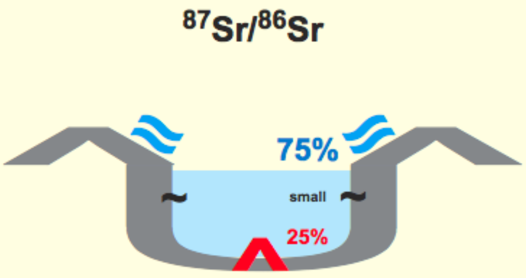
# Seawater Isotope Mass Balance

$$R_{box_{ss}} = (F_R\, R_R + F_H\, R_H + F_D\, R_D) / (F_R + F_H + F_D)$$



R = isotope ratio

F = flux

sub R = riverine

sub H = hydrothermal

sub D = diagenetic/boundary

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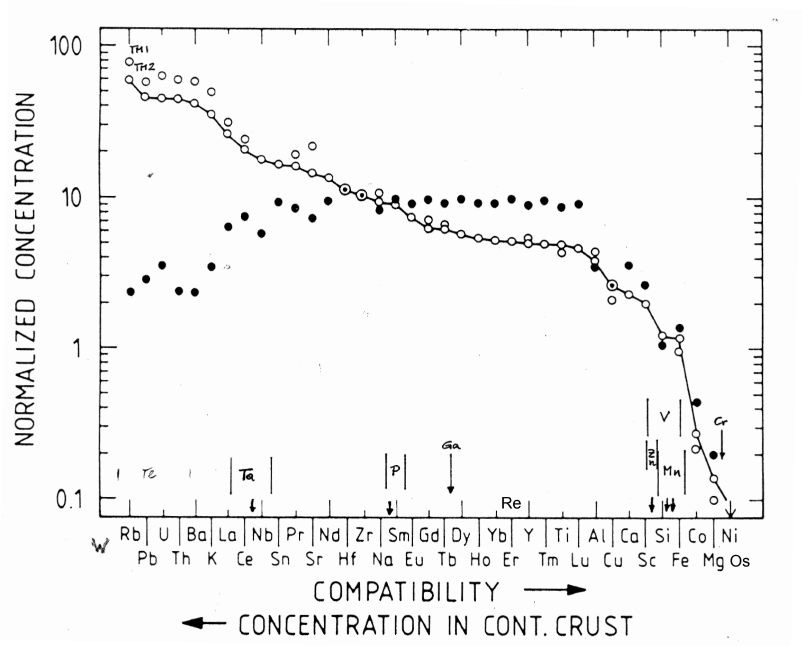
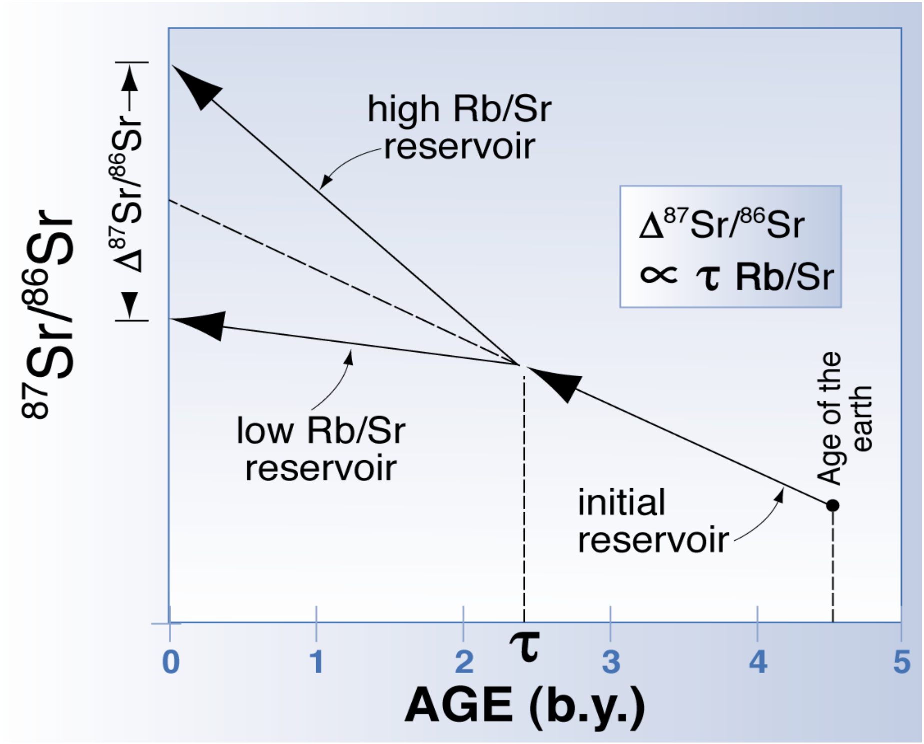
## Chemical differentiation of Earth: The relationship between continental crust, oceanic crust, and the mantle.



