“Perspective on Halogens”

Paul B. Shepson
Dept. of Chemistry, Purdue University
and
Purdue Climate Change Research Center

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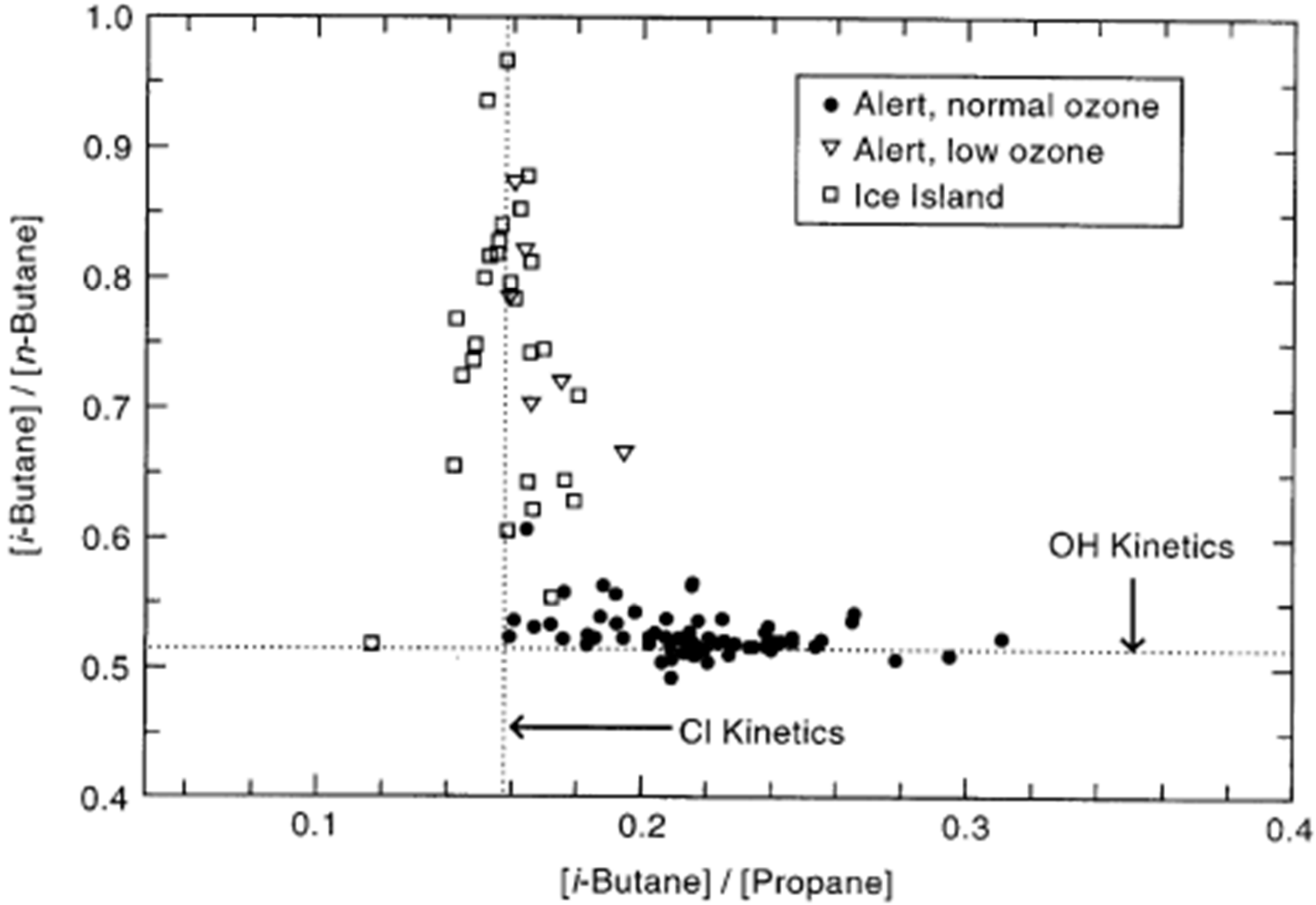
What things do we know?



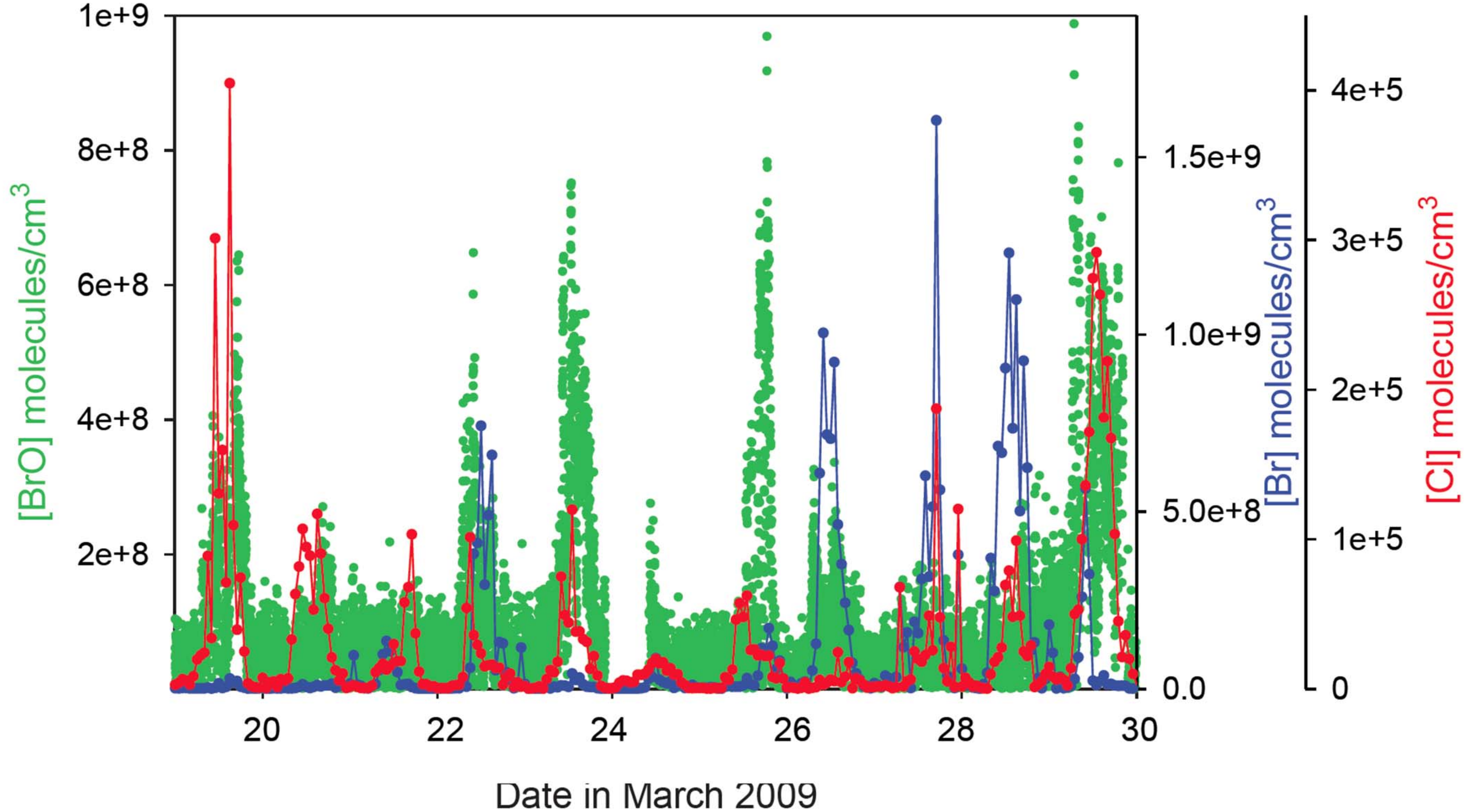
We know chlorine atom chemistry is occurring and it is important!
(Jobson et al., JGR, 1994)

OASIS09 – Measurements of “everything that matters”

$$[Cl]_{ss} = \frac{(2J[Cl_2] + J[BrCl] + J[ClO] + k[Cl_2][OH] + k[ClO][OH] + k[ClO][NO] + k[ClO][ClO])}{(k[HO_2] + k[O_3] + k[MEK] + k[CH_4] + k[C_2H_2] + k[C_2H_4] + k[C_2H_6] + k[C_3H_6] + k[C_3H_8] + k[iC_4H_{10}] + k[nC_4H_{10}] + k[HCHO] + k[CH_3CHO])}$$

$$[Br]_{ss} = \frac{(2J[Br_2] + J[BrCl] + J[BrO] + J[HOBr] + k[Br_2][OH] + k[BrO][NO] + k[BrO][ClO] + 2k[BrO][BrO] + k[BrO][OH])}{(k[HO_2] + k[O_3] + k[NO_2] + k[HCHO] + k[CH_3CHO] + k[C_2H_2] + k[C_2H_4] + k[C_3H_6])}$$

OASIS09 Measured and Calculated Radical Concentrations



For “typical” daytime peaks of [Cl] = 1x10^5 and [Br] = 4x10^8, [BrO] = 6x10^8

Calculated rate of O_3 destruction by Br = 0.26ppb/hr.

Calculated rate of O_3 destruction by Cl = 0.0.07ppb/hr.

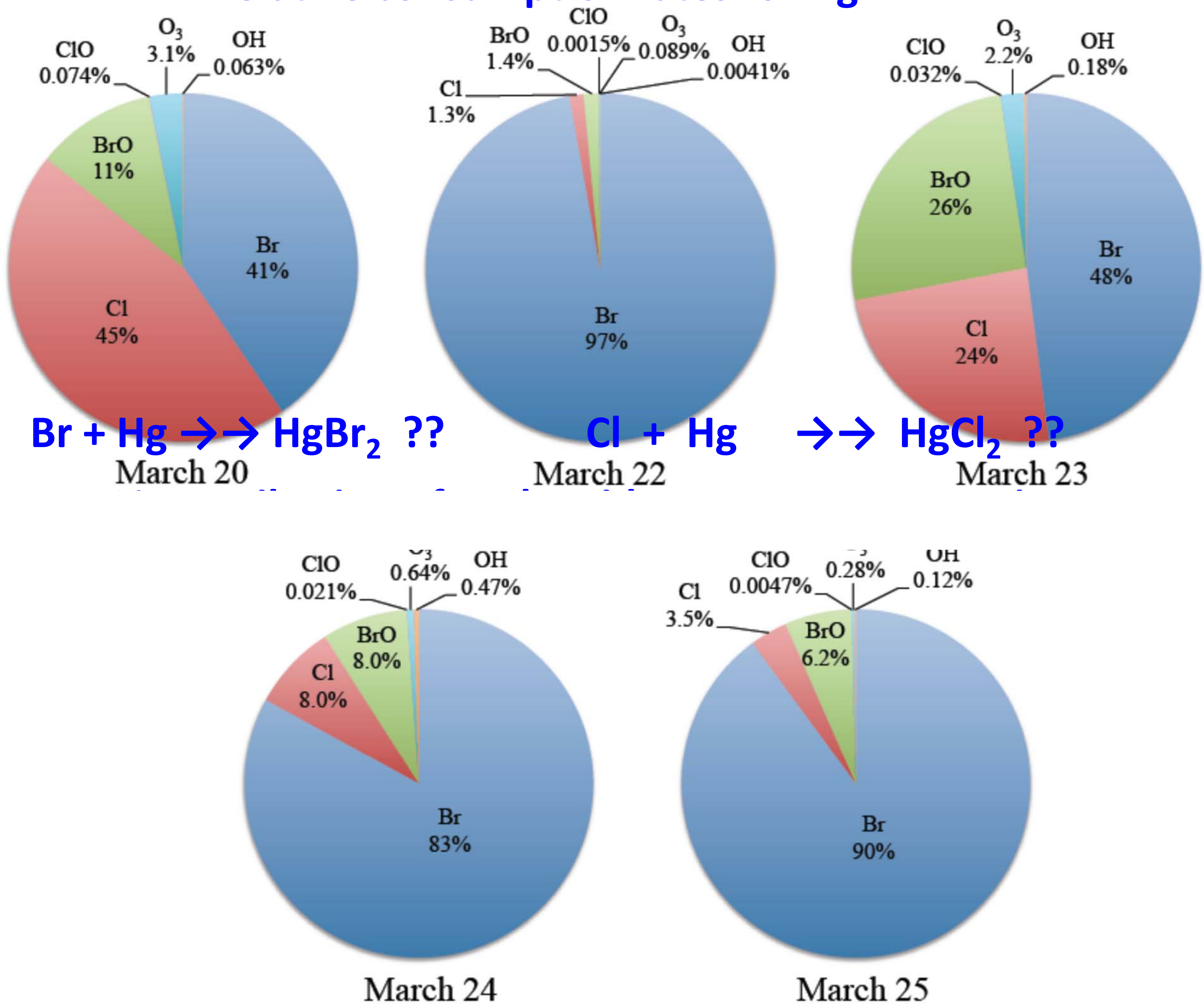
21%

$1x10^5$ cm^{-3} Cl represents a large oxidizing power.

