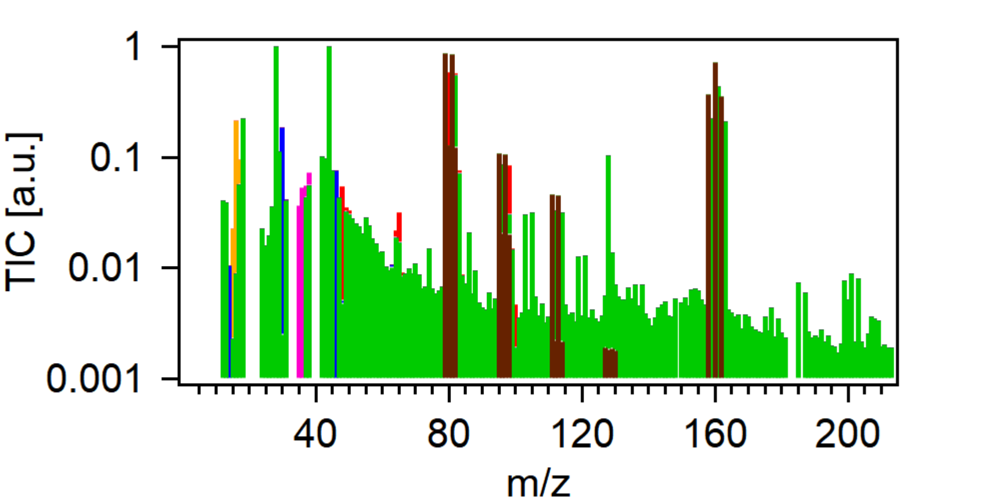
Finding Shiny Nuggets In The "Grass": Quantification of Halogen Species in the HR-AMS

- NaCl, ClO_3, ClO_4
- Br, BrO, BrO_3
- I, IO, IO_3



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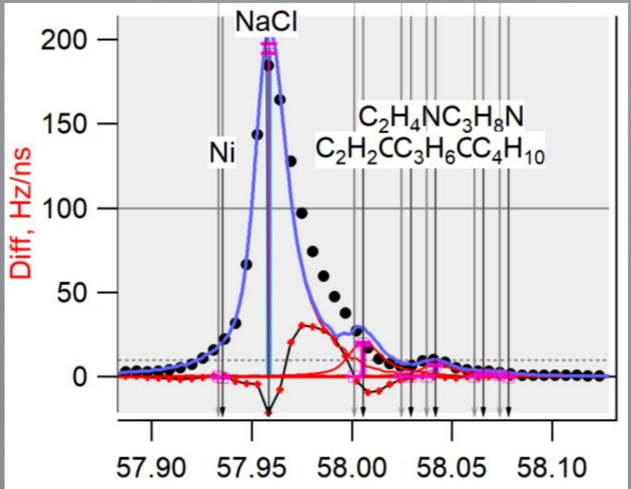
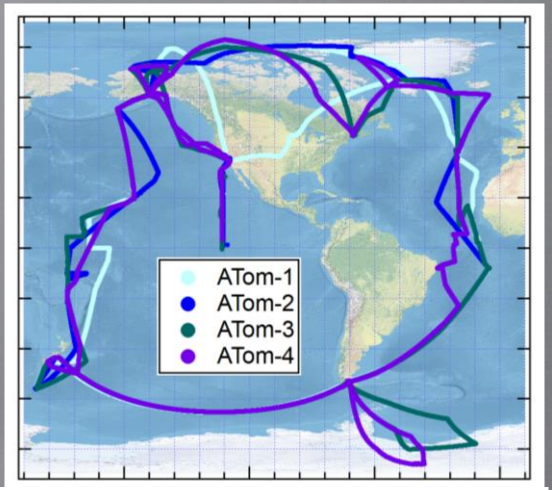
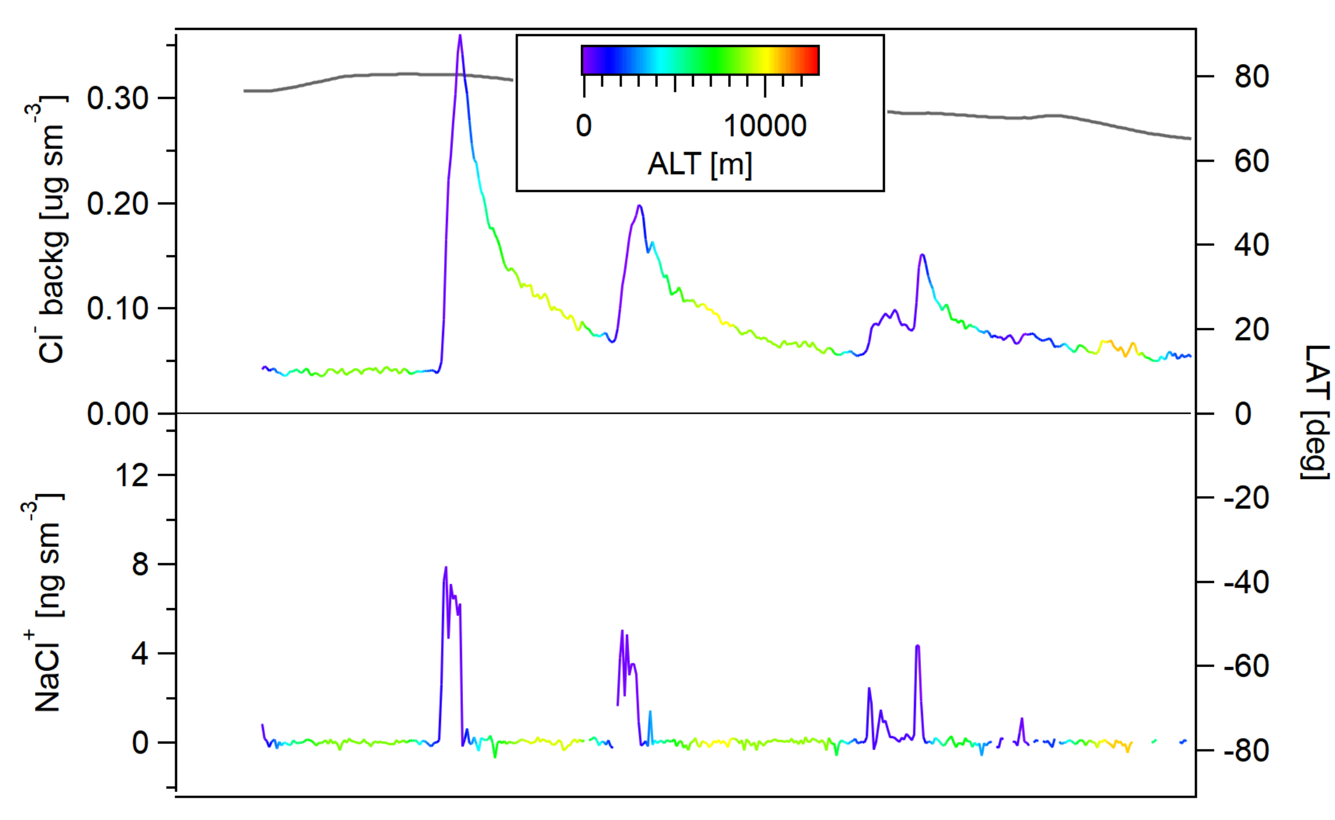
18th AMS Users Meeting
St Louis, MO, September 10th, 2018

Seasalt (NaCl)

- Refractory species, mostly leads to a slow increase in chlorine background in the AMS
- Ovadnevaite et al, 2012 showed that $NaCl^+$ ions are produced as well, with little background and fast response times.
- RIE is very low ($1/RIE_{Na^{57}Cl}=51$)
- During ATom, we saw both $NaCl^+$ (diff) as well as Cl (closed) increase in the MBL
- We also saw an "interference" of NaCl on AMS chloride







