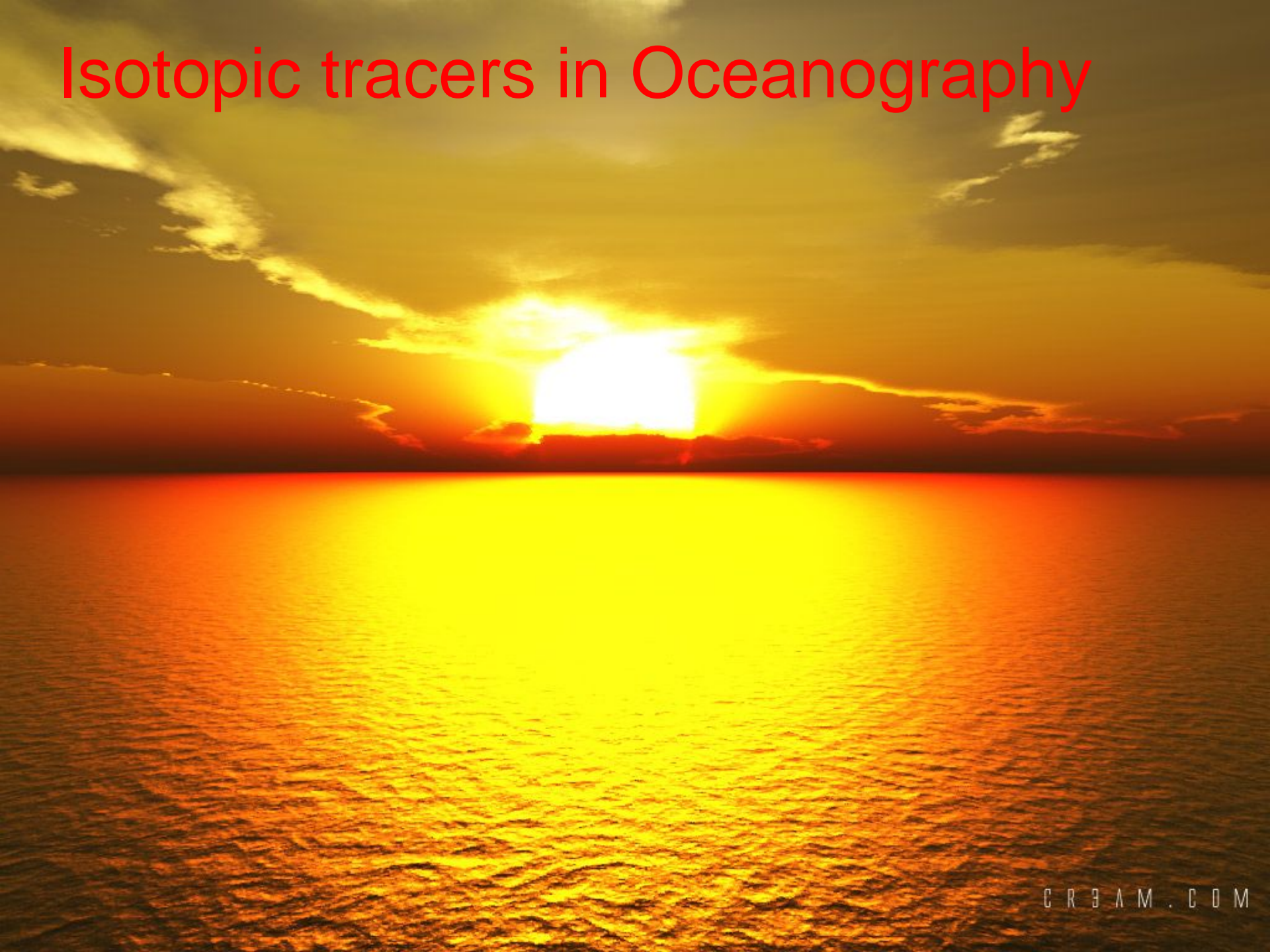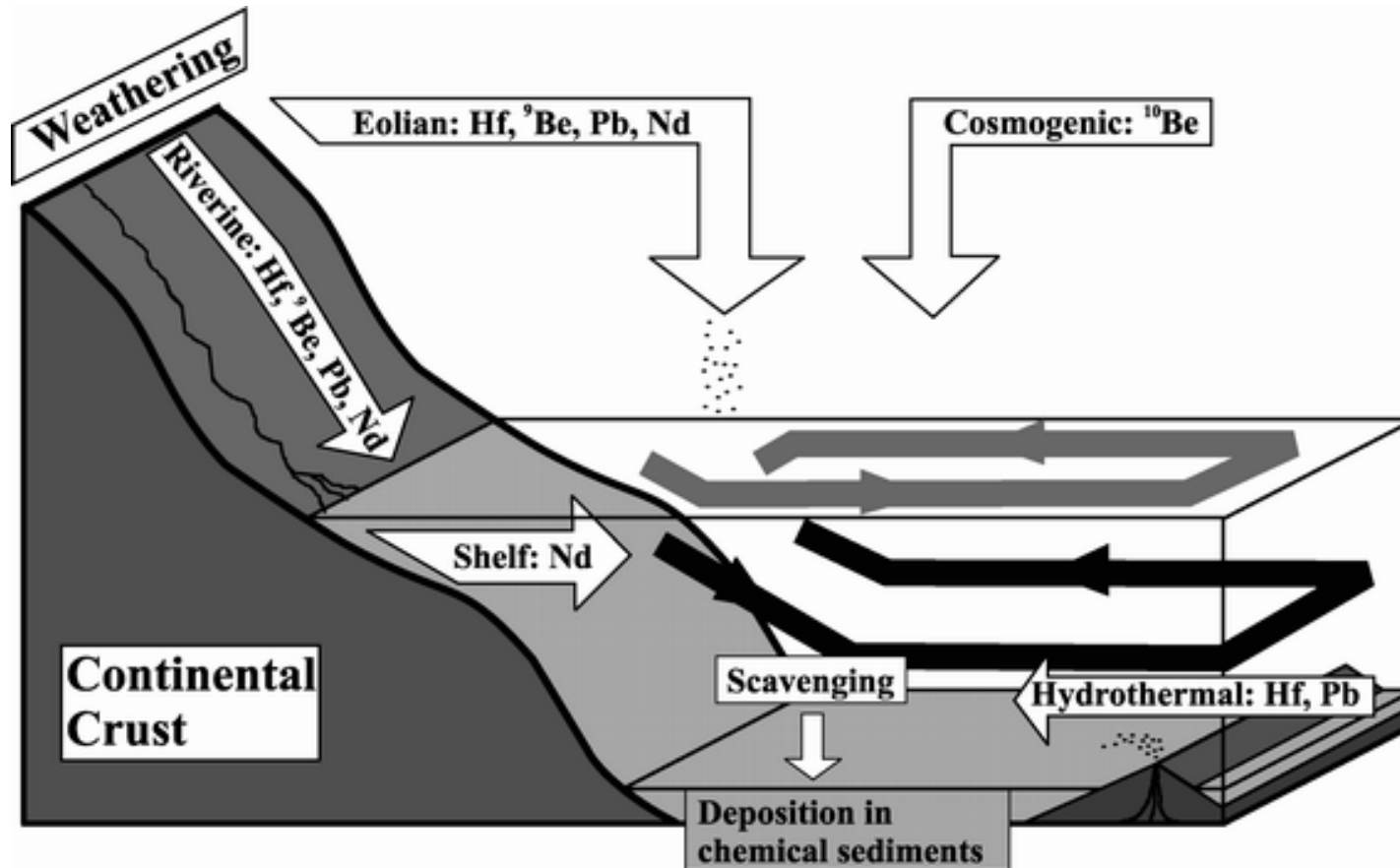# Isotopic tracers in Oceanography
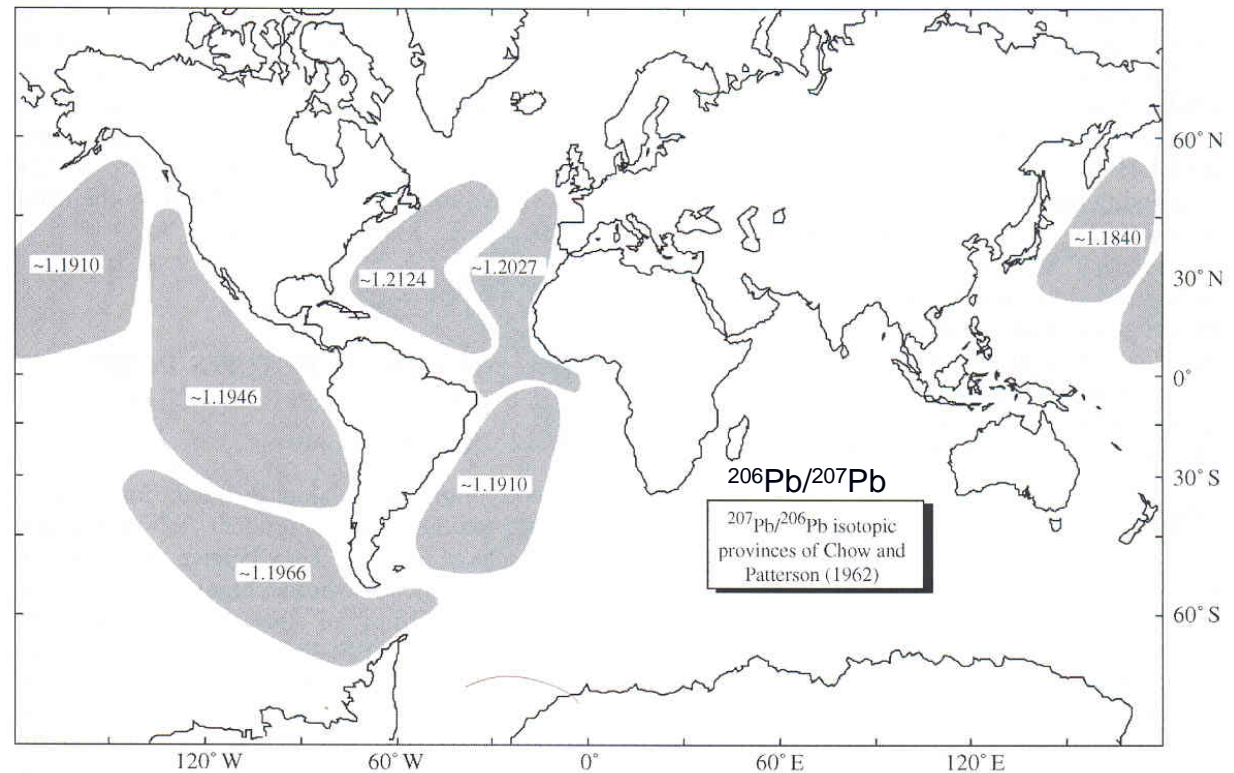
Isotopic tracers in oceanography

