SAND2015-4629C

Used Fuel Disposition Campaign

Environment on the Surface of SNF Dry Storage Canisters: Salt and Brine Stability

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Las Vegas, NV
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Overview

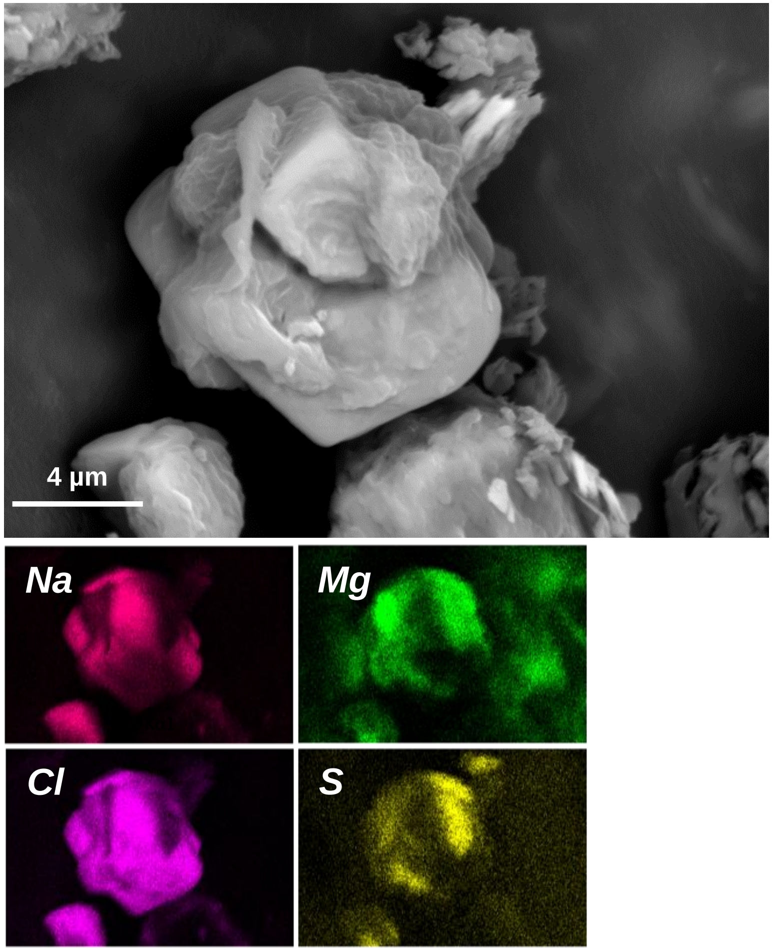
- **Typical salt assemblages**
  - Marine
  - Inland
- **Processes affecting salts and brines**
  - Gas-to-particle conversion reactions
    - *Evidence from in-service canister dust sampling*
  - Acid degassing
  - Ammonium mineral decomposition and brine degassing
    - *Experimental salt-brine stability tests*
      - Controlled Salt deposition
      - Degassing experiments.
    - *Results and Implications*

Composition of marine salt aerosols

Sea salt/spray — generally simulated with synthetic ocean water (ASTM D1141-98)

	Conc., mg/L	
Species	ASTM D1141-98	McCaffrey et al. (1987)
Na^+	11031	11731
K^+	398	436
Mg^{2+}	1328	1323
Ca^{2+}	419	405
Cl^-	19835	21176
Br^-	68	74
F^-	1	—
SO_4^{2-}	2766	2942
BO_3^{3-}	26	—
HCO_3^-	146	—
pH	8.2	8.2

Sea-salt aggregate on Diablo Canyon ISFSI storage canister



Inland salt compositions

Inland salts—ammonium, calcium, sulfate, and nitrate are the most abundant species. Chloride is present, but minor.

Inland site—continental salt aerosols. For example, data from an Iowa NADP site.

Species	Rain Conc., µeq/L
NH_4^+	29.217
Na^+	2.045
K^+	0.511
Mg^{2+}	3.208
Ca^{2+}	16.766
Cl^-	1.975
NO_3^-	15.565
SO_4^{2-}	17.685

Data from 5 selected IMPROVE Monitoring sites, showing relative abundances of nitrate, chloride, and sulfate (NRC 2014 NUREG/CR-7170).

