Gas and Condensation Chemistry in Astronomical Environments

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Outgassing Processes Workshop
Villefranche sur Mer, France, 27 May 2019

Overview

Dust & Gas in Astronomical Environments

Condensation Chemistry
Calculations
Examples: Solar Nebula,
Clouds in (sub)stellar objects,
Stellar Outflows (circumstellar shells, AGB)

Gas and dust chemistry important in many astronomical environments

For condensation/evaporation modelling major variables are:
overall elemental composition
temperature, pressure/density
gravitational effects; settling
Thermochemical vs. photochemical effects
kinetic effects
Quality of atomic/molecular parameters for thermodynamics, kinetics, photochemistry

Gas and Dust in Astronomical Environments

- **Galaxies** – Dust Lanes
  - Inter-Galactic & Interstellar Media (IGM,ISM)
- **Circumstellar Environs**
  - Star-forming Regions:
  - Proto-stellar & Planetary Accretion Disks
  - Dying Stars, Late-type/Evolved Stars:
  - AGB,PNe, SNe Ia, II; Release of elements
- Main-Sequence of Stars
  - Massive Stars (O,B,A) → Vega-type Debris Disks
  - Brown Dwarfs & Low-Mass Stars (M,L,T,Y) → Clouds
- **(Exo)-Planetary Systems:**
  - Planets, Moons, Asteroids, Comets, Meteorites, Interplanetary Medium (Zodiacal Light)
- **Planetary/Solid Objects Environs**
  - Atmospheres: Cloud-layer(s), Hazes, Aerosols
  - Surfaces: Hot & Cryo-Volcanism; Impact vaporization

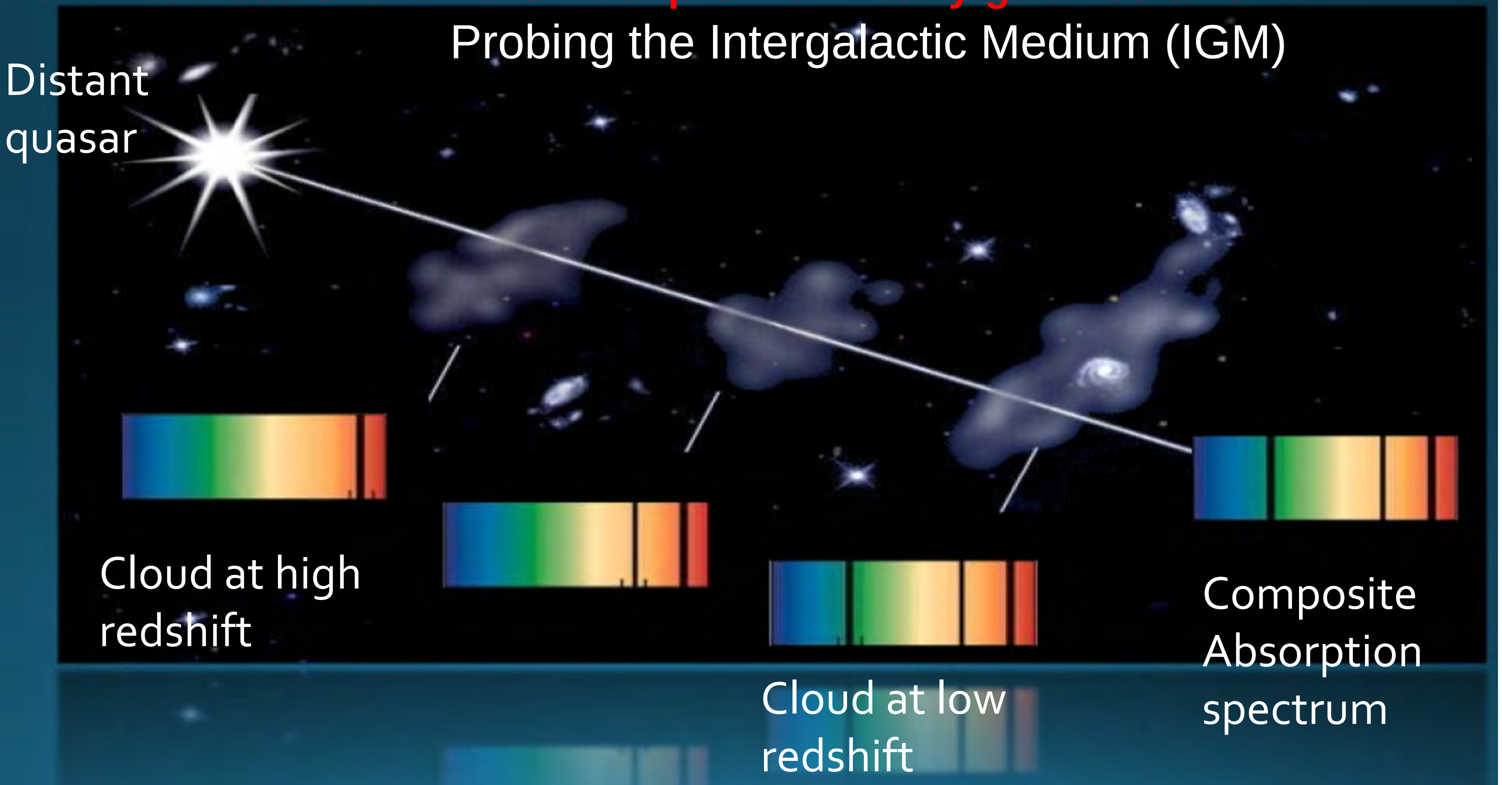
Ly-α absorption of neutral H-rich regions seen in spectra of background quasars (distant Active Galactic Nuclei) at early galaxy-forming times (at high redshift $2 < z < 5$)

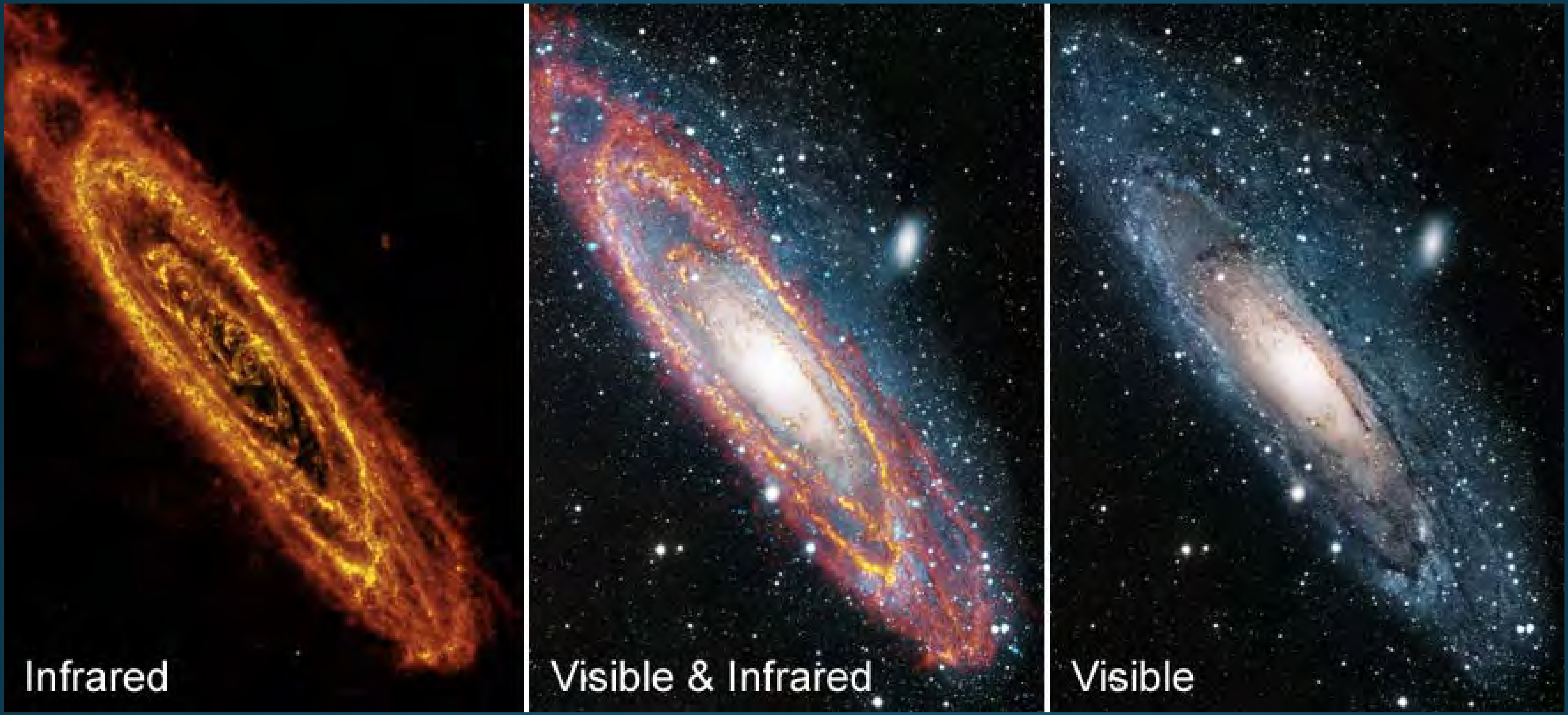
Mass density of neutral gas in DLAs is similar to mass density of stars found in galaxies today so DLAs are a measure of neutral matter for star formation in galaxies

Metal absorption lines: alpha elements made in core-collapse SNe II: Si and S
Fe-peak elements preferentially made in SN Ia: Fe and Zn

Elements made by same processes typically have similar relative abundances as seen in sun
But often found Si/S < (Si/S)sun and (Fe/Zn) < $(\text{Fe/Zn})_{\text{sun}}$
Gas has volatile S and Zn but less Si and Fe → dust prolific in early galaxies & IGM