Pathways of different trace metals from their sources to their sinks

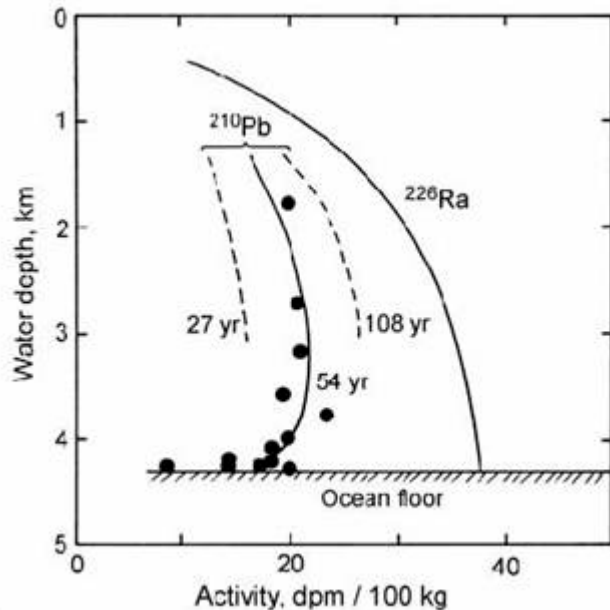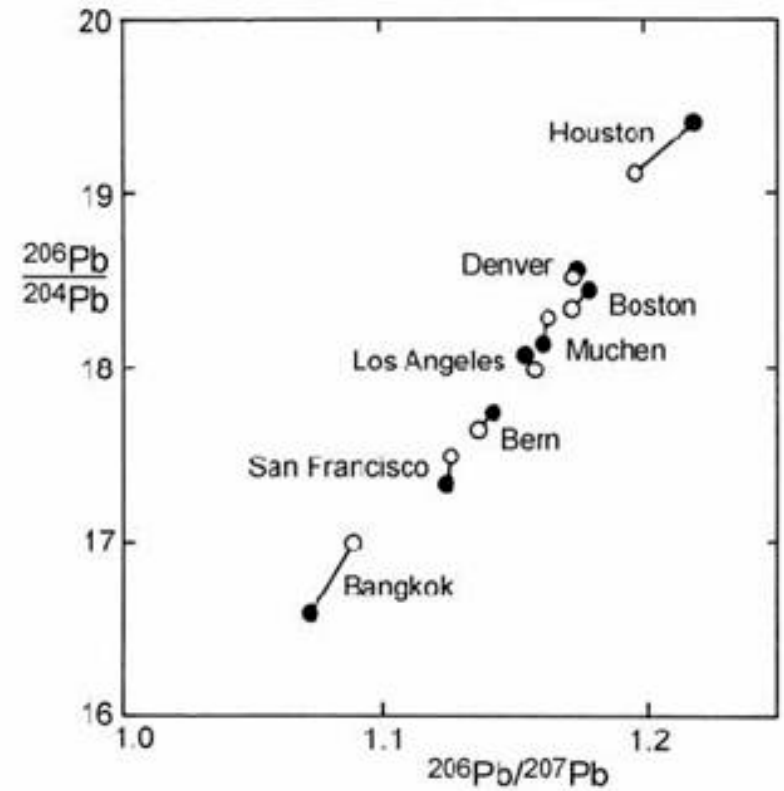# Pb isotopes in the ocean

Chow & Patterson 1959, 1962: First major Pb isotope studies on manganese nodules and pelagic sediments

$^{206}Pb/^{207}Pb$

$^{207}Pb/^{206}Pb$ isotopic provinces of Chow and Patterson (1962)

Result: General distinction between the Pb isotope signatures of Atlantic and Pacific samples. Within each ocean, manganese nodules and pelagic sediments give relatively consistent results

Conclusions: Pb has a relatively short residence time in seawater. Distinct Pacific and Atlantic Ocean signatures reflect average Pb isotope composition of the continents surrounding each ocean

from Goldstein & Hemming: Treatise on Geochemistry, Vol.6

Pb isotopes in the ocean
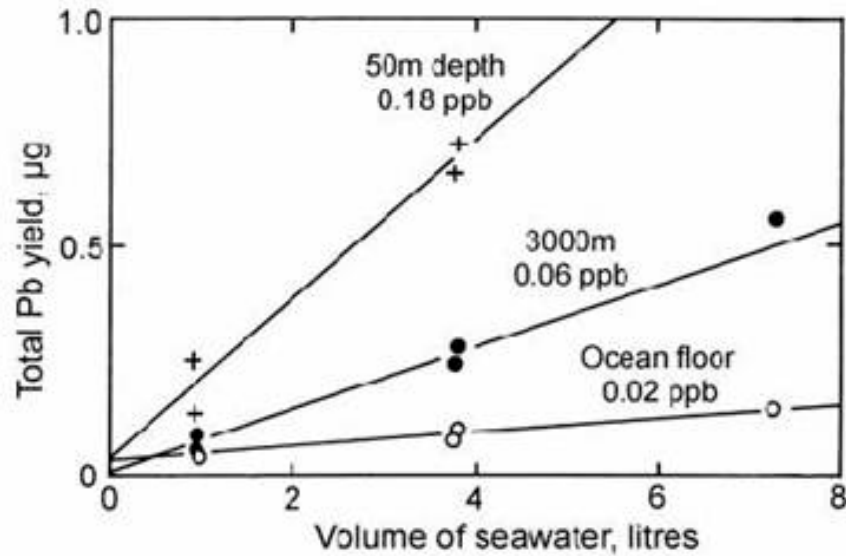
Correspondence between lead ore compositions (●) and gasolines (○) from different countries (Chow 1970)

Nd isotopes in the ocean
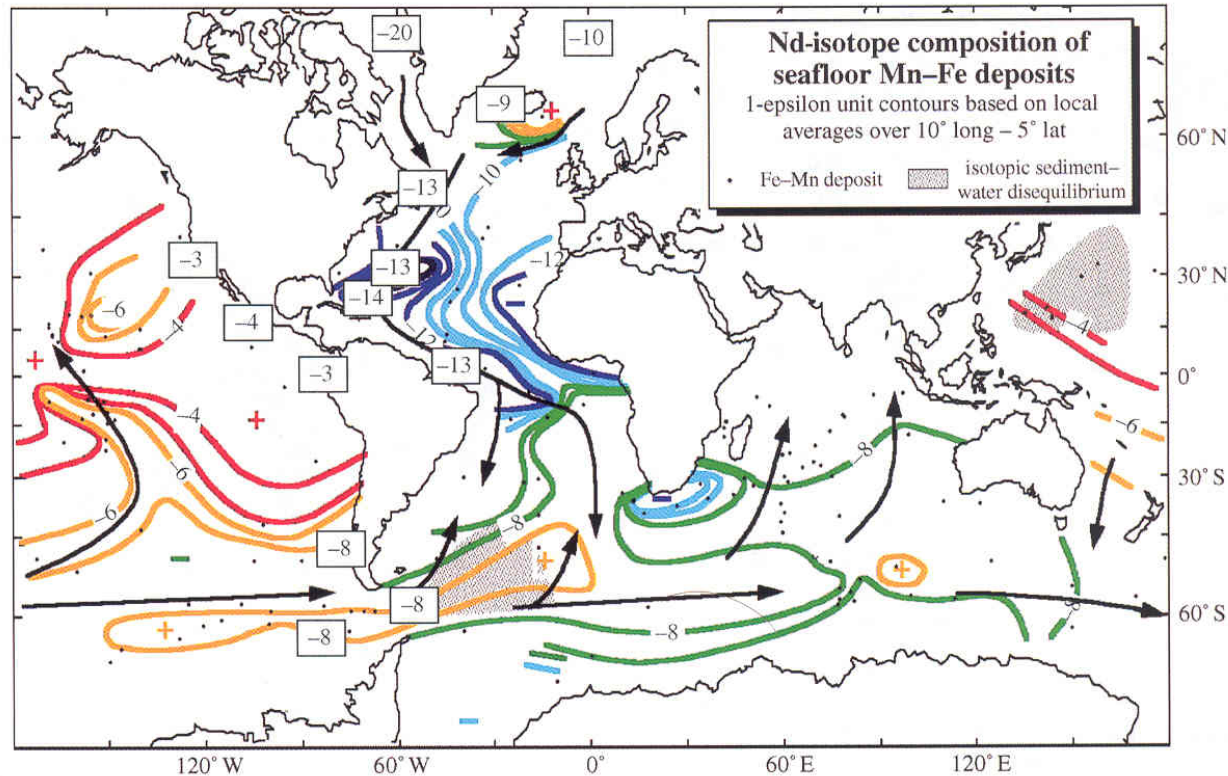
Nd has very short residence time in seawater (different from Sr)
Tracer for water mass circulation and for changes in ocean circulation pattern
^{143}Nd/^{144}Nd ratios allow identification of different source reservoirs
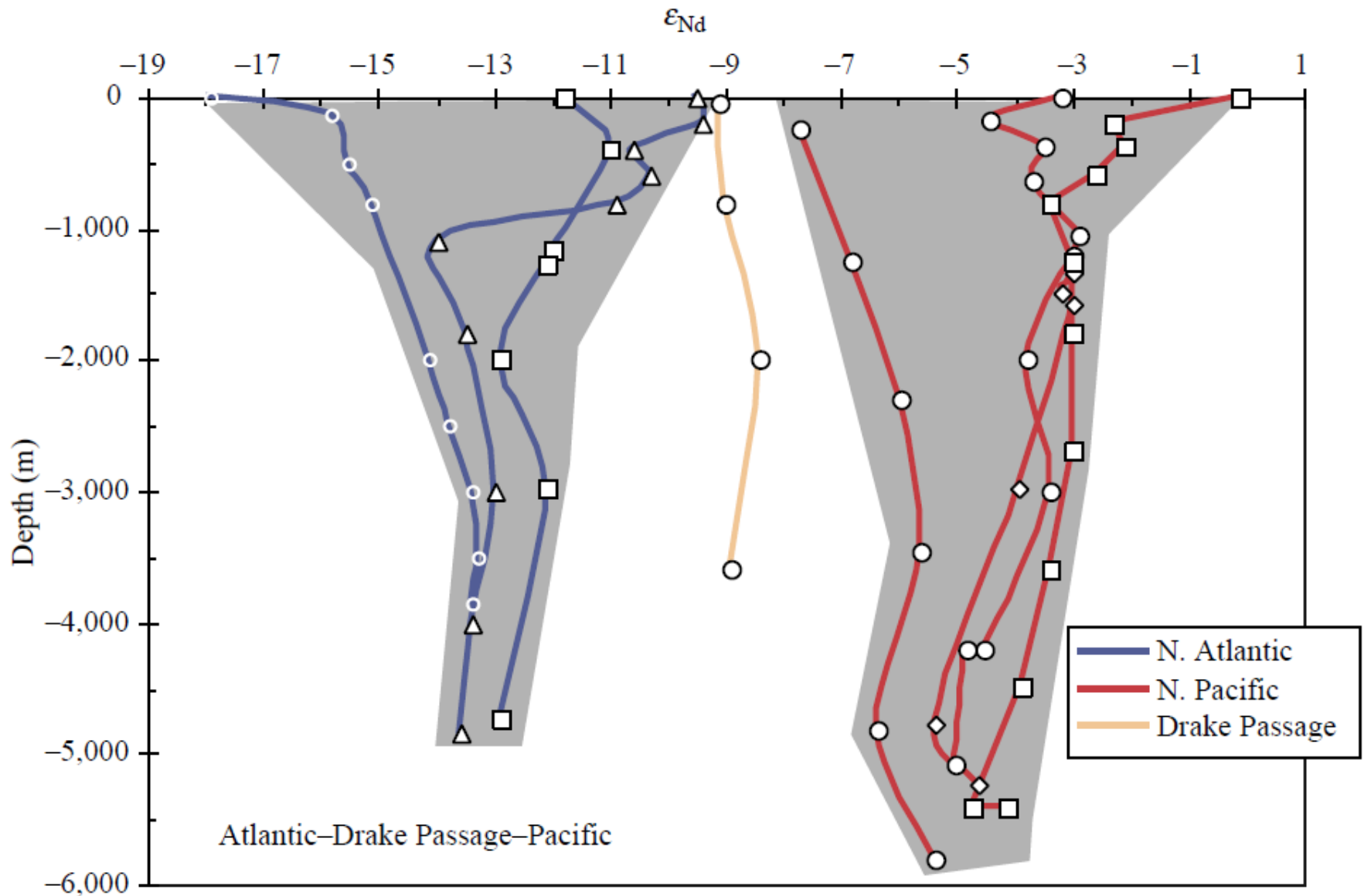
from Goldstein & Hemming: Treatise on Geochemistry, Vol.6

