

Volcanic gas emissions from Mount Erebus and their impact on the Antarctic environment

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Abstract. Emission rates of SO₂, HCl, and HF from the active volcano Mount Erebus, Antarctica, increased between 1986 and 1991; SO₂ from 7.7 to 25.9 Gg yr⁻¹, HCl from 6.9 to 13.3 Gg yr⁻¹ and HF from 4.0 to 6.0 Gg yr⁻¹. The emission rates of halogens from Mount Erebus are high relative to SO₂ emissions and are accompanied by relatively high emissions of trace gases and aerosols (Na, K, As, Zn, In, As, Se, and Au). Many elements (S, Cl, and metals) found in the Erebus plume are common impurities in Antarctic snow. Using a model which assumes a homogeneous distribution of the volcanic gas plume over Antarctica, we suggest that Erebus could be a source of the impurities. We calculate that Erebus could potentially contribute between 4 and 14 ng g⁻¹ snow of Cl at the south pole, and between 11 and 36 ng g⁻¹ snow of Cl at Dome C. Excess Cl (Cl in excess of that derived from marine NaCl aerosols) recorded in snow and firn cores from south pole and Dome C could be mainly derived from Erebus. Similarly, our predicted concentrations of Erebus-derived Cu, Zn, Cd, V, As, and Au in Antarctic snow are close to those reported. Trace element and Pb isotope compositions of Erebus aerosols are similar to those collected in remote regions of Antarctica. The volcanic gas plume emitted from Erebus appears to make a significant contribution to the Antarctic atmosphere and can be detected in the snow deposited over a wide area of the continent.

Introduction

Volcanoes are an important source of gases and aerosols to the atmosphere. Large volcanic eruptions which penetrate the stratosphere can bring about global changes [Lamb, 1970; Sear *et al.*, 1987; Simarski, 1993] which can lead to long-term changes in climate [Self *et al.*, 1981; Devine *et al.*, 1984; Self and Rampino, 1988; Stothers, 1989; Rampino *et al.*, 1988; Rampino and Self, 1992]. Small, passively degassing volcanoes, for which there are many currently active at any time, also contribute significant amounts of volatile elements as gases and aerosols to the troposphere. Although residence time of these gases and aerosols may be short (at least compared to those in the stratosphere), they

can affect the global climate system by increasing cloud cover in the troposphere [Volz, 1975; Pollack *et al.*, 1976; Baldwin *et al.*, 1976; Lazrus *et al.*, 1979; Turco *et al.*, 1982]. Increased cloudiness changes the Earth's albedo and thus affects the absorption of solar and terrestrial radiation. Passive volcanic degassing continuously contributes to the troposphere unlike the rare large eruptions which inject material into the stratosphere [Simkin *et al.*, 1993]. However, the potential impact of passive degassing is often ignored or overlooked because the gas plumes are small.

An understanding and characterization of volcanic emission rates is critical to an understanding of global inventories. As concern about anthropogenic emission rates of metals and environmentally sensitive materials like Cl, F, CO₂, and SO₄²⁻ increases, it becomes important to understand the natural sources of such materials. Volcanoes are one such natural source but, because of their diversity and episodic nature, it is difficult to estimate global volcanic outputs of gases and aerosols. Nriagu [1989] estimated that volcanic emanations contribute about 40–50% of Cd and Hg, and between 20 and 40% of As, Cr, Cu, Ni, Pb, and Sb emitted annually from natural sources. These estimates are based on scant data and it is likely they are low. If we are

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Paper number 97JB00155.
0148-0227/97/97JB-00155\$09.00

to estimate the extent of industrial pollution it is essential that the natural background is known accurately, and more data are needed on volcanic emissions.

Antarctica has become an important place to monitor the global impact of man on the Earth's atmosphere. Although still relatively pristine, the impact of man is starting to be recognized [Suttie and Wolff, 1993]. In order to understand and quantify anthropogenic impacts on the Antarctic atmosphere, it is essential that the local natural sources of metals and aerosols are characterized and quantified. Mount Erebus is the most active volcano on the Antarctic continent [Kyle, 1994]. Its location at 78°S makes it ideally suited to have a significant regional effect over much of Antarctica.

The goal of this study is to provide a detailed record of emission rates of some gases and aerosols from Mount Erebus and to evaluate their potential impact on the Antarctic environment. This has been achieved by monitoring SO₂ emissions by correlation spectrometer [Kyle et al., 1994] and by direct sampling of the volcanic plume using a combination of base-treated and particle filters. Here we report primarily the filter results collected between 1986 and 1991. Aspects of the degassing mechanism, comparison with other volcanoes, and short-term variations in the gas compositions are discussed by Zreda-Gostynska [1995].

Mount Erebus Volcano

Mount Erebus (77°33'S, 167°10'E, 3794 m above sea level) is the southernmost active volcano in the world. Although detailed observations of the volcanic activity did not start until the 1970s (and even that is sporadic and limited to a few months during the austral summer), historic observations suggest it has been passively degassing since 1841 and probably much longer [Kyle et al., 1982]. Mount Erebus is characterized by a permanent convecting lake of anorthoclase phonolite magma which was discovered in 1972 [Giggenbach et al., 1973] and continued to exist in December 1995. The lava lake was 60 m in diameter in 1978 but was buried in September 1984 by ejecta during a 4 month period of increased strombolian activity [Kyle et al., 1982; Dibble et al., 1984; Kyle et al., 1994]. The lava lake was exhumed in January 1985 and over the last 10 years has varied as one or more small pools from 10 to 25 m in diameter. Small strombolian eruptions from the lake(s) rarely (once or twice a month) eject bombs onto the Main Crater floor. However, during the period when samples were collected for this study, the lava lake was slowly convecting and quietly degassing with rare (one or two per week) small strombolian bubble bursts ejecting bombs 50-100 m distance.

Preliminary data [Kyle et al., 1990] showed the Erebus plume was rich in halogens and enriched in In, As, Hg, Zn, Au, Se, Co, W, Cs, Mo, Rb, Cu, Na, and K. Especially interesting is the occurrence of elemental gold in aerosol samples, possibly formed by reducing Au-Cl complexes by sulfur [Meeker et al., 1991]. The nature and origin of particulate aerosols emitted by Erebus are discussed by Chuan et al. [1986] and Chuan [1994]. Sheppard et al. [1994] gave preliminary estimates of outputs of several gases species from Mount Erebus.

Samples and Analytical Techniques

Forty-eight gas and aerosol samples were collected during December 1986, 1988, 1989, and January 1991 using

custom-made 110 mm and Nuclepore 47 mm filter packs [Finnegan et al. 1989; Kitto et al., 1988]. The packs consist of a particulate filter (one of the following filters were used: Fluoropore (1.0 μm), Zefluor (2.0 μm), and Sartorius (1.2 μm) teflon (PTFE) or Nuclepore polycarbonate aerosol (0.4 μm)) followed by two or more impregnated filters. The impregnated (treated) filters were prepared by saturating Whatman 41 (110 mm) and Whatman 541 (47 mm) filter papers with 1 molar (1 M) (1986 only) or 3 M ⁷LiOH solution prepared using purified ⁷Li metal, 80% deionized water and 20% glycerol [Finnegan et al., 1989]. Gas samples were collected on the north and northeast rim of the Main Crater using 12 V battery-powered pumps with attached flowmeters. Sampling times varied between 30 min and a few hours at an average flow rate of 0.05 m³ min⁻¹. After collection, the filters were unloaded, folded to protect their outer surface, and stored frozen in sterile plastic bags.

The filters were analyzed by instrumental neutron activation analysis (INAA) and ion chromatography (IC) [Finnegan et al., 1989; Kyle et al., 1990]. For INAA, a quarter of a 110 mm filter and half of a 47 mm filter were loaded in small polyethylene vials. Short half-lived (<12 hours) elements were analyzed using the automated pneumatic system at the Omega West Reactor, Los Alamos National Laboratory, and at the University of Missouri Research Reactor, Columbia. For analysis of longer half-lived elements, the sample vials were loaded in aluminum cans and irradiated for 14 hours at the Texas A&M reactor, and then counted at New Mexico Institute of Mining and Technology. Ion chromatograph (IC) was used to analyze sulfur (as sulfate ion) on all filters and F on particulate filters. A portion of each filter was leached in disposable plastic centrifuge tubes using 9 g of deionized water and 1 g H₂O₂ and shaken for at least 12 hours. The solution was filtered and analyzed using a Dionex 4000i model IC. All standards were prepared gravimetrically using K₂SO₄ and KF reagent grade salts dissolved in a matrix similar to the unknown samples.

