12.710 Marine Geology and Geophysics
Geochronology

Introduction

Course is intended as a broad overview of concepts central to marine geology and geophysics.

MTZ - structure of the Earth and plate tectonics
PC, JMc - near-shore sedimentation and stratigraphy
JMc - deep sea sediment processes and paleoceanography

Supplementary Readings

Stacey, Chapter 2
Fowler, Chapter 6

Concept of Time

-The accurate measurement of time is central to understanding the evolution of the Earth. There are a number of ways to measure time that will be covered over the course of the semester, one of which will be discussed in present lecture:

- **Biostratigraphy** - use fossils (type, number, diversity and distribution) to determine geologic period and environment. The method of choice for establishing the geologic record. McManus to cover.
- **Magnetostratigraphy** - use the time history of magnetization to trace the record of magnetic reversals. Used to determine the age of the sea floor. Zuber to cover in a later lecture.
- **Radioactive Age Dating** - Determine absolute ages of minerals using decay of radioactive substances. Most accurate method. Today's topic.

Geologic Time Scale

- Shows major periods of Earth history. Divided into Precambrian, Paleozoic, Mesozoic and Cenozoic eras. Eras are subdivided into periods. Periods are divided into epochs. Names taken from geographic locality in which formations were first discovered or best displayed, or from some characteristic of the formations.

- Life developed in Precambrian but was limited to simple organisms. At the beginning of the Paleozoic, specifically in the Cambrian era, great diversity ensued; understanding the conditions that led to the "explosion" in the number of species is an active research area. Mesozoic -- age of dinosaurs; Cenozoic -- age of mammals.

Age of the Oceans

Consider geologic time in the context of the oceans. From studies of meteorites we shall show that Earth has an age of 4.6 BY.

- oldest rock known (study done by Sam Bowring of MIT) is 4.03 BY. This is an igneous rock, *i.e.* of volcanic origin.
- oldest sedimentary rock has an age of 3.8 BY. So we know that as far back as 3.8 BY the ocean must have existed, because there is evidence of sedimentation. This sedimentary rock was found on a continent.

- Map of seafloor age shows that oldest preserved seafloor has an age of ~200 MY. So if we want to study the formation and earliest history of the oceans and we are looking for physical evidence we need to look somewhere else other than the ocean floor.

Radioactive Age Dating

Radioactivity was discovered by Henri Becquerel in 1896. By that time sedimentary layering was somewhat understood, at least to the point where it was known that observed sedimentary strata took hundreds of millions of years to accumulate. At that point the only known energy sources available to the sun and Earth, *i.e.* the energy associated with gravitational collapse, allowed a maximum age of 25 MY. For about 3 decades geologists debated whether to accept this age. The argument became moot due to the discovery of radioactivity. From the point of view of the evolution of the Earth, the discovery of radioactivity had two effects:

(1) it removed the short-term age limit of the Earth by providing a mechanism for long-term heating (the internal heat that drives mantle convection and thus plate motions); and

(2) it provided a means of determining absolute dates for rocks.

The stability of elements with respect to decay is related to the relative numbers of protons and neutrons. If the numbers of these are not approximately equal then element is prone to decay.

Element with same number of protons but a different number of neutrons are called **isotopes**.

Radioactive activity can be described by a simple rate law where the level of activity is proportional to the time rate of change of the number of atoms. The time rate of decay of N nuclei is proportional to N such that

$$\frac{dN}{dt} = -\lambda N$$

where t is time and the minus sign indicates that activity decreases with time. The rate of radioactive decay of an isotope is represented by a **decay constant**, λ, which is the probability that a constituent particle in the atomic nucleus will escape through the potential barrier that binds it to the nucleus. This probability of escape is solely a function of the properties of the nucleus. We may rewrite

$$\frac{dN}{N} = -\lambda dt.$$

We integrate both sides and see that

$$lnN = - \lambda t + c.$$

If we take the limit as $t \rightarrow 0$ it is apparent that $c=ln\, N_o$, where N_o is the initial number of radioactive atoms. Substituting and raising each side to an exponential, we get the **radioactive decay equation**

$$N = N_o e^{-\lambda t}. \qquad (1)$$

The relationship between λ and the **half-life** $\tau_{1/2}$ is obtained by substituting $N=N_o/2$ at $t=\tau_{1/2}$

$$\tau_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.69315}{\lambda}. \qquad (2)$$

Einstein taught us that energy *(E)* is equivalent to mass *(m)* with the simple and elegant expression $E = mc^2$, where *c* is the velocity of light. Radioactive decay occurs because some of the mass of an atom is held in **binding energy**.

