The Age of the Earth — NOT!

~~[illegible]~~

Absolute versus relative ages

Geologists have long been able to determine relative ages from cross-cutting relationships of rock units in outcrop.

Cartoon example Fig. 8.4 — discuss briefly
In practice, it requires careful observation to recognize such relations in the field

Absolute ages are more difficult — but there have been many attempts to answer the fundamental question — how old is the ⊕?

also J & R perspective 7.2

Figure 8.1 summarizes some of these ~~[illegible]~~ since the Renaissance — and with an emphasis on European ideas

Biblical chronologies exemplified by Archbishop James Ussher, ~~[illegible]~~ of Ireland 1581 – 1656

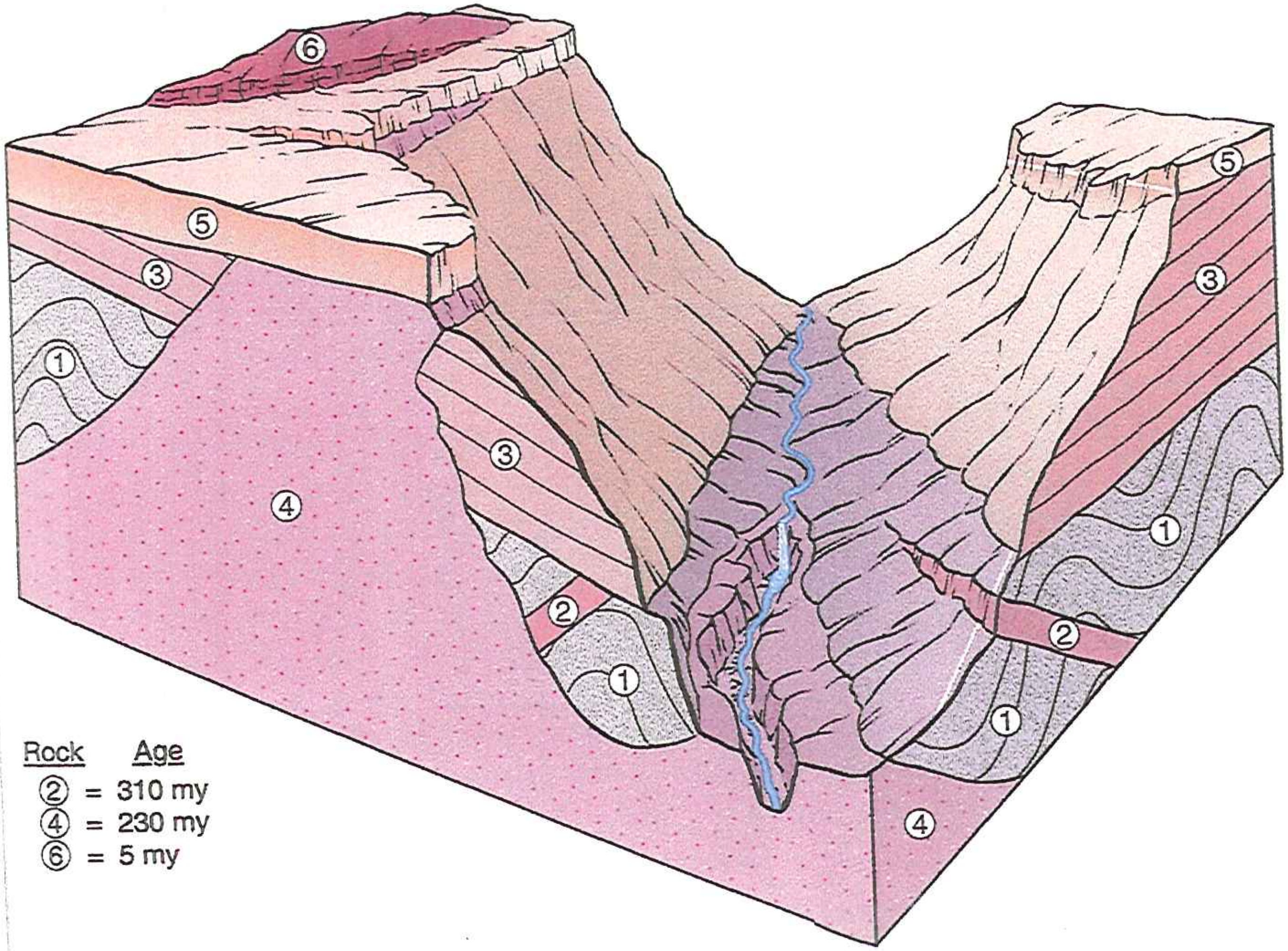


FIGURE 7.19
Radiometric dates obtained on igneous rocks can be fitted into the geologic time scale based on sedimentary rocks. This is done by bracketing the sedimentary rocks with the igneous rocks. In some instances radiometric dates can be assigned directly to the sedimentary rocks. See text for discussion.

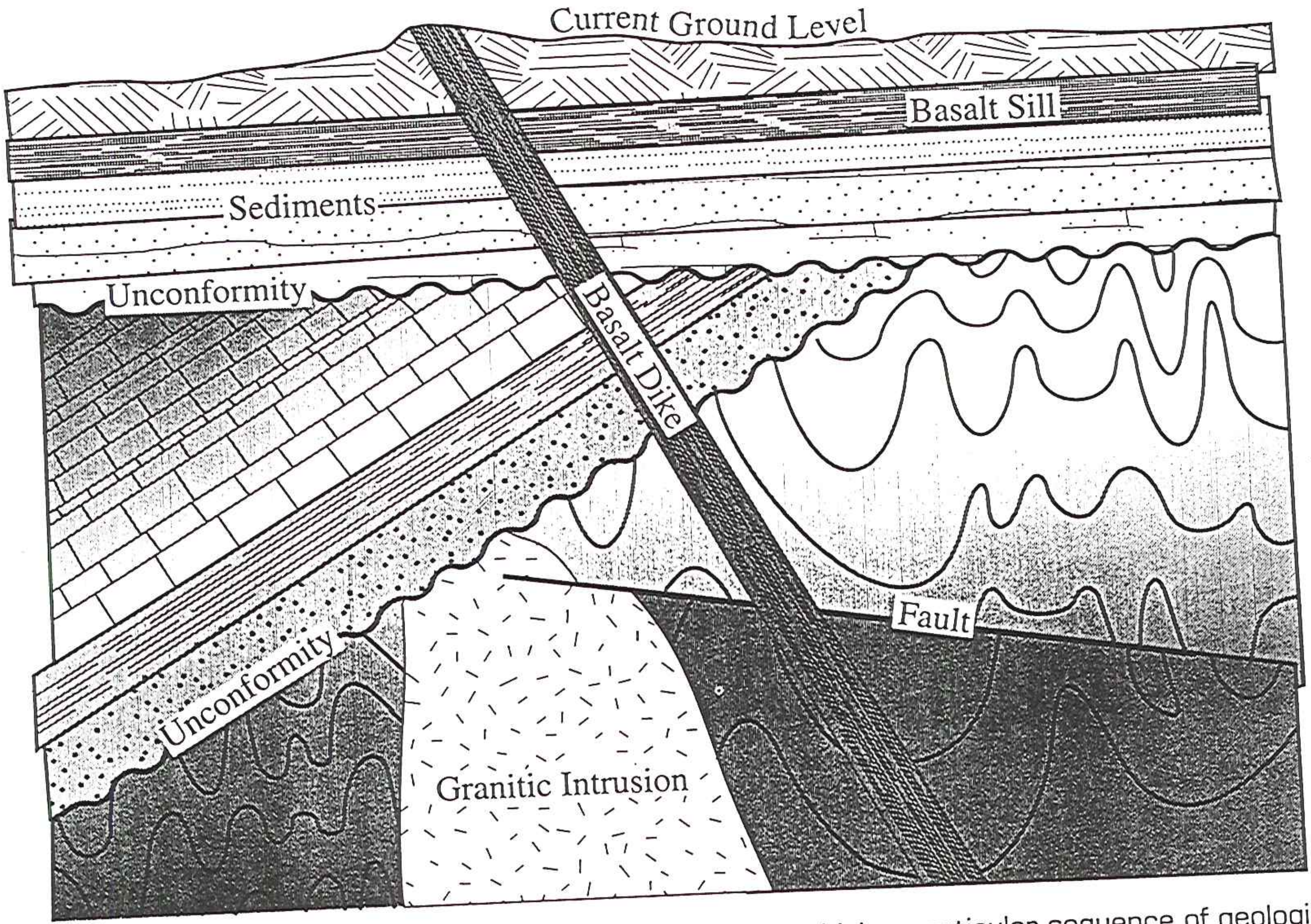


Figure 8.4. Idealized section of a geologic column from which a particular sequence of geologic processes may be inferred as described in the text. The section might be exposed, for example, as a roadcut, or as a cliff face on the side of a mountain. Adapted from Press and Siever (1978) by permission of W.H. Freeman and Company.

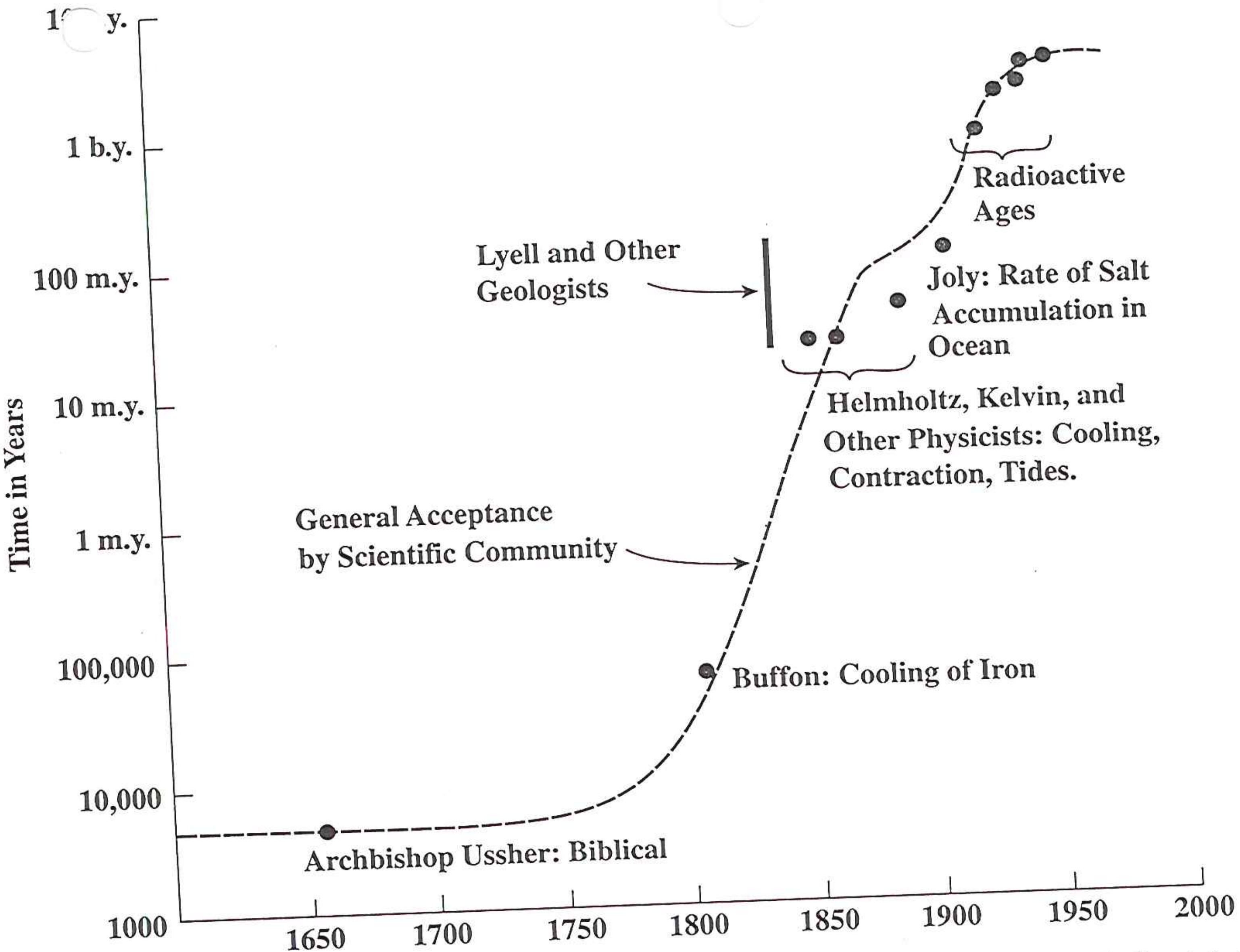


Figure 8.1. Age of Earth as estimated by various techniques since the Renaissance. Buffon tried to use rate of cooling of iron from a molten state to estimate the age of Earth, but the omission of as-yet undiscovered radioactive heating of Earth's interior (chapters 9 and 11) seriously shortened his cooling time. Joly worked out how long it would take to bring the oceans up to their current salinity based on the rate at which rivers carry salt to the sea; he ignored the precipitation of salt out of the ocean water into seafloor sediments. From Press and Siever (1978) by permission of W.H. Freeman and Company.

Genesis

1:1 In the beginning God created the heaven and the earth.

1:2 And the earth was without form, and void; and darkness was upon the face of the deep. And the Spirit of God moved upon the face of the waters.

1:3 And God said, Let there be light: and there was light.

1:4 And God saw the light, that it was good: and God divided the light from the darkness.

1:5 And God called the light Day, and the darkness he called Night. And the evening and the morning were the first day.

11:10 These are the generations of Shem: Shem was an hundred years old, and begat Arphaxad two years after the flood:

11:11 And Shem lived after he begat Arphaxad five hundred years, and begat sons and daughters.

11:12 And Arphaxad lived five and thirty years, and begat Salah:

11:13 And Arphaxad lived after he begat Salah four hundred and three years, and begat sons and daughters.

11:14 And Salah lived thirty years, and begat Eber:

11:15 And Salah lived after he begat Eber four hundred and three years, and begat sons and daughters.

11:16 And Eber lived four and thirty years, and begat Peleg:

11:17 And Eber lived after he begat Peleg four hundred and thirty years, and begat sons and daughters.

11:18 And Peleg lived thirty years, and begat Reu:

11:19 And Peleg lived after he begat Reu two hundred and nine years, and begat sons and daughters.

11:20 And Reu lived two and thirty years, and begat Serug:

11:21 And Reu lived after he begat Serug two hundred and seven years, and begat sons and daughters.

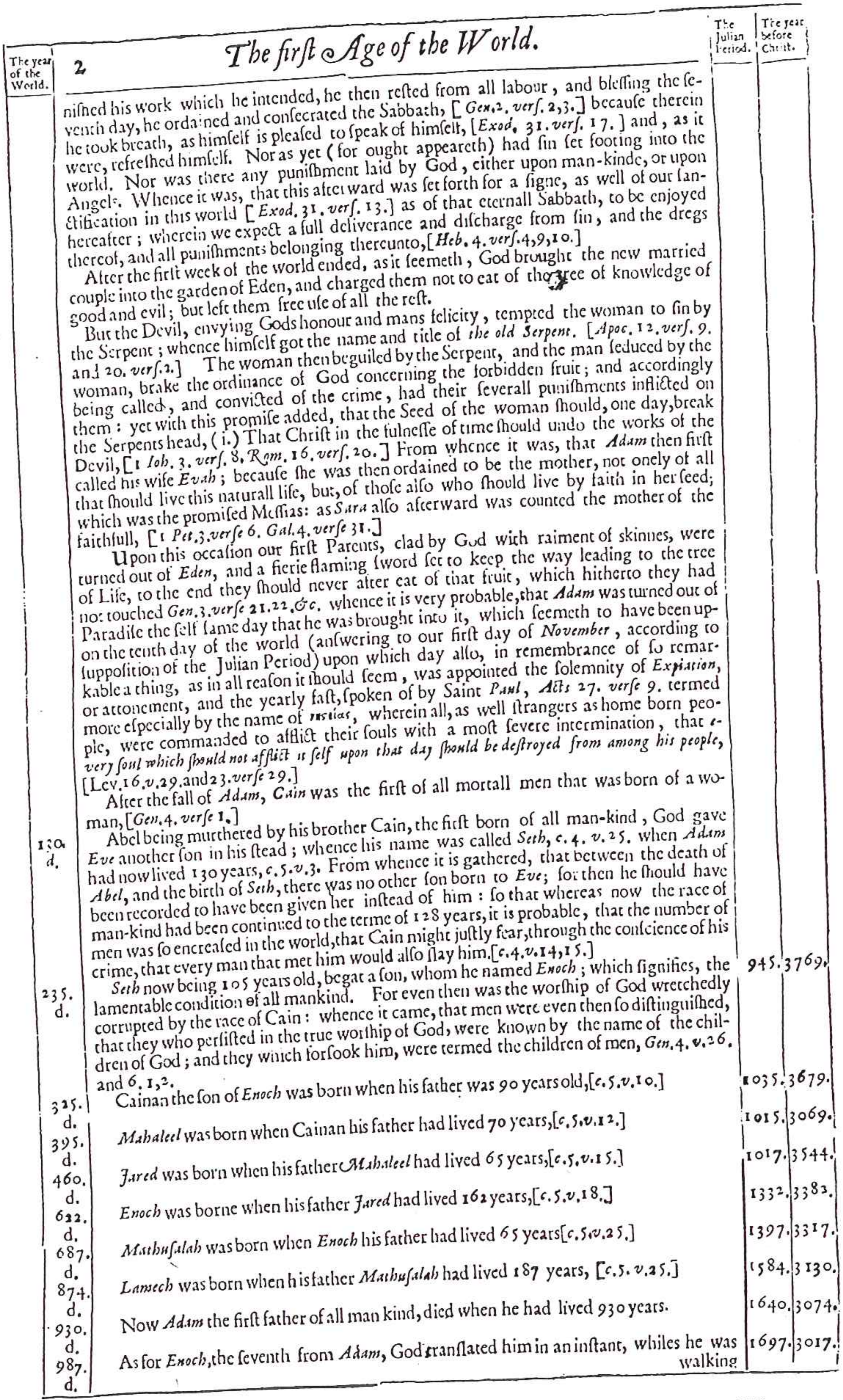
11:22 And Serug lived thirty years, and begat Nahor:

11:23 And Serug lived after he begat Nahor two hundred years, and begat sons and daughters.

11:24 And Nahor lived nine and twenty years, and begat Terah:

11:25 And Nahor lived after he begat Terah an hundred and nineteen years, and begat sons and daughters.

11:26 And Terah lived seventy years, and begat Abram, Nahor, and Haran.



The year of the World. | 2 | *The firſt Age of the World.* | The Julian Period. | The year before Chriſt.

niſhed his work which he intended, he then reſted from all labour, and bleſſing the ſeventh day, he ordained and conſecrated the Sabbath, [*Gen.* 2. *verſ.* 2,3.] becauſe therein he took breath, as himſelf is pleaſed to ſpeak of himſelf, [*Exod.* 31. *verſ.* 17.] and, as it were, refreſhed himſelf. Nor as yet (for ought appeareth) had ſin ſet footing into the world. Nor was there any puniſhment laid by God, either upon man-kinde, or upon Angels. Whence it was, that this afterward was ſet forth for a ſigne, as well of our ſanctification in this world [*Exod.* 31. *verſ.* 13.] as of that eternall Sabbath, to be enjoyed hereafter; wherein we expect a full deliverance and diſcharge from ſin, and the dregs thereof, and all puniſhments belonging thereunto, [*Heb.* 4. *verſ.* 4,9,10.]