For example, at T=245, for $1x10^5$ Cl and $1x10^6$OH

The first order k for consumption of n-butane is
$1.74x10^{-6}s^{-1}$ for OH (6.6 days)
and
$2.0x10^{-5}s^{-1}$ for Cl (0.56 days)

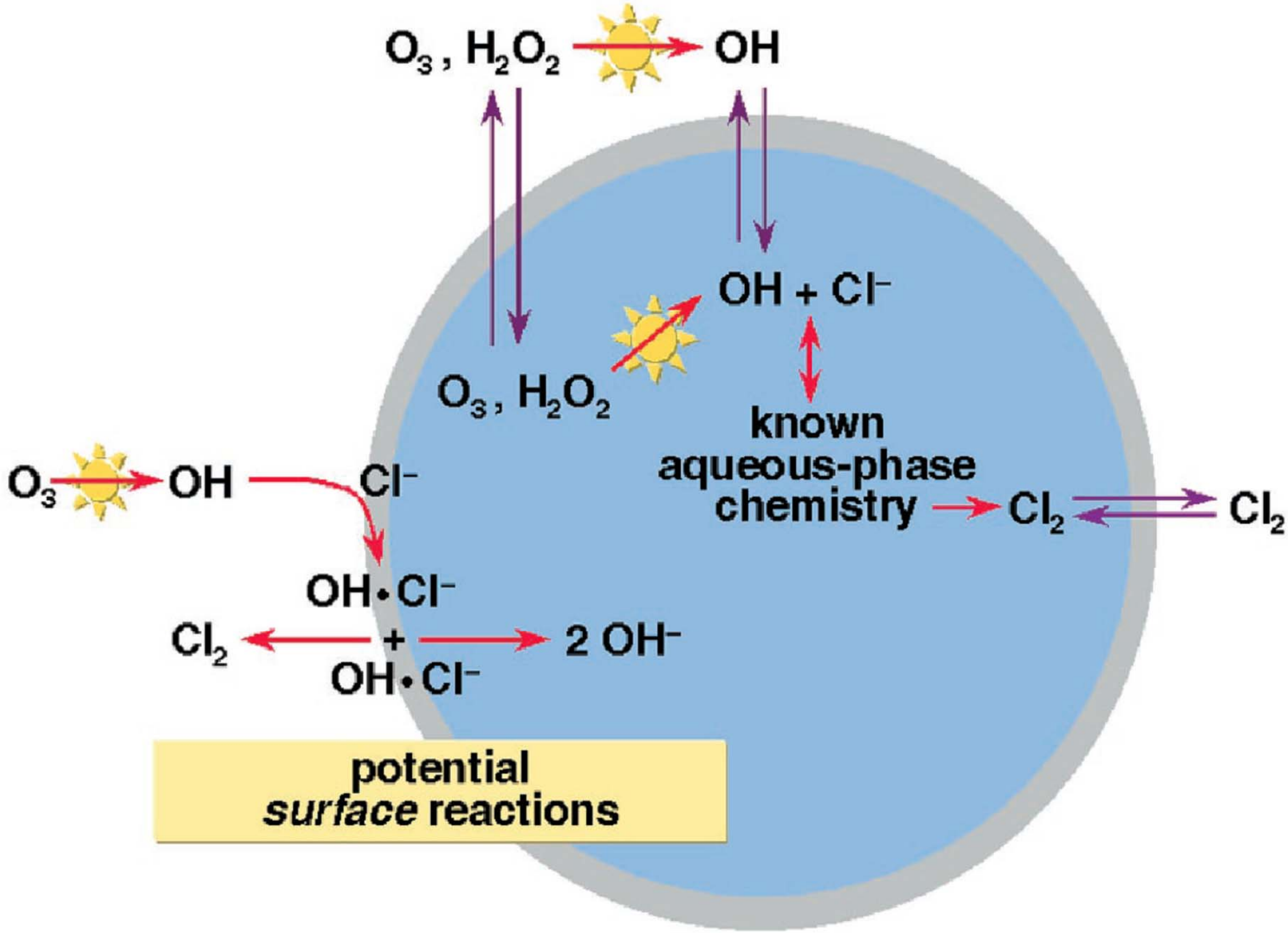
Relative consumption rates for Hg^o



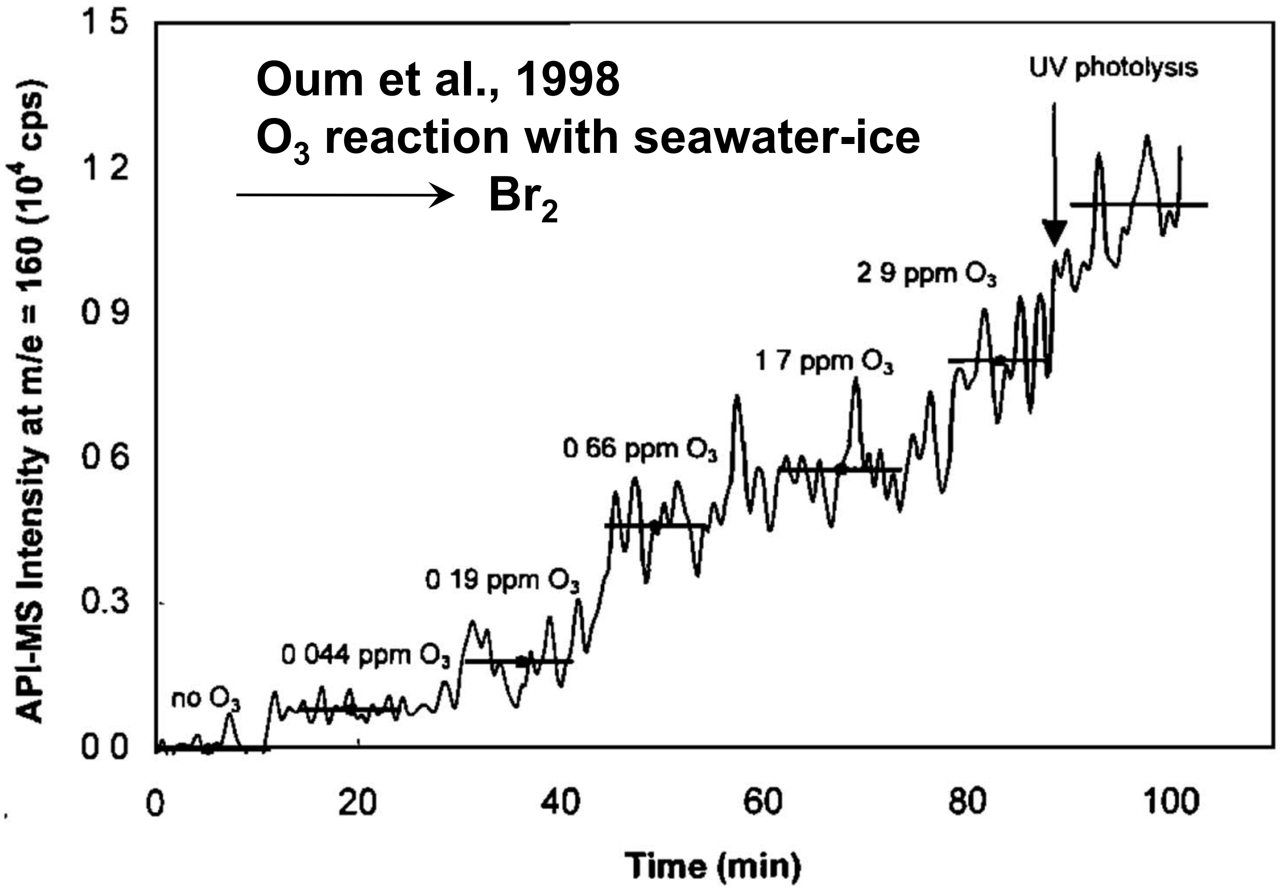
$Br + Hg \rightarrow\rightarrow HgBr_2$??

$Cl + Hg \rightarrow\rightarrow HgCl_2$??

We know that you can make Cl_2 by irradiating sea salt aerosols with 254nm radiation in the presence of O_3.
Knipping et al., 2000



We know, e.g. from Oum et al. and Wren et al. that Br^- at surfaces can be oxidized by O_3 to produce Br_2 (snow/sea ice/sea salt aerosols)

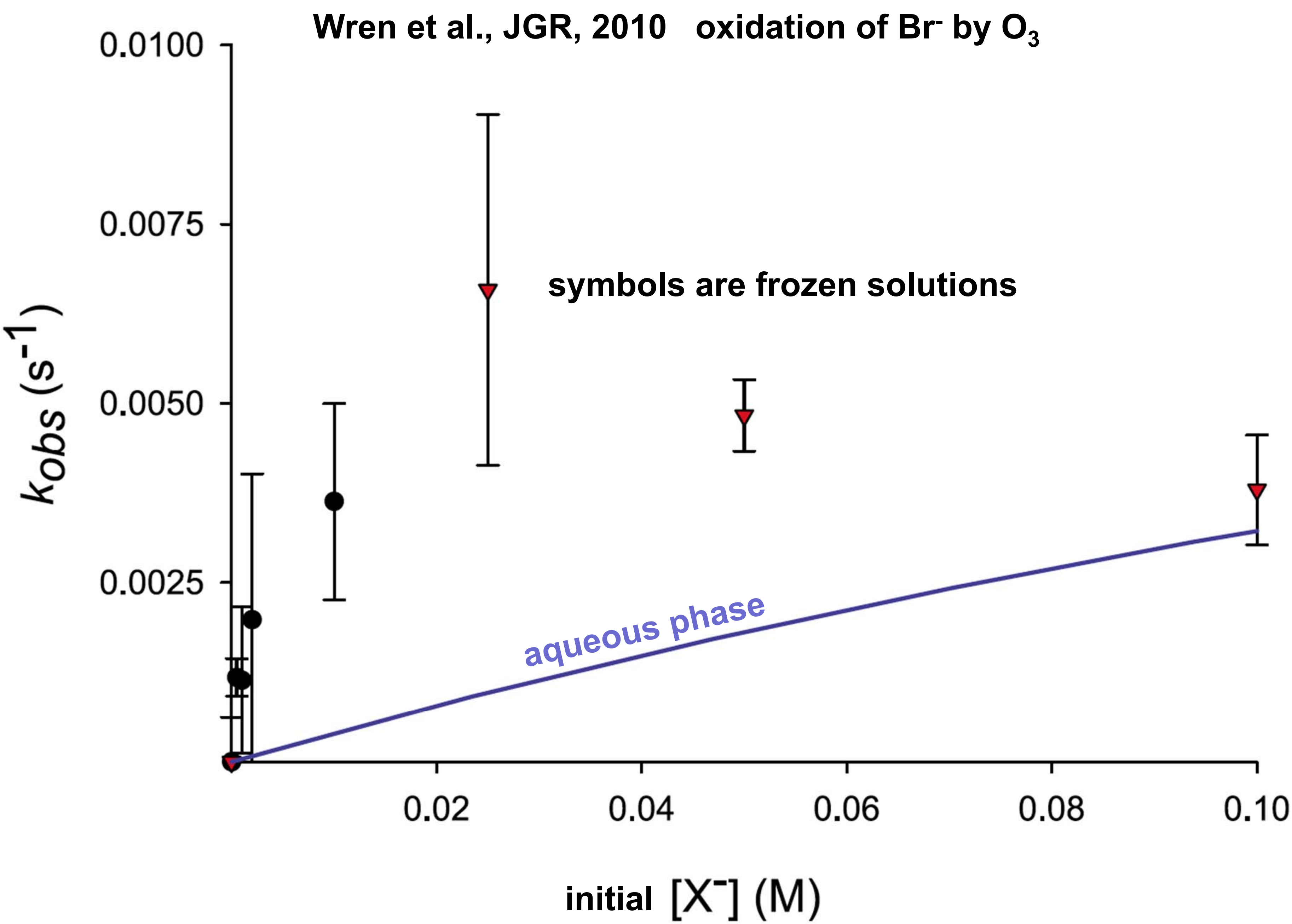


Hypothesis:

$Br^- + O_3 \rightarrow BrO^- + O_2$

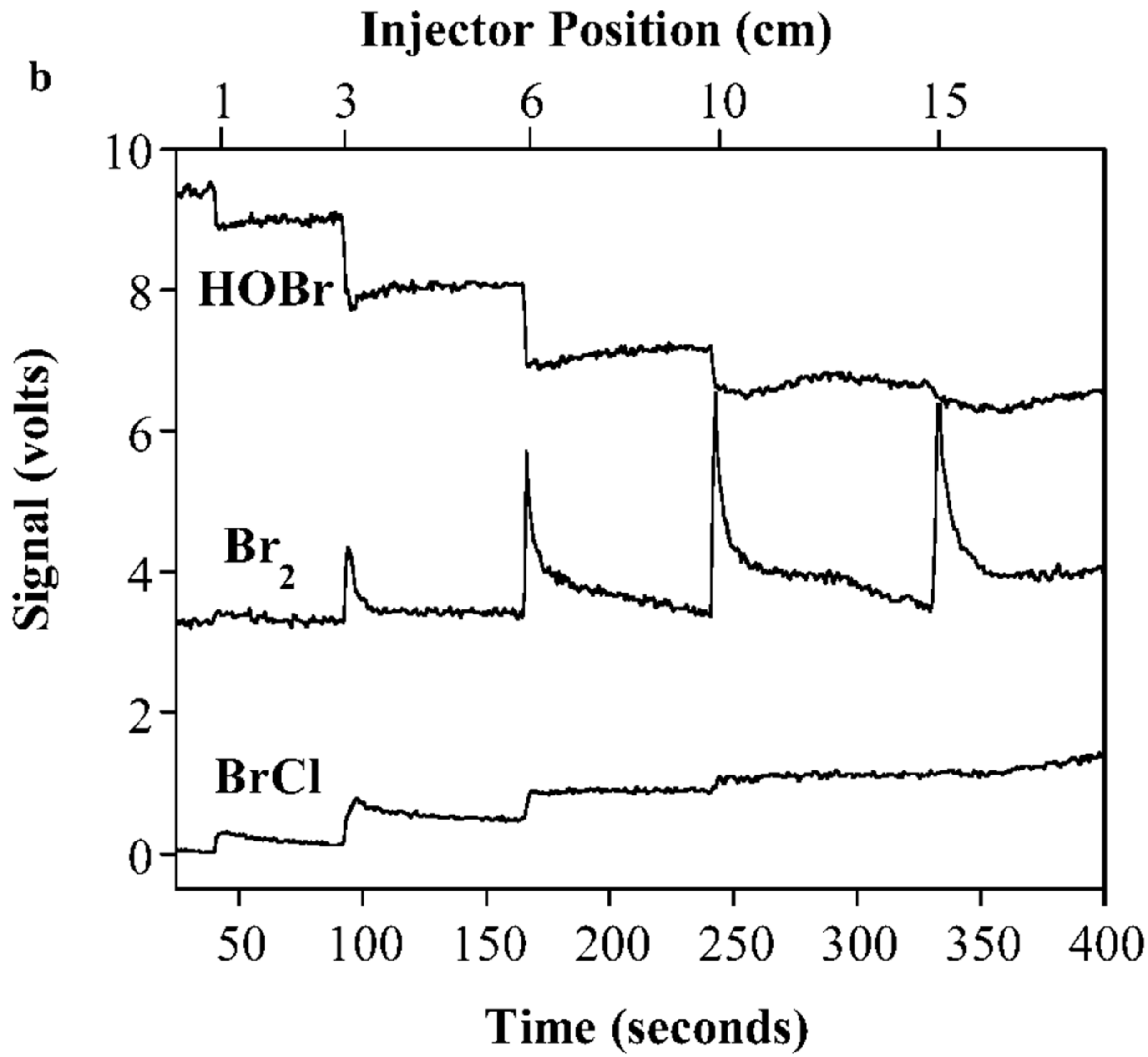
$BrO^- + H^+ \rightarrow HOBr$

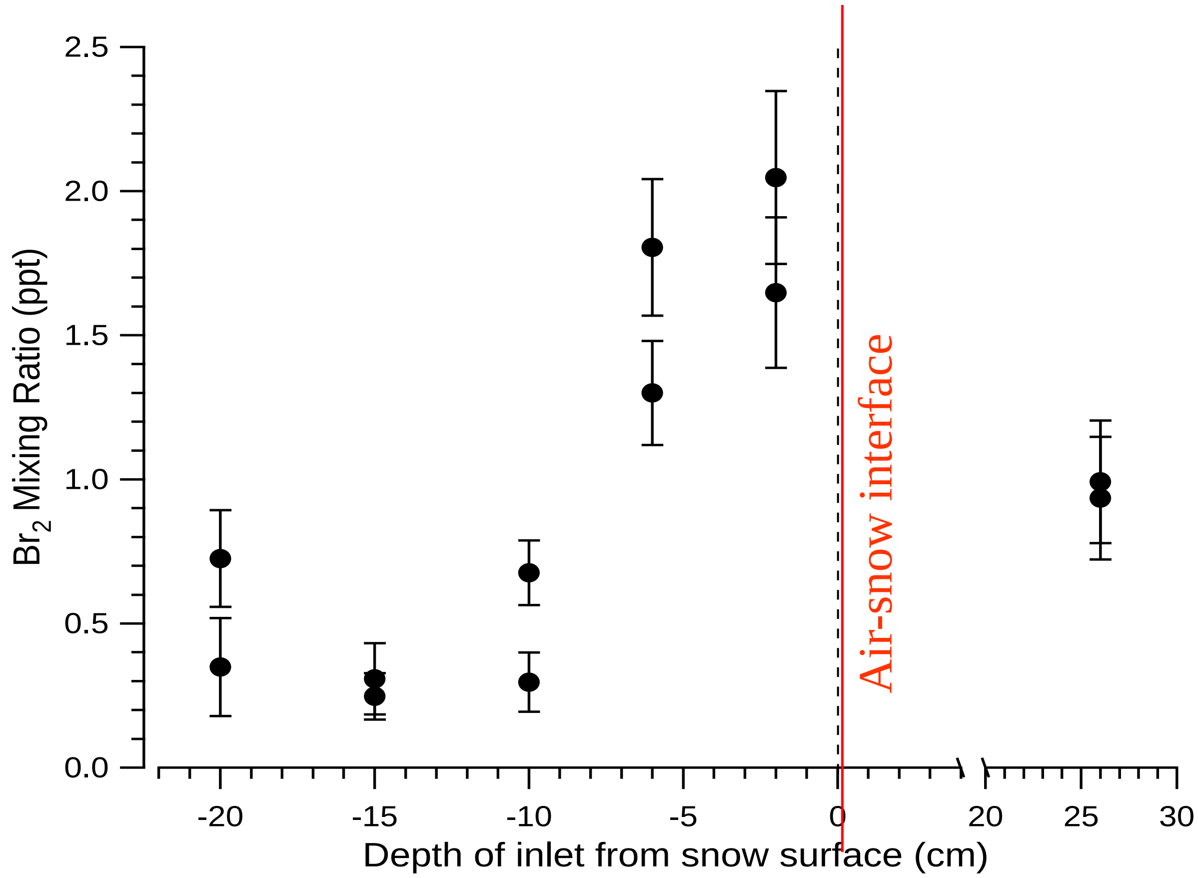
$HOBr + Br^- \rightarrow Br_2 + OH^-$


Wren et al., JGR, 2010 oxidation of Br⁻ by O3
0.0100
0.0075
0.0050
0.0025
kobs (s-1)
symbols are frozen solutions
aqueous phase
0.02
0.04
0.06
0.08
0.10
initial [X⁻] (M)

We know from Huff and Abbatt 2002 that

$$HOBr + H^+ + Br^- \text{ or } Cl^- \xrightarrow{\text{ice}} BrCl \text{ and } Br_2$$





We know that Br_2 is produced in saline snowpacks in the dark.

Foster et al., *Science*, *291*, 471-474, 2001.

FIGURE 2

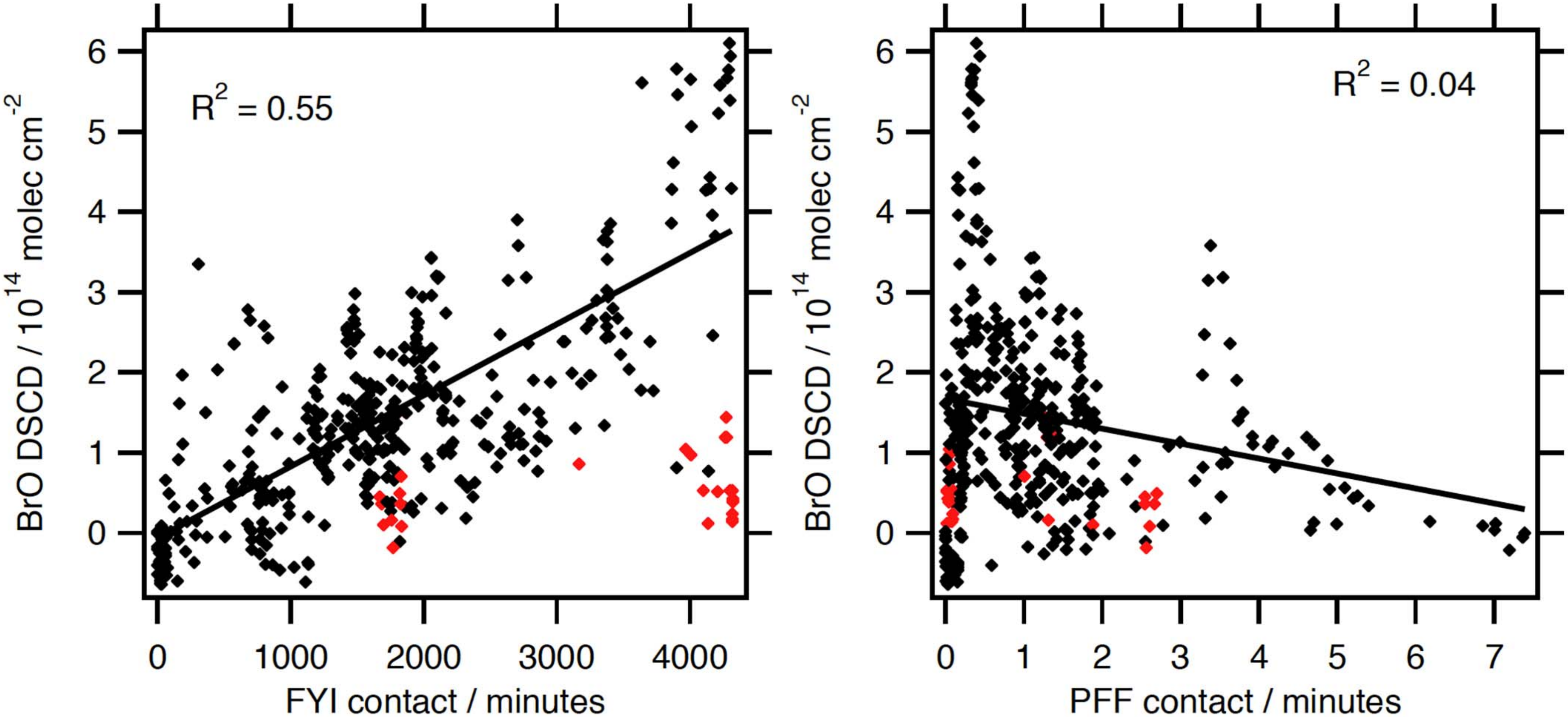
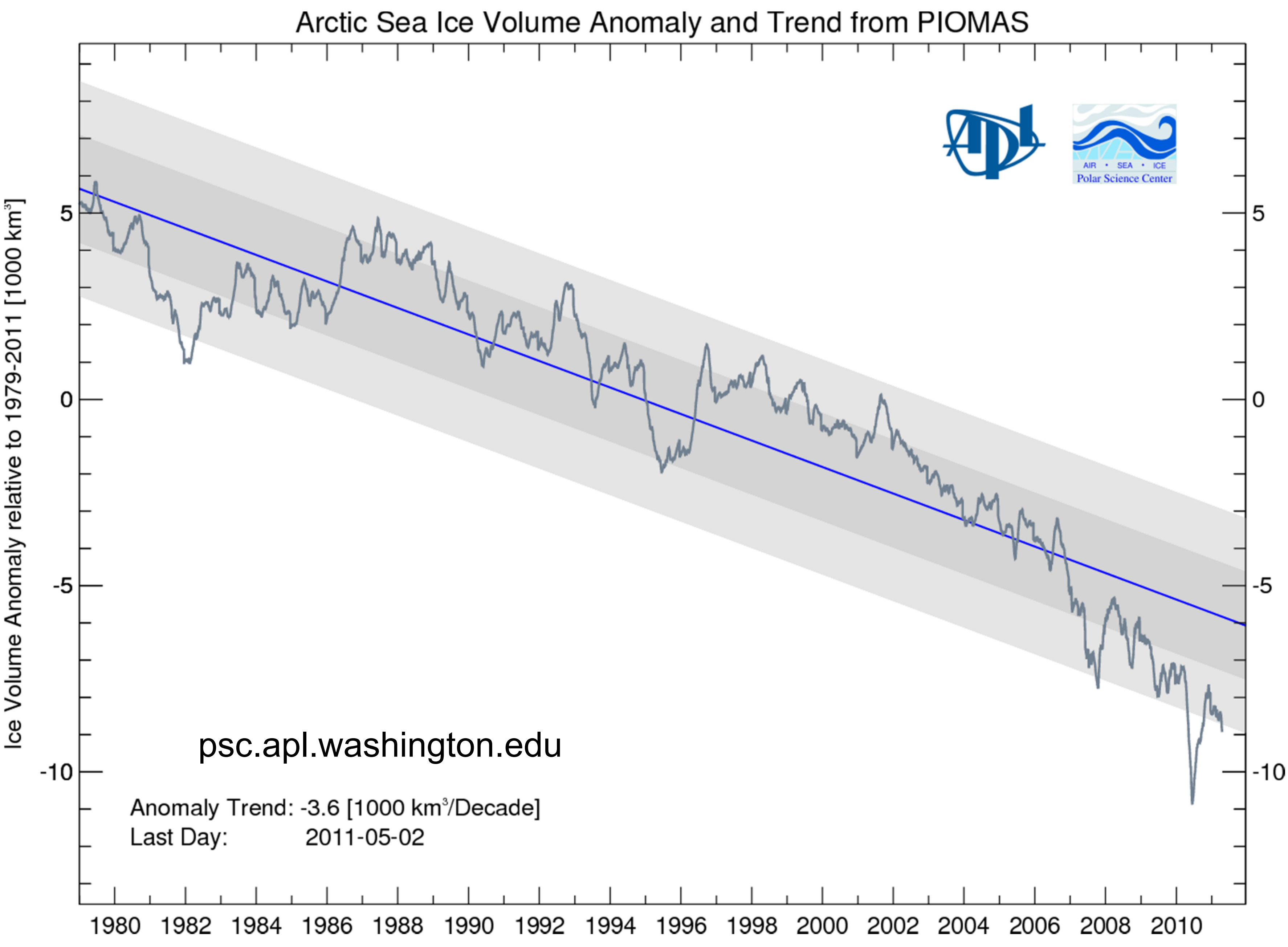


