Source Identification & Apportionment of PM via Isotope Measurements of Carbon Species (OC/EC)

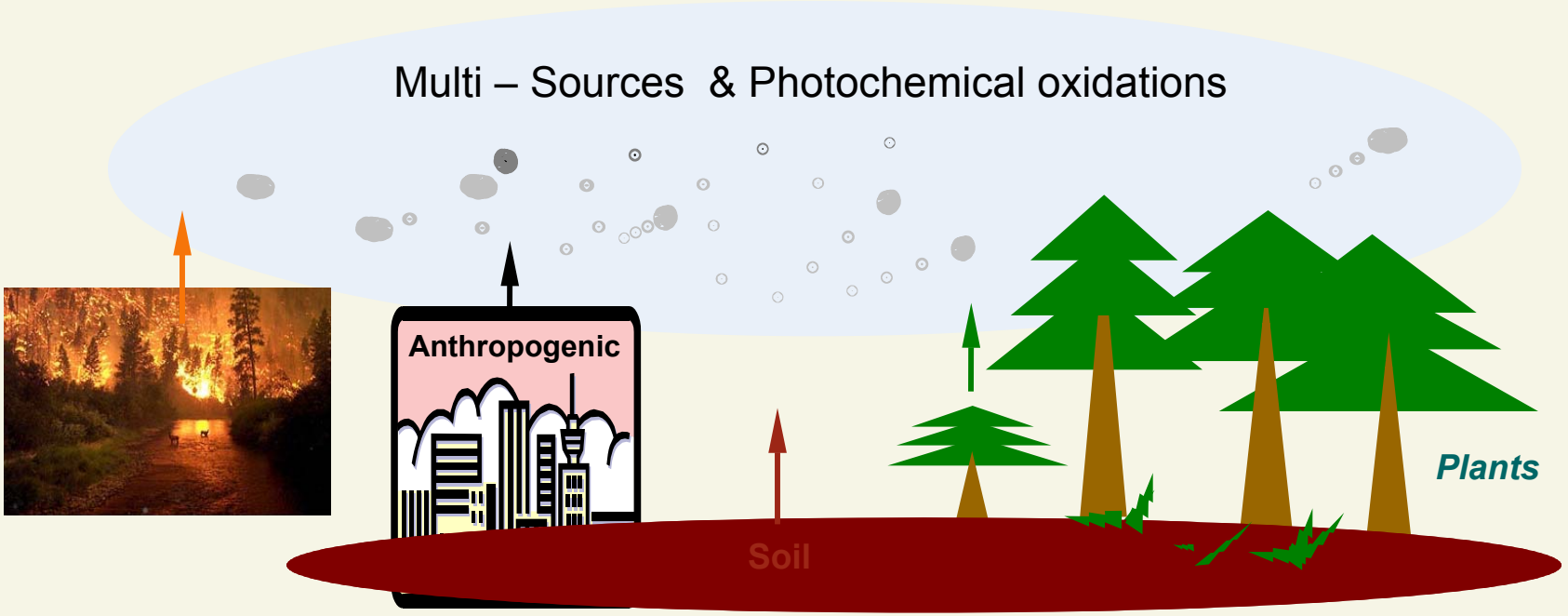
L. Huang, W. Zhang, J. Brook,
D. Ernst, A. Chivulescu, G. Lu, S. Sharma

Air Quality Research Branch
Atmospheric & Climate Science Directory
Meteorological Service of Canada

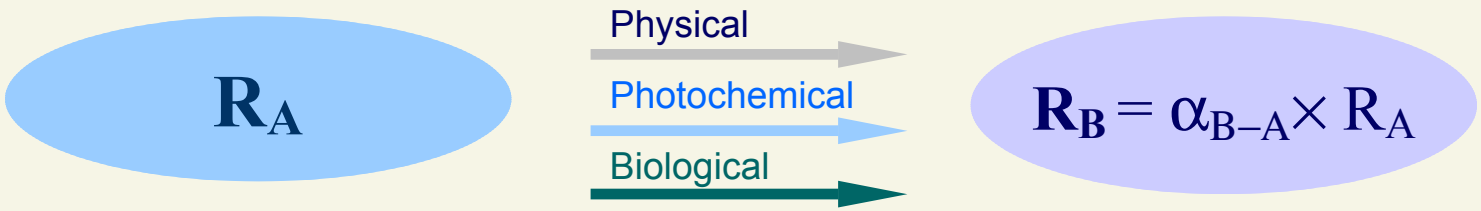
Environment Canada Environnement Canada

Why Carbonaceous aerosols ?

- **Regional Air Quality** (health and environment issues)
- **Global Climate Change**
- **Distribution of sources** (emission inventory) & **formation processes** (primary and secondary) **are not well understood**



Tracing Source and Process via Stable Isotopes



Source **Processes** **Measurements**

$$\alpha_{B-A} = R_B/R_A$$

The Primary Scale: **VPDB**

$\delta^{13}C = [(R_{sam}/R_{Std}) - 1]*10^3$, $R = {}^{13}C/{}^{12}C$

R ($^{13}C/^{12}C$)	$\delta^{13}C$	
0.0112934	**5**	***Carbonate***
0.0112372	**0**	***VPDB***
0.0111473	**- 8**	***ATMCO2***
0.0110799	**- 12**	***C3***
0.0109226	**- 28**	***C4***