Seasalt Calibrations

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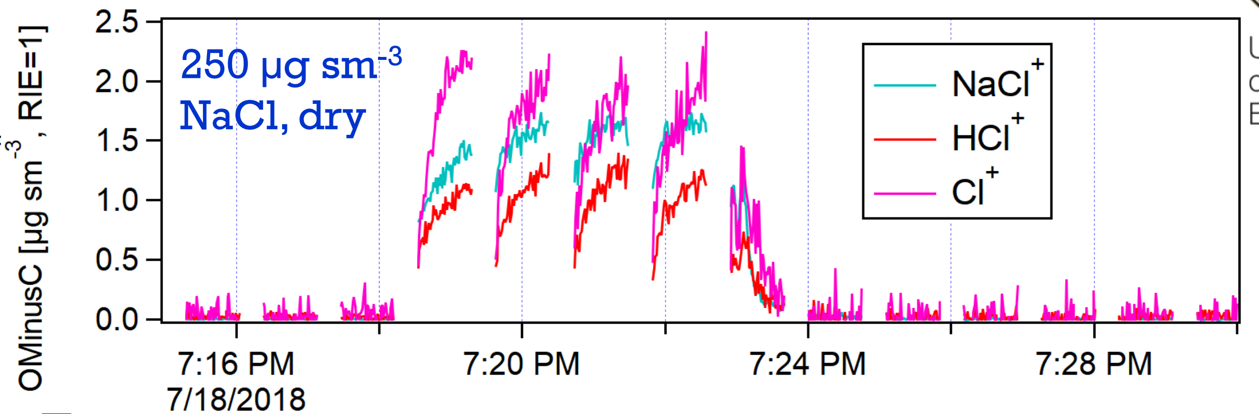
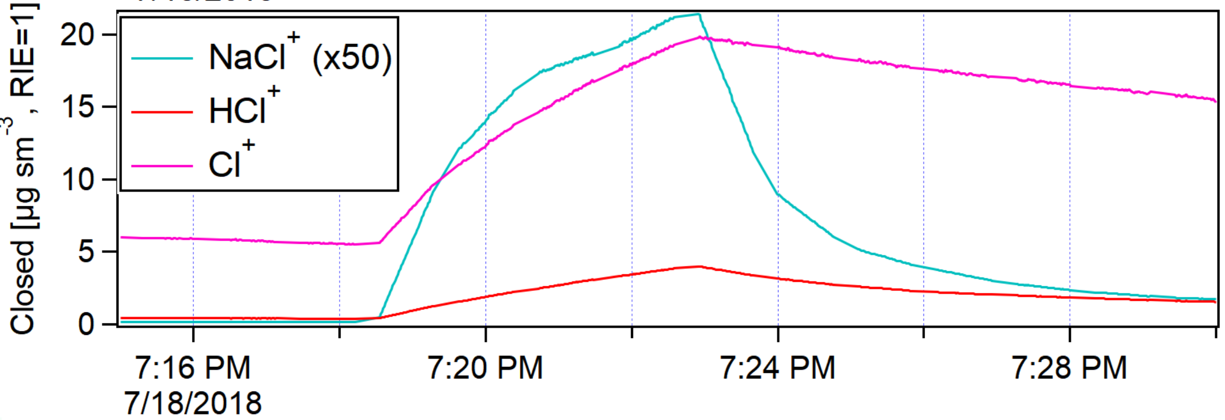
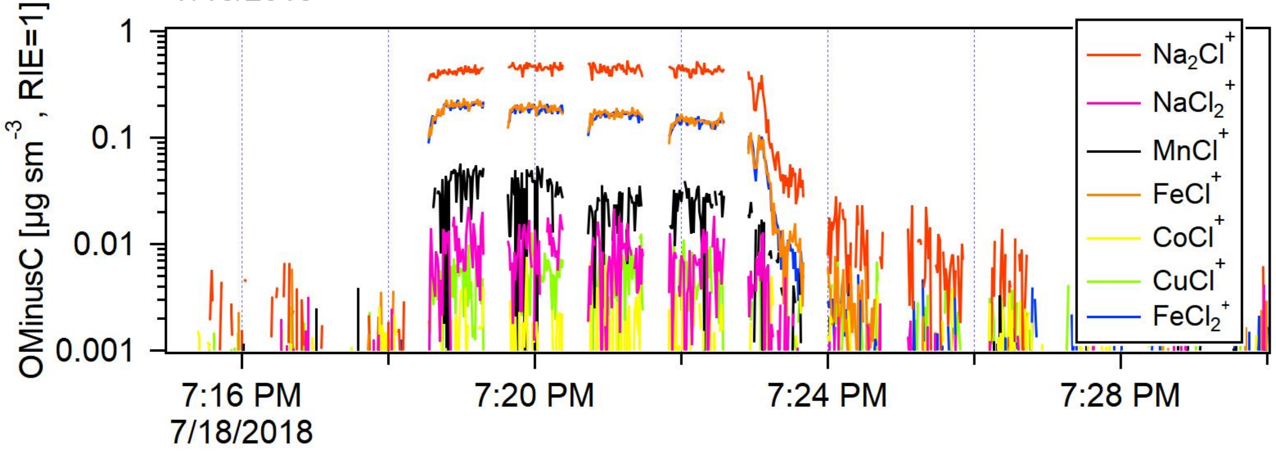
- Both dry (18% RH) and wet (~80% RH)
- Plenty of chloride ions present as well in OMinusC and Closed, but $NaCl^+$ is the least "sticky", hence preferred
- Vaporizer chemistry is important (Drewnick et al, 2015) and **independent** of phase
- Na_2Cl at m/z 81 and 83 is also fairly important (HSO_3 and perchlorate interference, Schmale et al, 2013)

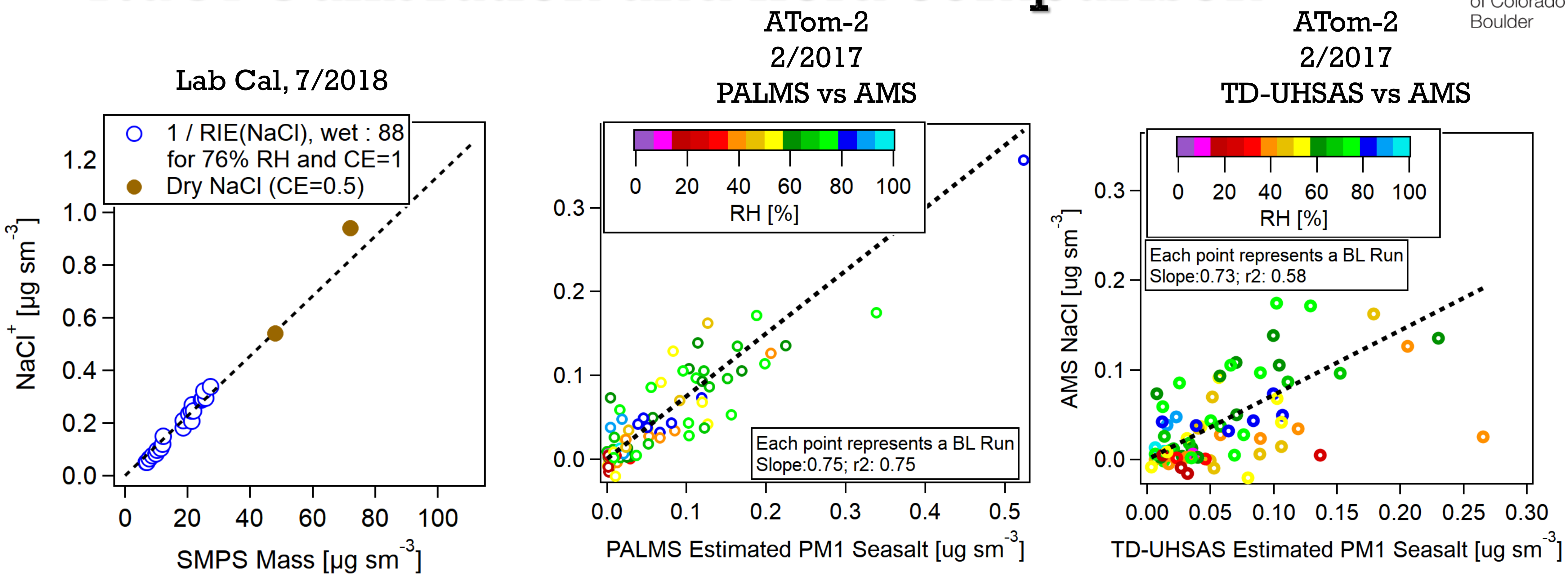






NaCl	ClO_3/ClO_4	Iodine	Bromine

NaCl Calibration and field comparison



- Agreement in the field data between PALMS and AMS is good, but suggest that the RIE for ATom-2 was higher
- Always calibrate as soon as possible!
- No evidence of CE ever being less than 1 in the field from PALMS comparison
- TD-UHSAS comparison ok in principle, but mass calculation still needs more work

Cl Closed (m/z 35) Cal and field data

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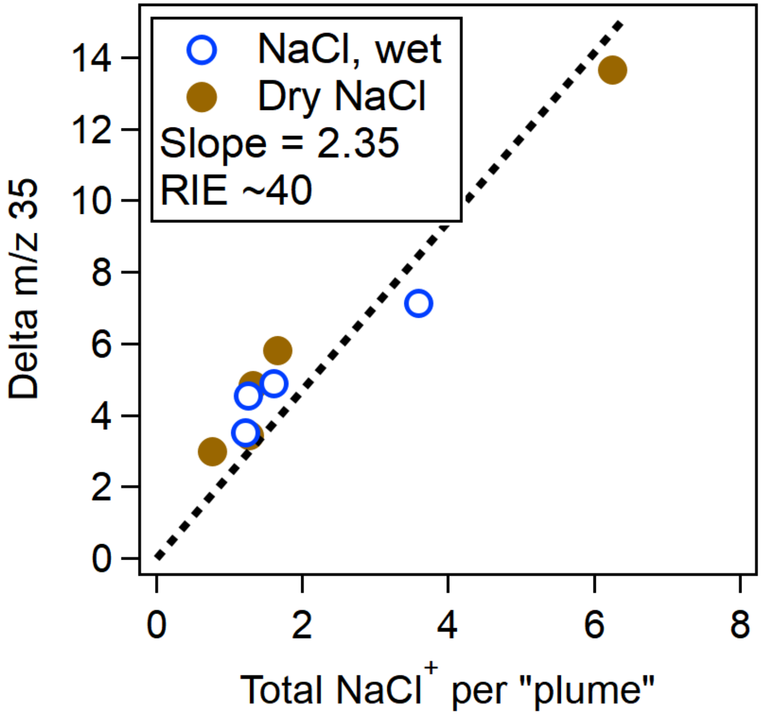
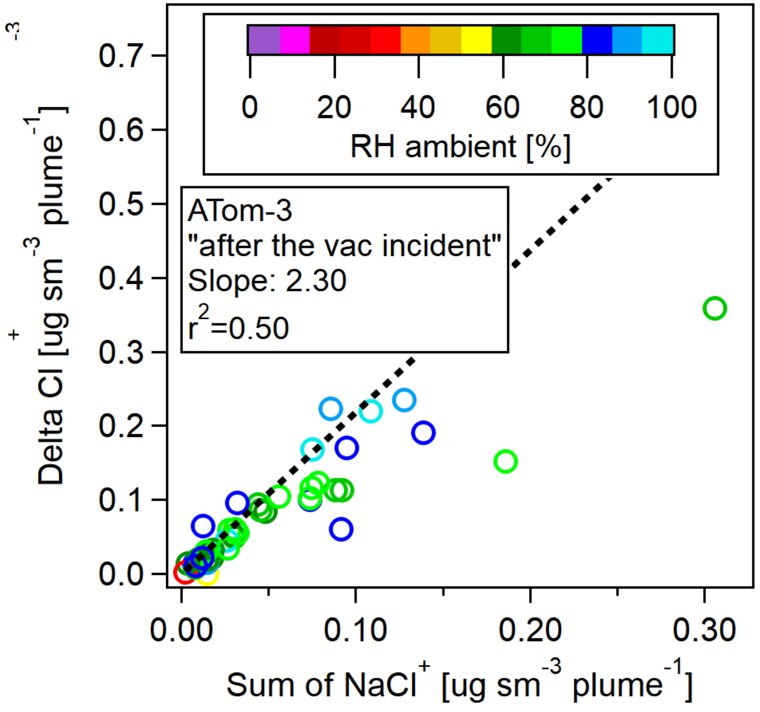
ACSM relevant