After the firſt week of the world ended, as it ſeemeth, God brought the new married couple into the garden of Eden, and charged them not to eat of the tree of knowledge of good and evil; but left them free uſe of all the reſt.

But the Devil, envying Gods honour and mans felicity, tempted the woman to ſin by the Serpent; whence himſelf got the name and title of *the old Serpent.* [*Apoc.* 12. *verſ.* 9. and 20. *verſ.* 2.] The woman then beguiled by the Serpent, and the man ſeduced by the woman, brake the ordinance of God concerning the forbidden fruit; and accordingly being called, and convicted of the crime, had their ſeverall puniſhments inflicted on them: yet with this promiſe added, that the Seed of the woman ſhould, one day, break the Serpents head, (i.) That Chriſt in the fulneſſe of time ſhould undo the works of the Devil, [1 *Ioh.* 3. *verſ.* 8. *Rom.* 16. *verſ.* 20.] From whence it was, that *Adam* then firſt called his wife *Evah*; becauſe ſhe was then ordained to be the mother, not onely of all that ſhould live this naturall life, but, of thoſe alſo who ſhould live by faith in her ſeed; which was the promiſed Meſſias: as *Sara* alſo afterward was counted the mother of the faithfull, [1 *Pet.* 3. *verſe* 6. *Gal.* 4. *verſe* 31.]

Upon this occaſion our firſt Parents, clad by God with raiment of skinnes, were turned out of *Eden*, and a fierie flaming ſword ſet to keep the way leading to the tree of Life, to the end they ſhould never after eat of that fruit, which hitherto they had not touched *Gen.* 3. *verſe* 21.22, &c. whence it is very probable, that *Adam* was turned out of Paradiſe the ſelf ſame day that he was brought into it, which ſeemeth to have been upon the tenth day of the world (anſwering to our firſt day of *November*, according to ſuppoſition of the Julian Period) upon which day alſo, in remembrance of ſo remarkable a thing, as in all reaſon it ſhould ſeem, was appointed the ſolemnity of *Expiation*, or attonement, and the yearly faſt, ſpoken of by Saint *Paul*, *Acts* 27. *verſe* 9. termed more eſpecially by the name of νηστιας, wherein all, as well ſtrangers as home born people, were commanded to afflict their ſouls with a moſt ſevere intermination, that *every ſoul which ſhould not afflict it ſelf upon that day ſhould be deſtroyed from among his people,* [Lev. 16. *v.* 29. and 23. *verſe* 29.]

After the fall of *Adam*, *Cain* was the firſt of all mortall men that was born of a woman, [*Gen.* 4. *verſe* 1.]

130. d. Abel being murthered by his brother Cain, the firſt born of all man-kind, God gave *Eve* another ſon in his ſtead; whence his name was called *Seth*, *c.* 4. *v.* 25. when *Adam* had now lived 130 years, *c.* 5. *v.* 3. From whence it is gathered, that between the death of *Abel*, and the birth of *Seth*, there was no other ſon born to *Eve*; for then he ſhould have been recorded to have been given her inſtead of him: ſo that whereas now the race of man-kind had been continued to the terme of 128 years, it is probable, that the number of men was ſo encreaſed in the world, that Cain might juſtly fear, through the conſcience of his crime, that every man that met him would alſo ſlay him. [*c.* 4. *v.* 14,15.]

235. d. *Seth* now being 105 years old, begat a ſon, whom he named *Enoch*; which ſignifies, the lamentable condition of all mankind. For even then was the worſhip of God wretchedly corrupted by the race of Cain: whence it came, that men were even then ſo diſtinguiſhed, that they who perſiſted in the true worſhip of God, were known by the name of the children of God; and they which forſook him, were termed the children of men, *Gen.* 4. *v.* 26. and 6. 1,2. 945. 3769.

325. d. Cainan the ſon of *Enoch* was born when his father was 90 years old, [*c.* 5. *v.* 10.] 1035. 3679.

395. d. *Mahaleel* was born when Cainan his father had lived 70 years, [*c.* 5. *v.* 12.] 1015. 3069.

460. d. *Jared* was born when his father *Mahaleel* had lived 65 years, [*c.* 5. *v.* 15.] 1017. 3544.

622. d. *Enoch* was borne when his father *Jared* had lived 162 years, [*c.* 5. *v.* 18.] 1332. 3383.

687. d. *Mathuſalah* was born when *Enoch* his father had lived 65 years [*c.* 5. *v.* 25.] 1397. 3317.

874. d. *Lamech* was born when his father *Mathuſalah* had lived 187 years, [*c.* 5. *v.* 25.] 1584. 3130.

930. d. Now *Adam* the firſt father of all man kind, died when he had lived 930 years. 1640. 3074.

987. d. As for *Enoch*, the ſeventh from *Adam*, God tranſlated him in an inſtant, whiles he was walking 1697. 3017.

Fig. 2.3. Old Testament chronology published by Bishop James Ussher (1658).

In the Beginning, God created Heaven and Earth, Gen. I.V.I. Which beginning of time, according to our chronology, fell upon the entrance of the night preceding the twenty third day of October in the year of the Julian calendar, 710 (Ussher, 1658).

Thus, Ussher arrived at the beginning of night (evening), October 22, 4004 B.C., for the date of Creation, giving a universe 5,994 years old in 1990.

Basically, he counted begats since Adam & Eve.

4004 BC at the beginning of night (in Greenwich ?) Oct 22!

~~A celebrated estimate is that of Lord Kelvin~~

Buffon — cooling of iron ~~[illegible]~~ sphere

Comte de Buffon 1707 – 1788
one of most productive &
best-known scientists of 18th century

laid the foundations for theory of probability

best known as a paleontologist

35 volume treatise Historie Naturelle

Had a whole theory — ⊕ formed when a ~~comet~~ comet struck the sun — began as a white-hot globe — how long would it take to cool to present temperature?

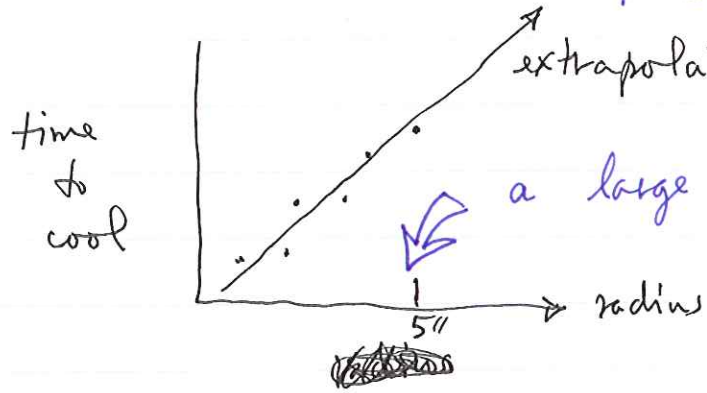
Surface cool enough to touch

10 iron spheres

$\frac{1}{2}''$ $1''$ $1\frac{1}{2}''$ . . . . $5''$

heated to white hot & observed time to cool to a touchable temperature

7-8 orders of magnitude



extrapolate to 6371 km!

a large cannonball

Table from Dalrymple — note the air of exactitude 74,832 years

Clear from his writings, though, that he was skeptical of this result.

Was aware of geological evidence, e.g. thick layers of sediments exposed in Alps.

<u>Lord Kelvin</u> born 1824 Belfast

Victorian equivalent of Einstein in the 20th century

Greatest scientist of Victorian age
Enunciated laws of thermodynamics
Kelvin = degrees above absolute zero

n globe. For more than half a century,
thinking about the antiquity of the
sha [illegible] n to subsequently, are among
mpts to determine a rational age for
lence. But the concept that a date for
d from calculations of cooling was in-
efore.

), English physicist and mathemati-
minating figure of the Enlightenment.
overies and inventions were the com-
ion and gravitation, the principles of
elescope. Newton was also interested
ieated bodies cooling in air, he con-
vas proportional to the difference in
and the surrounding medium. New-
to calculate an age for the Earth, but
Naturalis Principia Mathematica, pub-
a comet passing near the Sun would
ieat, which it would retain for an ex-
his point, he speculated on the length
iot iron the size of the Earth to cool:

> ter, exposed red hot to the open air, will
> time; but a greater globe would retain its
> neter, because the surface (in proportion
> of the ambient air) is in that proportion
> ie included hot matter; and therefore a
> th, that is, about 40,000,000 feet in diam-
> ıal r [illegible] er of days, or in above 50,000
> n of [illegible] may, on account of some latent
> ortion than that of the diameter; and I
> ortion was investigated by experiments

, or at least suspected, that the rela-
ze for bodies of planetary dimensions
peared at first glance. As we shall see
ven more complicated than Newton

n analog for the cooling Earth was a
aterial of everyday experience. Baron
646–1716), German philosopher and
h Newton) of the calculus and one of
rn world, was an early subscriber to
n Earth. He proposed that the Earth

solidified in stages similar to those he had observed in the cooling of large masses of metal. The cooling Earth, according to Leibniz, was sculpted by large bubbles, some of which hardened into mountains while others collapsed to form valleys (Haber, 1959: 84–88). Like Newton, Leibniz did not venture to determine an age for the Earth from cooling. That bold step was left to another prominent figure of the Enlightenment.

Georges-Louis Leclerc, Comte de Buffon, was born September 7, 1707, at Montbard in Burgundy. He was educated in the law at the College of Godrans in Dijon and went on to study medicine, botany, and mathematics at Angers. Buffon was a man of enormous talent and energy. In addition to his scientific interests, he managed his family land holdings at Buffon and Montbard, engaged in the business of harvesting timber, established a commercial tree nursery, and built and operated an iron foundry, which played an important role in his research into the age of the Earth. His business activities, however, did not detract from his interest in science.

Buffon

Buffon was one of the most productive and well-known scientists of the eighteenth century, and during his career he was elected to both the Royal Society and the Académie Française. He made fundamental contributions to the calculus of probability, plant physiology, and the scientific method, and laid the foundations for what would become the field of paleontology. He is best known, however, for an encyclopedic work in which he attempted, with considerable success, to synthesize all knowledge of nature and natural history into an intelligible whole. *Histoire Naturelle, Générale et Particulière* was originally intended to include an ambitious fifty volumes, of which Buffon actually completed 35 before his death in 1788. Among them were 12 volumes on mammals, nine on birds, and five on minerals as well as three introductory volumes and six lengthy supplements. The fifth supplement and the twentieth volume is *Epochs of Nature*, which was published in 1778 and is probably the best known. In it Buffon divided the history of the Earth into seven epochs. In the first epoch the Earth was a molten globe and the final epoch included the advent of man and the world as it is today; the intervening epochs included the formation of Earth's surface, the appearance of oceans and the beginnings of life, the formation of continents, the development of mammals, and the separation of the American and Eurasian continents.[7]

According to Buffon, the first epoch began when a comet collided with the Sun, causing the ejection of hot gases and liquid to

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[7] Both Albritton (1980: 84) and Haber (1959: 124–25) suggested that Buffon's use of seven epochs was a device to defuse church criticism of his concept of lengthy geological time, as the epochs are arbitrary and not an essential part of his synthesis of Earth history.

form the planets of the Solar System and their satellites. Buffon's proposition that the Earth began as a molten globe was consistent with accepted cosmogonies of the time. Leibniz had argued for a liquid primitive Earth, and in *Principia* Newton had furnished proof that the Earth was once fluid and had cooled in the shape of an oblate spheroid, thus explaining the equatorial bulge. Buffon also leaned heavily on the work of Jean-Jacques Dortous de Mairan, a French pioneer in atmospheric physics known for his work on the aurora. De Mairan had compiled more than a half century of measurements on temperatures of the atmosphere, of hot springs, in mines, and on the formation of ice in surface waters. These measurements, published in 1749, convinced Mairan and Buffon, with whom Mairan corresponded, that the Earth contained residual heat and was cooling. The next logical step was to calculate the time required for the Earth to cool from its initial to its present state.

Rather than speculate, Buffon had his foundry fabricate ten iron spheres whose diameters varied in half-inch increments up to 5 inches. These he heated to white heat and then observed the time required for them to cool, first to red heat, then to absence of glow, then to a point where they were cool enough to hold in his hand, and finally to room temperature. To ensure uniform conditions and minimize the daily temperature fluctuations caused by the Sun, Buffon performed his experiments in a cellar laboratory. He found an approximately linear relation between diameter and cooling time, which he then logically but naively extrapolated to a sphere the size of the Earth. On this basis he calculated that a mass of molten iron the size of the Earth would require 42,964 years to cool below incandescence and 96,670 years to cool to the present temperature of the Earth.

Buffon then performed similar experiments on a second set of graduated spheres composed of materials nearer the actual composition of the Earth. He corrected his calculations for the delaying effect of the Sun's heat and combined these data with some major events in Earth's history as reconstructed in *Epochs* to deduce the following scale of times, each in years from the beginning (Haber, 1959: 118):

Surface of Earth consolidated	1
Earth consolidated to center	2,936
Earth cool enough to be touched	34,270
Beginning of life	35,983
Temperature of present reached	74,832
End of life	168,123

Although the calculations were detailed and carried an air of exactitude, Buffon was suspicious of his results because he felt that the

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End of life	168,123	← too cold for life

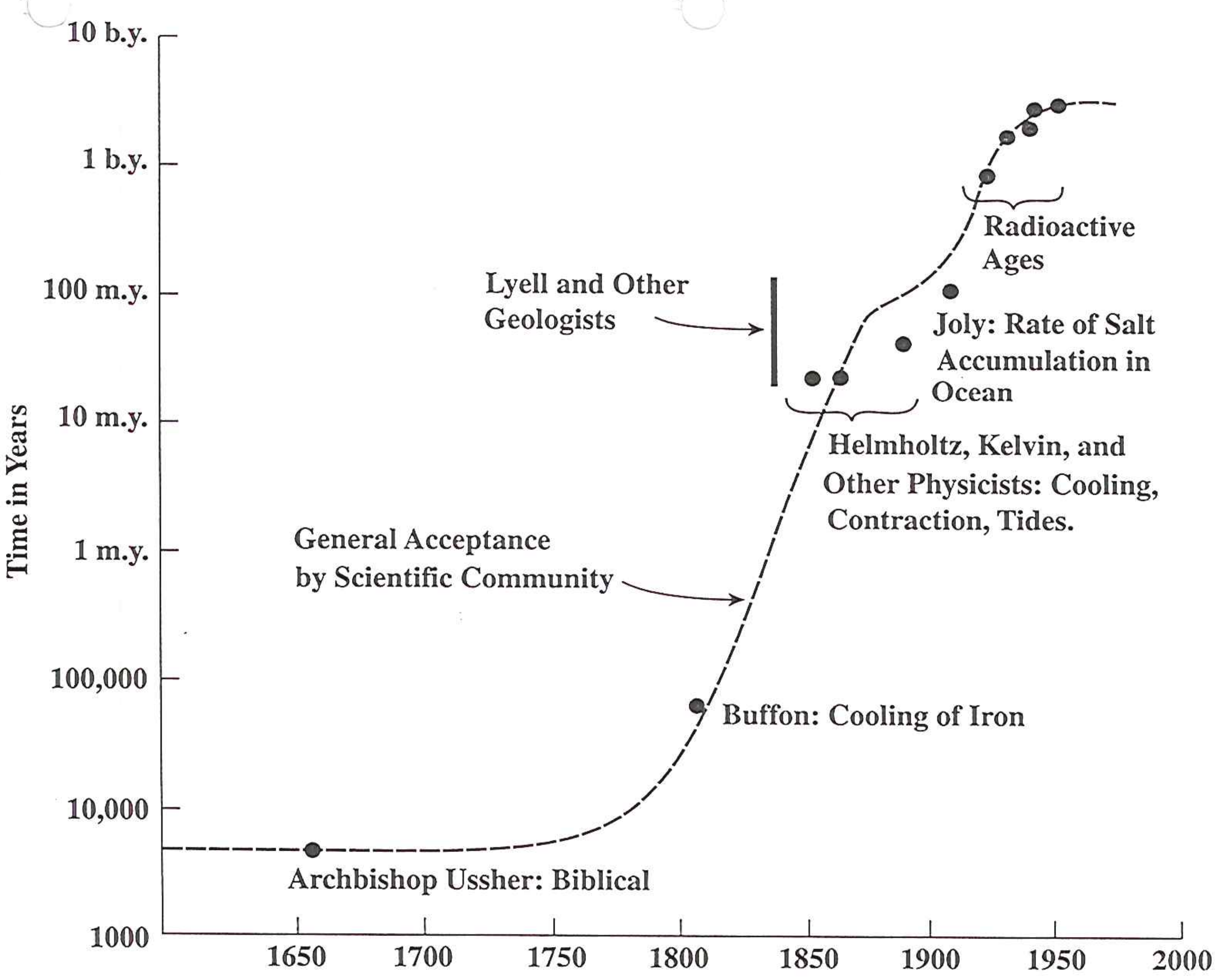


Figure 8.1. Age of Earth as estimated by various techniques since the Renaissance. Buffon tried to use rate of cooling of iron from a molten state to estimate the age of Earth, but the omission of as-yet undiscovered radioactive heating of Earth's interior (chapters 9 and 11) seriously shortened his cooling time. Joly worked out how long it would take to bring the oceans up to their current salinity based on the rate at which rivers carry salt to the sea; he ignored the precipitation of salt out of the ocean water into seafloor sediments. From Press and Siever (1978) by permission of W.H. Freeman and Company.

University of Glasgow at the age of ten, where he studied mathematics and became particularly interested in the work of Joseph Fourier, a French physicist who had devised mathematical methods of describing the physics of heat. In 1841 Thomson entered Cambridge University, from which he graduated in 1845 with high honors. Following graduation, he spent several months at the University of Paris, where he gained experience in laboratory methods by working with Henry Regnault, the French physicist. In 1846, largely through the efforts of his father, Thomson was appointed Professor of Natural Philosophy at Glasgow, a chair he held throughout his long and distinguished career.

Thomson was an unusually productive scientist, and at the time of his retirement in 1899 he had authored more than 600 scientific papers and books on electricity, magnetism, *thermodynamics*, hydrodynamics, atmospheric electricity, geomagnetism, *geodesy*, the thermal state and rotation of the Earth, tidal theory, and the age of the Earth. In 1848 he devised and described the absolute temperature scale, which still carries his name (the *Kelvin scale*). One of his most significant scientific achievements, a statement of the second law of thermodynamics, was published in 1851 under the title "On the Dynamical Theory of Heat." The cosmic implications of this fundamental principle later formed the basis for his calculations of the age of the Earth.

Kelvin

Thomson's work on electricity led him into the field of applied physics and to a role in the laying of the first trans-Atlantic telegraph cable. He became a director of the Atlantic Telegraph Company in 1856, served as the electrician aboard the *Agamemnon* in the first unsuccessful attempt to lay an Atlantic cable in 1858, and supervised the successful laying of the first cable by the *Great Eastern* in 1866, for which he was knighted that year by Queen Victoria. Thomson was also a prolific inventor, being responsible for the mirror galvanometer and siphon recorder used to receive telegraph signals, the stranded electrical conductor, the tide gauge, and an improved mariner's compass that allowed compensation for the magnetism of a steel ship. By the end of his career he held some 70 patents.

