

QCM THERMO-GRAVIMETRIC ANALYSIS (QTGA) COMPARISONS

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ABSTRACT

The ASTM E-1559 apparatus has been used for years at NASA/Goddard Space Flight Center (GSFC) to determine in situ outgassing rate information, as well as pertinent in situ TML and multiple VCM values. The apparatus also affords the opportunity to experimentally compute the evaporation rates of molecular species that are reemitted as the Quartz Crystal Microbalances (QCMs) are gradually warmed up at some controlled temperature. Typically the molecular mass that accumulates onto the test QCMs are a compilation of species that are outgassing from the sample due to their respective activation energies and the desorption processes that the sample undergoes at various tested temperatures. It has been speculated that if there is too much molecular buildup of condensed water vapor (ice) onto the QCM crystal that a significantly higher temperature would be needed to break these “ice” bonds. ASTM E-1559 data plots will be used to demonstrate the thermogravimetric effects of water and other miscible molecular species with various water/ice thicknesses and at different evaporation rates.

INTRODUCTION

The ASTM E-1559 setup at NASA/GSFC utilizes 4 QCMs to collect a molecular mass at 4 different temperature ranges. The coldest QCM is typically cooled to near liquid nitrogen (LN2), at ~90K, and condense most water vapor that impinges onto it and most other heavier weighted outgassed molecules from the sample. The other QCMs are typically set to common temperatures, warmer than the water condensation temperature under high vacuum (<1E-6 Torr). A variety of common aerospace materials and candidate samples were considered for this investigation. These samples have been exposed in the Molekit2 system within the past 2 years. The samples selected for this evaluation considered a variety of materials and varied the water accumulation rate from 100's of Hertz to 10000's of Hertz over a test period of 24 to over 100 hours. The reemission process, mass evaporating from the QCM crystal, was also performed with a steady increase in temperature. Under high vacuum the normal range that deposited water vapor begins to evaporate is around -125C. If there is 50,000 Hz or ~10,000 Angstroms (1000 nm) of accumulation on the QCM crystal does the water vapor take substantially longer to evaporate/reemit because of the thicker layer of contaminate? Does the thermogravimetric effects of water differ when other miscible molecular species are present?

ABBREVIATIONS and ACRONYMS

ASTM American Society of Testing Materials
CCD Charged Couple Device
GSFC Goddard Space Flight Center
EC Effusion Cell
LN2 Liquid Nitrogen
Molekit Molecular Kinetics
NASA National Air & Space Agency
QCM Quartz Crystal Microbalance
QTGA QCM Thermogravimetric Analysis
RGA Residual Gas Analyzer

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SYMBOLS

Å	Angstrom	cm ²	square centimeter
°C	degrees Celsius	g	gram
Hz	Hertz	K	degrees Kelvin
nm	nanometer (1 nm = 1E-9 m = 10Å)		

EXPERIMENTAL METHODS/SETUP

The GSFC setup for the ASTM E-1559 test procedure provides outgassing information and reemission data for evaluating spacecraft materials. The setup does have a limitation to the sample size. Currently the effusion cell can fit samples that are ~1" by ~1.5" by ~2". The effusion cell has an orifice diameter of ~1/8" and is located on the top of the "can". The EC can be heated rather instantaneously by heaters attached to the side, up to 300°C. The effusion cell can also be cooled and maintained at temperatures below ambient. One sample, included in this analysis was tested as low as -20°C, which involved attaching several thermal straps from the LN2 chamber to the EC and then adjusting the EC heaters as required. A schematic of the GSFC Molekit system is shown below in Figures 1A and 1B. GSFC has 2 molecular kinetics facilities for performing E1559 tests, which are practically identical, Molekit2 and Molekit3, respectively. Samples for this investigation include samples tested from both systems, which had the same QCM set cold for all samples.

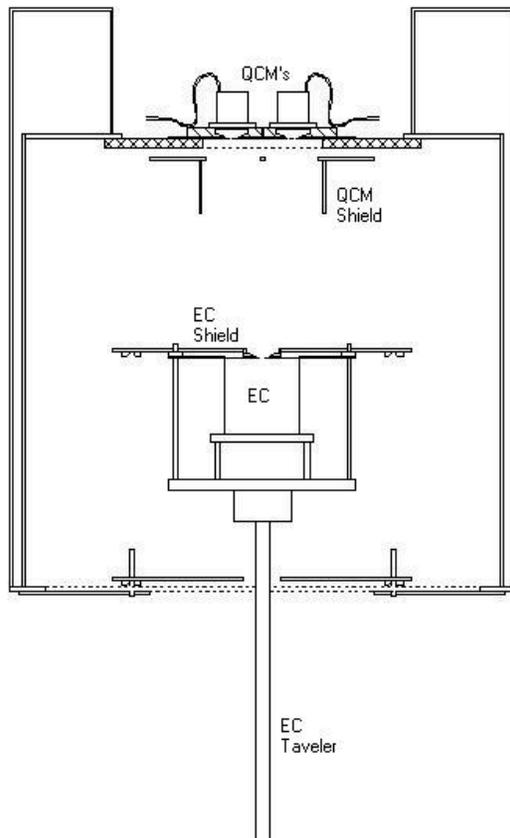


Figure 1A
Molekit 2 & 3 Shroud configuration

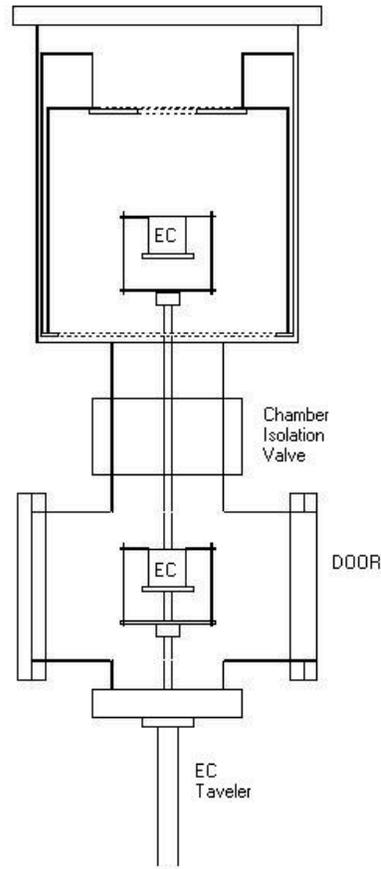


Figure 1B
Typical sample introduction from
The Interlock Chamber to Test chamber

The following is brief explanation of the Molekit test procedure. This is described in more detail in the actual ASTM E1559 procedure (ref. 1). GSFC follows the Test Method B option for most samples. A preweighed sample is placed inside an effusion cell in the Interlock chamber, which is at ambient pressure and ambient temperature. Once the QCMs, located in the Main chamber and under high vacuum, have stabilized at their desired setpoints, a slight vacuum is pulled on the Interlock chamber to $\sim 1\text{E-}3$ Torr, which occurs rather quickly (within minutes). The isolation valve is then opened and the sample is manually slide to a setpoint elevation inside the Test chamber, which places the EC orifice $\sim 6''$ away from the QCM crystal elevation. The EC is set to the desired temperature setpoint and outgassing from the sample through the orifice to the QCMs ensues. The outgassing from the sample exits the orifice in a lambertian manner. The four (4) QCMs are positioned approximately $6''$ away and centered equidistant from the $0.125''$ diameter EC orifice. The resultant viewfactor or form factor of the orifice to the QCMs for the GSFC Molekit 2 setup has been determined to be 635 cm^2 . (M3 was 610 cm^2). This setup is a line-of-sight (LOS) transport, with little to no reflected molecules affecting the net molecular gain by the QCMs. The chamber walls and QCM sink plate are flooded with LN2 and thus capture molecular mass that are dispersed from the orifice at angles more than $\sim 5^\circ$ from normal. The QCM shield is thermally coupled to the QCM sink plate and provides an additional protection from chamber shroud accidental warm-up, due to LN2 outage. The GSFC setup typically sets the 4 QCM Research QCMs to -183°C (90K), -113°C (160K), -60°C (213K), and -20°C (253K). The coldest QCM is capable of condensing water vapor and most other light weight molecular species. The chamber vessel typically obtains vacuum levels of $1\text{E-}6$ Torr or lower and water theoretically condenses at $\sim 116^\circ\text{C}$ at this pressure and lower with attainment of better pressures. Setting the 2nd coldest QCM to a level just above water condensation affords the attainment of the outgassing rate trend data for all non-water molecule species. The other temperature settings allow for computation of fractional condensing material. Since these are common setpoint temperatures for each sample, the same QCM is typically set to the same temperature. Therefore the QCMs have a history of condensing molecular mass at a common temperature. The coldest temperature setpoint has been the same QCM for all these comparisons. The following table indicates the QCM Research QCM type and serial numbers, and their common temperature setpoints for the Molekit 2 & 3 system.

Table 1
QCM serial numbers and common temperature setpoints in the MOLEKIT 2 & 3 setup

Molekit 2 QCM serial numbers	Molekit 2 QCM temperature setpoints	Molekit 3 QCM serial numbers	Molekit 3 QCM temperature setpoints
QCM1: Mark17 S/N 1096	-113°C (160 K)	QCM5: Mark17 S/N 2697	-113°C (160 K)
QCM2: Mark17 S/N 2697	-60°C (213 K)	QCM6: Mark17 S/N 2397	-60°C (213 K)
QCM3: Mark17 S/N 2297	-183°C (90K)	QCM7: Mark17 S/N 2297	-183°C (90K)
QCM4: Mark16 S/N 0691	-20°C (253K)	QCM8: Mark17 S/N 1096	-20°C (253K)

The molecular deposition onto all the QCMs, including the coldest QCM should be mixture of species dependent on their activation energies and perhaps influenced by the actual sample construction. A typical test deposition phase can vary from 24 hours to several days. The sample is then removed from the test setup, pulled back into the interlock chamber and the isolation valve is closed again, sample removed and a post test mass measurement is performed. The QCMs are maintained at their temperature setpoint for a period of several hours to monitor what sort of reemission occurs after the sample is removed from the test chamber. Typically there is little to no reemission of the deposited mass while maintained at the constant temperatures.

