1.3 Radioactivity and the age of the solar system

Most of you are familiar with the phenomenon of radioactive decay: Certain elements have *isotopes* in which the nucleus is not stable but rather decays, usually emitting some particle in the process. As an example, we have the "beta decay" of the carbon isotope ^{14}C,

$$^{14}\mathrm{C} \rightarrow {}^{14}\mathrm{N} + e^- + \bar{\nu}_e. \tag{1.124}$$

This means that the carbon nucleus decays into a nitrogen nucleus, giving off an electron (e^-) and a particle you might not know about called an anti–neutrino ($\bar{\nu}_e$); the subscript e means that this particular neutrino is associated with the electron.

To back up a bit, let's recall that most of the carbon around us is ^{12}C. If you look at the periodic table you can see that carbon has six electrons, and since the atom is neutral there must also be six protons in the nucleus; 6 is the "atomic number" of carbon. The "mass number" of 12 comes from these six protons plus six neutrons. The isotope ^{14}C has the same number of electrons and protons—that's what it means to be an isotope!—but two extra neutrons in its nucleus.

Looking again at the periodic table, nitrogen has seven electrons and hence seven protons; ^{14}N thus has seven neutrons. So what is happening in the beta decay of ^{14}C really is

$$6 \text{ protons} + 8 \text{ neutrons} \rightarrow 7 \text{ protons} + 7 \text{ neutrons} + e^- + \bar{\nu}_e, \tag{1.125}$$

or more simply the decay of a neutron (n) into a proton (p^+), an electron and an anti–neutrino,

$$n \rightarrow p^+ + e^- + \bar{\nu}_e. \tag{1.126}$$

If you just have a neutron sitting in free space, this takes about twelve minutes (!). But with all the particles trapped in the nucleus, it can take much longer: more than 5000 years for the decay of ^{14}C.

What you measure when you have a radioactive element is the extra emitted particle, the electron in the case of ^{14}C. So unlike the usual case in chemistry, you don't measure the concentration of each species, you actually measure the transitions from one species to the other. The particles that come out of radioactive decays often have enough energy that you can count the individual particles, so this is like observing chemical reactions one molecule at a time. As we will discuss later in the course, the behavior of individual molecules or individual nuclei is random, so if you watch 1000

^{14}C atoms for $t_{1/2} = 5730$ yr, you won't see exactly 500 decays, but rather some random number which on average is equal to 500. Let's not worry about this randomness for now.

Since every nucleus does its thing on its own, the average number of decays per second (or per year, or per millennium) must be proportional to the number of nuclei that we start with. Since ^{14}C decays but no other nuclei decay into ^{14}C, the dynamics of the concentration of these atoms in a sample is very simple:

$$\frac{d[^{14}\mathrm{C}]_t}{dt} = -\lambda[^{14}\mathrm{C}]_t, \tag{1.127}$$

where λ is the decay rate. By now we know the solution to this equation,

$$[^{14}\mathrm{C}]_t = [^{14}\mathrm{C}]_0 \exp(-\lambda t). \tag{1.128}$$

The concentration falls by half in a time $t_{1/2} = \ln 2/\lambda$, and again this is $t_{1/2} = 5730$ yr for ^{14}C.

You may know that ^{14}C is used to determine the age of fossils and other organic materials. The idea is that as long an organism is alive, it constantly is exchanging carbon with its environment (eating and excreting) and so the isotopic composition of the organism matches that of the atmosphere. Once the organism dies, this exchange stops, and the ^{14}C trapped in the system starts to decay. If we know, for example, that the $^{14}\mathrm{C}/^{12}\mathrm{C}$ ratio was the same in the past as it is today (which is almost true, but hang on for a surprise ...), then if we see less ^{14}C it must be because this isotope has decayed (^{12}C is stable). Since we know the decay rate, the amount of the decay can be translated back into a time, which is the time elapsed since the object "died" and stopped exchanging carbon with the atmosphere. This is the basis of radiocarbon dating.

