

REVISED MANUSCRIPT 4 - SUPPLEMENTAL

INFORMATION

Variations in snow and firn chemistry along US ITASE traverses and the effect of surface glazing

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S.1 Methodology

The DI-cleaning process for vials and jars consists of a triple rinse in DI, immediately followed by an overnight soak in DI, and finally another triple rinse in DI before drying under a class-100 HEPA clean bench and capping. The DI-cleaning process for sampling equipment is identical to the aforementioned DI-cleaning process for vials with the addition of a thorough scrub with a 2% Citranox detergent solution beforehand (Citranox was not used on the sample containers or vials). The acid cleaning process consists of soaking in 10% trace metal grade HNO₃ for one week, triple-rinsed in DI, then DI-soaked for one week, triple-rinsed in DI, and finally dried under a class-100 HEPA clean bench and capped.

The bags containing surface snow samples were kept at -20°C. Each one was opened under a class-100 HEPA clean bench located in our main freezer and the snow was mounted on a plastic lathe (at this point the snow had sintered into a fairly solid block). The outermost 2-3 cm of each snow block was removed using a DI-cleaned ceramic blade. The sample was then handled using DI-cleaned plastic tongs and a further 2-3 cm was removed from each end. Each clean sample was split between two pre-cleaned 60

mL polypropylene Nalgene wide mouth jars. The first 60 mL jar, for major ion and stable isotope analysis, was DI-cleaned. The second 60 mL jar, for trace element analysis, was acid cleaned. The two sets of jars were then transferred to our clean room and allowed to melt overnight at room temperature. The major ion and stable isotope samples were poured into their respective vials for analysis. The trace element samples were each acidified to 1% with Optima double-distilled HNO₃ under a class-100 HEPA clean bench, capped, shaken, left to digest for one week, and then poured into a set of acid cleaned polypropylene vials ready for analysis. Major ion, trace element, and stable isotope lab procedures follow those in (Osterberg et al., 2006).

The majority of the firn sections were manually or electromechanically drilled, the cores subsequently being subsampled for major ion analysis on a DI-cleaned plastic core tray using a DI-cleaned plastic knife to cut the core into slices (several test cores were drilled beforehand in order to clean the drill barrel). Each subsample of core was placed inside a new Whirl-Pak plastic bag, sealed, and stored at -20°C. Prior to analysis, the Whirl-Pak bags from each firn section were left to melt (upright in a clean lab) overnight. The following morning, under a class-100 HEPA clean bench, they were poured into DI-cleaned vials ready for major ion analysis. Firn section cores for trace element analysis were melted using the University of Maine continuous melter system (Osterberg et al., 2006).

Firn sections that were not drilled were collected from snow pits excavated using DI-cleaned plastic shovels and sampled using a DI-cleaned ultra-pure-nickel (Ni 270) blade. Each firn section snow pit sample for trace element analysis was collected directly into an acid-cleaned 60 mL polypropylene Nalgene wide mouth jar and treated in the same manner as the ITASE-06/07 surface snow trace element samples (above). Each firn section snow pit sample for major ion analysis was placed inside a new Whirl-Pak plastic bag, sealed and treated as the firn section core samples (above).

S.2 Chemistry Quality Control

We ran a series of method blanks, these are a series of vials prepared and treated in precisely the same way as the sample vials, the only difference being that they contain DI water instead of a snow sample. The results from the method blanks define our method

detection limits, whereby the Method Detection Limit (MDL) for each element is equal to three times the standard deviation of that element in a series of method blanks. We used seven method blanks to calculate the MDL for our IC samples and eight for our ICP-SFMS MDL (Table S1).

The mean surface snow concentrations for each traverse year are above the mean blank concentrations and MDL for each IC ion and ICP-SFMS element (Table S1). Additionally, the MDL and mean blank concentrations for each ICP-SFMS element are similar to, and in most cases lower than, published values using similar methods and identical/comparable instruments (Osterberg et al., 2006; Knusel et al., 2003; Krachler et al., 2005; Barbante et al., 1999)

The MDL, when expressed as a percentage of the mean surface snow sample concentration for each traverse year, is below 10% for the majority of the ions/elements (Table S1). For the ITASE-02 ions the MDL is 63%, 38%, and 20% of the mean concentrations for Mg, Ca, and Na, respectively. For the ITASE-03 ions, the MDL is 33% and 17% of Ca and Mg and for ITASE-06/07 the MDL is 35%, 32%, and 25% of Ca, K, and Mg ions, respectively (Table S1).

For the ITASE-02 elements the MDL is 61% and 59% of the Al and Fe; 47%, 34%, 33%, and 33% of the Co, Li, Cr, and As; and 18%, 18%, 16%, and 13% of the Ti, U, V, and Cd, respectively. For the ITASE-03 elements the MDL is 44%, 43%, 40%, and 28% of the Co, Cr, Li, and Al; 23%, 15%, 13%, 12%, and 10% of the Fe, Ti, Cd, V, and Ba, respectively. For ITASE-06/07 elements the MDL is 36% and 26% of the Li and Co; 13%, 11%, and 10% of the V, Al, and Fe, respectively. The MDL for the remaining elements is <10% of the mean surface snow concentration (Table S1).

The Mg enrichment during the ITASE-02 and ITASE-03 traverse years is artificially high as a result of the following factors. The ITASE-06/07 surface snow samples were analyzed for all trace elements presented here during their first ICP-SFMS analysis. However, surface snow samples from the ITASE-02 and ITASE-03 traverse years were re-run on the ICP-SFMS (after sitting unfrozen for >1-year) in order to obtain Na, Mg, Li, and K data (these four elements were not measured on the ITASE-02 and ITASE-03 samples during their initial ICP-SFMS analysis). The re-run Na and K data seem to be unaffected based upon the fact that the ICP-SFMS trace element concentrations are not

higher than the original IC major ion data. Unfortunately, we do not have any IC analyses with which to compare the re-run Li data. However, the original ITASE-06/07 Li data exhibit similar concentrations and $nssEF_c$ values to the re-run ITASE-02 and ITASE-03 Li data, so we assume that the re-run Li is unaffected. The re-run ICP-SFMS Mg samples exhibit significantly higher concentrations than the IC major ion data, but the original ITASE-06/07 ICP-SFMS Mg samples do not. There are two possible explanations: either the storage vials are leaching small amounts of Mg into the sample or a significant fraction of the total Mg is present in particulate form that takes longer than one week to dissolve in 1% HNO_3 . The latter explanation is the more likely of the two.