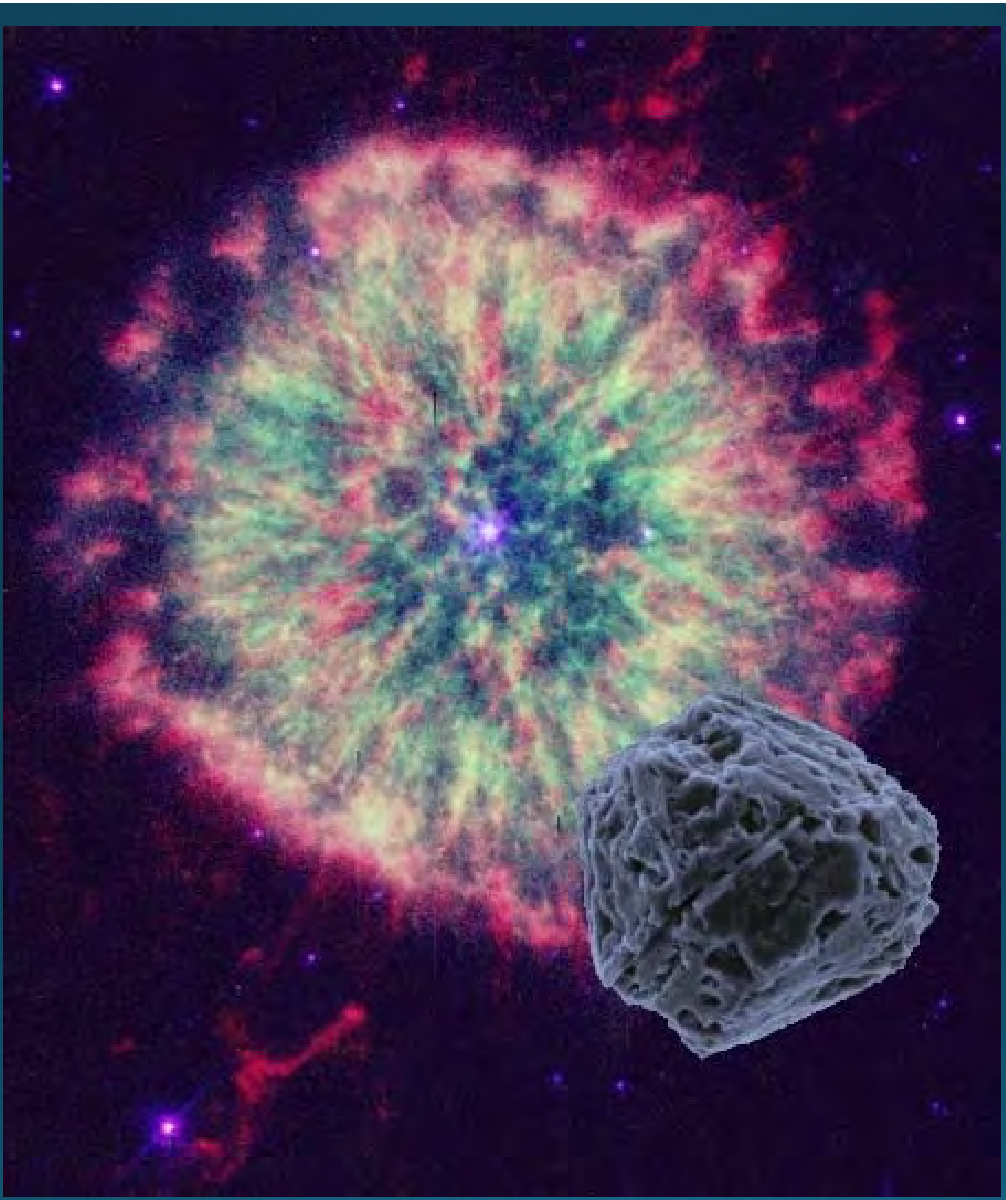
Damped Lyman alpha (DLA) systems





The Andromeda Galaxy shown in the far-infrared (left) and visible (right), with a composite image in the middle. *Image credit: Robert Gendler(visible) ; ESA / Herschel / SPIRE / HELGA (far-infrared).*

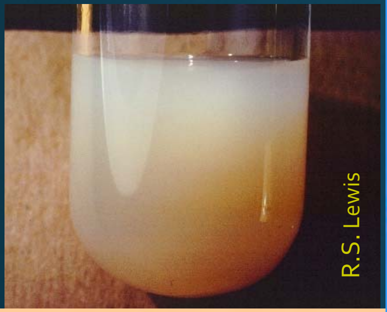
The Andromeda Galaxy from visible to far-infrared with a composite image in the middle.
Image credit: Robert Gendler(visible) ; ESA / Herschel / SPIRE / HELGA (far-infrared).

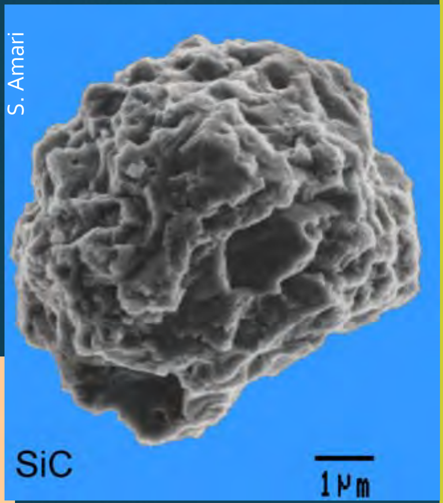


Studying the stars in the laboratory: A distant planetary nebula and a SiC grain isolated from meteorites that formed in such an environment

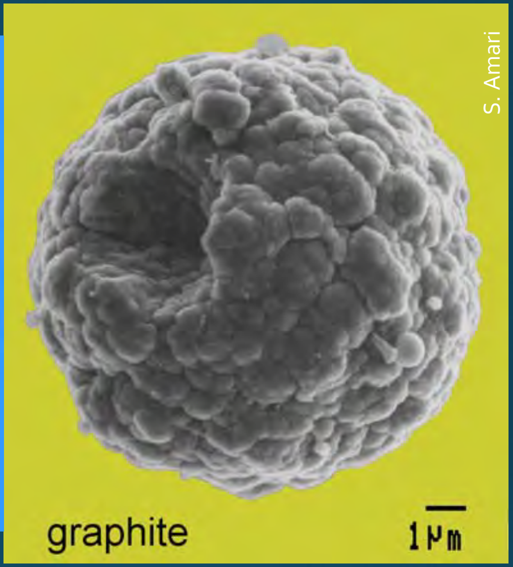
Genuine Star Dust in Meteorites

Nano-diamonds


R.S. Lewis



S. Amari



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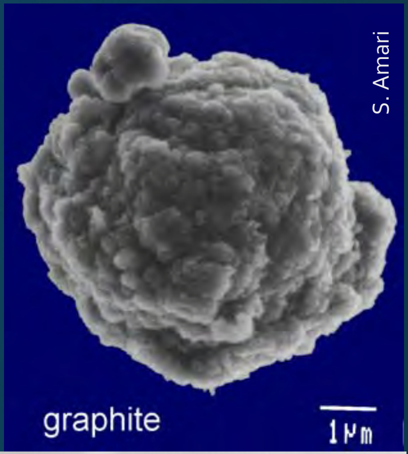

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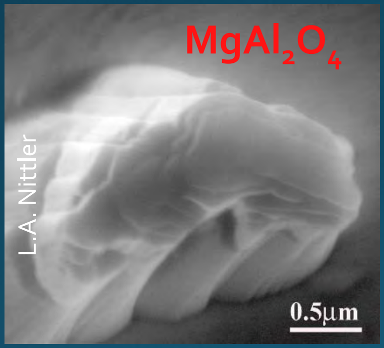
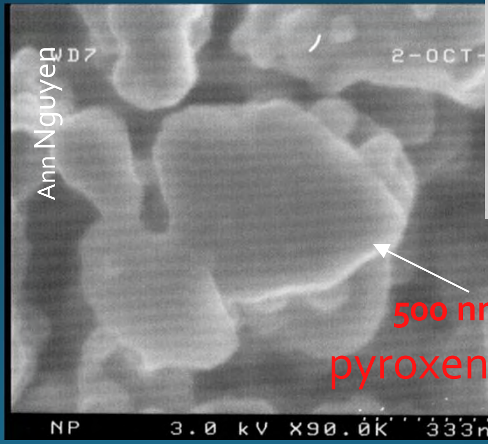


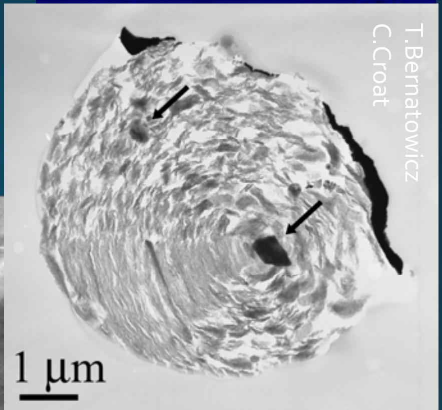
$MgAl_2O_4$

L.A. Nittler



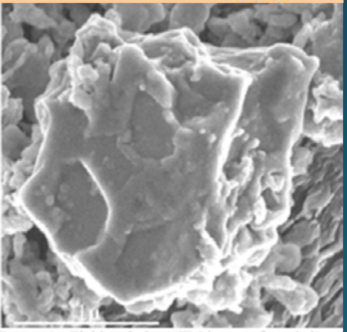
pyroxene

Ann Nguyen



T.Bernatowicz
C.Croat

Graphite with internal carbides


T.Bernatowicz

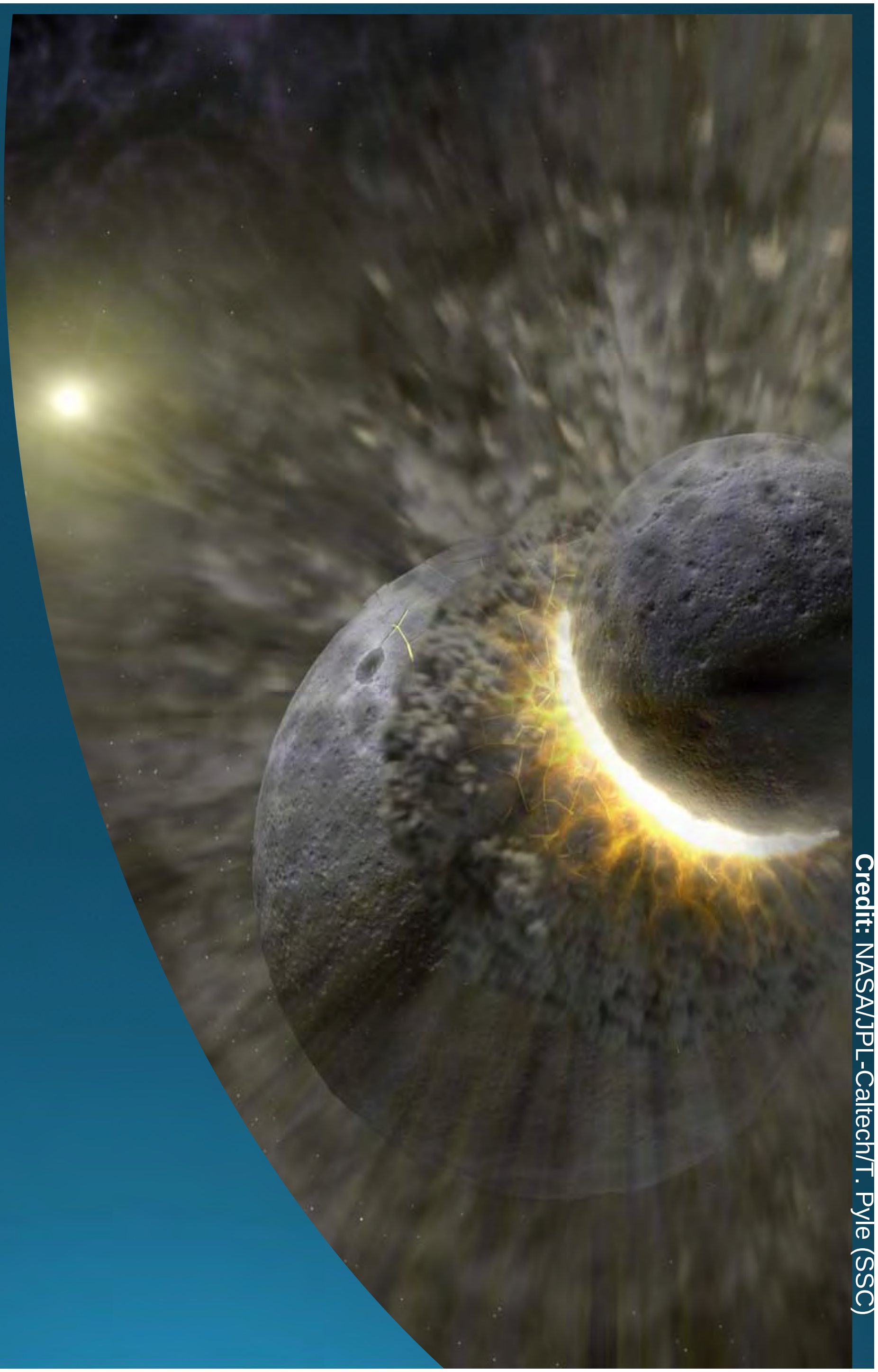
SiC in matrix

Vega-type debris disks

Proto Type System Vega (α-Lyr), A0V star, 2.1 M_{sun}

Stars with debris-disks, dust revealed by infrared excess emission to stellar radiation

- Dust from collisions of smaller objects in a planetary disk akin to Kuiper-Edgeworth belt in our solar system
- Remnant disk formed when stellar/planetary system formed
- Objects still dynamically active, need ongoing collisions to make dust
- Mechanical dust processing; impact heating effects akin seen in meteorites?
- Need very energetic events for evaporation; any signatures for recondensation of "fresh dust"?



