

Moisture sources and SO₂ oxidation pathways: Evidence from the snow pack sulphate from the Prince of Wales Icefield, Ellesmere Island

V.L. Wasiuta, A.L. Norman, S. Marshall
The University of Calgary

INTRODUCTION

Atmospheric sulfur is a key component to understand as climate change affects the productivity and spatial extent of open water versus sea ice in the Arctic. Decay of marine biota in the surface ocean is linked to the formation of dimethylsulphide (DMS), a gas that can escape into the atmosphere. Its oxidation is expected to increase the number of condensation nuclei, promoting cloud formation and scattering incident radiation back to space (Charlson et al., 1987). An increase in open water and sea ice leads with rising temperatures could result in an increase in DMS released to the atmosphere. Quantifying this potentially large negative feedback to global warming is difficult in the Arctic where coupled chemical, aerosol and transport model parameterizations do not necessarily apply. Characterization of the chemical and isotopic composition of sulphate in the snowpack at varying altitudes within the Arctic can provide key information on how much DMS is produced, the altitude at which this occurs, its transport, and its oxidation pathways. This study explores the isotope composition of snowpack sulphate, of the Prince of Wales Icefield (POW), to examine DMS oxidation and its relationship to moisture sources in a region adjacent to the North Water Polynya and northern Baffin Bay, Nunavut, Canada at 78.5° N (Figure 1).

BACKGROUND

High-resolution snow pit samples were collected between April 21 and June 10, 2004 for isotopic and chemical analyses of fall 2003 to spring 2004 accumulation. The Lower Leffert Glacier, with a low slope angle (~2.3°), was sampled every 150 m in elevation between sea level and 1450 masl. The adjacent steeper gradient Jewell Glacier was sampled every 300 m in elevation from 100 to 1300 masl. At each site, two sample suites were collected for each 10 cm depth interval, a small volume sample for ion chemistry and snow water isotopic analyses ($\delta^{18}\text{O}$ and $\delta^2\text{H}$), and a large volume sample for sulphate isotopic analyses ($\delta^{18}\text{O}$ and $\delta^{34}\text{S}$). Isotopic values were quantified by mass spectrometry at the University of Calgary Stable Isotope Laboratory. Ion concentration was quantified by IC for anions, and ICP-MS for cations at the University of Alberta.

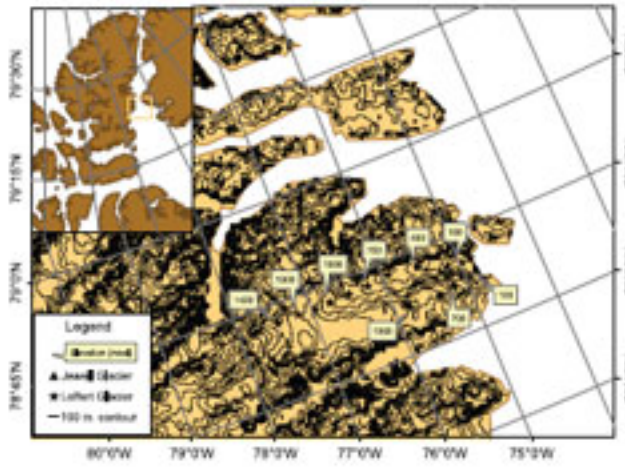


Figure 1. Map showing the location of the sampling sites on the Prince of Wales Icefield, Ellesmere Island

ISOTOPES

Variations in the natural abundances for isotope ratios of terrestrial materials are on the order of parts per thousand. Typically, the number of heavy to light isotopes in a sample (S) are compared to the same ratio in a reference material (R); VCDT for S, VSMOW for O. This ratio varies only slightly from unity and is therefore expressed on the delta (δ) scale in parts per thousand (per mil = ‰).

$$\delta_{n+2X} = \left(\frac{n+2X/nX}{n+2X/nX} \right) S / (n+2X/nX) R - 1 \times 103 \quad X = \text{Element} \quad n = \text{major isotope}$$

ISOTOPE VARIATIONS IN SULFATE SOURCES

S and O isotope variations for sources of sulfate in the Arctic are shown in Figure 2. Sea-salt sulfate is subtracted from the total sulphate using the mass ratio of sulphate to sodium in seawater as a tracer. This leaves DMS sulphate and anthropogenic (+volcanic) sulphate which can be apportioned using $\delta^{34}\text{S}$ values. Similarly sulphate formed at high temperatures (primary) can be distinguished from that formed at low temperatures (secondary) by their $\delta^{18}\text{O}$ values. The range in $\delta^{18}\text{O}$ values for secondary sulphate depends upon the O isotope composition of associated water and/or vapour of the molecules participating in the oxidation as described by Holt et al. (1991).

