Geologic Time and Stratigraphic Correlation

Relative Time

- Geologists first worked out the sequence of events recorded in the rock record using the principles of relative time:
 - original horizontality
 - original lateral continuity
 - superposition
 - fossil succession
 - cross-cutting and intrusive relationships
 - unconformities

What is the Geologic Time Scale, continued?

• Due to the fact that early geologists had no way of knowing how the discoveries of the Earth were going to develop, geologist over time have put the time scale together piece by piece. Units were named as they were discovered. Sometimes unit names were borrowed from local geography, from a person, or from the type of rock that dominated the unit.

Examples

• <u>Cambrian</u>: From the Latin name for Wales. Named for exposures of strata found in a type-section in Wales by British geologist Adam Sedgwick.

<u>Devonian</u>: Named after significant outcrops first discovered near Devonshire, England

• <u>Jurassic</u>: Named for representative strata first seen in the Jura Mountains by German geologist Humboldt in 1795)

• <u>Cretaceous</u>: From the Latin "creta" meaning chalk by a Belgian geologist

• The earliest time of the Earth is called the Hadean and refers to a period of time for which we have no rock record, and the Archean followed, which corresponds to the ages of the oldest known rocks on earth. These, with the Proterozoic Eon are called the **Precambrian Eon**. The remainder of geologic time, including present day, belongs to the **Phanerozoic Eon**.

• While the units making up the time scale are called geochronologic units, the actual rocks formed during those specific time intervals are called chronostratigraphic units. The actual rock record of a period is called a system, so rocks from the Cambrian Period are of the Cambrian system.

Principles Behind Geologic Time

 Nicholas Steno, a Danish physician (1638-1687), described how the position of a rock layer could be used to show the relative age of the layer. He devised the three main principles that underlie the interpretation of geologic time:

✓ <u>The principle of superposition</u>: The layer on the bottom was deposited first and so is the oldest

✓ <u>The principle of horizontality</u>: All rock layers were originally deposited horizontally.

✓ The principle of original lateral continuity: Originally deposited layers of rock extend laterally in all directions until either thinning out or being cut off by a different rock layer.

 These important principles have formed the framework for the geologic area of stratigraphy, which is the study of layered rock (strata).



Younger

 Decades later, other European scientists rediscovered 'Steno's Laws' and began applying them. Abraham Gottlob Werner became famous for his proposal that all rocks came from the ocean environment. He and his followers were called "Neptunists." An opposing view (by Voisins) argued that all rocks of the earth came from volcanic environments. These scientist were called "plutonists."

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Principles Behind Geologic Time, continued

• James Hutton, a Scottish physician and geologist (1726-1797), thought the surface of the earth was an ever-changing environment and "the past history of our globe must be explained by what can be seen to be happening now." This theory was called "uniformitarianism," which was later catch-phrased as "the present is the key to the past."

• William Smith was a surveyor who was in charge of mapping a large part of England. He was the first to understand that certain rock units could be identified by the particular assemblages of fossils they contained. Using this information, he was able to correlate strata with the same fossils for many miles, giving rise to the principle of biologic succession.

✓ <u>The principle of biologic succession</u>: Each age in the earth's history is unique such that fossil remains will be unique. This permits vertical and horizontal correlation of the rock layers based on fossil species.



Even though these two outcrops are separated by a large distance, the same rock layer can be correlated with the other because of the presence of the same shark teeth. This lets scientists know that the two layer were deposited at the same time, even if the surrounding rocks look dissimilar from each other.

Principles Behind Geologic Time, continued

 During the early 1800's, English Geologist, Charles Lyell published a book called "Principles of Geology," which became a very important volume in Great Britain. It included all of Hutton's ideas, and presented his own contemporary ideas such as:

✓ <u>The principle of cross-cutting relationships</u>: A rock feature that cuts across another feature must be younger than the rock that it cuts.

✓ **Inclusion principle**: Small fragments of one type of rock but embedded in a second type of rock must have formed first, and were included when the second rock was forming.

• <u>Charles Darwin</u> (1809-1882) was an unpaid naturalist who signed up for a 5-yr expedition around the world aboard the H.M.S. Beagle. On this trip, he realized two major points. In spite of all species reproducing, no one species overwhelmed the Earth, concluding that not all individuals produced in a generation survive. He also found that individuals of the same kind differ from one another and concluded that those with the most favorable variations would have the best chance of surviving to create the next generation.



• The theory of natural selection was credited to Darwin (along with Alfred Russel Wallace) and he went on to write the famous "Origin of Species." Darwin's two goals in that work were:

1. To convince the world that **evolution had occurred and organisms had changed over geologic time**

2. The mechanism for this evolution was natural selection.

Original Horizontality - Sedimentary rocks are horizontal because the original sediments were horizontal.



Original Lateral Continuity: a logical extension of original horizontality. Individual beds are the same age along an outcrop.



Unconformities: They are significant in that they are indicators of missing time in the rock record.



Trilobite (490 million years old)

Unconformities

Unconformities are surfaces in rock that represent periods of erosion or non-deposition. In other words, time has been left out of the <u>physical</u> geologic rock record.

There are three (3) principal types of unconformities:

Angular Unconformity

Rocks above and below unconformity have different orientations. Shows that there was a period of deformation, followed by erosion, and then renewed deposition. Easiest of the three types to recognize because the units are at an angle truncated with the units above them.

Angular Unconformity



Nonconformity

Rocks in a horizontal fashion were eroded down to igneous bedrock material at which time subsequent deposition of sedimentary layers commenced. Shows that there was a period of deformation, followed by erosion, and then renewed deposition. Represents the greatest amount of time left out of the geologic rock record.

Disconformity

Rocks in a nearly horizontal fashion were eroded and an erosional profile remains covered by subsequent sedimentary deposition. Shows that there was a period of erosion and then renewed deposition in nearly horizontal layers. Most difficult to recognize because the units are nearly horizontal and only a small discontinuous layer can be observed (rubble zone or soil profile).

Disconformity



Nonconformity







James Hutton, 18th Century founder of Geology

Siccar Point, Scotland, where Hutton discovered the meaning of unconformities.







Relative Age Dating

• "Relative age" means the age of one object compared to the age of another, not the exact age of an object. This method can only be used when the rock layers are in their original sequence.

• All six of the original stratigraphic principles may be applied to determine the age of a rock. This process is called age dating. <u>Correlation</u> of strata by rock unit type (lithology) or fossil type (biology) using species, composition, or texture leads scientists to extrapolate relationships over large areas of land. Because rock layers can be "matched up," we can guess that they were formed during the same period, so they usually are the same age.

 Using the principles of original horizontality and superposition, we can conclude that oldest rock is always on the bottom because is was deposited 1st.

• Deciphering the sequence of a rock outcrop is sometimes complicated by a features within the rock record called unconformities, which are specific contacts between rock layers. There are three types of unconformities that help us **determine relative ages of rock layers**:

- **1. Angular:** Horizontal beds are uplifted and tilted or eroded followed by new deposition of horizontal beds. The figure to the right is an angular unconconformity.
- 2. Disconformity: Episodes of erosion or nondeposition between layers
- **3. Nonconformity:** Sediment is deposited on top of eroded volcanic or metamorphic rock (indicates very long passage of time)



• Relative ages can also be determined using Lyell's principle of cross-cutting relationships. In the figure to the right, both the gray and the yellow horizontal strata needed to be in place for the pink layer to cut them, therefore, the pink layer is the youngest.



Relative Age dating with index fossils

Biostratigraphy is the correlation of stratigraphic units based on fossil content.
Biostratigraphically useful species are known as <u>index fossils</u> (or guide fossils) because they can be used as guides for recognition of chronostratigraphic units.