Because the half life of ^{14}C is about 5000 years, it's a great tool for archaeologists. It's hard, on the other hand, to use ^{14}C to date something more recent. How could we know, for example, if something were 10 or 50 years old? In 10 years there is only a $\sim 10/5000 = 0.002$ decay of the ^{14}C nuclei, so to distinguish things with 10 year accuracy means making measurements to an accuracy of nearly one part in 1000—not so easy. But, in fact, the isotopic composition of the atmosphere is changing rapidly. For a brief period of time in the 1950s and 60s, human beings tested nuclear weapons by exploding them in the atmosphere. This ended with the signing of the nuclear test ban treaty in 1963. The testing produced a significant increase in atmospheric ^{14}C, and since (roughly) 1963 this has been decaying exponentially as it mixes with the oceans and biomass (Fig 1.13) Recently

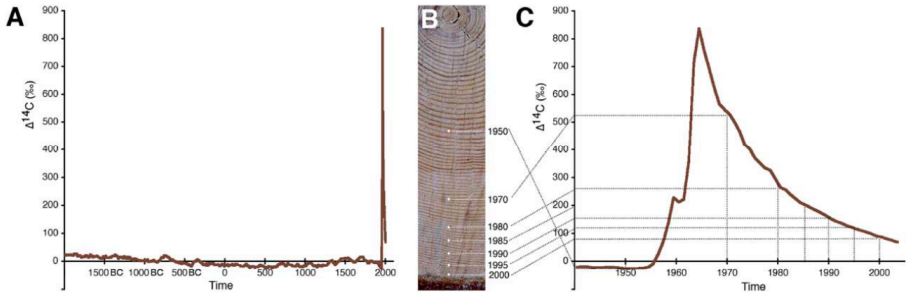

Figure 1.13: (A) Estimated ^{14}C composition of the atmosphere on a $\sim 1000\,$yr time scale. (B) Cross section of a swedish pine tree, from which ^{14}C composition can be measured in successive rings, as shown in (C). Complied by KL Spalding, RD Bhardwaj, BA Buchholz, H Druid & J Frísen, *Cell* **122,** 133–145 (2005).

it has been suggested that this provides a signal that one can use, for example, to determine the birth dates of cells from different tissues in recently deceased people. While slightly macabre on several levels, this technique offers the opportunity to address really crucial questions such as whether we are growing new cells in our brain even when we are adults, or if all the cells in the brain are born more or less when we are born.

Problem 16: The radioactive isotope ^{14}C has a half–life of $t_{1/2} = 5730\,$years. You find two human skeletons which you suspect are about $10,000\,$years old. The setting in which you find these skeletons suggests that they died in two events separated by roughly $20\,$years. How accurately do you need to measure the abundance of ^{14}C in the skeletons in order to test this prediction? State as clearly as possible any assumptions that are made in interpreting such measurements.

If we want to look at events that take much longer than 5000 years, it's useful to look for radioactive decays that have much longer half lives. If you poke around the periodic table, you find that heavy elements often have radioactive isotopes with half lives measured in billions of years. Let's focus

on the uranium isotopes which decay into lead. Specifically, ^{235}U decays into ^{207}Pb at a rate $\lambda_{235} = 9.849 \times 10^{-10}\,\mathrm{yr}^{-1}$, while ^{238}U decays into ^{206}Pb at a rate $\lambda_{238} = 1.551 \times 10^{-10}\mathrm{yr}^{-1}$:

$$^{235}\mathrm{U} \stackrel{\lambda_{235}}{\rightarrow} {}^{207}\mathrm{Pb} + \cdots \tag{1.129}$$

$$^{238}\mathrm{U} \stackrel{\lambda_{238}}{\rightarrow} {}^{206}\mathrm{Pb} + \cdots, \tag{1.130}$$

where in both reactions $\cdots$ refers to additional fragments that emerge in the fission of the uranium nucleus. If we imagine a hunk of rock that formed at time $t = 0$ in the distant past, then all of the uranium nuclei are decaying, so what we measure now at time t is

$$^{235}\mathrm{U}(t) = {}^{235}\mathrm{U}(0)\exp(-\lambda_{235}t) \tag{1.131}$$
$$^{238}\mathrm{U}(t) = {}^{238}\mathrm{U}(0)\exp(-\lambda_{238}t). \tag{1.132}$$

Every uranium nucleus that decays adds to the number of lead atoms that we find in the rock, so that

$$^{207}\mathrm{Pb}(t) = {}^{207}\mathrm{Pb}(0) + [{}^{235}\mathrm{U}(0) - {}^{235}\mathrm{U}(t)] \tag{1.133}$$
$$^{206}\mathrm{Pb}(t) = {}^{206}\mathrm{Pb}(0) + [{}^{238}\mathrm{U}(0) - {}^{238}\mathrm{U}(t)]. \tag{1.134}$$

Remember that we don't actually know what the isotopic compositions were when the rock was first formed. So in order to use these equations to analyze real data, we should try to get rid of all the terms that involve the isotopic compositions at $t = 0$.