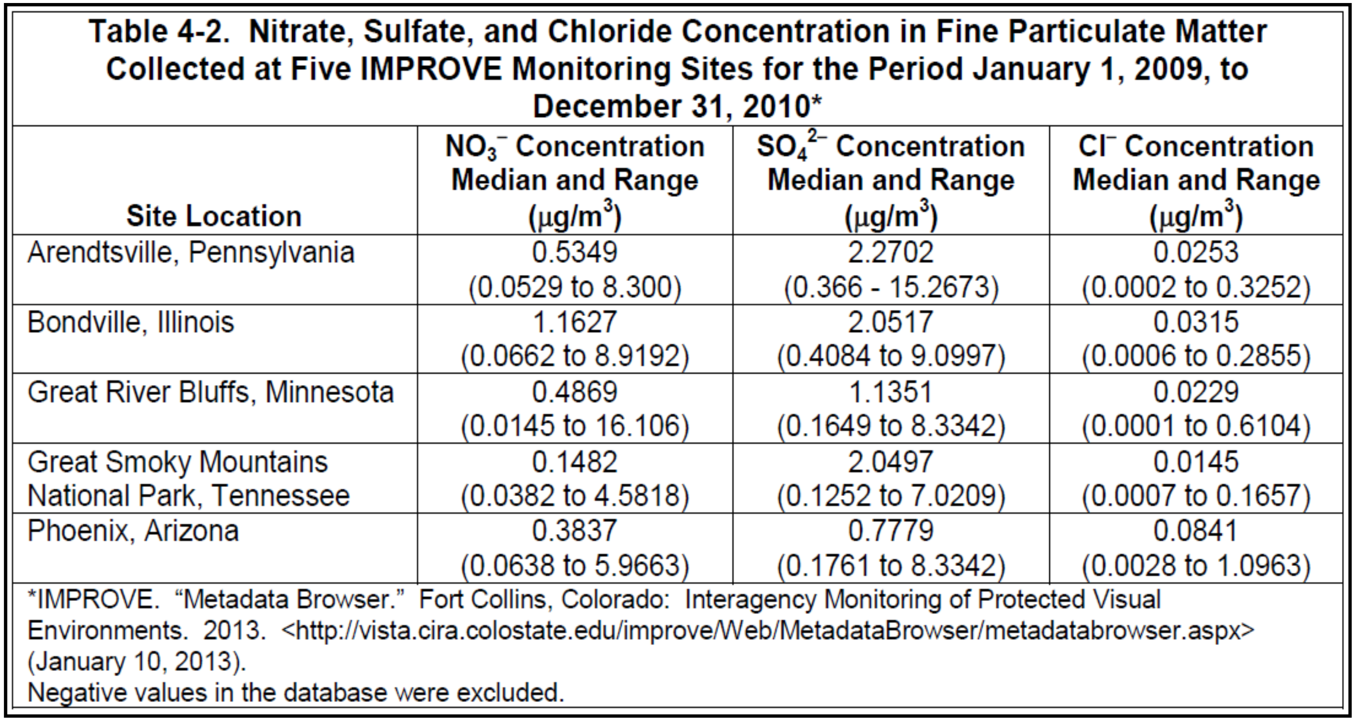


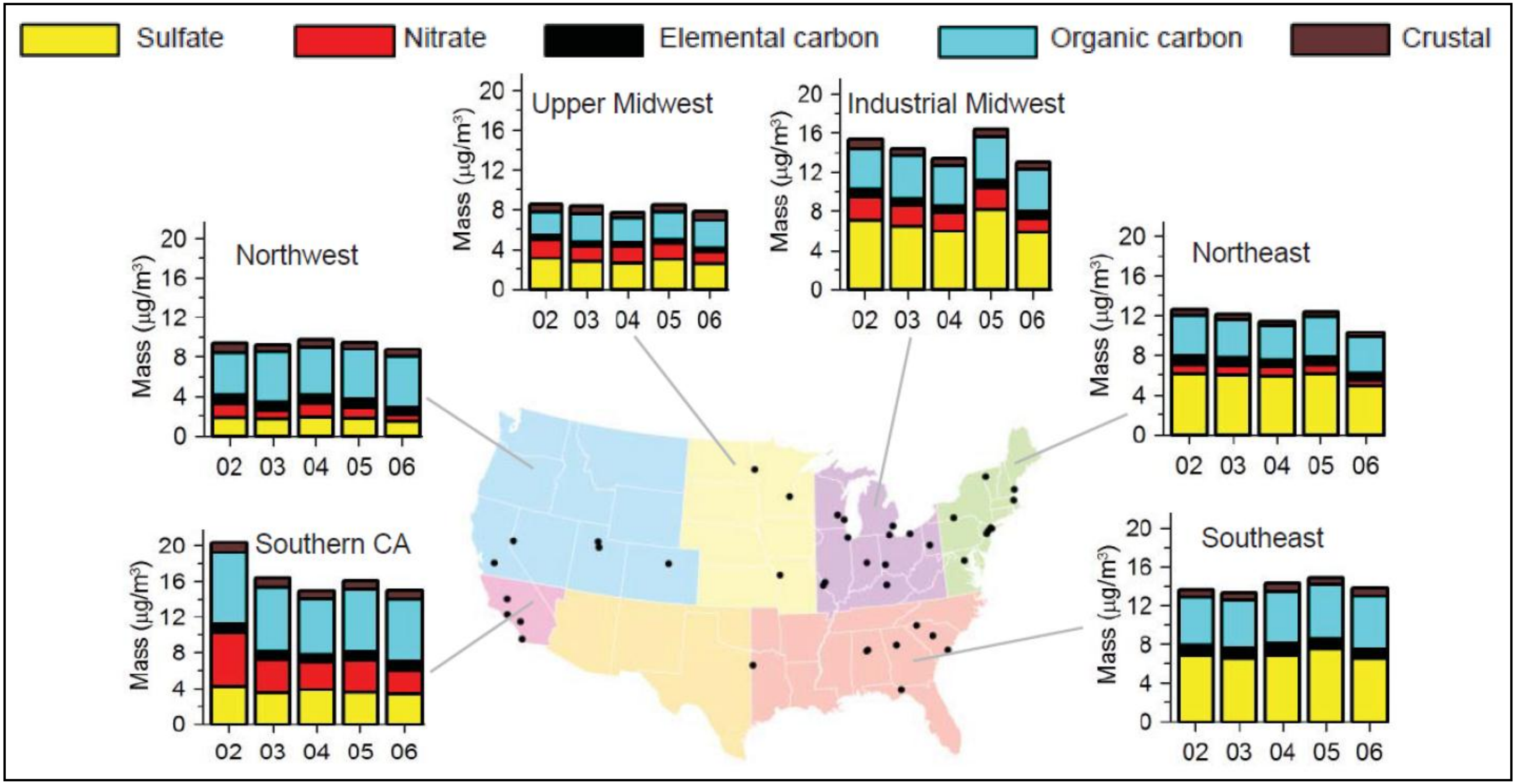
Table 4-2. Nitrate, Sulfate, and Chloride Concentration in Fine Particulate Matter Collected at Five IMPROVE Monitoring Sites for the Period January 1, 2009, to December 31, 2010*

Site Location	NO_3^- Concentration Median and Range (µg/m^3)	SO_4^{2-} Concentration Median and Range (µg/m^3)	Cl^- Concentration Median and Range (µg/m^3)
Arendtsville, Pennsylvania	0.5349 (0.0529 to 8.300)	2.2702 (0.366 - 15.2673)	0.0253 (0.0002 to 0.3252)
Bondville, Illinois	1.1627 (0.0662 to 8.9192)	2.0517 (0.4084 to 9.0997)	0.0315 (0.0006 to 0.2855)
Great River Bluffs, Minnesota	0.4869 (0.0145 to 16.106)	1.1351 (0.1649 to 8.3342)	0.0229 (0.0001 to 0.6104)
Great Smoky Mountains National Park, Tennessee	0.1482 (0.0382 to 4.5818)	2.0497 (0.1252 to 7.0209)	0.0145 (0.0007 to 0.1657)
Phoenix, Arizona	0.3837 (0.0638 to 5.9663)	0.7779 (0.1761 to 8.3342)	0.0841 (0.0028 to 1.0963)

*IMPROVE. "Metadata Browser." Fort Collins, Colorado: Interagency Monitoring of Protected Visual Environments. 2013. <http://vista.cira.colostate.edu/improve/Web/MetadataBrowser/metadatabrowser.aspx> (January 10, 2013).
Negative values in the database were excluded.

Composition of salt aerosols—inland sites

Important components in atmospheric aerosols, averages for 2002-2006 (EPA 2010).



Processes affecting aerosol/brine compositions

But, prior to or after deposition, a variety of reactions can modify the salt compositions

- **Gas-to-particle conversion reactions change chlorides to sulfates and nitrates (e.g., Gibson et al., 2006):**

$$NaCl(s,aq) + HNO_3(g) \xrightarrow{RH\%} NaNO_3(s,aq) + HCl(g)$$

$$MgCl_2(s,aq) + 2HNO_3(g) \xrightarrow{RH\%} Mg(NO_3)_2(s,aq) + 2HCl(g)$$

(and reactions with nitrous oxides)

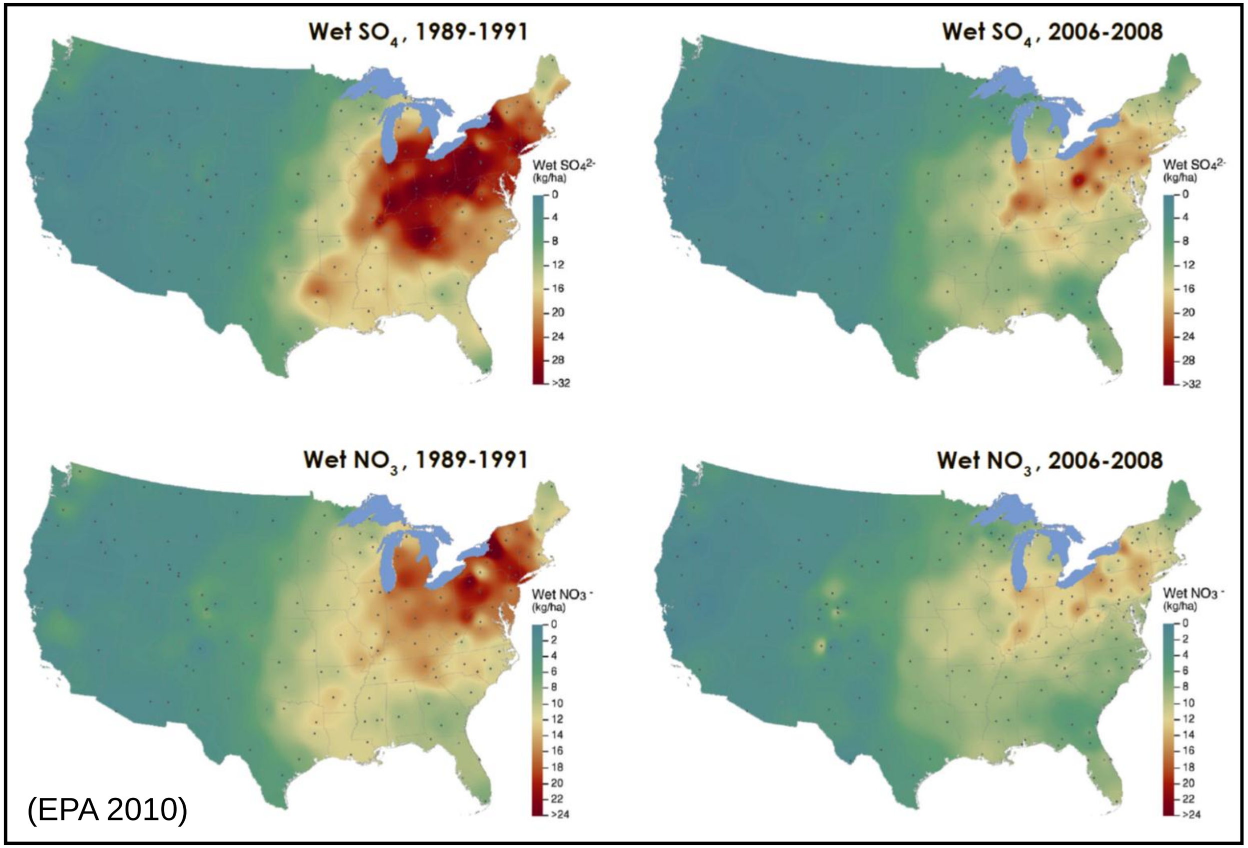
$$SO_2(g) + H_2O + ½O_2 + 2NaCl \rightarrow 2HCl(g) + Na_2SO_4$$

  - These reactions can be very efficient at converting chlorides to nitrates and sulfates
  - Even over oceans, atmospheric aerosols are deficient in chloride relative to sea salt (Hitchcock et al. 1980)
  - Coastal aerosols in Spain lose 24% (coarse particles) to 67% (fine particles) of their chloride prior to reaching the shoreline, ~11% per hour thereafter. (Pio and Lopes, 1998).
- **Carbonate mineral grains also react with NO_x, SO_2, and HCl/HNO_3 to form Ca, Mg nitrates/chlorides/sulfates. At higher temperatures, the reaction is reversed.**

SO_2 and NO_x power plant emissions

Despite improvements in emissions over the past few decades, SO_2 and NO_x are still high in the industrialized east. Gas-to-particle conversion reactions that change chlorides and carbonates to sulfates or nitrates may be especially important in the eastern US.

