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Air-snow exchange investigations at Summit, Greenland: An overview

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Abstract. The Greenland Ice Sheet Project 2 (GISP2) and Greenland Ice Core Project (GRIP) deep drilling programs at Summit, Greenland included support (both logistical and scientific) of extensive investigation of atmospheric transport and air-snow exchange processes of gases and particles relevant to the interpretation of the ice-core records. Much of the sampling for the air-snow exchange investigations was conducted at a unique solar-powered camp 30 km southwest of the GISP2 drill camp (even further from the GRIP camp) and was characterized by a high degree of international collaboration and cooperation. The wide range of expertise and analytical capabilities of the 20-plus investigators participating in these studies has provided important insight into the meteorological, physical, and chemical processes which interact to determine the composition of snow and firn at Summit. Evolving understanding of this system will allow improved reconstruction of the composition of the atmosphere over Greenland in the past from the detailed Summit ice-core records. This paper provides an overview of air-snow exchange investigations at Summit, including their development through the course of the drilling programs (1989-1993), significant findings related to both air-snow exchange issues and the present state of the Arctic free troposphere, as well as the major outstanding questions which are being addressed in ongoing experiments at Summit.

Introduction

Climate changes over timescales ranging from intraannual to glacial-interglacial transitions are recorded in the physical and chemical properties of glacial ice. Changes in ice chemistry are thought to largely reflect changes in atmospheric chemistry and dynamics resulting from variations in biogeochemical cycling due to climatic (and other) perturbations. However, variations in the properties measured down an ice core have to be translated first into corresponding variations of the atmospheric properties, before they can be used to estimate past climate signals.

In other words, full use of the remarkable records recently recovered at Summit, Greenland (discussed in many other papers in this special section) requires determination of transfer functions between air and snow, snow and firn, then firn and ice. The overall transfer function involves multiple physical and chemical processes. The composition of the atmosphere over any ice coring site is the result of horizontal and vertical transport from a variety of source types and regions, with the additional complication of ongoing modification by physical and chemical processes enroute. Another complication involves the effects of temporal averaging; the snowpack and ice usually preserve, at best, monthly or seasonal resolution, periods which may involve atmospheric transport from widely divergent source regions and pathways. Initial incorporation of atmospheric constituents into surface snow can result in significant

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fractionation; the relative importance of wet and dry deposition of aerosols and gases will differ between species present in the atmosphere and between sites. Reemission of some species to the atmosphere, mobilization and redistribution within the snowpack, and the potential for wind to redistribute, and perhaps import or export, surface snow will further modify any atmospheric signal that is eventually preserved in glacial ice. Thus the overall goal of understanding air-to-snow transfer functions involves developing an understanding of (1) source areas and transport pathways, (2) processes controlling incorporation of material into the snowpack, (3) temporal variations in these processes as related to observable atmospheric processes from the mesoscale to microscale, and (4) post-depositional modification of snow.

The field activities and logistic support associated with the Greenland Ice Sheet Project 2 (GISP2) and Greenland Ice Core Project (GRIP) deep drilling programs provided an unprecedented opportunity to conduct investigations into air-snow exchange processes at Summit, Greenland. This paper will present an overview of these investigations, starting with a brief history of the program but emphasizing the advances that have been made in our understanding of air-snow exchange. *Kahl et al.* [this issue] focus on questions of source areas and transport, so these issues will not be discussed here. The reader may also want to refer to *Jaffrezo et al.* [1995] and *Dibb* [1996] for earlier review articles on several aspects of air-snow exchange investigations in Greenland and to the special issue of *Atmospheric Environment* (27A (17/18) pp. 2703-2822, 1993) devoted to a similar investigation conducted at Dye 3 (south Greenland) in 1988-1989.

History of the Summit Program

Coordinated atmospheric and snow sampling began at Summit in the summer season of 1989, in conjunction with camp

construction and initial drilling activities for GISP2 and GRIP (the 1989 European drilling program was known as Eurocore, but major preparation was accomplished for GRIP in the same season). A large, integrated proposal for air-snow exchange investigations had been declined for funding, but the U.S. ice-core chemistry community, and particularly the GISP2 executive committee, strongly felt that improved understanding of the transfer functions would be an important contribution of the GISP2 program. With a small amount of funding from the National Science Foundation (NSF) Office of Polar Programs and much support from the GISP2 Science Management Office and all field personnel at Summit, a pilot project was conducted during this first season.

The authors and Paul Mayewski (chair of the GISP2 executive committee) recognized that a small atmospheric sampling program would have lower logistic impacts but could also produce higher-quality data through the elimination of local pollution. A decision was made to collect atmospheric samples (as well as surface and near-surface snow) at a remote camp with as few pollution sources as possible. It was also decided that an attempt would be made to operate all atmospheric sampling devices with clean power provided by photo-voltaics with battery storage. A tent camp, henceforth referred to as ATM, was established 28 km southwest (bearing 217° true) of the GISP2 drill camp for this purpose (Figure 1). The camp was set up 300 m beyond a snowmobile "parking lot" at the end of the flag line to the drill camp, no motorized traffic was allowed past this parking lot. Approximately 500 m beyond the camp a small trench was built to house batteries and sampling pumps. Sampling lines were run from the trench an additional 30-50 m further away from the tent camp. From 1989 to 1993 this camp was operated by only two people at a time, with a third staffer based at GISP2 in some seasons for processing of samples and cleaning equipment (Table 1). This small crew operated equipment and collected samples for as many as 20 different research teams (Table 2) [Jaffrezo et al., 1991].

In 1989 the power system consisted of 800 W of photovoltaic cells and twelve 100-amp-hour gel cell batteries. These were configured into a 24 V system that proved capable of powering two high-volume aerosol sampling systems (one for natural radionuclides and one for soluble ionic species) for the majority of time during the 10-week season [Dibb, 1990]. Snow samples were collected for these same analyses plus trace elements, carbon, insoluble aerosols, and stable isotope analyses. Several arrays of accumulation stakes were established and attempts to sample ice fog (for chemical analyses) were initiated.

After the successful "proof of concept" during 1989, NSF increased the size of the solar power system by four fold for the 1990 season. In addition, researchers from the Laboratoire de Glaciologie et Geophysique de l'Environment provided 1 kW of panels (with battery storage) for their preliminary investigation of acidic gases (sampled with denuder techniques) [Silvente, 1993; Silvente and Legrand, 1995]. During this season five bulk aerosol sampling lines and one impactor (to collect size-segregated aerosol samples) were operated in addition to the French denuders and nylon filter packs. Snow sample collection was similarly expanded to provide material for the investigators analyzing the various new atmospheric samples. During 1990 the solar power system was also used to operate an electromechanical drill and collect a firn/ice core to approximately 140-m depth. Samples from this core, and a companion 6-m-deep snowpit, were provided to several of the GISP2 and GRIP investigators to complement the results of their

sampling from the main cores or around the drill camps. New techniques for collection of ice fog were tested, and analysis of these samples was expanded to include stable isotopes as well as soluble ionic species.

Prior to the 1991 season the GRIP steering committee and the GISP2 executive committee decided to make the air-snow investigations a formal, joint undertaking of the two drilling programs. A memorandum of understanding was adopted to ensure access to the site by interested investigators from both communities, as well as shared logistics. As part of this agreement, ATM staff agreed to continue to make every effort to collect samples (atmospheric and/or snow) requested by investigators in either program if they were not able to place personnel at this unique site. At this point GRIP provided an additional 3 kW of solar panels and a 1500-amp-hour battery bank, bringing the total generation capacity to a nominal value of 7 kW, with 3000 amp hours of storage. The sampling program grew in parallel, with 10 atmospheric samplers, representing a constant load of approximately 2.5 kW, successfully operated throughout a 4-month (May-August) season. Regular meteorological soundings with a tether sonde system were initiated at the GISP2 camp.

