

## Summertime aerosol chemical components in the marine boundary layer of the Arctic Ocean

Zhouqing Xie,<sup>1,2</sup> Liguang Sun,<sup>1</sup> Joel D. Blum,<sup>3</sup> Yuying Huang,<sup>4</sup> and Wei He<sup>4</sup>

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[1] Samples of aerosols from the marine boundary layer of the Arctic Ocean were collected aboard the R/V *Xuelong* during summer on the Second Chinese Arctic Research Expedition (July–September 2003). Synchrotron radiation X-ray fluorescence (SR-XRF) was used to determine chemical compositions of aerosol particles. Multivariate analysis of the SR-XRF data resolved a number of components (factors), which, on the basis of their chemical compositions and from their affiliation with specific meteorological flow patterns, were assigned physical meanings. Five factors explaining 94.7% of the total variance were identified. Ship emissions accounted for 35.3% of the variance (factor 1 (F1)) and are loaded significantly with S, Fe, V, and Ni. The total Fe emitted from ships globally was estimated at  $8.60 \times 10^6$  kg yr<sup>-1</sup>. Heavy-metal-rich factors included 34.0% of the variance (F2 and F3) and were interpreted to be pollution carried into the Arctic Ocean by long-range transport. Anthropogenic contributions from industrial regions to the Arctic Ocean during the summer vary and depend on the source locations. Air mass backward trajectories indicate that the metals including Hg, Pb, Cu, and Zn come mainly from northern Russia. The third source controlling the chemical compositions of aerosols was sea salt (F4, 12.8%). The role of sea salt decreased from the open sea to areas near pack ice. On the basis of the factor scores of aerosol samples, we infer that chlorine volatilization from sea salt may occur, enhanced by nitrogen and sulfur contamination emitted from ships. Because the global inventories of nitrogen and sulfur for ship exhausts are large, and halogens could have important consequences in possible tropospheric ozone destruction, the role of ships in influencing halogen depression in sea salt should be further investigated. Finally, we also identified a crustal factor (F5, 12.6%) and suggest that crustal elements (e.g., Ca) contaminating sea ice may become reinjected into the atmosphere as windblown aerosols.

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### 1. Introduction

[2] Anthropogenic pollution of the Arctic troposphere is a well-documented phenomenon during the winter and spring periods of the year [Rahn, 1981, 1985; Barrie, 1986]. Numerous studies have shown that delivery of heavy metals and other contaminants from midlatitude sources to the Arctic can occur in a matter of days or weeks [Arctic Monitoring and Assessment Programme (AMAP), 1997]. In winter, meteorological conditions favor long-range transport of air masses with high concentrations of gaseous and

particulate species from the Eurasian continent to the Arctic [Talbot *et al.*, 1992]. In summer, pollutants are at a minimum compared to the wintertime, producing relatively “cleaner” air [Talbot *et al.*, 1992].

[3] In contrast to the intensively studied winter Arctic troposphere, especially the Russian sector, few data exist to describe the chemical state of the marine boundary layer during summer in the Arctic Ocean. In this study, aerosols in the marine boundary layer (MBL) in the Chuckchi Sea and Beaufort Sea were surveyed in summertime during the Second Chinese Arctic Research Expedition (July to September 2003).

[4] To achieve the abatement of aerosol pollution, it is necessary to identify sources of particulate matter pollution for which control measures may be possible. The method of source apportionment usually involves compositional analysis of aerosols. Conventional chemical methods such as neutron activation are commonly applied to measure compositions of bulk aerosol particles. Because of the complex nature of the aerosol samples and the low concentrations involved, synchrotron radiation X-ray fluorescence (SR-

<sup>1</sup>Institute of Polar Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei, China.

<sup>2</sup>Also at Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan, USA.

<sup>3</sup>Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan, USA.

<sup>4</sup>Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, China.

XRF) analysis was utilized for this study because it satisfies the requirements of being sensitive, element-specific, and accurate. SR-XRF is applicable to major, minor and trace constituents of atmospheric aerosols and is becoming an important tool in atmospheric chemistry [Cahill *et al.*, 1992; Reid *et al.*, 1994; Khodzher *et al.*, 2000; Bench *et al.*, 2002; Cahill, 2003; Yue *et al.*, 2004].

[5] In the present work, bulk aerosol samples collected in the marine boundary layer of the Arctic Ocean were analyzed by SR-XRF and their origins were identified by multivariate factor analysis. This is the first part of a study describing the summertime aerosols collected during the Second Chinese Arctic Research Expedition.

## 2. Experimental Methods

### 2.1. Sample Collection

[6] Aerosol collection was made aboard the Chinese Arctic and Antarctic Administration (CAAA) R/V *Xuelong* during the Second Chinese Arctic Research Expedition (July to September 2003). The cruise has been described in detail elsewhere [Zhang, 2004].

[7] Bulk aerosol sampling, namely total suspended particles (TSP), was conducted using a high-volume bulk aerosol sampler (Tianhong Instruments, Wuhan, China) and collected on 20–25 cm<sup>2</sup> Whatman 41 cellulose filters at a flow rate of 1.05 m<sup>3</sup> min<sup>-1</sup> [Xie *et al.*, 2002]. The sampler was installed in the foredeck about 20 meters above sea level. A wind direction controller was not used to limit sampling because prevailing winds flowed off the bow during most of the aerosol sampling period and therefore sampling would not have been possible. Continuous sampling periods lasted from 1 to 2 days, depending on the weather. All filter samples were retrieved from the sampler with strict contamination control procedures as outlined by Gao *et al.* [1996]. They were sealed in clean plastic bags and kept at 4°C until laboratory analysis. A total of 49 samples and 2 blanks were collected. Nineteen of the total samples were collected between 37°N and 65°N latitude on the cruise track to and from the Arctic ocean. Thirty samples were collected in the Arctic Ocean. The spatial distributions for half of the 30 samples were nearly overlapping in the Arctic region.

[8] In this paper, a subset of 15 aerosol samples, collected in the marine boundary layer in the Chuckchi and Beaufort Seas, chosen to maximize their spatial distribution, were selected for analysis. A location map for these samples is shown in Figure 1a, and detailed sampling information is listed in Table 1.

