Lecture 3: The age of the elements, and the formation of the earth and oceans

Looking Past the Veil

In a way it's ironic that we have more confidence in our ideas about what transpired in the first few nanoseconds of the creation of the universe some 14 Ga (billion years) ago than what we "know" about the first billion years of the earth's (or our solar system's) history. One of the reasons, of course, is that things were simpler (if rather exotic) at the beginning of the universe, whereas the early evolution of our solar system and planet are masked now by many complex events that have overprinted the record, obscuring our view. However, isotopes, and in particular radioactive and radiogenic isotopes, provide us with powerful constraints on the timing and mechanics of events. The name of the game is to use the fact that in general, radioactive transmutation involves a change in the elemental identity, and hence chemistry. We use this in a number of ways. Moreover, there are isotopic signatures of extinct radioactivities (elements with rather short half-lives that must have been freshly created prior to solar system formation) that are preserved in the record.

The table below is a list, in order of increasing half-life, of radionuclides that have been exploited to look at early earth and solar system history. Although there is a wide range of half-lives to choose from in the table of the isotopes, one might initially guess that an isotope needs a half-life ranging from several hundred million years to several billion years to be useful. At the low end, it must be long-lived enough to survive to be measured. At the high end, it must have a short enough decay time to have an appreciable change. Surprisingly, some of the very short-lived isotopes are of interest, particularly in the range of a million years or so, because we can see evidence of their past existence in isotopic signatures. These are known as "extinct radioisotopes".

Parent	**Daughter**	**Half-life (Ma)**
^{26}Al	^{26}Mg	0.730
^{60}Fe	^{60}Ni	1.5
^{53}Mn	^{53}Cr	3.7
^{107}Pd	^{107}Ag	6.5
^{182}Hf	^{182}W	9
^{129}I	^{129}Xe	15.7
^{244}Pu	Fission Xe	82
^{146}Sm	^{142}Nd	103
^{235}U	$\rightarrow ^{207}Pb$	704
^{40}K	^{40}Ca, ^{40}Ar	1,270
^{238}U	$\rightarrow ^{208}Pb$	4,469
^{232}Th	$\rightarrow ^{206}Pb$	14,010
^{187}Re	^{187}Os	41,600
^{87}Rb	^{87}Sr	48,800
^{147}Sm	^{143}Nd	106,000
^{190}Pt	^{186}Os	450,000

It is now generally accepted that our sun and solar system formed at the same time. The fact that the earth and inner planets consist largely of elements other than the primordial elements (hydrogen, helium and lithium) means that the material from which our sun and solar system was formed must have been previously produced within an earlier generation of stars, which in turn must have created the elements from a cataclysmic series of supernova events. (For a recent discussion of this, see Hester et al, 2004). It is likely that our solar system coalesced from a cloud of dust and gas that was the ashes of other exploding stars, and that the condensation was triggered by a shockwave from other exploding stars. It is also likely that the condensing solar nebula was peppered with freshly minted nuclei from additional supernovae, adding more material to the mix. This presents us with a number of challenges and caveats to our use of isotope systems:

- Non-closed system (addition, removal of material)
- Heterogeneity (material may not be mixed prior to incorporation or processing)
- Multiple events of differing physical or chemical character (what are we dating?)
- Overprinting by subsequent events (metamorphism, weathering, diagenesis, etc).

We will find that the solar system formed about 4.6 Ga ago, and that the earth was substantially formed within 100 Ma or so after that. We will examine a few isotope systems that tell us this, and consider the attributes of the information provided by them.

How Old are the Elements?