We can start with uranium, for which everything we observe today is just a decayed version of where things started; this means that we can invert Eq's (1.131) and (1.132):

$$^{235}\mathrm{U}(0) = {}^{235}\mathrm{U}(t)\exp(+\lambda_{235}t) \tag{1.135}$$
$$^{238}\mathrm{U}(0) = {}^{238}\mathrm{U}(t)\exp(+\lambda_{238}t), \tag{1.136}$$

and then we can substitute into our equations for the current amount of the two lead isotopes [Eq's (1.133,1.134)] to obtain

$$^{207}\mathrm{Pb}(t) = {}^{207}\mathrm{Pb}(0) + [{}^{235}\mathrm{U}(t)\exp(+\lambda_{235}t) - {}^{235}\mathrm{U}(t)] \tag{1.137}$$
$$^{206}\mathrm{Pb}(t) = {}^{206}\mathrm{Pb}(0) + [{}^{238}\mathrm{U}(t)\exp(+\lambda_{238}t) - {}^{238}\mathrm{U}(t)], \tag{1.138}$$

or more simply

$$^{207}\mathrm{Pb}(t) = {}^{207}\mathrm{Pb}(0) + {}^{235}\mathrm{U}(t)[\exp(+\lambda_{235}t) - 1] \tag{1.139}$$
$$^{206}\mathrm{Pb}(t) = {}^{206}\mathrm{Pb}(0) + {}^{238}\mathrm{U}(t)[\exp(+\lambda_{238}t) - 1], \tag{1.140}$$

This is almost a relationship between things we can measure—the current numbers of atoms of each isotope—but not quite. First of all, we still have the initial concentrations of the lead isotopes. Second, it's hard to make absolute measurements (how could we be sure that we got all the lead out, as it were), so it would be nice to express things in terms of isotopic ratios.

The key idea is that different rocks start out with different amounts of lead and uranium, because that involves the chemistry of formation of the rock, but if all these heavy elements were made in a single event such as a supernova then the ratios of the isotopes would have been the same in all materials at $t = 0$. Since all that happens to the uranium nuclei is that they decay, the ratio of ^{235}U to ^{238}U still is the same in all materials, although of course it might be very different from the ratio at $t = 0$. To make use of this fact, let's try to solve for the number of ^{238}U atoms as a function of the number of ^{206}Pb atoms:

$$\begin{aligned} {}^{206}\mathrm{Pb}(t) &= {}^{206}\mathrm{Pb}(0) + {}^{238}\mathrm{U}(t)[\exp(+\lambda_{238}t) - 1] \\ \Rightarrow {}^{238}\mathrm{U}(t) &= \frac{{}^{206}\mathrm{Pb}(t) - {}^{206}\mathrm{Pb}(0)}{\exp(+\lambda_{238}t) - 1}. \end{aligned} \tag{1.141}$$

But if we measure the ratio $^{235}\mathrm{U}(t)/^{238}\mathrm{U}(t)$ today and call this ratio $R_{235/238}$, we can say that

$${}^{235}\mathrm{U}(t) = R_{235/238}\frac{{}^{206}\mathrm{Pb}(t) - {}^{206}\mathrm{Pb}(0)}{\exp(+\lambda_{238}t) - 1}. \tag{1.142}$$

This relates the ^{235}U concentration in a sample to the ^{206}Pb concentration, both measured today. But we have seen that the ^{235}U concentration is related to the number of atoms of the *other* lead isotope, through Eq (1.139). So we can put these equations together:

$$\begin{aligned} {}^{207}\mathrm{Pb}(t) &= {}^{207}\mathrm{Pb}(0) + {}^{235}\mathrm{U}(t)[\exp(+\lambda_{235}t) - 1] \\ {}^{235}\mathrm{U}(t) &= R_{235/238}\frac{{}^{206}\mathrm{Pb}(t) - {}^{206}\mathrm{Pb}(0)}{\exp(+\lambda_{238}t) - 1} \\ \Rightarrow {}^{207}\mathrm{Pb}(t) &= {}^{207}\mathrm{Pb}(0) \\ &\quad + R_{235/238}\frac{{}^{206}\mathrm{Pb}(t) - {}^{206}\mathrm{Pb}(0)}{\exp(+\lambda_{238}t) - 1}[\exp(+\lambda_{235}t) - 1] \\ &= {}^{207}\mathrm{Pb}(0) - {}^{206}\mathrm{Pb}(0)R_{235/238}\frac{\exp(+\lambda_{235}t) - 1}{\exp(+\lambda_{238}t) - 1} \end{aligned} \tag{1.143}$$

$$+^{206}\mathrm{Pb}(t)\left[R_{235/238}\frac{\exp(+\lambda_{235}t)-1}{\exp(+\lambda_{238}t)-1}\right] \tag{1.144}$$