### 2.2. Synchrotron Radiation X-ray Fluorescence Analysis

[9] The SR-XRF measurements for the particles were carried out at the X-ray fluorescence station of beam line 4W1B of the Beijing Synchrotron Radiation Facility (BSRF) [Xie *et al.*, 2003]. The electron energy and maximum ring current of the BSRF storage ring were 2.2 GeV and 110mA, respectively. Monochromatic synchrotron radiation excitation with 13.1 keV X rays was used. The beam size, restricted by vertical and horizontal slits, was about 2 × 2 mm<sup>2</sup>. Electrostatic scanning of the incident beam was utilized to scan areas of 1 × 1 cm<sup>2</sup> using a point by point

raster mode with a beam size of 2 × 2 mm<sup>2</sup>. A computer-controlled three-dimensional sample stage was used, and a Si(Li) detector under liquid nitrogen and with an energy resolution of 165 eV (5.9 keV), was placed at 90° to the incident-beam direction. A schematic diagram of the BSRF 4w1B XRF facility is given by Xie *et al.* [2003]. The samples were measured in air, and the distance between the samples and the detector was about 1 cm. The beam dwelt at each point on a sample for 100 s before the sample was moved to the next location. A 2048 multichannel analyzer (MCA) was used to record and analyze the XRF spectra. The continuous X-ray spectrum was used for rapid multielement detection and was favorable for qualitative analysis as described in detail in previous references [Cahill *et al.*, 1992; Reid *et al.*, 1994; Khodzher *et al.*, 2000; Bench *et al.*, 2002; Cahill, 2003; Yue *et al.*, 2004].

[10] Data reduction was performed offline using the well-accepted international XRF code AXIL [Xie *et al.*, 2003], and the peak areas for various elements, corresponding to the concentration of elements, were generated. Peak areas less than 3σ of the background noise were considered below the detection limit, and were denoted as zero. The peak areas of elements were normalized by current intensity and sampling volume, yielding the relative concentrations of elements (Table 2). This qualitative data was adequate for source apportionment using multivariate statistics but did not yield quantitative concentrations because of a lack of standard materials for this type of sample. Elements that were below the detection limit for most samples are not included in Table 2.

### 2.3. Multivariate Statistics

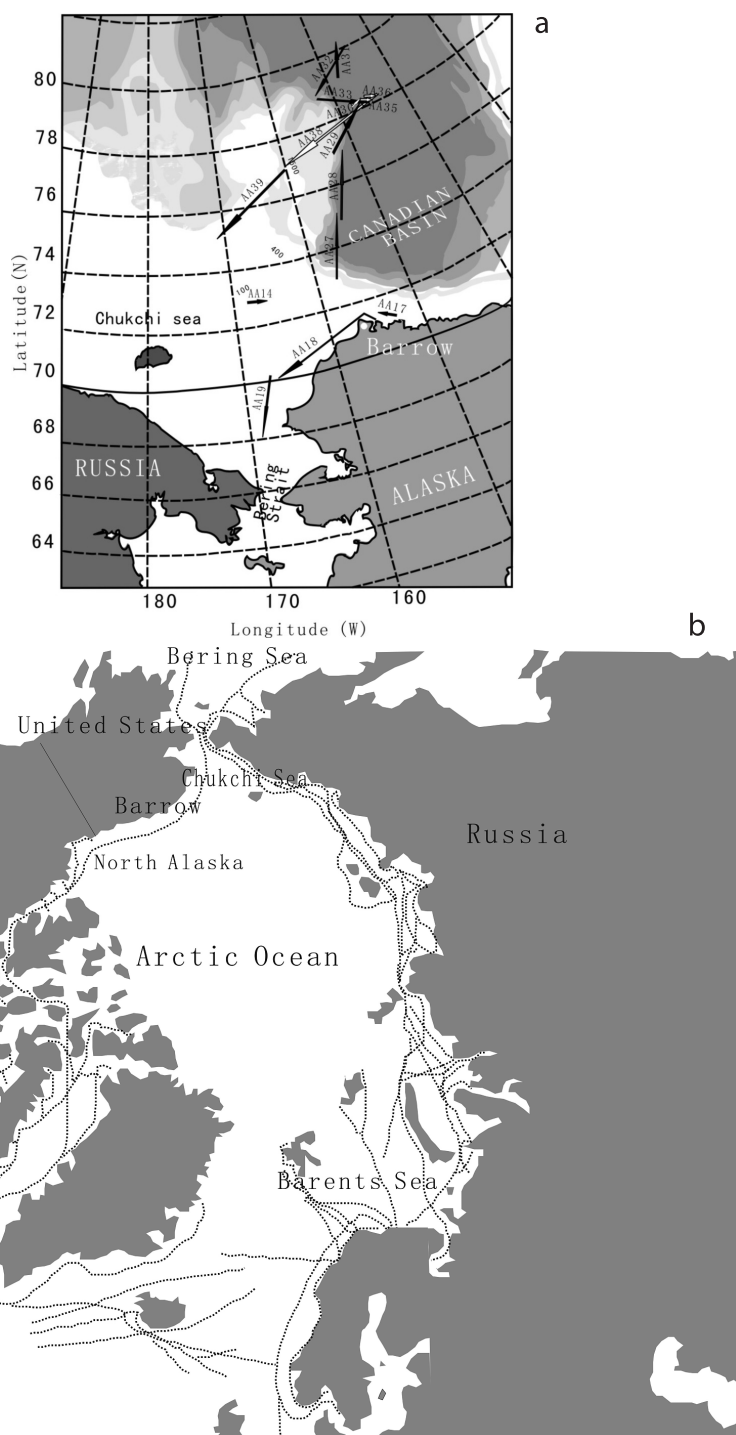
[11] Factor analysis was performed using SPSS software (version 10.0). Multivariate statistics were used to identify the origin of aerosols on the basis of their chemical composition following a widely used technique for the identification of the sources of chemical compounds [Sun *et al.*, 2000; Aiuppa *et al.*, 2003; Xie *et al.*, 2005]. The association of several geochemical parameters into a few independent variables (the so-called “factors”) as achieved by the application of factor analysis, often allows the different sources and/or processes that control the composition of aerosol to be distinguished [Gao *et al.*, 1996].

[12] Factor analysis was carried out on 15 samples for 10 selected elements with measurable concentrations in most samples, and represent the various sources of aerosols. Five factors explaining 94.7% of the variance in the data were obtained and rotated according to the orthogonal varimax method; their respective loadings are reported in Table 3 (factor loadings higher than 0.65 are shaded). The factor score indicates the relative impact from that factor on the sample composition. For example, if the sample has a high F1 score, this means that the sample was intensively impacted by the source identified as F1.