Results

Analyses of the particulate and treated filters were combined to give a total element concentration for each sample collected and recorded as micrograms of element per cubic meter of air (Tables 1 to 4). New analyses of S on filters collected in 1986 are presented in Table 1 and show previous reported analyses are in error [Meeker, 1988; Kyle et al., 1990].

Absolute concentrations of elements on the filters (expressed in $\mu\text{g m}^{-3}$) can be affected by plume dilution, sampling position in the plume, and LiOH concentrations on the impregnated filters. It is therefore more convenient to express the data as (1) relative concentrations by determining the element as a percentage of the total concentration of all elements analyzed on a filter, (2) as emission rates, or (3) as enrichment factors.

Relative concentrations for representative elements are shown on Figure 1. Although the measured concentrations of components show large changes between 1986 and 1991, changes in their relative proportions are smaller. The least variable of the elements are S, Cl, and F, which vary less than 10% between 1986 and 1991. Figure 1 also shows an increase in the alkali metals content in 1991. Similar

Table 1. Concentrations of Elements in Mount Erebus Plume Samples Collected in December 1986

	Sample 86-1, Dec. 19, 1986, Size 110 mm, Volume 1.38 m ³	Sample 86-2, Dec. 19, 1986, Size 110 mm, Volume 4.96 m ³	Sample 86-3, Dec. 20, 1986, Size 110 mm, Volume 3.15 m ³	Sample 86-4, Dec. 20, 1986, Size 110 mm, Volume 2.1 m ³	Sample 86-5, Dec. 21, 1986, Size 110 mm, Volume 3.8 m ³	Sample 86-6, Dec. 22, 1986, Size 110 mm, Volume 4.32 m ³	Sample 86-7, Dec. 23, 1986, Size 110 mm, Volume 1.8 m ³	Sample 86-8, Dec. 24, 1986, Size 110 mm, Volume 1.11 m ³	Sample 86-9, Dec. 24, 1986, Size 110 mm, Volume 5.07 m ³	Mean	S.d.	% Total
F	183	166	806	649	658	228	936	455	258	482	290	23
Na	27.6	32.1	126	128	132	30.9	52.9	63.7	64.3	73.1	43.9	3.5
Al	3.5	7.2	5.1	19.2	7.05	5	20.1	16.8	70.5	17.2	21.0	0.8
S	187.3	342.2	479.3	492.1	n.d.	516.1	469.8	595.7	1087.9	521.3	299.4	24.8
Cl	399	334	1830	1588	1784	664	670	444	448	907	634	43
K	26.1	25.9	113	79.1	134	26.1	39	43.8	29.2	57.4	41.4	2.7
Ca	n.d.	n.d.	14	23	n.d.	7.3	18.6	35.5	20.9	13.3	12.4	0.6
Sc	0.001	0.001	0.001	0.003	n.d.	0.001	0.002	0.003	0.008	2.1E-03	2.3E-03	1.0E-04
Ti	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	0	0
V	0.02	n.d.	0.02	0.005	n.d.	n.d.	0.03	0.08	n.d.	1.7E-02	2.6E-02	8.2E-04
Cr	1.2	0.09	0.05	0.1	0.16	0.01	0.18	0.11	0.4	0.26	0.37	0.01
Mn	0.08	0.4	0.55	0.86	0.34	0.13	0.45	0.52	1.6	0.55	0.46	0.03
Fe	19.9	14	7.4	18.9	9.1	6.8	20.6	26.2	42.2	18.3	11.2	0.9
Co	0.18	n.d.	n.d.	n.d.	n.d.	0.004	0.01	0.57	0.001	0.085	0.191	0.004
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	0	0
Cu	0.02	n.d.	3.8	4.9	n.d.	0.84	n.d.	0.008	n.d.	1.063	1.903	0.051
Zn	1.1	1.2	4	2.1	3	2.5	4.8	3.5	2.6	2.8	1.2	0.1
As	0.06	0.5	2	2	1.5	0.36	0.54	0.51	0.48	0.88	0.74	0.04
Se	0.08	0.01	0.05	0.03	0.04	0.05	n.d.	n.d.	0.03	0.03	0.03	0.00
Br	1.8	1	2.8	3.1	4.8	1.6	2.2	1.3	0.9	2.2	1.2	0.1
Rb	n.d.	0.23	0.72	0.68	0.81	0.16	n.d.	0.32	n.d.	0.32	0.33	0.02
Mo	n.d.	n.d.	n.d.	n.d.	0.02	0.07	0.9	5.4	0.04	0.71	1.78	0.03
Cd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	0	0
In	0.06	0.05	0.19	0.17	0.2	0.04	0.04	0.04	0.03	0.09	0.07	0.004
Sb	0.005	0.01	0.06	0.08	0.03	0.007	0.026	0.04	0.04	0.033	0.025	0.002
Cs	0.005	0.01	0.02	0.02	0.04	0.007	0.015	0.01	n.d.	0.014	0.012	0.001
La	0.004	0.05	0.02	0.04	0.02	0.011	0.046	0.06	0.14	0.043	0.041	0.002
Ce	n.d.	0.09	0.03	0.07	0.03	0.046	0.154	n.d.	0.27	0.077	0.087	0.004
Sm	n.d.	0.01	n.d.	n.d.	0.004	0.001	0.005	0.006	0.02	0.005	0.007	2.4E-04
Eu	n.d.	0.002	0.015	0.01	n.d.	0.001	n.d.	n.d.	0.002	0.003	0.005	1.6E-04
Yb	0.02	0.006	0.008	0.01	0.01	0.023	0.098	0.2	0.08	0.051	0.065	2.4E-03
Hf	0.02	0.003	n.d.	0.006	0.008	0.055	0.008	0.01	0.02	0.014	0.017	6.9E-04
Ta	0.03	0.006	0.002	0.04	0.01	n.d.	n.d.	n.d.	0.009	0.011	0.014	5.1E-04
W	0.015	0.01	0.08	0.006	n.d.	0.01	n.d.	0.004	n.d.	0.014	0.025	6.6E-04
Au	n.d.	0.00052	n.d.	0.00062	n.d.	0.00131	0.000122	0.00058	0.00075	4.3E-04	4.5E-04	2.1E-05
Total	851.10	925.08	3395.22	3011.53	2735.17	1490.13	2236.50	1693.39	2027.67	2098.57		

All values in $\mu\text{g m}^{-3}$. All data from Meeker [1988] except S concentrations. Abbreviation n.d., not detected; dash, not determined; read 2.1E-03 as 2.1×10^{-3}