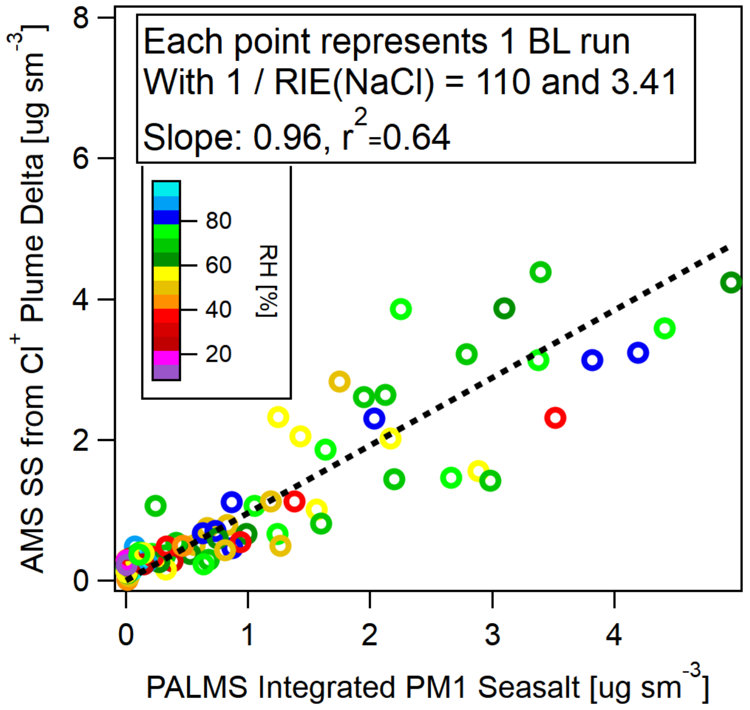
Lab Cal, 7/2018



ATom-2
2/2017
AMS vs AMS



ATom-2
2/2017
PALMS vs AMS



- Highly correlated behavior, PALMS comparison a little bit worse (r^2=0.64 vs 0.75)
- Almost no interferences at m/z 35, so this can be used to quantify seasalt with ACSM/mini-AMS/ cToFs as well (basically cal 58 vs 35)

NaCl	ClO_3/ClO_4	Iodine	Bromine

Chloride Corrections/Quantification

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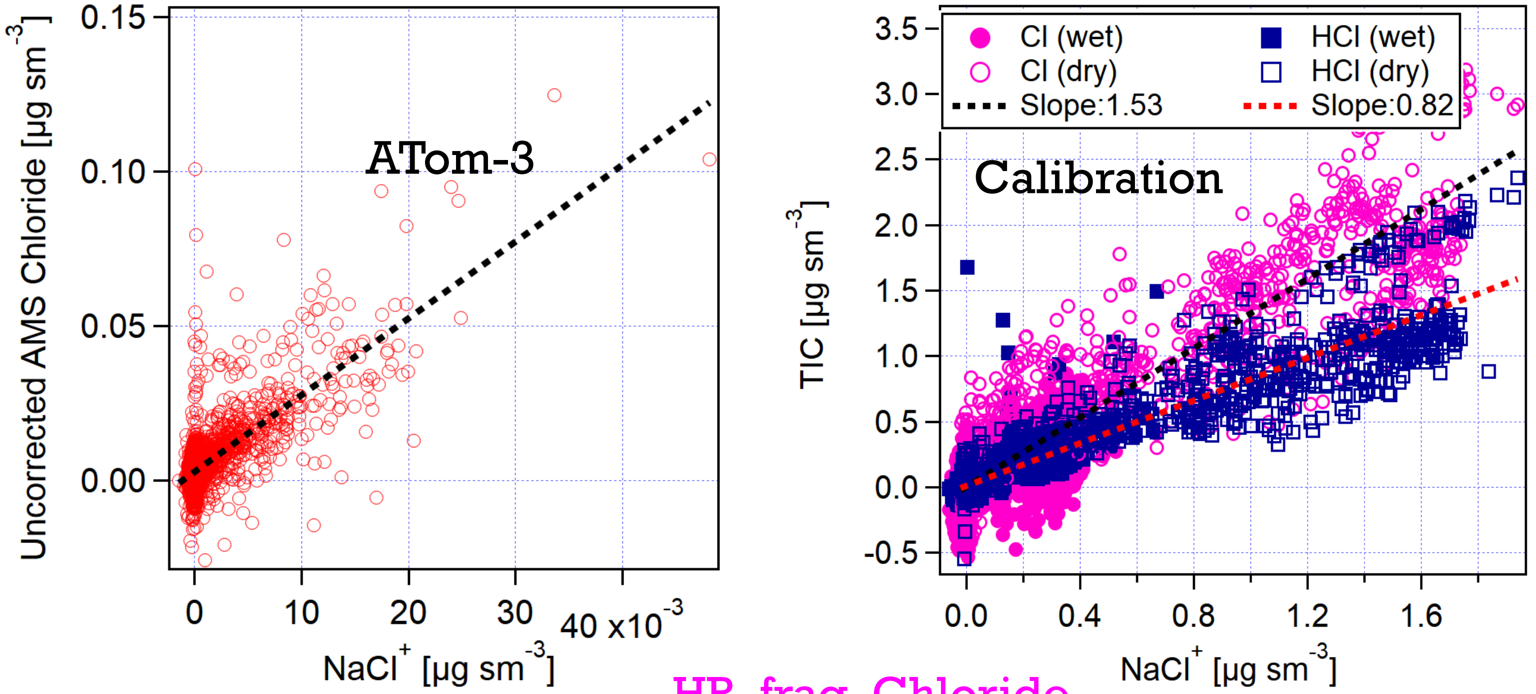
I feel strongly that AMS Chl should remain NR PM_1 Chloride (so NH_4Cl and organic chloride)
=> Need to correct for the SS contributions to Cl and HCl (and remove NaCl from familyCl!)



Correction factors change between AToms, but seem stable during each deployment

Implemented in the HR Frag table as illustrated below, happy to explain offline or tomorrow

		HR_frag_Chloride	HR_frag_seasalt
20	Cl	{Cl},-HR_frag_seasalt[{Cl}],HuClFrag*HR_frag_nitrate	ClNaClFrag*HR_frag_seasalt[{NaCl}]
21	HCl	{HCl},-HR_frag_seasalt[{HCl}],-HuHClFrag*HR_frag_nitrate	ClNaClFrag*HR_frag_seasalt[{NaCl}]
22	j37Cl	0.3198*HR_frag_chloride[{Cl}]	0.3198*HR_frag_seasalt[{Cl}]
23	Hj37Cl	0.3198*HR_frag_chloride[{HCl}]	0.3198*HR_frag_seasalt[{HCl}]

NaCl	ClO_3/ClO_4	Iodine	Bromine

Another chlorine species: Perchlorate (ClO_4)