Then the QCMs are warmed up at a specified ramp rate. This QCM Thermogravimetric Analysis (QTGA) can be performed any variety of ways. The ASTM E1559 procedure recommends a ramp rate of $1^\circ\text{C}/\text{min}$ for the coldest QCM from the set points up to a “bakeout” temperature of 80°C (353K). The GSFC setup was programmed to perform the QTGA on all the QCMs at ramp rates of $1^\circ\text{C}/\text{min}$. However, mainly for this investigation, a ramp rate of $0.2\text{ C}/\text{min}$ was selected. Typically the GSFC QTGA goes up to 110°C (383K), where the QCMs bakeout for period of time to remove any (tough) molecules. The QTGA setup can be programmed to “march” the QCMs up in temperature together, where QCM3 (set to -183°C) will initially begin warm-up and then at -113°C , QCM1 would also begin warm-up, and so on. The QCMs can also be programmed to warm-up all at once from their temperature setpoints, therefore QCM4, set at -20°C originally, will reach 110°C the quickest and remain in bakeout mode awaiting the attainment of the other QCMs to 110°C (383K).

Either method of warm-up is okay because the QCMs do not see each other and thus do not contribute/transfer deposition to any other QCM. QTGA for all these samples was performed under the “marching up together” method. Equations for computing the insitu outgassing rates, TMLs, VCMs, and evaporation rates are discussed in the ASTM E1559 procedure (ref. 1). Hundreds of tested samples for outgassing characteristics from various facilities across the US, including GSFC’s, are available through the NASA SEE program (ref. 2).

This slower method of QTGA takes ~21 hours to complete the warm-up to 110°C versus the standard QTGA method of 1°C/min, which takes less than 5 hours. This slower method was originally requested to simulate a potential on-orbit warm-up of a critical optical sensor, like a Charged Couple Device. CCDs may have a heater mounted on the retaining structural support and through passive means may be heated up in a slow manner. This investigation was also interested in addressing how warm does the QCM (or a pseudo CCD surface) have to get to remove molecular buildup from water/ice of various film thicknesses from its surface. Table 2 lists the samples considered for this investigation, which also includes the QTGA ramp rate.

Table 2
Samples considered for this investigation

Sample material	Exposed temperature (°C)	Effective sample size (cm ²) and pre-test mass (g)	Sample Outgassing duration (hrs)	QCM3 decay n-term	QCM3 buildup (Hz)	QCM3 buildup (Angstroms)	QTGA ramp rate (°C/min)
Carbon Phenolic Rocket Nozzle	80	22.84 cm ² 9.417 g	55.2	0.513	77905	15269	0.2
Carbon Phenolic Rocket Nozzle	50	21cm ² 8.218 g	78.7	0.535	39462	7735	0.2
Carbon Phenolic Rocket Nozzle	30	21.92 cm ² 8.657 g	52.2	0.49	20253	3970	0.2
JWST ISIM composite	50	105.75 cm ² 8.689 g	56	0.708	8743	1714	0.2
JWST ISIM composite w/Micro cracks	40	105.75 cm ² 8.645 g	146	0.605	9487	1859	0.2
JWST ISIM composite	-20	105.75 cm ² 8.689 g	265	0.5	2661	522	0.2
Swift Alum Honeycomb Carbon Composite	80	63.5 cm ² 4.283 g	72.8	0.971	3970	778	1.0
Swift Alum Honeycomb Carbon Composite	50	62.4 cm ² 4.684 g	77.4	0.768	2741	537	1.0
Swift Alum Honeycomb Carbon Composite	30	62.4 cm ² 4.933 g	96.6	0.71	2240	439	1.0
3M 1205 acrylic adhesive tape	80	42.41cm ² 0.562 g	50	1.02	2168	425	0.2
EC 2216 gray epoxy	80	5.82 cm ² 1.795 g	76.4	0.66	3695	724	0.2
EC 2216 gray epoxy	50	4.92 cm ² 1.714 g	73.3	0.678	2104	412	0.2
EC 2216 gray epoxy	30	5.22 cm ² 1.689 g	78.5	0.62	1232	241	0.2
Eccobond 285 w/ catalyst 9 (100:3.5) black epoxy	102	11.64 cm ² 6.603 g	76	0.616	1571	308	0.2
Eccobond 285 w/ catalyst 9 (100:3.5) black epoxy	80	11.64 cm ² 6.857 g	75.3	0.696	805	158	0.2
Z306 w/9924 primer on Al foil	80	31.3 cm ² 0.103 g	44	0.91	861	169	1.0
Z306 w/9924 primer on Al foil	50	71.1 cm ² 0.286 g	27.4	0.95	1465	287	1.0
Z306 w/9924 primer on Al foil	30	142.5 cm ² 0.537 g	71	1.06	1938	380	1.0

The samples had a variety of exposure temperature and lengths of exposures which characterized the outgassing effects. The effective surface area of the samples were premeasured as well as the pre-test mass without the substrate. The outgassing decay term ($1/t^n$) was determined by taking a power curvefit of the sample log OGR versus the log of exposure time (hrs). Some of the samples exhibited diffusion-limited outgassing characteristics, but one in particular, the JWST composite sample (w/Microcracks) at 40°C, was noticeably dropping off in outgassing after 100 hours of exposure. The molecular accretion onto QCM3 was also included and a simple film thickness conversion to Angstroms was included by assuming the average molecular density of 1.0 g/cm^3 . The QTGA ramp rate is also noted for each sample. Most similar samples had similar QTGA ramp rates.

RESULTS

A simple way of showing the results from all the samples is have them plotted onto a single graph that essentially plots the change in the QCM frequency (Hz) versus QCM temperature (°C). The change in QCM frequency is the subtraction of the sample tested QCM frequency at a temperature minus the baseline QCM frequency at the same temperature. This is also explained the ASTM E1559 procedure (ref.1). Figure 2 demonstrates the effectiveness of the QTGA evaporation for each sample considered. The QCM frequency was not normalized to demonstrate that there is still some non-water molecular mass on the crystal during QTGA up to -80°C and beyond. One can then take Figure 2 one step further and calculate the percentage (%) left on the crystal at each temperature of the QTGA process by normalizing the accumulated mass and multiplying by 100.

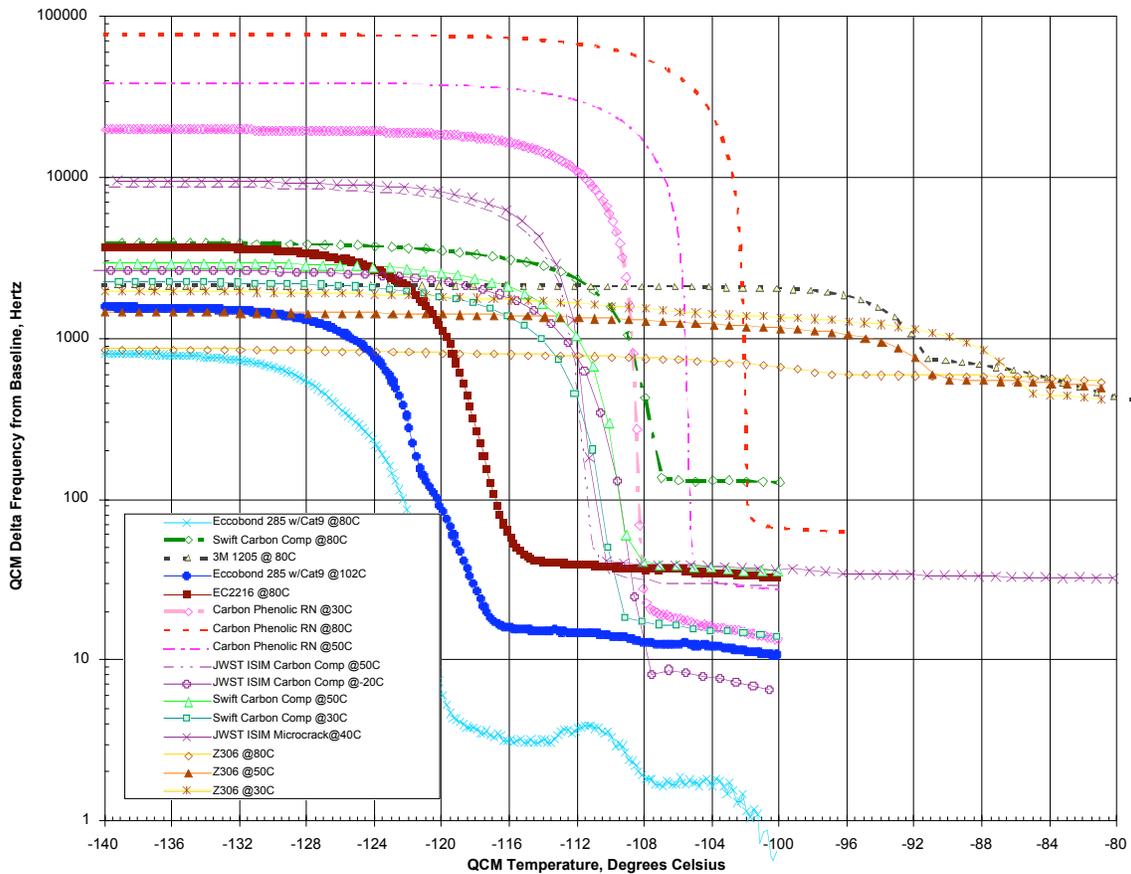


Figure 2
QCM Mass remaining in terms of Frequency during QTGA

Two quick inferences can be drawn from Figure 2 and from referencing the samples listed in Table 2.

1. The higher the molecular deposition levels on the QCMs tended to increase the QCM temperature required to remove the condensed water vapor. However, even thousands of Angstroms of ice/water mass can be removed by -100°C if the reemission rate is slow enough.
2. Samples with a higher percentage of non-water concentrations demonstrated that an even warmer QCM temperature ($>-100^{\circ}\text{C}$) is needed to remove the water from the surface. The reemission of the 3M 1205 acrylic tape residue on the QCM required a temperature of -91°C to be reached before the majority of water vapor was removed.

As mentioned the outgassing from these samples occurred over a period of days. Water and gases are known to outgas fairly quickly under vacuum. Therefore the bulk diffusion outgassing process took place after the initial surface desorption phase and thus formed mixed monolayers onto the QCM crystal over the top of water monolayers. The percentage of water that was deposited onto the QCMs was computed by a simple comparison of the respective sample's molecular deposition, in terms of Hertz, gained on QCM3, set to -183°C , versus the gain on QCM1, typically set to -113°C .

