Condensation Sequence : observations, pros and cons

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The plan of my two lectures

- Why everything we do is (generally)incorrect:
  - Equilibrium Calculations : formation of minerals
  - Kinetic Calculations: nucleation, growth & annealing
- Applications of Condensation Models
  - Circumstellar Outflows & Models of Protostellar Nebulae
  - Meteoritic Evidence & Comet Observations
- Experimental Observations & Limitations
  - SiO Vapor Pressure
  - Formation of large Pre-solar SiC and Graphite Grains
  - Rates of Thermal Annealing
  - Metastable Eutectic Condensates
- A short digression on carbon in the Solar Nebula

What is Equilibrium?

- Equilibrium comes in many forms: some forms are harder to achieve than others.
  - Minimal Physical energy of the system.
  - Minimal Chemical energy of the system.
  - Minimal Thermal energy of the system.
- Equilibrium can be “absolute” or “dynamic”
- Is the granite block sitting on the table at equilibrium?

No, the block is not at equilibrium:

- It is colder than it’s surroundings and is absorbing thermal energy from the room at an ever decreasing rate.
- The minerals in the block are very slowly becoming hydrated and are dissolving in the tiny film of adsorbed water.
- Application of some quantity of activation energy will release it’s gravitational potential.

Equilibrium is hard to achieve.

- The rate at which equilibrium is approached is usually driven by a gradient:
  - Thermal gradients drive heat flow,
  - Chemical gradients drive diffusion.
- The system can become trapped in localized “metastable” states if the gradient is not strong enough to provide the “kick” to overcome a barrier of some kind.

Our world is not in equilibrium.

- Graphite and Diamond: are both stable solids?
  - Less than 700 calories per mole separates bulk graphite and bulk diamond.
  - Graphite transforms to diamond at high temperature and pressure.
  - Diamond does not transform to graphite at lower temperature and pressure.
- Which one is at equilibrium?

The concept of surface free energy.

- With most minerals the surface/volume ratio is ~zero.
  - E.g. (#atoms on the surface)/(#atoms in the interior)
- Solids forming from the vapor are initially all surface.
- Free Energy of Formation
  - For a mineral this refers to the internal bond energy.
  - For a condensate, bonds at the surface will dominate.
  - Surface energy results from unfulfilled bonds at surfaces.
  - Surface free energy can be measured (but not very well).
- Surface energy does not matter for thermodynamic calculations, but does matter for kinetic models.

Why do nano-diamonds form?

- Diamond is significantly denser than graphite so a mole (6.02 x 10^{23} atoms) of diamond has less surface area than a mole of graphite for size "x" grains.
- Alternatively, fewer particles of diamond are needed to yield a mole of carbon atoms than would be needed for equal sized particles of graphite.
- Graphite has a larger surface area per mole.
- Surface area represents increased formation energy.
- As the average particle size decreases diamond becomes more stable compared to graphite.

An observational counter-argument

"That cannot possibly be correct. If it were true and I struck a match then I should see tiny particles of diamond formed rather than the graphitic soot that I always observe." (Ed Anders @ Washington Univ.)

- Which one (diamond or graphite) is at equilibrium?

An observational counter-argument

"That cannot possibly be correct. If it were true and I struck a match then I should see tiny particles of diamond formed rather than the graphitic soot that I always observe." (Ed Anders @ Washington Univ.)

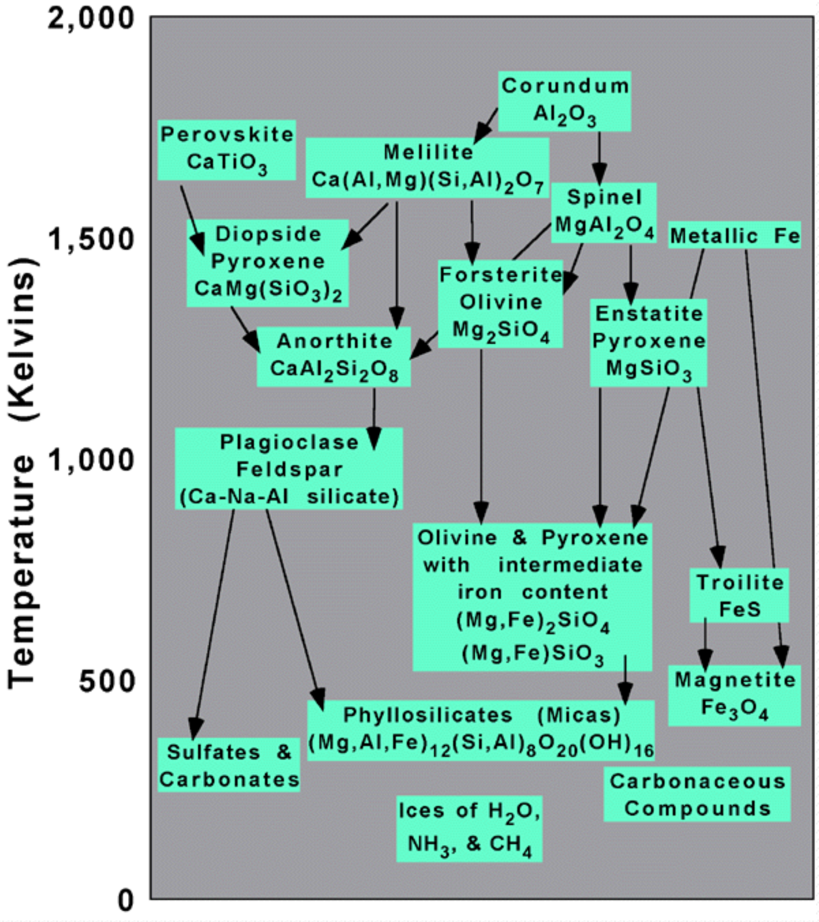
- Which one (diamond or graphite) is at equilibrium?

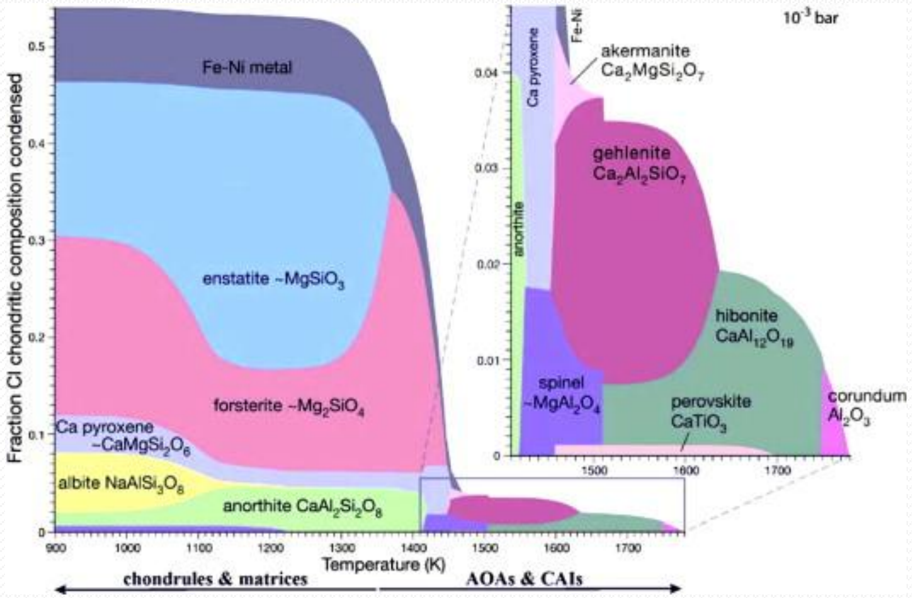
- **Neither** diamond or graphite is at equilibrium in an atmosphere of ~6 x 10^{18} O_2 molecules per cc.
- Carbon Dioxide is the most stable form of carbon on the earth's surface.

Equilibrium Condensation 1

- If the Solar Nebula became very hot (>3000K) during the collapse phase and if it cooled very slowly (Many x 10^6 years) then chemistry may have reached equilibrium at least for the rock forming minerals found in meteorites.
- If equilibrium is maintained then partition of the elements among various solids and the gas is calculable from tables of ΔG.

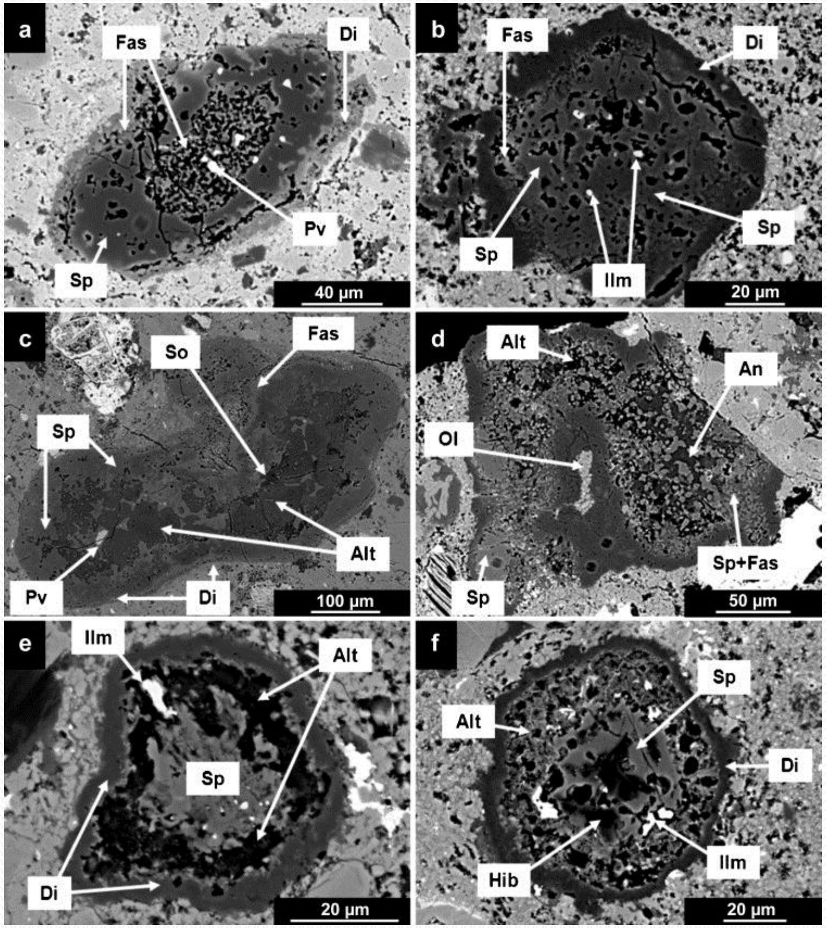
Equilibrium Condensation 2





Standard Model of the Thermodynamic Condensation sequence for the Primitive Solar Nebula predicts the condensates as a function of temperature and pressure.

Equilibrium Condensation 3



The Renazzo Chondrite (above) and (left) various CAIs showing zoning. Minerals used in thermodynamic calculations are based on such observations.

Equilibrium Condensation 4

- Advantages:
  - Allows very precise calculation of condensation temperatures in any well-specified environment.
  - There is no need to know the starting mineralogy or the chemical reaction sequence, just the composition.
- Disadvantages:
  - There is no information on physical parameters such as the particle size distribution or grain number density.
  - Only stable mineral species are considered: amorphous materials are not part of the model.

Equilibrium Condensation - 5

- Where are Equilibrium Calculations most applicable?
  - Under conditions that are either static or changing very slowly in temperature, pressure & composition.
- What are some natural examples where it might apply?
  - Slowly-cooling, intrusive dikes and plutons on Earth,
  - Slowly-evaporating, natural lakes with little input,
  - Cameron & Pine's original model of the Solar Nebula.
- What can be most easily calculated using this model?
  - Composition and sequence of the solid condensates.


COMPLAINT
DEPARTMENT
PLEASE TAKE A NUMBER
1

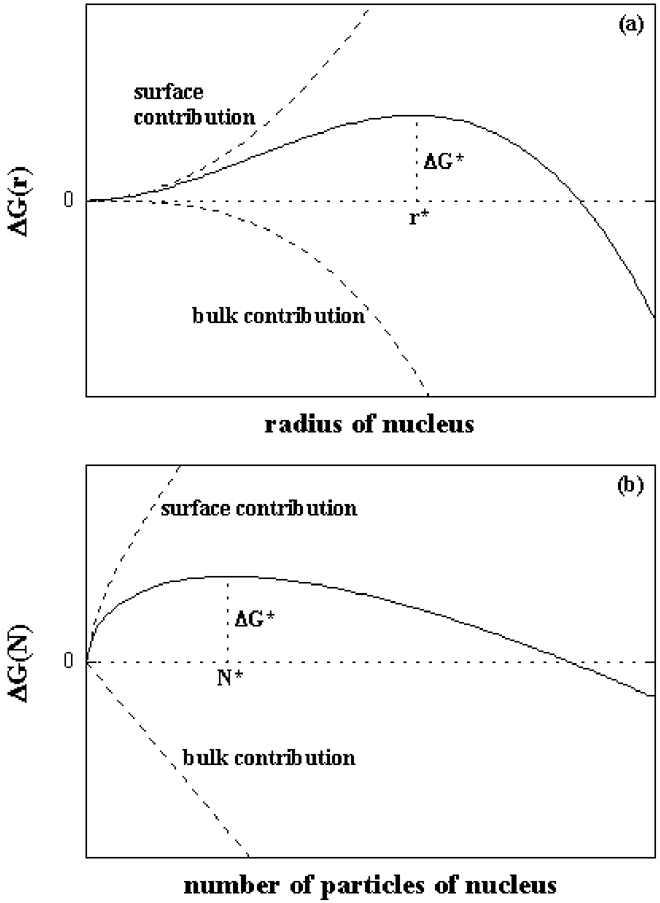
Kinetic Condensation Models 1

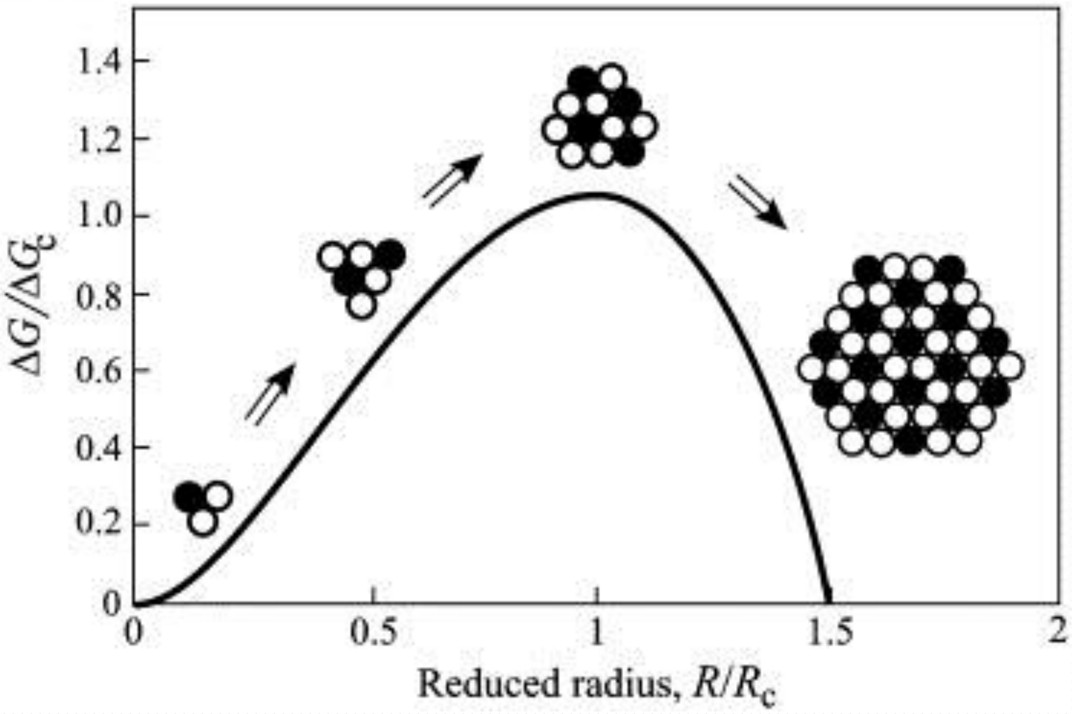
- The ideal chemical kinetic model:
    - Specify the concentration of all molecules and atoms.
    - Specify the initial temperature and density of the gas.
    - Calculate the collision rates for all relevant species.
    - Calculate the reaction rates for all relevant species.
    - Calculate the concentration changes for all species.
    - Specify the temperature and density of the gas.
    - Repeat *ad infinitum* as T & P change appropriately.
- For a specific cooling profile, this will yield the detailed chemical pathway and composition at any given time.

Kinetic Condensation Models 2

- Real World Problems:
- We have no source for the very large number of chemical reaction rates and partition coefficients for the growing refractory clusters and specific atoms and molecules – as a function of temperature.
- We do not know the composition or structure of the more important quasi-stable intermediate clusters that eventually grow into grains.
- If we add in nebular transport and mixing effects, there is simply too much information to track.

Nucleation Theory - Compromise





Use Thermodynamics to calculate a steady state cluster distribution and Kinetics to calculate the growth rate of stable clusters => grains,

Nucleation Theory 1

- Advantages:
  - No requirement for individual reaction rates.
  - Uses equilibrium assumption to calculate the distribution of precondensation clusters.
  - Only the “critical cluster” grows into a grain.
  - Specifically calculates grain sizes and distributions.
- Disadvantages:
  - Highly simplified kinetics and thermodynamics.
  - Growth calculations rely on idealized “sticking coefficient” that is dependent on grain structure.
  - Nucleation rates are highly dependent on surface energy.

Nucleation Theory - 2

- Where might Nucleation Theory be used?
  - In a situation where the starting composition, pressure and temperature are known and the time-temperature trajectory can be specified reasonably well.
- What are some natural examples where it might apply?
  - In a circumstellar outflow around an AGB star,
  - In a highly transient event in the Solar Nebula, such as a shock wave or lightning bolt,
  - In an impact plume on almost any scale.
- What can be predicted most readily?
  - Size distributions and number density of condensates.

Summary of Model Approaches

- Thermodynamic models predict the compositions of the condensates if equilibrium is attained under any given set of model parameters. They cannot predict grain sizes or distributions and can not predict the formation of amorphous solids.
- True Kinetic models are impossible for any multi-component natural system: too many unknowns.
- Nucleation models predict the formation rate and final particle size distributions of simple condensates in well specified natural systems: not compositions.

Applications of Condensation Models

- **Circumstellar Outflows**
  - These are “simple” well defined systems: great places to test condensation models.
- **Protostellar Nebulae**
  - These are complex, multi-process regions.
  - **Meteoritic Evidence:** must separate grain condensation from evaporation and nebular processes from parent-body processes.
  - **Comet Observations:** potentially contains pristine condensates but utility is limited.