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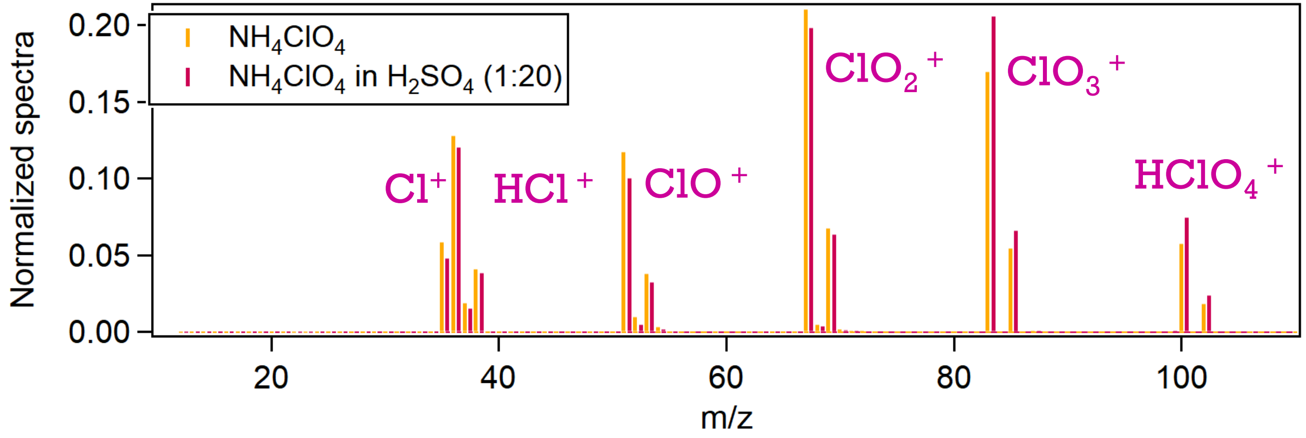
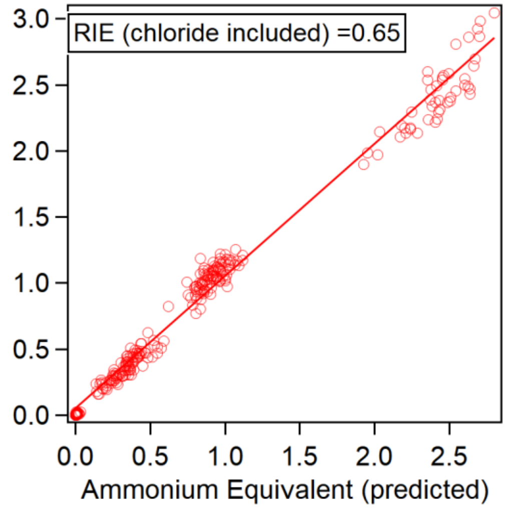
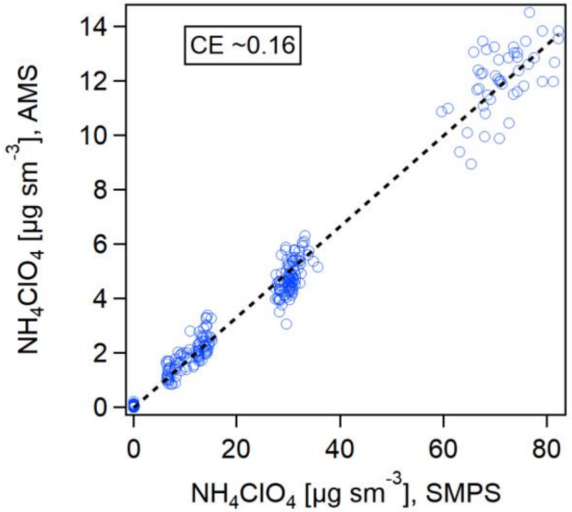
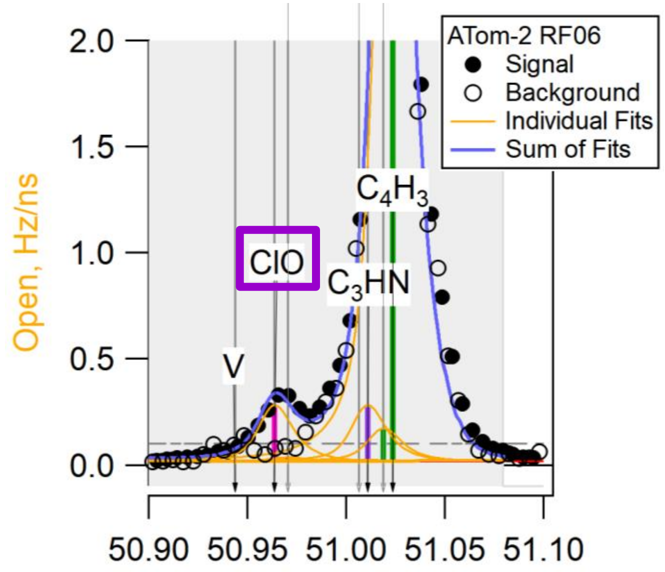
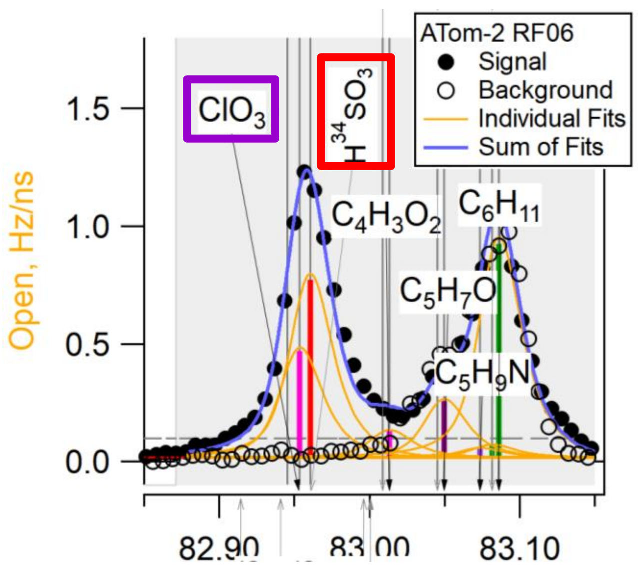




