

PARTICLE MORPHOLOGY, COMPOSITION AND ASSOCIATED ICE CHEMISTRY OF TEPHRA LAYERS IN THE BYRD ICE CORE: EVIDENCE FOR HYDROVOLCANIC ERUPTIONS

by

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ABSTRACT

In 1968 an ice core 2164 m long was recovered from Byrd station in West Antarctica. About 2000 tephra layers were observed in the core and have been differentiated into ash and dust bands according to the grain size and concentration of particles in the layers. Mount Takahe, a local volcano in Marie Byrd Land, Antarctica is the probable source.

Detailed examinations of the particle morphology, composition and ice chemistry associated with some of the tephra layers have led to the conclusion that the eruptions which produced the layers were probably hydrovolcanic. Melted glacier ice is considered the most likely source of the water involved in the eruptions.

Processes associated with hydrovolcanism such as particle aggregation (causing premature deposition of fine particles), rapid conversion of sulfur dioxide to sulfuric acid (in the presence of abundant moisture) and scavenging of acid droplets by the fine dust particles are inferred to have taken place. Such processes would greatly reduce the atmospheric residence time of the eruptive products and thus their atmospheric and climatic impact.

INTRODUCTION

Deep ice cores from the polar regions of Antarctica and Greenland contain extensive records of paleoclimate and paleoatmospheric composition in the form of soluble and insoluble impurities, stable isotope variations and gases trapped in air bubbles in the ice. The interpretation of these records from a global point of view requires knowledge of the local factors which could affect the record.

In 1968 an ice core 2164 m long was recovered from Byrd station in West Antarctica (80°01'S, 119°31'W, altitude 1530 m). In addition to studies of the ice-crystal size, fabric, density, air bubbles, stable isotopes, ice chemistry, microparticles and the basal ice (Gow and others 1968, Thompson and others 1975, Cragin and others 1977), preliminary examination of the core revealed the presence of about 2000 volcanic ash and dust layers (tephra) which were examined by Gow and Williamson (1971) and more recently by Kyle and Jezek (1978) and Kyle and others (1981, 1982).

The purpose of the present study is to seek supporting evidence that Mount Takahe in West Antarctica is the source of the tephra as proposed by Kyle and Jezek (1978) and to provide information regarding the probable nature of the eruptions and the likely atmospheric and climatic impact they had. In addition, the results of this study may establish criteria which should be useful in the interpretation of tephra layers in other deep ice cores. The results include studies of the particle morphology, composition and ice chemistry of several of the tephra layers in the Byrd core.

PREVIOUS WORK

Gow and Williamson (1971) made the first detailed study of the 25 dirt and other (c. 2000) cloudy layers in the Byrd core. These layers were differentiated into volcanic ash and dust bands according to the mean grain size and concentration of particles in the layers, as summarized below.

Parameter	Ash	Dust
Concentration (g cm ⁻³)	10 ⁻³	10 ⁻⁵
Mean size (μm)	50	1-2
Composition	lithic vitric crystal	vitric crystal
Approximate depth (m)	788, 1300-1800	911, 1200-2000 (especially 1300-1400)

The most likely source of these ash and dust (tephra) layers was believed to be the volcanoes of Marie Byrd Land although a more distant source for the dust layers was not ruled out.

Kyle and Jezek (1978) examined glass shards and lithic particles from three of the ash bands by electron microprobe analysis and classified the glass as peralkaline trachyte. They suggested that Mount Takahe, a young (<0.25 Ma BP (LeMasurier 1972)) volcano located about 450 km from Byrd station is the probable source. Kyle and others (1981) later confirmed these conclusions after studying several additional ash layers from the Byrd ice core and suggested that the eruptions were probably phreatomagmatic or surtseyan in nature.

Ragone and Finelli (1972), Cragin and others (1977) Kyle and others (1982) and Palais and Legrand (1985) have studied the major soluble impurities in the Byrd ice core. These studies have shown that most ionic species had elevated concentrations during the last glacial period. Ragone and Finelli (1972) speculated that the volcanism recorded in the core might be responsible for these elevated concentrations whereas Cragin and others (1977) appealed to important influxes of eolian dust into Antarctica from other parts of the globe.

