Lecture 29

High Temperature Geochemistry

Formation of the solar system

Reading this week:
White Ch 8.1 – 8.4.1(dig. 313-326) and
Ch 10.1 to 10.5.3 (dig. 421-464)

Today

1. Age and Origin of the Solar System

2. Condensation Sequence

Next time

3. Planetesimal Accretion and Early Solar System Evolution

Age and origin of the Universe and our solar system

There are **3 main** lines of evidence for how old the universe is:

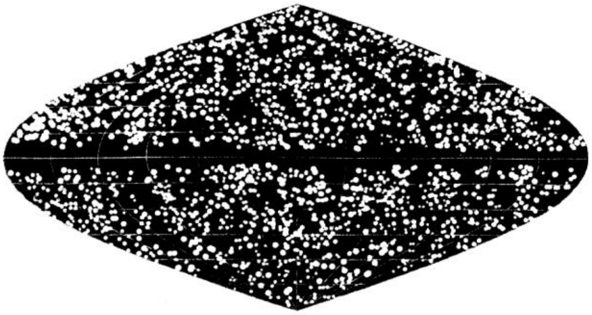
1. Astronomical approaches use measurements of globular clusters, old white dwarf stars, and the rate of expansion of the Universe (Hubble constant = velocity/distance, using the red shift of distant galaxies or variations in the cosmic microwave background temperature).

Recent estimates by different approaches yield ages from about **10-16 Ga.**

Cosmic microwave measurements suggest an age of 13.7 ± 0.2 Ga.

However, there are uncertainties in most of these methods related to poorly quantified amounts of dark matter in the universe (among other things).

Note: Ga = giga annum = 10^9 yrs



HOMOGENEOUS DISTRIBUTION of galaxies is apparent in a map that includes objects from 300 to 1,000 million light-years away. The only inhomogeneity, a gap near the center line, occurs because part of the sky is obscured by the Milky Way. Michael Strauss of the Institute for Advanced Study in Princeton, N.J., created the map using data from NASA's *Infrared Astronomical Satellite.*

Peebles et al., Scientific American, Oct 1994

Age and origin of the Universe and our solar system

Geochemical estimates can be made from

2. the rate of consumption (depletion) of nuclear fuel in the most distant stars within our galaxy,

or from

3. the radioactive decay of long lived r-process nulcides. Most of this work has been done with ^{232}Th, ^{238}U, and ^{235}U.

These methods give ages that are both ~15Ga.

Let's examine the last estimate a bit.

^{232}Th	$t_{1/2} = 1.4 \times 10^{10}$ yr	longer time
^{238}U	$t_{1/2} = 4.5 \times 10^{9}$ yr	medium time
^{235}U	$t_{1/2} = 7.1 \times 10^{8}$ yr	shorter time

We assume, for simplicity, that *supernovas have been distributed uniformly throughout the Universe*, so that a single mean r-process production rate applies everywhere for each of these three isotopes.

There are actually a range of estimates for the r-process production ratios of the long-lived Th and U isotopes based on various theoretical and observational lines of evidence.

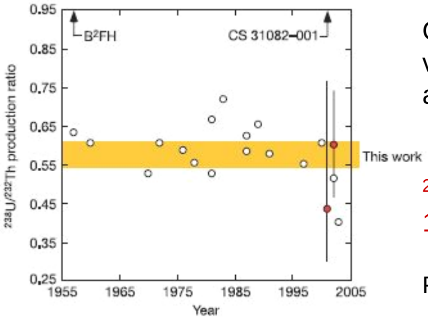


Figure 3 | Estimations of the ^{238}U/^{232}Th production ratio in r-process nucleosynthesis. The points are literature data (refs 1–8, see ref. 2 and references therein for publications before 1991) and the yellow band is the production ratio derived in this work ($0.571^{+0.037}_{-0.031}$, see text). The two arrows mark the first estimate of the U/Th ratio in the framework of r-process nucleosynthesis (labelled B^{2}FH, ref. 1) and the first determination of the U/Th ratio in a low metallicity star (CS 31082–001, ref. 10). The two red dots are state-of-the-art calculations aimed at estimating the U/Th production ratio and its possible uncertainty, arising primarily from uncertainties in the nuclear physics involved[5,6]. As shown, GCE and LMHS provide tight constraints on the U/Th production ratio that can be used in turn to refine nuclear mass formulae[5,6], to help determine the source of Galactic cosmic rays, and to date circumstellar grains[5]. ***Dauphas, Nature, 2005***

Our approximation assumes a typical value and yields this proportion right after the production ceases:

^{235}U	^{238}U	^{232}Th
100	66	127

Proportions are relative to 100 ^{235}U atoms:

We'll see next time that a group of meteorites known as the ***C1 chondrites*** have ratios of non-gaseous elements that nearly match those of the sun, so they yield an ***excellent estimate of our primordial solar nebula's composition.***

The ages of these meteorites (determined from radiometric-dating by the Rb-Sr, U-Pb, and Pb-Pb dating methods) are 4.55x to 4.6 x 10^9 yr.