 Index fossils are widespread, have short temporal durations resulting from rapid life spans, are abundant throughout their geographic and geologic ranges, and are easily recognized (unique).

• Trilobites are a commonly used index fossil because they are easy to recognize. We know exactly when certain species became extinct, such that we can compare rock layers that contain trilobites with a second rock layer and, based on position, determine if the second rock layer is younger. The photo to the right is a trilobite from the Mississippian period

• Fossils found in many rock layers have lived for long periods of time and cannot be used as index fossils.



Can you interpret the sequence of geologic events using superposition, intrusive relationships, and cross-cutting relationships?







What is the sequence of events?



Stratigraphic Thinking



From D. McConnell, Geologic Time, http://lists.uakron.edu/geology/natscigeo/Lectures/time/gtime1.htm

One possible interpretation...



What is the Geologic Time Scale?

What does the time scale represent?

• The geologic time scale divides up the history of the earth based on life-forms that have existed during specific times since the creation of the planet. These divisions are called **geochronologic units** (*geo*: rock, *chronology*: time).

• Most of these life-forms are found as <u>fossils</u>, which are the remains or traces of an organism from the geologic past that has been preserved in sediment or rock. Without fossils, scientists may not have concluded that the earth has a history that long precedes mankind.

The Geologic Time Scale is divided by the following divisions:

✓ Eons: Longest subdivision; based on the abundance of certain fossils

✓ Eras: Next to longest subdivision; marked by major changes in the fossil record

✓ Periods: Based on types of life existing at the time

✓ **Epochs:** Shortest subdivision; marked by differences in life forms and can vary from continent to continent.



Time Units

- Geochronologic Time Stratigraphic
- Era (Erathem)
 - -Period -System

-Age

- Epoch Series
 - -Stage
- Devonian Period Devonian System

Time Units of the Geologic Time Scale

- Time can be separated into "pure" time and "rock" time. Rock time is divided into time stratigraphic units. Pure time is divided into geochronologic units.
- Time stratigraphic units sometimes parallel formation boundaries, but often they cross formation boundaries.

Rock Units, not a part of the Geologic Time Scale

- Sedimentary rocks are divided into <u>formations</u>.
- Formations can be divided into <u>members</u>.
- Formations can be combined into groups.

INTERNATIONAL CHRONOSTRATIGRAPHIC CHART

International Commission on Stratigraphy





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4		Selection of the	Series / Epoch	Stage / Age	0. 0 numerical 0 age (Ma)					
	Paleozoic	Devonian	Upper	Famennian						
				Frasnian	372.2 ±1.6					
			Middle	Givetian 🧯	382.7 ±1.6					
				Eifelian	307.7 ±0.0					
			Lower	Emsian	353.3 11.2					
				Pragian 4	407.6 ±2.6 410.8 ±2.8					
				Lochkovian	410.2.42.2					
			Pridoli	4	419.2 13.2					
		Silurian	Ludlow	Ludfordian *	425.6 ±0.9					
				Homerian 4	427.4 ±0.5					
			Wenlock	Sheinwoodian 4	430.5 ±0.7 433.4 ±0.8					
			Llandovery	Telychian 🔒	8					
~				Aeronian 4	438.5±1.1 440.8±1.2					
ö				Rhuddanian 4	443.8 ±1.5					
ZO		Ordovician	Upper	Himantian 4	445.2 ±1.4					
haner				Katian 4	453.0 ±0.7					
				Sandbian 4	458.4 ±0.9					
"			Middle	Darriwilian	467.2 +1 1					
				Dapingian 🔹	470.0 ±1.4					
			Lower	Floian 🖕	477 7 +1 4					
			Lower	Tremadocian	485.4+1.9					
		ambrian		Stage 10	- 490.5					
			Furongian	Jiangshanian 🛓	400.5					
				Paibian 4	~ 494 ~ 497					
			Miaolingian	Guzhangian 🛓	5 E00 E					
				Drumian 4	~ 504.5					
				Wuliuan 🖌	500					
			Decise 6	Stage 4	~ 509					
		0	Series 2	Stage 3						
			Terreneuvian	Stage 2	~ 521					
				Fortunian	~ 529					
					041.0 ±1.0					



v 2020/03

Units of all ranks are in the process of being defined by Global Boundary Stratotype Section and Points (GSSP) for their lower boundaries, including those of the Archean and Proterozoic, long defined by Global Standard Stratigraphic Ages (GSSA). Italic fonts indicate informal units and placeholders for unnamed units. Versioned charts and detailed information on ratified GSSPs are available at the website http://www.stratigraphy.org. The URL to this chart is found below.

Numerical ages are subject to revision and do not define units in the Phanerozoic and the Ediacaran: only GSSPs do. For boundaries in the Phanerozoic without ratified GSSPs or without constrained numerical ages, an approximate numerical age (~) is provided.

Ratified Subseries/Subepochs are abbreviated as UIL (Upper/Late), M (Middle) and L/E (Lower/Early). Numerical ages for all systems except Quaternary, upper Paleogene, Cretaceous, Triassic, Permian and Precambrian are taken from 'A Geologic Time Scale 2012' by Gradstein et al. (2012), those for the Quaternary, upper Paleogene, Cretaceous, Triassic, Permian and Precambrian were provided by the relevant ICS subcommissions.

Colouring follows the Commission for the Geological Map of the World (www.ccgm.org)

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Chart drafted by K.M. Cohen, D.A.T. Harper, P.L. Gibbard, J.-X. Fan (c) International Commission on Stratigraphy, March 2020

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URL: http://www.stratigraphy.org/ICSchart/ChronostratChart2021-07.pdf



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4	San San	Space -	Se	ries / Epoch	Stage / Age	GSSP	numerical age (Ma)
		Jurassic			Tithonian		140.2 ±0.7
			Upper		Kimmeridgian	4	149.2 ±0.7
					Oxfordian	1	154.8 ±0.8
					Callovian		161.5 ±1.0
				Middle	Bathonian	3	168.2 ±1.2
			middle	Bajocian	2	170.9 ±0.8	
					Aalenian	٩	174.7 ±0.8
			Lower	Toarcian	4	101 0 -0 0	
				Dianchachian		184.2 ±0.3	
	0				2	192.9 ±0.3	
	S						
	8				Hettangian	3	199.5 ±0.3
	es				Rhaetian		201.4 20.2
	Σ				T G FOR G GRAFT	-	~ 208.5
		Triassic	Upper		Norian		. 997
					Camian		~ 221
				Garman	5	~ 237	
o			Middle		Ladinian	2	~ 242
20							247.2
2					Olenekian	-	251.2
e			Lopingian	Chanobsingian	2	251.902 ±0.024	
Ja		Permian		Wuchianingian	-	254.14 ±0.07	
à			Guadalupian		Casitanian	~	259.51 ±0.21
					Capitanian	2	264.28 ±0.16
					Wordian	2	266.9 ±0.4
					Roadian	5	272.01 ±0.14
			Cisuralian		Kungurian		275.01 10.14
	Paleozoic					-	283.5 ±0.6
					Artińskiań	5	290.1 ±0.26
					Sakmarian	2	200.120.20
					Asselian	2	293.52 ±0.17
			c		Cabolian	~	298.9 ±0.15
			-e	Upper	Kasimovian	-	303.7 ±0.1
			Av8	Middle	Massauian		307.0 ±0.1
		S	Pennsy	Middle	Moscovian		315.2 ±0.2
		ifero		Lower	Bashkirian	4	323.2 ±0.4
		Б	Mississippian	Upper	Serpukhovian		330.0 ±0.2
		Carb		Middle	Visean	-	999.9 IV.E
						~	346.7 ±0.4
				Lower	Tournaisian	5	358.9 ±0.4





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Communication of IUGS Geological Standards



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Ratification of Neogene subseries as formal units in international chronostratigraphy



Absolute Time: Geochronology

Radiometric Dating: the source of the dates on the Geologic Time Scale
Absolute Age Dating

• Absolute ages, or geochronometric ages, of rock can be assigned to the geologic time scale on the basis of properties of atoms that make up the minerals of a rock. Unlike relative dating, which relies on sequencing of rock layers (i.e. younger vs. older), absolute dating can produce an actual age in years.

