



HAL
open science

Volcanic layers in Antarctic (Vostok) ice cores: Source identification and atmospheric implications

Isabelle Basile-Doelsch, Jr Petit, S Touron, Fe Grousset, N Barkov

► To cite this version:

Isabelle Basile-Doelsch, Jr Petit, S Touron, Fe Grousset, N Barkov. Volcanic layers in Antarctic (Vostok) ice cores: Source identification and atmospheric implications. *Journal of Geophysical Research: Atmospheres*, 2001, 106 (D23), pp.31915-31931. 10.1029/2000JD000102 . hal-00726370

HAL Id: hal-00726370

<https://hal.science/hal-00726370v1>

Submitted on 25 Jan 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Volcanic layers in Antarctic (Vostok) ice cores: Source identification and atmospheric implications

Isabelle Basile,^{1,2} Jean Robert Petit,² Stéphanie Touron³, Francis E. Grousset,⁴ and Nartsiss Barkov⁵

Abstract. Fifteen visible volcanic ash layers (tephra) from Vostok ice cores have been analyzed for major elements, trace elements, and Sr and Nd isotope composition. Comparison of their geochemical signatures to lava composition from the inventory of Antarctic and subantarctic volcanoes, which have been active over the last 0.5 million years, indicates that nine layers originate from activity of the South Sandwich volcanic arc, three from southern South America, one from the Antarctic Peninsula (Bransfield Strait), and one from West Antarctica (Marie Byrd Land province). The large size of the tephra (up to 50 μm) requires rapid atmospheric transfer from the volcanic centers to East Antarctica. Rapid tropospheric transport from the southwestern Atlantic, penetrating East Antarctica, therefore predominates during the period studied, whether in glacial or interglacial climatic mode. In spite of the low frequency of occurrence of visible tephra layers in Vostok core (one event every 20 kyr), the overall atmospheric pathway of these ash events appears consistent with the almost continuous advection of continental dust from South America.

1. Introduction

The reconstruction of past atmospheric circulation patterns as well as the investigation of long-term links between volcanic aerosols and climatic change are today subjects of major interest and considerable debate. Representing potential archives of both climate and volcanic events, ice cores can be an important source of data for such studies. Although ash layers in ice cores do not always provide information on the climatic impact of volcanism, they do provide a record of atmospheric loading and the pathways taken by volcanic clouds.

Past volcanic activity is recorded as visible volcanic ash (tephra) layers and/or sulfate-rich layers. Sulfuric acid can be detected by an electrical method [Hammer, 1977] or by direct chemistry [Zielinski *et al.*, 1994, 1996, 1997]. The sulfuric acid record is an indicator of a large-scale atmospheric loading, and particular events, which are documented either by the observations or geological studies, are of interest because they could help in establishing the ice core chronology. Conversely, the dating of ice cores by independent methods (e.g., by varve or layer counting as for the Greenland ice records) can improve the documentation of the historical observations [Zielinski *et al.*, 1994].

However, the dating of ice cores is not always a straightforward task. This is particularly true for sites with low snow accumulation such as those in East Antarctica where the absence of seasonal variations of proxies prevents the detection of annual layers. Moreover, deep ice cores cover time periods of up to half a million years, and the tephrochronology beyond the last 2000 years is still poorly documented. Unlike sulfuric acid events, the tephra layers can potentially provide information on source location through the "fingerprints" left by their elemental and trace composition. This makes the study of tephra layers of particular interest for the documentation of eruptive volcanic events in the middle to late Pleistocene period. The amount of available material in ice is always very small, seldom exceeding a few milligrams. This restricts analytic methods and prevents the application of dating methods (e.g., ³⁹Ar/⁴⁰Ar). However, an inventory of the tephra in ice can provide event markers that are extremely useful when investigating the stratigraphic correlation between different ice cores [Fuji *et al.*, 1999] or between ice cores and marine sediment records [Zielinski *et al.*, 1997]. In addition, it should be possible to link the tephra with the volcanic source if the amount of lava materials is sufficient for absolute dating methods.

For the south polar regions, Smellie [1999] provides a review of upper Cenozoic tephra records. Focusing on the Antarctic ice records, volcanic ash layers from several cores have been already examined. In the Byrd ice core, in West Antarctica (Figure 1), Gow and Williamson [1971] identified almost 2000 visible ash layers, most of them concentrated in ice corresponding to the last glacial period. The vicinity of the Marie Byrd Land volcanic province and the possible triggering of eruptive activity from bedrock isostatic adjustment consecutive to the ice sheet thickening have been suggested to explain the abundance of volcanic layers at this time [Kyle *et al.*, 1981; Palais, 1985]. Among volcanoes, Mount Takahe, located 450 km away from the drilling site, has been proposed as a possible source [Kyle and Jezek, 1978;

¹Centre Européen de Recherche et d'Enseignement en Géosciences de l'Environnement, Europôle Méditerranéen de l'Arbois, Aix-en-Provence, France.

²Laboratoire de Glaciologie et Géophysique de l'Environnement, St. Martin d'Hères, France.

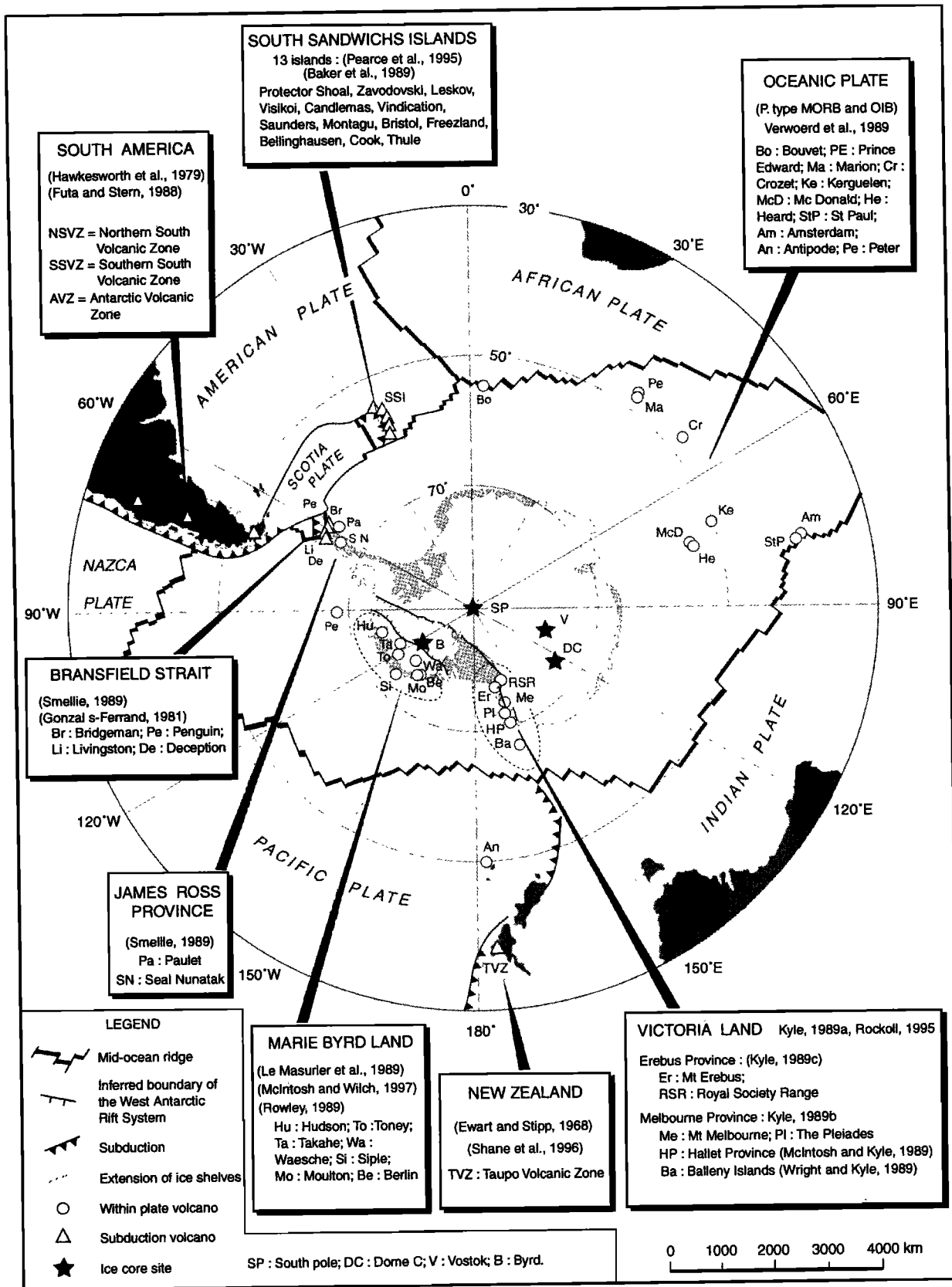
³Laboratoire de Géologie des Chaînes Alpines, Institut Dolomieu, Grenoble, France.

⁴Département de Géologie et Océanographie, Univ. of Bordeaux I, Talence, France.

⁵Arctic and Antarctic Research Institute, St. Petersburg, Russia.

Copyright 2001 by the American Geophysical Union.

Paper number 2000JD000102.
0148-0227/01/2000JD000102\$09.00



Kyle *et al.*, 1981; Palais, 1985]. In the Dome C ice core (East Antarctica), only one tephra was found. It was at a depth of 726 m and has been identified as coming from Mount Takahe [Kyle *et al.*, 1981]. In shallow ice cores from Vostok and South Pole, Kyle *et al.* [1984] and Palais *et al.* [1987] studied tephra layers by SEM-EDX and electron microprobe methods and compared their results with the major element composition of nearby sources. The authors suggested a common source (Candelmas Island in the South Sandwich Islands) for one event at 3200 years B.P. (before present), providing a visible tephra horizon for both sites. Therefore the tephra suggest an initial stratigraphic correlation between two Antarctic ice cores ~1200 km apart and ~5000 km from the direct source.

In a deep Vostok ice core (called "3G") covering the last 160 kyr, Palais *et al.* [1989] detected numerous cloudy and faint tephra layers after careful inspection of the core. The amount of available material was low, making quantitative analysis extremely difficult. As in previous studies, the source was identified for five layers by the major element composition. However, from a theoretical point of view, this method has a number of limitations for source identification: (1) the major element composition of tephra can be heterogeneous within a given layer; (2), different volcanoes and/or different volcanic provinces may produce tephra with similar major element composition; (3) conversely, for a given volcano, the composition may change from one eruption to another or even within a given eruption if there is a zoned magma chamber.

To mitigate these problems, a more complete geochemical identity card can be established using the analysis of trace elements and the strontium-neodymium isotopic signature. This provides complementary constraints to those from the major element composition and the comparison with sources. A matching source composition will, however, also be dependent on the data available from the literature and from the lava samples which have been analyzed and published for each potential source volcano (hereinafter PSV).

Vostok cores contain a total of ~20 levels of visible tephra with significant amounts of material. These layers are located almost randomly in ice from the interglacial period or glacial period (Figure 2). This strongly differs from the Byrd core, however Vostok is located in central East Antarctica, relatively far from volcanic centers. The Vostok ice core provides a climatic record of the last 400,000 years [Petit *et al.*, 1999], the longest climatic

sequence ever obtained. Climate is depicted by the isotope of the water and taken as a proxy of the temperature (Figure 2). Ice chronology was obtained by development of a glaciological model, and the age of the ice layers is estimated to within ~5% accuracy [Petit *et al.*, 1999].

In this paper we present results of the analysis of 15 levels to which we applied an extended geochemical tracer method (major elements, trace elements, and Sr and Nd isotopic compositions) for comparison with the composition of volcanic material of the source. First of all, the elemental composition and the geochemical signatures of glass shards are used to determine the layers exhibiting a similar tectonic setting with respect to their parental magma (subduction zone or within-plate volcanoes). Next, we establish an inventory of volcanoes surrounding Antarctica, located from 90°S up to 30°S latitude, which have been active at some time over the last 0.5 million years. All these volcanoes are considered as PSVs. This represents numerous volcanoes (see Figure 1) set within subduction or within-plate (continental or oceanic) provinces. We then compare the geochemical signatures of the tephra with available geochemical data for PSVs. We are aware that slight geochemical differences may result from the use of different analytical techniques [e.g., Kyle *et al.*, 1984] or from different eruption characteristics, i.e., lava flow or pyroclastic. Fortunately, they are not significant compared to the geochemical differences that exist between the two tectonic settings, which helps us rapidly analyze the PSVs and predict the source of the tephra. We will then discuss some of the implications in terms of atmospheric pathways of air masses for glacial and interglacial periods.