C1 Chondrites today have:

^{235}U	^{238}U	^{232}Th
100	13947	52632

i.e., going from most decayed to -------> least decayed

since formation 4.6 Ga ago (1Ga= 10^9 yr)

Correcting for radioactive decay in the last 4.6 Ga since solar system formation using a slightly modified form of the decay equation:

$N_1 = N_2\, e^{\Delta T/\tau}$

where τ is the mean life of $1/\lambda$, ΔT is the time interval,

N_1 = the r-process production values

N_2 = C1 Chondrite values @ 4.6 Ga of each of the three isotopes,

we estimate that that @ 4.6 Ga C1 Chondrites (and Earth) had:

^{235}U	^{238}U	^{232}Th
100	345	818

We can then solve to find that…

$\Delta T = 2.1 \times 10^9$ yrs before Earth formed, or 6.7×10^9 yrs old,

which is 6.7 Ga.

This is a <u>very low</u> estimate (too low) relative to astronomical estimates.

Furthermore, it’s badly inconsistent with the presence in our solar system of the decay products of extinct radioactive nuclides that were still “alive” at 4.6 Ga, when the earliest solids formed, such as:

$^{26}\text{Al} \rightarrow {}^{26}\text{Mg} \quad T_{1/2} = 700$ ka

$^{129}\text{I} \rightarrow {}^{129}\text{Xe} \quad T_{1/2} = 17$ ma

That such highly radioactive elements existed at 4.6 Ga in our solar nebula means that there must have been **at least one supernova** (and thus r-process event) in our neighborhood of the galaxy **shortly before our solar nebula formed** (i.e., within a few million years).

This has the effect of making our simple estimate of the age of Th and U in the solar system too low (young), more so if more than one supernova contributed elements to our solar nebula.

We can't really know when or how often earlier supernovas occurred, but if we <u>assume</u> that they occur regularly, at a <u>steady-state in frequency and size</u>, we can use historical observations over the last 2000 years to estimate that there are roughly 10^8 supernovas per 10 Gyr within our galaxy.

If the galaxy is well-mixed on very large scales, there will be a time for each isotope when production by the r-process is balanced by decay (i.e., steady state).

At steady state, it can be estimated that the isotopic proportions are:

^{235}U	^{238}U	^{232}Th
100	410	2460

The time needed for each isotope to reach steady state is indicated in this figure. Clearly, only ^{235}U has reached this condition so far.

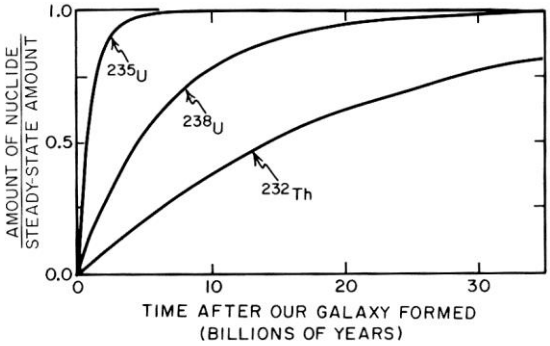


Figure 4-5. The evolution of the amounts of ^{235}U, ^{238}U, and ^{232}Th in our galaxy: The assumption is made that supernova events have occurred regularly over the entire history of our galaxy. The steady-state amounts correspond to the situation where the isotope is undergoing radiodecay at a rate that matches the new production in stars. *Broecker, "...Habitable Planet"*

noting that our own nebular values would have been "locked in" at 4.6 Ga (more recent novas have not affected the ratio in our solar system), we can again use the 4.6 Ga values in C1 chondrites (repeated from above)

^{235}U	^{238}U	^{232}Th
100	345	818

to find that ^{238}U and ^{232}Th were at 84% (= 345/410) and

33% (= 818/2460) of the way to

steady state at 4.6 Ga.