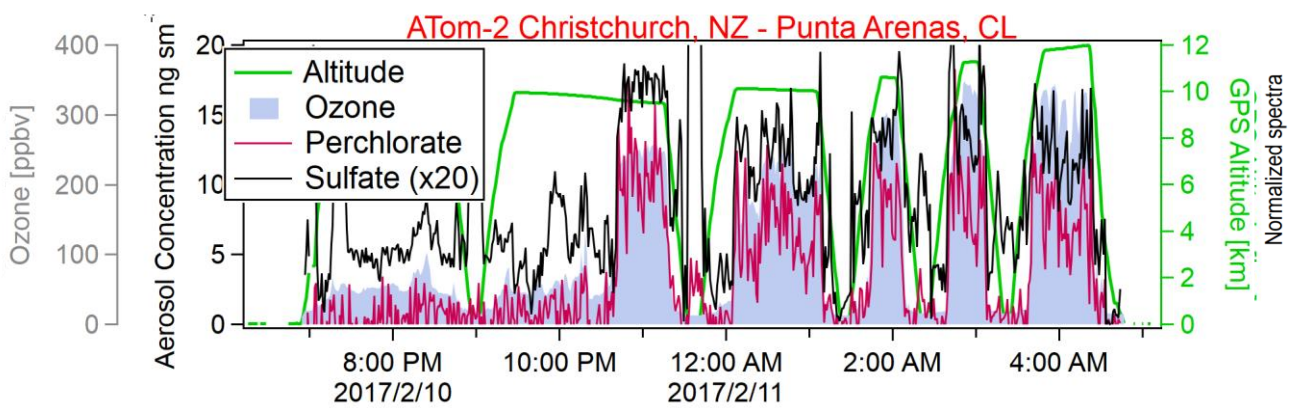


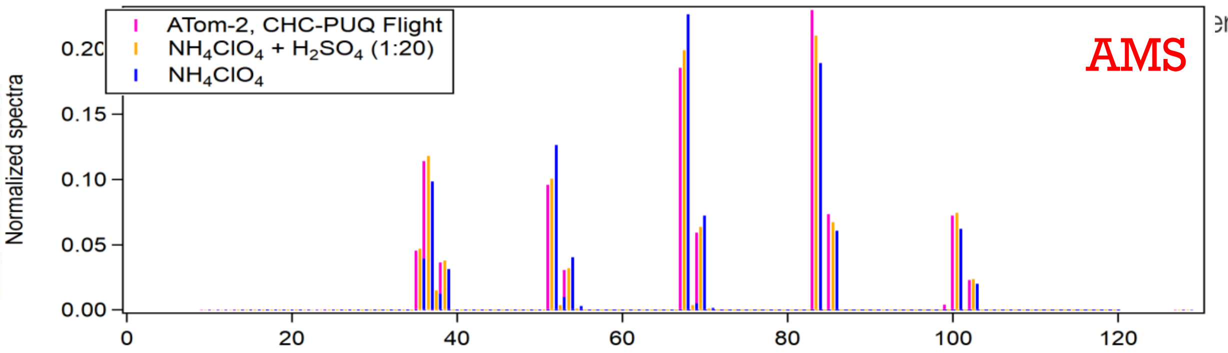


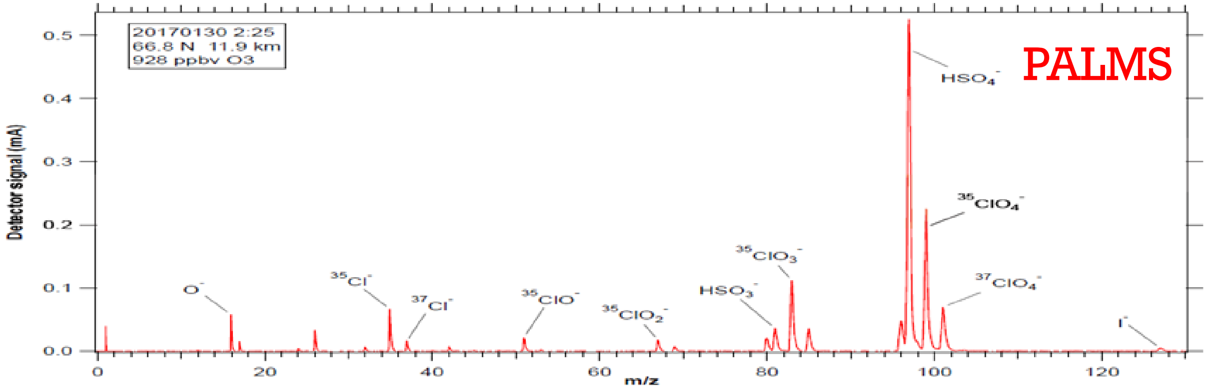


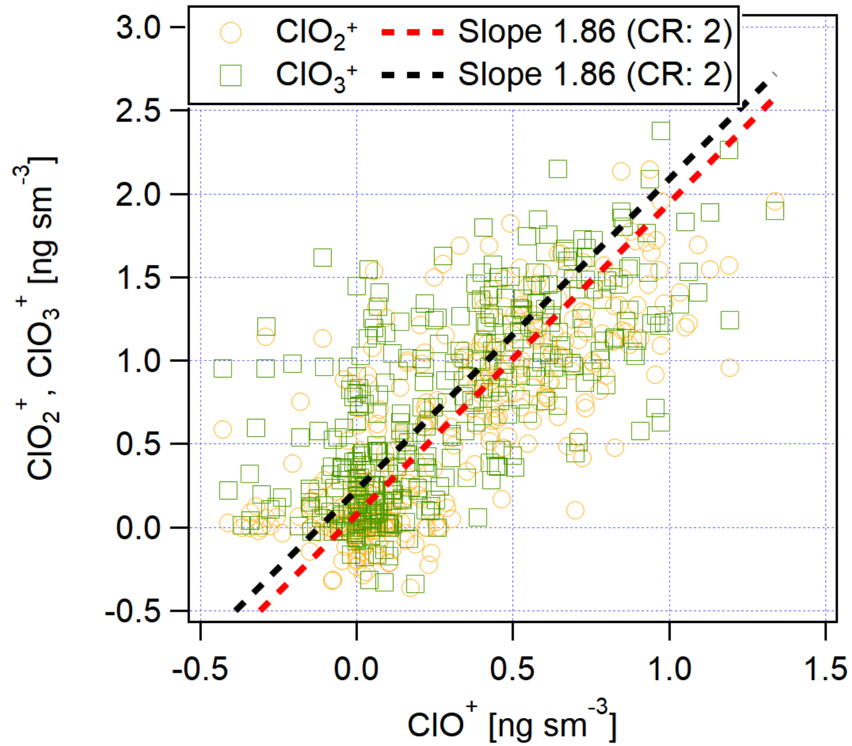
- High sensitivity
- Low CE for the neutral compound, worse than sulfate
- Fragmentation depends on acidity/CE, but less than sulfate
- Cl^+/HCl^+ contribution needs to be taken into account (and removed from Chl)
- $Na_2{}^{37}Cl^+$ interference with ClO_3^+
- Sulfate interferences for ClO_2^+ and ClO_3^+

Detection of Perchlorate during ATom





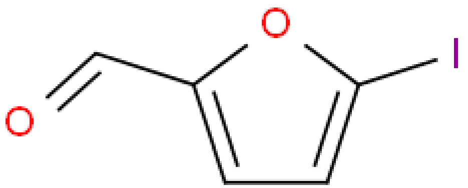




- Dan Murphy (PALMS instrument) saw this first during ATom-2 on the Southern Ocean flight
- We had previously calibrated for this (long story)
- Ion ratio analysis confirms proper quantification
- We sampled plenty (1-4 pptv) of perchlorate in the lower polar stratosphere during all AToms

NaCl	ClO_3/ClO_4	Iodine	Bromine

Iodine



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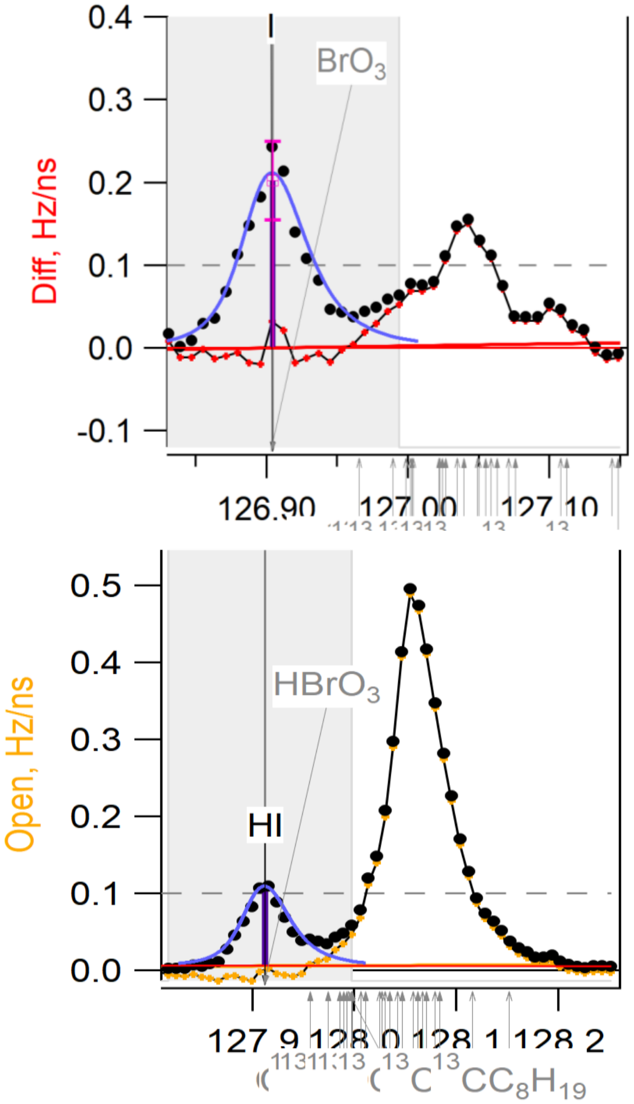
- Compounds we calibrated for:

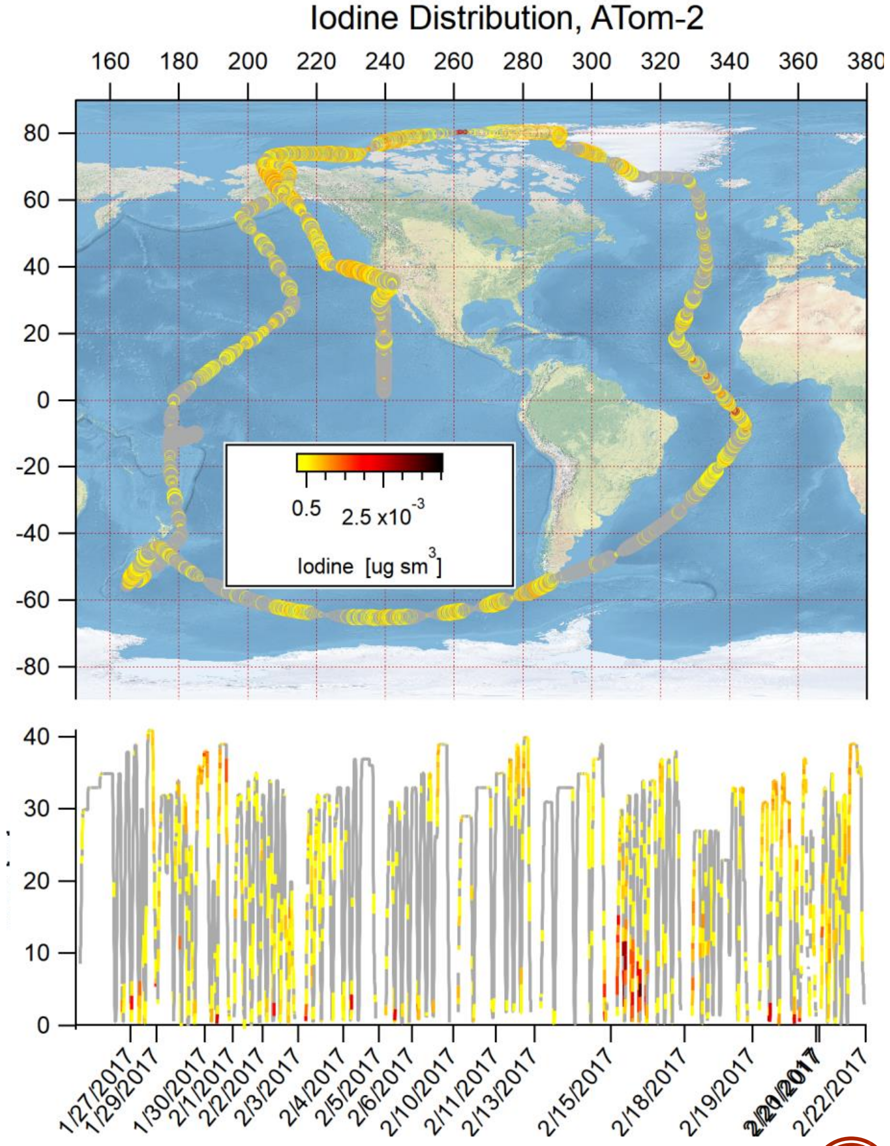
  NH_4I, NH_4IO, NH_4IO_3, $C_5H_3IO_2$

  up to m/z 450
- RIE was derived from ammonium balance

  RIE = 0.72

Iplus2
HIplus2
I
HI
CH3I
IO
HOI
IO2
HIO2
IO3
HIO3
I2





Quantifying Bromine

- Compounds we calibrated for:

  NH_4Br, NH_4BrO, $KBrO_3$

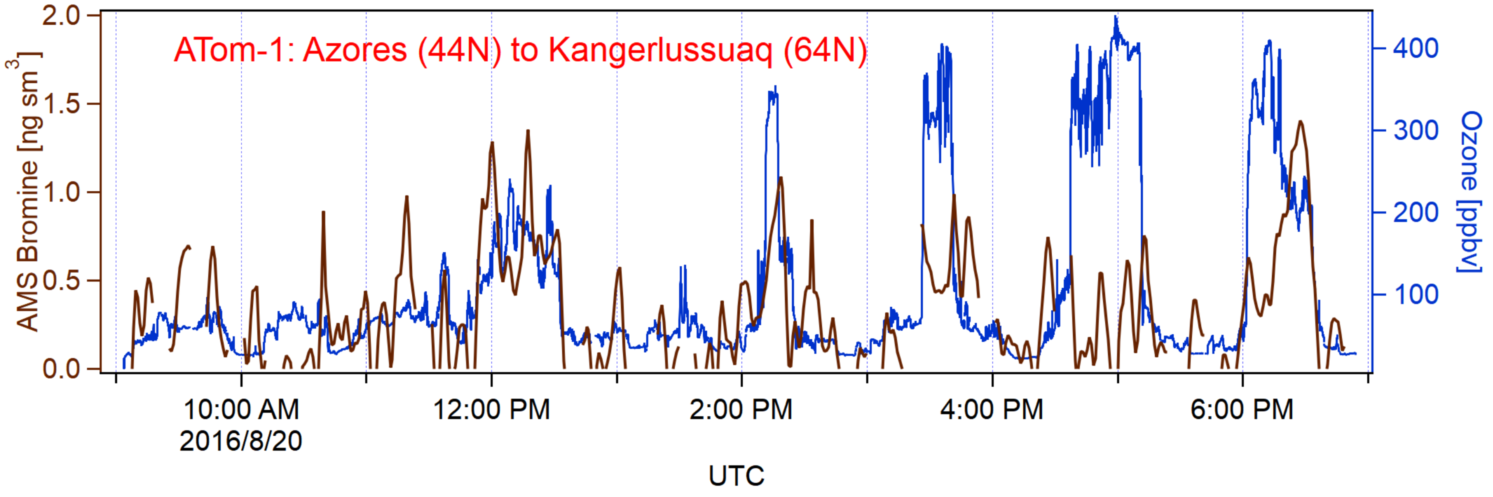
  up to m/z 450

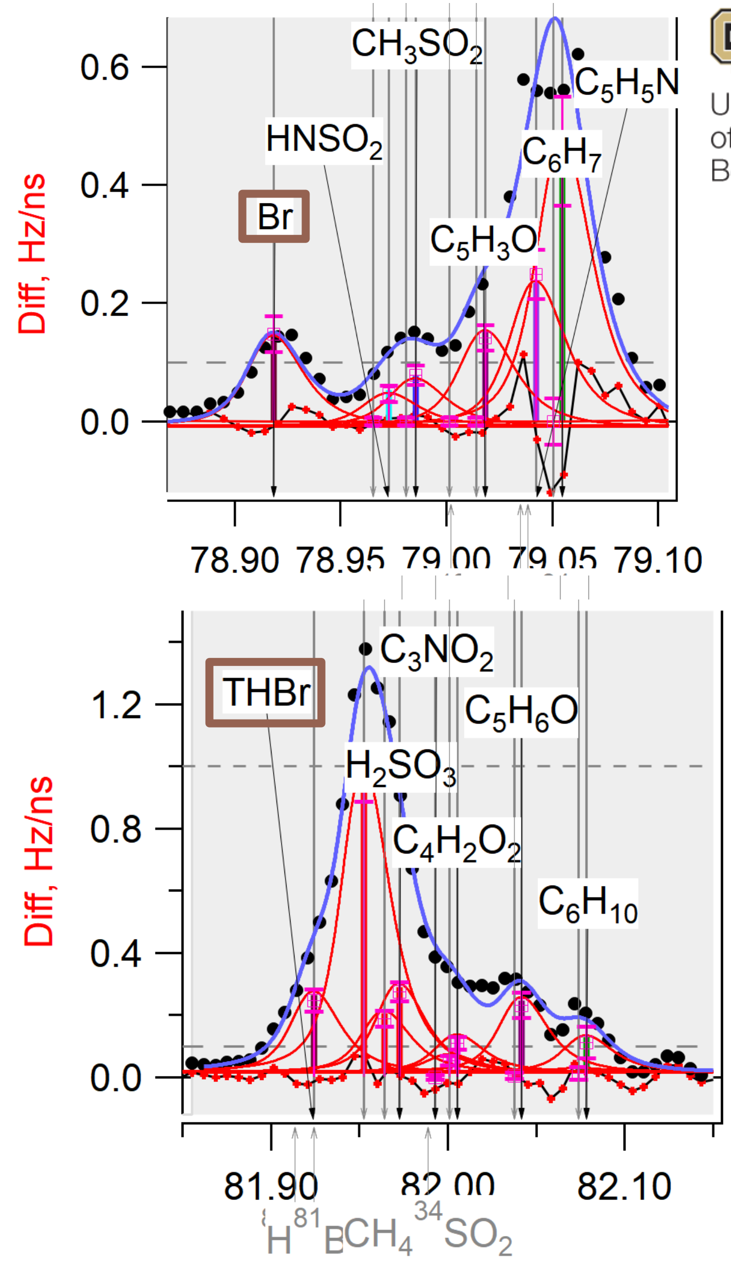
- RIE was derived from ammonium balance of Br(-1) and Br(+1)

  RIE = 0.68

- BrO_x^+ is almost negligible in all cases, unlike Br_2^+
- Careful when fitting HBr!

Br
THBr
BrO
HBrO
BrO2
HBrO2
TBrO3
THBrO3
Br2





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Tracking oxidation state of halogens by fragmentation

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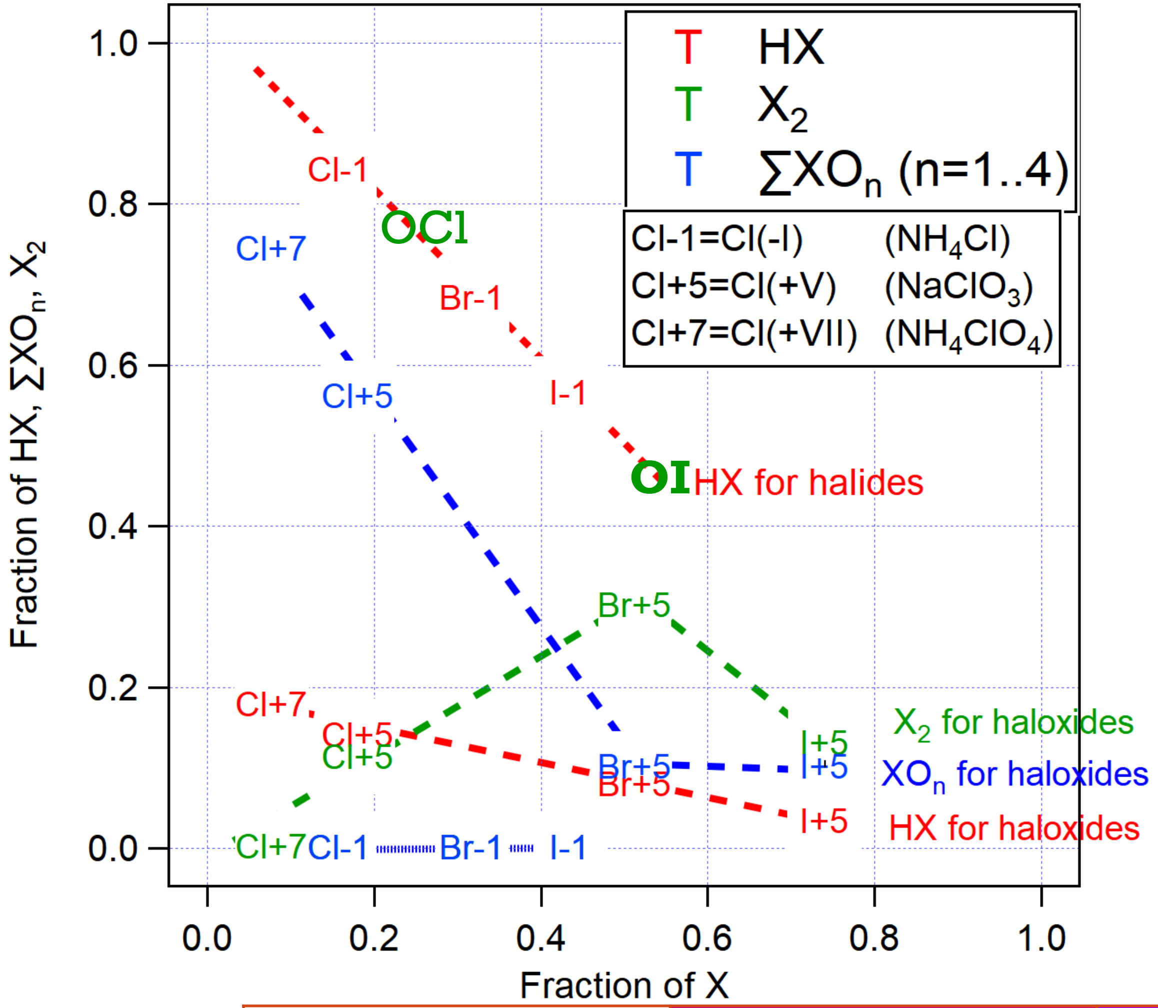
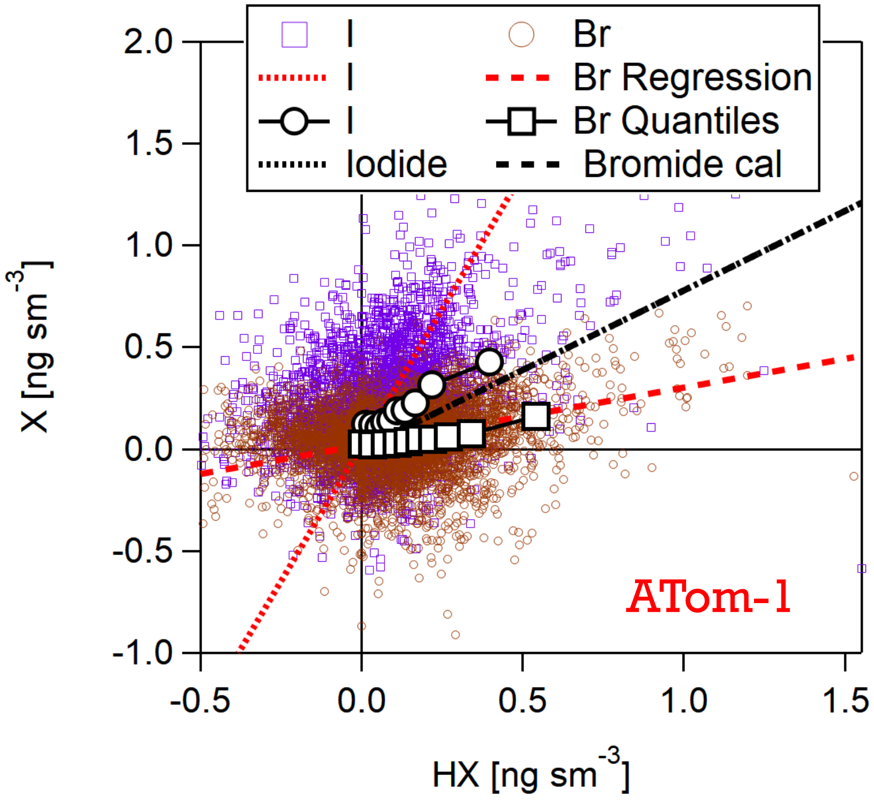
- HX is always the most important ion besides X
- Except for chlorate and perchlorate, XO_n ions are not very important
- Feasible to use HX/X as a marker for oxidation state (especially in low conc environments)
- BUT: Organic halogens complicate the picture, TBC