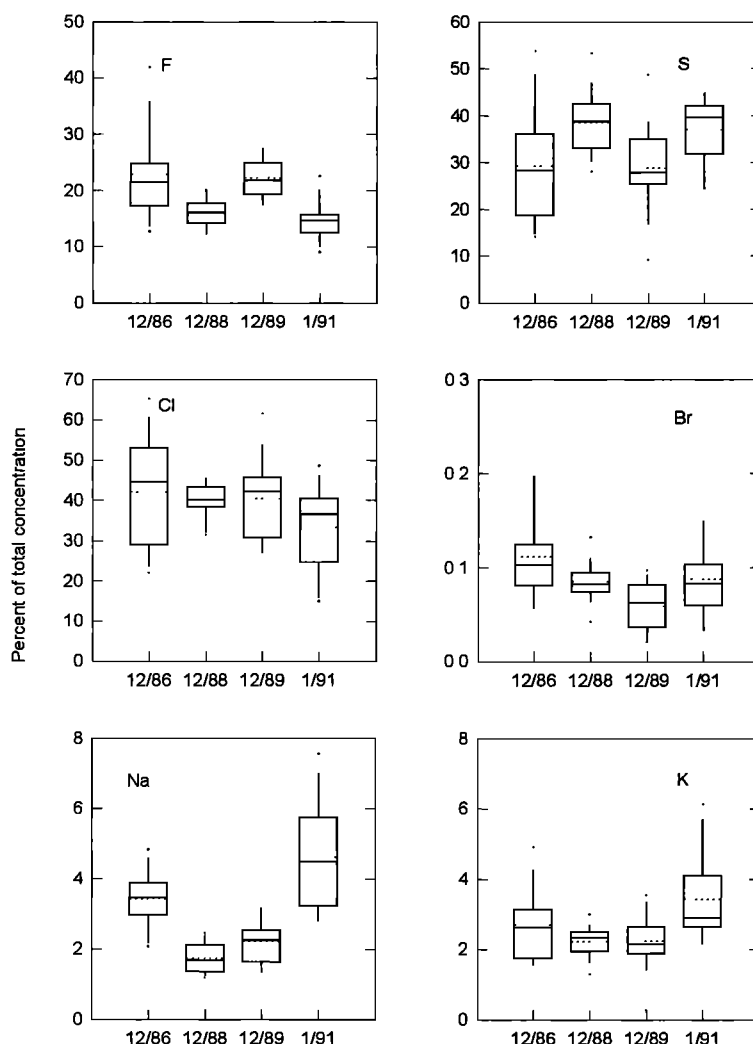


Figure 1. Representative distribution plots of elements as analyzed on filter packs collected at Mount Erebus in December 1986, 1988, 1989 and January 1991. Concentrations are expressed as the percentage of the total elements concentrations measured on the filters. Data for each year are represented as box plots with the size of each box determined by the spread of distribution of data between the 25th and 75th percentile. The "whiskers" are showing data between the 10th and 90th percentile, and points below and above the whiskers represent the outliers. The solid line in each box is a median, and the dotted line gives the average (arithmetic mean) for each data set. This representation allows "at a glance" comparison between samples collected during each sampling season, making season-to-season changes in composition of the plume more visible.

increases in the relative content of Al, Fe and Mn (not shown here) were also observed, and indicate an increase in ash content of the plume.

Element emission rates (Table 5) are calculated by using element/sulfur weight ratios determined on the filters and correlation spectrometer (COSPEC) measurements of SO_2 emission rates [Kyle *et al.*, 1994]. Uncertainties in the emission rates result from (1) analytical errors during filter analysis, (2) errors in SO_2 flux measurements, and (3) uncertainties associated with sample collection. The overall uncertainty in the emission rate for an element (σ_F) [Journel and Huijbregts, 1978] was calculated using

$$\sigma_F = \sqrt{x_\Phi^2 \sigma_r^2 + x_r^2 \sigma_\Phi^2 + 2x_\Phi x_r \sigma_\Phi \sigma_r} \quad (1)$$

where x_Φ and σ_Φ are mean and standard deviation values of S flux, and x_r and σ_r are mean and standard deviation values of element-to-sulfur ratio.

Emission rates of SO_2 and other volatiles have increased since 1985 (Table 5). The total amount of the three most abundant volatiles ($\text{SO}_2 + \text{HF} + \text{HCl}$) increased from 19 Gg yr^{-1} in 1986 to about 45 Gg yr^{-1} in 1991 ($1 \text{ Gg} = 10^9 \text{ g}$). Between 1986 and 1989, the emissions of HF increased from 4.0 to 9.2 Gg yr^{-1} , but then declined to 6.0 Gg yr^{-1} in 1991. Likewise the HCl emissions increased from 6.9 to 17.5 Gg yr^{-1} , and then decreased to 13.3 Gg yr^{-1} in 1991. Emissions of other components also show an increase between 1986 and 1991. For example, Na emissions increased from 0.5 to 1.7 Gg yr^{-1} and K emissions increased from 0.4 to 1.1 Gg yr^{-1} . Aluminum showed a sudden increase from 0.2 Gg yr^{-1} in December 1989 to 1.4 Gg yr^{-1} in January 1991, consistent with an increased ash content in the plume. Similar large

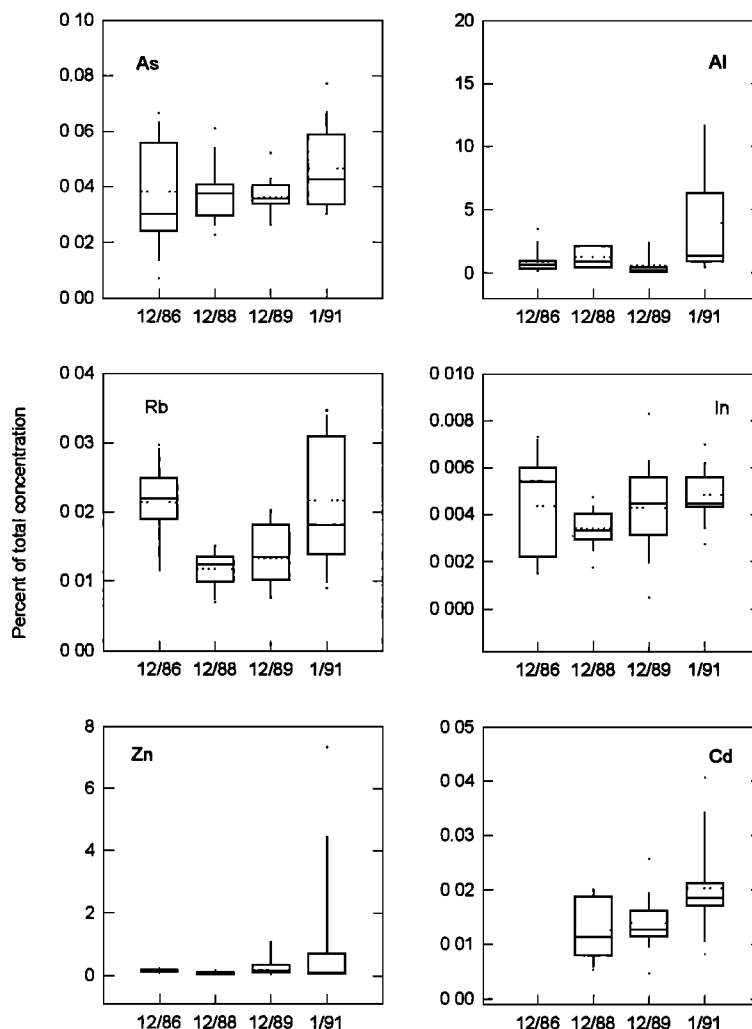


Figure 1. (continued)

increases, often of several orders of magnitude, were observed in 1991 for V, Cr, Mn, Fe, Co, Ni, Cu, Zn, rare earth elements, Hf, Ta, and Au also consistent with increased ash contents. The average emission rates (Table 5) do not use 1991 data for Au as these are unreasonably high, possibly due to contamination.

Enrichment factors are a convenient way to compare data from different volcanoes or even between samples collected at different times from the same volcano. Enrichment factor (EF) is defined as [Zoller *et al.*, 1983]

$$EF_{\text{sample}} = \frac{(X/R)_{\text{sample}}}{(X/R)_{\text{magma}}} \quad (2)$$

where EF_{sample} is the enrichment factor of element X in the sample; $(X/R)_{\text{sample}}$ is the ratio of element X to the reference element R in the sample, and $(X/R)_{\text{magma}}$ is the ratio of element X to the reference element in the magma. The composition of fresh lava or volcanic ash is often used as the reference material. This shows which elements in the gas are being preferentially volatilized and consequently enriched in the gas. However, such data cannot be used to make

comparisons between volcanic systems of differing magma composition or with ambient atmospheric aerosols. To allow such comparisons, EFs are calculated with respect to an average crustal composition.

