Lecture 28

High Temperature Geochemistry

Formation of chemical elements

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. Stellar processes

2. nucleosynthesis

Next time

3. Age and Origin of the Solar System:

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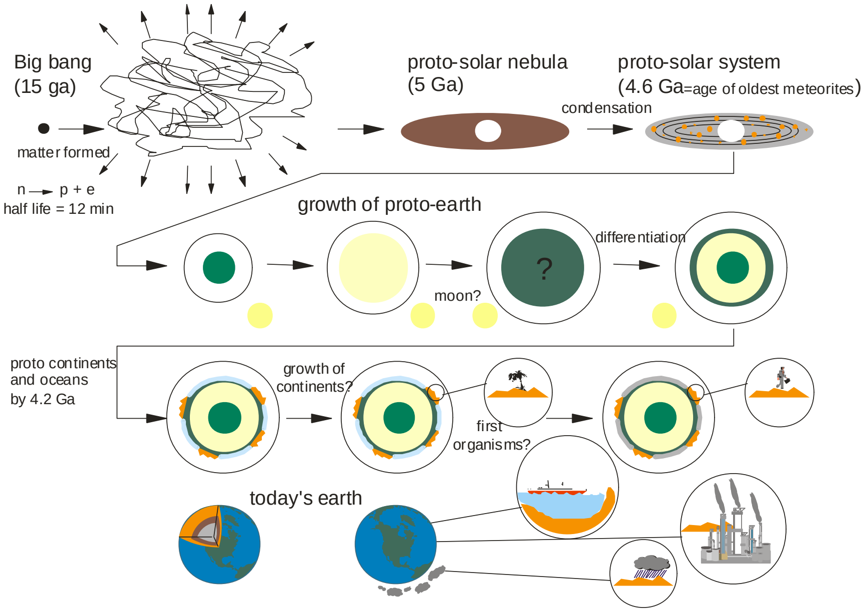
For the last 5 weeks of the semester we focus on the formation and differentiation of Earth, using high temperature and nuclear geochemistry



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Early Solar System History:

Our information includes:

1. **Physical properties** of matter (e.g., nuclear and electronic properties, temporal stability)

2. **Chemical composition** of the sun and other stars (mostly through spectral analysis of emitted light)

3. **Chemical composition** of the moon and other planets (mostly through spectral analysis of reflected light, direct analysis of lunar, Martian, and asteroid samples)

4. **Physical properties** of the Universe, our Galaxy, and our solar system (distribution and age of matter, masses, densities, velocities, orbits)

First step.... the origin of the elements:

Current theories about the origin of matter and time are based on informed speculation and theoretical physics.

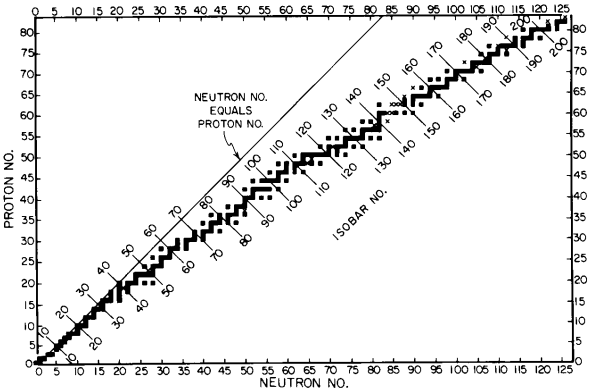
Understanding the construction of the Solar System and the matter it contains requires knowledge of the processes through which the chemical elements are made and the time period over which it occurs.

This process is called "nucleosynthesis"

To understand the formation and persistence of most matter we look to the **atomic nucleus** and the **energetics of nuclear processes**.

Nuclei are held together by strong forces between their subatomic particles. Only certain combinations of protons and neutrons make stable nuclei. *Unstable nuclei "decay" or break apart, by what we term radioactivity.*

The abundances of stable nuclei of odd and even masses gives clues as to their formation and stability: recall that A = Z + N



A	N	Z	# of nuclei
even	even	even	166
	odd	odd	8
odd	even	odd	57
	odd	even	53

Radioactivity and the stability of nuclei

In general, the less energetically favorable a nucleus is, the faster it typically decays (the shorter its lifetime) and the harder it is to make in the first place.

Radioactive decay is a statistical phenomenon, occurring at a rate that is characteristic of a given isotope.

