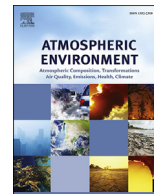




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Elements and inorganic ions as source tracers in recent Greenland snow



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HIGHLIGHTS

- Trace and major elements were measured by SF-ICPMS at 22 Greenland snow pits.
- Crustal element data suggests dust estimation from nssCa is accurate within 50%.
- S is anthropogenically enriched, but weakly correlated with other enriched elements.

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ABSTRACT

Atmospheric transport of aerosols leads to deposition of impurities in snow, even in areas of the Arctic as remote as Greenland. Major ions (e.g. Na^+ , Ca^{2+} , NH_4^+ , K^+ , SO_4^{2-}) are frequently used as tracers for common aerosol sources (e.g. sea spray, dust, biomass burning, anthropogenic emissions). Trace element data can supplement tracer ion data by providing additional information about sources. Although many studies have considered either trace elements or major ions, few have reported both. This study determined total and water-soluble concentrations of 31 elements (Al, As, Ca, Cd, Ce, Co, Cr, Dy, Eu, Fe, Gd, K, La, Mg, Mn, Na, Nb, Nd, Pb, Pr, S, Sb, Si, Sm, Sn, Sr, Ti, V, U, Y, Zn) in shallow snow pits at 22 sampling sites in Greenland, along a transect from Summit Station to sites in the northwest. Black carbon (BC) and inorganic ions were measured in colocated samples. Sodium, which is typically used as a tracer of sea spray, did not appear to have any non-marine sources. The rare earth elements, alkaline earth elements (Mg, Ca, Sr), and other crustal elements (Fe, Si, Ti, V) were not enriched above crustal abundances relative to Al, indicating that these elements are primarily dust sourced. Calculated ratios of non-sea salt Ca (nssCa) to estimated dust mass affirm the use of nssCa as a dust tracer, but suggest up to 50% uncertainty in that estimate in the absence of other crustal element data. Crustal enrichment factors indicated that As, Cd, Pb, non-sea-salt S, Sb, Sn, and Zn were enriched in these samples, likely by anthropogenic sources. Principal component analysis indicated more than one crustal factor, and a variety of factors related to anthropogenically enriched elements. Analysis of trace elements alongside major tracer ions does not change interpretation of ion-based source attribution for sources that are well-characterized by ions, but is valuable for assessing uncertainty in source attribution and identifying sources not represented by major ions.

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1. Introduction

Chemical analysis of stratigraphically layered Arctic snow and ice provides valuable insight into the composition of Arctic aerosols and deposition and exchange processes. As a more remote region of

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the Arctic and one of Earth's two ice sheets, Greenland is an important area for snow and aerosol research. Snow and ice core records provide insight into past climates, global biogeochemical cycles, and long-range atmospheric transport (Legrand and Mayewski, 1997). Recently, additional focus has been given to Greenland due to observed changes in albedo of, and melt on, the Greenland Ice Sheet (Box et al., 2012; He et al., 2013; Stroeve et al., 2013), and the potential contribution of light-absorbing contaminants to the overall energy balance of surface snow on the Greenland Ice Sheet (Flanner et al., 2007; Hansen and Nazarenko, 2004; Keegan et al., 2014; McConnell et al., 2007; Polashenski et al., 2015). Measurement and source attribution of chemical species in snow and ice in Greenland are key in these investigations.

Historically, aerosol source reconciliation has been approached using soluble ion data from ion chromatography (IC) and continuous flow analysis (CFA). Sodium (Na^+) is used as a sea salt tracer; calcium (Ca^{2+}) as a mineral dust tracer; ammonium (NH_4^+), potassium (K^+), and/or organic anions (e.g. acetate [CH_3COO^-] or formate [HCOO^-]) as biomass burning tracers; and sulfate (SO_4^{2-}) as a tracer for anthropogenic combustion-related emissions (Legrand and Mayewski, 1997). Covariance of these ions and concentrations of other common species, such as Mg^{2+} , Cl^- , and black carbon (BC), add further confidence to source attributions. Tracer ions provide insight into relative contributions of these different sources and their spatial and temporal variation, as well as air-snow exchange processes and post-depositional transformations (Bergin et al., 1995; de Caritat et al., 2005; Dibb et al., 2007, 1996; Fischer and Wagenbach, 1996; Krnavek et al., 2012; Whitlow et al., 1992). Ion measurement is commonly used because it is more readily available and less expensive than trace element measurements. However, this approach may have limitations in how much information can be inferred and with what certainty due to convolved effects. For example, the relationship between Ca^{2+} and dust depends on calcium solubility, dust source and mineralogy, and other aerosol components (Banta et al., 2008; Laj et al., 1997; Ruth et al., 2008, 2002).