2. Samples and Analytical Methods

Ash layers were recovered during successive expeditions at Vostok Station from a shallow ice core named "BH1," and from two deep ice cores named "4G2" and "5G" (Figure 2). The 15 tephra layers studied here (Table 1) were detected visually. The layers are from a few to 20 mm thick with a variable whitish, brownish, or grayish color. The total amount of material is about 1 to 5 mg. The selected ice samples were first decontaminated by washing with deionized water in a dust-free clean room. The inner part of the core was then melted, and two aliquots of the water were filtered through two Nucleopore® filters (13 mm diameter and

Figure 1. Location in the Southern Hemisphere of volcanic provinces and PSVs in their tectonic settings (activity dating back less than 500 kyr). The provinces and the main references on tectonic settings and dating are McMurdo volcanic group [Kyle, 1989a, 1989b and 1989c; Verwoed *et al.*, 1989; Rocholl *et al.*, 1995]; Marie Byrd Land province (MBL) [LeMasurier, 1989, Rowley *et al.*, 1989]; James Ross Islands volcanic group and Bransfield strait volcanoes [Smellie, 1989; Tokarski, 1991; Gonzales-Ferran, 1991]; South Sandwich Islands (SSIs) [Baker *et al.*, 1989; Pearce *et al.*, 1995]; New Zealand [Ewart and Stipp, 1968; Simkin and Siebert, 1994; Shane *et al.*, 1996]; South America [Hawkesworth *et al.*, 1979; Futa and Stern, 1988]. Additional references are given in the discussion (see text). Adapted from LeMasurier and Thomson [1989]. The locations of Antarctic drilling sites are also shown. V, Vostok; PS, Admunsen-Scott South Pole; B, Byrd; DC, Dome C.

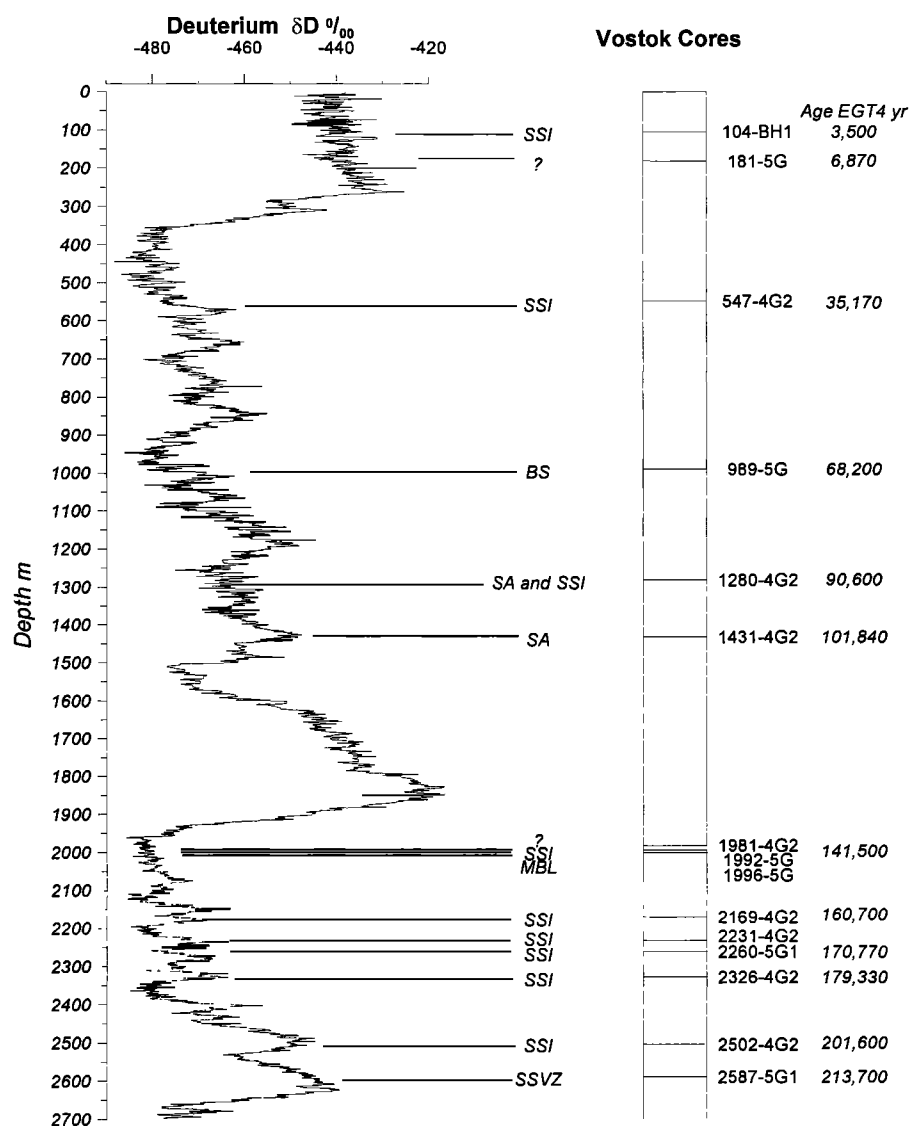


Figure 2. Position of the visible ash layers in the Vostok core studied, recorded along with the isotopic composition (deuterium) of the ice and the age of the layer [Petit *et al.*, 1999]. The identified sources of ash layers are SSIs (South Sandwich Island), BS (Bransfield Strait), SA (South America), SSVZ (southern part of southern volcanic zone), MBL (Marie Byrd Land).

0.4 μm porosity) fitted for microscope observations. For each layer, one filter was embedded with epoxy resin and polished using diamond pastes (grain size 6, 3, 1, and 0.25 μm) to obtain flat surfaces for quantitative microprobe analysis.

Tephra were observed with an optical microscope in transmission mode (with natural and polarized light) and in reflection mode. Additional observations were performed with a scanning electron microscope. The size of the tephra varies from a few micrometer up to 50 μm (see Table 1). Under the optical microscope, shards appear brown, orange, or colorless. All the observations indicated that the tephra layers are a mixture of three different types of particles: (1) glass shards (70 to 90%) resulting from the quenching of erupted magma (Figure 3b), (2) lithic fragments (5 to 30%) composed of cryptocrystalline glass (i.e., glass partly recrystallized) probably from prior eruptions (Figure 3a), and (3)

microlites of feldspar or ferromagnesian minerals which may or may not have been included in the glassy phase (Figure 3c).

The quantitative major element composition of glass shards was obtained using a wavelength-dispersive X-ray (WDX) electron microprobe. This method is more accurate and precise and was preferred to scanning electron microprobe (SEM) energy dispersive X-ray spectrometry [Palais *et al.*, 1987]. Analyses were performed on particles greater than 5 μm because of the limitation of the required minimum for analytical volume. To prevent the loss of Na under the beam [Nielsen and Sigurdsson, 1981], we set the beam current and the accelerating voltage to 6 nA and 15 kV respectively. The number of analyzed particles varies from 7 to 33 for each layer. Results are presented in Table 2.

Trace elements were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS- VG

Table 1. Ash Layers Sampled From Different Vostok Ice Cores: BH1, 4G2 and 5G^a

Depth (m)	Age EGT4 (years)	Number of Core	Number of Drilling	Thickness of Layer (mm)	Maximal Size of Ash (μm)
103.14	3 450	104	BH1	30	50
180.24	6 870	181	5G	15	20
546.24	32 170	547	4G2	20	40
988.45	68 190	989	5G	19	40
1279.16	90 600	1 280	4G2	2	20 ~ 50
1430.9	101 840	1 431	4G2	5	10
1980.37	140 040	1 981	4G2	7	10
1991.93	141 330	1 992	5G	2	50
1995.23	141 690	1 996	5G	20	50
2168.43	160 650	2 169	4G2	2	30
2230.29	168 180	2 231	4G2	20	40
2259.02	171 390	2 260	4G2	2	40
2325.4	179 250	2 326	4G2	5	40
2501.92	201 970	2 502	4G2	12	50
2586.15	213 700	2 587	5G1	8	20

^a Age "GT4" is from *Pettit et al.* [1999]. Ash layer label refers to the bottom depth of the 1 m long ice core increment containing the layer. Size of tephra was measured using an optical microscope.

Plasmaquad PQ 2 Turbo®) with a standard quantitative method. The tephra samples were first dried (~5 mg of sample obtained) then dissolved with a mixture of Teflon®-distilled acids [HF + HClO₄ + HNO₃] [*Falkner et al.*, 1995]. For five samples, the amount of available material was too small for accurate trace element analysis. Results are presented in Table 2.

Sr and Nd isotopic compositions were measured using a multicollector thermo-ionisation mass spectrometer (TIMS) (Finnigan MAT 261 ®). After dissolution, Sr and Nd were chemically separated using ionic chromatographic columns. We followed chemical and mass spectrometer procedures as previously described by *Grousset et al.* [1988]. Results are presented in Table 2. For convenience, measured (¹⁴³Nd/¹⁴⁴Nd)_{Meas} ratios were normalized with respect to a standard of CHondritic Uniform Reservoir (CHUR) with a value of 0.512636 [*Jacobsen et Wasserburg*, 1980] using the relationship $\epsilon_{\text{Nd}(o)} = ((^{143}\text{Nd}/^{144}\text{Nd})_{\text{Meas}} / (^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} - 1) \times 10^4$.

3. Tephra Composition and Groupings

3.1. Variability of the Major Element Composition

Microprobe analyses were performed only on glass shards because they represent the magma at the time of the eruption. To point out the variability in glass shard composition from a given layer, we represent, in Figure 4, the composition of several single shards from three different depths (1280, 2169 and 2260 m) on a plot of the concentration of K₂O and of MgO versus SiO₂. The other major elements are not represented because they show similar patterns and lead to the same conclusions. For the discussion, we use the classification of volcanic rocks based on alkaline elements versus SiO₂ concentrations (Figure 5a) as suggested by *Cox et al.* [1979] and adapted by *Le Maitre et al.* [1989].

The three samples illustrate different degrees of homogeneity inside a single tephra layer (Figure 4). The 2169 m layer is composed of basaltic andesite glass shards and appears very homogeneous. By comparison the 2260 m layer ranges from andesite to dacite: SiO₂ and MgO varying from 60 to 75% and from 3 to 0.3%, respectively. This straight-line trend probably results from fractional crystallization and the presence of a zoned magma chamber prior to the eruption [*Zielinski et al.*, 1995]. The third example is the 1280 m layer which shows two distinct compositions featuring dacite (K₂O ~ 0.51%, noted 1280a) and rhyolite (K₂O ~ 4.5%, noted 1280b), respectively. In addition, the size distribution of the shards is bimodal, showing one mode at 20-40 μm and another at 5-20 μm . This indicates that 1280 m tephra represents, in fact, two independent eruptive events, and the mixed volcanic cloud deposited tephra simultaneously at Vostok. This layer was divided into two subgroups: 1280a and 1280b.

3.2. Major Element Compositions and Classification of Tephra Layers

The major element compositions are given in Table 2 and represent for each layer the average value from multiple analyses. In Figure 5a we plot the mean composition of alkalis (Na₂O+K₂O) versus SiO₂ to classify the different tephra layers accordingly. Four main groups could be identified according to the increase of the total alkali content.

1. Set 1 contains two layers (1280a, and 2326 m) and is composed of dacite with a very low alkali content (K₂O ~ 0.5%). They belong to a low-K tholeiite series.

2. Set 2 contains nine layers (104, 181, 547, 1981, 1992, 2169, 2231, 2260 and 2502 m) and is also tholeiitic magma but slightly more alkaline (Na₂O+K₂O from 2 to 4%) than set 1.