Acknowledgements

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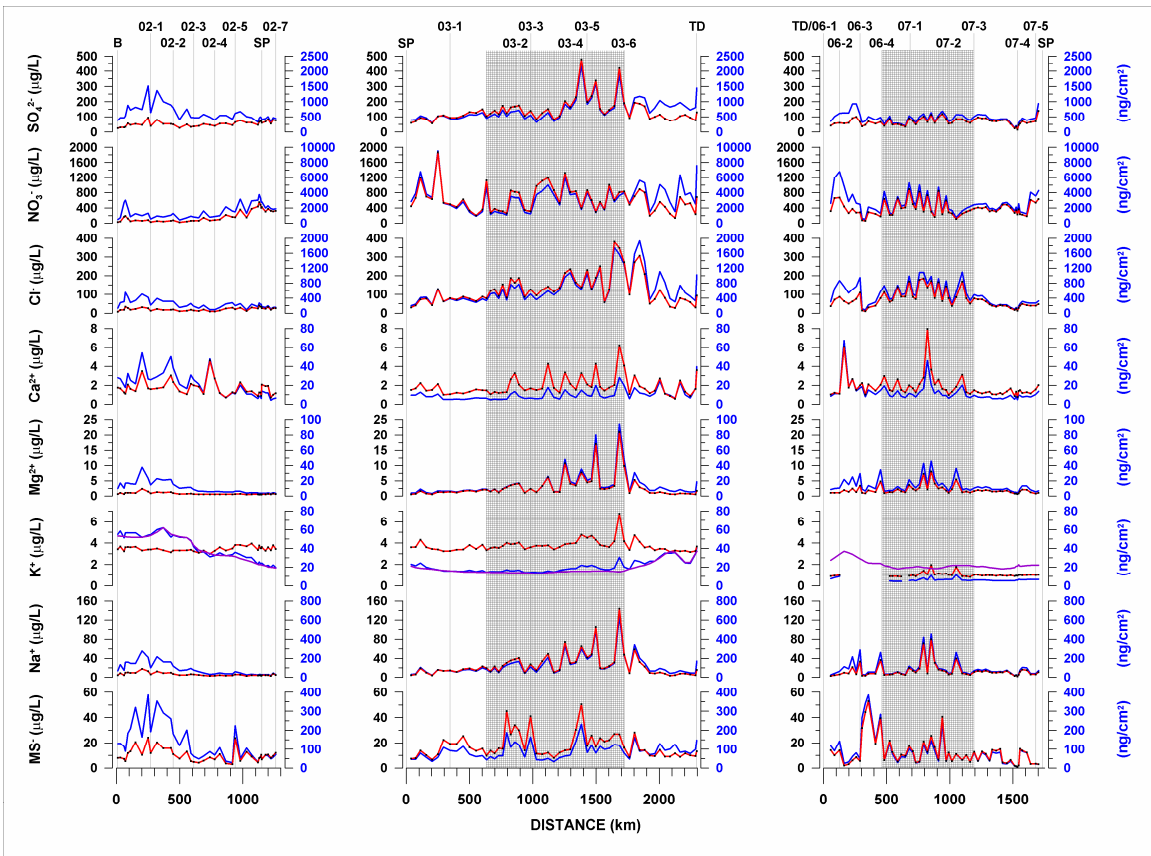


Figure S1. Same as Figure 2, except that the three y-axes for each ion are identical linear scales.

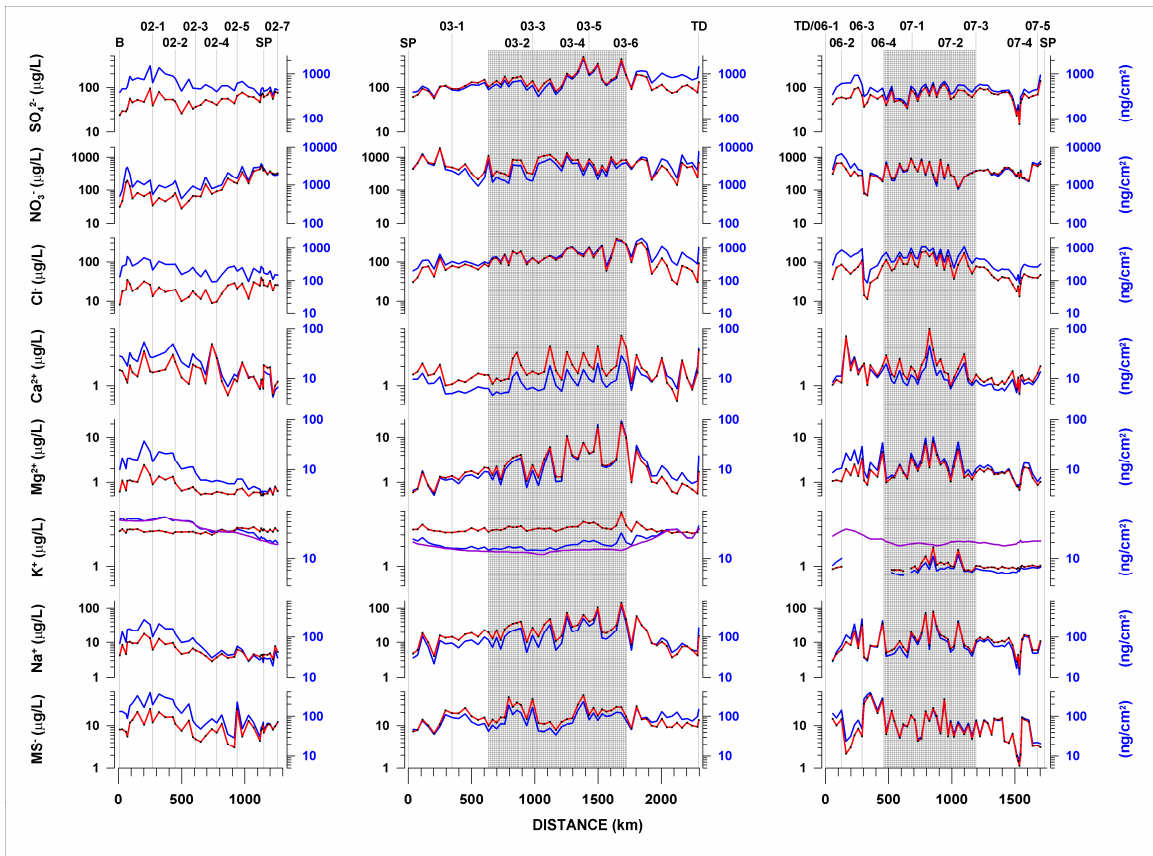


Figure S2. Same as Figure 2, except that the three y-axes for each ion are identical log scales.