There are 5 main mechanisms of radioactive decay:

β

- **β+ :** emission of a positron, changing a proton into a neutron (changes Z=atomic # but not A=atomic mass)
- **β- :** emission of an electron, changing a neutron into a proton (changes Z but not A)
- **K capture:** inner-shell electron enters nucleus, making a proton into a neutron
- **α :** emission of a $^{4}He_{2}$ particle from nucleus (changes A and Z)
- **Fission:** where a big nucleus splits into two smaller ones, both of relatively high mass

Radioactivity and the stability of nuclei

Radioactivity is quantified with the decay equation:

- ► $-dN/dt = \lambda N$
- ► $\ln N = -\lambda t + C$
- ► at $t=0$, $\ln N_0 = C$
- ► $\ln N = -\lambda t + \ln N_0$
- ► $\ln (N/N_0) = -t$
- ► $N = N_0 e^{-\lambda t}$

where t is time, N and N_0 are the number of atoms of some isotope present at time=t and time=0, and λ is a decay constant. λ is related to half life (the time it takes for 1/2 of the atoms present at any given time to decay away).

by substituting $N_0/2$ for N into above eqn, we derive

$$T_{½} = \ln 2/\lambda = 0.693/\lambda$$

The amount of radioactivity in a material is the number of decays per unit time. It is measured by Activity (A).

$A = \lambda N$ and $A = A_0 e^{-\lambda t}$

Making the chemical elements

The conditions for making and preserving chemical nuclei are a **function of their nuclear stability**.

The fundamental process through which neutrons and protons are combined to make atomic matter occur only in conditions of very high pressure and temperature.

These conditions do not exist on Earth. In fact, they occur only in the cores of some stars.

Even our own star is not massive or energetic enough to produce chemical elements heavier than He.

We must look *beyond our solar system* for the birth of the elements that comprise it.

Before we can understand the processes that make the chemical elements, we should look at the processes that formed matter itself.

The Big Bang

Theory has it that the first matter, **quarks**, was formed in the Big Bang, and that the Universe began to expand from an original singularity.

Quarks are estimated to have coalesced to **neutrons** within the first 10 μsec.

More Big Bang

Next, once a certain threshold of pressure and temperature was reached, the first decay reaction began (still involving subatomic particles): n → p + e.

This reaction has a 12 min. half life, so that 12 min. after the Big Bang equal numbers of p, n and e existed.

Remember that hydrogen is ${}^{1}_{1}H$.

All other atomic matter ultimately comes from **hydrogen** nuclei.

More Big Bang

Next, heavier nuclei were formed:

deuterium ($^{2}_{1}H$), tritium ($^{3}_{1}H$), and helium ($^{4}_{2}He$, $^{3}_{2}He$).

After day 1, it's estimated that ~24% of the mass was He and ~76% was H.

It's estimated to have taken ~300 kyr for the temperature to cool enough for electrically neutral atoms to be stable.

The Big Bang *(continued)*

Next, matter organized into clouds of gas, some of which were dense enough that they could contract under the force of gravity and become the first **proto-stars.**

As temperatures in the cores rose to $>10^{7}$ °, nuclear "burning" (fusion) began.

This is how other elements were (and are) made.

The first, and simplest, nuclear fusion reaction is **hydrogen burning**, the combination of $^{1}_{1}H$ with itself to make $^{2}_{1}H$, $^{3}_{1}H$, $^{3}_{2}He$, and $^{4}_{2}He$.

Overall: $^{1}_{1}H + ^{1}_{1}H + 2n \rightarrow ^{4}_{2}He$ + energy

(Net reaction; the actual mechanism involves 3 steps.)

Nuclear Energy

Stars that burn hydrogen need not be large. This is the reaction that produces our sun's energy and it is occurring in the vast majority of stars we can see.

How much energy is released in hydrogen nuclear burning?

We use $E = \Delta mc^2$ to calculate

nuclear mass of He ^4_2He:	6.64462×10^{-27} kg
rest mass of n:	1.67495×10^{-27} kg
rest mass of p:	1.67265×10^{-27} kg
C (speed of light):	2.9979×10^{8} m/s

Δm = mass(He) – 2 x [mass(p) + mass(n)] = 5.058×10^{-29} kg

$E = 4.546 \times 10^{-12}$ kg m^2/s^2 or J (or 1.0865×10^{-12} cal)
per He atom formed.

Nuclear Energy (*continued*)

$E = 4.546 \times 10^{-12}$ kg m^2/s^2 or J (or 1.0865×10^{-12} cal)
per He atom formed.

by comparison, an average 200g apple has ~50 kcal = **50 x10^3 cal** of energy stored in easily broken (digestible) bonds.

This amount of energy would be released when 4.602×10^{16} He atoms are produced or twice this number of H atoms are consumed.