3. Set 3 contains four layers (989, 2587, 1280b and 1431 m) and represents calc-alkaline magma. However, their SiO₂ content is significantly different (~55% and ~70%), and we therefore divide them into two subgroups: set 3a with two layers (989 and 2587 m) and set 3b with two layers (1280b and 1431 m). The high TiO₂ content (TiO₂ ~ 2.5%) in the 989 m layer (Table 2) could be a signature of tholeiitic or alkaline within-plate volcanism [*Albarède*, 1992] (see below).

4. Set 4 contains one layer (1996 m) with a composition much different from that of the other layers. It is a trachyte from an alkaline series (K₂O+Na₂O ~ 10%).

This classification gives an initial indication of the tectonic setting of the volcanic sources: tholeiitic and calc-alkaline series typically come from subduction-related provinces, whereas the alkaline series probably come from within-plate tectonic sources.

3.3. Complementary Discrimination Using Trace Element Composition

The formation of a magma follows three main steps: (1) the partial fusion of mantle rocks, (2) the collection and migration of the magma, and (3) the storage and fractional crystallization. Different additional processes may occur that modify the composition during magma genesis. Magma may be mixed and contaminated by

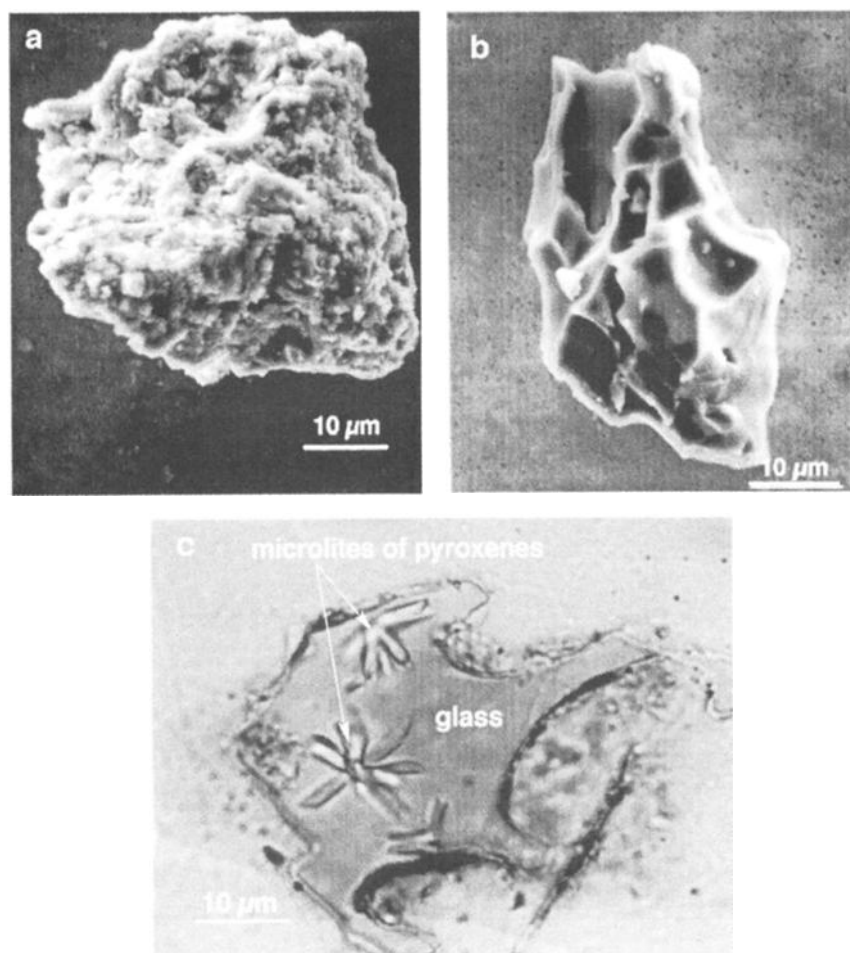


Figure 3. Microscope observations: (a) scanning electron microscope picture of lithic material composed of cryptocrystalline glass; (b) scanning electron microscope picture of glassy shard with a blocky morphology typical of phreatomagmatic ash grains [Heiken and Wohletz, 1985]; (c) picture of the polished surface of a glassy shard observed with an optical microscope using transmitted light; microlites of pyroxenes appear in a spherulite structure in the glass matrix.

various crustal rocks with different compositions of continental or oceanic origin. Trace element behavior is very sensitive to all these petrogenetic processes. This makes it possible for the origin of a magma to be characterized according to the tectonic setting (tholeiitic, calcalkaline or alkaline series). Moreover, in a given tectonic setting, each volcanic area inherits specific characteristics of trace elements. Among trace elements, rare earth element (REE) enrichment with respect to a standard (normalized chondrite composition), negative Europium anomaly, light REE (LRRE) enrichment or depletion given by the ratio of La to Gd, to Sm or to Tb, Nb to Zr ratio, as well as Sr and Nd isotopic signatures are the classical proxies used to characterize and discriminate between magmas and volcanic rocks [Wilson, 1989]. We apply this approach to the composition of the Vostok tephra. The REE profiles, the La/Gd versus Zr/Nb ratio and the isotopic composition of set 2, 3a and 4 are shown in Figure 5b, c, d. For set 1 and set 3b and the 181 m layer of set 2, the amount of

available material was unfortunately too small for ICPMS or TIMS analysis.

Among the nine layers of set 2, seven layers (104, 547, 1992, 2169, 2231, 2260 and 2502 m) differ from the 1981 m layer with respect to the REE profile. Their profile is enriched by 6 to 17 times the chondritic abundance (Figure 5b) and a slight LREE depletion occurs (La/Gd = 0.8) (Figure 5c). They also have a high Zr/Nb ratio (62-76) (Figure 5c) and a Nd isotopic composition ($\epsilon_{Nd}(0)$) from +6 to +8 as well as a $^{87}Sr/^{86}Sr$ ratio from 0.70393 to 0.70478 (Figure 5d), indicating a rather radiogenic signature. These data in addition to the tholeiitic composition indicate a typical parental magma from oceanic subduction zones. For convenience these seven layers will be called set 2* or "depleted LREE" layers hereinafter.

Set 3a includes the 989 and 2587 m layers. The REE concentration is 12 to 35 times higher than the chondritic abundance (Figure 5b) with a slight LREE enrichment (La/Gd = 1.9) (Figure 5c). They have an intermediate

Table 2. Analytical Results of Major and Trace Elements ^a

Depth-Drilling Number of Analyses	104-BH1		181-5G		547-4G2		989-5G		1280a-4G2		1280b-4G2		1431-4G2		1981-4G2	
	23	SD	14	SD	16	SD	31	SD	14	SD	33	SD	21	SD	13	SD
SiO ₂	60.23	1.52	53.16	1.05	60.90	1.20	55.50	1.93	64.62	1.15	66.62	0.96	66.30	0.88	56.12	0.95
TiO ₂	0.83	0.23	1.52	0.98	1.27	0.22	2.45	1.17	0.78	0.12	0.59	0.08	0.52	0.08	1.13	0.38
Al ₂ O ₃	15.62	0.69	14.59	0.79	14.66	0.97	17.08	2.02	14.74	0.69	14.71	0.64	14.68	0.31	15.01	0.46
FeO	9.31	0.79	11.68	1.64	9.50	1.25	8.09	1.74	8.55	0.99	9.11	0.44	8.88	0.49	10.22	0.52
MnO	0.22	0.11	0.24	0.08	0.28	0.24	0.15	0.10	0.20	0.09	0.34	0.09	0.34	0.09	0.23	0.09
MgO	2.51	0.42	5.41	1.12	2.30	0.57	3.13	0.86	1.95	0.25	0.08	0.05	0.01	0.01	4.51	0.47
CaO	6.97	0.52	10.11	1.35	6.44	0.46	7.49	1.25	6.29	0.38	1.50	0.35	1.70	0.41	8.87	0.31
Na ₂ O	3.42	0.35	2.36	0.27	3.29	0.73	4.78	0.62	2.20	0.45	2.34	0.27	2.68	0.42	2.79	0.28
K ₂ O	0.49	0.10	0.47	0.19	0.86	0.11	0.67	0.26	0.47	0.07	4.46	0.24	4.76	0.19	0.69	0.08
P ₂ O ₅	0.15	0.14	0.21	0.20	0.14	0.12	0.42	0.22	0.09	0.06	0.06	0.05	0.06	0.04	0.25	0.15
SO ₃	0.05	0.07	0.11	0.14	0.15	0.11	0.11	0.10							0.10	0.23
Cl	0.20	0.07	0.13	0.27	0.21	0.07	0.12	0.17	0.21	0.01	0.25	0.11			0.08	0.05
Total	100		100		100		100		100		100		100		100	
Rb	11.3						24.3								113.4	
Sr	142.7						356.8								244.5	
Zr	49.5						204.3								47.4	
Nb	0.7						5.9								43.0	
Ba	91.9				168.7		102.1								472.0	
La	2.4				3.8		11.2								97.1	
Ce	7.6				11.2		27.1								198.0	
Pr	1.3				1.9		3.8								23.1	
Nd	7.2				8.6		22.5								92.1	
Sm	2.6				2.4		5.3								18.6	
Eu	1.0				0.8		1.6								3.5	
Gd	3.3				2.9		5.5								16.3	
Tb	0.6				0.5		1.0								2.8	
Dy	4.3				3.5		5.1								16.4	
Ho	1.0				0.7		1.1								3.5	
Er	2.9				2.3		3.2								10.2	
Tm	0.4				0.4		0.4								1.4	
Yb	2.8				2.9		2.9								10.0	
Lu	0.5				0.4		0.4								1.4	
⁸⁷ Sr/ ⁸⁶ Sr	0.704776	35			0.703932	22	0.703412	19							0.703304	20
¹⁴³ Nd/ ¹⁴⁴ Nd	0.513046	12			0.513000	26	0.513003	13							0.512882	13
εNd(0)	8.00				7.10		7.16								4.80	

^a Major elements (% weight) measured with an electron microprobe. Results are normalized to 100%. Trace elements (in ppm) are measured by ICPMS. Isotopic compositions are measured by TIMS. Error is $2\sigma \times 10^{-6}$. Measured ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd ratios have been corrected for mass fractionation by normalizing to ⁸⁶Sr/⁸⁸Sr=0.1194 and ¹⁴⁶Nd/¹⁴⁴Nd=0.7219, respectively. Blanks were negligible. Our measurements for the strontium standard (NIST SRM 987) yielded an average value for ⁸⁷Sr/⁸⁶Sr equal to 0.710205 (+/-0.00002) for 6 measurements, compared to the certified value of 0.710245. The neodymium standard (La Jolla) was analyzed 5 times and gave an average value for ¹⁴³Nd/¹⁴⁴Nd equal to 0.511846 (+/-0.000015) compared to the certified value of 0.511865. The observed differences between our data and the certified values are within the range of the measurement uncertainty.

Zr/Nb ratio (~35, Figure 5c), but they differ by their Nd and Sr isotopic compositions, which however are both included in the array of the mantle composition (Figure 5d). These characteristics suggest a parental magma from a subduction setting, although the high TiO₂ content (TiO₂ ~ 2.5%, Table 2) of the 989 m layer is unusual for a subduction magma. These compositions possibly suggest a more complex tectonic environment [Albarède, 1992].

