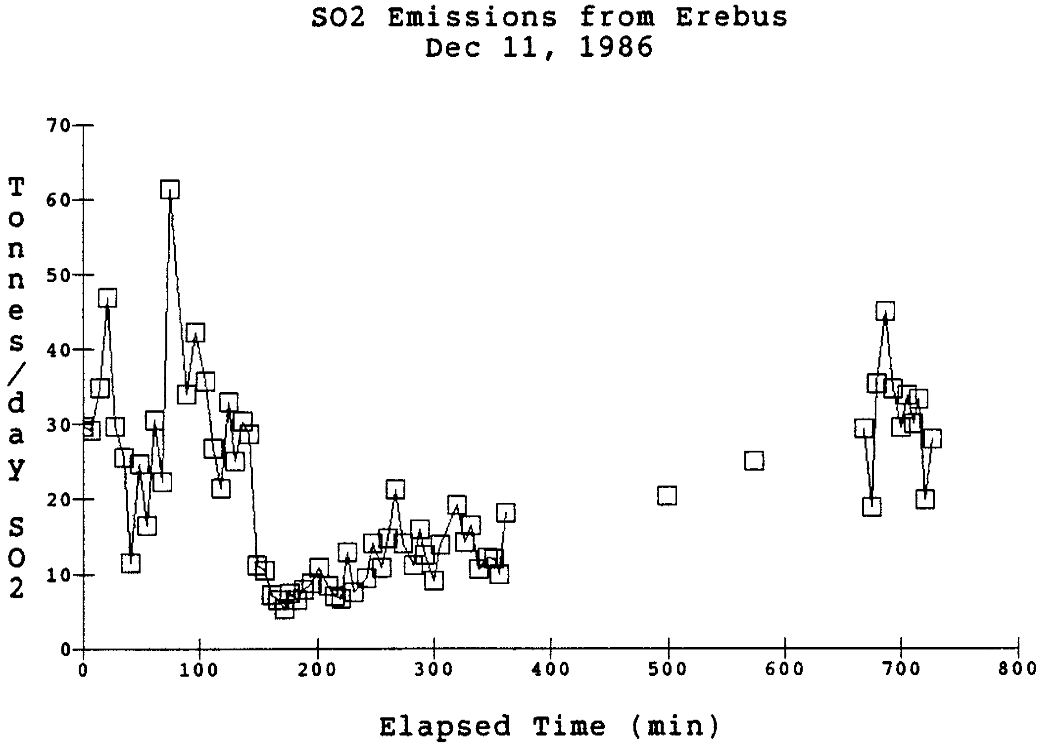
APPENDIX A-2

SO_2 Emission Rates

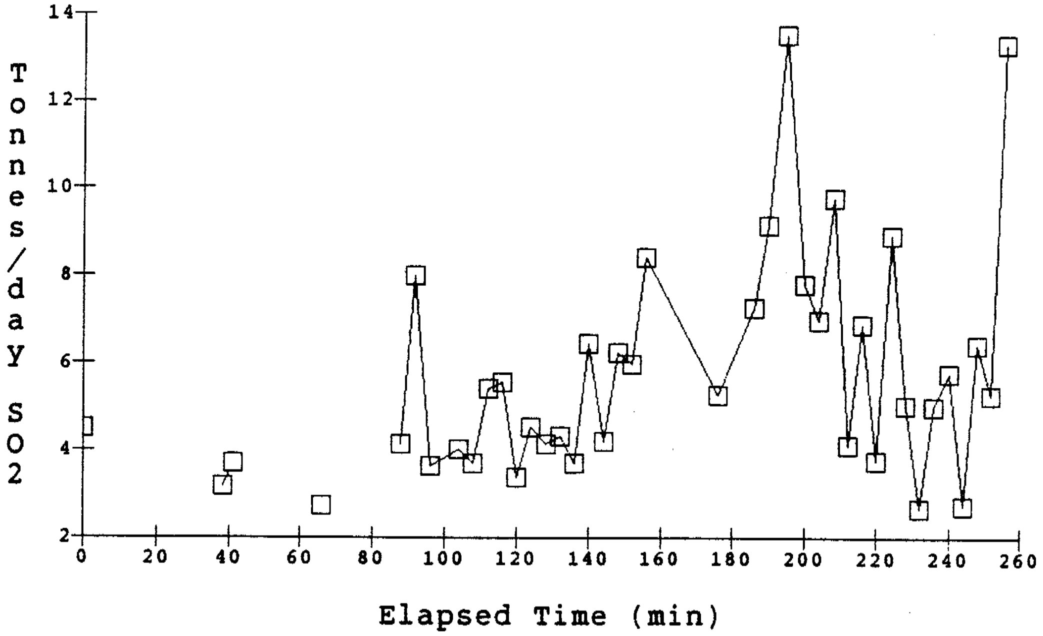
The following pages contain tables listing run number, time, plume width and SO_2 flux in tonnes/day for COSPEC measurements collected between 1985 and 1987. These are followed by a graphical representation of SO_2 flux versus elapsed time.