If there is "too much" binding energy (and quantum mechanics is needed to assess how much is too much), the nucleus will decay spontaneously -- by radioactive decay -- or by an induced nuclear reaction (neutron bombardment) to lower the energy state. Decay can occur by three classes of mechanisms:

- **Alpha decay** - escape of a He^4 nucleus
  The strong forces that bind nuclei dictates that it is difficult to escape from the potential well. α particles are not very energetic and cannot jump the potential well but Heisenberg's Uncertainty Principle tells us that a particle can sometimes exist outside the threshold due to uncertainty in position.
- **Beta decay** - escape of an electron or positron by:
  (1) Electron emission (β^-)
  $n \rightarrow p + e^- \uparrow + \bar{v}$
  - for nuclides over-rich in neutrons
  (1) Positron emission (β^+)
  $p \rightarrow n + e^+ \uparrow + v$
  - for nuclides depleted in neutrons
  (3) Electron capture (ec)
  $e^- + p \rightarrow n + \bar{v}$
  - S electron in K shell on an atom has finite probability of being inside nucleus.
- **Gamma decay** - emission of gamma radiation that occurs when nuclei are in excited energy states. Newly-produced nuclei are not in ground state and produce γ-rays.

Nuclear binding energies are huge(!) and nuclei are so small (~1 angstrom=10^{-8} cm) that radioactive decay is not greatly affected by physical conditions on the Earth such as temperature and pressure. However, the half-life can be changed somewhat by changes in bonding energy, etc.

E.g. solar wind studies have shown different λ's for Beryllium on sun and Earth.

Isotopes important for long-lived radioactive decay to produce heat within the Earth:

- ^{238}U, ^{235}U, ^{232}Th, ^{40}K

Isotopes important for radioactive dating (long timescales):

- $^{87}Rb/^{87}Sr$
- $^{147}Sm/^{143}Nd$
- $^{238}U/^{204}Pb$
- $^{235}U/^{207}Pb$
- $^{40}K/^{40}Ar$
- $^{232}Th/^{208}Pb$
- $^{182}Hf/^{182}W$

In these schemes the material that is the first step in the decay sequence is called the **parent** and the element that the parent decays to is the **daughter**.

In geologic studies we usually don't know the initial concentration of the radioactive parent. This complicates the use of radioactive isotopes to get ages. But it is possible to work around the problem using the daughter product. We can measure the concentration $D*$ of the daughter because

$D* = N_o - N$. We substitute from (1) so

$D* = N_o - N_o e^{-\lambda t} = N_o(1-e^{-\lambda t})$

where D* is the number or concentration of a radiogenic daughter product at time *t*. We want to eliminate N_o because we don't know it. So we divide by (1):

$$\frac{D*}{N} = \frac{N_o(1-e^{-\lambda t})}{N_o e^{-\lambda t}} = \frac{1-e^{-\lambda t}}{e^{-\lambda t}}$$

or

$$\frac{D*}{N} = e^{\lambda t} - 1. \qquad (3)$$

Equation (3) can be used directly in the determination of ages if there is no initial non-radiogenic daughter component, or if that initial component can be estimated.

K-Ar Dating

This method is useful for measuring igneous rocks with relatively simple cooling histories.

Most argon in the atmosphere is the radiogenic isotope ^{40}Ar, which is formed as the decay product of ^{40}K that has been outgassed from the crust and mantle as a consequence of volcanic activity. This is consistent with the thought that the atmosphere (and oceans) formed due to early outgassing of the Earth.