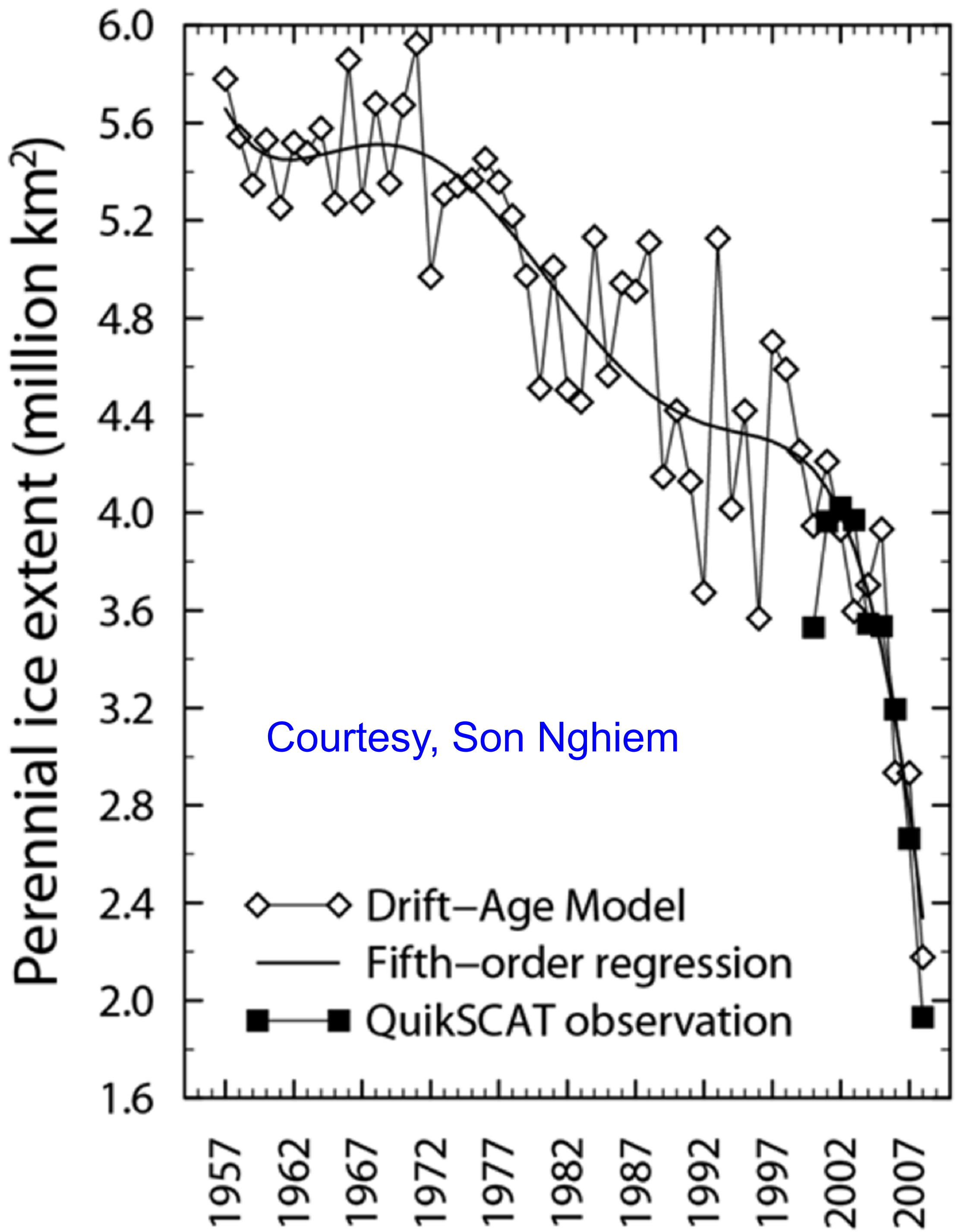
Fig. 3. Correlation plots of BrO versus first-year sea-ice contact (left) and potential frost flowers contact (right). Data colored in red occurred when ozone <1 ppbv and were ignored from the correlation analysis.

We know that BrO seems to correlated with First Year Sea Ice
Simpson et al., 2006

We know that sea ice mass is rapidly decreasing, and that process is accelerating.

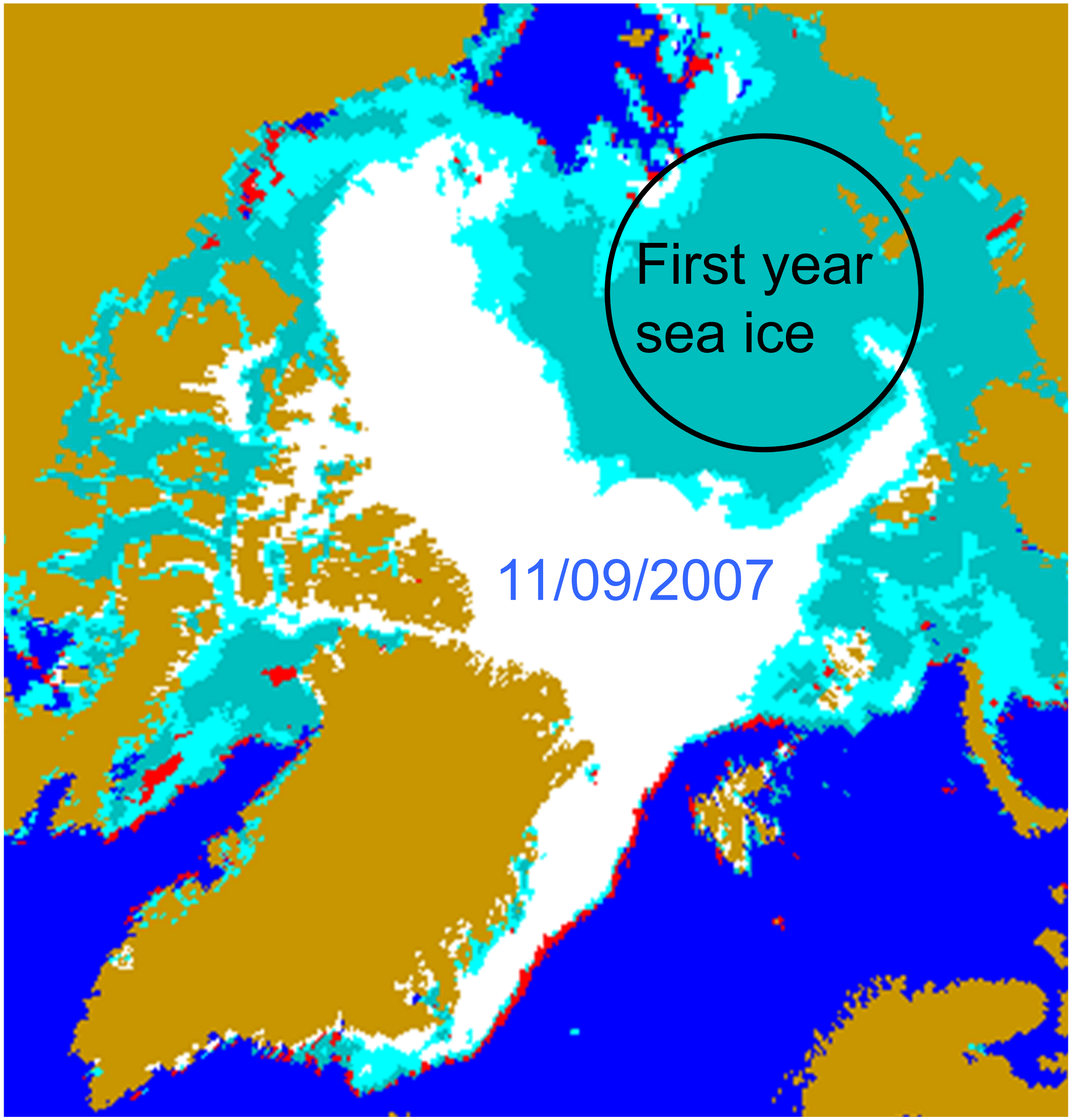


We know that
MYI is in very rapid decline



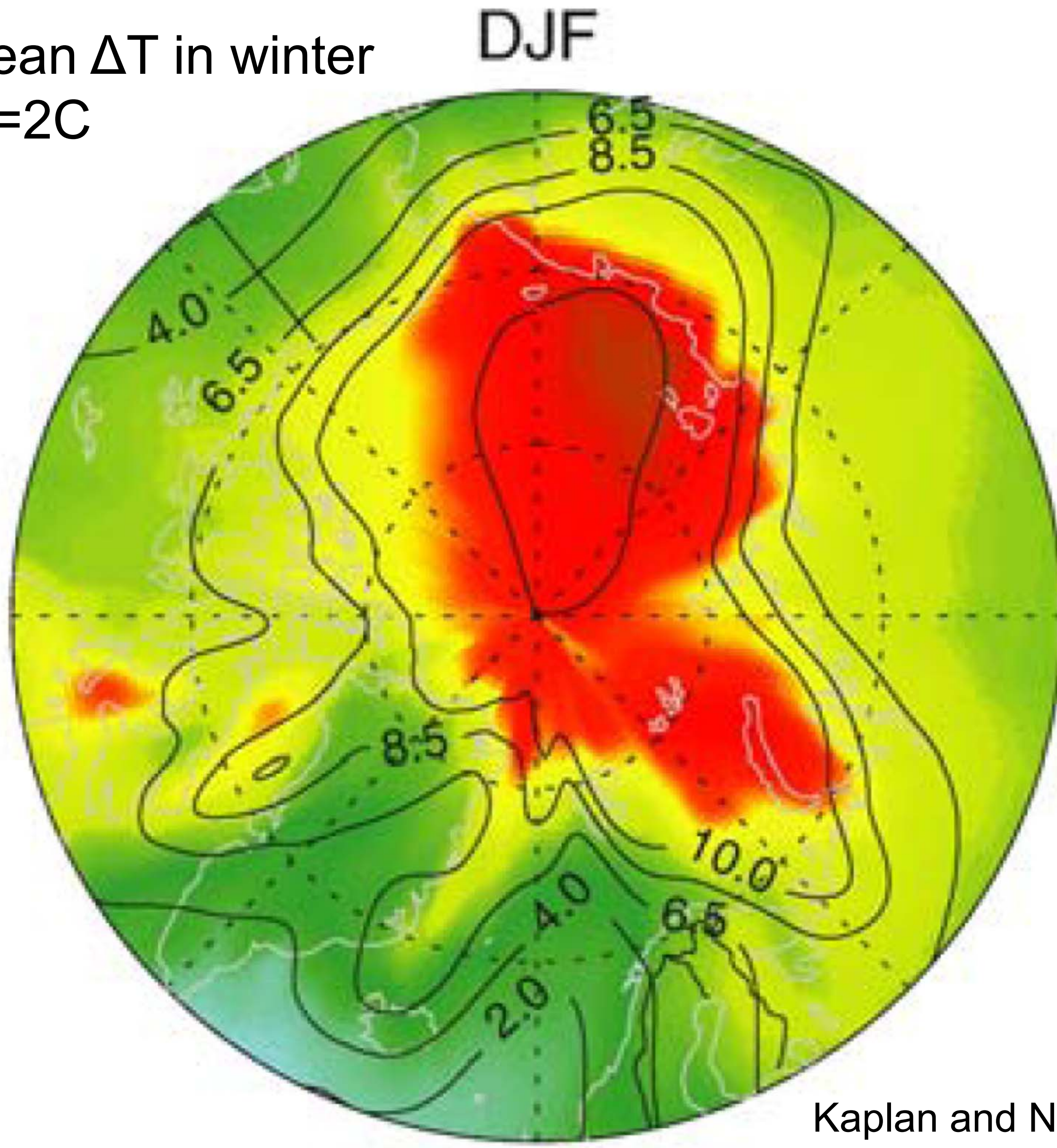
It will be replaced by First Year Ice

Courtesy
Son Nghiem




What will the future bring?