Credit: NASA/JPL-Caltech/T. Pyle (SSC)

Inputs to Chemical Equilibrium Computations

Elemental Abundances

→ for solar, see Palme, Lodders & Jones, 2014, Treatise on Geochemistry; Lodders, Palme, & Gail 2009, Landolt Boernstein

Temperature, Pressure/Density of System

→ Adiabats (Solar nebula, planetary accretion disks, planetary atmospheres, circumstellar outflows…)

→ Representative total pressure of system for studying relative stability trends

Thermodynamic Properties/Equations of State

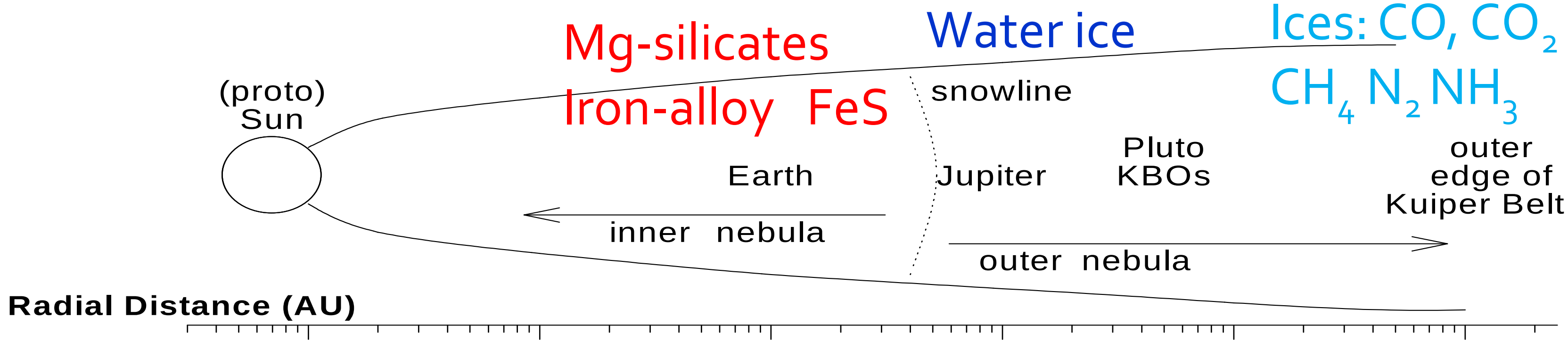
→ *Self-consistent set* of heats of formation, entropies, heat capacities as function of temperature for pure solid, liquid, and gaseous substances (e.g., Janaf Tables, Gurvich et al., primary literature); solid-solution properties/activity coefficients for trace elements dissolving in major mineral host phases, non-ideal fugacity coefficients for gases at high total pressures & near critical points.

Reliable Code

→ Gibbs-energy minimization codes (may not converge & run into local minima; number of possible coexisting phases may be limited to a few; may not return mass-balance.

→ Equilibrium-constant/Mass-action codes

Proto-Planetary Disks



Mg-silicates

Iron-alloy FeS

Water ice

Ices: CO, CO_2

CH_4 N_2 NH_3

(proto)
Sun

snowline

Earth

Jupiter

Pluto
KBOs

outer
edge of
Kuiper Belt

inner nebula

outer nebula

Radial Distance (AU)

0.01 0.1 1 10 100 1000

Temperature (K)	0.1	1	10	100	1000
Lewis 1969	7600	600	80	10	background
Cameron 1995	2200	470	100	20	background
Willacy et al. 1998	1500	700	50	background	→
Terquem et al. 2000	1500	600	50	background	→

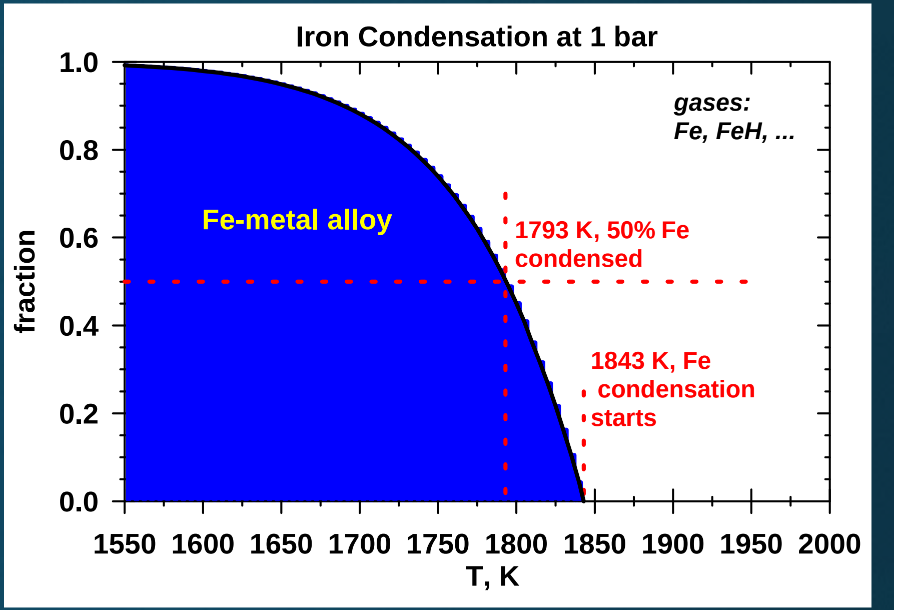
Pressure (bar)	0.1	1	10	100	1000
Lewis 1969	$7\text{x}10^{-1}$	10^{-4}	10^{-7}	$6\text{x}10^{-11}$	background
Cameron 1995	$3\text{x}10^{-2}$	$4\text{x}10^{-5}$	$6\text{x}10^{-8}$	$9\text{x}10^{-11}$	background
Willacy et al. 1998	$4\text{x}10^{-3}$	10^{-5}	10^{-8}	$3\text{x}10^{-10}$	background
Terquem et al. 2000	10^{-2}	$6\text{x}10^{-6}$	$2\text{x}10^{-8}$	10^{-11}	background

Thermochemistry vs. Photochemistry >>

Example Condensation & Evaporation:

Fe (g) = Fe (s)

For condensation: $a_{Fe} = 1 = K\ P_{Fe} = K\ P_{vap}$
or $P_{Fe} = P_{vap}$
Partial pressure of monatomic Fe must equal monatomic Fe saturation vapor pressure over pure solid or liquid Fe.



At thermodynamic equilibrium: $K = a_{Fe}/P_{Fe} = a_{Fe}/X_{Fe}\ P_{tot}$

K = equilibrium constant , T-dependent

a = thermochemical activity of solid or liquid , $a \equiv 1$ for pure substance;

$a_{Fe} = 1$ is the requirement for condensation.

P_{Fe} = partial pressure of condensing gas (here monatomic Fe)

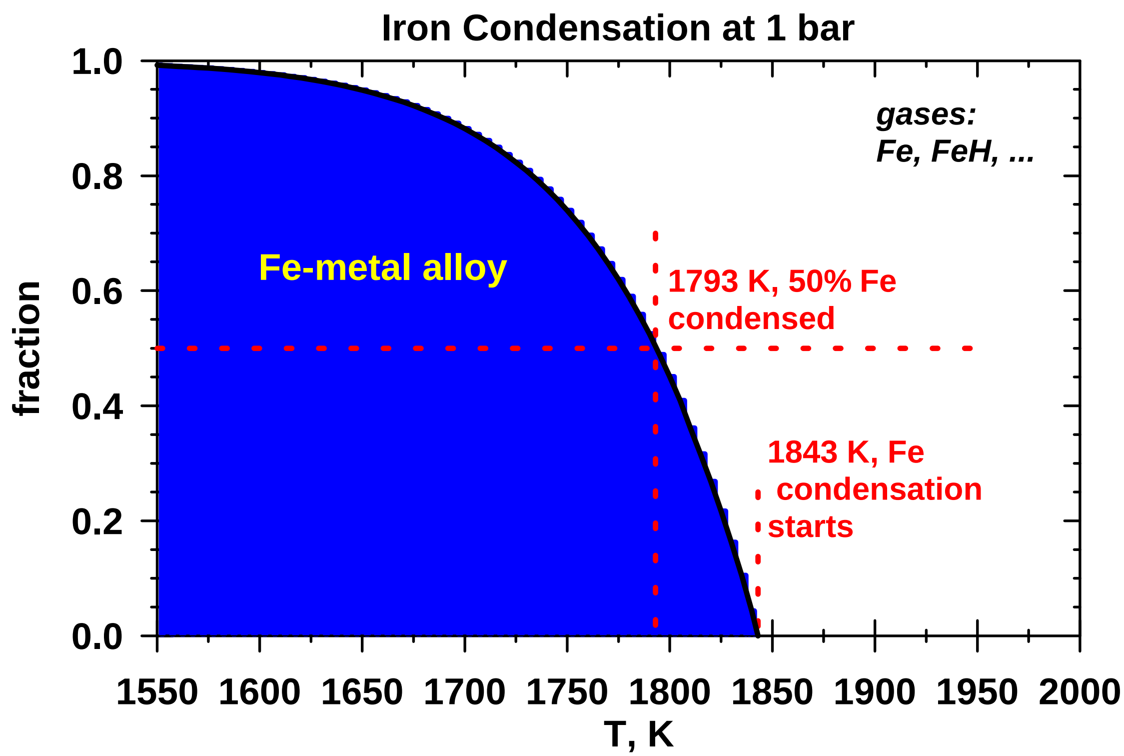
$P_{Fe} = X_{Fe}\ P_{tot}$

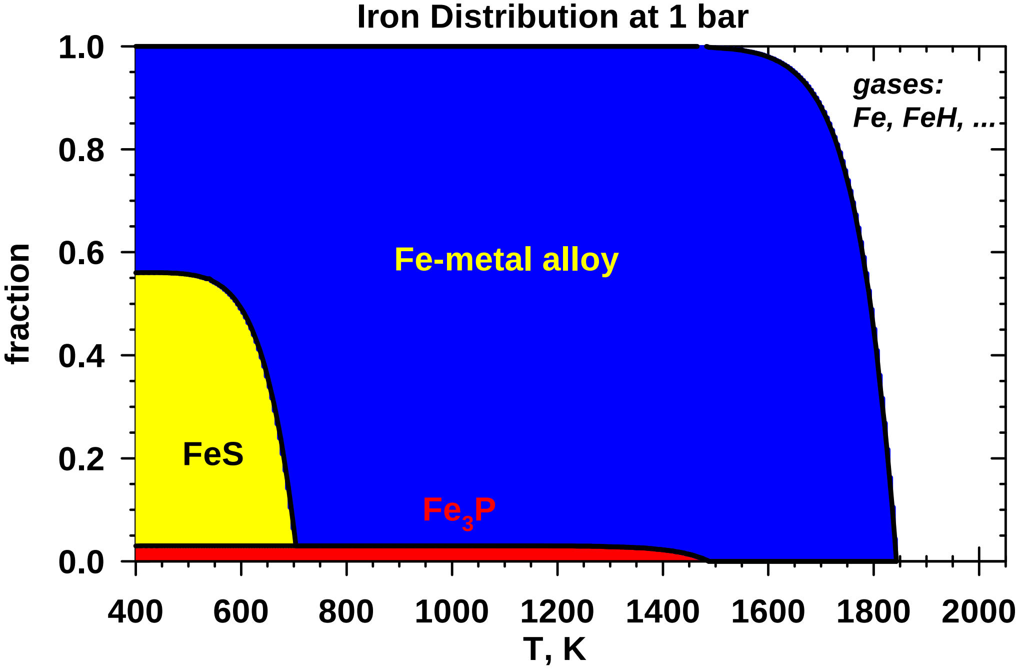
X_{Fe} = mole fraction of condensing gas in gas phase; follows from overall composition, X_{Fe} = Fe atoms / (Σ all other atoms + molecules in gas)

P_{tot} = total gas pressure of system; usually given/assumed

For $a_{Fe} = 1$, K is just the inverse of the saturation vapor pressure for iron gas: $K = 1/P_{vap}$

Saturation Ratio: $S = P_{Fe}/P_{vap,Fe} = 1$ at equilibrium
Kinetic inhibition may require super-saturation S > 1 for condensation.