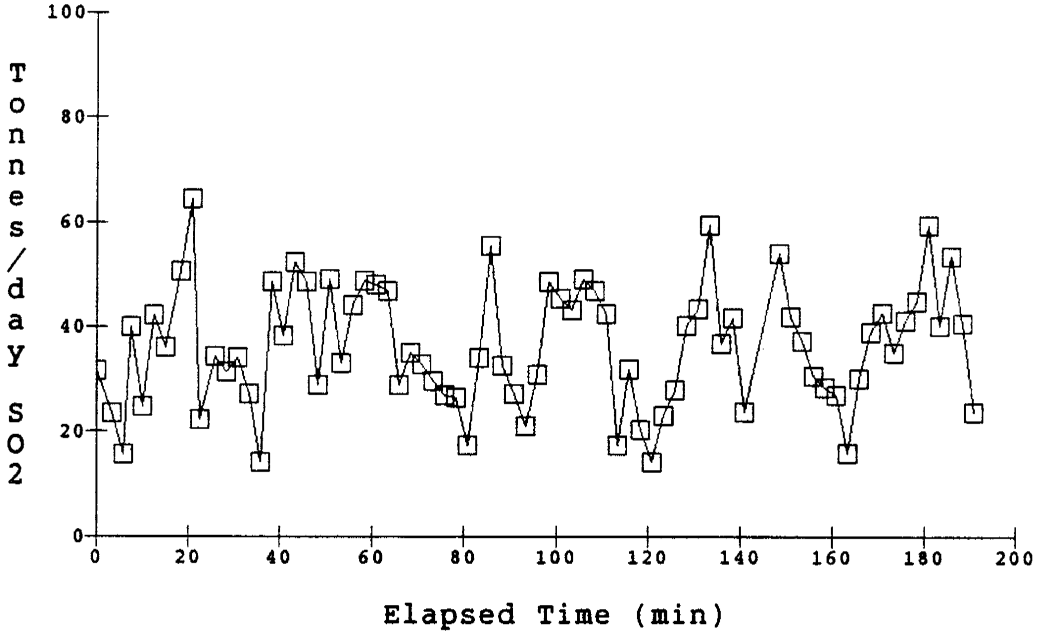
SO2 Emissions from Erebus
Dec 10, 1986



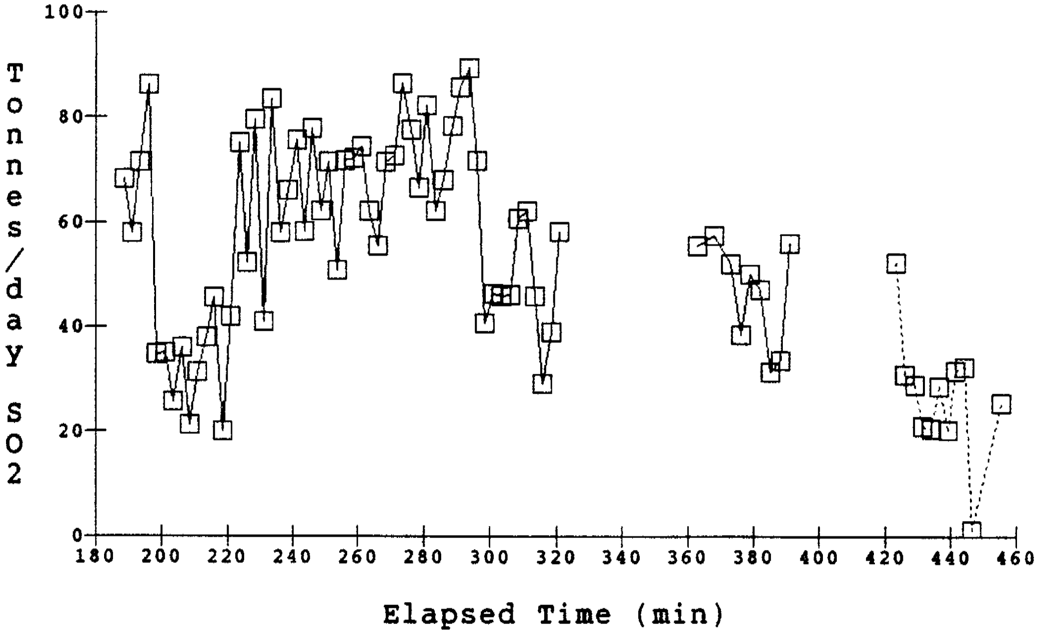
SO2 Emissions from Erebus
Dec 11, 1986



SO2 Emissions from Erebus
Dec 23, 1986



SO2 Emissions from Erebus
Dec 8, 1987



SO2 Emissions from Erebus
Dec 8, 1987

```
Dec 8, 1986         Vertical Scan
-----------------------------------------------------
Run        Time       Plume Width  Tonnes/day SO2
-----------------------------------------------------
1          16:12            478.52     12.82
2          16:28            428.79      6.00
3          16:35            303.12      4.99
4          16:37            318.37      4.25
5          16:46            303.12      3.34
6          16:50            428.79      3.97
7          17:26            461.76      4.22
8          17:31            318.37      3.25
9          17:36            258.03      4.73
----------------------------------------------------
                      Average               5.28
                      Standard Dev.         2.78
```