The reference element used in the calculation of EF should be characterized by well-established concentrations in the source and by the low reactivity of its compounds in the atmosphere. Usually, aluminum, scandium, iron and magnesium are used as the reference elements for normalizing atmospheric and volcanic plume data [Vie le Sage, 1983]. These elements are important constituents of both ash and crustal material, and have low chemical reactivity. However, these elements are not suitable for normalizing data collected in plumes that have high or variable ash content because the values obtained by the normalization depend on the amount of ash collected on filter. Crowe *et al.* [1987] found that the enrichment factors normalized to ash are minimum values and proposed the use of Br as the reference element. Collection of bromine appears to be sufficiently quantitative in filter collection systems, and because the release rate of Br is less subject to changes through the eruption cycle, Br provide constant calculations

Table 5. Average Emission Rates of Gases and Aerosols From Mount Erebus

	December 1986		December 1988		December 1989		January 1991		All Years	
	Mean	S.d.	Mean	S.d.	Mean	S.d.	Mean	S.d.	Mean	S.d.
SO ₂	7.7	4.0	9.8	3.3	19.0	7.7	25.9	7.3	15.6	8.4
HF	4.0	3.8	2.3	1.2	9.2	7.7	6.0	4.1	5.3	3.0
Na	0.5	0.5	0.2	0.1	0.9	0.8	1.7	1.0	0.8	0.6
Al	0.11	0.1	0.2	0.3	0.2	0.4	1.4	2.1	0.5	0.6
HCl	6.9	7.1	5.5	2.8	17.5	18.9	13.3	9.5	10.8	5.6
K	0.4	0.4	0.3	0.2	0.9	0.8	1.1	0.6	0.7	0.4
Ca	0.13	0.12	0.22	0.22	1.07	1.13	0.19	0.18	0.40	0.45
Sc	1.6E-05	1.4E-05	1.7E-05	3.8E-05	2.7E-05	3.9E-05	4.4E-05	4.1E-05	2.6E-05	1.3E-05
Ti			0.014	0.010	0.18	0.19	0.12	0.14	0.08	0.09
V	2.7E-04	2.9E-04	4.5E-04	4.6E-04	3.4E-04	2.4E-04	7.9E-03	1.5E-02	2.2E-03	3.8E-03
Cr	3.8E-03	9.6E-03	1.4E-03	1.5E-03	0.011	0.017	0.046	0.105	1.5E-02	2.1E-02
Mn	3.9E-03	3.4E-03	9.2E-04	6.2E-04	2.5E-03	2.8E-03	0.023	0.025	7.7E-03	1.0E-02
Fe	0.16	0.17	0.042	0.033	0.15	0.18	0.54	0.57	0.22	0.22
Co	1.5E-03	2.5E-03	3.7E-05	7.0E-05	7.1E-05	7.5E-05	0.030	0.071	7.9E-03	1.5E-02
Ni					4.8E-03	6.3E-03	0.010	0.003	3.8E-03	4.9E-03
Cu	0.02	0.02			4.7E-03	1.9E-03	0.15	0.29	4.3E-02	7.3E-02
Zn	0.02	0.02	9.9E-03	9.2E-03	0.11	0.14	0.38	0.81	0.13	0.17
As	6.3E-03	8.2E-03	5.0E-03	3.4E-03	0.014	0.012	0.017	0.011	1.1E-02	5.9E-03
Se	4.8E-04	7.4E-04	1.4E-04	4.6E-05	3.3E-04	2.8E-04	5.9E-03	1.3E-02	1.7E-03	2.8E-03
Br	0.017	0.017	0.011	0.006	0.023	0.024	0.034	0.029	2.1E-02	9.9E-03
Rb	3.4E-03	3.3E-03	1.5E-03	7.6E-04	5.4E-03	5.9E-03	7.1E-03	4.1E-03	4.3E-03	2.4E-03
Mo	1.1E-02	2.0E-02	2.2E-04	1.1E-04	2.1E-03	3.0E-03			3.3E-03	5.1E-03
Cd			1.6E-03	1.2E-03	5.8E-03	5.3E-03	7.9E-03	6.4E-03	3.8E-03	3.6E-03
In	7.1E-04	8.1E-04	4.4E-04	2.2E-04	1.8E-03	2.0E-03	1.7E-03	8.3E-04	1.2E-03	6.9E-04
Sb	2.5E-04	2.9E-04	2.0E-04	2.3E-04	7.1E-04	9.9E-04	1.3E-03	2.6E-03	6.3E-04	5.3E-04
Cs	1.1E-04	8.6E-05	5.4E-05	2.9E-05	2.5E-04	2.4E-04	3.1E-04	2.1E-04	1.8E-04	1.2E-04
La	3.1E-04	3.0E-04	2.2E-05	1.7E-05	1.5E-04	2.0E-04	1.7E-03	2.1E-03	5.6E-04	8.0E-04
Ce	7.3E-04	6.8E-04	7.3E-05	7.2E-05	3.2E-04	3.6E-04	5.1E-03	5.7E-03	1.6E-03	2.4E-03
Sm	5.4E-05	5.9E-05	3.5E-06	2.4E-06	1.7E-05	1.7E-05	2.3E-04	2.7E-04	7.7E-05	1.1E-04
Eu	4.7E-05	6.6E-05			5.8E-06	6.5E-06	5.6E-05	6.3E-05	2.7E-05	2.9E-05
Yb	4.0E-04	5.7E-04			1.5E-05	1.7E-05	1.3E-04	1.1E-04	1.4E-04	1.8E-04
Hf	1.6E-04	2.3E-04			7.5E-05	3.0E-05	4.4E-04	4.8E-04	1.7E-04	1.9E-04
Ta	2.1E-04	3.3E-04			1.8E-05	2.0E-05	2.1E-04	2.8E-04	1.1E-04	1.2E-04
W	2.0E-04	3.0E-04	1.0E-04	3.4E-05	5.7E-04	1.1E-03	2.8E-02	6.7E-02	7.3E-03	1.4E-02
Au	4.6E-06	4.7E-06	5.2E-05	7.3E-05	9.7E-05	1.3E-04	2.3E-02	4.1E-02	5.8E-03	1.1E-02

All data in gigagrams per year. Read 1.6E-05 as 1.6×10^{-5} .

of enrichment factors. Bromine-normalized values must be multiplied by a 10^5 factor which represents the approximate enrichment of Br in the gas phase and adjusts the enrichment factors for nonenriched ash elements to unity. This allows a comparison between Br-normalized and conventional EFs values [Crowe *et al.*, 1987].

Thanks to the low ash content of the Erebus plume, the use of either Al, Sc, or Br produces similar results in calculating EFs. Here we used Sc as the reference element because (1) Sc is easily analyzed by INAA even at very low concentrations, whereas in some cases high-precision determination of Br was a problem due to high blank concentrations; and (2) using Sc allows Br enrichment in the plume to be determined; this is important because Br may be important in volatilization of some metals [Gemmel, 1987].

Four yearly averaged EF values for the Erebus filter pack sample are compared with a sample collected in December 1978 [Germani, 1980] (Figure 2) and with aerosol samples collected at south pole and the Antarctic Peninsula (Figure 3). For Erebus there is generally good agreement between the four years with the January 1991 data showing higher enrichment of elements expected in ash. Indium, Cd, and S are the most enriched elements compared to the Erebus magma. The data from December 1978 show slightly higher EFs than our data. As the 1978 data set consists of a single sample and the analytical procedure was different from ours,

we do not know if the differences are real or due to sampling and analytical procedures.

Discussion

Sulfur Emissions

Sulfur is emitted from Mount Erebus mainly as SO₂ [Kyle *et al.*, 1994], although minor amounts of S-bearing aerosols are trapped on the particulate filters. Between December 1986 and January 1991 the SO₂ emission rates, as measured by COSPEC [Kyle *et al.*, 1994], increased from 7.7 to 25.9 Gg yr⁻¹ (Table 5), with an average SO₂ output of 22 Gg yr⁻¹ in the period 1983-1994 [Kyle *et al.*, 1994, 1996]. The SO₂ emission rates of Mount Erebus are extremely low compared to most volcanoes and insignificant compared to the global volcanic SO₂ emission rate of 13 Tg yr⁻¹ [Bluth *et al.*, 1993]. After emission, the SO₂ will convert to SO₄²⁻ and eventually be deposited onto the snow and sea surrounding Mount Erebus.