Our sun and solar system were formed as the result of a supernova shock wave travelling through the remains of other supernovae. The elements that make up the material from which the solar system formed were fabricated in the last few moments of a star's life. How long ago did this happen? How long did this material sit around before the sun and solar system formed? An upper bound for this time is the age of the universe, about 14-15 Ga. The lower bound for this is the age of the earth (about 4.5 Ga). It turns out we can do better than this. Thinking about the formation of the elements, especially the r-process, it can be argued that the major isotopes of U (235 and 238) and Th (232) are produced in roughly equal proportions. More thorough (and complicated) calculations provide us with an estimate of the primordial production ratio of

$$\left(\frac{^{235}U}{^{238}U}\right)_{Primordial} \approx 1.3$$

That is, the lighter isotope was initially more abundant. This makes sense, because the elements are built up from lower masses. However, present day isotopic ratios in the earth appear quite constant at

$$\left(\frac{^{235}U}{^{238}U}\right)_{Present} = 0.0072$$

The reason for this is quite simple. Both isotopes are radioactive, but the lighter isotope ^{235}U has a shorter half-life, 704 Ma, and has decayed away more rapidly than the heavier isotope ^{238}U, which has a half-life of 4.47 Ga. Over the time since the elements were created, more than 99% of the ^{235}U has decayed, while the ^{238}U is about half gone.

We can derive a simple relationship based on the radioactive decay equation. Here's how:

$$^{235}U = {^{235}U_0} e^{-\lambda_{235} t}$$

$$^{238}U = {^{238}U_0} e^{-\lambda_{238} t}$$

Now dividing the first equation by the second:

$$\left(\frac{^{235}U}{^{238}U}\right) = \left(\frac{^{235}U}{^{238}U}\right)_0 e^{-(\lambda_{235}-\lambda_{238})t}$$

Let's call the uranium isotope ratio "R", so that we have

$$R = R_0 e^{-(\lambda_{235}-\lambda_{238})t}$$

$$or$$

$$\frac{R}{R_0} = e^{-(\lambda_{235}-\lambda_{238})t}$$

and can be solved by taking the natural logarithm of both sides:

$$\ln\left(\frac{R}{R_0}\right) = -(\lambda_{235} - \lambda_{238})t$$

$$or$$

$$t = \frac{\ln\left(\frac{R}{R_0}\right)}{\lambda_{238} - \lambda_{235}} = \frac{\ln\left(\frac{0.0072}{1.3}\right)}{1.537x10^{-10} - 9.763x10^{-10}} = \frac{-5.196}{-8.226x10^{-10}} = 6.3Ga$$

The uncertainty in this number is about 0.2 Ga, which is due to uncertainties in the initial abundance ratio of about 20%.
A similar calculation can be done using the pair ^{232}Th:^{238}U, where the initial and present day ratios are 1.6 and 2.8 respectively. The equations are identical for this pair, but using the different half-lives (4.47 Ga for ^{238}U and 14.0 Ga for ^{232}Th). The result is an estimated age of 5.3 Ga, but this number is considerably more uncertain, about ± 2 Ga, due to the much longer half-lives involved, even thought the primordial ratios are still known to about ±20%. Moreover, there is an additional uncertainty introduced, because chemical/physical processes can also easily separate Th and U during the earth's formation and subsequent evolution.

The big problem, however, is that the ashes from which the solar system condensed are likely a mixture of materials that were fabricated over a range of times. The simple calculations done above must fail because it is probable that the ratios of the isotopes are substantially different from the primordial ratios. One could argue that for a more-or-less continuous formation process (stars exploding all the time), that the inventories of these isotopes would build up until their production would be balanced by radioactive decay. Thus at steady state, one would have

$$P_{235} = \lambda_{235} N_{235}$$

$$P_{238} = \lambda_{238} N_{238}$$

which, using the primordial production ratio of 1.3, we get

$$\left[\frac{N_{235}}{N_{238}}\right]_{initial} = 1.3\frac{\lambda_{238}}{\lambda_{235}} = 0.20$$

which, if we reapply this number to our original calculation, we get

$$t = \frac{\ln\left(\frac{R}{R_0}\right)}{\lambda_{238} - \lambda_{235}} = \frac{\ln\left(\frac{0.0072}{0.20}\right)}{1.537x10^{-10} - 9.763x10^{-10}} = \frac{-3.324}{-8.226x10^{-10}} = 4.04Ga$$