Table 3
Water percentage from samples

Sample material	Exposed temperature ($^{\circ}\text{C}$)	QCM buildup (Hz)	QCM buildup (Angstroms)	QCM decay n-term	Water evaporated by $^{\circ}\text{C}$	Estimated % of water from sample	QTGA ramp rate ($^{\circ}\text{C}/\text{min}$)
Carbon Phenolic Rocket Nozzle	80	77905	15269	0.513	-102	99.8	0.2
Carbon Phenolic Rocket Nozzle	50	39462	7735	0.535	-104	99.91	0.2
Carbon Phenolic Rocket Nozzle	30	20253	3970	0.49	-108	99.88	0.2
JWST ISIM composite	50	8743	1714	0.708	-111	99.4	0.2
JWST ISIM composite w/Micro cracks	40	9487	1859	0.605	-110	99.92	0.2
JWST ISIM composite	-20	2661	522	0.5	-107	99.7	0.2
Swift Alum Honeycomb Carbon Composite	80	3970	778	0.971	-106	96.7	1.0
Swift Alum Honeycomb Carbon Composite	50	2741	537	0.768	-108	98.6	1.0
Swift Alum Honeycomb Carbon Composite	30	2240	439	0.71	-109	99.2	1.0
3M 1205 acrylic adhesive tape	80	2168	425	1.02	-91	65	0.2
EC 2216 gray epoxy	80	3695	724	0.66	-115	98.8	0.2
EC 2216 gray epoxy	50	2104	412	0.678	-115	99.32	0.2
EC 2216 gray epoxy	30	1232	241	0.62	-117	99.45	0.2
Eccobond 285 w/ catalyst 9 (100:3.5) black epoxy	102	1571	308	0.616	-116	99.3	0.2
Eccobond 285 w/ catalyst 9 (100:3.5) black epoxy	80	805	158	0.696	-119	99.75	0.2
Z306 w/9924 primer on Al foil	80	861	169	0.91	-96	34	1.0
Z306 w/9924 primer on Al foil	50	1465	287	0.95	-90	63	1.0
Z306 w/9924 primer on Al foil	30	1938	380	1.06	-85	78	1.0

Table 3 indicates that the majority of molecular outgassing from the samples was predominately water vapor. Only the tape and the Z306 paint samples yielded sub 95% water concentrations. Muscari (ref. 3) and Glassford & Garrett (ref. 4) presented RGA and outgassing data that indicated similar findings for similar materials. There were ~20 samples of aerospace materials tested from each reference. If the source temperatures are not warm enough to drive out bulk contaminants, water was the primary source especially at low exposure temperatures. Z306 and acrylic tapes, have significant light weight molecules that outgas and condense at temperatures warmer than -113°C and create a mixture of outgassed monolayers over the initially outgassed water monolayers.

Table 3 doesn't appear to show a strong relation to QTGA ramp rate and water evaporation temperature (Column 6), but one would think if the ramp rate was too high, like 5°C/min there may be a noticeable lag in water vapor desorption. This work was done years ago by the QCM manufacturers whom computed the most logical ramp rate for a steady state QTGA. A slow ramp rate does allow the entrained water to "bubble" to the surface of the QCM and reemit. The outgassing decay term also shows some relation to the exposed sample temperature. The higher the source exposure temperature, the outgassing decay term is typically higher. This seems to hold true for composite samples (i.e. carbon phenolic rocket nozzle, the JWST ISIM composite samples, and the Swift Honeycomb samples), but not for epoxies and the Z306 paint.

An MSX-funded paper investigated a similar QTGA effect (ref. 5). Their miscible species included methanol and toluene mixed with water. The water/ice still evaporated by -100°C for both mixtures. The mixtures did show that the complete evaporation of water vapor lagged in desorbing from the QCM crystal than homogeneous layered depositions. Another interesting finding from that paper was the concept of a delayed evaporation due to pressure. The higher the pressure the higher the QCM temperature had to get to remove the water/ice buildup. However, a couple orders of magnitude increase in pressure only shifted the QCM temperature upwards a few degrees for water removal. An increase to 1E-1 Torr only required an increase of ~20°C, up to ~80°C, for complete water vapor removal from the QCM crystal.

Another way to review the evaporation or desorption of the water is to compare evaporation rates and evaporation curves. Figure 3 (next page) demonstrates a similar linear trend towards water evaporation from the crystal. This is characteristic of the kinetic constant of water evaporation. Several samples exhibit a minor bump in this linear trend, around -125°C (153K), where the phase change of ice to water (vapor) may be occurring. Water or then vapor is still continuing to be removed from the crystal until the majority of the gained water mass has been removed from the crystal. The sharp downward trends, on the right sides of the plots, are indicative that the majority of the water vapor has been depleted from the crystal, thereby leaving a smaller percentage of a variety of species. The softer bell-curve evaporative curves are more indicative of water evaporating from a mixed concentration, where the water evaporating has to move through monolayers of water/non-water mixtures. This water removal through a mixed monolayer takes a little longer based on the monolayer(s) buildup. The actual removal of the water (and vapor) from the critical volume is not addressed here but is typically a function of the vent paths from the volume, pressure between volumes, and surrounding surface temperatures.

SUMMARY

Water evaporation from a surface is dependent on the amount of molecular buildup, in terms of Angstroms or monolayers, and on whether the water must reemit through a miscible or mixed concentration. The results support the rationale that the thicker the miscible or mixed concentration, the slower the evaporative process of the water.

REFERENCES

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5. B. Barger, T.E. Phillips, and R.C. Benson, "Thermogravimetric Analysis of Selected Condensed Materials on a Quartz Crystal Microbalance," Proc. SPIE, Vol. 2261, 1984, pp. 188-199.