after Hofmann, EPSL 90, 297-314, 1988

## $^{87}$Rb-$^{87}$Sr Systematics



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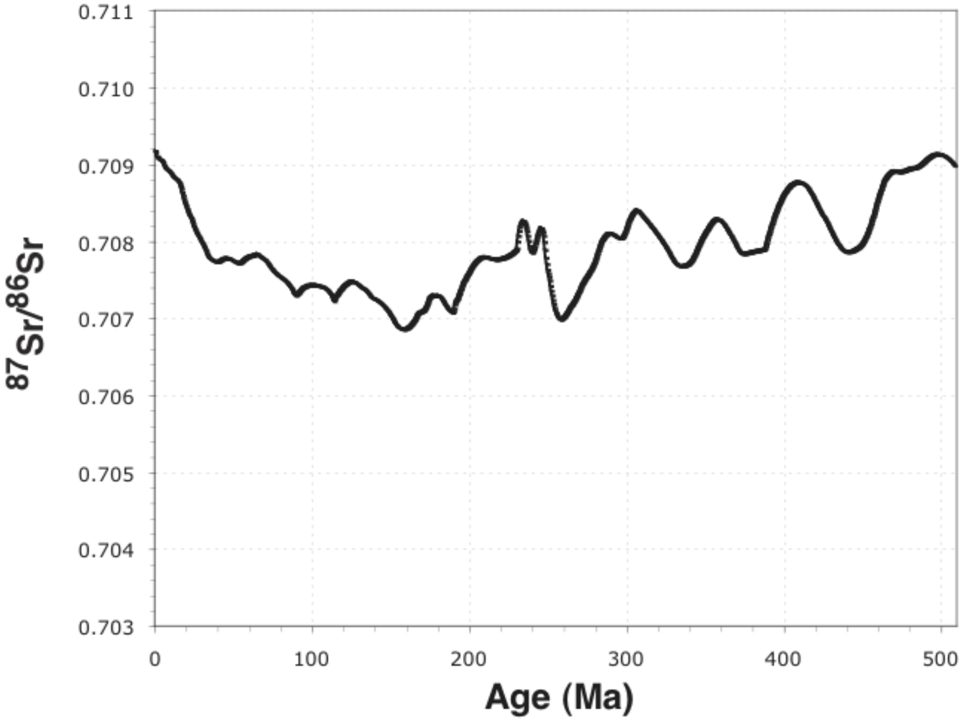
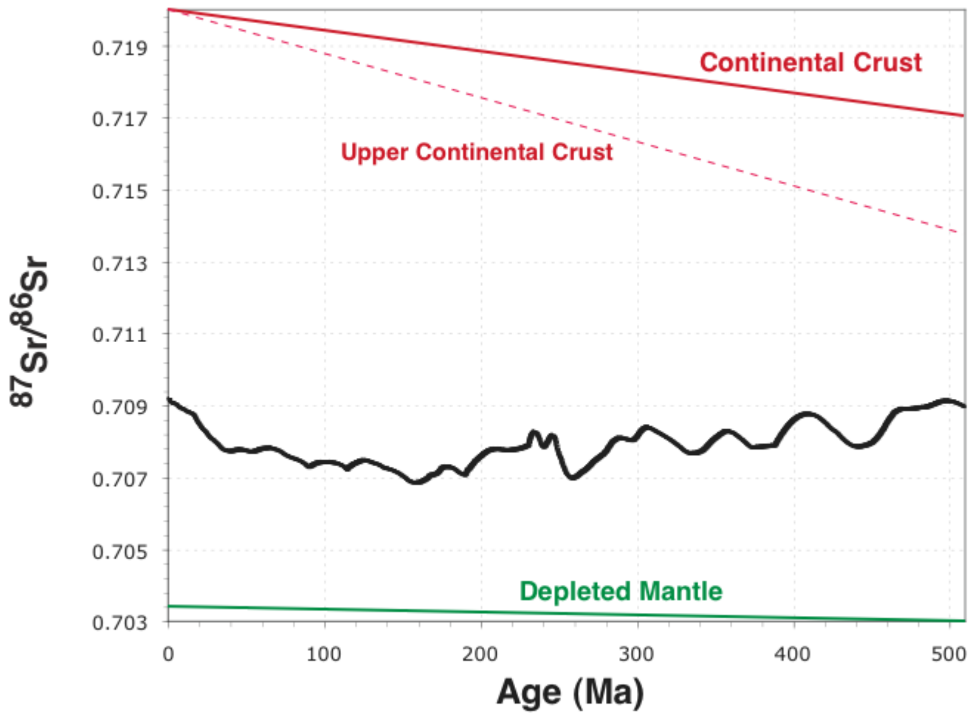
## The $^{87}$Sr/$^{86}$Sr Record of Seawater