## 3. Results and Discussion

### 3.1. Ship Emissions

[13] Heavy metals in aerosols were previously studied in the Russian Arctic during summer and autumn expeditions (July–October 1991–2000) on board Russian research vessels and the German icebreaker *Polarstern* [Shevchenko



**Figure 1.** (a) Sampling locations for aerosols collected in the Arctic Ocean during the Second Chinese Arctic Research Expedition. The arrows represent the location from the beginning to the end for each sample collection. Beside the arrows, sample numbers are marked. The Arctic Ocean is partially shaded with darker shading referring to deeper water. (b) Major navigational routes in the Arctic shown as dotted lines. (Redrawn after Figure 1 of *Norwegian Maritime Directorate* [2000].)

*et al.*, 2003]. It was suggested that particles enriched in Fe, Ni, Cu, Zn, Pb, and other metals may be derived from anthropogenic sources [Shevchenko *et al.*, 2003]. In this study, Cu and Zn, Fe and Ni, and Pb were separated with factor analysis, indicating that there are three distinct sources for this group of elements.

[14] Factor 1 (F1) explains 35.3% of the variance and is significantly loaded with S, V, Fe and Ni. F1 scores for each sample were calculated and are plotted in order of increasing latitude in Figure 2. Samples including AA30, AA35, AA36 and AA31 have the highest values. Soots from diesel combustion were observed on the surfaces of these filters,

**Table 1.** Parameters for Samples of Aerosols Collected in the Marine Boundary Layer in the Arctic Ocean During the Second Chinese Arctic Research Expedition

Sample Number	Start Date, UTC	Start Time, UTC	Sampling Duration, hours	Start Latitude, °N	Start Longitude, °W	Sampling Volume, m <sup>3</sup>	Atmospheric Temperature, °C
AA-14	2 Aug. 2003	0430	23	73.48	169.11	1449	0.4
AA-17	6 Aug. 2003	0430	23	71.55	153.65	1449	1.5
AA-18	7 Aug. 2003	0430	23	71.68	155.92	1440	4.2
AA-19	8 Aug. 2003	0430	23	70.49	167.18	1448	7.2
AA-27	19 Aug. 2003	0000	26	73.37	157.56	1638	0.4
AA-28	20 Aug. 2003	0300	24	75.73	155.39	1512	1.2
AA-29	21 Aug. 2003	0400	48	77.51	152.34	3023	0.2
AA-30	23 Aug. 2003	0600	48	78.34	148.76	2235	2.2
AA-31	25 Aug. 2003	2050	24	79.51	148.04	1512	0.2
AA-32	26 Aug. 2003	2200	26	80.22	146.75	1638	-1
AA-33	28 Aug. 2003	0100	48	79.32	151.70	3024	0.1
AA-35	31 Aug. 2003	0405	48	78.68	146.04	3023	4.8
AA-36	2 Sept. 2003	0600	48	78.74	145.32	3023	1.2
AA-38	5 Sept. 2003	0800	36	78.68	144.85	2268	-1.8
AA-39	6 Sept. 2003	2100	48	77.56	160.91	3025	-0.6

implying a potential contamination by ship emissions. During the past ten years, the International Maritime Organization has made attempts to address air pollution from ships. *Corbett and Fischbeck* [1997] were the first to assess the global inventory of ship emissions on the basis of emission test data for ships and a fuel-based approach similar to that used for automobile inventories. They estimated that ship sulfur accounts for 7.7% of the sulfur emitted by all fuel combustion sources and can equal or exceed land-based sources in coastal regions [*Corbett and Koehler*, 2003, 2004]. In the Northern Hemisphere shipping may generate more SO<sub>2</sub> above some parts of the oceans than is produced by dimethyl sulfide (DMS). DMS was previously considered to be the predominant source of marine sulphate aerosols, which influence cloud reflectivity in remote areas [*Corbett et al.*, 1999; *Huebert*, 1999; *Corbett and Koehler*, 2003, 2004; *Endresen et al.*, 2003, 2004]. Because of rapidly increasing ship traffic in the Arctic Ocean, the question arises as to the degree to which ship emissions may influence this remote region.

[15] In comparison with the extensive work on the role of ship emissions in the sulfur cycle of the marine atmosphere [*Corbett and Fischbeck*, 1997; *Corbett et al.*, 1999; *Capaldo et al.*, 1999; *Corbett and Koehler*, 2003, 2004; *Endresen et al.*, 2003, 2004], there are only a few reports on

the emissions of metals from ship diesel engines [*Cooper and Gustafsson*, 2004]. In this study, trace elements like Fe, V and Ni were observed to be controlled by diesel emissions from ships. This finding is in agreement with previous reports on the characteristics of residual fuel, which is burned in marine diesel engines [*Cooper and Gustafsson*, 2004] and has high contents of trace metals including Fe, V and Ni [*Cooper and Gustafsson*, 2004].

[16] For heavy metals, fuel analysis data normally includes only the metals Pb, Zn and Ni [*Gertler et al.*, 2002; *Cooper and Gustafsson*, 2004] because Fe and other metals are not required for reporting purposes. However, the importance of Fe in marine ecology and oceanography has now received substantial attention because Fe limits primary production in some parts of the ocean [*Boyd et al.*, 2000]. Fe is essential for nitrogen utilization and metabolism, chlorophyll biosynthesis, and numerous cellular respiratory functions in phytoplankton and therefore plays a critical role in the ocean “biological pump” [*Chen et al.*, 2003]. Aeolian mineral dust is presumed to be the chief source of marine iron in many areas. *Zhuang et al.* [1992] reported that Fe (II) contributed 56 ± 32% of the total iron in marine aerosol samples collected over the central North Pacific and 49 ± 15% at Barbados. To date, the role of ship emissions on Fe in the marine boundary layer has not received much

**Table 2.** Relative Concentrations of Elements, Represented by the SR-XRF Peak Areas Normalized by Current Intensity and Sampling Volume

Element	S	Cl	Ca	V	Fe (×1000)	Ni (×1000)	Cu	Zn	Hg	Pb (×1000)
AA14	0.0	15.3	245	6.9	0.600	2.030	6.2	26.2	11.8	8.31
AA17	0.0	2025	558	31.9	1.230	0.220	19.9	138	224	1.40
AA18	0.0	1095	413	0.0	0.250	0.020	373	331	0.0	7.65
AA19	12.6	41.7	214	12.1	0.290	0.250	8.3	8.8	410	1.49
AA27	0.0	0.0	101	0.0	0.520	0.020	7.8	62.2	98.4	1.02
AA28	0.0	8.0	157	0.0	0.780	0.020	52.7	0.0	0.0	1.13
AA29	8.9	33.4	162	92.7	0.290	0.230	33.3	58.6	8.1	5.85
AA30	370	14.0	123	741	0.120	0.140	19.2	248	0.0	6.40
AA31	0.0	17.6	430	159	0.650	0.400	12.3	112	183	1.33
AA32	0.0	211	193	0.0	0.380	0.020	82.3	128	0.0	6.92
AA33	2.5	222	331	208	0.600	0.280	30.6	127	5.3	3.56
AA35	369	0.0	976	2012	0.150	2.800	22.7	314	0.0	2.41
AA36	179	67.5	618	904	0.840	1.160	8.0	146	0.0	3.15
AA38	0.0	122	205	0.0	0.330	0.140	19.7	77.8	83.3	7.84
AA39	0.0	4.2	117	13.2	0.230	0.120	77.5	62.2	104	6.43