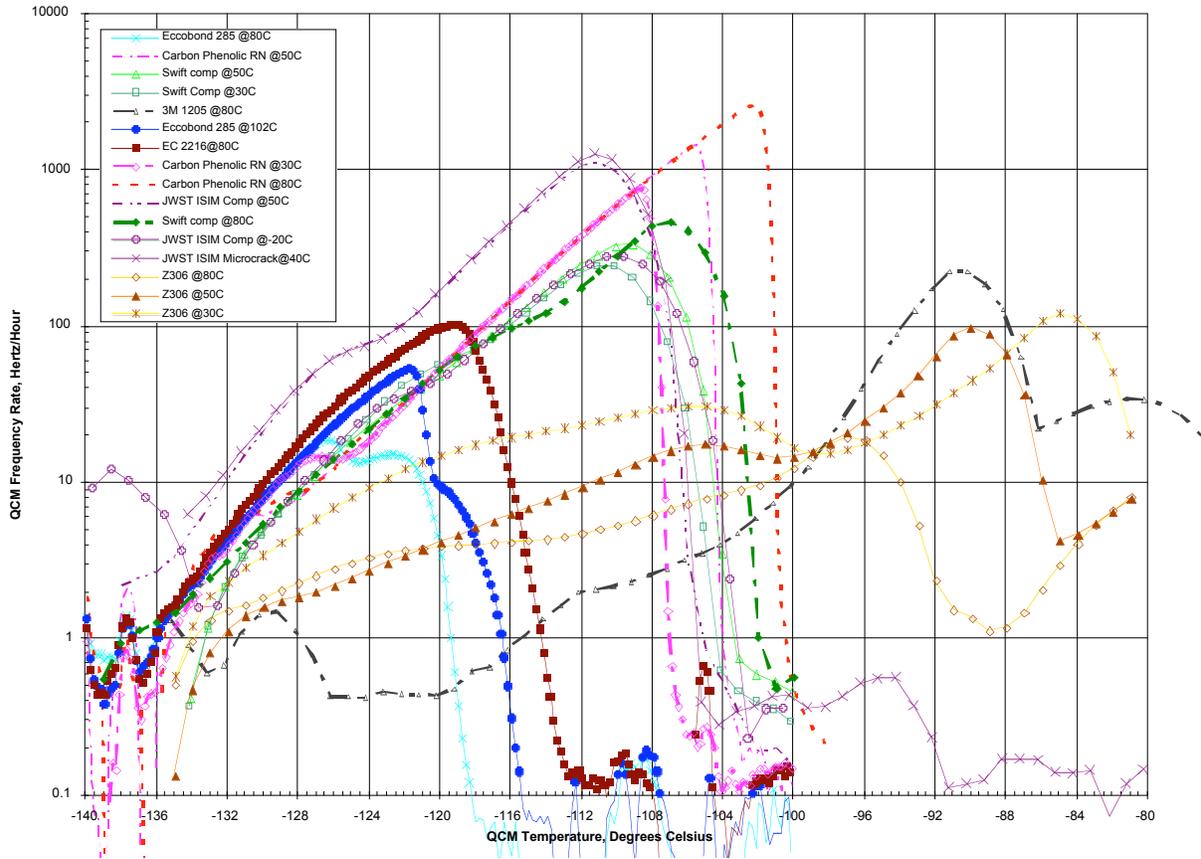


Figure 3
QCM Reemission Rates

QCM Thermo-gravimetric Analysis (QTGA) Comparisons

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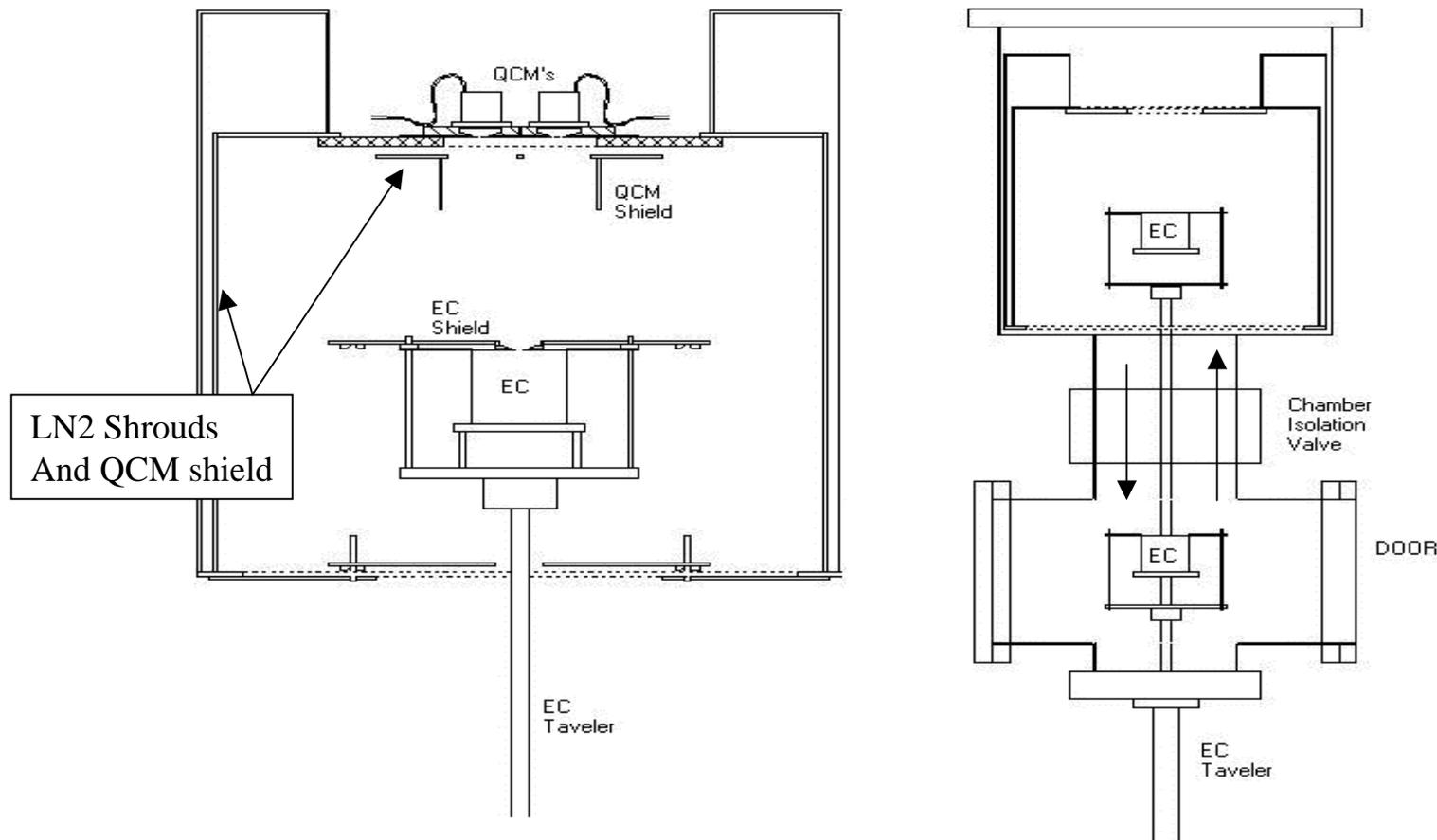
QTGA purposes

- A QCM can mimic a critical optical surface and through a controlled increase in temperature provide reemission characteristics of condensed molecular mass.
- QTGA data has been produced from various aerospace laboratories and from flight experiments for over 30 years providing various wealth of published documentation.
- Molecular outgassing is function of pressure and temperature. Critical molecular deposition is a function of receiver temperature with respect to source temperature. At pressures below $1\text{E-}6$ Torr and temperatures below 150K (-123C) water condenses. These condensed water/ice molecules are mixed with most other outgassed species to form miscible condensed monolayers.
- Pure species, like water, have distinctive desorption characteristics.
- How do the reemission traits of water change when a compilation of molecular species from various typical aerospace products are present?

Various GSFC tested samples

Sample material	Exposed temperature (°C)	Effective sample size (cm ²) and pre-test mass (g)	Sample Outgassing duration (hrs)	QCM3 decay n-term	QCM3 buildup (Hz)	QCM3 buildup (Angstroms)	QTGA ramp rate (°C/min)
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GSFC's ASTM E-1559 apparatus



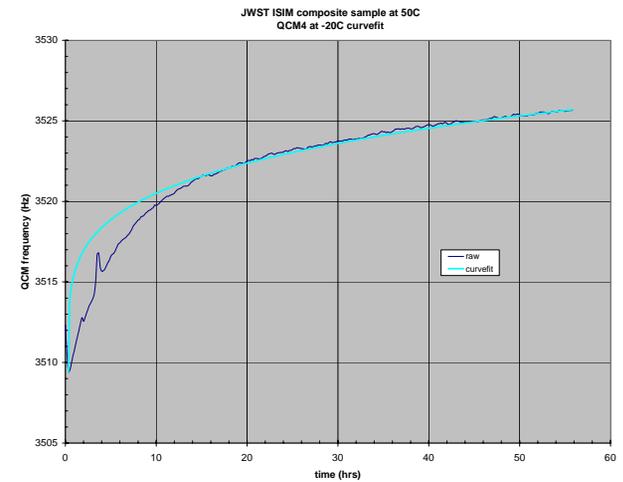
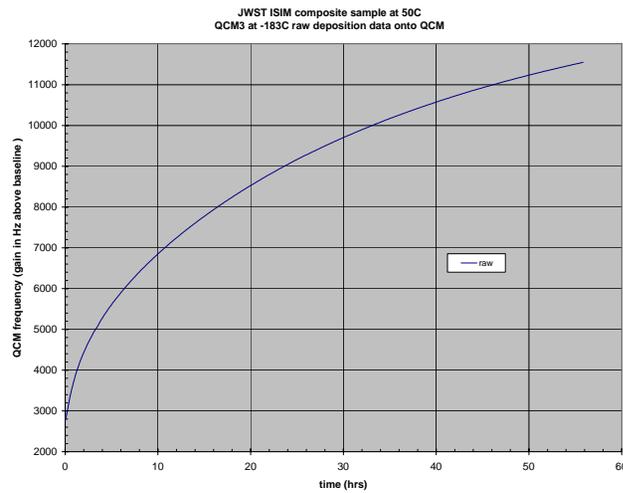
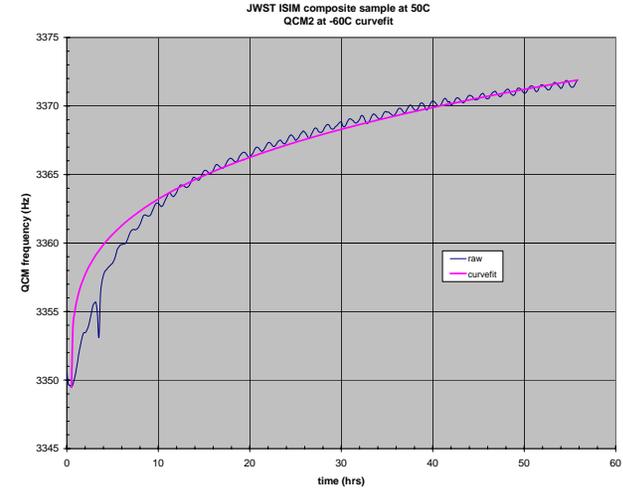
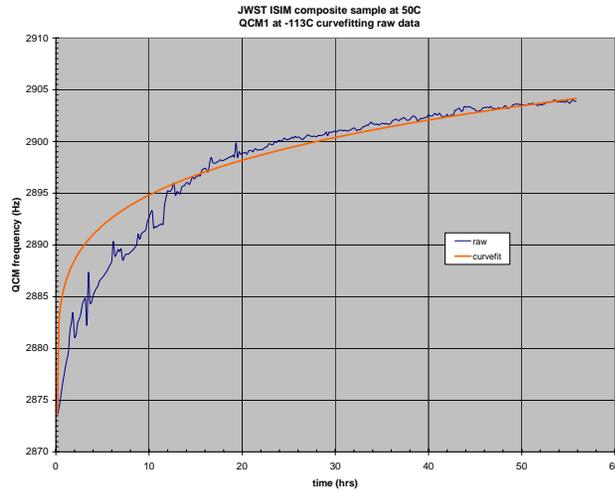
Typical Molekit 2 & 3 configuration

QCM settings

Molekit 2 QCM serial numbers	Molekit 2 QCM temperature setpoints	Molekit 3 QCM serial numbers	Molekit 3 QCM temperature setpoints
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QCM2: Mark17 S/N 2697	-60°C (213 K)	QCM6: Mark17 S/N 2397	-60°C (213 K)
QCM3: Mark17 S/N 2297	-183°C (90K)	QCM7: Mark17 S/N 2297	-183°C (90K)
QCM4: Mark16 S/N 0691	-20°C (253K)	QCM8: Mark17 S/N 1096	-20°C (253K)

- GSFC's ASTM E1559 setup uses 4 QCMs to gain a variety of partial condensations and reemission data.
- Note the same cold QCM has been used for both setups (at different times) for material testing

Typical QCM deposition phase



Raw and curvefit deposition phases

Deposition equations

$$QGR \left(\frac{g}{cm^2 s} \right) = \frac{[freq_{t2} (Hz) - freq_{t1} (Hz)]}{[time_{t2} (hrs) - time_{t1} (hrs)]} \times 1.96 \cdot 10^{-9} \left(\frac{g}{cm^2 Hz} \right) \times \frac{FF (cm^2)}{SA (cm^2)} \times \left(\frac{1hr}{3600s} \right)$$

where:

freq = QCM frequency at time 2 compared with frequency at time 1

time = time in hours of frequency data

QCM_{ms} = QCM mass sensitivity of a QCM Research 15 MHz QCM= 1.96E-9 g/cm²/Hz

FF = form factor of EC orifice to QCMs (Molekit2 FF = 635 cm²)

SA = source surface area (in EC, varies, units in cm²)

$$TMLorVCM(\%) = [freq_{t2} (Hz) - freq_{t0} (Hz)] \times 1.96 \cdot 10^{-9} \left(\frac{g}{cm^2 Hz} \right) \times \frac{FF (cm^2)}{SM (g)} \times (100)$$

where:

freq = QCM frequency at time 2 compared with initial frequency at time 0

QCM_{ms} = QCM mass sensitivity of a QCM Research 15 MHz QCM= 1.96E-9 g/cm²/Hz

FF = form factor of EC orifice to QCMs (Molekit2 FF = 635 cm²)