which is actually *younger* than the solar system. The answer is somewhere between the two extremes, because the activity ratio of the two isotopes will not have had time to really reach their "secular" equilibrium. The question now becomes more complex, since we are not asking at what specific time a nucleosynthetic event occurred, but rather over what range times, and what circumstances. For example, the young age above could be a signature of late addition of U isotopes to the earth/solar system, although we have arguments to explain it other ways as well. We've probably reached the limit of what we can realistically do with these isotopes (although that might not stop some people), so we ought to turn to other approaches. Before doing so, we need to consider other lines of evidence.

The Formation of the Solar System and the Earth

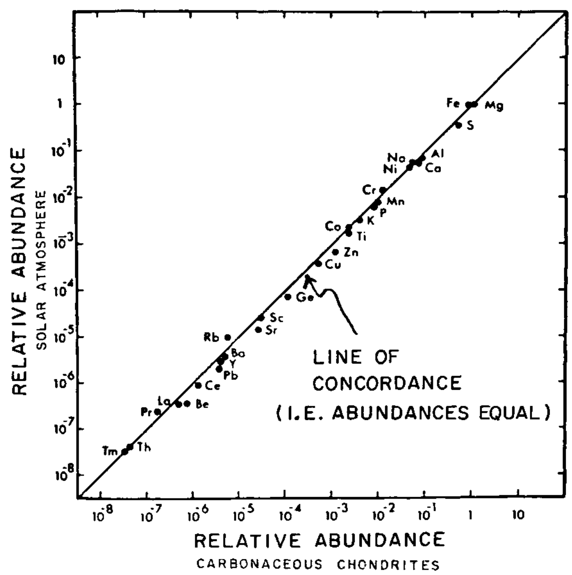
99.8% of the mass of the solar system is in the sun, although most of the angular momentum in the solar system resides in the planets. The solar system probably started as an equatorial disk of gas and small grains that commenced cooling from the outside inward. The planets themselves were probably formed from localized vortices set up in the cooling disk (Von Weizsacker's theory) or solar system-scale rings analogous to those formed around Saturn. The temperature gradient throughout the proto-system as the planets formed (cool in the outer regions, hotter near the centre) resulted in a characteristic pattern in planetary structure: planets with greater density and more "refractory" composition appear nearer the sun, and planets with lower density and more "hydrogenous" composition appear further out.

	Mercury	**Venus**	**Earth**	**Mars**	**Jupiter**	**Saturn**	**Uranus**	**Neptune**	**Pluto**
Mass (Earth = 1)	0.05	0.81	1.00	0.11	318	95	14.5	17.3	0.03
Density (g/cc)	5.1	5.0	5.5	3.9	1.33	0.71	1.27	2.22	2?

Jupiter is by far the most massive, and one of the least dense planets. Its composition is most similar to the sun, and in fact, may be regarded as a "failed star". That is, it did not have enough mass to become a star in its own right. This is not unusual. Paired stars, called "binary systems" or "binaries" for short, are quite common, with one of the stars being rather larger than the other. These stars orbit one another, and it is this orbital motion which provides the evidence for their existence. The detailed formation process of the terrestrial planets is still in debate (see Chambers, 2004).

