

# Natural variability of the atmospheric composition and anthropogenic influence in Patagonia. Contribution to the study of the transport along the Equator-Mid latitudes-Pole

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Scientific advice: Martine de Angelis

Grenoble, 19 January 2011



ENSO  
PDO

# The ice-archive



Fine resolution for  
paleo environmental  
reconstructions

Southern mid-  
latitudes information  
gap

35°-60°S

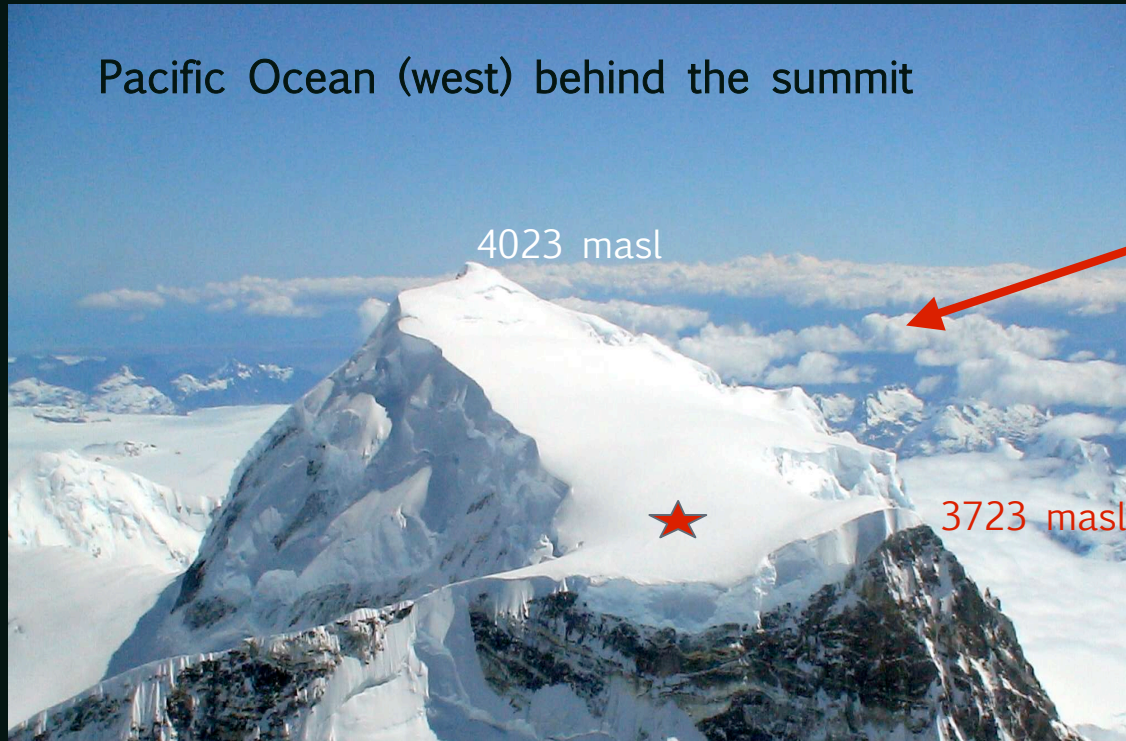
AAO

# Monte San Valentín

46°S 73°W

Cold site

Pacific Ocean (west) behind the summit

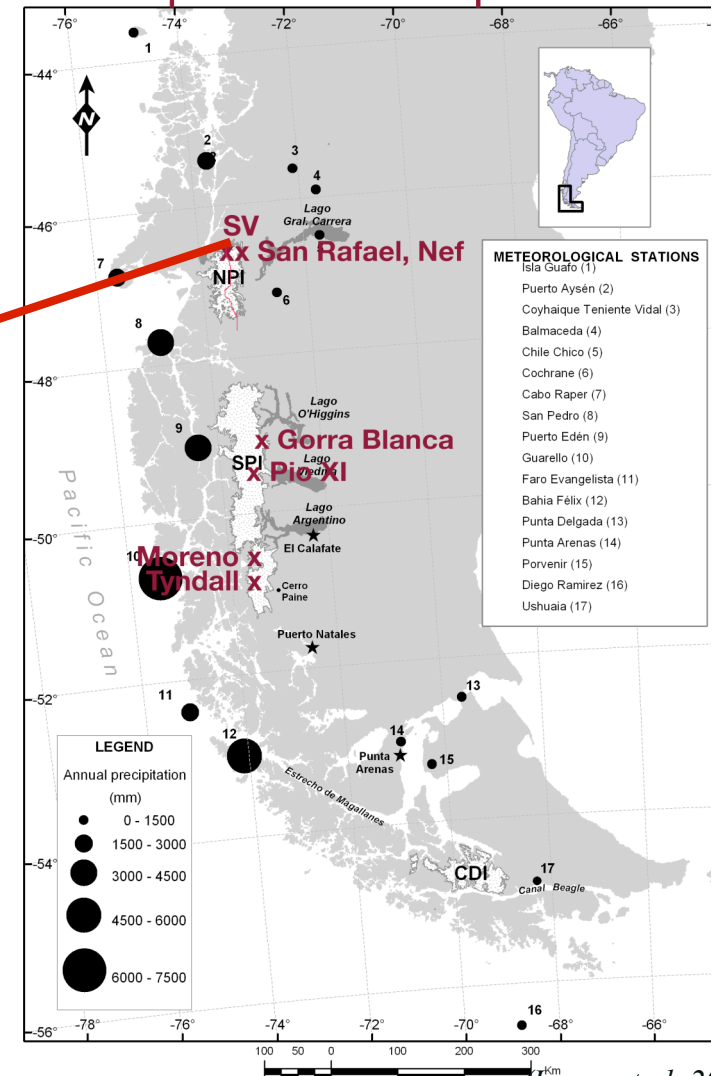


2005

15 m firn core



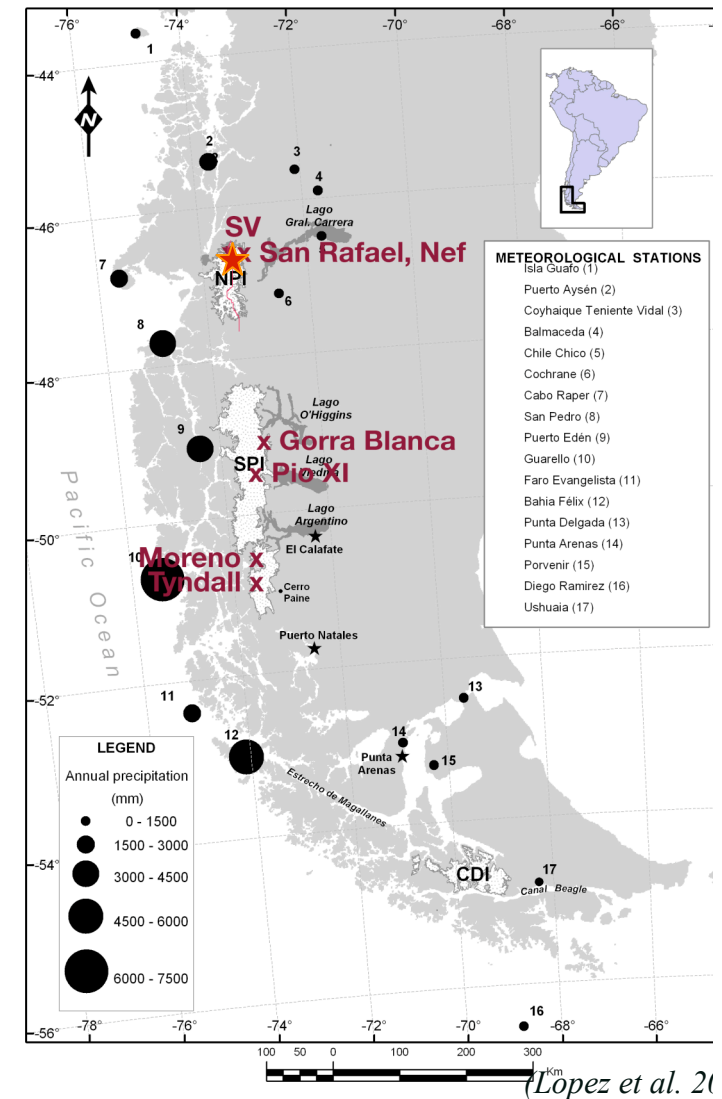
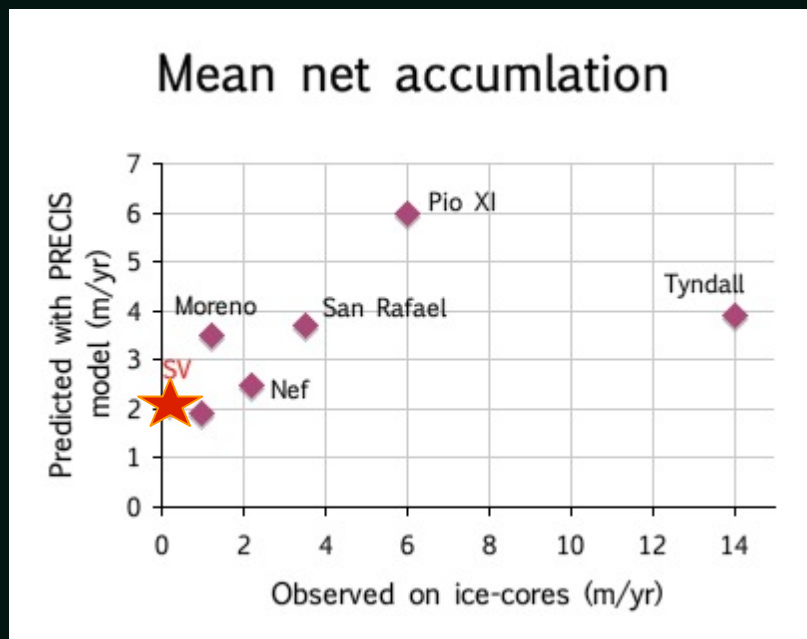
## Temperate sites + percolation



# Main results from the 2005 core:

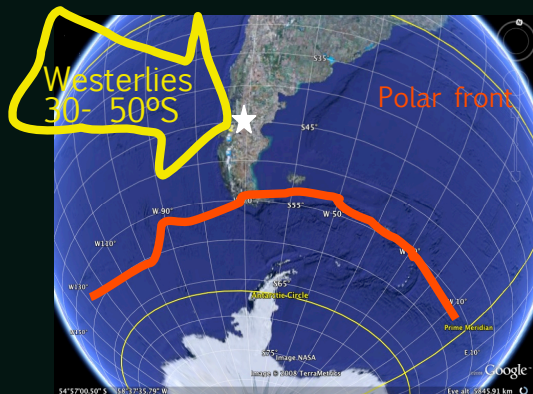
1. Low mean net accumulation [2005-1965] (*Vimeux et al 2008*)

19 cm w.e.  $\text{yr}^{-1}$   
(36 cm snow  $\text{yr}^{-1}$ )

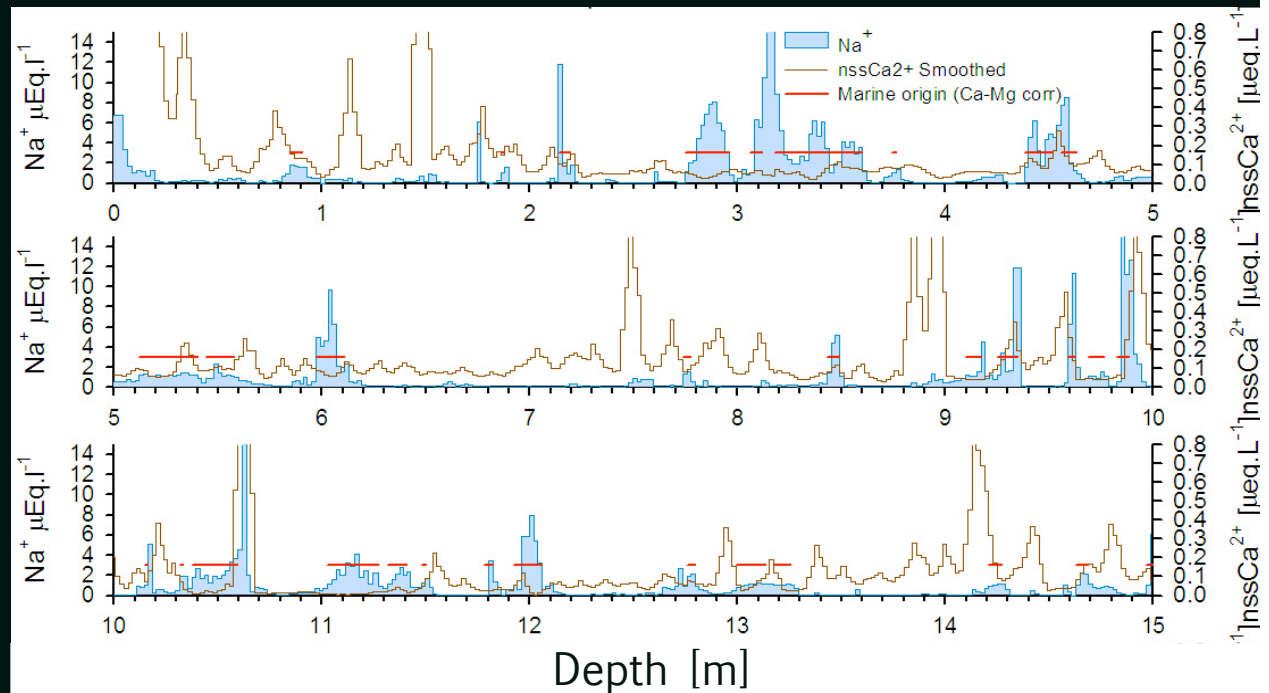


# Main results from the 2005 core:

## 2. Important continental register for a site under marine influence



Alternation of marine  $\text{Na}^+$  & continental  $\text{nssCa}^{2+}$



(Vimeux et al. 2008)

# Hypothesis 2005



## The SANVALLOR project

- Low accumulation + continental signal
- A deep ice core could cover the last millenium
- No years missing
- Marine storms partly eroded
- Continental inputs rather conserved

35°-60°S gap

→ generate  
environmental data

Document southern hemisphere  
mid-latitudes

- climatic variability?
- proxies for paleo environmental reconstructions?
- anthropogenic influence? sources?
- teleconnections ENSO-AAO?

# The SANVALLOR project

2007

- 20 m firn cores (5) → Pollen, algae, ions,  $\delta D$ ,  $\delta^{18}O$
- 50 m ice core
- 70 m ice core → Radiogenic species, metals
- 120 m ice core → Soluble ions,  $\delta D$ ,  $\delta^{18}O$



LGGE, LSCE  
LAMA, LMTG



CECs



U.Bern



# The SANVALLOR project

2007

- 20 m firn cores (5) → Pollen, algae, ions,  $\delta D$ ,  $\delta^{18}O$
- 50 m ice core
- 70 m ice core → Radiogenic species, metals
- 120 m ice core → Soluble ions,  $\delta D$ ,  $\delta^{18}O$



LGGE, LSCE  
LAMA, LMTG



CECs



U.Bern





# Objectives of this work

1. To reconstruct the paleoenvironmental conditions at southern mid-latitudes

- Holocene?
- Source identification

LGGE:

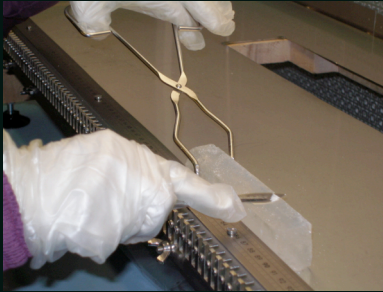
- 120 m core inorganic/organic ions (high resolution)
- Comparison with other available ice-core records

# Objectives of this work

2. To understand the processes responsible of the continental input
  - Air masses origin?
  - Precipitation conditions?

University of Chile, Geophysics Department :  
Backtrajectories + precipitation

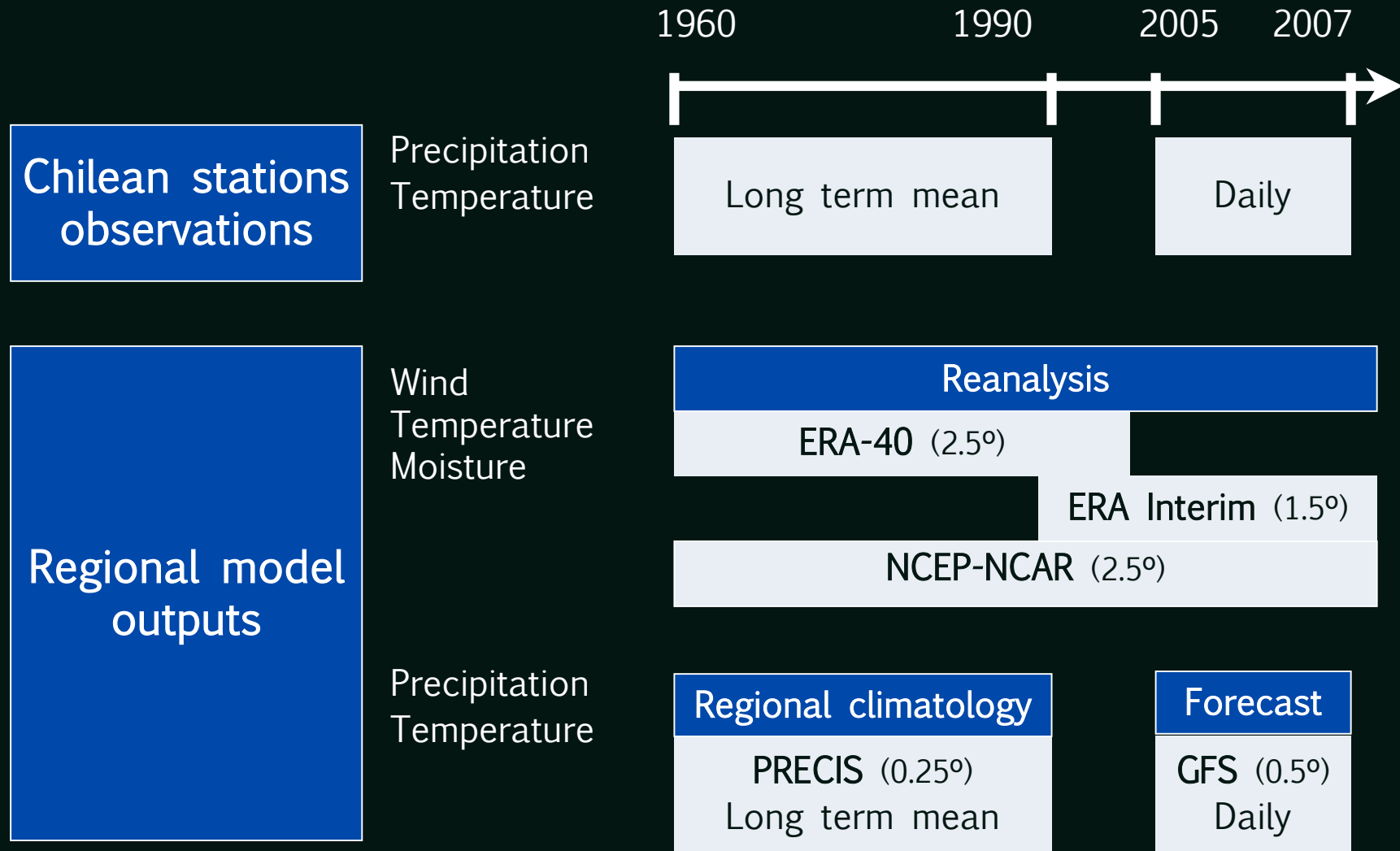
# Ion chromatography (IC)