These ratios are used to estimate galactic ages of 12 Ga from ^{238}U and 9 Ga from ^{232}Th **(average = 10.5**) [see red box in image at right]

Estimated age of universe: 10.5 + 4.6 Ga = **15 Ga** (before today)

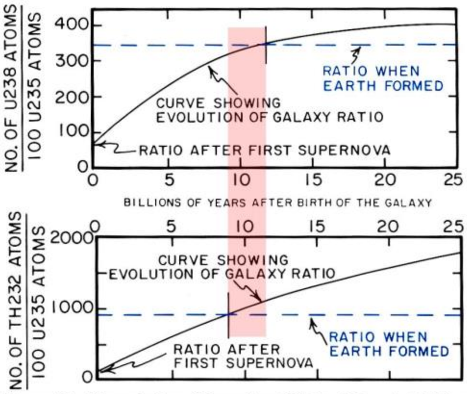


Figure 4-6. The evolution of the ratios of ^{238}U to ^{235}U and of ^{232}Th to ^{238}U in our galaxy if heavy-element production occurred at a constant rate: Very early in the galaxy's history the ratios were equal to the ratio in which they were produced in stars. With time the ratio changed favoring the longer-lived of the two isotopes. The horizontal dashed lines correspond to the ratios at the time the solar system formed. The intersection between the dashed line and the solid evolution curves should correspond to the time between the formation of our galaxy and the formation of our solar system. In the case of the ^{238}U-^{235}U pair, this time is about 12 billion years. In the case of the ^{232}Th-^{235}U pair, the time is about 9 billion years. Hence, about 10 billion years elapsed between galaxy and solar-system formation.

Broecker, "...Habitable Planet"

A more recent estimate for just the Milky Way galaxy uses similar reasoning by comparing the (1) temporal change in Th/U in very small low metal stars in our galaxy (the LHMS curve) and (2) a mean r-process production rate for stars throughout the galaxy, making various assumptions about how metals transfer among interstellar gas clouds, nebulae, and stars between supernovas to produce a chondritic Th/U ratio (GCE curve).

The intersection of the curves is the age of the Galaxy (**14.5** +2.8, -2.2 Ga)

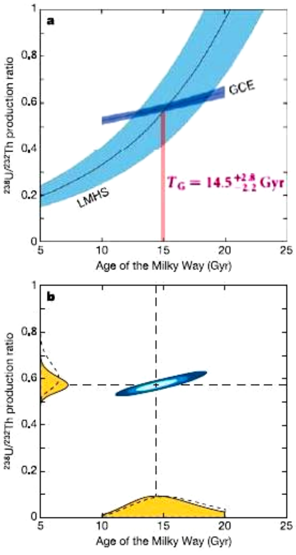


Figure 2 | Determinations of the U/Th production ratio and the age of the Milky Way. a, The light blue curve labelled LMHS is derived from the determination of the U/Th abundance ratio in a low metallicity halo star, CS 31082–001 (refs 10,11, equation (2)). The dark blue curve labelled GCE is derived from the solar U/Th ratio[9] and a GCE model[24] incorporating infall of low metallicity gas with a rate parameterized as a gaussian (equation (1)). For a given age of the Milky Way, a GCE model can be built on the basis of observations of the gas and the total surface densities[26,27] of the Galactic disk, the metallicity of the Sun[21], and the G-dwarf metallicity distribution[22]. This GCE model can then be used to calculate the U/Th production ratio required to explain the U/Th ratio measured in meteorites[9]. Repeating this procedure for a range of ages allows construction of the GCE curve. Because the U/Th ratio at Solar System formation integrates nucleosynthesis and decay over Galactic history, the position of the GCE curve is not very sensitive to the details of the GCE model. See Supplementary Information for details. **b**, The contours of the uncertainty ellipsoid of the intersection correspond to 20%, 38% and 68% confidence intervals. The curves filled in yellow are the marginal probability distributions of the U/Th production ratio ($P^{U/Th} = 0.571^{+0.037}_{-0.031}$) and the age of the Milky Way ($T_G = 14.5^{+2.8}_{-2.2}$ Gyr). The dashed curves are the marginal probability distributions if an exponential rate of infall is adopted ($P^{U/Th} = 0.602^{+0.058}_{-0.043}$ and $T_G = 15.1^{+2.8}_{-2.3}$ Gyr). Error bars are 68% confidence intervals.

Dauphas, Nature, 2005

Intra- and Extra Galactic Timescales Summarized:

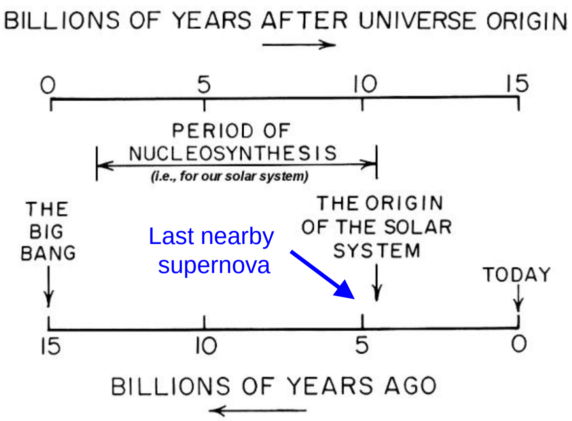


Figure 4-7. Summary of the chronology of universe events: The period of nucleosynthesis refers to the time interval over which the elements heavier than hydrogen and helium that are found in our solar system were produced. For the galaxy as a whole the period of nucleosynthesis extends right up to the present. The matter in the solar system was isolated from the galaxy 4.6 billion years ago. *Broecker, "...Habitable Planet"*

Next time we will discuss constraints on what I've labeled the "last nearby supernova".