Just a Few Observational Facts

- Almost all silicate grains formed in circumstellar outflows are amorphous: broad features at 10 &20 μm.
  - Rare, high-mass-loss-rate, stars produce some (5 – 40%) crystalline dust.
  - Crystalline dust is always a magnesium silicate mineral.
  - No crystalline dust has ever been observed to contain iron at detectable levels in a circumstellar outflow.
- Comet dust is both crystalline and amorphous: while some comets show magnesian mineral spectra, some show (iron, magnesium) olivine and enstatite.
  - Secondary processing may have been important here.


LODGING
NEXT RIGHT
State Prison

Experimental Approaches

- **All experiments are flawed at some level.**
- The low pressures of astrophysical systems are often ignored: experiments are done at higher pressures.
  - This can be an advantage if you can equate the number of collisions with total reaction time,
  - This can cause problems if the reacting systems do not "finish" one reaction before the next collision occurs.
- Sustained high temperatures are difficult to maintain.
  - Lab equipment melts, vaporizes or emits impurities while observation windows become obscured.
- Few experiments are done with "cosmic abundances."

What can experiments tell us?

- Basic physical parameters needed for models must be measured: vapor pressures, melting points, diffusion rates, etc.
- Models and theories can be tested.
- Chemical kinetic “fudge factors” & required reaction rates can be measured : sticking coefficients, annealing rates, etc.
- Sometimes an experiment reveals completely unexpected behavior: this is not typically why the experiment was done.

Some examples of experiments

- Crystalline grains generally do not appear from vapors.
- Many processes are required to make crystalline grains.
    - **Nucleation** – forms “stable” nuclei.
    - **Growth** - adds atoms to stable nuclei.
    - **Coagulation** – Grains stick together upon collision.
    - **Thermal Annealing** – can consolidate aggregates by partial melting and/or produce crystals from amorphous materials of different composition than condensates.
- Each of these processes can be tested independently,: sometimes on the actual materials of interest, but at other times it is more practical to test analog materials.

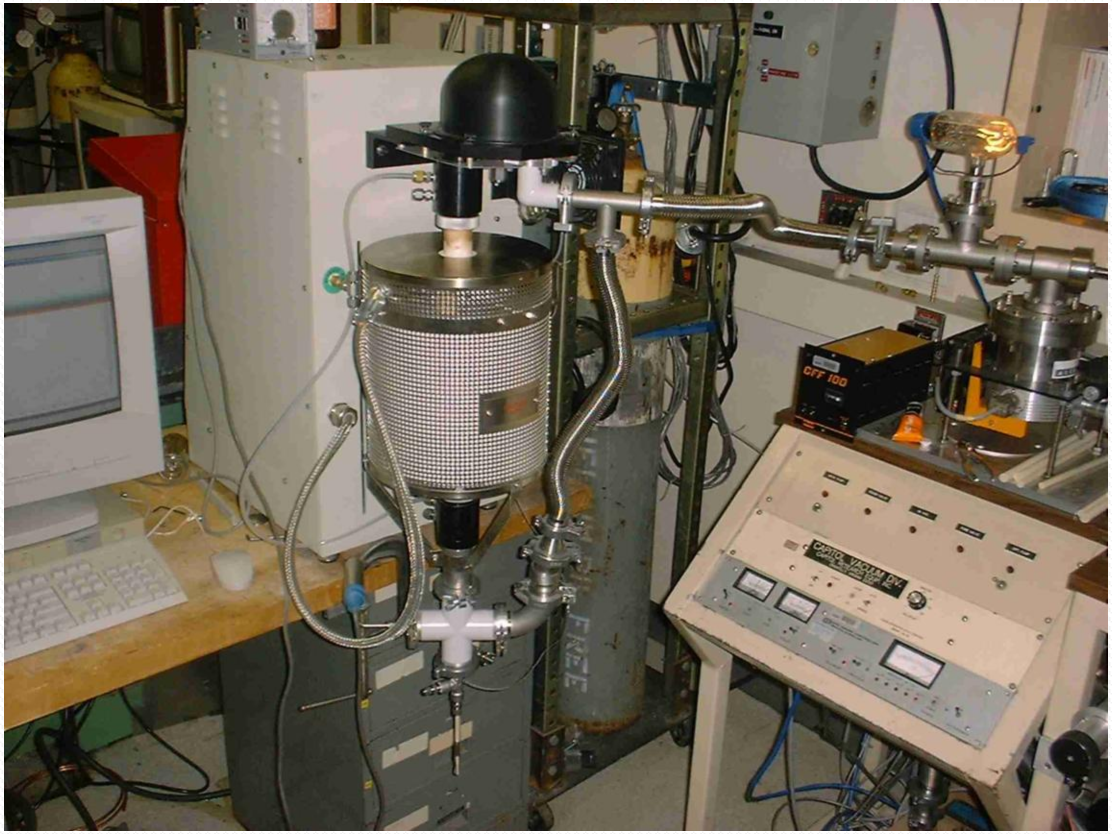
Measurement of Basic Data

- An example from astrophysics where the models conflict with observations.
    - SiO is the most important “dust-forming” molecule in oxygen-rich stellar outflows.
    - Silicates can not condense and are not stable until the concentration of SiO in the gas phase exceeds the vapor pressure of SiO.
    - Models could not make silicates form under conditions where they were observed!
- What is the vapor pressure of SiO?

Previous State-of-the-Art

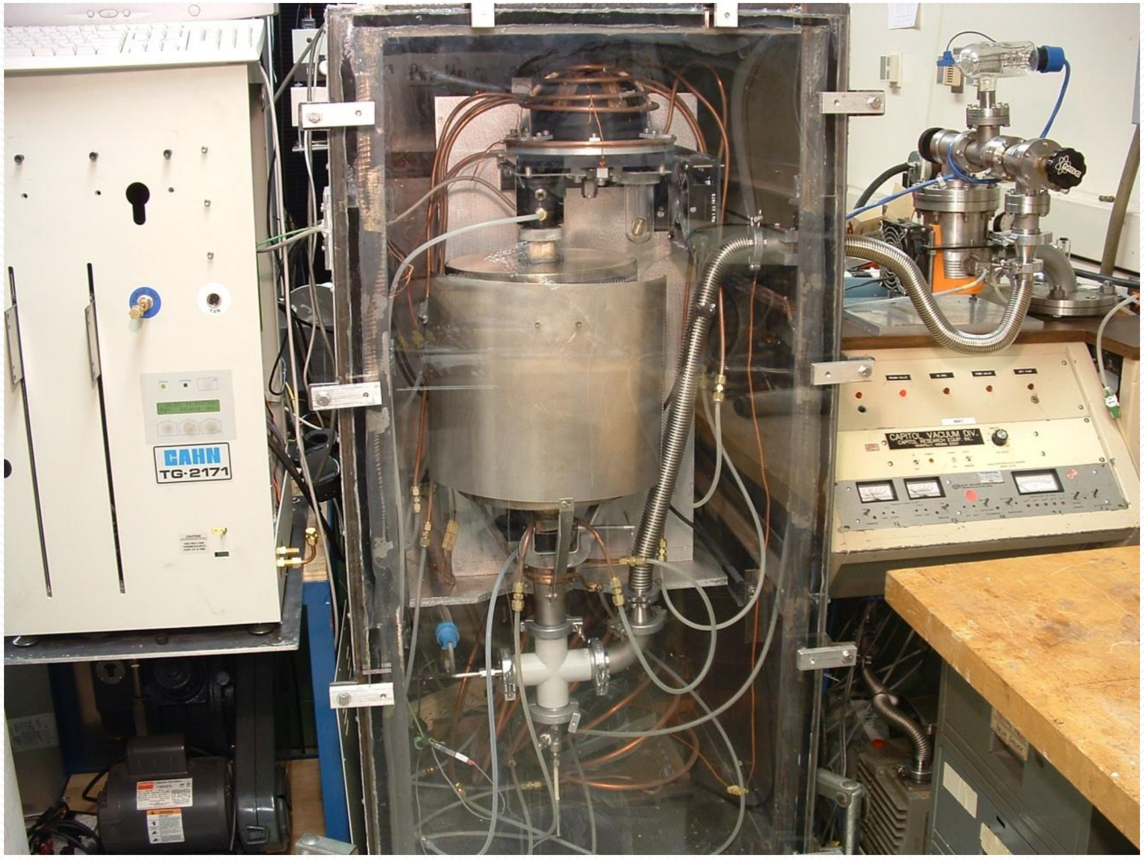
- SiO vapor pressure was derived from a broad thermodynamic treatment of silicate solid and gas phase chemistry for the steel industry (Schick, 1960).
- A single vapor pressure measurement made near 2000K anchors the equation.
- Extrapolation down to ~1000K where dust forms is based on a rough <u>estimate</u> of ΔH.
- Based on observational conflicts, a new set of vapor pressure data seemed to be required.

Current State-of-the-Art I



- **We bought a commercial Thermogravimetric system and gained experience measuring metal vapor pressures.**

Current State-of-the-Art II

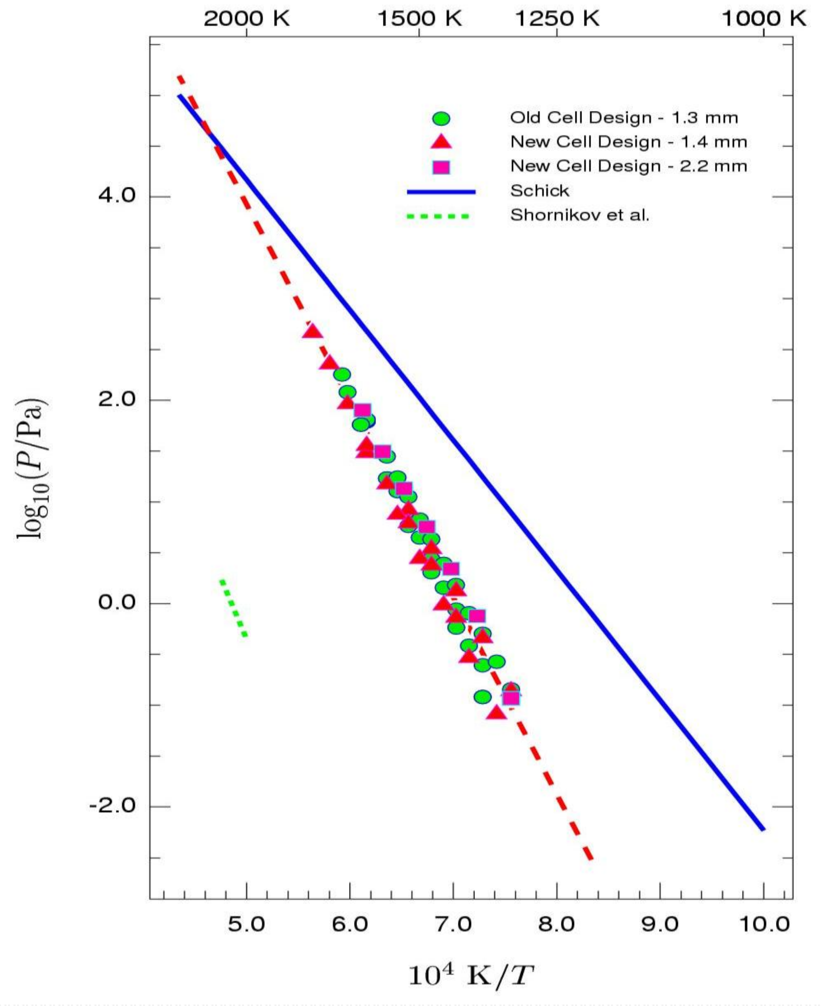


We rebuilt the system to eliminate oxygen contamination, then refined the techniques & data reduction methods.

Current State-of-the-Art III

- **We still had occasional experimental problems, but they were not intractable.**

Current State-of-the-Art IV

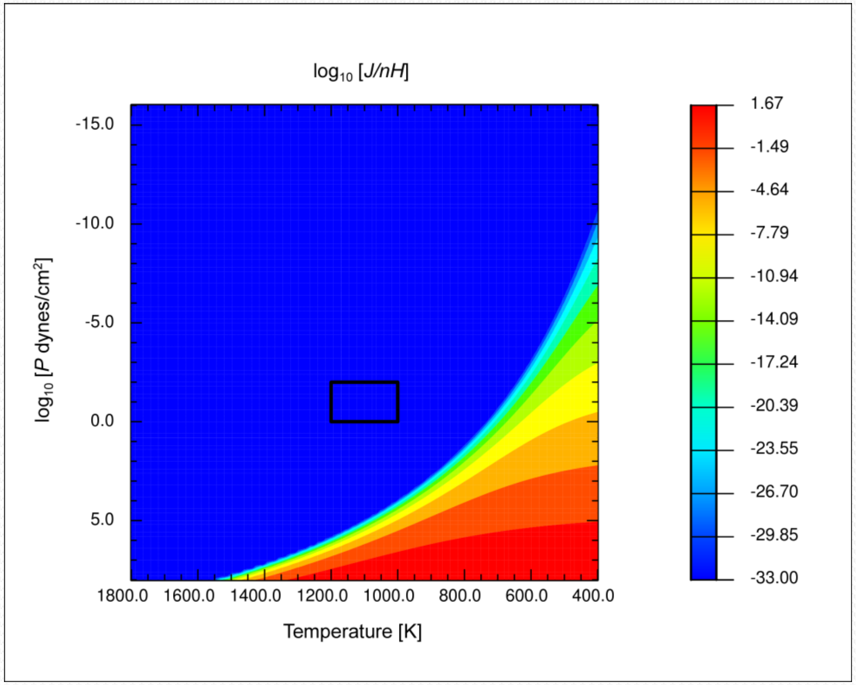


- **Three years later we were ready to measure SiO over the range 1273K < T < 1773K.**
- **Our new SiO vapor pressure extrapolates to *~5 orders of magnitude* less than Schick's at 1000K.**
- **Not quite there yet…**

What is Vibrational Disequilibrium?

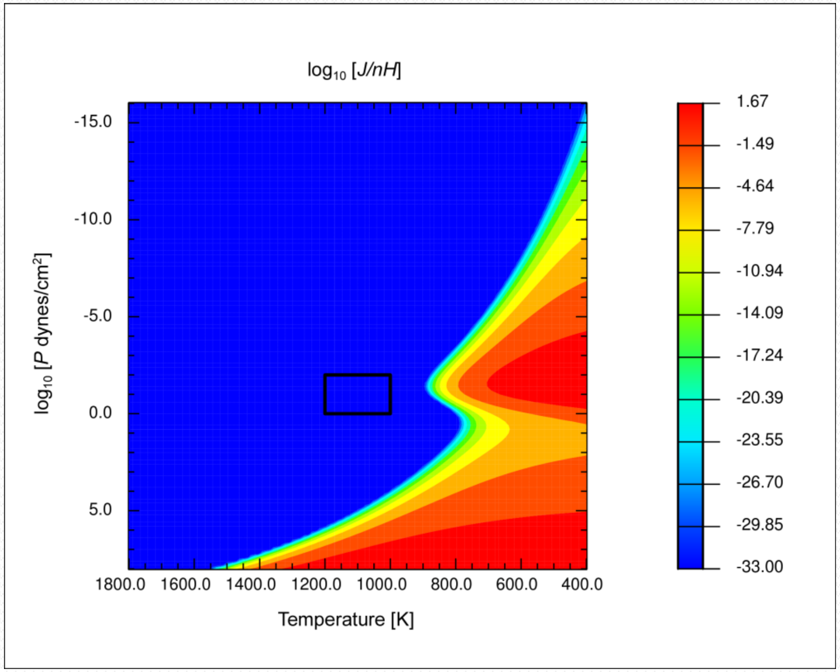
- For strong, energetic vibrational transitions at low pressure and in optically-thin environments, collisional excitation and photon absorption cannot balance the emission processes.
- In this case the population density in the upper vibrational levels drops dramatically.
- We assume that lower SiO vibrational temperature (T_v) promotes nucleation .
- We use T_v to calculate S.

Vibrational Disequilibrium (old)



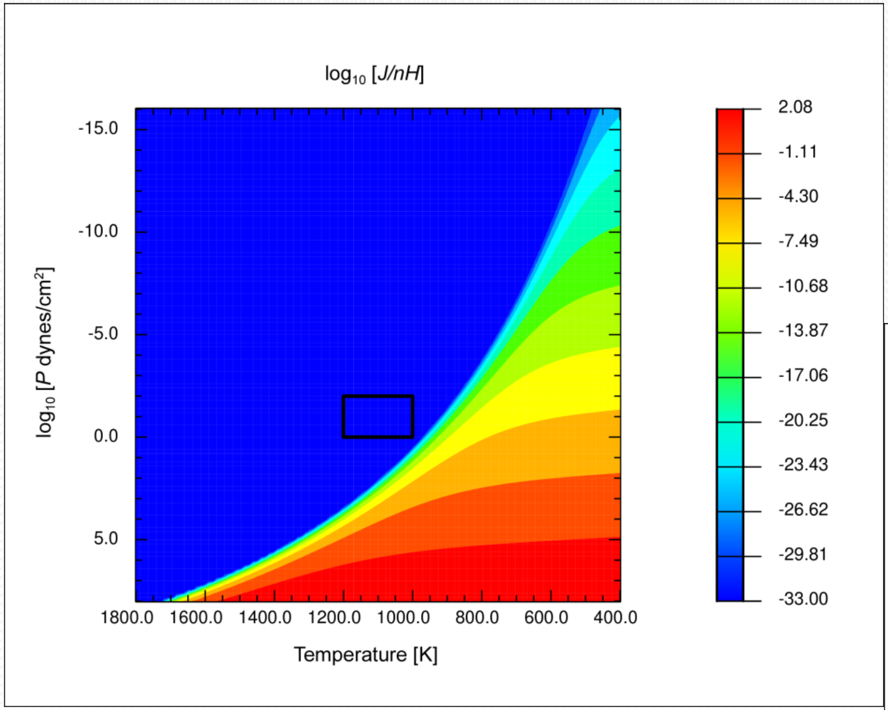
The black box is where dust formation is observed to occur.

Color indicates the rate of grain formation.



At low pressures spontaneous vibrational emission cools SiO molecules faster than they can be excited by collisions.