Although the 1981 m layer from set 2 and the 1996 m layer from set 4 belong to different major element trends, they both display a similar pattern for trace elements. The

REE profiles show an enrichment 30 to 300 times the chondritic abundance (Figure 5b) and a strong LREE enrichment (La/Gd = 5.3) (Figure 5c). They both display a negative Europium anomaly, a low (<7) Zr/Nb ratio, and similar εNd(0) signatures (4.76 and 4.97). Their ⁸⁷Sr/⁸⁶Sr compositions are different, and the 1996 m layer with a value of 0.70517 is more radiogenic than the 1981 m layer with 0.70330 (Figure 5d). We conclude for the parental magma that the two layers originate from a magma with a tectonic setting of continental within-plate volcanism, but for the 1981 m layer, there is a setting

Table 2. (Continued)

Depth- Drilling Number of Analyses	1992-5G		1996-5G		2169-4G2		2231-4G2		2260-4G2		2326-4G2		4G22502-		2587-5G1	
	26	SD	17	SD	20	SD	15	SD	20	SD	10	SD	16	SD	14	SD
SiO ₂	54.12	0.86	63.68	1.15	55.52	0.47	56.67	0.95	66.26	5.76	65.59	0.46	62.59	0.71	56.53	0.81
TiO ₂	0.88	0.29	0.41	0.16	1.23	0.07	1.29	0.11	0.74	0.27	0.91	0.07	0.74	0.30	1.43	0.47
Al ₂ O ₃	15.66	0.84	14.40	1.04	15.14	0.21	15.01	0.30	14.16	0.87	14.30	0.22	15.40	0.90	16.39	1.14
FeO	9.95	1.05	6.85	1.03	10.57	0.46	12.01	0.48	8.25	2.30	8.67	0.32	8.07	0.83	8.90	1.67
MnO	0.21	0.09	0.45	0.45	0.20	0.07	0.24	0.11	0.26	0.12	0.23	0.06	0.19	0.06	0.19	0.08
MgO	5.48	0.98	0.03	0.04	4.86	0.19	3.49	0.22	1.75	0.74	1.65	0.13	1.90	0.36	3.49	0.40
CaO	10.17	0.57	1.08	0.32	9.22	0.14	7.97	0.40	5.78	1.53	5.93	0.15	6.29	0.45	7.66	0.44
Na ₂ O	2.82	0.32	7.55	0.56	2.38	0.21	2.40	0.23	1.90	0.39	1.88	0.15	3.93	0.32	3.82	0.49
K ₂ O	0.42	0.11	5.08	0.34	0.61	0.07	0.62	0.06	0.51	0.15	0.47	0.04	0.48	0.08	0.98	0.22
P ₂ O ₅	0.16	0.17	0.15	0.13	0.15	0.04	0.15	0.07	0.09	0.05	0.14	0.04	0.14	0.15	0.39	0.25
SO ₃	0.04	0.05	0.04	0.07									0.06	0.07	0.13	0.11
Cl	0.09	0.06	0.25	0.13	0.07	0.02	0.11	0.02	0.26	0.07	0.20	0.03	0.21	0.08	0.09	0.07
Total	100		100		100		100		100		100		100		100	
Rb	10.0		191.2		16.2		15.2		19.1				11.2		26.1	
Sr	123.7		75.9		103.9		206.1		138.2				140.7		374.2	
Zr	59.6		560.6		94.9		91.4		89.5				68.7		136.0	
Nb	0.9		79.2		1.2		1.5		1.1				1.1		3.7	
Ba	84.5		107.5		97.4		150.4		97.5				98.8		270.0	
La	2.8		107.6		3.1		4.8		3.0				2.6		12.7	
Ce	7.7		218.6		8.9		13.6		8.5				7.7		29.4	
Pr	1.2		25.4		1.4		2.1		1.3				1.2		4.1	
Nd	7.2		100.1		10.3		12.2		9.7				8.5		21.2	
Sm	2.1		19.8		2.8		3.8		2.8				2.5		5.4	
Eu	0.7		2.3		0.8		1.3		0.9				0.9		1.4	
Gd	2.5		15.9		3.6		4.4		3.6				3.1		5.1	
Tb	0.5		2.7		0.7		0.9		0.8				0.6		0.9	
Dy	2.8		14.6		3.5		5.4		3.6				3.6		4.7	
Ho	0.6		3.0		0.8		1.2		0.8				0.8		1.0	
Er	2.0		8.5		2.4		3.7		2.6				2.5		3.1	
Tm	0.3		1.1		0.3		0.5		0.4				0.4		0.4	
Yb	1.9		7.8		2.4		3.8		2.6				2.5		3.0	
Lu	0.3		1.1		0.4		0.6		0.4				0.4		0.4	
⁸⁷ Sr/ ⁸⁶ Sr	0.704680	33	0.705172	37	0.704416	14	0.703971	12	0.704266	16			0.704247	10	0.704137	7
¹⁴³ Nd/ ¹⁴⁴ Nd	0.512941	41	0.512893	12	0.513014	30	0.513034	13	0.512985	38			0.512996	25	0.512827	12
εNd(0)	5.95		5.01		7.37		7.76		6.81				7.02		3.73	

with a low alkali content comparable to tholeiitic magmas.

At this step, we may already decipher two main tectonic settings for the studied tephra: first the 1996 m layer, which appears well apart, and probably the 1981 m layer, both correspond to a setting of within-plate magmatism; second, the “depleted LREE” layers (set 2*), the 989 m layer, and the 2587 m layer originate from different subduction zones.

4. Comparison With PSV Signatures

4.1. Inventory of PSVs

The location of the main volcanic centers with documented activity over the last 500 kyr is shown in Figure 1 (with references herein).

The volcanic provinces in a within-plate setting are James Ross Province, Marie Byrd Land, and Victoria Land on the Antarctic continental plate and the oceanic islands scattered over the Antarctic oceanic crust. The volcanic provinces in a subduction setting are the southern part of South America, the South Sandwich Islands (SSIs), the Bransfield Strait, and the New Zealand volcanoes.

The geochemical signatures of PSVs are taken from the literature. Unfortunately, some PSVs are poorly documented and cannot be compared directly with our data. We will therefore restrict comparisons by using only the available chemical data which seem to be the most pertinent.

First of all, we can already rule out some PSVs from the inventory regardless of the tectonic settings by using

the differentiation degree of the magmas. The least differentiated tephra at Vostok are basaltic andesites (Figure 5a) with a SiO₂ content higher than 52%. Thus the PSVs, which emitted only basalt (i.e., no differentiated products), are unlike the source for any of the Vostok layers. So we can already discard the following centers: Penguin, Greenwich, and Livingston Islands in the Bransfield Strait [Smellie, 1989; Gonzales-Ferran, 1991]; Seal Nunatak and Paulet Islands in the James Ross Province [Smellie, 1989]; and Antipodes Islands on the New Zealand continental shelf [Gamble and Thomson, 1989]. We now focus discussion on within-plate and subduction settings.

4.2. Within-Plate PSVs

Two tephra layers belong to this setting: 1981 and 1996 m. The within-plate volcanic provinces under consideration are Victoria Land, including Hallett, Melbourne, and Erebus volcanic provinces, the Marie Byrd Land province, and the intraoceanic volcanoes in the Indian part of the Antarctic plate and one in the Pacific part (Peter Island). In Figure 6 the geochemical signatures of the 1981 and 1996 m layers are compared to these PSVs. Peter Island is not included because only major elements (with a typical alkaline trend) are available in the literature [Verwoerd et al., 1989]. For both layers the REE enrichments (Figure 6a) are higher than REE profiles from all the provinces from Victoria Land [Rocholl et al., 1995] which we eliminate. They seem very close to REE from Marie Byrd Land province [LeMasurier et al., 1976] but the trace elements (Figure 6b) and the Sr-Nd isotopic data (Figure 6c) have different signatures.

For the 1996 m layer the REE (Figure 6a and 6b) profile is close to the Marie Byrd Land signature as well as the ¹⁴³Nd/¹⁴⁴Nd composition (Figure 6c) [LeMasurier

et al., 1989], but the ⁸⁷Sr/⁸⁶Sr isotopic composition (0.70517) seems more radiogenic. However, this difference could be nonsignificant because a radiogenic tendency for ⁸⁷Sr/⁸⁶Sr was already noted in the Marie Byrd Land province with values up to 0.70422. This was interpreted as contamination of the magma by continental crust [Panter et al., 1994; Kyle et al., 1994]. This, and the major elements composition which corresponds to an alkaline magma series [LeMasurier et al., 1989], appear therefore consistent with the Marie Byrd Land lava composition. Such an alkaline composition could also suggest Peter Island as a PSV, but the radiogenic ⁸⁷Sr/⁸⁶Sr isotopic signature is incompatible with its within-oceanic plate setting.

For the 1981 m layer the REE enrichment profile (Figure 6a) is similar to that of Marie Byrd Land, but trace element depletion (Zr/Nb<1, Figure 6b) points instead to Victoria Land Province with an intermediate signature between Hallett province and Melbourne/Erebus province signatures. Moreover, as the isotopic composition (Figure 6c) could not discriminate Hallett province from Marie Byrd Land province, no conclusion can be drawn for these within-continental plate provinces. On the other hand, concerning within-oceanic-plate volcanoes, Peter Island can be rejected because of its alkaline composition [Verwoerd et al., 1989]. Only the transitional tholeiites of Oceanic Island basalts could correspond to the major element signature of the 1981 m layer. Marion, Bouvet, and Prince Edward can also be rejected because of a Zr/Nb ratio between 6 and 18 [Verwoerd et al., 1989; Hart, 1988]. The other volcanoes of this province (Kerguelen, Heard Island, etc.) present the “DUPAL” anomaly [Dupré and Allègre, 1983] with enriched isotopic Pb and Sr signatures (Figure 6c) [Dosso and Muthy, 1980; Barling and Goldstein, 1990] which do not fit with the 1981 m layer (or with the 1996 m layer).

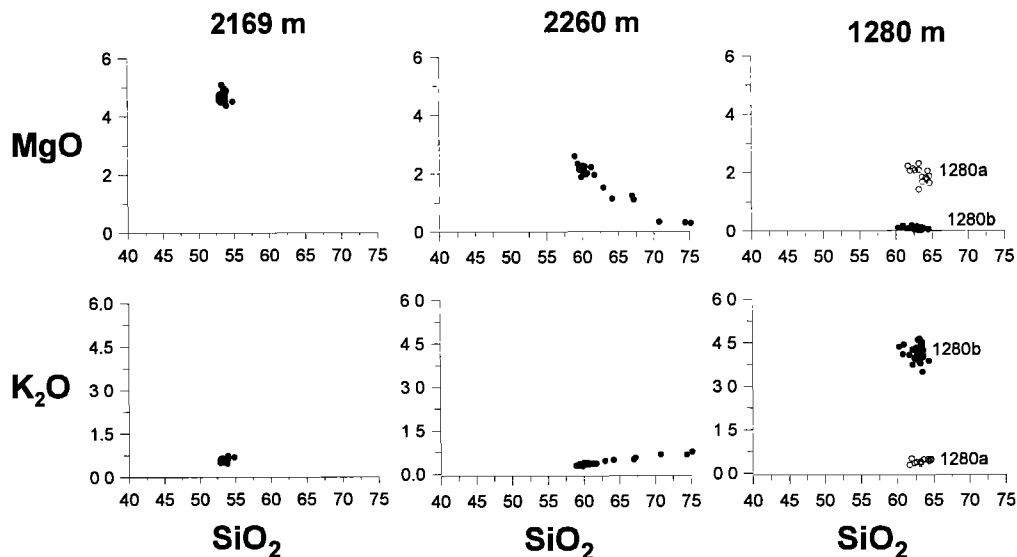


Figure 4. Electron microprobe analysis for layers at 2169 m (20 shards), 2260 m (20 shards), and 1280 m (47 shards) plotted on Harker diagrams of K₂O versus SiO₂ and MgO versus SiO₂. The 1280 m layer is divided in two subgroups 1280a and 1280b.