Implication of Isotopic Composition of Aerosols

Observation: R_{ob}

Photochemical Oxidation of OCs

$= \alpha * R_S$

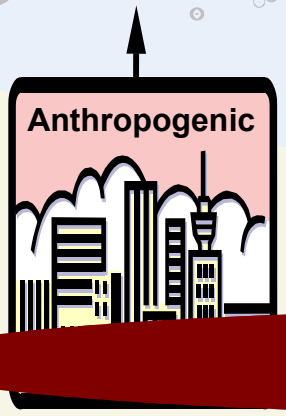
Sources

$\delta^{13}C^{s}_{EC} = (\delta^{13}C^{an}_{EC} \times F^{an}) + (\delta^{13}C^{bio}_{EC} \times F^{bio}) + (\delta^{13}C^{fire}_{EC} \times F^{fire}) + (\delta^{13}C^{at}_{EC} \times F^{at}) \ldots$

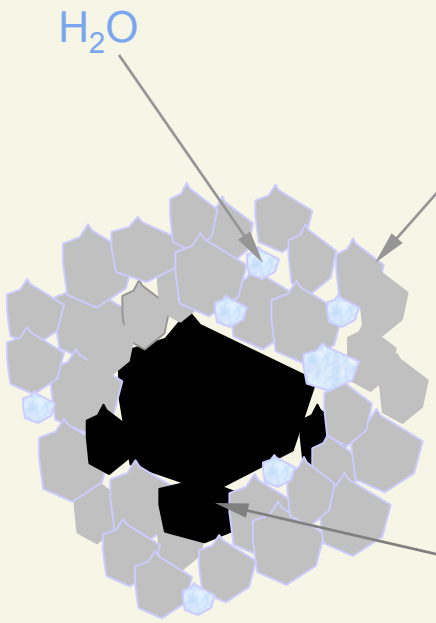
$\delta^{13}C^{s}_{1} = (\delta^{13}C^{an}_{1} \times F^{an}) + (\delta^{13}C^{bio}_{1} \times F^{bio}) + (\delta^{13}C^{fire}_{1} \times F^{fire}) + (\delta^{13}C^{at}_{1} \times F^{at}) \ldots$

……

$\delta^{13}C^{s}_{n} = (\delta^{13}C^{an}_{n} \times F^{an}) + (\delta^{13}C^{bio}_{n} \times F^{bio}) + (\delta^{13}C^{fire}_{n} \times F^{fire}) + (\delta^{13}C^{at}_{n} \times F^{at}) \ldots$



Implication of Isotope Analysis in Temperature Profiles of Carbonaceous Aerosols



Organic Carbon (OC)

- Condensed outside of the core as the coating;
- Could be primary or secondary aerosols;
- **Thermally released at relatively low temperature**;
- The isotopic composition reflects mainly process information.

Carbonate Carbon (CC)

- Usually from soil dust /cement;
- **Thermally decomposed at high temperature.**

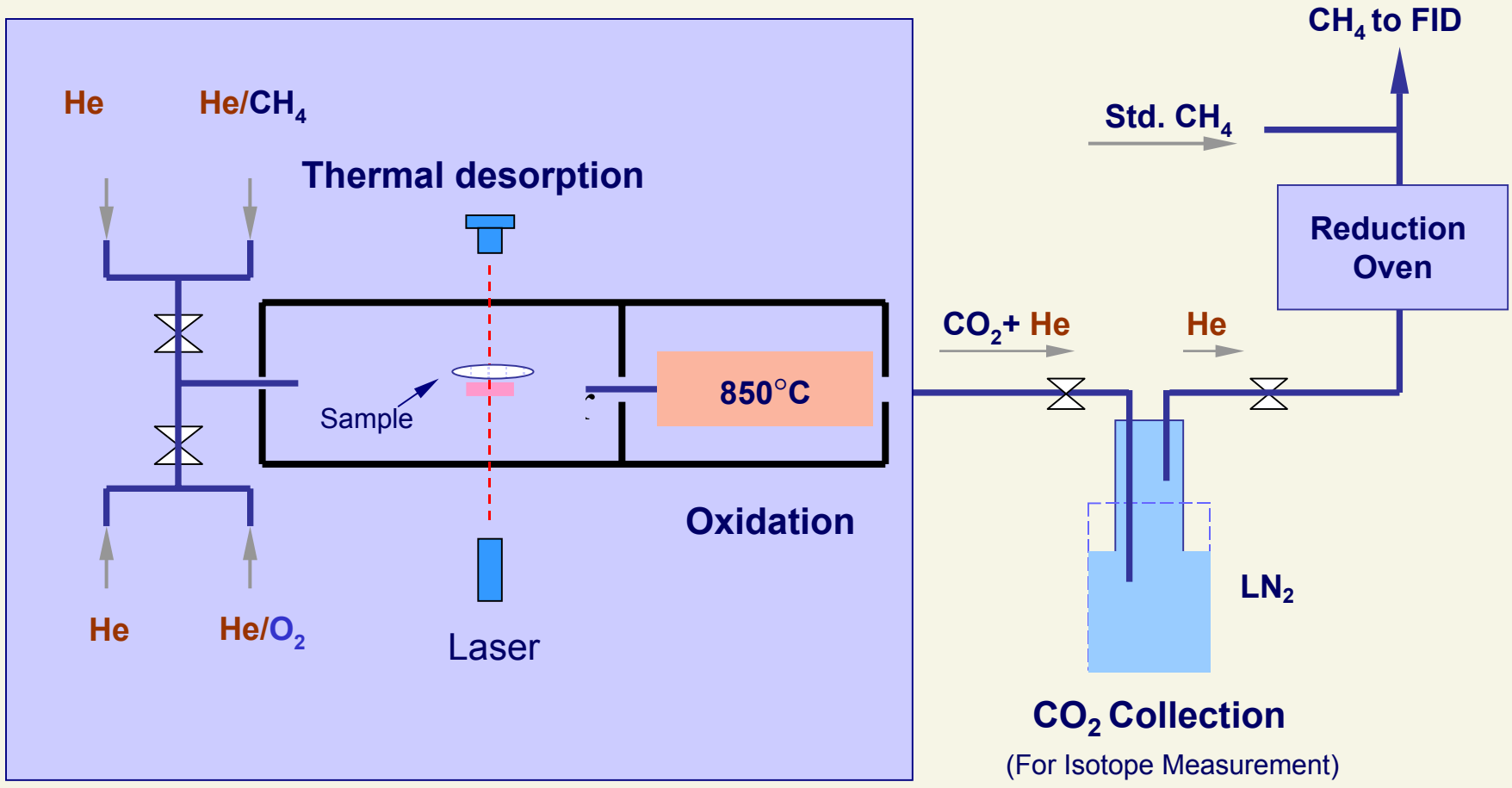
Black Carbon (BC) **or Elemental Carbon** (EC)