(which is **1.53×10^{-7} g** of H atoms).

Gram per gram, **1.3×10^9 times more energy** is released when ^1H is burned to make ^4He than when an apple is burned to make CO_2 and H_2O.

Hydrogen and Helium Burning

Because A=5 nuclei are not known to exist in nature, we presume that H-burning only makes predominantly masses 2-4.

Making heavier masses requires **He burning**, which only occurs in much more massive stars (**> 1.5 m_{sun}**).

Eventually He > H in the star, and H burning ceases in a star's core. The core of the star gets denser and hotter, $>10^{8}$ °, at which point He burning to Be and C can begin.

Note: Nuclear "Burning" makes heavier nuclei from lighter ones.

Hydrogen and Helium Burning

He burning to Be and C:

$^{4}_{2}He + ^{4}_{2}He \rightarrow ^{8}_{4}Be$ + energy

and

$^{4}_{2}He + ^{8}_{4}Be \rightarrow ^{12}_{6}C$ + energy or this net reaction:

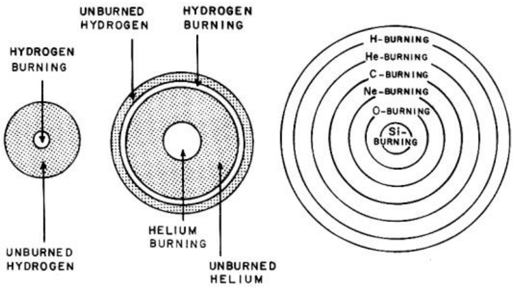
$3\ ^{4}_{2}He \rightarrow ^{12}_{6}C$ + energy

To make C the two reactions must occur quickly to overcome the instability of $^{8}_{4}Be$ (not found in nature, $T_{1/2} = 10^{-16}$ s).

Minor amounts of other isotopes are also made from combinations of $^{1}_{1}H$ and $^{4}_{2}He$.

Note that only small amount of elements with Z = 3, 4, or 5 (Li, stable Be, and B) are produced, which is why their abundance is relatively low on Earth.

More massive star = heavier elements it can burn.



Process	Fuel	Products	Temperature
Hydrogen-Burning	H	He	60 × 10^6 °K
Helium-Burning	He	C, O	200 × 10^6 °K
Carbon-Burning	C	O, Ne, Na, Mg	800 × 10^6 °K
Neon-Burning	Ne	O, Mg	1500 × 10^6 °K
Oxygen-Burning	O	Mg to S	2000 × 10^6 °K
Silicon-Burning	Mg to S	Elements near FE	3000 × 10^6 °K

Figure 2-5. Three stars with progressively hotter nuclear fires: Like our Sun, the star at the left burns hydrogen to form helium in its core; this core is surrounded by unburned fuel. The middle star is burning helium to form carbon and oxygen in its core. This core is surrounded by a layer of unburned helium. Outside of this is a layer in which hydrogen burns to produce helium. Finally there is an outer layer of unburned hydrogen. The star on the right has a multilayered fire. The successive nuclear fires are separated by layers in which no reaction occurs. These layers contain the same fuel as is being consumed in the underlying fire. These layers are depleted in the ingredient being consumed in the overlying fire. The approximate temperatures required to ignite the successive fuels are also given.

Burning makes even heavier nuclei.

Burning processes can account for elemental abundances up to and including Fe.

Hydrogen burning sequence:

$^1_1H + ^1_1H \rightarrow ^2_1H + \beta^+ +$ energy

$^2_1H + ^1_1H \rightarrow ^3_2He +$ energy

$^3_2He + ^3_2He \rightarrow ^4_2He + ^1_1H + ^1_1H +$ energy

Helium burning

$^4_2He + ^4_2He \rightarrow ^8_4Be +$ energy

$^4_2He + ^8_4Be \rightarrow ^{12}_6C +$ energy

(net reaction: $3\,^4_2He \rightarrow ^{12}_6C +$ energy)

Carbon Burning

$^{12}_6C + ^4_2He \rightarrow ^{16}_8O +$ energy

Late-stage burning reactions

Ne, O and Si

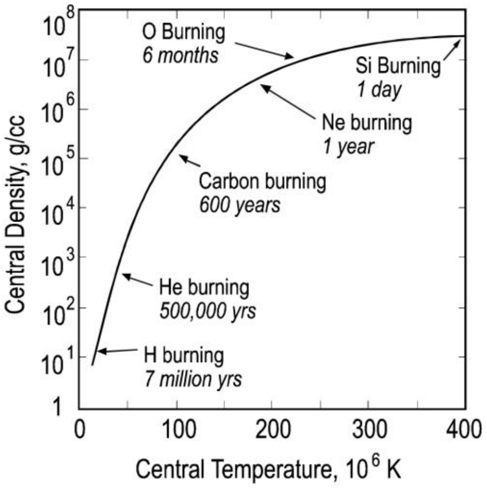


Figure 10.3. Evolutionary path of the core of star of 25 solar masses (after Bethe and Brown, 1985). Note that the period spent in each phase depends on the mass of the star: massive stars evolve more rapidly
modified from White, Geochemistry

The density and temperature at the center of a star must increase to initiate each successive nuclear burning step.