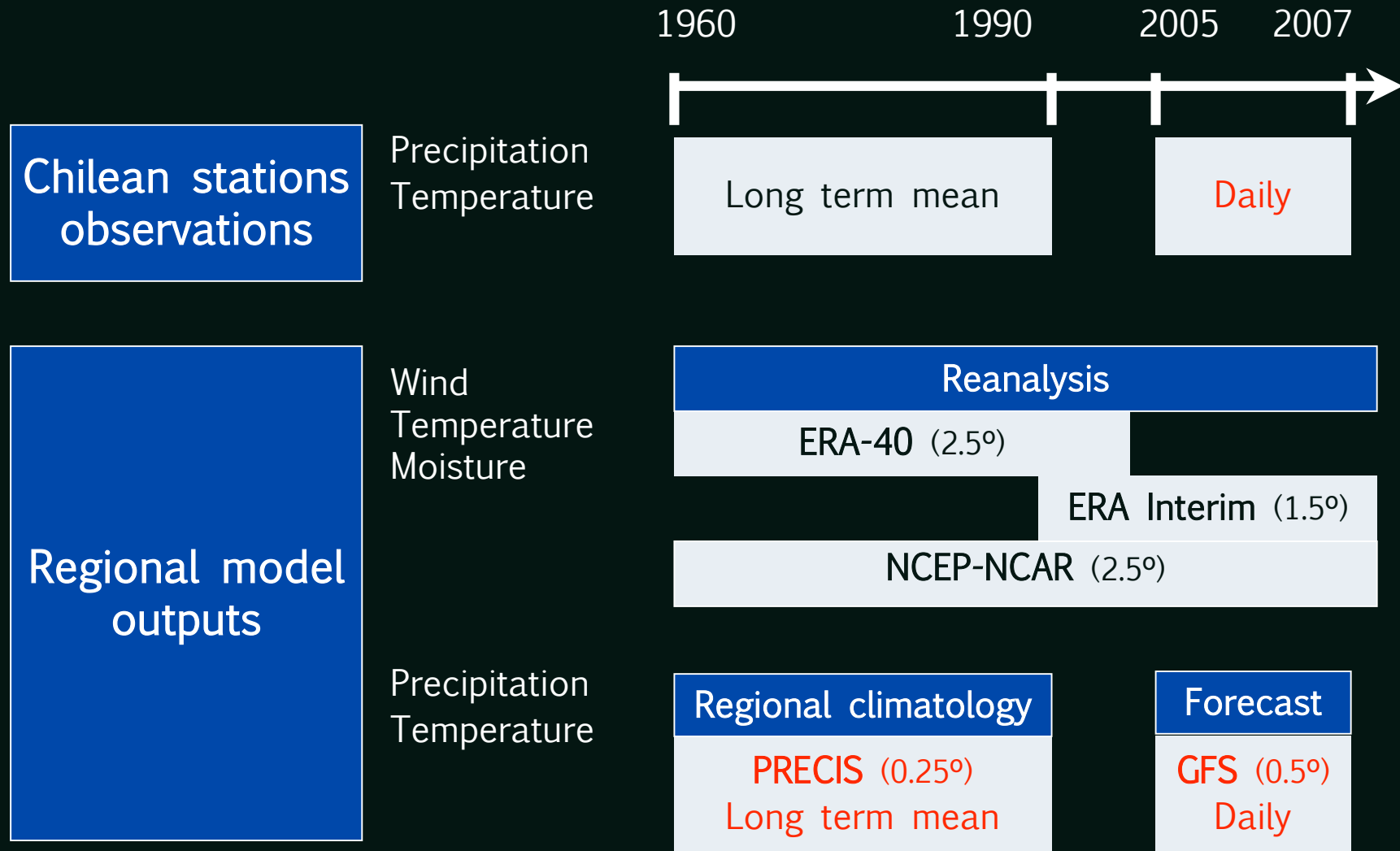
- Decontamination
- Soluble ions trace & ultratrace level: ng/g
  - Major ions  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ...
  - Other trace ions:  $\text{K}^+$ ,  $\text{Br}^-$ ,  $\text{NO}_2^-$ , mono and dicarboxylic acids

87 meters of ice  
> 4000 samples  
> 1 year analyses

# Datasets



# Datasets



# Plan

- Climate basis for the archive interpretation
- Complete chemical profile 2007 + comparison with 15m shallow core
- Marine contributions
  - Primary aerosol & biogenic (sources + seasonality)
- Continental contributions
  - Events (type + seasonality?)
  - Background trends

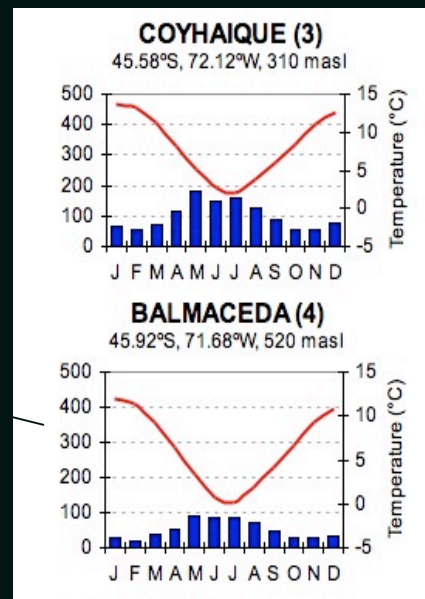
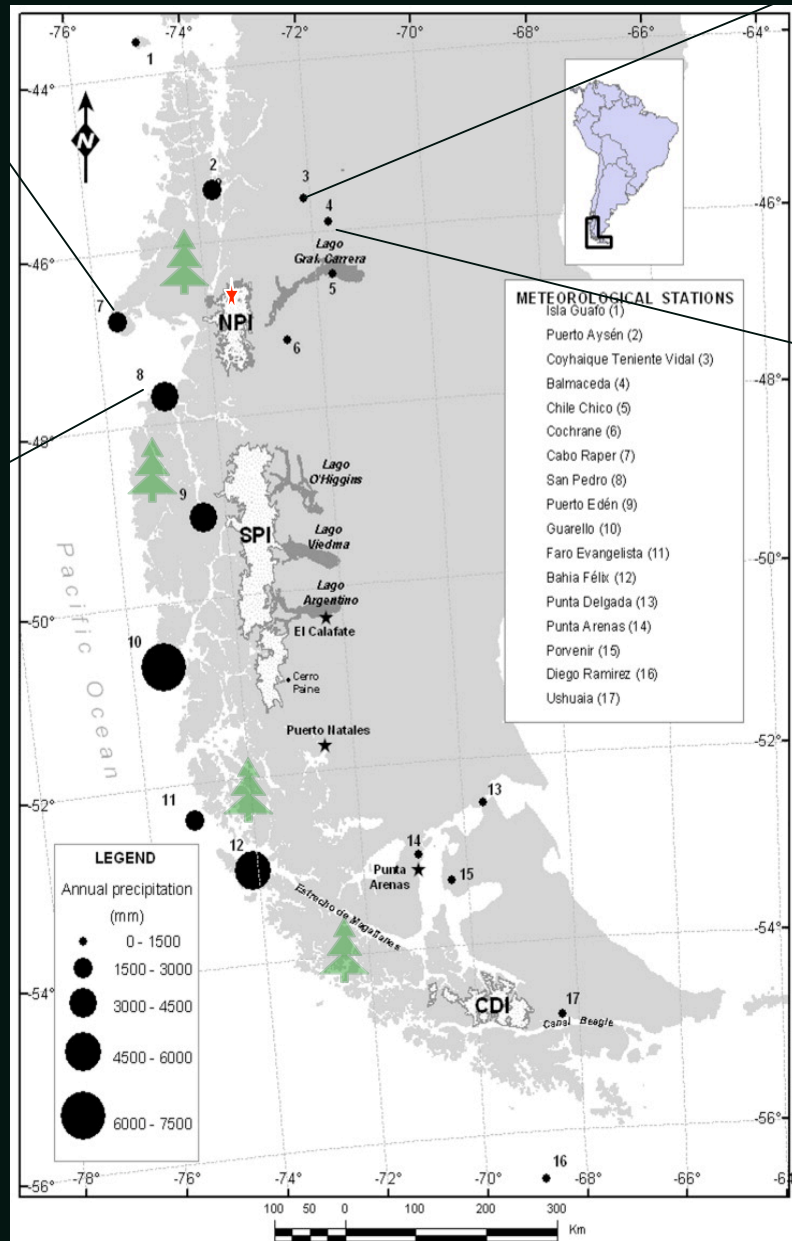
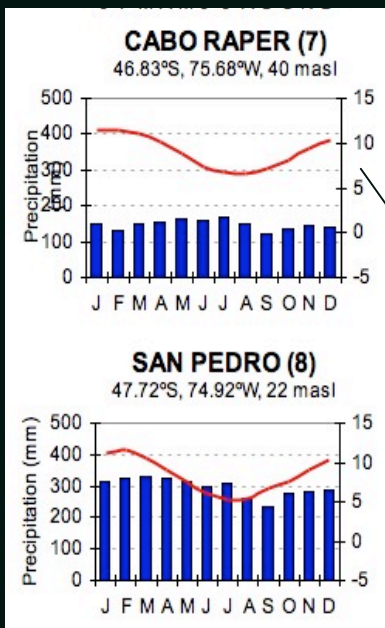
Climatology

120 m  
ice-core

Marine  
contribution

Continental  
contribution

Conclusions



$\delta D, \delta^{18}O =$   
seasonal  
temperature  
cycles  
(stations)

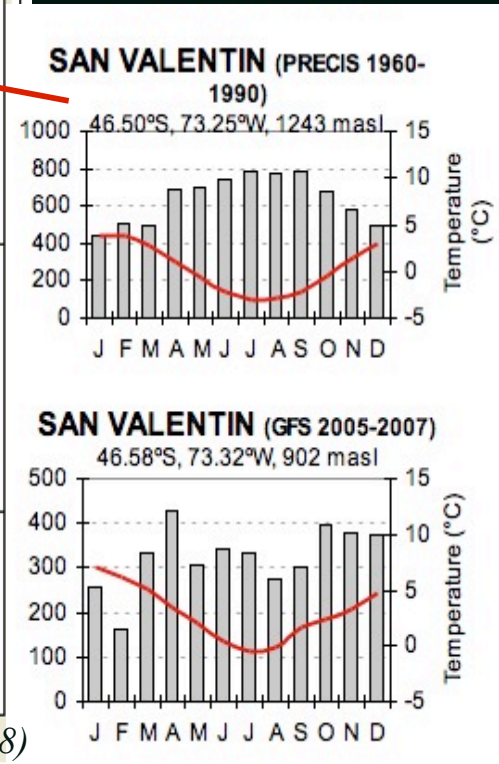
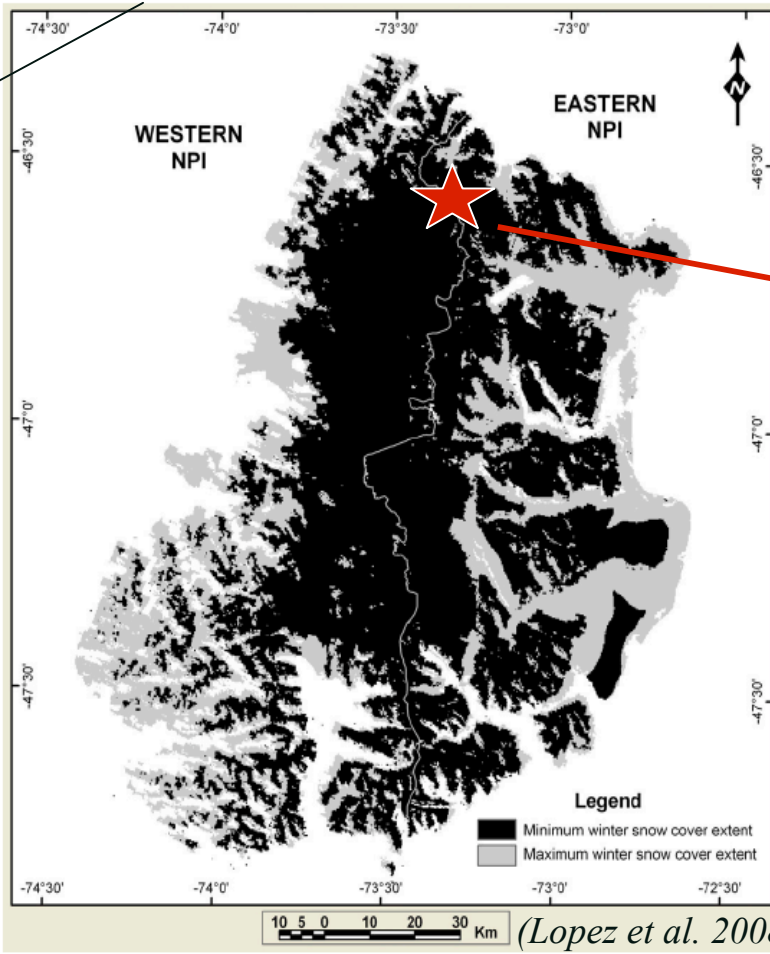
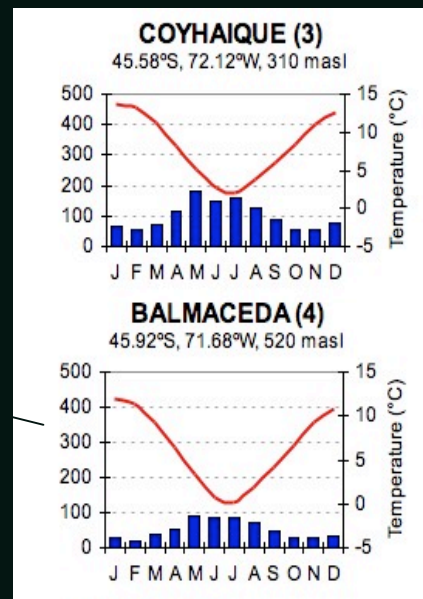
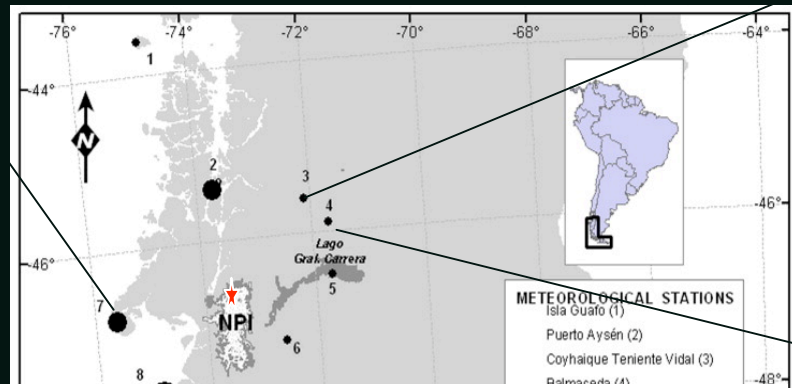
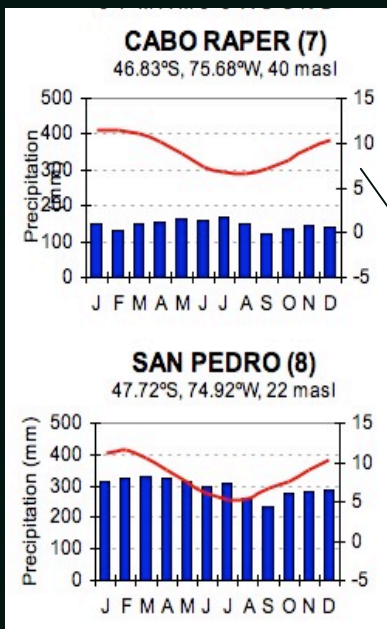
Climatology

120 m ice-core

Marine contribution

Continental contribution

Conclusions

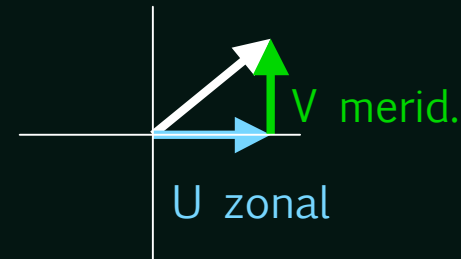


Annual pp  
4000 to  
8000 mm

(Lopez et al. 2008)