**Table 3.** Loadings for Factor Analysis of Various Elements<sup>a</sup>

	F1	F2	F3	F4	F5
S	<b>0.95</b>	-0.19	0.075	-0.17	0.066
V	<b>0.82</b>	-0.22	0.025	-0.17	0.48
Fe	<b>0.85</b>	-0.068	-0.24	0.39	0.22
Ni	<b>0.72</b>	-0.22	-0.16	-0.18	0.41
Hg	-0.14	<b>0.96</b>	-0.12	0.006	0.073
Pb	-0.25	<b>0.83</b>	-0.14	0.28	-0.26
Cu	-0.25	-0.14	<b>0.92</b>	0.17	-0.015
Zn	0.58	-0.24	<b>0.69</b>	0.21	0.22
Cl	-0.079	0.20	0.28	<b>0.91</b>	0.11
Ca	0.45	-0.036	0.11	0.25	<b>0.82</b>
Variance	35.30%	18.70%	15.30%	12.80%	12.60%

<sup>a</sup>Values of factor loading higher than 0.60 are in bold.

attention. According to *Corbett and Koehler* [2003, 2004], the annual world marine fuel (bunkers) usage is approximately  $2.89 \times 10^8$  t, or  $3.44 \times 10^{11}$  L (based upon a density of  $0.84 \text{ kg L}^{-1}$ ). Using the average Fe content of residual fuels, which is approximately 25 mg/kg [*Cooper and Gustafsson*, 2004], we estimate an annual emission rate (AER;  $\text{kg yr}^{-1}$ ) of Fe from ships of  $8.60 \times 10^6$ , (assuming that all Fe in the fuel is emitted in exhaust).

[17] Because of a lack of data on Fe emissions from other sources it is difficult to assess the significance of the AER that we have calculated. One of the few reports of Fe emissions in the literature is for Fe emissions from diesel engine vehicles in the Taiwan area, which is approximately 180 times smaller than our estimate for global Fe emissions from ships [*Wang et al.*, 2003]. It should be noted that the emission factor estimated here for Fe is highly uncertain, and therefore this estimate should be considered only as preliminary. More detailed measurement of metals emitted from ships should be made in the future.

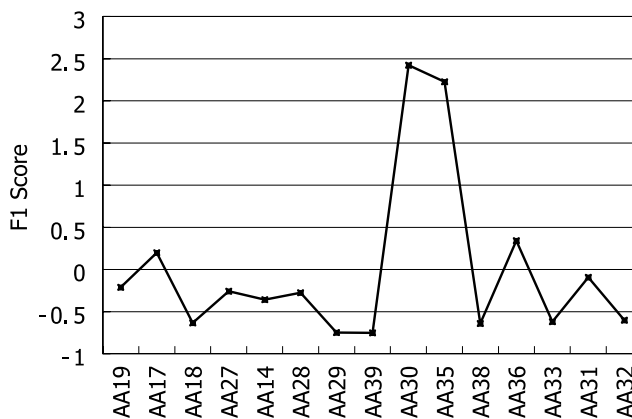
[18] In order to figure out whether the samples were contaminated by emissions from the R/V *Xuelong* or were sampling emissions from other ships, the frequency of the relative wind direction for each sampling period was calculated and is shown in a rose diagram (Figure 3) [*Xie et al.*, 2002]. In general, when the relative wind direction ranged between N-NE and N-NW of the stern of the ship (here, the direction of N refers to the wind flowing directly from the stern of the ship), it implied that a potential impact of R/V *Xuelong* emissions might occur. The relationship between the F1 score for each sample and the frequency of the relative wind direction from R/V *Xuelong* emission is showed in Figure 4. No significant correlation is observed, indicating that the ship emissions sampled cannot be attributed predominantly to the R/V *Xuelong*. Several samples received relatively high F1 scores, while the frequency of the relative wind direction indicated that these samples are likely not impacted by R/V *Xuelong* emissions during the sampling period. Therefore we suggest that F1 represents other sources of ship emissions in the Arctic Ocean. According to a report of the *Norwegian Maritime Directorate* [2000] (available at <http://uwweb.uwinnipeg.ca/index/cms-filesystem-action?file=pdfs/quest/north/shippingactivities.pdf>), shipping activities occur around almost the entire periphery of the Arctic Ocean (Figure 1b). The major constraint is sea ice, which determines the length of the shipping season. This is as short as two and a half months in some locations, but in the Russian

Arctic year-round navigation is possible and there is extensive shipping activity. A fleet of ice-strengthened freighters serviced by icebreakers carries cargo of several million tons annually to and from the ports of Murmansk and Vladivostok. In the Canadian Arctic, shipping activities are largely related to the transportation of crude oil. The preferred mode of transportation in the Beaufort Sea, Northwest Passage and Hudson Bay is by tugboat and barge. There are also deliveries of general cargo and petroleum products to eastern Arctic communities.