Palais and Legrand (1985) were able to show that, on the average, ionic impurities in the Byrd core are in charge balance and that marine NaCl and Na₂SO₄ are a major component of these impurities. The gas-derived acids HNO₃, HCl and H₂SO₄ were also found to be important in the ionic balance of the Byrd core ice. Palais and Legrand suggested that turbulence in the atmosphere, resulting from stronger meridional circulation increased the atmospheric loading of marine impurities during the last glacial period while increased biogenic productivity or local volcanism might have been responsible for the increase in gas-derived excess sulfate. These studies provide a useful foundation from which to examine whether the volcanism recorded in the Byrd core affected atmospheric chemistry and thus the composition of the precipitation deposited at Byrd station.

SAMPLING AND ANALYTICAL METHODS

Samples from 23 sections of the Byrd core were examined in this study. Because none of the 25 ash layers, originally described by Gow and Williamson (1971), have remained intact in the core, this sampling was limited to

ice with dust bands and clear ice. However, tephra samples which had been retained on filters from 15 of the 25 original ash layers were available for SEM, EDAX and electron microprobe analyses.

Samples were prepared using the "wet" cleaning procedure described by Langway and others (1974) for use with ice cores in which a drilling fluid had contaminated the core exterior. More than 50% of the original sample may have been removed in this process. Washed samples were placed in clean plastic cups and allowed to melt. Melted samples were placed in Coulter™ accuvettes and refrozen until the time of analysis. Two accuvettes of about 20 to 25 ml were obtained from each sample, one of which was used for ice chemistry and the other was used for grain-size analyses and filtering for examination of the dust.

Tephra morphology and composition

An ISI model S-111A scanning electron microscope equipped with a KeveX 7000 series Quantex ray™ ux analytical spectrometer was used to examine individual tephra particles. Working distances were typically 20 to 30 mm and an accelerating voltage of 15 kV was used for imaging and EDAX analyses. The Quantex ray standardless EDS analysis uses ZAF corrections via MAGIC (KeveX Corporation 1980). Oxide concentrations from elemental peak intensities and theoretical standards are calculated and compared. Unknown elemental concentrations are then approximated and given as oxide weight percents normalized to 100%.

Electron microprobe analyses of particles from five ash layers were made using a 3-channel Camebax automated microprobe. An accelerating voltage of 15 kV, specimen current of 0.012 μA , 10–15 μm beam size and a minimum of 5-second count times were used. Data were corrected using the Bence-Albee matrix correction procedure (Bence and Albee 1968). Several glass and feldspar standards were used to check accuracy and monitor Na_2O and K_2O concentrations. Typical precision for most elements was from 1 to 5% of the mean value.

Ice chemistry

Melted ice samples were measured for conductivity, acidity, sulfate, nitrate, total sodium and aluminum depending on the availability of liquid. Conductivity and acidity measurements were made using a method of standard addition developed by Legrand (1980) and discussed in detail by Legrand and others (1982, 1984). The precision of these measurements was estimated to be $\pm 0.03 \mu\text{S cm}^{-1}$ at the 95% confidence interval for conductivity and $\pm 0.2 \mu\text{eq l}^{-1}$ at the 95% confidence interval for acidity (Legrand and others 1984).

During these measurements a phenomenon was observed which deserves to be mentioned. It was noted that samples, which contained abundant silicate dust, consistently had low acidity and often high conductivity. During the measurements of these samples, readings of the conductivity meter and hydrogen ion electrode potential were very unstable as if reactions were taking place. Several experiments were undertaken in which known amounts of volcanic glass were added to solutions of known acidity and it was confirmed that the presence of silicate dust did affect the acidity and conductivity of samples with low (ppb) concentrations of ionic impurities. Acidities were found to decrease by 15 to 70% of the initial acidity for additions of dust between 30 to 430 ppm. The greater the concentration of dust the greater was the decrease of acidity. The reaction that causes this effect may be silicate hydrolysis which tends to neutralize the acidity initially present in the ice and could make the meltwater alkaline. The liquid conductivity of such samples may increase because of the liberation of ions from the silicate in exchange for H^+ ions.

Sulfate and nitrate were measured using a Dionex model 10 ion chromatograph. The working conditions and precision of these measurements are discussed in detail by Legrand and others (1984). In general the detection limit is about 1 ppb ($0.02 \mu\text{eq l}^{-1}$) for all ions and the precision is about $\pm 0.2 \mu\text{eq l}^{-1}$ for sulfate and $\pm 0.1 \mu\text{eq l}^{-1}$ for

nitrate. The concentrations of unknown samples were determined by comparing peak heights with those of calibration solutions.