# Precipitation events vs. wind speed (GFS)

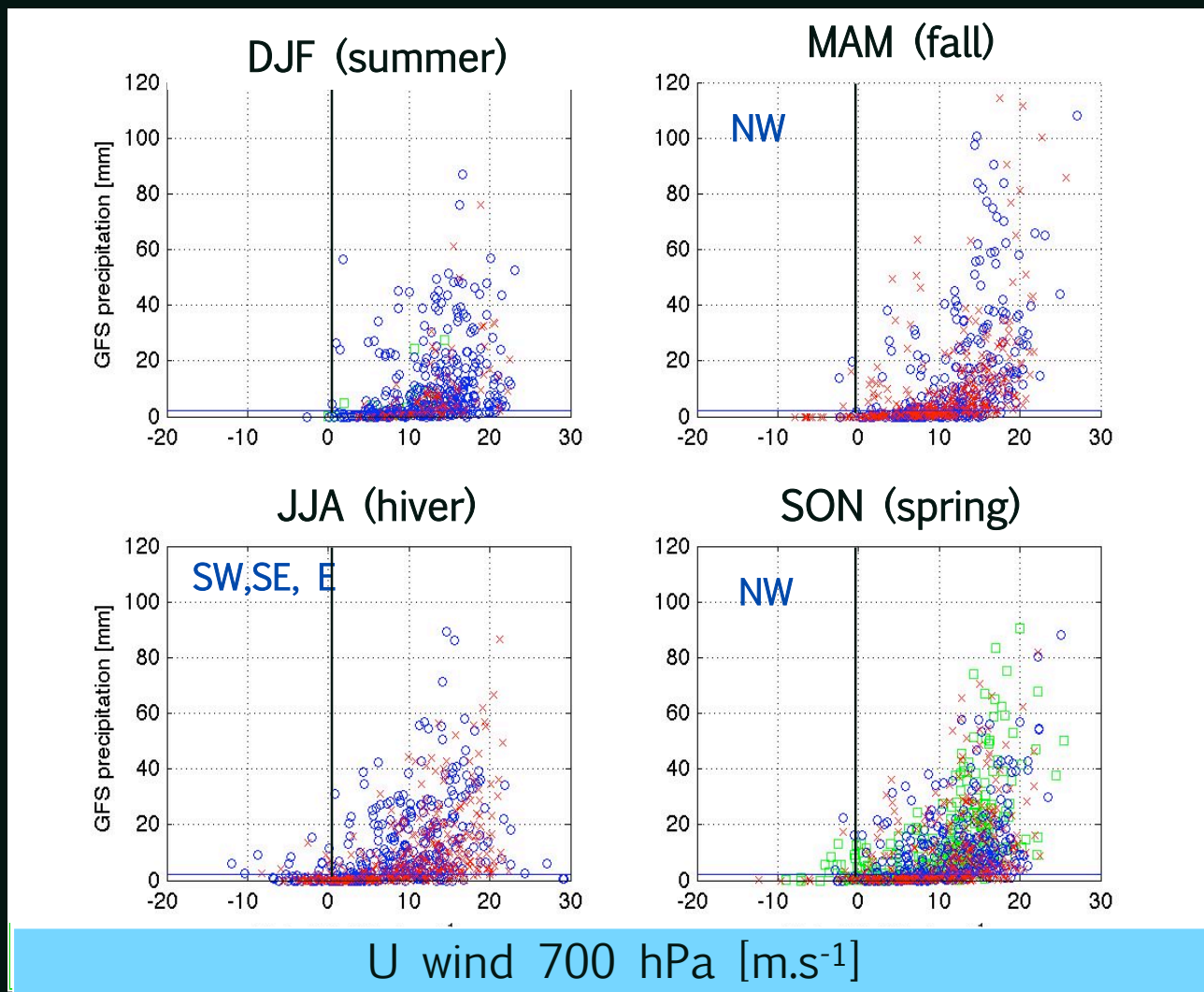


120 m ice-core

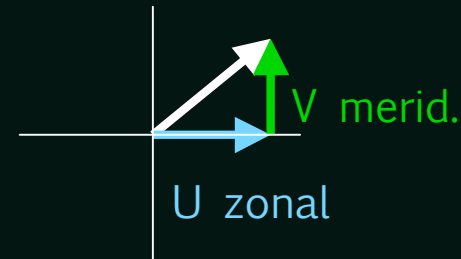
Marine contribution

Continental contribution

Conclusions



# Precipitation events vs. wind speed (GFS)

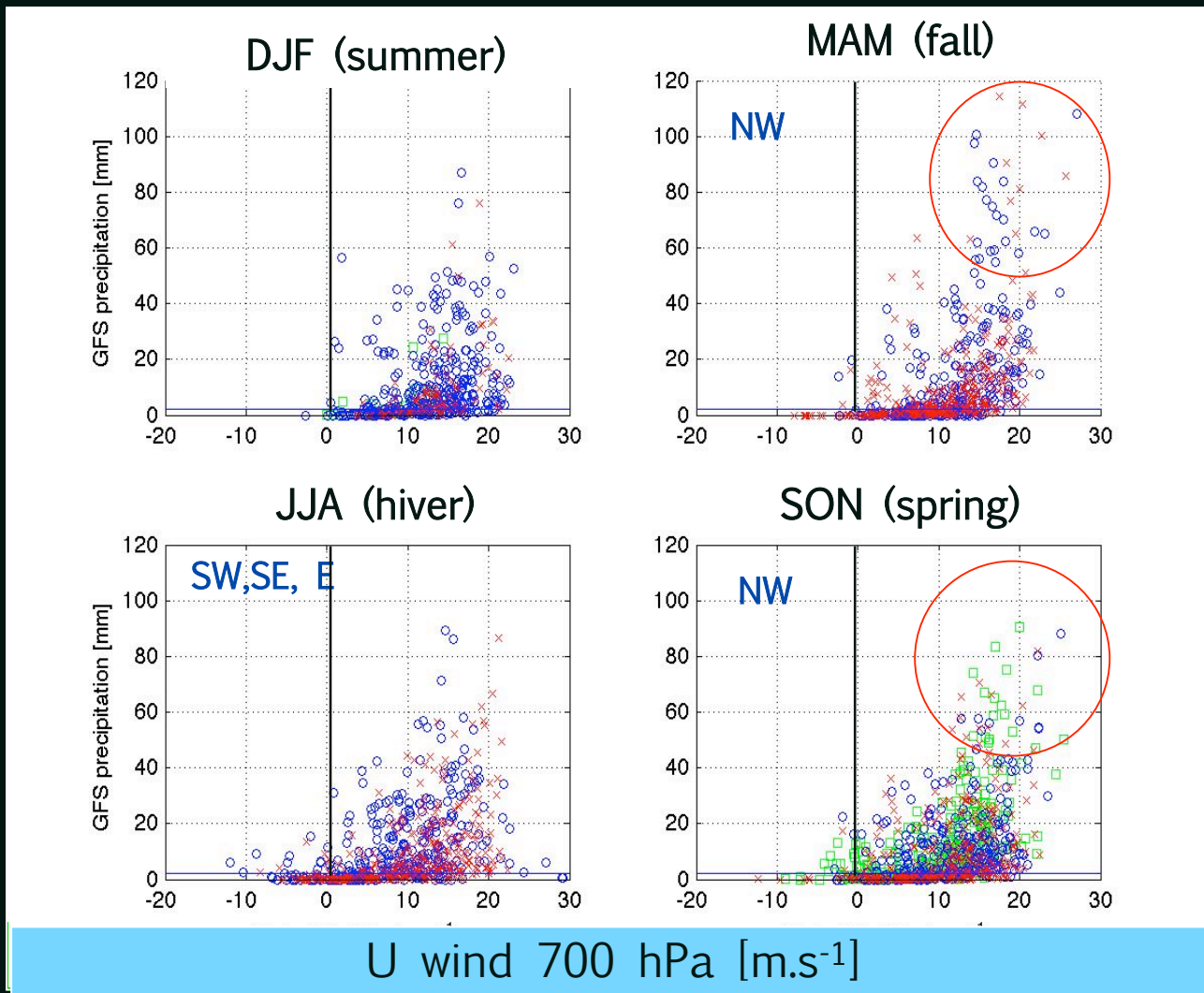


120 m ice-core

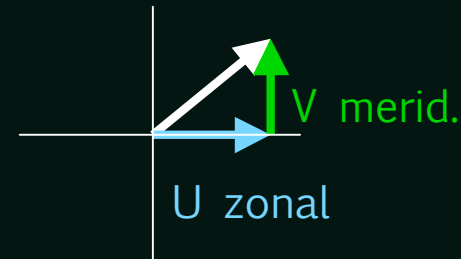
Marine contribution

Continental contribution

Conclusions



# Precipitation events vs. wind speed (GFS)

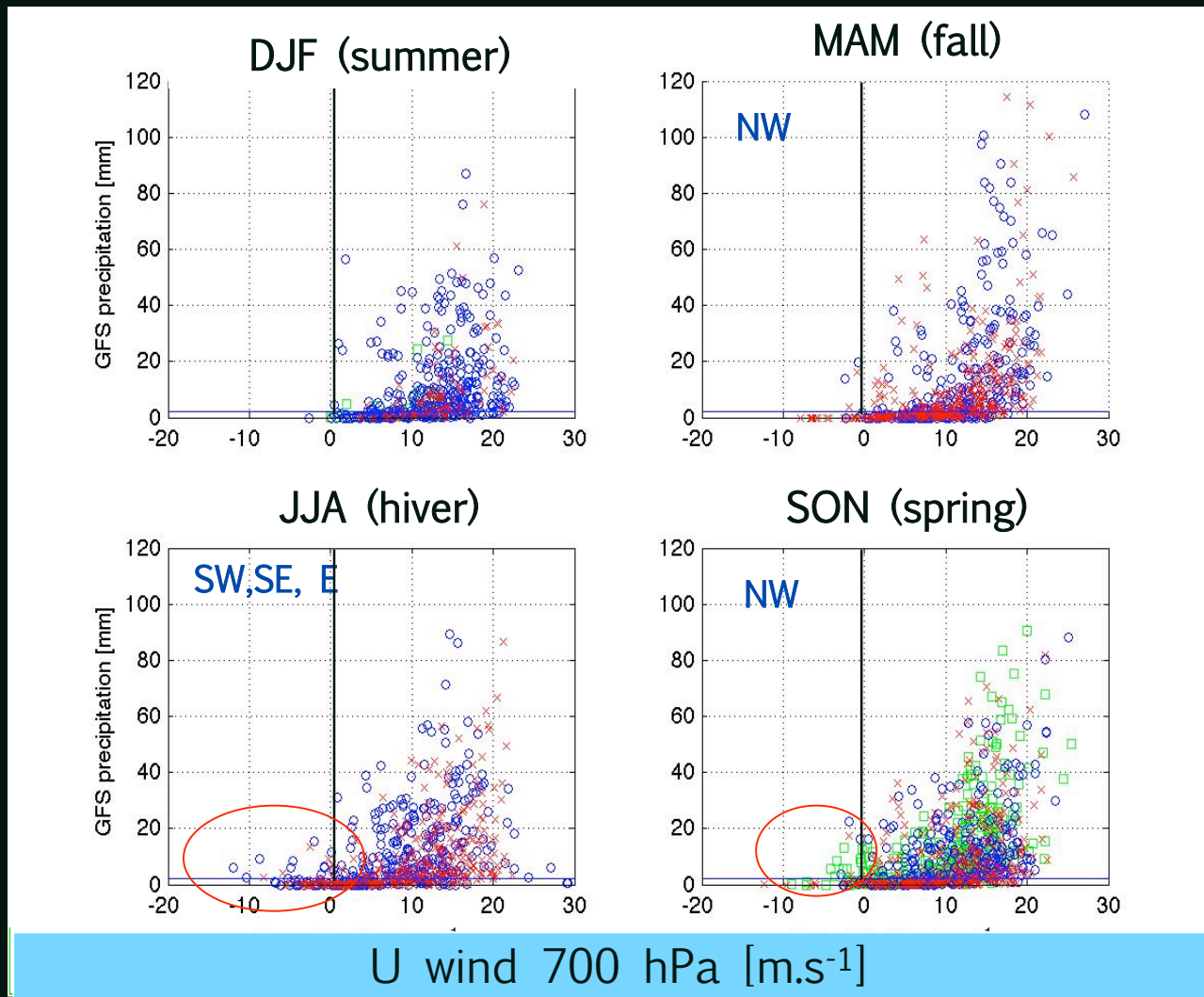


120 m ice-core

Marine contribution

Continental contribution

Conclusions



# Direction

2005-2007

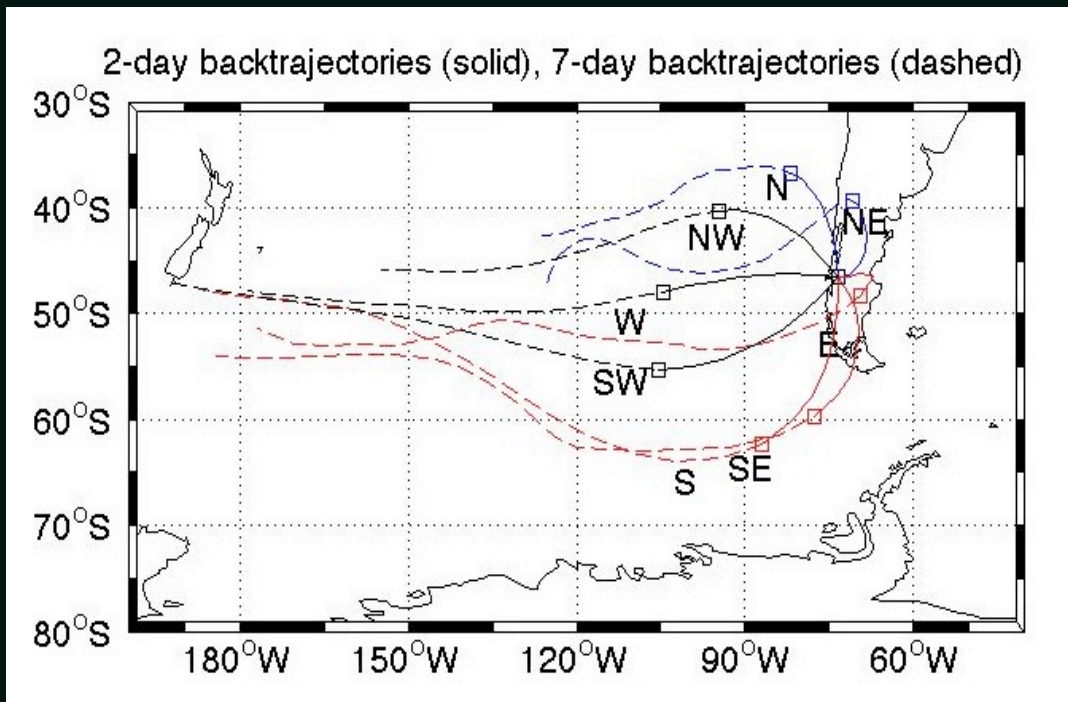
120 m ice-core

NCEP-NCAR  
backtrajectories  
Approximate (regional)

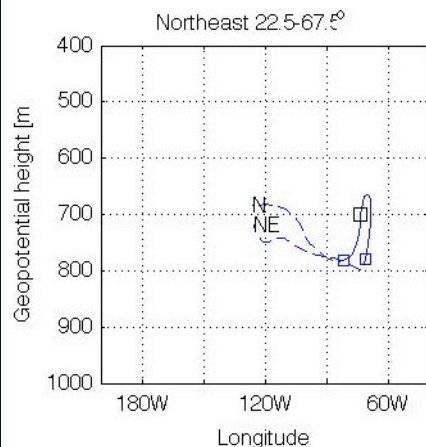
Marine contribution

Continental contribution

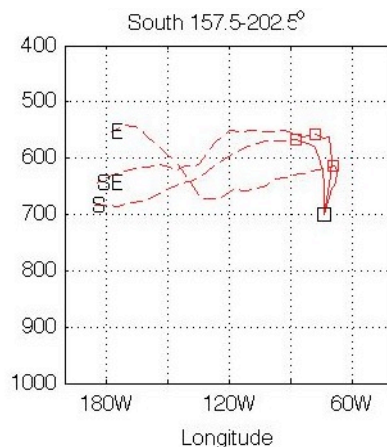
Conclusions



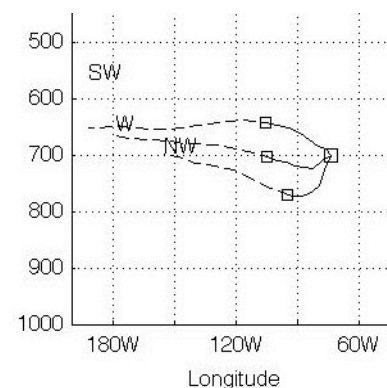
3% N, NE



5% E, SE, S



92% SW, W, NW



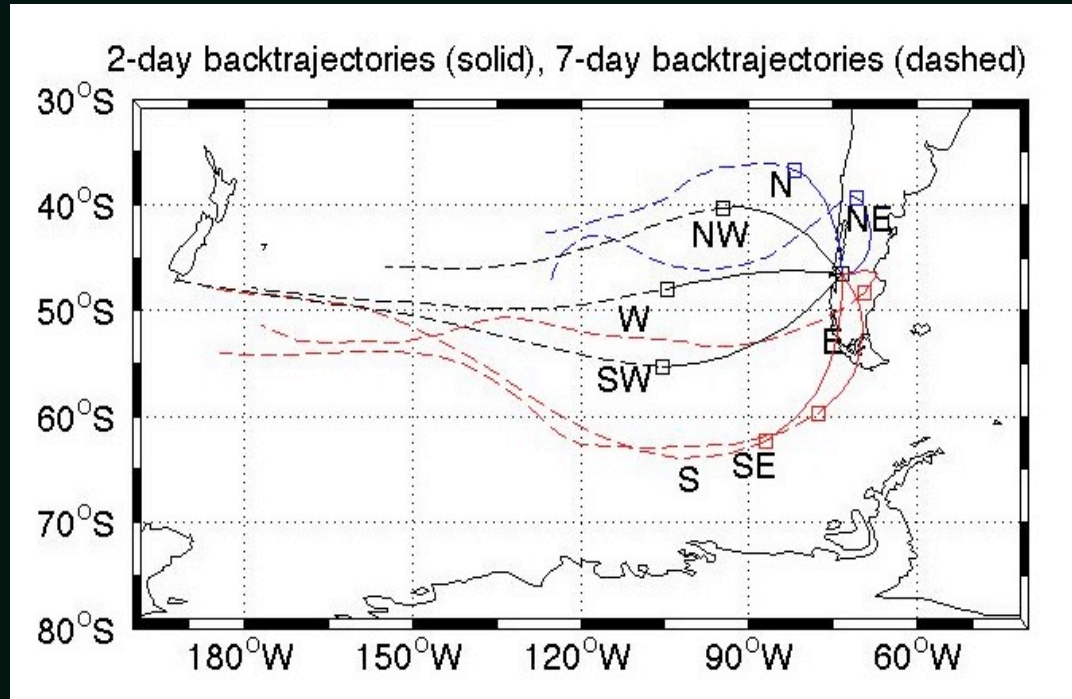
# Direction

120 m ice-core

Marine contribution

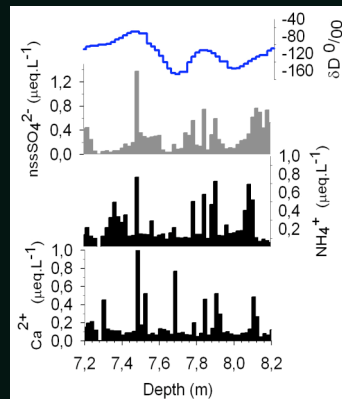
Continental contribution

Conclusions



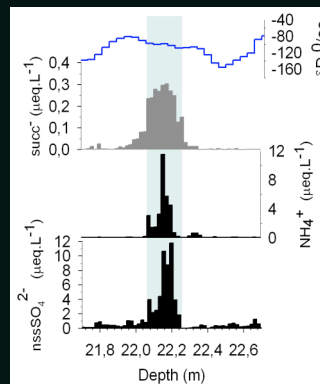
Easterly transport

NO precipitation  
Dry deposit



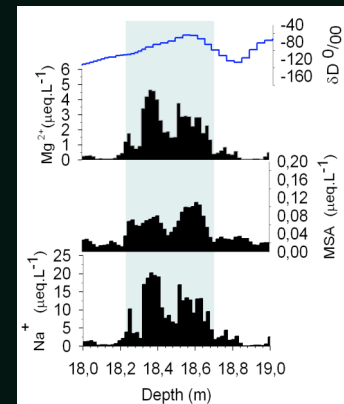
Northerly: NW, N

Continental  
Wide peaks



Westerly: W, NW, SW

Marine storms  
Wide peaks



# Conserved signal

120 m  
ice-core

Wide peaks: not seasons but events

- 19 cm w.e. Mean net accumulation
- 11 cm w.e. A single large biomass burning event
- 25 cm w.e. A single large marine event

Marine  
contribution

Continental contribution: S, NE, N, NW

Continental  
contribution

Lower precipitation / dry deposit  
Lower zonal wind → conservation

Important wind blowing

Conclusions

But no missing years.