In early spring of 1992, NSF sponsored a workshop, organized by the International Commission of Snow and Ice Working Group on Snow-Atmosphere Chemical Exchange, where progress on these issues at Summit was reviewed and a plan for the next several seasons was formulated [Bales et al., 1992]. The field season following this meeting was marked by the successful completion of the GRIP drilling program and continued growth of the air-snow exchange group activities at the GISP2 camp, including preliminary gas phase measurements of H_2O_2. GRIP transferred a containerized laboratory van and a snowmobile to the GISP2 site at the end of 1992 for our continued use. In 1993 the GISP2 drilling program recovered samples of bedrock under the ice sheet, the remote camp continued operation at full speed, and continuous measurements of HCHO and O_3 were initiated at the drill camp. Pilot studies were also conducted to determine the feasibility of using mist chamber sampling techniques to measure soluble acidic gases at Summit [Dibb et al., 1994], as well as measuring H_2O_2 and HCHO in the air filling the pore space of firn [Bales et al., 1995a]. A large-scale continuous, experiment to evaluate the fluxes of soluble ionic species to the snow surface from all main deposition processes was also initiated [Bergin et al., 1994, 1995a,b]. In preparation for air-snow investigations from a scaled-down GISP2 camp in 1994-1996, the remote camp was relocated to a site 11 km from GISP2 (along the same flag line) at the end of the 1993 season.

In the three seasons after the completion of drilling (1994 through 1996), air-snow investigations have continued to expand at Summit, with 8-10 researchers present throughout the summer season (Table 1). Five different U.S. research teams are participating with support from the NSF Office of Polar Programs, while the European Community (EC) has funded an international program on "Transfer of Aerosol and Gases to Greenland Snow and Ice" (TAGGSI) for the 1994-1996 period. The remote camp at 11 km distance is still operated for collection of aerosol-associated species (10 different sampling lines) and most surface and near-surface snow sampling. A 20-m tower was erected at GISP2 and is the focus of most experiments conducted in camp, including eddy correlation measurements of sensible heat, momentum, water vapor, and reactive nitrogen oxides (NOy); gradient measurements of acidic gases and aerosols; continuous monitors of CO and O_3; and operation of
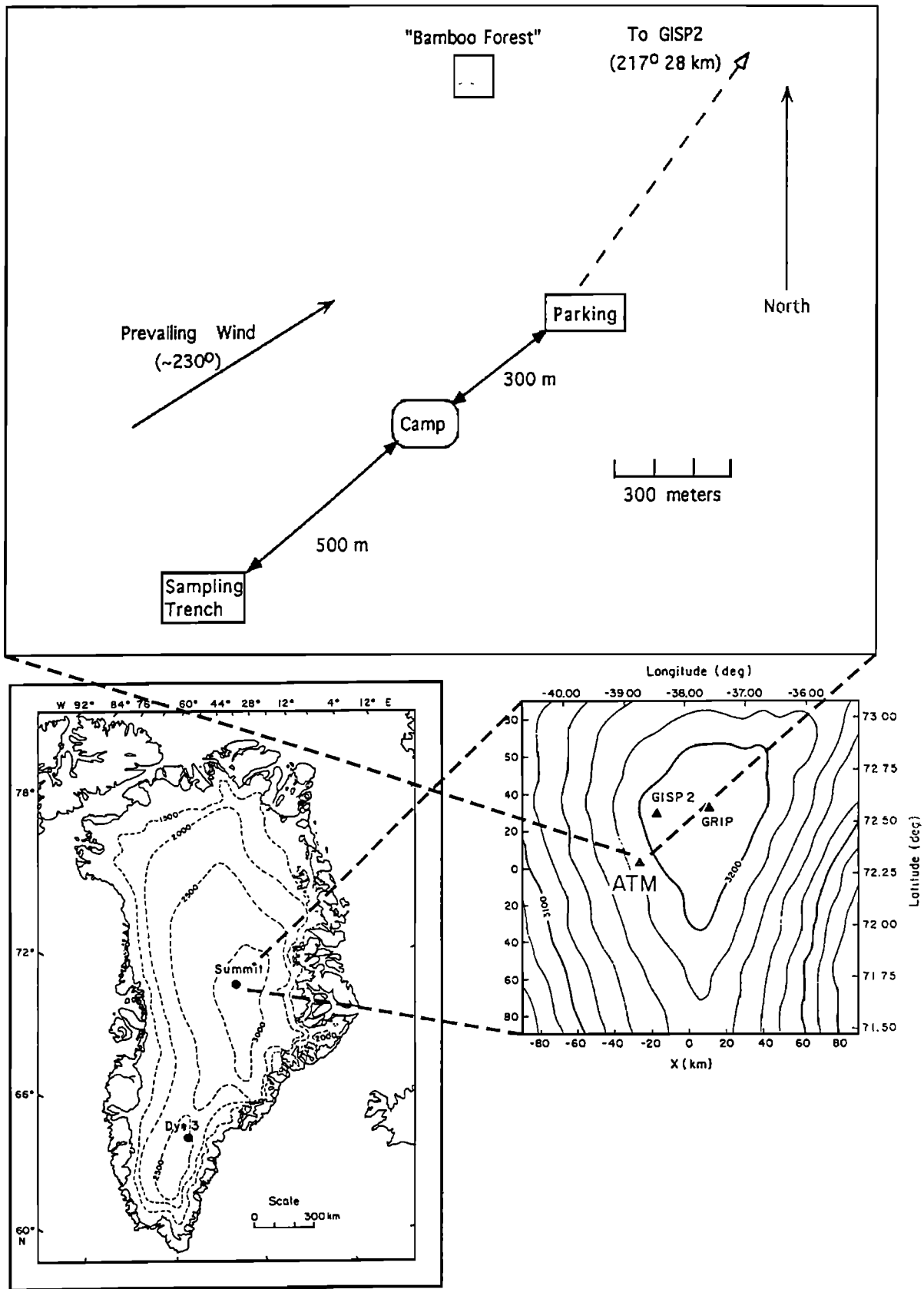
Figure 1. Location map showing the drill camps and atmospheric sampling sites at Summit, Greenland.

Table 1. Individuals Who Have Collected Atmospheric and Snow Samples at Summit as Part of These Investigations

The early (small crew) years	Additional Personnel in 1993-1995
J. Dibb[a,b]	M. Losleben[a]
J.-L. Jaffrezo[a,b]	V. Hart[a]
M. Pender[a]	J. Winterle[a]
S. Weyenberg[a]	J. McConnell[a]
E. Silvente[a]	M. Hutterli[a]
M. Bergin[a]	A. Colman[a]
D. Stanitski	J. W. Munger[a]
N. Fuller	H. Kuhns[a]
R. Schoen	M. Albert[a]
C.-S. Lin	P. Wahlin[a]
G. Marec	R. Bales
R. Borys	M. Anklin
	K. Fuhrer
	R. Mendelson
	S.-M. Fan
	M. Fowler
	B. Fontaine
	N. Barabas
	M. DeAngelis
	V. Hoyaux
	M. P. Clain
	F. LaPierre
	E. Aarons
	S. Decato
	R. Davis
	N. Heidam
	J. Choi

[a] These individuals participated in more than one season.
[b] Both of the authors have spent part of each season overseeing the program.

several different types of impactors. A separate warm lab houses instruments making gradient measurements of HCHO and H_2O_2. A 180° clean sector is established to the south of camp; this area is used for firn gas sampling and certain specialized snow sampling campaigns, and motorized traffic is prohibited in this zone. (Stationary emission sources are all in a relatively small sector (300°-360°) north of the tower.) An area 5 km northeast of camp has been set aside for detailed investigation of snow metamorphism and the exchange of energy and material between the atmosphere and snow. Two 16- by 20-foot heated temporary structures and the lab van from GRIP are shared by all groups, providing laboratory space for sample processing, chemical analyses, and data processing/manipulation.