Condensation of our Solar Nebula

We have learned that the elemental material that makes up our solar system is older than it.

We turn now to processes that occurred once our nebula formed from the galactic pool of elemental gas.

Elements can be categorized by behavior at assumed values of P and T throughout the solar system.

This table notes gross distinctions that are useful for considering planetary surfaces and atmospheres in our solar system.

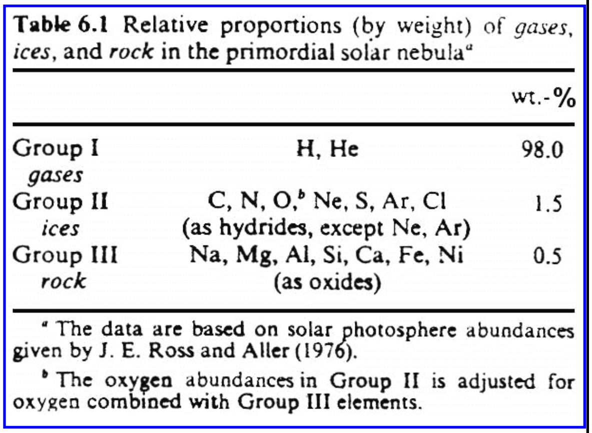


Table 6.1 Relative proportions (by weight) of *gases*, *ices*, and *rock* in the primordial solar nebula[a]

		wt.-%
Group I *gases*	H, He	98.0
Group II *ices*	C, N, O,[b] Ne, S, Ar, Cl (as hydrides, except Ne, Ar)	1.5
Group III *rock*	Na, Mg, Al, Si, Ca, Fe, Ni (as oxides)	0.5

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[a] The data are based on solar photosphere abundances given by J. E. Ross and Aller (1976).

[b] The oxygen abundances in Group II is adjusted for oxygen combined with Group III elements.

Condensation of our Solar Nebula

To do this more quantitatively, we must consider **what solids will condense from a hot vapor of elements in gaseous form.**

Step 1.

We can get at this question by determining what the main high-temperature solid phases are for each element.

The next slide shows examples of gas-solid phase diagrams for Si, Ca, and Al as a function of T at a very low pressure of 10^{-4} atm, similar to what we think pertained in much of the early pre-solar nebula.

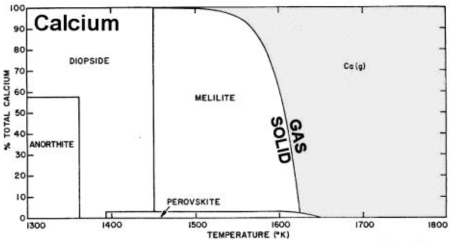


Fig. 1. The distribution of Ca between crystalline phases and vapor. Perovskite condenses at 1647°K, using up only a small fraction of the total Ca. Melilite rapidly consumes most of the Ca soon after appearing at 1625°K. Its Ca is transferred to diopside at 1450°K, when Mg-rich melilite is converted to spinel + diopside. The Ca released when perovskite is converted to Ti_3O_5 at 1393°K is consumed by diopside, which reacts with spinel to form anorthite at 1362°K.

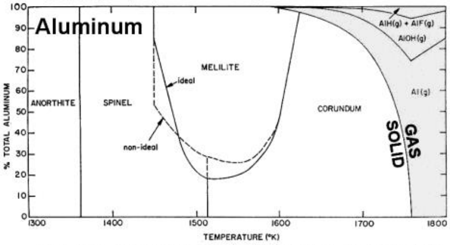
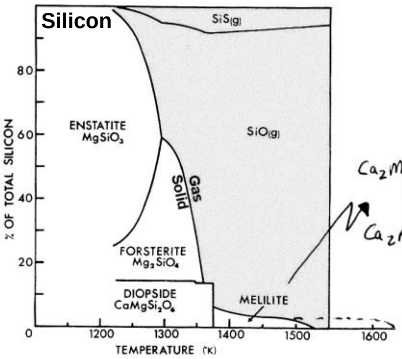