# The $^{87}$Sr/$^{86}$Sr Record of Seawater



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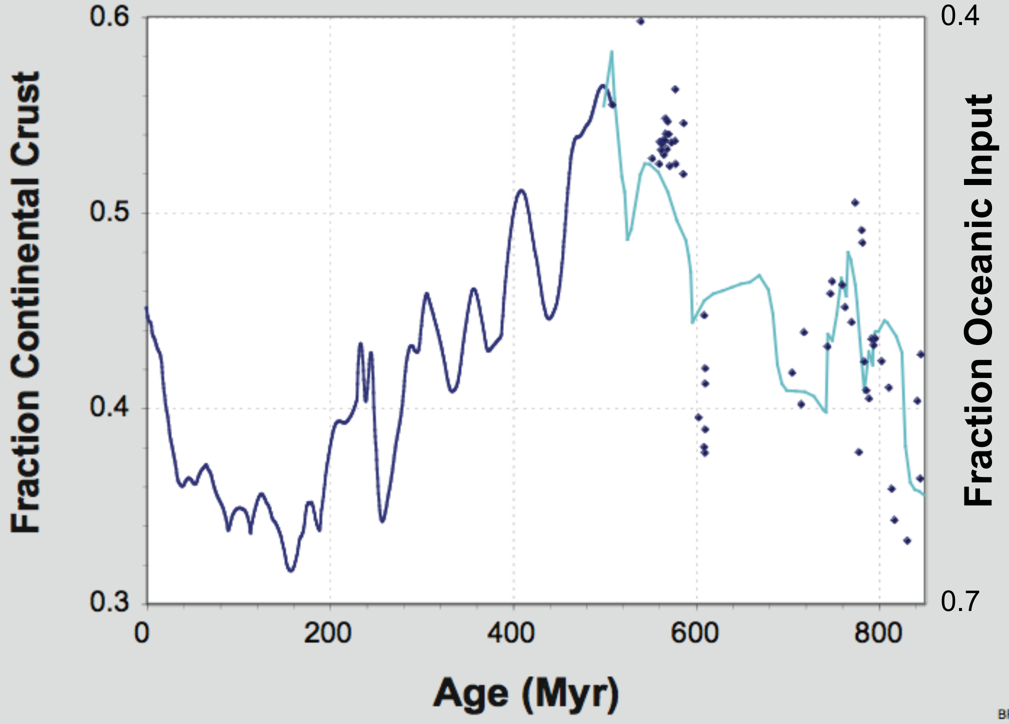
Albarede et al. (1980), and many others: hydrothermal flux vs continental runoff