Climatology

120 m  
ice-core

Marine  
contribution

Continental  
contribution

Conclusions

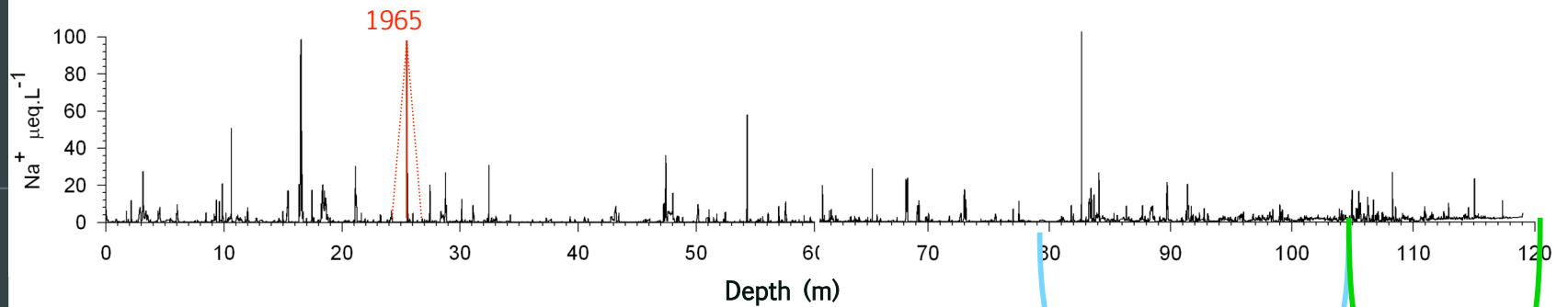
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# Chemical analysis

Climatology

# Chemical profile 120 m

120 m  
ice-core



Marine  
contribution

$^3\text{H}$ ,  $\beta$ ,  $\gamma$

Brittle  
zone

Older ice  
max. age 4ky  
( $\delta^{18}\text{O}$  air)

Continental  
contribution

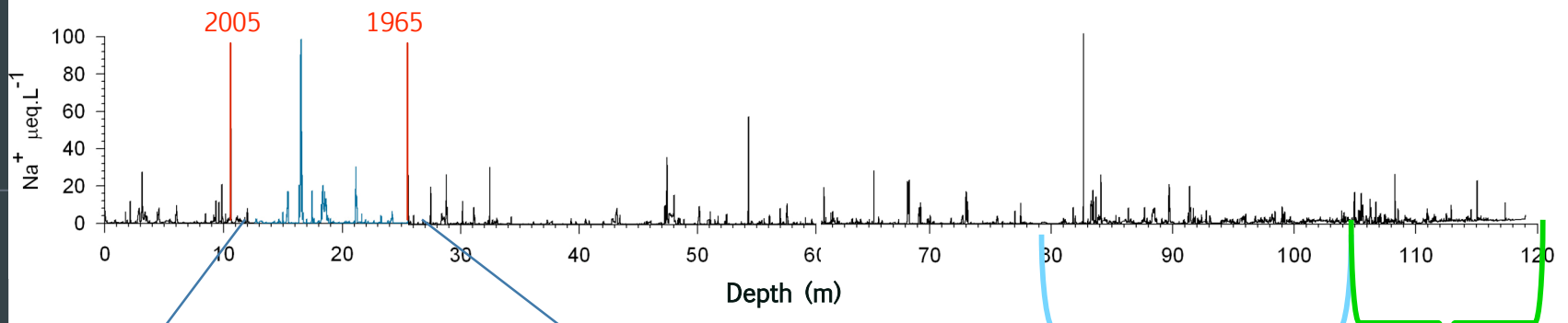
Conclusions



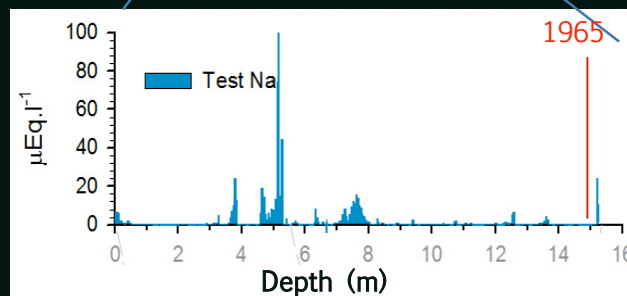
Climatology

# Chemical profile 120 m

120 m ice-core



Marine contribution



Continental contribution

Brittle zone

Older ice  
max. age 4ky  
( $\delta^{18}\text{O}$  air)

Conclusions

- Reliable paleo-register
- 12-meter of snow between both profiles

Climatology

120 m  
ice-core

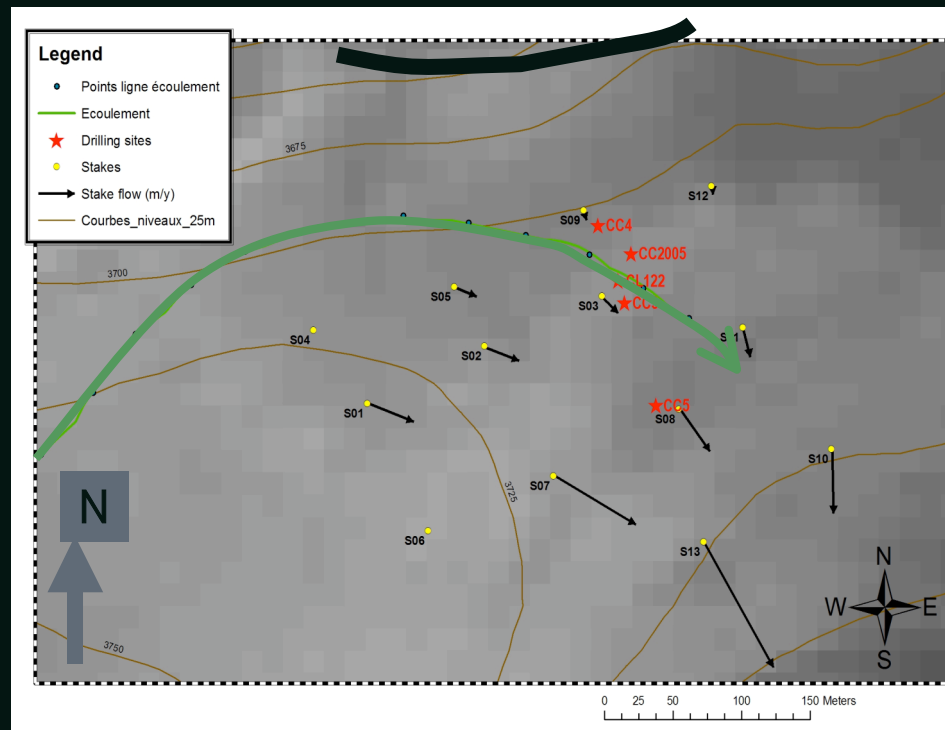
Marine  
contribution

Continental  
contribution

Conclusions



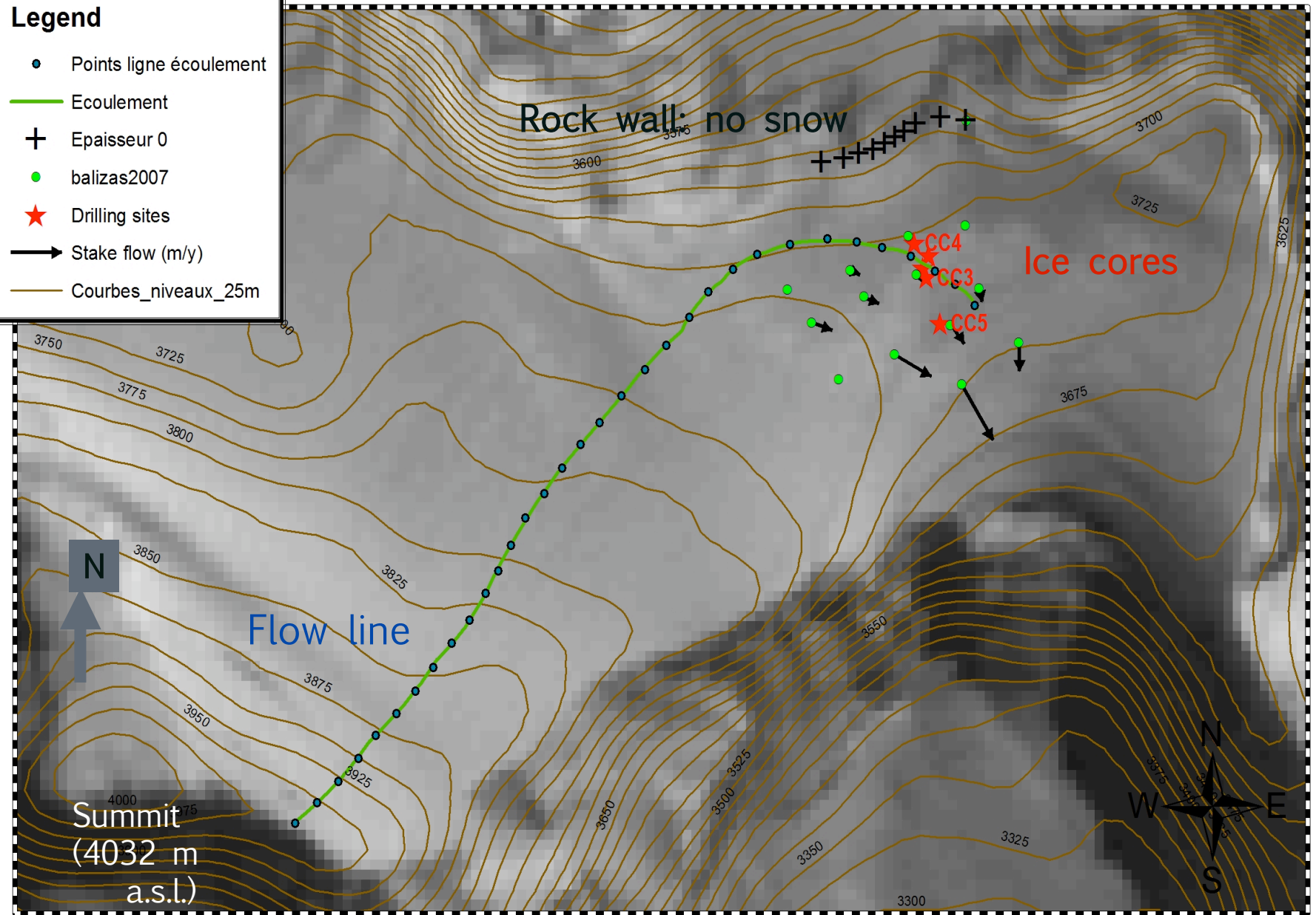
Current  
hypothesis:  
Geophysical  
effect



Spatial  
variation of  
the net  
accumulation

### Legend

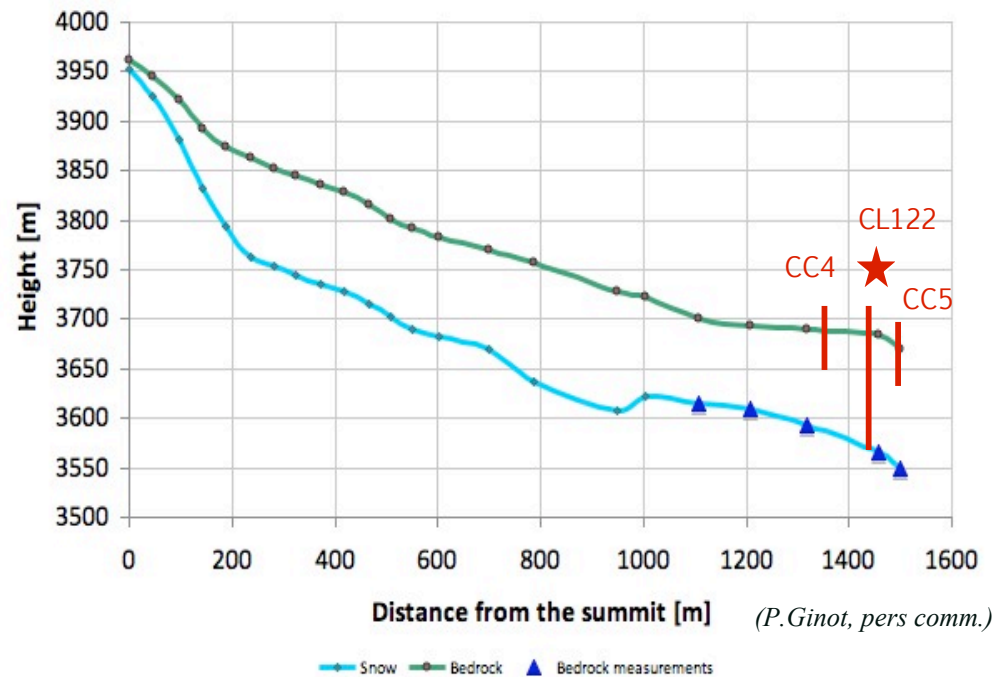
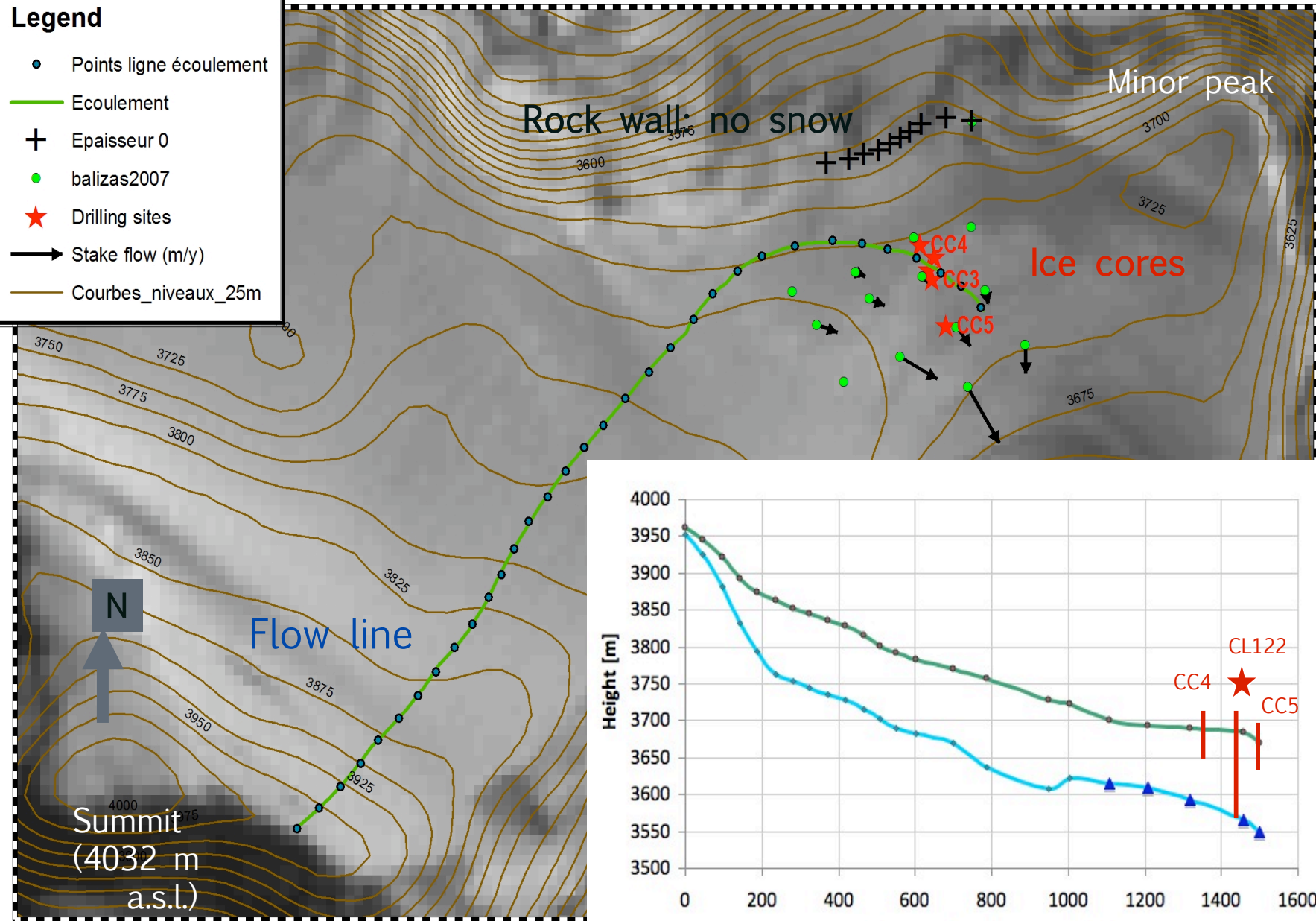
- Points ligne écoulement
- Ecoulement
- + Epaisseur 0
- balizas2007
- ★ Drilling sites
- Stake flow (m/y)
- Courbes\_niveaux\_25m



0 100 200 400 600 Meters comm.)

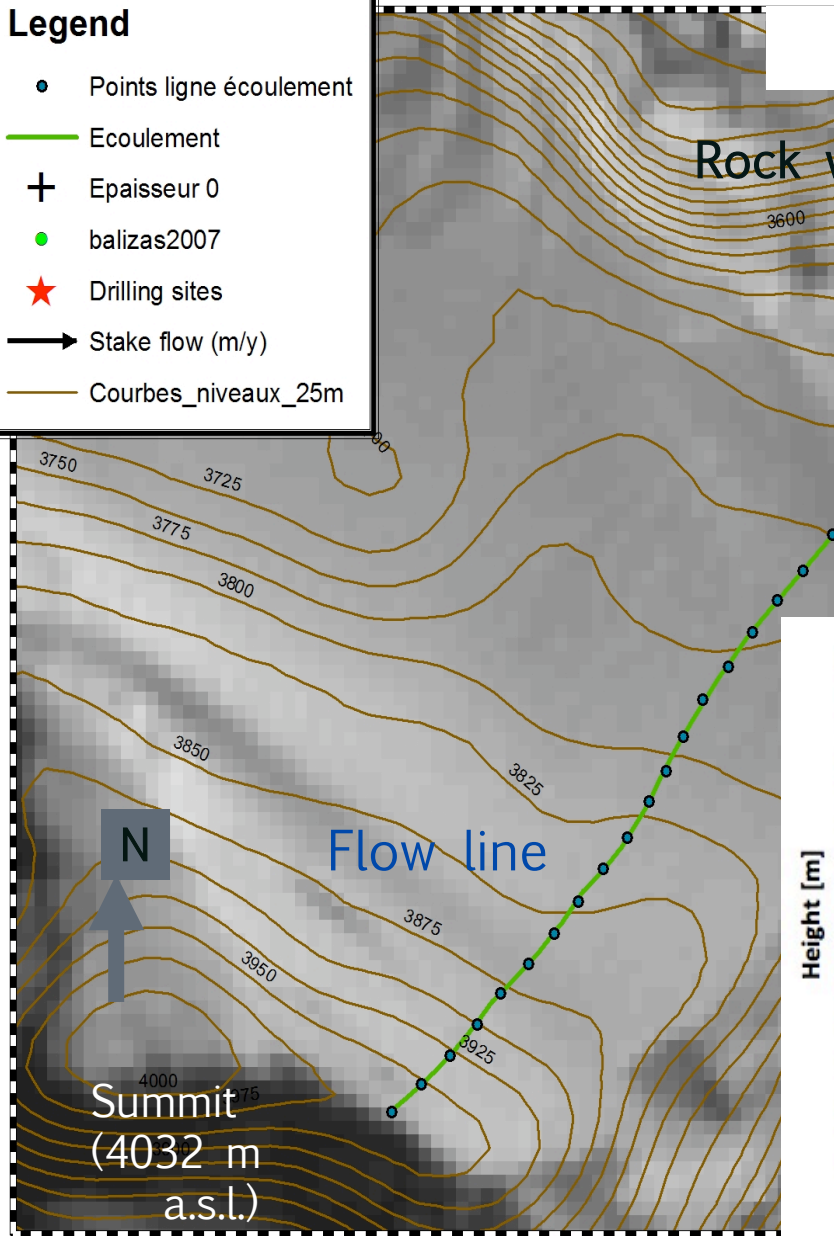
### Legend

- Points ligne écoulement
- Ecoulement
- + Epaisseur 0
- balizas2007
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- Courbes\_niveaux\_25m

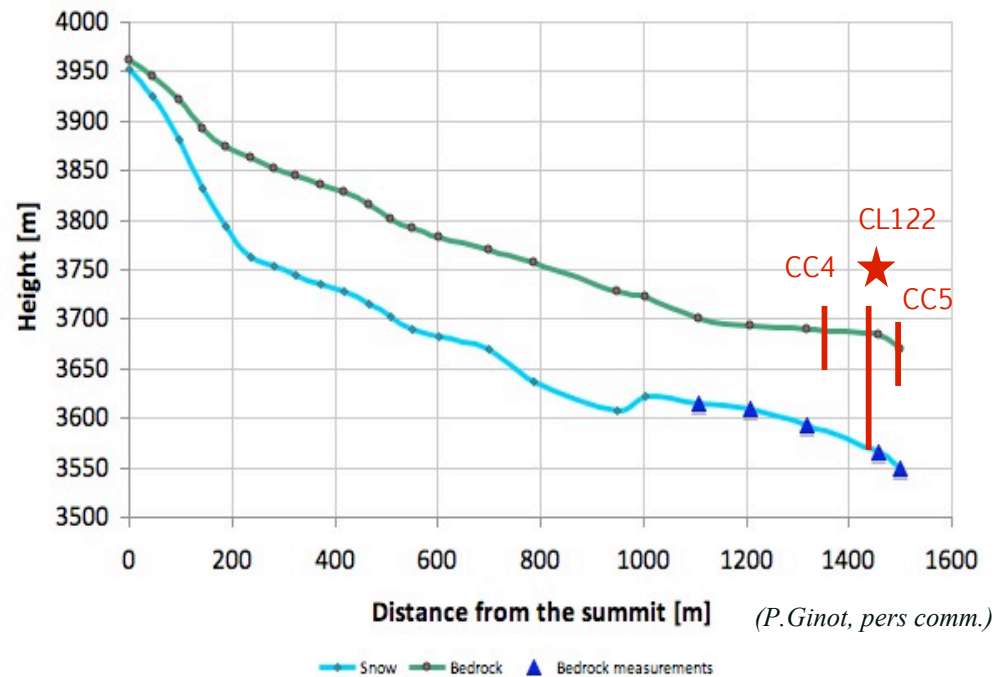
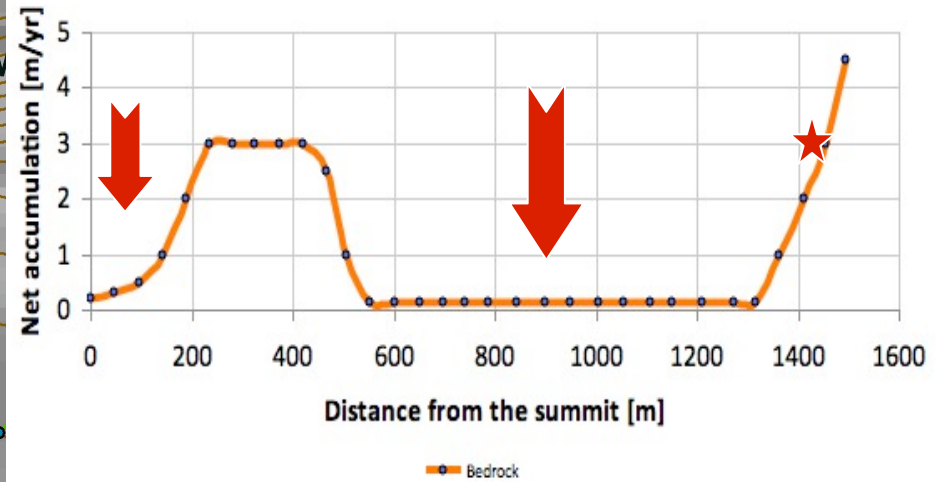