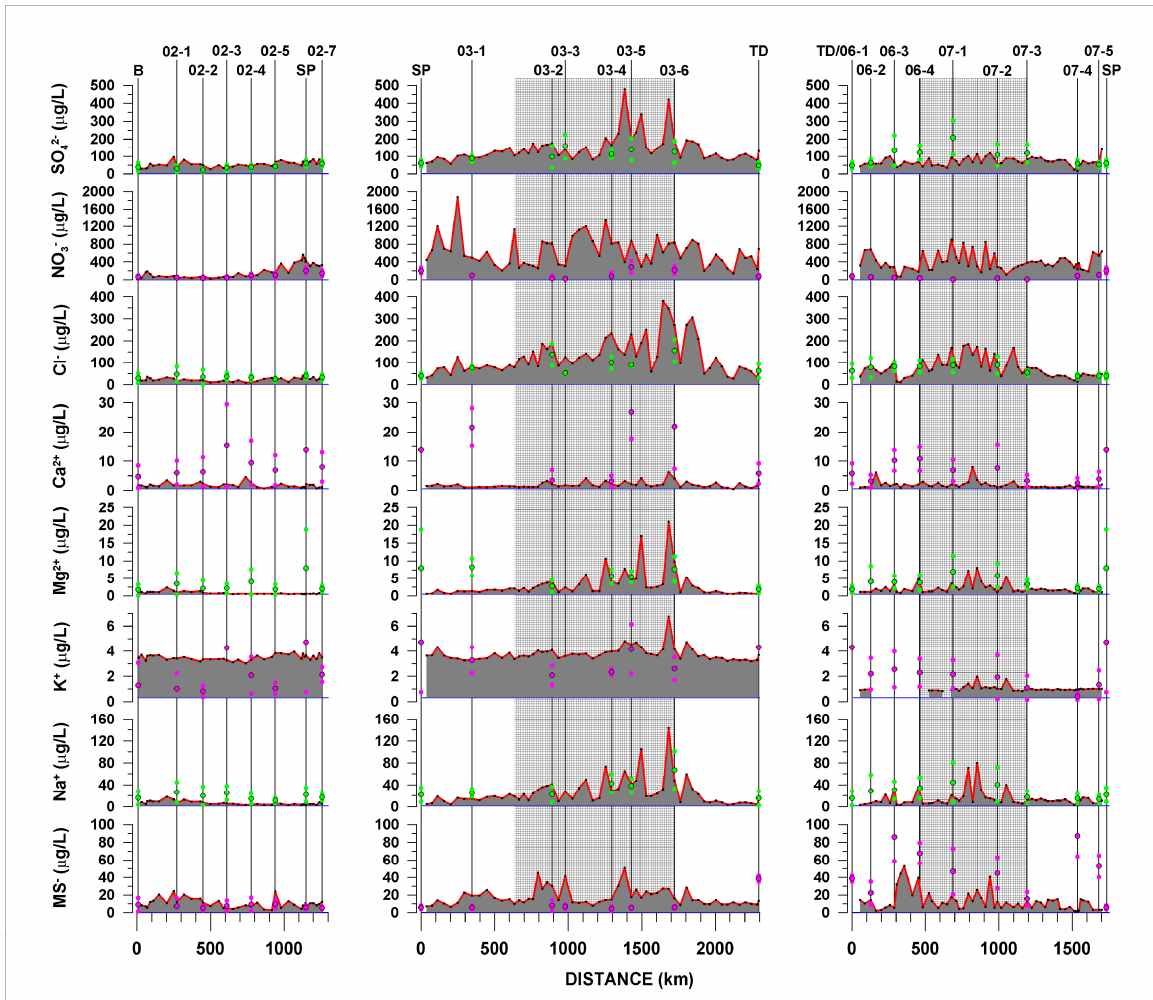


Figure S3. Same as Figure 4, except that the three y-axes for each ion are identical linear scales.

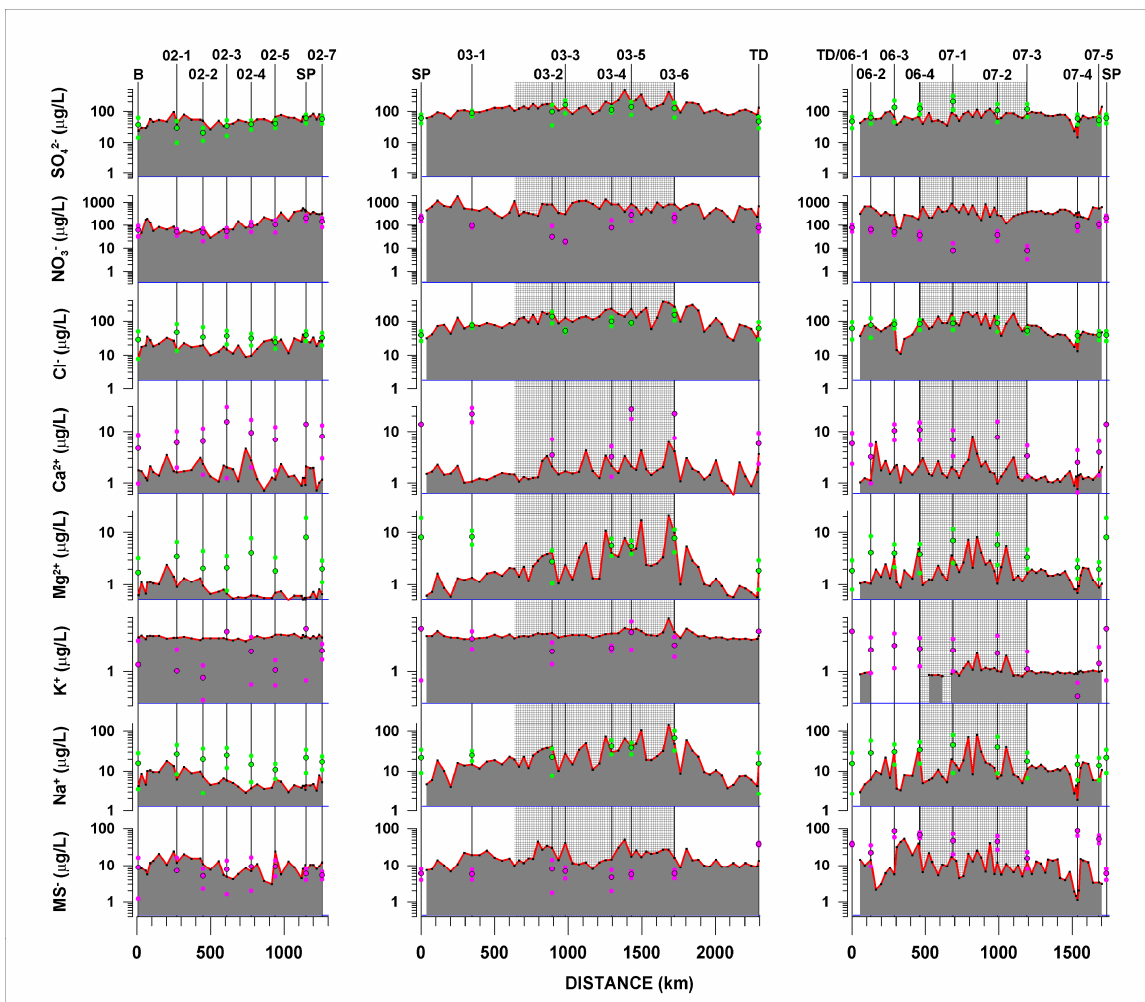


Figure S4. Same as Figure 4, except that the three y-axes for each ion are identical log scales.

