High Temperature Condensed Phase Mass Spectrometric Analysis

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Ongoing studies of ion emission from moderate temperature (~800°C) inorganic materials have resulted in several concepts

- Charge centers can shut down ion migration in the solid
- Acid/base conditions can shift the chemical species between ionic and non-ionic forms
- Combine these two concepts to synthesize waste forms that are self limiting in regard to high temperature ion migration

These concepts require new methods and instruments for realistic study

- Instrumentation and methods developed for the study of ion emitters demonstrates the types of research required to gain better understandings of these concepts
- Require identification of all species subliming and in the condensed state

This research requires unique new instrumentation

- Ions emitted from the surface need to be measured
- Neutral species subliming from the surface need to be measured
- Condensed phase species need to be identified

Concepts for the new instrument

- Neutrals subliming from the surface will be ionized by electron impact
- Positive and negative surface ion emission will be measured
- Dynamic and static SIMS analysis for positive and negative ions to gain understandings of the condensed phase

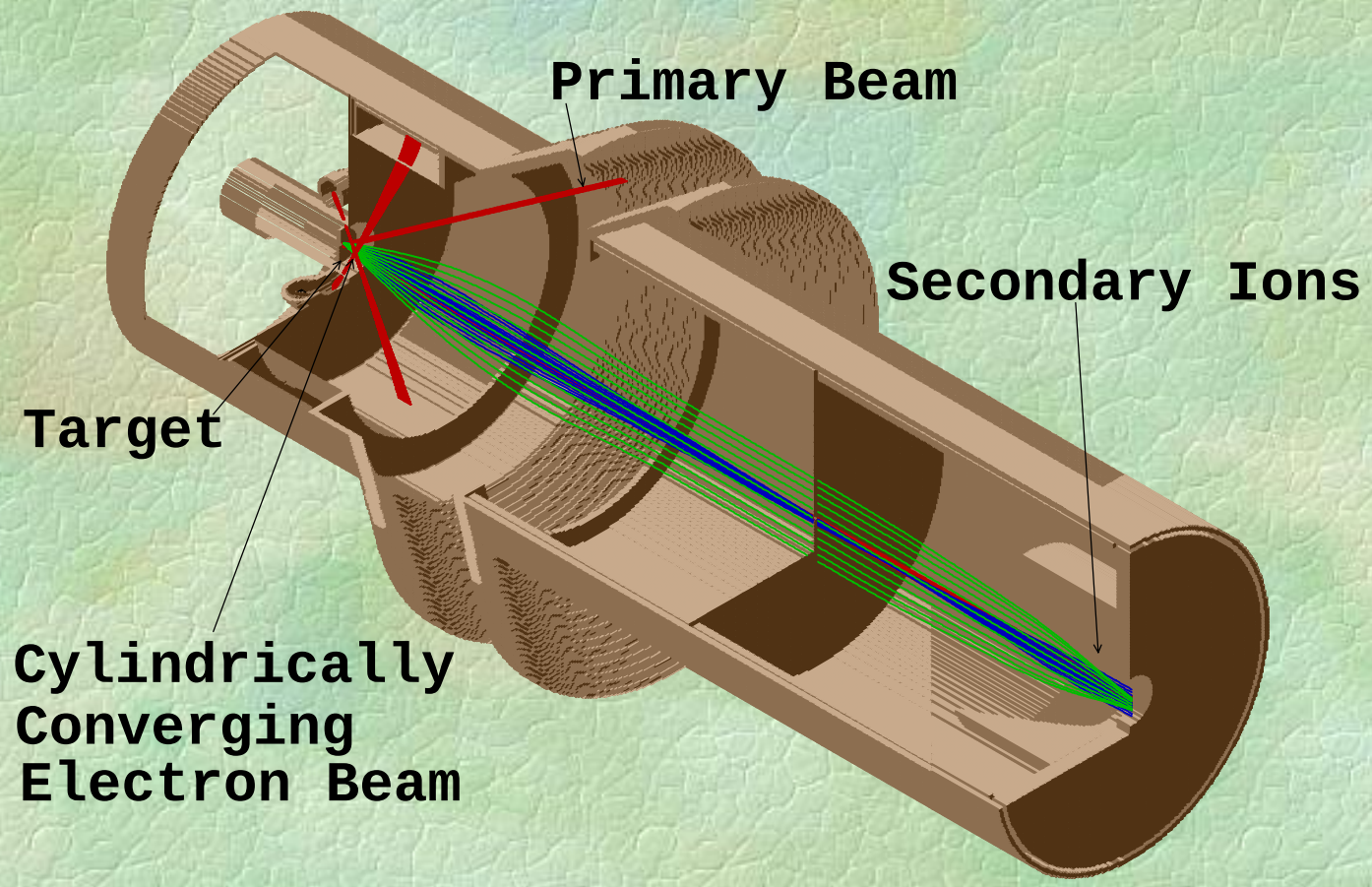
Miniaturized high temperature furnace acts as source