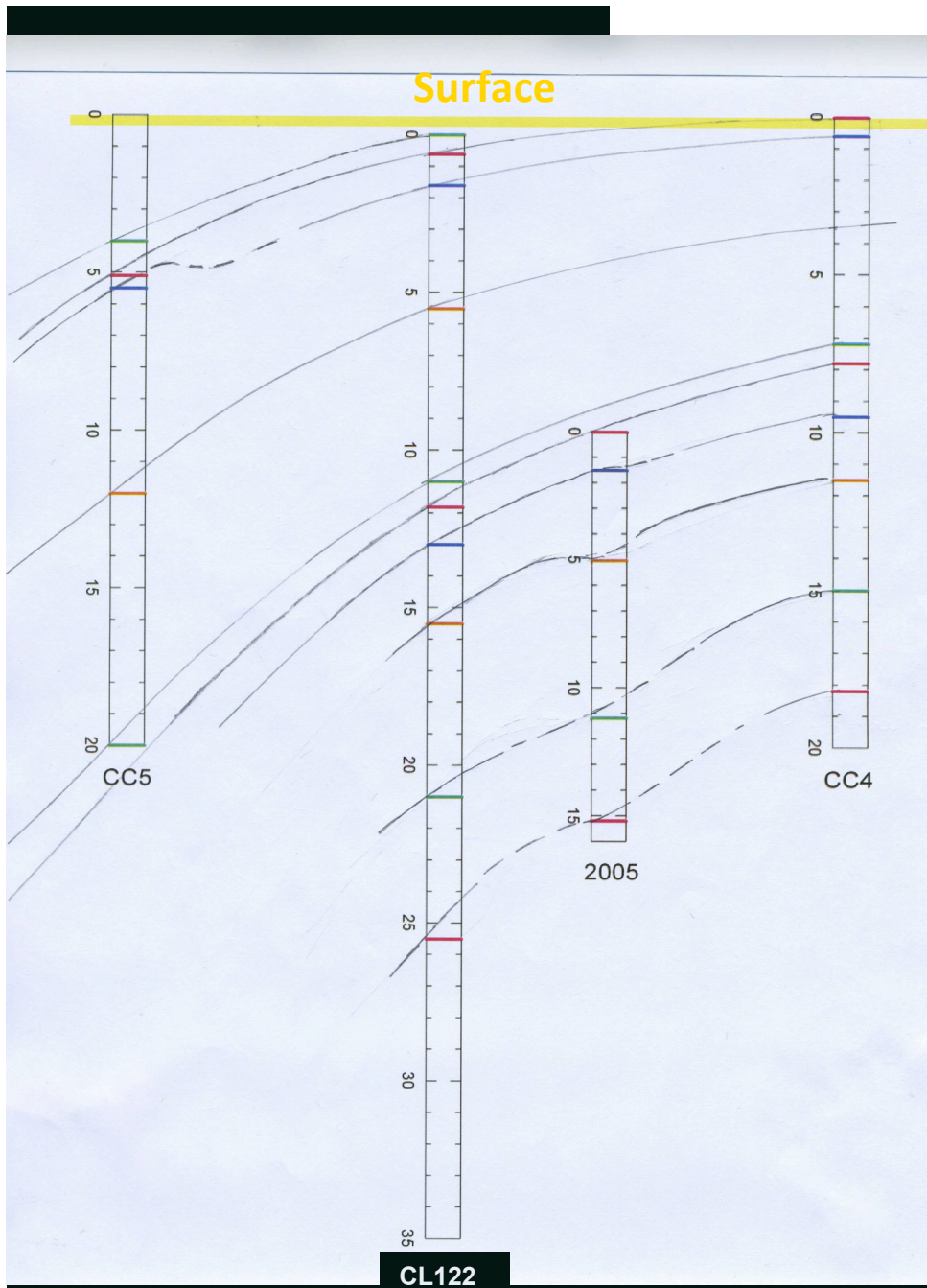
### Legend

- Points ligne écoulement
- Ecoulement
- ⊕ Epaisseur 0
- balizas2007
- ★ Drilling sites
- Stake flow (m/y)
- Courbes\_niveaux\_25m

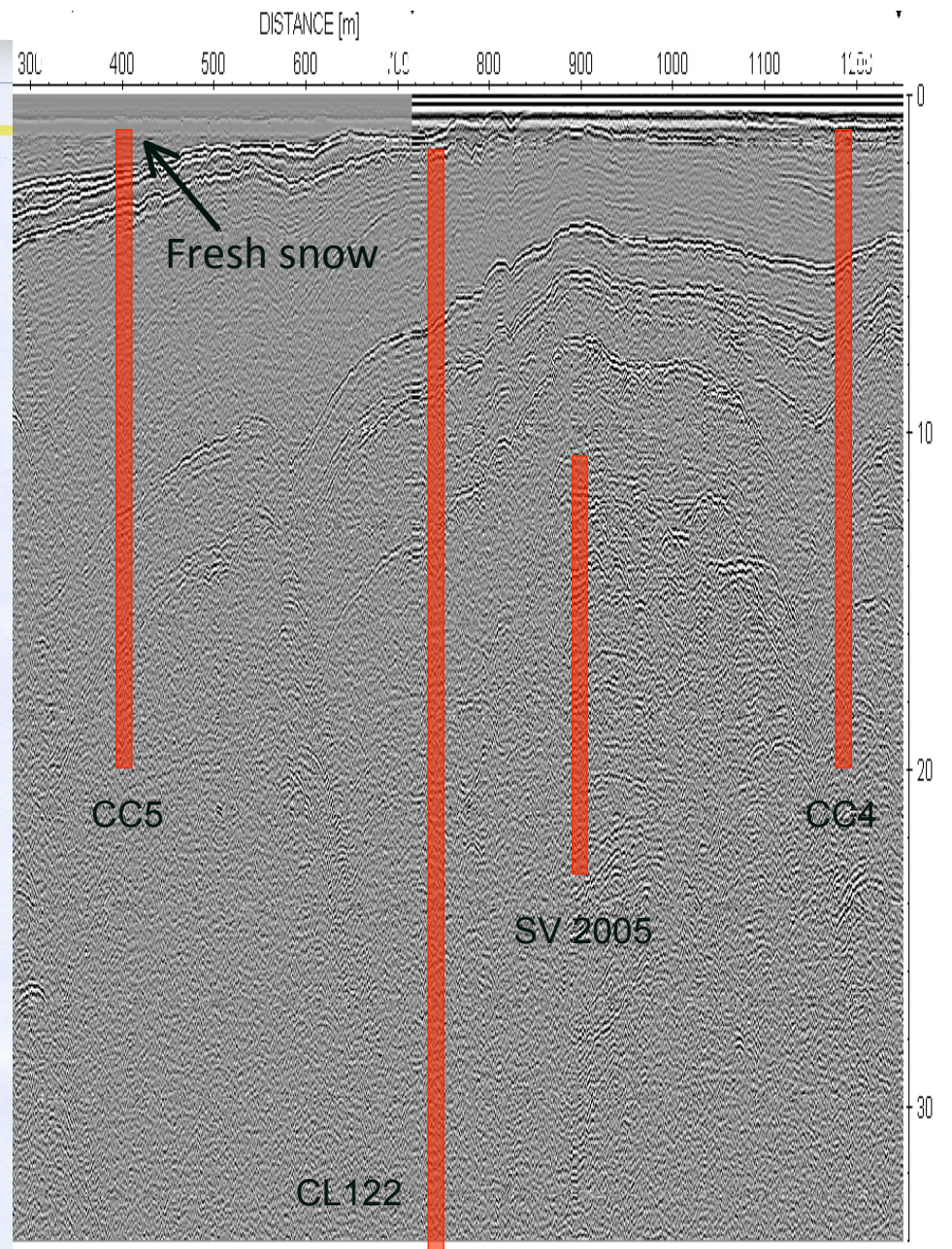


### Estimated net accumulation





(M. de Angelis, pers comm.)



(G. Cassasa, pers comm.)

# Implications

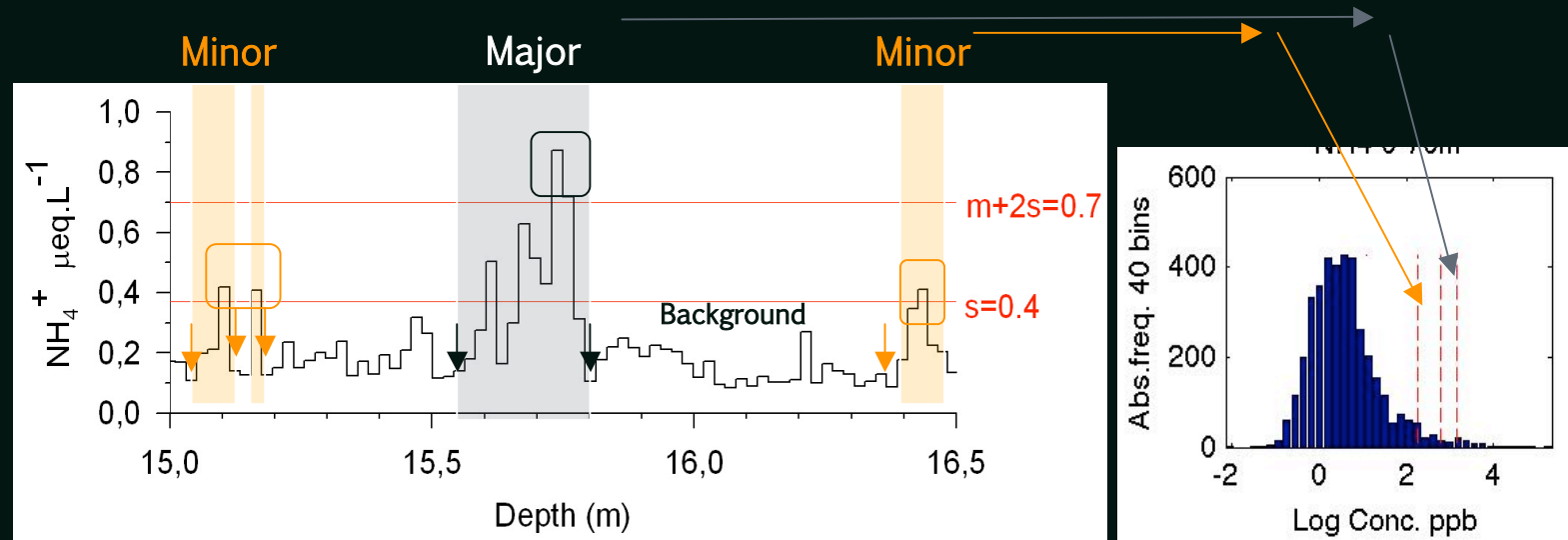
- Glaciological study ongoing: elements for dating
- This work:
  - Events
  - Sources identification + transport
  - Possible dating horizons

# Methodology

- Proxies:
  - Marine:  $\text{Na}^+$ , MSA
  - Continental:  $\text{NH}_4^+$ ,  $\text{nssSO}_4^{2-}$ ,  $\text{nssCa}^{2+}$ ,  $\text{F}^-$
- Peak sorting

Marine contribution

Continental contribution



Conclusions

- Correlation matrices



Climatology

120 m  
ice-core

Marine  
contribution

Continental  
contribution

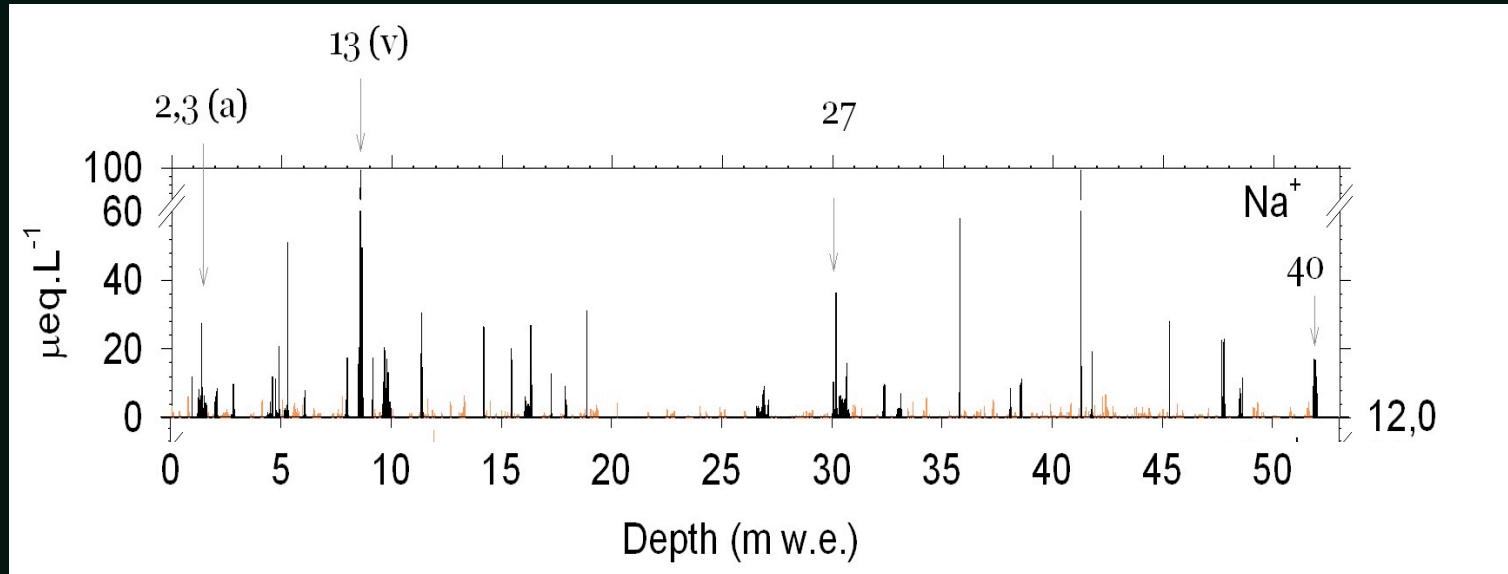
Conclusions

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# The marine component

# Primary marine inputs

120 m ice-core



Marine contribution

Continental contribution

Bubble bursting:  
primary marine aerosol  
 $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , ...

- Uplift by cyclonic perturbations
- Transport by Westerlies

Conclusions

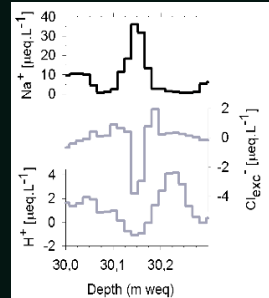
	$[\text{Na}^+] \mu\text{eq.L}^{-1}$
16°S Coropuna	0.8
46°S San Valentin	1.4
65°S James Ross I.	~5

$\text{Na}^+$  peak → marine storm  
~30 % of the register

# Primary marine inputs

120 m ice-core

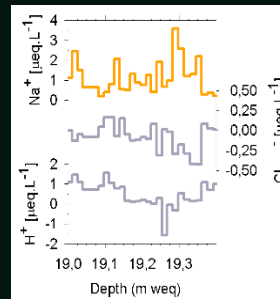
Major peaks



Na<sup>+</sup>, Cl<sup>-</sup>, Mg<sup>2+</sup> ...  
Na/Cl close to sea water  
→ fast transport

Marine contribution

Minor peaks



Na<sup>+</sup>, Cl<sup>-</sup>, Mg<sup>2+</sup> ...

NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>

Continental contribution

Background

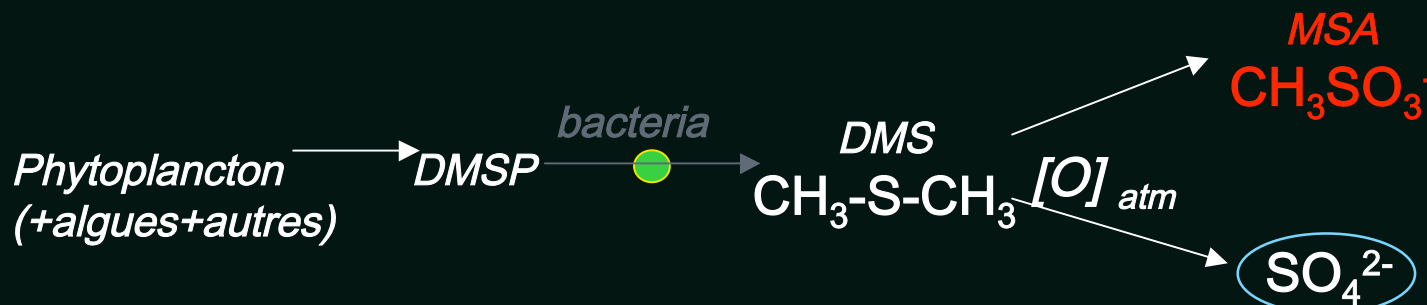
Organic species  
NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>

Conclusions

Climatology

# Marine biogenic aerosol

120 m ice-core



Fraction not related to sea-salt:

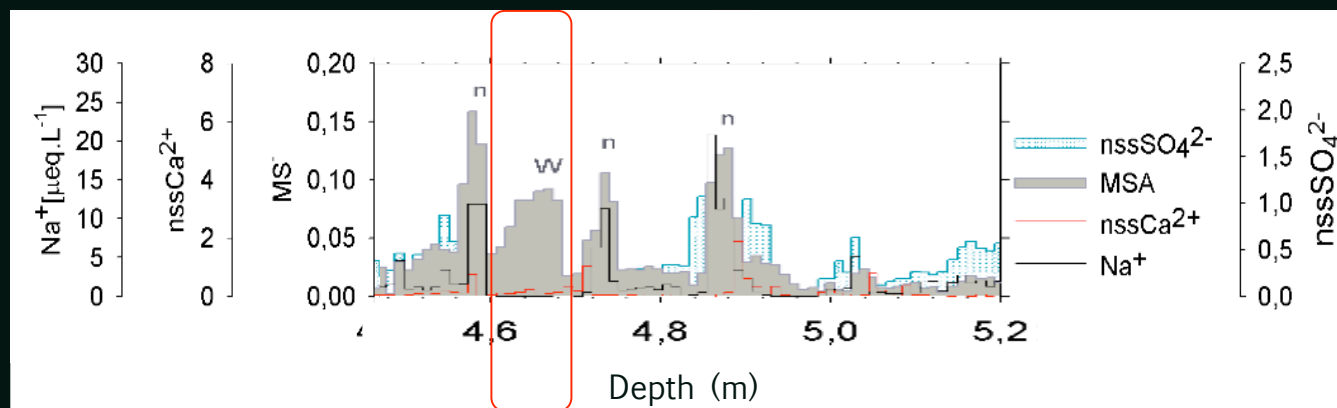
$$[nssSO_4^{2-}] = [SO_4^{2-}]_T - R_{BSW} * [Na^+]$$

Many sources

Marine contribution

Continental contribution

Conclusions



Climatology

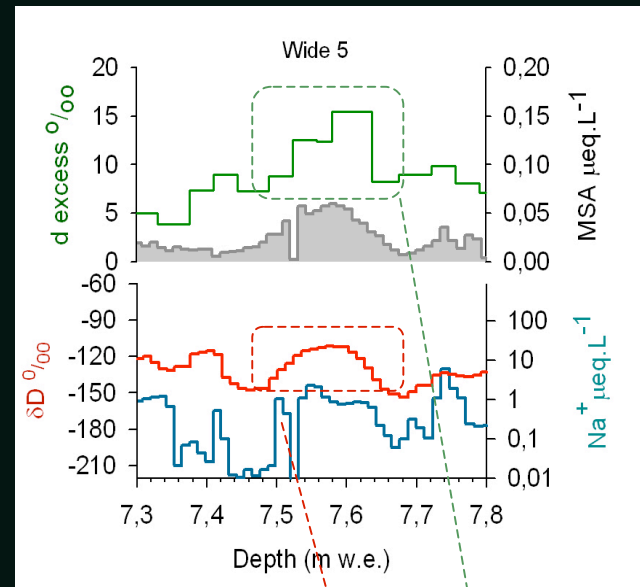
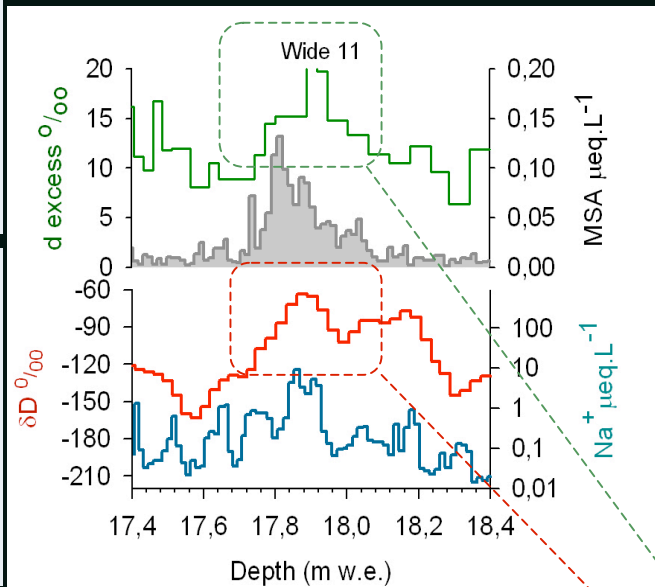
# Marine biogenic aerosol origin?