Fig. 2. The distribution of Al between crystalline phases and vapor. Corundum condenses at 1758°K and rapidly consumes most of the Al until it begins to react to form melilite at 1625°K. The ratio of Al in melilite to that in corundum gradually increases with decreasing temperature until 1513°K when the excess corundum is converted to spinel. Below 1513°K, spinel consumes the Al which is displaced from melilite by gaseous Mg. Two sets of curves are shown in this region, one for each melilite solid solution model. The non-ideal model predicts displacement of Al from melilite at temperatures high enough to precipitate corundum. At 1450°K, all the remaining Al in melilite is converted to spinel which is destroyed at 1362°K to form anorthite.

modified from Grossman 1972



$Ca_2MgSi_2O_7$

$\updownarrow$

$Ca_2Al_2SiO_7$

Figure 6.8 The calculated distribution of silicon between crystalline and vapor phases in a gas of solar composition at 10^{-4} atm. Nearly all magnesium has condensed at 1290°K (mainly as forsterite), whereas only 60 percent of the total silicon has condensed. Forsterite begins to react with silicon in the gas phase to form enstatite at 1290°K. This reaction continues with falling temperature until 95 percent total silicon is condensed at 1240°K. (Diagram kindly provided by L. Grossman.)

From: Ringwood, "Origin of the Earth and Moon"

We then consider the P-T stability relationships for the high temperature phases, recalling that P_{TOT} will essentially be set by P_{H2} so long as we are in a gas with solar abundances of the chemical elements (see notes from last lecture).

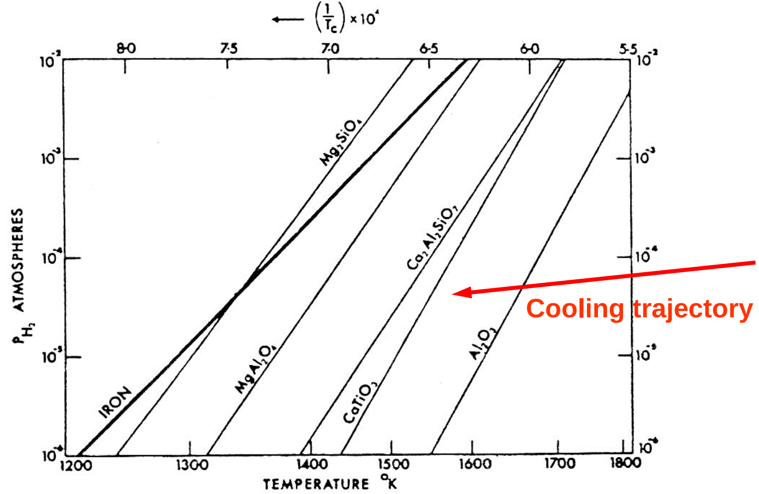


Figure 6.7 Pressure variation of condensation temperature for some major phases. (After Grossman and Larimer, 1974.) ***From: Ringwood, "Origin of the Earth and Moon"***

The Solar Condensation Sequence

Step 2.

We then estimate $\Delta G°_f$ and K_{eq} for each compound from the native elements as a function of T and P to determine its condensation temperature at a given pressure.

i.e.,

$$Al_2O_3\ (s) \leftrightarrow 2Al\ (g) + 3O\ (g)$$

$$K_{eq} = (P_{Al}^{2})(\underline{P_O^{3}})$$

So…

$$\log K = 2\log P_{Al} + 3\log P_O$$

Partial pressure of elemental O, cubed

The Solar Condensation Sequence

Step 3.

Next, we need to estimate the concentration of each element in the gas phase nebula with two assumptions.

1. the nebula was an ideal gas: $P_{total}V = n_{total}RT$
2. $P_{total} \sim P_{H2}$

We make this second assumption because at early nebular conditions these elemental abundances prevailed:

- $Abund_H \sim 94\%\ abund_{all\ elemental\ material}$
  For instance, $abund_{He} = 6\%\ abund_H$; $abund_{all\ other\ elements} \ll 0.1\%\ abund_H$
- $P_{H2} > 500\ P_{other\ H\ species}$, so that $n_{H2} = ½n_{H\ total}$
- $P_{total} \sim 10^{-4}$ to 10^{-3} atmospheres, depending on location in the gas cloud.