• The number of neutrons in a nucleus of an atom determines the isotope of the element, just like the number of protons determines the identity of an element.

• Some isotopes are unstable and break down into other isotopes through a process called radioactive decay. Radioactive decay is characterized by beta decay, where a neutron changes into a proton by giving off an electron, and alpha decay, when isotopes give off 2 protons and 2 neutrons in the form of an alpha particle and changes into a new product. The original isotope is called the parent and the new isotope product is called the daughter.

• What is a Half-Life?

• Each radioactive parent isotope decays to its daughter product at a specific and measurable rate. This measurement is reported in half-lives. The <u>half-life</u> of an isotope is the time it takes for ½ of the parent atoms in the isotope to decay.

• If an isotope has a half-life of 4000 years, then after 4000 years $\frac{1}{2}$ of the parent isotope remains. After another 4000 years, $\frac{1}{2}$ of $\frac{1}{2}$ remains, or $\frac{1}{4}$ of the original amount of parent isotope. In another 4000 years (12,000 years total), $\frac{1}{2}$ more of the remaining amount decays, so after 3 half-lives, there only remains $1/8 (\frac{1}{2} \text{ of } \frac{1}{2} \text{ of } \frac{1}{2})$ of the original parent isotope.

• If a scientist knows the half-life of the parent and measures the proportion of parent isotope to daughter isotope, he/she can calculate the absolute age of the rock. This valuable method is called **radiometric dating**.

Note: Radioactive isotopes can be found in the rock record because radioactive isotopes are incorporated into the crystals of igneous rock as it cools.

Radiometric Dating

- Actually a simple technique.
- Only two measurements are needed:
- 1. The <u>parent:daughter ratio</u> measured with a mass spectrometer.
- 2. The <u>decay constant</u> measured by a scintillometer.

Basis of the Technique

- Radioactive elements "decay." Decay occurs as an element changes to another element, e.g. uranium to lead.
- The parent element is radioactive, the daughter element is stable.
- The decay rate is constant.

What is Radioactivity?

- Radioactivity occurs when certain elements literally fall apart.
- Usually protons and neutrons are emitted by the nucleus.
- Sometimes an electron is emitted by the nucleus, which changes a neutron to a proton.
- Sometimes an electron is captured.

What causes radioactivity?

- Carbon-14 is produced by cosmic ray bombardment of Nitrogen-14 in the atmosphere.
- All other radioactive elements were produced by supernova explosions before our solar system formed. This is called <u>explosive nucleosynthesis</u>.



Radioactive Decay

Scientists used the <u>proportion</u> of parent material remaining to the <u>proportion</u> of daughter material produced in order to predict the age of the rock. During each halflife, only one-half of the parent material decays to the daughter product.

DECAY

→ DAUGHTER

■ Isotopes with very long half-lives are not suitable for dating rocks younger than ~1 million years because there are too few daughter atoms to be measured accurately.

• Experimental error limits measurements to those rocks younger than about 12 half-lives of the isotope used.

Radiocarbon Dating

PARENT

• Radiocarbon dating is a common method used to date anything that was once alive (including plants) and up to 70,000 years old.

All living things take in carbon from the environment in the form of carbon-12 and carbon-14.
 When an organism dies, carbon intake stops and the carbon-14 begins to decay at a known rate.
 Scientists can determine how much C-14 remains in an organism by measuring radiation emitted by the C-14 isotopes.

Carbon dating can be used on wood, plants, humans, and even old paper made out of papyrus.

The half-life of C-14 is 5,730 years. Because of this, it should not be used with material older than ~70,000 years or 12 half-lives.
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Commonly used radioactive isotopes

Parent	Daughter	half-life	Mineral or Material
Uranium238	Lead 206	4.56 BY	Zircon, Uraninite, Pitchblende
Uranium 235	Lead 207	704 MY	Zircon, Uraninite, Pitchblende
Potassium 40	Argon 40	1.251 BY	Muscovite, biotite, hornblende, K-feldspar, volcanic rock, glauconite, conodonts
Rubidium 87	Sr 87	48.8 BY	K-mica, K-feldspar, Biotite, Metamorphics
Thorium 230	Lead 206	75 KY	Ocean sediments
Thorium 232	Lead 208	1.39 BY	Zircon, Uraninite, Pitchblende
Carbon 14	Nitrogen 14	5730 yr	Wood, bone, shell

KY- thousand years. MY- million years. BY- billion years

Uranium-Lead decay series (U-Pb series)

 Unlike carbon-14 dating, uranium dating cannot be used to date formerly living things; however, it is the most commonly used method in igneous rock dating because of the abundance of zircon minerals.

• The subscripts of 235 and 238 are the atomic mass numbers of the element. Though each isotope has 92 protons in its nucleus, U-235 has 143 neutrons and U-238 has 146 neutrons.

• Igneous rocks, or the magma from which it was formed, often intrudes overlying sedimentary rocks. By dating the magma, one can get at least a minimum age for the sedimentary rock.

Key Term

• Half-Life: the amount of time for half the atoms of a radioactive element to decay. Doesn't matter how many atoms started, half will decay.











Some Half Lives

- Carbon-14: 5,728 years
- Uranium-235: 713 MY
- Potassium-40: 1.3 BY
- Uranium-238: 4.5 BY
- Rubidium-87: 48.8 BY

Setting the Radiometric Clock

- When an igneous melt crystallizes, parent and daughter elements are chemically separated into different crystals.
- Further radioactive decay keeps the parent and daughter elements in the same crystal.

Setting the Radiometric Clock

- Individual crystals of the same mineral are dated to give the age of crystallization or cooling. Examples include zircon, muscovite, and biotite.
- Note that whole rock analysis would not give the age of cooling.

Setting the Radiometric Clock

- Carbon-14 is different in that it occurs in organic remains rather than in rocks.
- Clock is set when an organism dies.
- Carbon-14 is absorbed by all living organisms from the atmosphere or the food they eat.
- Useful for about 10 half lives, or only about 57,000 years.







Fig. 8.12. Carbon-14 radiometric clock



	Charcoal, wood, twigs and seeds.
	Bone.
	Marine, estuarine and riverine shell.
	Leather.
	Peat
	Coprolites.
Materials dated	Soil.
	Pollen.
using the Carbon-14	Hair.
method	Pottery.
metrica	Wall paintings and rock art works.
	Avian eggshell.
	Corals and foraminifera.
	Speleothems.
	Blood residues.
	Textiles and fabrics.
	Paper and parchment.
	Fish remains.
	Insect remains.
	Resins and glues.
	Antler and horn.
	Water.

Calibrating the Geologic Time Scale

- Radiometric dates from igneous rocks can be used to indirectly date sedimentary rocks and their fossils.
 Principles such as superposition and cross-cutting relationships come into play.
- Thousands of radiometric dates have been obtained.



