

## Implications of ionic species from Styx glacier firn core, East antarctica

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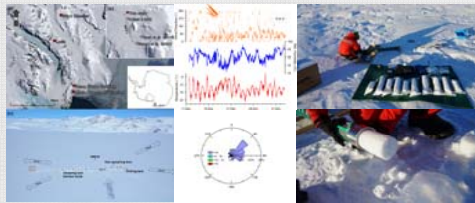
### Abstract

It has been known that ionic species in the ice core are critical to reconstruct atmospheric circulation, volcanic events, and sea ice extent in the past. In this study, the major ions from the Styx glacier firn core were determined and their implications were studied in order to present the preliminary results of shallow ice core drilled on the 10th December 2014 – 2nd January 2015 at the Styx glacier (73° 51.095' S, 163° 41.217' E, 1620m a.s.l.). It is located at the north of 80km from Jangbogo station at the seashore of the Northern Victoria Land, East Antarctica. The Ross sea is one of the few regions in the Southern Ocean experiencing a significant positive trend in sea ice extent and has been considered one of the most productive regions of the Southern Ocean, and also volcanic gas emissions from volcanoes are important source of gases and aerosols to the atmospheric environment of Victoria Land. It is thought that the multi-proxies of ice core from Styx glacier can represent the oceanic environment of Ross sea and atmospheric environment of Northern Victoria Land in the past because the prevailing winds are southerly and southwesterly.

In this work, the possibilities of ionic species from the Styx glacier firn core as the proxy to indicate the variabilities of sea ice extent and polyna area of Ross sea and also the characteristics of atmospheric environment of Victoria Land in the past were investigated. The initial chronology of the firn core was established combining annual layer counting based on sub-annual analyses of  $\delta^{18}O$ , major chemical species ( $Na^+$ , non sea salt  $SO_4^{2-}$ ,  $EF SO_4^{2-}$ ,  $Cl^-/Na^+$ , and  $theo-H^+$ ), as well as 1 reference horizon (the volcanic horizons related to the eruption of Pinatubo (1991)). This firn core encompassed the period –1988-2014. Variations in concentration and compositions of primary (sea spray) and secondary (biogenic emission from ocean area and atmospheric transformation from precursors) species was observed. Of ionic species,  $F^-$  and biogenic sulfur (MSA and nss  $SO_4^{2-}$ ) were investigated their implications to indicate volcanic emissions at the N.V. and ocean environment of Ross sea in the past.

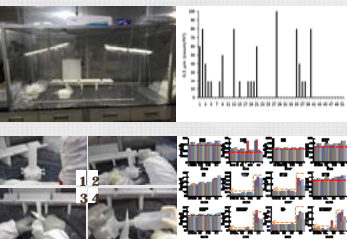
### Experimental

#### Styx glacier information and field activities



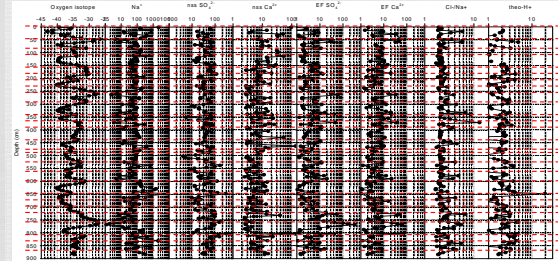
- ◆ **Accumulation Rate**  
~130  $kgm^{-2}a^{-1}$  (Han et al., 2015), ~138  $kgm^{-2}a^{-1}$  (this study)
- ◆ **Core location**  
Map of the Styx glacier of the Northern Victoria Land showing core location
- ◆ **Field campaign period:**  
10th Dec, 2014 – 4th Jan, 2015
- ◆ **Field activities:** GPR survey (Ice thickness over ~400m), Shallow ice coring (~210.5 m), Ice chip sampling, Snow pit sampling (~1.6 m depth), **Firn coring** (~10 m), Borehole temperature logging (SNU), Observation of weather parameters (WD, WS, RH, Temp), Firn gas trapping (SNU)

#### Sample preparation



- ◆ **Cleanliness of clean bench**  
The concentrations of dust with diameter larger than 0.5- $\mu m$  during firn core sample preparation: mostly less than ~3500 particles per  $m^3$  (ISO 5)
- ◆ **Decontamination of firn core sample**  
Cleaning method of sampling bottle (LDPE) and ceramic knife (FK-110WH, Kyocera): Rinse in DW, soaked in DW overnight, sonication in DW for 1 hour, triple-rinse in DW again, drying and storage under a class-10 clean bench  
The water purification system; MilliQ-Element system (Millipore, Milford, MA; >18.2 M $\Omega$ )  
Procedure: setting of firn core sample in the sample holder, first layer 2mm chiselling using first ceramic knife, second layer 2mm chiselling using second ceramic knife, third layer 2mm chiselling using third ceramic knife, cutting of inner firn core sample using fourth ceramic knife in the sampling bottle
- ◆ **Performance test**  
>  $Ca^{2+}$ ,  $NO_3^-$ , Organic anions,  $F^-$ : concentrations measured in the first layer are clearly higher than those observed in the second layer  
> Others: no clear change of concentrations from outer side to inner side