Sulfate aerosols which constitute about 70-80% of all polar aerosols by mass [Shaw, 1989] are produced by biogenic activity in the oceans (these are sometimes called non sea-salt sulfates or nss-S), whereas sea-salt sulfates, volcanic activity, and anthropogenic emissions are minor sources of SO₄²⁻. Most of the nss-S compounds are formed by oxidation of dimethyl sulfide (CH₃)₂S produced by algae

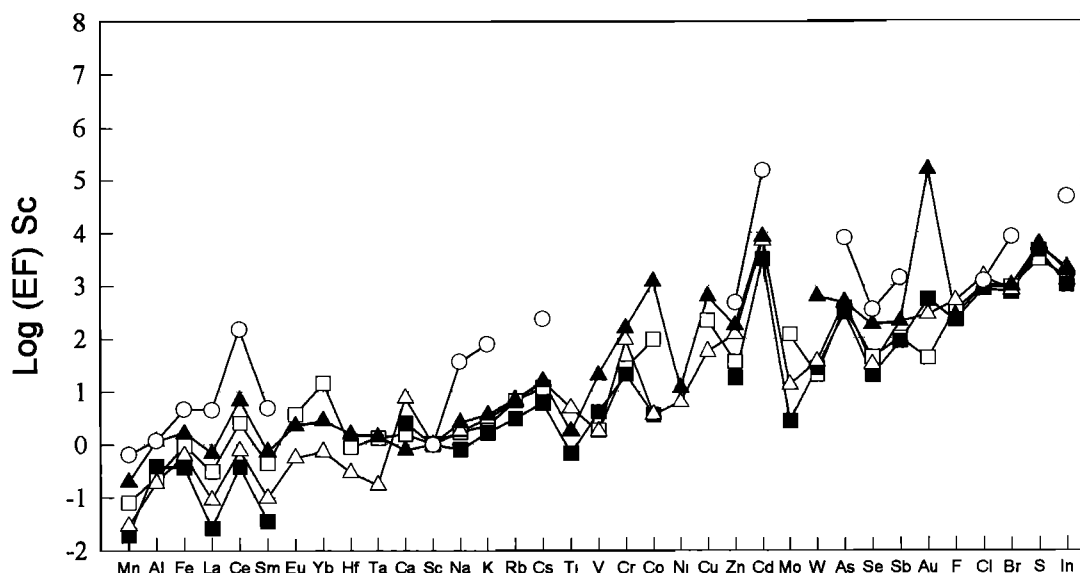


Figure 2. Comparison of enrichment factors ($EF_{\text{crust}}(Sc)$) relative to Erebus magma and normalized to Sc for yearly averages of Mount Erebus filter pack samples (Table 5) and a sample collected by *Germani* [1980] in December 1978. Open squares, December 1986; solid squares, December 1988; open triangles, December 1989; solid triangles, 1991; open circles, December 1978.

and phytoplankton in the oceans and by bacteria in the marine boundary layer with methane sulfonic acid (CH_3SO_3H) and H_2SO_4 being the main products [Shaw, 1989; Delmas, 1992].

The sulfate budget for Antarctica has been evaluated by *Delmas* [1982] using a simple box model in which the Antarctic atmosphere is represented as a rectangular box with a square base $A = 14 \times 10^6 \text{ km}^2$ ($\sim 3700 \times 3700 \text{ km}$) and height $h = 5 \text{ km}$. *Delmas* [1982] reported typical SO_2 and SO_4^{2-} concentrations of $0.1 \mu\text{g m}^{-3}$ (equivalent to $0.15 \mu\text{g m}^{-3}$ of SO_4^{2-}), and $0.3 \mu\text{g m}^{-3}$, respectively, in the Antarctic air. An input (Q) of S (as SO_4^{2-}) into the Antarctica atmosphere can be calculated using

$$Q = C_{\text{air}} v_{\text{wind}} A_c \quad (3)$$

where C_{air} is the SO_4^{2-} concentration in air of $0.45 \mu\text{g m}^{-3}$, v_{wind} is an average wind velocity of 5 m s^{-1} and A_c the vertical cross-section area of $3700 \text{ km} \times 5 \text{ km}$. This gives a total S input of 1300 Gg yr^{-1} as SO_4^{2-} .

The SO_2 emissions from Mount Erebus in January 1991 were $25.9 \pm 7.3 \text{ Gg yr}^{-1}$, equivalent to 39 Gg yr^{-1} of SO_4^{2-} . Because the estimated input of SO_4^{2-} into Antarctica is 1300 Gg yr^{-1} , it follows that Mount Erebus can contribute about 3 % of the total sulfur present in the Antarctic atmosphere.

The amount of S deposited in the snow by dry deposition (D_d), assuming homogeneous distribution over the continent, is calculated using the equation [Delmas, 1982]

$$D_d = C_{\text{air}} v_d A \quad (4)$$

where v_d is the deposition velocity ($v_d = 0.08 \text{ cm s}^{-1}$ [Delmas 1982]) and A is the area of the Antarctic ($14 \times 10^6 \text{ km}^2$). The calculated dry deposition of SO_4^{2-} is 160 Gg yr^{-1} .

The residence time (T_R) of S in the Antarctic atmosphere can be calculated using

$$T_R = \frac{C_{\text{air}} V_{\text{atm}}}{D_d} = \frac{C_{\text{air}} A h}{D_d} \quad (5)$$

where h can be assumed to be equal to 5 km . Equation (5) simplifies to

$$T_R = \frac{h}{v_d} \quad (6)$$

A v_d of 0.08 cm s^{-1} gives a T_R of 72 days to transport SO_4^{2-} in a 5 km thick atmosphere; this compares to a T_R of 50 days suggested by *Shaw* [1982]. It is apparent that although there is a considerable flux of S into Antarctica, the low deposition velocity means that only $\sim 10\%$ ends up in the snow. If the same deposition rate applies to aerosol derived from Mount Erebus, then it will only contribute a few percent of the sulfate in Antarctic snow and its contribution will be drowned out by marine derived SO_4^{2-} . However, gas emissions from Mount Erebus are unlikely to be evenly distributed over all of Antarctica and there will be areas of local enrichment. Therefore in the Ross Sea area the significance of Mount Erebus as a sulfur source may be larger.

Chlorine Emissions

The HCl emission rates from Mount Erebus ranged from 5.5 Gg yr^{-1} in 1988 to 17.5 Gg yr^{-1} in 1989 (Table 5). If this HCl was distributed homogeneously over the $14 \times 10^6 \text{ km}^2$ of Antarctica and deposited in the snow, it would contribute $0.38 \text{ kg km}^{-2} \text{ yr}^{-1}$ of Cl in 1988 and $1.2 \text{ kg km}^{-2} \text{ yr}^{-1}$ of Cl in 1989. *Legrand and Delmas* [1988] measured Cl concentrations in snow deposited between 1959 and 1969 at Dome C and south pole as $69 \pm 11 \text{ ng g}^{-1}$ and $45 \pm 13 \text{ ng g}^{-1}$, respectively (Table 6). Although these measurements were not made at the same time as our plume measurements, they are sufficiently close in time to allow comparison. Taking the

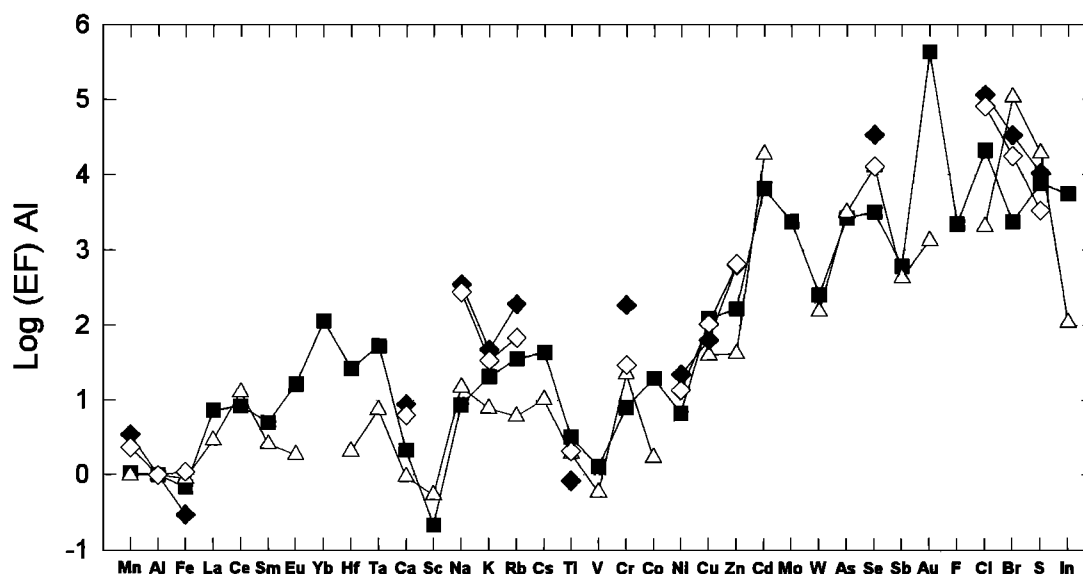


Figure 3. Comparison of enrichment factors ($EF_{crust}(Al)$) relative to average crust [Taylor and McLennan, 1985] and normalized to Al for the average of Mount Erebus filter pack samples (solid squares) and aerosol samples from south pole (1974-1975, open triangles) [Maenhaut et al., 1979], and two sizes of aerosols collected on the Antarctic Peninsula (solid diamond, fine; open diamond, coarse) [Artaxo et al., 1992].

range in Cl emission rates from Mount Erebus, we can calculate its concentration in the snow knowing the snow accumulation rates (Table 6). For south pole, the data in Table 6 would suggest that Mount Erebus could contribute between 10 and 32% of the total Cl in the snow. At Dome C the Cl contribution from Mount Erebus could be between 16 and 52%.