Simulated mean ΔT in winter for global ΔT=2C

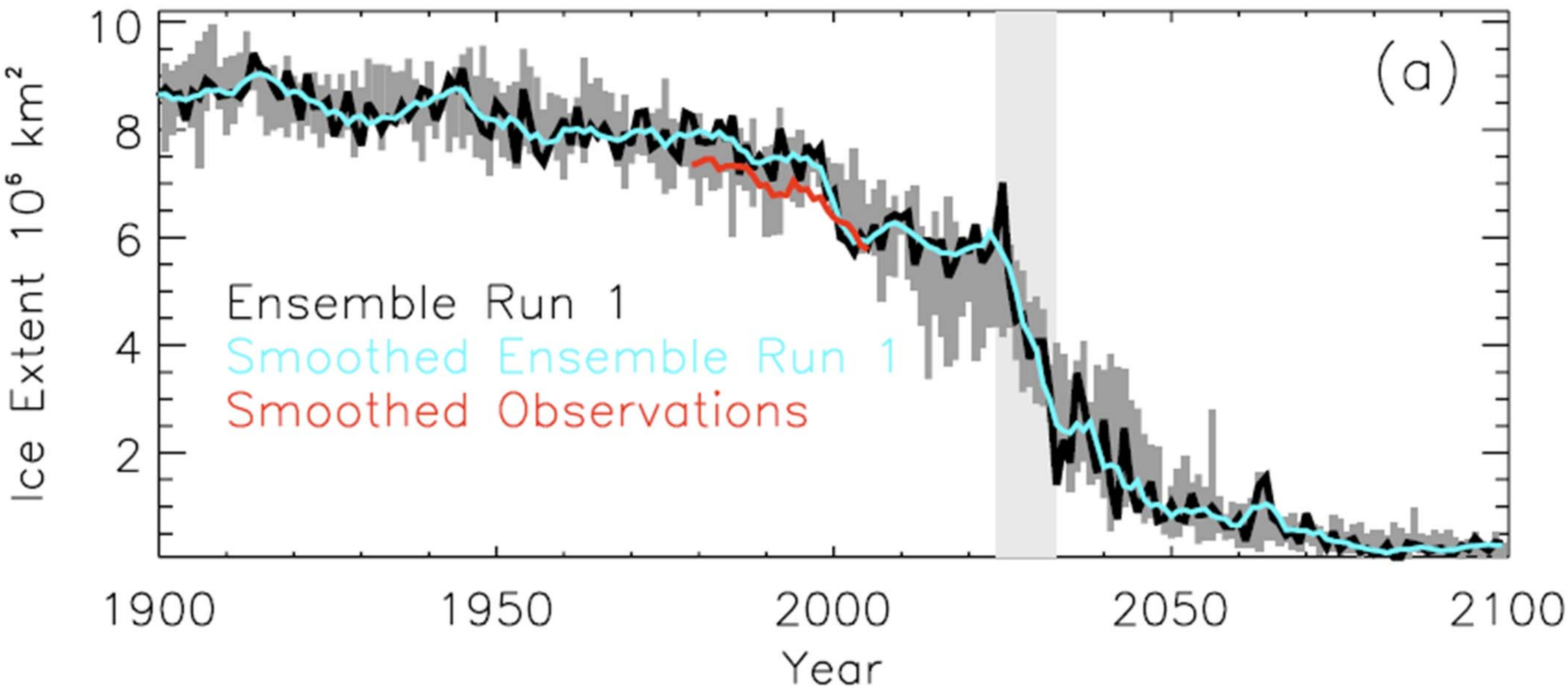


The Arctic
will experience
massive change

Kaplan and New
Climatic Change, 2006

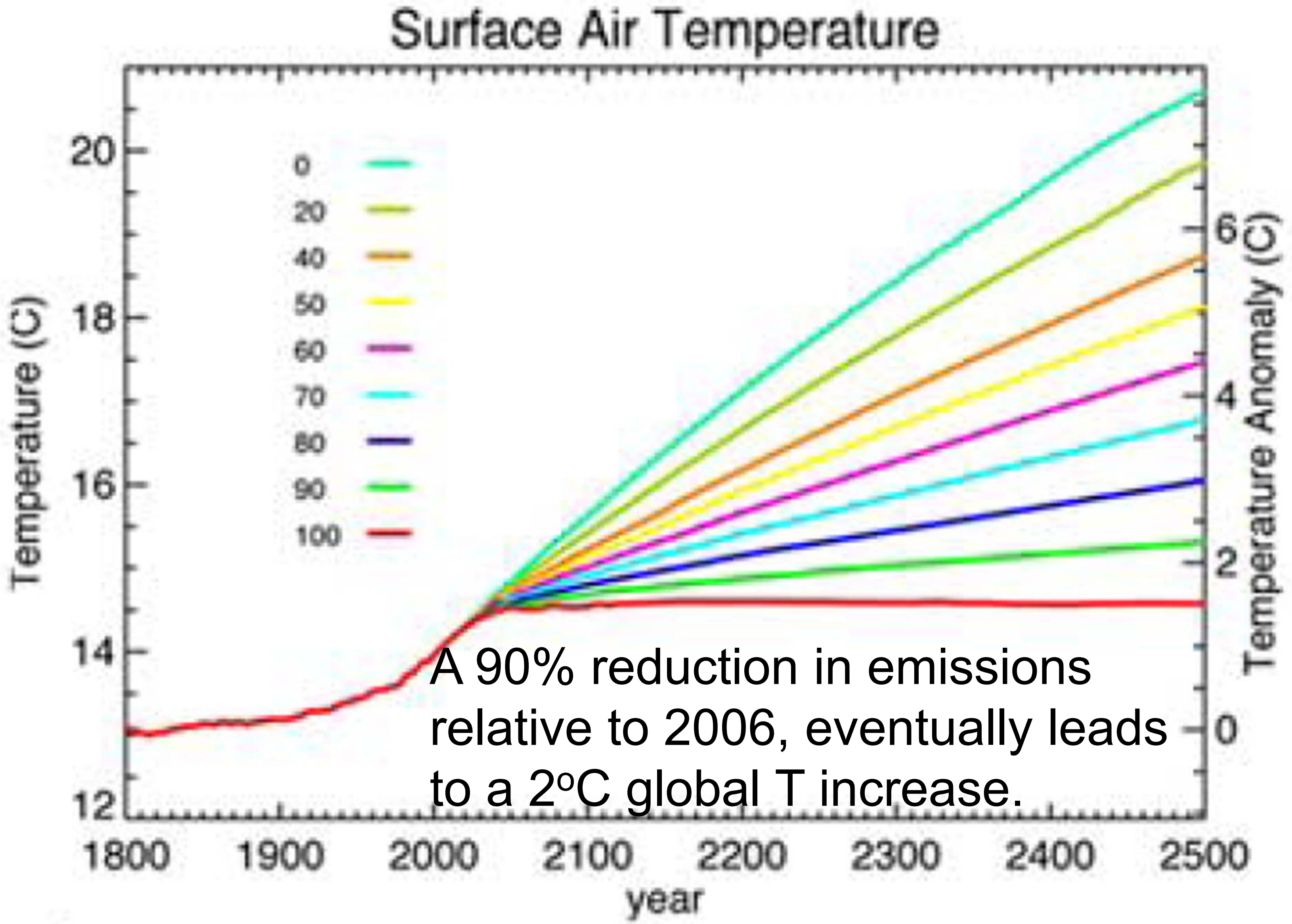
Holland et al., *GRL,* 2006

Arctic Sea Ice Extent Simulations



Weaver et al. (UVic) GRL 2007

Climate Change impacts of CO_2 emissions reductions relative to 2006 levels



A 90% reduction in emissions relative to 2006, eventually leads to a 2°C global T increase.

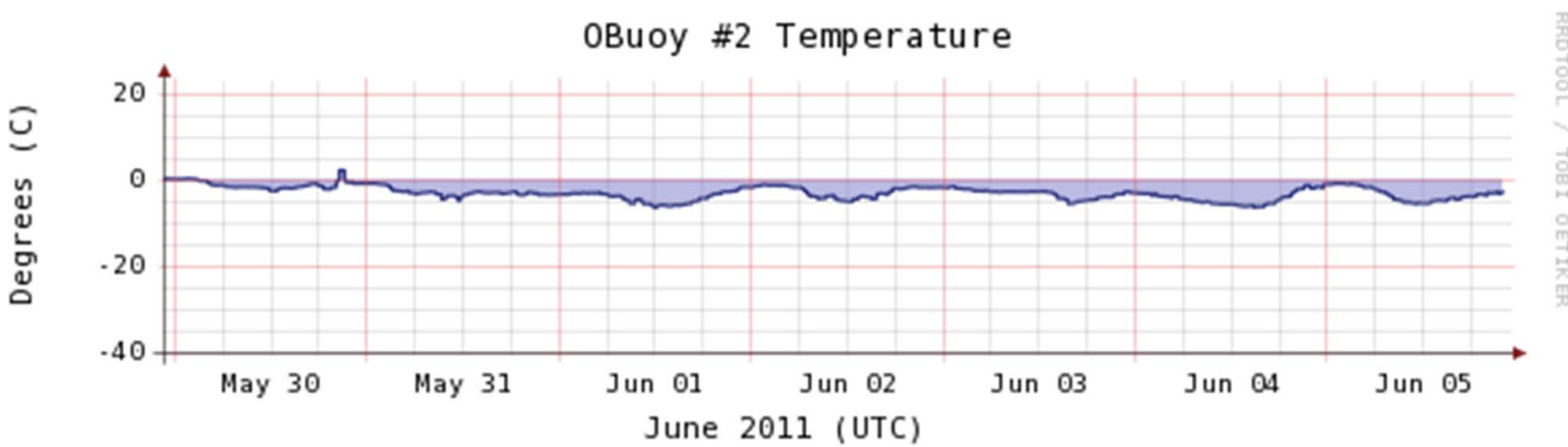
Eventually, the ice will be gone.

So, how to simulate the future?

How will an ice-free Arctic impact atmospheric composition?

- More O_3 at the surface?
- Smaller oxidation capacity
- Slower rate of production of CCN?
- But more water vapor? So, more cloud cover?
- Slower rate of Hg oxidation product inputs?
- Can we investigate these questions from measurements over polynyas?
- How to simulate this world?

We do know that ODEs can occur at relatively high T.
See, e.g. OBuoy number 2, currently in the Beaufort Sea:



We think we know that this chemistry occurs on surfaces. For ice, for lack of a good term, let's call it the QLL.

We think we know that this surface is a god-awful horrible mess.

Cho et al., *J. Phys. Chem.*, 2002.