SM = source surface mass (preweighed in EC, varies, units in g)

Curvefitting QCM raw data can be expressed with use of the following expression[1]:

$$freq_{cf} = [freq_{t0} (Hz)] + \left[\left(\frac{a}{b} \right) \times (time_{t2} - time_{t0})^b \right]$$

where:

freq = QCM frequency at time 0; curvefit frequency dependent on *a* and *b*

time = incremental time steps (hours) from time 0

$$b = \frac{\text{LOG} \left[\frac{freq_{t2} (Hz) - freq_{t0} (Hz)}{freq_{t1} (Hz) - freq_{t0} (Hz)} \right]}{\text{LOG} \left[\frac{time_{t2} (hr) - time_{t0} (hr)}{time_{t1} (hr) - time_{t0} (hr)} \right]}$$

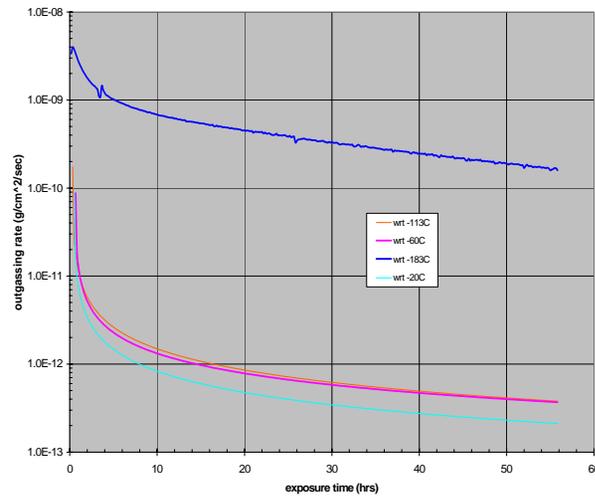
$$a = \frac{[freq_{t1} (Hz) - freq_{t0} (Hz)]^b}{(time_{t1} (hr) - time_{t0} (hr))^b}$$

Ref. [1] documented by M. Woronowicz in "Obtaining Model Outgassing Rate Parameters from Molekit Frequency Data," SAI-21030173/MSW-38, Swales Aerospace, 7 March 1999.

Typical Outgassing plots

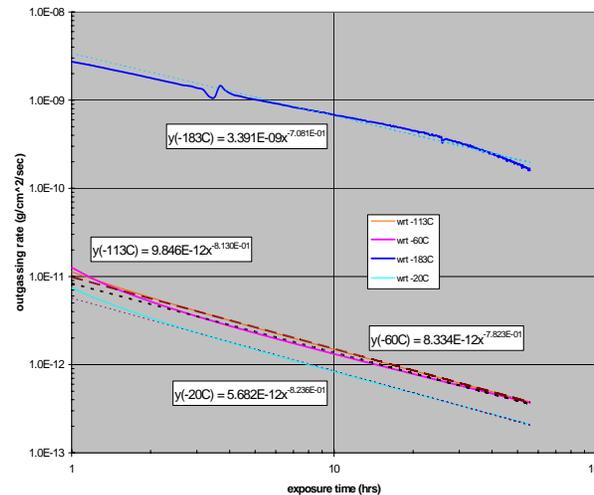
#1

Outgassing rate of JWST ISIM carbon composite at 50C



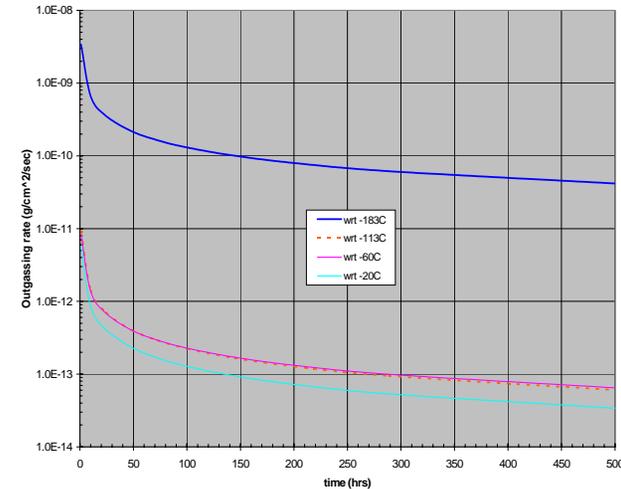
#2

Outgassing Rate decay of JWST ISIM carbon composite at 50C



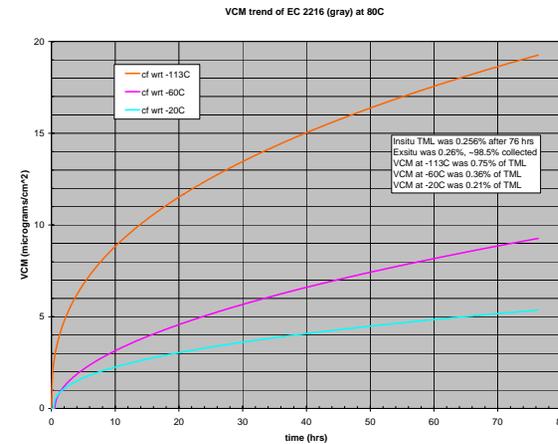
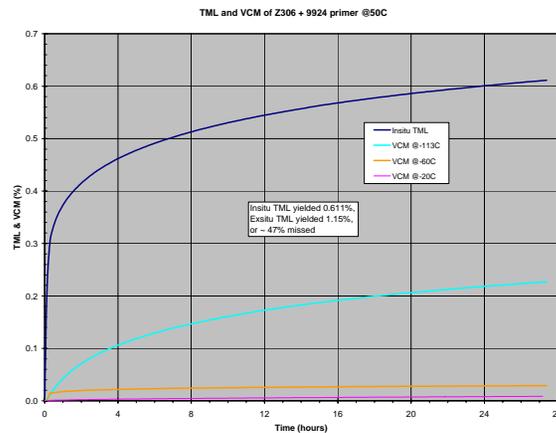
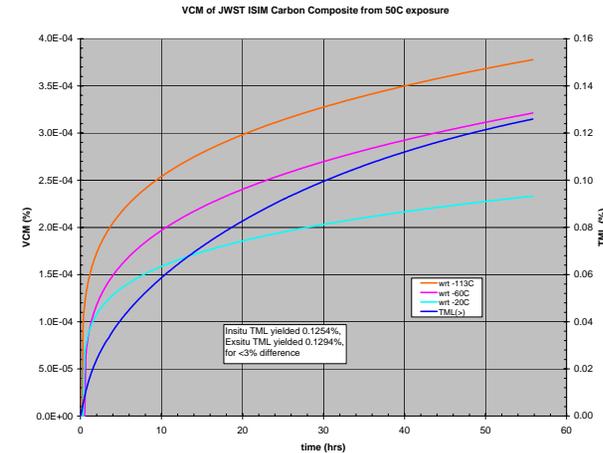
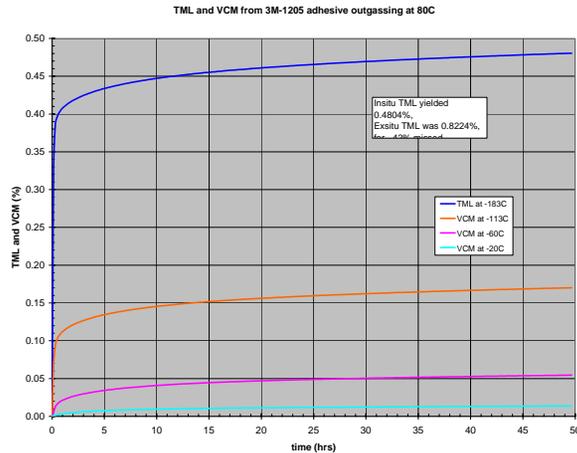
#3

Long term Outgassing of JWST ISIM Carbon Composite at 50C



- Plot 1) Using the equations listed in the ASTM E1559 one can convert the raw or curvefit QCM data into an Outgassing Rate ($\text{g}/\text{cm}^2/\text{sec}$) versus time
- Plot 2) One can then take the OGR plot and then plot it LOG (OGR) vs. LOG (time) to the determine the powerfit decay and gain the n-term ($1/t^n$).
- Plot 3) One can then take the decay term and conservatively estimate the long term OGR (i.e. diffusion limited processes are ignored)

Various Sample TML and VCM Plots



Evaporative processes (QTGA)

- The preprogramming of QTGA-like processes has been incorporated in many optical cavities and thermal systems
 - Tradeoff...Mechanical Design \$ vs. Increased Science Data.
 - Though the optical warmups typically suspend data collection, most systems rebound with optimal throughput. Subsequent diffusion processes continue to provide molecular mass over years to still condensed mass on various, thus necessitating additional warmups.
 - Condensed Water is of main concern for IR sensors
 - Hydrocarbons, silicones are of main concern for UV optics.
 - Lack of QTGA capability, Synergistic effects, and lack of product removal from the cavity (venting) may never correct molecular induced degradation (i.e. Chandra optics BO)
- The ASTM E-1559 process does provide a best case scenario for reviewing QTGA processes.
 - Preprogrammed Rates for all QCMs at 1.0C/min or 0.2C/min up to 110C
 - Reemitted mass condenses on cold walls/shields and doesn't return to any of the QCMs
 - Can load up realistic quantities of a molecular film within a relatively short period with possibly a cornucopia of materials

QTGA equations

$$\text{EvapRate} \left(\frac{\text{g}}{\text{cm}^2\text{s}} \right) = \left(\frac{[\text{freq}_{t_2}(\text{Hz}) - \text{freq}_{t_1}(\text{Hz})]}{[\text{bfreq}_{t_2}(\text{Hz}) - \text{bfreq}_{t_1}(\text{Hz})]} \right) \times 1.96 \cdot 10^{-9} \left(\frac{\text{g}}{\text{cm}^2\text{Hz}} \right) \left((t_2(\text{hrs}) - t_1(\text{hrs})) \times \left(\frac{1\text{hr}}{3600\text{s}} \right) \right)$$

where the evaporation rate is a function of the change in sample and baseline frequencies with respect to QCM temperature:

freq = QCM frequency from sample data at temp2 compared with frequency at temp1
 bfreq = QCM frequency from baseline data at temp2 compared with frequency at temp1
 t1, t2 = timesteps of QTGA process in hours
 QCM_{ms} = QCM mass sensitivity of a QCM Research 15 MHz QCM= 1.96E-9 g/cm²/Hz

* Evaporation rate can be expressed in terms of g/cm² as well (remove time from equation)

* Evaporation rate can be expressed in terms of g as well (remove time and multiply by area of QCM crystal area of ~0.32 cm²) and perhaps multiply by 1000 to get in terms of milligrams (mg).