Vibrational Disequilibrium (new)



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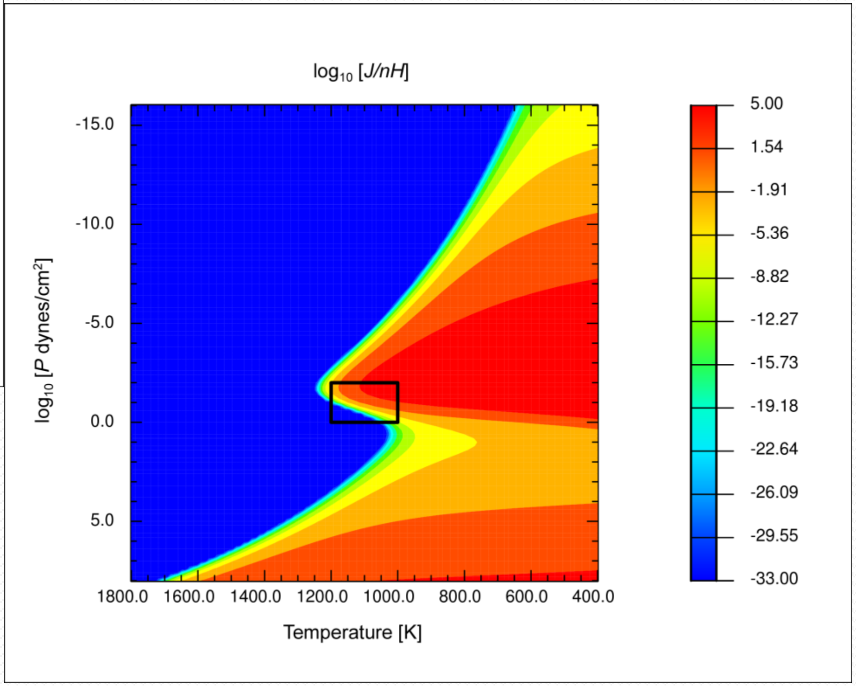


Application of New Data

- The new vapor pressure equation for SiO greatly increases the calculated level of supersaturation in circumstellar outflows.
- Even so, vibrational disequilibrium must also be invoked in order to nucleate refractory silicates under conditions observed in circumstellar outflows.
- Using vibrational disequilibrium with the Schick vapor pressure equation alone does not cause SiO to nucleate in circumstellar outflows.
- Using vibrational disequilibrium and our new vapor pressure equation works almost too well: within the uncertainties of classical nucleation theory and circumstellar observations dust DOES form.


Thank you for driving carefully through the village
CINQUE PORTS

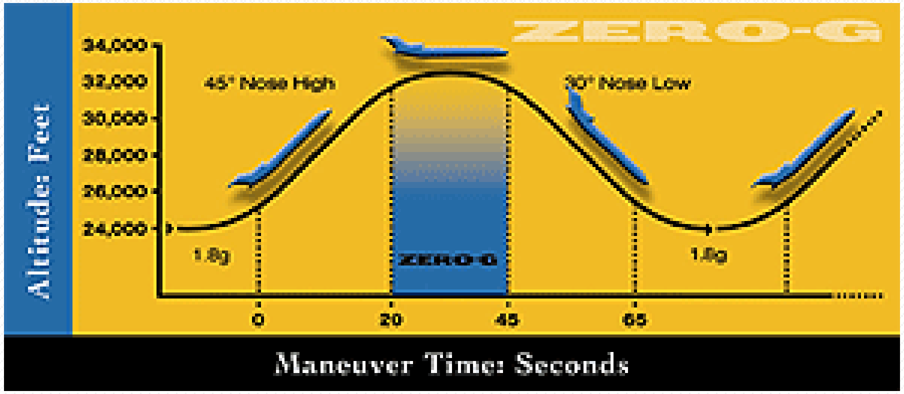
Measuring a Fudge Factor

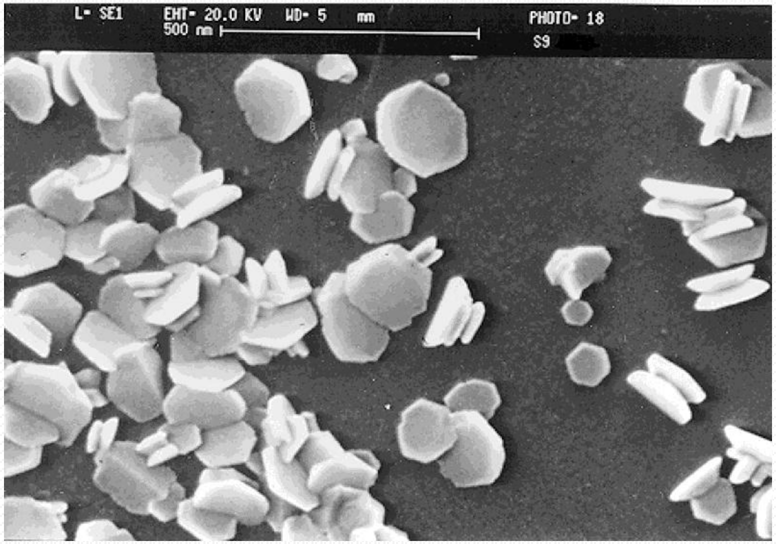
- Measurement of a sticking coefficient.
  - How much time is required to grow a 20 μm crystalline grain (e.g. presolar SiC or graphite) at equilibrium in a stellar outflow?
  - Large crystalline grains require about a year IF every atom that collides with a growing grain also sticks.
  - Crystalline SiC & graphite grains form in stars at very high temperatures (~1750K).
  - Temperatures found in stars are not easy to simulate in the laboratory!

Experimental Requirements, etc.

- Grow a crystalline grain from a vapor.
  - Preferably a refractory particle like graphite
- Measure the rate of particle growth
  - Must know the concentration of the vapor
  - Must follow growth from seed to large grain
- Growth should take place in steady state.
  - Must eliminate convection (or compensate)
  - Experiment should be repeated a few times.

Experiments on NASA's KC-135

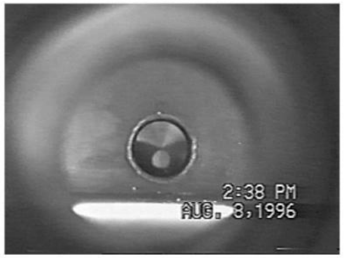




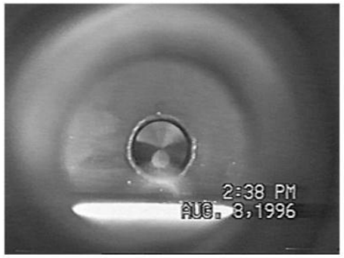
- The Vomit Comet can simulate zero-gravity for about 23 seconds.
- No gravity/No convection.
- Zinc vapor cloud can be produced at controlled temperature and pressure.
- Zinc vapor forms crystals.
- We measured the growth rate of zinc crystals.

Our Experiment on the KC-135

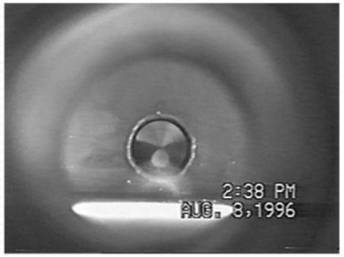
Our Experiment on the KC-135



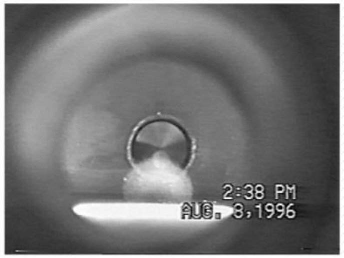
(a) Frame Before Nucleation Begins



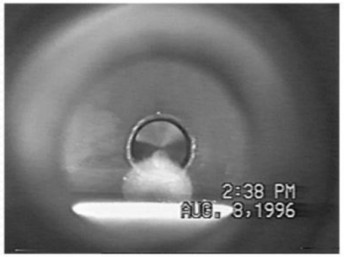
(b) Start of Nucleation



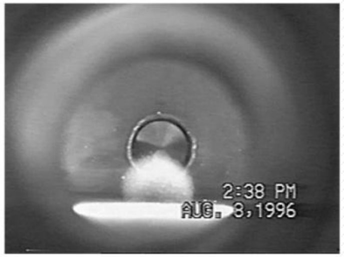
(c) 1/30 Second Later



(d) 2/30 Second Later



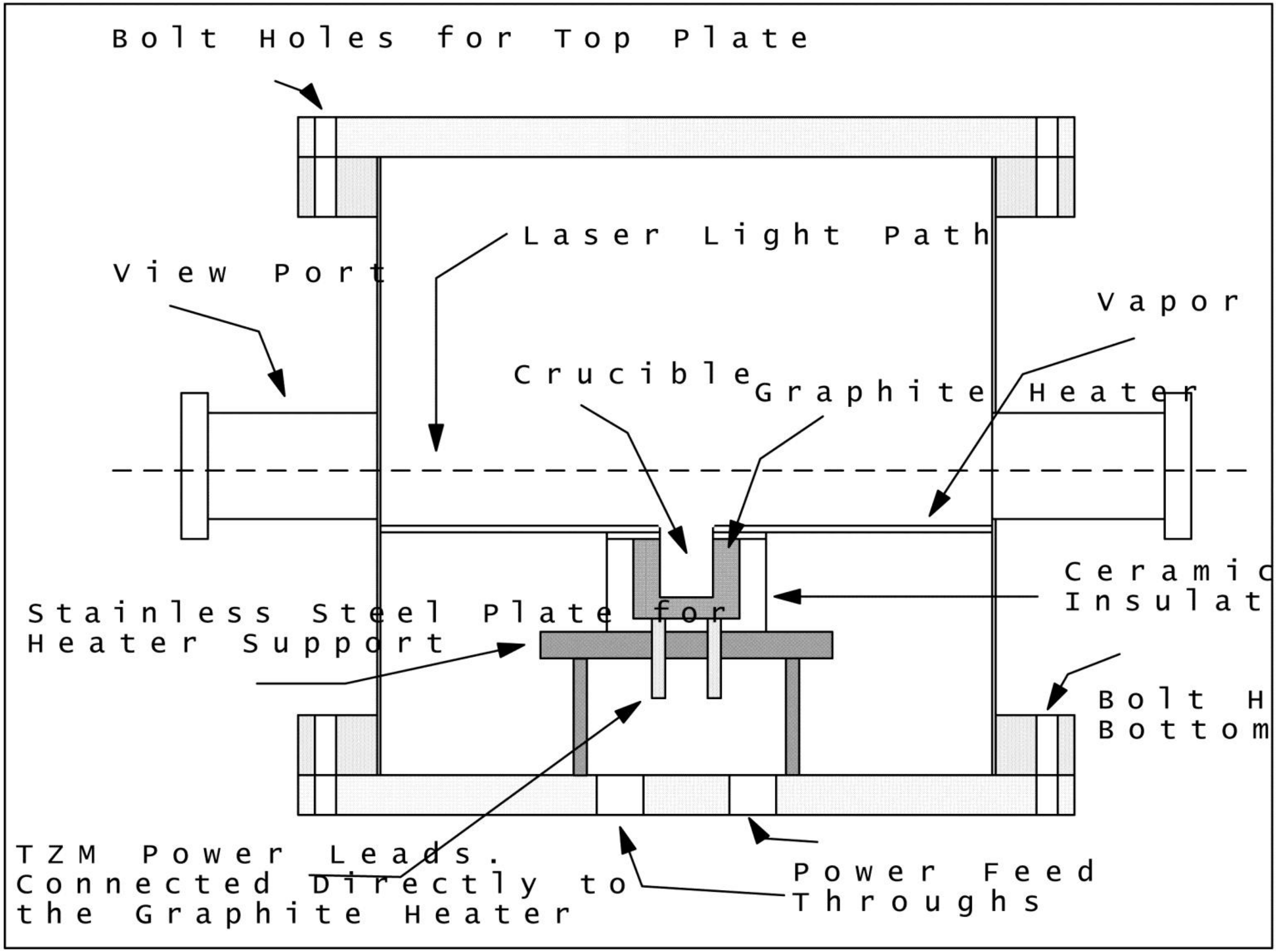
(e) 3/30 Second Later



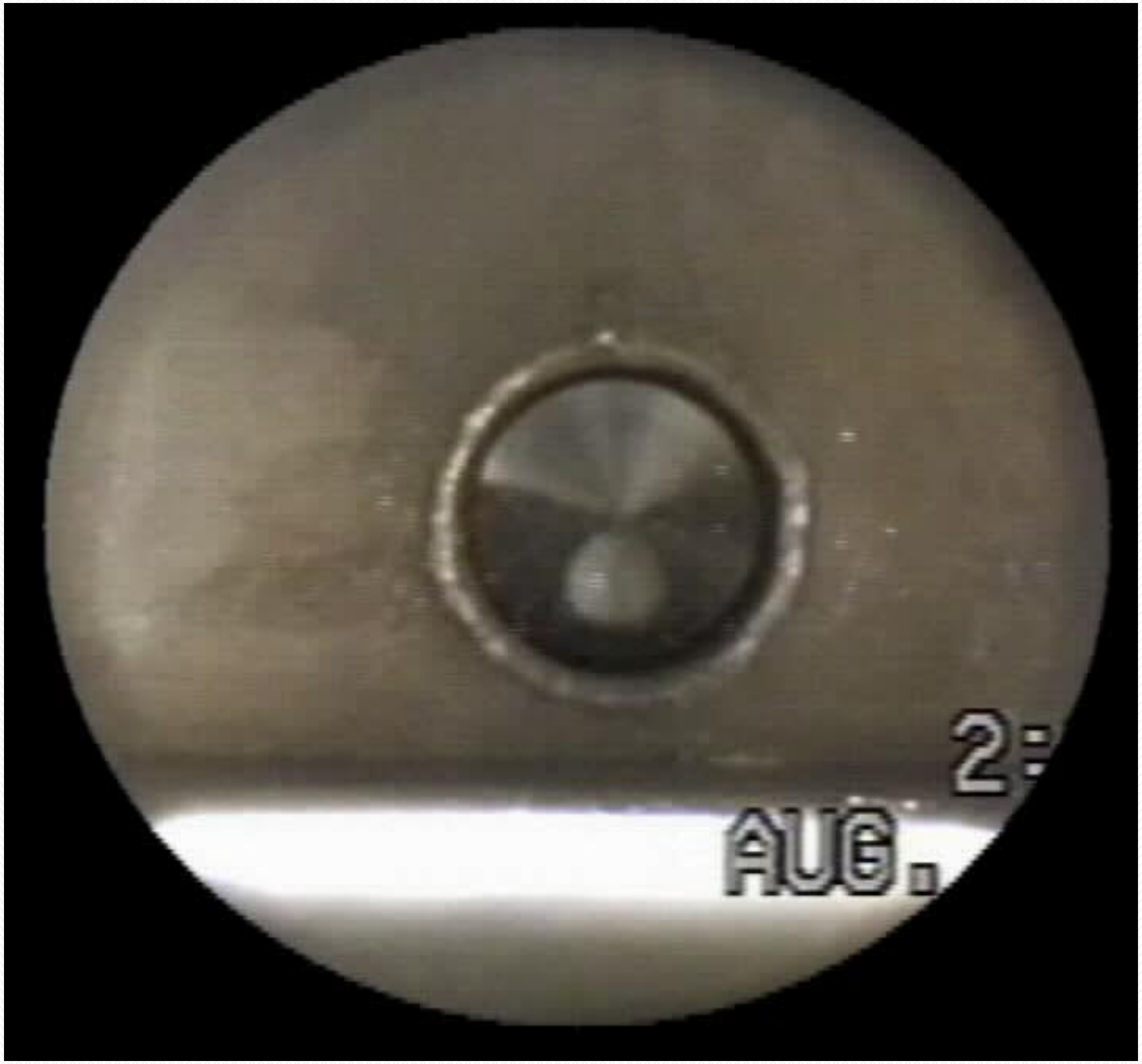
(f) 4/30 Second Later

- **We measured the zinc grain size distribution in a 1 cm^3 volume at the center of the nucleating cloud that formed in zero gravity as a function of time using laser scattering techniques.**

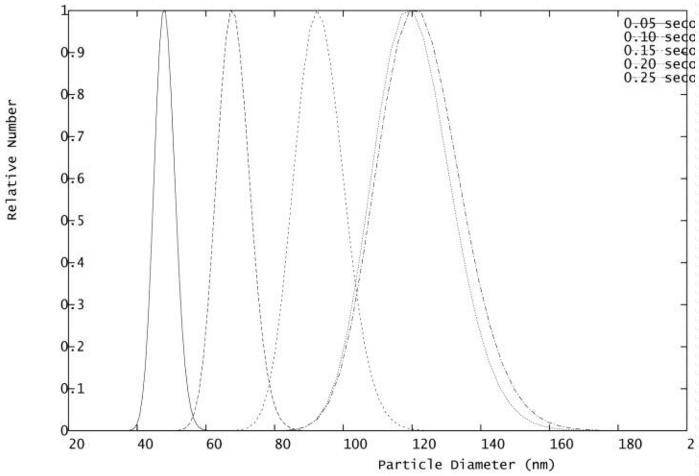
Schematic of Experimental System

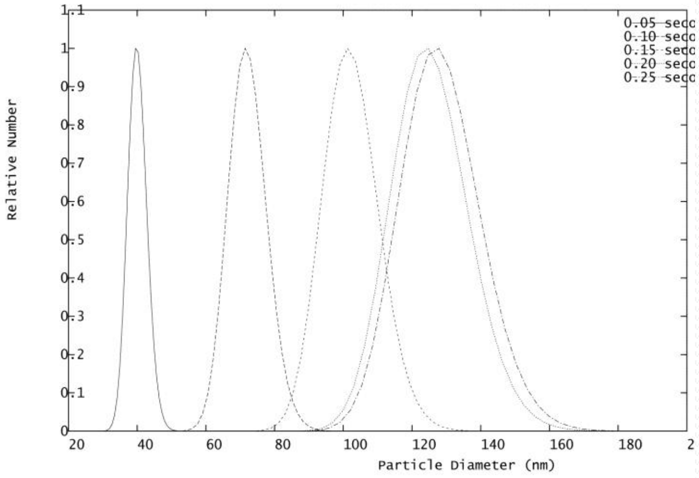


Our Experiment on the KC-135



Our Experiment on the KC-135



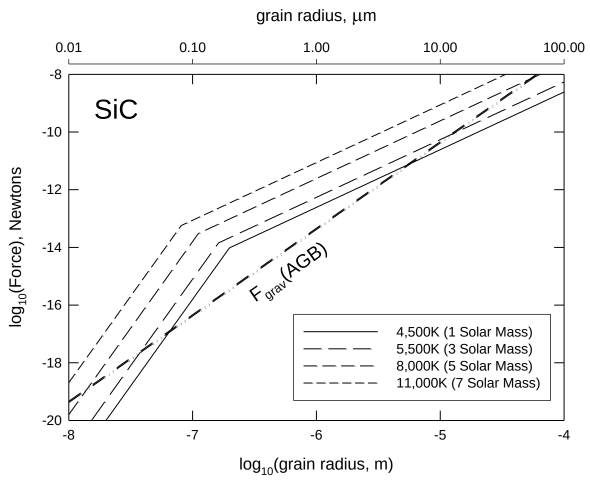


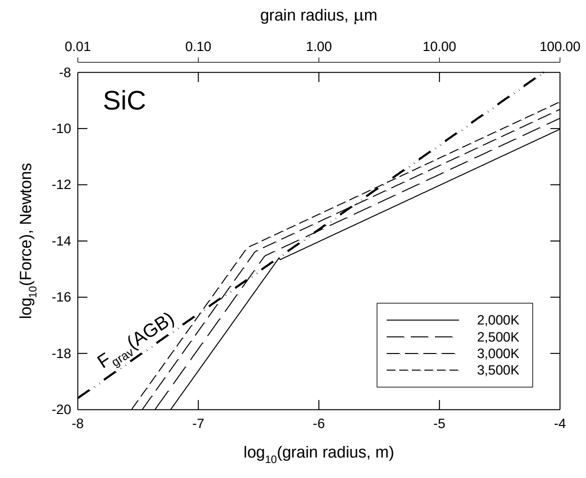
- Each experiment could be analyzed for at least three growth stages.
- We assumed spherical grains (overestimate).
- Temperature ~ 480K
- Zinc Pressure ~ 29 Torr
- Average Collision Rate was ~ $5 \times 10^{7}\ s^{-1}nm^{-2}$.