Thomson was probably the most honored British scientist in history, with countless awards, medals, and degrees. He was first elected president of the Royal Society in 1890 and was reelected to that office for five consecutive terms. In 1882 he was raised to the peerage and became Baron Kelvin of Largs, Ayrshire, and in 1896, on the fiftieth anniversary of his professorship at Glasgow, he was awarded the Grand Cross of the Royal Victorian Order. Because of his renown and the great respect in which he was held throughout the Western world, Kelvin's writings and opinions were accorded special significance. It

Also eminently practical — read from Dalrymple

- first submarine telegraph cable
- improved mariners' compass
- tide gauge

Estimated age of Sun — knew the rate at which it radiates energy in form of light waves

$\boxed{4 \cdot 10^{26}\ W}$ – ignores neutrinos

At the time only two known sources of energy available to power the sun

- chemical combustion, as in a coal furnace

Combustion of one kg of coal releases $3 \cdot 10^7$ J

$\boxed{\text{coal}: 3 \cdot 10^7\ J/kg}$

For how long could the sun burn if its energy were supplied by chemical processes, i.e. suppose the Sun is a coal furnace similar to homework problem

$$\underbrace{4\cdot 10^{26}\ \frac{J}{sec}}_{\text{heat release rate}} \times t\ (sec) = \underbrace{2\cdot 10^{30}}_{\text{mass of Sun}}\ kg \times 3\cdot 10^{7}\ \underbrace{J/kg}_{\text{released by burning}}$$

$$t = \frac{(2\cdot 10^{30})(3\cdot 10^{7})}{4\cdot 10^{26}} = 1.5\cdot 10^{11}\ sec$$

one year $\approx 3\cdot 10^{7}$ sec

$$\boxed{t = 4800\ \text{years}}$$

Pretty close to Archbishop Ussher!

~~Kelvin knew better than this, so he proposed that the source of the Suns heat was the only other then known process.~~

~~meteoric aggregation i.e. settling of masses to the Sun by the infall of meteorites & comets~~

- meteoric aggregation — i.e. constant infall of meteorites into Sun

Kelvin also eliminated this on the basis of detailed observations of the orbit of Mercury

He thus concluded that the Sun had to have formed hot, and that it is cooling off — all the radiated energy is simply this fossil initial heat

To estimate age of Sun from cooling need to know two things:

- average temperature of Sun
  $T = 15{,}000\ ^\circ C$
- specific heat of solar material

$$c - \frac{J}{kg\ ^\circ C}$$

amount of heat needed to raise T by 1°C — or amount that must be removed to cool it by 1°C

$$c(H_2O) \cong \overset{\text{actually 4184}}{\frac{4000\ J}{kg\ ^oC}}$$

If Sun has same specific heat of water, how much is cooling off ?

$$\frac{\overbrace{c\left(\frac{J}{kg}\right) M_\odot\,(kg)}^{c_{total\,\odot}}\ \overset{\text{in one year}}{dT}}{dt\ (3\cdot10^7\ sec = 1\ yr)} = 4\cdot10^{26}\ \frac{J}{sec}$$

or, better

$$\underbrace{\left(4\cdot10^{26}\ \frac{J}{sec}\right)\left(3\cdot10^{7}\ \frac{sec}{year}\right)}_{\text{heat lost in 1 yr}} = c\left(\frac{J}{kg}\right) M_\odot\,(kg)\ dT$$

$$dT = \frac{(4\cdot10^{26})(3\cdot10^{7})}{(4000)(2\cdot10^{30})}$$

$$\text{if } c_\odot = c_{H_2O} \rightarrow \boxed{dT = 1.5^oC\ /year}$$

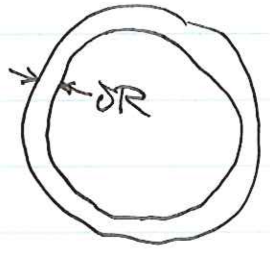
This would result in a <u>thermal</u> <u>contraction</u>

~~$\alpha_{H_2O} = 3.6 \cdot 10^{-4} (°C)^{-1}$~~

~~$\frac{\delta R}{R} = 3.6 \cdot 10^{-4}$ per °C cooling~~

~~$= 5.4 \cdot 10^{-4}$ per year~~

$\alpha_{H_2O} \approx 10^{-4}$ per °C



$\frac{\delta R}{R} = 10^{-4}$ per °C

$= 1.5 \cdot 10^{-4}$ per year

= 1% shrinking in 70 years

This could clearly be ruled out by observations.

Remember: Kelvin knew the mean density of the Sun from Kepler's 3rd law

$\bar{\rho}_\odot = 1400$ kg/m³

Concluded that $\boxed{c_{\text{solar material}} = 10^2 - 10^4 \times c_{H_2O}}$

Say $c_{\text{sun}} = 1000\ c_{H_2O} = 4 \cdot 10^6 \frac{J}{kg}$

Then cooling rate 1.5 °C / 1000 years

Age t: $\frac{c M_\odot\ 15{,}000\ °C}{t\ (\text{sec})} = 4 \cdot 10^{26} \frac{J}{\text{sec}}$

easier to note that
st no °C / 10^3 yrs °C
15,000 10^7 yr

$$t = \frac{\left(4\cdot 10^{6}\ \frac{\text{J}}{\text{kg}\ {}^\circ\text{C}}\right)\left(2\cdot 10^{30}\ \text{kg}\right)\left(15{,}000\ {}^\circ\text{C}\right)}{4\cdot 10^{26}\ \text{J/sec}}$$

$$= 3\cdot 10^{14}\ \text{sec} = \boxed{110\ \text{m.y.}}$$

Read ¶ from Dalrymple ← go to page 9½

We now know, of course, that the Sun's energy is provided by nuclear burning — see homework problem

John Joly 1857 – 1933 Geology professor at U. Dublin — best known for his work on the chemical extraction of radium & its use in treatment of cancer

$$\boxed{\text{age of } \oplus = \frac{\text{total Na}^{+}\text{ in ocean}}{\text{annual Na}^{+}\text{ influx from rivers}}}$$

It seems, therefore, on the whole most probable that the sun has not illuminated the earth for 100,000,000 years, and almost certain that he has not done so for 500,000,000 years. As for the future, we may say, with equal certainty, that inhabitants of the earth cannot continue to enjoy the light and heat essential to their life, for many million years longer, unless sources now unknown to us are prepared in the great storehouse of creation (W. Thomson, 1862a: 494).

This last statement was prophetic. There were indeed powerful and unknown sources of energy fueling the Sun's fires, but their discovery was still four decades in the future.

A few years later Kelvin returned to the problem.

Used observations of the rate of temp increase in mines — cooling of ⊕ rather than Sun

Do not discuss here since need to introduce concepts of heat flow and thermal conductivity

On this basis he obtained 98 m.y. In good agreement with his solar estimate but he felt it was considerably more certain — this is in fact his most famous estimate.

His 98 Myr age assumed a very high (molten) $T_0 = 3870$ °C

Clarence King (Director of USGS) improved upon this — evidence for a much lower $T_0 \approx 1200$°C

This lowered the age to 20–40 Myr

seems unlikely that the Moon was ever closer to the Earth than about 38 Earth radii (compared to the present 60).

Within the framework of late-nineteenth-century understanding of the Earth, Darwin's hypothesis was reasonable and appropriate, but we now know that tidal considerations are incapable of providing a basis for determining the Earth's age. One has the feeling that Sir George wouldn't have minded.

The Salt Clock

Physics was not the only discipline to provide early estimates of Earth's age; chemistry was also set to the task, and in a rather clever way.

Imagine a tub of water to which a chemical is continuously added. If you knew the amounts of the chemical in the water both now and when the tub was first filled, and the rate at which the chemical was added to the water, then you could calculate the time of origin, i.e. the age, of the tub of water. It was the possibility of just such a calculation that Edmund Halley (1656–1742), the Astronomer Royal who predicted the return of the comet that bears his name, had in mind when, in 1715, he proposed that the age of the Earth might be calculated from the salt content of the ocean and of certain kinds of lakes (Halley, 1715).[19]

Halley observed that all lakes that receive runoff from rivers but lack outflow contain salt in varying amounts. The concentration of salt in the waters of these lakes must increase, he said, because salt, picked up by the rivers in their passage over the Earth, is continuously added but not removed.[20] Water is removed by evaporation, but water vapor is fresh so the salt is left behind: "But the vapours thus exhaled are perfectly fresh; so that the saline particles brought in by the rivers remain behind, while the fresh evaporates; and hence it is evident that the salt in the lakes will be continually augmented, and the water grow salter and salter. . . ." (Halley, 1715, in G. F. Becker, 1910a: 460). If this was truly the cause of the saltiness of lakes, Halley reasoned, then it is probable that the same mechanism was responsible for the saltiness of the ocean.

Analytical methods were then incapable of measuring the minute quantities of salt in the rivers that supplied the ocean, but Halley

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[19] Lengthy excerpts from Halley's paper appear in G. F. Becker (1910a).

[20] The idea that the ocean was originally fresh and that its salt was dissolved out of the Earth's crust did not originate with Halley. Leibniz, among others, had incorporated the idea into his model of the Earth.

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had another method in mind. If the concentration of salt in the ocean was measured at different times, then the rate of addition and the age of the ocean, which he equated with the age of the Earth, could be determined. A repeat of the experiment at some later date, he noted, would not only check the constancy of the rate at which salt is added but would verify the hypothesis.

Halley observed, however, that the age of the Earth could not yet be calculated. The experiment would require a very long time, and he lamented that the ancient Greek and Latin authors had not provided information on the saltiness of the ocean 2,000 years ago. The only thing that could be done, advised Halley, was for the Royal Society to ensure that future generations would be provided with the necessary data: "I recommend it therefore to the society, as opportunity shall offer, to procure the experiments to be made of the present degree of saltness of the Ocean, and as many of these lakes as can be come at, that they may stand upon record for the benefit of future ages" (Halley, 1715, in G. F. Becker, 1910a: 461). Halley also observed that the method would provide only a maximum age for the Earth, because the ocean and some lakes might well have contained some salt when they first formed. The experiment, he said, was still worthwhile because "[it] is chiefly intended to refute the ancient notion, some have of late entertained, of the eternity of all things; though perhaps by it the world may be found much older than many have hitherto imagined" (Halley, 1715, in G. F. Becker, 1910a: 461).

Halley's idea was never pursued and seems to have been largely forgotten until 1876, when T. Mellard Reade rediscovered the method he called "chemical denudation." Reade proposed that the age of the ocean could be found from the concentrations of *chlorides* and *sulfates*. Instead of determining the rates of addition of these compounds by measuring their concentrations at different times, Reade proposed to find the values by estimating the annual amounts carried into the ocean by the rivers of the world. At the present annual rates of addition, he calculated that it would require 25 Ma for the sulfates of calcium and magnesium to reach their present concentrations in ocean water; for chlorides (principally of sodium) the comparable time was 200 Ma (Reade, 1876, 1879).

Reade's basic idea of dating the Earth from the progressive change in the chemistry of the ocean was carried to a high degree of refinement by John Joly (1857–1933), a professor of geology and mineralogy at the University of Dublin. The son of a clergyman, Joly was born in Holywood, Kings County, Ireland, and educated at Trinity College, Dublin, where he taught throughout his career. Joly was trained as a physicist but developed a keen interest in geology, an evolution that is reflected in his sequence of positions at Trinity College, where he held appointments as demonstrator in civil engineering (1883), in physics (1893), and finally as professor of geology and mineralogy (1897).

Joly's accomplishments were numerous. He developed a method of extracting radium and pioneered its use in the treatment of cancer. He invented a type of thermometer, a steam calorimeter to measure heat energy, and a photometer to measure light frequencies. He was the first to propose that convection, driven by the heat from radioactive decay in the Earth's interior, might play a major role in the energetics and evolution of the Earth's crust. During his distinguished career he was accorded many honors, including election as a Fellow of the Royal Society in 1892.

Joly's (1899) classic paper "An Estimate of the Geological Age of the Earth" was read to the Royal Dublin Society, of which Joly was then Secretary, on May 17, 1899. In it (p. 249) Joly proposed to measure the age of the Earth from the accumulation, not of a salt, but of an element in the waters of the ocean:

> Now, if any of the elements entering the ocean is not again withdrawn, but is, in a word, "trapped" therein, reappears as no extensive marine deposit, and is not laid down sensibly upon its floor, and if the amount of uniformity already defined is accepted, evidently in the rate of annual accretion by the ocean, from the rivers, of this substance and the amount of it now in the ocean, the whole period since the beginning of its supply can be estimated.

Such an element, he said, was sodium, and by using the pure element he avoided the questions and uncertainties of ionization and chemical form.

The result of Joly's calculations was an age for the Earth that differed little from Kelvin's:

> The quantity of sodium now in the sea, and the annual rate of its supply by the rivers, lead, it will be seen, to the deduction that the age of the earth is 99×10^6 years. Certain deductions from this are, it will be shown, warranted, so that the final result of this paper will be to show that the probable age is about 89×10^6 years. Also, that this is probably a major limit, and that considerable departure from uniformity of activities could hardly amend it to less than 80×10^6 years (Joly, 1899: 249).

How did Joly arrive at these values? The basic equation, lacking certain necessary corrections, is the soul of simplicity:

$$\text{age of Earth} = \frac{\text{total sodium in ocean}}{\text{annual sodium influx from rivers}}$$

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the soul of simplicity:

otal sodium in ocean
sodium influx from rivers

Joly began by arguing that the extrapolation of the rates of present processes into the past was warranted unless it could be shown that the rates had been interrupted by catastrophe or change. He pointed out that the approximate constancy of erosion of the land surface throughout geological time was a tenet whose validity had not seriously been questioned. Even so, his calculation required acceptance of this tenet only in part:

> . . . that part of it which refers to the removal of the land surface by solution. It has to be accepted as a preliminary step that this, on the whole, has been constant. Herein are involved a constancy, within certain fairly wide limits, of rainfall over the land areas; a constancy, within fairly wide limits (which can be roughly defined), of the exposed land area, and a constancy in the nature and rate of solvent actions going on over the land surfaces (Joly, 1899: 248).

The other tenet that must be accepted was that the primeval ocean did not contain sodium in the quantities now observed.

The determination of a value for the sodium in the modern ocean was not difficult. Sir John Murray, a British oceanographer and founder of the study of submarine geology, had made estimates of the mass and mean depth of the ocean, the total volume of river discharge, and the quantity of dissolved matter in a number of the world's rivers.[21] Joly used Murray's mean ocean depth of 3,797 m combined with Hermann Wagner's ocean area of 1.0372×10^8 km^2 and the density of sea water to calculate that the mass of water in the world's ocean was 1.3245×10^8 *metric tons*.[22] The salinity of the ocean was known to be 3.5%, of which sodium chloride, NaCl, constitutes 77.758% of the total salts. Since 39.32% by weight of NaCl is Na, Joly arrived at a value of 1.4177×10^{16} metric tons for the total mass of Na in the ocean.

Murray's estimate for the total annual discharge of rivers into the ocean was 2.7176×10^4 km^3. His estimate for the dissolved matter in river water was based on analyses of waters from 19 rivers of the world. These analyses showed that of the total salts in river water, three contain sodium, giving a combined mass of 5,250 metric tons of Na per cubic kilometer of river water. The annual discharge multiplied by the sodium content provided Joly with a value of 1.4268×10^8 metric tons of Na supplied per year by rivers to the ocean. Joly's uncorrected age for the Earth thus was

$$\text{age of Earth} = \frac{1.4177 \times 10^{16}\ \text{metric tons Na}}{1.4268 \times 10^{8}\ \text{metric tons Na/yr}} = 99.4 \times 10^{6}\ \text{yr}$$

---

[21] John Murray (1841–1914) was one of the organizers of the famed *Challenger* expedition of 1872–76 and served on board as a naturalist. He completed the report of the expedition after the death of the leader, Sir Wyville Thomson.

[22] Joly's 1899 data were expressed in English units of measurement. I have converted them to metric units.

But this was not the true age of the Earth; some corrections were necessary.

Joly applied a correction to the numerator for the amount of sodium in the original ocean. This correction was based on his estimate of the amount of sodium that would have been dissolved out of the primeval rocks as the crust and ocean were forming. Like Kelvin, Joly presumed that the Earth began as a molten globe. At a temperature of 1,500° C, the crust would have been molten and the material of the future ocean would have consisted primarily of free hydrogen, free oxygen, and HCl gas; NaCl would not exist at that temperature. As the crust and primitive atmosphere cooled, first water vapor then liquid water would form and the hot acidic rains (from the HCl dissolved in the rain) would react with the hot crustal rocks to form salts of Na, K, Mg, Ca, and Fe. From the abundances of these elements in what Joly took to be the average crustal rock, and presuming that all of the HCl would be neutralized by reactions with these elements in the crust, he concluded that only 14% of the Cl in the acidic rains, i.e. in the original ocean, would combine with Na to form NaCl.

The next quantity Joly had to find was the total amount of Cl available in the primeval ocean. To do this Joly assumed that the amount of Cl now in the ocean is the sum of the amount in the primeval ocean and the amount brought in by rivers since the ocean first formed. The amount of Cl in the present ocean was relatively easy to estimate; it was the sum of the amounts in the ocean's NaCl (21.913×10^{15} tons) and $MgCl_2$ (3.775×10^{15} tons).

The amount brought in by rivers over geologic time was a less certain calculation. Joly summed the amounts brought in each year as NaCl, LiCl, and NH_4Cl, but reduced the contribution from NaCl by 10% to account for recycling from the sea by evaporation. This sum, less the 10% correction, was about 69×10^6 tons of Cl per year. But for how many years? Joly chose 86 Ma as a reasonable value, which yielded 5.929×10^{15} tons of Cl added to the ocean by rivers since the world began. To summarize, Joly's estimate of the Cl in the primeval ocean was

now as NaCl	21.913×10^{15} tons
now as $MgCl_2$	3.775×10^{15} tons
from rivers in 86×10^6 years	-5.929×10^{15} tons
Cl in primeval ocean	19.759×10^{15} tons

Fourteen percent of this Cl, or 2.766×10^{15} tons, would combine with 1.789×10^{15} tons of Na, which was Joly's value for the original Na in the primeval ocean and was the amount to be subtracted from the numerator in his age equation.