Compositional Evidence from Solar/Stellar Spectroscopy and meteorites

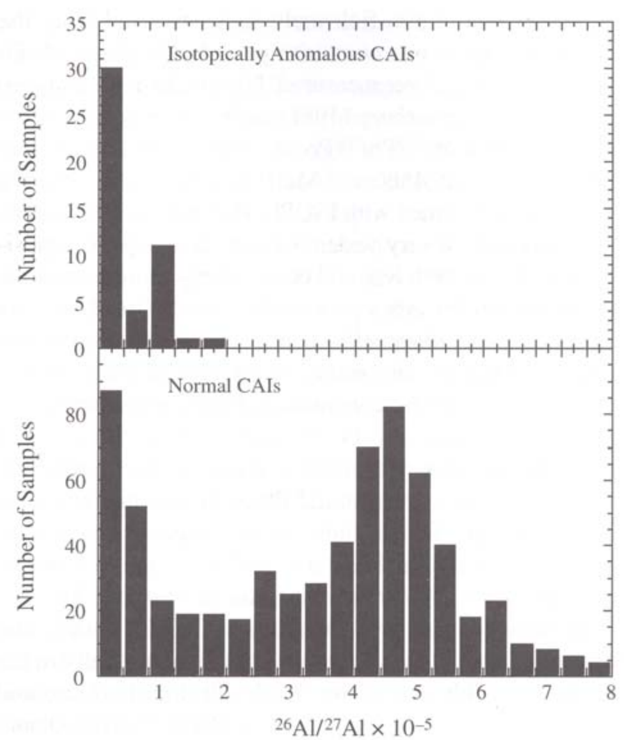
How do we know what the cosmic abundance of the elements is? All we have is some direct measurements of material scratched off the surface, plus indirect inferences about the material underneath. For that matter, how do we know the elemental abundances for our own sun? There's a nice summary article by Drake and Righter (2002) in Nature. One source of information lies in solar and stellar spectroscopic data. When you look at the spectrum of light from the sun, either using a prism or a diffraction grating, you see a characteristic rainbow-like colour pattern, with a series of black lines superimposed. The rainbow-like background results from the interior regions of the sun (or star) glowing with heat. Outside of the glowing shell is a cooler, unionized shell of gas. Some photons from the continuous spectrum of photons passing through the gas have exactly the right energy (wavelength) to excite the gas atoms into a higher excited state. Those photons are removed from the spectrum, leaving a "black" line. How black this line is (i.e., how many photons are removed from the stream) depends on the amount of the gas in its path. Now each element has a unique, identifiable pattern of lines associated with this excitation. The 19th and early 20th centuries saw a complete analysis of solar composition using this technique. In fact, the element Helium (from "Helos", for "sun") was discovered in the sun's spectrum in 1868, thirty years before it was isolated on the earth. An important, underlying assumption of this technique is that the outer layer of the sun (or star) that is cool enough to induce these adsorption lines has a composition representative of the remainder of the star. That is, it assumes that convection within the sun/star is vigourous enough to homogenise its composition.



Careful observations of some meteorite falls have allowed astronomers to back-calculate the orbits and hence origins of meteorites. Evidence points to the asteroid belt between Mars and Jupiter. This makes some sense, as the asteroid belt is thought to be the remnant of a failed planet: either one that hasn't formed or one that has broken up. There are two basic types of meteorites: stony and iron. About 90% of all meteorite falls are stony, but the iron meteorites are routinely much more massive. In fact, on a weight basis, about 65% of the material is iron meteorites.

Iron meteorites are metallic and rich in iron. Inasmuch as pre-solar material is unlikely to be refined by any simple processes, this implies that they originated in the breakup of a differentiated planetary body. The iron meteorites would then be part of the core of this putative planet. Considering this model of meteorite stony meteorites might be regarded as the mantle or crust of this assumed planet, but a significant sub-class of meteorites are clearly not from a differentiated parent body. These meteorites are called "chondrites" because they have "chondrules" distributed throughout them. Chondrules are small (0.1 to 1 mm sized) spherical entities resembling droplets that appear to have solidified from a melt. They are largely made up of olivine, and likely have condensed out at about 1250°K. Also embedded in the surrounding ground-mass (which has similar composition to the chondrules) are millimeter sized particles of nickel-iron. This mineralogical evidence points to a primitive, undifferentiated origin for chondritic meteorites.