Total sodium and aluminum were measured using a Perkin Elmer model 303 flameless atomic absorption unit equipped with a graphite furnace (model HGA-70). Calibration solutions (0 to 200 ppb) were prepared using Orion™ standards. These solutions were run systematically before and after each series of measurements to allow correction for instrument drift and to determine concentrations of unknown samples. Typical values of analytical precision are about 5% for both sodium and aluminum (de Angelis and others in press).

RESULTS

Tephra morphology and composition

The interaction of magma or magmatic heat in the near-surface environment with large quantities of water (sea-water, groundwater, lake-water or glacial ice) produces highly explosive volcanic eruptions and other phenomena known collectively as hydrovolcanism (Sheridan and Wohletz 1983). In hydrovolcanic eruptions the mixing of magma and water (phreatomagmatic eruptions vs phreatic, in which no fresh magma is discharged) and the high degree of fragmentation which accompanies such an eruption, produces an initial population of very fine-grained (millimeter to sub-millimeter) pyroclastic material composed of abundant lithic particles, crystals and glass shards (Walker 1971, Rose and Hoffman 1982, Rose and others 1983).

According to Heiken (1974), tephra produced in hydrovolcanic eruptions are characterized by equant, blocky grains with curvilinear surfaces and few vesicles. If vesicles do occur they range from spherical to elongate depending on the viscosity of the magma. Flat, elongate, pyramidal and drop-like particles are also common. Fine micron-size dust often adheres or is partially fused to the other particles. In extreme cases, aggregates are formed when fine ash particles of this kind become agglutinated or when fine particles coat larger ones (Wohletz 1983, K H Wohletz and D H Krinsley personal communication).

In addition to their shape, hydrovolcanic particles can be recognized by a number of surface microfeatures including conchoidal fractures, v-shaped depressions, upturned plates, grooves, cracks, adhering particles and chemical alteration (sublimates, clays and zeolites (palagonite)) which form during eruption, transport and deposition of the ash (Heiken 1974, Rose and others 1982, Wohletz 1983, K H Wohletz and D H Krinsley personal communication). The particles from the ash and dust layers examined in this study have many of the features characteristic of hydrovolcanic tephra. These are described below.

Ash

The most prominent feature of the tephra particles in the ash layers is their morphological and compositional homogeneity. Except for an occasional lithic or crystal most of the particles in the ash layers are blocky or platy shards of low vesicularity (Figs. 1(a) and (b)). Where vesicular particles do occur they are usually only fragments with thick bubble walls and ovoid, elliptical or elongate pipe vesicles (Figs. 1(c) and (d)). In some samples fine dust adheres to the ash particles (Figs. 1(a), (b), and (c) and some particles are aggregates of smaller fragments (Fig. 1(a)).

Electron microprobe analyses of particles from five ash layers (including four not previously analyzed) are listed in Table I. Comparison of these analyses with data from Kyle and others (1981) provides additional support for the conclusion that all ash layers in the core have the same source. Mount Takahe, one of the youngest volcanoes (<0.25 Ma) in the Marie Byrd Land province of West Antarctica is still the preferred source (Kyle and Jezek 1978). Figure 2 is a plot of the mean weight percent of SiO_2 in particles from the tephra layers analyzed in this study and by Kyle and others (1981). The compositional similarity of all the ash layers examined is particularly interesting for it suggests that the volcano maintained the same composition during the time that it was active (>20 ka).