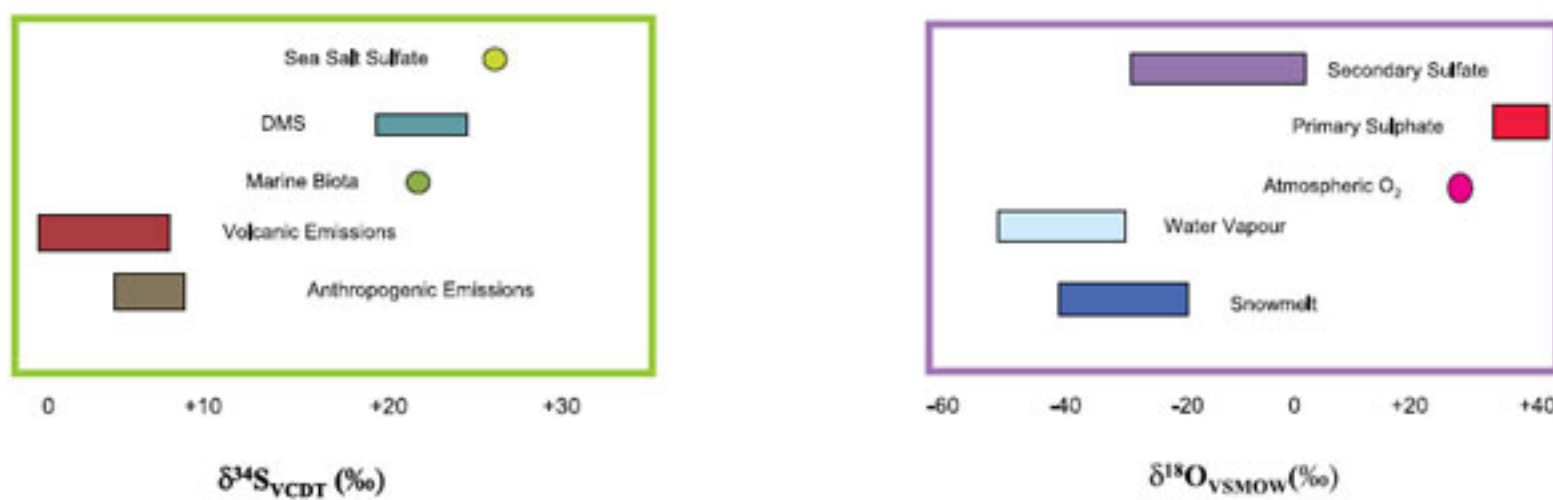


Figure 2. Potential contributors to the isotopic composition of $\delta^{34}\text{S}$ (a) and of $\delta^{18}\text{O}$ (b) of aerosol sulphate in the Arctic.

SNOW WATER $\delta^{18}\text{O}$ IN DEPTH PROFILE

Isotope fractionation in the hydrologic cycle during evaporation, transportation, and condensation creates precipitation that is more depleted in the heavier isotope (^{18}O) or isotopically lighter, with increased distance inland, increased latitude, increased elevation, and with colder temperatures (Dansgaard, 1963, and Yonge et al., 1989). Both POW depth profiles show relatively high $\delta^{18}\text{O}$ values at the base of the profile (in the late summer to early fall accumulation). Generally, $\delta^{18}\text{O}$ values decrease with height in the profile to more ^{18}O depleted values in the surface spring snow. This is interpreted as warmer temperatures during condensation of the fall snow and colder temperatures through the Arctic winter, possibly combined with increasing distance from moisture source. The spread in $\delta^{18}\text{O}$ values between the basal fall and surface spring snow is much larger on the Leffert Glacier than the Jewell Glacier. Local moisture, from the North Water polynya, would have a shorter more direct transportation and deposition route to the Jewell Glacier than a similar elevation on the gentler Leffert Glacier.