What We Have Learned

Aerosol

The composition of air along the crest of the Greenland Ice Sheet (Summit and Dye 3) does not reflect that in the better-studied Arctic Basin. In particular, the Arctic Haze phenomenon, which blankets the Arctic Basin with pollutants and dust for 3-4 months during late winter, is manifested at Dye 3 as brief episodes (a few days) of transport from the basin to the higher elevations of the ice sheet interior. Most of these events appear to occur in spring (i.e., toward the end of the Arctic Haze season), and they can contribute a large fraction of the annual deposition of anthropogenic and crustally derived species to the snow surface. Preliminary results from automated year-round aerosol sampling suggest that the same is true at Summit [Wahlin, 1996]. The Greenland Ice Sheet's orientation and

elevation (a tall obstruction perpendicular to the prevailing westerlies), and boundary layer dynamics mediated by the presence of the ice, are responsible for this decoupling between low-elevation Arctic sites and those on the ice sheet [Dibb, 1990; Davidson et al., 1993]; see also the special issue of Atmospheric Environment on "Arctic Air, Snow and Ice Chemistry," (27A (17/18) pp. 2703-2822, 1993). It is possible that the springtime maximum in dust transport to the crest of the Greenland Ice Sheet includes a contribution from a general increase in dust loading of the northern hemisphere troposphere by dust storms over the great deserts of Asia and Africa [e.g., Merrill et al., 1989; Gao et al., 1992; Swap et al., 1996], but the Dye 3 events examined in detail all seemed to originate in the Arctic Basin and were interpreted to be transporting pulses of Arctic Haze to higher elevations.

From the beginning of our work on the Greenland Ice Sheet, we observed unexpected covariance in the concentrations of ^{210}Pb and ^7Be in the aerosol [Dibb, 1990; Dibb and Jaffrezo,

Table 2. Measurements in the Air-Snow Exchange Investigations at Summit, 1989-1996

	Principal Investigators
Atmospheric Measurements	
Radionuclides (^{210}Pb, ^7Be)	Dibb
Major anions/cations	Davidson/Jaffrezo
Organic acids	Legrand/Jaffrezo/Dibb
Trace metals	Davidson/Jaffrezo/Boutron
Trace elements	Mosher/Colin/Winchester
MSA	Salzman
Size fractionated aerosol chemistry	Salzman/Maenhaut/Hillamo
Gas phase soluble acids	Legrand/Dibb/Talbot
PAH and heavy organics	Masclet
Aerosol number	Baltsenperger/Bergin
Aerosol black carbon	Cachier/Hansen
Cloud condensation nuclei	Bodhaine/Bergin
Trace gases	Rasmussen/Blake/Munger
Reactive N (NOy)	Munger/Jacob
H_2O_2, HCHO	Bales/Stauffer/Neftel
Hg (aerosol and gas phase)	Vandal/Boutron
Streaker sampling (year-round aerosol)	Heidam/Wahlin
Year-round Rn monitor	Wagenbach
Stable isotopes of Pb in aerosol	Rosmann
Fresh and Aging Snow Analyses	
Radionuclides	Dibb
Major anions/cations	Davidson/Jaffrezo/Dibb
Trace metals	Boyle/Boutron
Trace elements	Mosher/Colin
Organic acids	Legrand/Jaffrezo/Dibb
Microparticles	Zielinski
Carbon (total, soot, soluble)	Cachier
Stable isotopes (of water)	Grootes/White
PAH, heavy organics	Masclet
H_2O_2, HCHO	Bales/Stauffer/Neftel
Snow Related Studies	
Snowflake habit	Borys/Albert/Davis
Fog droplet size distribution	Borys
Chemistry of occult deposition	Borys/Davidson/Jaffrezo
Isotopic composition of vapor/fog/rime	Grootes/White
Accumulation network	Dibb/Jaffrezo/Gow/Meese
Snowpack microphysics	Albert/Davis
Meteorology	
AWS network and echo sounder	Stearns
Tether sonde profiling	Kahl
Back trajectory calculations	Harris/Kahl
Micrometeorology	Albert/Davis/Munger/Jacob

1993; *Dibb et al.*, 1992a]. At the outset, we hoped these natural radionuclides would serve as independent tracers of continental versus upper troposphere/lower stratosphere air masses reaching the crest of the ice sheet, reflecting their different sources (Rn daughter versus cosmogenic isotope for ^{210}Pb and ^{7}Be, respectively). We have determined that the surface level concentrations of these submicron aerosol tracers primarily reflect the influence of boundary layer dynamics over the ice sheet. Downward mixing of free tropospheric air results in elevated concentrations of both radionuclides, while the concentrations in air trapped below the near-surface inversion decrease over time until the next ventilation event [*Dibb et al.*, 1992a]. Throughout the Summit program we have continued to see high correlations between these two tracers; in fact, the past three seasons have shown the tightest relationships so far (Table 3). The connection, or lack of one, between the free troposphere and air sampled just above the snow surface must be considered on a case by case basis when examining air snow relations, since the formation of snow often "samples" airmasses hundreds to thousands of m above the surface of the ice sheet [*Borys et al.*, 1992].

The ^{7}Be data at Summit have nevertheless indicated that stratospheric intrusions can influence the free troposphere over Greenland, an inference that was supported by meteorological evidence in at least one case examined in detail [*Dibb*, 1993]. An episode of even higher ^{7}Be concentration (665 fCi m^{-3}) than discussed in the 1991 case study was observed on June 22, 1994 (Figure 2). Concentrations above 400 fCi ^{7}Be m^{-3} were not observed in free tropospheric (3-6 km) samples collected in the Canadian Arctic and Subarctic during the NASA Global Troposphere Experiment (GTE) Arctic Boundary Layer Expedition (ABLE) 3B airborne campaign [*Dibb et al.*, 1992b], implying a source in the extreme upper troposphere or stratosphere for the 1994 episode sampled at Summit. Figure 2 also illustrates the tendency for covariance of ^{7}Be and ^{210}Pb that has characterized all sampling at Summit (Table 3). (The low correlation in 1991 reflects extremely effective vertical mixing during a long series of storms in May and June, the usual covariance returned in July and August [*Dibb*, 1993].)

In general, the aerosol reaching the crest of the Greenland Ice Sheet reflects the remote location of this site. Concentrations measured for most of the species in summer are quite low, comparable to those determined in airborne campaigns sampling the northern hemisphere free troposphere far from source

Table 3. Monthly Mean Concentrations of the Aerosol Associated Natural Radionuclides at Summit

	n[a]	^{210}Pb fCi m^{-3}				^{7}Be fCi m^{-3}				corr[b]
		May	June	July	Aug.	May	June	July	Aug.	
1989	37		7.2	4.0			123	82		0.55
1990	79		4.6	4.0	3.0		91	102	65	0.60
1991	120	2.7	4.4	6.3	3.1	58	88	126	81	0.20
1992	89	5.4	4.8	4.3	2.4	110	101	126	71	0.57
1993	60	6.7	6.0	3.6		135	210	100		0.75
1994	113	5.6	7.9	5.0	3.7	130	208	168	118	0.77
1995	73	7.6	4.1			197	134			0.77
1996	34	8.5	4.2			247	108			0.87

[a] Number of samples collected. Generally 24-hour integration, but some intervals include three samples per day.
[b] Correlation coefficient between ^{210}Pb and ^{7}Be.

regions. Analysis of carbon (H. Cachier, unpublished data, 1991-1995) and minor organic species in the aerosol, both for concentration and speciation, confirms the aged character of the air masses reaching Summit. Most of the organic compounds have reached their final stage of oxidation during transport, with esters, ketones, and alcohol being the dominant families (P. Masclet et al., Speciation and quantification of the particulate organic matter in polar atmosphere, submitted to *Journal of Geophysical Research*, 1996), in sharp contrast to the characteristics of mid-latitude aerosol [*Clain et al.*, 1996; M. P. Clain, Composition of particulate organic matter in atmospheric aerosol: Comparative study, submitted to *Tellus, Series A*, 1996]. This aging is also reflected in the low concentrations of condensation nuclei measured in summer at Summit [*Kuhns*, 1997], as well as the characteristic loss of the nuclei mode and dominance of the accumulation mode for aerosol-associated species like $SO_4^=$ compared to $SO_4^=$ size distributions measured closer to source regions (Figure 3).