K-Ar dating is based on the decay of ^{40}K ^{40}Ar. 10.5% of ^{40}K decays to ^{40}Ar, while the rest goes to ^{40}Ca, which is a very common isotope. But there is almost no initial ^{40}Ar in rocks because it is a Nobel gas and chemically inert, so it doesn't combine with anything and so doesn't "stick" in crystal lattices. To correct for the fact that there are two daughter products of ^{40}K we may write:

$$\frac{\lambda_{Ar}}{\lambda} = \frac{\lambda_{Ar}}{\lambda_{Ar} + \lambda_{Ca}} = 0.105$$

where $\lambda = \lambda_{Ar} + \lambda_{Ca}$. ^{40}Ar is almost completely lost from outgassing from molten rock. When a volcanic rock forms its clock resets to *t=0.* For K-Ar dating the age equation is modified from (3) to be

$$^{40}Ar = \frac{\lambda_{Ar}}{\lambda} {}^{40}K(e^{\lambda t} - 1). \qquad (4)$$

So to determine the age of the rock it is necessary to know the ratio of ^{40}Ar/^{40}K, which can be done either directly or by measuring daughter products of another potassium isotope. The most common method for doing this requires the sample in two halves that (presumably) contain equal concentrations of ^{40}A and ^{40}K, and measuring the Ar in one and the K in the other. The argon measurement is done in a mass spectrometer. The rock is melted and the argon released in the presence of a known quantity of ^{38}Ar, know as a "spike". This is done because mass specs measure isotope ratios much better than absolute concentrations. By comparing these isostopes it is possible to correct for isotopic contamination, because atmospheric argon occurs in the proportion ^{40}Ar:^{38}AR:^{36}Ar = 100: 0.063: 0.337. Potassium is usually measured with a flame photometer, comparing the sample with a solution standard assuming that ^{40}K makes up 0.01167% of total K.

Where is application of this technique a problem?

- very young rocks – not much time to accumulate radiogenic argon.
- mineral assemblages where there isn't much ^{40}K in the system – produces insignificant amount of ^{40}Ar.
- deep sea – partial pressure dicates that non-radiogenic ^{40}Ar is retained in minerals. Yields over-estimate of age.

^{40}K/^{40}Ar measurements most commonly made on bitotite and hornblende.

^{40}Ar/^{39}Ar Technique

This technique allows measurement of step-wise cooling of a sample. It enables investigation of more complicated cooling histories (read: metamorphic history).

- Expose sample to neutron flux in reactor.
- Convert a fraction of ^{39}K (n,p) ^{39}Ar.
- ^{39}Ar is a measure of the potassium content so can use mass spectrometer to measure Ar/K ratio by measuring ^{40}Ar/^{39}Ar

Advantages: (1) analysis can be done on a single sample; (2) Don't need absolute concentrations, just need parent/daughter ratio.

Disadvantage: other reactions are also going on (K Ca) and corrections need be made.

- Argon is released as sample is heated. So ^{40}Ar/^{39}Ar will be lower for lower temperature release and dates metamorphic events.
- Correction for non-radiogenic argon is made by comparison with ^{36}Ar.

Use a standard dated by an independent method to get ^{40}Ar/^{39}Ar ratio for that and reference it to known age.

- A plot of ^{40}Ar/^{36}Ar vs. ^{39}Ar/^{36}Ar for argon released at different temperatures gives a linear plot with a gradient equal to ^{40}Ar*/^{39}Ar, where the asterisk gives the radiogenic ^{40}Ar required for the calculation of age.

E.g. Rims of mineral may be near pluton and partly degassed so will give artificially low age. Core of mineral may give true age. Degassing whole sample at once will give average age for whole mineral, which may be misleading.

Argon is a tracer for outgassing of the mantle:
Quenched submarine basalts from mid-ocean ridges and island hot spots have ^{40}Ar/^{36}Ar ratios that are generally much higher (~2000) than the atmospheric ratio (295). This indicates that primordial ^{36}Ar that accreted with the Earth is mostly in the atmosphere. We may assume that it has always been here or that the mantle is strongly outgassed and that much of the ^{40}Ar is also in the atmosphere. In either case the ratio points to a rapid early outgassing of the Earth.

K-Ar techniques have provided absolute ages that have "anchored" the timescale for geomagnetic reversals preserved in oceanic crust.

Rb-Sr System

Useful for old dating old rocks (Precambrian terranes and meteorites)

Rb is an alkali metal, a large ion. It is close in size to potassium and substitutes for it in crystal lattices. It commonly substitutes in between lattice sheets in amphiboles (like micas). Rb is also commonly found in potassium feldspar (orthoclase; $KAlSi_3O_8$).