Some compelling evidence for chondrite origins comes from the analysis of volatiles in a rare subclass called "carbonaceous chondrites". The isotopic ratios of noble gases, as well as other elements clearly indicate that these meteorites are indeed primitive, and represent unprocessed samples of the material from which the solar system has formed. Analysis of elemental abundances within these meteorites match closely cosmic abundance information obtained from spectroscopic techniques. However, detailed comparison of isotopic and composition evidence suggests that although there’s



Histogram of ^{26}Al/^{27}Al for normal and isotopically anomalous (the so-called FUN and UN inclusions) from Allende. After *MacPherson et al.* (1995).

some commonality, fundamental differences do exist, and that although similar, we don't as yet have unbiased samples of the "stuff" from which the earth was formed (see Drake and Righter, 2002).

These meteorites, however, are demonstrably primitive, and contain other clues about the formation of the solar system. Work has focused on calcium-aluminum inclusions, referred to as CAI's, which show evidence of extinct radioisotopes (notably ^{26}Al), and are the oldest known objects in our solar system. This shows up as anomalous increases in the daughter product ^{26}Mg, which can then be used to calculate the $^{26}Al/^{27}Al$ ratio of the material on formation. Even amongst the CAIs, there are anomalous types, suggesting a certain degree of heterogeneity in the solar nebula. This would arguably be the case if the nebula were peppered with debris from neighboring supernova events, since a relatively short half life (< 1 Ma) would be sensitive to this lack of uniformity.

Concerns were raised when the possibility was suggested that some of these extinct radionuclides could be produced by protosolar cosmic rays rather than by nucleosynthesis (e.g., see Lee et al, 1998). However, evidence of extinct ^{60}Fe, as reported by Tachibana and Huss (2003), which is not readily produced except by nucleosynthesis suggests that these concerns are not well founded.

Recently, long-chain hydrocarbons have been measured in carbonaceous chondrites that suggest that the planets condensed from the solar nebula at temperatures below 400°K. This comes from the fact that these compounds can form below this temperature from the schematic reaction below:

$$20\,CO + 41\,H_2 \Leftrightarrow C_{20}H_{42} + 20\,H_2O$$

whereas at higher temperatures (above 450°K), the following process occurs

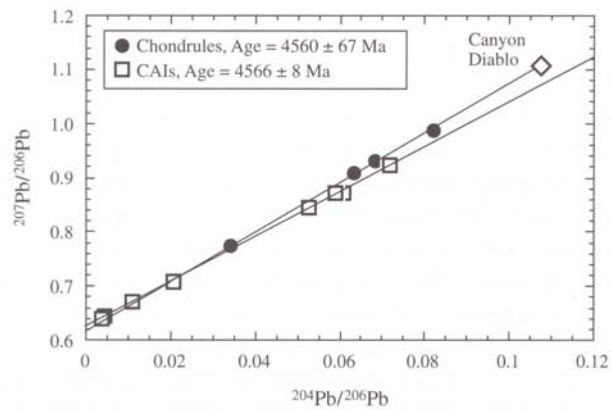
$$CO + 3\,H_2 \Leftrightarrow CH_4 + H_2O$$

Meteorites and the Age of the earth

How old is the earth? Can we do a similar calculation as we did for the age of the elements? The answer to the latter question is "not really", but we can come up with an answer to first question anyway. Uranium ultimately decays to lead in the following two reactions:

$$^{238}U \rightarrow {}^{206}Pb + 8\,\alpha$$
$$^{235}U \rightarrow {}^{207}Pb + 7\,\alpha$$

Lead has a variety of isotopes, amongst them is ^{204}Pb, which is not produced by any radioactive decay sequence, and hence must be primordial in origin. If we knew the primordial $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios, then we could determine how much radiogenic ^{207}Pb and ^{206}Pb has been created, and using the ^{235}U and ^{238}U concentrations, we can calculate the ages from the radioactive decay equation:



Lead-lead systematics for Allende CAIs (*Chen and Wasserburg,* 1981) and chondrules (*Chen and Tilton,* 1976) showing the widespread Pb-isotopic composition of the CAIs. The line defined by the CAI data pass to the unradiogenic side of Canyon Diablo Pb, indicative of a nonsolar initial Pb-isotopic composition in CAIs.