EDAX analyses of 12 ash layers were made to provide

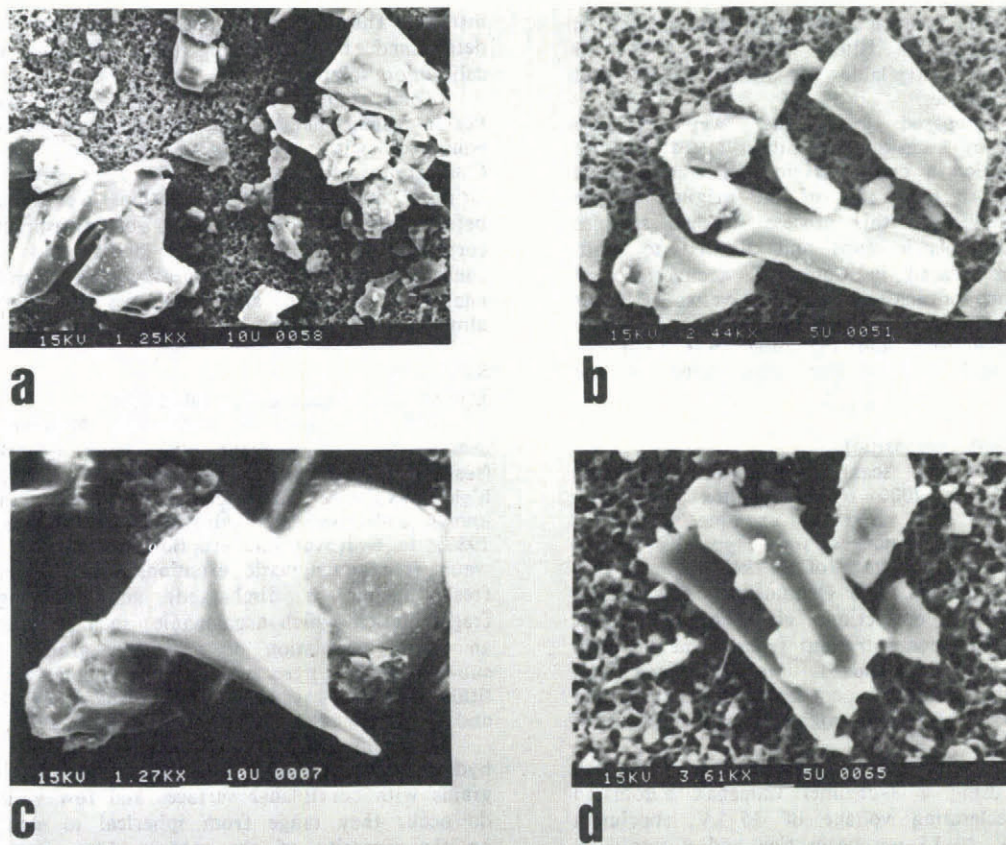


Fig. 1. SEM photographs of particles from ash layers: (a) 1581 m, blocky and platy shards, (b) 1558 m, blocky shards and crystals (?), (c) 1458 m, bubble wall shard, (d) 1616 m, pipe vesicles, elongate shard.

information on the surface chemistry of individual particles. Although such analyses are not as precise as those made with the electron microprobe, they confirm the compositional homogeneity of the ash layers suggested by the microprobe work. These data will be discussed in more detail by Palais in a later paper, now in preparation.

Trace amounts of S and Cl probably in the form of sublimate salts and other non-silicate phases such as those listed by Rose and others (1982) were found on the surfaces of some ash particles. Because the absolute values of S and Cl obtained by EDAX are uncertain, the ratio of S/Cl was calculated instead, to determine whether or not the presence of these elements is consistent with a volcanic source. These values are plotted on the right side of Figure 2 and range from 0.41 to 5.83. The S/Cl ratio on volcanic ash from magmatic eruptions is typically in the range from 0.14 to 3.8 (Stoiber and others 1980, 1981); the higher the ratio the greater the contribution from a magmatic gas component.

The S/Cl ratios calculated for the ash in this study are consistent with a volcanic origin for the S and Cl and in at least some ash layers an important magmatic gas component may have been present. Because the S/Cl ratio depends to a large extent on the initial concentration of volcanic gases (e.g. SO₂, HCl) in the magma (and in the plume) it is difficult to determine whether the variations in the ratio observed for the tephra layers are a function of the nature of the eruptions (phreatomagmatic vs phreatic) (see below) or the result of changes in the composition of the volcanic gases.

Dust

In contrast to the layer particles in the ash layers the dust-sized samples are morphologically and compositionally heterogeneous with a large variety of particle types including vitric, lithic and crystal fragments. Figure 3 shows several of the more common types of the dust particles. Although few, if any, of the blocky, platy or vesicular shard-like particles occur in these layers, many other types of particles do occur.

The particles which are most characteristic of the dust layers are the aggregates, such as those pictured in Figures 3(a) and (b). In Figure 3(a), the individual particles are probably a mixture of vitric and crystal fragments whereas in Figure 3(b) the particles seem to be entirely crystal fragments.

These aggregates are very similar to particles which have been described by Sorem (1982), Rose and Hoffman (1982) and Rose and others (1983) from hydrovolcanic eruptions. Several mechanisms have been proposed to explain the formation of these aggregates (Sorem 1982, Rose and Hoffman 1982). The presence of abundant moisture (including H₂SO₄ droplets) and fine dust (which promotes electrostatic attractions) such as would be present in a hydrovolcanic eruption are two features which seem to be characteristic of all eruptions in which aggregates have been found.

Other types of particles which are found in the dust layers include mineral fragments (Fig. 3(b)), spheres (Fig. 3(c)) and altered lithic fragments (Fig. 3(d)). Many of these particles have surface features like those described by Wohletz (1983) such as grooves, pits, cracks, plates, adhering particles and chemical alteration. These features are especially obvious in Figures 3(c) and (d).