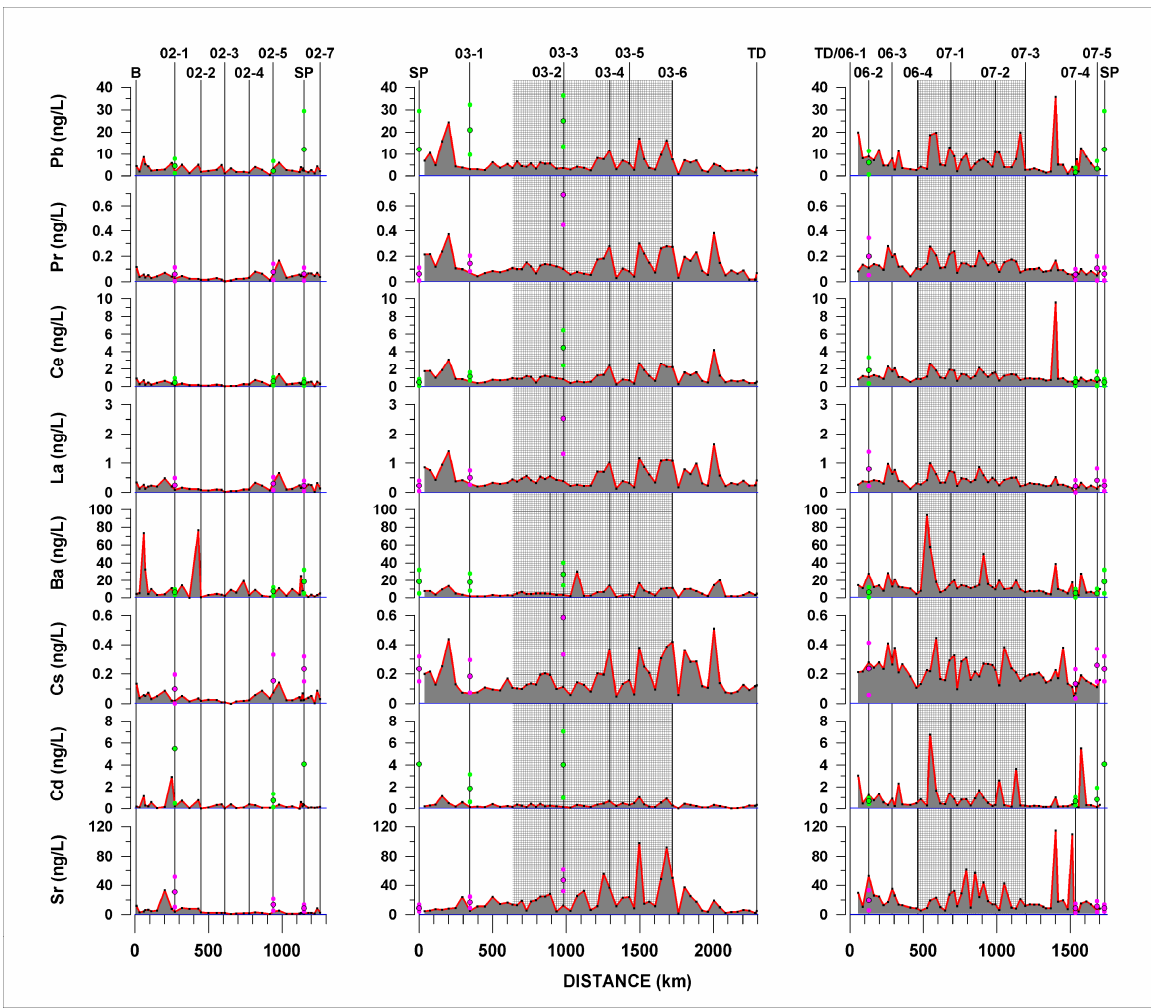


Figure S5. Same as Figure 5a, except that the three y-axes for each element are identical linear scales.

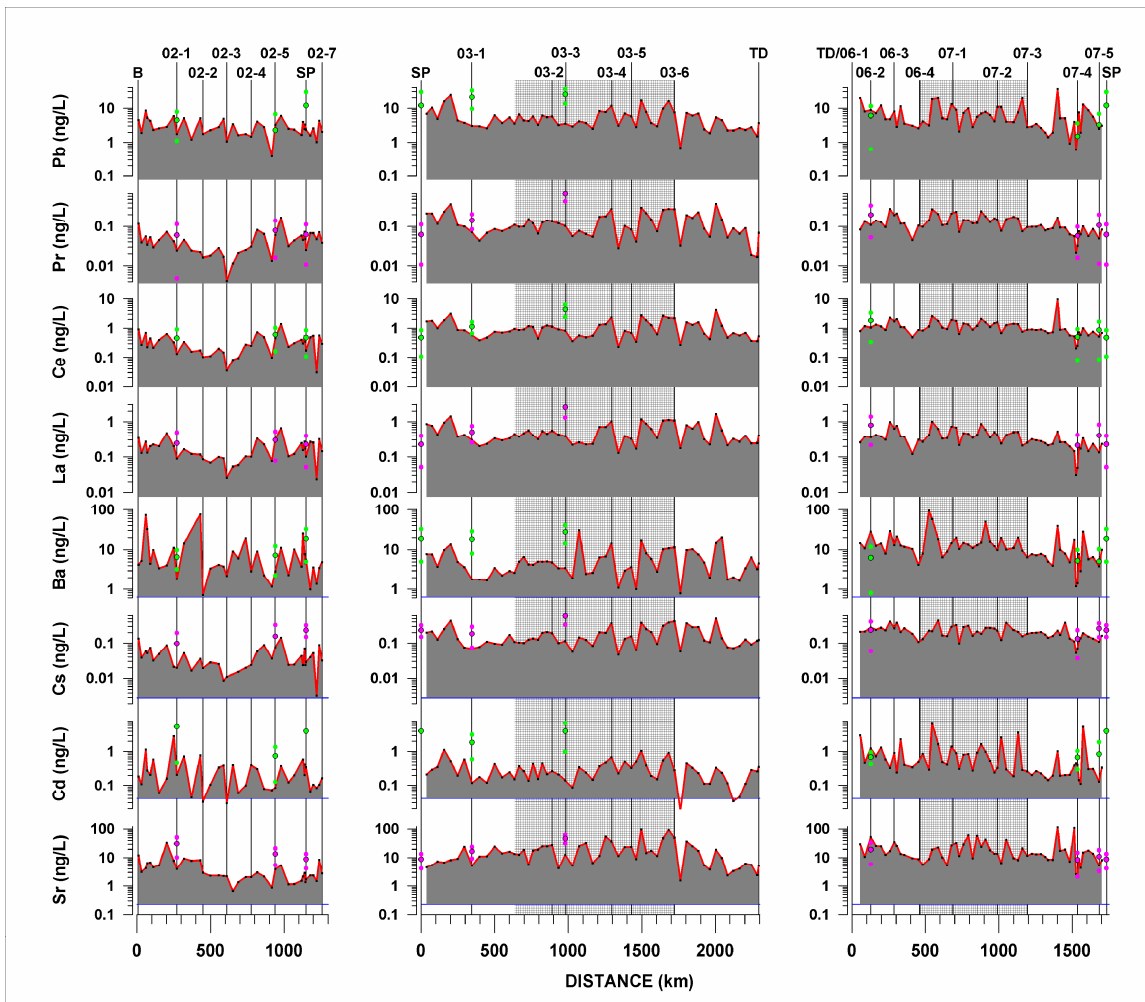


Figure S6. Same as Figure 5a, except that the three y-axes for each element are identical log scales.