Age of the Earth: 4.6 BY

- The oldest rocks found on earth are 4.0 BY from NW Canada.
- 4.3 BY detrital zircons have been found in younger sandstones in Australia.
- Meteorites and moon rocks are 4.6 BY.
- Rocks older than 4.0 BY on earth have apparently been destroyed by weathering and plate tectonics.

4.40 BY zircon grain from Australia, found in 3 BY sandstone



Correlation

- Determination of the equivalence of bodies of rock at different locations. There are two kinds of correlation:
- <u>Lithostratigraphic</u> matching up continuous formations.
- <u>Chronostratigraphic</u> matching up rocks of the same age. Usually done with fossils using <u>biostratigraphy</u>.

Correlation

- Over <u>short distances</u> lithostratigraphic correlation is the same as chronostratigraphic correlation.
- Over <u>medium distances they are not</u> the same.
- Over <u>long distances</u> only chronostratigraphic correlation can be used.

How Old is Old?

• From the time of Hutton, scientists were convinced that the earth was much older than the 6000 years predicted by the religious scholars.

- Charles Lyell tried to estimate the age of the earth through the amount of evolution exhibited by marine mollusks in a specific time system.
- Another method was to estimate the rate of deposition for sedimentary rocks.
- Sir Edmund Halley proposed to estimate the age of the earth using salt content of the oceans, assuming that the oceans were once non-saline and that salt addition to the oceans corresponded in some linear fashion with time.
- Lord Kelvin estimated the age of the Earth at 24-40 million years. He proposed that the Earth has been cooling since it formed, and he calculated the rate of cooling using principles of heat conduction.
- It wasn't until Henri Becquerel discovered radioactivity in 1896 and Madame Curie isolated radium 2 years later that people realized that the Earth had it's own source of heat. Thus it became one of the most useful tools for future scientists.
- The oldest rocks found so far on Earth (based on zircon grains from Australia) have been dated at 4.1-4.2 billion years.
- Meteorites have also been dated at 4.6 billion years. Meteorites are considered to be remnants of a plant or asteroid that originally formed at the same time as the Earth, so that the Earth's age is currently estimated to be 4.6 billion years.
- The oldest fossils are preserved remains of stromatolites, which are layers of lithified blue-green algae, dating to approximately 3.5 billion years before present.

Origin and Early Evolution of Life The lost record of the origin of Life? Few crustal rocks from > 3 Ga Half life of sediments 100-200 Ma so most destroyed



CRUSTAL GROWTH has proceeded in episodic fashion for billions of years. An important growth spurt lasted from about 3.0 to 2.5 billion years ago, the transition between the Archean and Proterozoic eons. Widespread melting at this time formed the granite bodies that now constitute much of the upper layer of the continental crust.

Taylor & McLennan (1996)

The Inhospitable Hadean Eon (4.6-3.8 Ga)

It is more useful to define the Hadean Eon as the time when impacts ruled the Earth than to define it as the time before the rock record. For decades now it has been obvious that the coincidence between the timing of the end of the lunar late bombardment and the appearance of a rock record on Earth is probably not just a coincidence. I doubt I am pointing out something that the reader hasn't long ago given thought to. While the Moon was struck by tens of basin-forming impactors (100 km objects making 1000 km craters), the Earth was struck by hundreds of similar objects, and by tens of objects much larger still. The largest would have been big enough to evaporate the oceans, and the ejecta massive enough to envelope the Earth in 100 m of rock rain. Smaller impacts were also more frequent. On average, a Chicxulub fell every 10⁵ years. When one imagines the Hadean one imagines it with craters and volcanos: crater oceans and crater lakes, a scene of mountain rings and island arcs and red lava falling into a steaming sea under an ash-laden sky. I don't know about the volcanos, but the picture of abundant impact craters makes good sense -- the big ones, at least, which feature several kilometers of relief, are not likely to have eroded away on timescales of less than ten million years, and so there were always several of these to be seen at any time in various states of decay. The oceans would have been filled with typically hundreds of meters of weathered ejecta, most of which was ultimately subducted but taking with them whatever they reacted with at the time --CO₂ was especially vulnerable to this sort of scouring. The climate, under a faint sun and with little CO₂to warm it, may have been in the median extremely cold, barring the intervention of biogenic greenhouse gases (such as methane), with on occasion the cold broken by brief (10s to 1000s of years) episodes of extreme heat and steam following the larger impacts. In sum, the age of impacts seems sufficiently unlike the more familiar Archaean that came after that it seems useful to give this time its own name, a name we already have, and that, if applied to the Hadean that I have described, actually has some geological value.

Zahnle (2001) The Hadean Atmosphere, EOS, AGU Fall Mtg, U51A-10

INTERNATIONAL WEEKLY JOURNAL OF SCIENCE Volume 384 No. 6604 7 November 1996 50

Oldest traces of life on Earth

How vertebrates tell left from right Controlling inflammation Science in South Africa S.J.Mojzsis et al. (1996), "Evidence for life on Earth before 3,800 million years ago" ...based on isotopically light carbon in graphite from apatite in rocks on Akilia Island, SW Greenland.

But ...

Sano et al. '99 report the apatite had U/Pb and Pb/Pb ages of only ~ 1.5 Ga.





measured log have also been examined. The

scale is in meters.

Geology Matters: 1

• Re-mapping of Akilia Island & new petrologic & geochemical analyses do not support sedimentary origin for these rocks.

They appear instead to be metasomatized ultramafic *igneous rocks* (not BIFs).
Therefore highly improbable that they hosted life at the time of their formation.

Fedo & Whitehouse (2002) Science, Vol. 296:1448-1452.

Geology Matters: 2

Fedo & Whitehouse (2002) Science, Vol. 296:1448-1452.

Quartz-pyroxene outcrop originated as igneous rock, compositionally modified during repeated episodes of metasomatism (= hot rock + water) & metamorphism (= high T +P)
Deformational petrologic features inconsistent with BIF



Geochemical evidence against Akilia rocks being BIFs

• REE pattern, elemental ratios & mineralogy all consistent with Akilia rocks being **igneous** & not sedimentary BIFs



0.10

0.00

0.20

P2O5 (wt. %)

С

0.30



quartz-pyroxene rock is similar to AK 38 in composition and abundance of REEs. Analyses for Eu are not plotted because of very inconsistent behavior of Eu. Eu/Eu* (chondrite-normalized) ranges from 0.25 to 1.61, suggesting that metamorphic conditions may have fluctuated near the Eu(II)-Eu(III) valence boundary. (B) The plot shows the relationships of the six BIF groups from Isua, average komatiite (19), AK 38, and four samples of ultramafic schist from Akilia. None of the six groups of Isua BIF have Cr/Th or Th/Sc ratios near those of AK 38 (a proxy for the entire quartz-pyroxene lithology), which are very similar to those of average komatiite. (C) The main plot shows data from Akilia, BIFs from Isua, and tholeiite-komatiite compositions from the Barberton greenstone belt (18) for TiO, versus P,Oe. Tholeiites and komatiites plot in consistent positions where TiO₂/P₂O₂ ≤ 10. AK 38 and Akilia ultramafic samples plot in the komatiite field; all samples of the quartz-pyroxene rock (except for a single boudin) plot near this field. Isua BIFs all lie in an unrelated field. The outlier point in the BIF data represents an aluminous BIF group, which has been interpreted to represent an admixture of BIF and mafic volcaniclastic component and so is not an exclusive BIF composition (17). The inset plot shows distinct fields for the different lithologies. Akilia ultramafic samples and AK 38 lie in the komatiite field. Note the distinct position of the Isua BIFs.