Detailed studies of the individual particles in the dust layers show that they have similar chemical compositions (when calculated on a S- and Cl-free basis) and probably have the same source as the ash layers. In addition to vitric dust particles with compositions nearly identical to the glass shards from the ash layers there are abundant crystal (e.g. feldspar, pyroxene, oxides) and lithic fragments.

In Figure 2, the mean SiO₂ (weight %) values of 10 of the dust layers which were examined are plotted. Although the mean SiO₂ of the dust layers in the interval between 1300 and 1350 m appears to be lower than the mean of the ash layers this is probably because of the abundant lithic and crystal fragments (which tend to have lower SiO₂) which have been averaged in with the analyses. On this figure is also plotted the mean SiO₂ of all the ash and dust samples from this study and the work of Kyle and others

TABLE I. MAJOR ELEMENT ANALYSES (WEIGHT %) OF VOLCANIC GLASS FROM TEPHRA LAYERS IN THE BYRD ICE CORE AND COMPARATIVE ANALYSIS OF VOLCANIC ROCKS FROM MOUNT TAKAHE

Sample	1	2	3	4	5	6	7
Tube number	915	959	1013	1047	1061		
Depth of sample (m)	1436	1500	1581	1631	1653		
Number of measurements on sample	21	8	10	12	8		
SiO ₂	63.61(0.59)	63.53(0.67)	62.17(0.35)	63.13(0.35)	64.04(0.69)	61.90(0.40)	61.22
TiO ₂	0.37(0.07)	0.43(0.05)	0.41(0.02)	0.44(0.04)	0.42(0.12)	0.54(0.06)	0.61
Al ₂ O ₃	15.46(0.51)	14.93(0.05)	14.24(0.19)	15.33(0.16)	15.59(0.77)	15.01(0.25)	15.16
FeO ^(a)	6.81(0.91)	7.07(0.51)	8.70(0.29)	6.99(0.35)	5.37(1.35)	7.90(0.25)	7.07
MnO	0.20(0.03)	0.34(0.03)	0.36(0.02)	0.25(0.01)	0.21(0.05)	not analyzed	0.29
MgO	0.02(0.01)	0.04(0.01)	0.06(0.01)	0.11(0.01)	0.08(0.03)	0.12(0.05)	0.12
CaO	0.91(0.14)	1.01(0.07)	1.02(0.03)	1.03(0.04)	0.80(0.14)	1.28(0.13)	1.30
Na ₂ O	9.65(0.22)	7.04(0.43)	7.01(0.60)	7.47(0.23)	6.35(0.70)	7.83(0.23)	7.97
K ₂ O	4.84(0.13)	4.74(0.28)	4.60(0.05)	4.90(0.04)	5.25(0.28)	4.51(0.06)	4.80
P ₂ O ₅	not analyzed	not analyzed	not analyzed	not analyzed	not analyzed	0.09(0.02)	0.11
Total	99.86	99.12	98.57	99.65	98.11	99.18	98.65 ^(d)
CIPW norms (wt %) ^(b)							
Q	0.12	1.98	0.54	-	3.42	0.61	-
Or	28.36	27.80	27.24	28.91	31.14	26.62	28.36
Ab	52.92	50.30	47.68	51.35	50.83	50.46	50.15
Ne	-	-	-	-	-	0.89	0.60
Ac	5.08	5.08	6.47	5.08	2.31	6.16	5.67
Ns	1.34	0.85	0.98	1.34	00	1.66	2.27
Di	2.11	2.38	2.38	2.34	1.85	5.13	5.08
Hy	9.87	10.66	13.80	10.50	7.59	3.24	-
Ol	-	-	-	-	-	3.36	5.29
Mt	-	-	-	-	0.70	0.10	-
Il	0.76	0.76	0.76	0.91	0.76	0.92	1.16
Ap	-	-	-	-	-	0.20	0.26
Total	100.56	99.81	99.85	100.43	98.60	99.35	98.84
DI ^(c)	81.4	80.1	75.5	80.3	75.4	78.6	79.1

Key 1-5: ash layers from Byrd station, 6: mean of analyses of six ash layers (788 m, 1457 m, 1487 m, 1500 m, 1594 m, 1711 m, number of samples: 101) from Byrd station analyzed by Kyle and others (1981), 7: peralkaline trachyte (66A) from Mount Takahe (W LeMasurier personal communication to P Kyle and others 1981), number in parentheses ($\bar{\sigma}$) represents one standard deviation of the mean.