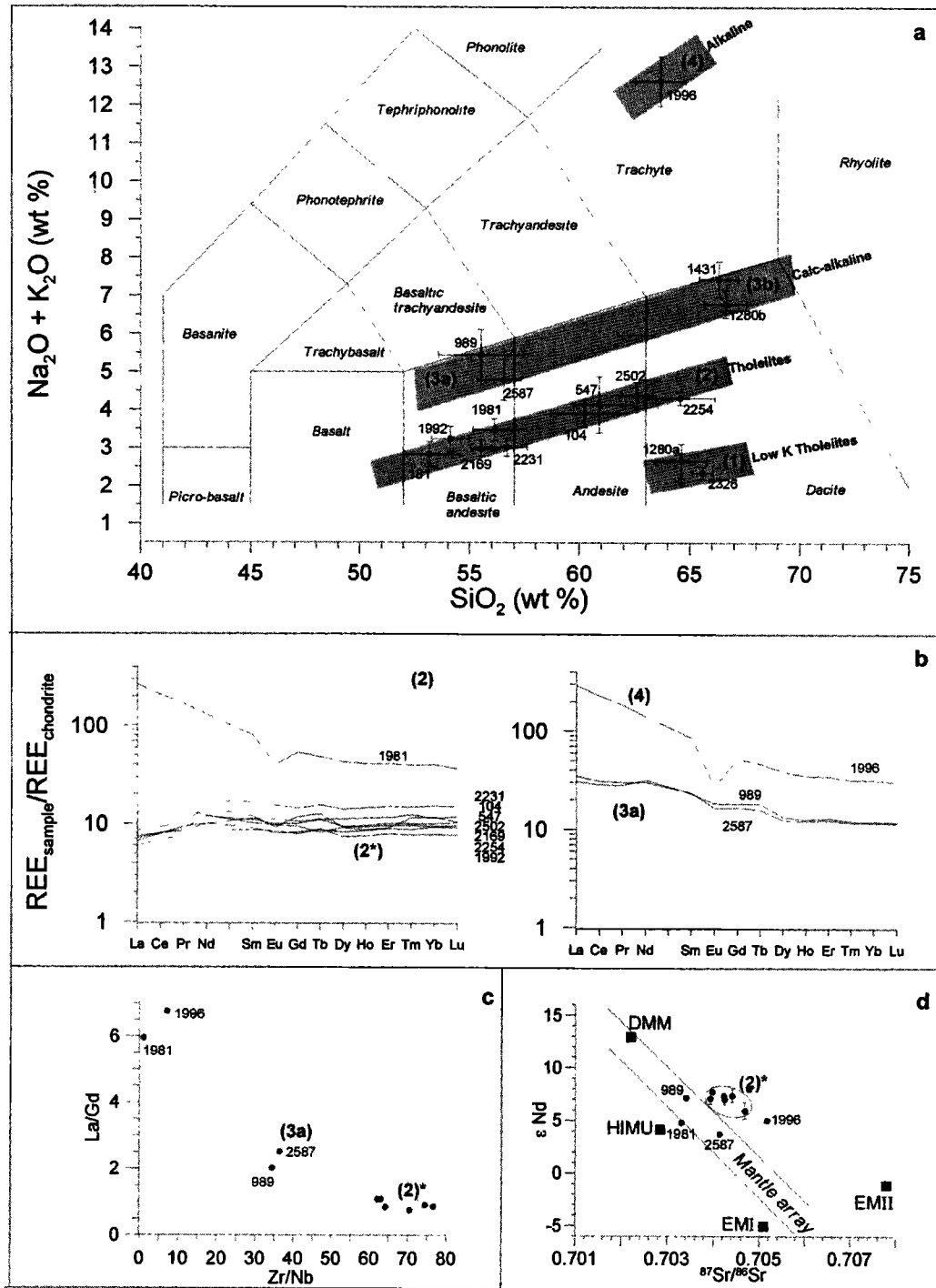


Figure 5. Geochemical characteristics of Vostok ash layers. The ash layer label refers to the bottom depth of the 1m long ice core increment containing the layer. See text for definition of sets 1 to 4. Set 2* represents set 2 without 1981 m. (a) Alkali content versus SiO_2 . Error bars represent the standard deviation obtained from our measurements. (b) REE profiles normalized to chondrite composition [Taylor and McLennan, 1985]. (c) La/Tb versus Zr/Nb . (d) Isotopic compositions in the theoretical model reservoirs [Hart et al., 1992]: DMM, depleted mantle; HIMU, U/Pb enriched mantle; EMI, enriched mantle with lower crust affinity; EMII, enriched mantle with upper crust affinity; mantle array represents the signature of a large number of oceanic basalts [Rollinson, 1993]. Errors bars (2σ) are smaller than the symbol size.

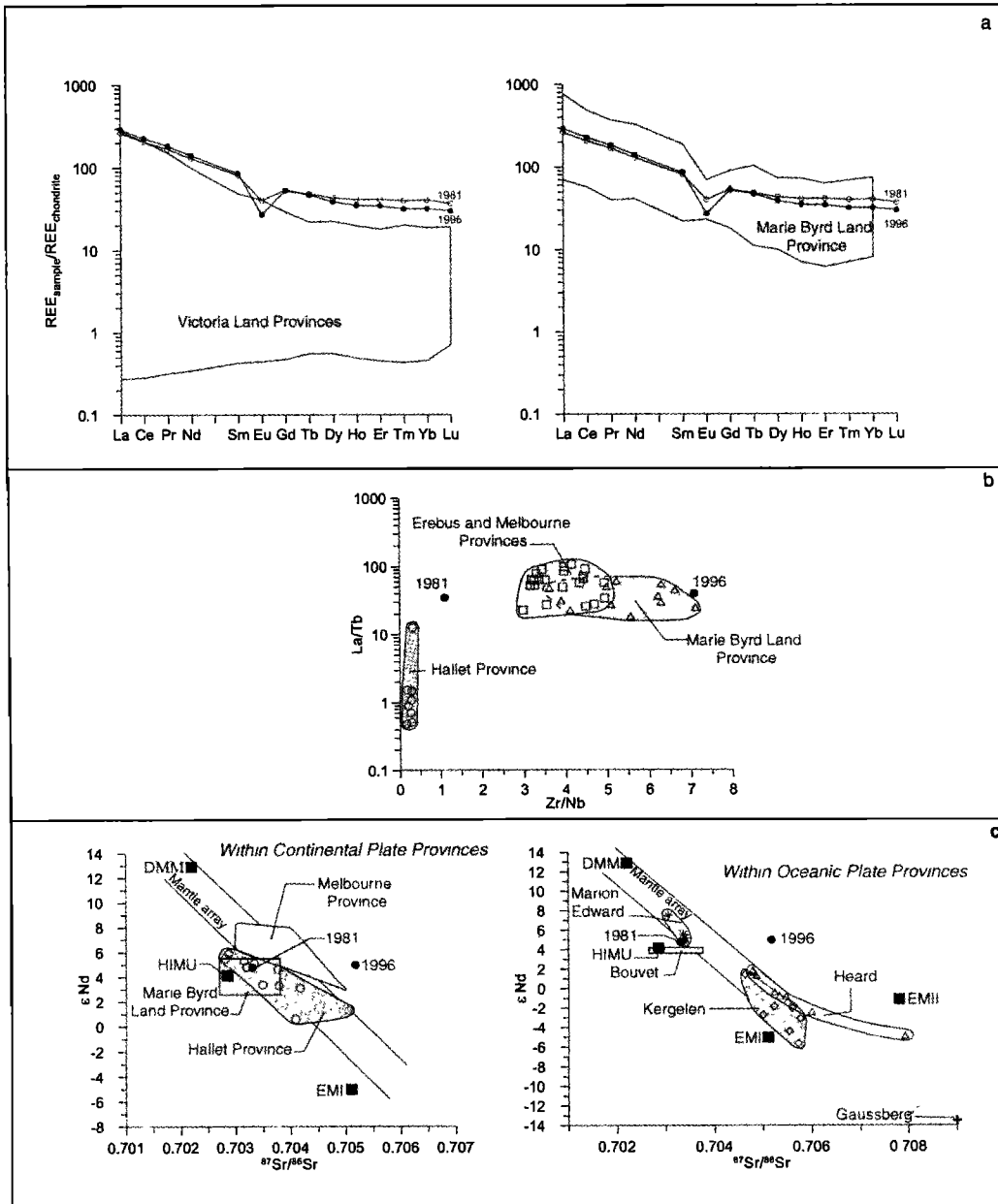


Figure 6. Geochemical characteristics of within-plate Potential Source Volcanoes and related ash layers (black circles). (a) REE profiles for 1981 and 1996 m layers; shaded areas represent the limits of most and least enriched profiles of Victoria Land provinces [Rocholl *et al.*, 1995] and Marie Byrd Land province [Lemasurier *et al.*, 1976]. (b) La/Tb versus Zr/Nb signatures of 1981 and 1996 m layers of Victoria Land provinces (open circle, Hallett province [Rocholl *et al.*, 1995]; open square, Erebus province and Melbourne province [Kyle, 1989b, 1989c] and Marie Byrd Land province (open triangle) [Lemasurier *et al.*, 1989]. (c) Isotope signature of the 1981 and 1996 m layers (black circles); within continental (right) and oceanic plate (left) provinces are separated for legibility. See Figure 5d for reservoir definitions. Hallett province [Rocholl *et al.*, 1995], Melbourne province [Wörner *et al.*, 1989], Marie Byrd Land province [Kyle *et al.*, 1994], Kerguelen Islands [Dosso and Muthy, 1980], Heard Island [Barling and Goldstein, 1990], Bouvet Island [Verwoerd *et al.*, 1989], Marion and Edward Islands [Hart, 1988].

We conclude that the source of the 1996 m layer is very likely located in Marie Byrd Land province. The source of the 1981 m layer is probably restricted to a within-continental plate source (Victoria Land or Marie Byrd Land province), but we cannot discriminate in any greater detail.

4.3. Subduction Zone PSVs

For subduction PSVs the provinces are the SSIs, the Bransfield Strait, the South American and the New Zealand provinces. Set 2* contains seven “depleted REE” Vostok layers that appear to correspond to the signature of SSIs by their REE enrichment profiles (Figure 7a),

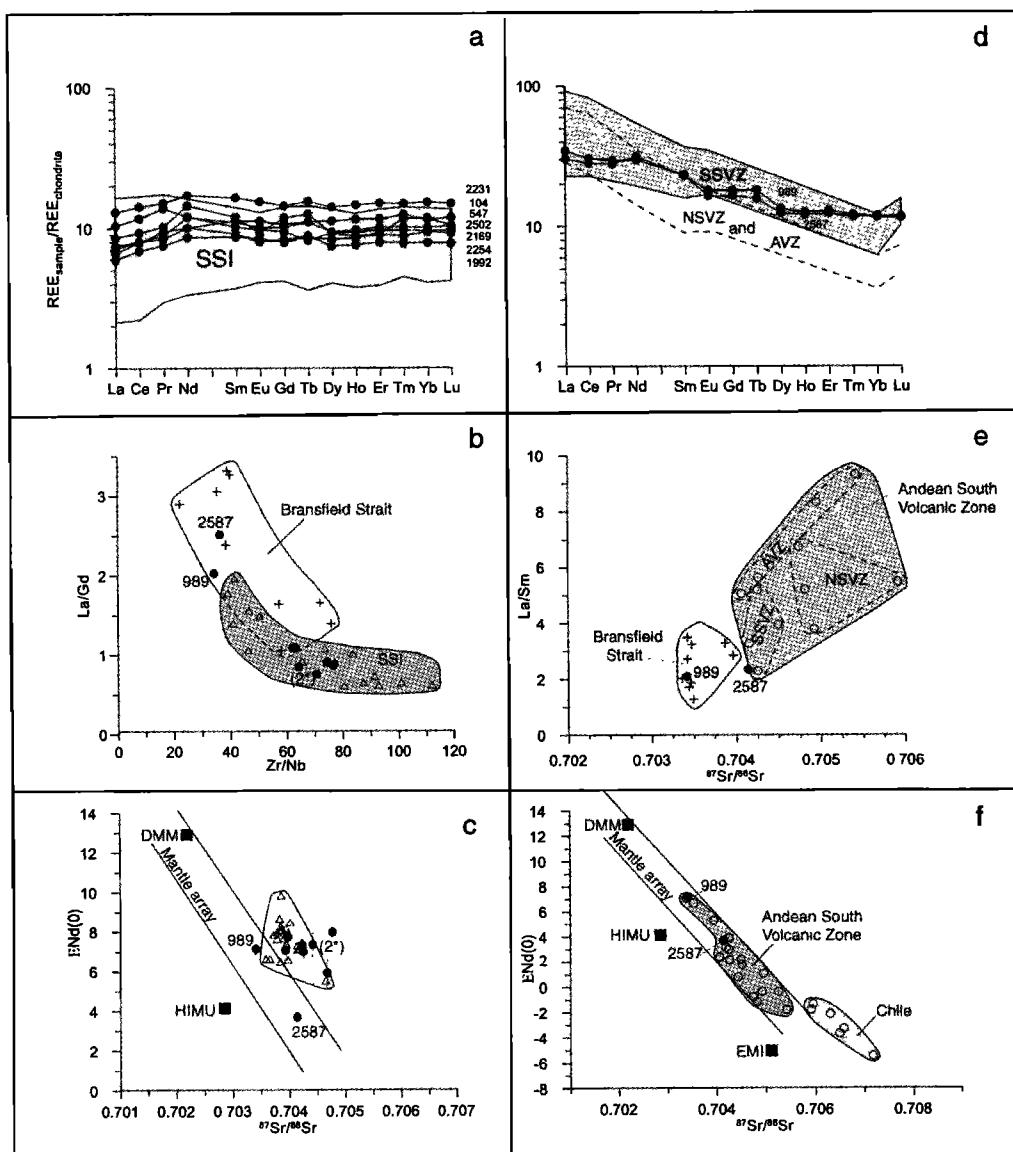


Figure 7. Geochemical characteristics of subduction potential source volcanoes. (a-c) signatures of the SSIs and the "depleted LREE" layers (black circles). (b, d, e, f) show the Bransfield Strait and the Andean signatures with the 989 and 2587 m layers. Shaded areas represent the limits of most and least depleted REE profiles for each province. Crosses, Bransfield Strait [Weaver *et al.*, 1979]; open triangle, SSIs [Pearce *et al.*, 1995]; open circles, South America [Hawkesworth *et al.*, 1979; Futa and Stern, 1988].

their trace elements (Figure 7b) and their isotope compositions (Figure 7c). Some Vostok layers display a Sr composition slightly more radiogenic than the SSIs lava composition given by Pearce *et al.*, [1995]. However, such an isotopic signature is typical of young oceanic subduction for which the SSIs (age < 3Ma) are the unique candidate among the PSVs. We have no explanation for this difference, but such a shift between the in situ lavas and their relative pyroclastics has already been observed [e.g., Ewart and Stipp, 1968] and points out the limits of the comparison between pyroclastics and lavas.