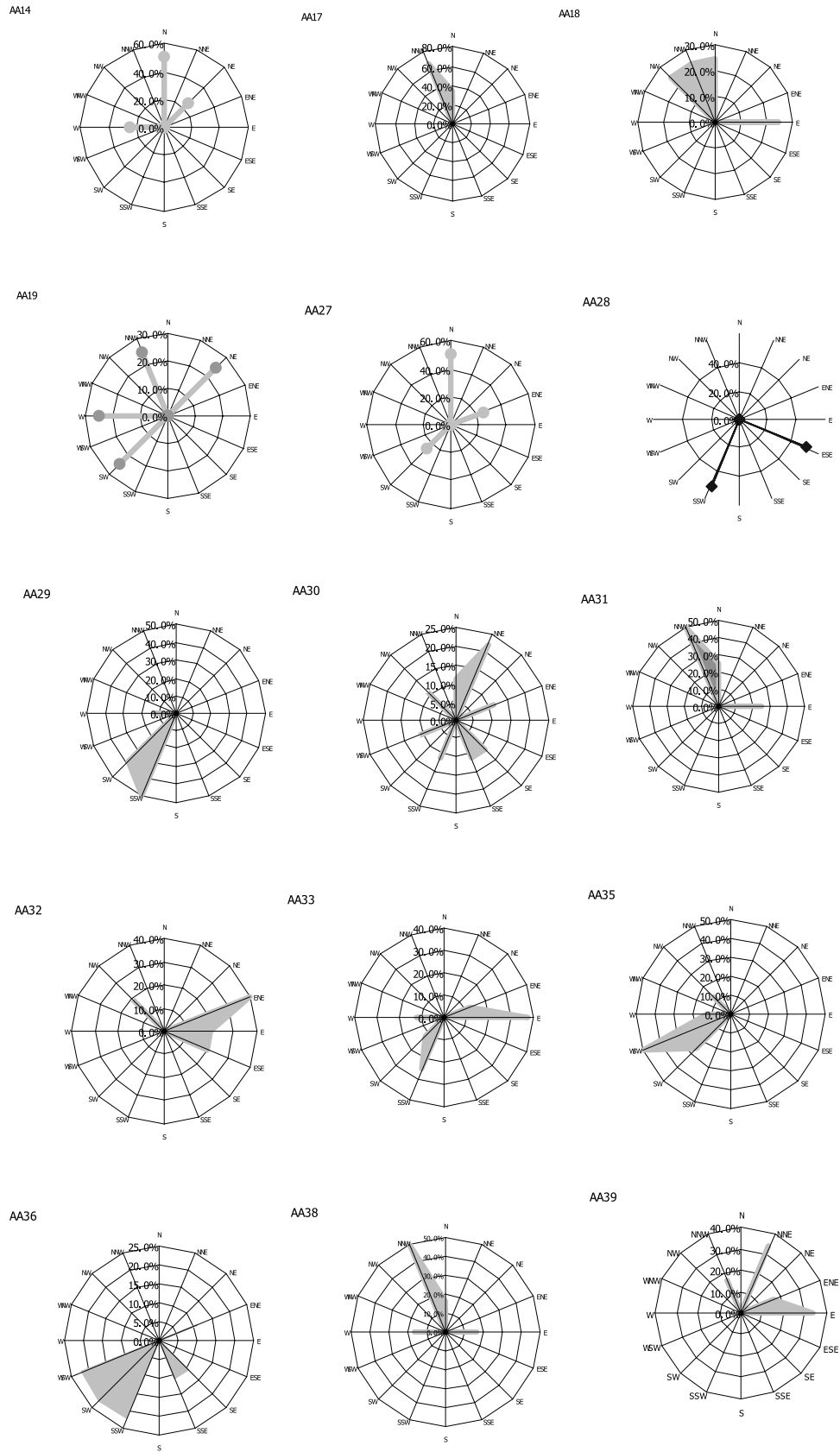
[19] Most shipping in the U.S. Arctic region is from southern Alaska or the west coast of Canada and the United States. Cargo vessels normally travel through the Bering Strait along the northern coast of Alaska to Barrow or Prudhoe Bay, Alaska; there is no tanker transport of crude oil in the U.S. Arctic. Shipping activities in the Barents Sea are expected to increase substantially during the next 10 to 20 years [*Norwegian Maritime Directorate*, 2000]. This is mainly expected to result from (1) increases in petroleum traffic from Russia to Europe and the United States, (2) increases in traffic caused by petroleum activities in the Norwegian sector of the Barents Sea, and (3) increases in cruise and speed boat traffic [*Norwegian Maritime Directorate*, 2000]. Although the main navigation routes in the Arctic are known, there is insufficient data available on ship traffic and fuel usage to accurately estimate the impact of ship emissions on the chemical compositions in the marine boundary layer in the Arctic Ocean.

### 3.2. Anthropogenic Sources

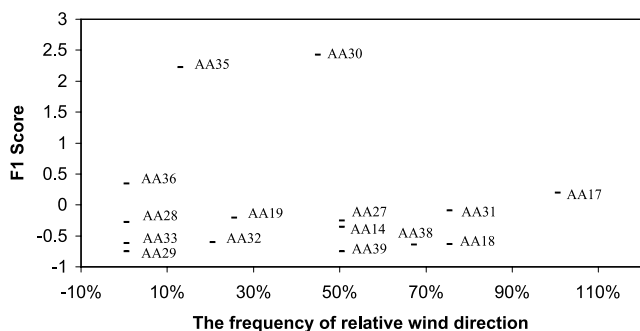
[20] Trace elements like Cu, Zn and Pb are often regarded as “anthropogenic elements,” and *Cooper and Gustafsson* [2004] suggest that they can be emitted in significant amounts from diesel engines. However, in this study, Cu, Zn and Pb had relative low loadings for F1, and thus these elements must be controlled by other processes. Table 3 shows that factor 2 (F2) was characterized by the association of Pb and Hg, accounting for 18.7% of the total variance, while factor 3 (F3) was characterized by high loadings of Cu and Zn and accounted for 15.3% of the total variance. Factor analysis results indicate that although Cu, Zn and Pb are anthropogenic elements, their source in the marine boundary layer may also vary. F2 and F3 scores for each sample were calculated and plotted in Figure 5 and



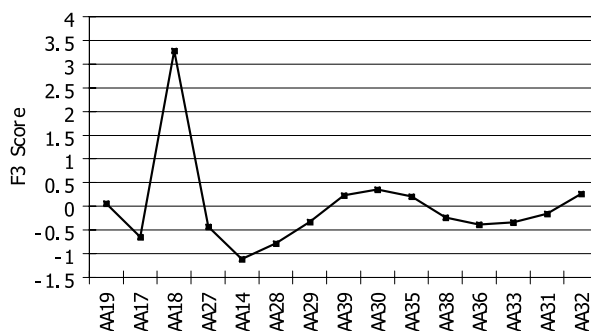
**Figure 2.** F1 scores versus aerosol samples, which are arranged from low latitude to high latitude.



**Figure 3.** Rose diagrams representing the frequencies of the relative wind direction during aerosol sampling periods. The relative direction of N refers to the wind flowing from the stern of R/V *Xuelong*.



**Figure 4.** F1 scores versus the frequency of the relative wind direction for contaminating the samples by R/V *Xuelong* emission.