Fig. 3 (A) Plot of chondrite-normalized (39) REE abundances for the quartz-pyroxene rock. Note the concave-down behavior of the LREEs in the Akilia quartz-pyroxene samples and the concave-up behavior of the LREEs and the entire pattern for average Isua BIF (heavy red line). The scatter of REE abundances in the quartz-pyroxene samples is due to quartz dilution (AK 46 has 71.9 wt % SiO_; AK 41 has 95.5 wt % SiO₂). The average value of extracted boudins from the



<u>Geology</u>

Matters:

Fedo & Whitehouse (2002) Science, Vol. 296:1448-1452.

Bottom Line: No evidence for a Biogenic Origin of Reduced Carbon in 3.8 Ga Isua (SW Greenland) Rocks

A biogenic origin of graphite in carbonate-rich rocks in Isua1-4 was inferred from the assumption that these rocks had a sedimentary origin. However, recent field and laboratory investigations have shown that most if not all carbonate in Isua is metasomatic in origin. Petrographic and isotopic analyses show that graphite in the metacarbonate rocks, serving as a basis for earlier investigations, is produced abiogenically by disproportionation of ferrous carbonate at high temperature and pressure and at a time later than the formation of the host rock. This type of graphite, including graphite inclusions in apatite, therefore cannot represent 3.8 Gyr-old traces of life. Stepped-temperature combustion accompanied by isotope

 $\mathbf{6FeCO_3} \rightarrow \mathbf{2Fe_3O_4} + \mathbf{5CO_2} + \mathbf{C}$

Van Zuilen et al (2002) Nature Vol. 418:627-630

Morphological Evidence for Antiquity of Life

WARRAWOONA PROKARYOTIC MICROFOSSIL PILBARA CRATON WA ~ 3.5 Ga (J.W. SCHOPF, 1983)





Figure 1 Optical photomicrographs showing carbonaceous (kerogenous) filamentous microbial fossils in petrographic thin sections of Precambrian cherts. Scale in **a** represents images in **a** and **c**-**i**; scale in **b** represents image in **b**. All parts show photomontages, which is necessitated by the three-dimensional preservation of the cylindrical sinuous permineralized microbes. Squares in each part indicate the areas for which chemical data are presented in Figs 2 and 3. **a**, An unnamed cylindrical prokaryotic filament, probably the degraded cellular trichome or tubular sheath of an oscillatoriacean cyanobacterium, from the ~770-Myr Skillogalee Dolomite of South Australia¹². **b**, *Gunflintia grandis*, a cellular probably oscillatoriacean trichome, from the ~2,100-Myr Gunflint Formation of

Ontario, Canada¹³. **c**, **d**, Unnamed highly carbonized filamentous prokaryotes from the ~3,375-Myr Kromberg Formation of South Africa¹⁴: the poorly preserved cylindrical trichome of a noncyanobacterial or oscillatoriacean prokaryote (**c**); the disrupted, originally cellular trichomic remnants possibly of an *Oscillatoria*- or *Lyngbya*-like cyanobacterium (**d**). **e**-**i**, Cellular microbial filaments from the ~3,465-Myr Apex chert of northwestern Western Australia: *Primaevifilum amoenum*^{4,5}, from the collections of The Natural History Museum (TNHM), London, specimen V.63164[6] (**e**); *P. amoenum*⁴ (**f**); the holotype of *P. delicatulum*^{4,5,15}, TNHM V.63165[2] (**g**); *P. conicoterminatum*⁵, TNHM V63164[9] (**h**); the holotype of *Eoleptonema apex*⁵, TNHM V.63729[1] (**i**).

Biogeochemistry That's life?

This could be a picture of one of the earliest-known fossils a microbe, 60 μ m long, that is almost 3,500 million years old. On the other hand, it could be just a flaw in the rock. It all depends on whom you talk to, as epitomized by two papers in this issue.

The more optimistic view is taken by William Schopf and colleagues (Nature 416, 73-76; 2002). In the early 1990s. Schopf caused a sensation with reports of a diverse bacterial flora from the 3.465-millionvear-old Apex cherts of Western Australia. At the time. all he had to go on was morphology. This was always controversial, given that bacteria have little morphology to begin with. As a consequence, it is hard to tell the difference between a



the controversy, however, as demonstrated by the report from Martin Brasier and colleagues (*Nature* **416**, 76–81: that the fossils, as a whole, have a random orientation that is not characteristic of bacterial behaviour. in which the cells

Schopf's "microfossils" seem to have formed hydrothermally (hot water + rock)

Non-biologic Origin of 3.5 Gyr "Microfossils"?

bacterium — especially a fossil bacterium — and a bubble. This is why Schopf has devised authenticity criteria that are based on bacterial habit. If you have one bacterium, for example, you will usually have hundreds: isolated blobs purporting to be bacteria usually turn out to be artefacts.

Since then, Schopf and colleagues have sought to back up the morphology using laser-Raman imaging, a technique in which the chemical composition, as well as the structure of the fossils, can be mapped in two dimensions. After several tests of the technique on less controversial fossils, Schopf et al. have used the method on the Apex chert material. They find that the fossils have the composition to be expected if they were made of organically derived carbon.

This will not be the end of

2002). Using the original Apex chert material, as well as newly collected specimens, they find that the rocks in which the fossils were found come from a vein that may have been produced hydrothermally, that is, by the action of heated water on minerals. The carbonisotope signature is consistent with a biogenic origin, one derived from living organisms. But other studies suggest that this was an environment in which carbon dioxide produced by volcanic action was transformed into isotopically light carbon at 250-350 °C. The bottom line is that although the carbon looks organic, it need not be. Similarly, Raman spectroscopy shows that although the material in the fossils could be biogenic, it could equally well be amorphous graphite. Brasier et al. even dismiss the morphology. They suggest

tend to line up in one direction or another: the individual cells have a range of strange, even branched, morphologies; and what look like filaments with internal divisions may be the result of interleaving guartz and graphite sheets. Many authors agree that there is isotopic evidence for biogenic activity in the Archaean (that interval of Earth history before 2,500 million years ago). But Brasier and colleagues, at least, say that the Apex chert fossils aren't really fossils at all.

Given that Schopf was one of the first to cast doubt on the biogenicity of another celebrated suite of purported microfossils — in the martian meteorite ALH84001 — it is ironic that his own work should be subjected to such scepticism. But that is the name of the game for claims of life at the extremes of time and space. Henry Gee

Gee (2002) Nature, 416:28. Brasier et al. (2002) Nature, 416:76-81.



Questioning the authenticity of 3.465 Ga Apex fossils: 2

"Many of these filamentous structures [from the apex chert] are branched or formed in ways not shown in the original descriptions because of the choice of focal depth and/or illustrated field of view."

Brasier et al. (2002) Nature, Vol. 416: 76-81.

Figure 2 Automontages of inferred artefacts from the Apex chert. **a**, **b**, **o**, **u**, **v**, **x**, Pseudoseptate and branched filamentous artefacts from vein chert (NHM V.63127, 63164, 63165, 63127, 63164, 63164). **i**, Artificial graphite filament (63166). **e**, **k**, **l**, Filamentous artefacts from felsic tuff (**e** and **k** from chalcedony matrix; **l** from within devitrified rim of volcanic glass shard). **p**, Pseudoseptate filament from clast in stratiform chert. **c**, **d**, **f**–**h**, **j**, **m**, **n**, **q**–**t**, **w**, **y**, **z**, New images of previously illustrated structures (refs 2, 3; holotypes*): **c**, *Primaevifilum amoenum*; **d**, *A. disciformis*; **f**, *P. laticellulosum**; **g**, *P. delicatulum**; **h**, *P. attenuatum**; **j**, *P. amoenum**; **m**, *P. conicoterminatum**; **n**, type C narrow filament; **q**, *Archaeotrichion septatum**; **r**, **s**, 'trichome showing bifurcated cells'; **t**, type A broad filament; **w**, cf. *A. grandis**; **y**, 'type B' broad filament; **z**, *Archaeoscillatoriopsis maxima**. Bright-field transmitted light. Scale bar, 40 µm; arrows indicate anomalies (see the text).