Iron Condensation at 1 bar


Iron Distribution at 1 bar

Corundum Condensation -- see Lodders 2003 for details

$2\,Al\,(g) + 3\,H_2O = Al_2O_3\,(s) + 3\,H_2\,(g)$

$\log K_{eq}\,(T) = \log a_{Al2O3} + 3 \log X_{H2} - 2 \log X_{Al} - 3 \log X_{H2O} - 2 \log P_{tot}$
$= A + B/T$

** Find K_{eq} (T) data

** Calculate the X_{Al} the from gas chemistry for all elements and gases

for given T and P_{tot} *equilibrium AND mass-balance*

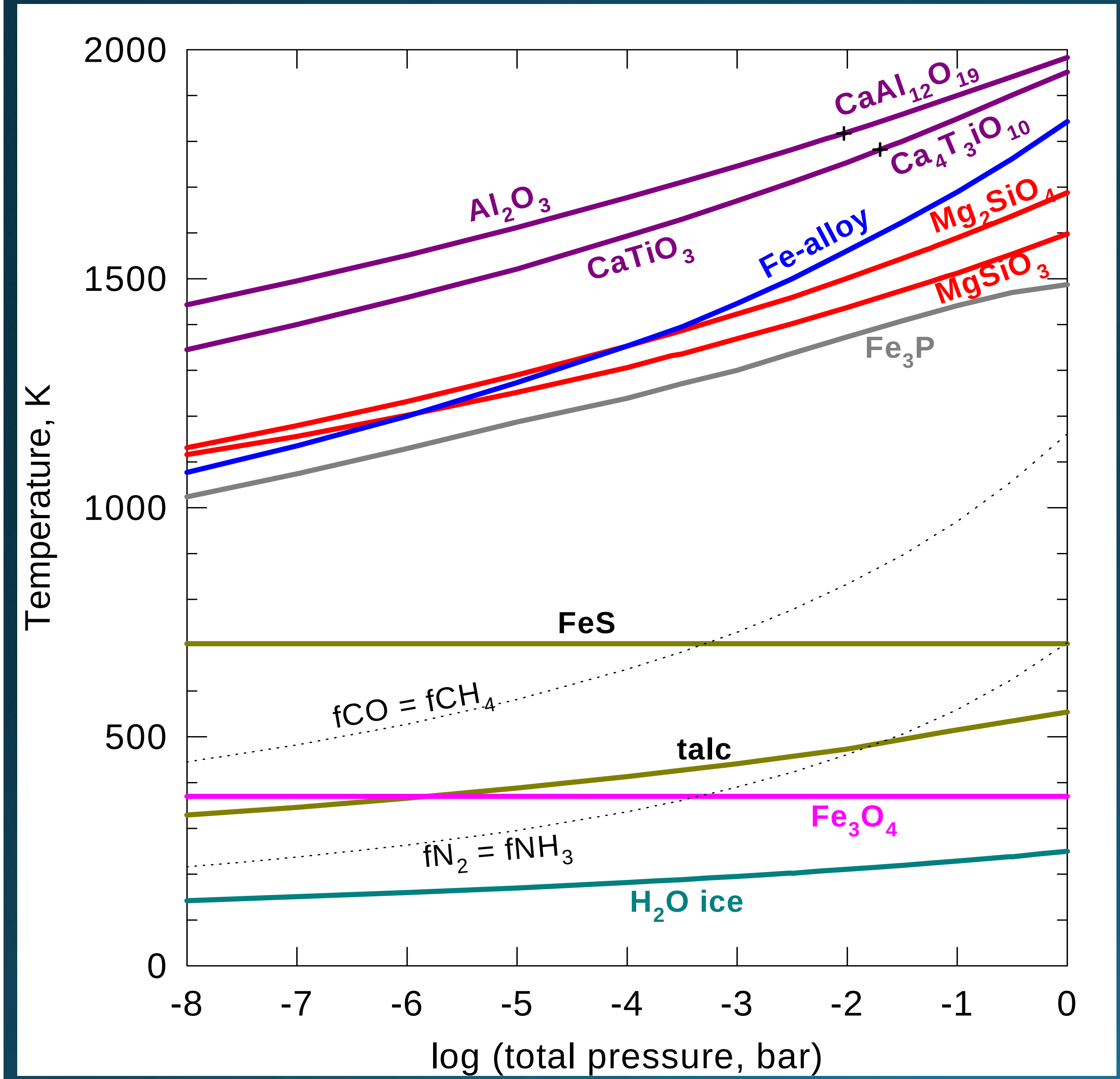
** also calculate corundum activity with K_{eq}

** Find solution where $a_{Al2O3} = 1$

$P_{Al} = P_{tot} X_{Al}$ and approx. $X_{Al} \approx P_{Al} / (P_{H2} + P_{He}) = P_{Al} / (A_H/2 + A_{He})$
where A_i = abundance

Set $P_{Al} \approx A_{Al}$ ONLY IF P_{Al} is the **major/only** Al-bearing gas
– but lots of abundant Al-gases Al, AlO, HAlO, Al2O…

Solar Composition System: Condensation/Evaporation Sequence



Ca-Al-Ti oxides

Change in sequence
Above ~10^{-4} bar, **metal alloy** before **Mg-silicates**

High-T phases > 600 K in solar composition make ~0.5% of total mass

Troilite (FeS)

FeO into silicates: higher H_2O/H_2 ratio or higher dust/gas ratios
Magnetite, Hydrated silicates, e.g talc →
KINETICS

Water Ice
~ 130 – 180 K

All That is in the Planets was in the Disk,
But Not All That was in the Disk is in the Planets

Start with Solar system **elemental abundances**
(e.g., Palme, Lodders, Jones 2014, Treatise of Geochemistry)

Chemical & physical fractionation
***** of compounds *in* the accretion disk**
Condensation & Evaporation, Phase Stabilities f(T,P,r,z,t)
Dynamical & Density Sorting (gravity), Radial Mixing (ices)
→ feed-back into disk structure (opacity, redox state)
****** of planet-building blocks**
Thermal stabilities of solids and liquids (volatile retention)
Iron oxidation/reduction reactions (metal content)
Extent of gas-solid equilibria at low temperatures,
e.g, sulfides, hydrated silicates
gas giant planets also H_2 & He gas accretion efficiencies with time
******* fractionations *after* dissipation of the gaseous disk**
Outgassing, impact processing (Moon), debris disks

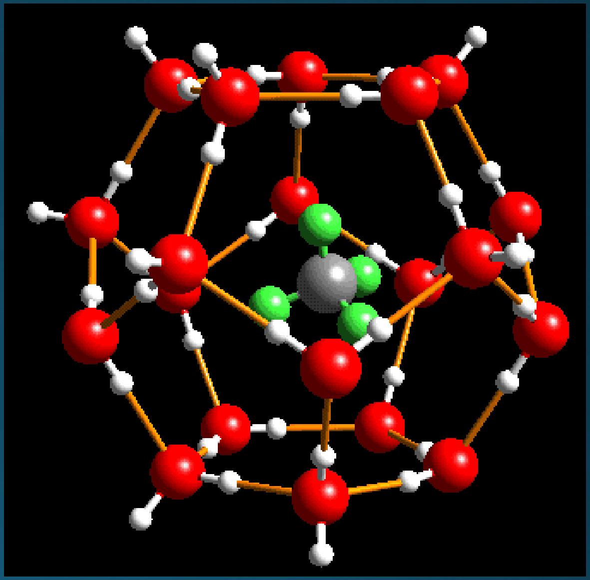
Major components for solar composition

Gases H_2, He not condensing

Rock: Metal, Silicate, Sulfide(s). Trace element into solid-solution(s).

Ices: H_2O; CO, CH_4, CO_2, NH_3, N_2, and/or clathrates or hydrates thereof

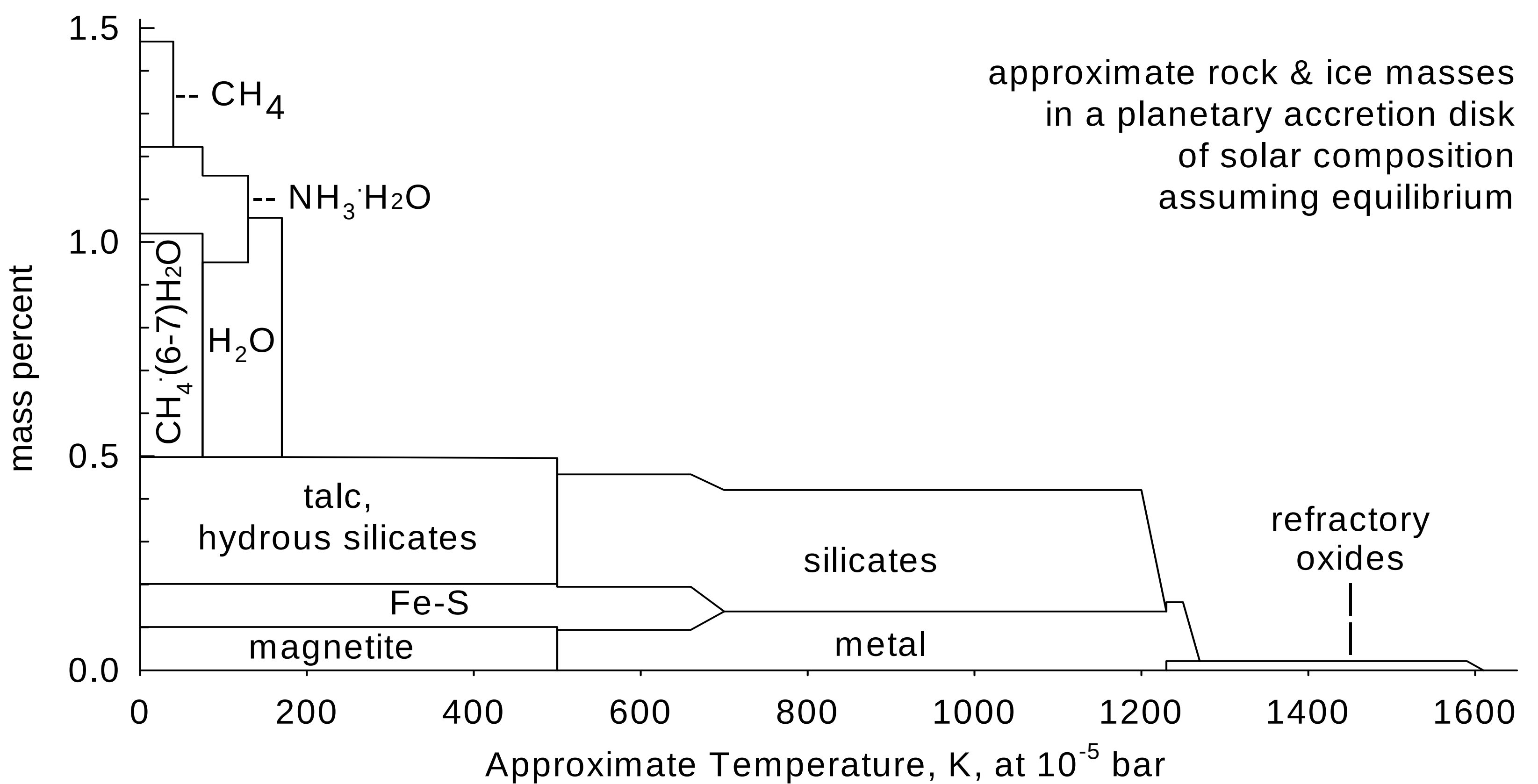
also noble-gas clathrates



Methane Clathrate:
Methane is a guest molecule
Water molecules form a cage
through H-bond bridging.