Dec 10, 1986

Run	Time	Plume Width	Tonnes/day SO2
1	7:23	343.60	12.65
2	7:27	343.60	8.64
3	7:30	722.86	18.66
4	7:43	874.63	14.47
5	7:49	828.25	24.57
6	7:52	737.69	20.74
7	7:57	620.89	21.41
8	8:01	797.75	15.49
9	8:06	649.71	34.28
10	8:11	921.82	23.23
11	8:16	592.31	18.18
12	9:17	828.25	37.06
13	9:27	493.93	31.90
14	9:31	620.89	26.67
15	9:36	678.77	25.57
16	9:41	493.93	25.93
17	9:44	635.27	26.04
18	9:49	859.09	41.51
19	12:42	236.67	8.50
20	12:47	381.45	9.99
21	12:53	289.93	7.99
22	13:04	661.30	18.66
23	13:17	241.98	8.39
24	13:22	332.83	12.13
25	13:32	241.98	11.89
26	13:37	146.84	5.48
27	13:42	354.39	19.05
28	14:01	392.31	29.58
29	14:06	535.79	26.63
30	15:12	343.60	23.46
31	15:27	419.56	28.00
32	15:33	425.03	22.21
33	15:39	603.71	34.47
34	15:45	457.97	29.58
35	15:51	530.19	31.63
36	18:36	183.74	12.23
37	18:40	125.81	8.84
38	18:45	178.46	9.43
39	18:49	110.05	5.45
40	18:53	953.74	4.40
41	19:03	953.74	6.37
42	19:08	131.06	5.93
43	19:12	146.84	10.61
44	19;16	257.93	8.41
45	19:28	167.91	11.68
46	19:32	173.19	14.83

Dec 10, 1986

Run	Time	Plume Width	Tonnes/day SO2
47	20:04	189.02	12.89
48	20:12	178.46	8.55
49	20:19	199.59	14.75
50	20:25	152.11	13.71
51	20:31	115.30	6.42
		Average	17.83
		Std Dev	9.57

Dec 11, 1986

Run	Time	Plume Width	Tonnes/day SO2
1	10:16	569.60	29.65
2	10:23	558.30	29.21
3	10:30	719.90	34.83
4	10:37	1154.44	46.98
5	10:44	684.61	29.79
6	10:51	446.97	25.57
7	10:57	327.45	11.55
8	11:04	403.19	24.69
9	11:11	338.21	16.45
10	11:18	381.45	30.62
11	11:24	189.02	22.29
12	11:31	865.29	61.40
13	11:45	649.71	33.97
14	11:53	626.64	42.35
15	12:01	708.09	35.81
16	12:08	535.79	26.71
17	12:15	535.79	21.47
18	12:21	731.75	33.00
19	12:27	638.15	25.12
20	12;33	661.30	30.43
21	12:39	791.69	28.63
22	12:47	189.02	11.08
23	12:54	210.17	10.42
24	12:59	210.17	7.26
25	13:05*	425.03	6.41
26	13:10	210.17	5.29
27	13:15	252.61	7.30
28	13:21	189.02	6.56
29	13:27	210.17	7.84
30	13:33	273.91	8.75
31	13:40	359.79	10.72
32	13:47	189.02	8.40
33	13:53	189.02	6.96
34	13:58	220.76	6.74
35	14:04*	355.47	12.92
36	14:09	381.45	7.49
37	14:20	338.21	9.41
38	14;26	414.10	14.09
39	14:33	469.00	10.77
40	14:39	446.97	14.67
41	14:45	684.61	21.28
42	14:52	603.71	13.98
43	15:01	252.61	11.16
44	15:06	457.97	16.04
45	15:11	370.61	12.46
46	15:18	295.28	9.06

Dec 11, 1986

Run	Time	Plume Width	Tonnes/day SO2
47	15:24	524.59	13.82
48	15:38	569.60	19.16
49	15:44	491.15	14.18
50	15:50	558.30	16.50
51	15:56	231.36	10.60
52	16:04	469.00	12.25
53	16:10	603.71	12.05
54	16:14	480.06	9.97
55	16:19	569.60	18.12
56	18:37	524.59	20.50
57	19:52	359.79	25.13
58	21:26	231.36	29.42
59	21:32	189.02	18.82
60	21:37	316.71	35.43
61	21:45	469.00	45.10
62	21:51	414.10	34.76
63	21:58	359.79	29.61
64	22:03	359.79	33.84
65	22:08	252.61	29.98
66	22:13	381.45	33.37
67	22:18	189.02	19.84
68	22:25	295.28	28.05
		Average	20.71
		Standard Dev.	11.79