*To gain the percent mass lost (%) from the QCM during the QTGA process use the following expression, which compares the delta frequency in sample and baseline at each temp/time step to the (maximum) delta frequency that should occur at time zero.

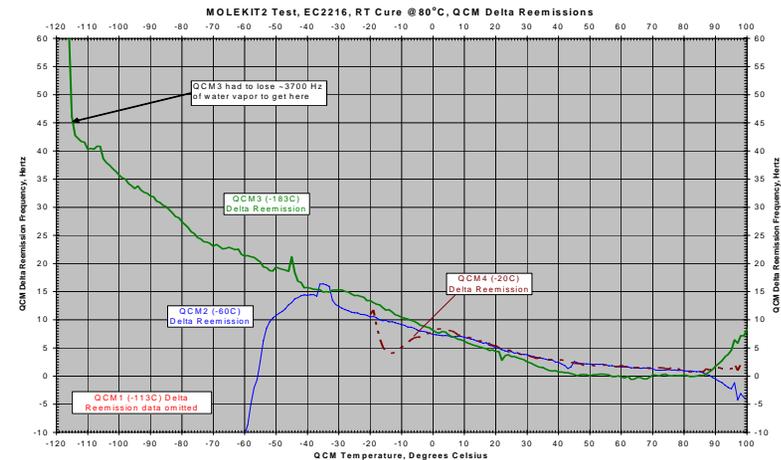
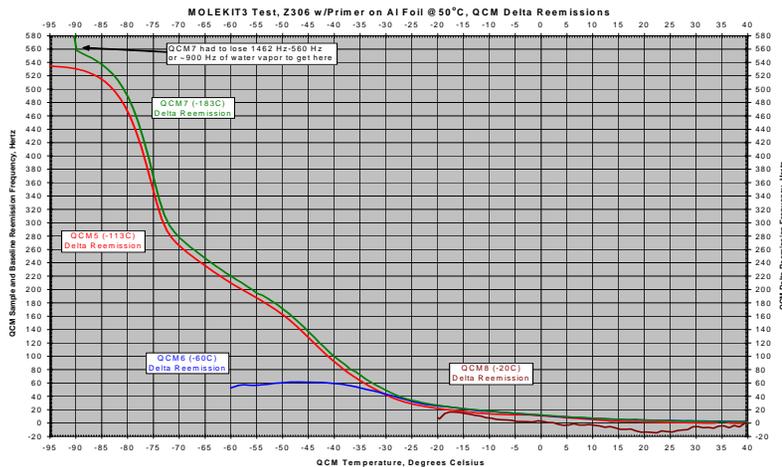
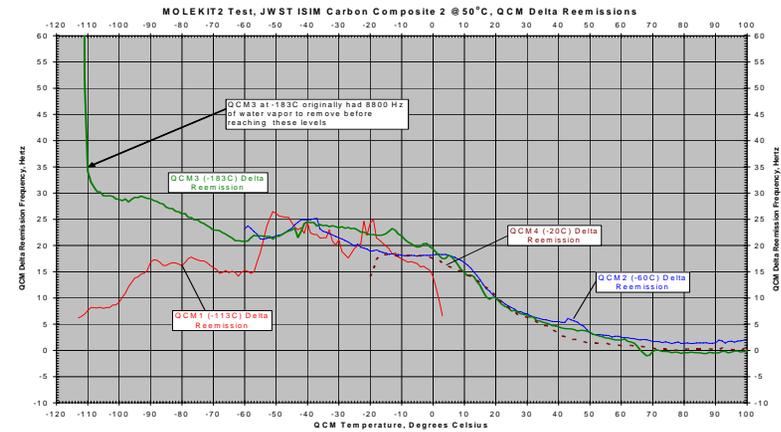
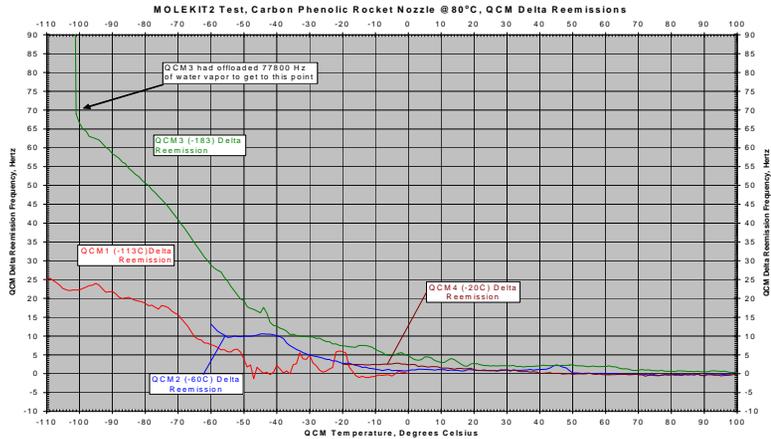
$$\text{Percent Remaining}(\%) = \left(\frac{[\text{freq}_{t_1}(\text{Hz}) - \text{bfreq}_{t_1}(\text{Hz})]}{[\text{freq}_{t_0}(\text{Hz}) - \text{bfreq}_{t_0}(\text{Hz})]} \right) \times (100)$$

* To just look at the change in frequency (Hz) during the QTGA just consider the difference between sample and baseline frequencies at each temp/time step, freq_{t1}-bfreq_{t1}.

* To gain the evaporation rate of the mass in terms of Hz/hr, just consider the incremental change in sample to baseline frequencies per temperature/timestep (t₂ to t₁) considered.

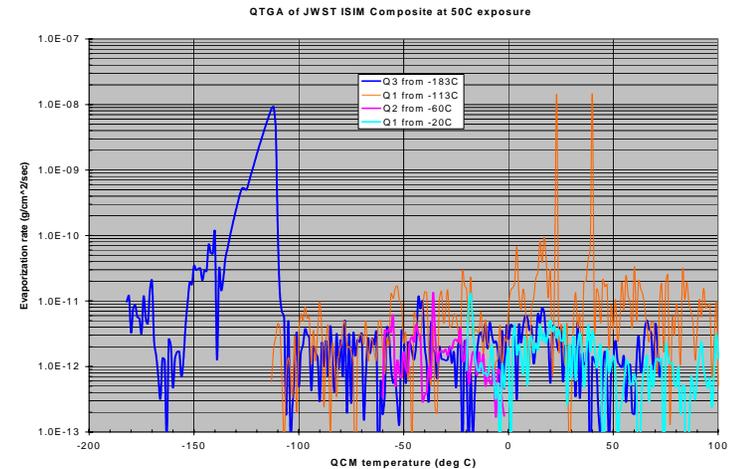
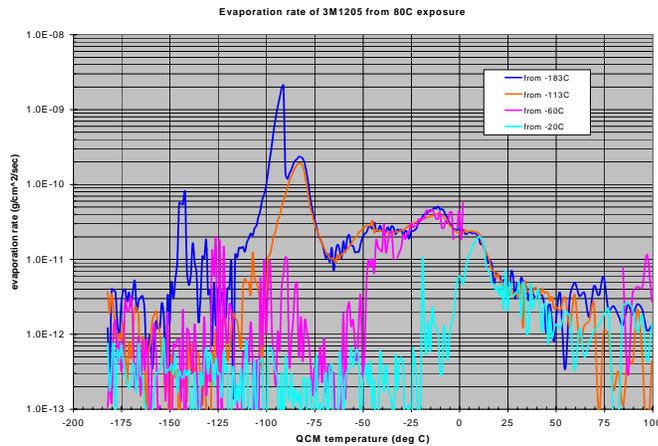
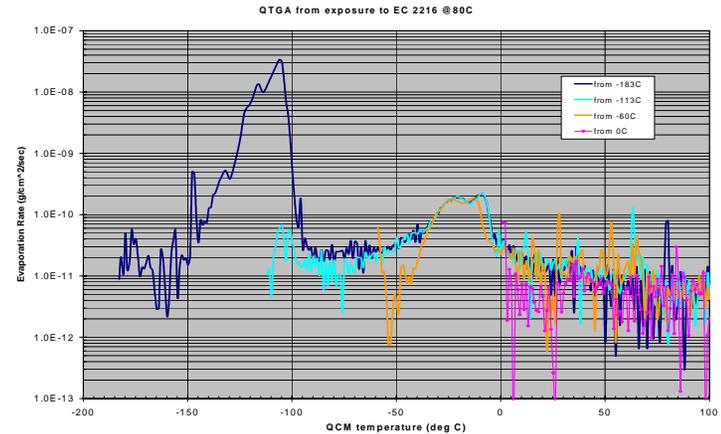
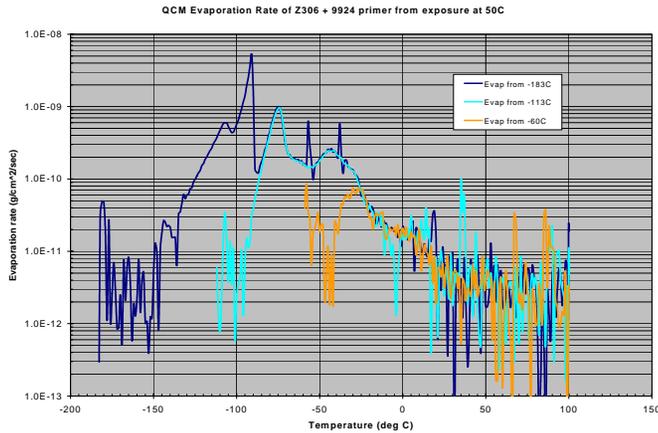
$$\text{EvapRate} \left(\frac{\text{Hz}}{\text{hr}} \right) = \left(\frac{[\text{freq}_{t_2}(\text{Hz}) - \text{freq}_{t_1}(\text{Hz})]}{[\text{bfreq}_{t_2}(\text{Hz}) - \text{bfreq}_{t_1}(\text{Hz})]} \right) / ((t_2(\text{hrs}) - t_1(\text{hrs})))$$