Schopf's 'microfossils' #2: Raman Spectroscopy to the rescue?



Figure 2 Digital optical images and corresponding Raman images. a-i, Optical images (left) and Raman 'G' band intensity maps (right), of areas of fossils indicated by the squares in Fig. 1a-i, respectively.

Raman spectra & spectral maps (G band) of 0.7-3.5 Ga 'microfossils'
Indicates presence of reduced carbon (graphite) associated with 'microfossils'.

Figure 3 Typical spectral bands of parts of fossils shown in Fig. 1 used for Raman imaging (Fig. 2) and the spectrum of immersion oil used to enhance the optical image of some specimens. **a**, **b**, Point spectra of the Skillogalee filament shown in Fig. 1a, without (above) and with (below) a covering veneer of immersion oil; and of *Gunflintia grandis* (Fig. 1b), without (above) and with (below) an oil veneer (showing a broad 'D' band and its substructure, <u>typical of the kerogen in this relatively unmetamorphosed</u>, subgreenschist facies, geologic unit). **c**–**i**, Point spectra of other fossils from which Raman images were acquired: unnamed filamentous prokaryotes from the Kromberg Formation (**c**, **d**; shown in Fig. 1c, d, respectively); cellular filamentous prokaryotes from the Apex chert (**e**–**i**; shown in Fig. 1e–**i**, respectively). **j**, Spectrum of immersion oil used to enhance the optical image of some specimens.



Schopf et al. (2002) *Nature*, vol. 416:73-76.

Abiotic origin of microfossil-like structures #2



a,b: Apex chert (3.5 Ga, WA) microfilament images from Schopf et al (2002) & Brasier et al. (2002), respectively (10 μm and 40 μm scale bars, respectively).

c,d: SEM micrographs of self-assembled silica-carbonate aggregates (scale bars = $40 \mu m$)

Garcia-Ruiz et al. (2003) Science Vol. 302: 1194-1197.

Abiotic origin of microfossil-like structures #3





<u>Above</u>: Optical micrographs of silica-carbonate 'biomorphs' taken under same illumination (scale bars = $50 \mu m$)

a

(a) As prepared; (b) after hydrothermal absorption of organics; (c) baked after exposure to organics (as in b).

<u>Right</u>: Raman spectra of (Top) heat-cured biomorph and (Bottom) Schopf et al. (2002) 3.5 Ga Apex microfilament.



Garcia-Ruiz et al. (2003) Science Vol. 302: 1194-1197.


Animal, Vegetable or Mineral ("Biomorph") #1 ?

> Garcia Ruiz et al. (2002) Astrobiology, Vol. 2(3): 353-369.

Animal, Vegetable or Mineral #2?



(j-l)

Garcia Ruiz et al. (2002) Astrobiology, Vol. 2(3):353-369.

Animal, Vegetable or Mineral #3?



Garcia Ruiz et al. (2002) Astrobiology, Vol. 2(3):353-369.

What are Stromatolites & how do they form?







Stromatolites









W. Australia location of
stromatolites & Schopf
'microfossils'

Hofman et al. (1999) Geol.
Soc. Am. Bull. Vol. 111(8): 1256-1262.
http://www.dme.wa.gov.au/anc ientfossils



Stromatolites-1

• 1.5 Ga stromatolite from Ozarks

http://www.stlcc.cc.mo.us/fv/ geology/text/25.html

• Stromatolites are fossils which show the life processes of cyanobacteria (fomerly called bluegreen algae). The primitive cells (Prokaryotic type), lived in huge masses that could form floating mats or extensive reefs. Masses of cyanobacteria on the sea floor deposited calcium carbonate in layers or domes. These layered deposits, which have a distinctive "signature" are called laminar stromatolites. This is an example of a layered stromatolite from the Ozark Precambrian. Most often, stromatolites appear as variously-sized arches, spheres, or domes. Ozarkcollenia, a distinctive type of layered Precambrian stromatolite, pushes the appearance of life in the Ozarks to well over 1.5 Ga.

Stromatolites-2



• Kona Dolomite (Michigan) 2.2 Ga stromatolite

• Schematic of stromatolite structure

• Mary Ellen Jasper (Minnesota) 2.1 Ga stromatolite

• Stomatolites are colonial structures formed by photosynthesizing cyanobacteria and other microbes. Stromatolites are prokaryotes (primitive organisms lacking a cellular nucleus) that thrived in warm aquatic environments and built reefs much the same way as coral does today.

http://www.wmnh.com/wmel0000.htm

Oldest Microfossils on Earth?



Warrawoona Group, N. Pole Dome/ Marble Bar, WA; 3.5 Ga





FILAMENTOUS MICROFOSSILS -- WARRAWOONA GROUP (APEX BASALT) -- WESTERN AUSTRALIA --- 3.5 Ga

Courtesy Joe Kirschvink, CalTech

Warrawoona Stromatolites May be the Oldest Convincing Evidence for Life on Earth*

Grotzinger & Knoll '99 argue that Archean stromatolites could be simple inorganic precipitates!

*My opinion & that of many geologists

Examples of 800 million year-old stromatolites from the Officer Basin, Western Australia. *LEFT:* Acaciella australica - a form with narrow columns in bioherms up to 1 metre in diameter.



ABOVE: Baicalia burra - a form with broad, irregular branching columns



More W. Australian Stromatolites

LEFT: Detail of a branching column formed on the side of a stromatolite cone. <u>Complex structures such as these rule</u> <u>out formation by means such as the</u> <u>folding of soft sediments</u>.

 BELOW LEFT: The outcrop of <u>"egg-carton"</u> <u>stromatolites</u> when first discovered, before removal of the overlying rocks.
 BELOW RIGHT: The "egg-carton" rock face after the overlying rocks were removed. Although today the "eggcartons" are tilted at an angle of about 70 degrees, they were originally flat lying.





Macroscopic Remains of Proterozoic Stromatolites



CONOPHYTON STROMATOLITES MCARTHUR BASIN, AUSTRALIA ~ 1.6 Ga (M.R. WALTER)

A possible abiotic origin for stromatolites?

 Seems statistically feasible that the morphology of stromatolites can occur through non-biological processes.

Grotzinger & Rothman (1996) "An abiotic model for stromatolite morphogenesis," *Nature*, Vol. 382: 423-425.



A Modern Analog, though, provides support for the interpretation of stromatolites as fossil life forms: Modern Living Stromatolites in Shark Bay, Australia

• Hamelin Pool's stromatolites result from the interaction between microbes, other biological influences and the physical and chemical environment.

• The cyanobacteria trap fine sediment with a sticky film of mucus that each cell secretes, then bind the sediment grains together with calcium carbonate which is separated from the water in which they grow. Because the cyanobacteria need sunlight to grow and they have the ability to move towards light, their growth keeps pace with the accumulating sediment.

http://www.sharkbay.org/terrestial_enviroment/page_15.htm

The majority view seems to be that stromatolites are the first good evidence for life, placing its origin in the vicinity of 3.5 Ga.

By 3.47 Ga there is additional evidence for microbial life in the form of isotopicallydepleted sulfur minerals....