Step 4, some algebra

The ideal gas law tells us that in a unit volume of solar nebula

$n_{H2} = P_{H2}/RT$ and so.......... $½n_{H\ total} = P_{H2}/RT$

using the mole fraction of each other element

$X_i = n_i/n_{total}$ which is $X_i \sim n_i/n_H$

we get an expression for the moles of i in a unit volume:

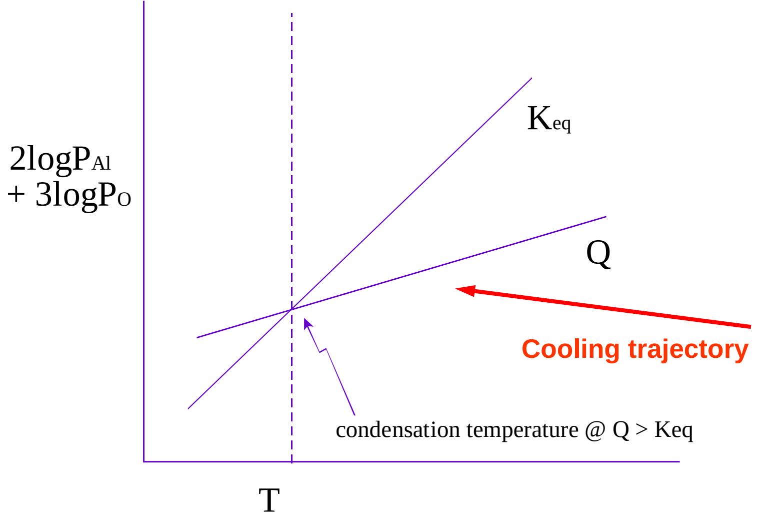
$$\boxed{n_i = X_i\,(2P_{H2}/RT)}$$

In other words, we can estimate the *equilibrium molar concentration* of **any element** *per unit volume*, given the gas pressure and temperature of the nebula, and the element's abundance ratio to H_2.

For stable elements, we can get the original abundance ratio directly from the present-day composition of the sun (which contains 99.8% of the mass of the solar system).

Step 5.

Finally, we estimate the T of condensation for each element in its highest temperate phase by comparing K_{eq} as a function of T with Q (the reaction coefficient) based on actual nebula abundances.



Results, summarized:

key parts of the condensation sequence estimated by this method

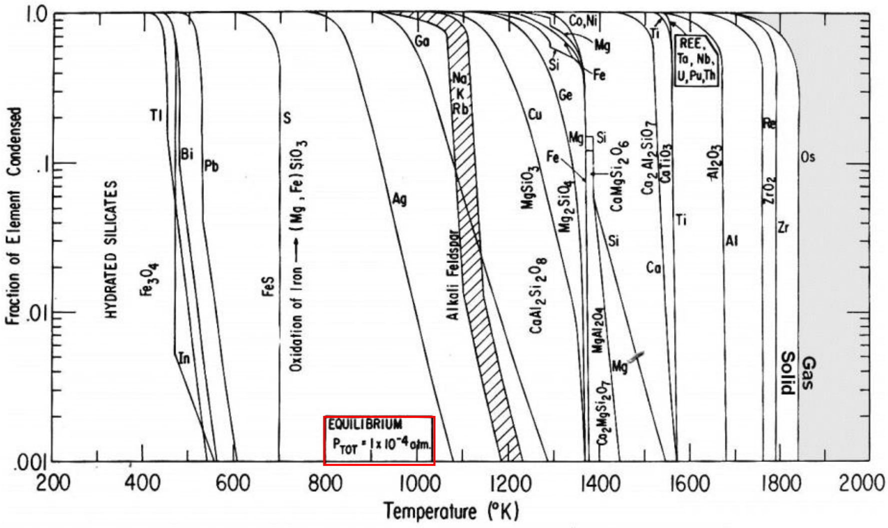


Figure 6.6 Condensation of the elements from a gas of solar composition at 10^{-4} atm. (From Grossman and Larimer, 1974, with permission.)

The condensation sequence also takes into account the fact that some high-temperature solids react to form others as the temperature continues to drop.