QTGA via Molekit

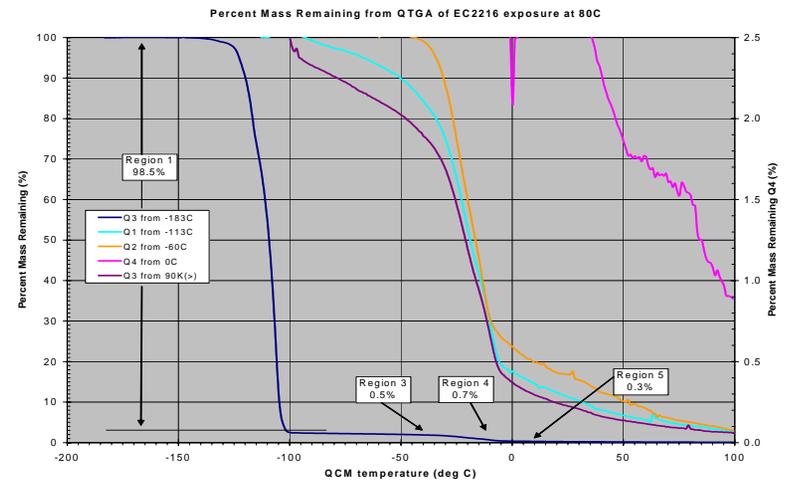
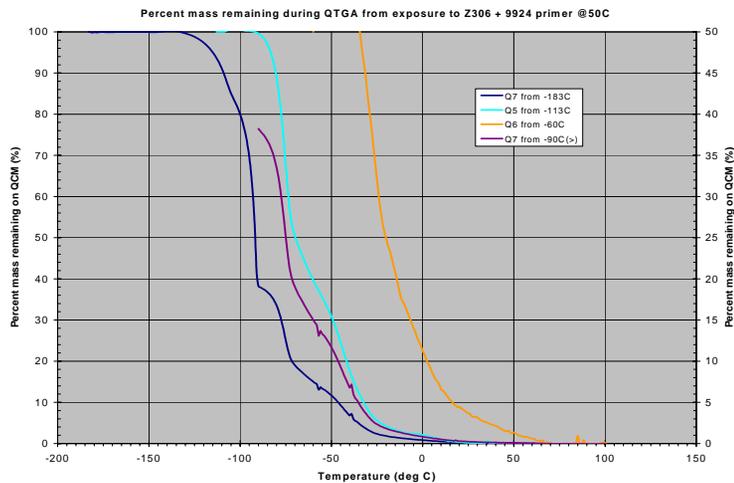
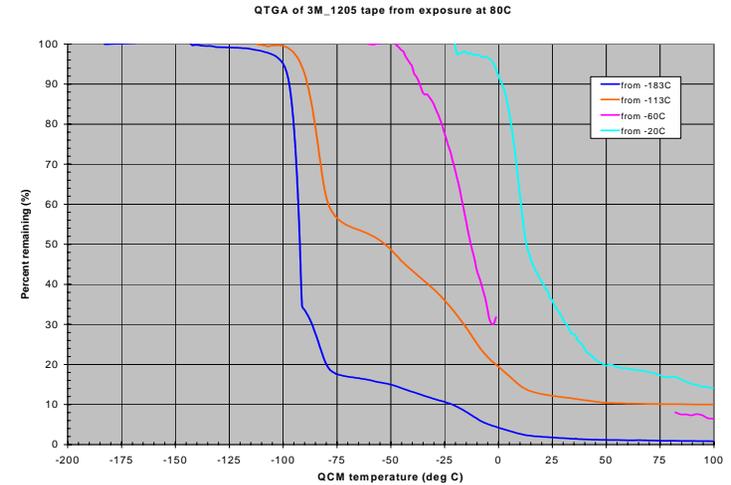
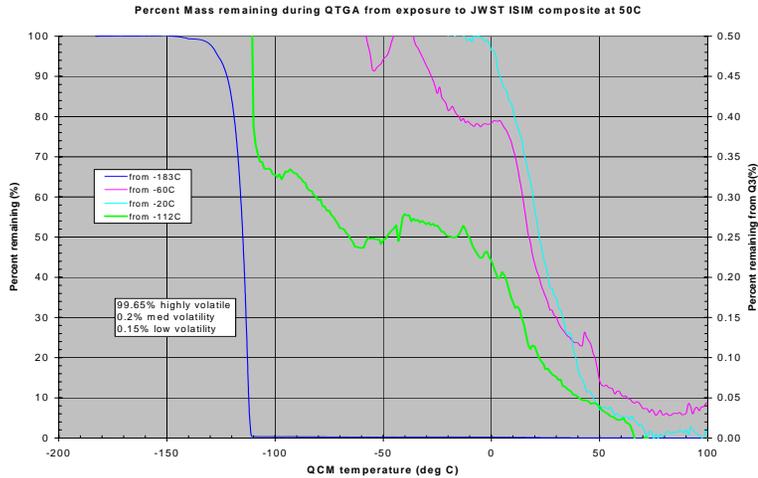


Non-water vapor QTGA, typically trend together on reemissions

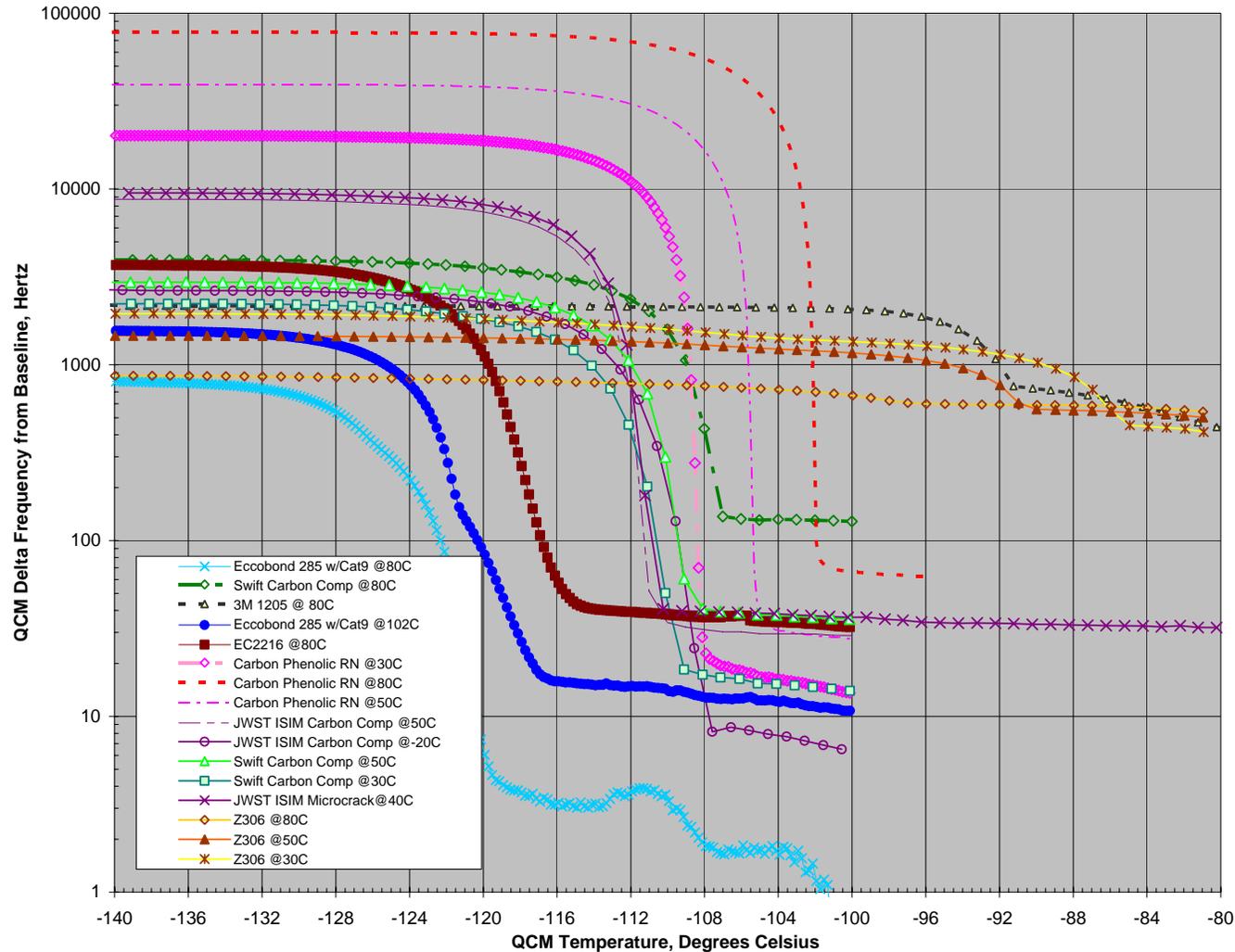
QTGA (evaporation rates vs. temp)



QTGA Plot (Percent Remaining)