- Located at the core;
- Usually considered as primary aerosols;
- **Oxidized at relatively high temperature** stage;
- The isotopic composition reflects mainly source information.

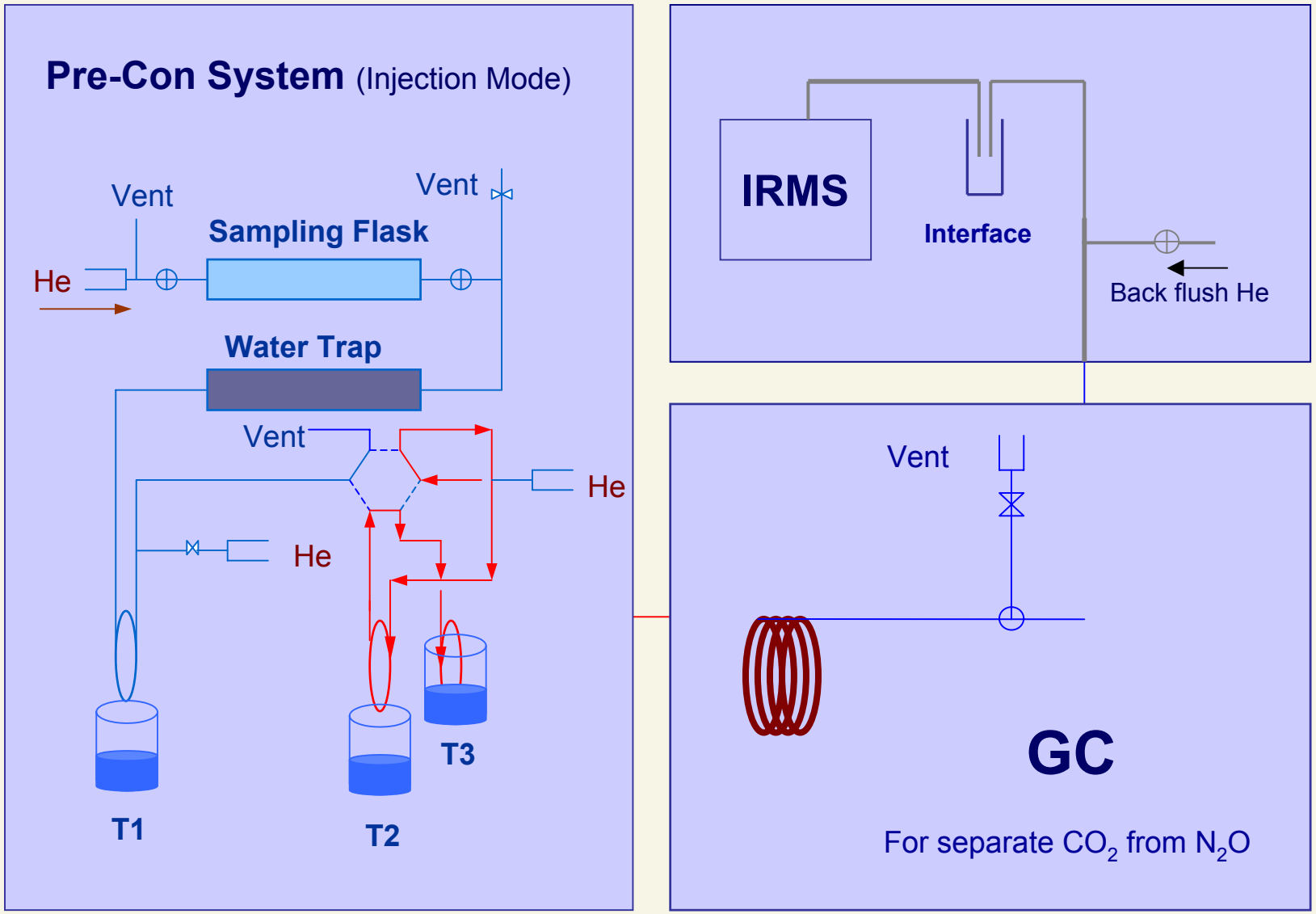
* The distributions of carbon isotopic composition in a temperature profile may release the information on the sources and the processes of PM.