Wet deposition of sulfate and nitrate, 1989-1991 (left) and 2006-2008 (right)

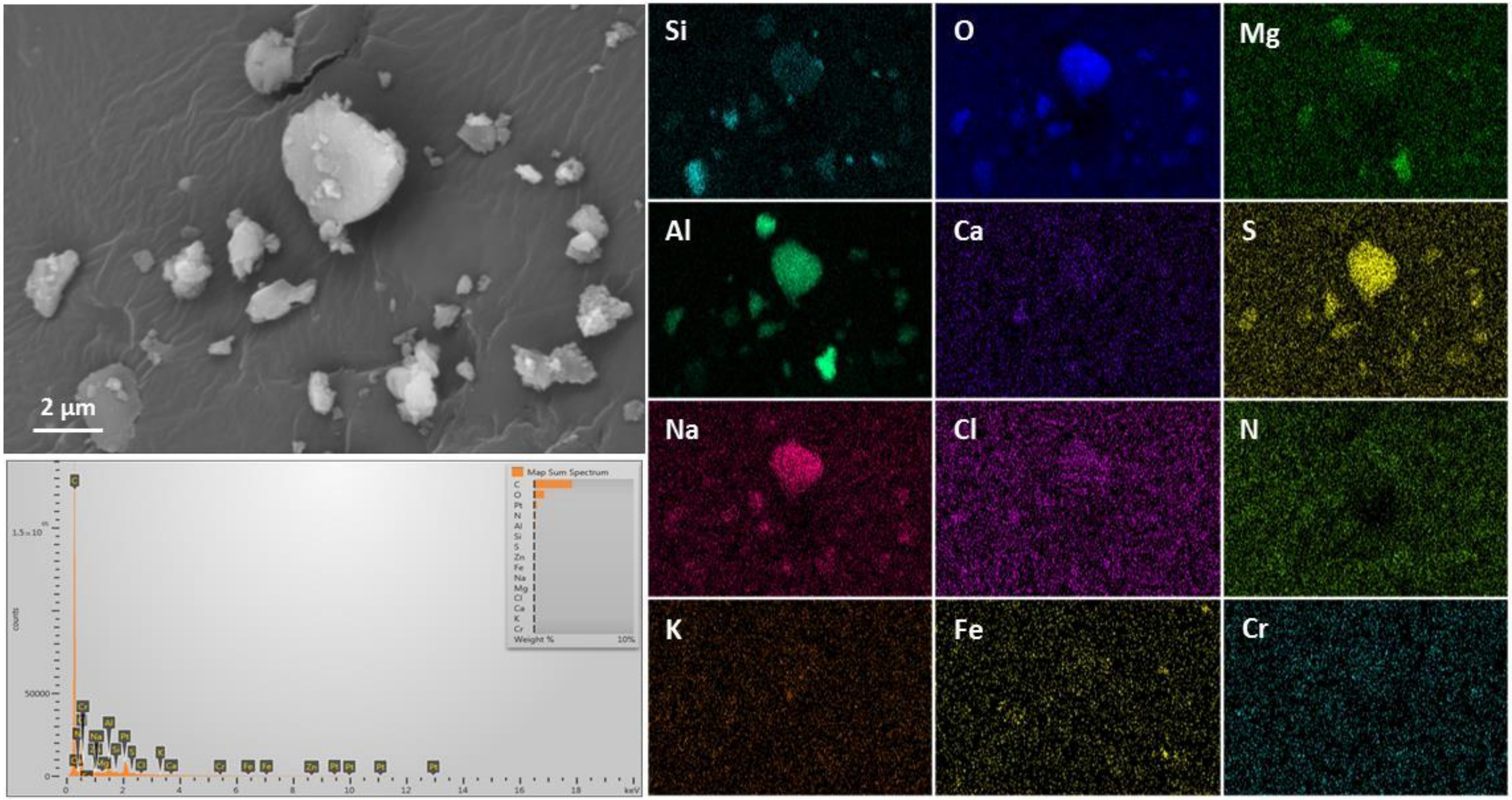


(EPA 2010)

Evidence for conversion reactions from canister dust sampling

- Calvert Cliffs in-service canisters. Soluble salts strongly dominated by Ca and SO_4, with abundant NO_3 and sparse Cl (less than Na). SEM analysis shows abundant Ca-SO_4 phase. Possibly formed by $CaCO_3$ reactions with SO_2 or with $(NH_4)_2SO_4$).
- Hope Creek in-service canisters. Soluble salts dominated by Ca, SO_4, and NO_3. Ca-SO_4 and Ca-Mg-SO_4 commonly observed by SEM. Formed by conversion of carbonates?
- Diablo Canyon in-service canisters. Sparse mixed Cl-NO_3 phase—partially converted NaCl?
- Hope Creek unused canister (analyzed this FY). Light salt loads, dominantly Ca-SO_4-Na-NO_3. Sparse but varied salt assemblage, sparse nitrates and chlorides, and abundant sulfates, including Ca-SO_4, K-SO_4, Na-K-SO_4, and several grains of Na-Al-SO_4. These are not common salts, and can only have formed by gas-to-particle conversion reactions (probably prior to deposition). Na-Al-SO_4 probably sourced to Al smelter emissions (Hall-Heroult process) An Al smelter is in Camden NJ, less that 40 miles from the site.

Dust collected from the FME cover, Hope Creek unused canister. Note the Na-Al-SO_4 phase.



Other processes affecting aerosol/brine compositions

- **Acid degassing:**
  - Loss of acid gas anions (Cl, NO_3 from solution)
  - pH rises, until buffering reactions (e.g., precipitation of carbonate or hydroxy-chlorides, concommitant ammonium degassing) stabilize it
  - Evaluated in SNL (2008) (Analysis of Dust Deliquescence for FEP Screening) for NO_3-rich salt assemblages, and EPRI (2006) for marine environments
  - Generally only considered important (for ~ seawater) below pH ~ 3 (Hitchcock et al., 1980)
- **Decomposition of ammonium minerals and ammonium degassing**
  - Loss of ammonium plus:
    - *The associated anion if mineral decomposition in the solid state occurs*
    - *Anions in proportion to their acid gas fugacities over the solution of interest, if a deliquesced solution is present.*
- **Reactions with other dust components**
  - Organics—reactions consume nitrate (Yucca Mountain dusts; Peterman 2008, 2009)
  - Mineral phases (e.g., silicates)—reactions buffer pH to near neutral values (SNL 2008)

Experimentally Evaluating Salt and Brine Stability

Experimentally evaluate salt and brine stability on the canister surface

- *Salt decomposition in the solid state*
- *Brine stability*
  - *Degassing*
  - *Reactions with other dust phases or atmospheric gases*

Reactions may result in:

- *Mass/compositional changes in soluble salts and brine chemistry*
- *Changes in RH_D (dryout?)*

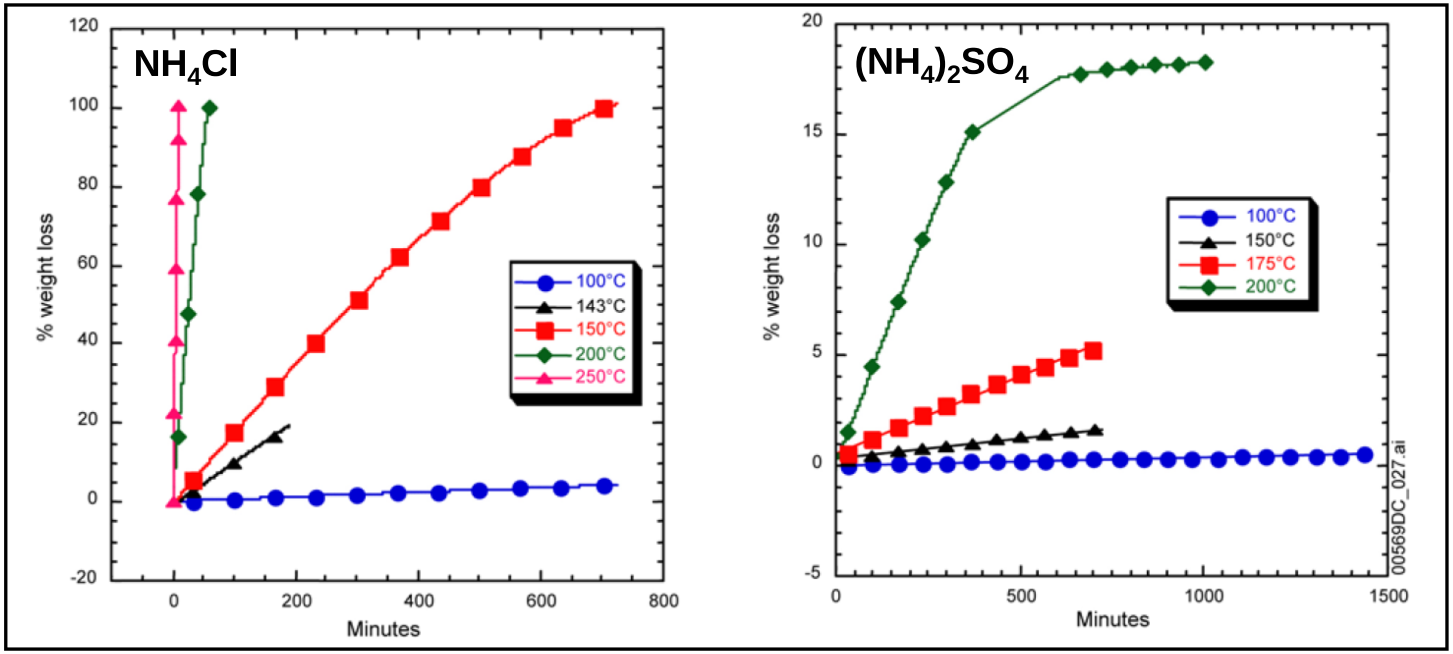
Experimental methods:

- *Deposit salts as aqueous solution using an airbrush mounted on an automated 3-D printer platform.*
- *Simultaneously deposit onto quartz crystal microbalance (QCM) wafers and metal coupons*
  - *QCM wafers—monitor deposit deposition mass, later used to monitor deliquescence and mass loss in the environmental chamber*
  - *Metal coupons—Much larger area, used to measure salt compositional changes during exposure in the environmental chamber. (soluble salts leached off and analyzed)*

Initial experiments: Evaluating inland salts—ammonium minerals

- **Ammonium salts decompose in the solid state to release NH_3 and acid gas:**

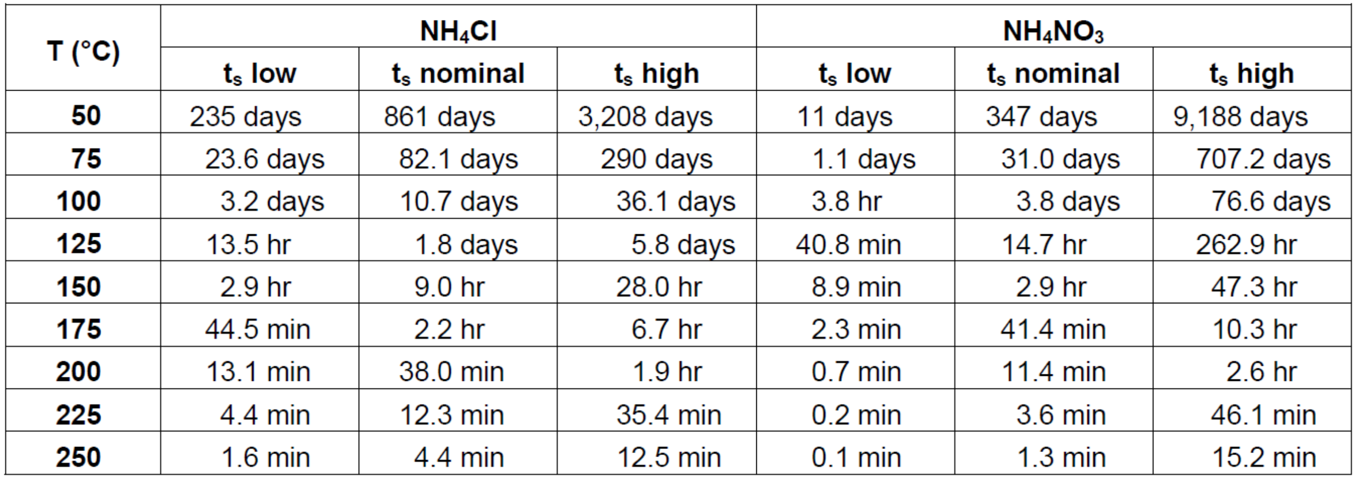
$NH_4Cl \rightarrow NH_3 + HCl$ $NH_4NO_3 \rightarrow NH_3 + HNO_3$ $(NH_4)_2SO_4 \rightarrow 2NH_3 + H_2SO_4$



SNL 2008, Figure 6.1-2

Initial experiments: Evaluating inland salts—ammonium minerals

- **Decomposition of ammonium salts is rapid (SNL 2008, Table 6.1-1)**



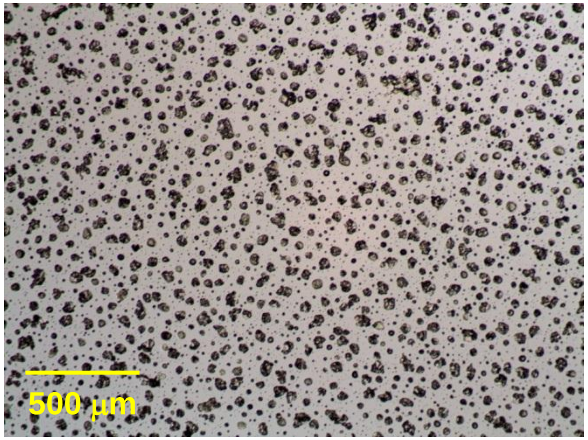
T (°C)	NH_4Cl			NH_4NO_3		
	t_s low	t_s nominal	t_s high	t_s low	t_s nominal	t_s high
50	235 days	861 days	3,208 days	11 days	347 days	9,188 days
75	23.6 days	82.1 days	290 days	1.1 days	31.0 days	707.2 days
100	3.2 days	10.7 days	36.1 days	3.8 hr	3.8 days	76.6 days
125	13.5 hr	1.8 days	5.8 days	40.8 min	14.7 hr	262.9 hr
150	2.9 hr	9.0 hr	28.0 hr	8.9 min	2.9 hr	47.3 hr
175	44.5 min	2.2 hr	6.7 hr	2.3 min	41.4 min	10.3 hr
200	13.1 min	38.0 min	1.9 hr	0.7 min	11.4 min	2.6 hr
225	4.4 min	12.3 min	35.4 min	0.2 min	3.6 min	46.1 min
250	1.6 min	4.4 min	12.5 min	0.1 min	1.3 min	15.2 min

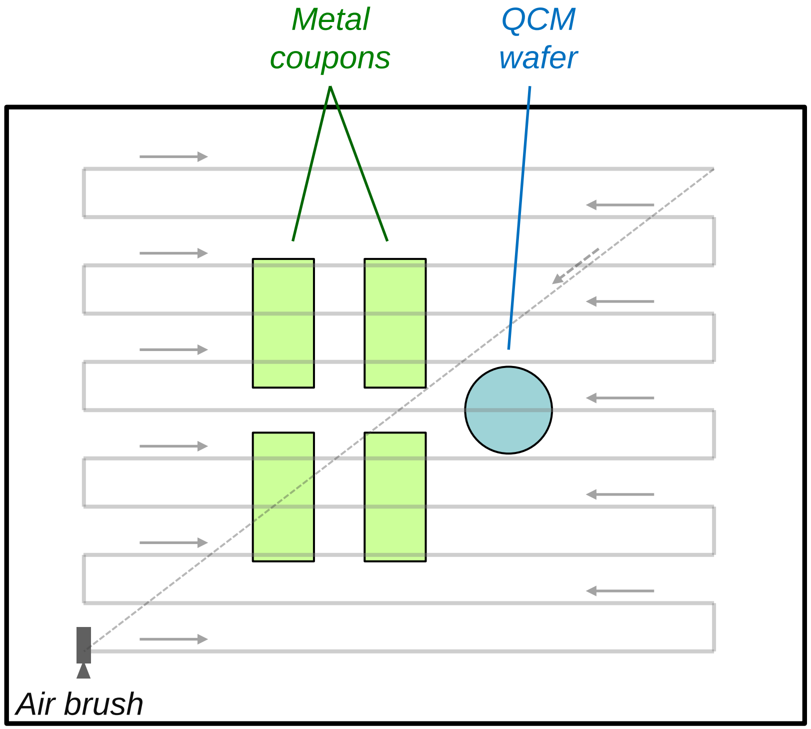
- **Once deliquescence conditions are achieved, ammonium salts will dissolve upon contact with the canister surface:**
  - The deliquescent solution will degas ammonia and acid gases
  - Acid gas loss is no longer tied to the identity of the deposited ammonium salt
  - Acid gases will be lost in proportion to their partial pressures above the deliquesced brine

Salt Deposition

- *Deposition of soluble salts using an airbrush*
  - *Aqueous solutions—for individual salts (0.1M)*
  - *Deposited mass monitored using a QCM*
  - *25-50 multiscan passes = 100 ± 2 µg/cm^2 (1 g/m^2)*
  - *Each pass is ~20 mg/m^2 (depends on salt FW)*
  - *Lower surface loads, down to perhaps a few mg/m^2, can be achieved using a more dilute starting solution*

NH_4NO_3



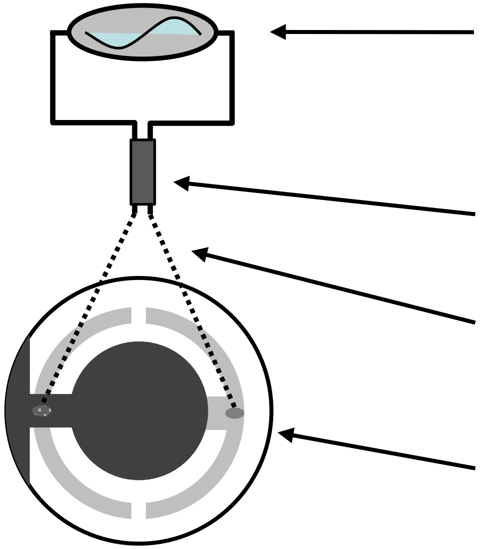


Good for single salts. For multiple salts, to avoid reactions during deposition, may have to deposit as alcohol suspensions, or dry deposition?