### Age Dating

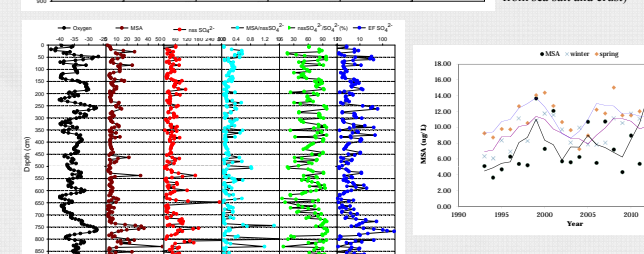
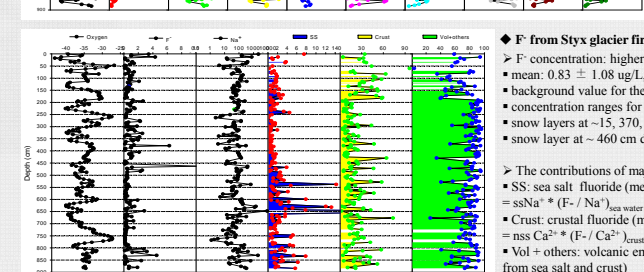
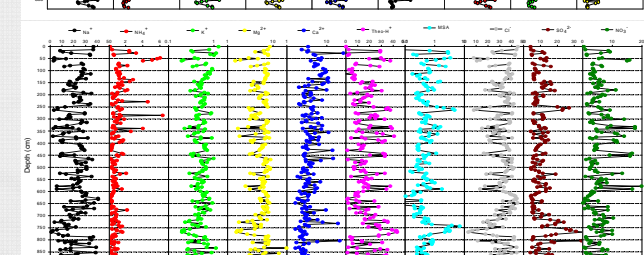
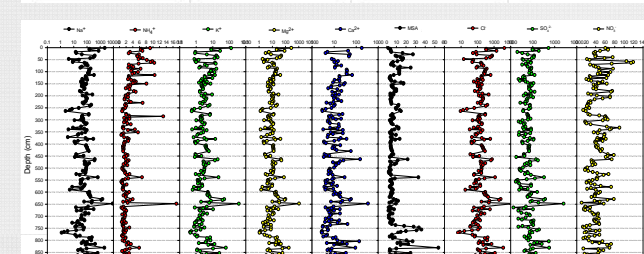
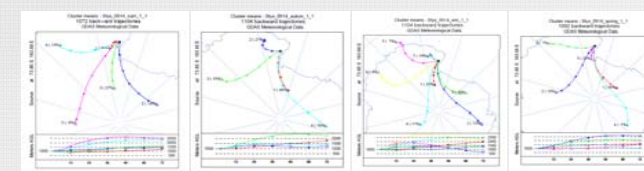


- ◆ **2015**  
> nss  $SO_4^{2-}$  (non-sea salt sulfate)  
 $= SO_4^{2-} - (SO_4^{2-} / Na^+)_{sea\ water} * Na^+$ ,  $(SO_4^{2-} / Na^+)_{sea\ water} = 0.25$
- ◆ **2010**  
> nss  $Ca^{2+}$  (non-sea salt calcium)  
 $= Ca^{2+} - (Ca^{2+} / Na^+)_{sea\ water} * Na^+$ ,  $(Ca^{2+} / Na^+)_{sea\ water} = 0.038$
- ◆ **2005**  
> EF  $SO_4^{2-}$  (Sulfate enrichment factor)  
 $= (SO_4^{2-} / Na^+)_{sample} / (SO_4^{2-} / Na^+)_{sea\ water}$
- ◆ **2000**  
> EF  $Ca^{2+}$  (Calcium enrichment factor)  
 $= (Ca^{2+} / Na^+)_{sample} / (Ca^{2+} / Na^+)_{sea\ water}$
- ◆ **1995**  
>  $theo-H^+$   
> Anions sum (equivalent concentration) – Cations sum
- ◆ **1990**  
> Red dot line: summer season

#### from austral winter of 1988 to austral summer of 2015

- > Annual layer counting based on sub-annual analyses of  $\delta^{18}O$ ,  $Na^+$ , non sea salt  $SO_4^{2-}$ ,  $EF SO_4^{2-}$ ,  $Cl^-/Na^+$ ,  $theo-H^+$  combined with 1 volcanic horizons related to the eruption of Pinatubo (1991)
- > Maximum concentrations for  $Na^+$  during winter season and Synchronous maximum values for  $\delta^{18}O$  and non sea salt  $SO_4^{2-}$
- > Snow layer at surface, ~110, 290, 470, 570, 600, 645, and 755 cm depth: synchronous increase of  $Na^+$  and nss  $SO_4^{2-}$  during summer season
- > Snow layer at ~670-810 cm depth: Pinatubo eruption based on the seasonal pattern of  $\delta^{18}O$ , nss  $SO_4^{2-}$ , and Enrichment Factor for  $SO_4^{2-}$  relative to sea water composition. The  $SO_4^{2-}$  level in the winter of the eruption year (1991) was not significantly elevated. However, the EF  $SO_4^{2-}$  showed clear variations to be affected by volcanic eruption and the majority of the volcanic  $SO_4^{2-}$  was deposited in the first four years following the eruption.
- >  $Cl^-/Na^+$  ratio: clearly higher during summer season, the possibility of additional deposition of gaseous HCl (secondary formed species by the reaction of  $H_2SO_4$  and NaCl or emitted from volcanoes)
- >  $theo-H^+$ : clearly higher during summer season due to secondary formed acidic species (mainly non sea salt  $SO_4^{2-}$ )