- Sample is pressed into rhenium tube 1/16” OD, 1/32” ID with rear plug
- Rhenium tube is supported from rhenium ribbons that double as heaters
- Face of tube contains sample and sits at focal point of lens
- Langmuir sublimation occurs as opposed to Knudsen effusion

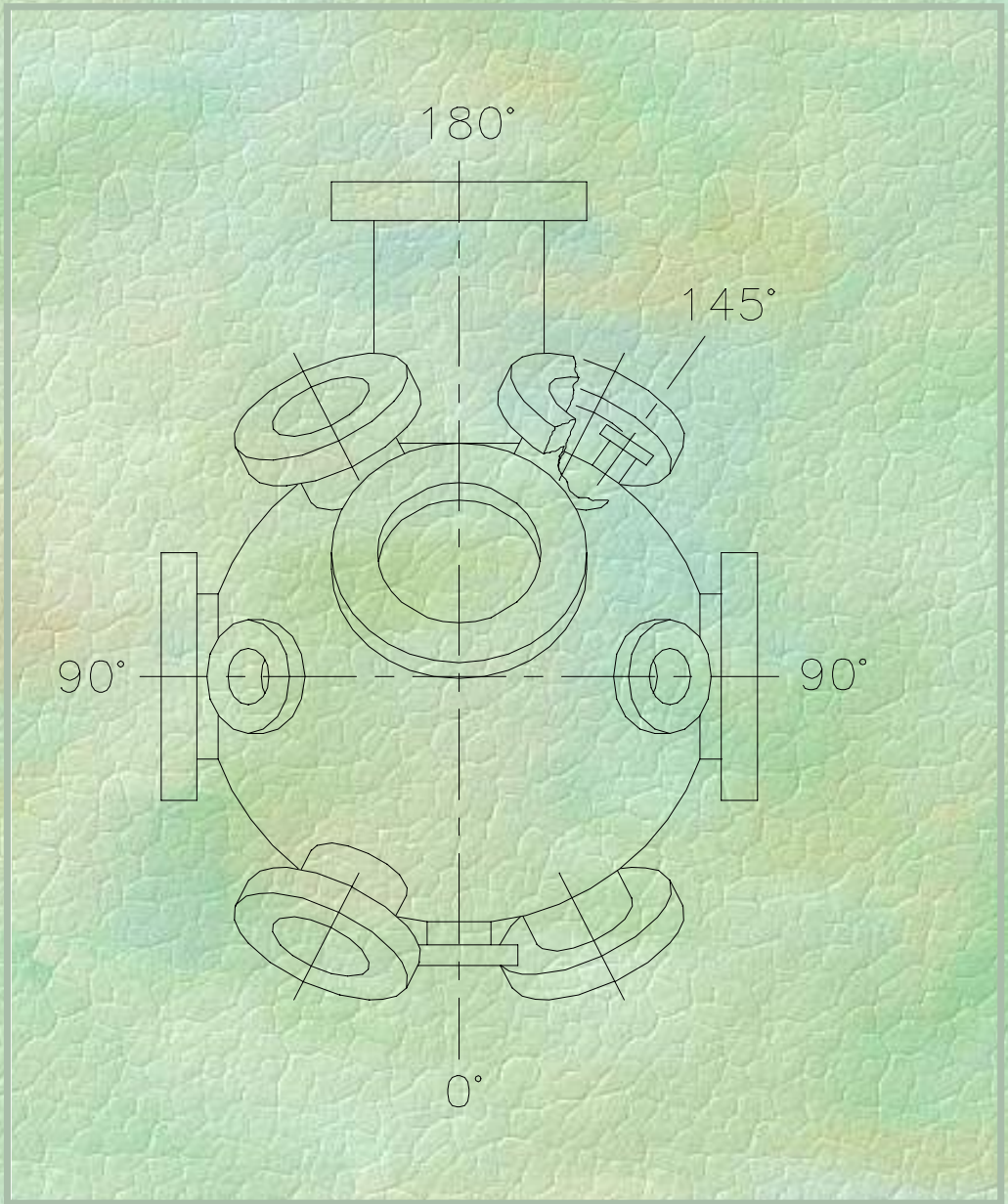
An instrument has been designed and is under construction that combines these features