**Figure 6.** F3 scores versus aerosol samples, which are arranged from low latitude to high latitude.

Figure 6, respectively. Both of these figures show that samples collected in the Beaufort Sea had lower scores, indicating the long-range transport of anthropogenic elements in this area is insignificant. Samples collected in the marine boundary layer in the Chukchi Sea had relatively high loadings. For example, the sample with the maximum F2 value was AA19 (latitude: 70.48°–68.00°N; longitude: 167.18°–168.98°W), while the F3 score peaked at AA18 (latitude: 71.68°–70.50°N; longitude: 155.92°–167.00°W).

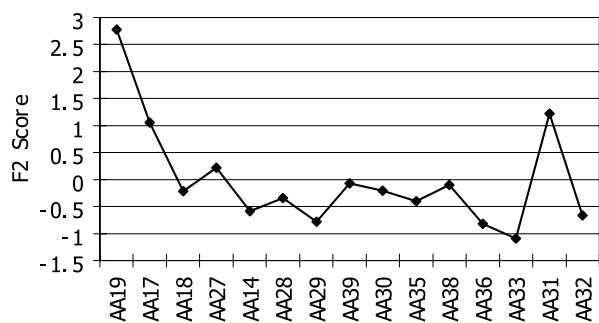
[21] We analyzed 7-day isentropic air mass back trajectories for each sample location. The trajectories were calculated for 24-hour intervals using HYSPLIT4 on the Air Resources Laboratory of the National Oceanic and Atmospheric Administration Web site (<http://www.arl.noaa.gov/ready/hysplit4.html>; R. R. Draxler and G. D. Rolph, HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory), 2003; G. D. Rolph, Real-time Environmental Applications and Display System (READY) Web site, 2003). During the sampling period of AA19, air masses flowed from Russia and northwestern Alaska (Figure 7). This suggests that the sources of Hg and Pb in the Chukchi Sea in summertime may come from both Russia and northwestern Alaska. It has been reported that the main source of air pollution in the Russian Arctic is anthropogenic, namely, the Norilsk industrial region [Shevchenko et al., 2003]. Norilsk mining and metallurgical works is one of the world’s largest plants for mining and processing of copper-nickel ore [Shevchenko et al., 2003]. This plant is one of the

main sources of pollution in the northeastern part of Russia and emits S, Se, Cu, Ni, Co, Sb, As, Pb, Zn and Hg into the atmosphere [AMAP, 1997]. In contrast, there are no major local emission sources for these elements in northwest Alaska [Douglas and Sturm, 2004]. An important source of these environmental contaminants in this area is instead arctic haze [Shaw, 1995; Douglas and Sturm, 2004]. Measurements of atmospheric concentrations at Barrow and Resolute (Arctic Canada) confirm the presence of these metals in haze in the North American sector of the Arctic [Davidson et al., 1989, 1993; Polissar et al., 1998; Xie et al., 1999]. During late winter and early spring when the Polar Front extends southward and a cold dry air mass blankets the Arctic, Eurasian industrial emissions migrate into the Arctic Basin where they accumulate. The pollutants are scavenged from the atmosphere, accumulate in the snow pack [Douglas and Sturm, 2004], and enter arctic ecosystems [Xie et al., 1999]. Thus northwest Alaska should not be a significant source of Hg and Pb to the marine boundary layer in the Chukchi Sea during summer, even though the air mass back trajectory crossed this area during the time that sample AA19 was collected. The sources of Hg and Pb in this sample are uncertain but seem more likely to have come from Russia.

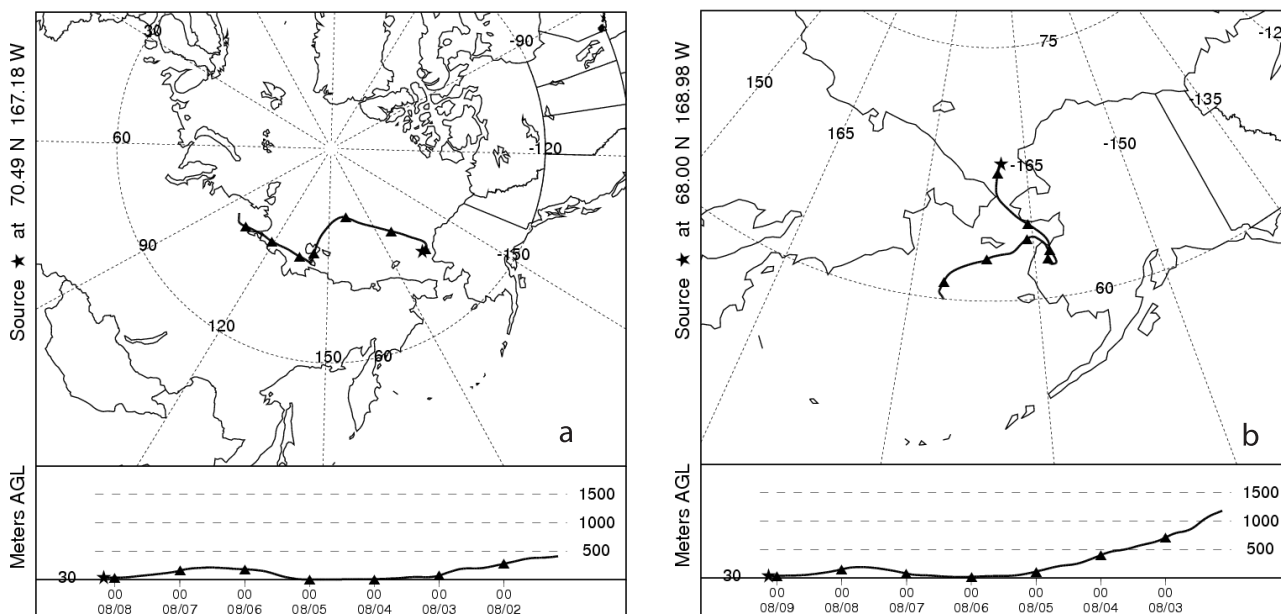
[22] The factor 3 score is the highest for sample AA18, the sampling period of which corresponds to an air mass back trajectory from Russia, in the general vicinity of the Norilsk industrial region (Figure 8). Factor 3 displays the highest loadings of Cu and Zn and is distinct from factor 2, which has heavy loadings of Hg and Pb, implying that the contributions from industrial regions to Arctic atmospheric pollution vary. The difference is controlled not only by changes in the source of emissions, but also depends on the efficiency of atmospheric pollution transport to the sampling sites.