More massive stars evolve faster

The rate of each successive step is progressively shorter.

Very massive stars last for only a few million years, whereas small stars continue to burn H for many billions of years.

Only super-massive stars (>8 m_{sun}) can progress to Si burning (Fe production).

The relationship between stellar mass, temperature, and rate of hydrogen burning.

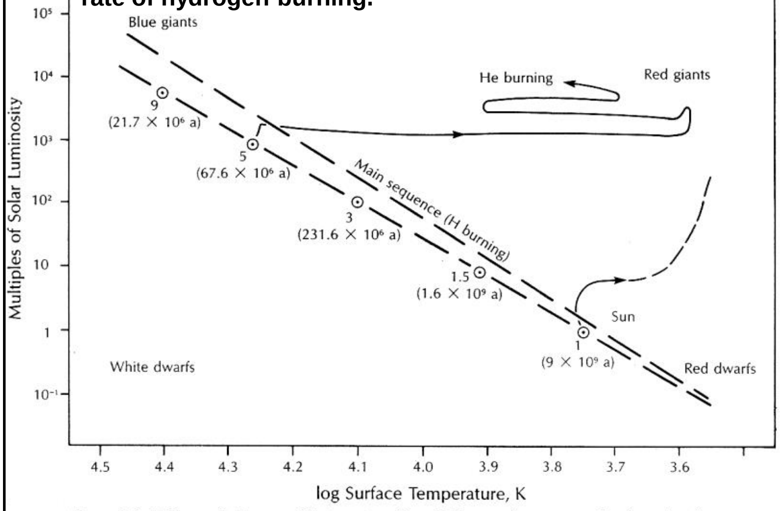
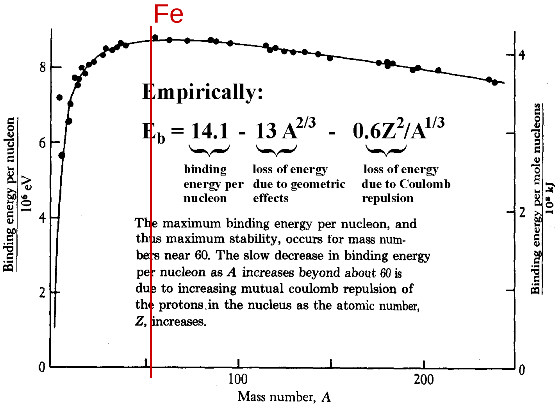


Figure 2.1 Stellar evolution on a Hertzsprung–Russell diagram for stars ranging from 1 to 9 solar masses. When a star has used up the hydrogen in its core, it contracts and then moves off the main sequence and enters the realm of the red giants, which generate energy by helium fusion. The evolutionary track and the life expectancy of stars are strongly dependent on their masses. Stars five times more massive than the sun are nearly 1000 times brighter, have surface temperatures of about 18,000 K—compared to 5800 K for the Sun—and remain on the main sequence only about 68 million years. Their evolution to the end of the major phase of helium burning takes only about 87 million years (Iben, 1967).

Nuclear burning beyond He involves primarily nuclear fusion of He to other nuclei or combinations of two like nuclei

The addition process stops at Fe because after that, energy is no longer gained by making heavier nuclei.



Empirically:

$$E_b = \underbrace{14.1}_{\text{binding energy per nucleon}} - \underbrace{13\,A^{2/3}}_{\text{loss of energy due to geometric effects}} - \underbrace{0.6Z^2/A^{1/3}}_{\text{loss of energy due to Coulomb repulsion}}$$

The maximum binding energy per nucleon, and thus maximum stability, occurs for mass numbers near 60. The slow decrease in binding energy per nucleon as *A* increases beyond about 60 is due to increasing mutual coulomb repulsion of the protons in the nucleus as the atomic number, *Z*, increases.