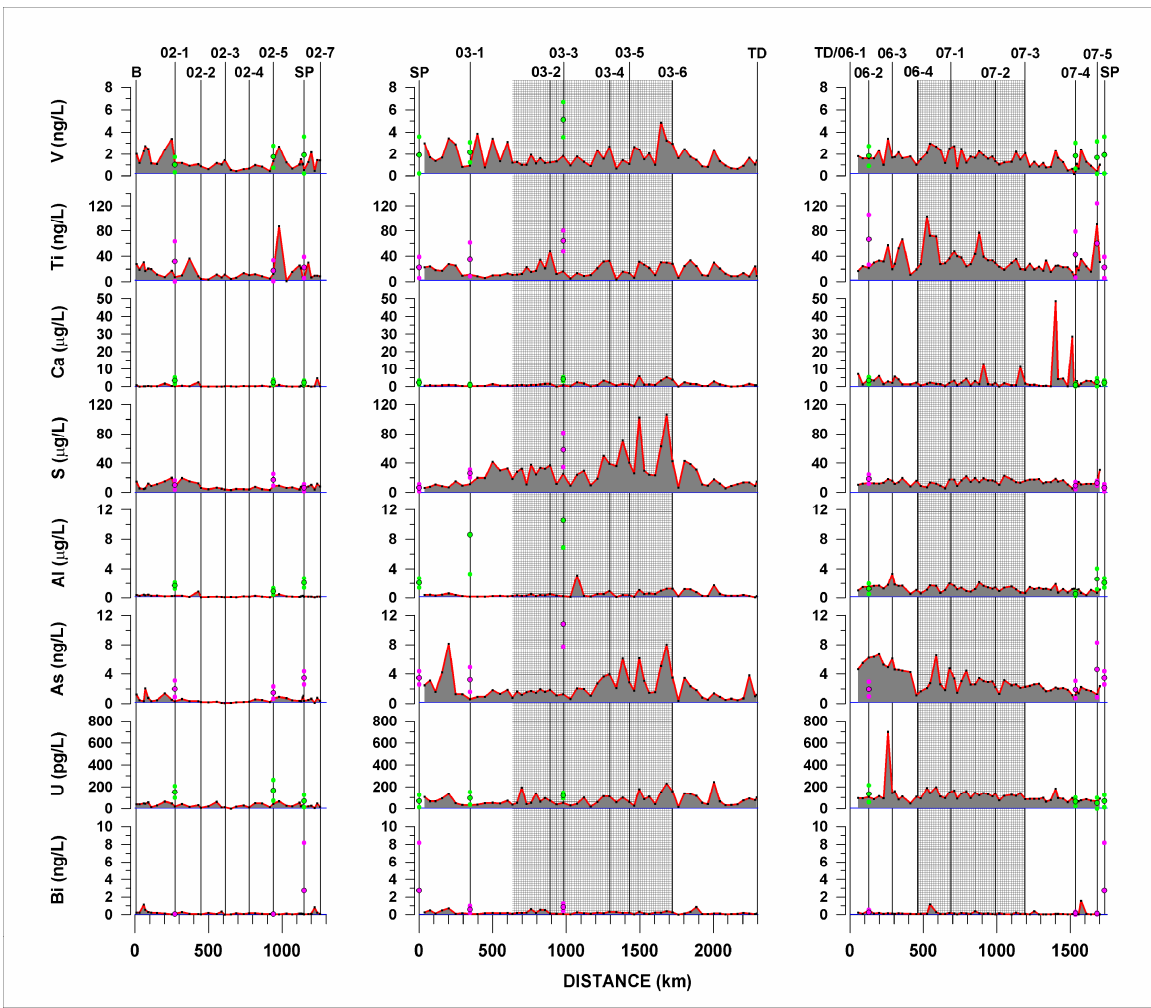


Figure S7. Same as Figure 5b, except that the three y-axes for each element are identical linear scales.

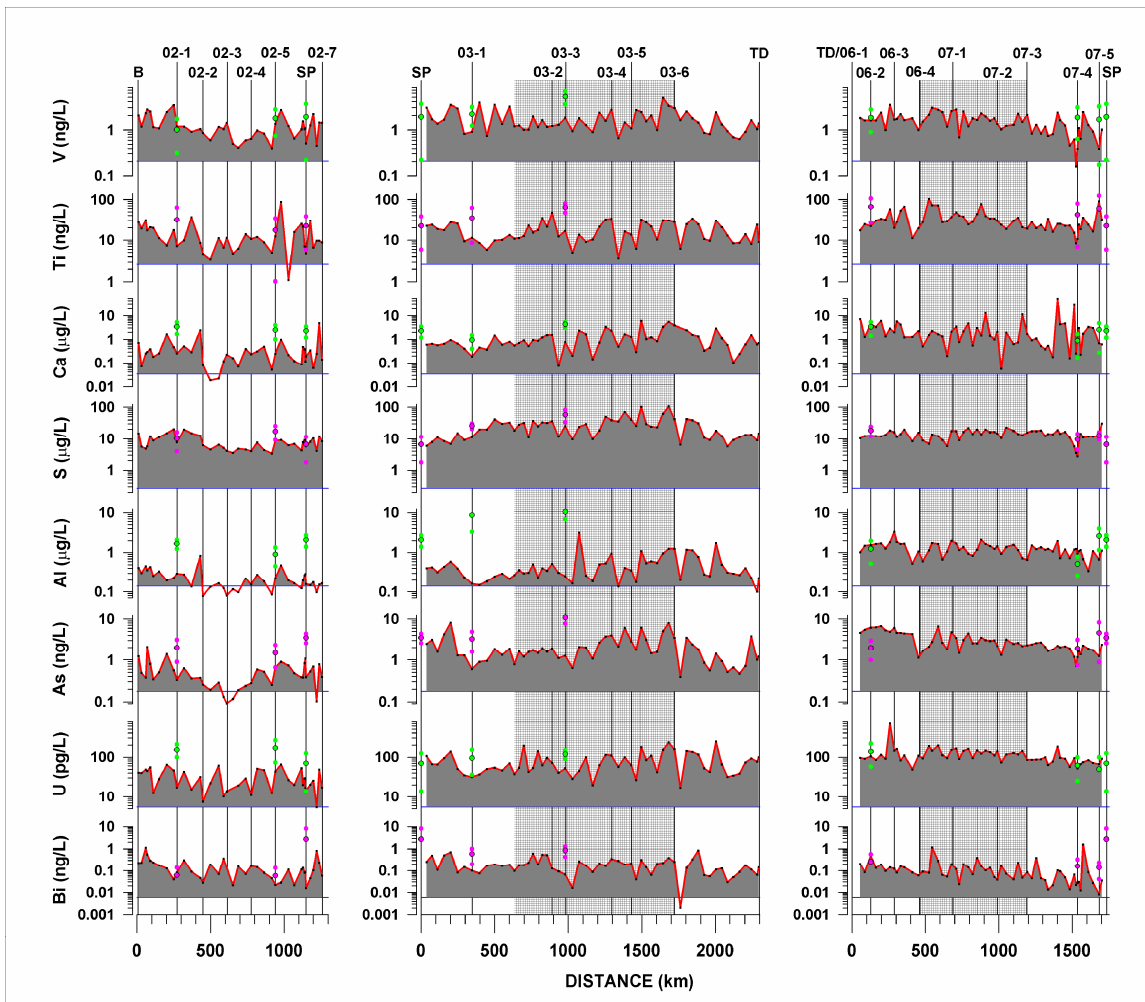


Figure S8. Same as Figure 5b, except that the three y-axes for each element are identical log scales.