The Schematic of OC/EC Measurement in Aerosols

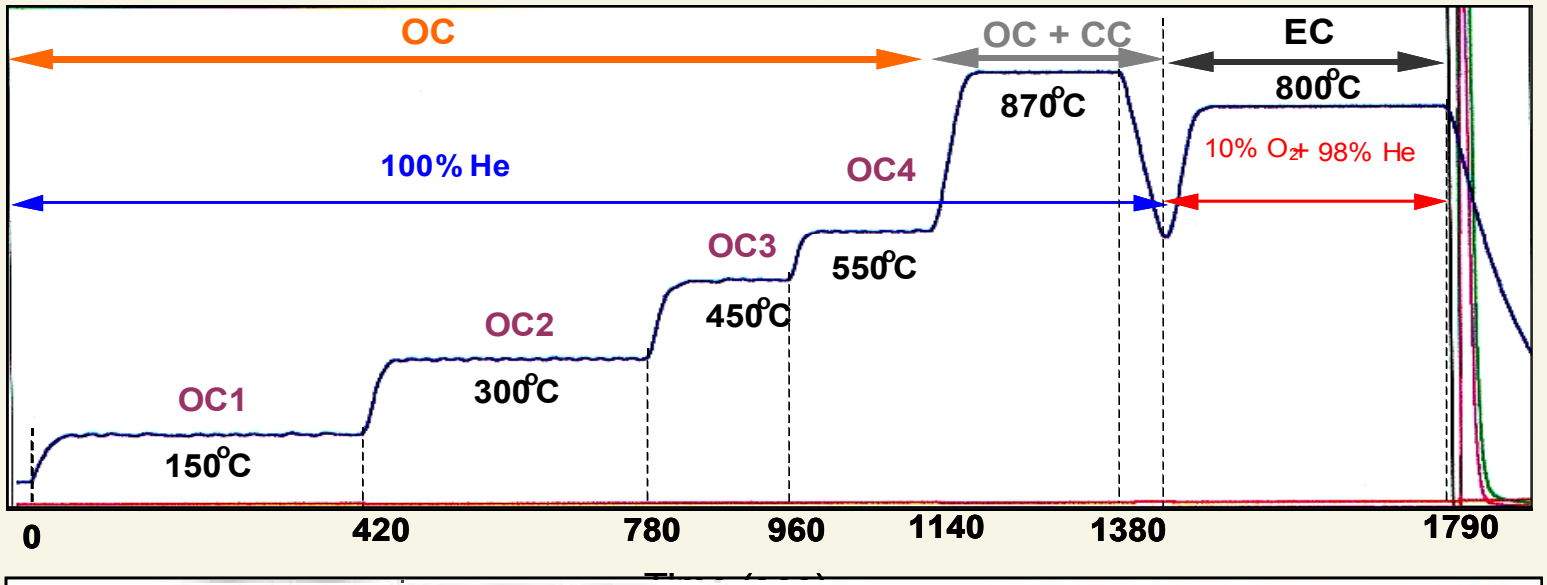
(by Thermal Desorption-Optical Method)