Figure 28-3 Binding Energy per Nucleon for Stable Nuclei

Modified from Waser, et al. "Chem One"

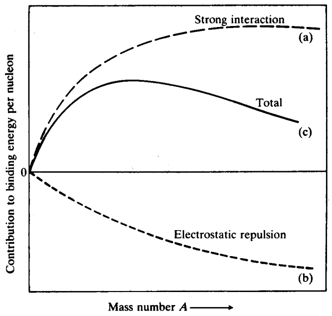
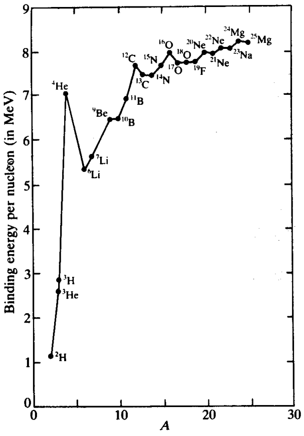


Fig. 2.3. Major contributions to the binding energy curve, Fig. 2.2. (a) Contribution of the attractive strong interaction. (b) Contribution of the electrostatic repulsion between protons. (c) Sum of (a) and (b).

modified from Cox, "The Elements"

Binding energy per nucleon in detail:



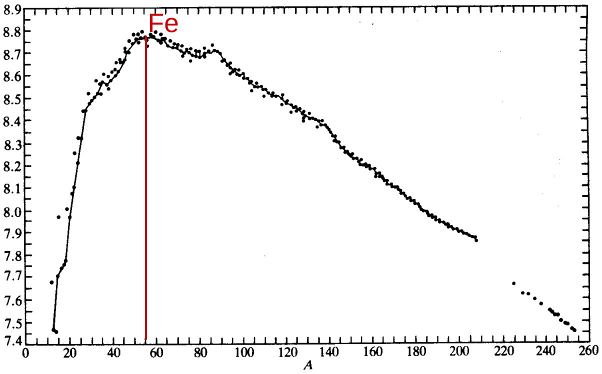


Fig. 2.2. The binding energy per nucleon for stable nuclides, plotted as a function of mass number, *A*. (From Friedlander *et al.* 1981.)

modified from Cox, "The Elements"

Note the plateau around Fe mass. Several other elements (e.g., Cr, Mn, Co and Ni) are similar in energy.

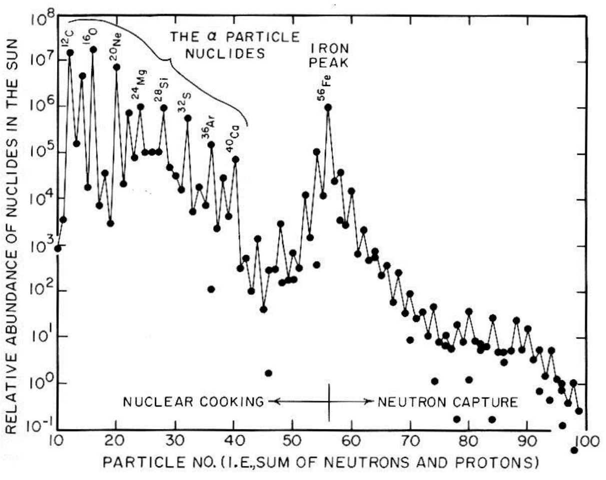


Figure 2-10. Relative abundances of individual nuclides: In the mass range 10 to 50, nuclides with particle numbers divisible by 4 (i.e., 12, 16, 20, 24, 28, 32 . . .) have abundances far above those of their neighbors. They are referred to as the *α*-particle nuclides. In the particle number range 50 to 100 the abundances of nuclides with an even particle number stand about a factor of 3 above those for their odd-numbered neighbors. Where more than one point is shown at a given mass number, two different nuclides with the same neutron-plus-proton number exist. *Broecker, "..Habitable Planet"*

In our solar system, we can account for the relative abundances of nearly all the elements up to Fe by a combination of:

- H burning
- He burning
- heavier-element burning

in ancient stars that existed before the sun.

The most abundant nuclei up to ^{56}Fe are based on combinations of $^{4}_{2}$He nuclei and have masses that are multiples of 4.