This is an interesting equation, because it says that the amount of ^{207}Pb that we find today in a rock should be related to the amount of ^{206}Pb that we find in that same piece of rock. But we still have those pesky initial values to deal with.

There is yet a third isotope of lead which is both stable and *not* the product of other radioactive decays, and this is ^{204}Pb. So the amount of this isotope that we measure today is the same as we would have measured when the rock was formed. This means that we can take our expression for $^{207}\mathrm{Pb}(t)$ in Eq (1.144) and normalize by $^{204}\mathrm{Pb}(t)$,

$$\begin{aligned}\frac{^{207}\mathrm{Pb}(t)}{^{204}\mathrm{Pb}(t)} &= \frac{^{207}\mathrm{Pb}(0)}{^{204}\mathrm{Pb}(t)}-\frac{^{206}\mathrm{Pb}(0)}{^{204}\mathrm{Pb}(t)}R_{235/238}\frac{\exp(+\lambda_{235}t)-1}{\exp(+\lambda_{238}t)-1}\\ &\quad+\frac{^{206}\mathrm{Pb}(t)}{^{204}\mathrm{Pb}(t)}\left[R_{235/238}\frac{\exp(+\lambda_{235}t)-1}{\exp(+\lambda_{238}t)-1}\right],\end{aligned} \tag{1.145}$$

but then we are free to rewrite $^{204}\mathrm{Pb}(t) \rightarrow {}^{204}\mathrm{Pb}(0)$ anyplace where it would make thing look better. So this last equation becomes

$$\begin{aligned}\frac{^{207}\mathrm{Pb}(t)}{^{204}\mathrm{Pb}(t)} &= \frac{^{207}\mathrm{Pb}(0)}{^{204}\mathrm{Pb}(0)}-\frac{^{206}\mathrm{Pb}(0)}{^{204}\mathrm{Pb}(0)}R_{235/238}\frac{\exp(+\lambda_{235}t)-1}{\exp(+\lambda_{238}t)-1}\\ &\quad+\frac{^{206}\mathrm{Pb}(t)}{^{204}\mathrm{Pb}(t)}\left[R_{235/238}\frac{\exp(+\lambda_{235}t)-1}{\exp(+\lambda_{238}t)-1}\right],\end{aligned} \tag{1.146}$$

This looks complicated, but it's not. We can rewrite this equation as

$$\frac{^{207}\mathrm{Pb}(t)}{^{204}\mathrm{Pb}(t)} = A + B\frac{^{206}\mathrm{Pb}(t)}{^{204}\mathrm{Pb}(t)}, \tag{1.147}$$

where the first important point is that A and B should be the same in all rocks (!).

Actually, Eq (1.147) contains a prediction of tremendous power. You should go back over the derivation and see what we had to assume:

- Uranium isotopes decay into lead isotopes as observed in the lab.
- Nothing else decays into lead, which is stable, and no processes produce any new uranium; again these are statements based on laboratory observations.

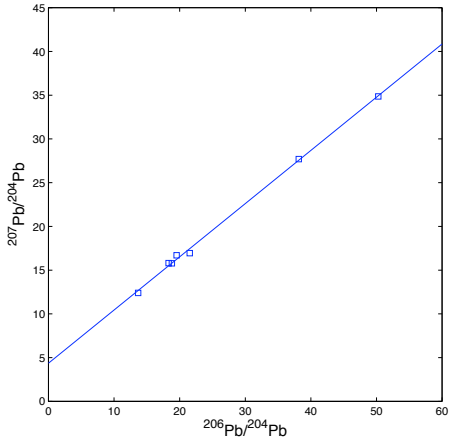

Figure 1.14: Isotopic compositions of some stone meteorites and terrestrial rocks. The fact that the data fall on a straight line is consistent with a single 'moment of creation' for the heavy elements, and the slope determines that this origin was 4.55×10^9 yr in the past. From data in V RamaMurthy & CC Patterson, Primary isochron of zero age for meteorites and the earth, *Journal of Geophysical Research* **67,** 1161 (1962).