Marine aerosols are a major source of Cl (as NaCl) in the Antarctic atmosphere and snow. Legrand and Delmas [1988] detected excess Cl (Cl_{ex}) in snow deposited during summer months on the East Antarctic Ice Sheet. Cl derived from marine aerosols will be accompanied by Na and have a Cl/Na ratio of 1.8; when this ratio is exceeded, the additional Cl (assumed to be HCl) is termed Cl_{ex} . Legrand and Delmas [1988] estimated Cl_{ex} deposition at south pole to range from 1 to 2 kg km² yr⁻¹. The Cl_{ex} occurs in snow accumulated during summer months and was explained as a product of a reaction between sea-salt and biogenic H₂SO₄ [Legrand and Delmas, 1988]. However, our calculated Cl deposition rate of 1.2 kg km² yr⁻¹ from Mount Erebus in 1991 lies within the range of Cl_{ex} observed at south pole.

An estimate of Cl_{ex} at south pole and Dome C can be calculated knowing the Na concentration in the snow (Table 6) [Legrand and Delmas, 1988] and using the expression

$$Cl_{ex} = Cl - 1.8Na \quad (7)$$

We calculate 18 ng g⁻¹ of Cl_{ex} at south pole and 40 ng g⁻¹ at Dome C (Table 6). Using our January 1991 emission rate data, this suggests that almost all the Cl_{ex} could be derived from Mount Erebus. The lowest Cl emission rates were measured in December 1986, and these could account for about a third of the Cl_{ex} at both south pole and Dome C. It seems reasonable to suggest that Mount Erebus could be the source of most of the Cl_{ex} in recent snow to fall on the East Antarctic Ice Sheet.

The amount of Cl dry deposited (D_d) in the snow can be calculated using

$$D_d = C_{snow} k_{snow} A \quad (8)$$

where C_{snow} is the Cl concentration in snow, k_{snow} is the snow accumulation rate (in g cm² yr⁻¹) and A is the area of the Antarctic continent (14 × 10⁶ km²). To obtain an approximate D_d for Cl for the East Antarctic Ice Sheet, we have used the average of C_{snow} and k_{snow} for South Pole and Dome C (Table 6). A C_{snow} of 57 ng g⁻¹ and k_{snow} of 5.95 g cm² yr⁻¹, results in a D_d for Cl of 47.5 Gg yr⁻¹.

Rearranging (4), the deposition velocity of Cl on snow can be estimated:

$$v_d = \frac{D_d}{C_{air} A} \quad (9)$$

Using a C_{air} of 10 ng m⁻³ [Duce et al., 1973], area A as given above and D_d of 47.5 Gg yr⁻¹, the calculated v_d is 1.08 cm s⁻¹. This is lower but within the error of the experimental measurements of Dasch and Cadle [1986; after Davidson, 1989], who obtained values of 4.3 ± 6.1 and 5.1 ± 4.0 cm s⁻¹ from measured Cl⁻ deposition velocities on surface snow and on a snow/water mixture, respectively.

Using (6), the residence time of Cl in the Antarctic atmosphere is 5.4 days. It is generally thought that volatile Cl injected into the troposphere by volcanoes has a short lifetime and is quickly removed by wet deposition [Tabazadeh and Turco, 1993]. However, in the dry desert environment of Antarctica, wet deposition should not be a factor. We are not aware of any published T_R data for Cl in the Antarctic atmosphere. Duce et al. [1973] stated that gaseous Br may have a residence time of 2-3 weeks. Because it is likely that gaseous Cl behaves similarly to Br, the T_R value calculated above may be low. The calculated T_R indicates there is sufficient time for Cl emissions from Mount Erebus to be quite widely dispersed and consistent with its deposition on the East Antarctic Ice Sheet.

Table 6. Na and Cl Concentrations and Calculated Cl_{ex} in Antarctic Snow and Estimates of Cl Deposition from Mount Erebus Using Emission Rate Data From December 1988 and December 1989

Location	Snow Accumulation Rate, $g\ cm^{-2}\ yr^{-1}$	Observed Concentrations, $ng\ g^{-1}\ snow$			Estimated Cl Deposition From Mount Erebus					
					Minimum Flux = $5.32\ Gg\ yr^{-1}\ (1988)$			Maximum Flux = $17.07\ Gg\ yr^{-1}\ (1989)$		
		Na	Cl	Cl_{ex}^*	$ng\ g^{-1}$	% Cl Total	% Cl_{ex}	$ng\ g^{-1}$	% Cl Total	% Cl_{ex}
South pole (1959-1969)	8.5	15 ± 6	45 ± 13	18	4.5	10	25	14.3	32	80
Dome C (1959-1969)	3.4	22 ± 9	69 ± 11	29	11.2	16	38	35.9	52	122

The deposition rates were calculated assuming an area of deposition of $14 \times 10^6\ km^2$ and are given in nanograms per gram and as percent of the Cl and Cl_{ex} in the snow at south pole and Dome C. Accumulation rates, Na and Cl data in snow from south pole and Dome C from *Legrand and Delmas* [1988].

* $Cl_{ex} = Cl - 1.8Na$.

Fluorine Emissions

Mount Erebus emits significant quantities of F which could be used as a tracer and should be also present in the atmosphere and snow deposited in Antarctica. Unfortunately, F has not been measured in Antarctic atmosphere or snow and ice samples. *Herron* [1982] measured large concentrations of F in Greenland ice cores that correlate with peaks from volcanic eruptions showing that F, like Cl and SO_4^{2-} , is deposited in snow/ice and provides a record of volcanic activity. *De Angelis and Legrand* [1994] also measured F in Greenland snow and confirmed the volcanic source for high concentrations of F. They postulate that the source of background F concentrations present during nonvolcanic periods is probably associated with soil dust and biomass burning and that some F in recent snow samples may be of anthropogenic origin.

If Mount Erebus is the source of the excess Cl in snow, then it should be accompanied by an enhanced F content, unless the two gases are fractionated in the atmosphere. Thus analyzing the F content of snow could help to identify the source of the excess Cl. Between December 1986 and January 1991 the HF emission rates from Mount Erebus range from 2.3 to $9.2\ Gg\ yr^{-1}$. Using a maximum value of $9.2\ Gg\ yr^{-1}$ HF ($=8.7\ Gg\ yr^{-1}$ F), and assuming similar reasoning to that presented above, this gives about $0.62\ kg\ km^{-2}\ yr^{-1}$ of F deposited in the snow. At a snow accumulation rate of $8.5\ g\ cm^{-2}\ yr^{-1}$ for the south pole (Table 6), we estimate the amount of F in the snow as about $7.3\ ng\ g^{-1}$. Unfortunately, we are not aware of any published analyses of F on the Central Antarctic snow samples. However, the published major cation and anion analyses of the snow do show a deficiency in anions of $0.8\ \mu eq\ L^{-1}$ when the ionic mass balance is calculated [*Delmas et al.*, 1982]. Our estimated value for F is $0.4\ \mu eq\ L^{-1}$ and is therefore within the uncertainty of the published ionic mass balance.