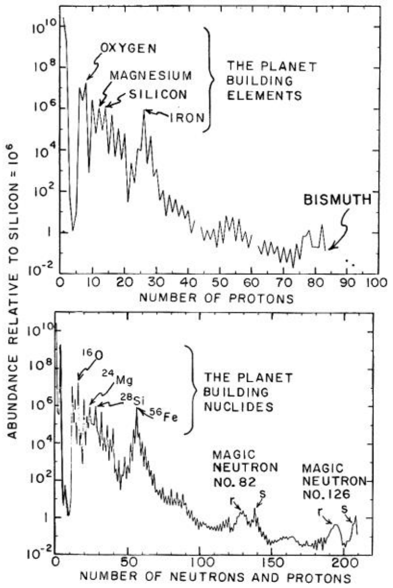


Figure 2-12. The raw material for planet formation: The upper diagram shows the relative abundances of the elements. Up to bismuth there are only two elements not found in nature; technetium (element 43) and promethium (element 61). The lower diagram shows the relative abundance, of the isobars. Only two isobars of nuclear number less than 208 are not represented in nature, those of mass 5 and of mass 8. *Broecker, "..Habitable Planet"*

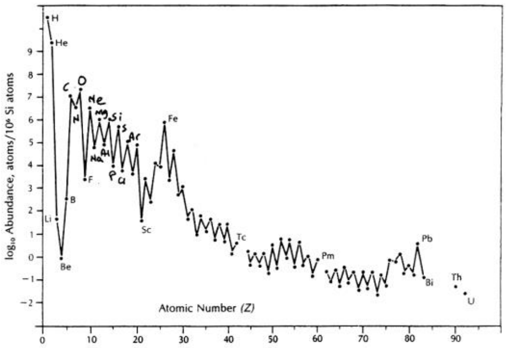


Figure 2.2 Abundances of the chemical elements in the solar system in terms of atoms per 10^6 atoms of Si. The data were derived primarily by analysis of carbonaceous chondrite meteorites and by optical spectroscopy of light from the Sun and nearby stars (Anders and Ebihara, 1982).

<u>Elements heavier than Fe</u> are nearly all made by nuclear processes involving direct ***neutron addition*** to a target nucleus, sometimes interspersed with radioactive decay.

The sources of neutrons for these reactions are:

(1) side reactions in the late-stage burning processes

(2) the very high neutron fluxes that occur during a supernova of a very massive stars.

Nuclei with the “magic” neutron numbers of 82, 126, and 184 are unusually stable, producing kicks or jogs in the neutron addition pathways.

There are two main neutron-addition pathways: the **s-process** and the **r-process.**

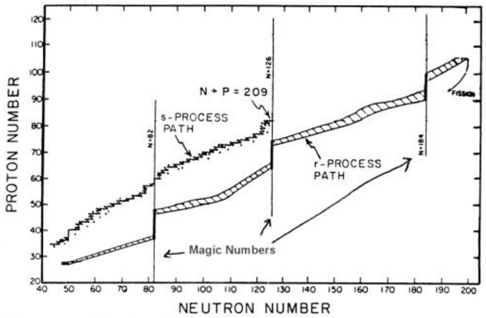


Figure 2-6. The elements heavier than iron were built by neutron irradiation: Two quite different processes contributed to this production. One, the s-process (i.e., slow process), occurs concurrently with the production of iron in the stellar core. As in a nuclear reactor, the reaction proceeds in a controlled way. Neutron hits are spaced out in such a way that the nuclides have time to achieve stability through beta decay. Thus, the buildup path follows the belt of stability shown in Figure 2-2. For the same reason it terminates at ^{209}Bi, the heaviest stable nuclide.

The r-process (i.e., the rapid process) occurs during the supernova explosion. Thus, it is akin to an atomic bomb. No sooner has a nuclide absorbed one neutron than it is hit by another. No time exists between hits for radiodecay. Rather, radiodecay occurs only when the nuclide becomes so neutron-rich that it cannot absorb any more. This leads to a buildup path displaced from the stability belt as shown. It also allows the buildup to proceed beyond particle number 209. Instead, the buildup goes just beyond particle number 300. At this point the colliding neutrons cause the nuclides to fission. The jogs in the r-process pathway occur at the so-called magic neutron numbers, 82, 126, and 184. They are "magic" in the sense they give the nuclide unusual stability. *Broecker, "..Habitable Planet"*

Three main heavy-element forming processes:

- **The s-process**.

This neutron addition process is slow enough for decay to occur between steps. It occurs only in neutron dense environments, such as large stars collapsing before death. The s-process only produces nuclides to n+p = 209 (which is Bi).

$^{A}_{z}X + ^{1}_{0}n \rightarrow ^{A+1}_{z}Y$ + energy (slow). $^{A+1}_{z}Y$ is stable enough to not decay before the next neutron addition. *Produces relatively neutron poor nuclides.*

- **The r-process**.

Neutron addition is so rapid that it bypasses nuclear decay with sheer speed. This only occurs during high neutron flux events such as supernovae, that then disperse the products into the neighboring region of the galaxy.