The aerosol is nearly always distinctly acidic, with $SO_4^=$ dominating the total mass [*Dibb et al.*, 1992a; *Bergin et al.*, 1995b; *Kuhns*, 1997], except during unusual events like the advection of biomass burning plumes [*Dibb et al.*, 1996], when large quantities of organic acids (formate, acetate, oxalate) together with potassium and ammonium are found in the particulate phase (Figure 4). In summer, soluble acidic gases are generally even more abundant than particulate $SO_4^=$, with HCl and HNO_3 dominant relative to their aerosol-associated anions [*Silvente*, 1993; *Dibb et al.*, 1994]. However, the concentrations of these inorganic acids tend to be more than an order of magnitude lower than those of the carboxylic acids formic (HCOOH) and acetic (CH_3COOH) [*Dibb et al.*, 1994, 1996, J. E. Dibb et al., Air-snow exchange of HNO_3 and NO_y at Summit, Greenland, submitted to *Journal of Geophysical Research*, 1997; hereafter referred to as Dibb et al., submitted manuscript, 1997; M. Legrand, unpublished data, 1995].

Determination of the content of the aerosol at Summit has confirmed some aspects of the seasonality of transport previously inferred from snowpit studies but also has pointed out some apparent discrepancies. Automatic weekly year-round measurements showed that large concentrations of $SO_4^=$ in the atmospheric aerosol at Summit seem restricted to spring only [*Wahlin*, 1996], as is the case for south Greenland [*Davidson et al.*, 1993]. Daily measurements during the late spring-summer seasons showed low concentrations of sea salt aerosols [*Dibb et al.*, 1992a; *Silvente*, 1993; *Bergin et al.*, 1995b], and decreasing concentrations of sulfate [*Kuhns*, 1997] and crustal aerosols like Ca^{2+} and K$^+$ from spring into summer. However, the levels of these dust tracers can stay high well into June, somewhat at odds with the timing of the "spring" peak recorded in the snow [*Dibb*, 1996]. Also, high concentrations found in "summer" layers in snowpits for NH$_4$$^+$ are not measured in the aerosol at that time [*Kuhns*, 1997]. Better agreement is seen for the timing of large oscillations in the concentrations of methylsulfonate (MSA) in air and snow at Summit, with this species tending to show two annual concentration peaks, spring and late summer [*Jaffrezo et al.*, 1994]. Similar timing has been reported for MSA concentration peaks at several other Arctic sites, suggesting that MSA episodes at Summit are strongly linked with processes occurring at low elevations in the Arctic Basin. Indeed, *Kuhns* [1997] has shown that these episodes are associated with rapid transport from the seas surrounding Greenland.

Progress has been made in the characterization of the source regions influencing Summit. Air mass back trajectories were
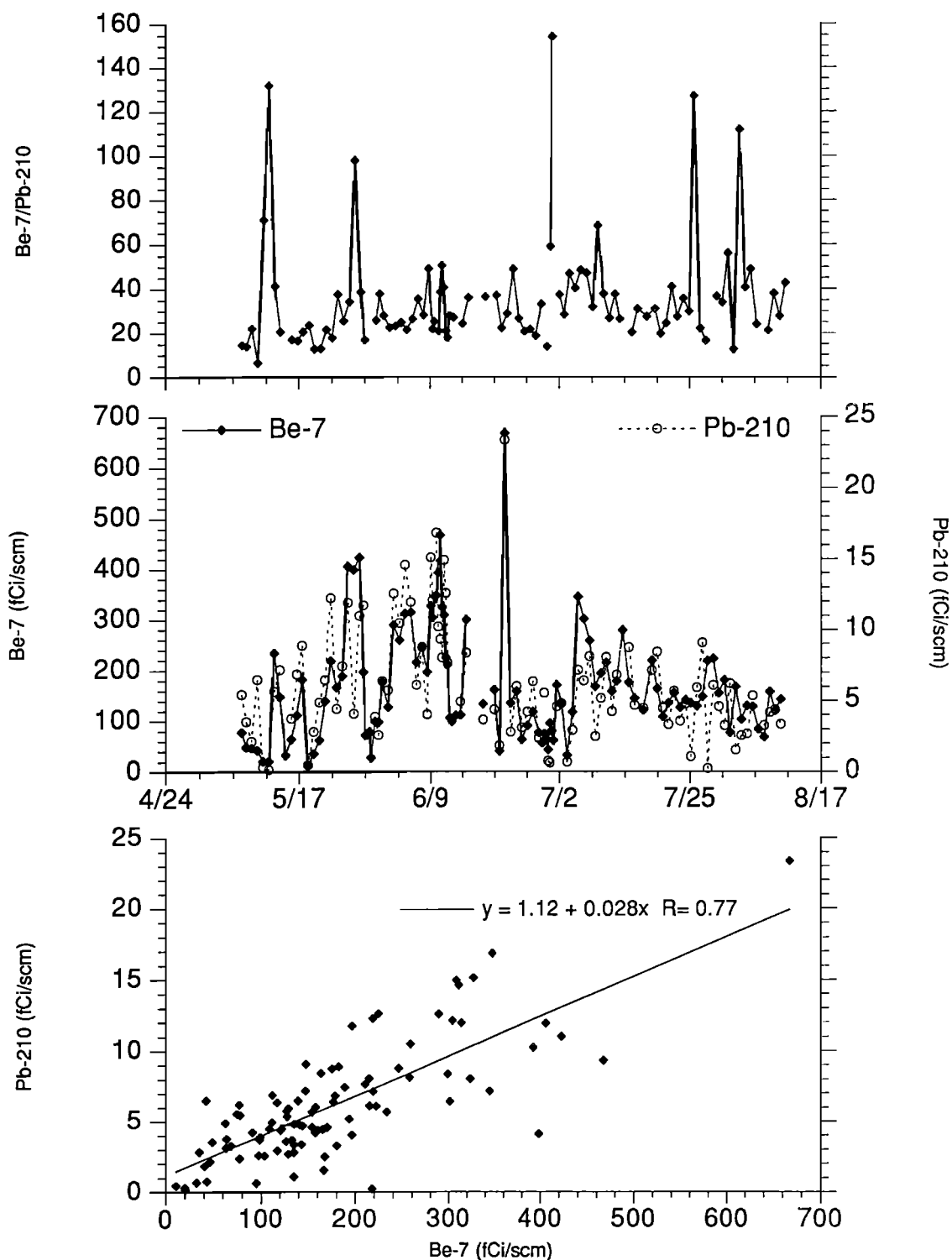
Figure 2. Aerosol-associated natural radionuclide tracers at Summit during the 1994 summer season. The middle panel presents concentrations measured mainly on filters exposed for 24-hour intervals, but filters were changed every 8 hours for several intensive sampling periods during the season. The two time series tend to covary, as is reflected in the scatterplot in the bottom panel (see also Table 3). The $^7Be/^{210}Pb$ ratio plotted in the top panel emphasizes those periods when the concentrations of these two tracers of submicron aerosols are not so tightly linked.
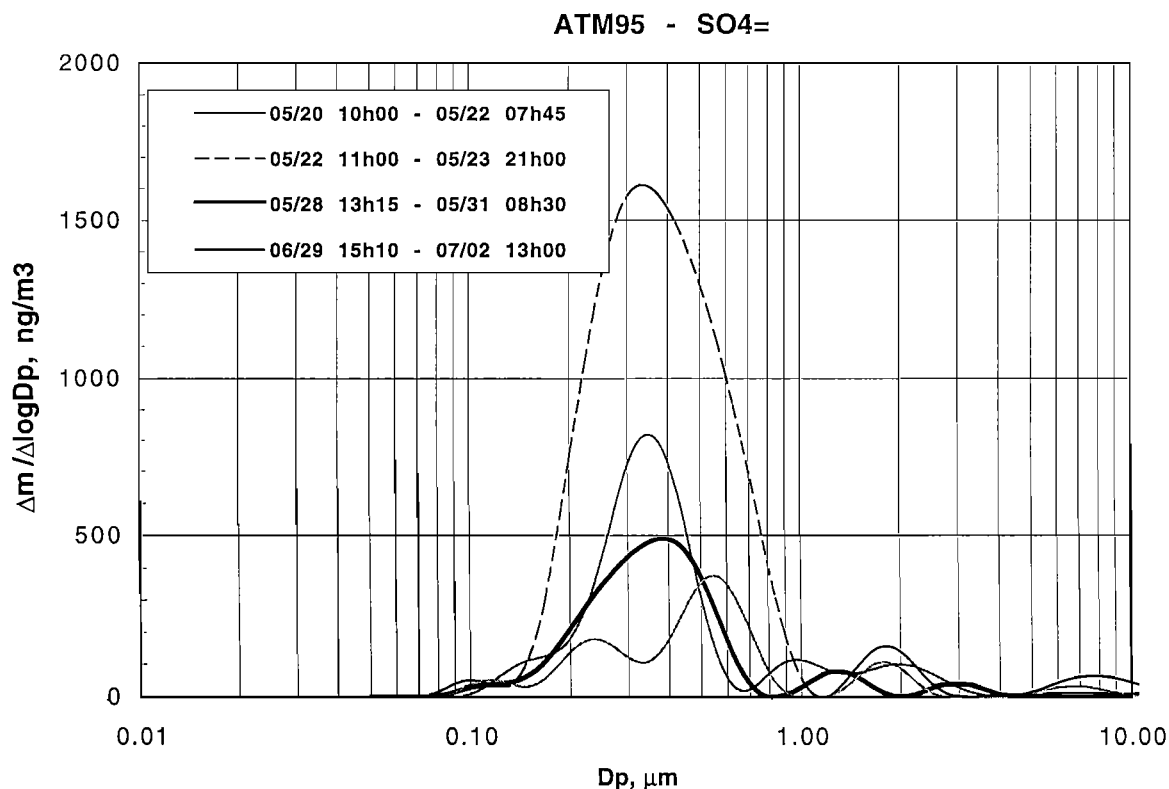
Figure 3. Smoothed size distribution for $SO_4^=$ measured at Summit during ATM95 (prepared from data discussed by *Maenhaut et al.* [1996]).