Brass (1976): “granitic” vs “basaltic” runoff from continents



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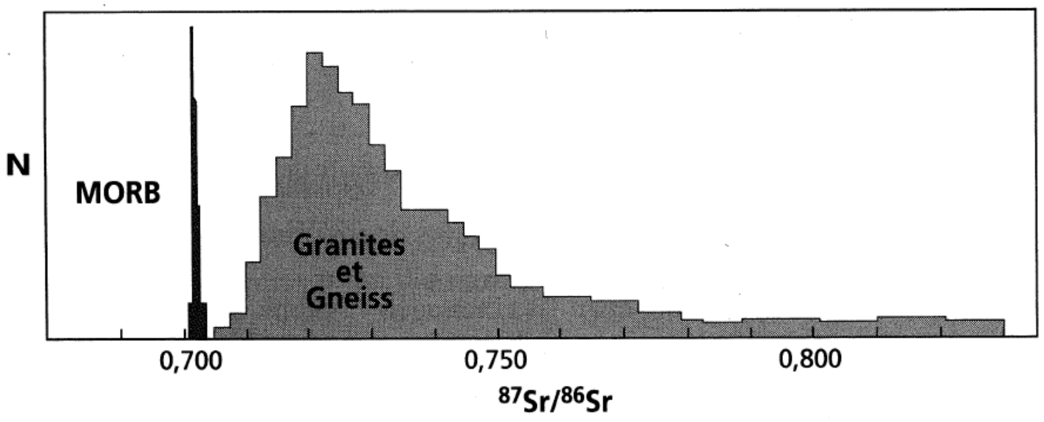
# Isotopic variability of the continental vs. the oceanic crust



Claude Allègre, 2005, Géologie isotopique

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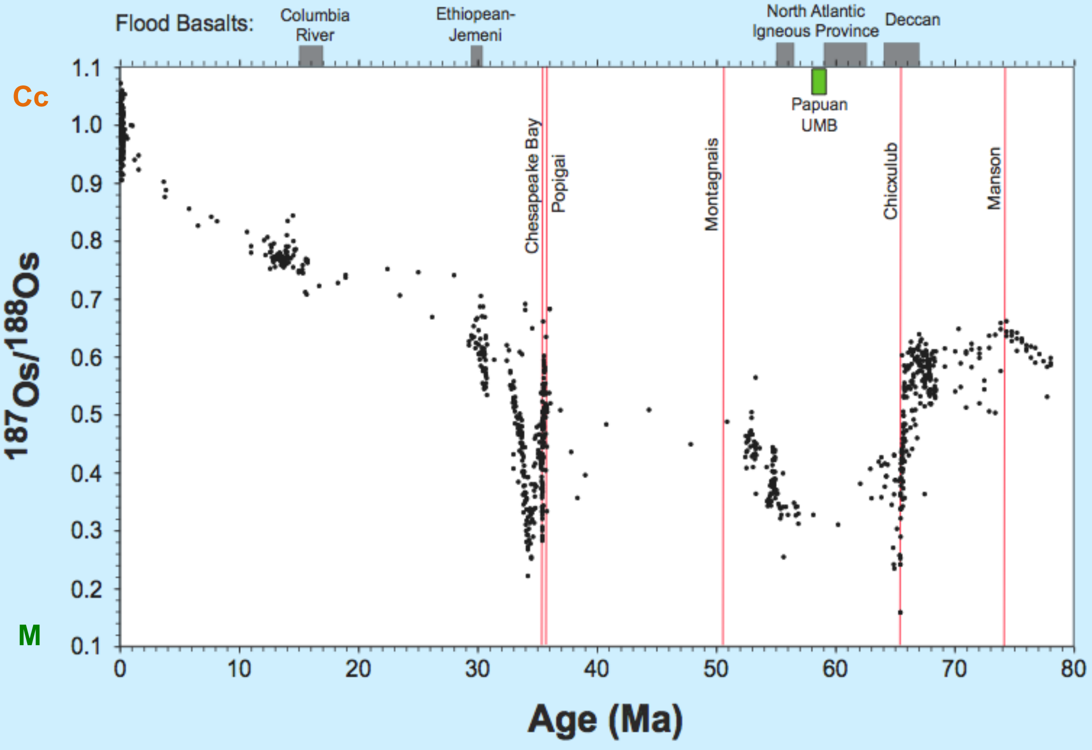
# Seawater - Osmium



## Isotope mass balances

Isotope mass balances for elements with long residence times in seawater are generally described in terms of simple one-box models. The temporal change in the number of atoms of an element in our box is described by

$$(1)\quad \frac{dN}{dt} = \sum F_{\text{in}} - \sum F_{\text{out}}$$

with $N$ = number of atoms of an element in the box and $F$ = flux (in or out)