A number of studies of Greenland snow have examined trace elements, most often as a means of assessing the influence of sources with unique fingerprints, such as platinum group metals following the widespread adoption of catalytic converters in vehicles (Barbante et al., 2001). Existing studies of trace element data have provided important information about inputs of potentially toxic elements into Arctic ecosystems and global transport patterns of specific sources (Barbante et al., 2003, 2001; Boutron, 1979; Boutron et al., 1994, 1993; Candelone et al., 1996), as well as how melt percolation affects trace element records in ice cores (Wong et al., 2013). Analyzing trace elements to supplement the information inferred from major ions has rarely been applied in studies of polar snow and ice, with the exception of a few studies that have examined trace crustal element concentrations and/or isotopic data to infer source regions and other properties of dust (Biscaye et al., 1997; Bory et al., 2003a; Ruth et al., 2008).

Here, we present data on total and water-soluble concentrations of 31 elements and more common tracer ion concentrations in selected layers of 22 snow pits in a transect from central Greenland near Summit Station to northwest Greenland. The primary goals of this paper are to provide a survey of the major and trace elemental composition of recent Greenland snow from sites distributed across the ice sheet, and to explore relationships between the more commonly determined major tracer species and trace elements that are less commonly measured.

2. Methods

2.1. Sample collection

For elemental analysis, 133 samples were collected in 3 cm intervals at 22 snow pits across central and northwest Greenland (Fig. S1) over the periods 1 May – 5 June 2013 and 8–30 April 2014, targeting layers deposited in summer 2013 and 2014 and in spring 2012 and 2013 to assess stratigraphy with the highest likely BC and dust levels respectively. Colocated samples were collected for analysis of stratigraphy, black carbon (BC), and major ions, alongside these samples and at many other sites in Greenland as part of a larger bulk chemical analysis effort (Polashenski et al., 2015). All samples, placed into polyethylene bottles cleaned according to the planned chemical analysis, were transported while frozen to Durham, NH or Madison, WI and kept frozen until analysis.

2.2. Processing and chemical analysis

Samples collected for trace element analysis were stored and subsampled in the trace element clean lab facility at the University of Wisconsin State Laboratory of Hygiene (Madison, WI). The frozen samples were apportioned by weight into subsamples and placed into bottles cleaned appropriately for subsequent analyses. A summary of all analytes and chemical analyses conducted is presented in Table S1.

Trace and major element concentrations were determined using high resolution magnetic-sector Inductively Coupled Plasma-Mass Spectrometry (SF-ICPMS; Thermo-Finnigan Element 2) for paired filtered and unfiltered samples, in order to determine water-soluble and total element concentrations (Kerr et al., 2008; Okuda et al., 2014). Samples were thawed in small batches under a HEPA hood, mixed to ensure homogeneity, and divided into two aliquots. One was transferred directly into an acid-cleaned polypropylene tube for unfiltered measurement, and the other was filtered through a pre-cleaned 0.22 μm polypropylene syringe filter. It must be noted here that while we refer to the measurements of filtered samples as “water-soluble,” this does include concentrations of colloids that are not truly soluble. Both aliquots were acidified with ultrapure nitric acid and then digested at 60 °C for 24 h. Filters used for SF-ICPMS analysis of 2013 samples were later discovered to be contaminated with Ca, and thus Ca was subsequently determined from a separate aliquot of snow using IC, following the protocol used for the colocated samples at UNH (Dibb et al., 2007).

SF-ICPMS analysis of samples was performed in triplicate with quality control checks including matrix (bottle) and method blanks, sample matrix and blank spikes, sample duplicates, and calibration verification checks. Reported concentrations are the average of at least three replicate acquisitions, and have been blank-subtracted using the average bottle blank, excluding one bottle blank that exhibited uncharacteristic contamination in a few elements. Reported uncertainties were propagated from the standard deviations of sample replicates and multiple blanks. Sample concentrations were deemed significant if the blank-subtracted value was statistically different from zero. Only elements for which at least 80% of measurements were significant were included in the analyses we report, which excluded sixteen elements (Ag, Ba, Cs, Cu, Ho, Li, Mo, Ni, P, Pt, Rb, Rh, Sc, Th, Tl, and W). For the remaining elements, bottle blanks contributed no more than 10% of average sample values except for Co (17%), Nb (12%), and S (14%). Average spike recovery was $99.5 \pm 10\%$, and on average relative uncertainty of blank-subtracted concentrations was 14%.

In colocated samples, major water-soluble ions (Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^-) were measured by ion chromatography

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