Nd isotopes in seawater

from Goldstein & Hemming: Treatise on Geochemistry, Vol.6

Nd isotopes in seawater

from Goldstein & Hemming: Treatise on Geochemistry, Vol.6
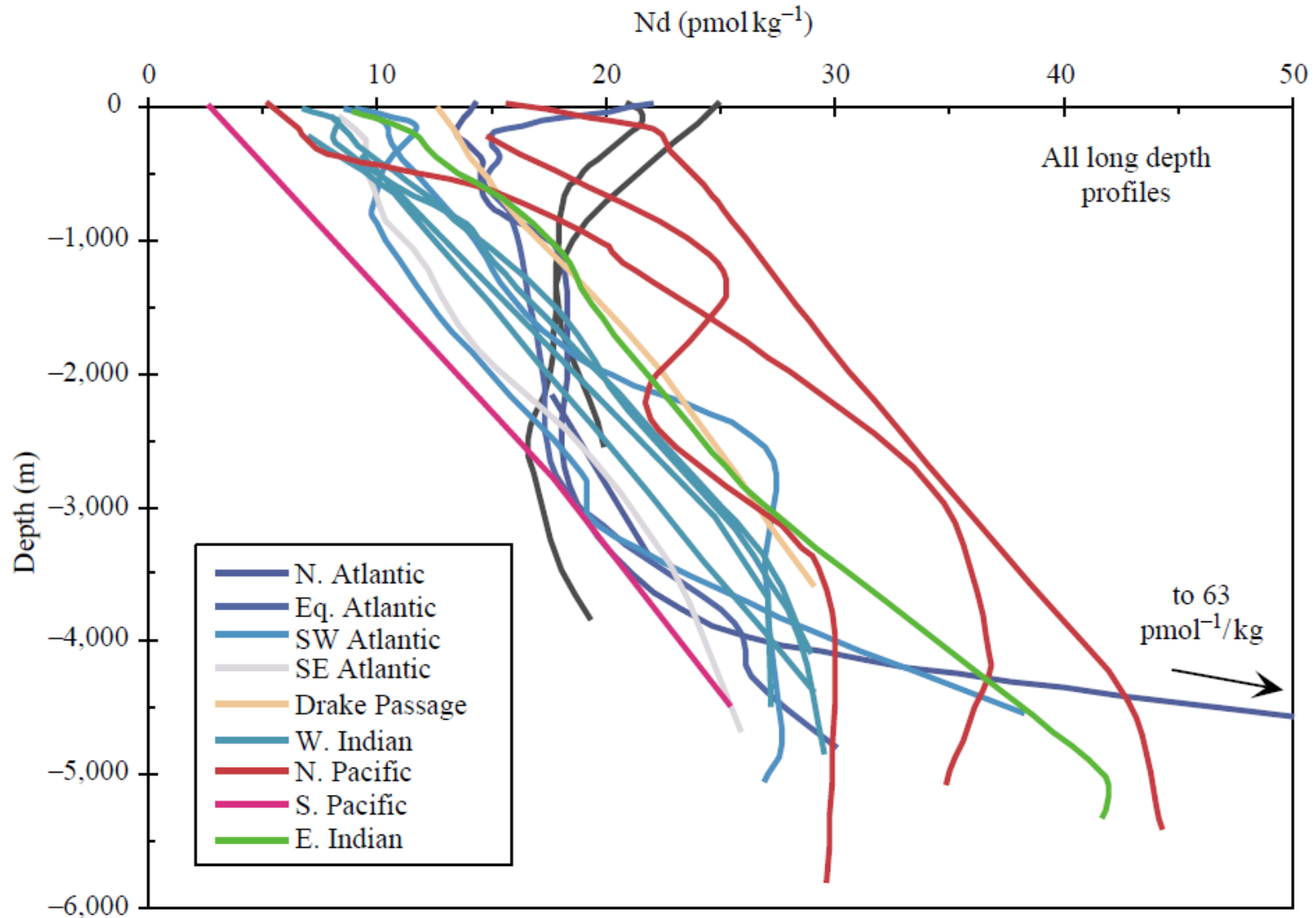
Nd isotopes in seawater
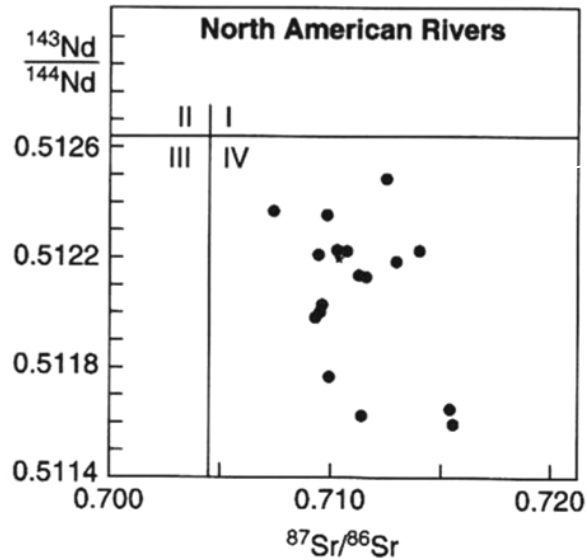
All rivers plotted drain a variety of continental crusts. Relatively low Nd ratio, relatively high Sr ratio

Table 19.3. Average Weighted Concentrations and Isotope Ratios of Nd in River Water Prior to Losses due to Sorption in Estuaries

River Water	Discharge, km^3/y	Nd, ppt	$^{143}Nd/^{144}Nd^a$
Atlantic Ocean rivers	20,323	55.7	0.511991
Pacific Ocean rivers	13,123	27.8	0.512489
Indian Ocean rivers	4,878	26.6	0.512191
Arctic Ocean rivers	4,115	21.6	0.511319
All rivers	42,439	40.5	0.511330

Source: Goldstein and Jacobsen, 1987.

[a] Relative to 0.512638 for CHUR-Nd.

Atlantic – drains continental crust silicates (low Nd ratio)

Pacific – drains rocks that were mantle derived volcanics (high Nd ratio)

Nd isotopes in seawater

Salinity West Atlantic Basin (psu)