Dec 21, 1986

Run	Time	Plume Width	Tonnes/day SO2
1	13:14	502.27	20.50
2	13:21	469.00	26.11
3	13:33	381.45	11.42
4	13:39	580.94	30.91
5	13:59	580.94	15.68
6	14:06	491.15	27.80
7	14:10	615.16	33.33
8	14:19	979.58	66.92
9	14:28	649.71	34.43
10	14:37	649.71	37.33
11	14:43	626.64	30.82
12	14:49	603.71	41.49
13	14:55	580.94	41.72
14	15:01	580.94	37.56
15	15:07	649.71	26.69
16	15:16	684.61	36.94
17	15:22	865.29	53.34
18	15:29	558.30	33.08
19	15:38	767.57	52.30
20	15:46	580.94	36.20
21	15:52	992.59	37.56
22	15:59	626.64	32.95
23	16:05	502.27	22.95
24	16:11	649.71	36.74
25	16:17	435.99	18.08
26	16:27	535.79	32.79
27	16:32	381.45	18.57
28	16:37	425.03	24.74
29	16:42	480.06	23.16
30	16:46	524.59	20.22
31	16:51	491.15	17.39
32	15:55	425.03	14.17
33	16:59	403.19	19.42
34	17:03	502.27	16.10
35	17:07	580.94	28.41
36	17:13	491.15	20.46
37	17:19	469.00	8.33
38	17:24	558.30	12.73
39	17:35	469.00	19.10
40	17:39	425.03	17.95
41	17:48	403.19	21.55
42	17:52	469.00	11.97
43	17:59	381.45	17.75
44	18:02	513.41	18.04
45	18:07	547.03	23.16
46	18:11	558.30	26.01

Dec 21, 1986

Run	Time	Plume Width	Tonnes/day SO2
47	18:21	425.03	23.07
48	18:27	446.97	18.97
49	18:47	457.97	17.50
50	18:51	295.28	5.72
51	18:55	469.00	7.94
52	19:00	403.19	10.80
53	19:04	480.06	5.16
54	19:09	446.97	7.00
55	19:13	425.03	8.52
56	19:18	547.03	10.89
57	19:23	491.15	12.42
58	19:27	425.03	10.76
59	19:32	615.16	19.64
60	19:38	535.79	20.31
61	19:43	491.15	22.42
62	19:49	348.99	14.30
63	19:55	502.27	17.04
64	20:03	252.61	7.78
65	20:12	403.19	27.79
66	20:19	316.71	15.59
67	20:26	370.61	1.80
68	20:31	305.98	19.48
69	20:37	327.45	18.70
70	20:43	491.15	25.28
71	20:52	295.28	17.44
72	20:58	263.25	16.44
73	21:04	316.71	13.08
74	21:11	359.79	16.82
75	21:17	480.06	18.27
76	21:23	252.61	9.07
		Average	22.30
		Standard Dev.	11.77

Dec 23, 1986

Run	Time	Plume Width	Tonnes/day SO2
1	10:54	316.71	4.51
2	11:32	316.71	3.17
3	11:35	263.25	3.69
4	12:00	178.46	2.74
5	12:22	178.46	4.13
6	12:26	231.36	8.00
7	12:30	189.02	3.63
8	12:34	178.46	4.02
9	12:38	220.76	3.72
10	12:42	220.76	5.40
11	12:46	189.02	5.55
12	12:50	231.36	3.38
13	12:54	252.61	4.52
14	12:58	189.02	4.13
15	13:02	231.36	4.33
16	13:06	199.59	3.69
17	13:10	231.36	6.45
18	13:14	241.98	4.21
19	13:18	295.28	6.24
20	13:22	241.98	5.98
21	13:26	263.25	8.43
22	13:46	273.91	5.27
23	13:56	316.71	7.28
24	14:00	252.61	9.16
25	14:05	316.71	13.51
26	14:10	316.71	7.80
27	14:14	231.36	6.98
28	14:18	305.98	9.79
29	14:22	231.36	4.10
30	14:26	295.28	6.89
31	14:30	210.17	3.77
32	14:34	273.91	8.92
33	14:38	231.36	5.03
34	14:42	189.02	2.67
35	14:46	263.25	5.00
36	14:50	273.91	5.76
37	14:54	273.91	2.74
38	14:58	252.61	6.41
39	15:02	305.98	5.26
40	15:06	305.98	13.31
		Average	5.74
		Standard Dev.	2.55