ice composition very dependent on kinetics

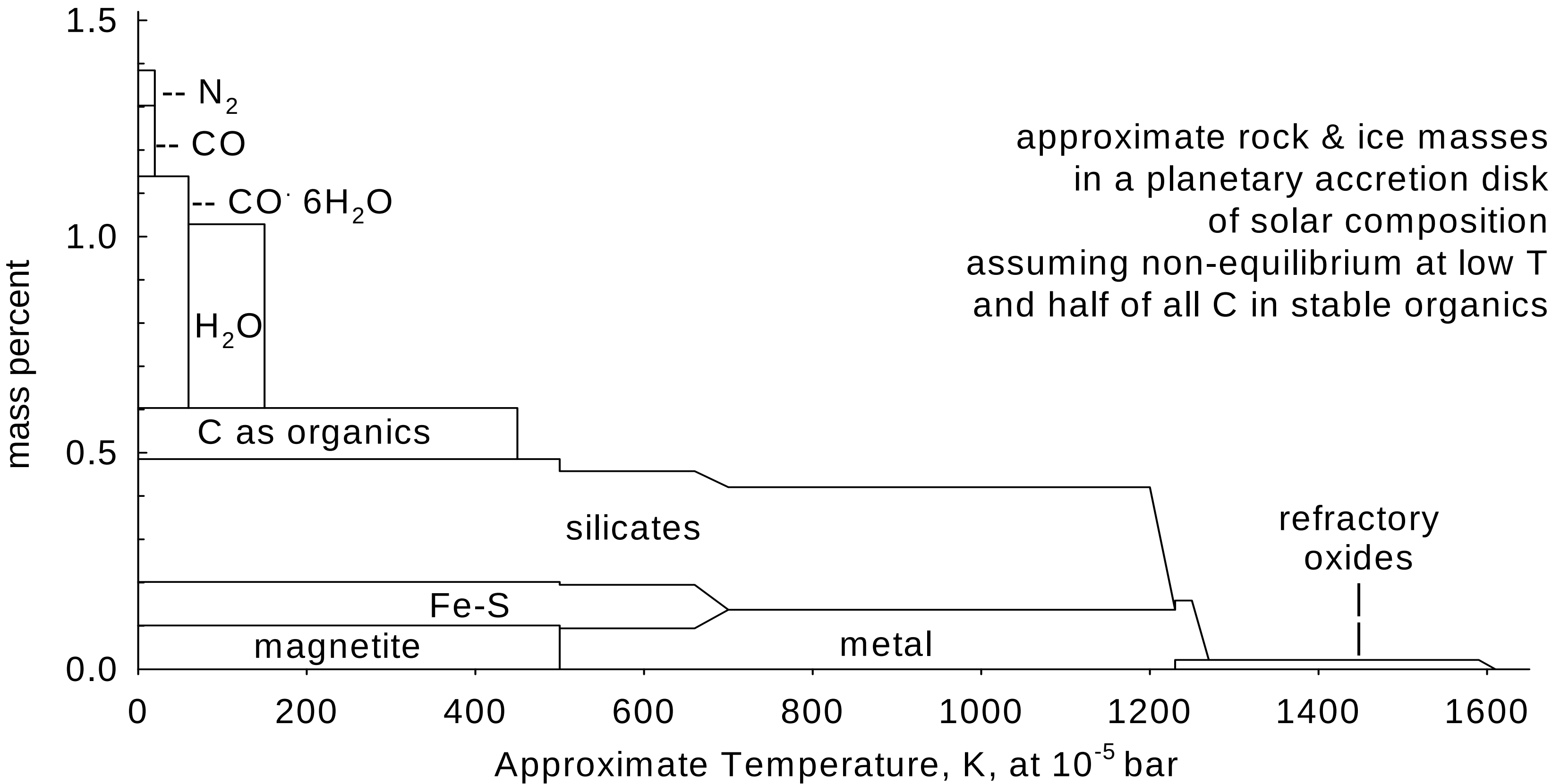
Conversion of CO (gas) to CH4 (gas); N2 (gas) to NH3 (gas)



equilibrium condensate mass distribution

But: not all low-T phases can form within the solar nebula lifetime

No hydration of silicates in “vacuum”; only little methane gas, little ammonia gas

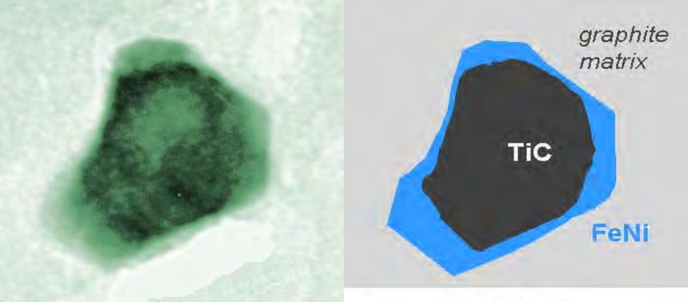


Non-equilibrium condensate mass distribution
Half of all C in condensed organics

ISM-organics require 350-450 K for complete evaporation, Nakano et al. 2003

Solid organics could be important for core accretion model, Lodders 2004, ApJ

No hydrous silicates, no methane and ammonia bearing ices



A *slice* of a presolar graphite grain with metal and carbide inclusions (Croat 2007). Chemical condensation model can explain formation (Lodders 2007)

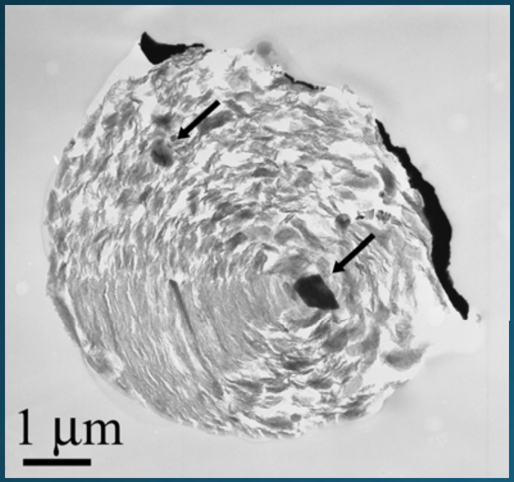


Photo: C. Croat & T. Bernatiwicz

Presolar graphite with internal Ti-Mo-Zr-carbides

Condensation and Evaporation: Kinetic inhibition may require super-saturation to initiate condensate formation

Homogeneous condensation: Condensate forms directly from gas phase; refractory phases observed in presolar grains

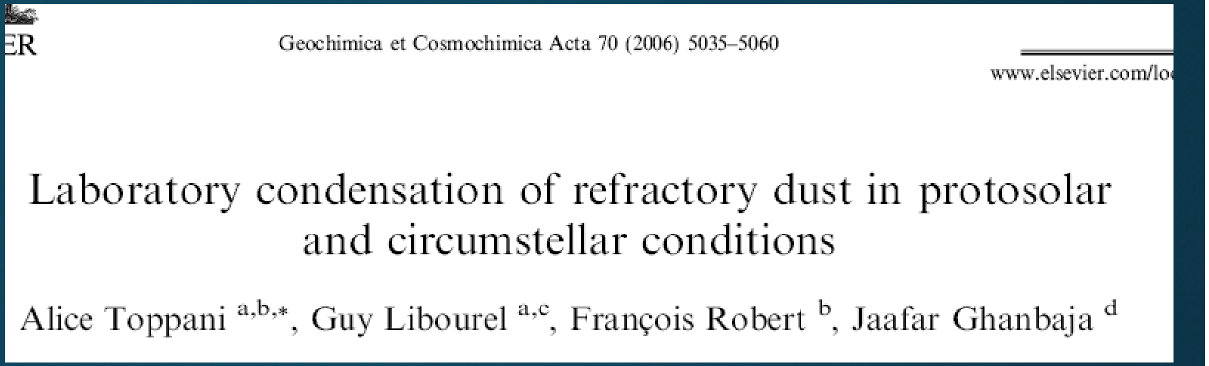
Heterogeneous condensation: Condensate grows onto existing grains; nucleation seeds

Grain growth: Deposition, coalescence, coagulation

Combine observed phase info & calculations to find overall composition and physical conditions (T,P) of the condensate source

Do Equilibrium Calculations Apply?

Application of equilibrium condensation calculations is supported experimentally


ER

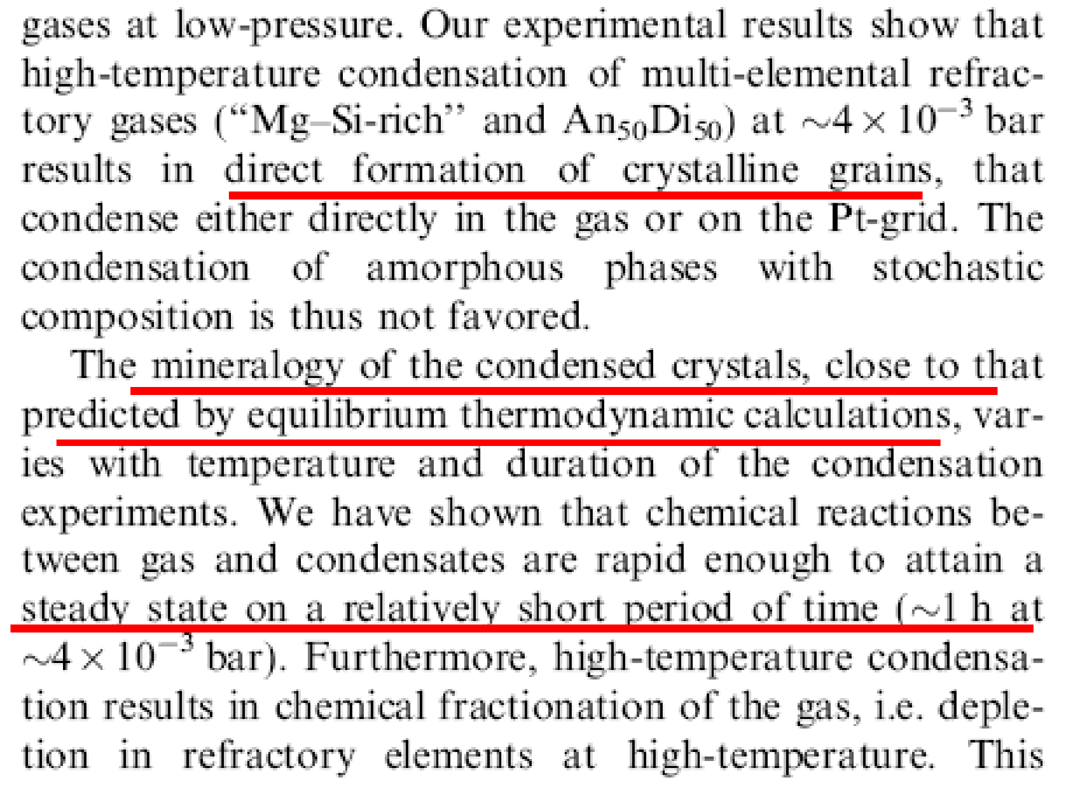
Geochimica et Cosmochimica Acta 70 (2006) 5035–5060

www.elsevier.com/lo

Laboratory condensation of refractory dust in protosolar and circumstellar conditions

Alice Toppani [a,b,*], Guy Libourel [a,c], François Robert [b], Jaafar Ghanbaja [d]

Condensation experiments at high T and low total pressure (1000-1285K, ~0.004 bar) yield many expected condensates in crystalline form; steady-state attained within an hour


gases at low-pressure. Our experimental results show that high-temperature condensation of multi-elemental refractory gases (“Mg–Si-rich” and $An_{50}Di_{50}$) at $\sim 4 \times 10^{-3}$ bar results in direct formation of crystalline grains, that condense either directly in the gas or on the Pt-grid. The condensation of amorphous phases with stochastic composition is thus not favored.