**3.3. Sea Salt**

[23] Factor 4 (F4) explains 12.8% of the variance and is loaded significantly with Cl, suggesting a marine origin. This factor score is highest in sample AA17 (Figure 9). The synoptic situation observed from the satellite nephogram indicated a cyclone occurrence during the sampling period. Strong winds can result in a high content of sea salt in the air in the marine boundary layer. This phenomenon is often observed in the North Pacific. The marine boundary layer of the North Pacific is presumed to be charged with some of



**Figure 5.** F2 scores versus aerosol samples, which are arranged from low latitude to high latitude.



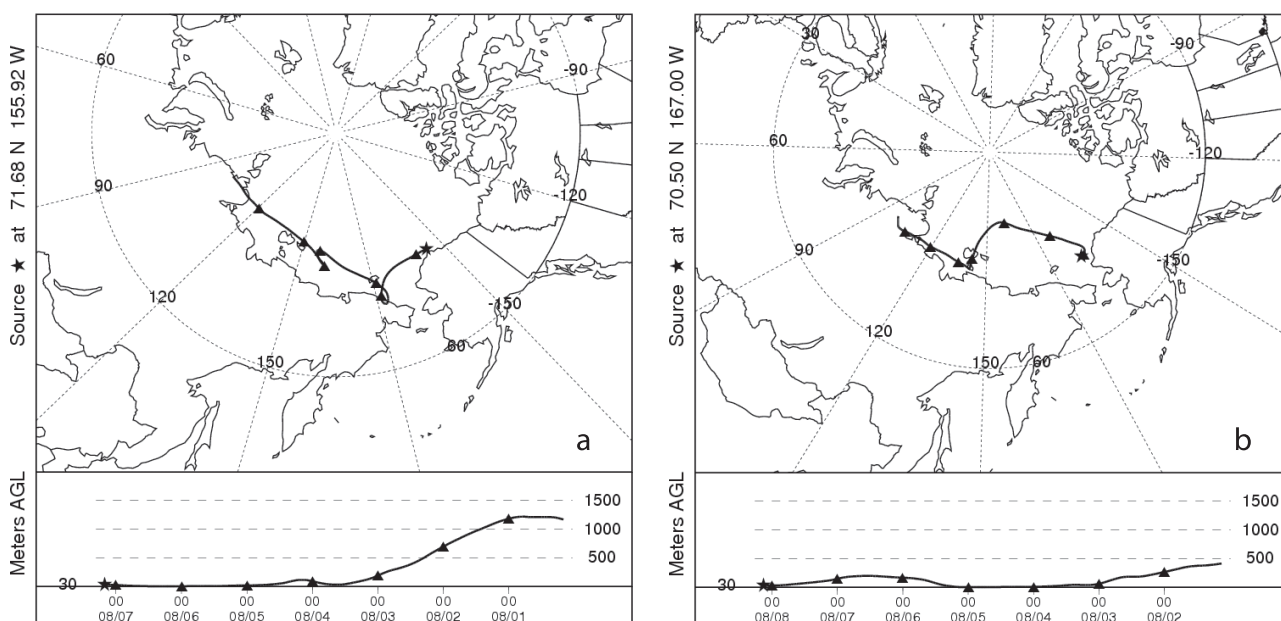
**Figure 7.** Back trajectories of air mass transport to the area of sample AA19. Trajectories have been calculated for the point at (a) the beginning of sampling and (b) the end of sampling. AGL refers to the above-ground level.

the highest concentrations of sea salt on Earth because of the windswept seas associated with the Aleutian low cyclonic system [Erickson *et al.*, 1986].

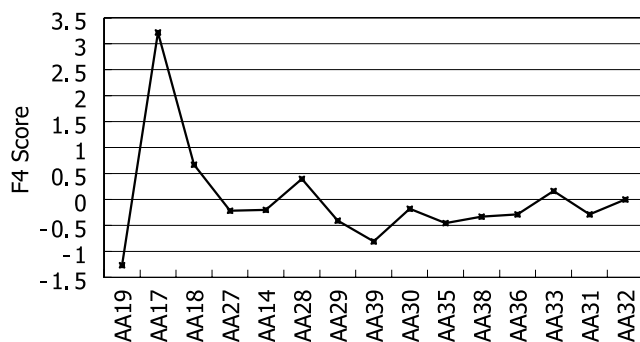
[24] In comparison with sample AA17, the other samples have relatively low F4 scores. This may be attributed to several phenomena. During the summertime, sea ice in the southern Arctic Ocean thaws and the area of pack ice usually retreats to a location at about 75°N. Samples collected to the north of this latitude were located in areas

of pack ice and thus did not have the high levels of sea salt observed in the open ocean.

[25] Shaw [1991] found that chlorine depression in marine aerosols was associated with air pollution containing strong acids. Similar halogen depressions in aerosols collected in the marine boundary have also been reported by Hitchcock *et al.* [1980], McInnes *et al.* [1994], Sander and Crutzen [1996], and Ayers *et al.* [1999]. The reaction between sea salt and acidic nitrate and sulfate is expected



**Figure 8.** Back trajectories of air mass transport to the area of sample AA18. Trajectories has been calculated for the point at (a) the beginning of sampling and (b) the end of sampling.



**Figure 9.** F4 scores versus aerosol samples, which are arranged from low latitude to high latitude.

to liberate HCl gas to the atmosphere leaving the particles enriched in nitrate and non-sea-salt sulfate, and thus depleted in chloride following the reactions:

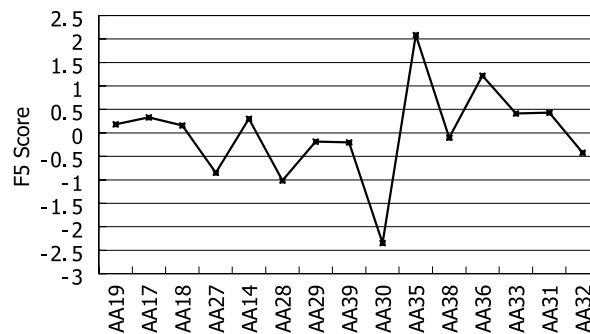


where g and p refer to gas and particle, respectively [Eriksson, 1959]. Correlations of gaseous HCl and sea-salt chloride depletion were obtained from bulk filter collections [Keene *et al.*, 1990] implying that sea-salt particles were the major source of volatile inorganic chlorine.