Most geologic clocks are complicated by the occurrence of initial as well as radiogenic daughter nuclides. When this occurs we need more than one measurement of the daughter/parent ratio. The decay scheme must meet two conditions:

(1) Several minerals in the rock must have different ratios of parent/daughter and it must be possible to separate them.

(2) A non-radiogenic reference isotope of the daughter must be present for comparison.

For the ^{87}Rb-^{87}Sr clock we rewrite (4) $N={}^{87}Rb$ and $D^*={}^{87}Sr$. We also add initial strontium $^{87}Sr_o$ and rewrite equation (3)

$$^{87}Sr={}^{87}Sr_o+{}^{87}Sr^*={}^{87}Sr_o+{}^{87}Rb(e^{\lambda t}-1).$$

We divide by the abundance of reference isotope ^{86}Sr, which gives the **isochron** (equal time) equation

$$\frac{^{87}Sr}{^{86}Sr}=\left(\frac{^{87}Sr}{^{86}Sr}\right)_o+\frac{^{87}Rb}{^{86}Sr}\left(e^{\lambda t}-1\right). \qquad (5)$$

The initial strontium ratio $(^{87}Sr/^{86}Sr)_o$ is the same for all minerals in an igneous rock because the two isotopes are chemically identical and when a rock is melted the ratio is almost uniform throughout. Equation (5) represents the variation with time of $^{87}Sr/^{86}Sr$ in a suite of samples that were isotopically homogeneous at $t=0$.

At age t graph of (5) is linear with intercept $(^{87}Sr/^{86}Sr)_o$ and gradient $(e^{\lambda t}-1)\sim\lambda t$, which gives the age t. The gradient is always <<1 because the time for ^{87}Rb decay is long compared to the age of the Earth (10x longer).

Graphical methods help visualize the significance of isochrons. *Stacey* describes an example for a situation in which the original emplacement and subsequent metamorphism of a suite of co-genetic rocks can be dated.

- Consider three rocks from a common igneous source that are produced rapidly such that they have approximately the same age. Their initial whole rock compositions are *A, B* and *C*. These rocks are chemically different, though, and so have a range of Rb/Sr, but because they are from a common source their initial strontium ratios $(^{87}Sr/^{86}Sr)_o$ are the same.
- As the rocks age ^{87}Rb atoms decay and ^{87}Sr atoms are produced, causing the compositions to move along dashed lines with slope=-1. They reach the points *A', B'* and *C'* after time *T*. The line through these points is the T-isochron, with gradient $(e^{\lambda T}-1)$.
- Now suppose at some time $t<T$ all of the rocks were reheated sufficiently to re-homogenize the isotopes within their minerals (on a scale of cm), but not sufficiently to

cause mixing between their rocks (on a scale of hundreds of m to km). In this circumstance the whole rock analyses would be unaffected, but the mineral clocks would have been reset to zero *t* years ago and now give an age of *t*. The whole rock isochron would still give an age of *T*.
- The figure also provides information concerning the interpretation of initial strontium ratios. Note that Rock *C* has a high Rb/Sr ratio so accumulates more ^{87}Sr than rocks *A* and *B* when it decays. When its clock is reset it has a higher $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_o$ ratio than *A* and *B* although all three rocks had the same initial ratio *T* years ago. A high $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_o$ ratio characterizes a rock that was derived from a source region rich in Rb relative to Sr. An example of this is the Earth's continental crust. Young igneous rocks w/high initial Sr ratios are likely to be reworked crustal material with long crustal residence times while low initial Sr ratios (<0.705) indicate mantle-derived rocks.

The long half-life of Rb ($t_{1/2}$ =4.88x10^{10} years) means that variations of $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ are small and very high Rb/Sr ratios are required to measure young ages. The Rb-Sr method is best suited for measurements of several BY-old rocks because neither Rb or Sr diffuses quickly and the clock is not easily reset. This method is particularly useful for Precambrian geology.

U-Pb System

Has wide use for a range of applications; crustal studies, meteorites, etc.