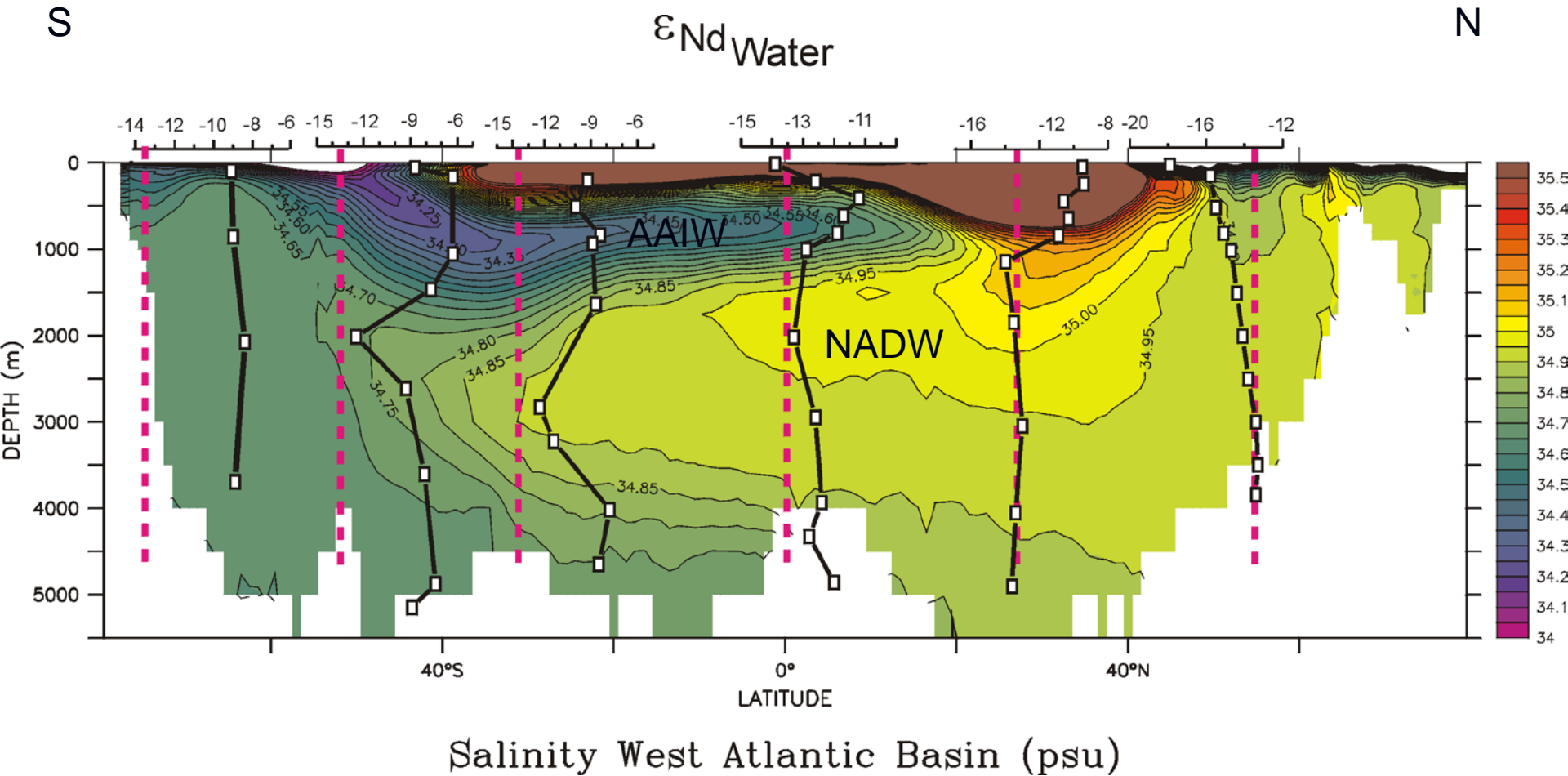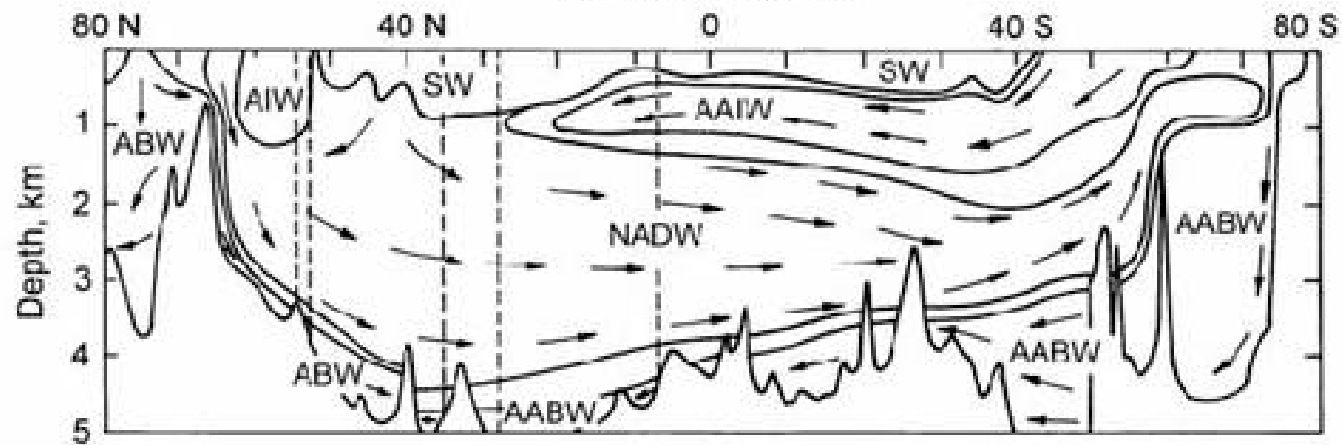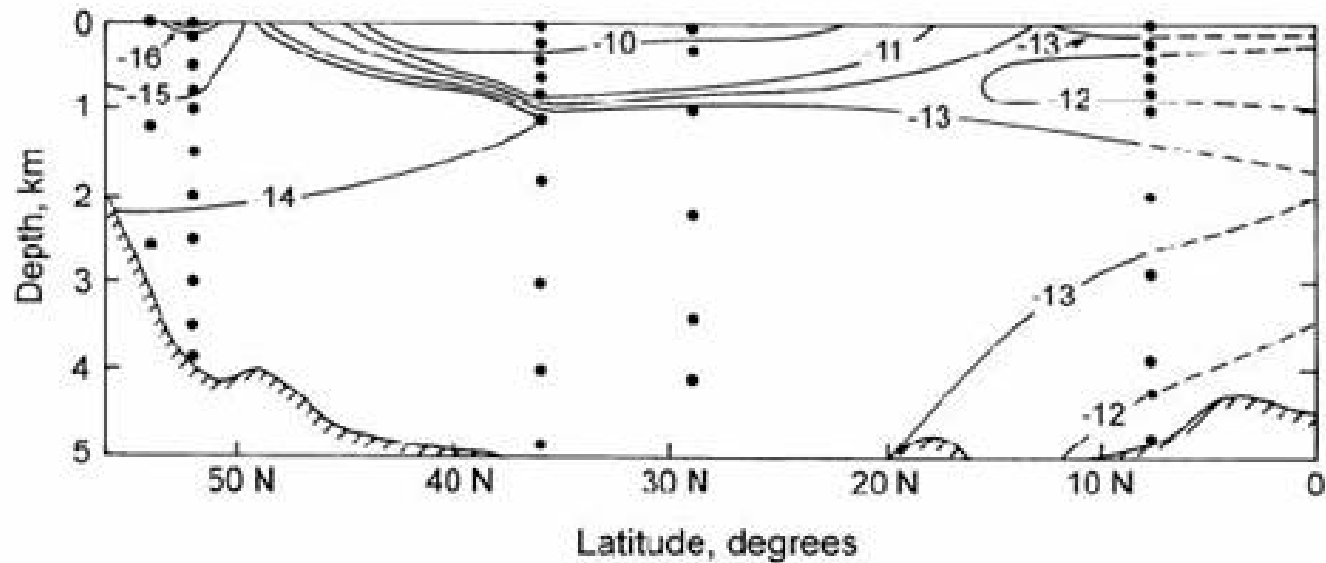*from Goldstein & Hemming: Treatise on Geochemistry, Vol.6*

Nd isotopes in seawater

Nd isotopes in seawater

Comparison of seawater isotope compositions with sea floor Fe-Mn nodules and possible source reservoirs.

seawater

manganese
nodules

crustal sources
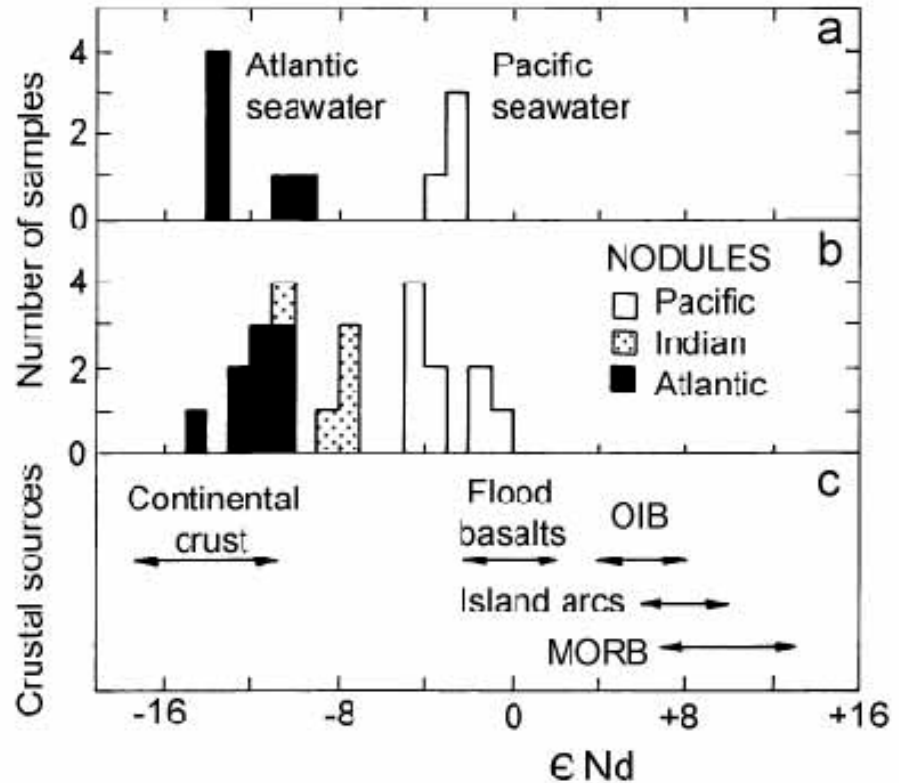
Conclusion: Nd in Atlantic seawater is primarily continental in origin. Consistent with greater discharge of river water into the Atlantic. ~50% of Nd in Pacific seawater appears to be derived from basaltic crustal sources, either from erosion of mafic rocks or from some form of exchange with ocean floor basalts.

from Alan P. Dickin: http://www.onafarawayday.com/Radiogenic/

Nd isotopes in seawater
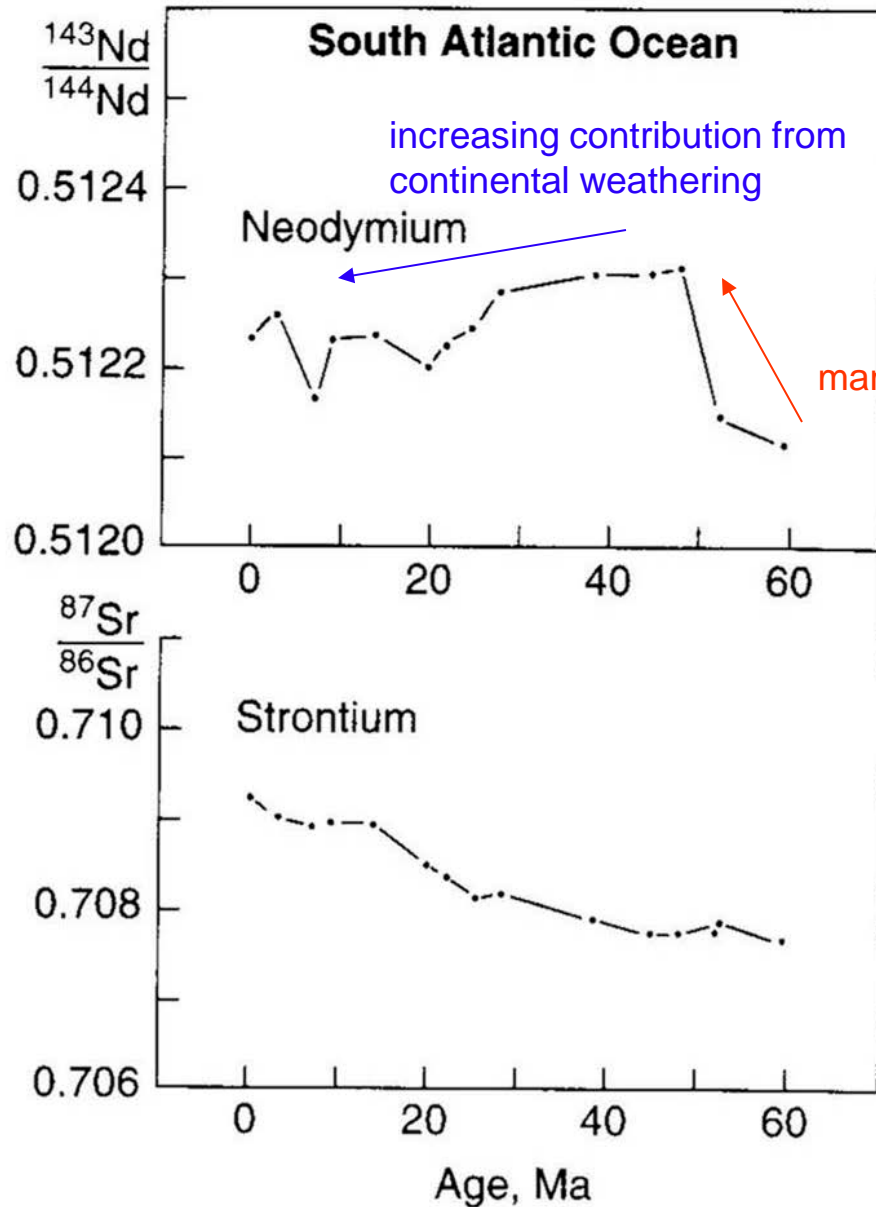
From ferromanganese oxyhydroxide coatings on the foram tests.