Dec 8, 1987

Run	Time	Plume Width	Tonnes/day SO2
1	0857	620.89	31.58
2	0900:30	563.95	23.61
3	0903	592.31	15.65
4	0905:30	708.09	39.97
5	0908	828.25	24.69
6	0910:30	890.27	42.09
7	0913	828.25	36.00
8	0915:30	797.75	50.65
9	0918	828.25	64.37
10	0920:30	620.89	22.29
11	0923	1018.83	34.45
12	0925:30	828.25	31.27
13	0928	797.75	34.17
14	0930:30	767.57	27.11
15	0933	828.25	14.24
16	0935:30	953.74	48.71
17	0938	1085.67	38.24
18	0940:30	986.08	52.28
19	0943	1225.32	48.50
20	0945:30	1189.60	28.83
21	0948	1154.44	49.13
22	0950:30	1225.32	33.14
23	0953	1189.60	44.28
24	0955:30	1154.44	48.92
25	0958	1154.44	48.03
26	1000:30	649.71	46.81
27	1003	953.74	28.99
28	1005:30	1154.44	35.05
29	1008	592.31	32.95
30	1010:30	737.69	29.60
31	1013	592.31	26.87
32	1015:30	708.09	26.38
33	1018	425.03	17.43
34	1020:30	649.71	34.13
35	1023	953.74	55.35
36	1025:30	828.25	32.64
37	1028	592.31	27.32
38	1030:30	767.57	21.02
39	1033	767.57	30.93
40	1035:30	767.57	48.52
41	1038	986.08	45.42
42	1040:30	986.08	43.18
43	1043	1534.26	49.12
44	1045:30	1452.72	46.99
45	1048	1336.04	42.41
46	1050:30	678.77	17.50

Dec 8, 1987

Run	Time	Plume Width	Tonnes/day SO2
47	1053	797.75	31.85
48	1055:30	1154.44	20.33
49	1058	535.79	14.16
50	1100:30	620.89	23.10
51	1103	1189.60	27.83
52	1105:30	1225.32	40.26
53	1108	1018.83	43.35
54	1110:30	953.74	59.42
55	1113	1018.83	36.71
56	1115:30	563.95	41.71
57	1118	1154.44	23.74
58	1120:30	1413.11	53.90
59	1123	953.74	42.01
60	1125:30	592.31	37.29
61	1128	592.31	30.66
62	1130:30	620.89	28.36
63	1133	828.25	26.98
64	1135:30	620.89	15.91
65	1138	452.47	30.28
66	1140:30	890.27	39.04
67	1143	828.25	42.60
68	1145:30	620.89	35.02
69	1148	828.25	41.15
70	1150:30	828.25	44.90
71	1158	890.27	59.31
72	1155:30	953.74	40.17
73	1158	649.71	53.44
74	1200:30	767.57	40.68
75	1203	592.31	23.79
76	1205:30	737.69	68.34
77	1208	737.69	58.02
78	1210:30	1052.02	71.44
79	1213	767.57	86.17
80	1215:30	859.09	34.80
81	1218	767.57	35.05
82	1220:30	767.57	25.68
83	1223	1018.83	36.13
84	1225:30	737.69	21.29
85	1228	425.03	31.46
86	1230:30	953.74	38.01
87	1233	737.69	45.58
88	1235:30	708.09	20.11
89	1238	1225.32	41.87
90	1240:30	1374.23	75.21
91	1243	767.57	52.29
92	1245:30	1452.72	79.45

Dec 8, 1987

Run	Time	Plume Width	Tonnes/day SO2
93	1248	592.31	40.87
94	1250:30	1154.44	83.49
95	1253	986.08	58.02
96	1255:30	986.08	66.04
97	1258	1261.61	75.62
98	1300:30	986.08	58.07
99	1303	1534.26	77.87
100	1305:30	1225.32	62.03
101	1308	986.08	71.38
102	1310:30	649.71	50.90
103	1313	828.25	71.63
104	1215:30	797.75	72.20
105	1318	1189.60	74.41
106	1320:30	953.74	62.14
107	1323	953.74	55.50
108	1325:30	1225.32	71.49
109	1328	1298.51	72.71
110	1330:30	1452.72	86.35
111	1333	1225.32	77.54
112	1335:30	986.08	66.58
113	1338	953.74	82.31
114	1340:30	953.74	62.15
115	1343	828.25	68.01
116	1345:30	859.09	78.33
117	1348	828.25	85.75
118	1350:30	1225.32	89.46
119	1353	1298.51	71.72
120	1355:30	828.25	40.79
121	1358	480.06	46.43
122	1400:30	797.75	45.90
123	1403	708.09	46.13
124	1405:30	797.75	60.56
125	1408	986.08	62.21
126	1410:30	797.75	45.84
127	1413	797.75	29.07
128	1415:30	1154.44	39.10
129	1418:30	1298.51	58.24
130	1500:30	828.25	55.53
131	1505:30	890.27	57.41
132	1509	890.27	52.03
133	1512	890.27	38.42
134	1515	828.25	50.02
135	1518	708.09	47.02
136	1521	480.06	31.48
137	1524:10	316.71	33.49
138	1527	767.57	55.97