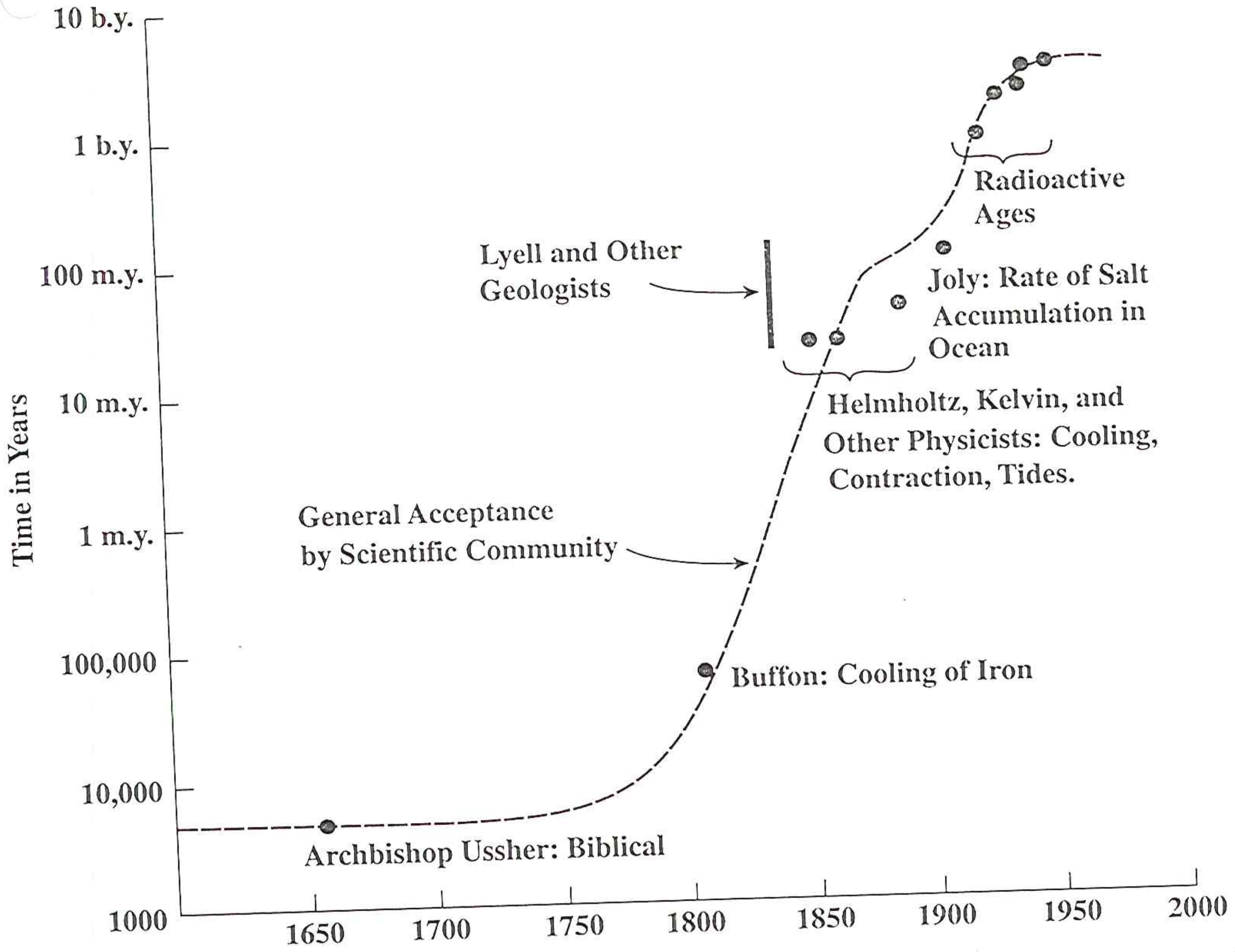


Figure 8.1. Age of Earth as estimated by various techniques since the Renaissance. Buffon tried to use rate of cooling of iron from a molten state to estimate the age of Earth, but the omission of as-yet undiscovered radioactive heating of Earth's interior (chapters 9 and 11) seriously shortened his cooling time. Joly worked out how long it would take to bring the oceans up to their current salinity based on the rate at which rivers carry salt to the sea; he ignored the precipitation of salt out of the ocean water into seafloor sediments. From Press and Siever (1978) by permission of

Table 8.1 dissolved species in sea water — except in estuaries very constant

Main cations

$$\underbrace{Ca^{++},\ Mg^{++},\ Na^{+},\ K^{+}}_{\text{derived from weathering of feldspars and other minerals}}$$

Total dissolved solids 35 g/kg

Solidity = 35 ‰ (per mille)

How much Na^+ in oceans?

$$\text{Volume} = 4\pi\,(6371)^2\,(0.7)\,\overset{\leftarrow \text{ mean depth}}{4}$$

$$= 1.4 \cdot 10^{9}\ km^3$$

$$= 1.4 \cdot 10^{27}\ \text{liters}$$

$$\#\ \text{moles } Na^+ = \left(1.4 \cdot 10^{27}\ l\right)\left(0.479\ \frac{\text{moles}}{l}\right)$$

$$= 6.7 \cdot 10^{20}\ \text{moles } Na^+ \text{ in ocean}$$

To find riverine influx need to measure average Na^+ conc. in river water × total discharge

Fig. 5.3 & Table 5.9 show average composition of dissolved species in river water

cations: Ca^{++}, Mg^{++}, Na^{+}
anions: Cl^{-}, SO_4^{-}, HCO_3^{-}

Note the effect of road salt in winter

Na natural 6.5 mg/l
polluted 8.4 mg/l } in NA rivers

Also Cl^{-} same season

SO_4^{-} pollution due to fertilization of fields — sulfuric acid used in fertilizer production
Also coal combustion

Na^{+} in average world rivers

5.2 mg/l

$$\frac{(5.2 \cdot 10^{-3}\ g/l)}{23\ g/mole} = 2.3 \cdot 10^{-4}\ mole/l$$

2000 times less than seawater

Table 5.1 lists major rivers in order of discharge km³/year H_2O

Total all rivers 37,400 km³/yr

Amazon alone 1/5 of this

$$37{,}400 \text{ km}^3/\text{yr} = 3.7 \cdot 10^{16} \text{ l/yr}$$

Na^+ addition:

$$\left(3.7 \cdot 10^{16} \text{ l/yr}\right)\left(2.3 \cdot 10^{-4} \text{ moles/l}\right)$$

$$= 8.5 \cdot 10^{12} \text{ moles } Na^+ \text{ added/yr}$$

$$\boxed{\text{Age of } \oplus = \frac{6.7 \cdot 10^{20} \text{ moles}}{8.5 \cdot 10^{12} \text{ moles/yr}} = 79 \text{ million years}}$$

Joly used somewhat different data and found 99×10^6 years

"Certain deductions..." — he applied a small correction for <u>initial</u> Na^+ in oceans

$$\boxed{t_{\text{Joly}} = 89 \times 10^6 \text{ years}}$$

TABLE 8.1 Major Dissolved Components of Seawater for a Salinity of 35‰

Ion	Concentration		Percent Free Ion
	g/kg	mM[a]	
Cl^-	19.354	558	100
Na^+	10.77	479	98
Mg^{++}	1.290	54.3	89
SO_4^{--}	2.712	28.9	39
Ca^{++}	0.412	10.5	99
K^+	0.399	10.4	98
HCO_3^{-}[b]	0.12	2.0	80

[a] mM = millimoles per liter at 25°C.

[b] For pH = 8.1, $P = 1$ atm, $T = 25$°C.

Sources: Wilson 1975; Skirrow 1975; Millero and Schreiber 1982.

TABLE 5.6 Chemical Composition of Average River Water

By Continent	River Water Concentration[a] (mg/l)									Water Discharge (10^3 km³/yr)	Runoff Ratio[b]
	Ca^{++}	Mg^{++}	Na^+	K^+	Cl^-	SO_4^{--}	HCO_3^-	SiO_2	TDS		
Africa:											
Actual	5.7	2.2	4.4	1.4	4.1	4.2	26.9	12.0	60.5	3.41	0.28
Natural	5.3	2.2	3.8	1.4	3.4	3.2	26.7	12.0	57.8		
Asia:											
Actual	17.8	4.6	8.7	1.7	10.0	13.3	67.1	11.0	134.6	12.47	0.54
Natural	16.6	4.3	6.6	1.6	7.6	9.7	66.2	11.0	123.5		
S. America:											
Actual	6.3	1.4	3.3	1.0	4.1	3.8	24.4	10.3	54.6	11.04	0.41
Natural	6.3	1.4	3.3	1.0	4.1	3.5	24.4	10.3	54.3		
N. America:											
Actual	21.2	4.9	8.4	1.5	9.2	18.0	72.3	7.2	142.6	5.53	0.38
Natural	20.1	4.9	6.5	1.5	7.0	14.9	71.4	7.2	133.5		
Europe:											
Actual	31.7	6.7	16.5	1.8	20.0	35.5	86.0	6.8	212.8	2.56	0.42
Natural	24.2	5.2	3.2	1.1	4.7	15.1	80.1	6.8	140.3		
Oceania:											
Actual	15.2	3.8	7.6	1.1	6.8	7.7	65.6	16.3	125.3	2.40	—
Natural	15.0	3.8	7.0	1.1	5.9	6.5	65.1	16.3	120.3		
World average:											
Actual	14.7	3.7	7.2	1.4	8.3	11.5	53.0	10.4	110.1	37.4	0.46
Natural (unpolluted)	13.4	3.4	5.2	1.3	5.8	8.3 (5.3)[c]	52.0	10.4	99.6	37.4	0.46
Pollution	1.3	0.3	2.0	0.1	2.5	3.2 (6.2)[c]	1.0	0	10.5	—	—
World % pollutive	9%	8%	28%	7%	30%	28% (54%)[c]	2%	0%	—	—	—

road salt

fertilizer + coal

---

[a] *Actual* concentrations include pollution. *Natural* concentrations are corrected for pollution.

[b] Runoff ratio = average runoff per unit area/average rainfall (calculated from Meybeck).

[c] We have raised pollutive contribution; see Table 5.11. (Our values are in parentheses.)

Source: All river water concentrations and discharge values from Meybeck (1979) except "actual" concentrations by continent, which were calculated from Meybeck's data. (M. Meybeck, "Concentrations des eaux fluviales en éléments majeurs et apports en solution aux oceans," *Rev. Géol. Dyn. Georgr. Phys.*, 21(3), 220, 227. Copyright © 1979. Reprinted by permission of the publisher.)

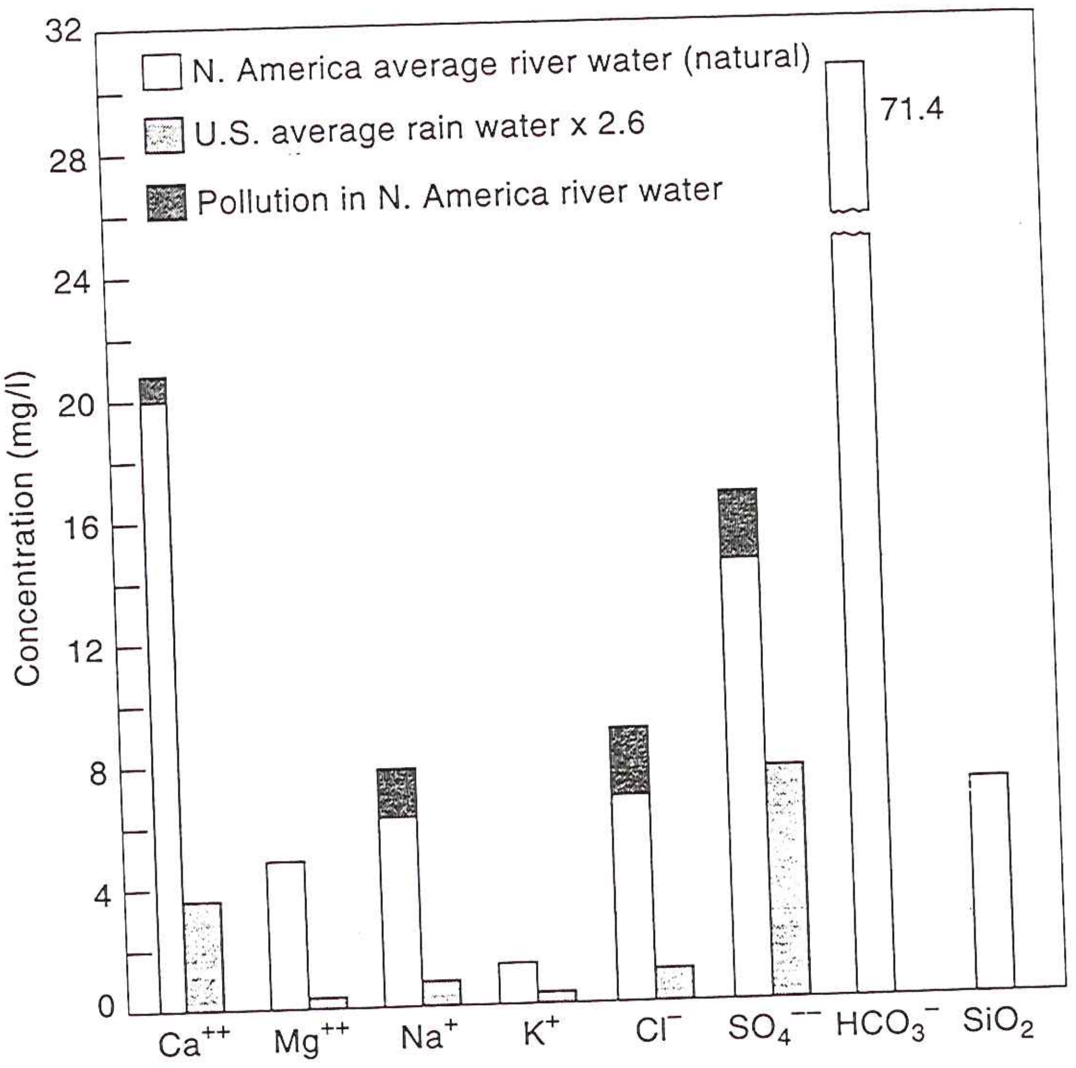


Figure 5.3. Comparison of dissolved composition of North American natural and polluted river water (data from Meybeck 1979) with U.S. rainwater (concentrations in mg/l). Rainwater concentrations are multiplied by 2.6 to correct for evaporation from the continents (see text).

TABLE 5.1 Major Rivers that Flow to the Sea, Listed in Order of Discharge

River	Location	Water (km^3/yr)
1. Amazon	S. America	6300
2. Zaire (Congo)	Africa	1250
3. Orinoco	S. America	1100
4. Yangtze (Chiang)	Asia (China)	900
5. Brahmaputra	Asia	603
6. Mississippi	N. America	580
7. Yenisei	Asia (Russia)	560
8. Lena	Asia (Russia)	525
9. Mekong	Asia (Vietnam)	470
10. Ganges	Asia	450
11. St. Lawrence	N. America	447
12. Parana	S. America	429
13. Irrawaddy	Asia (Burma)	428
15. Mackenzie	N. America	306
17. Columbia	N. America	251
20. Indus	Asia (India)	238
Red (Hungho)	Asia (Vietnam)	123
Huanghe (Yellow)	Asia (China)	59

Note: Tributaries are excluded.

Total discharge all the world's rivers:

37,000 km^3/yr = $3.7 \cdot 10^{16}$ liters/yr

The result of Joly's calculations was an age for the Earth that differed little from Kelvin's:

> The quantity of sodium now in the sea, and the annual rate of its supply by the rivers, lead, it will be seen, to the deduction that the age of the earth is 99 × 10^6 years. Certain deductions from this are, it will be shown, warranted, so that the final result of this paper will be to show that the probable age is about 89 × 10^6 years. Also, that this is probably a major limit, and that considerable departure from uniformity of activities could hardly amend it to less than 80 × 10^6 years (Joly, 1899: 249).

Joly considered other possible sources of error, including the Na pos- permanently removed from the system as salt deposits and the pos- sible violations of his assumption of a constant rate of Na influx, but concluded that, taken as a whole, they probably were insignificant. He concluded

> We think that it is at least justifiable to claim that our present knowledge of solvent denudation of the earth's surface points to a period of between eighty and ninety millions of years having elapsed since water condensed upon the earth, and rain and rivers and the actions continually progressing in the soils began to supply ocean with materials dissolved from the rocks (Joly 1899: 287).

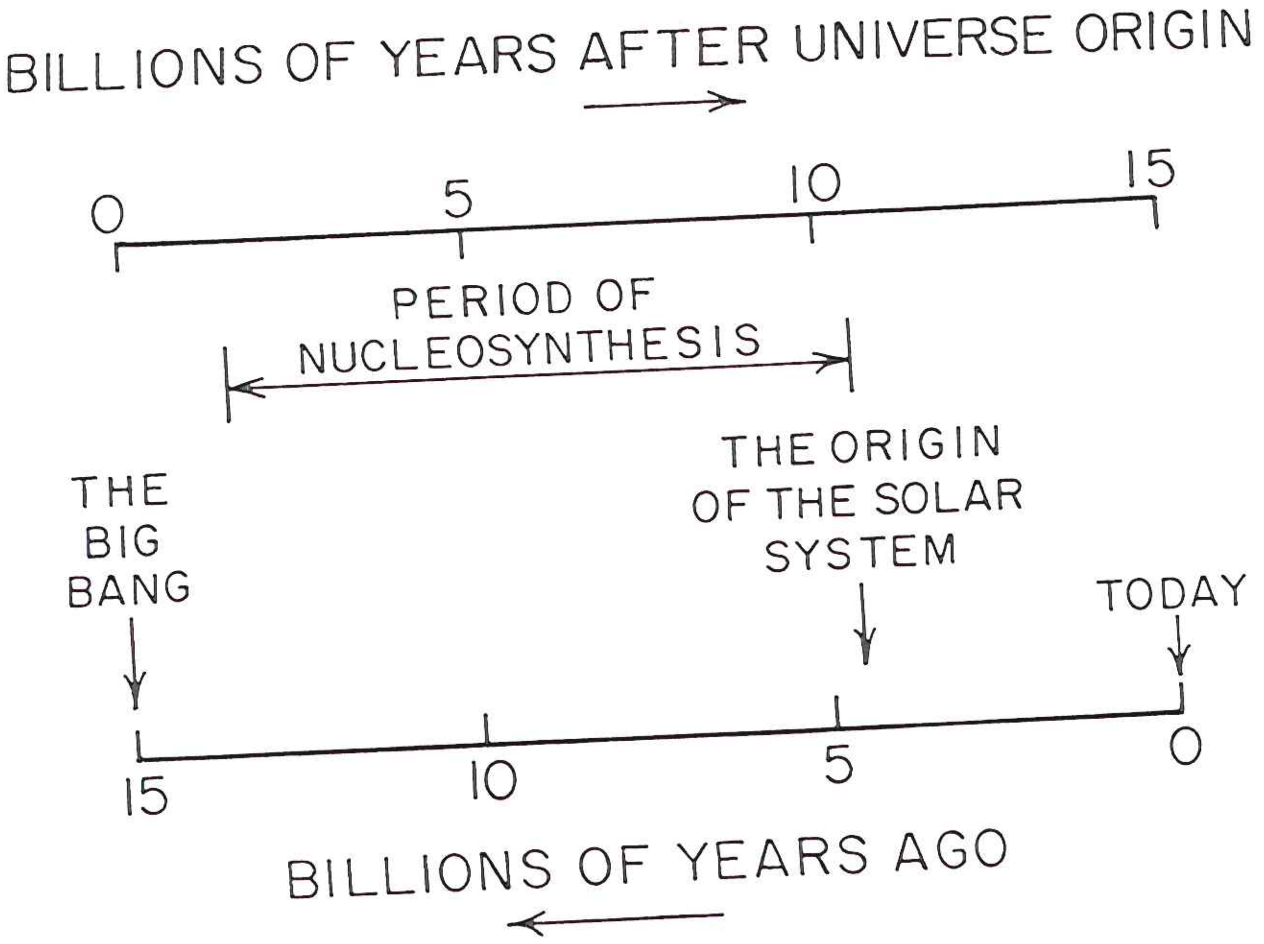


Figure 4-7. Summary of the chronology of universe events: The period of nucleosynthesis refers to the time interval over which the elements heavier than hydrogen and helium that are found in our solar system were produced. For the galaxy as a whole the period of nucleosynthesis extends right up to the present. The matter in the solar system was isolated from the galaxy 4.6 billion years ago.