(a) ΣFe , total Fe as FeO.

(b) for the norm calculation Fe₂O₃ standardized at 0.25 x ΣFeO .

(c) differentiation index 9Thornton and Tuttle 1960).

(d) includes H₂O⁺ = 0.37.

(1981). The SiO₂ value from Mount Takahe is also plotted. The similarity of these mean values is a good indication that all the tephra layers (ash and dust) in the Byrd core were erupted from Mount Takahe.

The S and Cl surface alteration which was found on some ash particles was also present on many of the dust particles and is believed to be related to processes that occurred during the eruptions which deposited S- and Cl-bearing compounds of the particle surfaces. The S/Cl ratios calculated for the particles in the dust layers range from 0.57 to 1.89 and are plotted on the right side of Figure 2. These ratios are somewhat lower and have a much narrower range than the values calculated for the ash layers. As discussed by Gandrud and Lazrus (1981), abundant water in a volcanic plume would tend to reduce the solubility of

SO₂, increase the solubility of HCl, and cause a selective enrichment of Cl (lower S/Cl ratio) on acid-coated particles. The differences between the S/Cl ratios on the ash and dust particles may be due in some cases to changes in the composition or the contribution of the magmatic gas component in the eruptions. However if a large amount of water were involved in the eruption of some of the layers this could have the same effect on the S/Cl ratios as compositional changes in the magma. Based on the finer grain size and the morphology of particles in the dust layers as well as the low S/Cl ratios on the dust particles it is believed that water may have been more abundant and the eruptions may have been more explosive in the dust as compared to some of the ash eruptions.

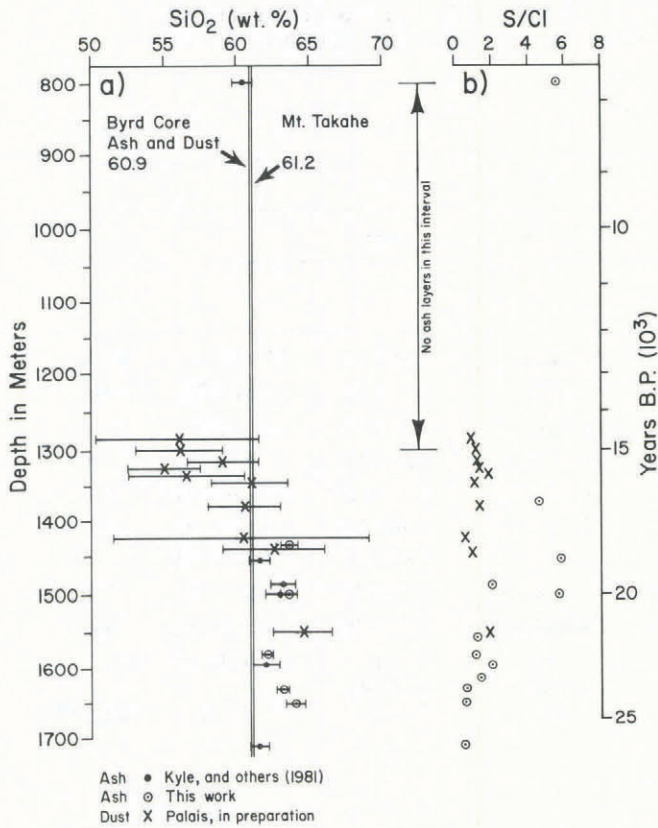


Fig. 2. (a) Mean SiO₂ (weight %) of particles in the ash and dust layers of the Byrd core ($\pm 2\sigma$) vs depth (age). Time scale from Lorius and others (1984). Mean SiO₂ of all particles in ash and dust bands is 60.9% and from Mount Takaha 61.2%. (b) Mean S/Cl ratio on particles from ash and dust layers.

Ice chemistry

In Figures 4(a), (b), and (c) the ice chemistry of three representative core sections with tephra (dust) layers (indicated by the arrows) is shown. Because of limitations in sample volume the profiles are not complete for all parameters. However, some general observations regarding the relationship between the concentration of ionic species in the ice to the presence of tephra layers can be made.

In general, conductivity and acidity of the ice are not well correlated with one another. However, the presence of dust seems to have affected the acidity and liquid conductivity of samples and has imposed an inverse relationship between them. Acidities typically range from -2 to $+2 \mu\text{eq l}^{-1}$ with peaks up to $6 \mu\text{eq l}^{-1}$ while conductivities are usually in the range -1 to $2 \mu\text{S cm}^{-1}$ with peaks up to $4 \mu\text{S cm}^{-1}$. Although the neutralization of the acidity in these samples occurred in part during the analyses, a significant amount of neutralization probably also occurred in the atmosphere and in situ in the ice sheet.