We can extend the SSIs comparison to layers for which no trace elements are available. Pearce *et al.* [1995] have shown that SSIs lava follows three distinct magmatic trends in major elements: a low-K tholeiitic

series, a tholeiitic series, and a calc-alkaline series of oceanic arcs. SSIs are also the only volcanoes that produce low-K tholeiitic magmas among the PSVs. Thus using these arguments, we classify the two events of set 1 as low-K tholeiitic (1280a and 2326 m) originating from the SSIs.

The 989 and 2587 m layers (set 3a) are basaltic andesites (Figure 5) from calcalkaline series lava which do not correspond to SSIs composition (Figure 7a, 7b, and 7c). They neither correspond to a New Zealand signature since the Taupo volcanic zone produced only rhyolitic emissions ($\text{SiO}_2 > 70\%$) over the last 0.5 million years [Ewart and Stipp, 1968; Simkin and Siebert, 1994]. Thus only the Bransfield Strait or volcanic zones in South America could be the sources. Both are associated with a similar subduction setting (oceanic crust subducted under

continental plate). There is a slight geochemical distinction between those two volcanic provinces, as illustrated by the La/Sm versus $^{87}\text{Sr}/^{86}\text{Sr}$ plot (Figure 7e), where the Bransfield Strait displays a less radiogenic strontium isotope signature and a lower LREE enrichment than the Andean volcanoes (see appendix for tectonic justification). Thus regarding the isotopic information and the high content of TiO_2 (Table 2), the 989 m layer seems to correspond to the Bransfield Strait signature [Smellie, 1989]. Unfortunately, for the Bransfield Strait, REE profiles and $^{143}\text{Nd}/^{144}\text{Nd}$ data are not available to confirm our suggestion. For the 2587 m layer, the REE profile (Figure 7d) suggests South America and probably the southern south volcanic zone (SSVZ) as a possible source.

We may also suggest a source for the 1280b and 1431 m layers (set 3b) for which we do not have trace element data. These layers belong to the calc-alkaline series, and taking into account their relative acidity ($\text{SiO}_2=66\%$), their low TiO_2 content, and the rather small size of the particles, we may suggest with confidence an Andean origin. The 181 m layer belongs to set 2, which includes both within-plate and subduction volcanoes. In this case, the major elements are not sufficient to discriminate, and no source can be proposed.

5. Discussion

5.1. Source Volcanoes

We finally suggest that the subduction volcanoes of the SSIs are sources of the "depleted LREE" layers (104, 547, 1992, 2169, 2231, 2254, and 2502 m) as well as the 1280a and 2326 m layers. Sources for the 1280b, 1431, and 2587 m layers are probably located in the Andean cordillera. The 2587 m layer is probably restricted to the southern south volcanic zone of South America. Bransfield Strait is the source for the 989 m layer. The 1996 m layer originates from Marie Byrd Land province, while the 1981 m layer is from West Antarctica.

The SSIs appear therefore as an important source for visible tephra layers discovered in the Vostok ice core (i.e., more than 65% of the events). The SSIs signature has already been suggested for two Vostok layers found at depths of 100.8 and 550 m from previous cores adjacent to our Vostok ice cores. Kyle *et al.* [1984] and Palais *et al.* [1987] studied one layer at 100.8 m from a shallow ice core that is equivalent to our 104 m layer on BH1, and Palais *et al.* [1989] analyzed the 550 m layer in the "3G" Vostok core that is equivalent to our 547 m layer from "4G2." From the major element composition these authors proposed the Candlemas volcano (one of the 13 SSIs volcanoes) as the source for the two layers. Our data also suggest a SSIs source but from other volcanoes. From the study of Pearce *et al.* [1995], Candlemas volcano belongs to the low-K tholeiitic trend ($\text{K}_2\text{O}\sim 0.35\%$ at $\text{SiO}_2\sim 60\%$) and has a high LREE depletion ($\text{La}/\text{Sm}<0.8$). By comparison our results show for the 104 m layer a similar composition for major elements ($\text{K}_2\text{O}=0.5\%$ at $\text{SiO}_2\sim 60.23\%$) but a low LREE depletion ($\text{La}/\text{Sm}=0.92$). This composition corresponds more closely to tholeiitic SSIs volcanoes such as Bellingshausen, Saunders, or Visokoy Islands as defined

by Pearce and coworkers. It was also found that lava from Cook and Thule Islands with tholeiitic signatures could also be the source. The 547 m layer ($\text{K}_2\text{O}=0.86\%$ at $\text{SiO}_2\sim 60.90\%$ and a $\text{La}/\text{Sm}=1.58$) corresponds more closely to a calcalkaline series in which Leskov and Freezland are represented [Pearce *et al.*, 1995]. These two examples show once again the interest of the traces and at the same time the limitation of the interpretation when only major element composition is used and only scarce data on sources are available in the literature.

5.2. Atmospheric Transport

It is obvious that in addition to the frequency of the eruptions, the height of injection, the circulation of tropospheric air masses, and the distance between the volcanic center and the location of the studied Antarctic ice core site also greatly affects the occurrence of tephra in central Antarctica. For example, the Byrd ice core is located ~ 500 km from the Marie Byrd volcanoes, and the ice record, which covers the last ~ 100 kyr contains ~ 2000 tephra events. This gives an overall frequency of 1 per 50 years. For Vostok, a total of ~ 20 tephra have been detected, mostly from SSIs and ~ 5000 km away. Over the 400 kyr of the ice record, this gives a frequency of 1 per 20,000 years. It is of interest to note the decrease by 3 orders of magnitude in occurrence of tephra when the distance to the source changes by 1 order of magnitude. Interestingly, the occurrence of tephra in the Dome-F core also in East Antarctica but closer to SSIs centers is 50% higher (1.5 per 20000 years) than in the Vostok core [Fuji *et al.*, 1999]. However, the transport is not in a direct line to Antarctica, and it is necessary to take into account not only the distance between the volcanic center and the Antarctic site but also the circulation of tropospheric air masses.

The transport of volcanic clouds from the SSIs to East Antarctica seems a priori consistent with the general atmospheric circulation with tropospheric air masses spiraling southward toward Antarctica. However, the size of particles restricts the duration of transport because most of the ash particles are found in the first hundred kilometers around volcanoes [Fisher, 1964]. For example, $20\ \mu\text{m}$ particles settle rapidly in the atmosphere and according to Stoke's law fall by 500 to 1000 m per day. Taking into account the 4000 m elevation of the East Antarctic plateau, the volcanic ash would have to reach a very great height after eruption. So assuming that SSIs volcanic eruptions can inject tephra up to a 6000 m altitude in the troposphere, corresponding to a volcanic explosivity index (VEI) of 2 to 3 [Newhall and Self, 1982], the transport duration to Vostok should not exceed 2 to 4 days. This represents direct advection with an apparent average horizontal speed of ~ 100 km/h, a value that increases with particle size and with the lower level reached by the volcanic cloud. Thus the tephra event in the ice core is probably associated with a particular synoptic situation leading to high eddies and strong tropospheric perturbations which penetrate almost directly to the center of Antarctica (Figure 8). This scheme of transport can be extended to South America (1280b, 1431 and 2587 m layers) and to Antarctic Peninsula (989 m layer) which represent more distant

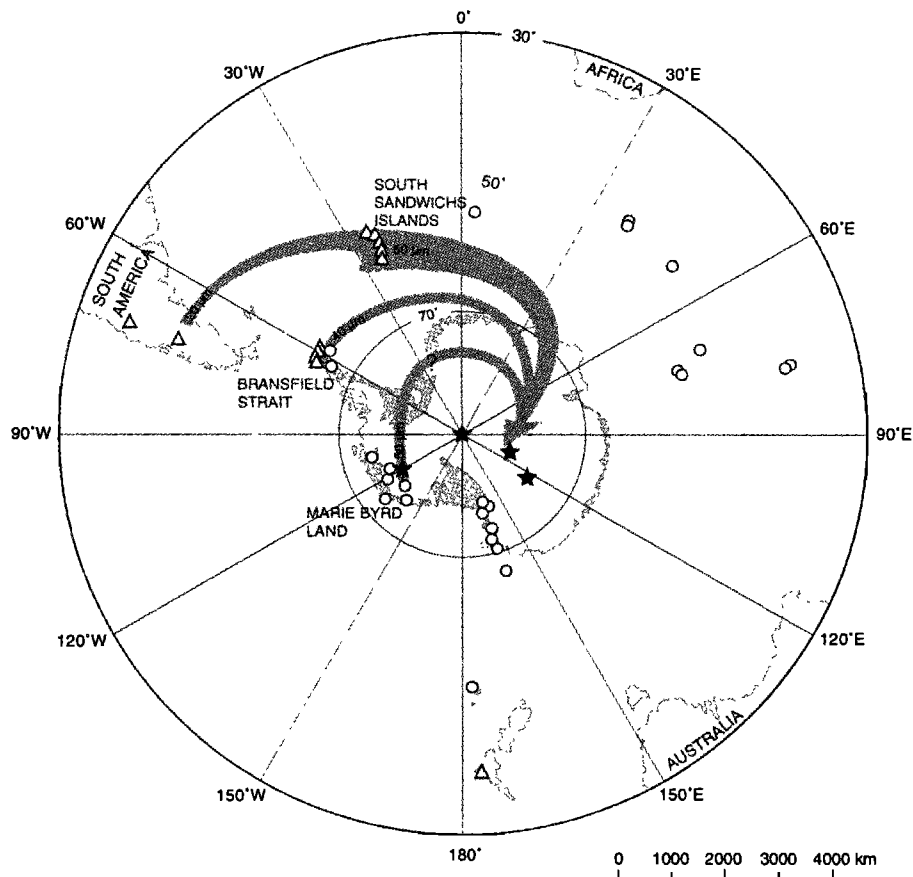


Figure 8. Sketch of possible atmospheric paths suggested from the identification of the sources of the 15 volcanic ash layers. The width of each arrow is proportional to the occurrence of the pathways. The maximum particle size is indicated in the arrows. While the transport to Vostok is probably more direct (a straight line), the shapes of the trajectories are inspired from reverse trajectory models (C. Genthon, personal communication 2001) and *Adriani et al.* [1995]. See Figure 1 for volcano and drilling site abbreviations.

sources, but corresponding tephra layers in ice contain smaller particles ($20\ \mu\text{m}$ for maximum size)(Figure 8).