Isotopic evidence for microbial sulphate reduction in the early Archaean era

Yanan Shen*, Roger Buick† & Donald E. Canfield*

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Sulphate-reducing microbes affect the modern sulphur cycle, and may be quite ancient^{1,2}, though when they evolved is uncertain. These organisms produce sulphide while oxidizing organic matter or hydrogen with sulphate3. At sulphate concentrations greater than 1 mM, the sulphides are isotopically fractionated (depleted in ³⁴S) by 10-40‰ compared to the sulphate, with fractionations decreasing to near 0‰ at lower concentrations^{2,4-6}. The isotope record of sedimentary sulphides shows large fractionations relative to seawater sulphate by 2.7 Gyr ago, indicating microbial sulphate reduction7. In older rocks, however, much smaller fractionations are of equivocal origin, possibly biogenic but also possibly volcanogenic2,8-10. Here we report microscopic sulphides in ~3.47-Gyr-old barites from North Pole, Australia, with maximum fractionations of 21.1‰, about a mean of 11.6‰, clearly indicating microbial sulphate reduction. Our results extend the geological record of microbial sulphate reduction back more than 750 million years, and represent direct evidence of an early specific metabolic pathway-allowing time calibration of a deep node on the tree of life.

Microbial Activity ~3.47 Ga Suggested by Sulfur Isotopes

H_2S in Barite = $BaSO_4$



Microbial sulphate reduction? $SO_4^{2-} + 2CH_2O = S^{2-} + 2CO_2 + 2H_2O$

• Sulfide is depleted in heavy isotope (³⁴S) relative to sulfate precursor when biological enzymes reduce it.

Shen et al (2001) Nature, Vol. 410:77-81

By 3.5 Ga then there is evidence for life from stromatolites (Warrawoona, NW Australia) & isotopically-depleted sulfur in barite (N. Pole, Australia)

By 3.2 Ga there is new and different evidence for life... Only this time it did not form at the surface....

Rather microbial life seems to have evolved in a submarine thermal spring system...

Filamentous microfossils in a 3,235-million-year-old volcanogenic massive sulphide deposit

Birger Rasmussen

Department of Geology and Geophysics, University of Western Au Nedlands, Western Australia 6907, Australia

letters to nature

3.2 Ga Hyperthermophilic Microbes from W. Australia

"A biogenic origin is inferred for the filaments from their sinuous morphology, length-wise uniformity and intertwined habit..."



Figure 3 Photomicrographs of filaments from the Sulphur Springs VMS deposit. Scale bar, 10 μm. a-f, Straight, sinuous and curved morphologies, some densely intertwined.

g, Filaments parallel to the concentric layering. h, Filaments oriented sub-perpendicular to banding.

Rasmussen (2000) Nature, Vol. 405:676-679.

Location & Images of 3.2 Ga hydrothermal microbes



Figure 1 Location and geology of the Sulphur Springs deposit. a, Map showing the geology of the northern Soanesville belt and the location of the Sulphur Springs deposit (after ref. 16). b, Stratigraphic column of the Sulphur Springs group (after ref. 18).



Figure 2 Remnant cores and bands containing filaments. **a**, Silica-rich colloform cores containing filaments, surrounded by replacive pyrite (gold). Combined transmitted and reflected light (TL and RL) photographic montage. **b**, Thin banded layer containing filaments within paragenetically early chert (TL and RL). **c**, Detail of **a** showing the partial replacement of quartz-rich colloform structures displaying fine-scale lamination (TL and RL). Scale bar is 1 mm for **a**, **b** and 0.1 mm for **c**.

Rasmussen (2000) Nature, Vol. 405:676-679.

By 2.7 Ga there is excellent evidence for both microbial life, eukaryotes & oxygenic photosynthesis from molecular fossils



•Archean Molecular Fossils from the 2.7 Ga Roy Hill Shale

PILBARA CRATON

"Archean Molecular Fossils & The Early Rise of Eukaryotes" Jochen J. Brocks, Graham A. Logan, Roger Buick & Roger E. Summons *Science*, 285, 1033, 1999

GEOCHEMISTRY vs STRATIGRAPHY



Summons, Brocks, et al.

2.7 Ga Cyanobacterial & Eukaryote Biomarkers

Steranes

Hopanes







Kalahari Manganese Member, Hotazel Fm., Manatwan Mine, S. Africa

Oxidation (+2 to +4) $Mn^{+2} \longrightarrow Mn^{+4}$ insoluble $O_2 \longrightarrow H_2O$ Reduction (0 to -2)

> Caryopilite (Mn,Mg)₃Si₂O₅(OH)

At 2.4 Ga this is the oldest constraint on free O₂ in earth history...

Modified from Joe Kirschvink, CalTech

Cyanobacteria Bloom Causes Electrochemical Stratification in Ocean, Depositing Manganese in Upwelling Areas on Continental Shelves





Red Beds

Hematite: Fe₂O₃
Fe²⁺ --> Fe³⁺
O₂ --> H₂O
Requires free O₂ to oxidize Fe(II) & produce (red) iron oxides

- Oldest red beds ~ 2.2 Ga
- Sedimentary rock
- Reddish, sandy sediment deposited by rivers &/or windblown dust.

Photos: Kansas Geological Survey



Paleosols ("Ancient Soils")

> 2.2 Ga: Fe-deficient
Soluble Fe(II) removed by groundwater

- < 2.2 Ga: Fe-rich
- Fe(III)-oxides insoluble

H. Holland (Harvard) >2.2 Ga: $O_2 < 0.01$ PAL <1.9 Ga: $O_2 > 0.15$ PAL %Attempt to develop quantitative indicator of O_2 based on Ref Beds

Kump et al. (1999) *The Earth System*, Prentice Hall. http://www.gly.uga.edu/railsback/FieldImages.html



Banded Iron Formations (BIFs)



ron Ore Mine, W. Au.

• Most BIFs > 1.9 Ga; indicates free O₂ existed by then

- Laminated sedimentary rocks
- Alternating layers of magnetite / hematite & chert (SiO₂)
- Most Fe in steel comes from BIFs in Canada & Australia

Hematite (Fe₂O₃) & magnetite (Fe₃O₄) : Fe²⁺ --> Fe³⁺
O₂ --> H₂O
Requires free O₂ to oxidize Fe(II)

Precambrian Banded Iron Formations (BIFs)

(Adapted from Klein & Beukes, 1992)



Time Before Present (Billion Years)

Abundance of BIF Relative

Courtesy Joe Kirschvink, CalTech

How did BIFs form?

•A big open question in geology!

One favored scenario:

- Anoxic deep ocean containing dissolved Fe(II)
- Seasonal upwelling brings Fe(II) to the surface where it is oxidized to Fe(III) by O_2 produced by cyanobacteria/algae.
- Insoluble Fe(III) precipitates out of seawater
- SiO₂ precipitated by algae during non-upwelling season

Image: http://web.uct.ac.za/depts/geolsci/dlr/hons1999/sishen2.jpg

Geochemical **Evidence** for Atmospheric Oxygen

Sulfur Isotopic Evidence for O₂ After 2.3 Ga

• S cycle > 2.3 Ga controlled by **mass-independent fractionation** of S isotopes

> Oxidizing Atmosphere

Mass-dependent processes

Reducing Atmosphere • S has 4 stable isotopes: ³²S-95.02%, ³³S-0.75%, ³⁴S-4.21%, ³⁶S-0.02%

• Only known source of mass-independent fractionation of S isotopes is gas phase photolysis of SO₂ (from volcanoes) w/ UV light in near absence of O₂

• During biological, thermodynamic & kinetic processes S isotopes are fractionated in a predictable manner according to mass differences (i.e., Δ^{33} S=0)

-measured on sulfates & sulfides

 $\Delta^{33}S = \delta^{33}S_{meas} - \delta^{33}S_{exp} = \delta^{33}S_{meas} - 0.518 + \delta^{34}S_{meas}$

Farquhar & Wing (2003) *Earth Planet. Sci. Lett.* **213** 1-13 in Canfield (2005) *Ann. Rev. Earth Planet. Sci* Vol. 33: 1-36.