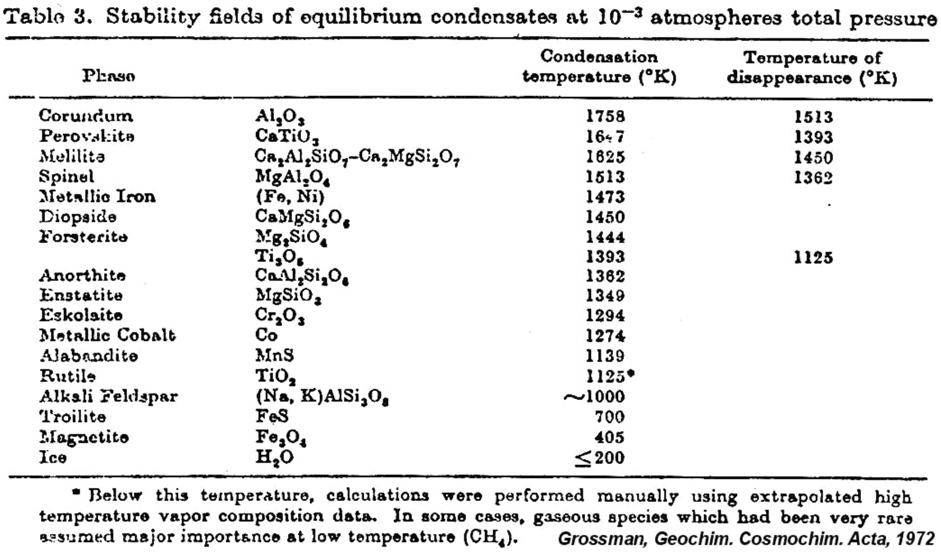


Table 3. Stability fields of equilibrium condensates at 10^{-3} atmospheres total pressure

Phase		Condensation temperature (°K)	Temperature of disappearance (°K)
Corundum	Al_2O_3	1758	1513
Perovskite	$CaTiO_3$	1647	1393
Melilite	$Ca_2Al_2SiO_7$–$Ca_2MgSi_2O_7$	1625	1450
Spinel	$MgAl_2O_4$	1513	1362
Metallic Iron	(Fe, Ni)	1473	
Diopside	$CaMgSi_2O_6$	1450	
Forsterite	Mg_2SiO_4	1444	
	Ti_3O_5	1393	1125
Anorthite	$CaAl_2Si_2O_8$	1362	
Enstatite	$MgSiO_3$	1349	
Eskolaite	Cr_2O_3	1294	
Metallic Cobalt	Co	1274	
Alabandite	MnS	1139	
Rutile	TiO_2	1125*	
Alkali Feldspar	(Na, K)$AlSi_3O_8$	~1000	
Troilite	FeS	700	
Magnetite	Fe_3O_4	405	
Ice	H_2O	≤200	

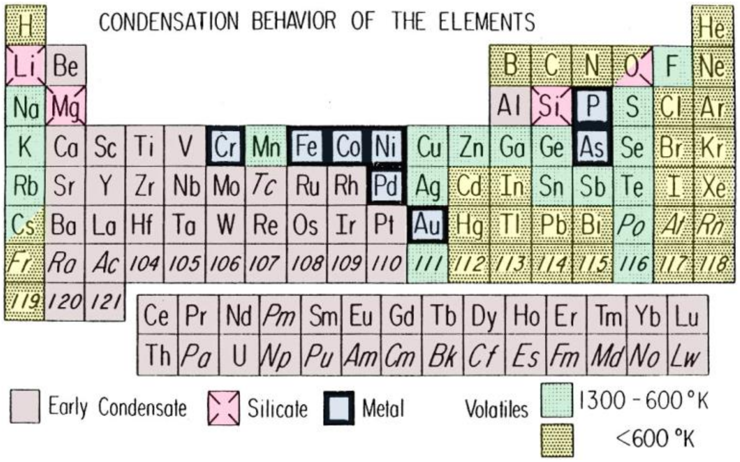
* Below this temperature, calculations were performed manually using extrapolated high temperature vapor composition data. In some cases, gaseous species which had been very rare assumed major importance at low temperature (CH_4).

Grossman, Geochim. Cosmochim. Acta, 1972

Solid materials in this sequence can be divided into 3 subcategories:

✓ early condensate ✓ silicates and ✓ metals

volatiles are separated into higher-T (1300-600°K) and lower-T (<600°K) groups. The lower-T volatile group can be subdivided further into “ices” and “gases” based on condensation point, if desired.



the condensation sequence: the sequence of phases we might expect if condensation occurred in a closed system at chemical equilibrium.

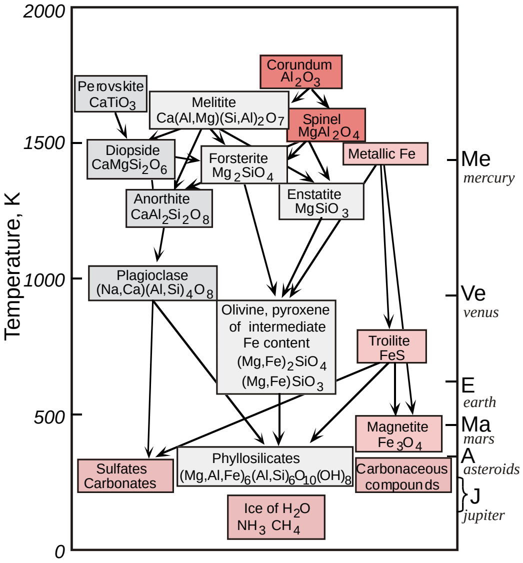


Figure 10.33. Simplified mineralogical condensation sequence.
modified from White, Geochemistry