The ratio of two isotopes of an element in seawater is then simply a function of input and removal terms. In essence, this is analogous to a simple titration experiment. The temporal change in the isotope ratio in our box is described by

$$(2)\quad \frac{dNR_{\text{box}}}{dt} = \sum F_{\text{in}} R_{\text{in}} - \sum F_{\text{out}} R_{\text{out}}$$

Where $R$ is the isotope ratio of the input (in), the output (out), and the reservoir (box)
Applying the product rule on the left hand side yields

$$(3)\quad R_{\text{box}}\frac{dN}{dt} + N\frac{dR_{\text{box}}}{dt} = \sum F_{\text{in}} R_{\text{in}} - \sum F_{\text{out}} R_{\text{out}}$$

Replacing $dN / dt$ with the right hand side of equation (1) yields

$$(4)\quad R_{\text{box}}\left(\sum F_{\text{in}} - \sum F_{\text{out}}\right) + N\frac{dR_{\text{box}}}{dt} = \sum F_{\text{in}} R_{\text{in}} - \sum F_{\text{out}} R_{\text{out}}$$

or

$$(5)\quad R_{\text{box}}\sum F_{\text{in}} - R_{\text{box}}\sum F_{\text{out}} + N\frac{dR_{\text{box}}}{dt} = \sum F_{\text{in}} R_{\text{in}} - \sum F_{\text{out}} R_{\text{out}}$$

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It is often assumed that the isotopic composition of the flux out of the box is equal to the isotopic composition of the box (i.e., $R_{\text{box}} = R_{\text{out}}$). In the case of the marine Sr isotope record this means that the calcium carbonate precipitating from seawater (i.e., the major sink) has the same isotopic composition as seawater itself (no fractionation). Then $R_{\text{box}}\,\Sigma\, F_{\text{out}} = \Sigma\,(F_{\text{out}}\, R_{\text{out}})$ and equation (5) can be reduced to

$$(6)\quad N\frac{dR_{\text{box}}}{dt} = \sum F_{\text{in}} R_{\text{in}} - R_{\text{box}}\sum F_{\text{in}}$$

divide by $N$

$$(7)\quad \frac{dR_{\text{box}}}{dt} = \frac{[\,\sum F_{\text{in}}\,(R_{\text{in}} - R_{\text{box}})\,]}{N}$$

### Steady-state

Assuming steady-state (ss), i.e., $dR_{\text{box}} / dt = 0$ and solving for $R_{\text{box-ss}}$, equation (7) becomes

$$(8)\quad R_{\text{box-ss}} = \frac{\sum F_{\text{in}} R_{\text{in}}}{\sum F_{\text{in}}}$$

The flux into the ocean box generally is composed of riverine (subscript R), hydrothermal (subscript H), and groundwater and/or diagenetic inputs (subscript D). Atmospheric or extraterrestrial inputs in most cases are negligible. The total flux to the ocean box is the sum of the individual isotope ratios weighted by the individual fluxes (water flux times concentration).

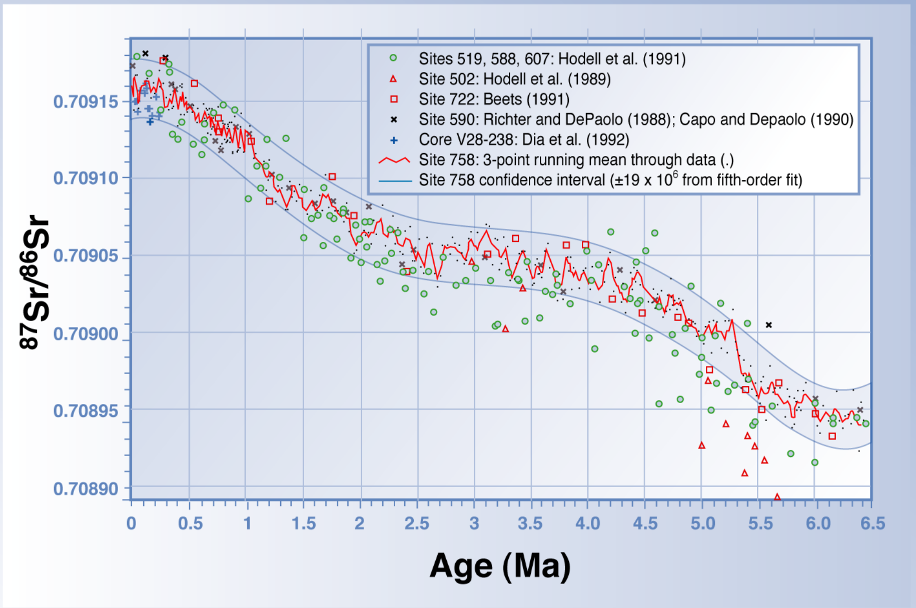
$$(9)\quad \sum F_{\text{in}} R_{\text{in}} = F_{\text{R}} R_{\text{R}} + F_{\text{H}} R_{\text{H}} + F_{\text{D}} R_{\text{D}}$$