Show regional changes in the S. Atlantic Basin.

From foram tests $CaCO_3$

Global change

Nd isotopes in seawater
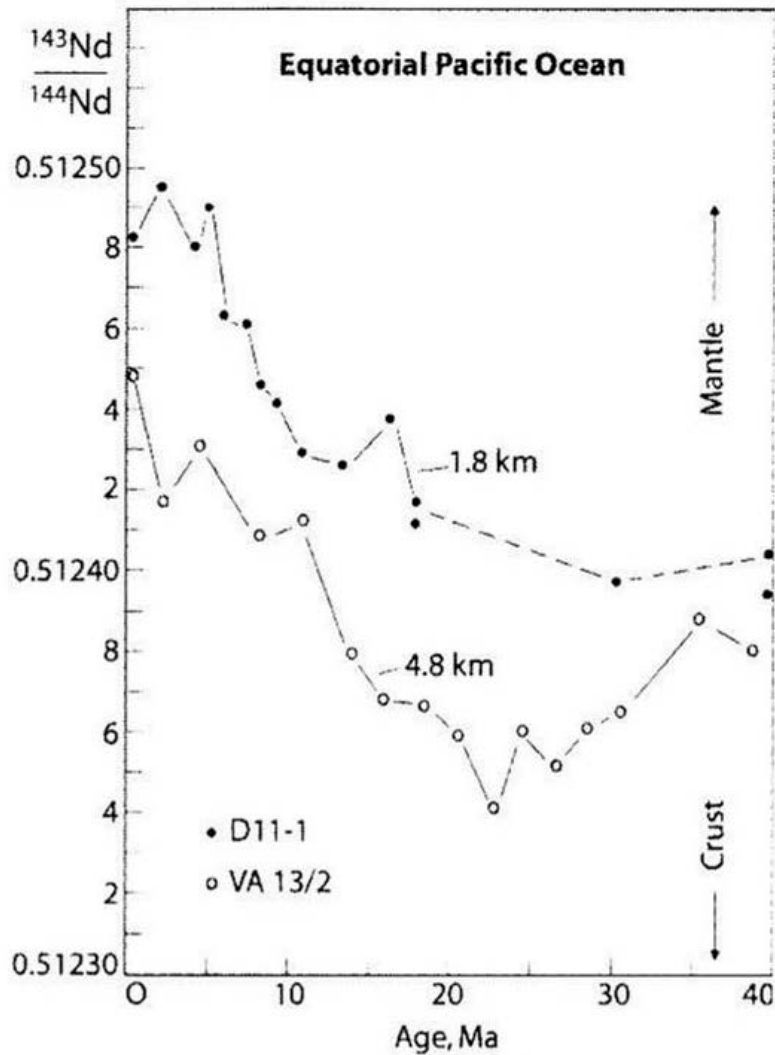
Rise of volcanic (mantle source) inputs to the Pacific

Some differences due to bottom water inputs…deep circulation.

it is the short residence time of Nd in the ocean relative to ocean mixing rates that allows to get basin specific information

Nd isotopes in seawater

Paleo-seawater Nd curves
(derived from conodonts, fish debris, forams or BIFs)
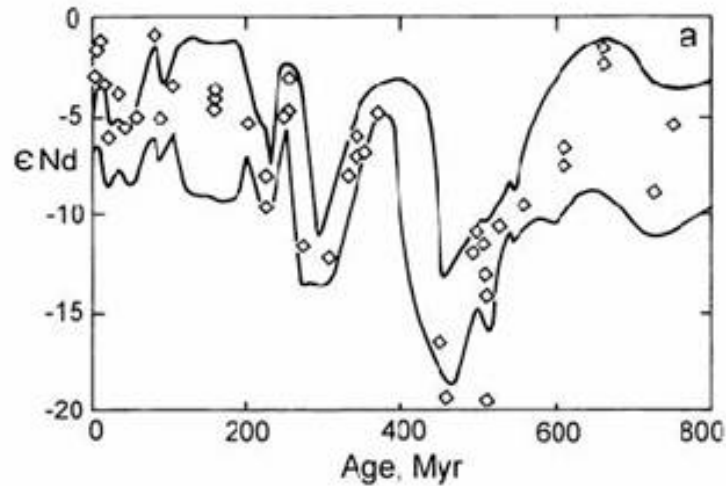
Phanerozoic

Archean & Proterozoic

from Alan P. Dickin: http://www.onafarawayday.com/Radiogenic/

Panama isthmus started to close ca. ~5 Ma ago.
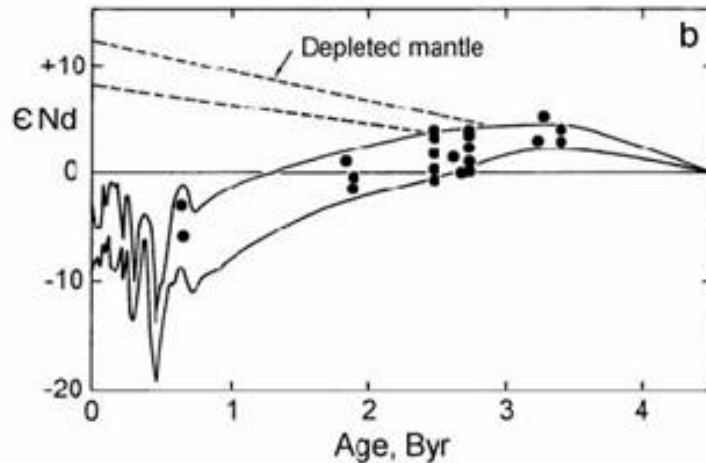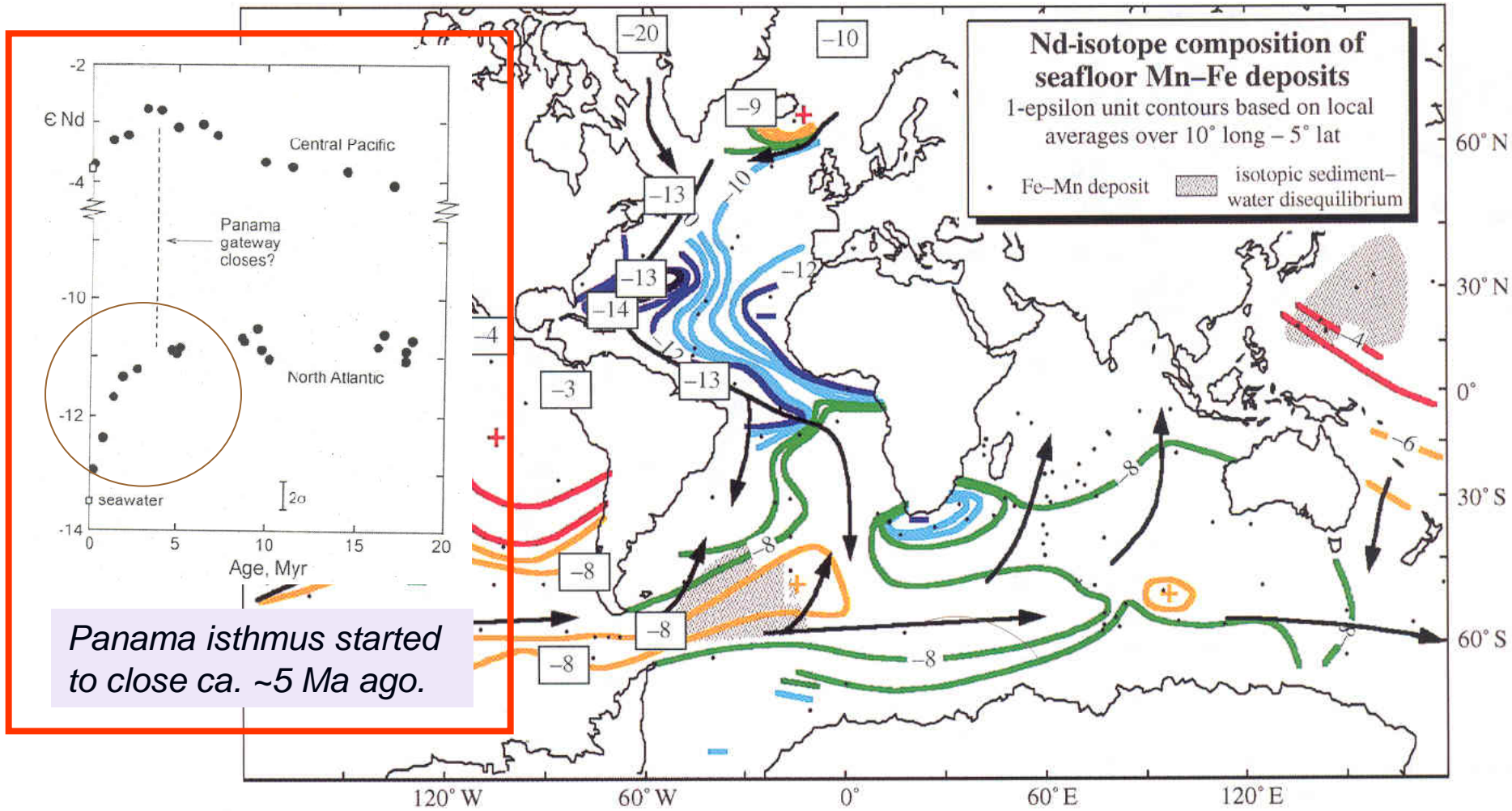
Nd isotopes in seawater
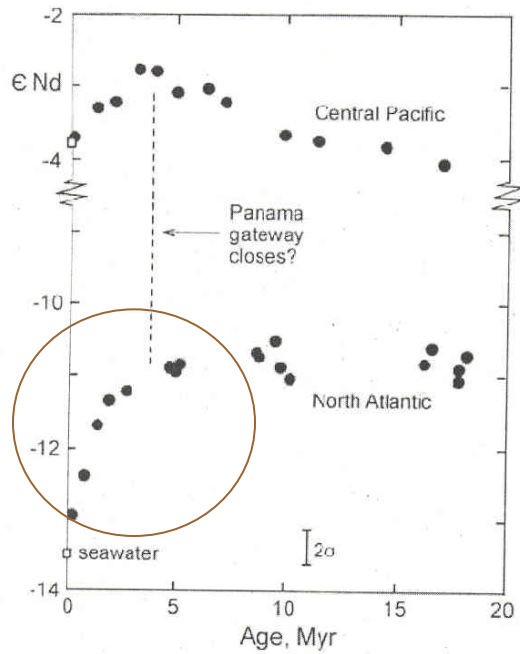
Nd-isotopes Pacific & Atlantic ocean:
closure of Panama gateway at 10-3 Ma.