### Results and Discussion



#### Air mass trajectories

- > Cluster analysis of once every two days (00 UTC) 3-day back trajectories (HYSPPLIT model developed by NOAA) during 2009-2014
- > Few JBS air masses had recent fetch outside of continental Antarctica
- > Mostly southerly and south westerly winds caused by the combination effect of an anticyclone over Victoria Land and cyclonic system off Cape Adare

#### Concentrations (ug/L) of ionic species

	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>2</sub>
Mean	171.07	2.72	7.38	20.86	17.88	8.12	339.42	91.63
S.D.	671.04	2.34	28.59	77.66	32.45	7.13	1239.97	188.53

#### Compositions (%) of ionic species

	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	theo-H <sup>+</sup>
Mean (ueq/L)	7.54	0.14	0.18	1.73	0.89	2.13
Compositions (%)	20.83	1.05	0.53	5.71	4.44	17.39
	Acce	For	MSA	Cl	SO <sub>4</sub> <sup>2-</sup>	NO <sub>2</sub>
Mean (ueq/L)	0.08	0.14	0.08	9.69	1.92	0.66
Compositions (%)	0.71	1.19	0.71	31.07	10.54	5.54

- > Primary (marked by  $Na^+$ ,  $Cl^-$ , partially  $SO_4^{2-}$ ) and Secondary ( $SO_4^{2-}$ , MSA) marine sources are the major contributions to the chemical composition of the aerosol deposited at the coast area (primary sea spray: ~60%, secondary biogenic emission: ~11%)
- >  $NH_4^+$ , Organic anions, and  $NO_3^-$  accounts for 1.1, 1.9, and 5.5 % of the ionic budget
- > The compositions of  $NH_4^+$ ,  $Ca^{2+}$ , MSA,  $SO_4^{2-}$ ,  $NO_3^-$ , and  $theo-H^+$  clearly increase during summer season and those of  $Na^+$ ,  $Cl^-$ ,  $K^+$ , and  $Mg^{2+}$  from sea spray aerosol increase during winter season
- >  $theo-H^+$ : mean concentration: 2.13 ueq/L (~17.4%), concentration range: mostly less than ~3 ueq/L, antarctic snow acidity: ~2.4 ueq/L for most locations
- > Acid-base chemistry:  $theo-H^+ = 0.94 * (\text{acidic anions sum} - \text{nss } Ca^{2+} + NH_4^+)$ ,  $0.01$  ( $r^2 = 0.97$ ), acidic anions sum = nss  $SO_4^{2-}$  + nss  $Cl^-$  +  $NO_3^-$  + MSA + organic anions +  $F^-$

#### F<sup>-</sup> from Styx glacier firn core

- >  $F^-$  concentration: higher than those from other glaciers of antarctica
- mean:  $0.83 \pm 1.08$  ug/L, range: 0.13 - 10.26 ug/L
- background value for the Antarctic ice sheet: 0.19 ug/L (Saigne et al., 1987)
- concentration ranges for the snow pits from N.V.: ~ 0.1 - 3 ug/L (Severi et al., 2014)
- snow layers at ~15, 370, 460, 650, 830 cm depth: synchronous increase of  $F^-$  and  $Na^+$
- snow layer at ~460 cm depth: the possibility of volcanic signal from Mt Erebus (~2001 year)
- > The contributions of major sources
- SS: sea salt fluoride (mean: 2.2%)  
 $= ssNa^+ * (F^- / Na^+)_{sea\ water} - (F^- / Na^+)_{sea\ water} = 0.00012$  (w/w)
- Crust: crustal fluoride (mean: 22.0%)  
 $= nss Ca^{2+} * (F^- / Ca^{2+})_{crust} - (F^- / Ca^{2+})_{crust} = 0.012$  (w/w)
- Vol + others: volcanic emissions or long-range transported input (mean: 75%) = total  $F^-$  - ( $F^-$  from sea salt and crust)

#### Biogenic sulfur

- > MSA/nss  $SO_4^{2-}$  and nss  $SO_4^{2-}/SO_4^{2-}$  are in the range of ~0.2 (summer season) - ~0.8 (winter season) and ~30 (winter season) - ~90% (summer season), respectively
- > Weak correlation ( $r = \sim 0.42$ ) between MSA and Ross sea ice area during winter and spring season (period: 1993-2008) (S.I.A: Ross sea ice area from Satellite (NOAA data center))
- > snow layer at ~750 (period: ~1991/92), ~830 (period: ~1989/90) cm depth: MSA high concentrations might be connected to the ENSO-associated changes in high latitude circulation