At steady state the isotopic composition of an element in our box ocean is thus given by

$$(10)\quad R_{\text{box-ss}} = \frac{F_{\text{R}} R_{\text{R}} + F_{\text{H}} R_{\text{H}} + F_{\text{D}} R_{\text{D}}}{F_{\text{R}} + F_{\text{H}} + F_{\text{D}}}$$

# Steady State?

## Seawater Evolution



Comparison of Site 758 $^{87}Sr/^{86}Sr$ data with results from prior studies on Berggren et al. (1985) time scale. All $^{87}Sr/^{86}Sr$ are plotted relative to Hodell et al. (1990) SRM-987 value of 0.710 235, or to their U.S. Geological Survey Tridachna Standard (EN-1) value of 0.709 172

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## Non steady-state

Geochemists like steady-state models because it simplifies the math. Steady-state is, however, a very special case. A system's response to perturbations is a function of the magnitude of the perturbation and the response time of the element in question (i.e., residence time, τ). Evaluating a system in transition to a new steady-state therefore yields clues to some important properties of the system. To consider the general case of non steady-state we need to go back a few steps (equation 6). The residence time of an element in our box ocean is defined by

$$(11) \quad \tau = \frac{N}{\sum F_{\text{in}}}$$

Dividing equation (6) by $N$ and introducing $\tau$ the mass balance becomes

$$(12) \quad \frac{dR_{\text{box}}}{dt} = \frac{\sum F_{\text{in}} R_{\text{in}}}{N} - \frac{R_{\text{box}}}{\tau}$$

This can be rearranged first to

$$(13) \quad \frac{dR_{\text{box}}}{dt} = \frac{\sum F_{\text{in}} R_{\text{in}} - R_{\text{box}} \sum F_{\text{in}}}{\tau \sum F_{\text{in}}}$$

then to

$$(14) \quad \frac{dt}{\tau \sum F_{\text{in}}} = \frac{dR_{\text{box}}}{\sum F_{\text{in}} R_{\text{in}} - R_{\text{box}} \sum F_{\text{in}}}$$

and finally, by expanding with ($\Sigma F_{\text{in}} / \Sigma F_{\text{in}}$) on the ride hand side, to

$$(15) \quad \frac{dt}{\tau \sum F_{\text{in}}} = \frac{\frac{1}{\sum F_{\text{in}}} \sum F_{\text{in}}\ dR_{\text{box}}}{\sum F_{\text{in}} R_{\text{in}} - R_{\text{box}} \sum F_{\text{in}}}$$

The term ($1 / \Sigma F_{\text{in}}$) can now be canceled on both side and the equation can be integrated

$$(16) \quad \int \frac{dt}{\tau} = \int \frac{(\sum F_{\text{in}}\ dR_{\text{box}})}{\sum F_{\text{in}} R_{\text{in}} - R_{\text{box}} \sum F_{\text{in}}}$$

resulting in

(17) $\frac{t}{\tau} + C' = \ln\left(\sum F_{\text{in}} R_{\text{in}} - R_{\text{box}} \sum F_{\text{in}}\right)$

with the integration constant C'. If we introduce $C'' = e^{C'}$ and simplify, we get

(18) $C'' e^{\frac{t}{\tau}} = \sum F_{\text{in}} R_{\text{in}} - R_{\text{box}} \sum F_{\text{in}}$

If we set $C'' = C\, e^{\frac{t0}{\tau}}$ with $t_o$ the time at our initial condition, equation (18) becomes

(19) $C\, e^{\frac{t-t0}{\tau}} = \sum F_{\text{in}} R_{\text{in}} - R_{\text{box}} \sum F_{\text{in}}$