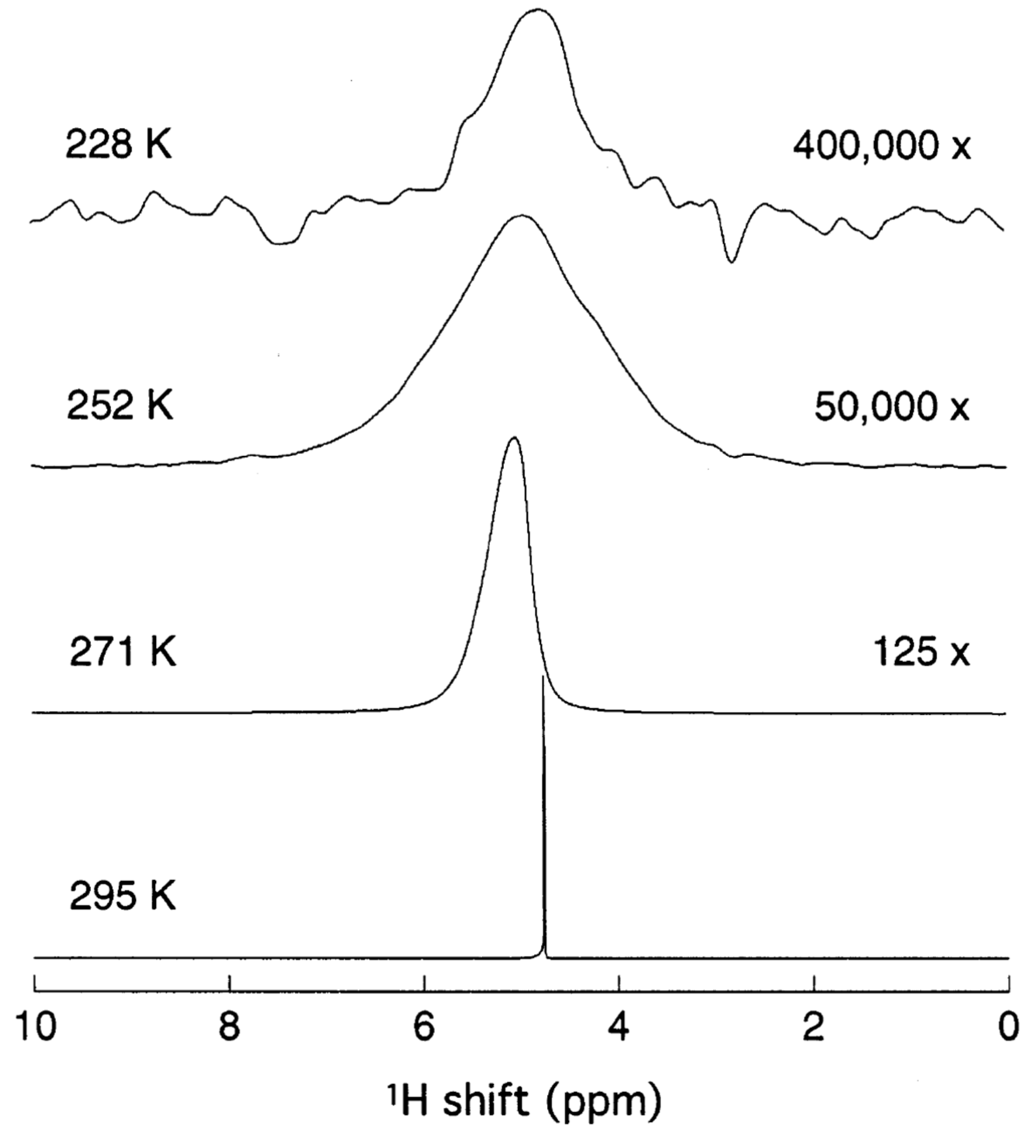
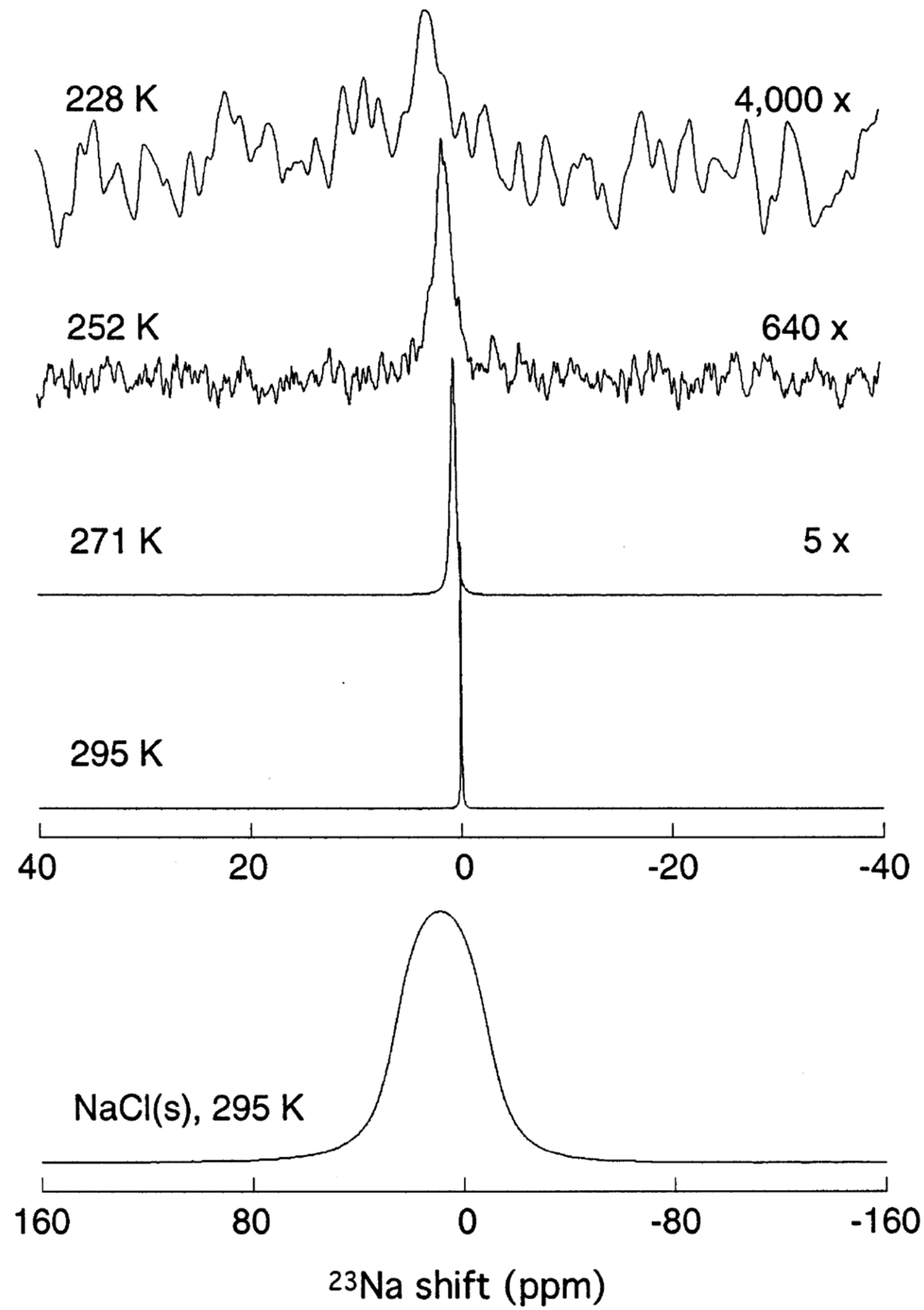
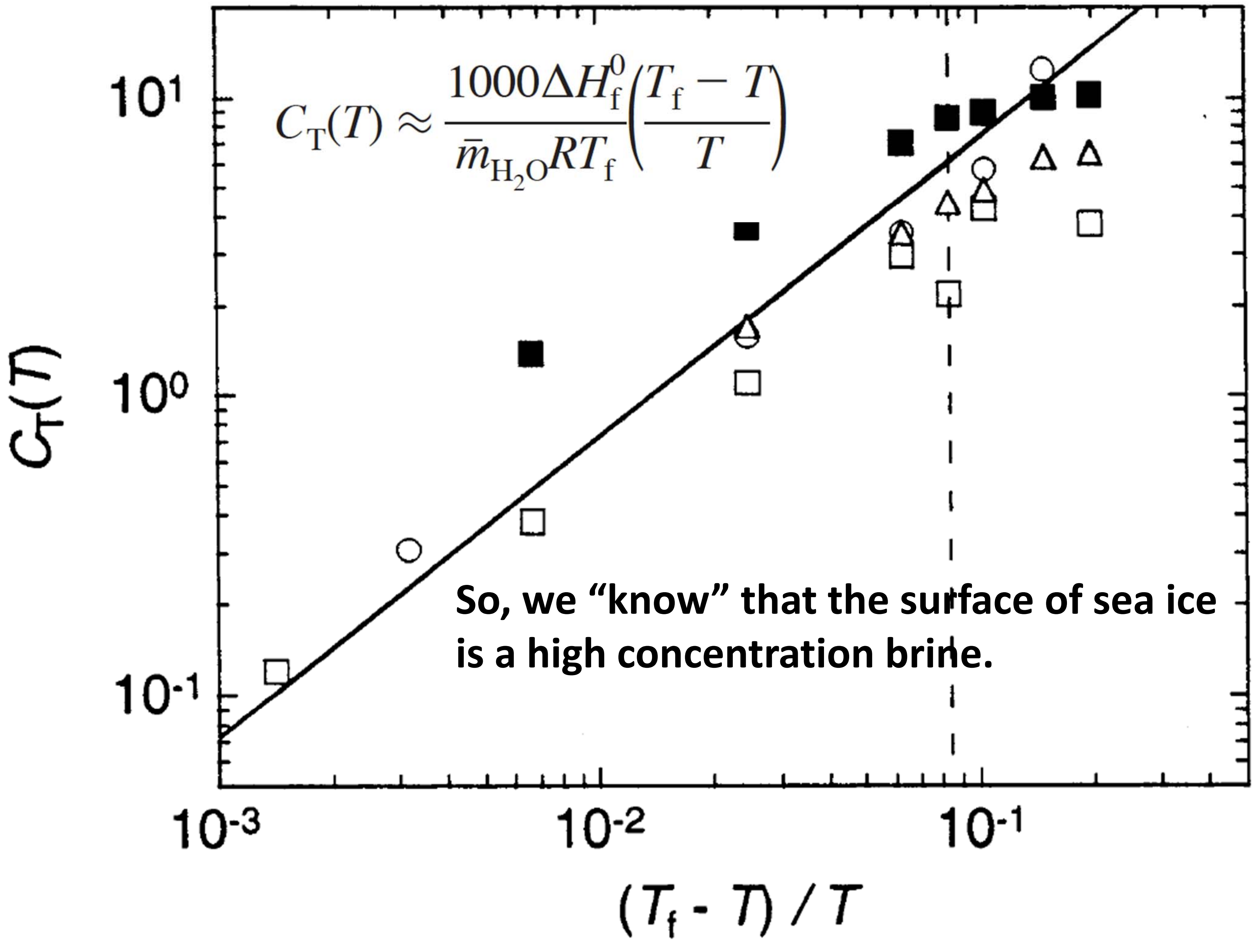


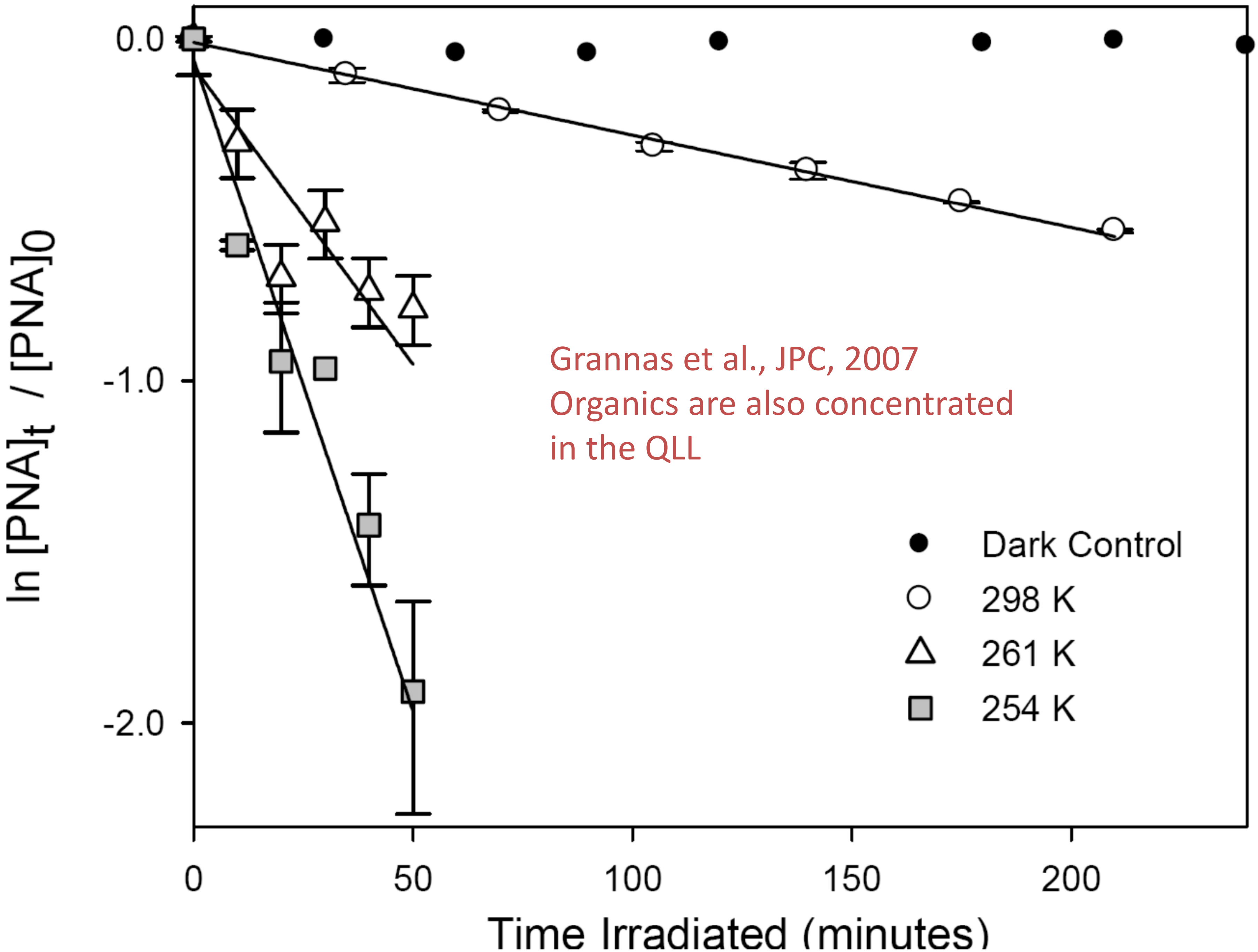
Figure 2. ^{1}H NMR spectra of a brine solution ([NaCl] = 0.500 M) at different temperatures. Relative intensity scales are given by the factors on the right. Each spectrum is an average of four scans. The time domain signals were apodized, but in no case was the width of the apodization function more than 20% of the intrinsic width of the ^{1}H line.