Figure 4(a) is a representative section from about 1317 m depth in the core and shows that the samples in which tephra layers occur are alkaline and have relatively high conductivity although a general positive or negative correlation between the two parameters (acidity vs conductivity) does not exist. For example, a different pattern is shown in Figure 4(b), which shows a core section from about 1380 m depth where the tephra layers seem to be associated with ice having varying levels of acidity. Sporadic peaks in conductivity are not well correlated with the acidity peaks in this core interval. The difference in the ice chemistry of these two layers probably reflects variations in the amount of acids and tephra associated with the eruptions which produced them. Although the profiles are not complete, the evidence from these figures and the other ice-chemistry profiles, which will be discussed by Palais (in preparation), show that sulfate concentrations are only occasionally elevated in association with the tephra layers (compare sulfate profiles in Figures 4(a), (b), and (c)). Taken together with the low acidity of the ice, this evidence suggests that sulfur gases may have been only a

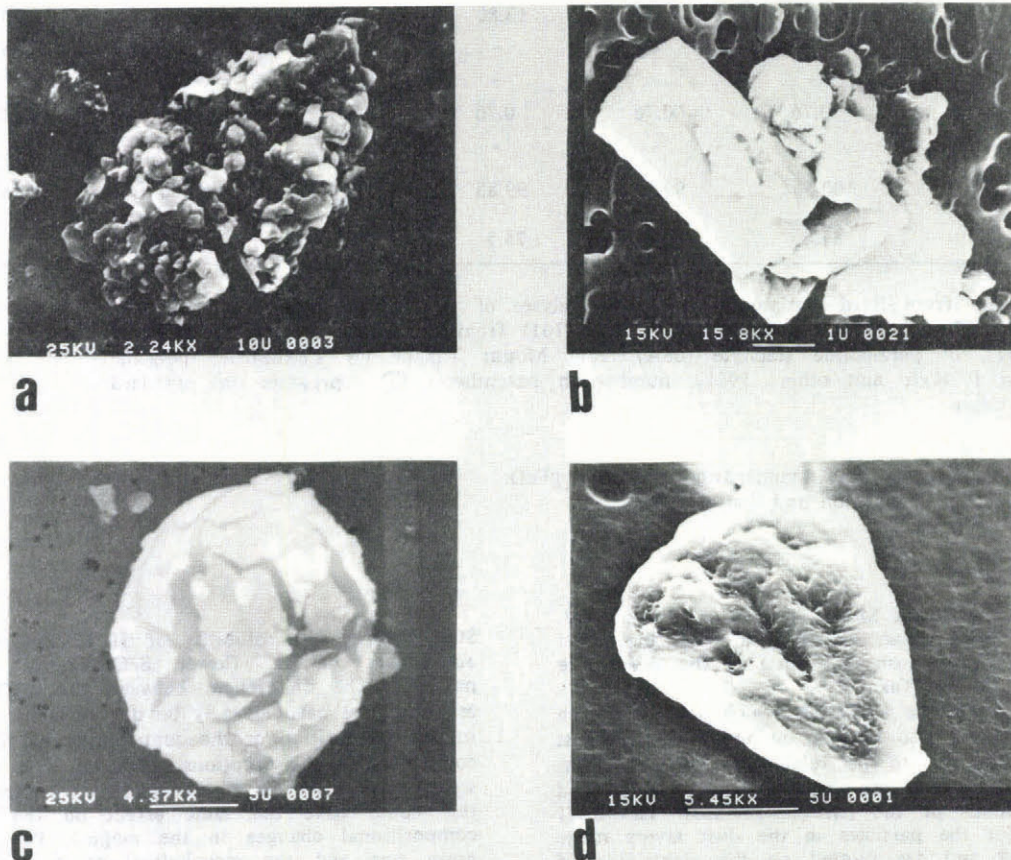


Fig. 3. SEM photographs of particles from the dust layers: (a) 1301 m, aggregate of rounded vitric fragments, (b) 1317 m, aggregate of crystal fragments, (c) 1301 m, sphere with surface cracks and adhering particles, (d) 1347 m, lithic fragment, surface alteration.