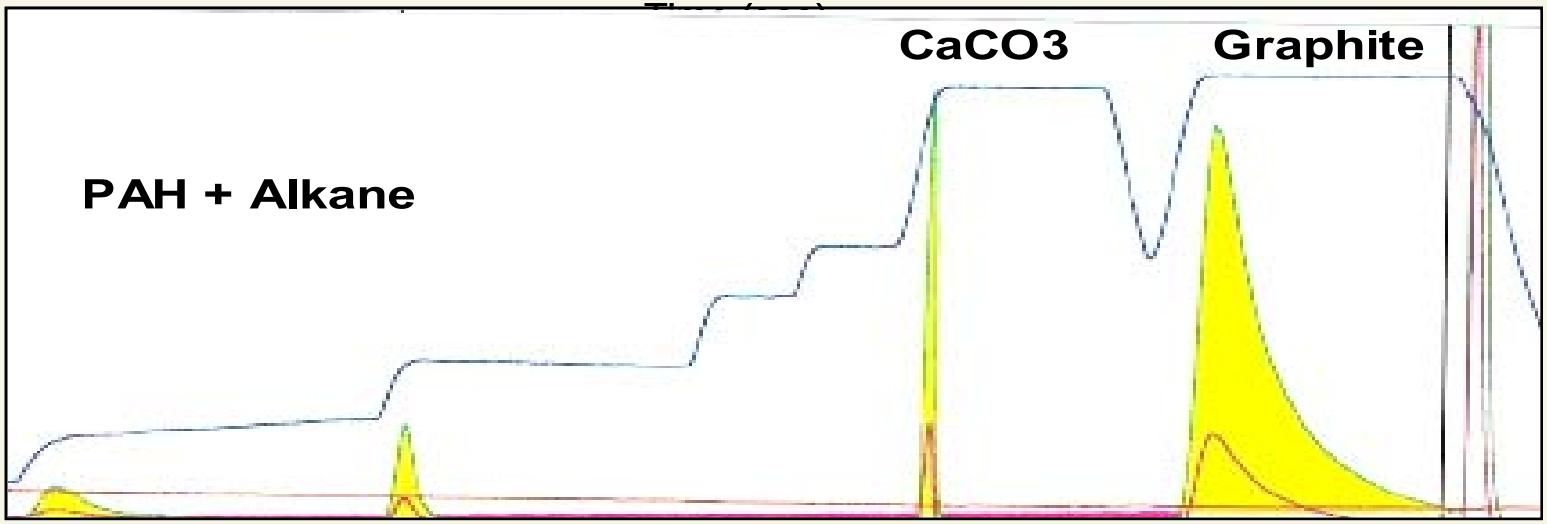


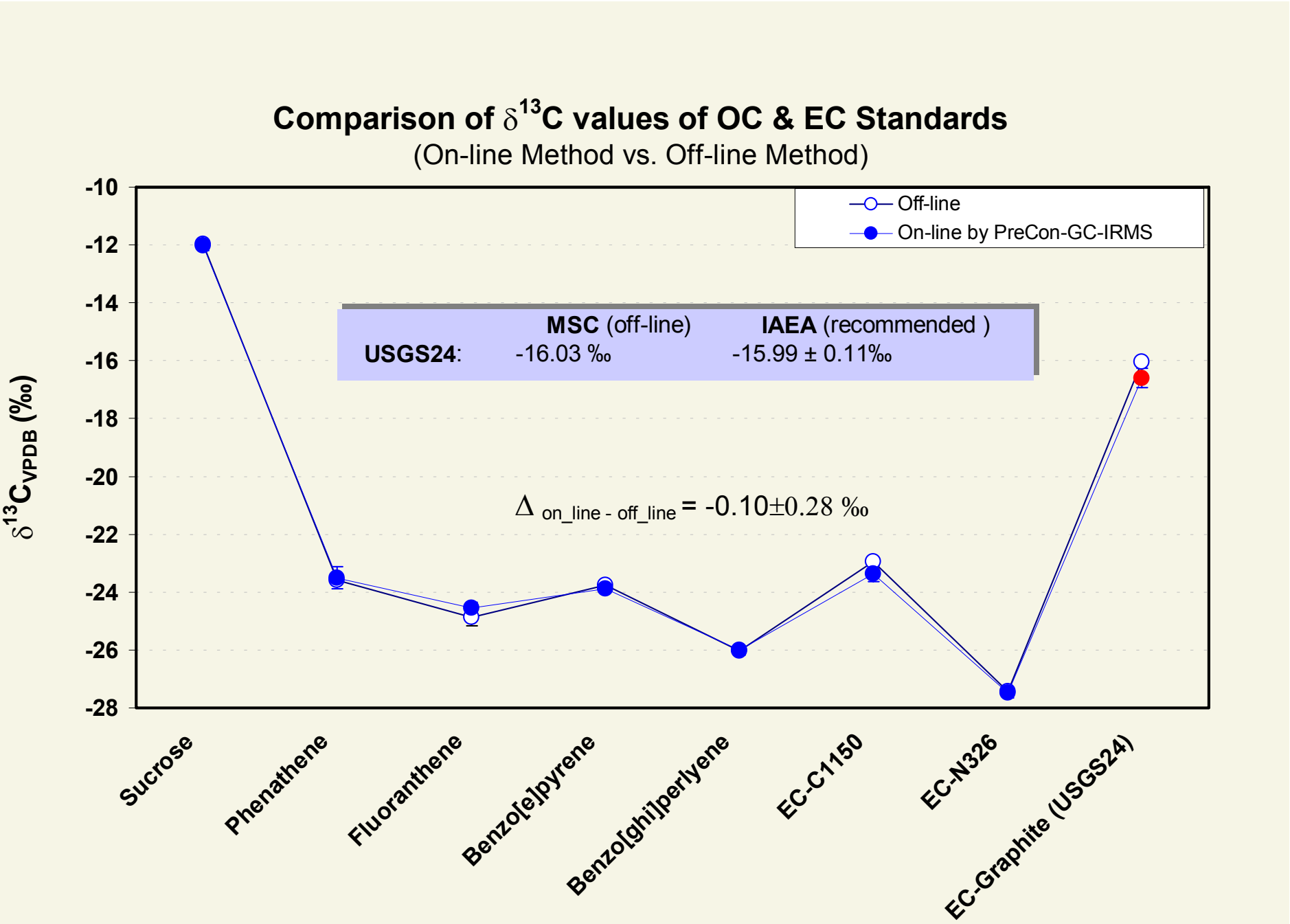
Schematic of On-line Isotope Measurement System for OC/EC in Aerosols