Experimentally Evaluating Salt and Brine Stability

Quartz Crystal Microbalance (QCM)

Tiny mass changes are measured by a change in the vibrational frequency of the piezoelectrically stimulated quartz wafer. The active area is the area of overlap between the two electrodes (38 mm^2)

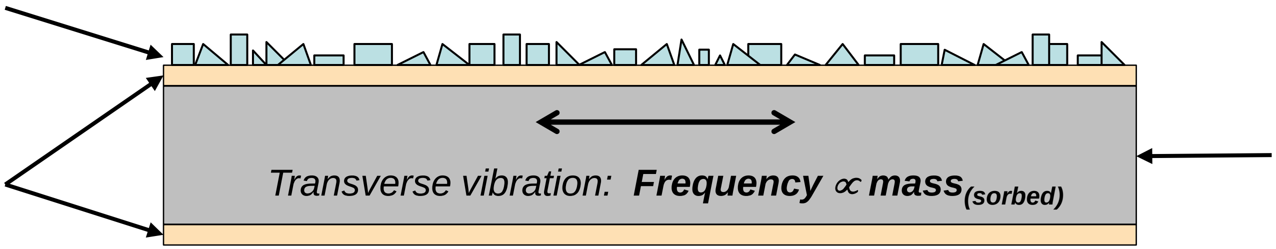


Oscillator circuit, frequency monitor, and power supply

Cable

Electrical leads

QCM Wafer



Deposited mass

Gold electrodes

Transverse-cut (AT) quartz wafer

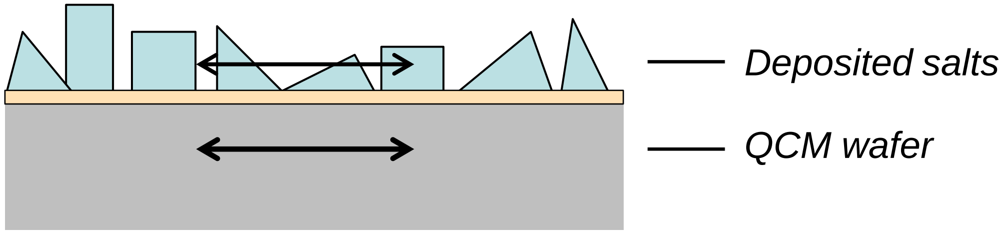
Transverse vibration: ***Frequency*** $\propto$ ***mass***$_{\textbf{(sorbed)}}$

Experimentally Evaluating Salt and Brine Stability

Quartz Crystal Microbalance (QCM): Limitations

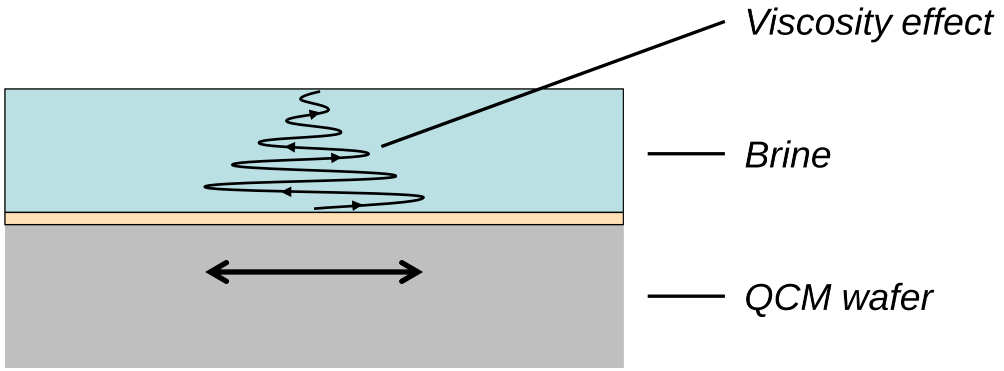
QCM accurately measures mass for solids that couple with the wafer, and vibrate with it.

- *Measure mass of deposited salts*
- *Measure weight loss as salts decompose from the solid state.*



QCM cannot measure mass of liquids (e.g., deliquescent brines), which do not couple with the surface of the wafer.

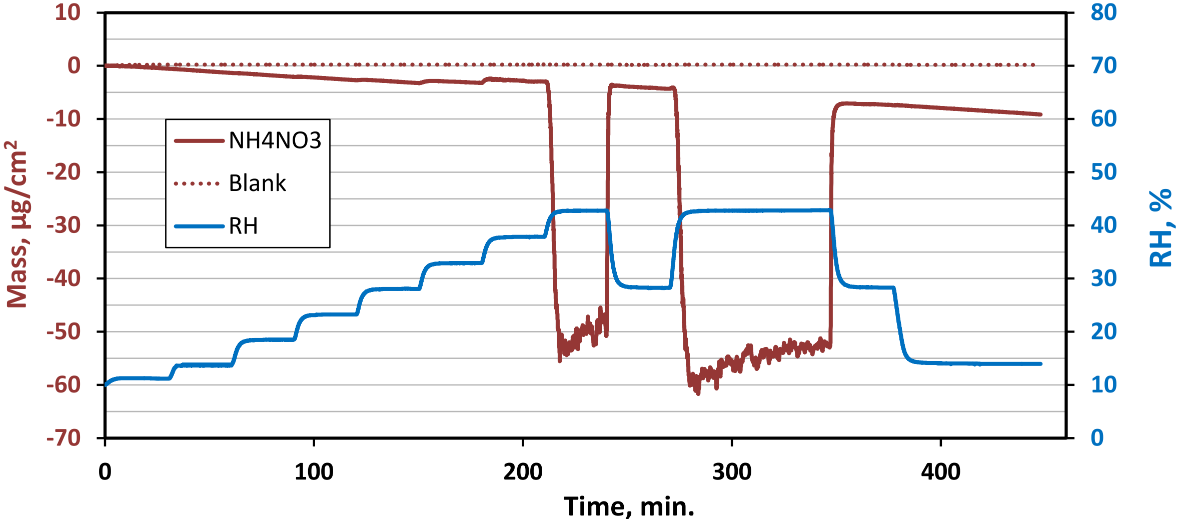
- *Cannot directly measure mass gain/loss of deliquesced brines*
- *Recorded mass is too low, while viscous drag results in high electrical resistance*
- *However, can measure mass prior to deliquescence and after dryout, and determine mass loss during deliquescent phase.*

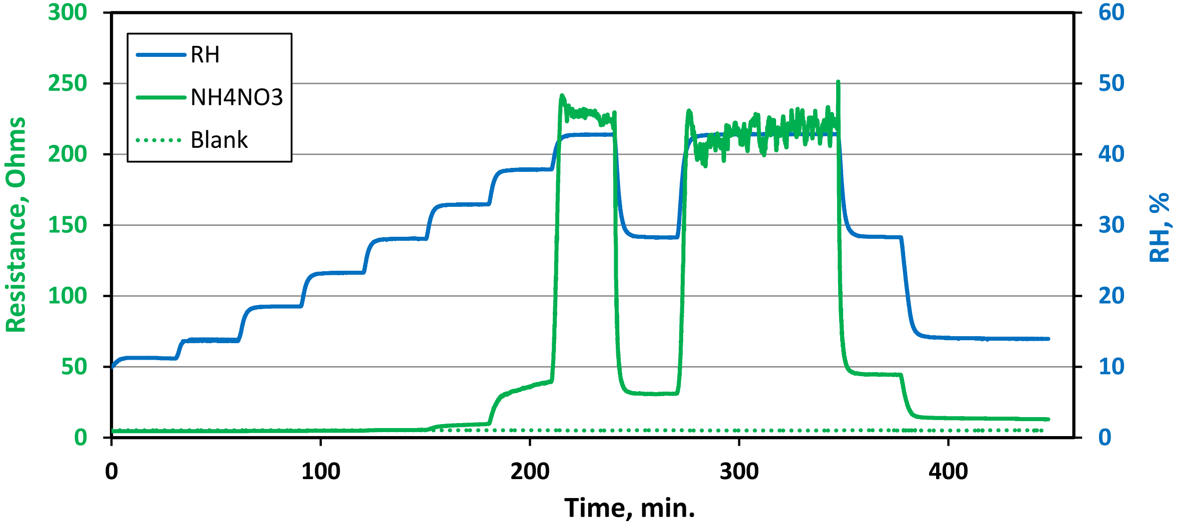


Initial experiments: NH_4NO_3

Deliquescence—increase RH in 5% increments.