Dec 8, 1987

Run	Time	Plume Width	Tonnes/day SO2
139	1559	4825.39	52.19
140	1601	425.03	30.88
141	1604	397.75	29.04
142	1606:30	452.47	21.06
143	1609	480.06	20.69
144	1611:30	828.25	28.76
145	1614	425.03	20.40
146	1616;30	480.06	31.55
147	1619	563.95	32.47
148	1621:30	452.47	1.23
149	1630:30	452.47	25.50
150	1701	370.61	18.27
151	1703:30	563.95	35.02
152	1706	859.09	23.98
153	1708:30	507.84	40.26
154	1711	767.57	38.47
155	1713:30	828.25	56.69
156	1716	797.75	53.43
157	1718:30	767.57	40.42
158	1721	592.31	27.32
159	1723:30	767.57	48.46
160	1726	828.25	37.90
161	1728:30	828.25	53.09
162	1731	767.57	60.17
163	1833:30	737.69	50.34
164	1737	1154.44	77.28
165	1738:30	649.71	38.99
166	1741	828.25	53.72
167	1743:30	678.77	47.66
168	1746	828.25	34.84
169	1748:30	737.69	24.62
170	1751	592.31	26.60
171	1753:30	1119.80	45.81
172	1756	620.89	33.13
173	1758:30	797.75	44.90
174	1801	986.08	60.74
175	1802:30	797.75	45.25
176	1805	1336.04	71.58
177	1807:30	1298.51	76.84
178	1810	1336.04	56.37
179	1812:30	1452.72	39.61
180	1815	828.25	48.77
181	1817:30	1018.83	57.47
182	1820	1119.80	58.23
183	1822:30	1052.02	58.53
184	1825	1261.61	57.64

Dec 8, 1987

Run	Time	Plume Width	Tonnes/day SO2
185	1827:30	828.25	62.51
186	1830	986.08	52.22
187	1832:50	890.27	55.20
188	1835	1052.02	67.37
189	1837:30	890.27	64.59
190	1840	1189.60	98.41
191	1842:30	1225.32	93.74
192	1845	1225.32	98.12
193	1847:30	1018.83	83.25
194	1850	1085.67	56.96
195	1852:30	1225.32	56.75
196	1855	737.69	45.27
197	1857:30	1225.32	79.24
198	1900	986.08	65.78
199	1902:30	986.08	87.34
200	1905	986.08	76.70
201	1907:30	1052.02	81.08
202	1910	767.57	78.68
203	1912:30	1261.61	71.67
204	1915	592.31	52.84
205	1917:30	797.75	64.06
206	1920	828.25	54.19
207	1925:30	953.74	67.79
208	1928	1154.44	88.92
209	1930:30	797.75	52.93
210	2016	1298.51	102.87
211	2018:30	649.71	48.13
212	2021	953.74	98.17
213	2023:30	1261.61	125.81
214	2026	1154.44	125.80
215	2028:30	1298.51	124.48
216	2031:30	1018.83	90.56
217	2034	678.77	56.25
218	2036:30	1052.02	99.58
219	2039	797.75	82.42
220	2041:30	1018.83	88.58
221	2044	1225.32	93.92
222	2046:30	480.06	52.17
223	2049	708.09	54.52
224	2051:30	1154.44	92.61
225	2054	1298.51	123.59
226	2056:30	953.74	68.26
227	2059	890.27	92.47
		Average	51.28
		Standard Dev.	22.84

APPENDIX A-3

Particle Morphology and Chemistry

The following pages contain the results of SEM and EDXRA analysis of particles collected by QCM from the crater rim, airborne plume and ambient air (South Pole flight) during the 1986/87 and 1987/88 field seasons. The tables present the morphology and chemical composition for the various sizes of particles.

Erebus 1986/87 Season
Crater Rim Sample

Stage #	Morphology	Si	Ag	S	Na	Cl	K	Zn	Au	Cu	Sn	Pb	Ce	Mg	Al	Fe	Ca
S-1	>2.0 microns																
1	bulbous to column.								xx								
2	subhedr. platey to amorph.					x			xx								
3	elongate spongy								xx								
4	no pic								xx								
5	flakey, spiral, maleable								x								
S-2	0.9 microns																
6	fluffy aggreg.			x		t?		t		x							
7	bimodal																
8	fuzz. + subhedr.		x	xx				xx									
9	fluff																
10	subhedr. plate w/ acid coat			x				x									
11	branched, bulbous	x	x	xx				xx									
12	crumbly, amorph.			x													
13	evap. agglom.			x		x									x		
14	agglom + tetrag. part.			xx				x									
15	column. + spongy								xx								
16	fluff			x		x											
17	monoclinic, w/ evap.			t											x	x	
S-3	0.3 microns													x		x	x
18	precipt.			x	x	x	x									x	
19	rhomb.?			xx	x		x								x		
20	evap + wet spot			t			t										
21	fluff (evap?) + tiny spheres			t		t	t										
22			x														
23	fuzz, amorph.			t	x	x	x										
S-4	0.1 microns																
24	ave spot			x	x	xx	x										
25	evaporites			x	x	xx	xx										
26	total stage																
27	massive aggreg.																