$^{A}_{z}X + ^{1}_{0}n \rightarrow ^{A+1}_{z}Y$ + energy (fast). $^{A+1}_{z}Y$ is unstable and would decay away except that neutron addition is faster than the decay rate. *Produces neutron rich nuclides.*

As far as we know, none of the naturally-occurring elements above 209 (Bi) would be present in the universe without the r process.

- **The p-process**.

This less frequent process involves p addition. *Produces protron rich nuclides.*
For instance $^{72}_{32}Ge + 2\,^{1}_{1}H \rightarrow ^{74}_{32}Se$

A slow process reaction sequence:
$^{62}_{28}Ni + ^{1}_{0}n \rightarrow ^{63}_{28}Ni + \gamma$ followed by
$^{63}_{28}Ni \rightarrow ^{63}_{29}Cu + \beta^{-}$

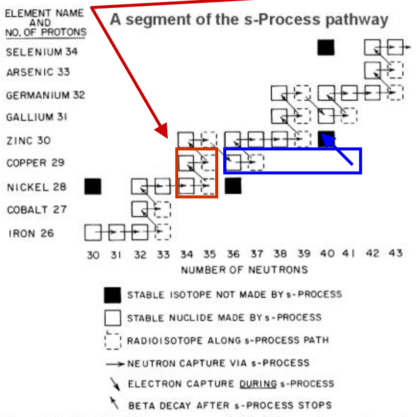


Figure 2-8. Details of the s-process path: Each time neutron capture produces a radioactive isotope, radiodecay occurs changing either a neutron into a proton or a proton into a neutron. Not all of the stable isotopes found in solar-system matter can be produced in this way. Those stable isotopes lying below the s-path are produced by the r-process. Those stable isotopes lying above the s-path are produced by proton bombardment.

Broecker, "..Habitable Planet"

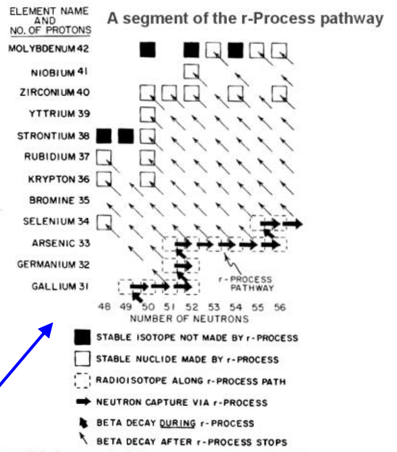


Figure 2-7. A segment of the r-process pathway: Rapid-fire neutron bombardment adds neutrons until a nuclide cannot hold any more. Only then does the nuclide undergo beta decay to become the next heavier element. This process—neutron capture to saturation followed by beta decay—is repeated over and over again, producing successively heavier elements. The r-process buildup occurs during the explosion that destroys the red giant. Hence it ends abruptly. The neutron flux stops and the highly radioactive isotopes on the r-process pathway emit beta particles one after another until stability is achieved. Note that in the case of those isobars for which two stable nuclides exist, only the neutron-rich nuclide of the pair is produced by the r-process.

Broecker, "..Habitable Planet"

A rapid process reaction sequence:
$^{65}_{29}Cu + 5\,^{1}_{0}n \rightarrow ^{70}_{29}Cu + 5\gamma$ followed by $^{70}_{29}Cu \rightarrow ^{70}_{30}Zn + \beta^{-}$
The 2nd reaction must happen quickly, before $^{69}_{30}Zn$ decay

Odd vs Even Nuclei:

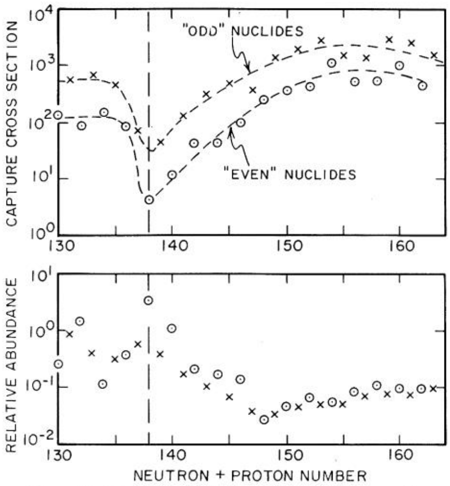


Figure 2-11. The relationship between neutron-capture cross sections and abundance: In the upper panel is shown the neutron-capture cross sections of nuclides produced by the s-process as a function of mass of the nuclide. Note the smoothness of the trend; note also that nuclides with an even number of nuclear particles have lower cross sections than those of their odd-numbered neighbors. Finally, note the minimum in the cross sections for both the even and odd nuclides near mass 138. Nuclides with this and neighboring masses have 82 neutrons, one of the magic numbers (see Fig. 2-6). As can be seen there is an inverse correlation between abundance and cross section. Nuclides with low capture cross section are higher in abundance. *Broecker, "..Habitable Planet"*