NaCl	ClO_3/ClO_4	Iodine	Bromine

Revisting the Pieber effect

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Pieber (ES&T 2016, AMS vaporizer):

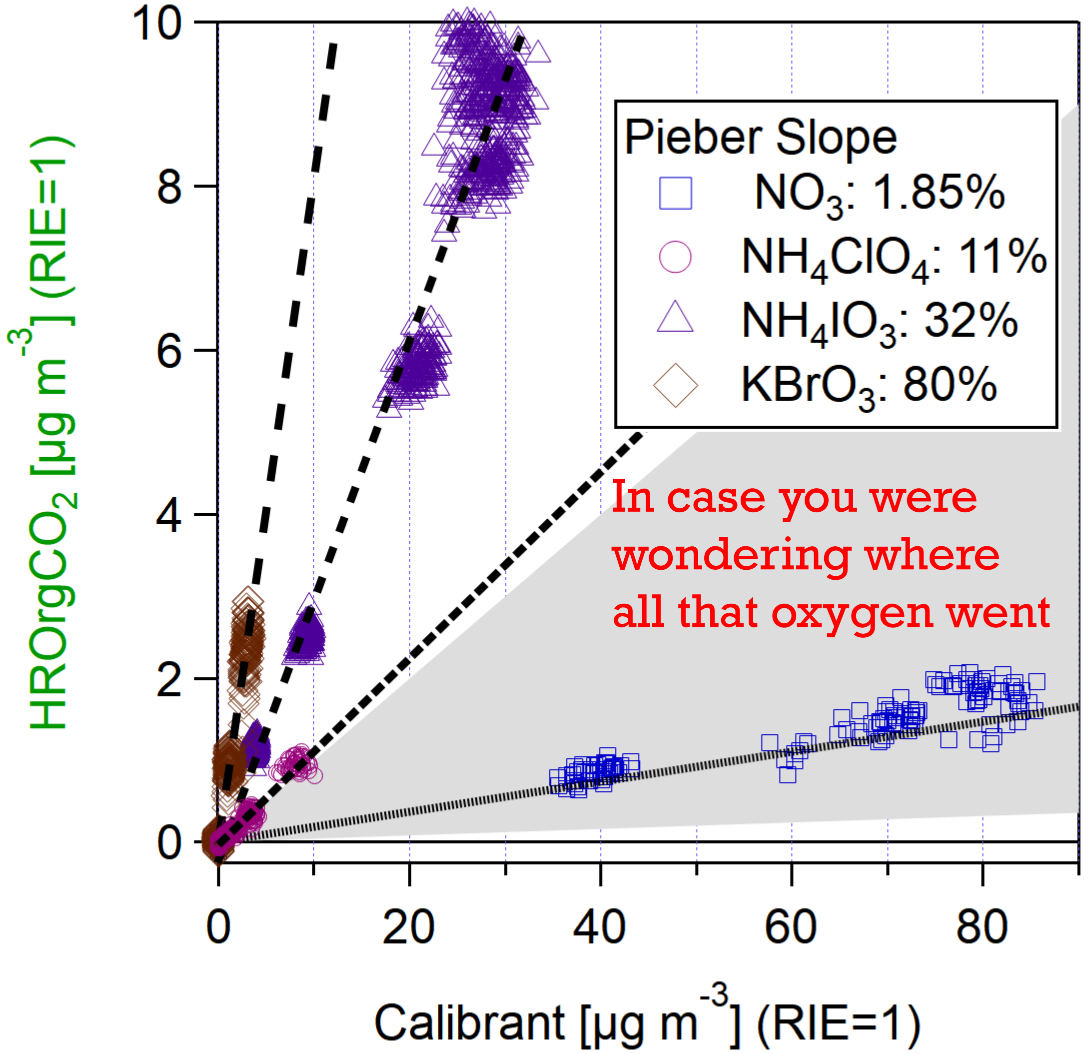
NH_4NO_3 + "$C_{x, heater}$" => CO_2 + products (at 600 C)

Gunpowder ignition (at ~1300 C):

$2NH_4NO_3 + C + S \Rightarrow CO_2 + SO_2 + 2\,H_2O + 2N_2$

Perchlorate and bromate are well known as oxidizers in "boutique" explosives, and are much stronger oxidizers than nitrate

Anion	E° [V]
NO_3^-	0.96
MnO_4^-	1.49
ClO_4^-	1.2
IO_3^-	1.19
BrO_3^-	1.50



NaCl	ClO_3/ClO_4	Iodine	Bromine

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ADDITIONAL SLIDES

Looking again at the Hu effect (AS&T, 2017)