Nd-(and ^{18}O)-isotopes in foraminifera, Indian ocean: *monsoonal activity*
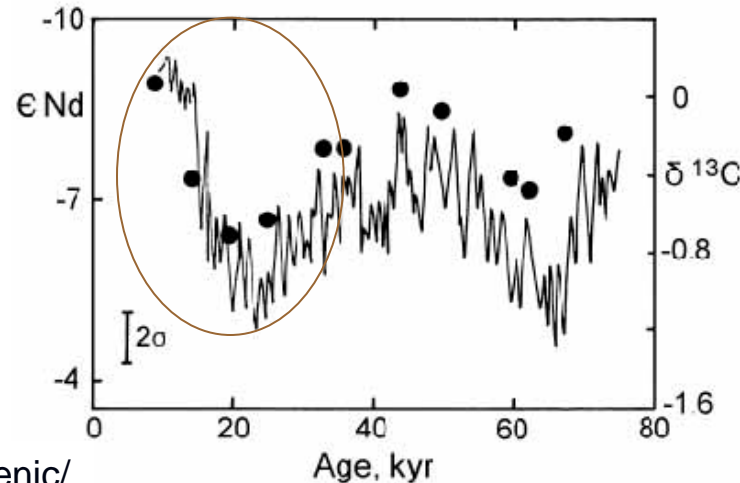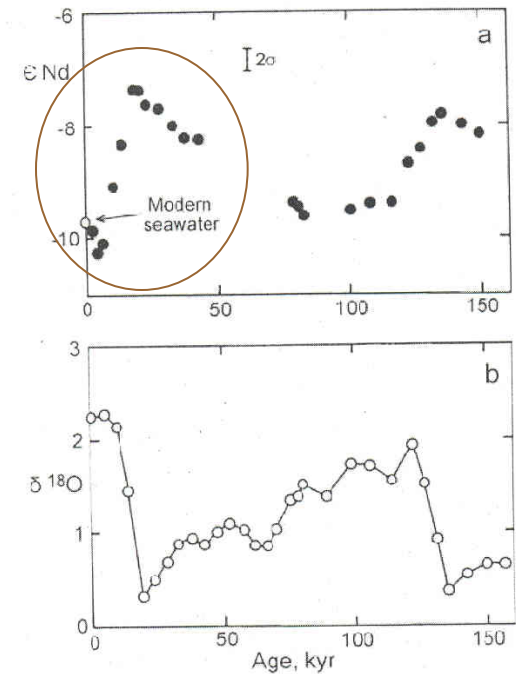
Nd isotopes S-Atlantic: proxy for NADW.

http://www.onafarawayday.com/Radiogenic/

Nd-Hf isotope ratios in rocks and Fe-Mn deposits

Hf: shows relative homogeneous signature in seawater.
Mixing between crustal (negative) and mantle (basaltic crust, pos. Hf values) sources. Crustal source reflects composition of **non-zircon-**bearing sediments.
Mantle-like end member with high εHf (~ +16).
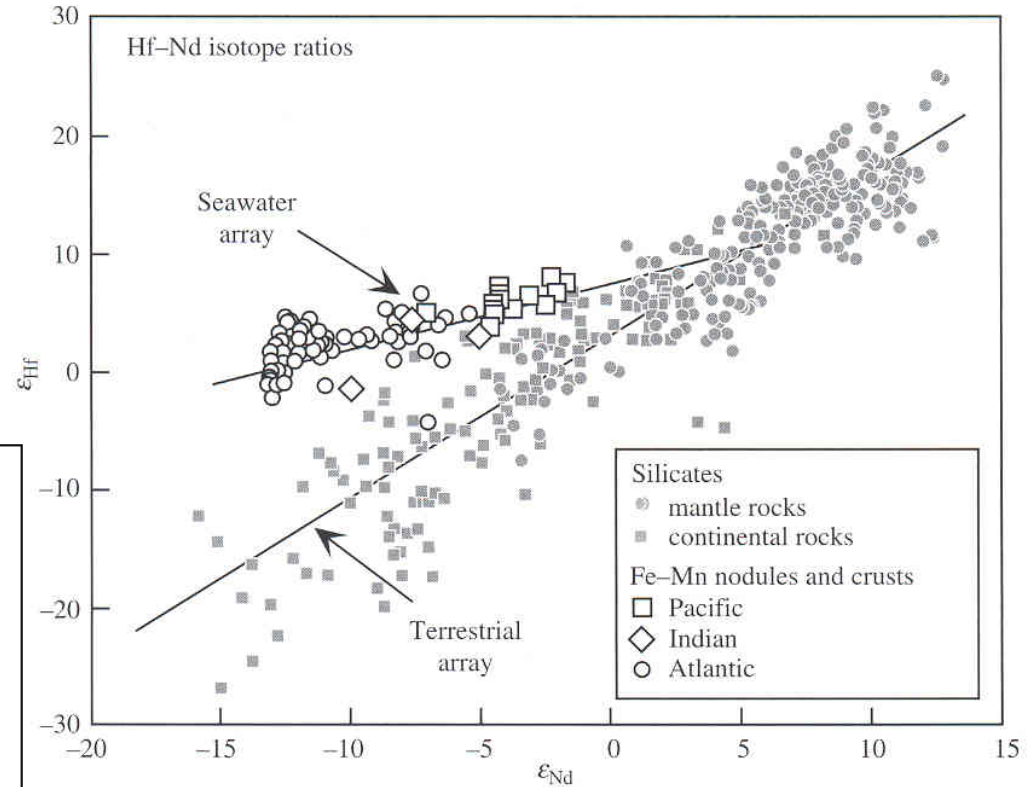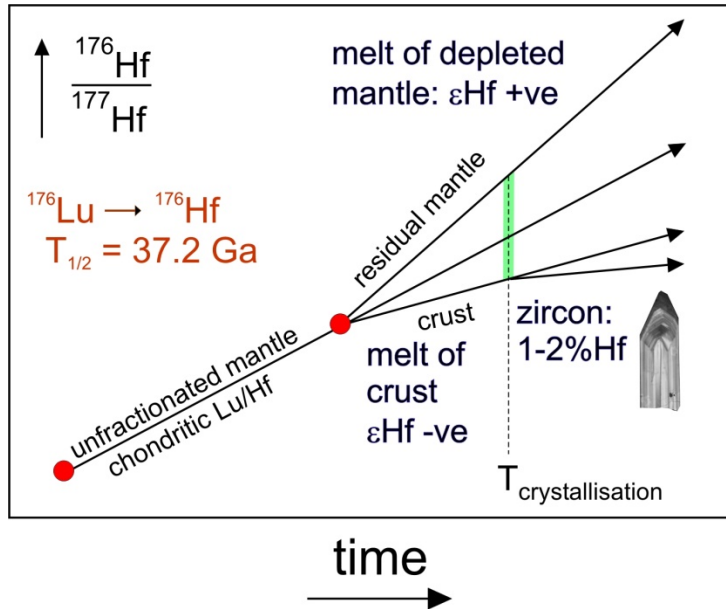
from Goldstein & Hemming (2004): Treatise on Geochemistry, Vol.6

Sr in the oceans

^{87}Sr/^{86}Sr of modern (and ancient) seawater is homogeneous on a global scale. Residence time (~4 Ma, Hodell et al. 1990) is long compared to mixing time (1-2 ka)

Sr isotope composition of the oceans is determined by the relative contributions of Sr from river waters and hydrothermal vents
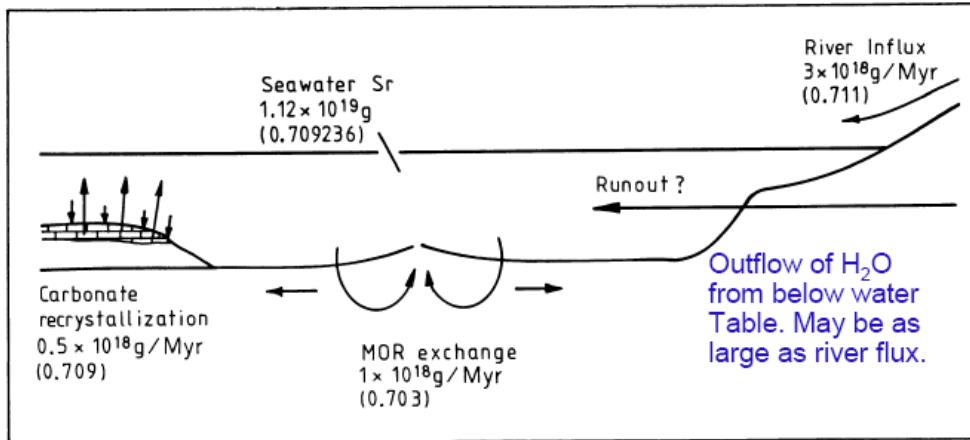
Burke et al. 1982

DePaolo 1987
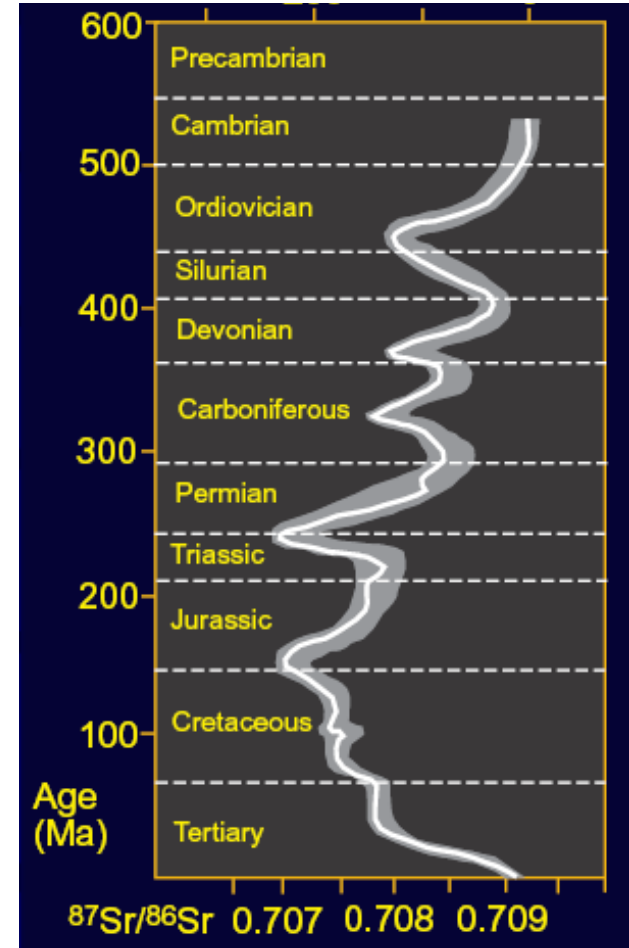
Based on brachiopods, belemnites, conodonts, foraminifera, micritic matrix