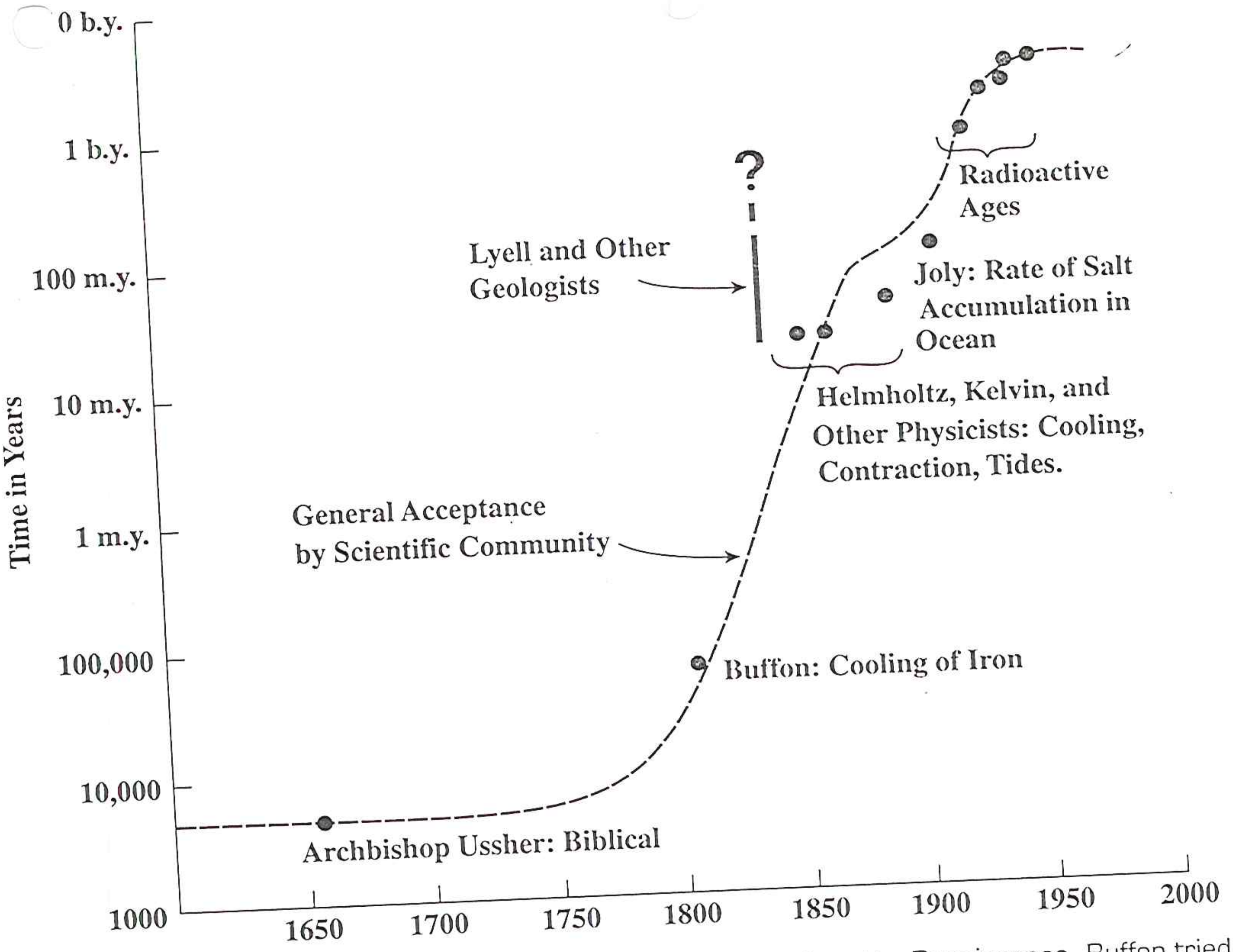


Figure 8.1. Age of Earth as estimated by various techniques since the Renaissance. Buffon tried to use rate of cooling of iron from a molten state to estimate the age of Earth, but the omission of as-yet undiscovered radioactive heating of Earth's interior (chapters 9 and 11) seriously shortened his cooling time. Joly worked out how long it would take to bring the oceans up to their current salinity based on the rate at which rivers carry salt to the sea; he ignored the precipitation of salt out of the ocean water into seafloor sediments. From Press and Siever (1978) by permission of W.H. Freeman and Company.

Actual age of ⊕ (Broecker Fig 4-7)
is 4.7 billion years

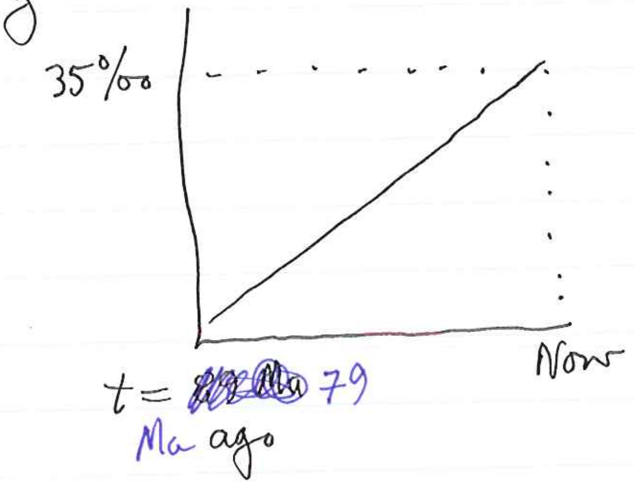
So Joly is off by a factor of 50
(Lunine Fig. 8.1 again)

What is wrong — Joly neglected
salt **deposition** ← see his quote — he
actually considered it but regarded it as small

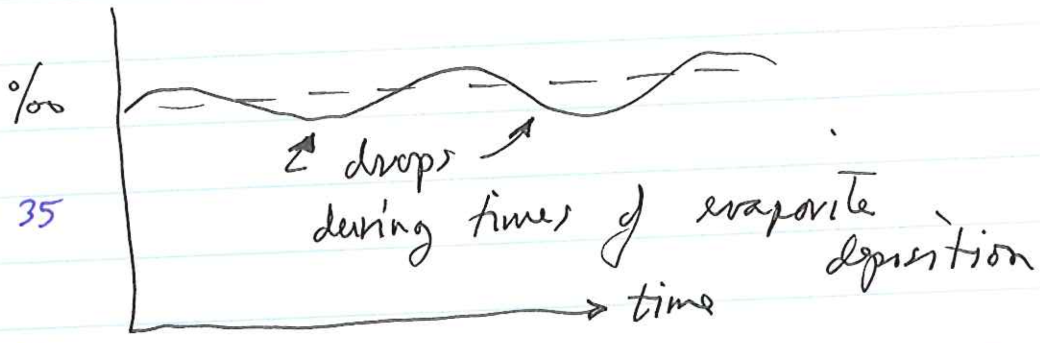
Evaporite deposition commonly occurs
in silled basins in warm arid
climates

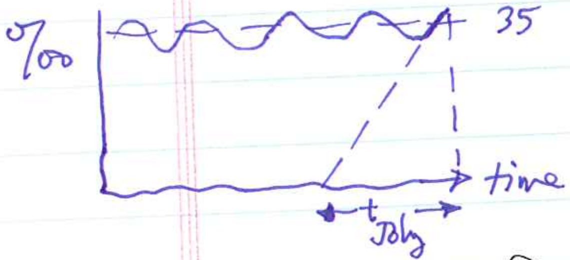
Evaporation of H_2O leaves behind
the salts $NaCl$, $CaSO_4$
halite , gypsum

Joly imagined that the salinity
of the ocean was constantly
increasing



In fact the long-term average salinity is essentially constant in time





~~Joly's "age" of the "ocean" really a residence time for Na^+ in the oceans~~

For example, entire Gulf of Mexico underlain by ~ 1 km thick layer of evaporite (salt)

Area of Gulf $1.6 \cdot 10^6$ km^2 (World Almanac)

$$1.6 \cdot 10^6 \text{ km}^3 \text{/salt}$$
$$= 1.6 \cdot 10^{15} \text{ m}^3$$
$$= 3.5 \cdot 10^{18} \text{ kg salt}$$

$\rho_{NaCl} = 2200$ kg/m^3

$$\frac{3.5 \cdot 10^{21} \text{ g}}{(24 + 35.5) \text{ g/mole}} = 6 \cdot 10^{19} \text{ moles}$$

1/10 as much Na^+ in this one evaporite deposit as in all oceans

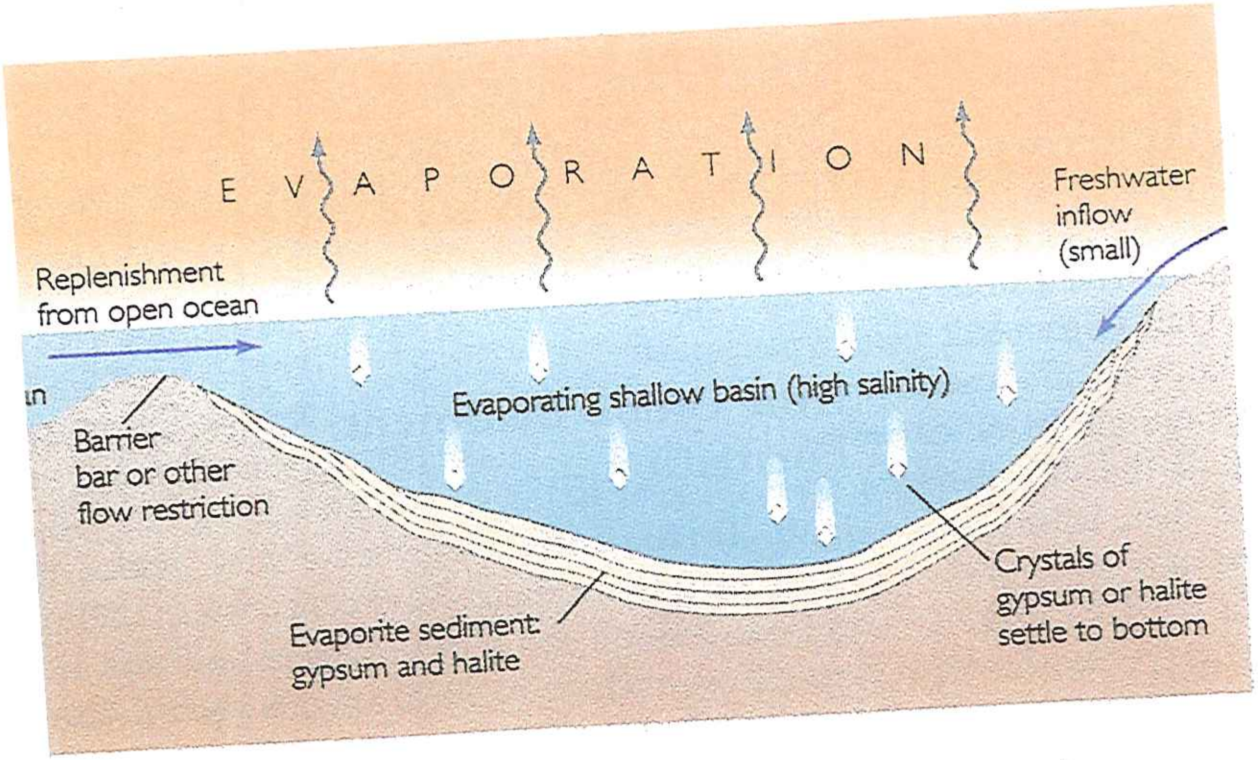


FIGURE 7.21 When seawater evaporates in a shallow basin with a restricted connection to the open ocean, gypsum and halite form as evaporite sediments. Evaporation removes much more water than the fresh water flowing in can replace. As the evaporating basin gets appreciably more saline than the water of the open sea, gypsum is precipitated. A further increase in salinity leads to the crystallization of halite.

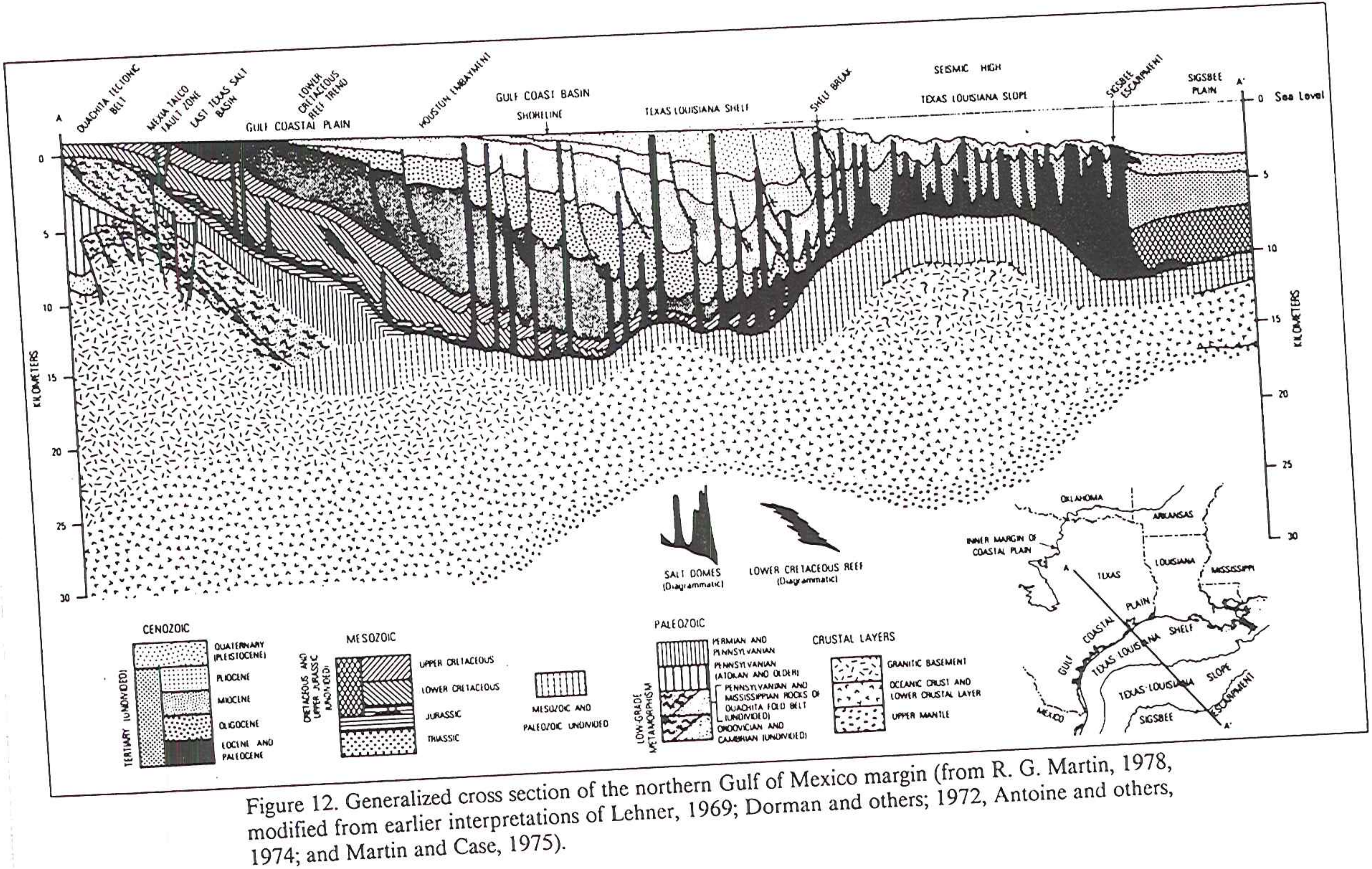


Figure 12. Generalized cross section of the northern Gulf of Mexico margin (from R. G. Martin, 1978, modified from earlier interpretations of Lehner, 1969; Dorman and others; 1972, Antoine and others, 1974; and Martin and Case, 1975).

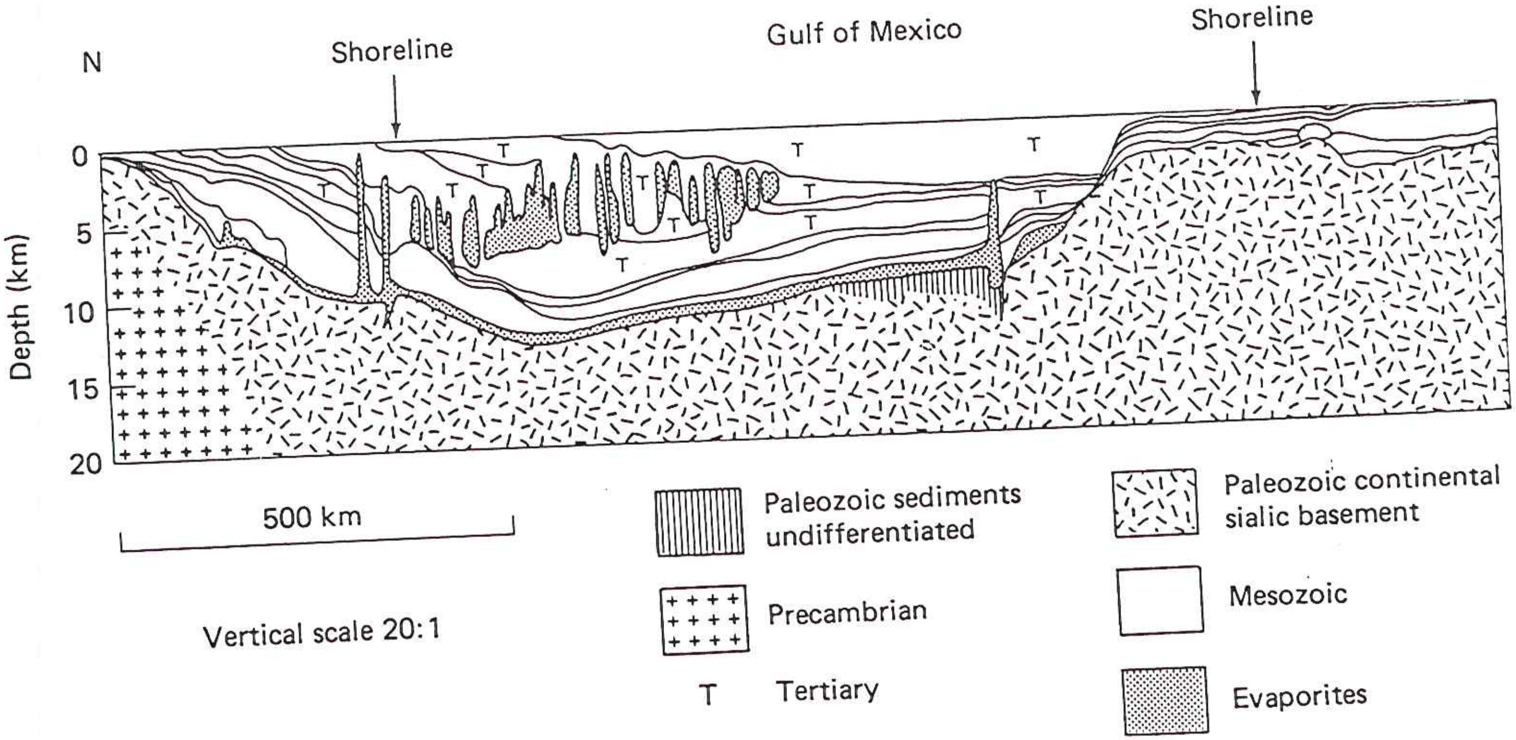


Figure 11-18 Geological cross section for the Gulf of Mexico. Vertical exaggeration is 20:1. (After Bally, 1979)