calculated for some specific episodes: they point to areas in northern Canada as potential sources for biomass burning plumes advected over Summit (Hudson Bay lowlands [*Dibb et al.*, 1996] and Mackenzie area (J.-L. Jaffrezo, unpublished data, 1993) for episodes in early August 1994 and late June 1993, respectively (Figure 4)). *Kahl et al.* [this issue] present the results of a climatology of trajectories arriving at Summit and tentatively link it with changes in aerosol chemistry observed at the surface of the ice sheet. Recent analyses of stable Pb isotopes in the aerosol at Summit indicate a change in the source regions that parallels the decrease of the concentrations observed from spring into summer (K. J. R. Rosman et al., unpublished data, 1993-1995), complementing similar observations for fresh snow in South Greenland (K. J. R. Rosman et al., Seasonal variations in the origin of lead in fresh and aged snow from Dye 3 in Greenland, submitted to *Earth and Planetary Science Letters*, 1996).

Snow Composition and Relationship to Atmospheric Chemistry

A large number of experiments have been performed over the years at Summit to characterize deposition of chemical species with fresh snow. A fundamental consideration is determination of any spatial and temporal patterns in deposition of snow itself. Long (up to 7 years) records of accumulation on several stake networks show that the variability in the local deposition is essentially the same at different scales: 10, 100, and 1000 m [*Kuhns*, 1997]. Also, year-round automatic measurements tend to indicate that accumulation is relatively low in winter, with a disproportionate amount of snow accumulation in the spring period [*Kuhns*, 1997; C. R. Stearns, unpublished data, 1993-

1996], in line with results from independent chemical studies (see below).

In the surface layer of snow, replicate samples separated by at most a few tens of centimeters typically show 10-30% variability in concentration of soluble ions during the summer. In general, the variability of "reversibly deposited" species (e.g., H_2O_2, Cl⁻, NO_3^-, see discussion below) is significantly less than that of aerosol-associated species (e.g., Na⁺, Ca^{2+}, Mg^{2+}; see season means in Table 4; H_2O_2 concentrations usually vary only a few percent on these spatial scales). Interestingly, the variability of snow concentrations on the centimeter scale represents a significant fraction of the variability found when samples were collected from a single layer at 92 points separated by distances ranging from 10 to 900 m (Figure 5). The fraction of overall spatial variability seen on the small scale of adjacent replicates was also found to be larger for the aerosol-associated soluble ionic species than those present mainly in the gas phase.

Concentrations of some aerosol-associated species showed variation of over 100% at a given depth in snowpits over horizontal distances of a few meters [*Dibb et al.*, 1992a]. The increased variability observed in these pits reflects sampling of different layers at the same level in the snow (i.e., in contrast to the surface snow samples where distinct stratigraphic layers are selected, any fixed depth sampling scheme can mix different events). Departures of snowpack stratigraphy from uniform, planar layers are largely due to small-scale topographic control of snow accumulation, particularly during drifting of the surface material, but such variability is probably inherent in any ice core sampling scheme that attempts to resolve subannual events. In 1995, the spatial survey described above was expanded to determine variability in the entire 1994 spring layer and the
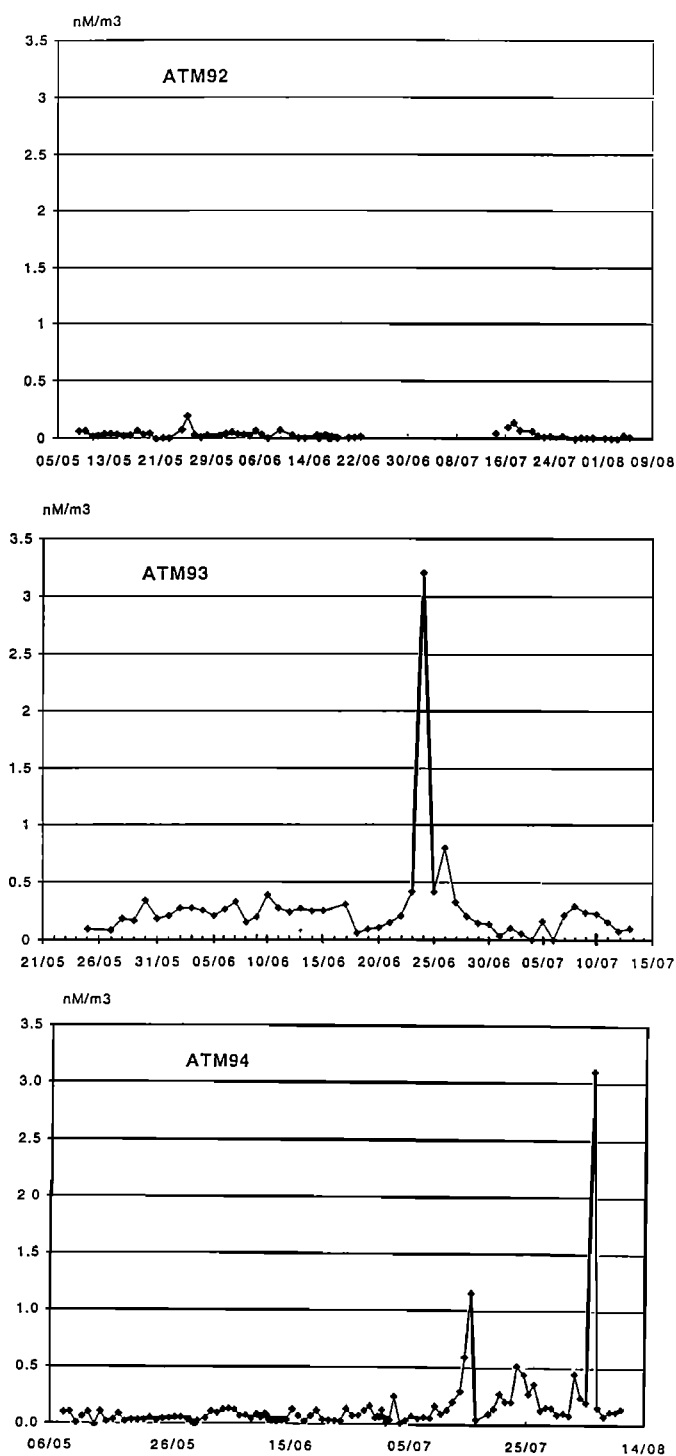
Figure 4. Time series of oxalate concentrations in the aerosol at Summit during the field seasons 1992-1994. Large oxalate concentrations are unambiguous tracers of biomass burning plumes advected over Summit.