- Surface and SIMS ions are collected simultaneously, and differentiated by deflecting the primary ion beam
- Positive and negative surface and SIMS ions are collected in an interlaced fashion
- Neutrals are ionized by EI in an alternate mode with the sample biased against surface ions

SIMION plot of the ion source



AutoCAD drawing of main chamber



Combination instrument is based upon 3 existing instruments

- Ion/neutral mass spec measures surface ions and neutrals via EI, using furnace source
- Hot SIMS measures SIMS spectra at elevated temperatures with furnace source and with charge leakage ring for analysis of heavily insulating samples
- TQ SIMS provides layout for new instrument with multiple ion gun ports

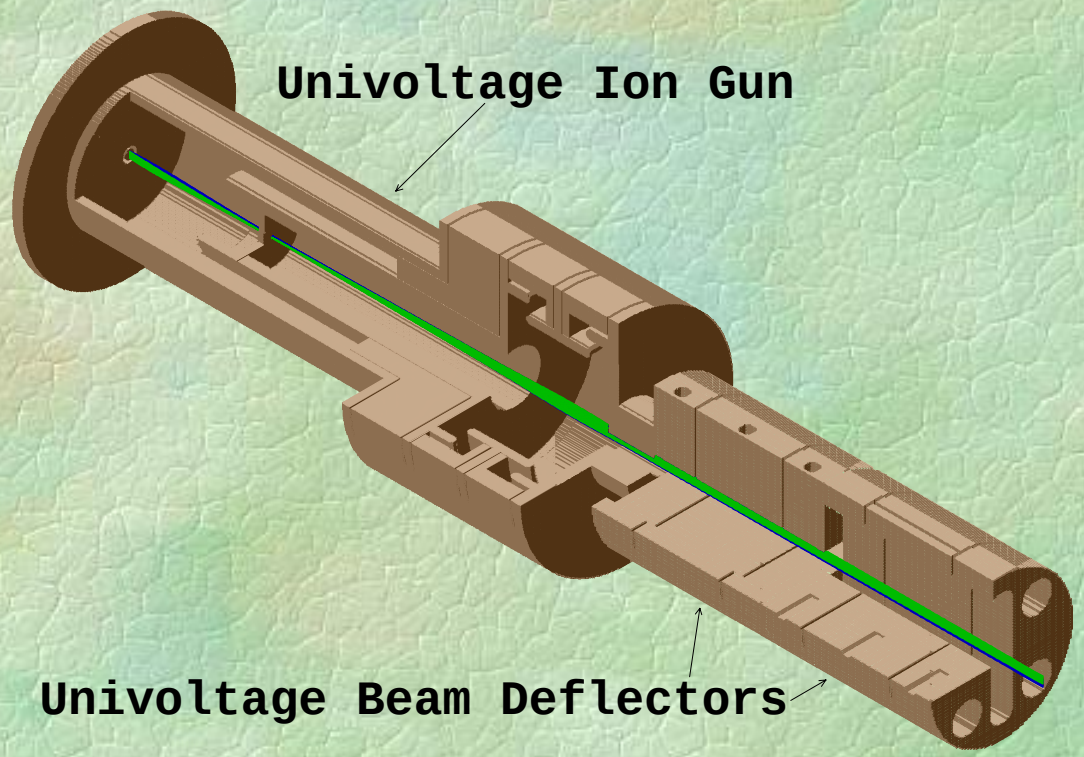
Vacuum System

- Ultra high vacuum system built around the central 12” sphere, all ports aligned to the center of the sphere
- Quadrupole mass spectrometer on top port
- Four ion gun ports at 35º to quad, 3 have analysis ports
- 500l/s triode ion pump
- Cryo shroud in line with hot samples
- Sublimator
- Turbo pump for pre and differential pumping
- Vacuum lock to insert miniature furnace source
- Entire system bakeable

Large Molecular Ions provide superior results when used as surface probes

- We have developed a primary ion gun that uses the ReO_4^- (250 daltons) anion for bombarding samples
- This ion gun produces an abundance of large molecular fragment ions upon impacting a surface
- The anion beam greatly simplifies maintaining charge neutrality on insulating surfaces
- This ion gun will be used for all static SIMS analyses
- An inert gas ion gun will be used to clean the sample surface and for dynamic SIMS

Ion optic design of perrhenate solid state ion gun



This instrument will permit self limiting ion migration concepts to be explored

- Adjust acid/base conditions to shift species into ionic forms (TcO_4^- <=> Tc_2O_7)
- When the temperature gets high enough to cause ion migration, charge centers remain
- Study the matrix effects that neutralize or keep intact these charge centers
- If charge centers are sufficiently numerous, further ion migration is shut down