History of Atmospheric Oxygen on Earth



Modified from Joe Kirschvink, CalTech

Biotic Evidence for Atmospheric Oxygen

Evolution of Eukaryotes

• Eukaryotes require free O₂ in excess of 0.1% PAL for respiration



• Prokaryote

• Eukaryote

Kump et al. (1999)
2.7 Ga Cyanobacterial (Prokaryote) & Eukaryote Biomarkers

Diagenetic products of Hopanols & Sterols



Brocks, et al. (1999)

Multicellular Algal Fossils--2.1 Ga



Grypania: genus of coiled multicellular <u>eukaryotic algae</u>. From 2.1 Ga rocks in Michigan.

Stanley (1999)

Sources of **Oxygen to** the Atmosphere

General Photosynthetic Equation

Photosynthesis $6CO_2 + 6H_2O + Solar Energy - C_6H_{12}O_6 + 6O_2$ ie. algae Carbohydrates + Oxygen as products 1 mole of CO₂ consumed as 1 mole of O₂ produced Controls surface water ocean chemistry of inorganic carbon and nutrients and, when combined with respiration, controls atmospheric CO₂ concentration.



http://courses.cm.utexas.edu/emarcotte/ch339k/fall2005/Lecture-Ch19-3/Slide2.JPG

Other Archean O₂ Sinks #1



Monolith Chimney, Juan de Fuca Ridge Mt. Pinatubo, Philippines **Oxidative Weathering** lhttp://www.pmel.noaa.gov/vents/ http://en.wikipedia.org/wiki/Image:W eathering_9039.jpg

http://eos.higp.hawaii.edu/index.html <u>Today</u>: Whereas oxidative weathering of reduced minerals in rocks (i.e., Fe²⁺, S²⁻, CH₂O) removes 75% of O₂ generated by C_{org} burial today (the

other $\sim 25\%$ sink consists of volcanic outgassing at 14% & hydrothermal vents at $\sim 10\%$), oxidative weathering was not quantitatively important during Archean.

> <u>During Archean</u>: Volcanic Outgassing (H₂, CO, SO₂) & Hydrothermal Vent Fluids (Fe²⁺, S²⁻)

-Holland (1978) The Chemistry of the Atmosphere and Oceans. John Wiley, NY, 351 pp. -Holland (1984) The Chemical Evolution of the Atmosphere and Oceans. Princeton University Press, Princeton, NJ, 582 pp.



• O₂ sink decreases with increasing oxygen partial pressure in mantle source region.

Figure 2. Model of Late Archean mantle structure and dynamics, depicting heterogeneity of mantle redox states. Basalts erupted at Earth's surface become oxidized. The oxidized slabs of oceanic lithosphere are subducted, penetrating into the lower mantle and accumulate at the core-mantle boundary. Plumes carry oxidized mantle back to the surface. Source regions for mid-ocean ridge basalts remain reduced through the Archean. Interior structure (but not redox characteristics) after *Albarede and van der Hilst* [1999].

Kump et al. (2001) Geophys Geochem. Geosyst., Vol. 2: 2000GC000114

The Rise of Atmospheric Oxygen

- Photosynthesis by cyanobacteria began ~ 3.5 Ga $CO_2 + H_2O ---> CH_2O + O_2$
- Organic carbon & pyrite burial release O_2 to atmosphere / ocean
- No evidence for free O_2 before ~2.4 Ga
- \bullet Reduced gases in atmosphere & reduced crust consume O_2 produced during 1.2 Gyr
- Hydrogen escape irreversibly oxidizes atmosphere
- Mantle dynamics & redox evolution reduce O₂ sink over time
- Geologic & geochemical evidence for O₂ :

Oxidized Fe & Mn mineral deposits

Detrital uraninite & pyrite

Paleosols

Redbeds

Sulfur & Iron isotopes

Eukaryotes

• <u>Conclusion</u>: Rapid rise of free O₂ 2.4-2.2 Ga

Eons:

Precambrian: Earliest span of time Phanerozoic: Everything since



We are living in the Phanerozoic Eon, Cenozoic Era, Quaternary Period, Holocene Epoch......BUT

The Earth Through Time

The Proterozoic:

- No life possible as the Earth initially forms 4.6 billion years ago.
- Simple, single-celled forms of life appear 3.8 billion years ago, becoming more complex and successful over the next 3 billion years:
- Prokaryotes then Eukaryotes
- Cyanobacteria begins producing free oxygen (photosynthesis)
- Land masses gather to make up a continent called "Rodinia"

Cambrian:

- Explosion of life
- All existing phyla come into being at this time
- Life forms in warm seas as oxygen levels rise enough to support life
- Dominant animals: Marine invertebrates (trilobites and brachiopods)
- Supercontinent Gondwana forms near the South Pole (note position of present-day Florida)





Ordovician:

- The 1st animals with bones appear, though dominant animals are still trilobites, brachiopods and corals
- The beginning of the construction of South Carolina
- A very cold time in Earth's history: there was a great extinction due to ice caps in present-day Africa
- Four main continents: Gondwana, Baltica, Siberia and Laurentia





- First land plants appear and land animals follow
- Laurentia collides with Baltica and closes Iapetus Sea.
- Coral reefs expand and land plants begin to colonize barren land.
- First millipede fossils and sea scorpions (Euryptides) found in this period



Devonian (Age of the Fish)

Pre-Pangea forms. Dominant animal: fish

- Oceans still freshwater and fish migrate from southern hemisphere to North America.
- Present-day Arctic Canada was at the equator and hardwoods began to grow.
- Amphibians, evergreens and ferns appear
- The Acadian Orogeny, leading to S.C. metamorphism

Mississippian:

First seed plants appear

 Much of North America is covered by shallow seas and sea life flourishes (bryoza, brachipods, blastoids)

Pennsylvanian:

- Modern North America begins to form
- Ice covers the southern hemisphere and coal swamps formed along equator.
- Lizards and winged insects first appear.





Permian:

- Last period of the Paleozoic
- Pangea forms. Reptiles spread across continents.
- The Appalachians rise

 90% of Earth's species become extinct due to volcanism in Siberia. This marks the end of trilobites, ammonoids, blastoids, and most fish.



Triassic:

- First dinosaurs appear
- First mammals- small rodents appear
- Life and fauna re-diversify
- Rocky Mountains form.
- First turtle fossil from this period
- Pangea breaks apart







Jurassic:

- Pangea still breaking apart
- Dinosaurs flourish "Golden age of dinosaurs"
- First birds appear
- North America continues to rotate away from Africa



Cretaceous:

- T-Rex develops
- First snakes and primates appear
- Deciduous trees and grasses common
- First flowering plants

• Mass extinction marks the end of the Mesozoic Era, with the demise of dinoaurs and 25% of all marine life.



Tertiary:

First horses appear and tropical plants dominate (Paleocene)

 Grasses spread and whales, rhinos, elephants and other large mammals develop. Sea level rises and limestone deposits form in S.C. (Eocene)

- Dogs, cats, and apes appear (Oligocene)
- Horses, mastadons, camels, and tigers roam free in S.C. (Miocene)
- Hominids develop and the Grand Canyon forms (Pliocene)

Quaternary:

- Modern humans develop and ice sheets are predominant- Ice age (Pleistocene)
- Holocene Humans flourish (Holocene)