We can then solve for ($R_{\text{box}}$) at any time ($t$) according to

(20) $R_{\text{box-t}} = \frac{(\sum F_{\text{in}} R_{\text{in}}) - C\, e^{\frac{t-t0}{\tau}}}{\sum F_{\text{in}}}$

(21) $R_{\text{box-t}} = \frac{(\sum F_{\text{in}} R_{\text{in}})}{\sum F_{\text{in}}} - \frac{C}{\sum F_{\text{in}}} e^{\frac{t-t0}{\tau}}$

We can now solve for ($R_{\text{box}}$) at time ($t_o$) by setting the boundary conditions for $F_{\text{in}}$ and $R_{\text{in}}$ at the steady state (ss) values, i.e. $F_{\text{in-ss}}$ and $R_{\text{in-ss}}$

(22) $R_{\text{box-t0}} = \frac{(\sum F_{\text{in-ss}} R_{\text{in-ss}})}{\sum F_{\text{in-ss}}} - \frac{C}{\sum F_{\text{in-ss}}} e^{\frac{t-t0}{\tau}}$

Using equation (10) to replace the first term on the right hand side we simplify equation (22)

(23) $R_{\text{box-t0}} = R_{\text{box-ss}} - \frac{C}{\sum F_{\text{in-ss}}}$

with

(24) $C = \sum F_{\text{in-ss}} \left(R_{\text{box-ss}} - R_{\text{box-t0}}\right)$

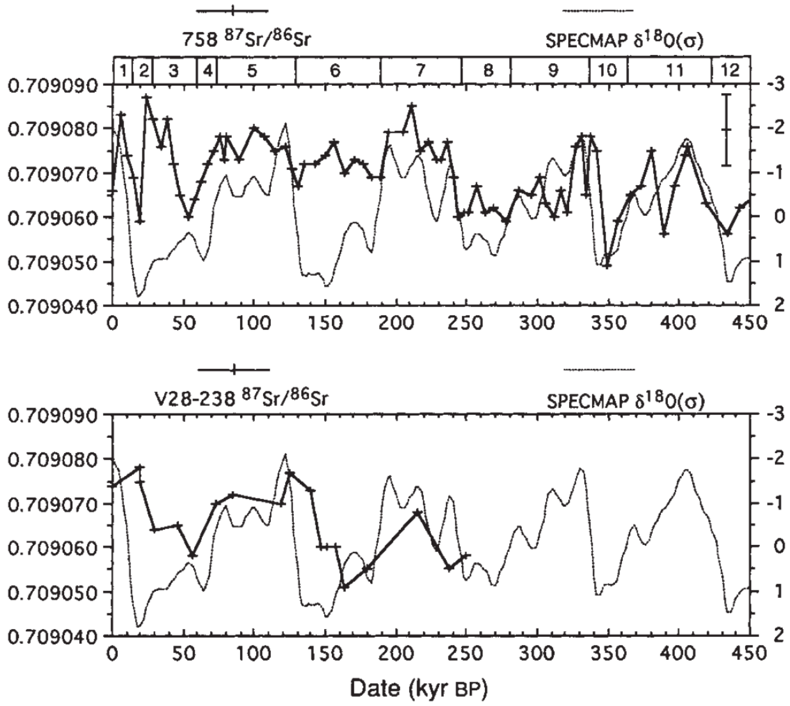
and equation (20) becomes

(25) $R_{\text{box-t}} = R_{\text{box-ss}} - (R_{\text{box-ss}} - R_{\text{box-t0}})\, e^{(t - t0)/\tau}$

Equation (25) is powerful because it allows us to calculate the isotopic composition of our box ocean at any time ($t$) after the system was disturbed from steady-state. Return to a new steady-state will occur within about 5 residence times ($\tau$). The equation also allows us to calculate the isotopic composition of a steady state box ocean from the isotopic composition of our box ocean at two times ($t$ and $t_o$). The isotopic composition of our box ocean at steady state will depend on the input fluxes and isotopic composition. If we hold all but one of the parameters constant that influence the isotopic composition of our box at steady state, the new value for the changed parameter can be calculated.

However, the new steady state isotopic composition can only be calculated iteratively, because changes in $F_{\text{in}}$ affect the residence time $\tau$ (remember: $\tau = N / \Sigma F_{\text{in}}$). An example for such an iterative solution is given by Hodell et al. (1989, EPSL 92, 165-178) for the response of the Sr isotope record of seawater to perturbations.