Primary goal for this 3 year program is to complete instrument, test and demonstrate the various operating modes

- Face of furnace source at focal point
- SIMS is most difficult, hence will be implemented first
- Surface ions obtained with SIMS mode
- EI will be implemented last, but not least

Secondary goal is to demonstrate acid/base effects in shifting chemical species

- Demonstrate shifting of chemical species between ionic/non ionic forms by synthesis followed by observation of ions/neutrals
- Accomplished by measuring shifts in ion/neutral ratios of species entering gas phase from furnace source
- Rhenium (Re) as +7 will be test element

Third goal is to demonstrate charge centers shutting off further ion migration

- Current evidence indicates that chemical reactions inside the solid matrix can neutralize charge centers
- Develop strategies to prevent neutralization of charge centers by studying known neutralization reactions
- This will occur at the end of the program, possibly requiring a follow-on program

A known mechanism for neutralizing charge centers

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- $Ba(ReO_4)_2 + Eu_2O_3 + 2e^- \Rightarrow$
- $2ReO_4^-$(gas phase) + 2EuO + BaO
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- This reaction, desirable in an ion emitter, needs to be avoided in a waste form if migration of the waste element is to be self limiting

Final goal of program is to develop technology for predicting which waste forms will be self limiting in regard to migration and sublimation

- This will have to occur in a subsequent program
- To develop linkages to other program areas where these concepts might be of interest
- Technetium is a good candidate since it requires multi-million year storage, and the +7 state is readily shifted between ionic and non-ionic forms
- Re and Tc have very similar chemistries, hence we have a convenient surrogate

Potential Applications

- Licensing waste forms for long term storage is problematic
- Over a million years much can happen, including geologic heating to high temperatures
- Waste forms which are self limiting for migration may be much easier to license