U-series disequilibrium methods
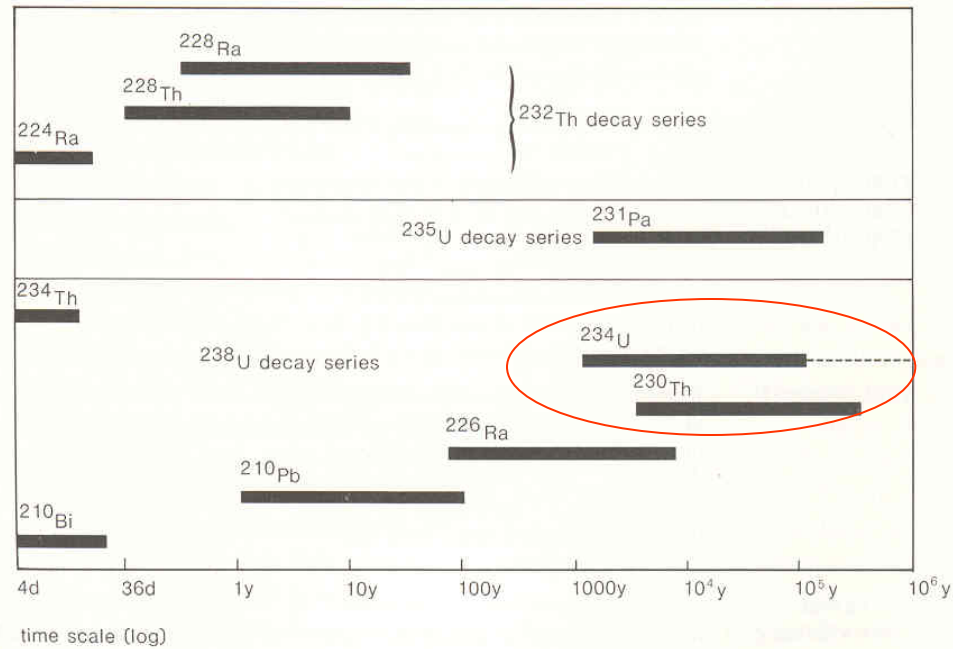
Potts 1987

Nuklid	Halbwertszeit [a]	λ [a^{-1}]
^{234}U	2.48×10^5	2.794×10^{-6}
^{230}Th	7.52×10^4	9.217×10^{-6}
^{226}Ra	1.622×10^3	4.272×10^{-4}
^{231}Pa	3.248×10^4	2.134×10^{-5}
^{210}Pb	22.26	3.11×10^{-2}

U-series disequilibrium methods

$$^{238}U \rightarrow {}^{234}U \rightarrow {}^{230}Th \rightarrow {}^{206}Pb$$
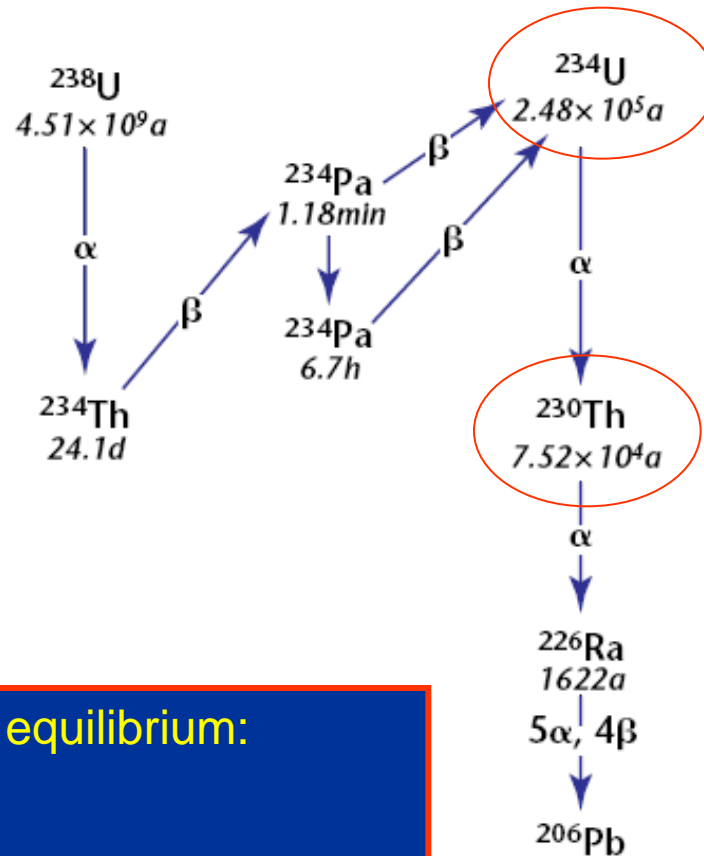
In case of secular equilibrium:
$\lambda_1 N_1 = \lambda_2 N_2$
$A_1 = A_2$
or $A_i = \lambda_i N_i$
e.g. $(^{230}Th/^{238}U) = 1$

U-series disequilibrium methods

Uranium "Parent"

Inset:

"Daughter"

"Grand-daughter" ~5 half-lives
2 half-lives
1 half-life

Uranium "Parent"

"Daughter"

"Grand-daughter"

Lead

In case of secular equilibrium:
$\lambda_1 N_1 = \lambda_2 N_2$
$A_1 = A_2$
or $A_i = \lambda_i N_i$
e.g. $(^{230}Th/^{238}U) = 1$

$$^{238}U \rightarrow {}^{234}U \rightarrow {}^{230}Th \rightarrow {}^{206}Pb$$

Isotopes in the decay series can become fractionated relative to one another, due to variations in their chemistry (seawater) or the structural site (crystal) → secular disequilibrium.

Such a situation can be utilised in two different ways as a dating tool, the "daughter-excess" and "daughter-deficiency" dating methods. The concentration in excess of the equilibrium is called "unsupported" or "an excess" of a nuclide

U-series disequilibrium methods

^{238}U $\rightarrow$ ^{234}U $\rightarrow$ ^{230}Th $\rightarrow$ ^{206}Pb (excluding some "shorties")

$T_{1/2} = 75$ ka
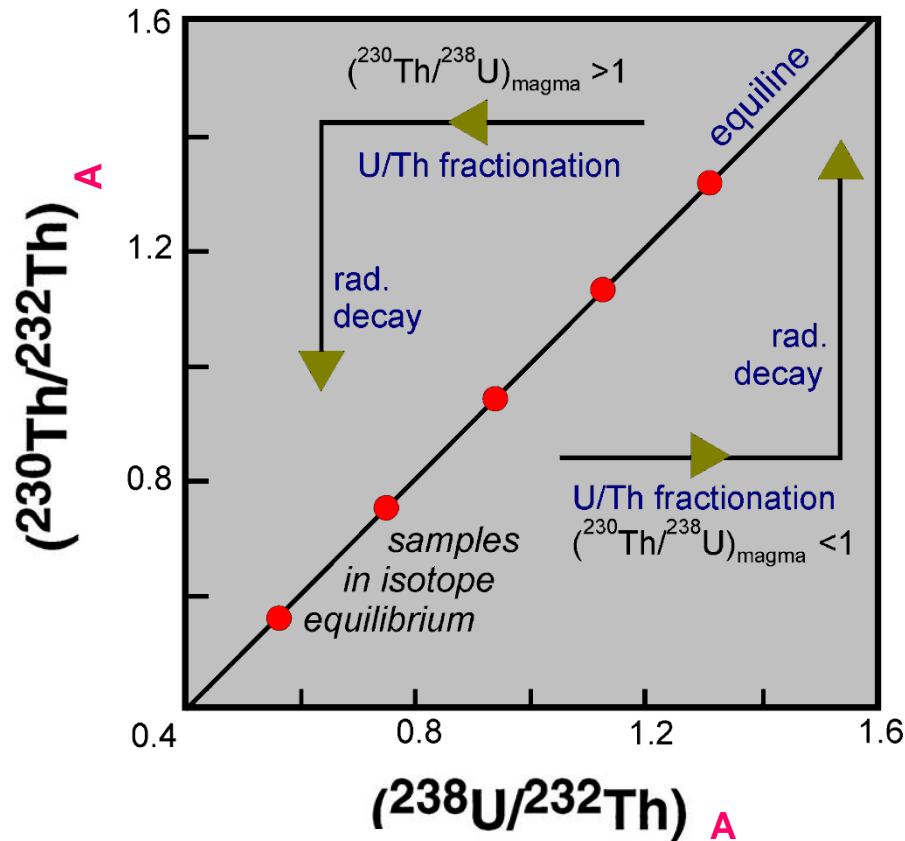
Equilibrium:
$\lambda_1 N_1 = \lambda_2 N_2$
$A_1 = A_2$
$(^{230}Th/^{238}U) = 1$

Allègre & Condomines (1976) EPSL 28, (1982) Nature 299

$$\frac{A(^{230}Th)}{A(^{232}Th)} = \left[\frac{A(^{230}Th)}{A(^{232}Th)}\right]_{excess} \cdot (e^{\lambda 230 t}) + \frac{A(^{238}U)}{A(^{232}Th)} \cdot (1 - e^{\lambda 230 t})$$

^{230}Th aus excess Th ^{230}Th aus ^{238}U-Zerfall

U-Serien-Ungleichgewichtsmethoden

$$^{238}U \rightarrow {}^{234}U \rightarrow {}^{230}Th \rightarrow {}^{206}Pb$$

$^{222}Rn \longrightarrow {}^{210}Pb$ $^{222}Rn \longrightarrow$

$^{238}U \longrightarrow {}^{234}U \longrightarrow {}^{230}Th \longrightarrow {}^{226}Ra$

Gelöst in Meerwasser
U: ~ 3 ppb
Th: < 0.0015 ppb

- In oxidized waters, U is soluble as U(VI), Uranyl ions = UO_2^{++}, strong complexes with carbonates
- Th is present as Th(IV); highly insoluble; sorbs to surfaces

Residenzzeit:
U: 0.5-3 Ma
Th: ~300 a

$$RT = \frac{\text{Total amount of dissolved element}}{\text{Rate of influx or efflux of element}}$$

^{226}Ra

^{230}Th

Aufgrund der schnellen Sedimentation von Th aus dem Meerwasser weisen junge pelagische Gesteine einen **^{230}Th-Überschuß** auf!