In spite of the low number of tephra events in the Vostok ice core, the occurrence of volcanic events coming from the southwestern part of the Atlantic does not significantly change with climate (Figure 2). During glacial periods we found six layers coming from SSIs and one from the Antarctic Peninsula. During warm periods we found three layers coming from SSIs and three from South America. This rapid transport from the southern part of the South Atlantic toward East Antarctica does not seem to be dependent on the climatic conditions nor on the probable northward position of the polar front during glacial times [Petit *et al.*, 1999]. This global pathway seems consistent with the almost continuous tropospheric transport of continental dust to Vostok [Grousset *et al.*, 1992; Basile *et al.*, 1997; Basile, 1997] since continental dust originates mostly from southern parts of South America for glacial as well as for interglacial periods [Basile, 1997]. However, unlike the volcanic pyroclastics injected at high altitude by the eruption, continental particles are mobilized at surface level and injected in the atmospheric circulation. Their transport probably follows the general circulation pattern, and transport to Antarctica is longer allowing dust deposition and removal by

precipitation. The size of the dust particles in the ice core is barely greater than $\sim 2\ \mu\text{m}$ and their corresponding gravitational settling velocity only $5\ \text{m/d}$. Moreover, as continental dust deposition in Antarctic seems to be affected by seasonal variations, [Thompson *et al.*, 1979], we can deduce that the same is true for volcanic ash deposition. Our data do not, however, allow us to discuss the seasonal effect of atmospheric circulation on the occurrence of volcanic dust at Vostok.

Only one layer in the Vostok core (1996 m) and probably one event (726 m) in the Dome C core [Kyle *et al.*, 1981] originated from Marie Byrd Land volcanoes. This suggests that tropospheric conditions carrying air masses from West to East Antarctica can occur. However, considering the very high frequency of eruptions in Marie Byrd Land province [Gow and Williamson, 1971] and the relatively close distance ($\sim 2300\ \text{km}$ in direct line), such a pathway seems very unusual. Finally, note the absence of visible New Zealand tephra (distance New Zealand-Vostok: $6000\ \text{km}$ in direct line) in spite of the frequency and violence of eruptions from the active Taupo volcanic province [e.g., Walker, 1981; Simkin and Siebert, 1994].

Tephra events from this study do not make it possible to reconstruct a step-by-step trajectory, as we identify

only the source and the size of particles. They probably correspond to a particular atmospheric circulation pattern. It would be of interest to know what synoptic conditions led to such events and simulate them using a general circulation model. Besides this, these ash layers represent stratigraphic markers which are independent of climate. Their geochemical composition opens possibilities for a reliable ice core correlation with the existing or the ongoing East Antarctic ice coring projects (e.g., Dome Fuji, EPICA, etc.). The abundance of SSIs layers in the Vostok core, with different geochemical signatures of magmas, also opens possibilities of correlation with South Atlantic marine sediment cores documenting leads and lags between ocean and ice climatic records. An additional use is the possible absolute dating of the Vostok core. In fact, Marie Byrd Land appears to be a good candidate (1996 m layer) since the alkaline composition of the lava near the source is favorable for the application of the $^{39}\text{Ar}/^{40}\text{Ar}$ method for this volcanic area, a possibility that is under study [Wilch *et al.*, 1999].

6. Conclusion

We have attempted to identify the volcanic source of fifteen ash layers of the Vostok ice cores. We used a more systematic method than previous studies, first by using trace element and isotopic signatures in addition to major element composition and, second, by considering all the Antarctic and subantarctic volcanic provinces active over the last 0.5 Myr.

We first show the importance of making precise major element analyses on a large set of glass shards. It is possible to detect heterogeneous layers such as tephra from a zoned magma chamber or those that are the result of the mixing of plumes from different eruptions.

The geochemical identity card of each ash layer represents a fingerprint of the tectonic conditions that govern the magma genesis. We deduced that the 104, 547, 1280a, 1992, 2169, 2231, 2326, 2254, and 2502 m layers as well as the 989, 1280b, 1431, and 2587 m layers originate from subduction volcanoes. In contrast, the 1981 and 1996 m layers originate from within-plate volcanoes. The comparison of the tephra signatures with Antarctic and subantarctic volcanic signatures show that the main sources of Vostok volcanic tephra are the volcanoes of the South Sandwich Islands since nine layers (the "depleted LREE" layers) originate from this volcanic arc. The other sources are the southern Andean volcanic province (1280b, 1431 and 2587 m layers), the Marie Byrd Land Province (1996 m layer), and the Bransfield Strait (989 m layer). The source of the 1981 m layer is probably restricted to a continental within-plate source but has not yet been identified. We show that the source can be identified with a higher level of confidence when using trace elements and isotopic composition rather than major elements alone.

The occurrence of tephra events suggests preferential atmospheric transport from the southern part of the western Atlantic toward the East Antarctic ice cap associated with strong eddies penetrating Antarctica. Occurrence of this transport does not appear to be dependent on climate, but our data are insufficient to discuss the seasonal effect. This atmospheric scheme

appears to be consistent with the almost continuous advection of continental dust from South America, but the latter is probably governed by the spiraling that takes place around Antarctica circulation. The atmospheric pathway from West to East Antarctica for clouds containing volcanic ash appears only once in the Vostok core, and there is no event from New Zealand.

Besides being used as atmospheric tracers, ash layers represent stratigraphic markers that are also independent of climate. Thus precise and complete geochemical analyses performed on tephra open new fields of research for core correlation and absolute dating of ice cores.

Appendix: Bransfield Strait and South American Geochemical Signatures

The South American and Bransfield Strait volcanic provinces are associated with the subduction of oceanic crust under continental crust. However, a slight geochemical distinction exists between the two since the subduction stopped under the Antarctic Peninsula around 4 Myr ago [Tokarski, 1991]. The Bransfield Strait, still active, is related to the opening of an asymmetric marginal basin located between the paleovolcanic arc (South Shetland Islands) and the within-plate volcanic area of the James Ross province [Hole *et al.*, 1995]. Thus the composition of the magma integrates the composition of the subducted fossil plate and a MORB (mean oceanic ridge basalt) composition. This transitional signature is slightly different from that of the South American subduction volcanoes. These chemical differences are illustrated in Figure 7 by the La/Sm versus $^{87}\text{Sr}/^{86}\text{Sr}$ plot. The Bransfield Strait has a less radiogenic strontium isotopic signature and a lower LREE enrichment than the Andean volcanoes. This is probably related to a higher continental crust contribution in Andean lava.

Acknowledgments. Vostok is a joint project among Russia, France, and the United States. We acknowledge the Russian Antarctic Expedition, the IFRTP (Institut Français de Recherche en Territoire Polaire), and the Office of Polar Program of NSF for logistic support. The project is supported in Russia by the Russian Ministry of Sciences. This work was funded by the French INSU-CNRS Programme National d'Etude de la Dynamique du Climat and VariEnte (Variabilité de l'Environnement de la Terre) programs. We are grateful to Jean Philippe Eissen for his help in the major element analyses carried out in Brest (Institut de Recherche et de Développement). We are also grateful to C. Jeandel for access to the thermo-ionisation mass spectrometer at Paul Sabatier University (Toulouse). We thank F. Keller and M. Revel for their help in inductively coupled plasma mass spectrometry at the Institut Dolomieu of Joseph Fourier University, Grenoble, and J.P. Balestrieri for technical help. We thank F. Albarède, H. Lapière, M. Paterne, F. Guichard, and C. Genthon for fruitful discussions as well as the anonymous reviewers for their suggestions and improvements.

References

- Adriani, A., T. Deshler, G. Donfrancesco, and G.P. Gobbi, Polar stratospheric clouds and volcanic aerosol during spring 1992 over McMurdo Station, Antarctica: Lidar and particle counter comparisons, *J. Geophys. Res.* **100**, 12, 25877-25897, 1995.
- Albarède, F., How deep do common basaltic magmas form and differentiate?, *J. Geophys. Res.* **97**, 10,997-11,009, 1992.