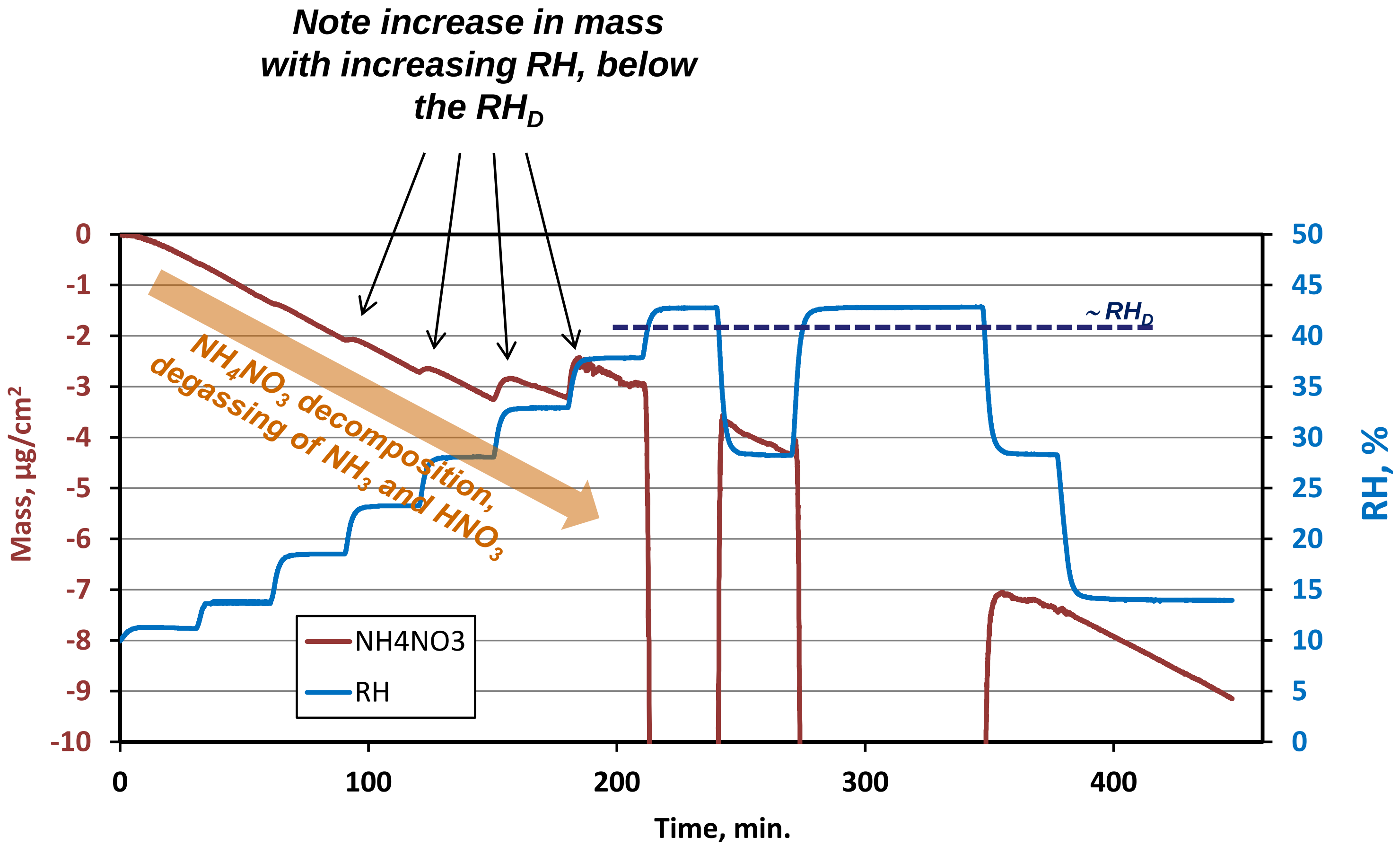
- *Blank wafer shows no weight change.*
- *Wafer loaded with NH_4NO_3 shows consistent weight loss*
- *When deliquescence occurs (~40-45% RH), brine decouples from the surface*
- *Apparent large weight loss.*
- *Concurrent large increase in resistance (viscosity effects)*
- *Upon dryout, salts re-couple to the surface, and mass can be measured*