t = trace
x = common
xx = abundant

Erebus 1986/87 Season
Airborne Plume Sample

Stage #	Morphology	Si	Ag	S	Na	Cl	K	Zn	Au	Cu	Sn	Pb	Ce	Mg	Al	Fe	Mn
S-1	>2.0 microns no particles seen																
S-2	0.9 microns																
1	amorphous	x															
2	conchoidal, glassy													x	x	x	
3	botriodal to columnar								xx								
4	subhedral, platey					x											
5	fuzzy, amorphous		x			x										x	
6	cylinder, relict?																
7	conchoidal particles	xx															
8	fuzzy, amorphous									t							
S-3	0.3 microns																
9	amorphous			x							x						
10	overview, aggregates			t													
11	amorphous															x	
12	amorphous												x				
13	bright spot		x														
14	fluff																
15	monoclinic to amorphous		x														
16	coagulated mass + tetrag. part.			xx							x						
17	fuzzy aggregates												x				
18	fluffly aggreg. + conchoid part.			t												x	x
19	coagulated mass			xx				xx									
20	evap. + conchoid. part.			x					x	x					x		
21	amorph. to flakey																
22	monoclinic		xx				x										
23	evap. from wet spot										x						
24	amorph. mass w/droplets		x						x	t							
S-4	0.1 microns																
25	overview																
26	overview			x													
27	fuzzy aggregates																
28	fuzz and wet spots			x?						x?							
29	fuzz and larger spherical part.			t													

t = rare
x = common
xx = abundant

Erebus 1987/88 Season
Crater Rim Sample

Stage #	Morphology	S	Na	Cl	K	Au	Cu	Ag	LZ*	Al	Fe	Si	Ca	Ti
S-1	>2.0 microns													
1	monoclinic, star	xx						x						
2	etching around S													
3										x		x		
4	spongy					xx								
5	rhomb. to amorph	x		x	x								x	
summary	> 90% elemental sulfur, also Al-silicates,Au,salts and sulfates													
S-2	0.9 um													
6	irreg aggl w/ shard	xx		t	x					x			x	
7	densely packed rhombs (S)	xxx												
summary	> 80% elemental and assoc sulfur, densely packed xls also Ca-Mg ,Fe silicates (ash) and salt agglomerates													
S-3	0.3 um													
8	glass w/ reaction surface	t	x	xx		xx			xx	t	x			
9	homog. spheres						t	x						
10	euhedral xl													
11	sphere													
12	amorph. evap. in LZ spheres		x	xx	x			x						
summary	majority is monodispersed, homgeneous particles Low Z													
S-4	0.1 um													
13	rhomb xls + cubic xls	xx	x	x	xx									
14	subhedr. rhomb. walls blown out on salts	xx	x		xx									
15	cubes w/moats precipitates			xx	xx									
16	massive amorph. w/ cubes	x	x	xx	x									
17	higher K,S on edge of above		x		xx									
summary	mostly salts and sulfates of Na, S, K and Cl.													

*LZ = Low atomic number, not detected by EXDRA

Erebus 1987/88 Season
Airborne Plume Sample

Stage/#	Morphology	S	Cl	LZ*	Cr	Fe
S-6	1.6 um					
1	poor pic	x		x?		
	fuzzy, amorph					
summary-	low particle concentration, elusive streaks,					
	agglom with weak S and maybe tr Cl					
S-4	0.4 um					
2	stage pic					
	few particles					
	fuzzy, round					
summary-	weak images, S,C?,					
	also Ca sulfate? and Ca rich particles					
S-2	0.1 um					
3	lg particle	x?		xx		
	low density,low count					
4	crumbly aggregate				xx	x
	oxide?					
5	similar aggreg				x?	xx
summary-	random particles, not representative?					
	also saw Al-silicates,noisy,low Z, poor image strings					
	tr of Fe and Cu (oxides?)					
	same rounded particles as on s-4					

* Low Z (atomic number), not diagnosed by EDXRA
t = trace
x = common
xx = abundant