Results of KC-135 Experiments

- **Based on the average observed rate of zinc particle growth and on the conditions of the experiment, only 3 atoms of every 100,000 that hit a growing zinc crystal actually stick.**
- **Previous calculations showed that presolar SiC grains required about 1 year to grow to 20μm.**
- **These experiments imply that ~10,000 - 100,000 years are required for growth at equilibrium.**
- **<u>Grains must form in the stellar atmosphere.</u>**
- ***Stellar clouds? Stellar air pollution?***

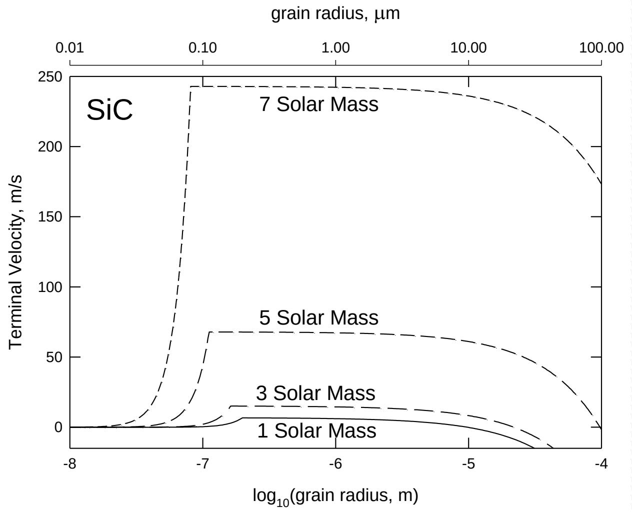
Stability of Stellar Cloud Particles I

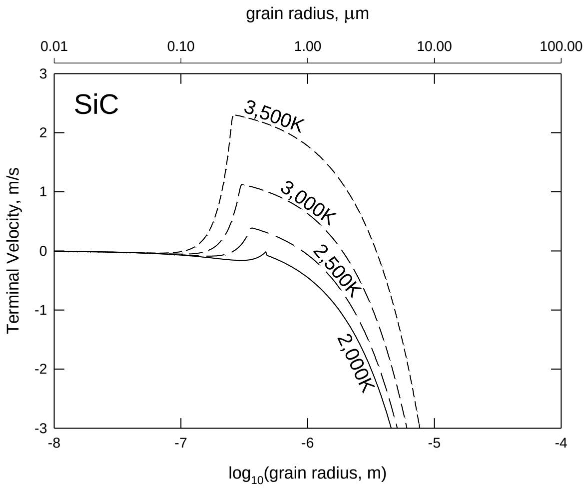




- How do growing SiC particles stay suspended in stellar atmospheres?
- Radiation Pressure on small grains ~ r^6.
- Radiation Pressure on large grains ~ r^2.
- Gravitational pull on all grains ~ r^3.
- Radiation Pressure can occasionally exceed Gravity.

Stability of Stellar Cloud Particles II





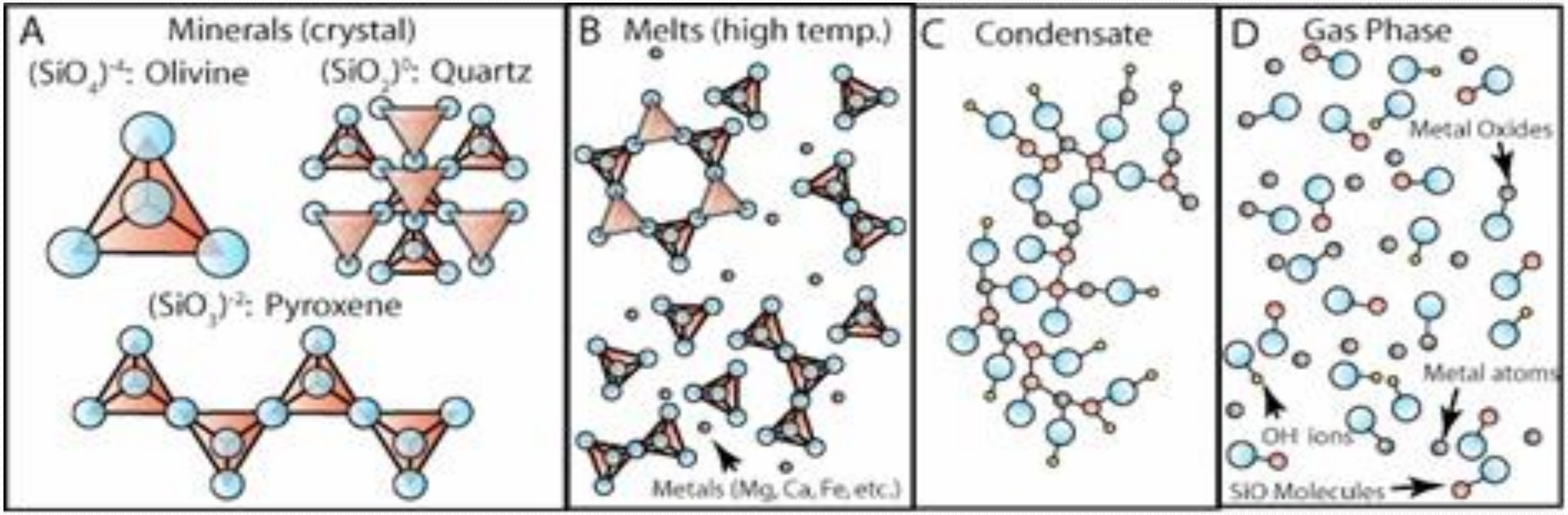
- What happens as SiC grains grow?
- Terminal Velocity is proportional to the force on a grain divided by the number density of the gas and r^2.
- Large stars rapidly eject very small grains.
- Only low mass AGB stars grow large grains.

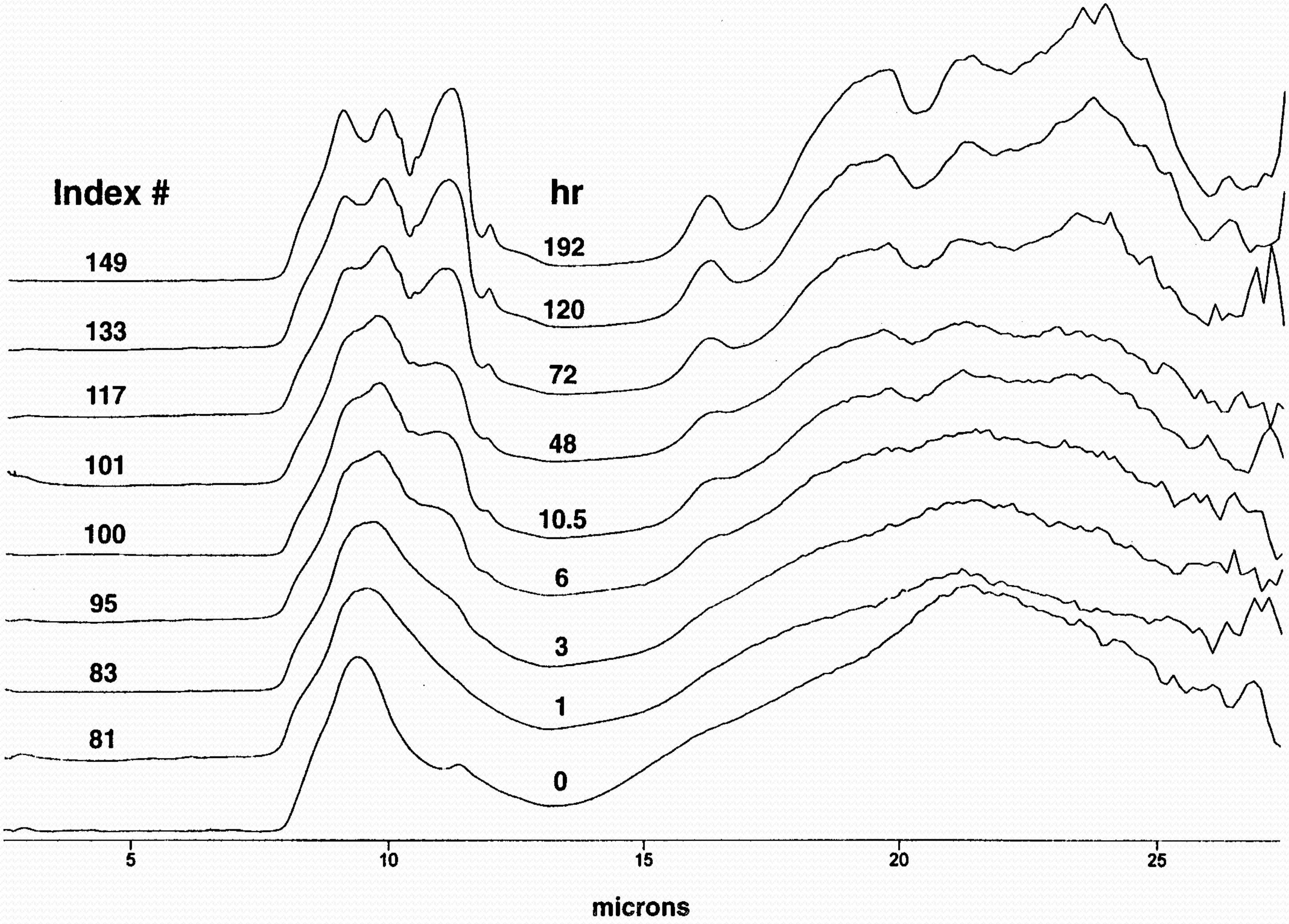
New Type of Grain Formation

- We propose that the large, refractory crystalline grains found in meteorites formed slowly in low mass AGB or Red Giant stars under equilibrium conditions.
- These particles are analogous to those found in atmospheric clouds.
- They have a natural size distribution determined by the stellar radiation field and the level of stellar turbulence.

Amorphous to crystalline transition

- What is required to transform a fresh silicate condensate into a crystalline grain?
- SiO => $(SiO_4)^{-4}$; Metals => Ions ; Establish short range order (glass) ; Establish long-range order (crystal).

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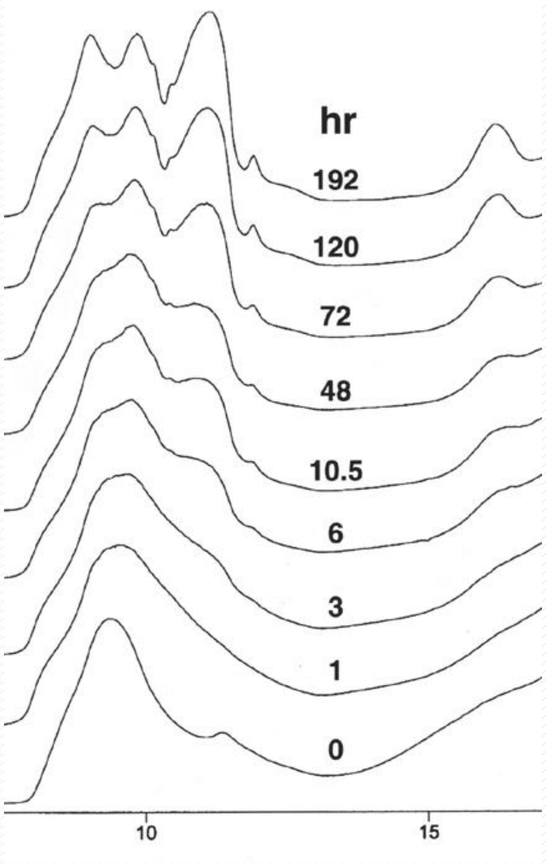
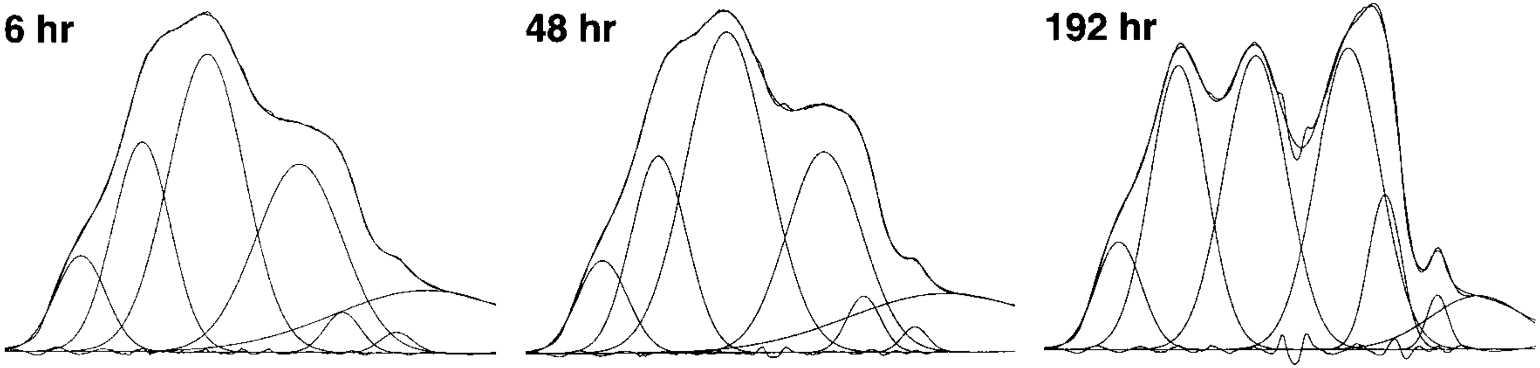
Evolution of Silicate Spectra

- The spectral evolution of fresh magnesium silicate smokes was characterized as a function of both time & temperature (1027K) in the mid-infrared region.
- Magnesium silicate smoke spectra evolve much more rapidly than do equivalent iron silicate spectra.
- Fe-SiO requires T~1300K to get the same rate of change.



Deconvolution of the 10 μm Silicate Feature

(Mg silicate smokes annealed at 1027 K)



6 hr

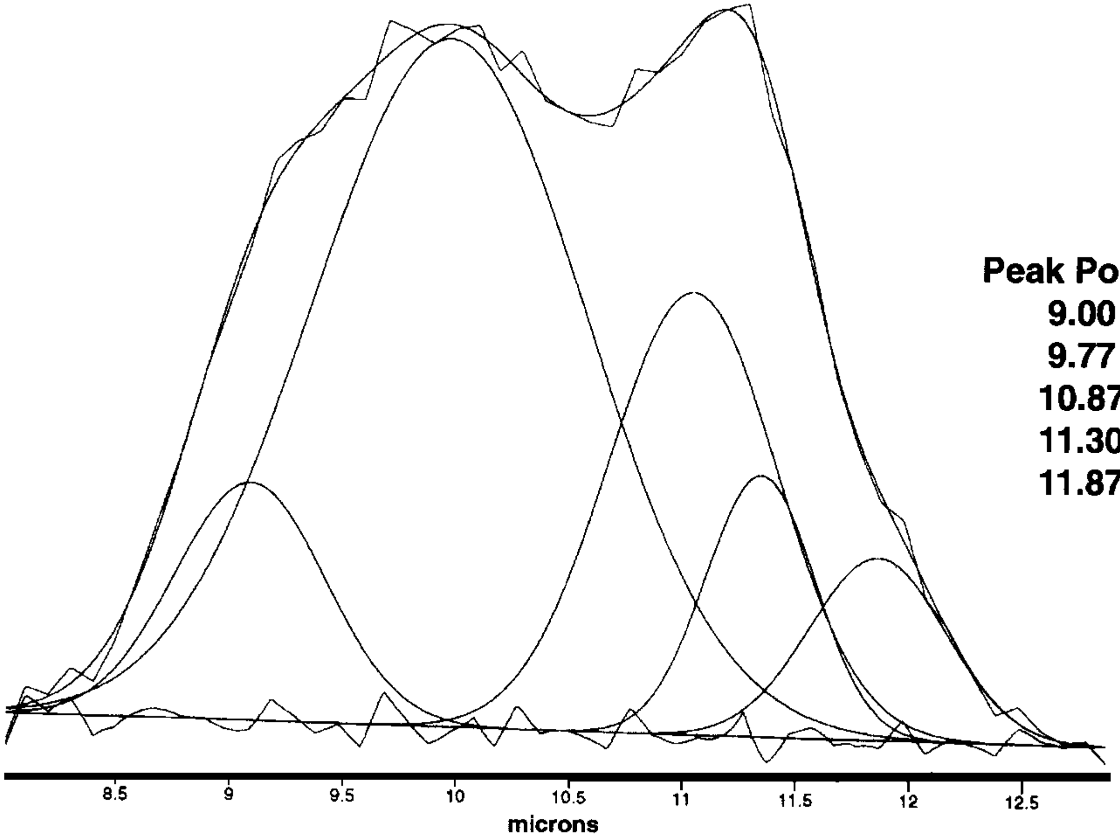
48 hr

192 hr

Peak Positions:

8.35, 9.00, 9.77, 10.87, 11.30, 11.87, 12.22 μm

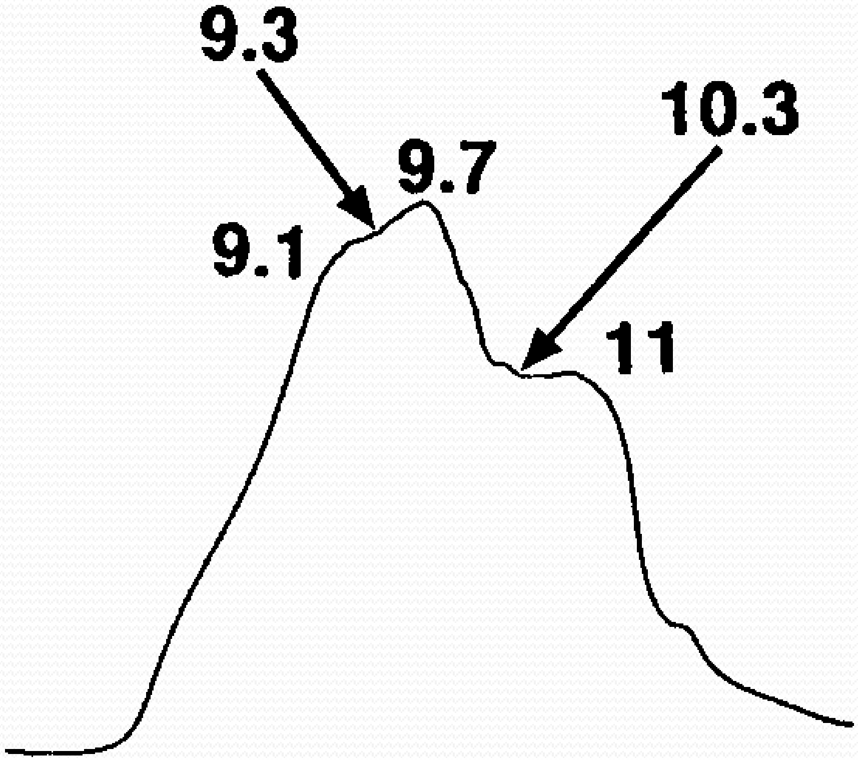
Deconvolution of the 10 µm Feature of Comet Halley



Peak Positions:
9.00 µm
9.77 µm
10.87 µm
11.30 µm
11.87 µm

Quantifying Spectral Changes

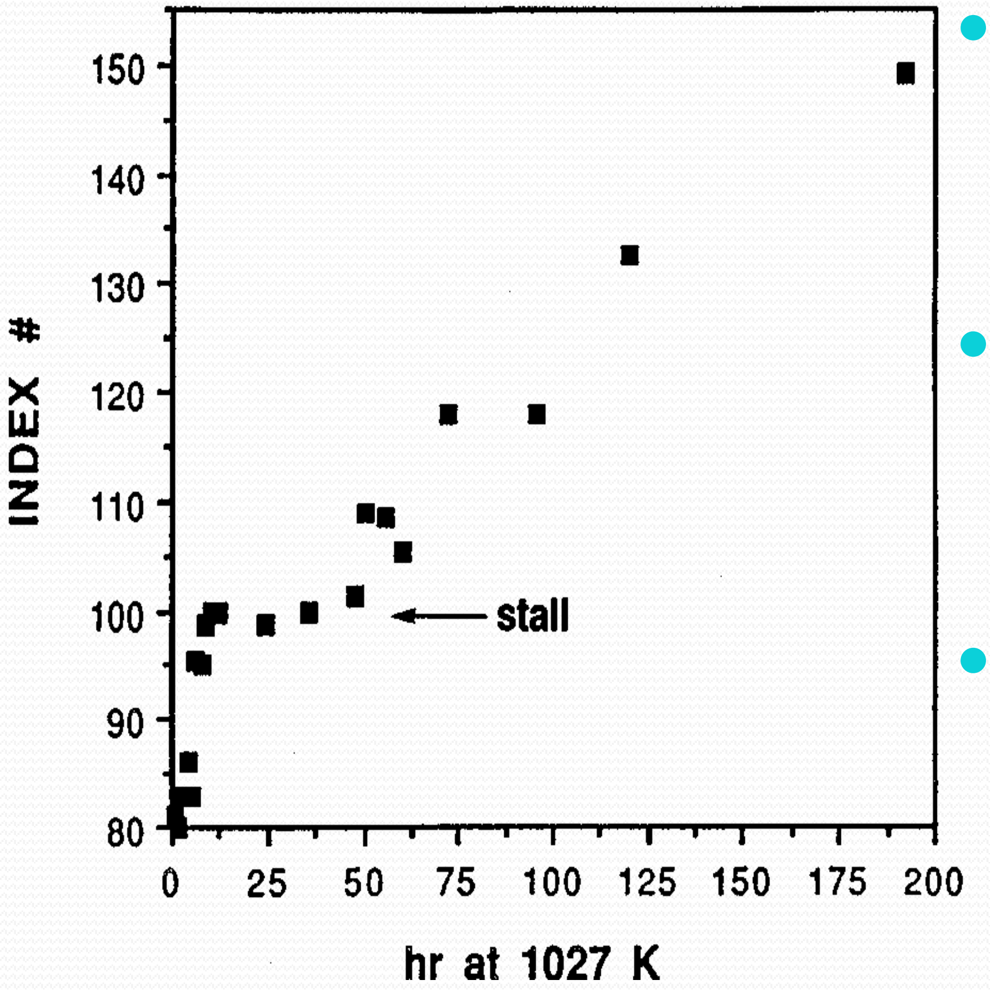
Stall spectrum



Constructing an Index

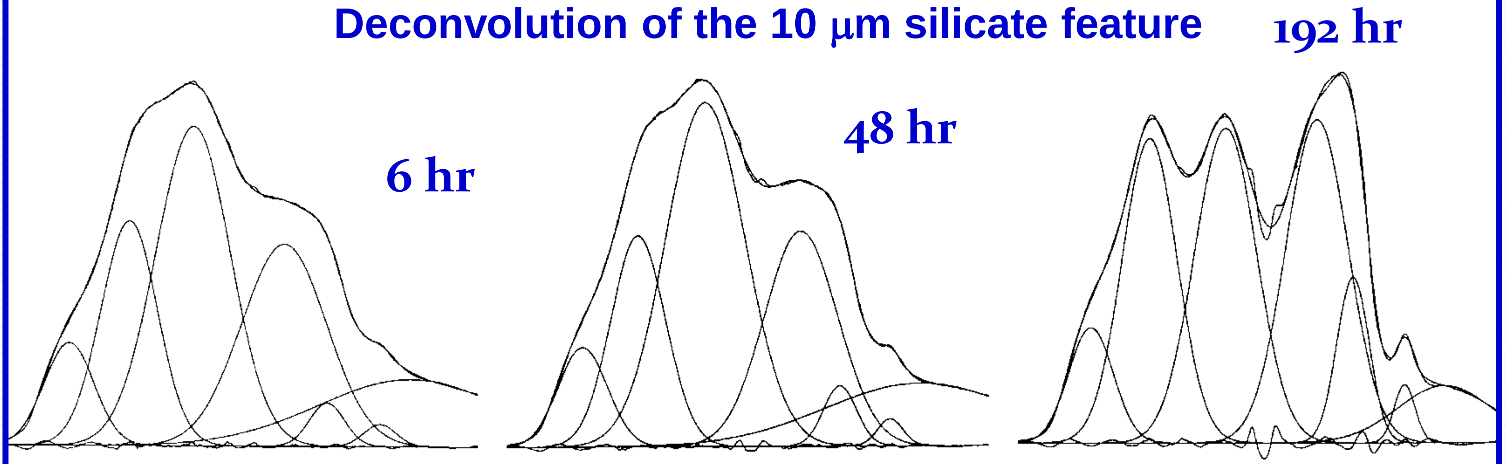
- 11 em/9.7 em, 11 em/9.1 em, 11 em/10.3 em, 9.1 em/9.3 em
- Divide ratios by Stall Ratios:
  - 11 µm/9.7 µm = 0.73;
  - 11 µm/9.1 µm = 0.81;
  - 11 µm/10.3 µm = 1.01;
  - 9.1 µm/9.3µm = 0.97
- Take the average of the ratios where stall values are defined to equal 100.

Index Spectral Sub-Components



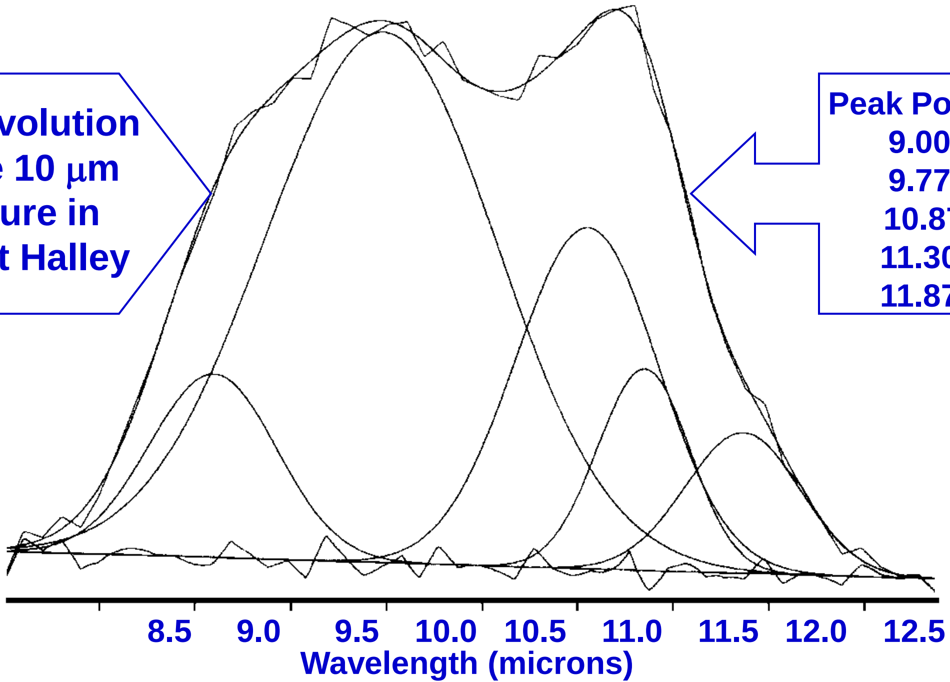
- Spectral features at 8.35, 9.0 and 12.25 microns also appeared in pure SiO and SiO2 smokes.
- Spectral features at 9.77, 10.87, 11.30 and 11.87 only appear in Mg-SiO smokes.
- A "stall" spectrum appears in all Mg-SiO runs for times that vary with T.

Deconvolution of the 10 μm silicate feature



Peak Positions: 8.35, 9.00, 9.77, 10.87, 11.30, 11.87, 12.22 μm

Deconvolution of the 10 μm Feature in Comet Halley

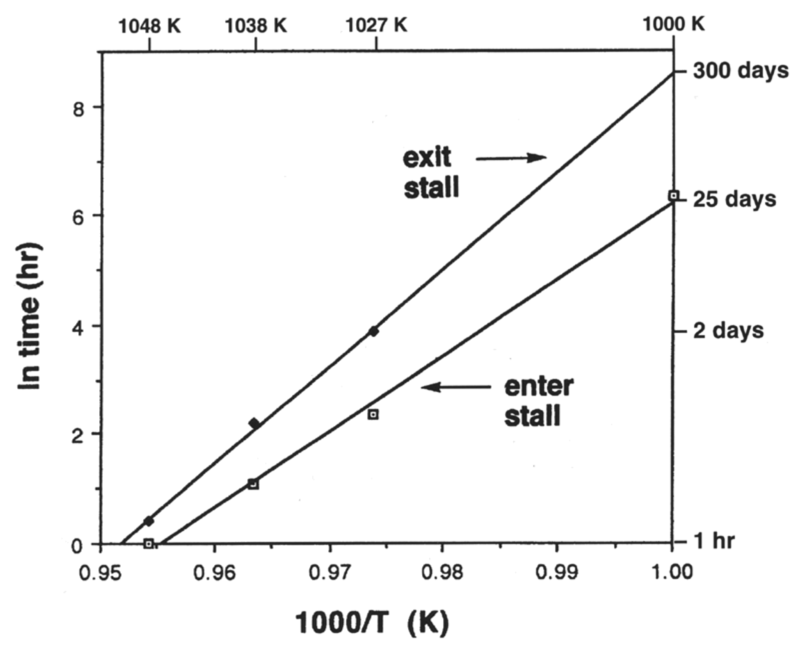


Peak Positions:
9.00 μm
9.77 μm
10.87μm
11.30 μm
11.87 μm

Evolution of Silicate Spectra

- Time to Stall vs. T

5.4 seconds	1100K
40 minutes	1050K
22.7 days	1000K
103 years	950K
39 centuries	900K
3.89 eons	850K
6137 U(20Ae)	800K

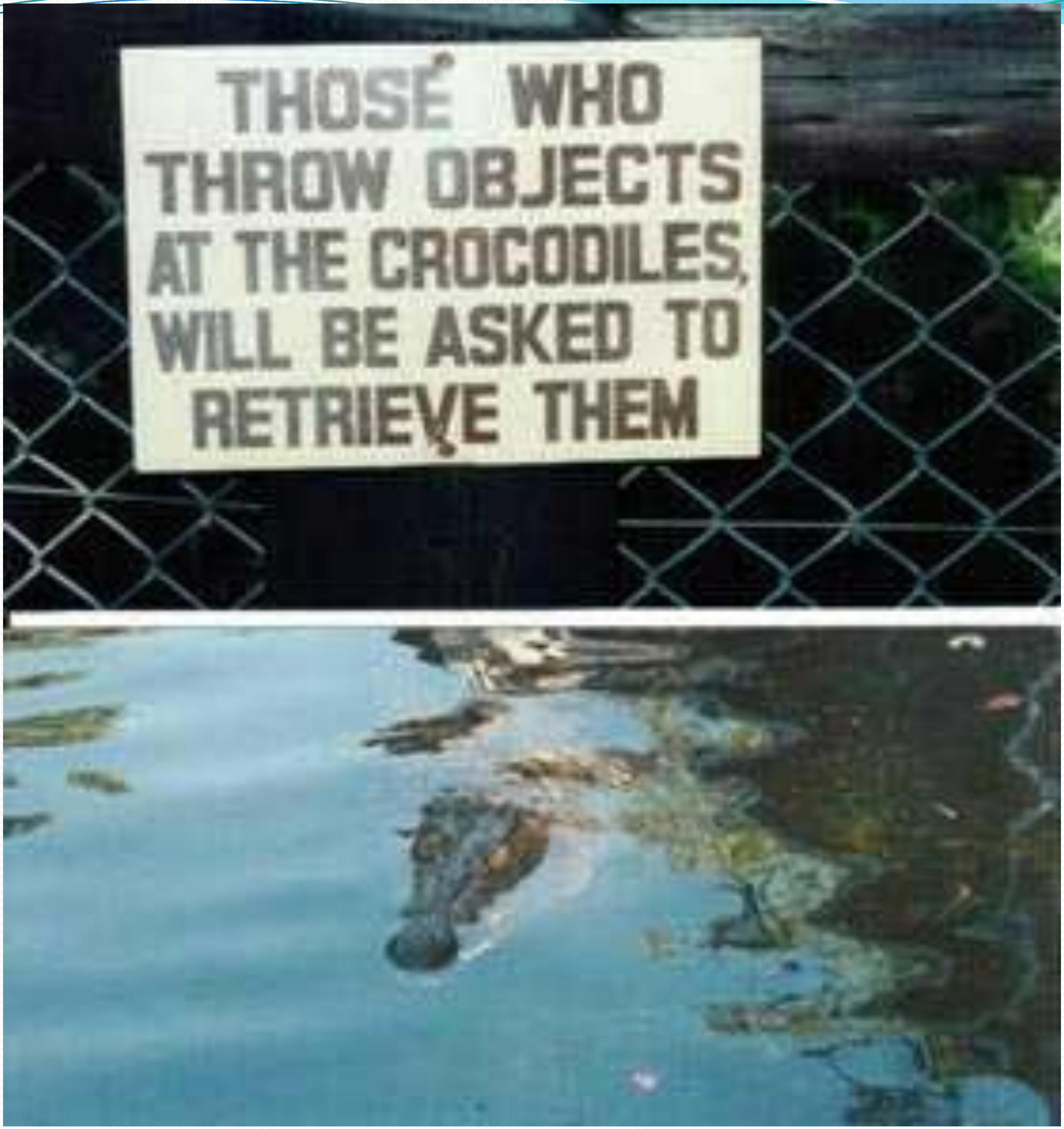


Silicate Evolution Index 1

- $T_{in} = 1.3 \times 10^{-55} \exp(140{,}870/T)$ (1)
- $T_{out} = 1.7 \times 10^{-70} \exp(177{,}430/T)$ (2)
- $F_{in} = 7.77 \times 10^{54} t \exp(-140{,}870/T)$ (3)
- $F_{out} = 5.88 \times 10^{69} t \exp(-177{,}430/T)$ (4)

The silicate evolution index (SEI) tracks the cumulative degree of annealing using both equations (3) and (4) in the following fashion : SEI = A + B (5) where

- $A = f_{in}$, $B = 0$ for $0 <= f_{in} <= 1$, $T < 1067$ K ;
- $A = 1$, $B = f_{out}$ for $f_{in} > 1$, $T < 1067$ K ;
- $A = 1$, $B = f_{out}$ for $T > 1067$ K .
- SEI < 1, pre-stall; 1 < SEI < 2, stall; SEI > 2, post-stall


THOSE WHO
THROW OBJECTS
AT THE CROCODILES
WILL BE ASKED TO
RETRIEVE THEM

New Phenomena

- Revelation of totally unexpected behavior
  - Amorphous silicates are observed in most oxygen-rich circumstellar outflows.
  - We assume that the composition of the grains is dependent on the composition of the gas.
  - Observations show that ~pure magnesium silicate crystals form in some stars.
  - One would expect to see iron-magnesium(1/1) silicate minerals in these systems.