Even mass nuclei are more stable and thus less likely to capture a neutron during r and s neutron addition processes. This is why even nuclei are more abundant in nature

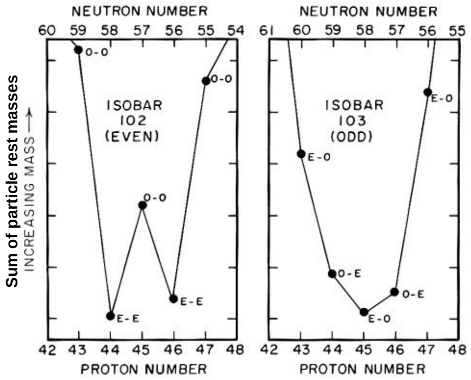


Figure 2-14. Odd–even particle number systematics: Shown here are the masses for two sets of nuclides. On the left are shown nuclides of particle number 102 (an even number). On the right are shown nuclides of particle number 103 (an odd number). The smaller the mass the more strongly the nuclide is bound together. For odd isobars, of the various possible neutron–proton combinations, one always has a lower mass than both its adjacent neighbors. For even isobars, there are usually two such nuclides. The reason for this difference is that odd–odd neturon–proton combinations are less tightly bound than even–even combinations. *Broecker, "..Habitable Planet"*

The chain of nucleosynthetic events summarized:

Start with a young, large H-burning star. This star eventually undergoes supernova death after the sequence depicted in the figure.

Initially, a star enters the nuclear burning stages, during which fuel is burned, the star becomes more massive, it collapses gravitationally, and then it enters the next, hotter burning stage, until finally Si is burned to Fe.

s-process neutron addition also occurs in the later stages of this sequence.

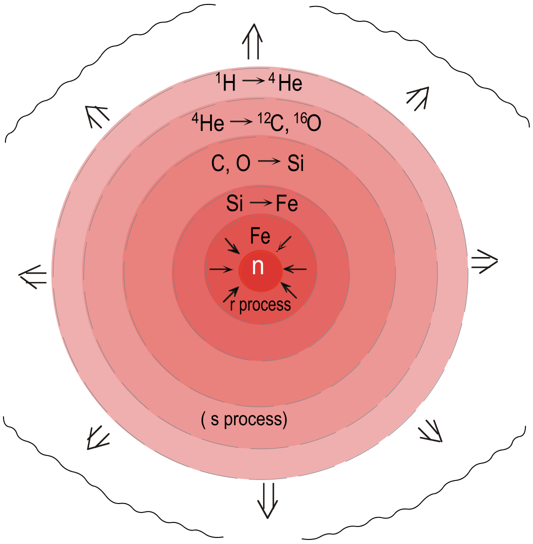


Figure 10.4. Schematic diagram of stellar structure at the onset of the supernova stage. Nuclear burning processes are illustrated for each stage. *modified from White, Geochemistry*

Eventually, the star's core exhausts its nuclear fuel, collapses gravitationally, and r-process nucleosynthesis initiates. The star implodes and then explodes in a supernova, ejecting its elements into nearby space.

Resulting atomic abundances summarized:

Those due to α-burning include:
H and He are most abundant, H/He ~12.5
The abundance of the first 56 elements (to Fe) decreases roughly exponentially, with 4 amu local peaks in abundance
Those due to the r- and s- processes include:
Abundances of >Z=56 elements are low are vary much less with Z
No stable isotopes above z=83 (Bi), but long-lived radioactive Th and U, + their transient radioactive daughter isotopes, still exist in our solar system today. Other radioactive transuranics (U-Pa-Th-Np...) produced by the r-process before our solar system formed, have subsequently all decayed away by fission, α or β decay
Th and U decay through various daughter to various (stable) isotopes of Pb, which accounts for the seeming overabundance of the Pb.
Those due to general nuclear stability include:
Even atomic #s are more abundance than odd ones.
Li, Be, B are very low compared to other low Z elements
Fe is high compared to similar Z elements
Tc and Pm do not exist

Here's a summary of all nucleosynthetic processes, including the rare ones we haven't discussed, and the resulting abundance vs. mass: relationship in our solar system.