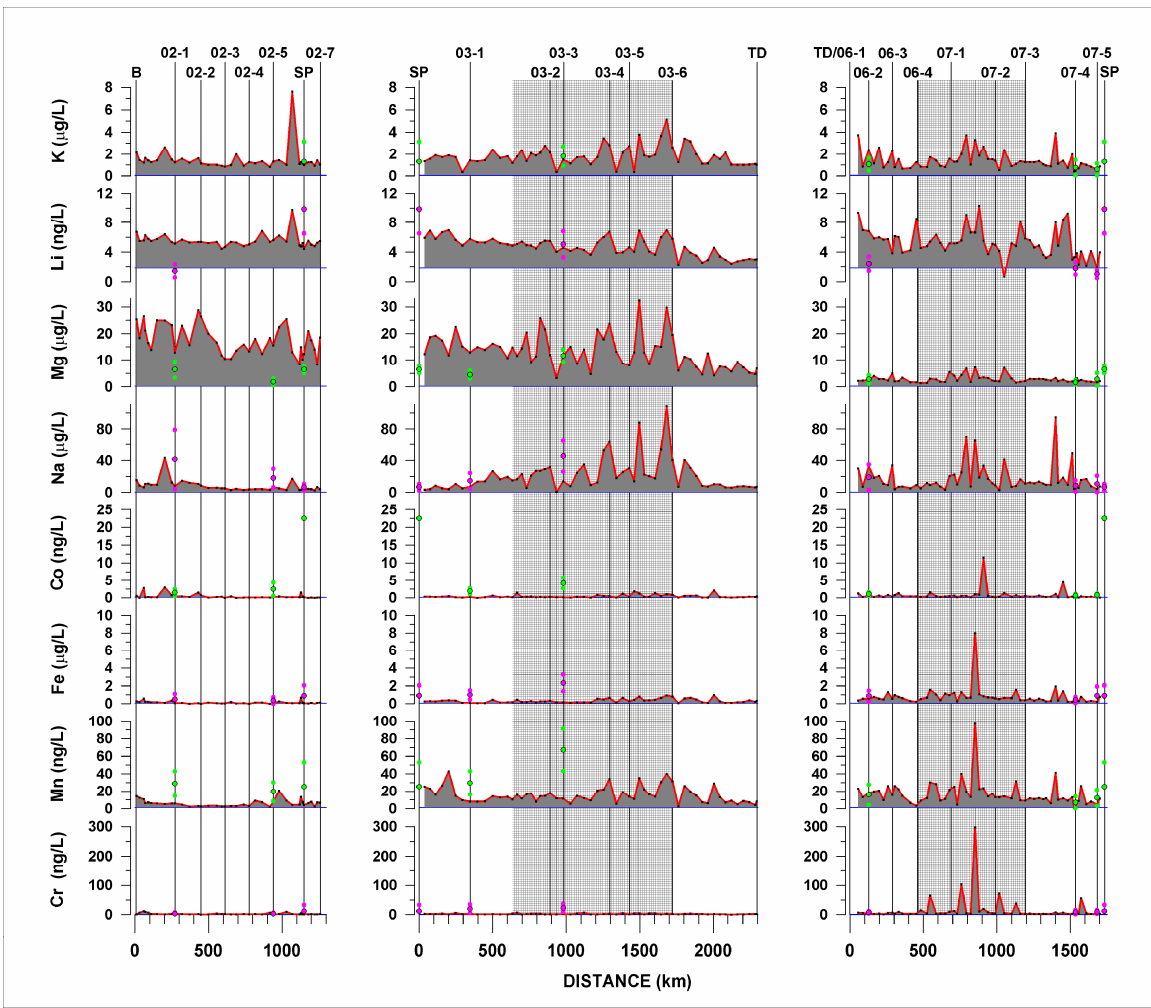


Figure S9. Same as Figure 5c, except that the three y-axes for each element are identical linear scales.

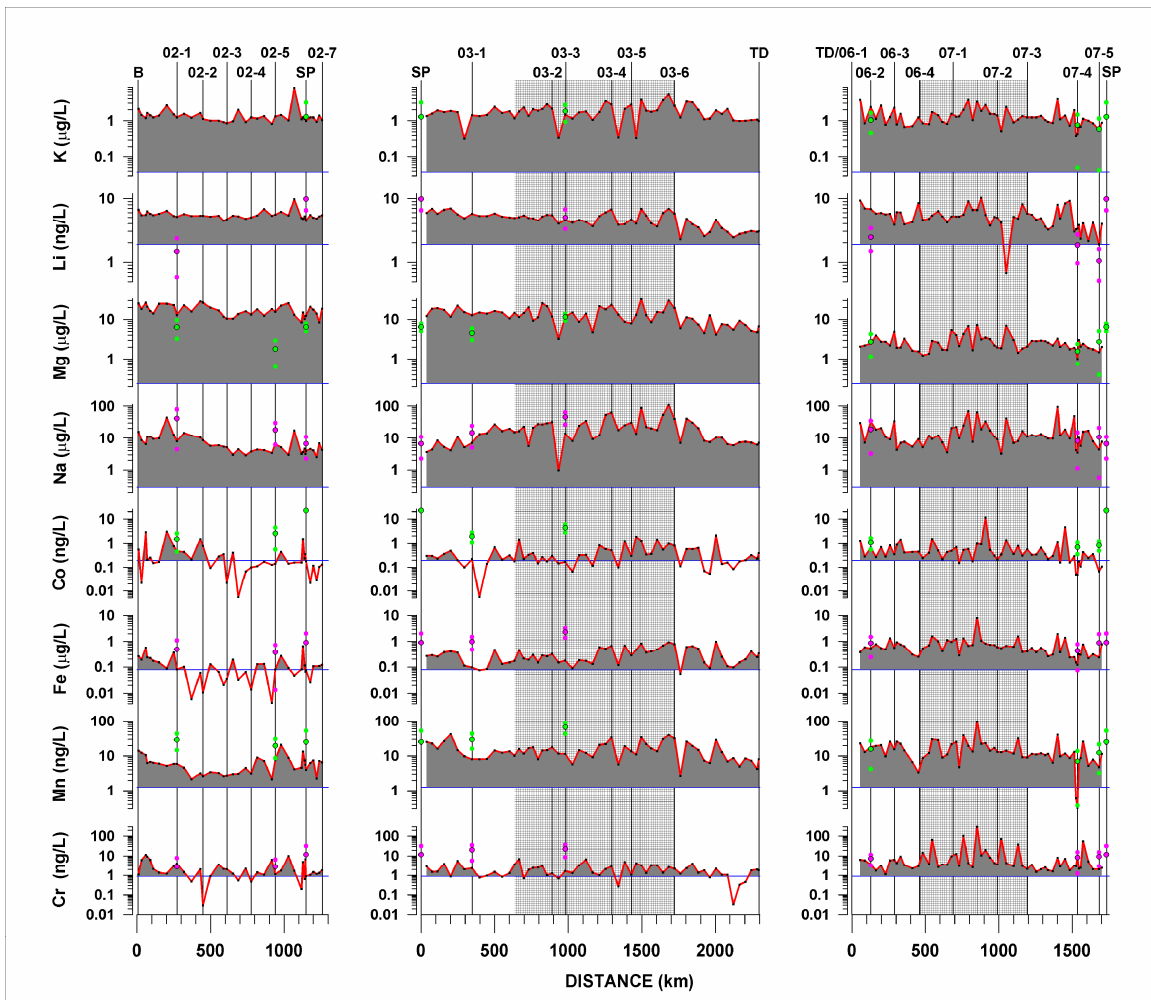


Figure S10. Same as Figure 5c, except that the three y-axes for each element are identical log scales.