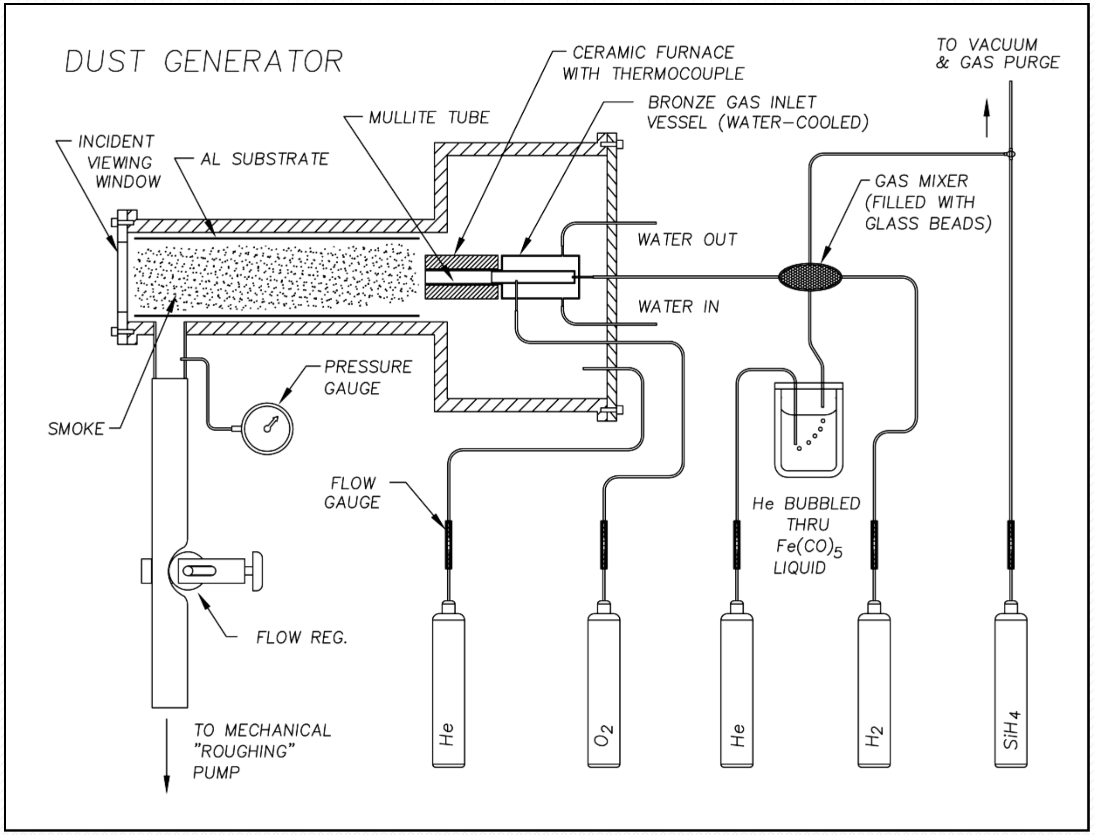
The best laid plans of mice & men

- NASA and ESA planned a series of infrared missions .(IRAS, ISO, SIRTF, JWST, KAO, SOFIA) to observe numerous stellar sources.
- We proposed to make a series of silicate grains of varying composition, then measure their infrared spectra to learn how to use spectral data to obtain the compositions of the grains near the stars.
- We built the Grain Condensation Apparatus in order to make large quantities of amorphous silicate smokes.

Vapor compositions we have used in the grain condensation apparatus

- $SiO-H_2-O_2$
- $Mg-SiO-H_2-O_2$
- $Fe-SiO-H_2-O_2$
- $Mg-Fe-SiO-H_2-O_2$

- $AlO-H_2-O_2$
- $Al-SiO-H_2-O_2$
- $Al-Fe-SiO-H_2-O_2$

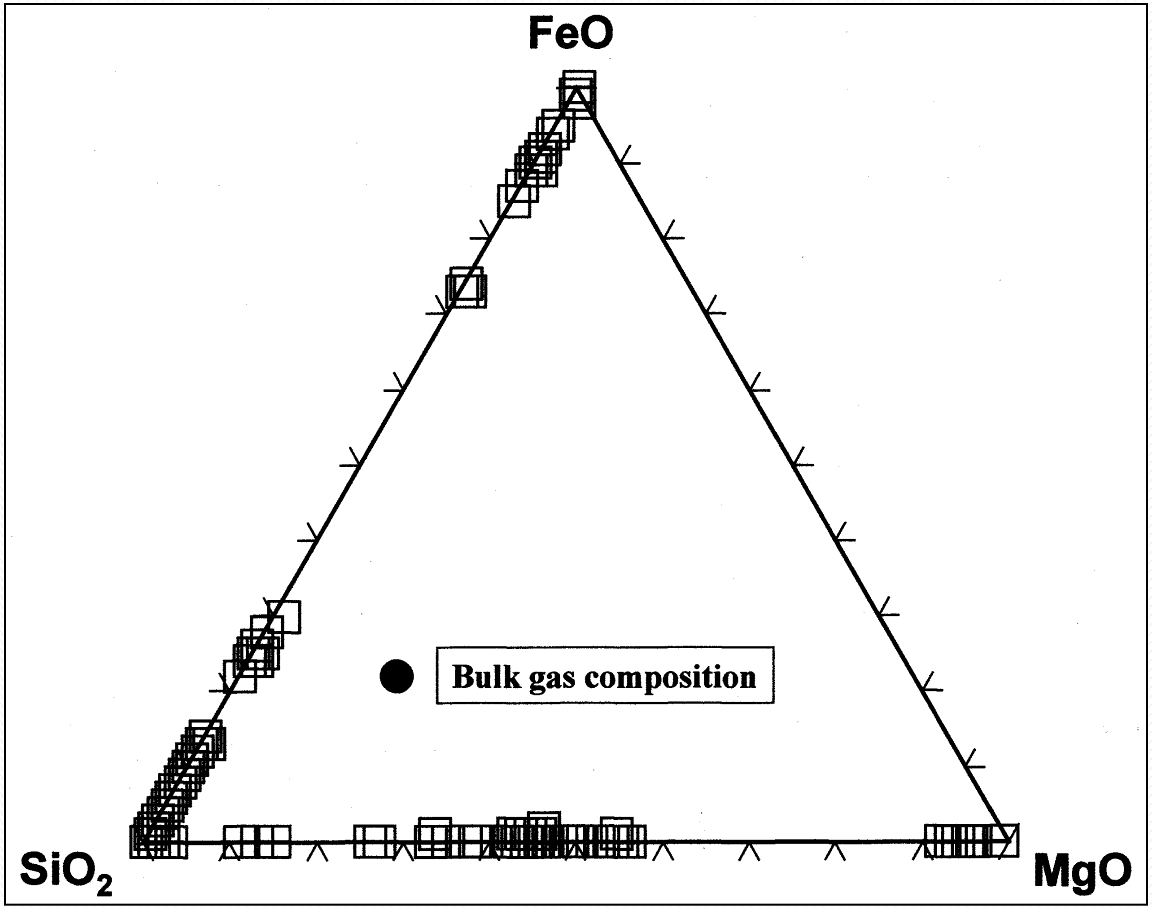


Everything worked as planned but the experiment failed…

- We produced amorphous oxide smokes of varying Mg, Fe, Al and Si composition quite easily and reproducibly.
- These grains were good starting materials for thermal annealing and hydrous alteration experiments.
- Changes in the IR spectra of these materials did not correlate with bulk composition…

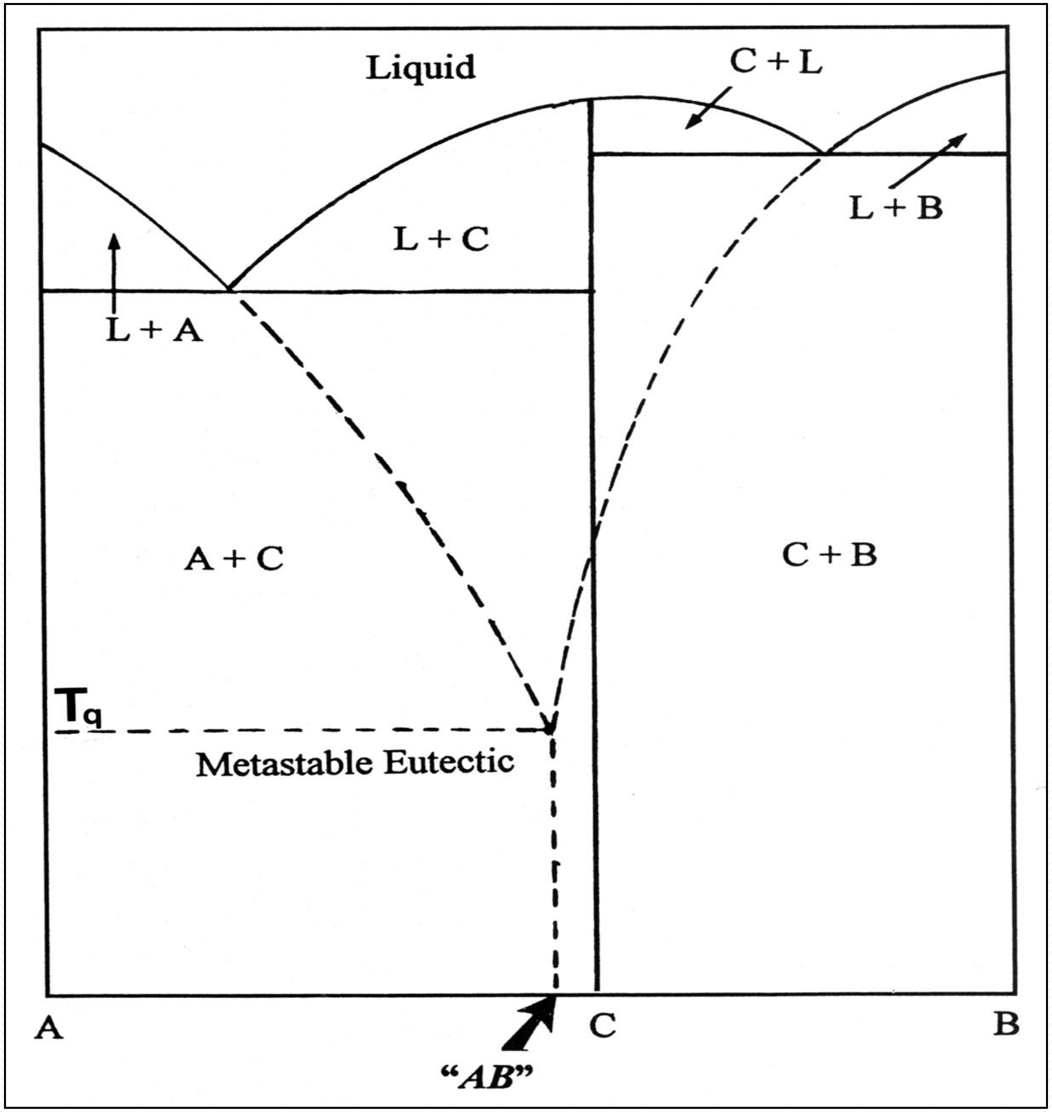
Mg-Fe-SiO-H_2-O_2 System:

Observed compositions of condensates less than 20 nm in diameter



Total mixing in the vapor phase, but NO mixing in the individual smokes.

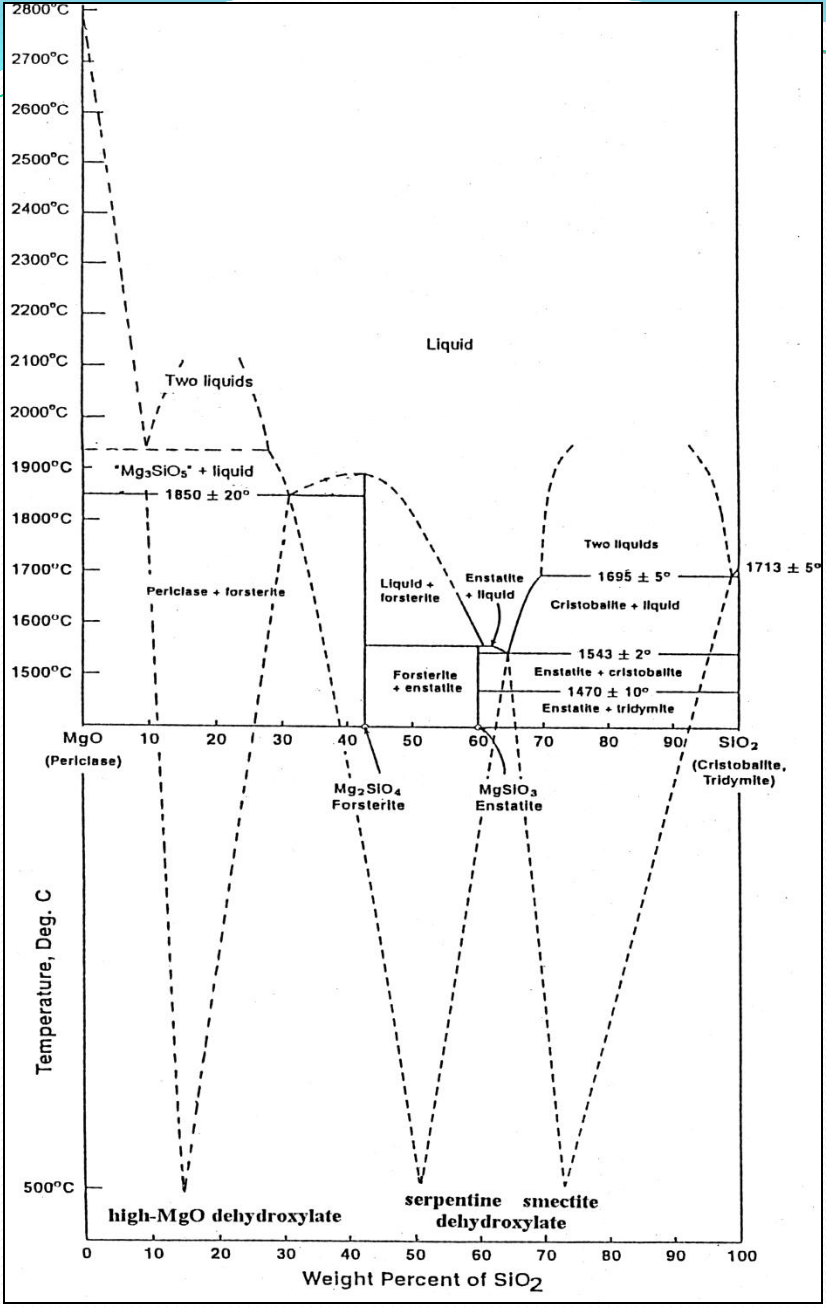
Metastable Eutectic Condensates

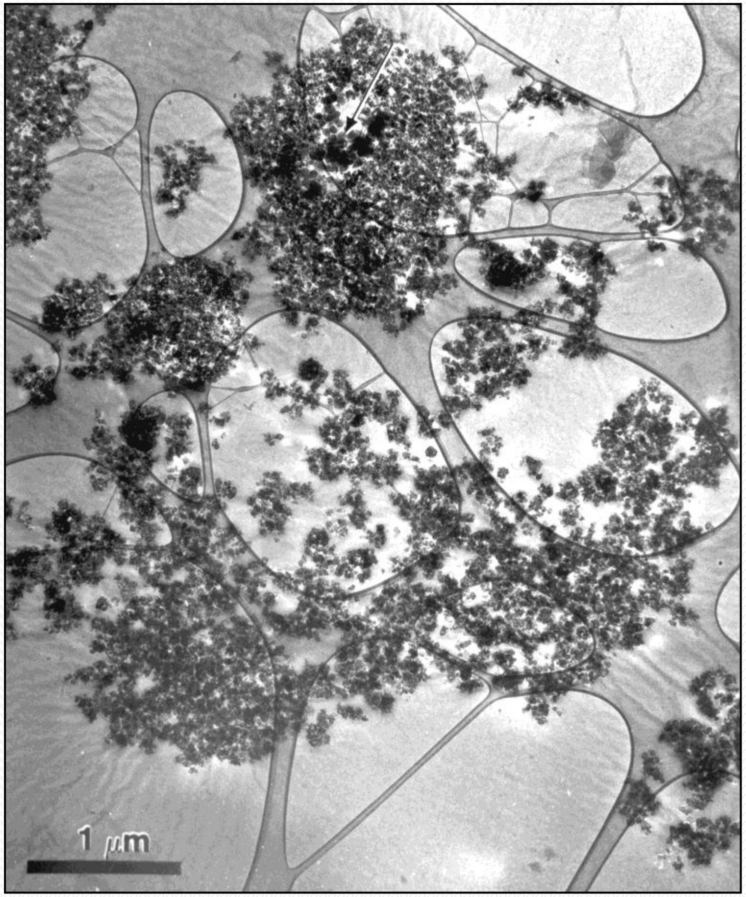


Condensates occur at specific chemical compositions even though they are amorphous.

These compositions correspond to extensions of stable phase boundaries.