120 m ice-core

Marine contribution

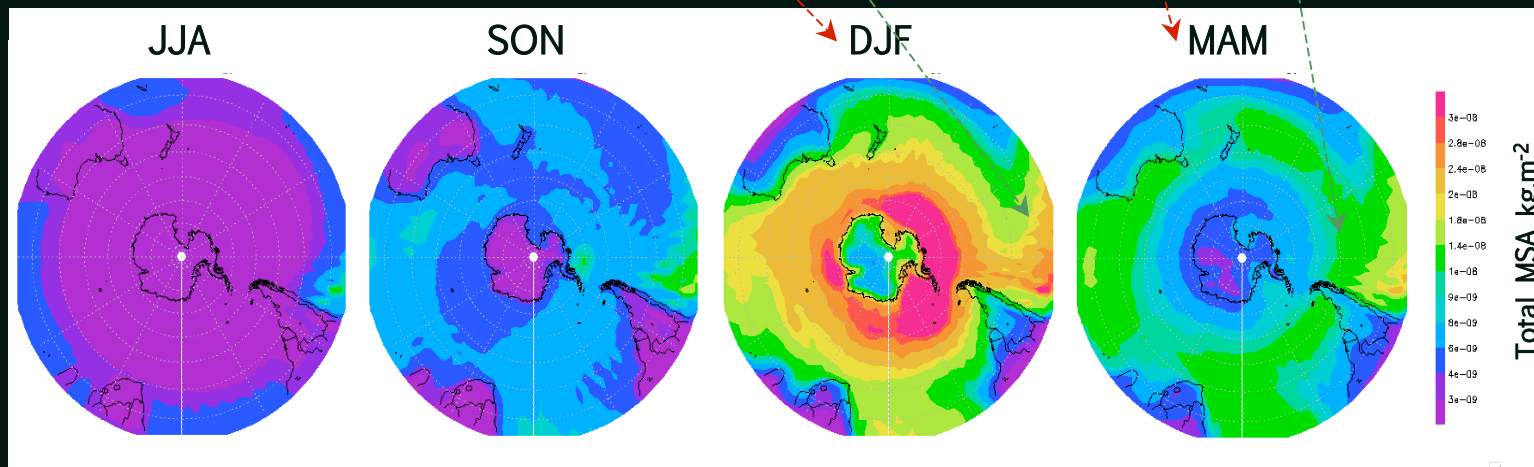
Source?

Regional T?



Continental contribution

Conclusions

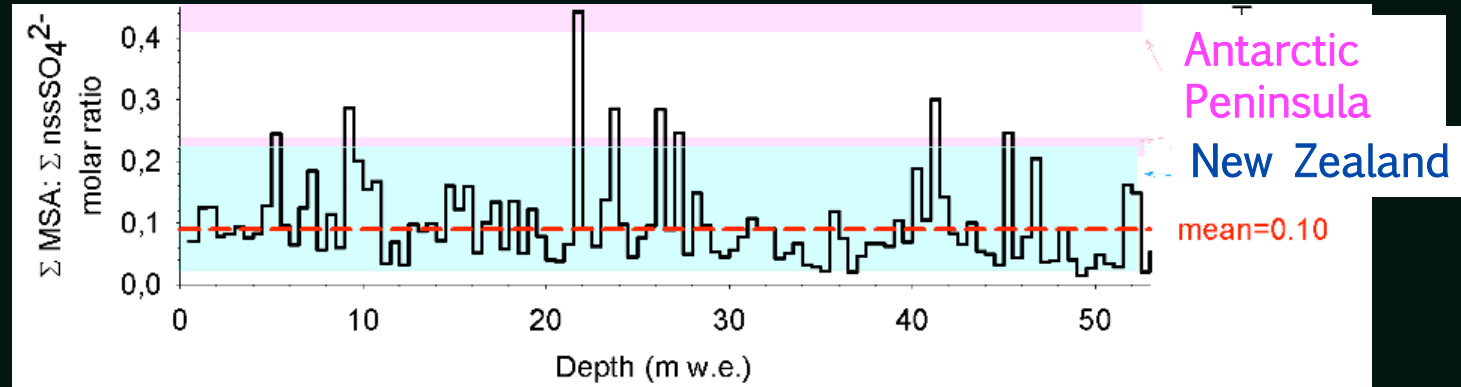


MOCAGE simulations (M.Ménégoz, pers. comm.)

Climatology

# Secondary marine aerosol

120 m ice-core



Marine contribution

MSA:nssSO<sub>4</sub><sup>2-</sup> = 0.10 - 0.16 (molar)  
→ mid-latitudes

Continental contribution

>90% marine transport expected  
45% important contributions observed  
30% Na  
15% MSA

Conclusions

Climatology

120 m  
ice-core

Marine  
contribution

Continental  
contribution

Conclusions

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# The continental component

Climatology

# Continental inputs

120 m  
ice-core

- $nssCa^{2+}$ 
  - almost insoluble
  - 5-20% IC/ICPMS

Marine  
contribution

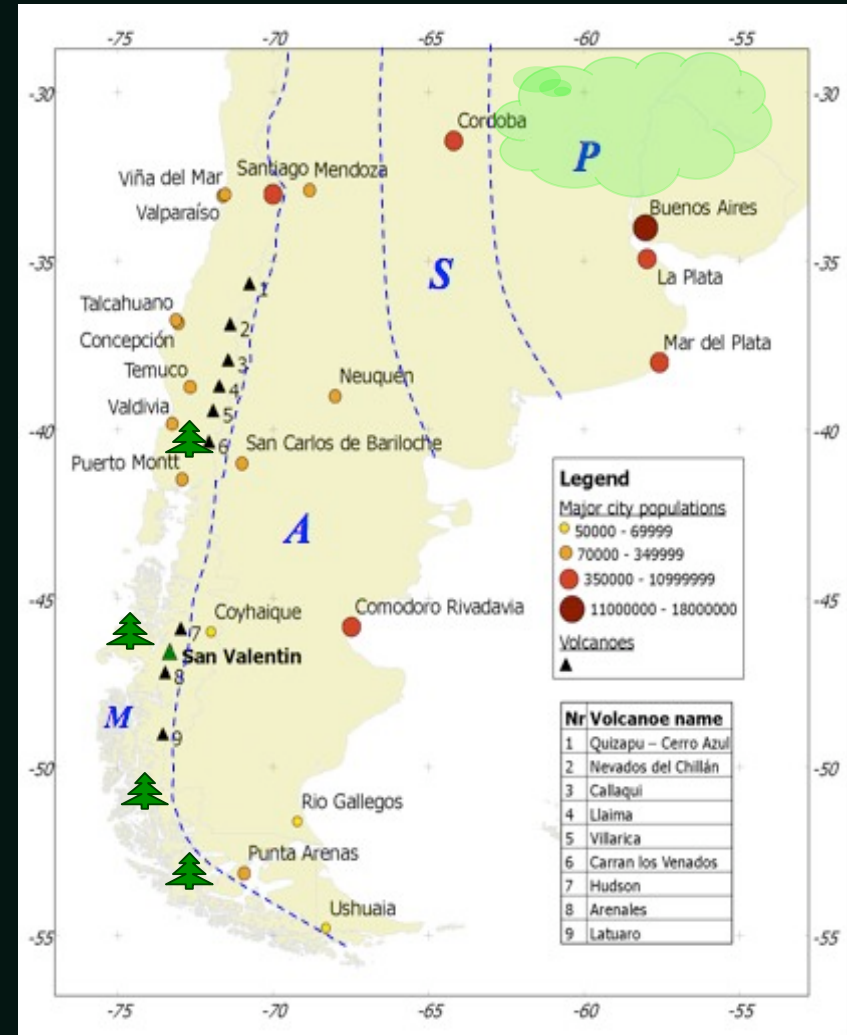
- $nssSO_4^{2-}$ 
  - 50-70% non marine biogenic
  - various sources influence

Continental  
contribution

- volcanism
- urban/industrial (?)

- $SO_4^{2-}$ ,  $NH_4^+$ ,  $NO_3^-$ ,  
 $HCl$

Conclusions



(Map: J.Gardelle.)



Climatology

# Volcanic contributions

120 m  
ice-core

- $F^- + SO_4^{2-}$
- Secondary gypsum formation
- $NH_3$  neutralization

Marine  
contribution

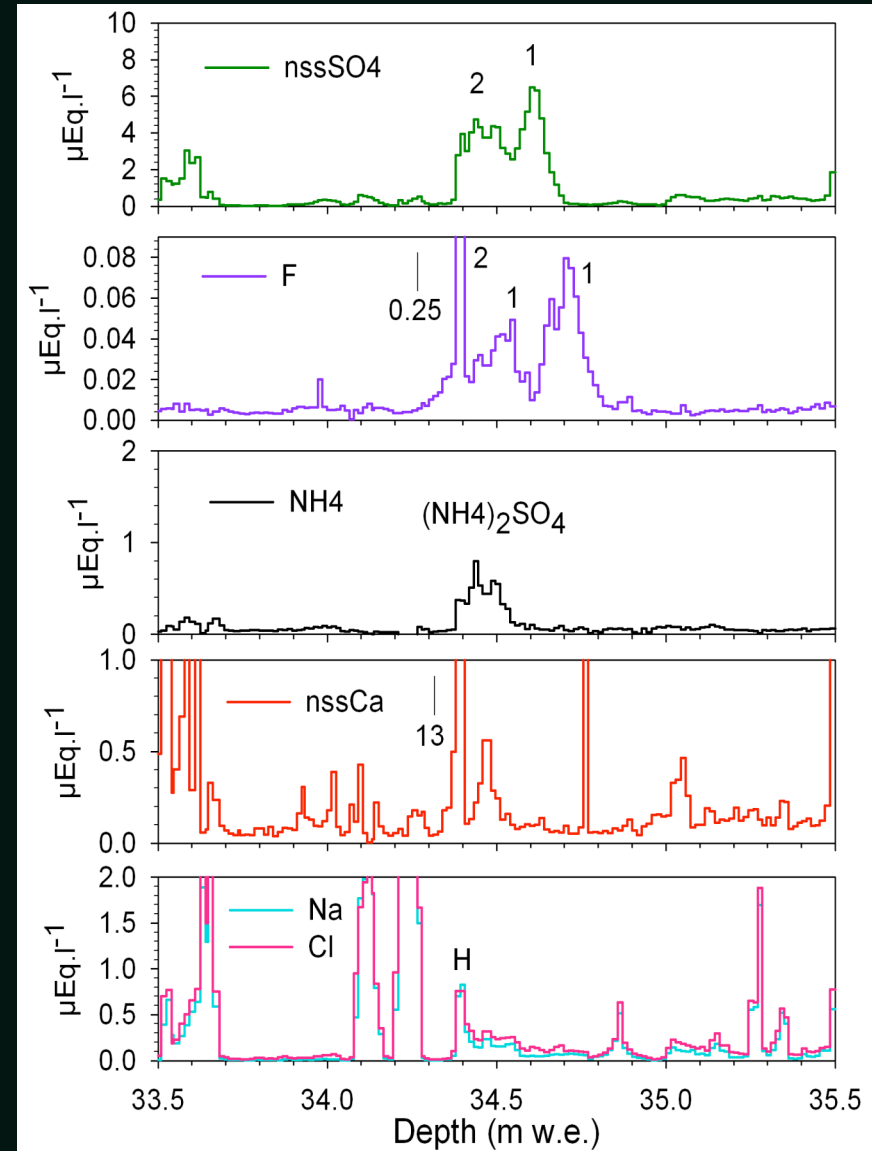
Continental  
contribution

Conclusions



Quizapu?: 1915-1932

35-40 m w.e.



Climatology

# Volcanic background

120 m  
ice-core

- Secondary gypsum formation

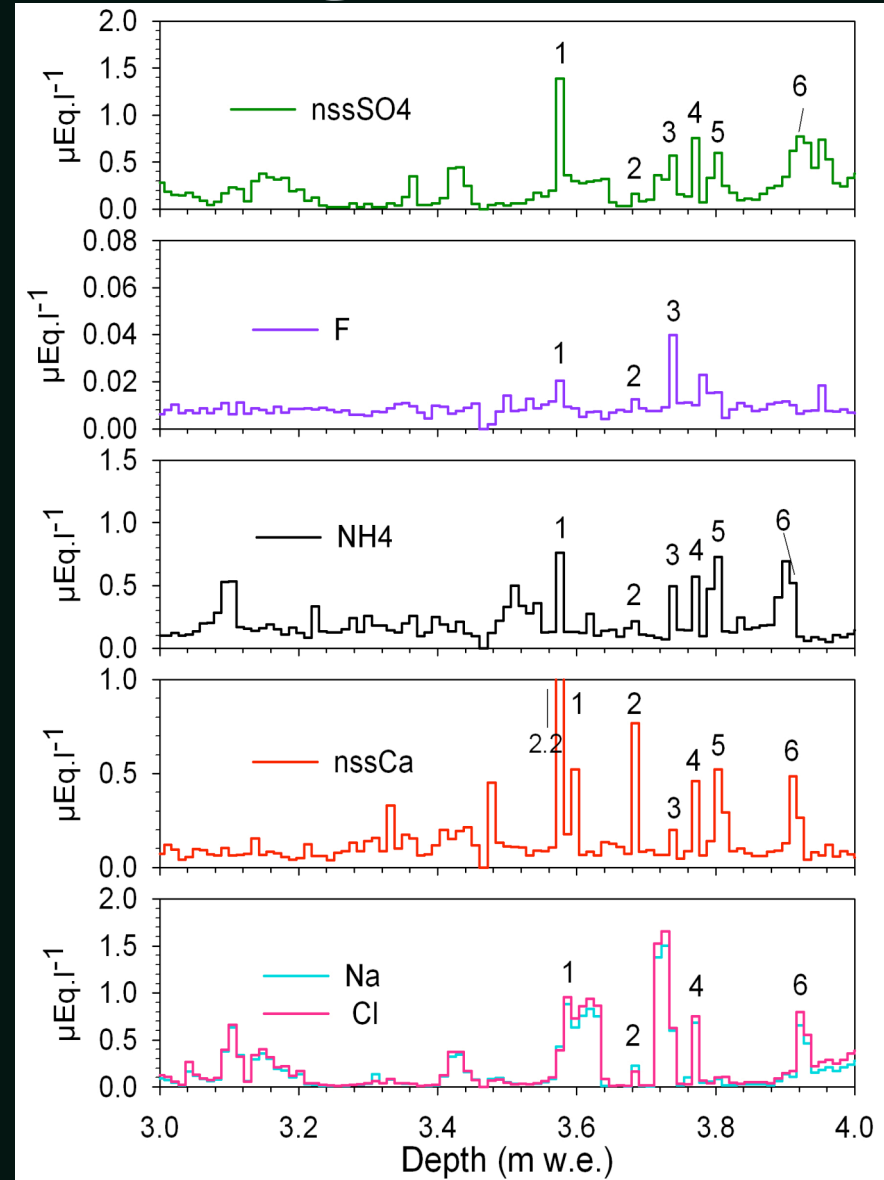
Marine contribution

nssCa<sup>2+</sup> acid attack:  
solubilisation

Continental contribution

- Dry deposit?