$$^{238}U = {}^{238}U_0 e^{-\lambda t}$$

or

$$^{238}U = \left({}^{238}U + {}^{206}Pb^*\right) e^{-\lambda t}$$

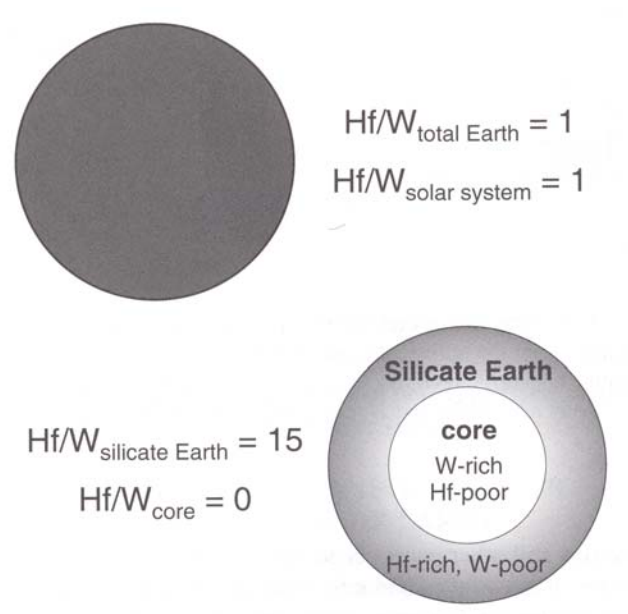
where the Pb* is the lead attributable to radiogenic decay. Now if only we could separate the radiogenic Pb from the original ("primordial") lead, because any lead that we *do* see in a sample will be a mixture of primordial and radiogenic lead.

Iron meteorites have virtually no uranium, but lots of lead. Thus we can look to the iron meteorites to provide us with the primordial lead isotope ratios. Turning to our old friends the carbonaceous chondrites, which are rich in U and poor in Pb, we can then date the meteorites, which presumably formed at the same time as the earth. This age is close to 4.5 Ga (see a definitive study by Allegre et al, 1995). Other radioisotope clocks, specifically ^{40}K-^{40}Ar and ^{87}Rb-^{87}Sr have been used to give consistent results.

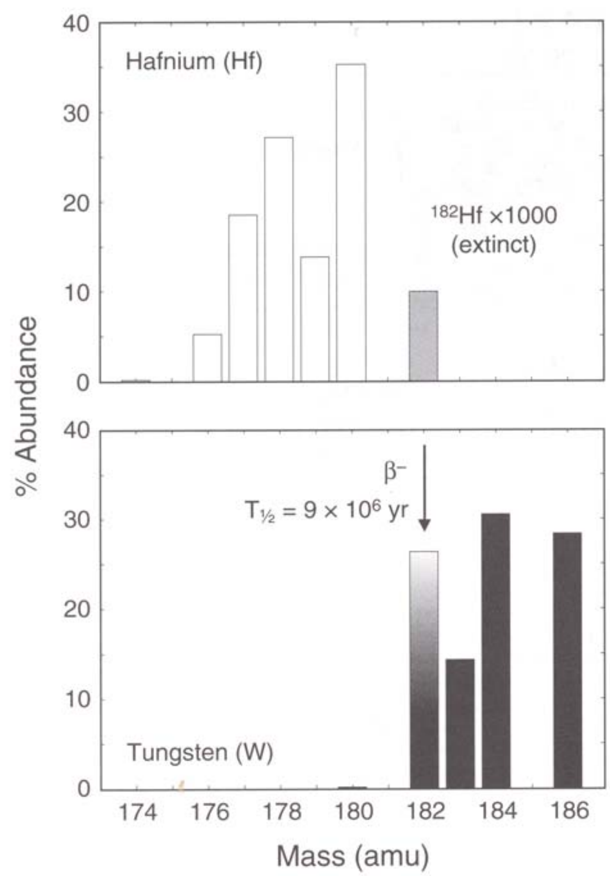
Meteorite (particularly the CAI and other phases such as chondrules) evidence gives timescales between the formations of the most primitive phases as a few million to a few tens of millions of years, depending on the isotope system you use. See, for example work on ^{53}Mn-^{53}Cr systematics by Lugmair and Shukolyukov (1998). These differences are not surprising considering the fact that each isotopic system will tend to respond to different chemical events and on different timescales (raising issues of homogeneity etc).