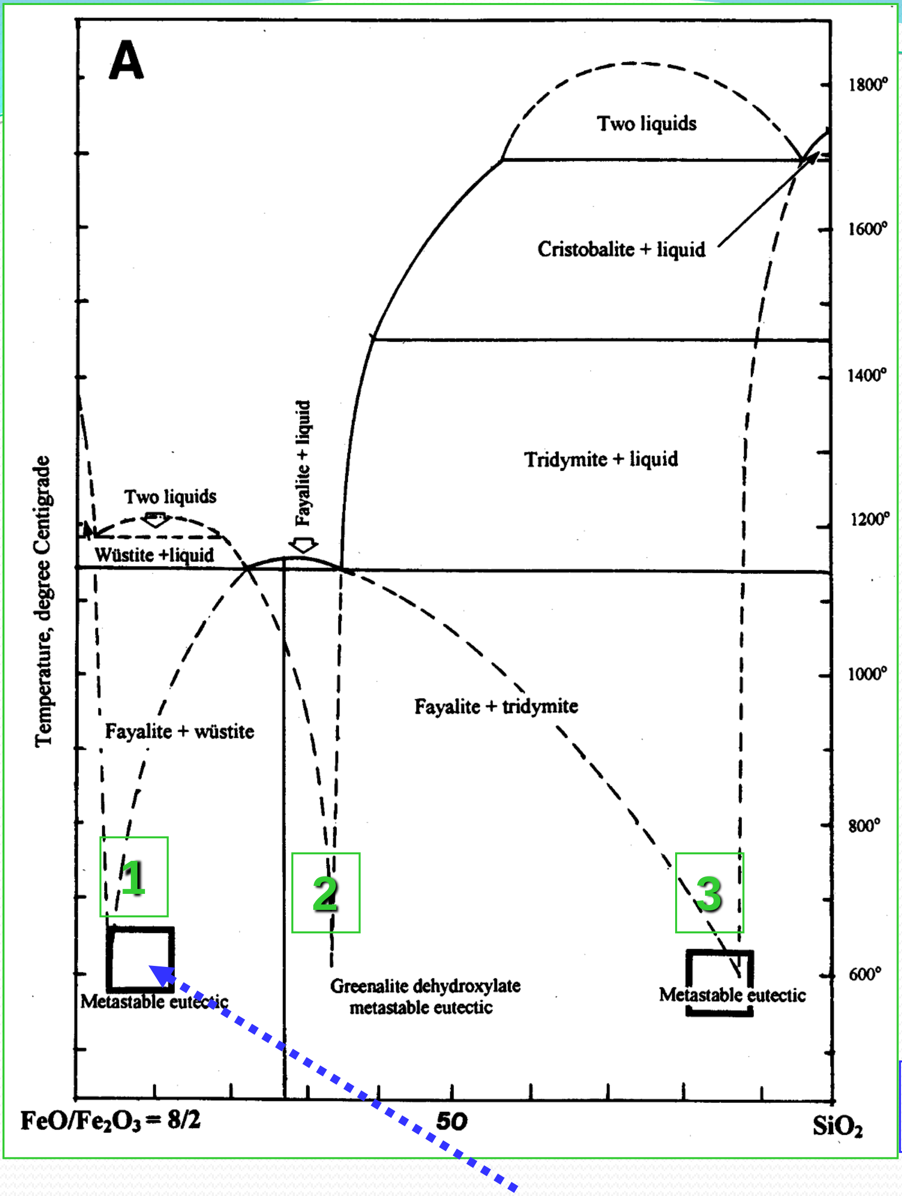
Mg-SiO-H_2-O_2

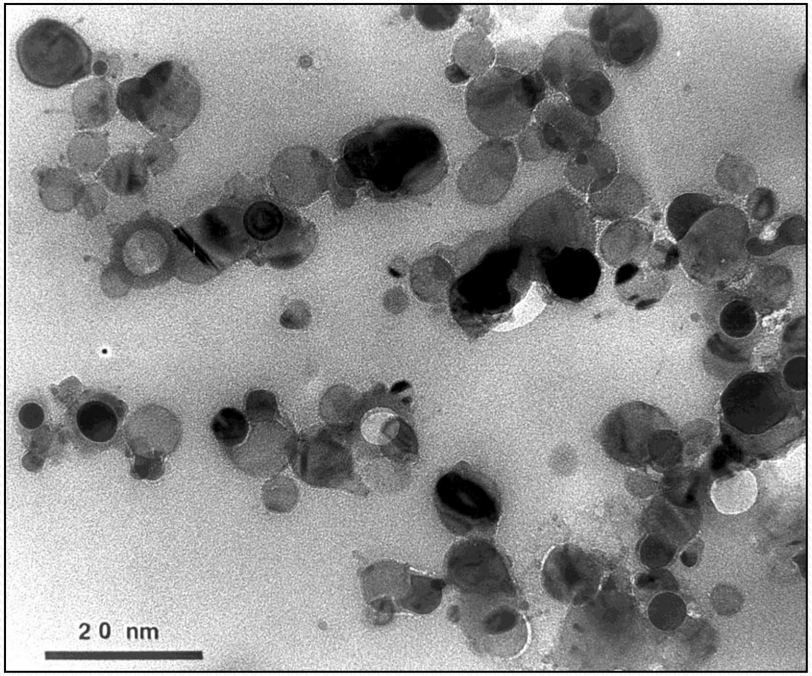




An ultrathin smoke section in epoxy on a holey carbon support film

Fe-SiO-H_2-O_2



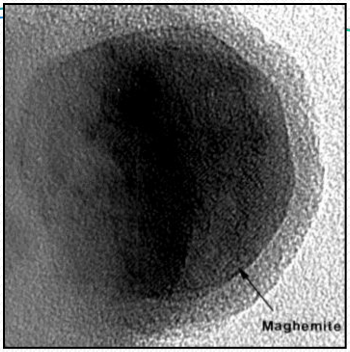


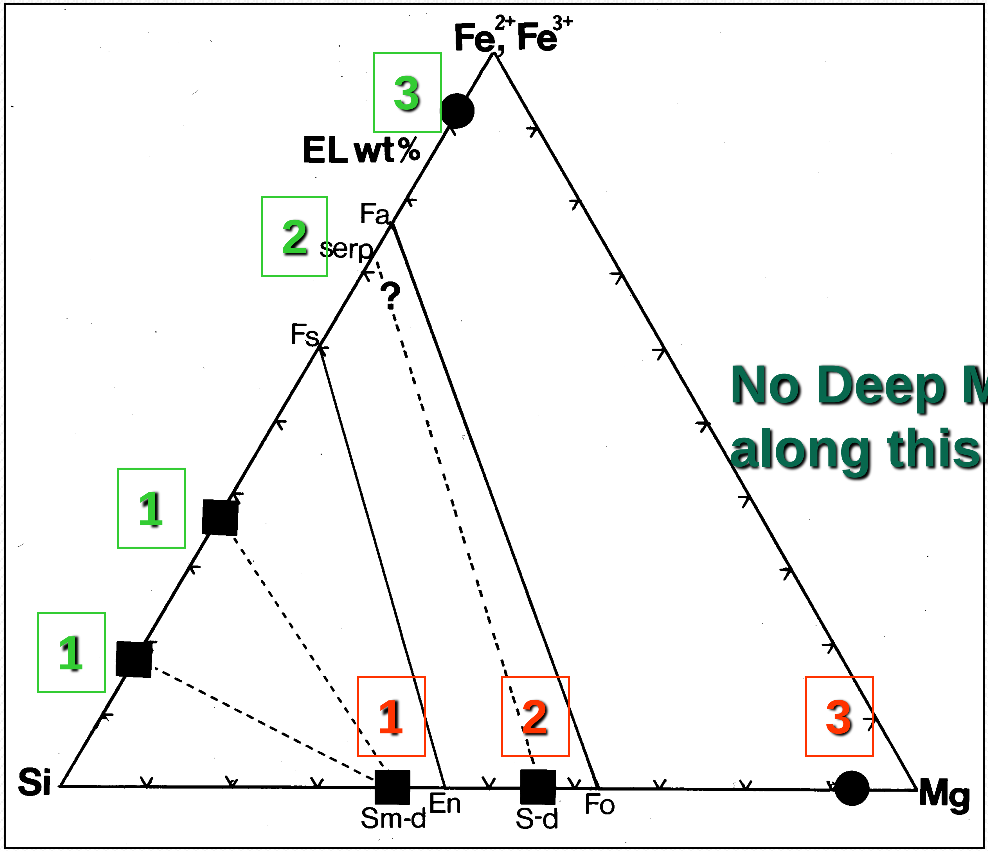
Gray background: embedding epoxy

Position shifts as a function of the FeO/Fe_2O_3 ratio

Metastable Condensate compositions in MgSiO and FeSiO smokes

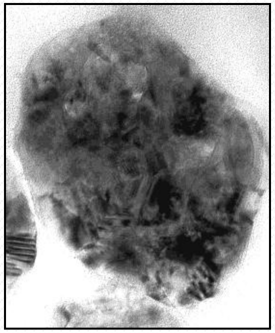
Fe_2O_3 (30 nm)



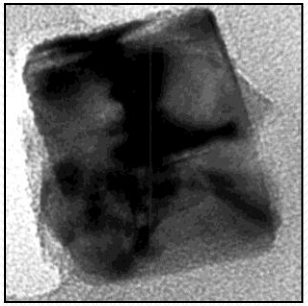


No Deep Metastable Eutectic along this join of the diagram

Tridymite (100 nm)



Periclase (55 nm)

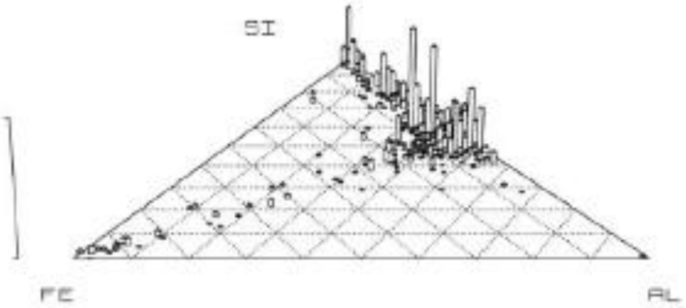


“Natural” Metastable Eutectics

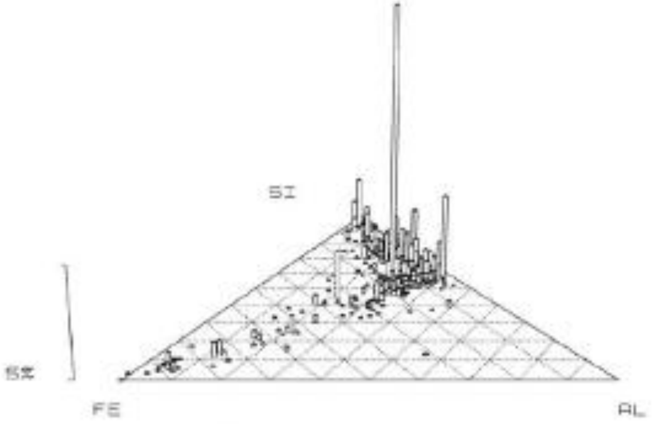
- ✓ **Volcanic ash**
- ✓ **Shocked materials (impact craters)**
- ✓ **Tektites**
- ✓ **Quenched meteors**
- ✓ **(coal-fires) Buchites**
- ✓ **Coal Fly ash**

Photo: Anupma Prakash © 2000

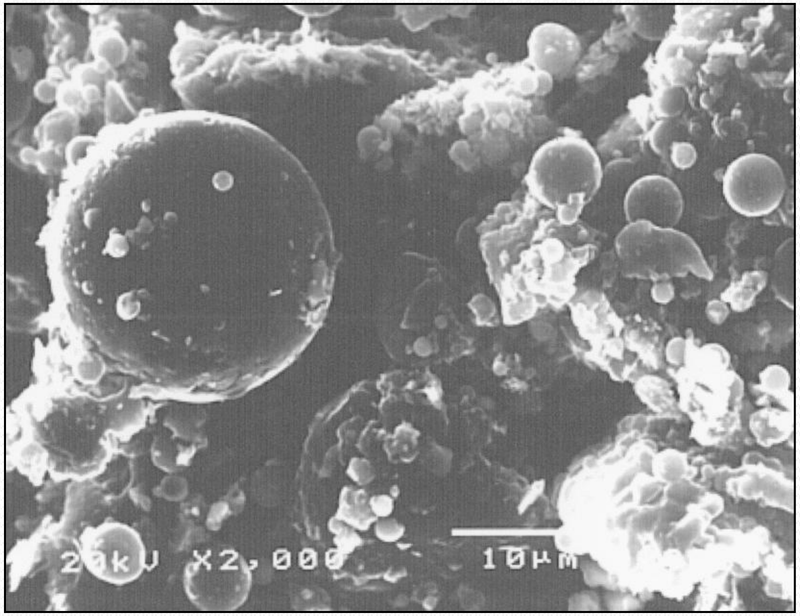
Coal Fly Ash (pm 2.5)



Ohio $PM_{2.5}$



Western Kentucky $PM_{2.5}$



Source: Chen et al. (2004) Fuel Proc. Technology, 85, 743-761

Who knew this happens?

- Deep Metastable Eutectics seem to be the preferred condensate compositions when refractory solids form from the vapor.
- Particles with Deep Metastable Eutectic compositions result from many natural and man-made vapor to solid transitions.
- We “discovered” this process completely by accident: our simple experiment failed and we went looking for an explanation.

Application to Silicate Spectra

- These experiments predict that amorphous iron silicate and magnesium silicate grains will condense as separate, but very well mixed populations in stellar outflows or in protostellar nebulae.
- Experiments demonstrate that magnesium silicates anneal faster than iron silicates.
- Therefore we have a natural explanation for the observation of pure magnesium silicate crystals in circumstellar outflows. & comets.

A Model of Nucleation & Growth

- Assume SiO is the primary nucleating species
  - Calculate nucleation flux based on SiO supersaturation
  - Calculate flux of Fe and MgO to ensure it is < SiO
  - Add Mg & Fe in proportion to their abundance to SiO clusters to make separate grain populations
  - Add an appropriate quantity of O to the grains
  - Track grain growth and composition over time
- Allow grains to coagulate both during & after growth
- Calculate Silicate Evolution Index to get the spectrum.


Hell

A Short Discussion of Nebular Carbon

- Set the stage:
  - Cosmic abundances and ISM grain models
  - Dust processing in protostars.
- Massive amounts of CO should be generated:
  - H_2/CO ratio should decrease by a factor of 7 – 20
- Why is there no observational evidence for a massive increase in nebular CO?
- I will argue for the existence of massive carbon cycles in protostellar nebulae that convert solid carbon to CO, then convert CO to organics.

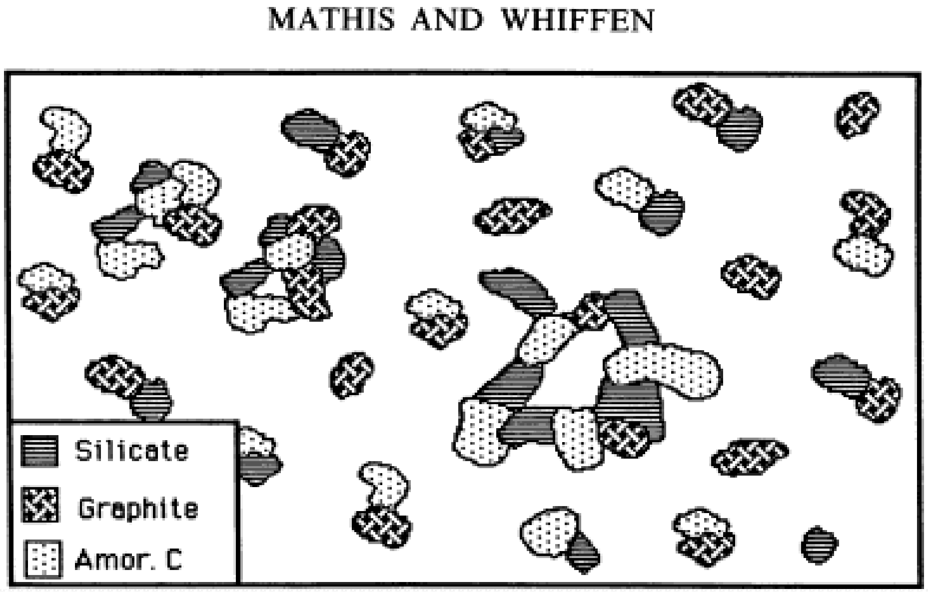
Just a Few Numbers to Get Started (all numbers in atoms: Si = 10^6)

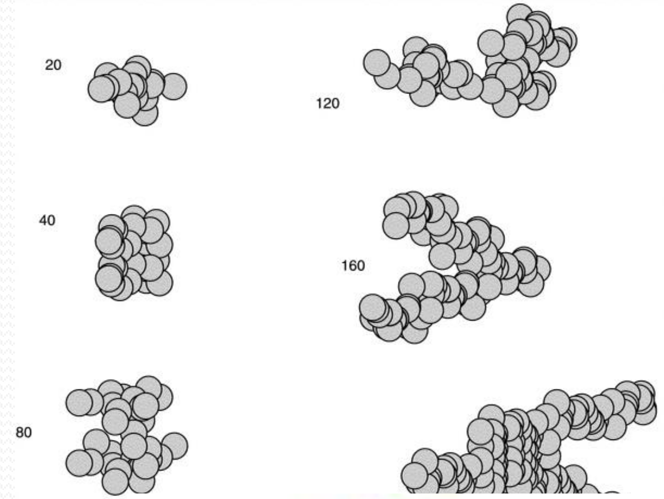
- Hydrogen Cosmic Abundance = 2.79×10^{10}
- Carbon Cosmic Abundance = 9.23×10^6
- Oxygen Cosmic Abundance = 18.8×10^6 so that oxygen is twice as abundant as carbon.
- Si + Mg + Fe Cosmic Abundance = 2.974×10^6 so that if Si(+4), Mg(+2) and Fe(+2=+3) then the amount of oxygen in dust = 4.087×10^6
- This leaves 14.7×10^6 atoms of oxygen in CO, CO_2, H_2O, OH and other oxides.

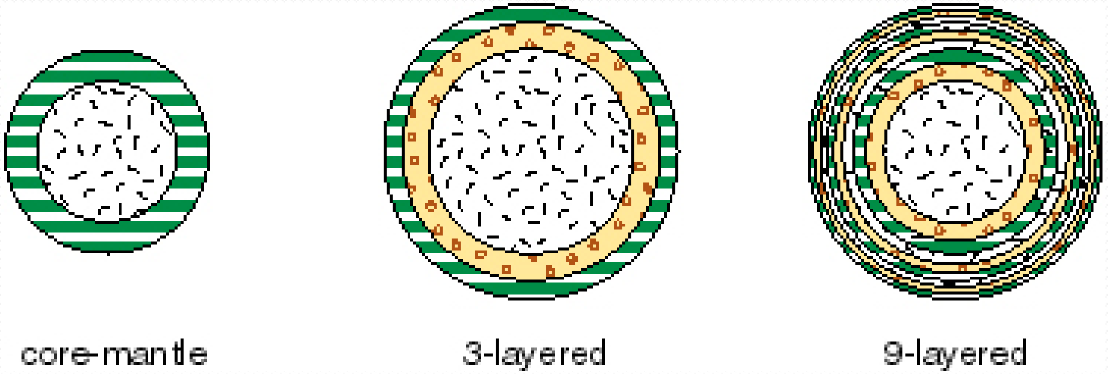
What is the abundance of the ISM's Carbonaceous Dust?

- For many interstellar grain models "90%" of the carbon abundance is in the dust in the ISM: this leaves a total of < **0.923×10^6** atoms of carbon in the gas phase.
- More carbon deposits on grains in cold clouds.
- The canonical H_2/CO ratio = 1.0×10^4: however $H_2/CO = 1.40 \times 10^{10} / 0.923 \times 10^6 = 1.51 \times 10^4$ so ~33% of this C is not present as CO (PAHs, CI, etc.).
- If ***ALL*** of the carbon were in CO then H_2/CO would be 1.51×10^3, ~7 times lower than the canonical value of 1.0×10^4.

How Are Carbonaceous Materials Related to Silicate Grains in the ISM?