Conclusions



Climatology

# Volcanic $\text{H}_2\text{SO}_4$

120 m  
ice-core

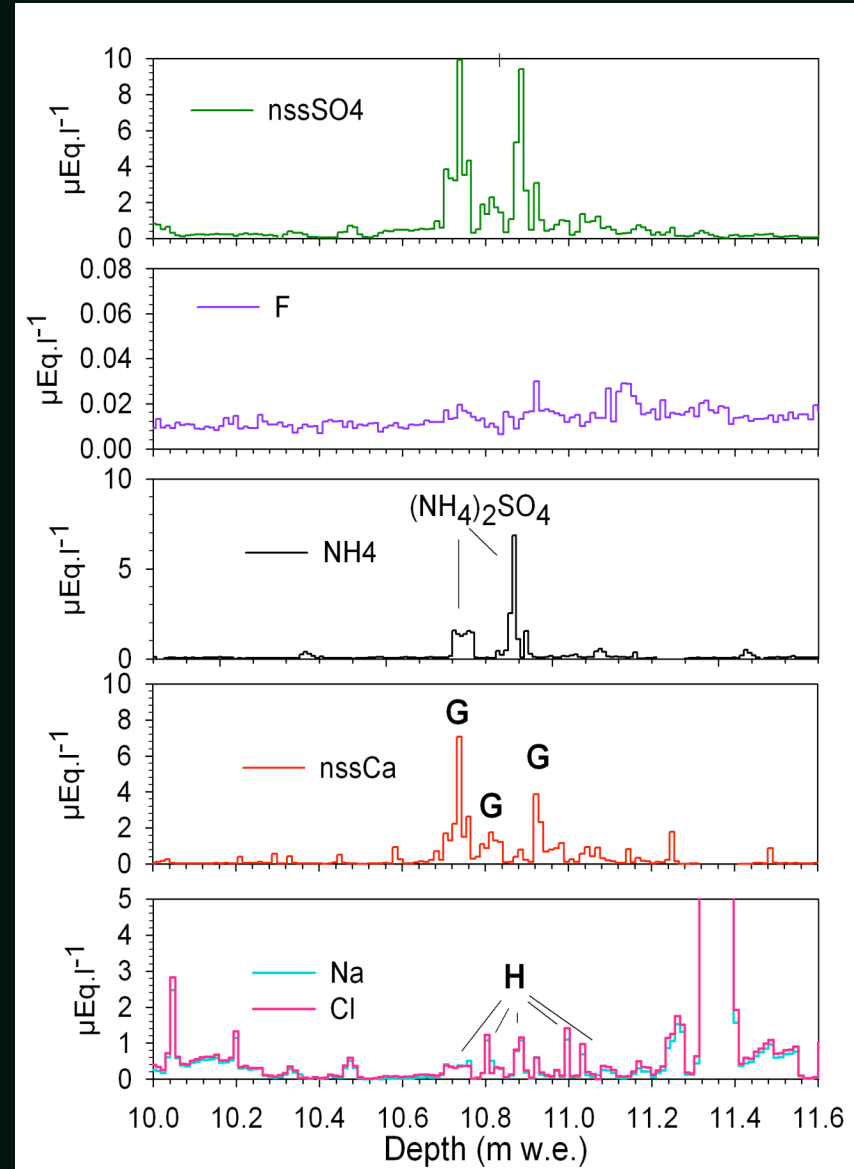
G = secondary  
gypsum formation

Marine  
contribution

H = halite  
formation

Continental  
contribution

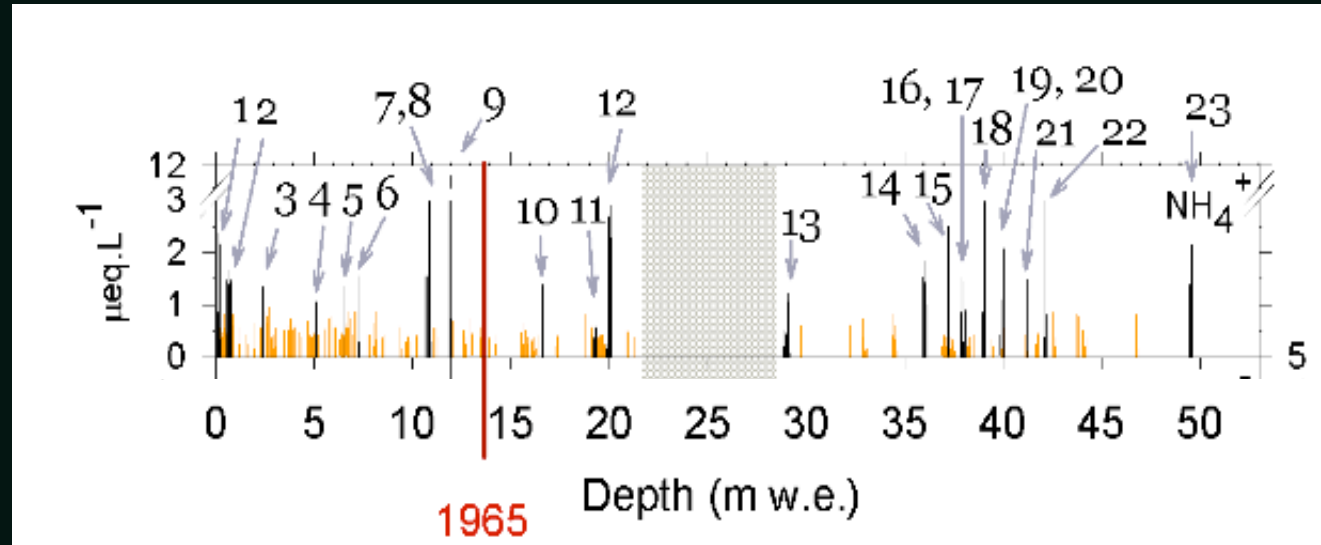
Conclusions



# Query of combustion events

120 m ice-core

Marine contribution



Continental contribution

- $\text{NH}_4^+$  complex proxy
  - Associated with high  $\text{SO}_4^{2-}$  (unusual)
  - Neutralized by volcanic  $\text{SO}_4^{2-}$

Conclusions

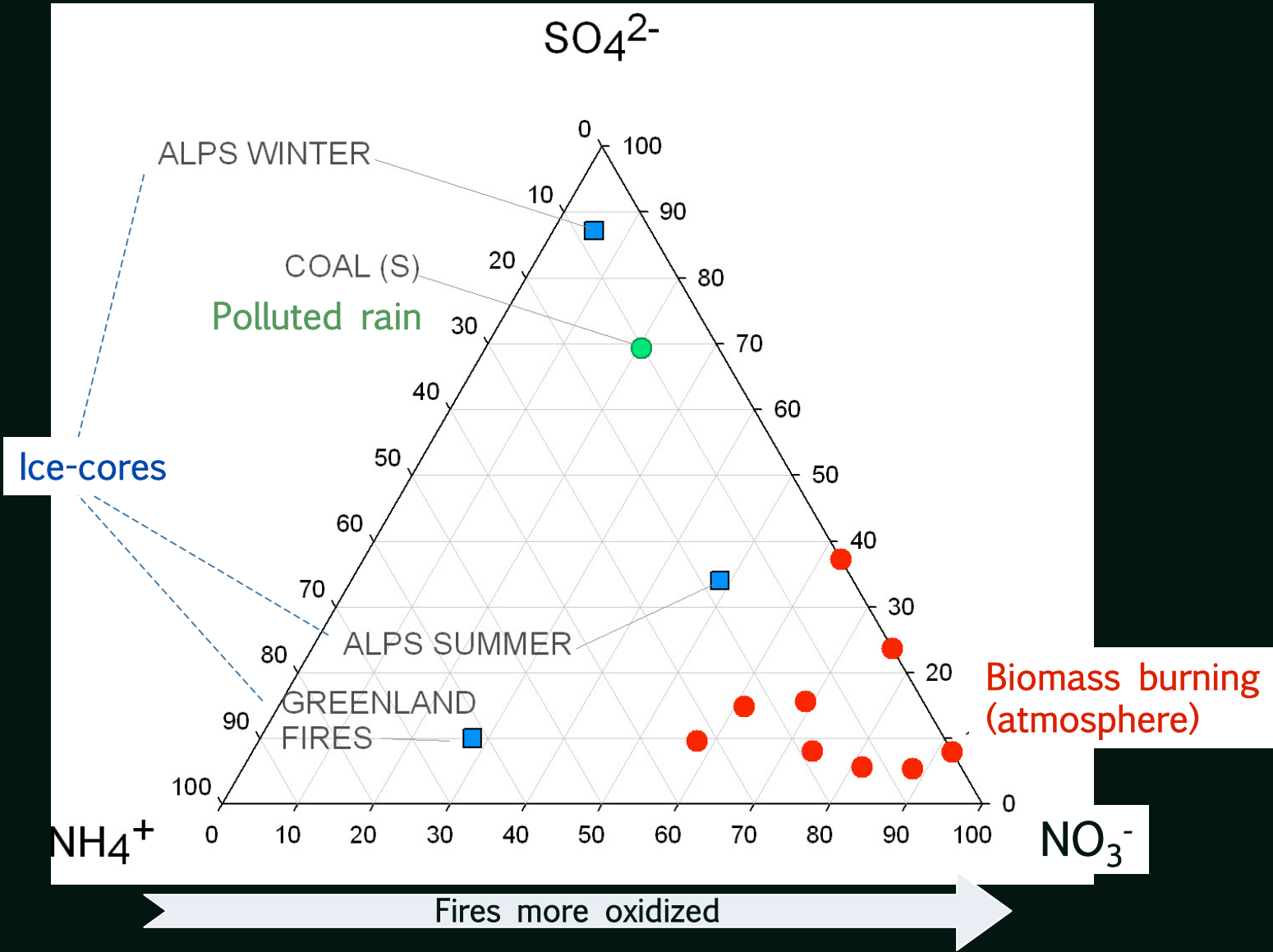
# Intricate continental fingerprint

120 m ice-core

Marine contribution

Continental contribution

Conclusions



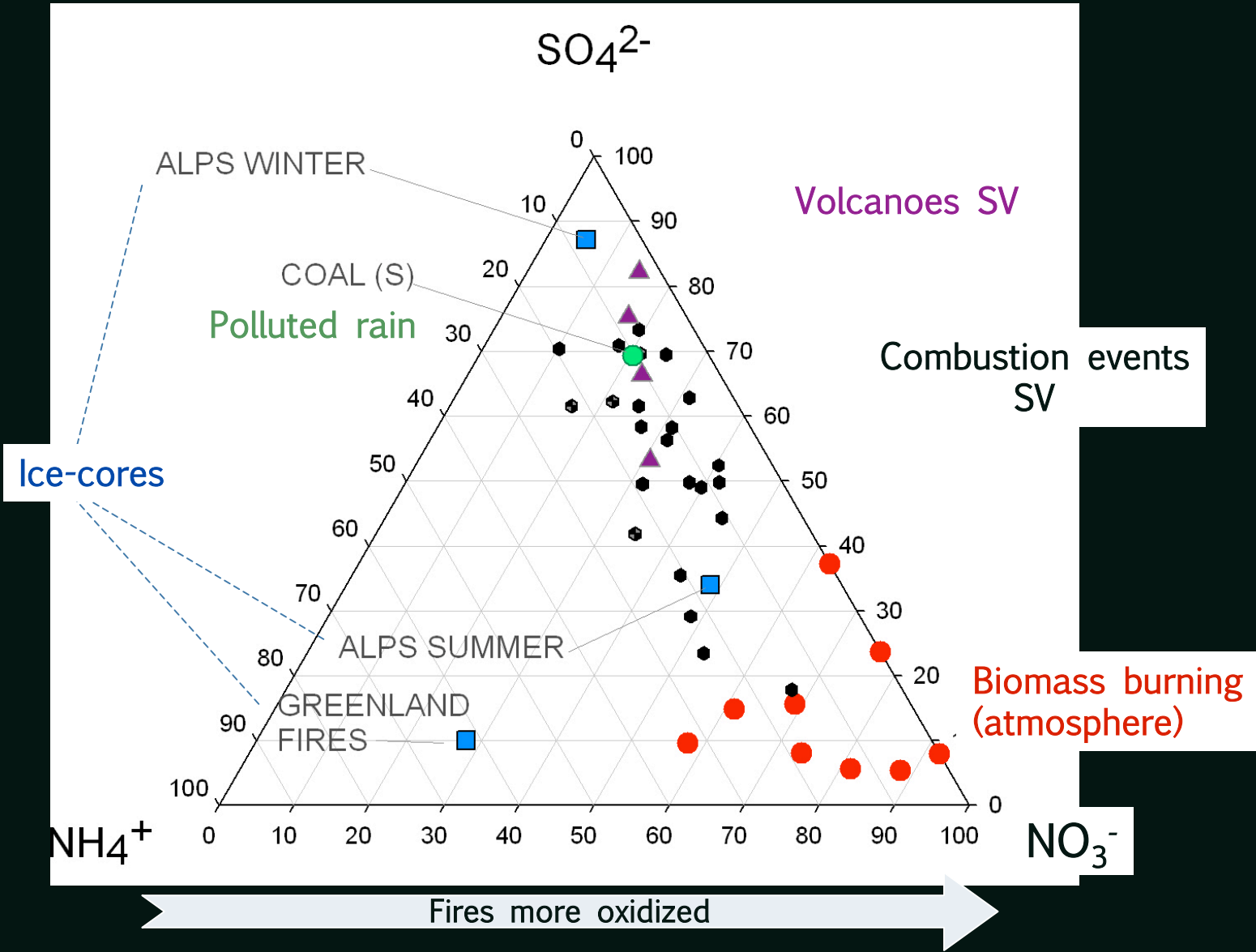
# Intricate continental fingerprint

120 m ice-core

Marine contribution

Continental contribution

Conclusions



Climatology

# Biomass burning

120 m  
ice-core

Absent:

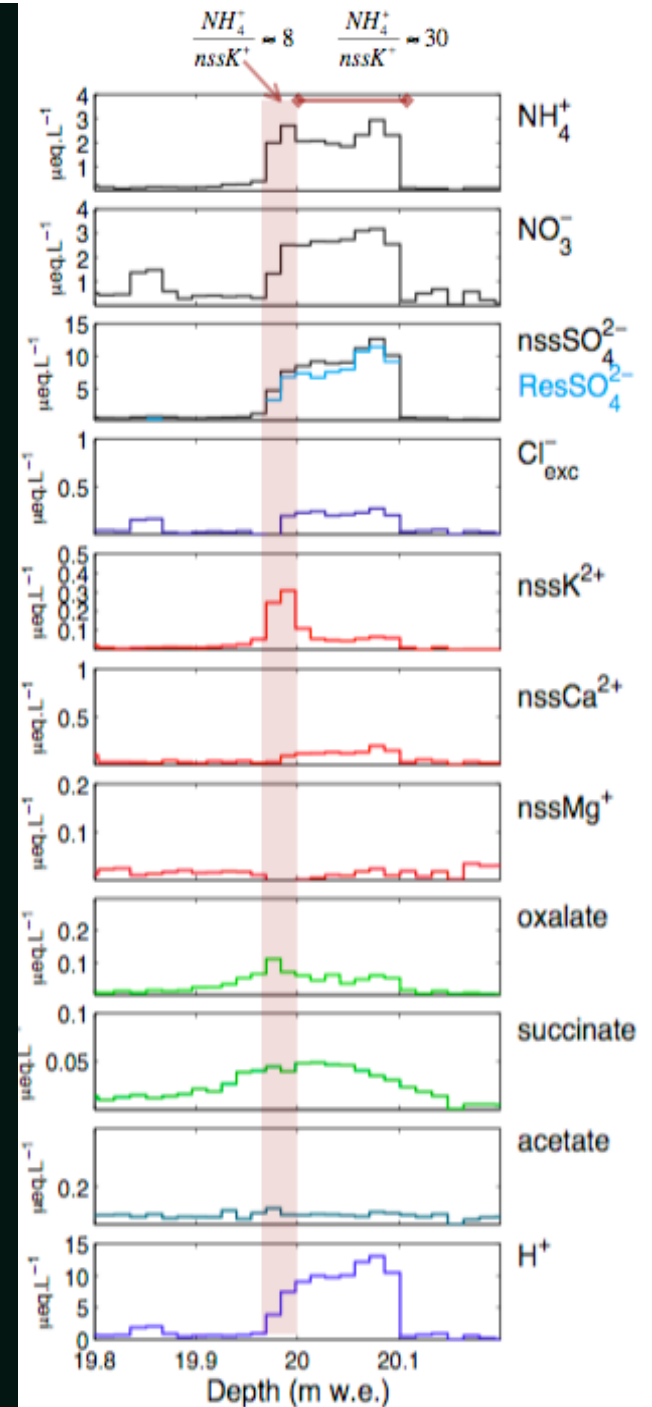
- Marine markers
- Monocarboxylic acids
- $H^+ > 10 \mu\text{eq.L}^{-1}$

Marine  
contribution

- Present:
- Levoglucosan
  - BC
  - Soot
  - Dicarboxylic acids

Continental  
contribution

Conclusions



Climatology

# Biomass burning

120 m  
ice-core

Absent:

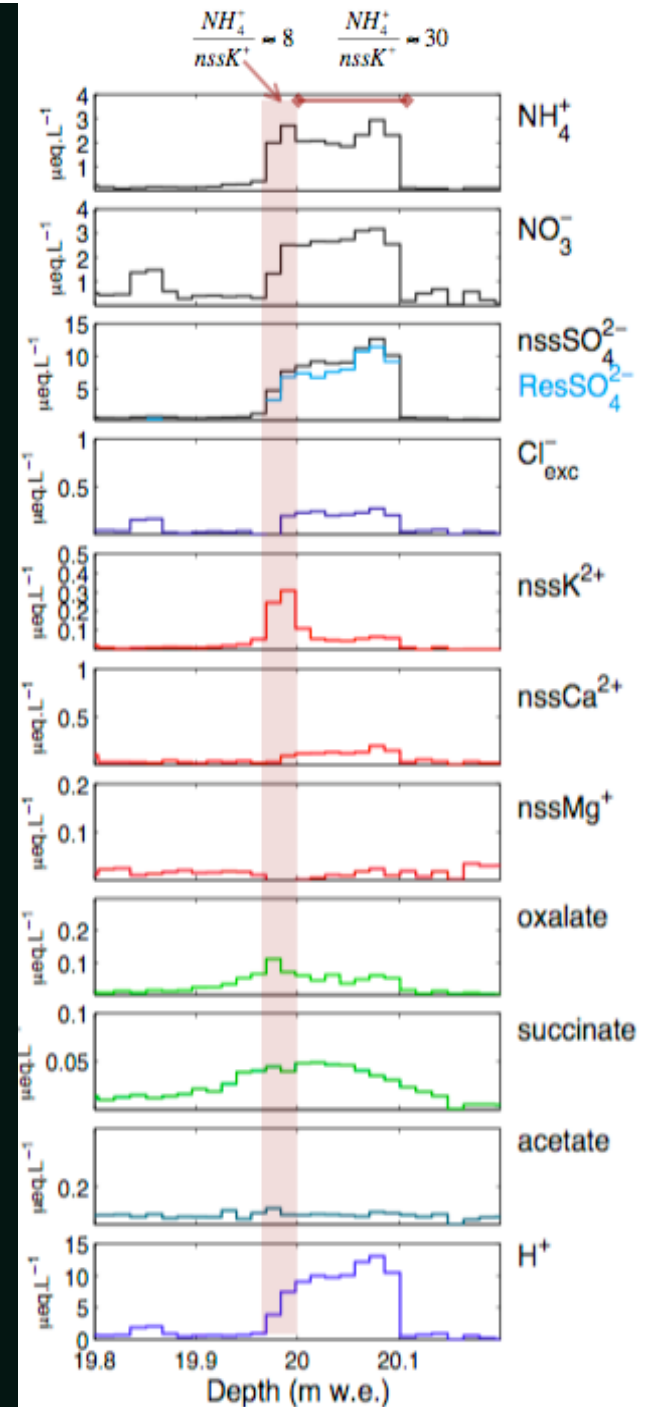
- Marine markers
- Monocarboxylic acids
- $H^+ > 10 \mu\text{eq.L}^{-1}$

Marine  
contribution

- Present:
- Levoglucosan
  - BC
  - Soot
  - Dicarboxylic acids

Continental  
contribution

Conclusions

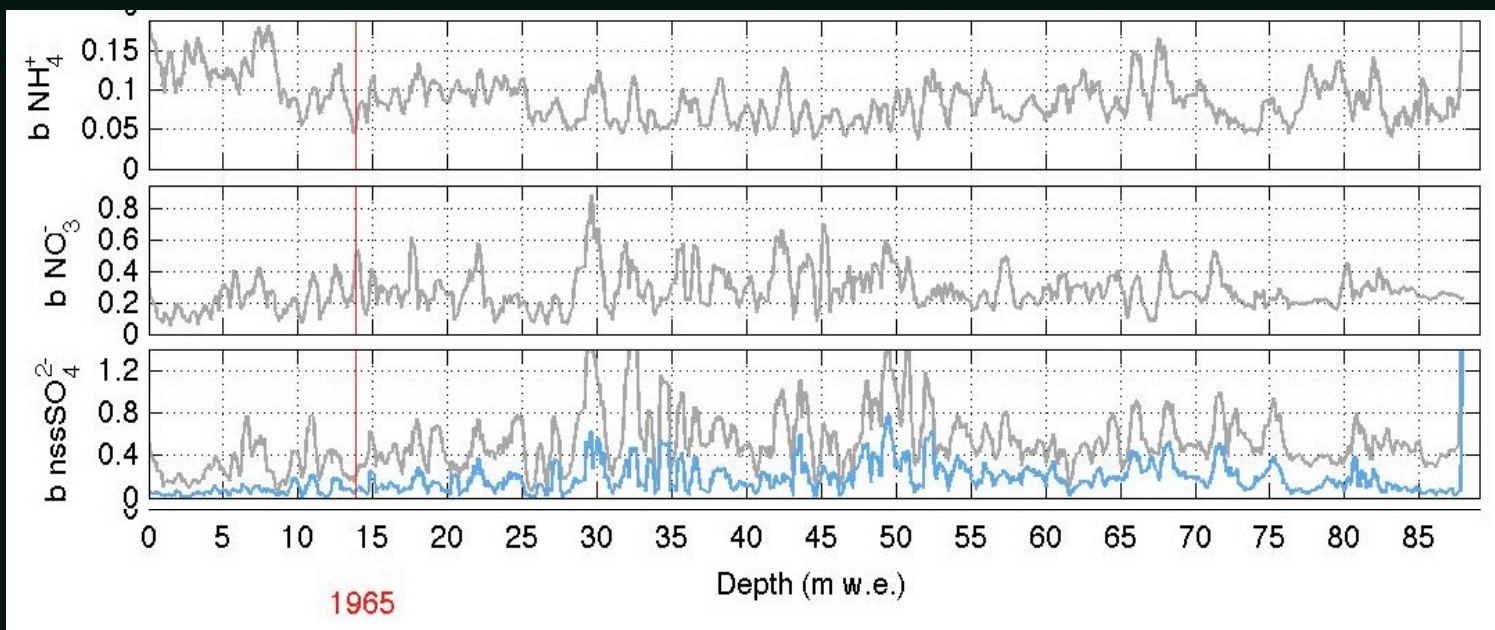




# Continental background

120 m ice-core

Marine contribution



Continental contribution

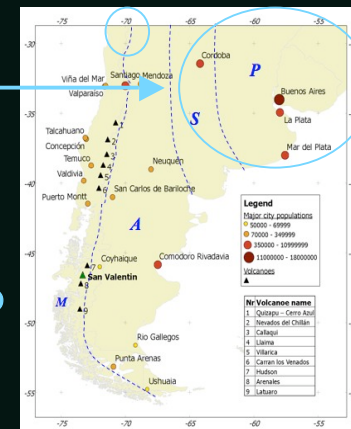
$\text{NH}_4^+$   
Soils emissions

→ Fertilizer use?