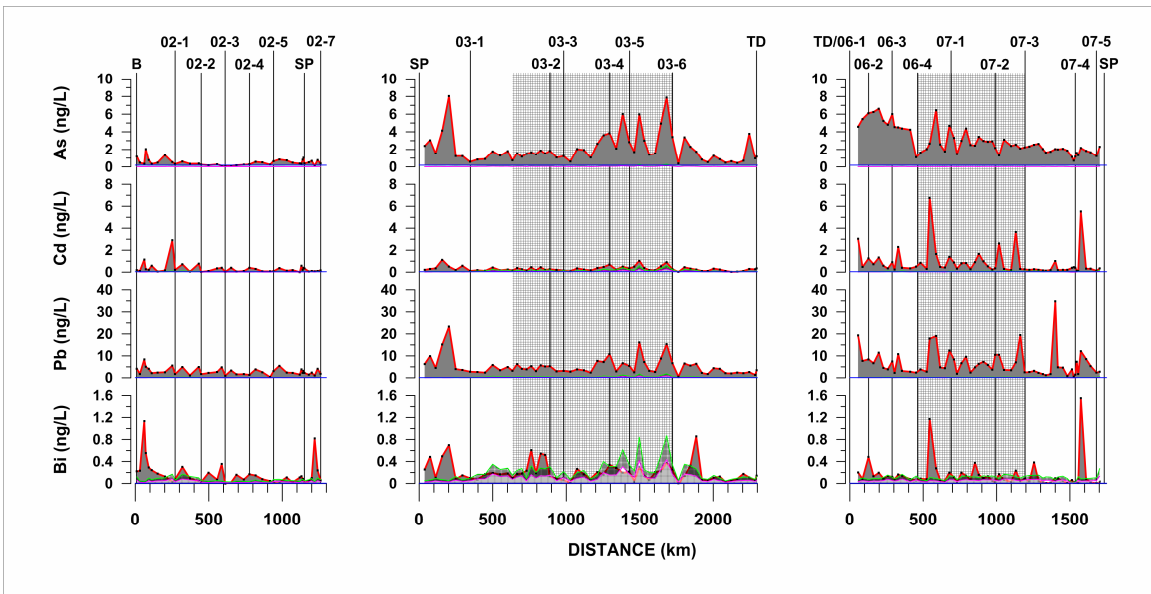


Figure S11. Same as Figure 6, except that the three y-axes for each element are identical linear scales.

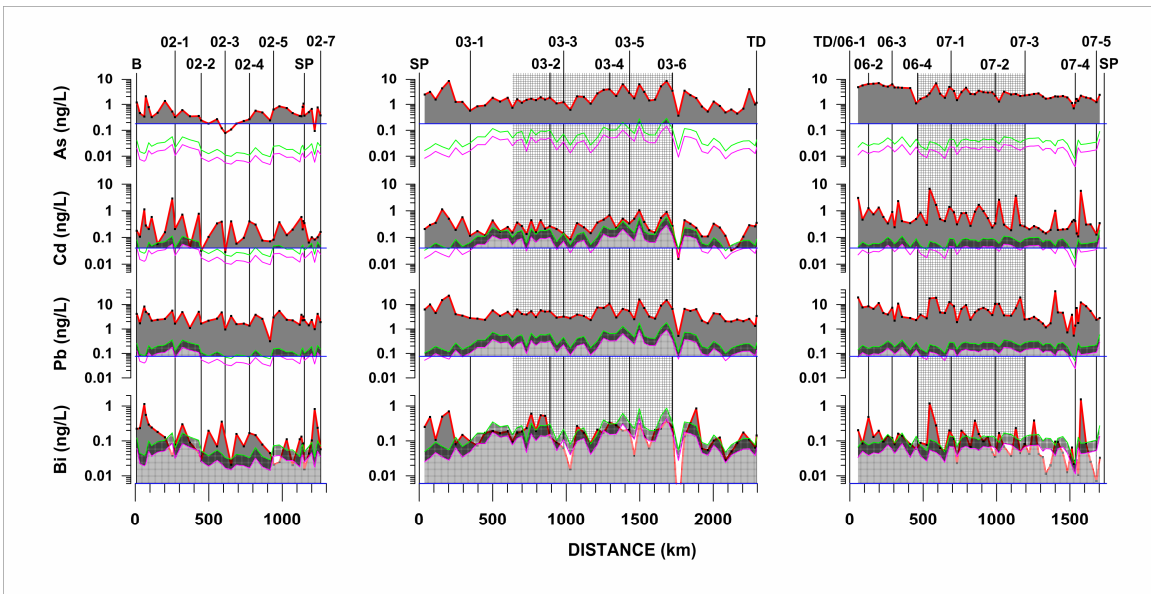


Figure S12. Same as Figure 6, except that the three y-axes for each element are identical log scales.

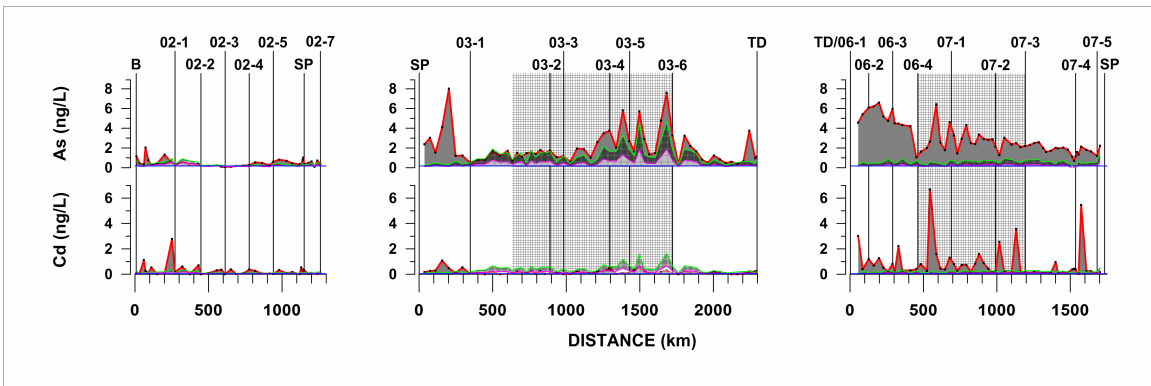


Figure S13. Same as Figure 7, except that the three y-axes for each element are identical linear scales.

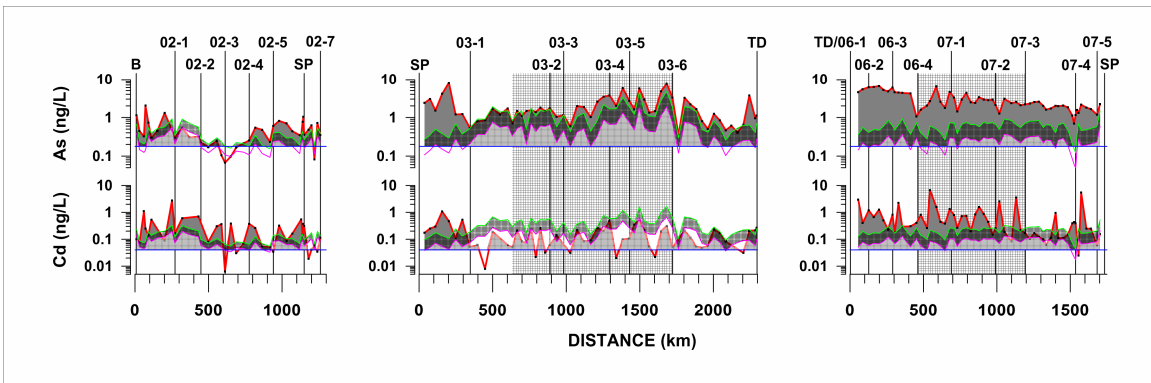


Figure S14. Same as Figure 7, except that the three y-axes for each element are identical log scales.

Table S1. Average method blank concentration (blank), method detection limit (MDL), minimum, maximum and mean sample concentration for each traverse year, and a MDL-mean concentration comparison (MDLC) for each surface snow IC ion and ICP-SFMS element measured in this study. MDLC = method detection limit as an approximate percentage of the mean ion or element concentration.