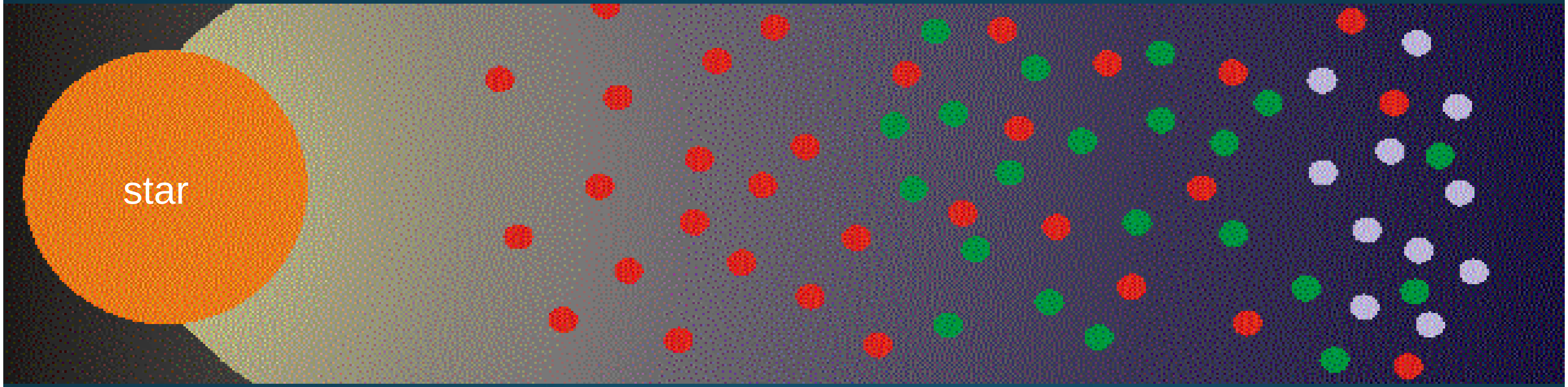
The mineralogy of the condensed crystals, close to that predicted by equilibrium thermodynamic calculations, varies with temperature and duration of the condensation experiments. We have shown that chemical reactions between gas and condensates are rapid enough to attain a steady state on a relatively short period of time (~1 h at $\sim 4 \times 10^{-3}$ bar). Furthermore, high-temperature condensation results in chemical fractionation of the gas, i.e. depletion in refractory elements at high-temperature. This

Equilibrium thermodynamics also explains presolar grain mineralogy and their trace element contents. They formed in low pressure winds of giant stars, so eq. thermo. should work well in high P atmospheres