Earth Evolution, core formation, and Age of the Atmosphere

A simple calculation shows that the gravitational potential energy that would be released by the accretion of the earth's mass from the solar nebula is enough to melt the earth completely three times over. It turns out that most of this energy was dissipated by black body radiation. Nonetheless there was enough heat to partially melt the earth, and this is likely resulted in the early segregation of the core from the mantle, and possibly some early version of the crust. Here, the Hf-W system, with a 9 Ma half-life sets a valuable constraint. The difference between the chemistry of the parent and the daughter is that the latter would preferentially move into the core: tungsten is a "siderophile" element, whereas Hf is more comfortable in a silicate phase. Thus we would have the following scenario:



Schematic showing the fractionation of Hf from W in the early solar system.



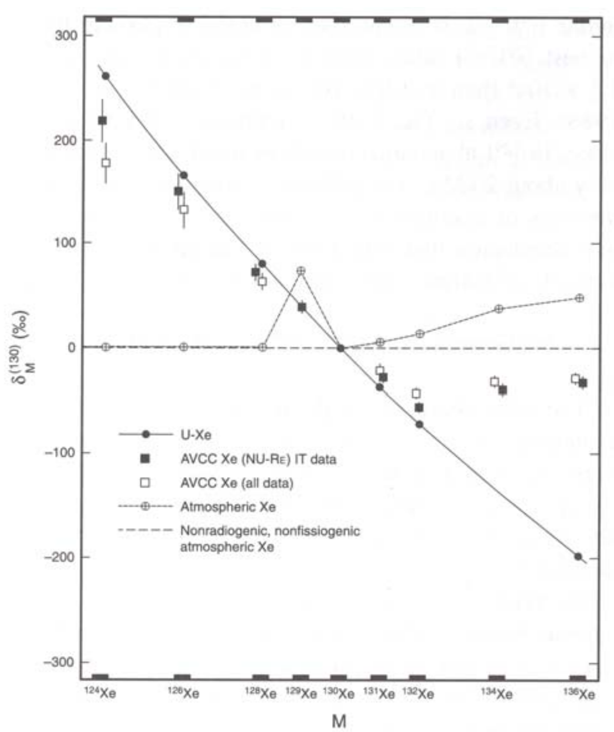
Isotopic abundances of Hf and W. Also shown is the amount of ^{182}Hf at the start of the solar system, magnified by a factor of 1000.

Work by Halliday and co-workers suggests very short time scales (a few million years) between planetary accretion and core formation. However, arguments can be made that lack of homogenization of incoming material with the rapidly differentiating earth may result in spuriously short time-scale determinations from this isotope system. (See the *Nature* article by Halliday).

In addition to the gravitational energy released as heat, the earth has been "fuelled" by radioactive decay of naturally occurring radionuclides. The energy that arises from radio-decay ultimately becomes heat. The thermal time constant of the earth is measured in millions of years (that is, it would cool down to ambient temperatures in a short time compared to its age), and all of the heat-flow observed at the earth's surface is due to these radionuclides. Mantle convection and plate motion are all driven by the heat produced from the decay of these isotopes. The primary heat producing radionuclides are:

Radionuclide	**Half-life (Ma)**
^{26}Al	0.73
^{129}I	15.7
^{244}Pu	82
^{235}U	704
^{40}K	1270
^{238}U	4469
^{232}Th	14010

Heat production was much greater early in the earth's history. Note that because these isotopes have different half-lives, their relative contributions will vary with time: the first few isotopes were very important in heat generation early in the earth's history, and the latter three have become more important later. As a result of this, partial melting of the earth, and the segregation of the core from the mantle likely occurred early in the earth's history. This process may well have played a role in the formation of the earth's atmosphere. Clearly the atmosphere has evolved since then, as we know that degassing of the earth is going on even today, and due to chemical evolution (weathering and biological reactions). However, geological evidence suggests that the atmosphere likely formed within the first few hundred million years of the earth's history. We ought to be able to refine that estimate based on other isotopic information.