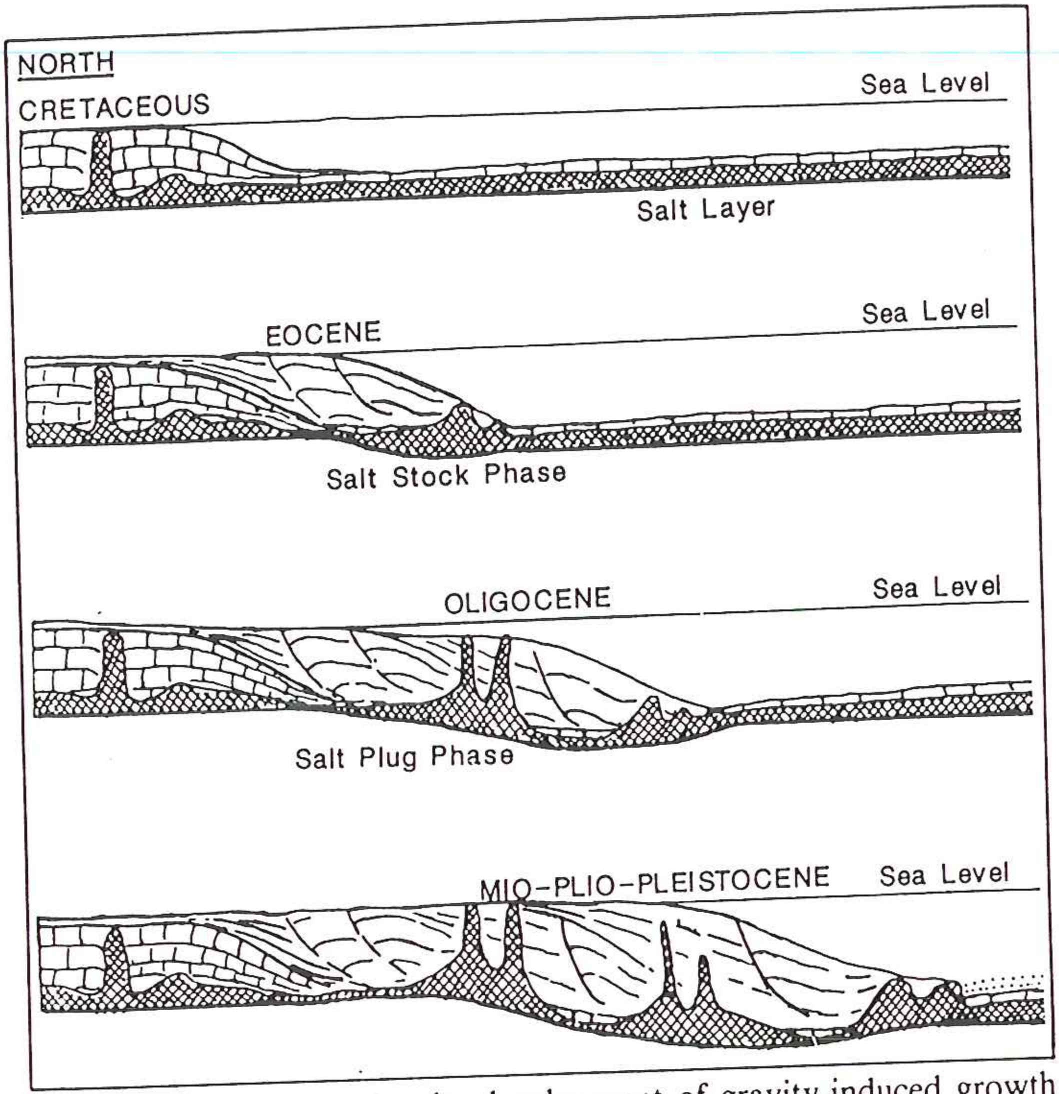


Figure 10. Hypothesis for the development of gravity-induced growth faults on a deep mobile salt layer, northern Gulf of Mexico (from Wilhelm and Ewing, 1972).

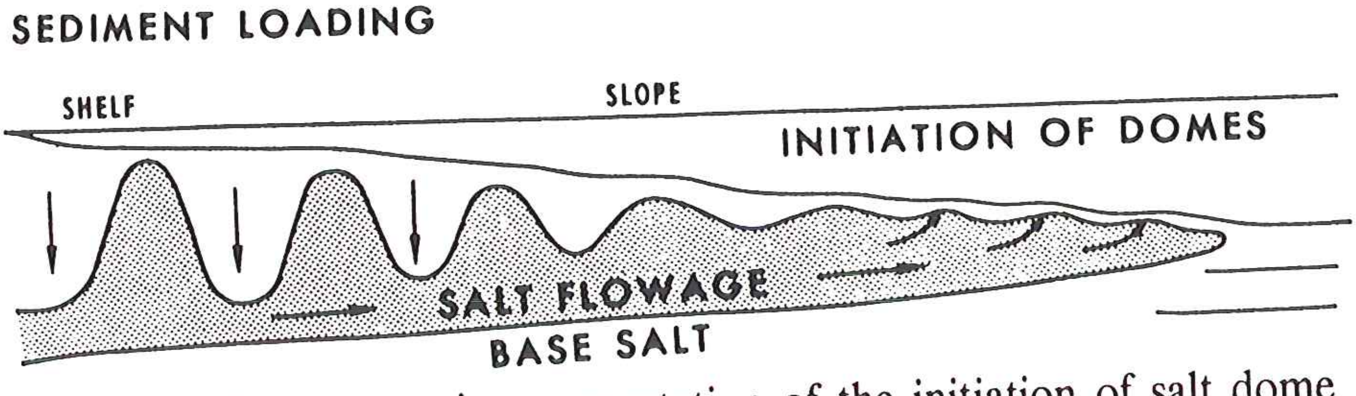


Figure 13. Diagrammatic representation of the initiation of salt dome growth on the continental slope as a result of sediment loading on the shelf–upper slope (from Humphris, 1978, 1979).

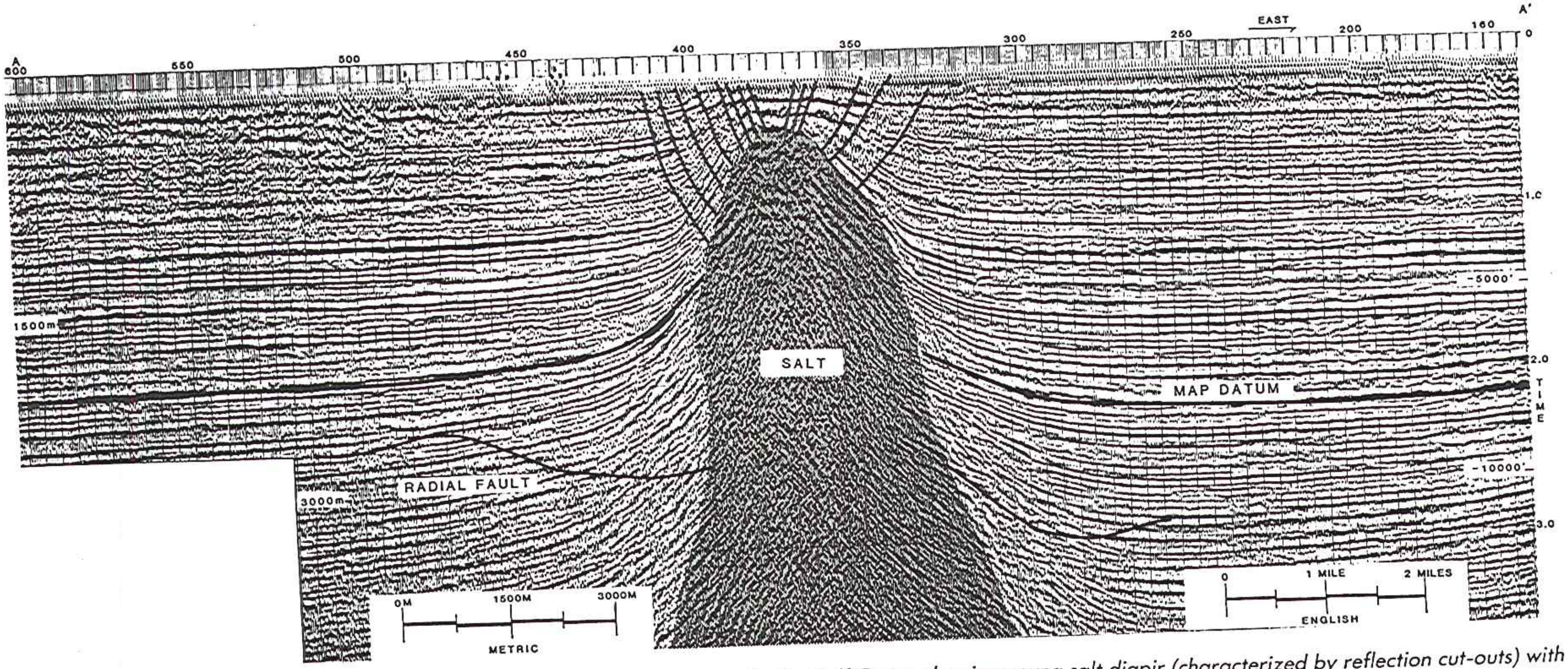
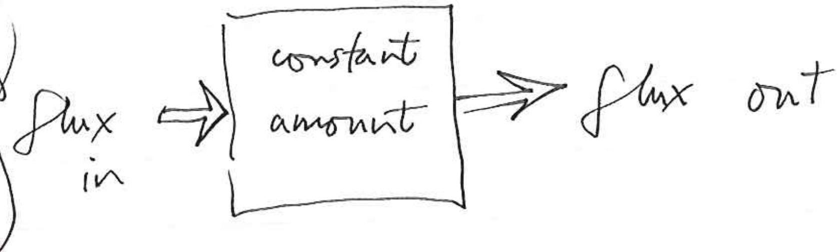


Fig. 8-31 (Sunwall et al., 1983)—Seismic line from offshore Louisiana, U. S. Gulf Coast, showing young salt diapir (characterized by reflection cut-outs) with superjacent normal faults and lower radial faults which strike parallel to seismic line. Salt configuration based on well control, gravity, and reflection and refraction seismic. Note that stratigraphic thinning toward diapir begins early (below 2 sec), but secondary rim synclines are not developed. Permission to publish by American Association of Petroleum Geologists.

Joly's "age of the ⊕" now viewed as a determination of the residence time of an Na^+ atom in the oceanic reservoir

Steady-state box model:

Blackboard discussion *before* showing box model transparency



Example — students at Princeton

- observe # Princeton students = 4400
- observe # incoming freshmen = 1100
- or # caps & gowns on Nassau Green on Commencement day = 1100

Chevy Suburbans disgorging furniture at beginning of Orientation Week

Residence time = $\frac{4400 \text{ students}}{1100 \text{ students/yr}}$ = 4 yrs

Show Berner Tables 8.1 and 8.6 again.

Can be used to determine the residence

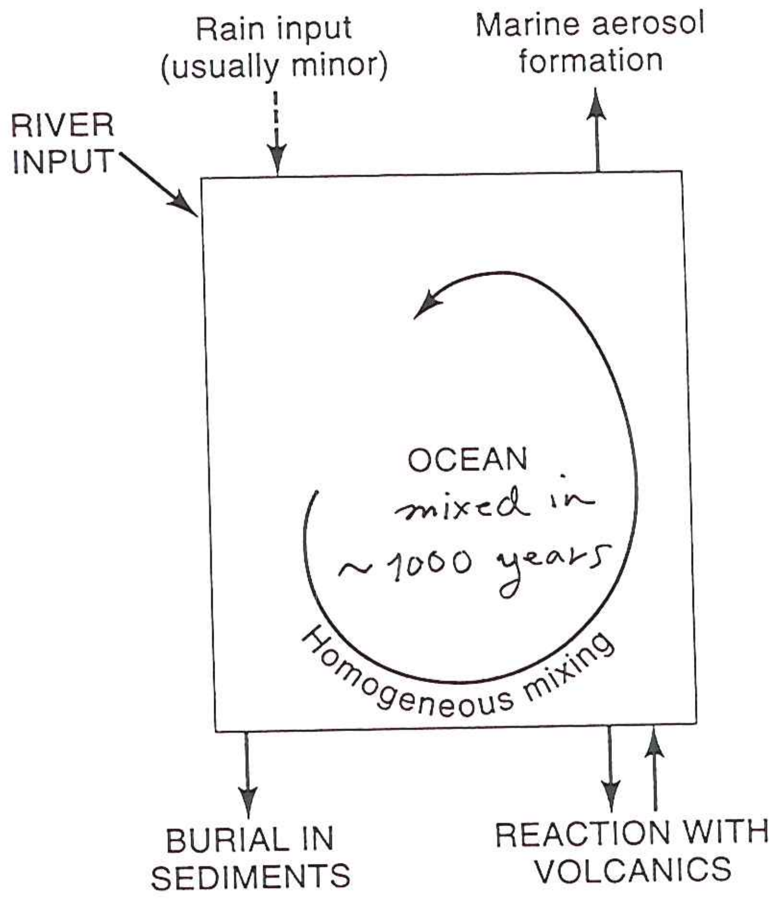


Figure 8.3. Simple box model appropriate for conservative elements in seawater. Note that, compared with the Sillèn model of Figure 8.2, fluxes enter and leave the box, and the atmosphere and sediments are considered to be outside the box. Also note that, in contrast to lakes, there is no outlet, so dissolved materials carried in by rivers can be removed only by sea–air transfer (marine aerosol formation), burial in sediments, or reaction with volcanics.

TABLE 8.3 Replacement Time with Respect to River Addition, τ_r, for Some Major and Minor Dissolved Species in Seawater

	Concentration (μM)		
Component	River Water	Seawater	τ_r [a] (1,000 yr)
Cl	230	558,000	87,000
Na^+	315	479,000	55,000
Mg^{++}	150	54,300	13,000
SO_4^{--}	120	28,900	8,700
Ca^{++}	367	10,500	1,000
K^+	36	10,400	10,000
HCO_3^-	870	2,000	83
H_4SiO_4	170	100	21
NO_3^-	10	20	72
Orthophosphate	1.8	2	40

← why not $79 \cdot 10^6$?

uses flux value including modern pollution

---

[a] $\tau_r = ([SW]/[RW])\ \tau_w$, where τ_w = replacement (residence) time of H_2O = 36,000 yr; RW = river water; SW= seawater, and [ ] = concentration in μmoles per liter = μM.

times of several species

Table 8.3 gives those — uses the modern (polluted) riverine inputs

- $\frac{Na^+ \text{ (polluted)}}{Na^+ \text{ (natural)}} = \frac{8.4}{6.5} = 1.3$ times as great a flux

$\frac{79 \text{ my}}{1.3} = 61$ myr — Berner gives 35 myr

A major aim of geochemistry is to balance the books on a given element. Briefly consider four

- $\boxed{\bullet\ Cl^- \quad \text{chlorine}}$ — all processes well identified — not incorporated in silicate minerals — only in evaporites NaCl

Table 8.13 one Tg (teragram) $= 10^{12}$ g $= 10^9$ kg

net air – sea transfer

sea breeze picks up aerosols & can smell the ocean near the shore

TABLE 8.13 The Oceanic Chloride Budget (Rates in Tg Cl^-/yr)

Present-Day Budget			
Inputs		Outputs	
Rivers (natural)	215	Net sea–air transfer	40
Rivers (pollution)	93	Pore-water burial	25
Total	308	Total	65
Long-Term (Balanced) Budget			
Inputs		Outputs	
Rivers	215	NaCl evaporative deposition	163
		Net sea–air transfer	40
		Pore-water burial	12
		Total	215

Note: Tg = 10^{12} g. Replacement time for Cl^- is 87 million years.

TABLE 8.12 Rates of Addition via Rivers of Major Elements to the ocean (as Dissolved Species) and Rates of Net Loss from the Ocean by Transfer of Sea Salt to the Continents via the Atmosphere

Species	Rate of Addition from Rivers[a] (Tg/yr)	Rate of Net Sea Salt Loss to Atmosphere (Tg/Yr)
Cl^-	308	40
Na^+	269	21
SO_4-S	143	4
Mg^{++}	137	3
K^+	52	1
Ca^{++}	550	0.5
HCO_3^-	1980	—
H_4SiO_4-Si	180	—

sea breeze

Note: $Tg = 10^{12}$ g.

[a] Based on river water input of 37,400 km^3/yr: includes pollution

Sources: River-water data from Meybeck 1979; cyclic salt data from Chapter 5.

TABLE 8.13 The Oceanic Chloride Budget (Rates in Tg Cl⁻/yr)

Present-Day Budget			
Inputs		Outputs	
Rivers (natural)	215	Net sea–air transfer	40
Rivers (pollution)	93	Pore-water burial	25
Total	308	Total	65
Long-Term (Balanced) Budget			
Inputs		Outputs	
Rivers	215	NaCl evaporative deposition	163
		Net sea–air transfer	40
		Pore-water burial	12
		Total	215

Note: Tg = 10^{12} g. Replacement time for Cl^- is 87 million years.

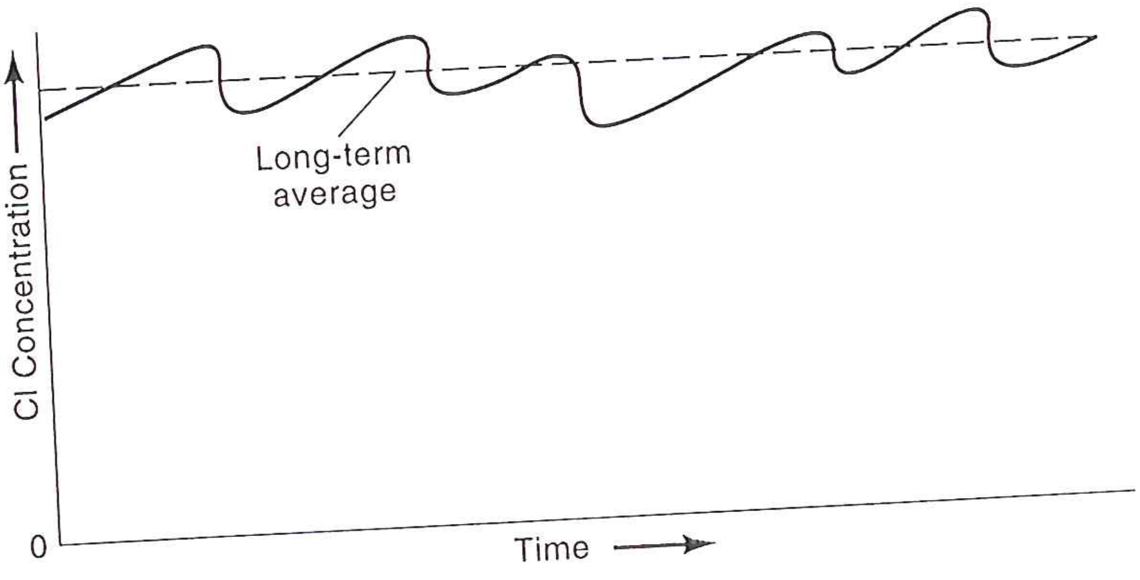


Figure 8.12. Schematic representation of change of chloride (Cl^-) concentration in seawater with geologic time. Sudden drops are due to the rapid precipitation of NaCl in evaporite basins.