Proto-Planetary Disk

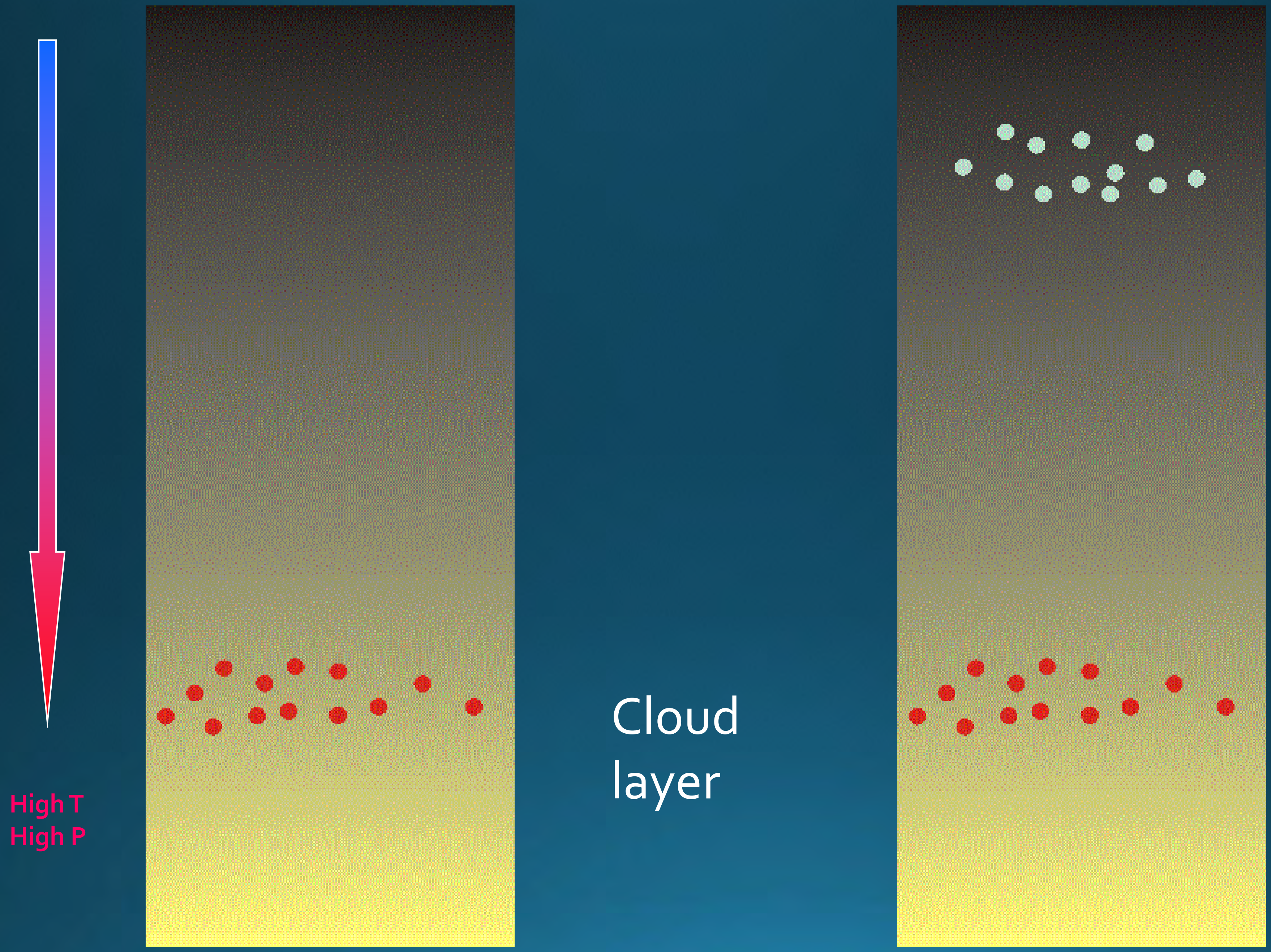
Dust Formation

(1) Condensates from gas (2) Gas-grain reactions

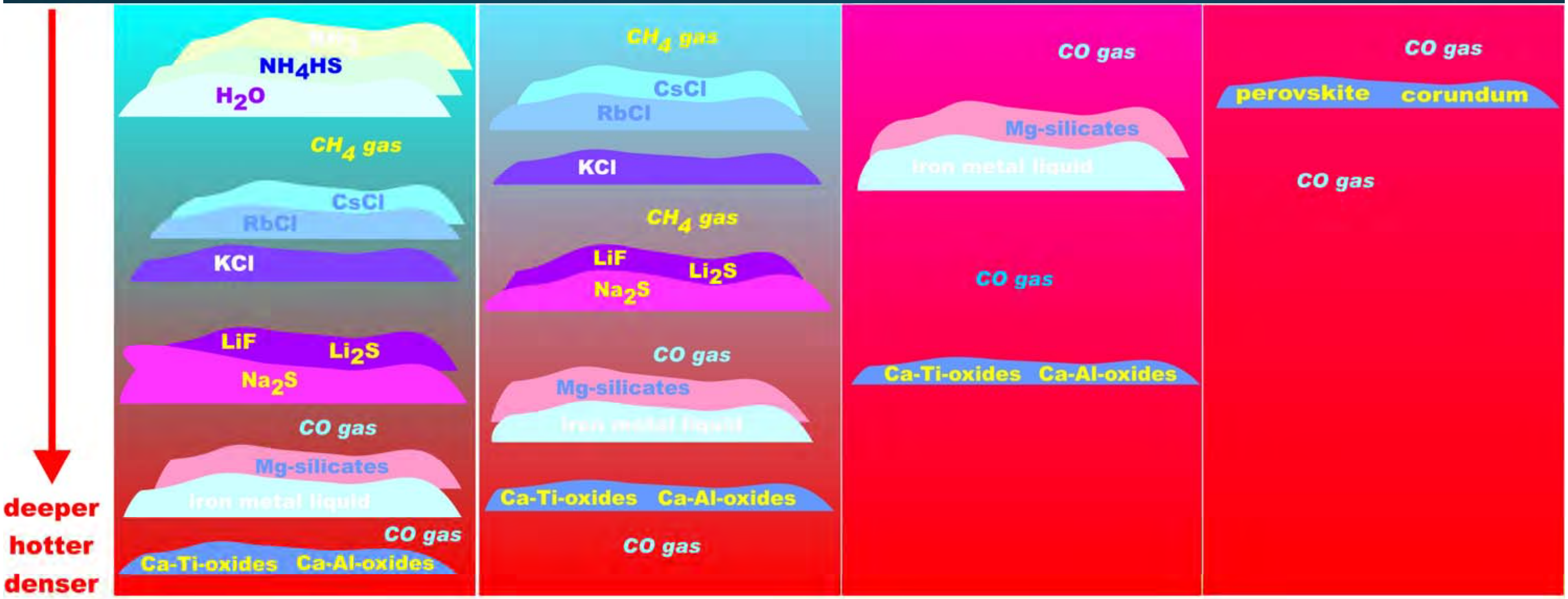


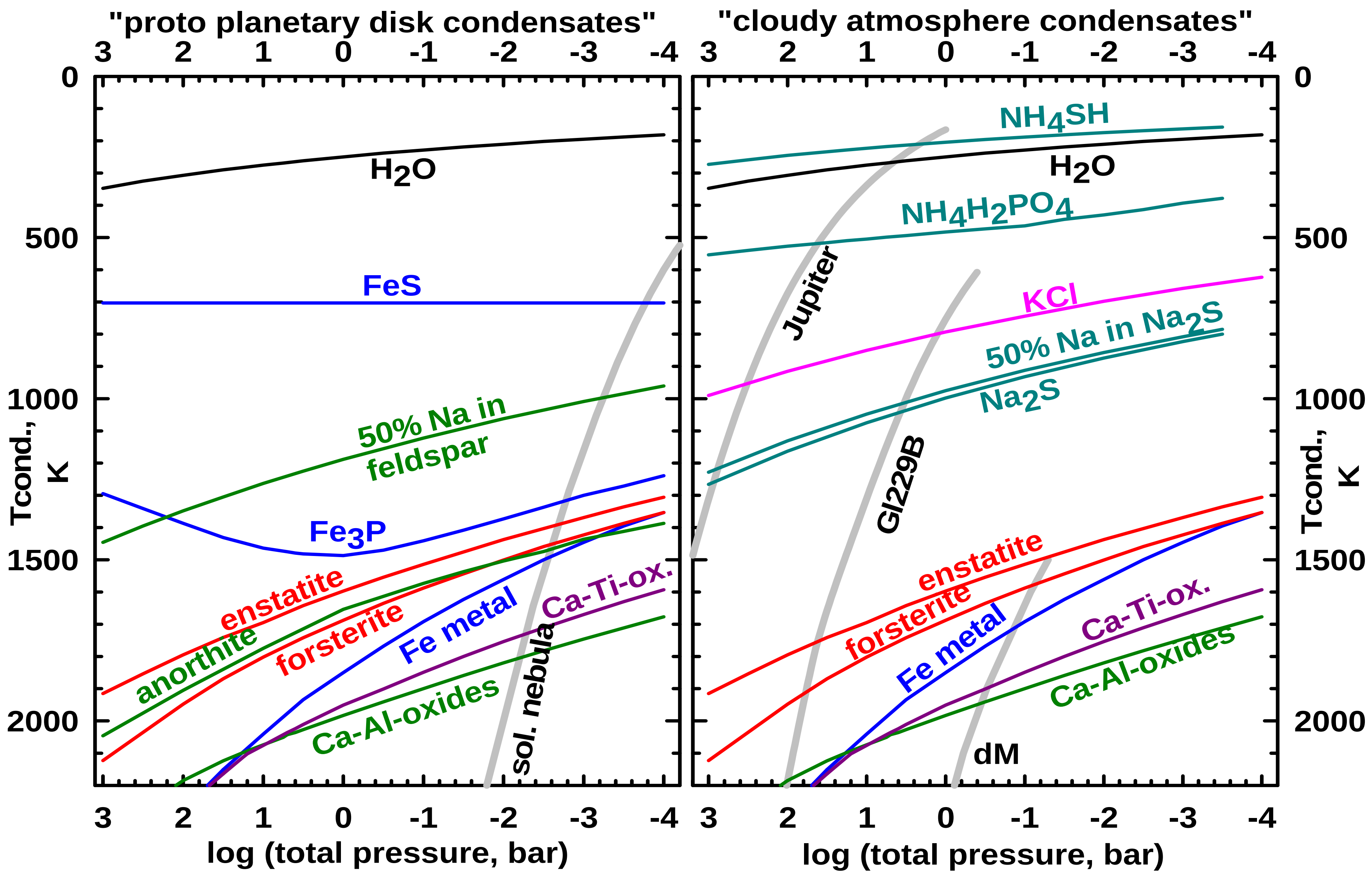
Fe-metal → FeS; sulfur removal

corundum → gehlenite → feldspar; Na, K removal

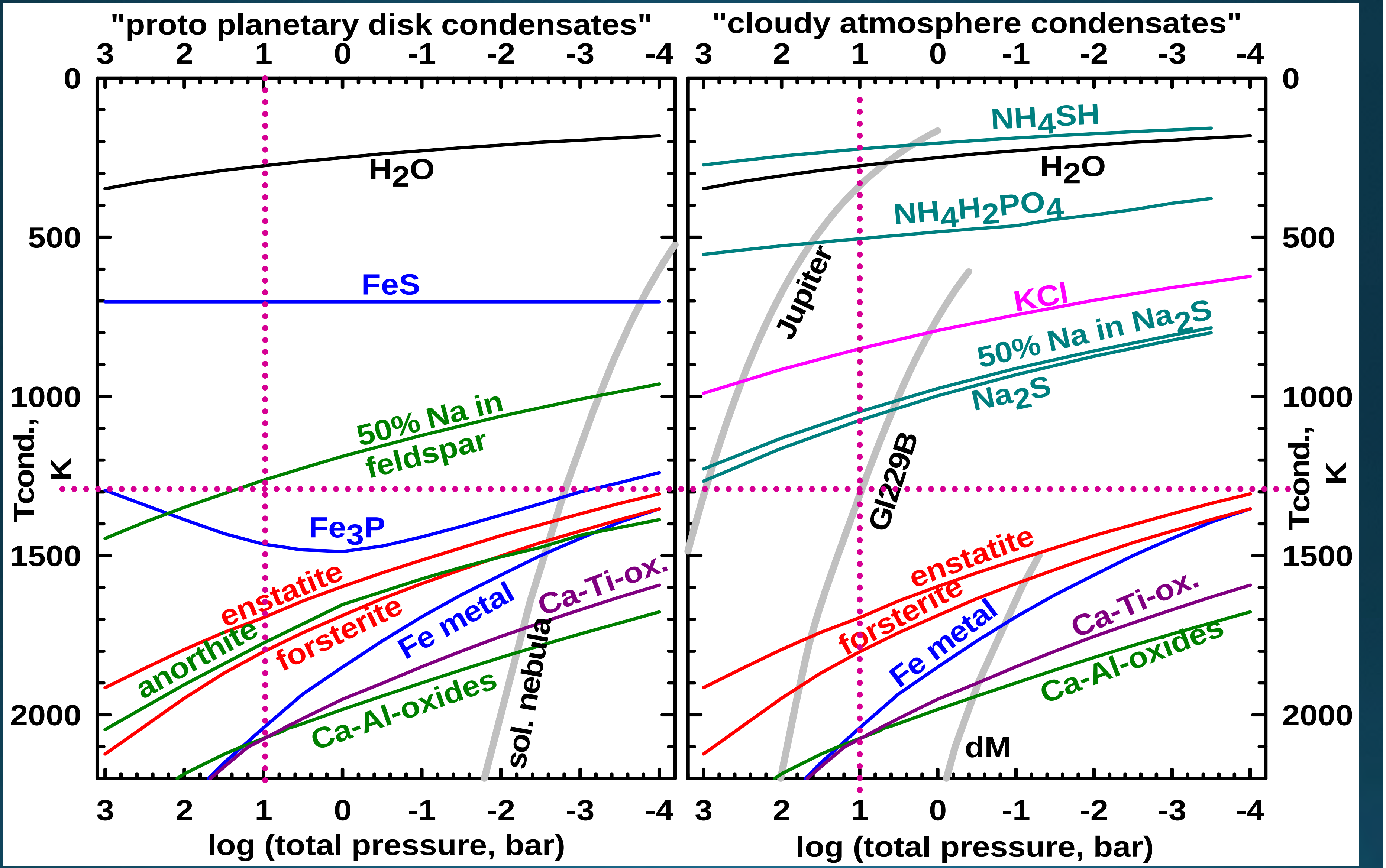


Cloud
layer


deeper
hotter
denser
NH3
NH4HS
H2O
CH4 gas
CsCl
RbCl
KCl
LiF
Li2S
Na2S
CO gas
Mg-silicates
iron metal liquid
CO gas
Ca-Ti-oxides
Ca-Al-oxides
CH4 gas
CsCl
RbCl
KCl
CH4 gas
LiF
Li2S
Na2S
CO gas
Mg-silicates
iron metal liquid
Ca-Ti-oxides
Ca-Al-oxides
CO gas
CO gas
Mg-silicates
iron metal liquid
CO gas
Ca-Ti-oxides
Ca-Al-oxides
CO gas
perovskite
corundum
CO gas



S into	FeS (troilite)	NH_4SH
P into	Fe_3P (schreibersite)	$NH_4H_2PO_4$
Na, K	into feldspar	Na_2S, KCl



Dotted line at ~1300K, ~10 bar for Na (and also K) removal into feldspar in solar nebula
But in brown dwarfs, need lower T for Na and K removal by Na_2S & KCl condensation

An astronomer's summary about potassium condensation in brown dwarfs:

… . If elements such as Al, Ca, and Si were not lost via such condensate-cloud formation at higher temperatures, neutral potassium would not have been seen as a major absorber in late-L and T dwarfs because it would have been removed by silicate condensates like orthoclase ($KAlSi_3O_8$, …). **Such is the bizarre and intricate dance of the condensates in M, L, and T dwarf atmospheres.** For more information on this topic, the reader is referred to the detailed papers by Lodders (2002) and Lodders & Fegley (2002) and the review by Burrows et al. (2001)

D. Kirkpatrick 2005, Annual Rev. Astron. Astrophys. 43, 195-245

Hot Exoplanets – Rock Vapor Atmospheres

- Most terrestrial accretion theories suggest that the Earth was at least partially molten
  - Many accretion models suggest presence of magma ocean
- Giant impacts, e.g. Moon-forming impact generate magma oceans which are hot enough to vaporize
  - evidence for large impacts in exo-planetary systems (Song et al., 2006, Nature)
- Terrestrial-type planets should get hot (T > 2000 K) and vaporize during accretion
  - Vaporization generates silicate atmospheres containing gases such as SiO that may be detectable spectroscopically

Core – Accretion Model Gas Giant Planets

Fast build-up of protocore facilitated if surface mass density in disk is increased
need up to 5-10 times the rock surface density
(Lissauer, 1987, Pollack et l 1996, Hueso & Guillot 2003)

Water Ice: Mass density of solids higher at the **snowline** and beyond

Solar abundances allow for factor 2-3 mass increase
2014: rock ~ 0.5% and *water* ice ~ 0.6% of all mass
AG89: rock ~ 0.5% and *water* ice ~ 0.9% of all mass

Diffusive redistribution of water from inner solar system and ice cold-trapping at the snow line and beyond can increase mass density (Stevenson & Lunine 1988, Cyr et al. 1998)

If Jupiter formed with a lot of water ice:
Where is the water now?

The Tar-line

Carbonaceous condensation/evaportion front

Organic solids more stable than water ice during condensation and more stable against evaporation

Carbonaceous matter is more refractory than water
Gooey sticky properties

Jupiter's observed envelope composition
high carbon abundance: C/H ~ 3-4x solar
low-solar oxygen: O/H = 0.5 – 1 x solar

Compared to methane, water abundances increase more strongly from Jupiter to Uranus suggesting water ice pile-up in the outer solar system.

Overall Composition Matters!

Condensation temperatures for solar composition may only apply to H and He-rich systems with similar metallicity and C/O ratios!

Types of condensates and sequence of their appearance as function of T depend on total pressure and overall composition.

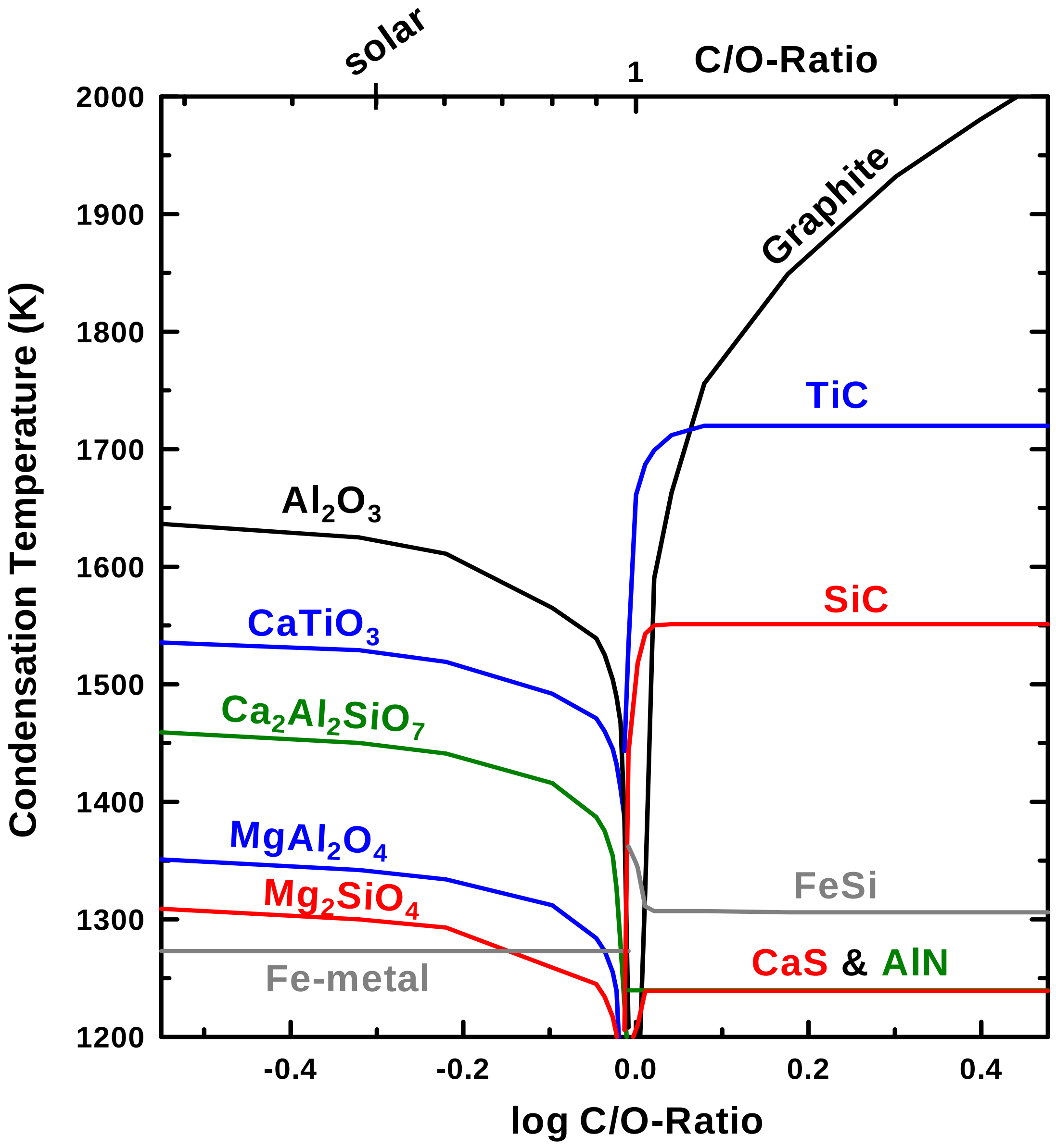
An increase of C/O in a gas of otherwise solar composition changes condensates of many elements from oxides and metals to carbides, nitrides, sulfides, and silicidies.