Thermograph for OCs, CC and EC Separation & Standards



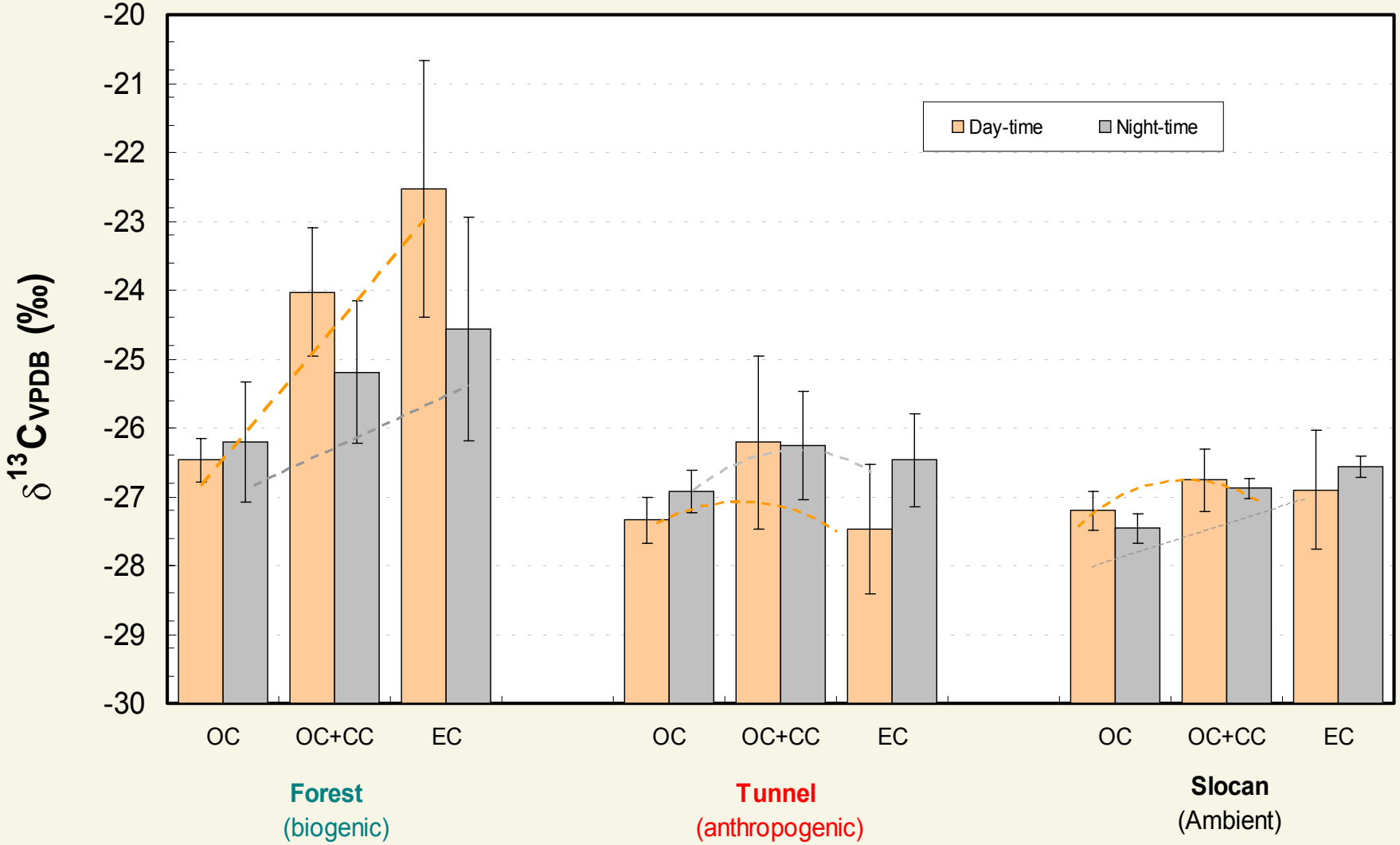



Comparison of δ13C values of OC & EC Standards
(On-line Method vs. Off-line Method)
δ13CVPDB (‰)
-10
-12
-14
-16
-18
-20
-22
-24
-26
-28
Off-line
On-line by PreCon-GC-IRMS
MSC (off-line)
IAEA (recommended)
USGS24: -16.03 ‰
-15.99 ± 0.11‰
Δ on_line - off_line = -0.10±0.28 ‰
Sucrose
Phenathene
Fluoranthene
Benzo[e]pyrene
Benzo[ghi]perlyene
EC-C1150
EC-N326
EC-Graphite (USGS24)