Same samples for ^{23}Na-NMR





So, we "know" that the surface of sea ice is a high concentration brine.



Grannas et al., JPC, 2007
Organics are also concentrated in the QLL

^{13}C NMR results for carboxylic acids

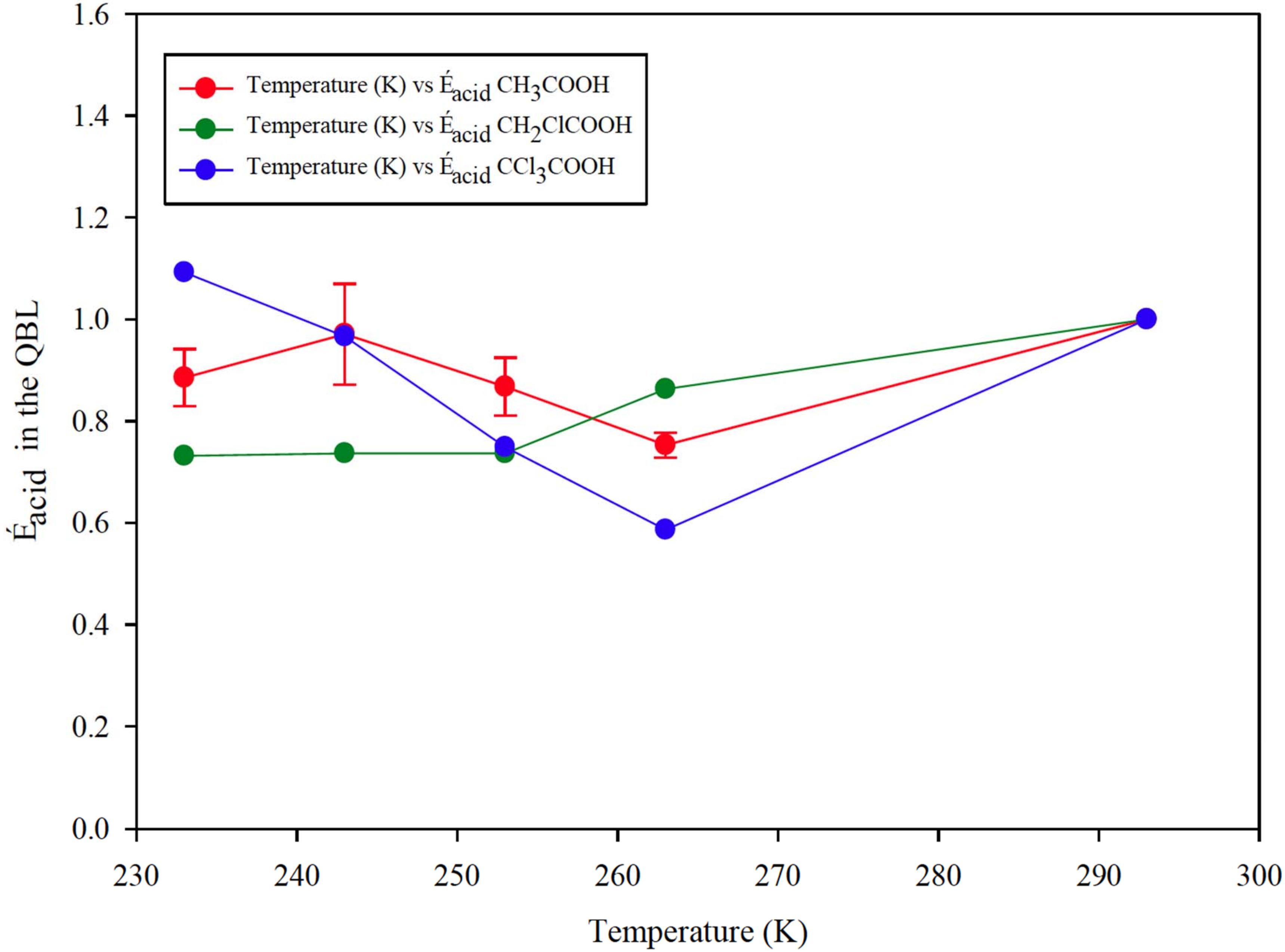
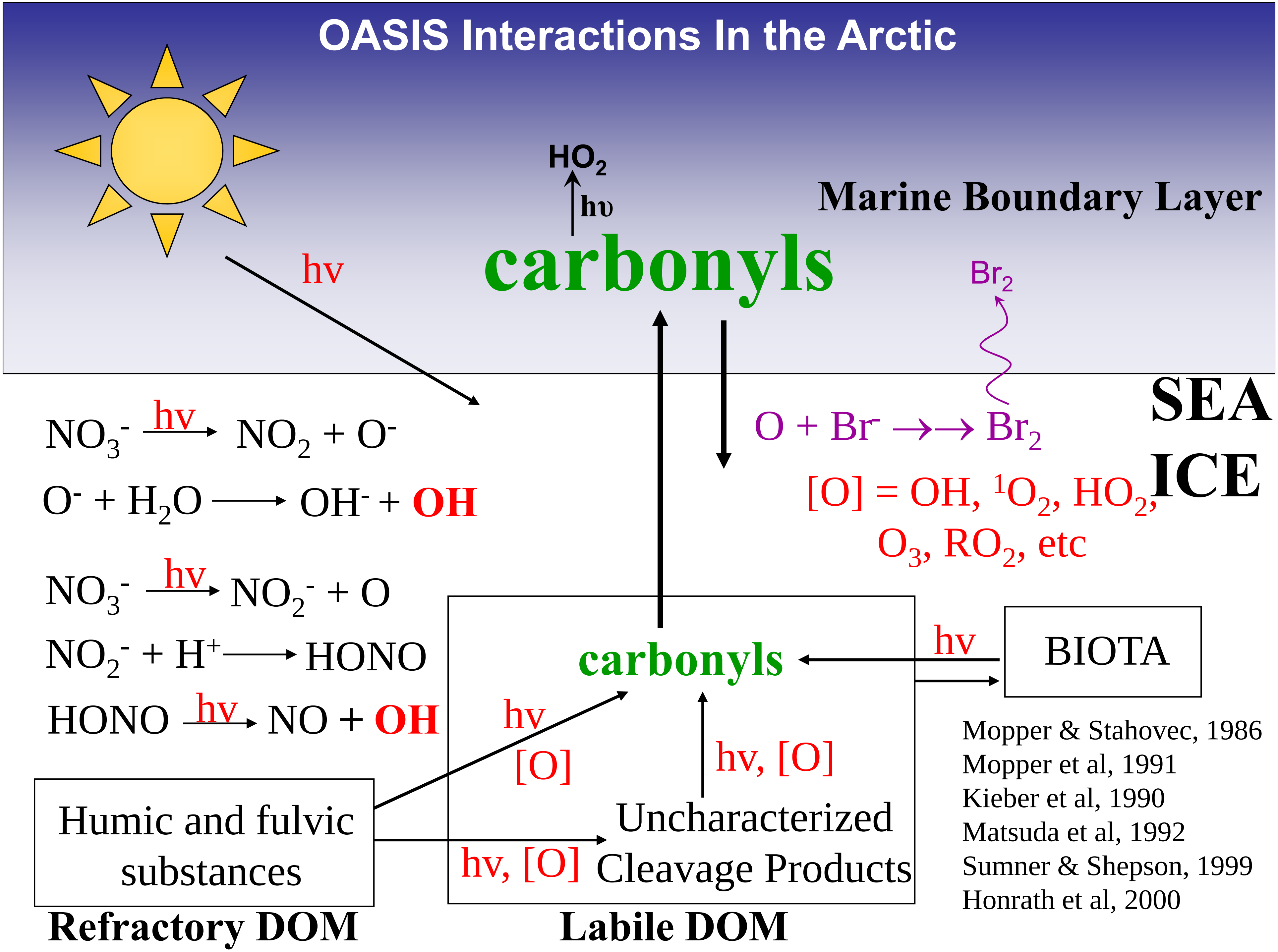


Table 1. Most Abundant Molecular Formulas Identified in Both Ice Core Samples[a]

1950 Core Sample						1300 Core Sample		
Formula	Error in Formula Mass, ppm	Peak Abundance	Formula	Error in Formula Mass, ppm	Peak Abundance	Formula	Error in Formula Mass, ppm	Peak Abundance
$C_{28}H_{40}O_4$	0.3	100	$C_{25}H_{20}SO$	−0.1	0.06	$C_{28}H_{40}O_4$	0.2	100
$C_{29}H_{42}O_4$	0.0	47.9	$C_{25}H_{22}SO$	−0.2	0.04	$C_{29}H_{42}O_4$	−0.2	52.4
$C_{26}H_{36}O_4$	0.2	45.4	$C_{25}H_{24}SO$	0.1	0.06	$C_{26}H_{36}O_4$	0.2	35.7
$C_{24}H_{18}O_{10}$	0.4	26.5	$C_{25}H_{26}SO$	0.0	0.04	$C_{19}H_{34}O_6$	−0.3	14.3
$C_{24}H_{44}O_{12}$	0.2	24.2	$C_{25}H_{20}SO_2$	−0.5	0.17	$C_{26}H_{48}O_{13}$	0.2	13.7
$C_{26}H_{48}O_{13}$	0.3	21	$C_{25}H_{22}SO_2$	0.6	0.11	$C_{24}H_{44}O_{12}$	0.2	12.7
$C_{27}H_{26}O_{13}$	0.4	10.4	$C_{25}H_{24}SO_2$	0.4	0.07	$C_{22}H_{40}O_{11}$	0.1	10.7
$C_{30}H_{44}O_4$	0.4	8.3	$C_{25}H_{20}SO_3$	0.2	0.09	$C_{29}H_{46}O_7$	0.1	9.9
$C_{24}H_{40}O_4$	0.1	7.8	$C_{25}H_{22}SO_3$	−0.6	0.06	$C_{30}H_{44}O_4$	0.1	8.7
$C_{29}H_{46}O_7$	0.2	5	$C_{25}H_{24}SO_3$	0.5	0.06	$C_{20}H_{36}O_{10}$	0.2	7.7
$C_{26}H_{42}N_4O_4$	0.2	4	$C_{26}H_{24}SO_3$	0.5	0.10	$C_{27}H_{42}O_6$	−0.2	6.9
$C_{29}H_{50}O_4$	0.0	3.6	$C_{26}H_{26}SO_3$	0.8	0.06	$C_{35}H_{58}O_{10}$	0.6	6.0
$C_{25}H_{30}O_{11}$	0.1	3.2	$C_{27}H_{22}SO_3$	0.0	0.13	$C_{24}H_{40}O_4$	−0.1	5.9

∴ **The QLL for all environmental samples will be a god-awful mess!**


OASIS Interactions In the Arctic
HO2
hυ
Marine Boundary Layer
hv
carbonyls
Br2
SEA
ICE
NO3- hv → NO2 + O-
O- + H2O → OH- + OH
O + Br- →→ Br2
[O] = OH, 1O2, HO2,
O3, RO2, etc
NO3- hv → NO2- + O
NO2- + H+ → HONO
HONO hv → NO + OH
carbonyls
hv
BIOTA
hv
[O]
hv, [O]
Uncharacterized
Cleavage Products
hv, [O]
Humic and fulvic substances
Refractory DOM
Labile DOM
Mopper & Stahovec, 1986
Mopper et al, 1991
Kieber et al, 1990
Matsuda et al, 1992
Sumner & Shepson, 1999
Honrath et al, 2000

We do know from a number of people, like Domine et al., and Ammann et al., and Kahan et al., that the QLL water does not behave like aqueous water!

So, to simulate this world, we have to address the things we don't know.

Some of the things we don't know

•What the actual chemistry is that produces Br_2 and Cl_2

•For the chemistry, e.g.
$HOBr + H^+ + Br^- \rightarrow Br_2 + H_2O$
What rate constants do we use?

•For the important equilibria, like:
Br_2 (QLL) $\leftrightarrow$ Br_2 (gas)
What equilibrium constants do we use?

•Where are the reactants? At the ice/QLL interface? At the QLL/air interface?

•What are the diffusion coefficients?