$\text{NO}_3^-$ ,  $\text{nssSO}_4^{2-}$   
Car exhaust  
Industrial emissions

- Not recorded at this altitude?
- Atmospheric dilution?
- Sources?
- Accumulation?

Conclusions



# Proposed dating horizons

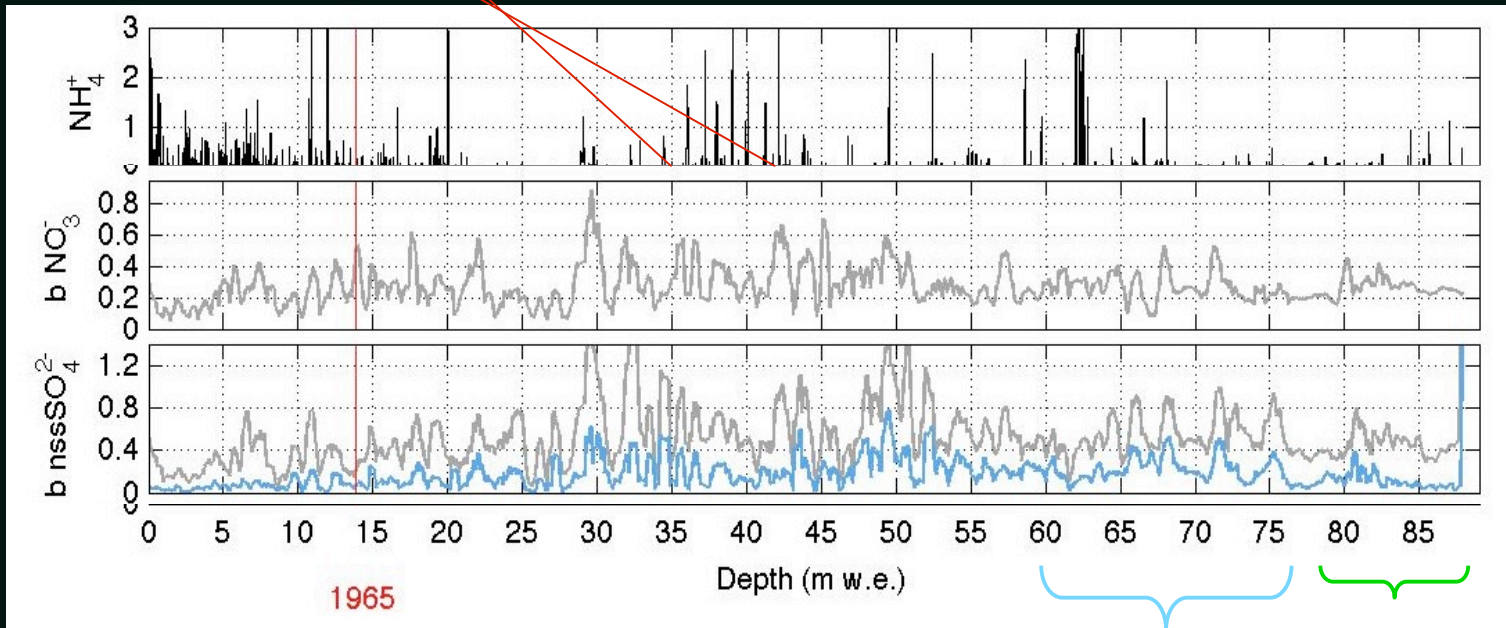
120 m ice-core



Marine contribution

Continental contribution

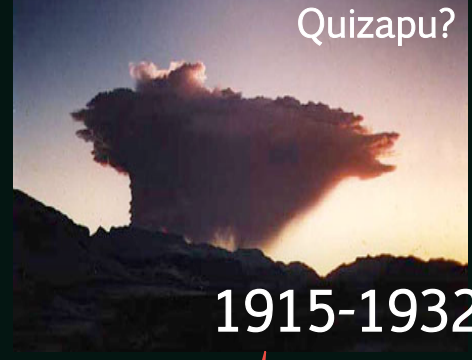
Conclusions



Brittle zone  
Old ice zone

# Proposed dating horizons

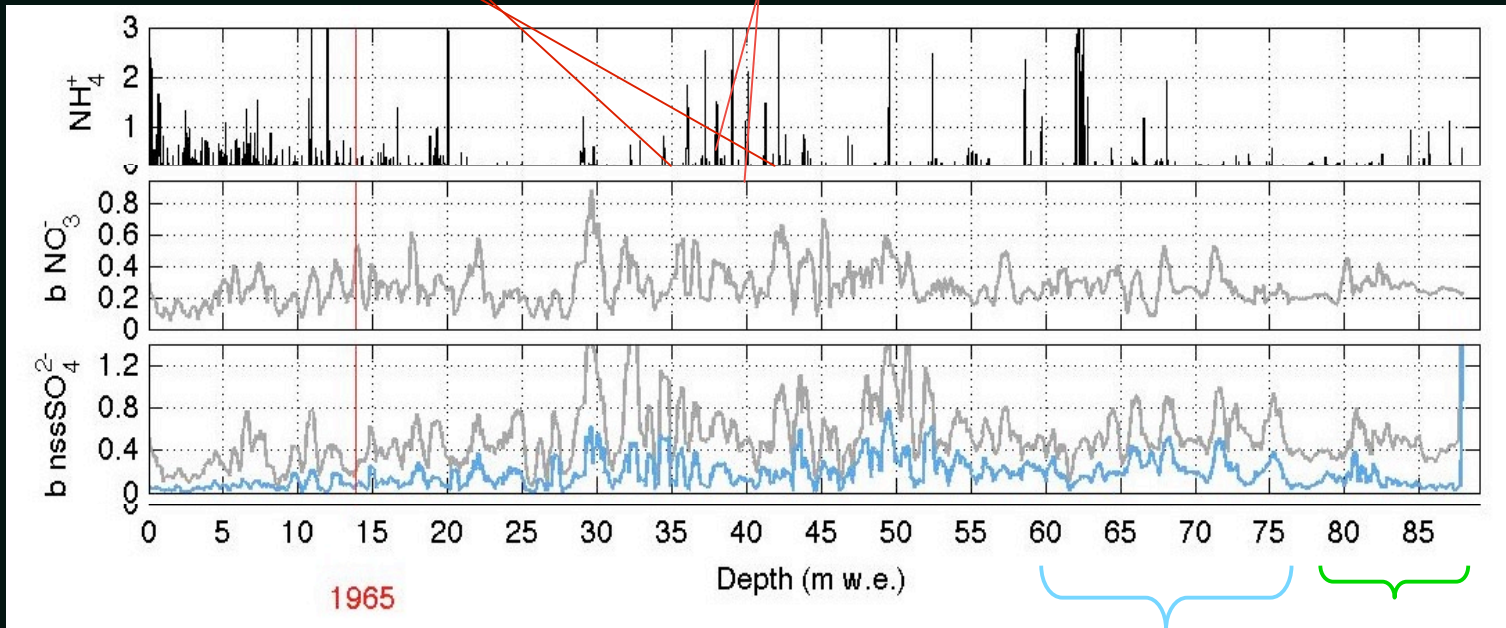
120 m ice-core



Marine contribution

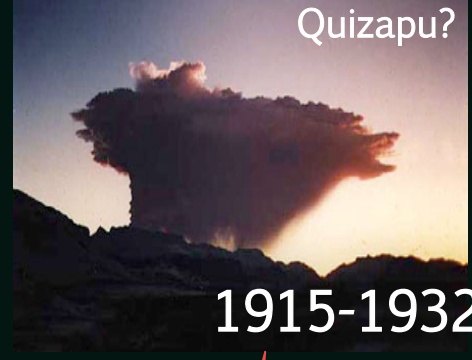
Continental contribution

Conclusions



# Proposed dating horizons

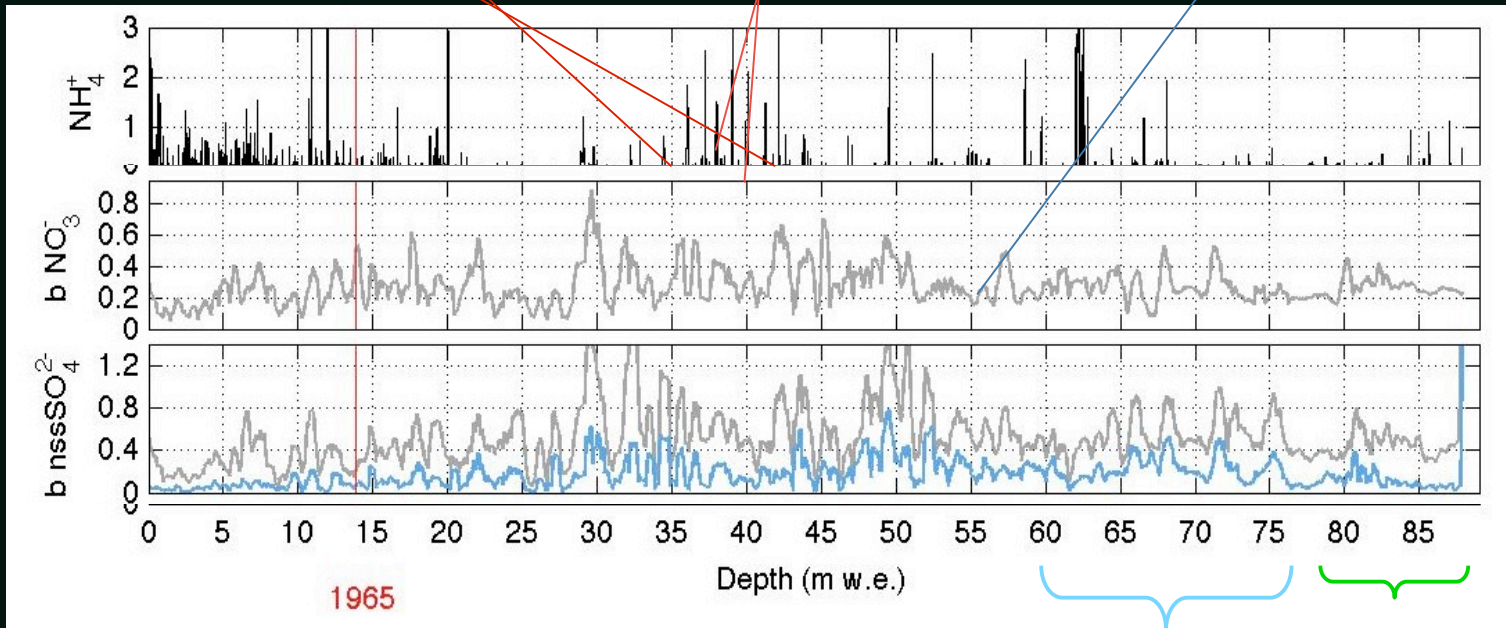
120 m ice-core



Marine contribution

Continental contribution

Conclusions



# Conclusions

Complete ionic dataset produced

+

General transport

- Holocene? → 73 m → 120 years
- Ice-core interpretation in terms of events
- Site under strong marine influence
  - Expected : 90% (backtrajectories)
  - Conserved: 45%
- $\text{MSA:nssSO}_4^{2-}$  molar ratio (0.10-0.16) is closer to the mid-latitudes marine values than Antarctic peninsula values

# Conclusions

Complete ionic dataset produced

+

General transport

Continental sources: N, NE, NW

$\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , HCl?

$\text{SO}_4^{2-}$  ubiquitous:

- \* Volcanic events, background,
- \* Fires

$\text{NH}_4^+$  complex:

- \* Ammoniac neutralization by volcanic  $\text{H}_2\text{SO}_4$
- \* Fires, anthropogenic (settlers arrival) influence

# Perspectives...

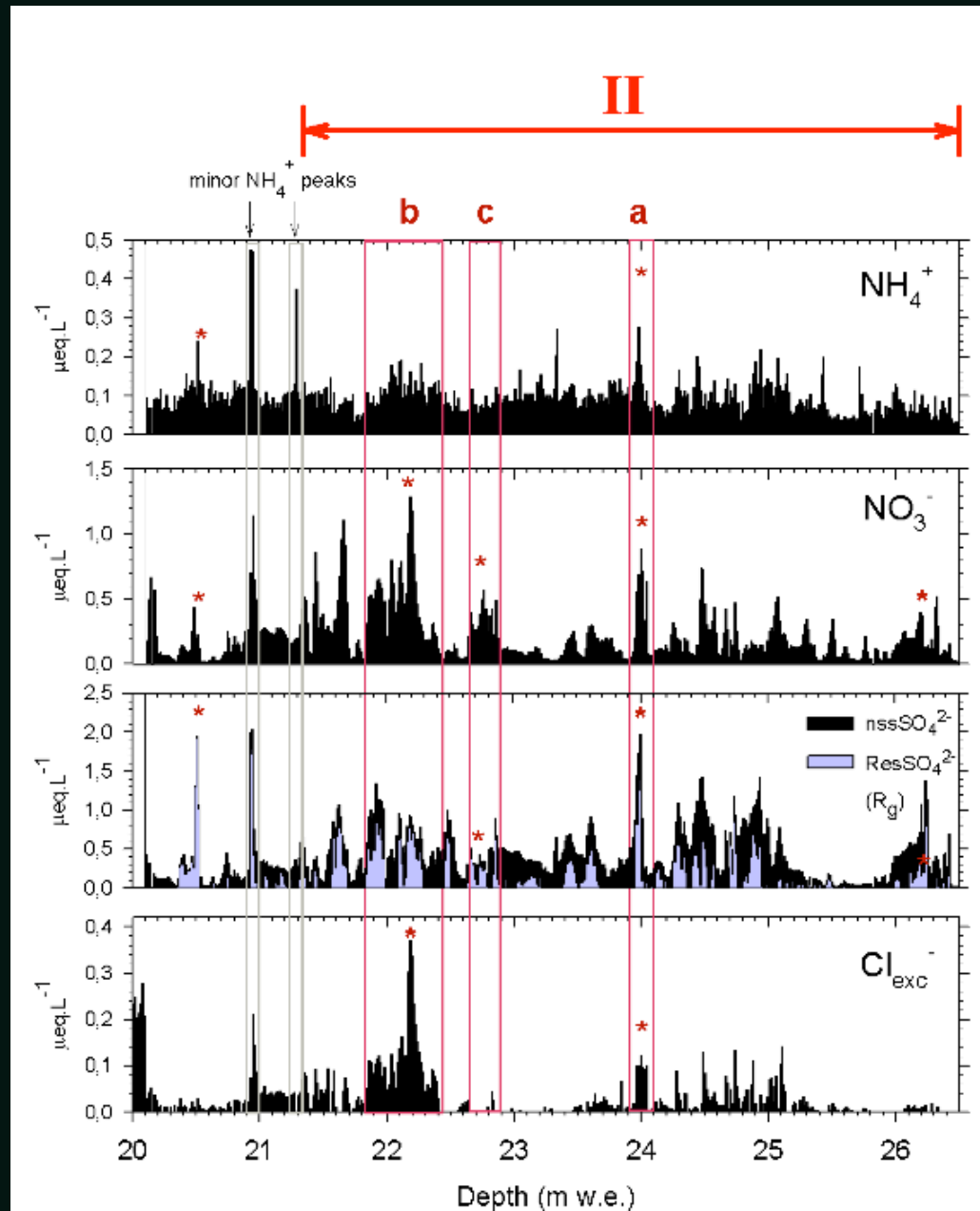
- 73-120 m Bottom ice
- Flow model, glaciological setting needed
  - Basis for climatic interpretation
- New elements: trace elements LMTG
- Climatic modes, isotopes: ENSO, AAO
- Which is the origin of the association of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{HCl}$ ?
  - Sources?
  - Mechanisms?
  - Regional chemical models?
- Stable isotopes: S, N



Thank you for your attention

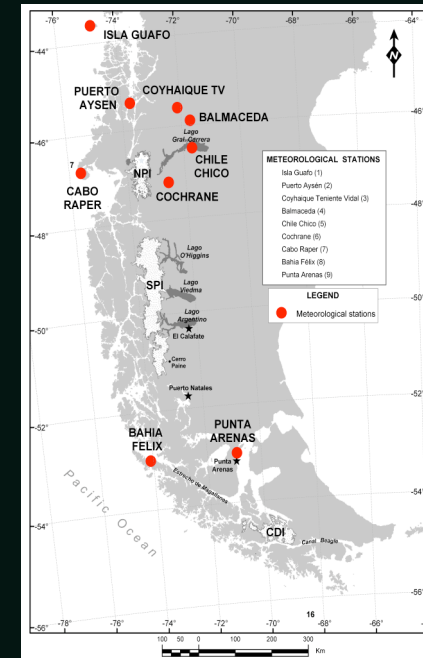


Continental  
ubiquitous  
cluster:  
 $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  
 $\text{HCl}$

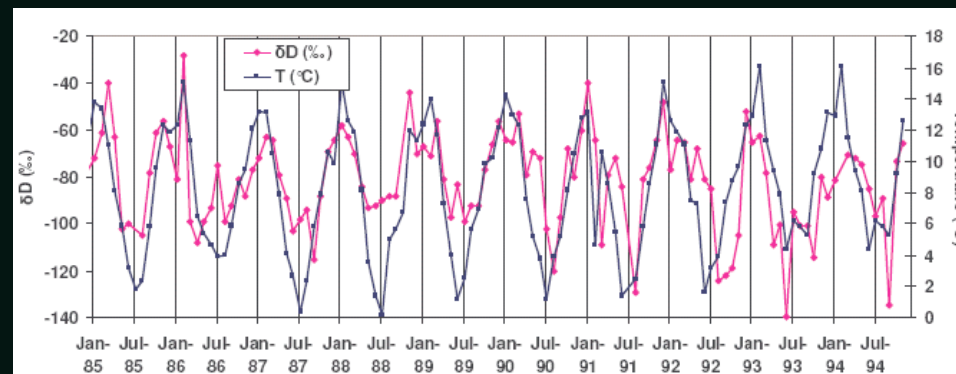


# What can we expect from stable isotopes?

- Clear isotopic seasonal cycles for precipitation collected at Coyhaique [45°50S; 75°70W, 310m]. Cycles at the summit also expected.
- Correction for isotopic diffusion needed.
- Ground temperature is representative for high altitude sites at mid-latitudes (*Falvey et al., 2008*)



(Lopez, pers. comm.)



(Herreros, pers. comm. IAEA data)