[26] Corbett *et al.* [1999] and Corbett and Koehler [2003, 2004] estimated the global inventory of ship emissions, using emission test data for ships and a fuel-based approach similar to that used for automobile inventories. They estimated global annual  $\text{NO}_x$  and  $\text{SO}_2$  emissions from ships to be 6.87 Tg (or  $10^{12}$ g) as N and 6.49 Tg as S. Nitrogen emissions from ships are shown to account for more than 31% of all nitrogen emissions from fossil fuel combustion, and sulfur emissions exceed 7.7% of sulfur emitted by all fuel combustion sources including coal. Ship sulfur emissions correspond to about 31% of biogenic DMS emissions. In regions of the Northern Hemisphere annual sulfur emissions from ships can be of the same order of magnitude as estimates of the annual flux of DMS [Chin *et al.*, 1996]. The role of sulfur emitted by ships in the global sulfur budget and the influence that this has on the Earth's radiation budget has received some attention [Capaldo *et al.*, 1999]. However, the role of sulfur and nitrogen from ship emissions in the depression of Cl in aerosols has not been reported. Inorganic halogens emitted from the reaction of sea salt and acid could also have consequences for tropospheric ozone destruction. Moreover, changes in physiochemical characteristics of sea salt may effect cloud condensation nuclei (CCN). Measurements obtained from the Arctic [O'Dowd and Smith, 1993] under high wind speeds showed that the CCN accumulation mode could at times be dominated by sea-salt particles. We suggest that the role of ship emissions in chlorine depression in marine aerosols should be more thoroughly investigated in the future.

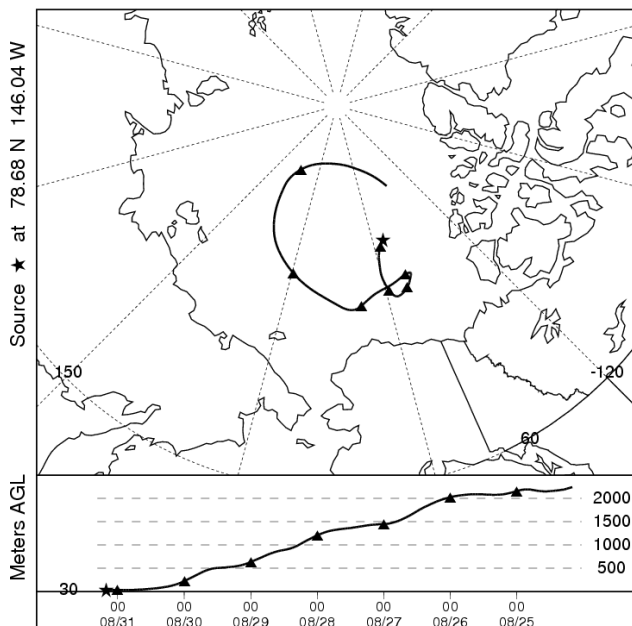
### 3.4. Crustal Elements

[27] Factor 5 (F5) was characterized by the highest loading of Ca, which explains 12.6% of the total variance.



**Figure 10.** F5 scores versus aerosol samples, which are arranged from low latitude to high latitude.

The factor 5 score for each sample was calculated and is plotted in Figure 10. Samples AA35, AA36, AA33 and AA31 had the highest F5 scores and were mostly collected while in the pack ice rather than in the open ocean. It is well known that Ca is an important crustal element. Seven day isentropic back trajectories of air mass transport were calculated to determine the source of Ca (Figure 11). Surprisingly, the trajectories showed that the relatively high levels of Ca were found in air that had not been in contact with large continental landmasses during the prior 7 days. It is tentatively suggested that the elevated levels of the crustal element Ca were the result of local windblown coarse aerosols generated from crustal materials previously deposited onto or incorporated within the ice rather than long-range transport.



**Figure 11.** Back trajectories of air mass transport to the area of sample AA35. Trajectories have been calculated for the point at the beginning of sampling. The location for the end of sampling was nearly the same region, so that trajectory is not shown.

[28] During a cruise of the R/V *Polarstern* icebreaker in July and August 1987, *Pfirman et al.* [1989] found that the ice north of 83°N was very much affected by particle-rich surface accumulations, and analyses of samples scraped from the surface indicated that they contained lithogenic (including also coal and heavy minerals) and biogenic materials. Large patches of particle-laden ice have previously been reported by many Arctic researchers [e.g., *Clark and Hanson*, 1983; *Maenhaut et al.*, 1996]. As indicated by *Reimnitz and Kempema* [1987], coarse shelf surface sediments, organic matter and river effluents can be incorporated into sea ice as a consequence of freeze-up storms and the formation of anchor ice. The latter may rise to the surface, and in the process lift materials that are attached to it. The contaminated sea ice can be transferred to the high-Arctic region by ocean currents. An alternative explanation may be that the crustal elements were deposited on the ice during Arctic haze episodes in late winter, and were then reinjected into the atmosphere as windblown aerosols. In this study, the highest level of Ca (Sample AA35) was found to occur in the region where the most intensive frequency distribution of Arctic haze was reported [*Raatz*, 1984; *Shaw*, 1995].

#### 4. Summary and Outlook

[29] Aerosols were collected from the marine boundary layer of the Arctic Ocean in the summer during the Second Chinese Arctic Research Expedition. Factor analysis results suggest that the chemical compositions of aerosols contain contributions from ship emissions, long-range transported anthropogenic emissions, sea salt, and a crustal component. Elements including S, Fe, V and Ni are emitted from ship diesel engines operated in the Arctic ocean. A preliminary estimate of total Fe emitted from ships globally is  $8.60 \times 10^6 \text{ kg yr}^{-1}$ . Because Fe plays a significant role in the ocean “biological pump” the source of Fe from ship exhausts should receive further attention. Heavy metals such as Hg, Pb, Cu and Zn may be carried into the Arctic Ocean by long-range transport. Air mass back trajectories indicate that Hg, Pb, Cu and Zn come mainly from Russia. The role of sea salt in the chemical composition of aerosols in the summer decreased from the open sea to the areas near pack ice. Because of contamination by nitrogen and sulfur emitted from ships, chlorine volatilization from sea salt may occur even in the high Arctic Ocean. Because the global inventory of nitrogen and sulfur in ship exhausts is large, and halogens could have important consequences for tropospheric ozone destruction, this role of ships in effecting halogen depression in sea salt should be further evaluated. Finally, we find evidence that the sea ice contaminated with crust elements may reinject crustal elements into the atmosphere as windblown aerosols.

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J. D. Blum, Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109, USA.

W. He and Y. Huang, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China.

L. Sun and Z. Xie, Institute of Polar Environment, School of Earth and Space Sciences, University of Science and Technology of China, Jinzai Road 96, Hefei, Anhui 230026, China. (zqxie@ustc.edu.cn)