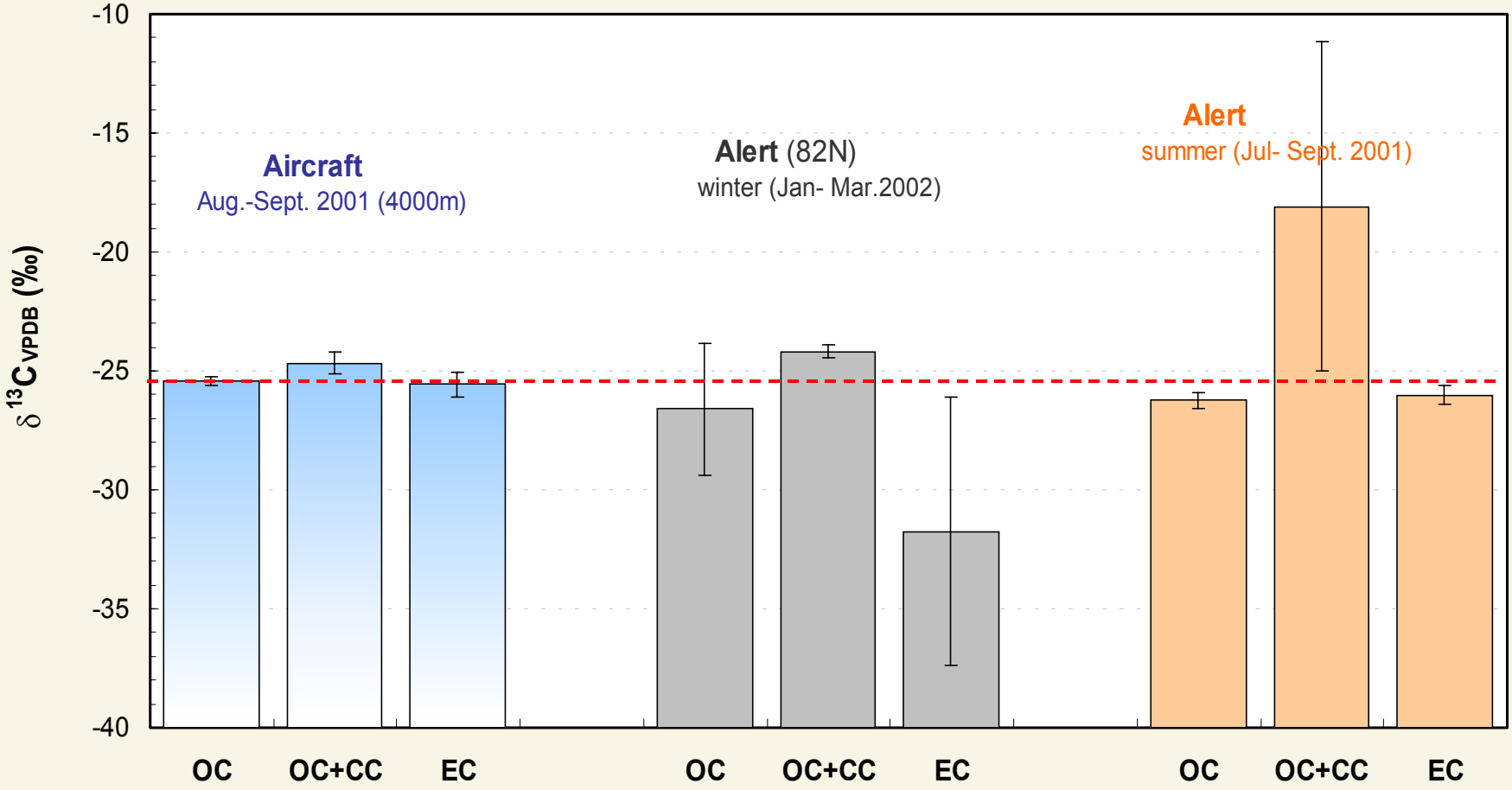

Pacific 2001 Ground Sites
Cssiar Tunnel
Golden Ears Park
Slocan Park
1
2
3
4
5
GVRD
FVRD
Whatcom County
Legend
Scale 1:550000

Isotope compositions in Source Profile and Ambient Air

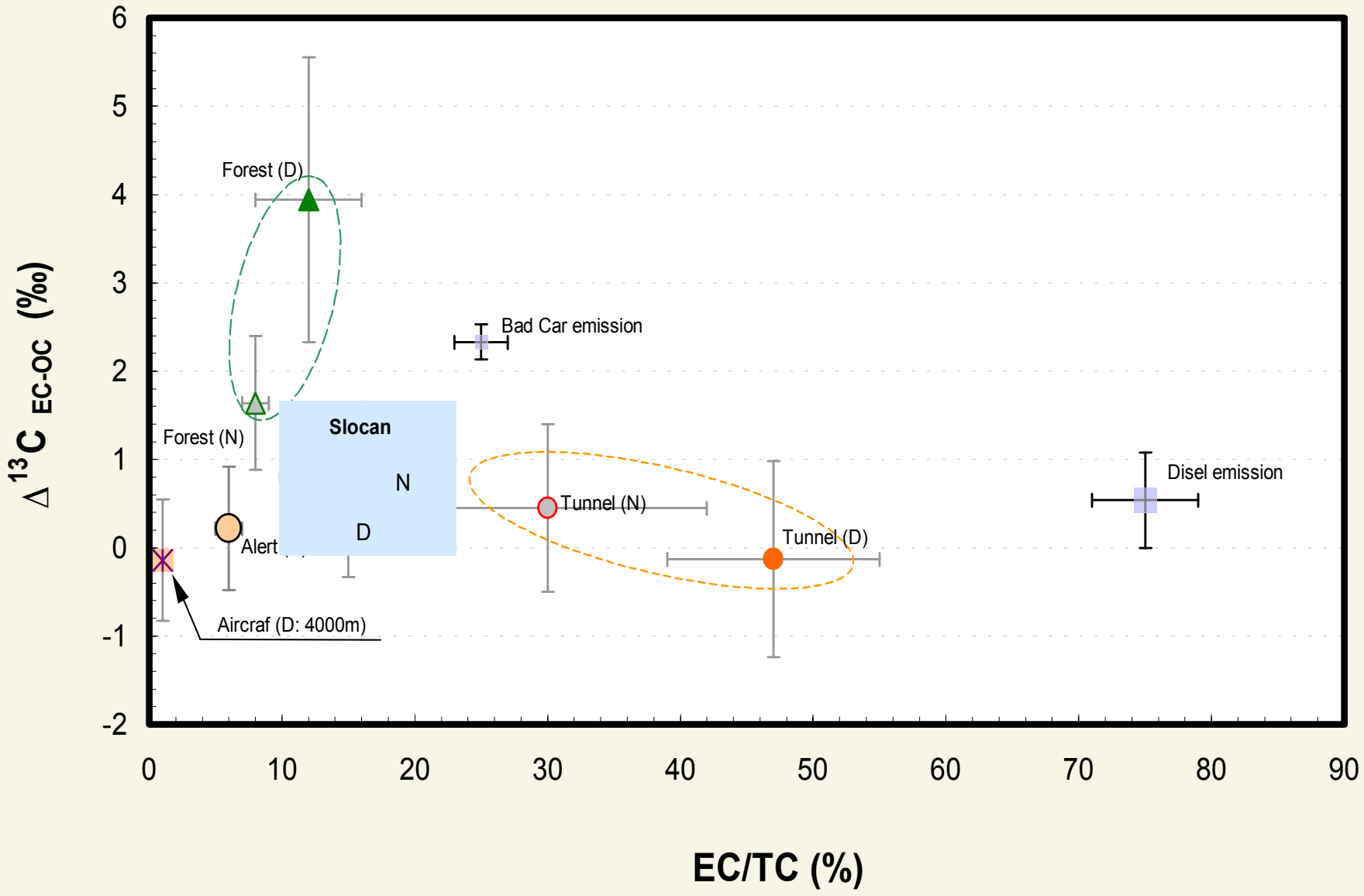
(Pacific2001 Campaign at Vancouver, BC)