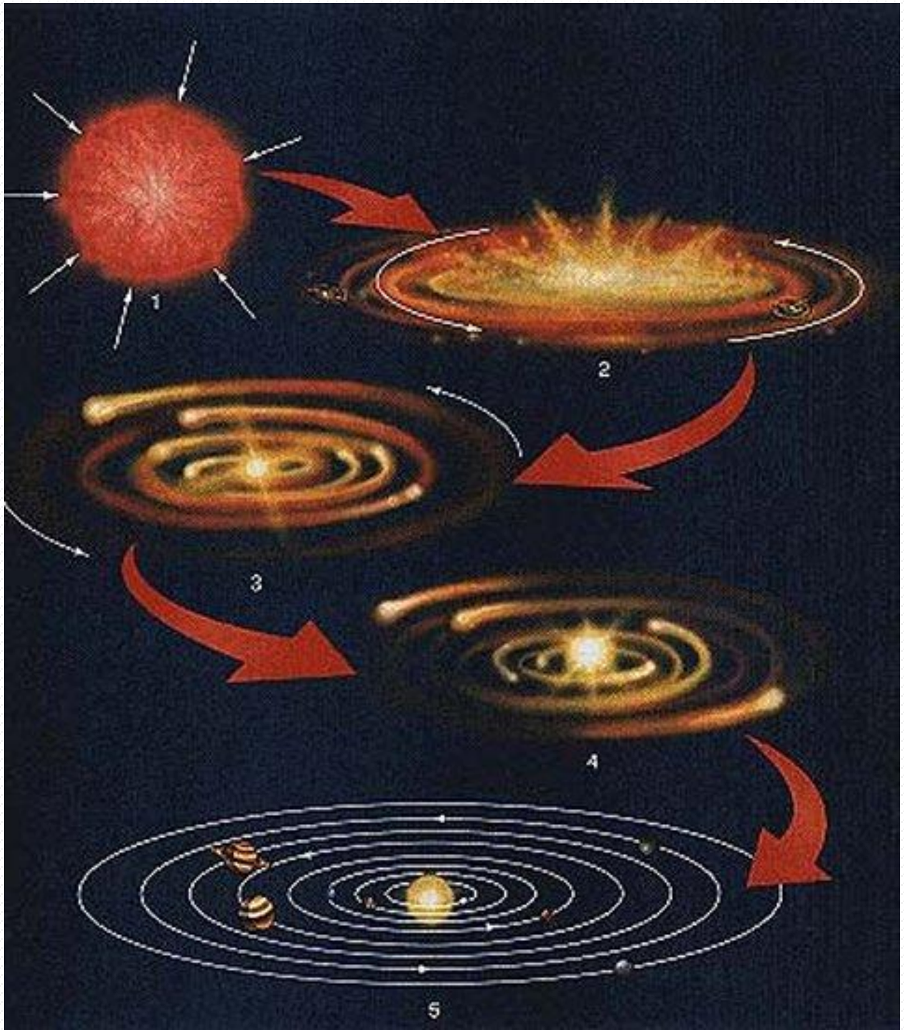






J.S. Mathis, G. Whiffen Composite interstellar grains Astrophysical Journal, 341 (1989), 808–822

What Happens to these Grains as the Solar Nebula Evolves?

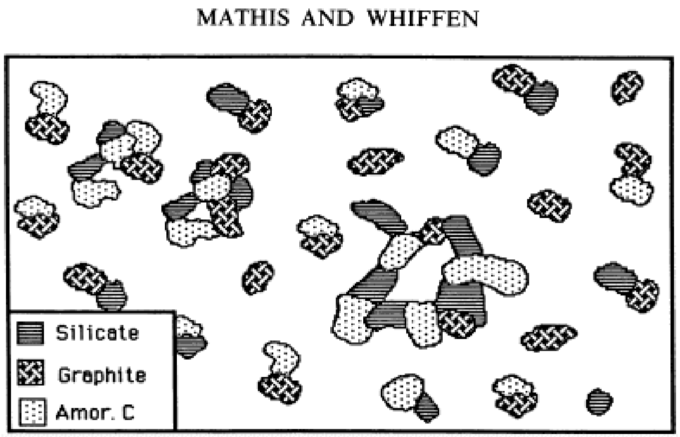


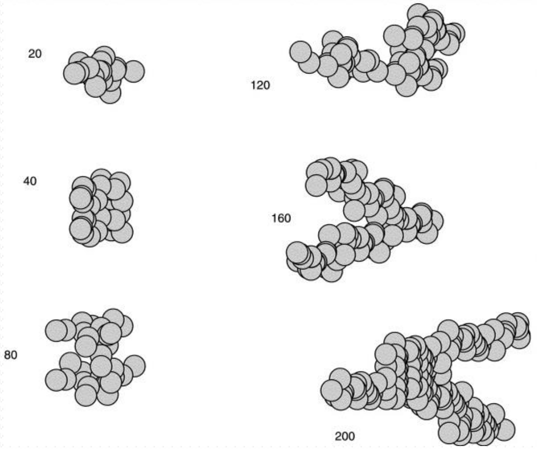
<u>In the Nebular Gas</u>:
Proximity to the Sun in the inner nebula, shocks, lightning, magnetic reconnection events heat the dust to high temperatures.

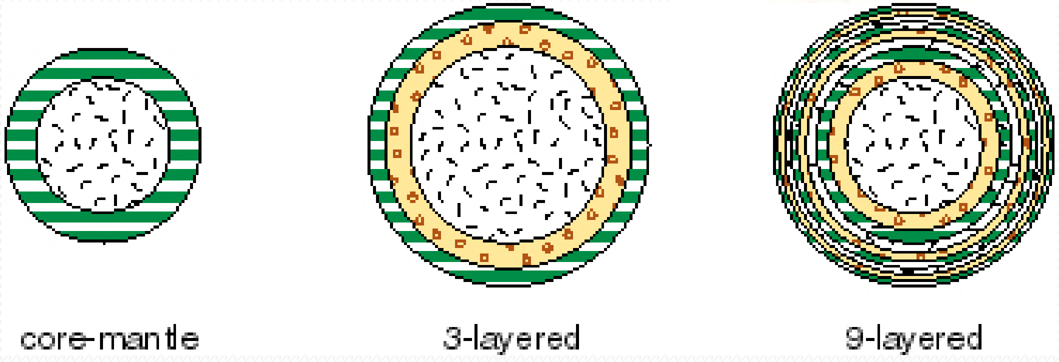
<u>In a Planetesimal:</u>
Gravitational accretion energy, decay of short-lived radioactive isotopes, large scale collisions, release of gravitational potential energy during differentiation all bring solids to high temperatures.

<u>Meteoritic Evidence:</u>
It has been known for many decades that more than 95% of matrix materials in even the most primitive meteorites was once either molten or totally vaporized.

An intimate mixture of metal oxides and carbonaceous material taken to high temperatures yields…







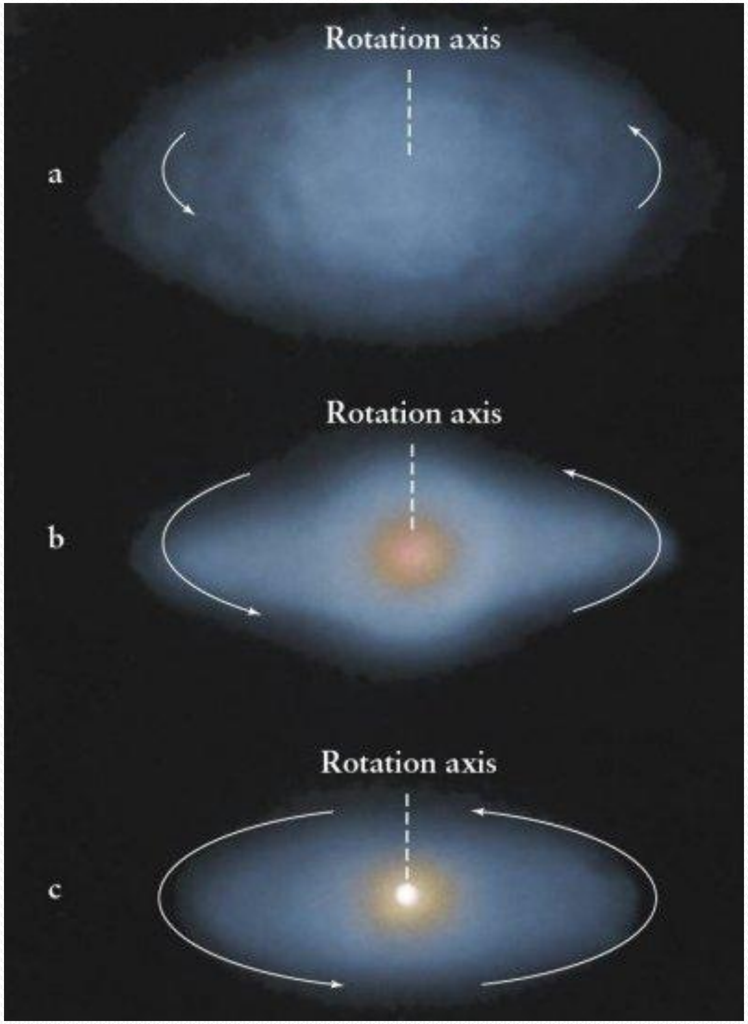
Metals plus CO

Where is the CO in protostars?

As the GMC collapses and the interior gets hot, the disk material in the inner regions of the nebula should release large quantities of CO.

The ratio of H_2/CO should decrease from the canonical value of 1×10^4 to ~1.5×10^3 as the nebular disk becomes less obscured by the collapsing molecular cloud and starts to dominate the molecular emission.

There are no reports of increased CO abundance in protostellar systems and no evidence for this process in meteorites.



The real CO increase should be much larger than the previous estimate.

- If, instead of working from the 'canonical' value of 10^4 for the H_2/CO ratio & cosmic abundances we used the fraction of carbon in dust:
    - If we assume that 90% of the carbon is dust and the rest is CO, then CO abundance (and the H_2/CO ratio) should increase by a factor of 10,
    - If we assume that only about half of the remaining carbon is in CO, then the H_2/CO ratio increases by a factor of 20 going from the GMC to the disk.

What might be the problem?

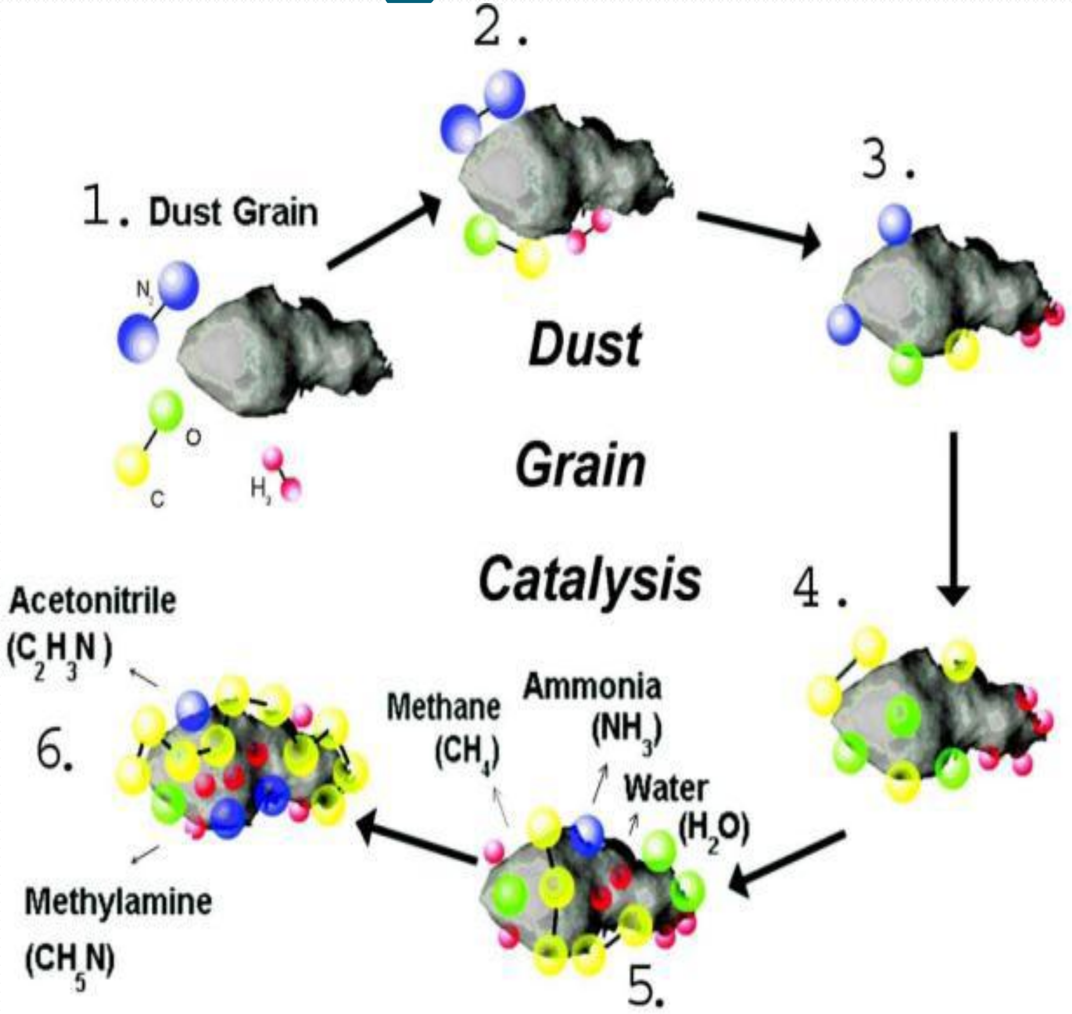
Radio Astronomers assume a H_2/CO ratio of 10^4 in their analyses. If they do not directly measure the ratio, they might not notice a change.

The change in H_2/CO ratio is going to occur very gradually since only the innermost region of the disk is hot enough to melt or vaporize rock.

There is evidence for melting, reduction and differentiation in meteorites, but it is hard to get a complete mass balance. Even if all carbon is converted to CO, there is still enough oxygen to oxidize all of the metals (by a factor of 3).

Some primitive meteorites contain >10% carbon as macromolecular "kerogen-like" material – a contradiction?

Fischer-Tropsch Type (FTT) Catalysis Might Provide a Solution



FTT synthesis has been discussed for many years as a source of carbon in meteorites.

Note: carbon in meteorites forms via many different processes, not just by FTT reactions.

If FTT is the solution, then it is a very important but little discussed process.

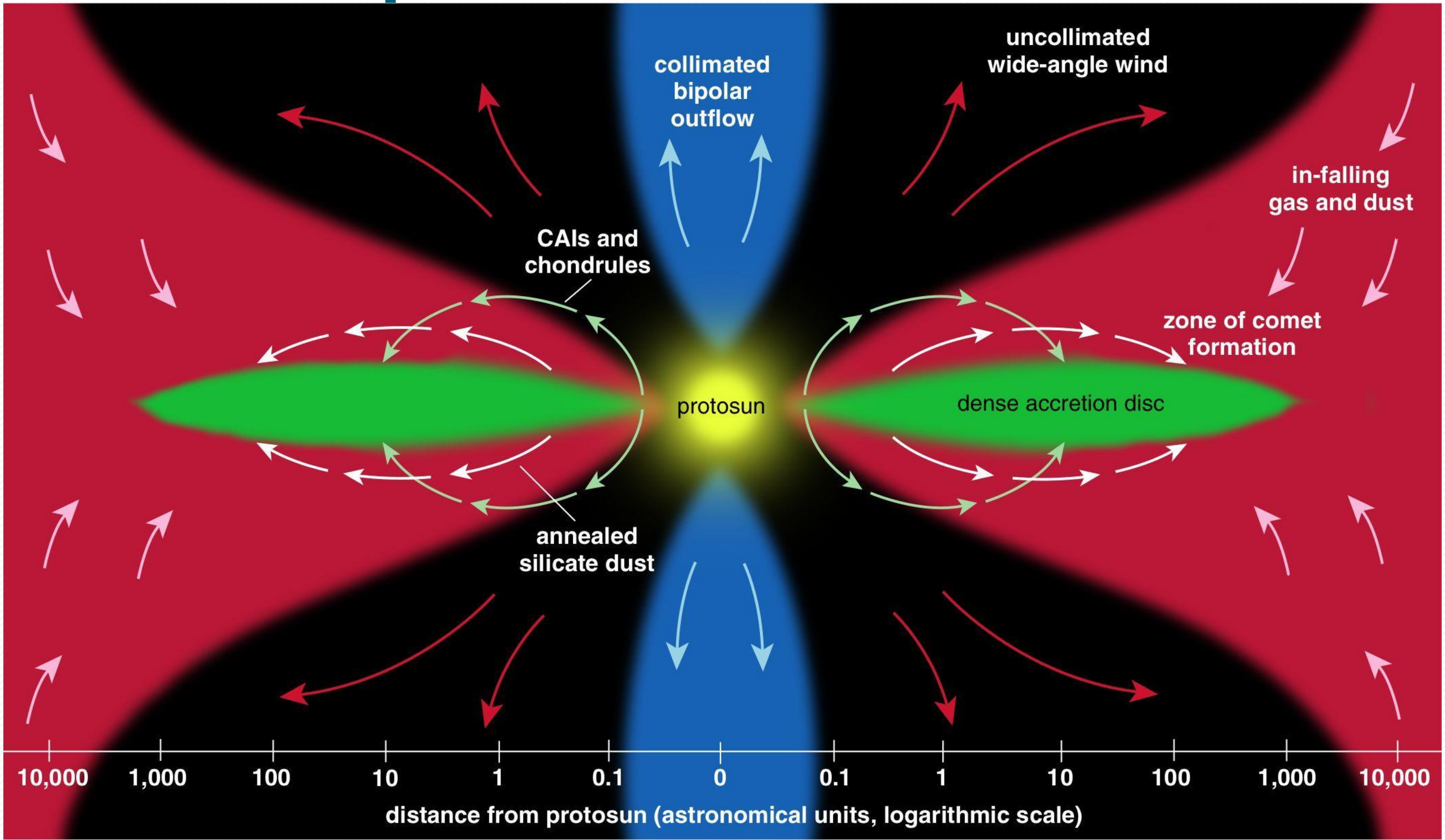
- Presolar graphite, silicon carbide and other solids comprise <1% of meteoritic materials.
- More than 90% or more of the carbon atoms in the presolar cloud were present as solid carbon.
- Energetic processes in the solar nebula should have converted most of the presolar carbonaceous dust into CO.
- If FTT processing then converted the CO back into solids, then >90% of the carbon is effected.

This implies a massive Carbon Cycle operating in protostellar nebulae…

The cycle continuously converts presolar carbon grains to CO – while also melting or vaporizing more than 95% of presolar silicates.

FTT reactions (on freshly condensed grain surfaces) then convert the CO into both organic molecules and macromolecular grain coatings.

Most activity occurs in the inner nebula, but the products circulate outward.



Carbon in Protostellar Nebulae

- ISM models predict that >90% of presolar C is in solids, yet <1% remains in primitive meteorites.
- Solid C is intimately mixed with presolar oxides: >95% of the oxides were melted or vaporized.
- High temperature processing of carbonaceous solids intimately mixed with oxides should produce massive quantities of CO – These are not reported.
- A carbon cycle that converts the CO into organics via FTT reactions could explain the loss of presolar carbon dust and the presence of meteoritic organics.

Thanks for your attention!