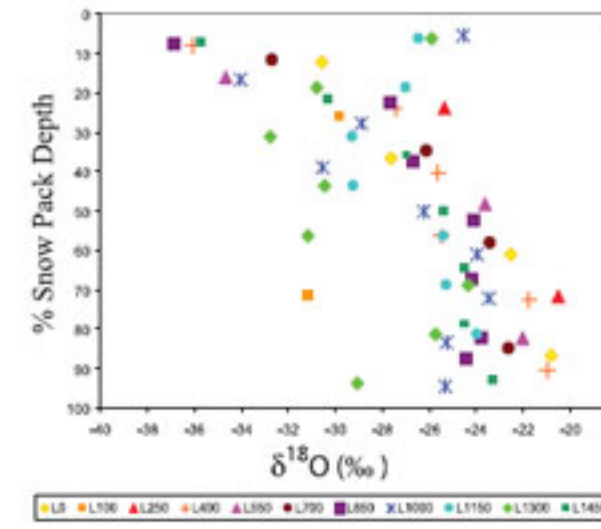


Figure 3a. Snow water $\delta^{18}\text{O}$ with snowpack depth on the Leffert Glacier. Illustrated by sampling site elevation.

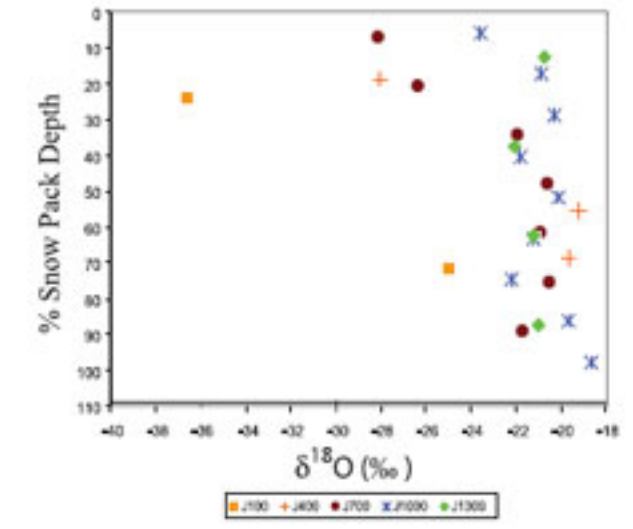


Figure 3b. Snow water $\delta^{18}\text{O}$ with snowpack depth on the Jewell Glacier. Late summer to early fall accumulation forms the base of the snowpack and spring snowfall the surface.

SULPHATE $\delta^{18}\text{O}$ VERSUS SNOWMELT $\delta^{18}\text{O}$: EVIDENCE OF SO₂ OXIDATION

The range in $\delta^{18}\text{O}$ values for Arctic snowmelt shown in Figure 3, is reflected in a wide range of sulphate $\delta^{18}\text{O}$ values on both glaciers. A general trend is observed in Figure 4 toward more positive $\delta^{18}\text{O}$ values for both sulphate and snowmelt. This is consistent with SO₂ oxidation in association with the snow layer in which it was found: SO₂ formed or transported into the region is likely oxidized to sulphate during snowfall events. The addition of a constant proportion of primary sulphate to that from secondary processes could explain the upward shift from the region for secondary sulphate shown on the plots below. However, extensive research has shown that Arctic sulphate is largely secondary – only 5% is primary sulphate from long range transport (Sirois and Barrie, 1999). This apparent contradiction can be resolved if we recognize that ozone oxidation was not included in the studies by Holt (1991). Tropospheric ozone has an isotope composition of ~100 ‰. A mixture of sulphate formed from SO₂ ozone reactions with secondary sulphate from other oxidation processes, shown in Figure 4, would result in sulphate with elevated $\delta^{18}\text{O}$ values that also follow the $\delta^{18}\text{O}$ precipitation trend. Ozone is a major oxidant of SO₂ in winter. At Polar Sunrise, ozone is depleted and other oxidation pathways such as H₂O₂, HOBr and OH oxidation become more important (Jin and Chu, 2005, Morin et al., 2005). A very interesting feature is the strong relationship between $\delta^{18}\text{O}$ sulphate and $\delta^{18}\text{O}$ precipitation at 1450 m ($r^2 = 0.65$) on the Leffert Glacier – an excellent indication that sulphate at this location is secondary.