TABLE 4.7 Origin of Major Components of Groundwater (Major Processes Only)

Component	Origin
Na^+	NaCl dissolution (some pollutive)[a] Plagioclase weathering Rainwater addition
K^+	Biotite weathering K-feldspar weathering Biomass decreases Dissolution of trapped aerosols
Mg^{++}	Amphibole and pyroxene weathering Biotite(and chlorite) weathering Dolomite weathering Olivine weathering Rainwater addition
Ca^{++}	Calcite weathering Plagioclase weathering Dolomite weathering Dissolution of trapped aerosols Biomass decreases
HCO_3^-	Calcite and dolomite weathering Silicate weathering
SO_4^{--}	Pyrite weathering (some pollutive)[a] $CaSO_4$ dissolution Rainwater addition
Cl^-	NaCl dissolution (some pollutive)[a] Rainwater addition
H_4SiO_4	Silicate weathering

Note: Order presented is approximate order of decreasing importance.

TABLE 5.11 Sources of Major Elements in World River Water (in Percent of Actual Concentrations)

Element	Atmos. Cyclic Salt	Weathering			Pollution[b]
		Carbonates	Silicates	Evaporites[a]	
Ca^{++}	0.1	65	18	8	9
HCO_3^-	<<1	61[c]	37[c]	0	2
Na^+	8	0	22	42	28
Cl^-	13	0	0	57	30
SO_4^{--}	2[d]	0	0	22[d]	54
Mg^{++}	2	36	54	<<1	8
K^+	1	0	87	5	7
H_4SiO_4	<<1	0	99+	0	0

[a] Also includes NaCl from shales and thermal springs.

[b] Values taken from Meybeck (1979) except sulfate, which is based on calculation given in the text.

[c] For carbonates, 34% from calcite and dolomite and 27% from soil CO_2; for silicates, all 37% from soil CO_2; thus, total HCO_3^- from soil (atmospheric) CO_2 = 64% (See also Table 5.13).

[d] Other sources of river SO_4^{--}; natural biogenic emissions to atmosphere delivered to land in rain, 3%; volcanism, 8%; pyrite weathering, 11%.

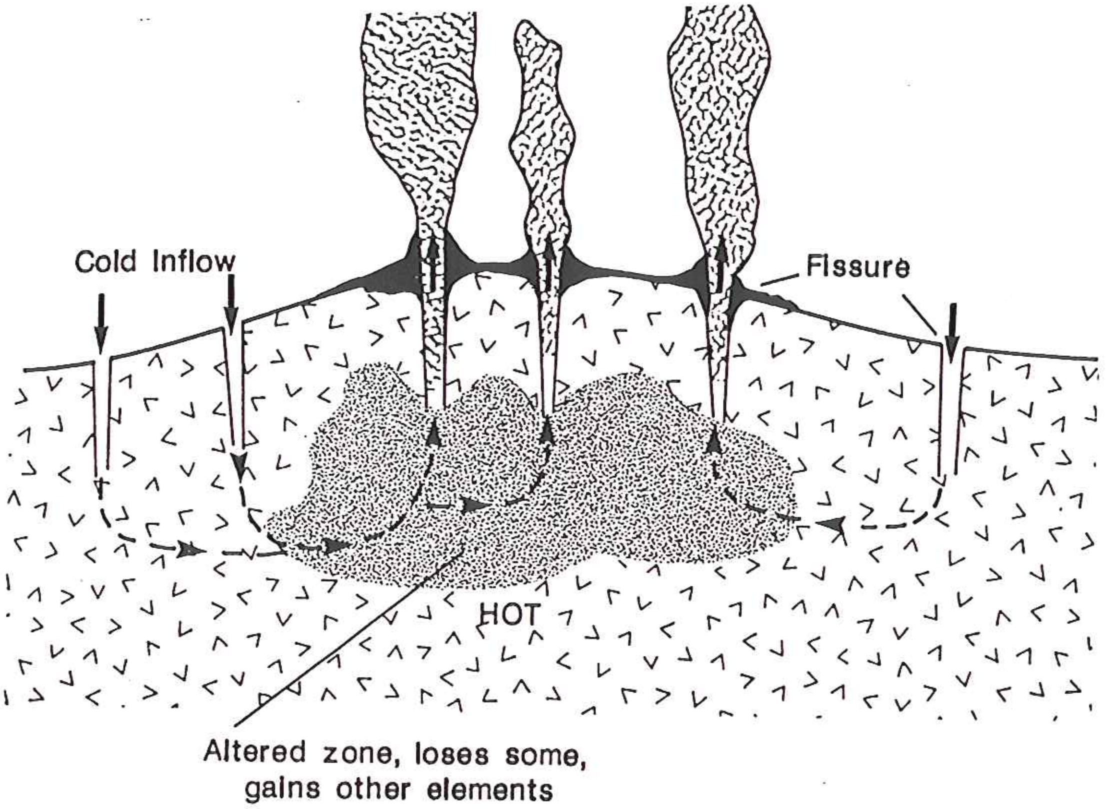


TABLE 8.8 Removal or Addition Fluxes of Some Major Seawater Constituents as a Result of Basalt-Seawater Reaction Near Midocean Ridges

	Flux (Tg/yr)		
Constituent	Edmond et al. (1979)	Thompson (1983)	Present Study
Mg^{++}	−187	−60	−119
Ca^{++}	140	73	191
K^{+}	51	−27	53
SO_4^{--} as S	−120	—	—[a]
H_4SiO_4 as Si	90	82	56

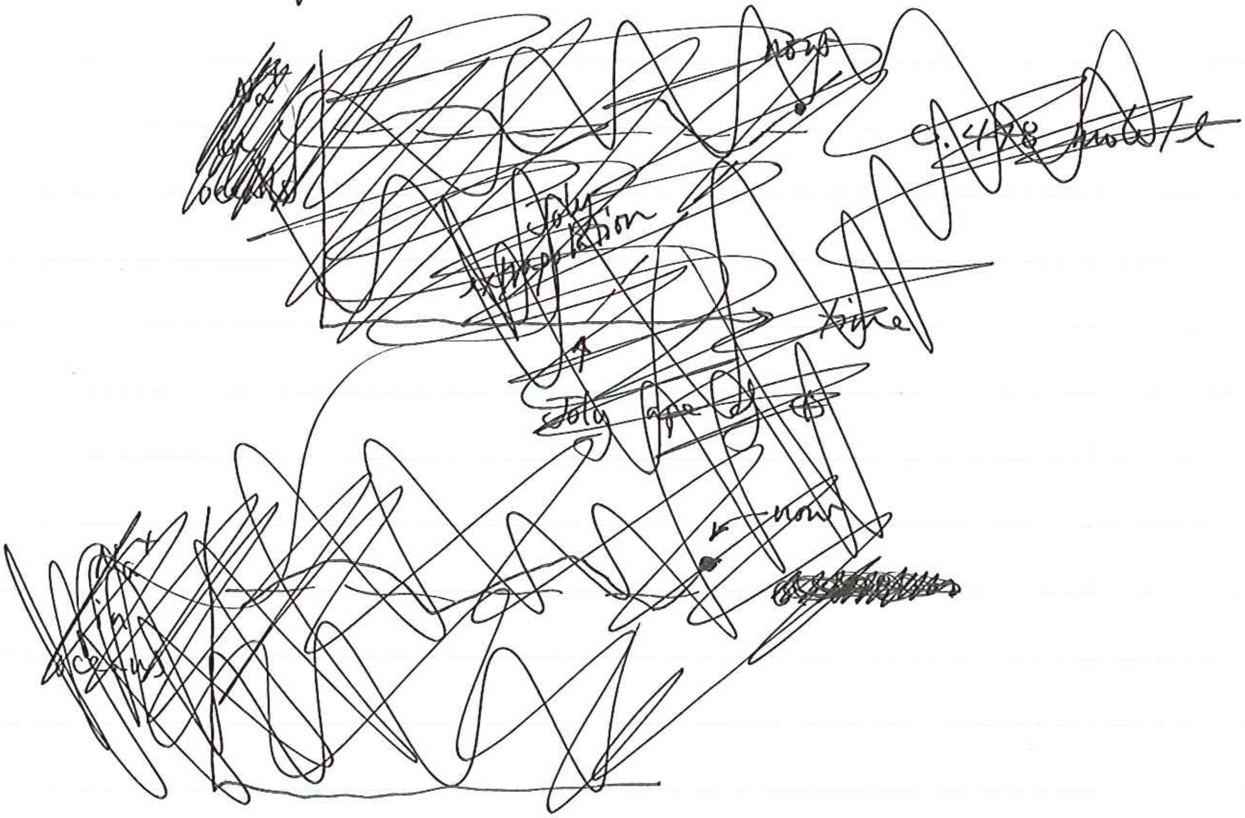
Note: Removal values shown as negative numbers. Tg = 10^{12}g.

[a] Less than 10% of Edmond et al. (1979) value

burial in pore sediments

Major imbalance at present time

- NaCl road salt 93/308
- time of reduced evaporite deposition



why — sea level particularly high now
interglacial

- Na⁺ — Joly's element

Table 4.7

more sources & sinks
Na in feldspars — ocean basalt
Na in clays

plagioclase $NaAlSi_3O_8$

Table 8.14 — present day out of balance as for Na^+

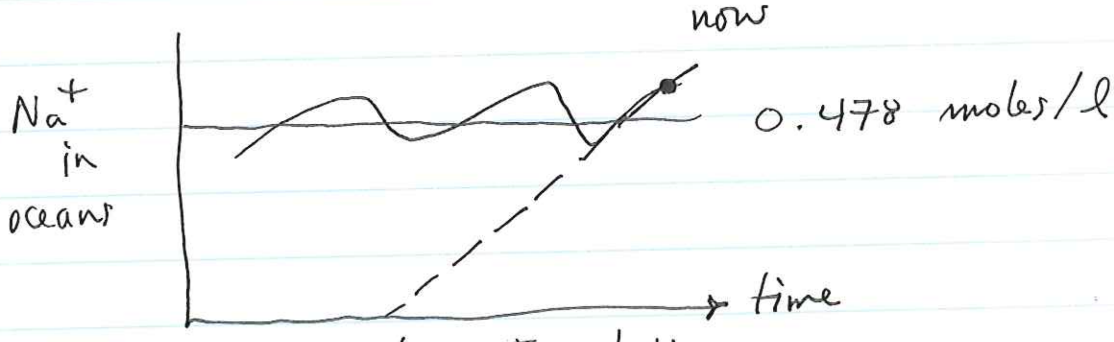
long-term NaCl deposition fixed using Na^+

$$163 \times \frac{24}{35.5} = 106$$

cation exchange — clay minerals in estuaries

basalt — seawater reaction — black smokers
removes Na^+ from seawater

For both Na^+ and Cl^- the picture is the same



Joly extrapolation
"age of ⊕"

Consider two more cations

TABLE 8.14 The Oceanic Sodium Budget (Rates in Tg Na^+/yr)

Present-Day Budget			
Inputs		Outputs	
Rivers (natural)	193	Cation exchange	42
Rivers (pollution)	76	Net sea–air transfer	21
		Pore-water burial	16
Total	269	Total	79
Long-Term Budget			
Inputs		Outputs	
Rivers	193	NaCl deposition	106
		Net sea–air transfer	21
		Cation exchange	21
		Pore-water burial	8
		Basalt–seawater reaction	37
		Total	193

Note: Tg = 10^{12} g. Replacement time for Na^+ is 55 million years.

• Mg^{++} magnesium

Table 8.16

Before discovery of MOR hot springs
∃ a serious imbalance problem

Now known that almost all
Mg^{++} added by rivers
(119 out of 137 Tg/yr)
is <u>removed</u> by reactions with
volcanic rock at ridges

• Ca^{++} calcium

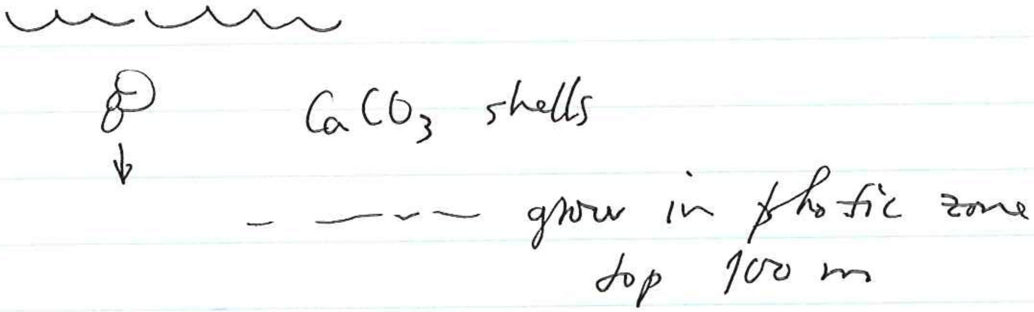
Ca^{++} and Mg^{++} same column
periodic table — Table 8.3

both μM

	conc in river water	conc in seawater
Mg^{++}	150	54,000
Ca^{++}	367	10,500

Much more Ca^{++} coming in rivers
but much less present in oceans

Reason — Ca^{++} is preferentially
incorporated into corals and the shells
of marine <u>plankton</u> — Fig. 8.9



Shell growth removes Ca++ from seawater
Die & sink to bottom.

Berner's budget is balanced to within the uncertainties

Most input from rivers
Ca++ also added to ocean by clay basalt – seawater reactions (opposite of Na+ and Mg++)

Most output as $CaCO_3$ limestone

- shallow water – shelves – coral reefs, etc.
- deep water – plankton

Below ~4 km depth the oceans are undersaturated with respect to $CaCO_3$

The solubility increases with pressure

As a result deep-sea sediments below ~4 km depth dissolve back into water column — calcite compensation depth

See map of Atlantic Fig. 8.13

Think of mid-ocean ridges like "snow"- capped peaks

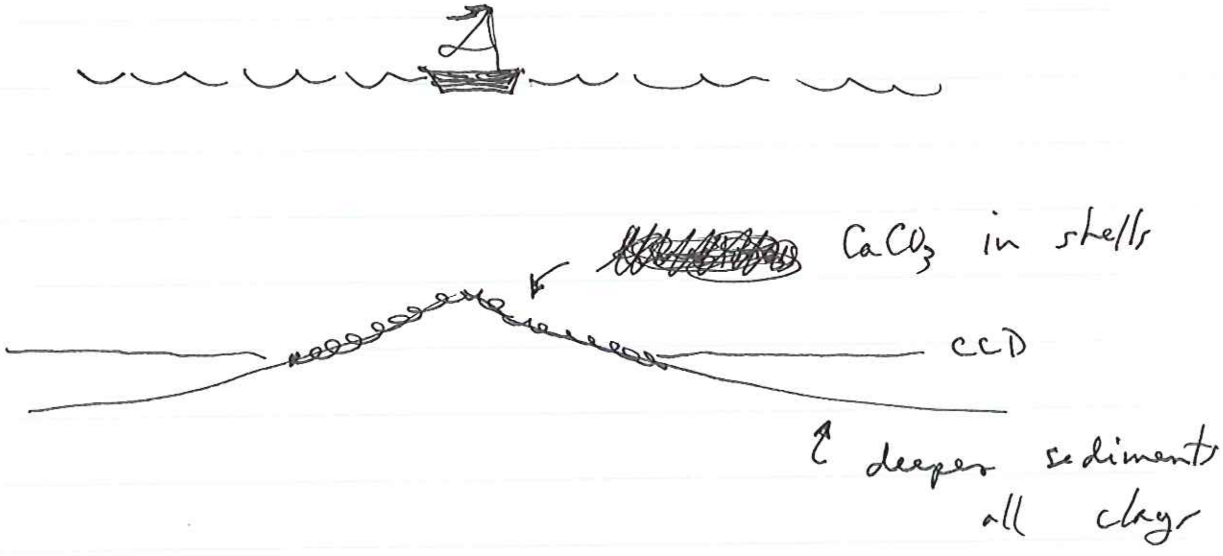


TABLE 8.16 The Oceanic Magnesium Budget (Rates in Tg Mg^{++}/yr)

(Balanced) Budget for Past 100 Million Years			
Inputs		Outputs	
Rivers	137	Volcanic–seawater reaction	119
		In biogenic $CaCO_3$	15
		Net sea–air transfer	3
		Total	137

Note: Tg = 10^{12} g. Replacement time for Mg^{++} is 13 million years.

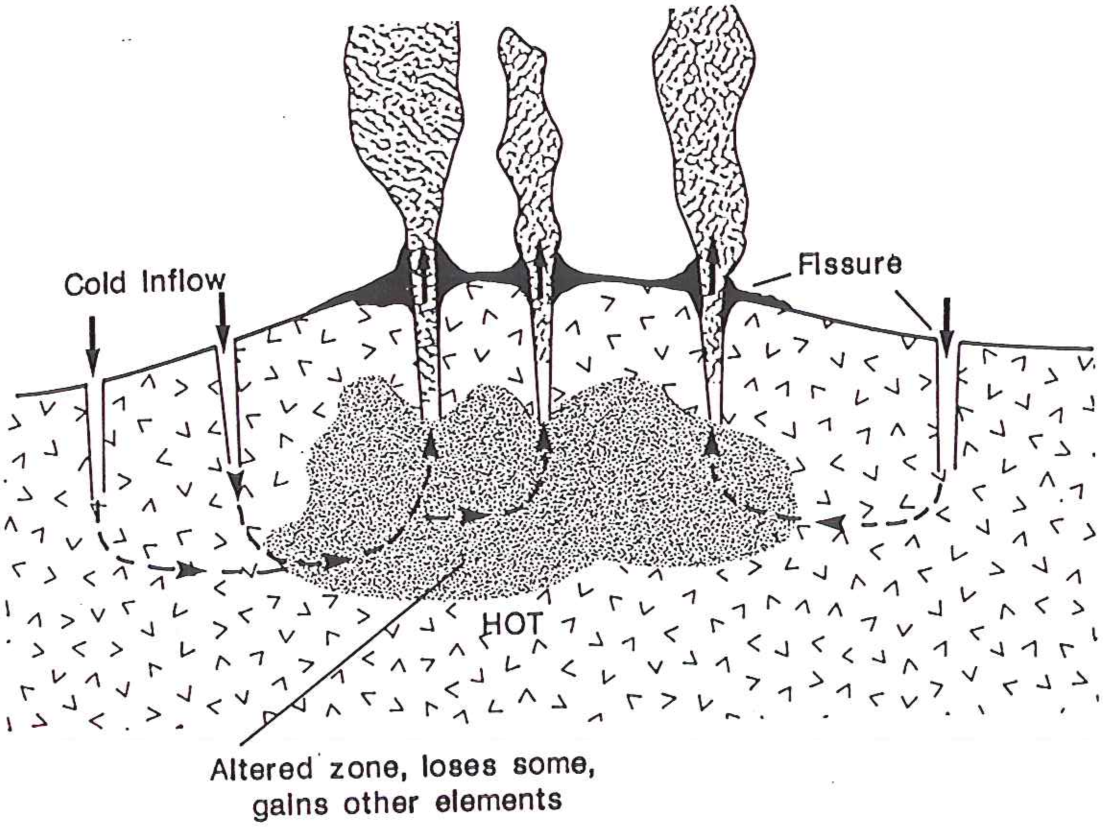


TABLE 8.16 The Oceanic Magnesium Budget (Rates in Tg Mg^{++}/yr)

(Balanced) Budget for Past 100 Million Years			
Inputs		Outputs	
Rivers	137	Volcanic–seawater reaction	119
		In biogenic $CaCO_3$	15
		Net sea–air transfer	3
		Total	137

Note: Tg = 10^{12} g. Replacement time for Mg^{++} is 13 million years.