Erebus 1987/88 Season
Ambient Air Sample

Stage/#	Morphology	S	Na	Cl	K	Au	Cu	LZ*	Al	Si	Ca	Fe	Ti	Co	Cr	Cd
S-2	: >12 um															
1	: rhomb	xx									xx					
2	: rhomb.										xx					
3	: bulbous, bright	xx		x?							xx			x		
4	: low dens. sphere							x								
S-4	: 6.2 um	xx									xx					
5	: tabular.layered	x									x					
6	: spongy oxide?	x								x						
7	: irreg shard (AlCl3?)			xx					xx	x?						
8	: hi Al,flocculant								xx			x				xx
9	: bright spongy aggreg											x			xx	
10	: delicate, tabulate								xx							
	: irreg, xl Al2O3?															
summary-	: spongy oxides to more xline															
	: CaSO4,CaCO3?															
	: rare to no elemental sulfur															
	: tr Cl assoc with Al															
S-6	: 1.6 um	t					x									
11	: v sm flakes	x														
12	: fuzzy,skelet.															
13	: typical columnar Au					xx										
S-8	: 0.4 um							x				x				
14	: field - irreg. flakes															
15	: irreg, bulbous						x				x	x				
16	: elong., Al>>S,	x						x	x							
17	: spongy cluster						x					x			xx	
18	: tiny agglom	x										x				
19	: acid bumps															
20	: amorph	x						x				x				

summary- also saw tiny agglom of Mg,Al,S?? low signal sulfates?

*Low Z (atomic No) no diagnosed by EXDRA

Key
t = trace
x = common
xx = abundant

APPENDIX A-4

Distribution of Elements on Particle and Base-treated Filters

The following table lists the μg/sample for each element collected on particle and treated filters during nine sampling periods between December 19 and December 24, 1986.

Erebus Filters 1986/87

filter	:	1	2	3	4	5	6	7	8	9
Element:					Ug/Sample					
F	:	252.68	825.65	2540.36	1363.32	2501.66	985.97	1684.45	504.60	870.93
Na	:	38.09	169.51	395.26	268.39	501.65	133.41	95.21	70.76	217.21
Al	:	4.87	35.31	16.22	40.36	26.79	21.48	36.19	18.63	238.40
S	:	613.30	27.50	470.60	377.70	649.50	270.90	19.70	35.20	51.60
Cl	:	550.53	1659.00	5766.47	3334.10	6778.98	2869.38	1206.80	492.44	1513.09
K	:	36.14	128.46	355.89	166.05	507.78	112.79	70.27	48.57	98.73
Ca	:			45.62	48.35		31.93	33.49	39.46	70.52
Sc*	:	1.45	3.39	2.67	6.22	0.00	3.33	4.21	3.08	25.40
V	:	0.03	0.00	0.05	0.01			0.05	0.04	
Cr	:	1.62	0.45	0.15	0.21	0.60	0.04	0.33	0.12	1.36
Mn	:	0.12	1.98	1.72	1.80	1.29	0.55	0.82	0.58	5.53
Fe	:	27.51	69.54	23.31	39.80	34.68	29.41	37.11	29.10	142.68
Co*	:	251.79	0.00	0.00	0.00	0.00	17.24	23.81	632.37	4.46
Cu	:	0.03		12.04	10.30		3.64		0.01	
Zn	:	1.53	6.09	12.73	4.44	11.29	10.90	8.66	3.89	8.81
As	:	0.09	2.48	6.18	4.13	5.65	1.58	0.98	0.56	1.61
Se*	:	115.63	33.11	170.35	63.61	162.55	218.84	0.00	0.00	87.78
Br	:	2.48	4.90	8.94	6.48	18.09	6.80	3.95	1.42	3.04
Rb	:	0.00	1.16	2.27	1.43	3.08	0.68	0.00	0.36	0.00
Mo*	:	0.00	0.00	0.00	0.00	65.49	290.97	1612.63	5955.70	141.10
In*	:	83.27	240.00	586.80	356.67	756.82	154.81	75.89	44.78	117.12
Sb*	:	7.22	62.13	189.15	174.45	128.19	29.84	46.30	39.85	137.23
Cs*	:	7.38	35.28	78.62	50.47	160.87	30.10	26.92	15.58	0.00
La*	:	5.93	239.84	52.19	91.38	87.48	47.27	83.12	63.97	463.67
Ce	:	0.00	0.47	0.09	0.16	0.12	0.20	0.28	0.00	0.91
Sm*	:	0.00	35.10	0.00	0.00	13.79	5.84	8.29	6.94	55.10
Eu*	:	0.00	10.71	47.12	28.81	0.00	3.19	0.00	0.00	8.09
Yb*	:	24.46	28.18	25.22	20.94	36.31	98.47	176.29	221.58	267.93
Hf*	:	23.32	17.29	0.00	11.88	31.51	237.16	14.45	11.05	76.70
Ta*	:	42.04	29.37	4.95	77.04	39.71	0.00	0.00	0.00	29.45
W*	:	20.05	63.46	244.26	12.24	0.00	41.61	0.00	4.34	0.00
Au*	:	0.00	2.60	0.00	1.30	0.00	5.66	0.22	0.64	2.54
Hg*	:	0.00	28.93	0.00	0.00	11.17	23.46	0.00	35.72	0.00

* ng/filter

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