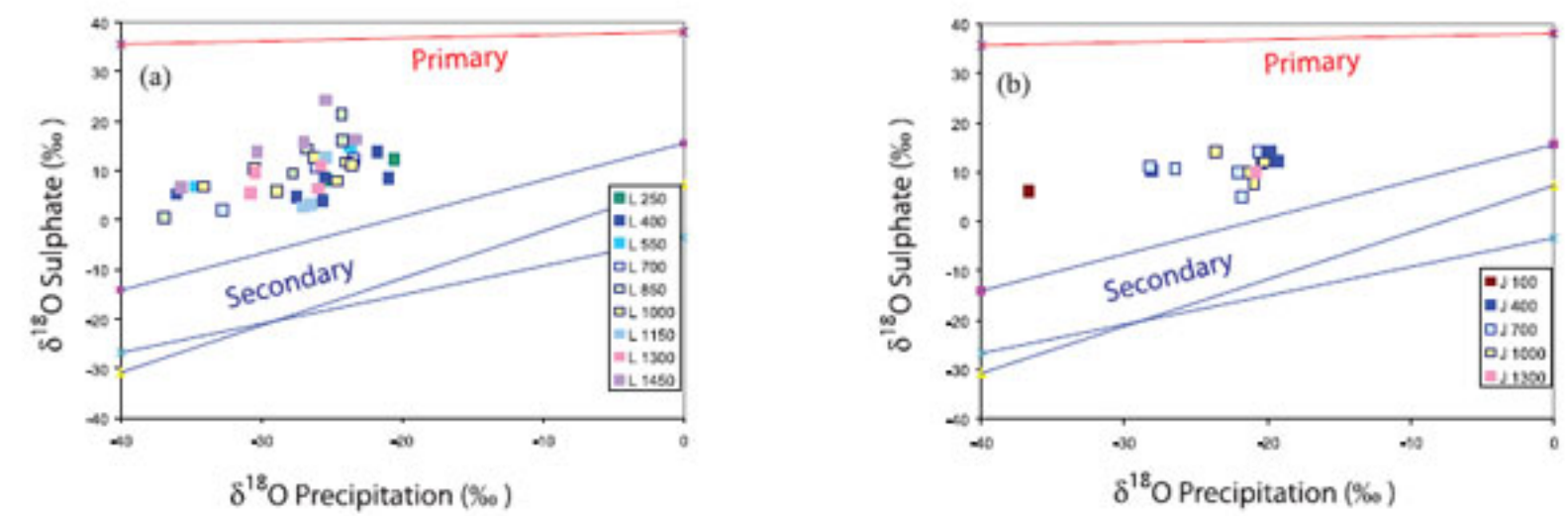


Figure 4. The oxygen isotope composition of snowpack sulphate from the Leffert (a) and Jewell (b) glaciers are shown versus the oxygen isotope composition of snowmelt and these data are compared to the relationships shown by Holt (1991) that are expected from various sulphate oxidation processes (see text).

CONCLUSIONS

Results from this study provide information on how reduced sulphur compounds, such as DMS and SO₂ are oxidized in the vicinity of Jewell and Leffert glaciers. It demonstrates that a considerable portion of SO₂, either from DMS or from long range transport of Eurasian pollutants, is oxidized in association with water vapour or on the surface of ice crystals. Further, the moisture source for the water vapour or ice crystals is most likely the nearby North Water Polynya in Smith Sound. The best correlation between precipitation and sulphate oxygen isotope compositions is seen at the highest elevation site (L 1450) and strongly suggests SO₂ oxidation as the main sulphate source at this site. In summary, DMS-sulphate at high elevations on the Leffert Glacier is very likely a good proxy for open sea ice conditions in the nearby Strait.

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