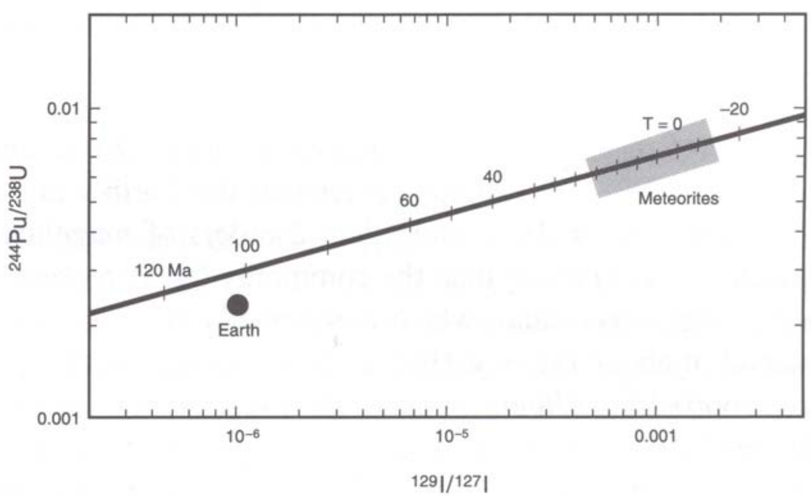
This information arises from consideration of the second isotope in this list: ^{129}I. This isotope was created during nucleosynthesis, and existed in the pre-solar cloud of gas and material when the solar system started to form. Now we know the radioactive decay is

$$^{129}I \rightarrow {}^{129}Xe + \beta^- + \bar{\nu}$$

It turns out that there are several isotopes of Xe, so that if there were significant amounts of ^{129}I around, then there would be anomalous amounts of ^{129}Xe relative to the other isotopes. Typically, data are related to ^{130}Xe, a non-radiogenic isotope of xenon.

There is plenty of Xe in the atmosphere for sampling. The challenge, in fact, is to decide on what the solar nebula unfractionated end-member Xe pattern is (referred to as "U-Xe"; see the diagonal line in the figure here). This is obtained by careful analysis and interpretation of primitive meteorites. It turns out that the atmosphere has a strongly mass fractionated isotope distribution of Xe (about 3.5% per amu), and evidence of excess ^{129}Xe. Moreover, there's also a signature of fissionogenic Xe from extinct ^{244}Pu decay. There are three features in the atmospheric pattern that need consideration.

- The relative enrichment (non-radiogenic) of the heavier isotopes is due to a catastrophic loss of atmospheric Xe (probably 90%) early in the earth's history, probably associated with the impact formation of the moon
- The presence of radiogenic ^{129}Xe suggests that the atmosphere was formed in the presence of significant amounts of radioactive ^{129}I, i.e., with several half-lives of nucleosynthesis
- The presence of fissionogenic Xe (primarily ^{136}Xe) suggests a similar time frame, but allows us to set quantitative limits on the timing.



In combination, the isotopes demonstrate that the atmosphere did not form a closed isotopic system for I-Xe-Pu until about 100 Ma after the earth's formation. (See Ozima and Podosek, 1999). This may in fact be an upper bound, because if one includes the possibility that radiogenic isotopes were lost during the moon-formation event, this time decreases to 50-60 Ma. Nevertheless it is remarkable that we are now beginning to constrain processes that occurred during the first 1 or 2% of the life of the planet.

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