TABLE 8.3 Replacement Time with Respect to River Addition, τ_r, for Some Major and Minor Dissolved Species in Seawater

Component	Concentration (μM)		τ_r[a]
	River Water	Seawater	(1,000 yr)
Cl	230	558,000	87,000
Na^+	315	479,000	55,000
Mg^{++}	150	54,300	13,000
SO_4^{--} why?	120	28,900	8,700
Ca^{++}	367	10,500	1,000
K^+	36	10,400	10,000
HCO_3^-	870	2,000	83
H_4SiO_4	170	100	21
NO_3^-	10	20	72
Orthophosphate	1.8[b]	2	40

---

[a] $\tau_r = ([SW]/[RW])\ \tau_w$, where τ_w = replacement (residence) time of H_2O = 36,000 yr; RW = river water; SW= seawater, and [ ] = concentration in μmoles per liter = μM.

[b] Includes input from solubilization of solids.

TABLE 5.12 Sources of Ca and Mg in World Average River Water

Source	Percent of Total Ca	Percent of Total Mg
Weathering		
Calcite, $CaCO_3$	52	—
Dolomite, $CaMg(CO_3)_2$	13	36
$CaSO_4$ minerals	8	—
Ca-silicates (plagioclase)	18	—
Mg-silicates	—	54
Cyclic sea salt	<<1	2
Pollution	9	8
Total	100	100

Source: Data for rock sources from Berner et al. 1983. Cyclic sea salt from Table 5.10 and pollution from Meybeck 1979.

TABLE 5.13 Sources of Rock Weathering-Derived HCO_3^- in World Average River Water

Weathering Source	Percent of Total HCO_3^- from Soil CO_2	Percent of Total HCO_3^- from Carbonate Minerals
Calcite + Dolomite	27	34
Ca-silicates	13	—
Mg-silicates	15	—
Na-silicates	6	—
K-silicates	3	—
Total	64	34

Note: For method of calculation, see text. (An additional 2% of total HCO_3^- is added by pollution; see Table 5.11.)

TABLE 8.18 The Oceanic Calcium Budget (Rates in Tg Ca^{++}/yr)

Present-Day Budget			
Inputs		Outputs	
Rivers	550	$CaCO_3$ deposition:	
Volcanic–seawater reaction	191	Shallow water	520
Cation exchance	37	Deep sea	440
Total	778	Total	960
Budget for Past 25 Million Years			
Inputs		Outputs	
Rivers	550	$CaCO_3$ deposition:	
Volcanic–seawater reaction	191	Shallow water	240
Cation exchance	19	Deep sea	440
		Evaporitic $CaSO_4$ deposition	49
Total	760	Total	729

Note: Tg = 10^{12} g. Replacement time (rivers only) for Ca^{++} is 1 million years.

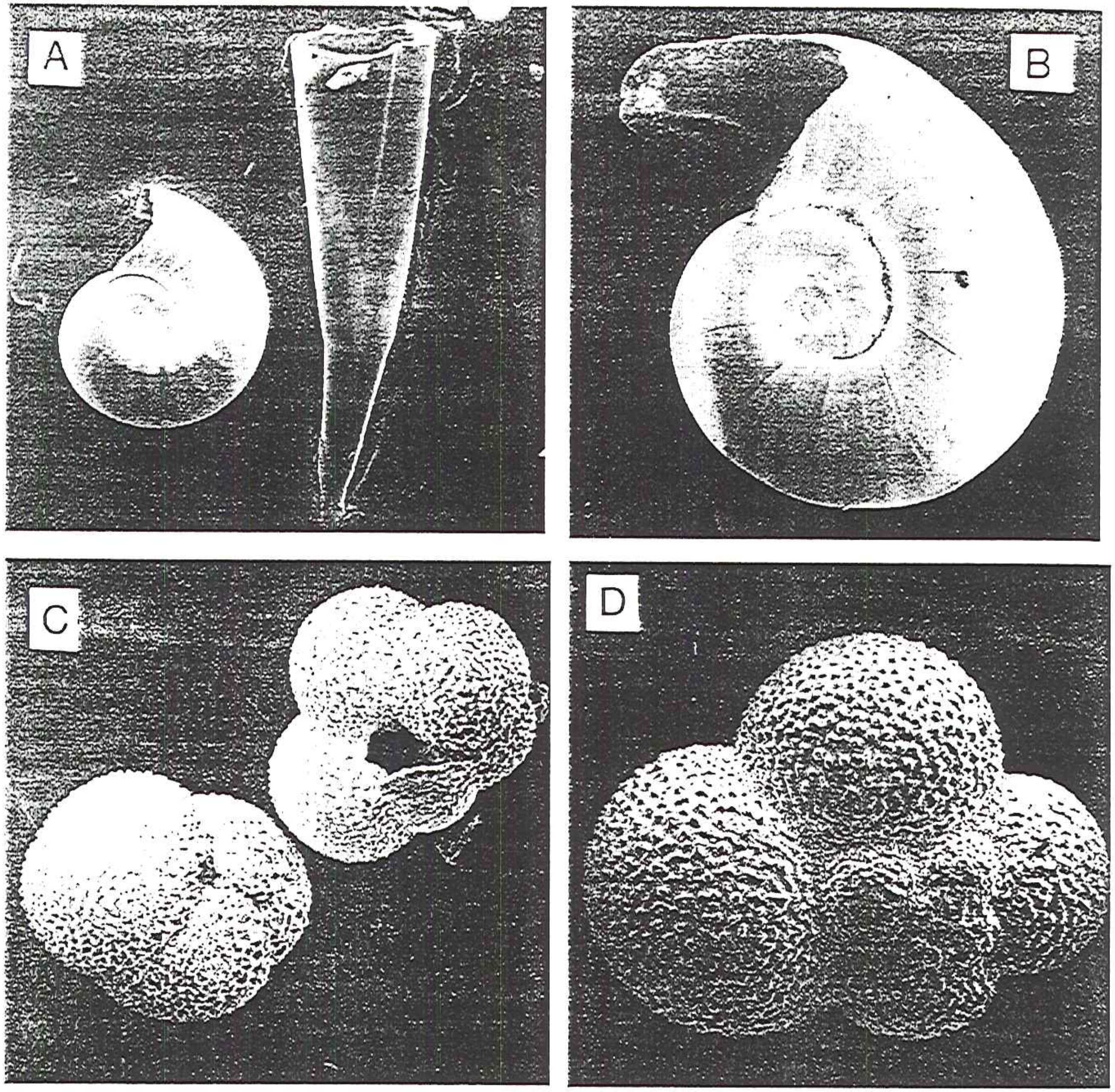
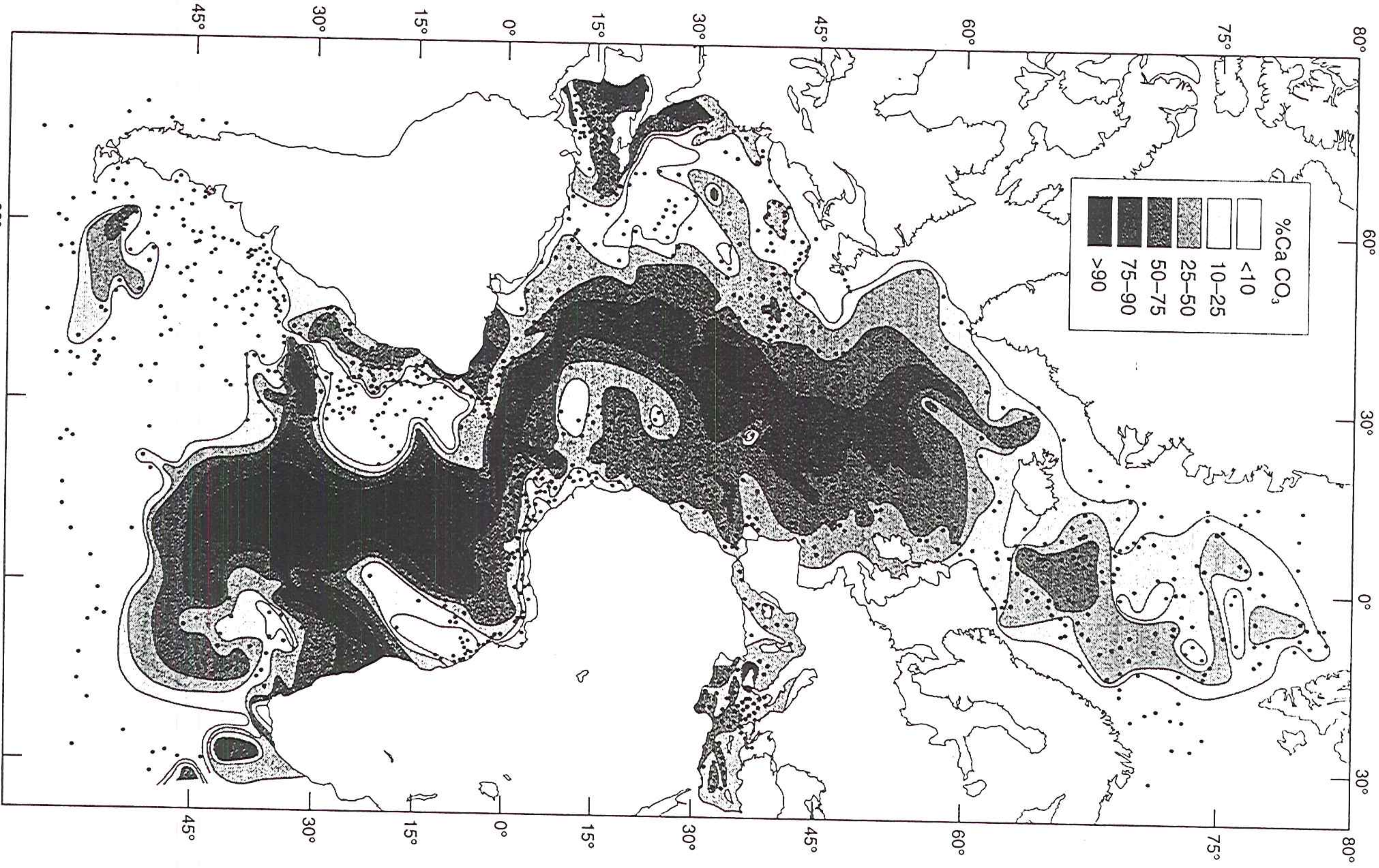


Figure 8.9. Photomicrographs of some planktonic $CaCO_3$-secreting organisms: (a) pteropod shells (aragonite) × 20; (b) pteropod shell (aragonite) × 10; (c) foram tests (calcite) × 70; (d) foram test (calcite) × 100.



igure 8.13. Distribution of $CaCO_3$ in deep-sea sediments of the Atlantic Ocean. Note that the highest concentrations are located at the hallowest depths atop the Mid-Atlantic Ridge. (After P. E. Biscaye, V. Kolla, and K. K. Turekian, "Distribution of Calcium Carbonate in urface Sediments of the Altantic Ocean." *Journal of Geophysical Research* 81: 2596. Copyright © 1976 by the American Geophysical Union, eprinted by permission of the publisher.)

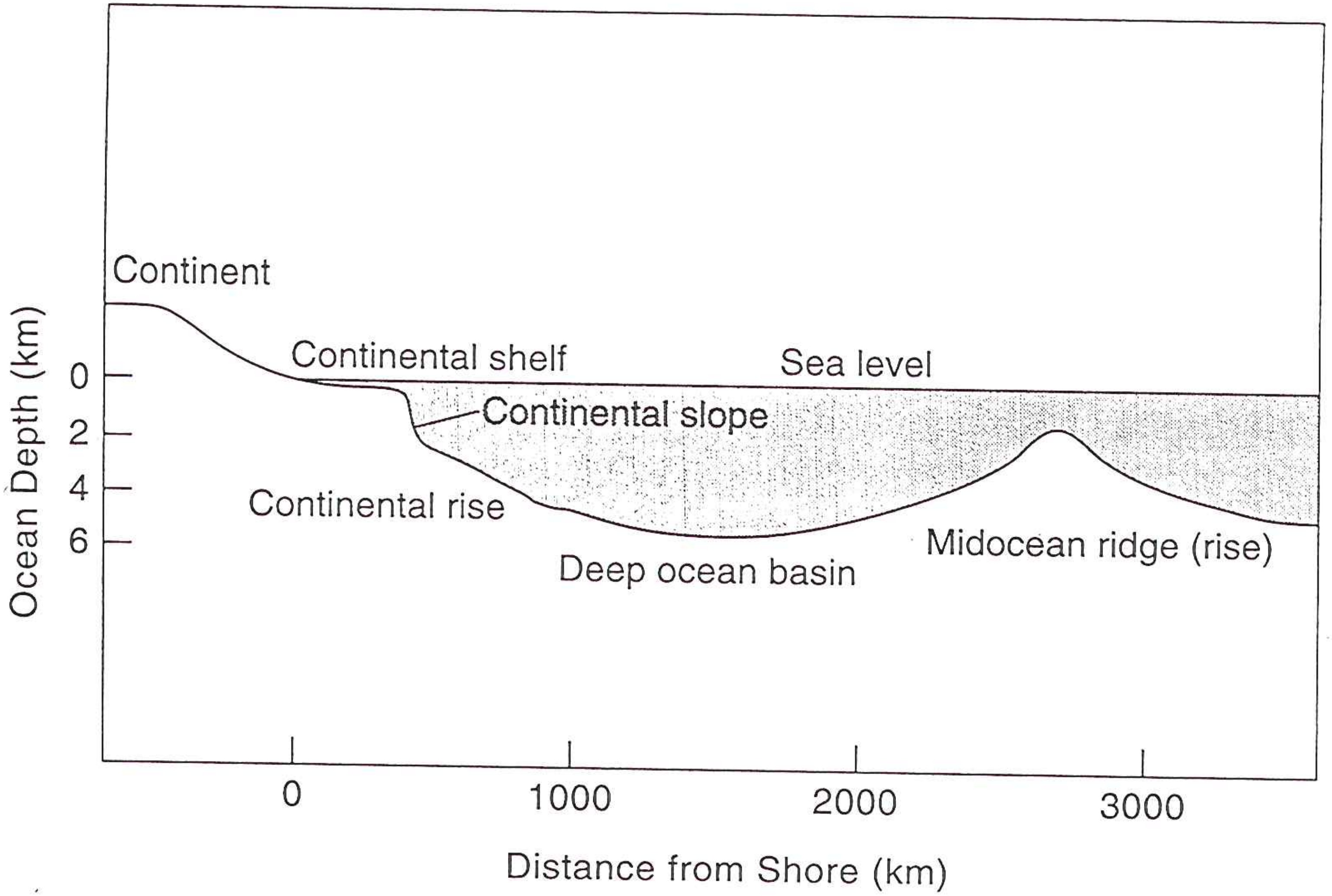


Figure 8.1. Generalized schematic cross section of the oceans showing major physiographic features. Note large differences in vertical and horizontal scales.

PERIODIC TABLE OF THE ELEMENTS

Mn — Chemical Symbol
25 — Atomic Number
Manganese — Element Name
54.94 — Atomic Weight

Strong tendency for outermost electrons to be lost to make full outer shell

Transition elements: valence electrons not in outer shell

Tendency to fill outer electron shell by electron sharing and gain or loss of electrons

Strong tendency to gain electrons to make full outer shell

Noble gases: outer shells filled; no tendency to gain or lose electrons

H 1 Hydrogen 1.01																	He 2 Helium 4.00
Li 3 Lithium 6.94	Be 4 Beryllium 9.01											B 5 Boron 10.81	C 6 Carbon 12.01	N 7 Nitrogen 14.01	O 8 Oxygen 16.00	F 9 Fluorine 19.00	Ne 10 Neon 20.18
Na 11 Sodium 22.99	Mg 12 Magnesium 24.31											Al 13 Aluminum 26.98	Si 14 Silicon 28.09	P 15 Phosphorus 30.97	S 16 Sulfur 32.06	Cl 17 Chlorine 35.45	Ar 18 Argon 39.95
K 19 Potassium 39.10	Ca 20 Calcium 40.08	Sc 21 Scandium 44.96	Ti 22 Titanium 47.90	V 23 Vanadium 50.94	Cr 24 Chromium 52.00	Mn 25 Manganese 54.94	Fe 26 Iron 55.85	Co 27 Cobalt 58.93	Ni 28 Nickel 58.70	Cu 29 Copper 63.55	Zn 30 Zinc 65.38	Ga 31 Gallium 69.72	Ge 32 Germanium 72.59	As 33 Arsenic 74.92	Se 34 Selenium 78.96	Br 35 Bromine 79.90	Kr 36 Krypton 83.80
Rb 37 Rubidium 85.47	Sr 38 Strontium 87.62	Y 39 Yttrium 88.91	Zr 40 Zirconium 91.22	Nb 41 Niobium 92.91	Mo 42 Molybdenum 95.94	Tc 43 Technetium (98)	Ru 44 Ruthenium 101.07	Rh 45 Rhodium 102.91	Pd 46 Palladium 106.4	Ag 47 Silver 107.87	Cd 48 Cadmium 112.41	In 49 Indium 114.82	Sn 50 Tin 118.69	Sb 51 Antimony 121.75	Te 52 Tellurium 127.60	I 53 Iodine 126.90	Xe 54 Xenon 131.30
Cs 55 Cesium 132.91	Ba 56 Barium 137.33	* (see below)	Hf 72 Hafnium 178.49	Ta 73 Tantalum 180.95	W 74 Tungsten 183.85	Re 75 Rhenium 186.21	Os 76 Osmium 190.2	Ir 77 Iridium 192.22	Pt 78 Platinum 195.09	Au 79 Gold 196.97	Hg 80 Mercury 200.59	Tl 81 Thallium 204.37	Pb 82 Lead 207.2	Bi 83 Bismuth 208.98	Po 84 Polonium (209)	At 85 Astatine (210)	Rn 86 Radon (222)
Fr 87 Francium (223)	Ra 88 Radium 226.03	** (see below)	Rf 104 Rutherfordium 261.11	Db 105 Dubnium 262.11	Sg 106 Seaborgium (263)	Bh 107 Bohrium (262)	Hs 108 Hassium (264)	Mt 109 Meitnerium (266)									
IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA

Lanthanide (Rare Earth) Elements

La *57 Lanthanum 138.91	Ce 58 Cerium 140.12	Pr 59 Praseodymium 140.91	Nd 60 Neodymium 144.24	Pm 61 Promethium (145)	Sm 62 Samarium 150.4	Eu 63 Europium 151.96	Gd 64 Gadolinium 157.25	Tb 65 Terbium 158.93	Dy 66 Dysprosium 162.50	Ho 67 Holmium 164.93	Er 68 Erbium 167.26	Tm 69 Thulium 168.93	Yb 70 Ytterbium 173.04	Lu 71 Lutetium 174.97

Actinide Elements

Ac **89 Actinium 227.03	Th 90 Thorium 232.04	Pa 91 Protactinium 231.04	U 92 Uranium 238.03	Np 93 Neptunium 237.05	Pu 94 Plutonium (244)	Am 95 Americium (243)	Cm 96 Curium (247)	Bk 97 Berkelium (247)	Cf 98 Californium (251)	Es 99 Einsteinium (252)	Fm 100 Fermium (257)	Md 101 Mendelevium (258)	No 102 Nobelium (259)	Lr 103 Lawrencium (260)