The depositional velocities and residence time of F in Antarctica can be calculated using the procedures described above for Cl. If all F present in Antarctica is emitted from Erebus, then the dry deposition (D_d) is $6.1\ Gg\ yr^{-1}$. To use equation 9, the concentration of F in air (C_{air}) must be known; however, no published data exists. The comparison of Erebus output and the total flux of Cl into the Antarctic atmosphere shows that Erebus could produce ~50% (4 - 100%) of Cl present in the atmosphere. In the best case, 50-

100% of all Cl measured in the air would be from Erebus, which gives $5-10\ ng\ m^{-3}$ if the Cl content of air given by *Duce et al.* [1973] is used. The average F/Cl ratio in Erebus gas is ~0.5, so if no fractionation occurs between the two halogens, F concentration in the air could measure between 2.5 and $5\ ng\ m^{-3}$. Substituting these values into (9), the obtained deposition velocities are between 0.28 and $0.55\ cm\ s^{-1}$. Both values are similar to that obtained for Cl. The calculated residence times of F (equation (6)) range between 10 and 21 days. Finally, from the estimated concentration of F in air and (3), the total F input in the Antarctic atmosphere could range from 7 to $15\ Gg\ yr^{-1}$, in agreement with the assumption that Erebus is probably the only source of this element in Antarctica.

Discussion

Mulvaney and Wolff [1994] examined the spatial variability of sulfate and chloride on the Antarctic ice sheet. They found that Cl concentrations decreased away from the sea, consistent with the Cl being derived from marine aerosols. Excess SO_4^{2-} , assumed to be marine derived H_2SO_4 , does not decrease away from the coast in East Antarctica. *Mulvaney and Wolff* [1994] note the anomalous behavior of the excess SO_4^{2-} and attribute it to dry deposition. Overall, this compilation does not show any evidence of possible contributions of Cl or SO_4^{2-} from Mt. Erebus to the Antarctic ice sheets. Locally, it is noticeable that Cl concentrations are higher in the Ross Sea area and do not decrease away from the sea at a rate observed in East Antarctica. A possible interpretation is that this could be partly due to Cl emissions from Mount Erebus.

Mount Erebus as the Source of Metals

Mount Erebus emits various metals which may be dispersed as aerosols across Antarctica. Because of their diverse nature the trace metals may be the best marker of the Erebus plume in the atmosphere and snow/ice. The concentrations of metals in the atmosphere are minute and range from a few nanograms ($10^{-9}g$) to fractions of picograms ($10^{-12}g$) per cubic meter of air sampled. Most of the trace elements are present as particulates, although some may be also in gaseous form (for example, As and Se compounds).

The average composition of aerosols over south pole can be compared with the Erebus plume by using $EF_{crust}(Al)s$. The EFs for the Erebus plume have similar trends to aerosol samples collected at South Pole except Br and Se, which probably are of marine origin (Figure 3). Zoller *et al.* [1974] noted that several elements (Cu, Zn, Se, Br, Sb, and Pb) detected in atmospheric samples from Antarctica were anomalously enriched when compared to the composition of the crust. Duce *et al.* [1975] extended this list to include S, Cl, I, As, Cd, In, W, Ag, Au, and Hg after comparing the enrichment factors calculated relative to both crust and mean oceanic material. Analyses by Maenhaut *et al.* [1979] support the older results.

Average emission rates (Table 5) show that many of the elements, notably Zn, As, Se, Br, Cd, In, W, and Au, commonly found in anomalously high quantities in the snow and atmosphere, are emitted from Erebus. The presence of metals in the Erebus plume is attributed to the high halogen content of the Erebus magma [Meeker *et al.*, 1991; Zreda-Gostynska, 1995], which probably allows the metals to exsolve as halogenated compounds. Other factors which may be important are reducing conditions in the plume that may inhibit precipitation of aerosols and the low ash content

of the plume which would limit scavenging of aerosols and also prevent aggregation of aerosols.

The potential contribution of metals from Mount Erebus to East Antarctic snow can be estimated assuming the homogeneous distribution of the plume and the typical snow accumulation rates for the south pole and Dome C [Legrand and Delmas, 1988]. We use the average trace element emission rates (Table 5), with the exception of S emissions for which we believe the average for the 1983-1991 period is more representative. Our calculated concentrations are compared to literature values in Table 7. Analyses of metals in polar snow and ice by Boutron and Lorius [1979], Boutron [1980], and Delmas [1982] contrast with the new estimates of Wolff and Peel [1985] and Palais *et al.* [1994]. Wolff and Peel [1985] questioned the earlier analyses of snow and ice collected in remote Antarctic sites, and attributed the high concentrations of many metals to contamination during sampling. The new values, all markedly lower than earlier estimates, are currently considered to be the best values of trace element concentrations in the uncontaminated Antarctic snow.

The Erebus plume could easily account for the concentrations of Cu, Cd, V, and As, for which the predicted concen-

Table 7. Estimated Concentrations of Erebus Plume Components in the Antarctic Snow Calculated Using Model Explained in Text and Comparison With Available Measurements of SO_4 , F, Cl, and Trace Metals in Snow and Ice

	Estimated Concentrations in Snow for Erebus, pg g ⁻¹ Snow		Measured Concentrations, pg g ⁻¹ Snow			
	Snow Accumulation Rate (g cm ⁻² yr ⁻¹)	Snow Accumulation Rate (g cm ⁻² yr ⁻¹)	Palais <i>et al.</i> [1993]	Boutron and Lorius [1979]	Wolff and Peel [1985]	Legrand and Delmas [1988]
	8.5	3.4				
F	4270	10,675				
Na	688	1720	4733	7700		15,000
Al	406	1014	1310	1070	1000	
SO ₄	27,731	69,328	40,680		63,333	70,000
Cl	8828	22,071	35,500			45,000
K	567	1418		370		
Ca	340	849	1657	510		
Sc	0.02	0.05				
Ti	66	164				
V	1.89	5	2.7			
Cr	13	32				
Mn	6	16	47	18		
Fe	187	467	4000	760		
Co	7	16	1067			
Ni	3	8				
Cu	36	90		47	1.8	
Zn	111	276		6.8	3.3	
As	9	22	11			
Se	12	4	337			
Br	18	45	663			
Rb	15	9				
Mo	2.7	6.9				
Cd	3.2	8.0		3.8	0.26	
In	1.0	2.4				
Sb	0.53	1.32				
Cs	0.15	0.38				
La	0.47	1.17	3.3			
Ce	1.3	3.3				
Sm	0.06	0.16				
Eu	0.02	0.06				
Yb	0.11	0.29				
Hf	0.14	0.35				
Ta	0.09	0.23				
W	6	15				
Au	0.04	0.11				

trations are close to those measured in snow samples. Thus the values reported by *Boutron and Lorius* [1979] and *Boutron* [1980] do not necessarily have to be a result of contamination. Predicted concentrations of less volatile elements (Al, Ca, Fe, Mn, and La) cannot account for the concentrations observed in the snow samples. These elements are usually associated with crustal weathering and are transported and deposited as dust.

Artaxo et al. [1992] measured trace elements in aerosols sampled on the Antarctic Peninsula (Figure 3). When the $EF_{crust}(Al)$ are compared to the Erebus plume and to aerosols from the south pole, they show more enrichment in Ca, Cr, and Mn (regarded as an effect of crustal weathering) and in Na, Cl, Se, and Br associated with sea-spray. Unfortunately, there are no data on elements such as As, In, and Au which could be used as markers of the Erebus plume. Therefore it is not possible to recognize the Erebus influence on aerosol composition in this region.

Pb Isotopic Data

Rosman et al. [1994] made Pb isotopic analyses on Antarctic snow samples including samples from south pole and 7500 year old ice from Dome C. The data reproduced in Figure 4 were interpreted as showing that the snow was heavily contaminated by anthropogenic Pb. *Flegel et al.* [1993] suggest that Pb isotope analysis of Antarctic seawater show evidence of a component that could be derived from Mount Erebus.