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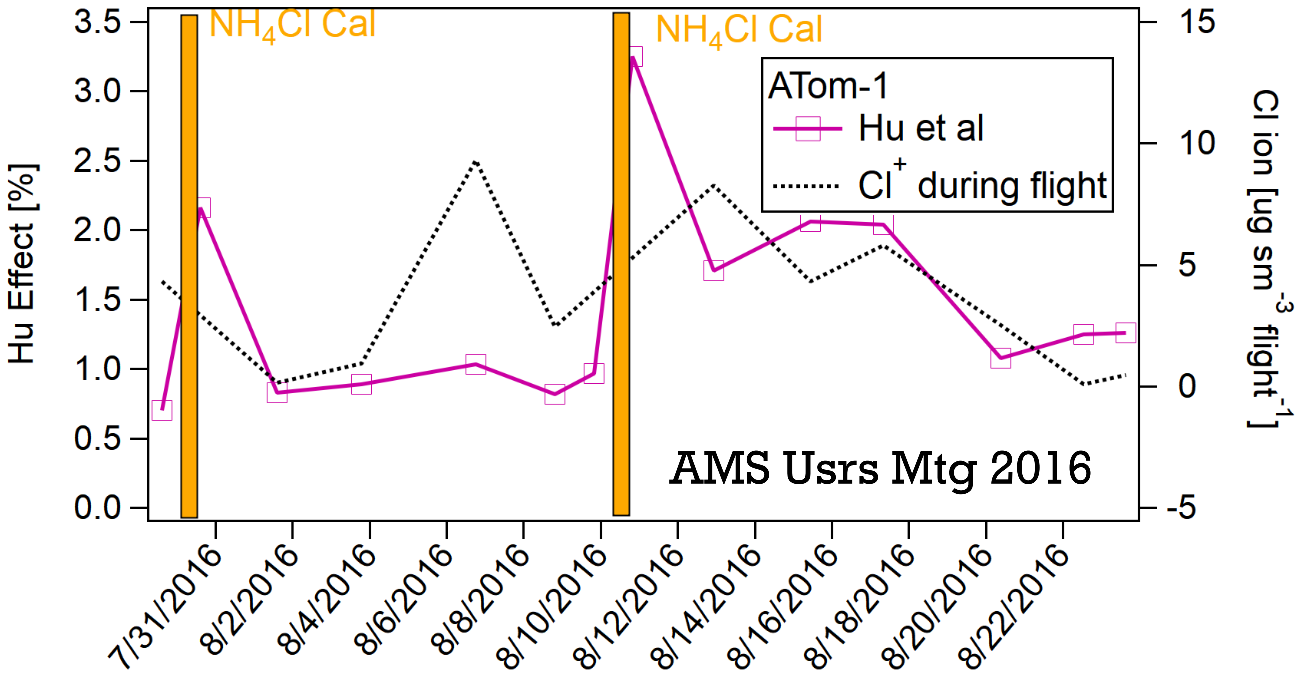
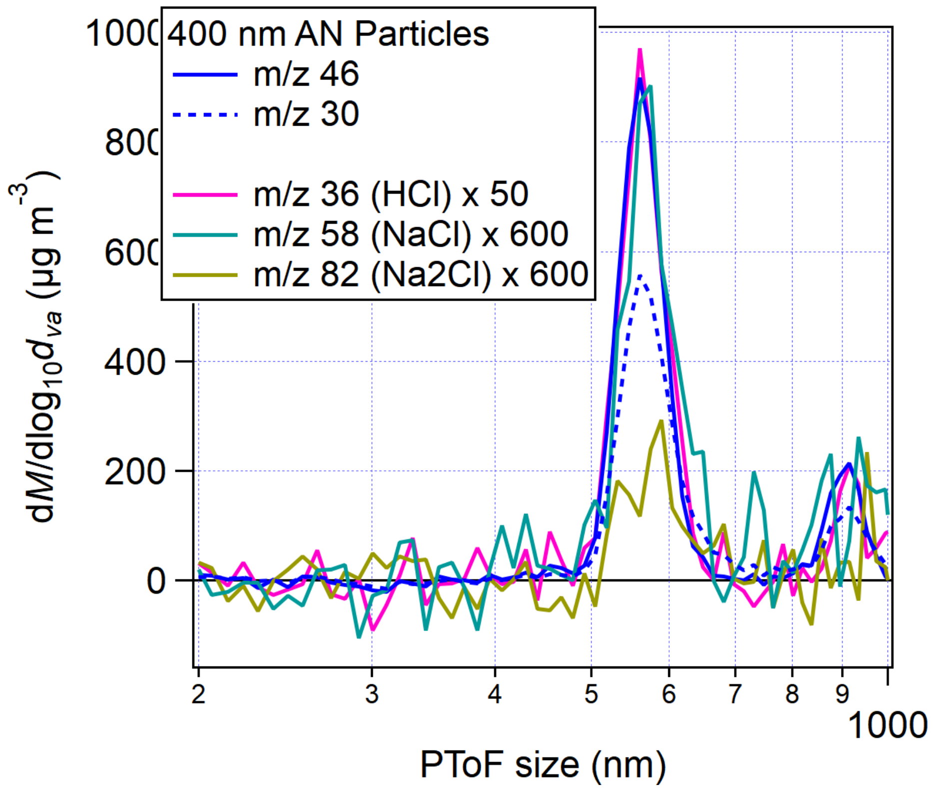
When performing AN calibrations, some fun heater chemistry is observed:

$$Cl_{(heater)} + HNO_{3(g)} \Rightarrow HCl_{(g)} + \text{products}$$

Refractory species are prime candidates. In ATom, we see this mostly after lots of SS exposure (and cals)



AN Calibration After SS Cal



NaCl	ClO_3/ClO_4	Iodine	Bromine

Can we determine Mg/Na ratios

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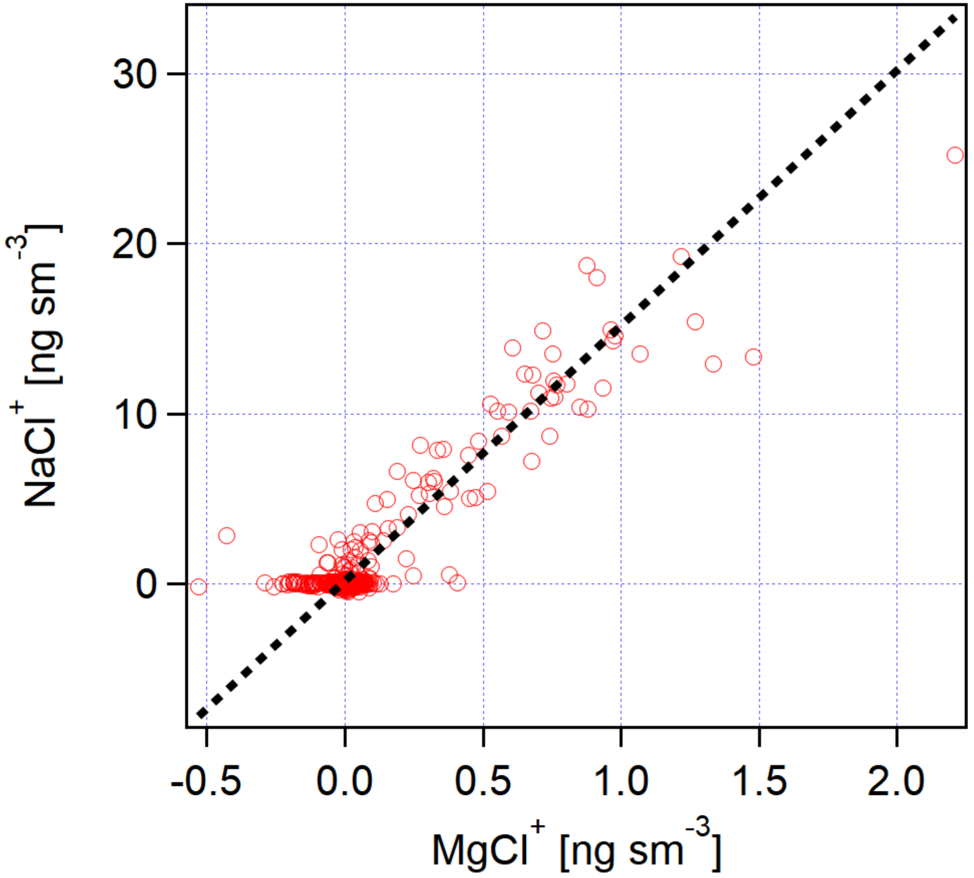
ATom-3, RF311, NE Atlantic (44-60N)



Posfai et al, JGR 1995

Table 3. Differences Between Atomic Ratios of Na to Mg, K, Ca, S, and Cl Relative to the Values of Seawater

Sample Number	Group Number	Δ Cl/Na	Δ S/Na	Δ A⁻/Na	Δ Mg/Na	Δ K/Na	Δ Ca/Na
9	I	-0.34	0.02	0.32	0.01	0.001	0.001
	II	-0.87	0.03	0.83	0	0	0.001
	V	-1.03	0.62	-0.12	0.03	0.005	0.011
11	I	-0.19	0.03	0.16	0.01	0.005	0.005
18	II	-0.86	0.07	0.74	0.01	0.001	0.009
	IV	-1.10	0.20	0.71	0.01	0	0.001
	V	-1.15	0.48	0.23	0.01	0.006	0.008
19	I	-0.39	0.04	0.34	0.02	0.004	0.002
	II	-0.68	0.17	0.37	0.01	0.002	0.004
	III-IV	-1.07	0.11	0.89	0.02	0.006	-0.002
	V	-1.13	0.46	0.24	0.01	0	-0.005
20	I	-0.26	0.03	0.23	0.01	0.002	0.001
	II	-0.54	0.13	0.30	0.01	0.003	0
	III	-1.09	0.02	1.03	–0.01	–0.001	-0.002
	IV	-1.02	0.16	0.68	0	–0.001	-0.003
	V	-1.14	0.37	0.36	–0.01	–0.005	-0.008
25	I	-0.43	0.07	0.34	0.02	0.002	0.003
	II	-0.80	0.07	0.69	0.02	0.003	0.001
	III	-1.09	0.04	0.97	–0.02	–0.002	0
	IV	-1.12	0.16	0.82	0.01	0	-0.001
	V	-1.15	0.49	0.19	0	0.002	0.002
28	I	-0.36	0.06	0.27	0.02	0.005	0.004
	II	-0.71	0.09	0.56	0.01	0 003	0.009
	III	-1.10	0.06	1.01	0.01	0.004	0.002
29	I	-0.36	0.04	0.33	0.02	0.005	0.004
Seawater		Cl/Na= 1.16	S/Na= 0.06	A⁻/Na= 0.007	Mg/Na= 0.11	K/Na= 0.022	Ca/Na= 0.022

Ratios are given for compositional groups I to V in each sample as determined from EDS analyses. The column under Δ A⁻/Na contains calculated values; A⁻ stands for anions other than Cl^- and $SO_4^=$ (see text). The ratios for seawater (as listed in the bottom row) are obtained from *Millero and Sohn* [1992].

- Should consider calibrating with seasalt instead of NaCl next time around
- Ratio observed for Mg/Na is about 6.7% about halfway between seawater and aged seasalt for that part of the North Atlantic (Posfai et al, 1995)