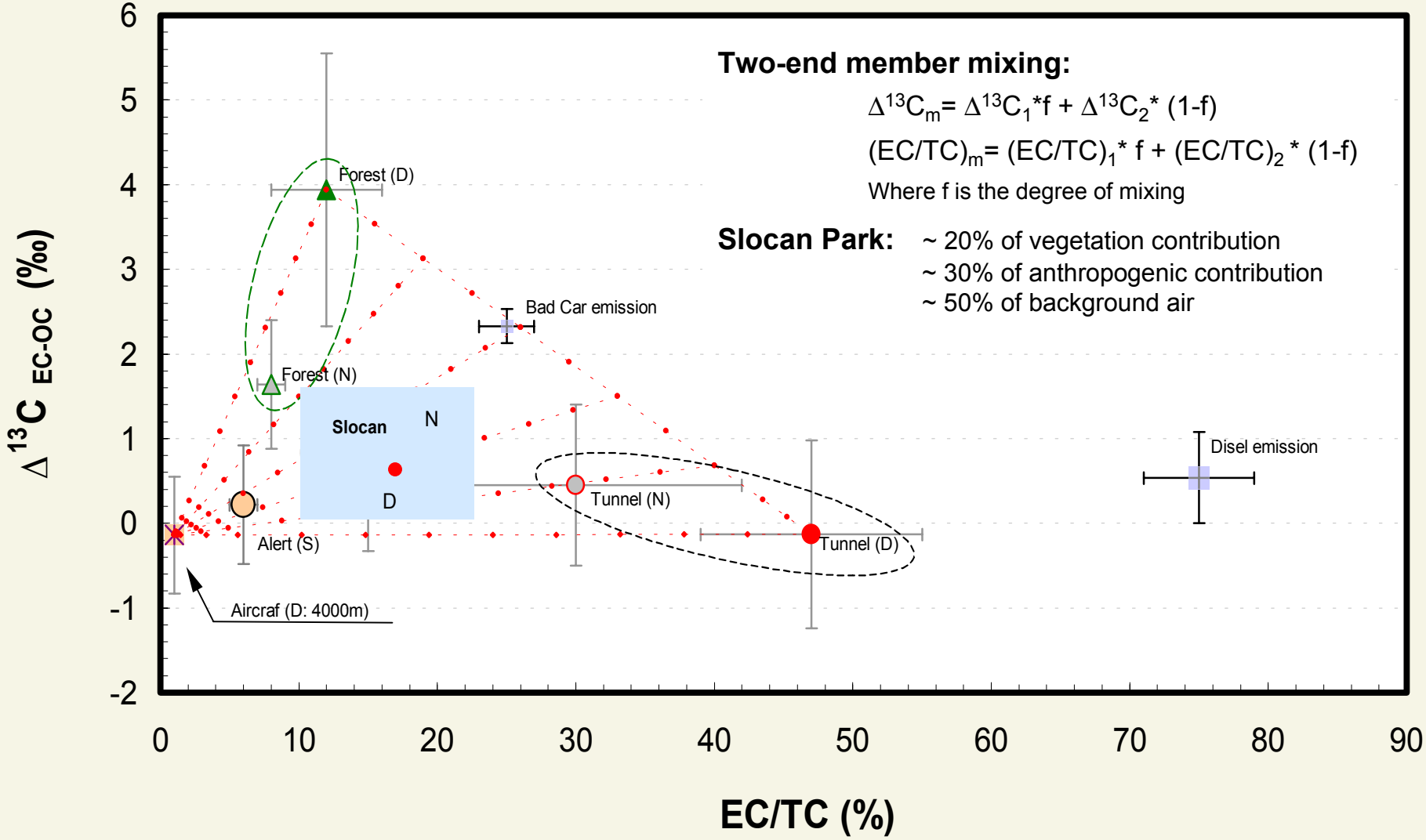
Isotopic Compsition of Background Air



OC/EC Abundances and Isotopic Compositions in Ambient PM and Their Sources



Source Apportionment via Isotope Measurements in OC/EC of PM



Summary

- Stable isotopic compositions of OC/EC in aerosols can be measured via coupling an OC/EC analyzer with GC-IRMS
  - **Overall accuracy: ~ 0.3 ‰**
  - **Overall precision: ~ 0.3 ‰**
- **There are obvious different patterns** in distributions of carbon components and their isotopic compositions between a **biogenic source** (Golden Ears) and an **anthropogenic source** (Cassiar Tunnel):
  - **the $\delta^{13}C$ value of EC in tunnel samples tends to be close to the value of OC**, indicating very small isotopic fractionation between different components in high temperature processes;
  - **the $\delta^{13}C$ value of EC in the forest samples is obviously different from that of OC**. The reason is not well understood yet;
  - the $\delta^{13}C$ value of OC/EC in aircraft samples are very close to those of Alert samples, indicating **homogeneous isotope composition of free troposphere aerosols**;

It is suggested that combining EC concentration and the isotope compositions of OC/EC can provide valuable information to source identification and apportionment for ambient aerosols.

Acknowledgement

- **Pacific 2001 Project from MSC for financing;**
- R. Leaitch's group, K. Anlurf, L. Grahem for **sampling** at Pacific 2001;
- S. Irei for assisting **sample analysis**;
- D. Lane for **sharing instrument**;
- Dr. B. E. McCarry for **sharing** carbon black **standards**;
- L. Grahem and T. Harner for **sharing** samples;
- S.M. Li, and R. Leaitch for **valuable discussion.**

The End