Lead isotope analyses of the gas plume from Erebus have not been made; however, data for the lavas from Mount Erebus are available [*Sun and Hanson*, 1975]. Lead will be emitted as aerosol particles which condensed from gas phases emitted from the lava lake or in ash particles. We assume the Pb isotopes of the aerosols will be identical to the magma. Lavas from Mount Erebus have $^{206}Pb/^{207}Pb$ which range from 1.27 to 1.29 and $^{208}Pb/^{207}Pb$ from 2.52 to 2.54 (Figure 4). This is significantly higher than normal crustal rocks (e.g., pelagic sediments) and reflects a large HIMU (High U/Pb Mantle Component, see *Zindler and Hart*, [1986]) mantle source component in the magmas (Figure 4) [*Zindler and Hart*, 1986]. *Rosman et al.* [1994] attribute the Pb isotopic ratio in the Dome C core to terrestrial dust. The similarity of the Pb isotopic ratios of Dome C ice with Erebus lavas is consistent with Erebus being the source of the aerosols. It is significant that Mount Erebus Pb isotopic compositions plot on an extension of the linear array defined by most of the snow and ice data. We therefore suggest that Mount Erebus is the source of the background aerosol and the variation in Pb isotopes in the snow and ice is due to two component mixing between marine (seawater) aerosols and those derived from Mount Erebus. We do not accept the conclusion that the snow and ice is heavily contaminated by anthropogenic Pb.

Dispersal of the Erebus Plume

The dispersal directions of the Erebus plume are unknown. The Cl, F, and Pb isotopic data suggests they could be good tracers of the Erebus plume. Unfortunately, the general scarcity of Cl and F data in both the snow/ice and the atmospheric aerosols, makes it impossible to evaluate the

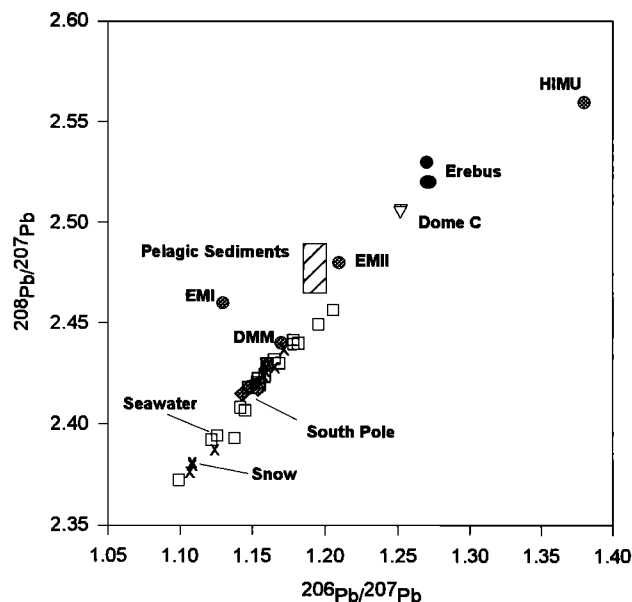


Figure 4. Plot of $^{208}Pb/^{207}Pb$ versus $^{206}Pb/^{207}Pb$ for rocks from Mount Erebus (solid circles) [*Sun and Hanson*, 1975], Antarctic snow (crosses), Dome C dust (inverted triangles), south pole snow (rhombuses) [*Rosman et al.*, 1994], Antarctic seawater (squares) [*Flegel et al.*, 1993], pelagic sediments [*Chow and Patterson*, 1962] and the four end-member (EMI, EMII (enriched mantle I and II), DMM (depleted MORB-mantle; MORB=Midocean Ridge Basalt), HIMU (High U/Pb mantle) mantle compositions proposed by *Zindler and Hart* [1986] (gray circles). Note the Antarctic snow and Dome C samples appear to lie on a mixing line between Mount Erebus rocks (presumably the same as Mount Erebus aerosols) and seawater.

extent of plume transport, and possible changes in its halogen content. From the preliminary estimates of the halogens residence times one can surmise that both Cl and F can remain in the atmosphere for days to weeks. One can also assume that dry deposition would be the most likely removal process of halogens in Antarctica, because their removal via wet deposition (which includes scavenging by forming snow/ice crystals) is precluded by the extreme aridity of air and absence of ice crystals [*Tabazadeh and Turco*, 1993]. Therefore, given a favorable pattern of air mass movement, the Erebus plume could be dispersed throughout the Antarctic atmosphere.

How could the Erebus plume reach the interior of the Antarctic continent? The circulation of air masses over Antarctica varies between summer and winter seasons. Analysis of monthly deviations from the mean annual pressure over the continent indicates that there is a net inflow of air into Antarctica during summer (October through January) and that during winter (from February through September) the air is moving away from the continent [*Schwerdtfeger*, 1970; after *Mroz et al.*, 1989]. In winter this movement of air masses is due to the presence of the circumpolar vortex which disappears in spring. Additionally, there is also evidence for the existence of meridional transport of air. In the lower atmosphere (corresponding to pressure > 600 mbar) air masses are moving outward from the continent; this movement is balanced by inflow from the oceans at higher altitudes (< 600 mbar). At the

center of the continent the air masses sink delivering the aerosols from the upper troposphere and lower stratosphere. Partly due to the establishment of the polar vortex, the meridional pattern weakens during the winter and seems to be stronger during summer months, as reflected in the composition of summer aerosols which show enrichment in crustal dust, sea salt, volcanic emissions, and radionuclides from the stratosphere [Mroz *et al.*, 1989]. Strong winter storms can occasionally penetrate the circumpolar vortex and transport aerosols toward the inside of the continent, but such events are rare. Atmospheric tracer experiments [Mroz *et al.*, 1989] and the study of tropospheric flow patterns by Harris [1992] indicate the presence of rapid (lasting few days) poleward movement of air masses during the Antarctic summer which strengthens the hypothesis that the Erebus plume can be transported inland. It also shows some evidence for vertical mixing of air masses on the edge of the continent, again a condition favorable for the plume because it allows for long-range transport.

Conclusions

The data presented here suggest that Mount Erebus is a significant source of aerosols and gases to the Antarctic environment. Although we are aware of the limitations of the simple modeling calculations presented above, we feel that the results thus obtained are realistic. Erebus-derived Cl could be responsible for as much as 80% of Cl_{ex} at south pole and all of the Cl_{ex} at Dome C. The Cl_{ex} should be accompanied by F at these locations. Fluorine has the potential to be the best tracer of the Erebus plume, and we have estimated its concentrations in the snow as 7.3 ng g^{-1} snow, which is within the limit of ionic mass balance calculated from analyses of Antarctic snow samples. The estimated residence times for both Cl and F (5 and 7 days, respectively) are sufficient for the halogens to participate in long-range transport processes over the Antarctica.

Mount Erebus could also be a potential source of Cu, Cd, V, and As found in Antarctic snow and atmospheric samples. Our modeled concentrations are close to those reported from snow/ice samples collected in various regions of Antarctica. That, together with the similarity of trace element and Pb-isotope composition of Erebus aerosols with aerosols collected in the remote regions of Antarctica, indicates that Erebus plume provides a significant component in the Antarctic system.

Further studies of trace elements in snow and ice will be helpful in evaluating the importance of Mount Erebus as a source of gases and aerosols to the Antarctic atmosphere. Especially helpful would be more data on elements, such as As and In, both of which are enriched in the Erebus plume. By combining the trace element analysis with that of more abundant anions (Cl^- , SO_4^{2-} , and F^-) it should be possible to trace the patterns of Erebus plume dispersal and to resolve the question of the source of some contaminants often detected in snow samples.

Acknowledgments. Many people contributed to the success of this project both in the field and in the lab. Sampling of the plume at Mount Erebus was assisted by Nelia Dunbar, Bill McIntosh, Bob Andres, Buzz Caldwell, and Kurt Panter. Field work was made possible by logistic support from the U.S. Navy VXE-6 squadron

and numerous individuals working with the civilian contractors supporting the U.S. Antarctic Program. At New Mexico Tech, assistance with lab work was provided by Lynn Brandvold, Jenny Verploegh, and Sandy Swartz. Mike Glascock and Jeff Denison were invaluable in making neutron activation analyses for short half-lived elements at the Research Reactor Facility, University of Missouri. Irradiation costs at the University of Missouri and the Nuclear Science Center, Texas A & M University, were covered by the reactor-sharing program of the Department of Energy. We also thank the staff of the Omega West Reactor, Los Alamos National Lab, for assistance. Helpful reviews and comments on the manuscript have been provided by Nelia Dunbar. This work was made possible through grants from the Polar Earth Science program, Office of Polar Programs, National Science Foundation. We thank Scott Borg for his support, encouragement, and continued assistance.

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(Received July 22, 1996; revised January 10, 1997; accepted January 15, 1997.)