annual (summer 1994 to summer 1995) accumulation in order to examine whether temporal averaging more similar to the schemes commonly applied in core sampling diminishes the effect of spatial heterogeneity seen in single events. Detailed analysis of these data is in progress, but it appears that the mean concentrations in this particular annual layer vary less than was found for the three individual events sampled on the same grid in

summer, 1994, though the apparent temporal smoothing does not reduce the large-scale spatial variability below the level defined by adjacent replicates over the three summer seasons (Table 4) [*Hart*, 1997].

Ice cores represent the premier archive of whole air samples preserving past concentrations of various radiatively active gases [e.g., *Pearman et al.*, 1986; *Chappelaz et al.*, 1990; *Etheridge et al.*, 1996]. These samples are trapped as bubbles within the ice as the pores in the firn become closed off. In general, the processes that may modify the composition of air during burial are well understood [e.g., *Battle and Sowers*, 1996; *Butler et al.*, 1996], though there are some open questions about the long-term integrity of CO_2 storage in Greenland ice from glacial times [*Delmas*, 1993; *Smith et al.*, this issue]. There is also a suite of reactive gaseous species that are central to understanding tropospheric chemistry and are preserved in snow and ice (i.e., H_2O_2, $HCHO$, HNO_3, HF, HCl, CH_3COOH, $HCOOH$). These reactive gases appear to be incorporated in or on the ice crystals rather than being trapped in bubbles. In contrast to nonvolatile aerosol particles, these species can be reemitted into the gas phase and return to the atmosphere from the snow. The potential for two-way exchange between air and snow adds complexity to the overall transfer function, and model development has focused on two classes of atmospheric constituents: those that stick to the snow once they encounter the surface (irreversibly deposited species) and those that can go back and forth (reversibly deposited species) [*Bales et al.*, 1992]. This division is merely a convenient starting point, since even a dust particle (which would be considered irreversibly deposited in this scheme) can be reentrained from the surface or released from a blowing snow crystal that sublimates completely [*Pomeroy and Jones*, 1996], and there are large differences in volatility of the reactive species of interest in snow and ice chemistry investigations.

With increasing degree of reversibility the concentrations of gaseous species seem to be determined by postdepositional adjustment of the upper snow layer to the air ventilated through the firn [*Neftel et al.*, 1995; *Neftel*, 1996; *Bales and Choi*, 1996]. In the case of H_2O_2, which is considered the archetypal "reversibly deposited" species, the timescale to reach equilibrium appears to be at least weeks as the snow responds to seasonal patterns of temperature, water accumulation, and photochemically controlled variations in the atmospheric concentration of H_2O_2. In general, H_2O_2 concentrations in the air a few meters above the snow at Summit during the summer (1-2 parts per billion by volume (ppbv)) are too high to be explained by homogeneous photochemistry, yet too low to be in equilibrium with surface snow [*Conklin et al.*, 1993; *Neftel et al.*, 1995; *Bales et al.*, 1995a, b]. Out-gassing to bring the snow into equilibrium with low atmospheric concentrations could cause increased airborne concentrations. However, measurements in 1993 did not reveal the gradients expected if rapid outgassing from the snow accounts for the elevated concentrations observed. *Bales et al.* [1995a, b] suggested that reequilbration between air and snow must continue into fall and winter even after burial, with grain-scale processes dominating the kinetics of equilibration at Summit. On the other hand, sampling during 1994 and 1995 frequently showed H_2O_2 gradients in the bottom 3 m of the atmosphere over the snow surface, with the apparent direction of flux changing from out of the snow when concentrations in air were observed to increase (most mornings) to downward in the afternoon and evening when concentrations decrease to the nighttime minima (J. McConnell, personal communication June, 1995). Calculation of the fluxes implied

Table 4. Coefficients of Variation (Standard Deviation/Mean) in the Concentrations of Soluble Ionic Species in Snow at Summit, Greenland

	Na+	K+	Mg^{2+}	Ca^{2+}	NH$_4$+	SO$_4$=	Cl-	NO$_3$-
1992 Season[a]	0.36	0.32	0.26	0.28	0.19	0.10	0.13	0.08
1993 Season[a]	0.30	0.30	0.18	0.22	0.13	0.10	0.11	0.09
1994 Season[a]	0.20	0.20	0.14	0.16	0.12	0.08	0.09	0.07
May 23, 1994 survey[b,c]	0.38	0.49	0.30	0.21	0.27	0.26	0.13	0.17
June 23, 1994 survey[b,d]	0.37	0.62	0.21	0.22	0.21	0.17	0.27	0.27
June 28, 1994 survey[b,e]	0.53	0.44	0.46	0.65	0.20	0.14	0.16	0.17
Annual Cores, 1995[b,f]	0.34	0.31	0.23	0.29	0.22	0.25	0.25	0.13

[a] The season means are the average coefficent of variation for replicate samples of surface snow collected within a few tens of centimeters at each sampling (similar to the replicates in Figure 5), while the 1994 surveys and the 1995 cores involved sampling at 92 points in a 600 x 700 m^2 grid.A sample set consisted of 3three-six adjacent replicates, each approximately 100 cm^2. Each sample set was collected from the single dominant, surface layer present at the time of sampling. At least one, but up to seven, sample sets were collected per day. A total of 86, 87, and 196 sample sets were collected in the 1992, 1993, and 1994 seasons, respectively.

[b] from *Hart* [1997]

[c] Sampled after wind storm.

[d] Layer aged 6 days in fine weather.

[e] Fresh snow fall.

[f] Cores were collected in precleaned tubes inserted from the surface down to a plate inserted into the walls of shallow pits in the middle of the prominent 1994 hoar layer. Insofar as the hoar layer represents a unique time horizon, all cores contained snow that accumulated over the same time period (within 2 weeks, as cores were collected in two groups in June 1995).

by these gradients and assessment of their potential impact on concentrations of H$_2$O$_2$ in near-surface air are in progress, but it appears that some portion of the postdeposition air-snow exchange of H$_2$O$_2$ may be quite rapid.