Uranium-lead evolution follows equations with the same form as equation (5) with two parallel decay schemes. There are four isotopes of lead and only one (^{204}Pb) does not have a radioactive progenitor. The following decay schemes occur:

$^{238}\mathrm{U} \rightarrow {}^{206}\mathrm{Pb}$ $8\alpha, 6\beta$	λ=1.55x10^{-10} yr^{-1}	$t_{1/2}$= 4.5 BY
$^{235}\mathrm{U} \rightarrow {}^{207}\mathrm{Pb}$ $7\alpha, 4\beta$	λ=9.85x10^{-10} yr^{-1}	$t_{1/2}$= 0.7 BY
$^{232}\mathrm{Th} \rightarrow {}^{208}\mathrm{Pb}$ $6\alpha, 4\beta$	λ=4.95x10^{-11} yr^{-1}	$t_{1/2}$= 14 BY

Note that decay of lead is not immediate but proceeds as a series of steps via intermediate daughter products. The longest half-life among the intermediate products is ^{234}U, the great-grand daughter of ^{238}U which has $t_{1/2}$= 2.5x10^5 yr.
- Here it is appropriate to note that there is also an isotope of (gaseous) radon in the both uranium decay series. Radon is a noble gas and tends to escape from crystal lattices. Fortunately the half-life of the radon is not long and doesn't give radon much time to escape. To use these isotopes in dating it is essential that the rocks to be dated remain as a "closed system".
- Sometimes ^{234}U and other intermediate daughters can be used as tracers in marine sedimentation.

The U-Pb dating system has two independent clocks, but we will show that it is simpler in practice to combine them to avoid the need to measure uranium content at all.

We start with equation (3) and describe the decay of ^{238}U:

$$\frac{^{206}Pb}{^{238}U} = e^{\lambda_{238}t} - 1$$

or

$$^{206}Pb = {}^{238}U\left(e^{\lambda_{238}t} - 1\right).$$

Then add the initially occurring ^{206}Pb:

$$^{206}Pb = {}^{206}Pb_o + {}^{238}U\left(e^{\lambda_{238}t} - 1\right).$$

Now reference to the non-radiogenic isotope ^{204}Pb:

$$\frac{^{206}Pb}{^{204}Pb} = \left(\frac{^{206}Pb}{^{204}Pb}\right)_o + \frac{^{238}U}{^{204}Pb}\left(e^{\lambda_{238}t} - 1\right). \tag{6}$$

Now similarly using equation (6) we can write the expression for the decay of ^{235}U:

$$\frac{^{207}Pb}{^{204}Pb} = \left(\frac{^{207}Pb}{^{204}Pb}\right)_o + \frac{^{235}U}{^{204}Pb}\left(e^{\lambda_{235}t} - 1\right). \tag{7}$$

We take the ratio of (6) and (7) and re-arrange to give:

$$\frac{\frac{^{207}Pb}{^{204}Pb} - \left(\frac{^{207}Pb}{^{204}Pb}\right)_o}{\frac{^{206}Pb}{^{204}Pb} - \left(\frac{^{206}Pb}{^{204}Pb}\right)_o} = \frac{^{235}U}{^{238}U}\frac{\left(e^{\lambda_{235}t} - 1\right)}{\left(e^{\lambda_{238}t} - 1\right)}. \tag{8}$$

Now we have a ratio of lead isotopes that can be used to provide information about times in Earth history when a particular lead sample was in a system w/uranium. Early on ^{207}Pb increased faster because of the shorter half-life of ^{235}U. But now there is less ^{235}U around to make ^{207}Pb so ^{206}Pb is increasing faster. We need to add to equation (8) terms for initial lead, which come from studies of meteorites:

$$\frac{^{207}Pb}{^{204}Pb} = \left[\frac{^{235}U}{^{238}U}\cdot\frac{\left(e^{\lambda_{235}t} - 1\right)}{\left(e^{\lambda_{238}t} - 1\right)}\right]\cdot\frac{^{206}Pb}{^{204}Pb} + \left[\left(\frac{^{207}Pb}{^{204}Pb}\right)_o - \frac{^{235}U}{^{238}U}\cdot\frac{\left(e^{\lambda_{235}t} - 1\right)}{\left(e^{\lambda_{238}t} - 1\right)}\cdot\left(\frac{^{206}Pb}{^{204}Pb}\right)_o\right]. \tag{9}$$

In equation (9) the ratio $^{235}U/^{238}U=1/137.9$ and this term is very nearly constant in all natural materials. So the terms in brackets are constant for a series of samples that have the same age, *i.e.* that were isotopically homogeneous at time *t* and have remained a closed system.