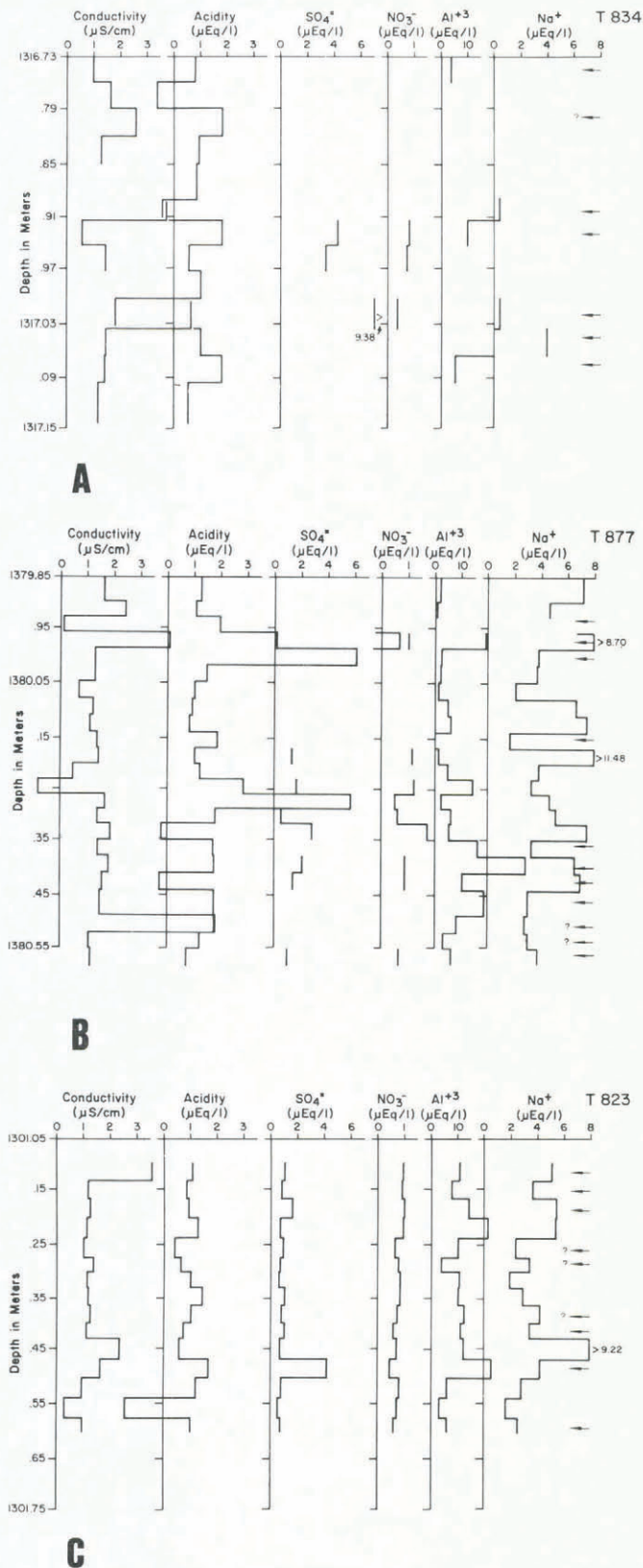


Fig. 4. Ice-chemistry profiles from A) 1317 m, B) 1380 m, C) 1301 m in the Byrd core. The profiles include conductivity ($\mu\text{S cm}^{-1}$), acidity ($\mu\text{Eq l}^{-1}$), sulfate, nitrate, aluminum and sodium ($\mu\text{eq l}^{-1}$). Arrows represent tephra layers.

minor product of the dust eruptions. Nitrate concentrations are unaffected by the presence of the tephra layers as shown in Figure 4(c) while Figures 4(b) and (c) demonstrate that the concentrations of aluminum and sodium are usually elevated in association with the tephra layers.

CONCLUSION

Evidence presented in this study suggests that the

eruptions which produced the tephra layers in the Byrd core were from hydrovolcanic eruptions of Mount Takahe. This is based on detailed examinations of the particle morphology, composition and ice chemistry associated with tephra layers in the core. Melted glacier ice is the most likely source of the water for the hydrothermal system which may have existed at Mount Takahe.

Processes such as particle aggregation, rapid conversion of SO_2 to H_2SO_4 and efficient scavenging of acid droplets by the abundant fine dust are characteristic of hydrovolcanic eruptions and are inferred to have taken place at Mount Takahe. Rapid aggregation and deposition of the fine acid-coated volcanic dust implies a short residence time for the tephra and gases and suggests that the eruptions had a minimal atmospheric-climatic impact.

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