- Baker, P.E., South Sandwich Island, in *Volcanoes of the Antarctic Plate and Southern Oceans*, edited by *Antarct. Res. Ser.*, vol. 48, W. E. LeMasurier and J. W. Thomson, pp. 361-395, AGU, D. C., 1989.
- Barling, S. and S.T. Goldstein, Extreme isotopic variations in Heard Island lavas and the nature of mantle reservoirs, *Nature*, 348, 59-62, 1990.
- Basile, I., Origine des aérosols volcaniques et continentaux de la carotte de Vostok (Antarctique), Ph.D. thesis, 270 pp., Univ. of Joseph Fourier, Grenoble, France, 1997.
- Basile, I., F.E. Grousset, M. Revel, J.R. Petit, P.E. Biscaye and N.I. Barkov, Patagonian origin of glacial dust deposited in East Antarctica (Vostok, Dome C) during glacial stages 2, 4 and 6, *Earth Planet. Sci. Lett.*, 146, 573-589, 1997.
- Cox, K. G., J. D. Bell, and R.J. Pankhurst, *The Interpretation of Igneous Rocks*, 450 pp., Allen and Unwin, Concord, Mass., 1979.
- Dosso, L., and V.R. Murthy, A Nd isotopic study of the Kerguelen Islands: Inferences on enriched oceanic mantle sources, *Earth Planet. Sci. Lett.*, 48, 268-276, 1980.
- Dupré, B. and C.J. Allègre, Pb-Sr variation in Indian Ocean basalt and mixing phenomena, *Nature*, 303, 142-146, 1983.
- Ewart, A., and J.J. Stipp, Petrogenesis of the volcanic rocks of the Central North Island, New Zealand, *Geochim. Cosmochim. Acta*, 32, 699-736, 1968.
- Falkner, K.K., G.P. Klinkhammer, C.A. Ungerer, and D.M. Christie, Inductively coupled plasma mass spectrometry in geochemistry, *Annu. Rev. Earth Planet. Sci.*, 23, 409-449, 1995.
- Fisher, R.V., Maximum size, median diameter, and sorting of tephra, *J. Geophys. Res.*, 69, 341-355, 1964.
- Fuji, Y., M. Kohno, H. Motoyama, S. Matoba, O. Watanabe, S. Fujita, N. Azuma, T. Kikuchi, T. Fukoaka, and T. Suzuki, Tephra layers in the Dome Fuji (Antarctica) deep ice core, *Ann. Glaciol.*, 29, 126-130, 1999.
- Futa, K. and C.R. Stern, Sr and Nd isotopic and trace element composition of Quaternary volcanic centers of the southern Andes, *Earth Planet. Sci. Lett.*, 88, 253-262, 1988.
- Gamble, J.A., and J.W. Thomson, Subantarctic volcanoes of the Pacific Plate, in *Volcanoes of the Antarctic Plate and Southern Oceans*, edited by *Antarct. Res. Ser.*, vol. 48, W. E. LeMasurier and J. W. Thomson, pp. 361-395, AGU, D. C., 1989.
- Gonzales-Ferran, M.O., The Bransfield rift and its active volcanism, in *Geological Evolution of Antarctica*, edited by M. R. A. Thomson, J. A. Crame and J. W. Thomson, pp 505-509, Cambridge Univ. Press., New York, 1991.
- Gow, A.J., and T. Williamson, Volcanic ash in the Antarctic ice sheet and its possible climatic implications, *Earth. Planet. Sci. Lett.*, 13, 210-218, 1971.
- Grousset, F.E., P.E. Biscaye, A. Zindler, J. Prospero, and R. Chester, Neodymium isotopes as tracers in marine sediments and aerosols : North Atlantic, *Earth Planet. Sci. Lett.*, 87, 367-378, 1988.
- Grousset, F.E., P.E. Biscaye, M. Revel, J.R. Petit, K. Pye, S. Joussaume and J. Jouzel, Antarctic (Dome C) ice core dust at 18 ky BP: Isotopic constraints on origins, *Earth Planet. Sci. Lett.*, 111, 175-182, 1992.
- Hammer, C.U., Past volcanism revealed by Greenland Ice Sheet impurities, *Nature*, 270, 483-486, 1977.
- Hart, R., Heterogeneous mantle domains: Signatures, genesis and mixing chronologies, *Earth. Planet. Sci. Lett.*, 90, 273-296, 1988.
- Hart, S.R., E.H. Hauri, L.A. Oschmann, and J.A. Whitehead, Mantle plumes and entrainment isotopic evidence, *Science*, 256, 517-520, 1992.
- Hawkesworth, C.J., M.J. Norry, J.C. Roddick, P.E. Baker, P.W. Francis, and R.S. Thorpe, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and incompatible element variations in calc-alkaline andesites and plateau lava from South America, *Earth Planet. Sci. Lett.*, 42, 45-57, 1979.
- Heiken G., and K. Wohletz, *Volcanic ash*, Los Alamos Nat. Lab., Univ. of California Press, Berkeley, Calif., 246 pp., 1985.
- Hole, M.J., A.D. Saunders, G. Rogers, and M.A. Sykes, The relationship between magmatism, lithospheric extension and slab window formation along continental destructive plate margins, *Volcanism Associated With Extension at Consuming Plate Margins*, edited by J.L. Smellie, Geol. Soc. Spec. Pub., 81, 265-285, 1995.
- Jacobsen, S.B., and G.J. Wasserburg, Sm-Nd isotopic evolution of chondrites, *Earth Planet. Sci. Lett.*, 50, 139-155, 1980.
- Kyle, P.R., McMurdo Volcanic Group, Western Ross Embayment, Introduction, in *Volcanoes of the Antarctic Plate and Southern Oceans*, *Antarct. Res. Ser.*, vol. 48, edited by W. E. LeMasurier and J. W. Thomson, pp. 19-25, AGU, Washington D. C., 1989a.
- Kyle, P.R., Melbourne Volcanic Province, in *Volcanoes of the Antarctic Plate and Southern Oceans*, *Antarct. Res. Ser.*, vol. 48, edited by W. E. LeMasurier and J. W. Thomson, pp. 48-80, AGU, Washington D. C., 1989b.
- Kyle, P.R., Erebus Volcanic Province, in *Volcanoes of the Antarctic Plate and Southern Oceans*, *Antarct. Res. Ser.*, vol. 48, edited by W. E. LeMasurier and J. W. Thomson, pp. 81-145, AGU, Washington D. C., 1989c.
- Kyle, P.R., and P.A. Jezek, Composition of three tephra layers from the Byrd Station ice core, Antarctica, *J. Volcanol. Geotherm. Res.*, 44, 225-232, 1978.
- Kyle, P.R., P.A. Jezek, E. Mosley Thompson, and L. Thompson, Tephra layers in the Byrd Station ice core and the Dome C ice core, Antarctica and their climatic importance, *J. Volcanol. Geotherm. Res.*, 11, 29-39, 1981.
- Kyle, P.R., J. Palais, and E. Thomas, The Vostok tephra: An important englacial stratigraphic marker?, *Antarct. J. U. S.*, 19, 64-65, 1984.
- Kyle, P.R., R.J. Pankhurst, S. Mukasa, K. Panter, J. Smellie, and W. McIntosh, Sr, Nd and Pb isotopic variations in the Marie Byrd plume, west Antarctica, *U.S. Geol. Surv. Circ. 1107*, *ICOG8*, p. 184, Berkeley, Calif., 1994.
- Le Maitre, R.W., et al., A Classification of Igneous Rocks and Glossary of Terms, Blackwell, Malden, Mass., 1989.
- LeMasurier, W.E., Marie Byrd Land, in *Volcanoes of the Antarctic Plate and Southern Oceans*, *Antarct. Res. Ser.*, vol. 48, edited by W. E. LeMasurier and J. W. Thomson, pp. 147-256, AGU, Washington D. C., 1989.
- LeMasurier, W.E., and D.C. Rex, Evolution of linear volcanic ranges in Marie Byrd Land, West Antarctica, *J. Geophys. Res. Lett.*, 94, 7223-7236, 1989.
- LeMasurier, W.E., D.C. Kyle P.R., and P.C. Rankin, Rare earth element geochemistry of volcanic rocks from the Executive Committee Range Marie Byrd Land, *Antarct. J. U. S.*, 11(4), 263-267, 1976.
- LeMasurier, W.E. and J.W. Thomson, *Volcanoes of the Antarctic Plate and Southern Oceans*, *Antarct. Res. Ser.*, vol. 48, edited by W. E. LeMasurier and J. W. Thomson, AGU, Washington D. C., 1989.
- Newhall, C.G., and S. Self, Volcanic explosivity index (VEI): An estimate of explosive magnitude of historical volcanism, *J. Geophys. Res.*, 87(2), 1231-1238, 1982.
- Nielsen, C. H. and H. Sigurson, Quantitative method for electron microscope analysis of sodium in synthetic glasses, *American Mineralogist*, 66, 547-552, 1981.
- Palais, J., Particle morphology, composition and associated ice chemistry of tephra layers in the Byrd ice core: Evidence for hydrovolcanic eruptions, *Ann. of Glaciol.*, 7, 42-48, 1985.
- Palais, J., P. Kyle, E. Mosley Thompson, and E. Thomas, Correlation of a 3200 year old tephra in ice cores from Vostok and South Pole stations, Antarctica, *Geophys. Res. Lett.*, 14(8), 804-807, 1987.
- Palais, J., J.R. Petit, C. Lorius, and Y.S. Korotkevitch, Tephra layers in the Vostok ice core: 160,000 years of southern hemisphere volcanism, *Antarct. J., Rev.*, 24, 98-100, 1989.
- Panter, K.S., R. Pankhurst, P.R. Kyle, J. Smellie, S. Mukasa, and W. McIntosh, Sr, Nd, O, and Pb isotopes from the Mount Sidley volcano, Marie Byrd Land, Antarctica, (abstract), *U.S. Geol. Surv. Circ. 1107*, *ICOG8*, p 241, Berkeley, California, 1994.
- Pearce, J.A., P.E. Baker, P.K. Harvey, and I.W. Luff, Geochemical evidence for subduction fluxes, mantle melting and fractional crystallisation beneath the South Sandwich Island Arc, *J. Petrol.*, 36, 1073-1109, 1995.
- Petit, J.R., et al. Climate and atmospheric history of the past

- 420,000 years from the Vostok ice core, Antarctica, *Nature*, 399, 429-436, 1999.
- Rocholl, A., M. Stem, M. Molzahn, S.R. Hart, and G. Wörner, Geochemical evolution of rift magmas by progressive trapping of a stratified mantle source beneath the Ross Sea Rift, Northern Victoria Land, Antarctica, *Earth Planet. Sci. Lett.*, 131, 207-224, 1995.
- Rollinson, H.R., Using geochemical data: Evaluation, presentation, interpretation, in *Geochemistry Series*, 352 pp., Addison-Wesley-Longman, 1993.
- Rowley, P.D., J.W. Thomson, J.L. Smellie, T.S. Laudon, K.E. La Prade, and W.E. LeMasurier, Alexander Island, Palmer Island and Ellsworth Land, in *Volcanoes of the Antarctic Plate and Southern Oceans*, *Antarct. Res. Ser.*, vol. 48, edited by W. E. LeMasurier and J. W. Thomson, pp. 257-300, AGU, Washington D. C., 1989.
- Shane, P.A.R., T.M. Black, B.V. Alloway, and J.A. Westgate, Early to middle Pleistocene tephrochronology of North Island, New Zealand: Implications for volcanism, tectonism and paleoenvironments, *Geol. Soc. Am. Bull.*, 108(8), 915-925, 1996.
- Simkin T., and L. Siebert, *Volcanoes of the world*, 349 pp., Geosci. Press, Inc., Tucson, Arizona, 1994.
- Sinclair, M., An objective cyclone climatology for the southern hemisphere, *Am. Meteorol. Soc.*, 122, 2239-2256, 1994.
- Smellie, J.L., Graham Land and South Shetland Islands, in *Volcanoes of the Antarctic Plate and Southern Oceans*, *Antarct. Res. Ser.*, vol. 48, edited by W. E. LeMasurier and J. W. Thomson, pp. 303-355, AGU, Washington D. C., 1989.
- Smellie, J.L., The upper Cenozoic tephra record in the south polar region: A review, *Global Planet. Change*, 21, 51-70, 1999.
- Taylor, S.R., and S.M. McLennan, *The continental crust : its composition and evolution*, 312 pp., Blackwell Sci., Malden, Mass., 1985.
- Thompson, L.G., E. Mosley Thompson, and J.R. Petit, Glaciological interpretation of microparticle concentrations from the French 905 m Dome C, Antarctica core, in *Sea level, ice and climatic change*, 131 pp., IAHS Publ., Bentbrugge, Belgium, 1979.
- Tokarski, M.A.K., The late Cretaceous-Cenozoic structural history of King George Island, South Shetland Islands, and its plate tectonic setting, in *Geological evolution of Antarctica*, edited by M. R. A. Thomson, J. A. Crame, and J. W. Thomson, pp. 493-497, Cambridge Univ. Press., New York, 1991.
- Verwoerd, W.J., L. Chevallier, and J.W. Thomson, Oceanic islands on the Antarctic plate, Bouvetoya, in *Volcanoes of the Antarctic Plate and Southern Oceans*, *Antarct. Res. Ser.*, vol. 48, edited by W. E. LeMasurier and J. W. Thomson, pp. 405-410, AGU, Washington D. C., 1989.
- Walker, G.P.L., Characteristics of two phreatomagmatic ashes and their water-flushed origins, *J. Volcanol. Geotherm. Res.*, 9, 395-407, 1981.
- Weaver, S.D., A.D. Saunders, R.J. Pankhurst, and J. Tarney, A geochemical study of magmatism associated with the initial stages of back-arc spreading, *Contrib. Mineral. Petrol.*, 68, 151-169, 1979.
- Wilch, T. I., W. C. McIntosh, and N. W. Dunbar, Late Quaternary volcanic activity in Marie Byrd Land: Potential $^{40}\text{Ar}/^{39}\text{Ar}$ -dated time horizons in West Antarctic ice and marine cores, *Geol. Soc. Am. Bull.*, 111, (10), 1563-1580, 2000.
- Wilson, M., *Igneous Petrogenesis : A Global Tectonic Approach*, 466 pp., Chapman and Hall, New York, 1989.
- Wörner G., H. Niephaus, J. Hertogen, and L. Viereck, The Mt Melbourne volcanic field (Victoria Land, Antarctica), II: Geochemistry and magma genesis, *Geol. Jahrb.*, E38, 395-433, 1989.
- Zielinski, G.A., P.A. Mayewski, L.D. Meeker, S.I. Whitlow, M.S. Twickler, M. Morrison, D.A. Meese, A.J. Gow, and R.B. Alley, Record of volcanism since 7,000 B.C. from the GISP2 Greenland ice core and implications for the volcano-climate system, *Science*, 264, 948-952, 1994.
- Zielinski, G.A., M.S. Germani, G. Larsen, M.G.L. Baillie, S.I. Whitlow, M.S. Twickler, and K. Taylor, Evidence of the Eldgja (Iceland) eruption in the GISP2 Greenland ice core: Relationship to eruption processes and climatic conditions in the tenth century, *Holocene*, 5, 129-140, 1995.
- Zielinski, G.A., P.A. Mayewski, L.D. Meeker, S.I. Whitlow, and M.S. Twickler, 110,000 yr record of explosive volcanism from the GISP2 (Greenland) ice core, *Quat. Res.*, 45(2), 109-118, 1996.
- Zielinski, G.A., P.A. Mayewski, L.D. Meeker, K. Grönvold, M.S. Germani, S.I. Whitlow, M.S. Twickler, and K. Taylor, Volcanic aerosol records and tephrochronology of the Summit, Greenland, ice cores, *J. Geophys. Res.*, 102, 625-26, 640, 1997.

N Barkov, Arctic and Antarctic Research Institute, 38 Bering St., 199226 St. Petersburg, Russia.

I. Basile, Centre Européen de Recherche et d'Enseignement en Géosciences de l'Environnement, Europôle Méditerranéen de l'Arbois, B.P. 80, 13545 Aix-en-Provence, France (basile@cerege.fr).

F. E. Grousset, Département de Géologie et Océanographie, Av des Facultés, Univ. Bordeaux I, 33405 Talence, France.

J. R. Petit, Laboratoire de Glaciologie et Géophysique de l'Environnement, BP 96, 38402 St. Martin d'Hères, France.

S. Touron, Laboratoire de Géologie des Chaînes Alpines, Institut Dolomieu, 15 rue Maurice Gignoux, 38301 Grenoble, France.

(Received November 2, 2000; revised March 9, 2001; Accepted March 19, 2001.)