1. Refractory elements primarily associated with corundum, Al_2O_3, and perovskite $CaTiO_3$, (Ti, Al, Ca, Os, Zr, Th, U, REE, platinum group metals)

2. Fe + Ni as a metal alloy and the first silicates (Mg, Ca-Mg)

3. Alkalis/alkaline earths as feldspars

4. Sulfide minerals, oxides like magnetite, oxidized Fe into olivine, pyroxene.

5. Hydrated phases (silicate minerals) below about 550°K; sulfates, carbonates below this

6. Ices below about 200°K

We see remnants of this high T condensation sequence in C1 Chondrites.

These meteorites are basically sedimentary rocks or metamorphosed sediments formed of the phases predicted by the condensation sequence.

However in detail multiple aspects of the simple equilibrium condensation sequence have been called into question over the last ~20 years, primarily due to evidence in meteorites such as:

1. multiple pulses of heating during cooling of the nebula
2. chemical reactions and kinetic control on processes within some of the materials
3. inheritance of some pre-solar grains in C1 chondrites

Nevertheless the notion of a condensation sequence and its general proof in observed materials remains one of the remarkable accomplishments of geochemistry/cosmochemistry.

What was the setting in which condensation occurred? Imagine dust-size particles forming as the pre-solar nebular gas cools. Models indicate that the cooling cloud collapses into a lens shaped body rather quickly.

During equilibrium condensation, the first-formed refractory phases become nucleation sites for lower-T condensates.

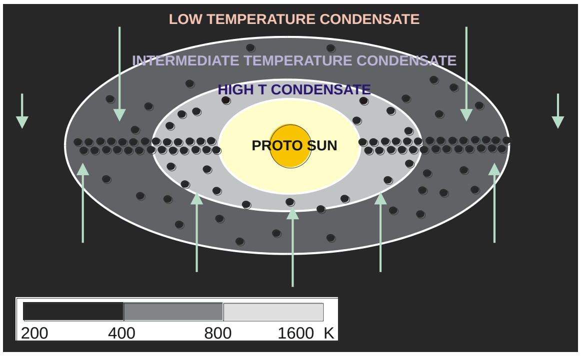
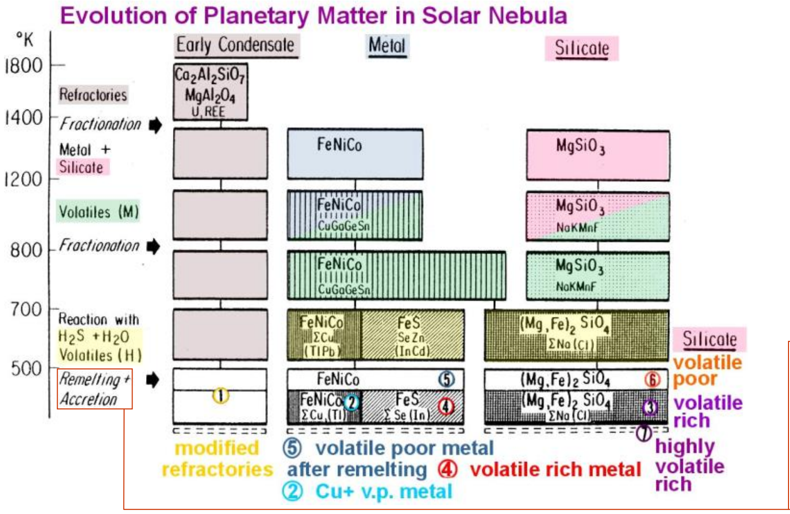


Figure 6.4 Diagram showing notational temperature distribution in "cocoon" nebula surrounding sun, and prior to collapse into discoidal configuration. Small first-generation planetismals form within the shell and sink towards the ecliptic plane in general direction indicated by white arrows (note that actual paths are more complex than this). An important result is that at any given distance from the sun in the ecliptic plane, the solids that collect may have been subjected to a wide range of temperature and pressure conditions.

Dust-size particles fall toward the disk, collide & aggregate.

They do this in the context of a temperature gradient from the center to the rim of the nebula, giving rise to a range of time-temperature-pressure paths for the initial agglomerations of condensed matter.

At ***non-equilibrium*** conditions, condensation sequence as applied to the accretion of planetary bodies considers that the primary "rock" phases would partially separate (fractionate) from each other at various steps during cooling of the nebula, and that each class of material can interact with volatiles at lower temperatures.



note: The final low T step, remelting/ accretion, is a later topic.