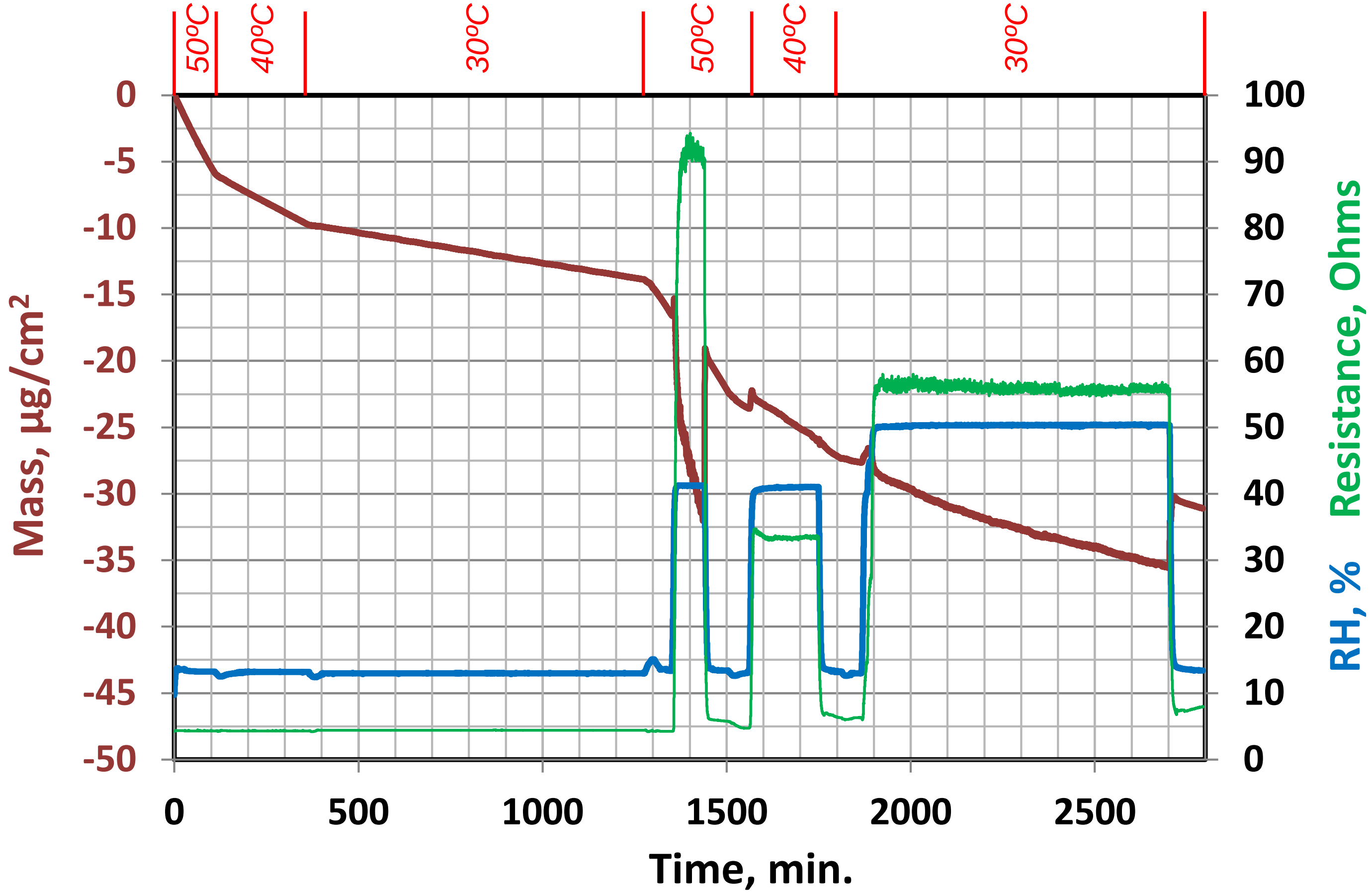


NH_4NO_3 Stability

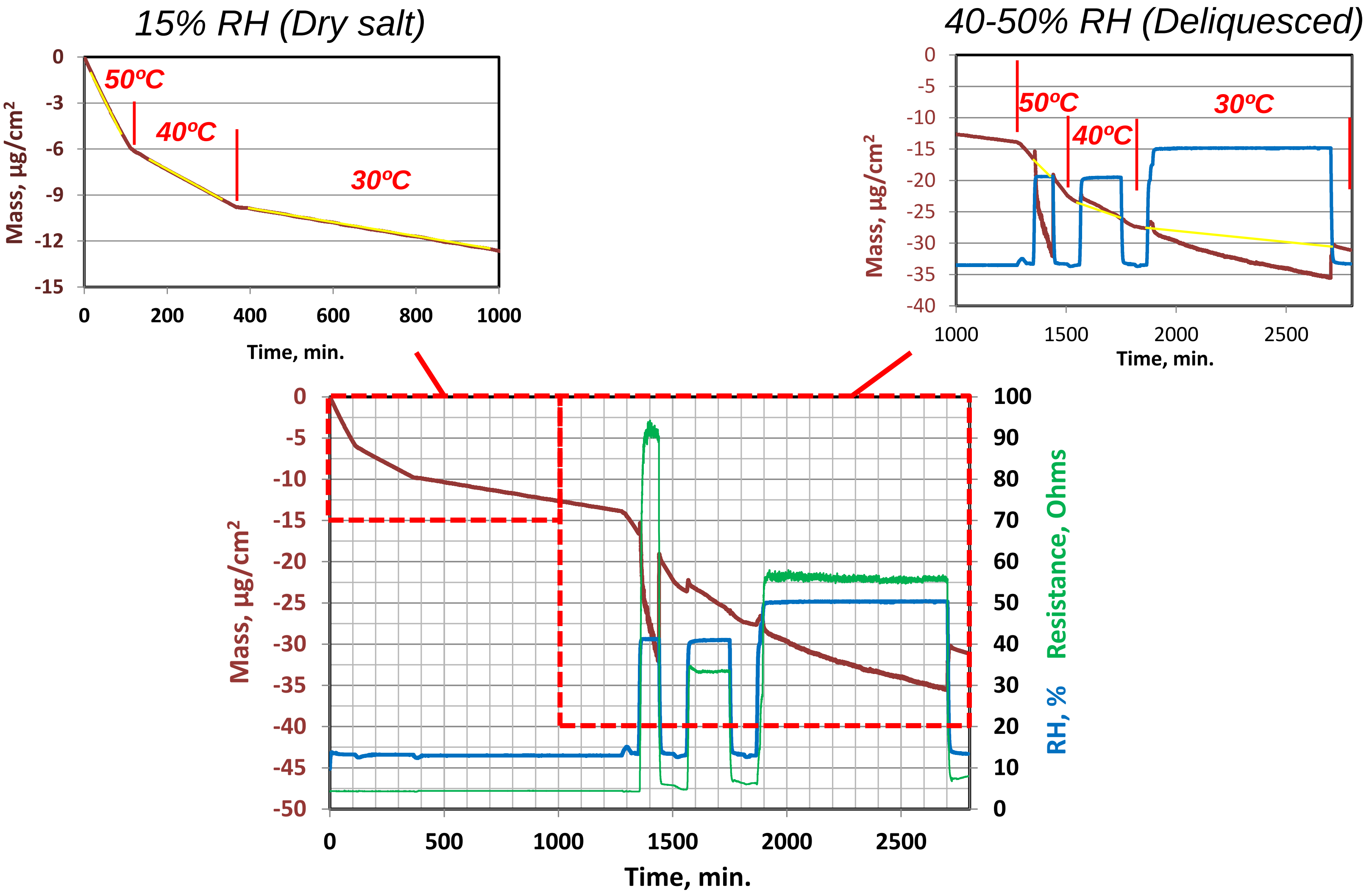
Close-up of previous plot



NH_4NO_3 Stability



NH_4NO_3 Stability



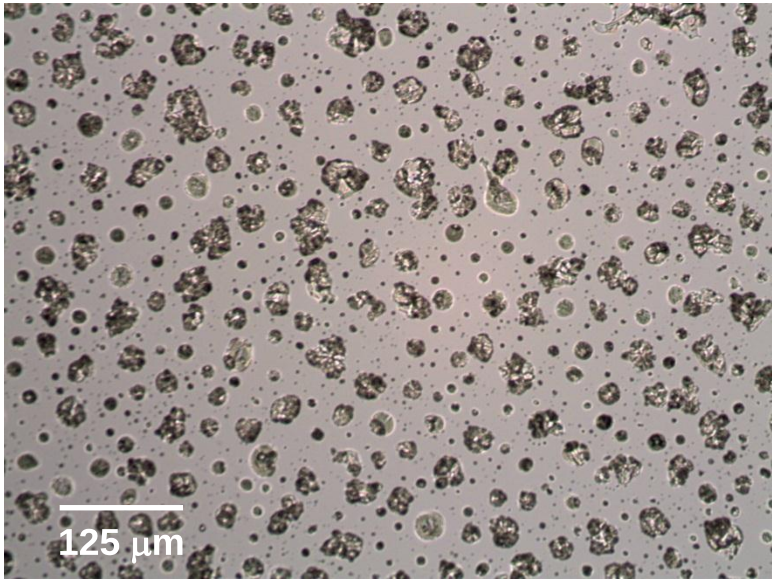
15% RH (Dry salt)

40-50% RH (Deliquesced)