Nitrate is the dominant ion in summer snow at Summit. This is reflected in pit and core studies, but NO$_3$- concentrations in surface snow during summer are generally much higher than those in "summer" layers of the snowpack, suggesting some post-deposition loss process [*Dibb et al.*, 1994; *De Angelis and Legrand*, 1995; J.-L. Jaffrezo, unpublished data, 1989-1996]. The summer surface snow concentrations appear too high to be readily explained by the low atmospheric concentrations of HNO$_3$ and aerosol-associated NO$_3$- that are observed during this season. (Total inorganic nitrate concentrations in the atmosphere at Summit rarely exceed 100 parts per trillion by volume (pptv) and are usually nearer 10 pptv [*Dibb et al.*, 1994, submitted manuscript, 1997; *Silvente and Legrand*, 1995].) However, gas phase concentrations of total reactive nitrogen (NO$_y$) and carboxylic acids (CH$_3$COOH and HCOOH) are surprisingly high, with NO$_y$ usually near and above 1 ppbv and both carboxylics consistently present in concentrations greater than 500 pptv [*Dibb et al.*, 1994, submitted manuscript, 1997; *Leopold*, 1995; *Munger et al.*, 1995]. The ratio HNO$_3$/NO$_y$ rarely exceeds 1%, a very unusual finding for remote atmospheric sampling. Limited measurements of ambient NO at Summit indicate that NO$_x$/NO$_y$ is also very small, in line with previous measurements in other parts of the Arctic. These results suggest that NO$_3$- in snow at Summit is reflecting poorly understood tropospheric nitrogen chemistry and postdepositional air-snow reequilibration, with organic nitrates playing a key role [*Dibb et al.*, 1994, submitted manuscript, 1997; *Munger et al.*, 1995].

The 1993-1995 gas phase sampling focusing on HNO$_3$ has also provided interesting insights into the carboxylic acids. The high "background" concentrations mentioned above are poorly understood but may prove to be related to organic nitrate species. The source of spikes in HCOOH and CH$_3$COOH as high as 6

ppbv in August 1994 has been traced to biomass burning plumes advected over Summit from fires in the Hudson Bay lowland [*Dibb et al.*, 1996]. These 1994 plumes also carried unique signatures in terms of other organic acids (e.g., oxalic, glycolic,
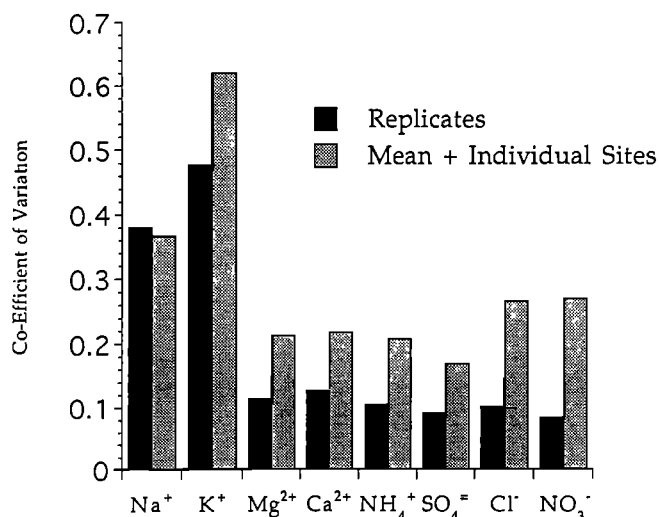

Figure 5. Spatial variation of the concentrations of soluble ionic species in surface snow at Summit. During the 1994 season, three spatial surveys were conducted on a 600 x 700 m^2 grid with 92 sampling points. For each survey, five contiguous replicate samples were collected from the discrete, dominant surface layer at every other sampling site, with a single sample collected at each of the intervening sites. The coefficient of variation (standard deviation/mean) was calculated for eight soluble ionic species from the five replicates at each of the 46 sites; then these were averaged to give the mean coefficient of variation on small spatial scales (centimeters to a few tens of centimeters) (solid black bars). The mean concentrations at these sites were merged with the 46 sites where only one sample was collected to calculate a coefficient reflecting spatial variability for samples separated by 10 - 900 m (shaded bars) (prepared from data presented by *Hart*, [1997]).

glutaric, succinic) (J.-L. Jaffrezo and H. D. Kuhns, unpublished data, 1994). Similar plumes appear to have been sampled in 1995 (J. E. Dibb, unpublished data, 1995; M. DeAngelis, personal communication, July 1995). Comparisons between the composition of the air during plume passage, surface snow, samples from pits, and the deep ice cores at Summit confirm that anomalous spikes of $HCOO^-$, NH_4^+, and dicarboxylic acids must be reflecting past forest fire activity in the source regions influencing air over Summit [*Legrand et al.*, 1992, 1995; *Whitlow et al.*, 1994; *Dibb et al.*, 1996].

During the summer season, snowfall is the dominant process delivering soluble species to the ice sheet. However, fog carries down a significant fraction (up to 40% of the total) of the summertime flux of some species, despite constituting a negligible fraction of the water budget [*Bergin et al.*, 1995b]. Contribution of dry deposition is insignificant for the summer season in recent years but might be more important in spring when aerosol loading increases or during periods of reduced snowfall [*Borys et al.*, 1992; *Bergin et al.*, 1994, 1995a, b]. An empirical model that considers all three of these processes has shown promise for reconstructing past atmospheric concentrations from snow chemistry, with agreement between estimated and measured mean airborne concentrations well within a factor of 2 for $SO_4^=$ and Ca^{2+} during the 1993 and 1994 seasons [*Bergin et al.*, 1995c]. A more elaborate cloud chemistry model has also been applied to the data sets from Summit; this exercise reinforced the fact that N chemistry is poorly understood and highlighted the need for more laboratory work to determine reactions and their rates operating in the extreme conditions (cold, dry, intense sun) over Summit in summer [*Bergin et al.*, 1996]. Laboratory results regarding the incorporation of some gaseous compounds into monocrystalline ice under controlled conditions have recently been reported [*Domine and Thibert*, 1995; *Domine et al.*, 1995, 1996].

Despite clear evidence for drifting throughout the year, the small-scale topography at Summit is very subdued compared to the Antarctic plateau where erosional bed forms (sastrugi) are dominant. The modest relief at Summit suggests a small impact of "wind-pumping" [*Cunningham and Waddington*, 1993] and might imply limited opportunities for air-snow exchange below a very shallow surface layer of the snowpack. However, the vertical permeability of the snowpack has been found to be much greater than expected and increases with depth down to at least 2 m [*Albert*, 1996; *Albert et al.*, 1996]. This may allow significant, rapid exchange of heat and air (carrying chemical species) to depths of several meters [*Albert et al.*, 1996; C. R. Stearns, unpublished data, 1987-1996]. It has also been shown, for the first time, that permeability must be treated as a tensor, since horizontal permeability can be severalfold higher than vertical permeability in thin layers including depth hoar. These findings are being incorporated into a three-dimensional model of the energy budget in polar firn, with the addition of chemical reactions planned for the near future (M. Albert, personal communication, May 1995).

Discrepancies between the seasonal variation of several chemical species in the atmosphere over Greenland and the seasonal patterns inferred from depth profiles measured in snowpits suggest that the winter season is underrepresented in the snowpack at Summit [*Dibb et al.*, 1992a; *Dibb*, 1993, 1996; Jaffrezo et al., 1994]. Nonuniform accumulation of snow through the year may create substantial biases in reconstruction of atmospheric concentrations, particularly if the phase

relationships between annual cycles in snow accumulation and airborne concentrations vary over time (i.e., small changes in the relative amount of snow falling and accumulating during a given season could have disproportionate impacts on the annual flux to the snow of those species whose airborne concentrations are at minima or maxima during that season) [*Dibb*, 1996]. Another example suggesting that depth in the snowpack is not a linear function of age is provided by the penetration of ^7Be below 60 cm in a pit sampled June 19, 1995 (Figure 6). Markers set out on July 15, 1994 were encountered at 65 cm in this pit, suggesting an age of 10.5 months at 60 cm if accumulation was linear over time. The ^7Be activity will decay to less than 2% of its initial value in 10.5 months; hence activities as high as 2 pCi kg^{-1} at 60 cm suggest that the snow is not so old as its depth indicates (or that the initial concentration was much higher that anything we observed in the summer of 1994).