- All of the heavy elements that we find in our neighborhood were made at some moment $t = 0$ in the past, and this event set the initial isotopic ratios for each element.

- Different materials start with different amounts of uranium and lead.

Notice that the first two assumptions are based on direct measurements. The last item is the assumption that nothing special happens to force a relationship between the lead and uranium content of different materials, so it isn't really an assumption. The only really startling claim on the list is that all the heavy elements were made at some specific time in the past. So this assumption—literally a hypothesis about the creation of the materials in our local corner of the universe—makes a prediction about what we will see if we measure the isotopic composition of many different materials: if you plot $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$, you'll see a straight line. As you can see in Fig 1.14 this works!

One can in fact do a little more with the data from Fig 1.14 and related experiments. Our simple form in Eq (1.147) hides the fact that the constants A and especially B have meaning. Referring to Eq (1.146), we see that the slope B involves the current ratio $R_{235/238}$ of uranium isotopes, the decay rates λ_{235} and λ_{238} of the uranium isotopes, and the time t since the creation of the elements. All of these things except the time t have been measured independently. So, by analyzing the slop of the line in Fig 1.14, we determine the time that has elapsed since the heavy elements were formed. The result

is $t = 4.55 \times 10^9$ yr. Even better is that you can do all this same analysis with other combinations of isotopes (e.g., rubidium and strontium) and you get the same answer for t even though everything else is different. This is impressive evidence that there really was some discrete event several billion years ago that created the heavy elements in our neighborhood.

Just to avoid confusion, what we have just calculated is *not* the time of the big bang. The heavy elements were formed only once the universe had developed to the point of having stars that could "cook" the light elements into more bigger nuclei. Actually, it's not automatic that these estimates for the age of heavy elements in the solar system should come out younger than the age of the universe as a whole (that is, the time since the big bang), which is estimated from very different kinds of data. There have been some tense moments in the history of the subject, but everything now is consistent; the big bang happened 13.7 billion years ago, with an uncertainty of about 1% (!).

It is worth remembering, at this point, that our whole line of argument leading to this remarkable conclusion hinges on the fact that we can solve the simple first order differential equation that describes radioactive decay. We know that this is the right equation because we have made measurements in the laboratory, but these measurements cover a range of (at best) a few years. Trusting the equations, we extrapolate the solutions over billions of years, and we obtain a wonderfully consistent view of the data.

An interesting question is whether there is any other evidence that the relevant parameters are constant over a period that is a significant fraction of the age of the universe. In fact, many people have considered the possibility that what we call "fundamental constants" of nature—including the constants that determine the rates of radioactive decay—might be changing slowly as the universe ages (and, as we now know, expands). Small rates of change obviously would have big consequences over such long time scales. For better or worse, there is no positive evidence for such changes, despite many ingenious, high precision measurements. This remains, however, a place where people are looking for cracks in our otherwise quite solid understanding.

Problem 17: The Allende chondrites are carbonaceous meteorites that fell near the town of that name in Mexico on February 8, 1969. Chondrites are a class of meteorites composed of tiny, rounded spheres containing silicate minerals (called chondrules). The chondrules are believed to have formed early in the solar nebula and many geochemical

studies have been performed on them. Mass spectrometric data obtained from these chondrules has allowed the determination of their elemental compositions. Shown in Table 1.2 are typical data for isotope ratios of rubidium and strontium obtained by Gray and coworkers in 1973.

(a.) Derive a simple, integrated expression relating the age of such a sample to the isotope ratios.

(b.) Calculate the age of these samples from this data using the known half–life for radioactive decay of ^{87}Rb to ^{87}Sr of 48.8 billion years. Note that the strontium isotopes are stable and do not decay.

^{87}Rb/^{86}Sr	^{87}Sr/^{86}Sr
0.00014	0.698770
0.00019	0.698810
0.00075	0.698890
0.00393	0.698990
0.00432	0.699030
0.00660	0.699250
0.00776	0.699140
0.00853	0.699330
0.05213	0.702140
0.00017	0.698770

Table 1.2: Isotopic ratios from the Allende chondrites.

Intriguingly, these chondrites have been found to contain both natural and unnatural amino acids. But that is a topic for another day.