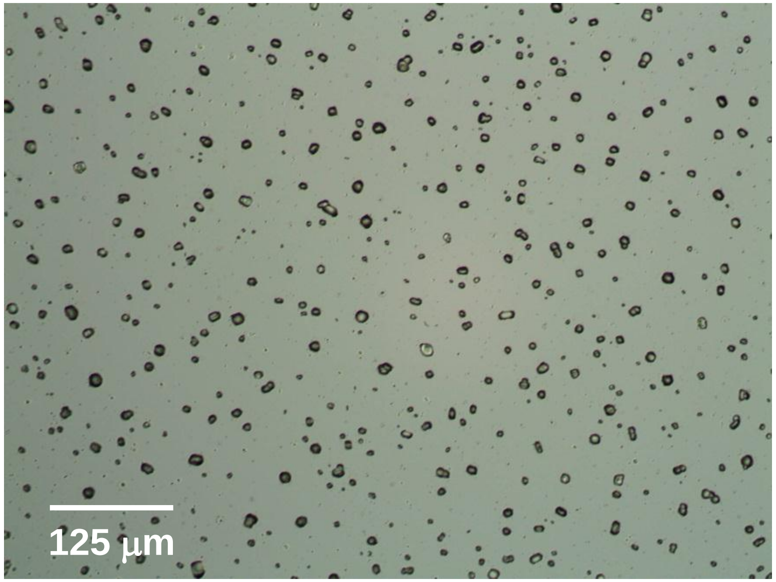
Deposited salts

NH_4NO_3

Before



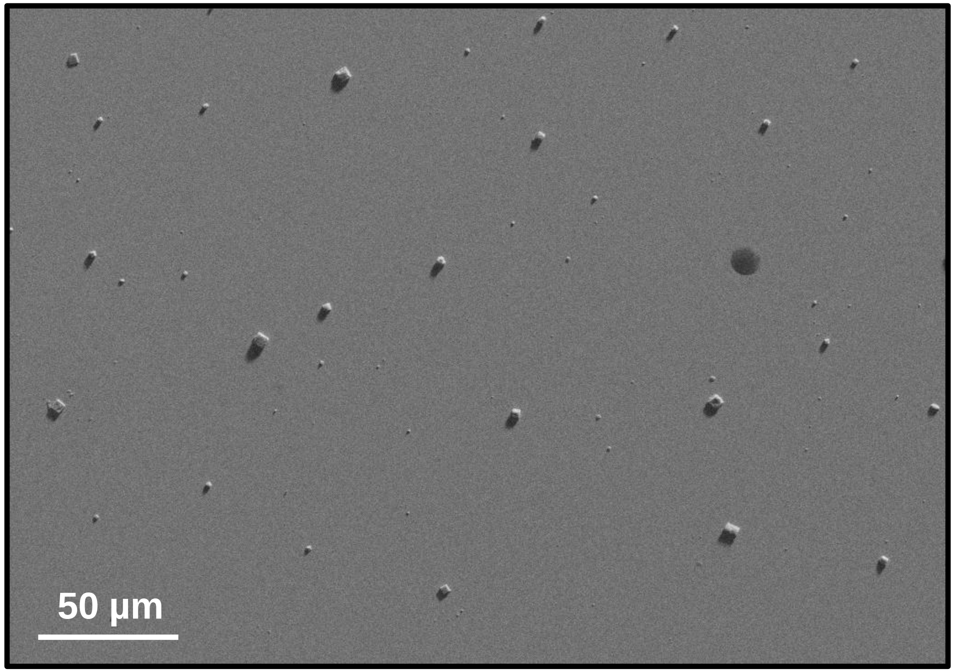
After

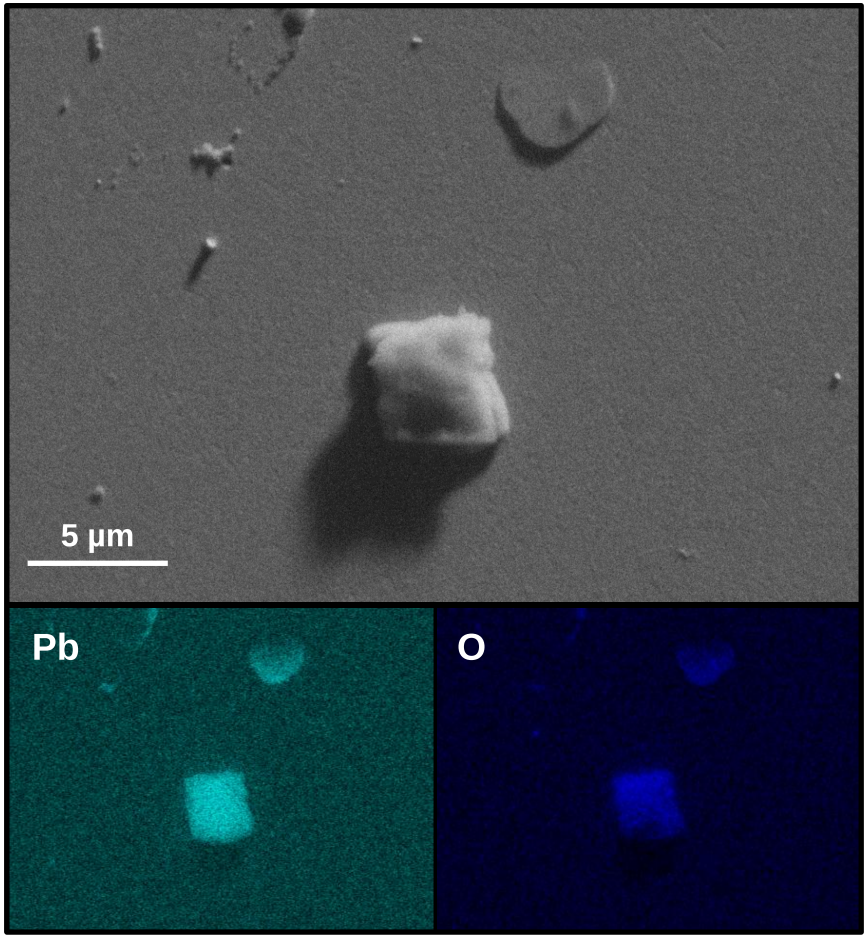


NH_4NO_3 experiment

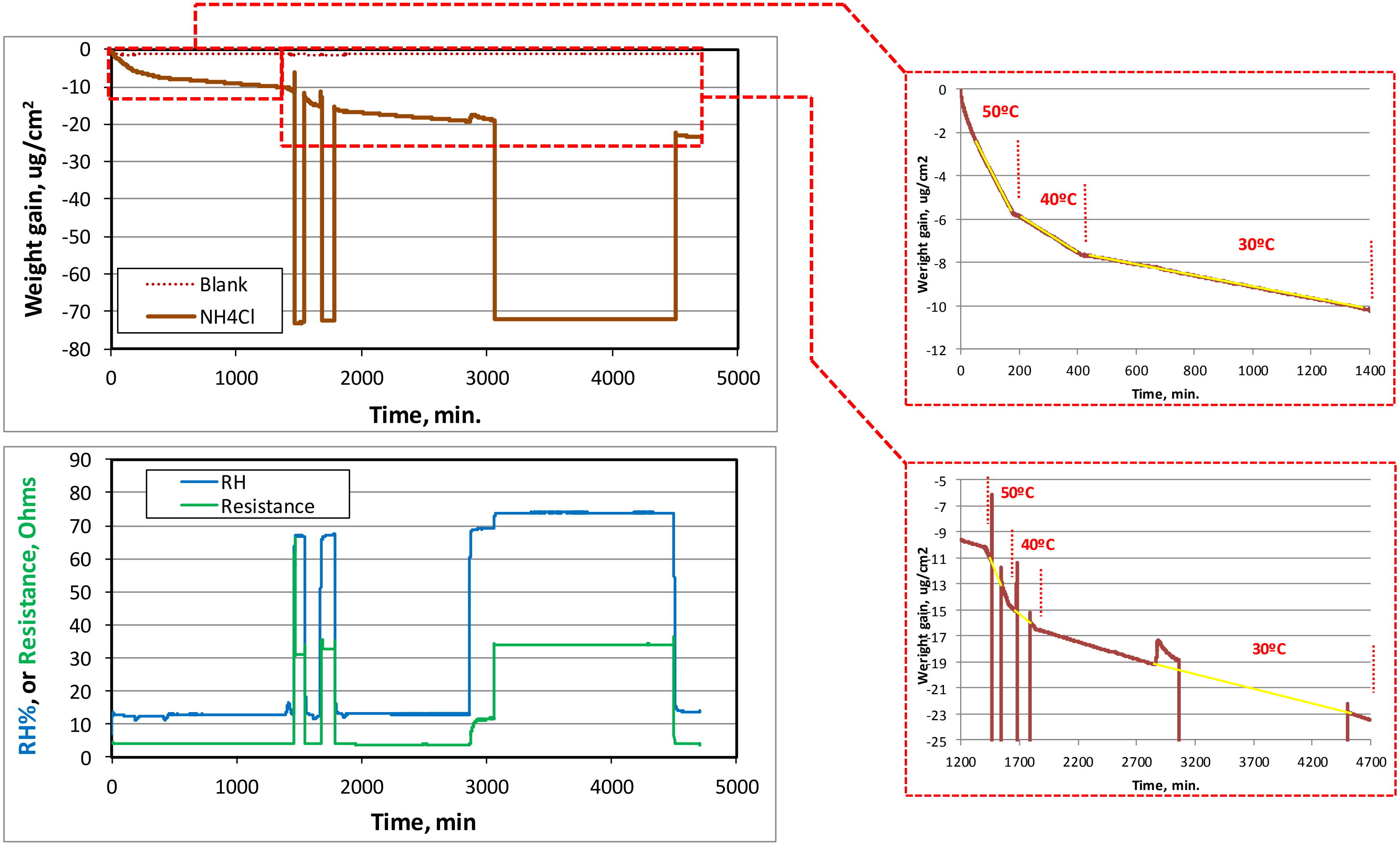
SEM photo of QCM wafer once degassing is complete (mass stabilizes)

Apparent residual salts are a Pb phase from solder fumes that condensed onto the wafer.





NH_4Cl experiment



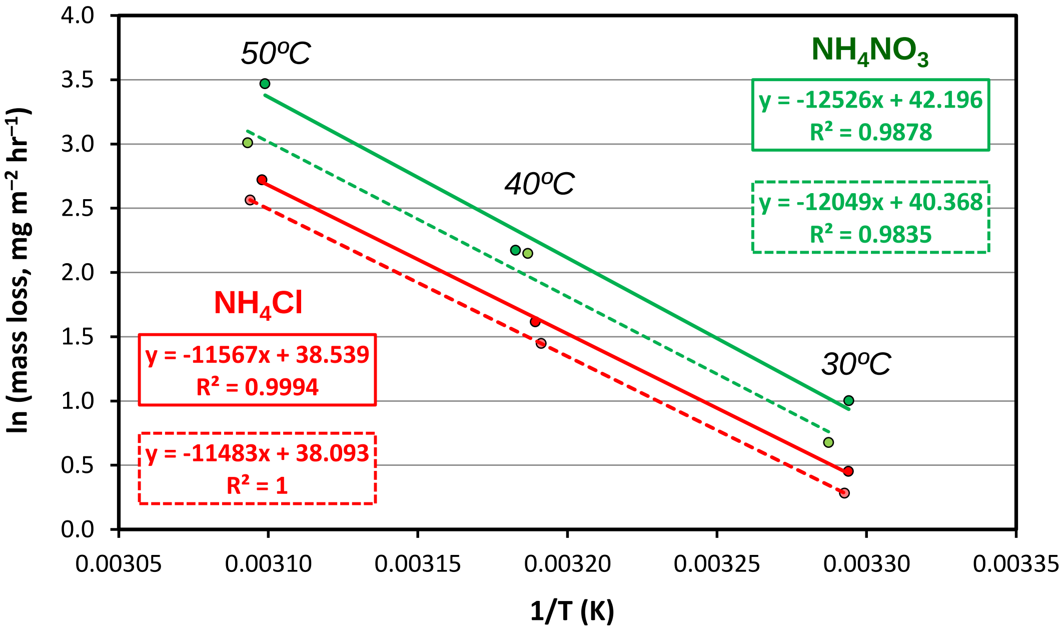
NH_4NO_3 and NH_4Cl degassing rates

NH_4Cl

T, ºC	RH	Rate, $mg/m^{-2}\ hr^{-1}$	Days to degas $1\ g/m^{-2}$
Dry			
49.8	12.6	-15.20	2.7
40.6	12.5	-5.03	8.3
30.6	13.0	-1.57	26.5
Deliquesced			
50.2	63.9	-12.98	3.2
40.4	62.1	-4.26	9.8
30.7	72.9	-1.33	31.4

NH_4NO_3

T, ºC	RH	Rate, $mg/m^{-2}\ hr^{-1}$	Days to degas $1\ g/m^{-2}$
Dry			
49.7	13.2	-32.10	1.3
41.2	13.2	-8.78	4.7
30.6	13.0	-2.72	15.3
Deliquesced			
50.3	41.2	-20.28	2.1
40.8	41.0	-8.56	4.9
31.2	50.3	-1.97	21.2



Salt	E_a, kJ/mol
NH_4NO_3, dry	104.1
NH_4NO_3, deliquesced	100.2
NH_4Cl, dry	96.2
NH_4Cl, deliquesced	95.5

Degassing is faster here that in the YMP experiments because particles sizes are smaller (higher surface area). Real dust aerosols much smaller, and will degas even more rapidly.

Implications

- NH_4NO_3 and NH_4Cl are unstable at elevated temperatures, decomposing rapidly in the solid state.
- Preliminary data suggest $(NH_4)_2SO_4$ does not decompose rapidly.
- NaCl, $MgCl_2$, $CaCl_2$ do not decompose in the solid state.
- Salt assemblages containing ammonium + chloride or nitrate are not representative of conditions that can occur and persist on the canister surface (except perhaps at ambient temperatures).
- If Cl-bearing salts are deposited on inland storage canisters, a chloride-rich brine can only form and persist if the deposition rate of chloride is greater than that of ammonium sulfate, the most common salt in inland aerosol salt assemblages.

On a hot canister, prior to deliquescence, NH_4NO_3 and NH_4Cl will not persist. *If deposited*, other chloride salts will accumulate, and $(NH_4)_2SO_4$ may accumulate.

***However*, upon deliquescence, brines containing NH_4^+ and NO_3^- or Cl^- will rapidly degas until either NH_4^+ or (NO_3^- + Cl^-) are consumed. For $(NH_4)_2SO_4$:**

$$(NH_4)_2SO_4 + NaCl \rightarrow \tfrac{1}{2}Na_2SO_4 + \tfrac{1}{2}(NH_4)_2SO_4 + NH_3(g) + HCl(g)$$

What about NH_4NO_3?

$$NH_4NO_3 + NaCl \rightarrow XNaNO_3 + (1\text{-}X)NaCl + NH_3(g) + (1\text{-}X)HNO_3(g) + XHCl(g)$$

Other planned experiments

- **Evaluate $(NH_4)_2SO_4$ and $(NH_4)HSO_4$. Little or no degassing?**
- **Evaluate multi-salt assemblages containing ammonium minerals and chloride salts (NaCl, $MgCl_2$)**
  - Degassing rates
  - Compositional changes
  - Changes in RH_D
- **Evaluate sea salts.**
  - Acid degassing and carbonation reactions—is $MgCl_2$ in deliquesced sea salts converted to Mg carbonate? Concommitant changes in RH_D?