$(^{231}Pa, {}^{210}Pb, etc.)$

^{230}Th/^{232}Th (ionium) method

$$^{238}U \rightarrow \ ^{234}U \rightarrow \ ^{230}Th \rightarrow \ ^{206}Pb$$

1. Preferential removal of Th from seawater

2. Freshly deposited sediment contains unsupported ^{230}Th

3. Decay of excess ^{230}Th in the sediment (see figures)

4. Allows to determine sedimentation rates

$$R = R_o e^{-\lambda t}$$
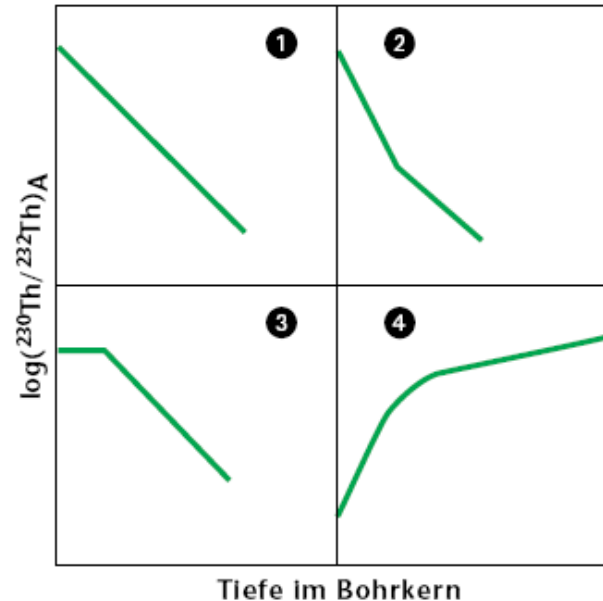
$$T = 1/\lambda \ \ln(R_o/R)$$

sedimentation rate:

$$a = h/t \ (h = depth)$$
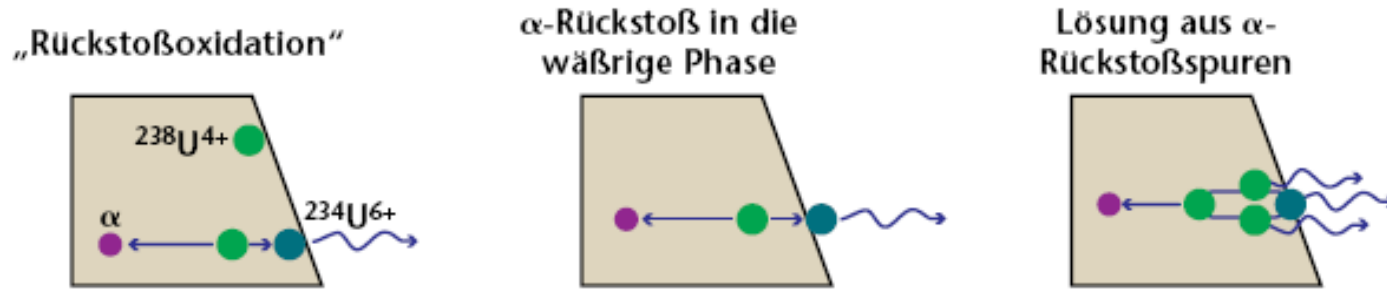$$R = R_o e^{-\lambda h/a}$$
$$\ln R = \ln R_o - \lambda h/a$$

Tiefe im Bohrkern

1   Normal pattern
2   change in sedimentation rate
3   Mixing of sediments (e.g. bioturbation) at top
4   dominance of U-supported ^{230}Th

^{238}U-^{234}U disequilibrium method

„Rückstoßoxidation"

α-Rückstoß in die wäßrige Phase

Lösung aus α-Rückstoßspuren

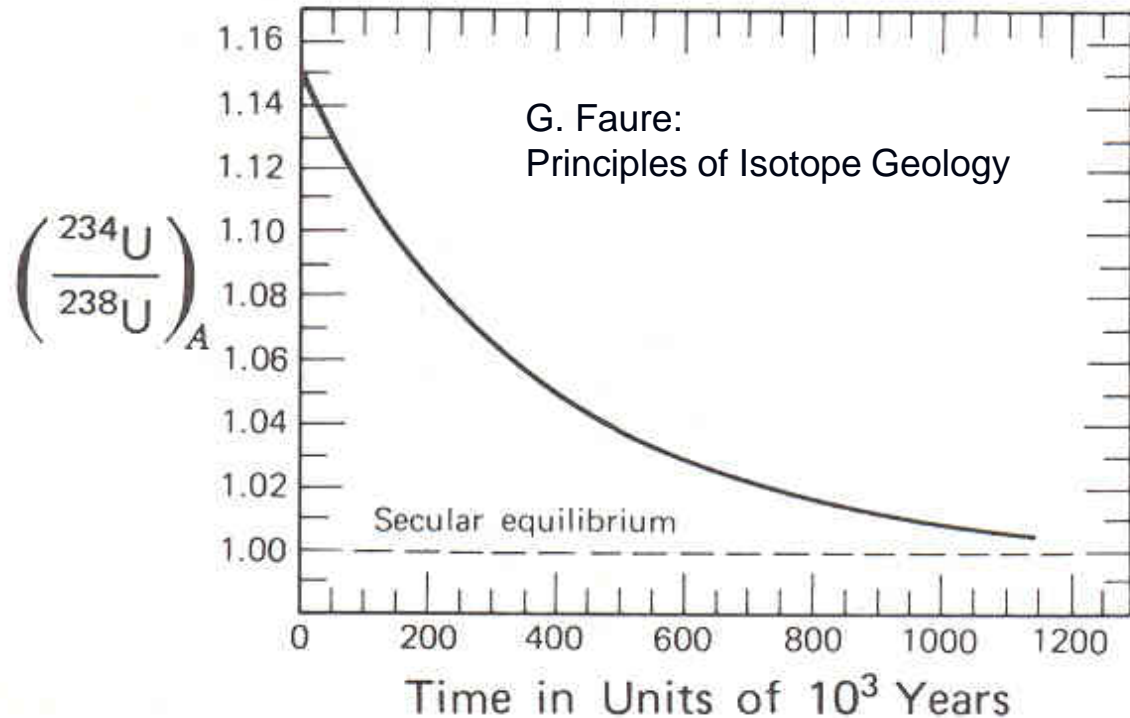**Stosch:** http://www.dmg-home.de/Ressourcen/Internet-Kurse/Isotopengeochemie.pdf

The activity of ^{234}U in seawater not in secular equilibrium with that of ^{238}U

^{234}U is preferentially leached out of radiation damaged crystal lattice sites during weathering

The $^{234}U_A/^{238}U_A$ ratio of sea water is about 1.15

^{238}U-^{234}U disequilibrium method

Activity disequilibrium between ^{234}U and ^{238}U isotopes in seawater

$$\left(\frac{^{234}U}{^{238}U}\right)_A$$

G. Faure:
Principles of Isotope Geology

Secular equilibrium

Time in Units of 10^3 Years
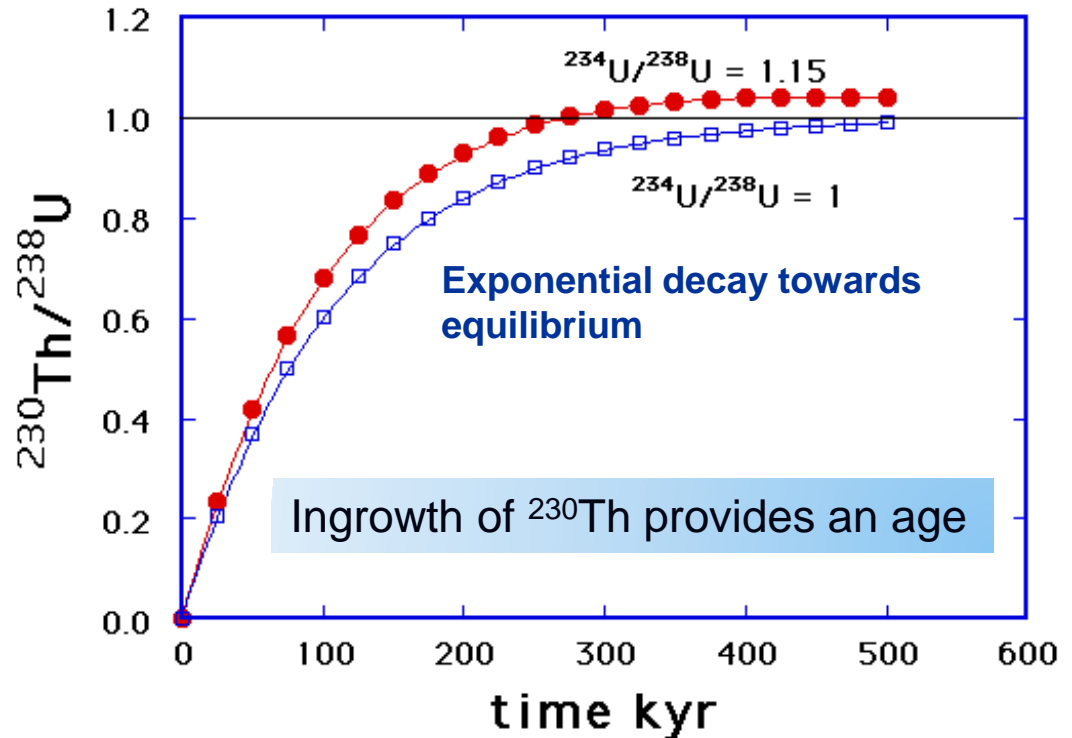
1. $^{234}U/^{238}U$ activity ratio of seawater is ~1.15 (contains excess ^{234}U)

2. When $CaCO_3$ is produced by coral or foraminifera it incorporates some U from seawater but almost no Th

3. When e.g. a coral is separated from seawater, excess ^{234}U decays into ^{230}Th
The limit of the dating range is reached when secular equilibrium between ^{234}U and ^{238}U is established

^{230}Th-^{238}U and ^{230}Th-^{234}U methods

$$^{238}U \rightarrow {}^{234}U \rightarrow {}^{230}Th \rightarrow {}^{206}Pb$$

Th/U isotope ratio can be used to date carbonates provided we know:

(1) the initial ^{234}U/^{238}U ratio

(2) that the initial ^{230}Th/^{238}U ratio was close to zero and that the sample has remained closed with respect to U, Th and their intermediate isotopes

^{234}U/^{238}U = 1.15

^{234}U/^{238}U = 1

Exponential decay towards equilibrium

Ingrowth of ^{230}Th provides an age

y-axis: ^{230}Th/^{238}U

x-axis: time kyr

Must account for initial Th (by measuring ^{232}Th) and initial seawater ^{234}U/^{238}U