Note that equation (9) takes the form $y=mx+b$.
The first bracketed term is the slope and the second bracketed term is the y-intercept.

- So the age can be determined from lead ratios with no information at all about the amount of uranium in the sample if the initial lead ratios are known.

How to get initial lead ratios?
Want to look for the most primordial lead so the search leads to analyses of meteorites. Iron meteorites have virtually no uranium and the least radiogenic lead [lowest $(^{207}Pb/^{204}Pb)_o$ and $(^{206}Pb/^{204}Pb)_o$ ratios] is found in troilite (*i.e.* iron sulfide) in the **Canyon Diablo meteorite**. This is by definition **primordial lead**, aka the lead ratio in the initial solar nebula. Note that Earth and the meteorites fall on the same lead-lead isochron, which is evidence that lead and uranium were both isotopically homogeneous in the solar nebula before the accretion into the planets, etc.

If we use the decay constants for uranium, the $^{235}U/^{238}U$ ratio given above, and the initial lead ratios from Canyon Diablo this gives a date of $(4.54\pm0.03)\times10^9$ years. This is the time when isotopically homogeneous lead was isolated from the solar nebula in various bodies with different U/Pb ratios. This is how we estimate the age of the Earth.

- For the purpose of tracing the development of lead in the Earth, primoridal lead in Canyon Diablo proves to be a good starting point. The meteorites were a closed system but on Earth geologic activity has redistributed lead and uranium. But studies of ocean sediments seem to provide a good estimate of the crustal average. The assumption was demonstrated that erosion, mixing and deposition homogenized the sample and produce an estimate of crustal lead.

Advantages of Pb-Pb approach:
(1) No need to measure absolute uranium concentrations. This is a plus because uranium is an incompatible element and thus mobile. Lead is not as mobile and thus using only that element makes it easier to find closed systems. Zircon crystals are relatively common and are very resistant to diffusion. They are commonly used for dating.
(2) Thanks to "national security considerations" the decay constants of uranium in equation (9) are the best determined of any isotopic system.
(3) Decay constants/half-lives are in range favorable for finding the age of Earth, ancient terranes on Earth, solar system, etc.

Radioactivity as a Long-Term Heat Source

We now know that radioactive decay is the primary contributor to long-term heating of the Earth. The isostopes ^{238}U, ^{235}U, ^{232}Th, ^{40}K are important in this regard. The decay energy H is

$$H_i = E_i \frac{N\lambda_i}{m_i} \qquad (10)$$

where E is the decay energy per atom, N is Avogadro's number ($=6.022\times10^{23}$ mol^{-1}), λ is the decay constant, and m is the atomic weight of the isotope. The subscript i indicates that the contributions from all four isotopes are to be summed. Abundances are usually taken to be **chondritic**, which is that in meteorites called **chondrites**. Chondrites are the most primordial meteorites and represent the closest preserved materials to the composition of the solar nebula.

Note that these elements are **large ion lithophiles (LILs)**. That is, they are large ions that are among the first to exit the crystal matrix of a mineral upon melting. The element ^{40}K

has an affinity for continental crustal rocks and its abundance is such that it must be taken into account in thermal models of the continental crust.

We will show how radioactive heating terms are handled when we study the thermal structure of the lithosphere.

Isotope	E Energy Decay per atom (10^{-6} erg)	λ Decay Constant (10^{-10} y $^{-1}$)	H Decay Energy (erg g^{-1} s^{-1})	Radioactive Isotope Abundance	Present terrestrial Abundance (10^{20} g)	Half-Life (Ga)
^{238}U	75.9	1.55125	0.940	0.9928	1.82	4.47
^{235}U	72.4	9.8485	5.79	0.0072	0.0132	0.71
^{232}Th	63.8	0.49475	0.26	1.0	6,79	14.01
^{40}K	1.14	5.543	0.302	1.167×10^{-4}	2.14	1.25