Ion/Element	Blank	MDL	ITASE-02 min-max (mean)	ITASE-02 MDLC (%)	ITASE-03 min-max (mean)	ITASE-03 MDLC (%)	ITASE-06/07 min-max (mean)	ITASE-06/07 MDLC (%)
IC								
Na (µg/L)	0.44	1.29	2.89 - 17.9 (6.38)	20	3.74 - 144 (25.7)	5	1.85 - 79.9 (13.6)	9
K (µg/L)	<0.33	0.33	3.00 - 3.95 (3.47)	9	3.17 - 6.77 (3.77)	9	0.84 - 1.95 (1.02)	32
Mg (µg/L)	0.4	0.51	0.49 - 2.42 (0.80)	63	0.56 - 21.0 (3.03)	17	0.68 - 8.04 (2.02)	25
Ca (µg/L)	0.79	0.63	0.71 - 4.60 (1.69)	38	0.58 - 6.25 (1.92)	33	0.76 - 7.97 (1.81)	35
MS (µg/L)	<0.43	0.43	3.02 - 24.3 (10.3)	4	6.73 - 50.5 (17.4)	2	1.13 - 52.9 (12.4)	4
Cl (µg/L)	2.68	1.78	8.25 - 40.4 (21.9)	8	27.5 - 381 (128)	1	11.1 - 185 (72.8)	2
NO3 (µg/L)	<0.35	0.35	27.6 - 554 (185)	<1	140 - 1869 (628)	<1	68.4 - 896 (388)	<1
SO4 (µg/L)	<0.76	0.76	24.3 - 95.8 (54.7)	1	57.6 - 478 (143)	1	14.7 - 140 (68.7)	1
ICP-SFMS								
Sr (ng/L)	0.23	0.23	0.67 - 33.0 (4.51)	5	1.55 - 98.1 (18.4)	1	2.21 - 115 (21.2)	1
Cd (ng/L)	0.12	0.040	0 - 2.90 (0.32)	13	0.017 - 1.13 (0.31)	13	0.11 - 6.76 (0.88)	5
Cs (ng/L)	0.0059	0.0029	0 - 0.14 (0.043)	7	0.047 - 0.51 (0.17)	2	0.053 - 0.45 (0.21)	1
Ba (ng/L)	0.35	0.63	0 - 76.6 (10.1)	6	0.78 - 30.3 (6.12)	10	1.19 - 94.0 (14.9)	4
La (ng/L)	0.0055	0.0074	0.024 - 0.66 (0.18)	4	0.13 - 1.64 (0.53)	1	0.031 - 1.00 (0.38)	2
Ce (ng/L)	0.18	0.0095	0.030 - 1.41 (0.35)	3	0.23 - 4.19 (1.11)	1	0.21 - 9.58 (1.24)	1
Pr (ng/L)	0.0074	0.0036	0.0042 - 0.17 (0.045)	8	0.017 - 0.38 (0.13)	3	0.022 - 0.28 (0.12)	3
Pb (ng/L)	0.36	0.076	0.39 - 8.60 (3.05)	3	0.69 - 24.3 (5.66)	1	0.60 - 35.8 (7.00)	1
Bi (ng/L)	0.013	0.0060	0 - 1.14 (0.17)	3	0.0021 - 0.86 (0.21)	3	0.0082 - 1.55 (0.15)	4
U (pg/L)	11.3	5.52	0 - 65.5 (30.2)	18	16.9 - 245 (81.4)	7	48.7 - 700 (117)	5
As (ng/L)	0.35	0.18	0.092 - 2.08 (0.54)	33	0.39 - 8.15 (2.17)	8	0.71 - 6.69 (2.98)	6
Li (ng/L)	3.14	1.88	4.40 - 9.75 (5.48)	34	2.26 - 6.93 (4.68)	40	0.68 - 10.3 (5.24)	36
Al (µg/L)	0.21	0.14	0.079 - 0.82 (0.23)	61	0.10 - 3.14 (0.51)	28	0.35 - 3.34 (1.28)	11
S (µg/L)	1.13	0.27	3.37 - 20.0 (8.20)	3	5.71 - 106 (26.4)	1	2.78 - 31.1 (14.0)	2
Ca (µg/L)	0.095	0.034	0.018 - 4.81 (0.47)	7	0 - 5.95 (1.21)	3	0.055 - 48.6 (3.62)	1
Ti (ng/L)	3.81	2.65	1.11 - 87.0 (14.8)	18	3.68 - 47.7 (17.8)	15	8.38 - 104 (32.8)	8
V (ng/L)	0.49	0.21	0.41 - 3.37 (1.29)	16	0.63 - 4.85 (1.72)	12	0.16 - 3.40 (1.54)	13
Cr (ng/L)	0.72	0.90	0.028 - 11.5 (2.75)	33	0.033 - 6.68 (2.11)	43	1.13 - 298 (15.3)	6
Mn (ng/L)	0.45	1.25	2.15 - 20.7 (6.21)	20	2.67 - 42.9 (15.8)	8	0.32 - 97.3 (16.4)	8
Fe (µg/L)	0.12	0.077	0 - 0.65 (0.13)	59	0.055 - 0.98 (0.33)	23	0.12 - 8.01 (0.78)	10
Co (ng/L)	0.17	0.19	0 - 3.03 (0.41)	47	0.0055 - 2.06 (0.44)	44	0.051 - 11.5 (0.74)	26
Na (µg/L)	0.38	0.30	2.52 - 43.4 (7.74)	4	0.97 - 108 (20.7)	1	3.21 - 94.3 (17.0)	2
Mg (µg/L)	0.42	0.24	8.31 - 28.7 (17.3)	1	3.27 - 32.4 (13.1)	2	1.01 - 7.21 (2.70)	9
K (µg/L)	0.26	0.038	0.82 - 7.61 (1.44)	3	0.33 - 5.15 (1.82)	2	0.39 - 3.92 (1.39)	3

Table S2. Average elemental abundances in the global ocean (Lide, 2005) and Earth's upper crust (Wedepohl, 1995).

Element	Symbol	Ocean Water (ppb)	Upper Crust (ppb)
Strontium	Sr	7900	316000
Cadmium	Cd	0.11	102
Caesium	Cs	0.3	5800
Barium	Ba	13	668000
Lanthanum	La	0.0034	32300
Cerium	Ce	0.0012	65700
Praseodymium	Pr	0.00064	6300
Lead	Pb	0.03	17000
Bismuth	Bi	0.02	123
Uranium	U	3.2	2500
Arsenic	As	3.7	2000
Aluminium	Al	2	77440000
Sulphur	S	905000	953000
Calcium	Ca	412000	29450000
Titanium	Ti	1	3117000
Vanadium	V	2.5	53000
Chromium	Cr	0.3	35000
Manganese	Mn	0.2	527000
Iron	Fe	2	30890000
Cobalt	Co	0.02	11600
Lithium	Li	180	22000
Sodium	Na	10800000	25670000
Magnesium	Mg	1290000	13510000
Potassium	K	399000	28650000

Table S3. Element-Sulphur ratios for the global mean volcanic quiescent degassing background (Hinkley et al., 1999) and the Mount Erebus plume (Zreda-Gostynska et al., 1997).

Element	Global	Erebus
Cd	0.00006	0.000346183
Pb	0.00019	
Bi	0.00009	
As	0.00003	0.00097364