•What are the organic reactants and how much is there?

•Is microbiology important?

So, in other words:
We don’t understand our container.
We don’t understand the bulk solvent.
We don’t know what our reactants are.
We don’t know where they are in the container or what their concentrations are.

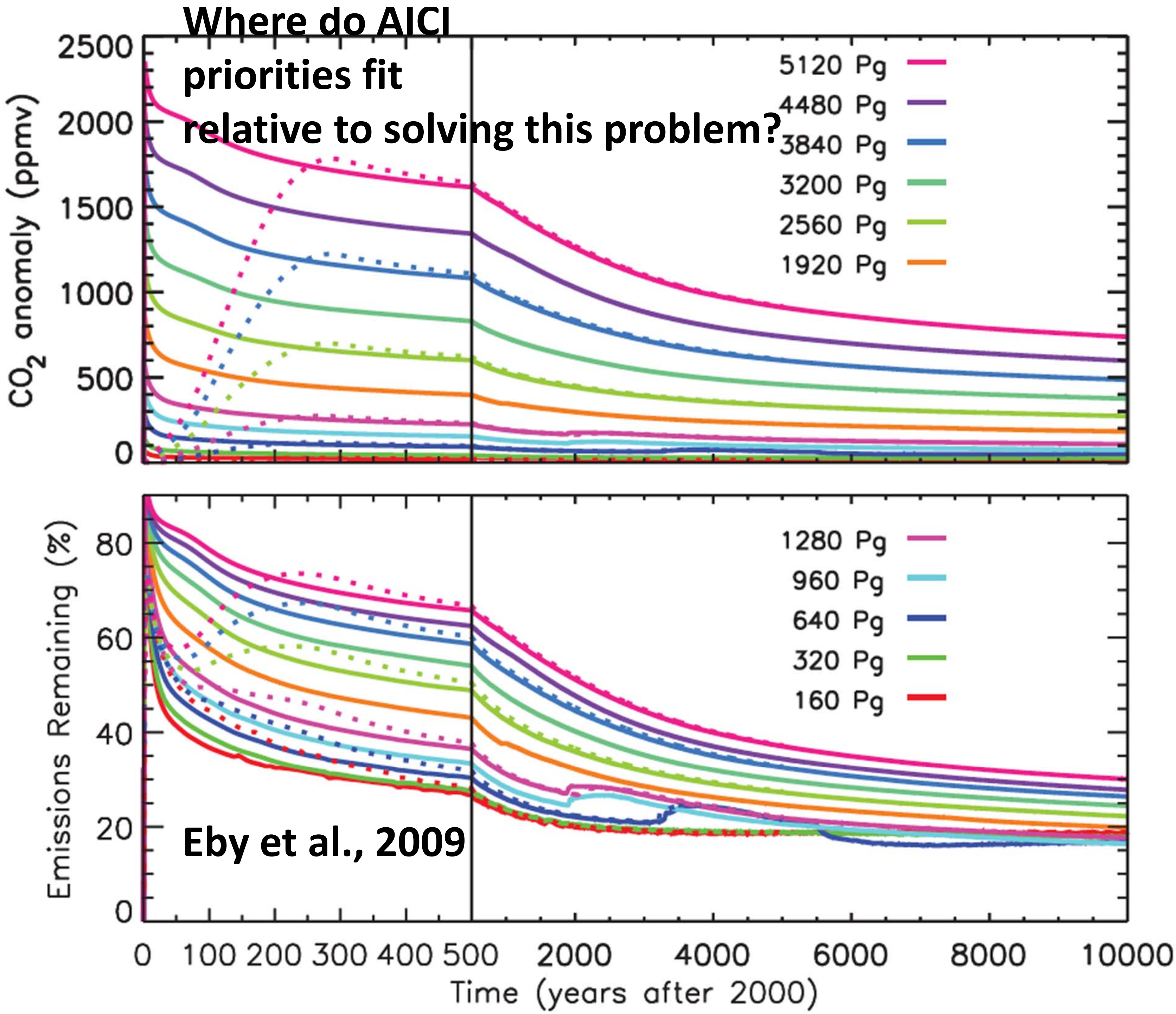
Simulating the current polar surface photochemistry is very difficult. Simulating it for the future will be even harder. Given this....

I think we need to first have a really good answer to the following questions:

Why should we?

Why should we invest the effort?
Why is it important to be able to simulate O_3 at the poles in the future?
Or does the justification hinge on Hg?
Or something else?

The answers to these questions influence what you work on, and how much funding the community gets.

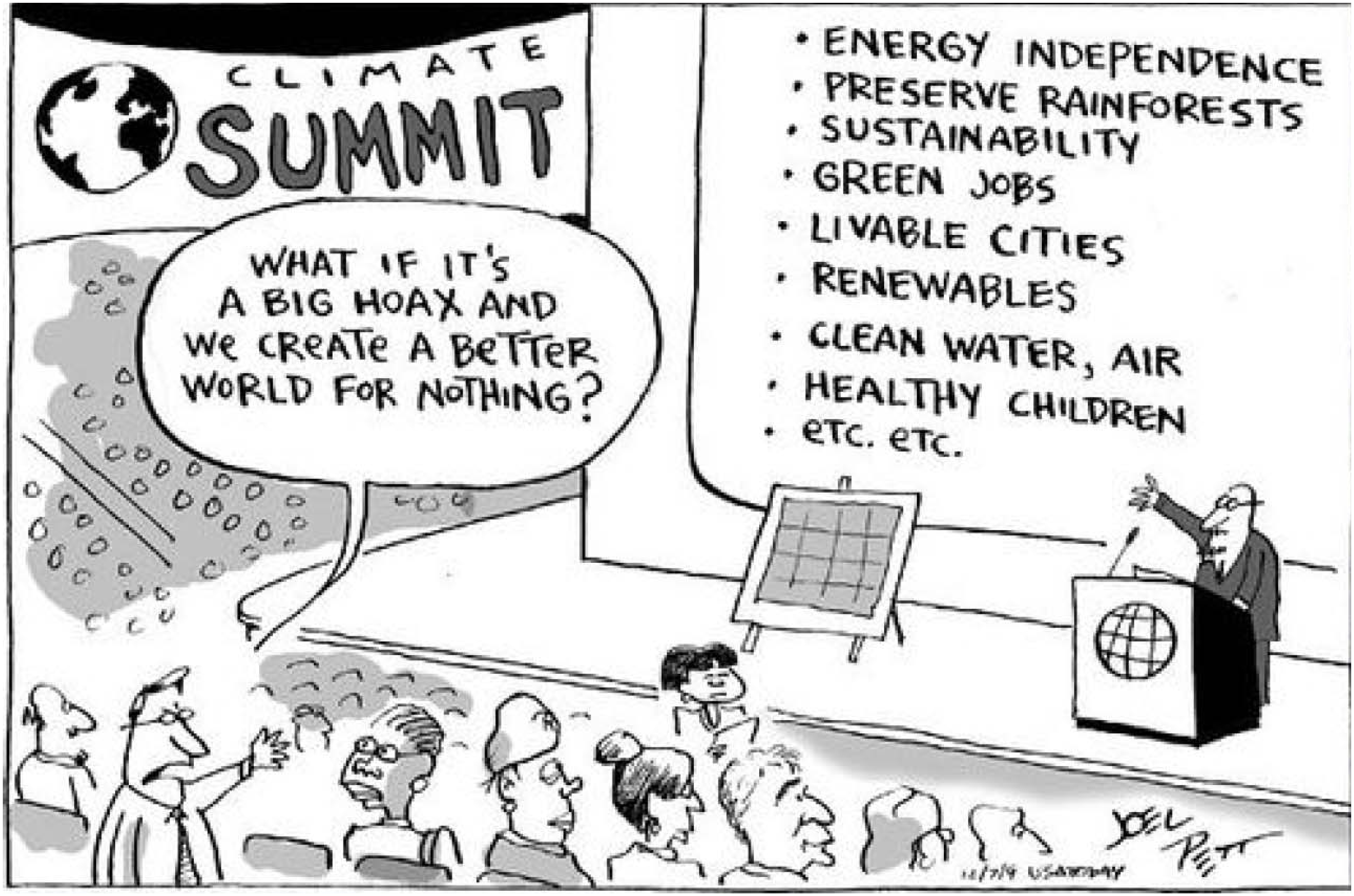


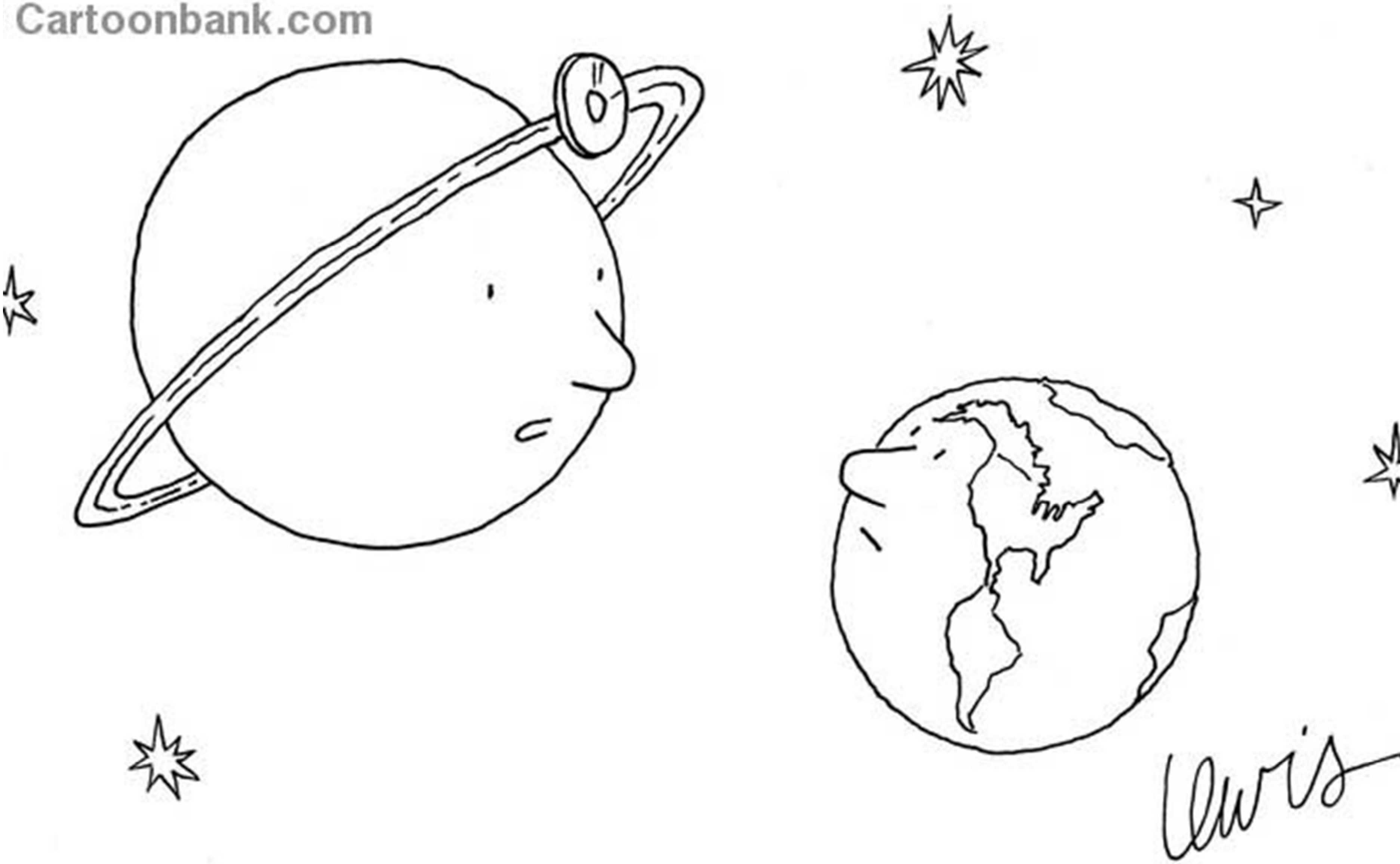
Where do AICI priorities fit relative to solving this problem?
Eby et al., 2009
5120 Pg
4480 Pg
3840 Pg
3200 Pg
2560 Pg
1920 Pg
1280 Pg
960 Pg
640 Pg
320 Pg
160 Pg
CO2 anomaly (ppmv)
Emissions Remaining (%)
Time (years after 2000)

Conclusions

- The future will be interesting and surprising!

- We have work to do!


CLIMATE
SUMMIT
WHAT IF IT'S A BIG HOAX AND WE CREATE A BETTER WORLD FOR NOTHING?
• ENERGY INDEPENDENCE
• PRESERVE RAINFORESTS
• SUSTAINABILITY
• GREEN JOBS
• LIVABLE CITIES
• RENEWABLES
• CLEAN WATER, AIR
• HEALTHY CHILDREN
• etc. etc.
JOEL PETT



"I'm afraid you have humans."