# Can this be real?



Clemens et al., 1993, Nature

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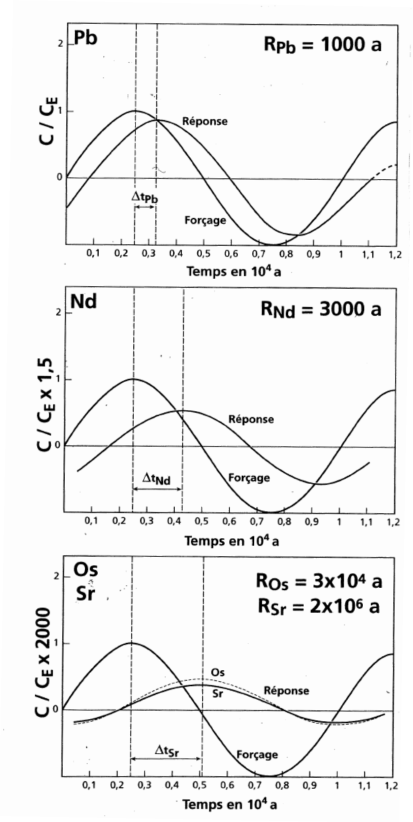
# System's response to perturbation

$dM/dt = J – kM$

with sinusoidal forcing $J = J_0 + \sin(\omega t)$
And with $\omega = 2\pi/T$

$dM/dt = J_0 + b \sin(\omega t) - kM$

C. Allegre, 2005, p. 450



## Examples of responses to forcing:

(1) $dC / dt = a + b \sin(\omega t) - kC$

For all elements a = 1, b = 1
With $k = 1/R$, (R is residence time)
T = 100,000 yrs, (period of forcing)
Time unit = 1000 yrs, e.g. $\omega = 2\pi/T = 0.0628$

With sufficiently long t (e.g. >3R)

Integration of (1) yields:

(2) $C = a / k + bk / (k^2\ \omega^2) \sin(\omega t) - k\omega / (k^2\text{-}\omega^2) \cos(\omega t)$

$k_{Pb} = 1$ (= reference)
$k_{Nd} = 0.33$
$k_{Os} = 0.033$
$k_{Sr} = 0.0005$

Relative sensitivities to magnitude of perturbation:
Pb (90%), Nd (65%), Os (0.2%), Sr (0.15%)

Phase lag increases approximately with ln R

C. Allegre, 2005, p. 453

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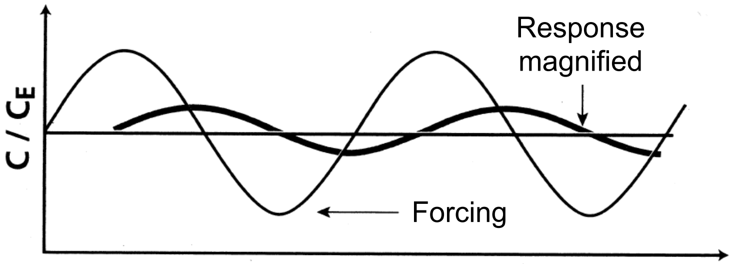
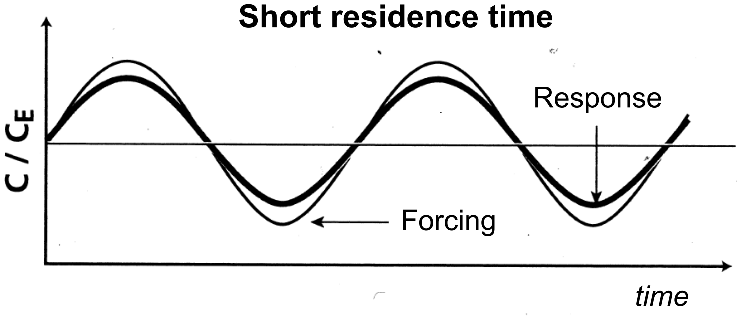
## System's response to perturbation as function of residence time

### Long residence time



(Sr, Ca, Mg, Li, B)

### Short residence time



(Pb, Fe, Nd, Os)

C. Allégre, 2005, p. 452