A decrease in hydrogen (increase of metallicity) in an otherwise solar composition gas makes the gas more oxidizing and favors oxide stabilities.

Essentially hydrogen-gas free systems at high temperatures (silicate magma oceans, volcanic gases) have different gas species coexisting than “astronomical condensates” in a H, He rich gas.

Condensate phases will also depend on the relative amounts of sulfur, nitrogen, halogens depending on the overall fractionation/differentiation history of the system under consideration.

Inner Circumstellar Chemistry of Red Giant Stars



Condensate mineral is determined by C/O

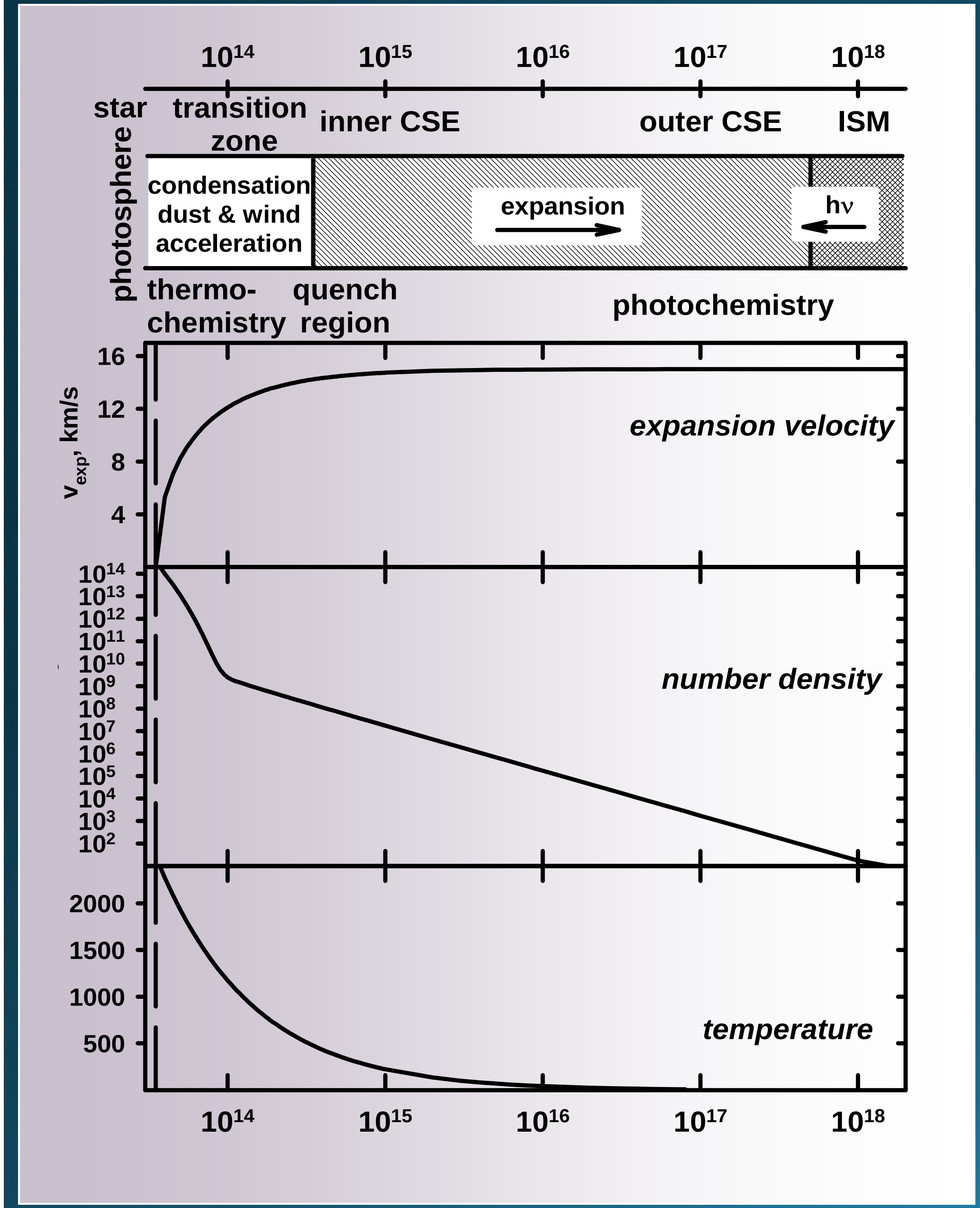
M stars, C/O <1 oxides, silicates, metal

C stars, C/O >1 graphite, carbides, nitrides, sulfides, silicides

Several of these minerals observed in CSE and among presolar grains

10^{-5} bar; C/O > 1, MgS at 1030K

Conditions in the Circumstellar Envelopes of Red Giant Stars



In the CSE, densities drop more than ten orders of magnitude.
Temperature also drop steeply in the CSE.

Photospheric equilibria become quenched as required reaction timescales become larger than expansion timescales

Outermost CSE receives interstellar UV
→ photochemistry

Circumstellar Envelope Chemistry of Red Giant Stars

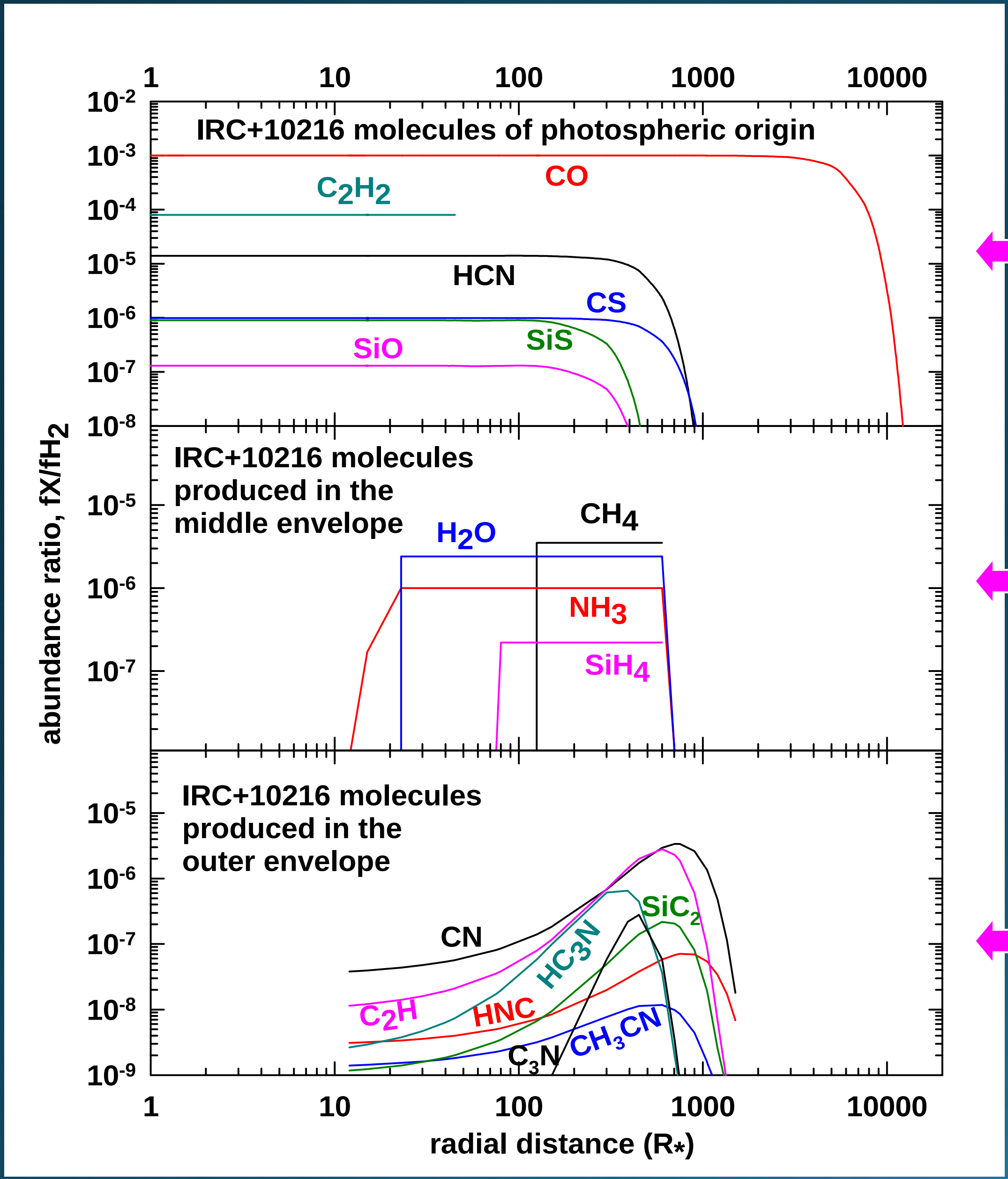
Photospheric and inner shell region:
At a given distance R, equilibrium is reached if reaction times are shorter than expansion timescales
$\tau_{chem}(R) < \tau_{expand}(R)$

Thermochemical equilibrium abundances become frozen in at distances where
$\tau_{chem}(R) = \tau_{expand}(R)$

Different reactions have different quench distances. Endothermic reactions and reactions with high activation energies quench closer to the star than exothermic reactions, e.g., CO, SiO, SiS, HCN difficult to destroy at low temperatures and pressures

Models require kinetic reaction networks

Observed Circumstellar Chemistry of the Carbon-rich Giant Star IRC+10216



Observed abundances consistent with quenched photospheric equilibrium abundances

Abundances higher than expected from equilibrium at given R, also higher than quenched equilibria from closer-in; grain-surface reactions?
Remains a mystery

Photochemically produced radicals and molecules; any dust destruction?

Keady & Ridgway 1993, Bieging & Tafalla 1993, Monnier et al. 2000, Woods et al. 2003

Summary

Astronomical environments display huge diversity in Dust & Gas Inventories over time and in physical settings

Condensation Chemistry
Calculations are useful to model observations
Examples: Solar Nebula,
Clouds in (sub)stellar objects,
Stellar Outflows (circumstellar shells, AGB)

Major dependencies for condensation/evaporation modelling:
overall elemental composition
temperature, pressure/density
gravitational effects; settling
thermochemical vs. photochemical effects
kinetic effects
Quality of atomic/molecular parameters for thermodynamics, kinetics, photochemistry