An alternative explanation for deep penetration of ^7Be would be aerosol deposition at some depth below the surface in the snowpack, which could introduce an age offset between a given layer of snow and the chemical impurities it contains [*Dibb*, 1993]. Wind pumping through the permeable upper layers of the snowpack might introduce aerosols at depth, with the possibility that a lower permeability layer would preferentially collect the airborne material. However, experiments at South Pole indicate that the firn is a highly efficient filter and appears to trap even submicron aerosols in the first few millimeters to centimeters [*Harder et al.*, 1996].

Foci of Ongoing Research

Despite the progress that has been made on many aspects of air/snow exchange at Summit, some of the important questions we began with remain open, and new ones have been revealed.
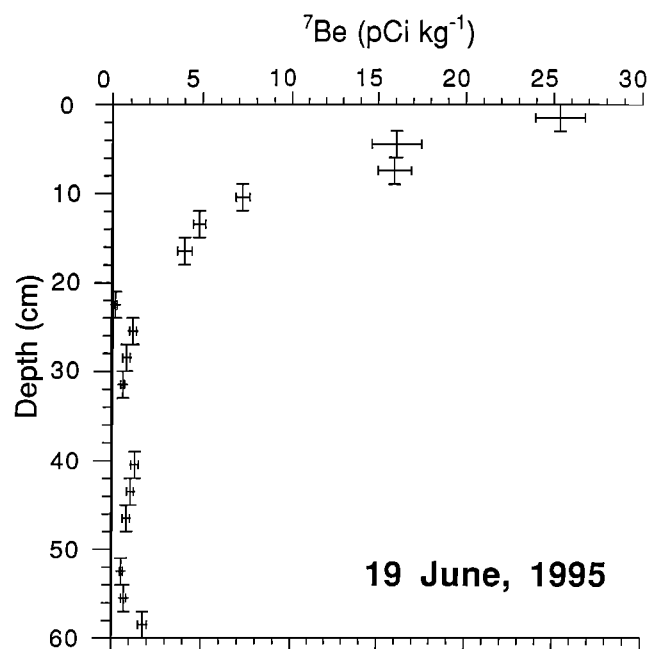

Figure 6. Depth profile of ^7Be in the snowpack at Summit on June 19, 1995. A marker set out on July 15, 1994, was at a depth of 65 cm in this pit. One would not expect to detect ^7Be at 60 cm if the snow at this depth was deposited nearly 1 year previous.

Uncertainties about the air to snow transfer function have prevented quantitative interpretation of NO_3^- profiles in terms of reactive N chemistry in the atmosphere [*Wolff*, 1995]. It has long been hypothesized that HNO_3 is the source of most NO_3^- in polar firn, yet it is now clear that HNO_3 concentrations are quite low just above the ice sheet. Apparent post depositional changes in NO_3^- concentrations further cloud the issue. Measurements of NO_y concentrations and fluxes along with concentrations and gradients of HNO_3 have shown that HNO_3 is a very small fraction of a surprisingly large pool of reactive nitrogen and that some fraction of this pool is fluxing into and out of the snow, with flux direction changing on timescales of a few hours. In 1995, HNO_3 gradients between 1 and 8 m above the snow were measured and the implied direction of HNO_3 flux often opposed the flux of NO_y. These data suggests that HNO_3 is not the only reactive nitrogen species exchanging with surface snow at Summit, and it may not be the dominant source of NO_3^- [*Dibb et al.*, submitted manuscript, 1997]. Speculation centers on the role of one or more organic nitrate species which must account for a significant fraction of the measured NO_y. In order to understand the relationship between NO_3^- in snow and reactive N in the atmosphere, it is imperative to measure organic nitrate species including PAN and alkyl nitrates. Proposals to make such measurements at Summit are currently pending.

Examination of stratigraphic features in snowpits around Summit indicates that most of the snow is drifted by wind before burial. Beyond the obvious potential for mixing snow from different events plus importing or exporting snow, the drifting process can modify the chemical composition of the snow [e.g., *Jaffrezo et al.*, 1995; *Pomeroy and Jones*, 1996]. Our investigations of spatial variability of snow composition have suggested the potential importance of such modifications on the preserved records. Sampling techniques to collect drifting snow at several heights have been developed and tested the past several seasons at Summit. These now allow quantification of the horizontal mass flux of wind blown snow and characterization of its composition as a function of wind speed, temperature, etc. Analysis of 1995 samples is in progress and a more extensive sampling program is planned for 1996.

Two major shortcomings of the work at Summit are recognized: the exclusive focus on summer and the lack of measurements at heights greater than 20 m above the snow surface (except for the meteorological soundings up to 1 km). Logistic considerations have dictated the summer field campaigns, but efforts have been made to use autonomous systems for key measurements year-round. Moderate success has been achieved for standard meteorological variables and it appears that the streaker sampler may provide low resolution aerosol composition data through the winter [*Wahlin*, 1996]. A continuous Rn monitor was deployed for the 1995-1996 winter over period, the device was still running in spring 1996 but the winter data was lost. Two different approaches to monitoring snow accumulation have been tested, both have been prone to failure and agreement between them (when both were operating) was poor (H. Kuhns, personal communication, June 1995). Snow sampling for chemical analyses presents even greater technical challenges. Maintaining a small manned camp at Summit through at least one winter was one of the summary recommendations of the NATO Advanced Research Workshop on "Processes of Chemical Exchange between the Atmosphere and Polar Snow" and NSF OPP is supporting an experimental year-round experiment at Summit from June, 1997 through April, 1998.

Vertical profiles of key atmospheric constituents over the ice sheet appear to require an aircraft sampling platform. The best prospect would be to convince a larger airborne campaign in the North Atlantic region to include one or more flights over Summit. Discussions with investigators in NOAA's ongoing North Atlantic Region Experiment, NASA's proposed Tropospheric Arctic Photochemisty Experiment: Seasonal Transitions and Regional Impacts, and the Canadian Atmospheric Environment Service are ongoing. Unfortunately, the schedule for NARE is already quite firm, while the timelines for NASA and AES missions in this part of the world may be too far in the future to ensure that the Summit site would still be an active ground station meriting an overflight. The NASA SASS Ozone and Nitrogen Oxide Experiment in fall 1997 will coincide with the year-round deployment at Summit, but the focus on the north Atlantic flight corridor will probably keep any flights over Greenland well to the south.

Conclusions

The GISP2 and GRIP drilling programs were tremendously successful and have resulted in unparalleled records of snow and ice chemistry at the Summit of the Greenland Ice Sheet. Full use of these records requires quantification of the relationships between a given ice-core parameter and the atmospheric parameter it is a proxy for. The air/snow investigations described herein focused on improving our understanding of these relationships.

Greater effort must now be devoted to the synthesis of field and laboratory results. Conceptual and numerical models are being developed for exchange of energy and chemicals between the air and snow [e.g., *Bales and Choi*, 1996; *Albert*, 1996; *Albert et al.*, 1996; *Bergin et al.*, 1995c, 1996]. These must be tested with the data sets now in hand in order to identify whether the proper parameters have been characterized adequately, both in the field and laboratory. When it is possible to quantify the accuracy with which snow concentrations can be predicted for a given set of atmospheric conditions, the critical task of working the problem in reverse and backing out past atmospheric concentrations from ice core measurements will be at hand.

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