QTGA of Samples Considered



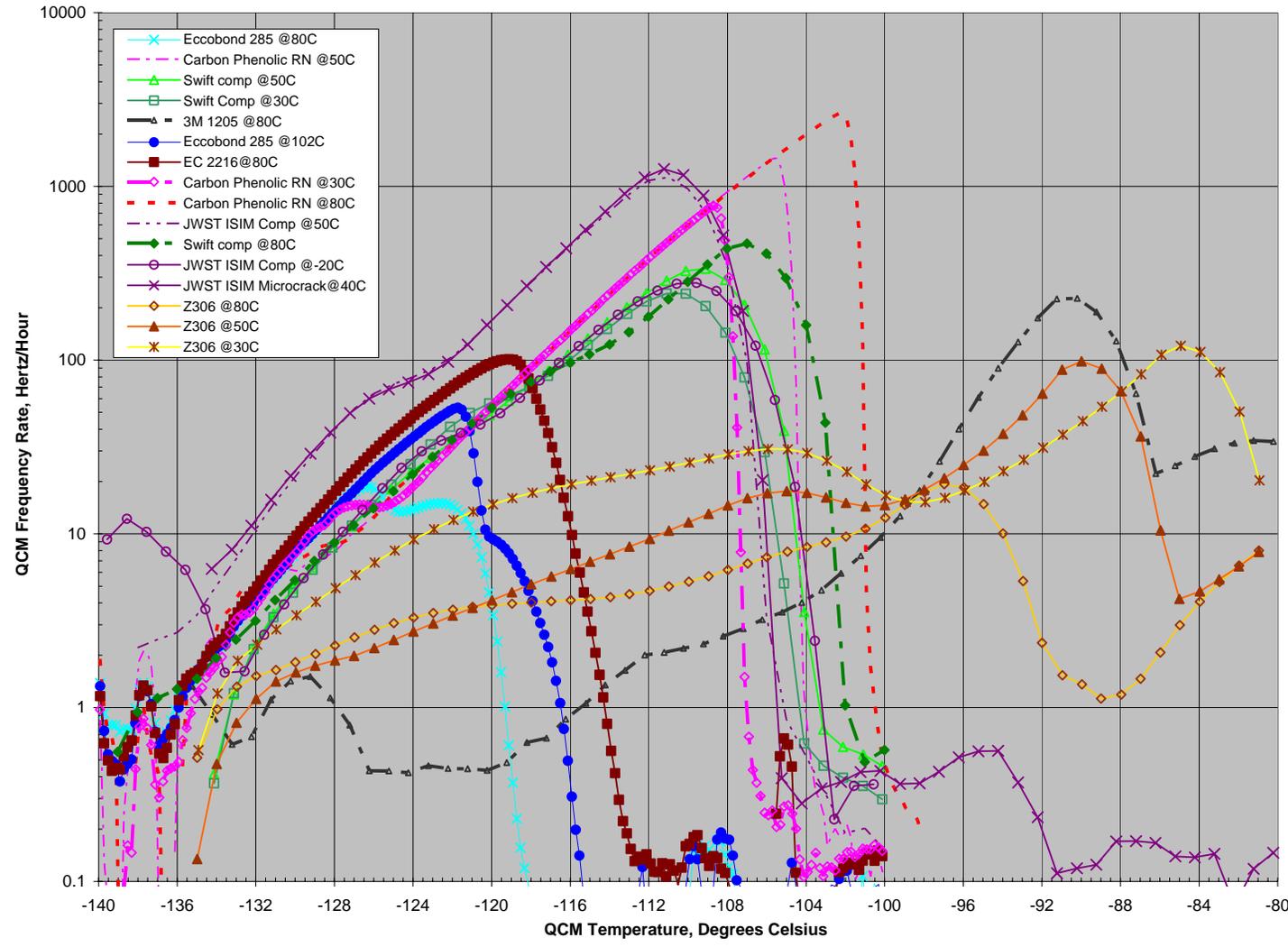
Water Evaporation temperatures

Sample material	Sample Temp	DFreq (Hz)	n-term	Angstroms	microns	micrograms	Evap Temp	% water	(degC/min)
Eccobond 285 w/cat 9	80C	805	0.696	158	0.016	0.500	-119	99.75	0.2
EC2216 gray epoxy	30C	1232	0.62	241	0.024	0.765	-118	99.45	0.2
Eccobond 285 w/cat 9	102C	1571	0.616	308	0.031	0.975	-116.5	99.3	0.2
EC2216 gray epoxy	80C	3695	0.659	724	0.072	2.294	-115	98.8	0.2
EC2216 gray epoxy	50C	2104	0.678	412	0.041	1.306	-115	99.32	0.2
JWST ISIM carbon composite	50C	8743	0.708	1714	0.171	5.427	-111	99.4	0.2
JWST ISIM carbon comp w/MCs	40C	9487	0.605	1859	0.186	5.889	-110	99.92	0.2
Swift Al HC carbon comp	30C	2240	0.71	439	0.044	1.390	-109	99.2	1
Carbon Ph Rocket Nozzle	30C	20253	0.49	3970	0.397	12.572	-108	99.88	0.2
Swift Al HC carbon comp	50C	2741	0.768	537	0.054	1.701	-108	98.6	1
JWST ISIM carbon composite	-20C	2661	0.5	522	0.052	1.652	-107	99.7	0.2
Swift Al HC carbon comp	80C	3970	0.971	778	0.078	2.464	-106.7	96.7	1
Carbon Ph Rocket Nozzle	50C	39462	0.535	7735	0.773	24.495	-104	99.91	0.2
Carbon Ph Rocket Nozzle	80C	77905	0.513	15269	1.527	48.358	-102	99.8	0.2
Carbon Ph Rocket Nozzle	50C	98082	0.71	19224	1.922	60.883	-101	99.91	0.2
Z306 w/9924 on Al foil	80C	861	0.907	169	0.017	0.534	-96	34	1
3M 1205 (Acry. Adh.)	80C	2168	1.02	425	0.042	1.346	-91	65	0.2
Z306 w/9924 on Al foil	50C	1465	0.95	287	0.029	0.909	-90	63	1
Z306 w/9924 on Al foil	30C	1938	1.06	380	0.038	1.203	-85	77.8	1

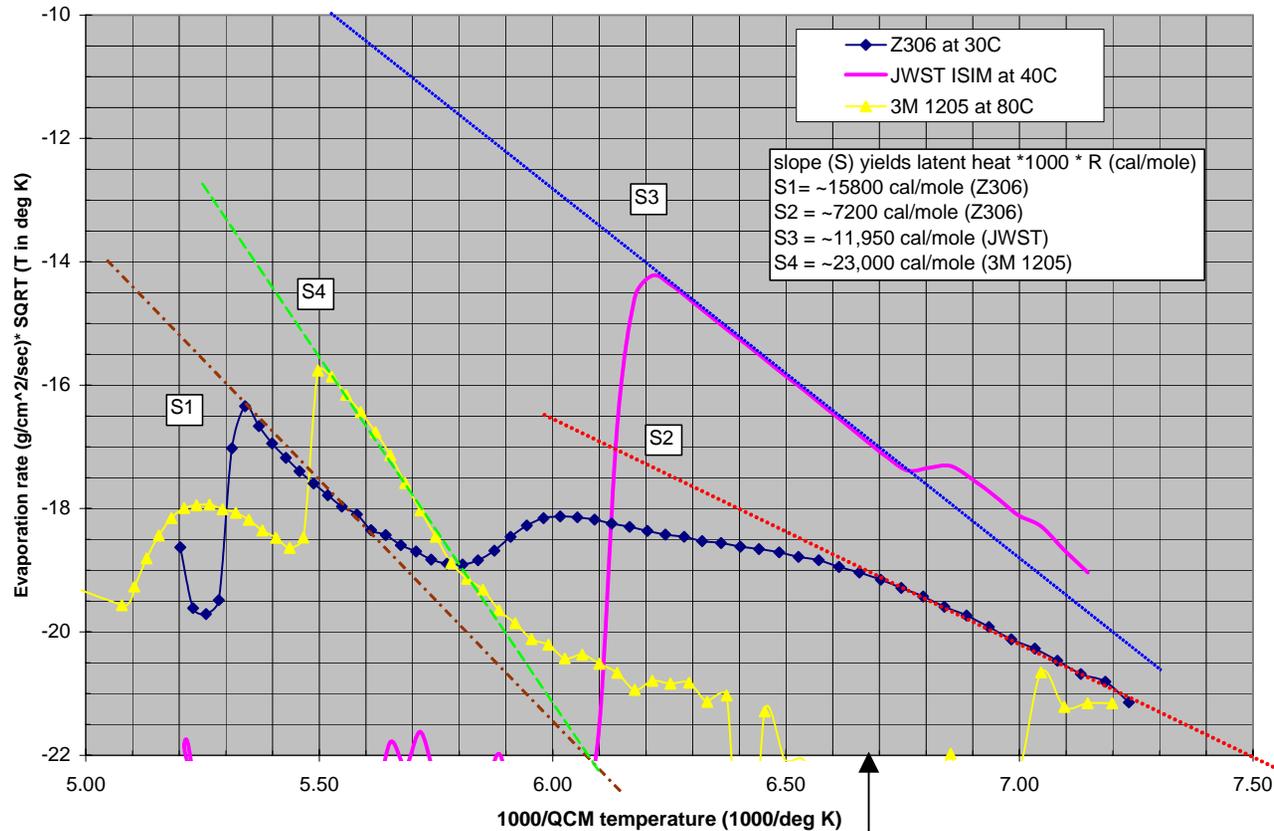
Earlier table sorted by ascending (complete) evaporation temperature.

- faster reemission rate drags evap temp
- Thicker water accretion drags evap temp
- higher n-term indicates less water, higher misc. VCM %

QCM Reemissions Rates (samples)



Arrhenius plots from samples



- Water evaporation rates are difficult to distinguish when multiple molecular species are mixed in the water monolayers.

Summary

- QTGA is a function of chemical composition deposited on a surface and the surface at which the source begins its evaporation
- Water evaporation is inhibited by the thickness of the molecular buildup, however the water evaporation can be a complete process at a fairly cold temperature (by -90C as long as venting is sufficient).
- Water molecules will work its way through more volatile layers of deposited mass but its complete reemission will be inhibited.
- Other non-volatile molecular residue only becomes “volatile” as the appropriate temperature is attained to activate the molecule(s) and may effect the evaporative processes of pure substances.
- An experimental QTGA process can be used to assist in programmatic decisions on warm-up capabilities and operational requirements.

Paper References

- ASTM E1559-00, Standard Test Method for Contamination Outgassing Characteristics of Spacecraft Materials, published by ASTM, maintained by ASTM subcommittee E21.05, January 2001.
- NASA Space Environments & Effects (SEE) Program, website <http://see.msfc.nasa.gov/>
- “Non-metallic Materials Contamination Studies Final Technical report,” MCR-80-637, the late Joe Muscari, Martin Marietta Corp., 16 Dec 1980.
- “Characterization of Contamination Generation Characteristics of Satellite Materials,” WRDC-TR-4114, Peter Glassford and Jeff Garrett, Lockheed Missiles & Space Company, Inc., 22 November 1989.
- “Thermogravimetric Analysis of Selected Condensed Materials on A Quartz Crystal Microbalance,” B. Bargeron, T.E. Phillips, and R.C. Benson, Proc. SPIE, Vol. 2261, 1984, pp. 184-189.

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