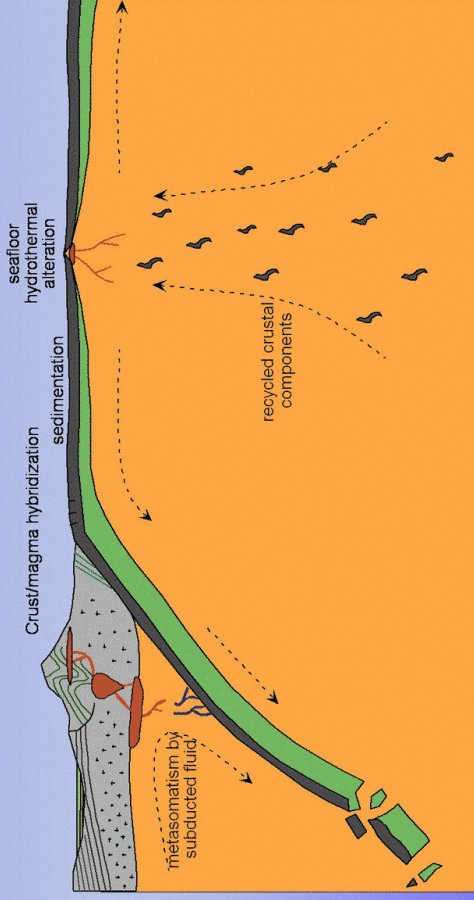


Stable isotope geochemistry

The idea:

Isotopic diversity is produced by physical chemistry and biochemistry in the near-surface environment and imposed on mantle-derived materials by subduction or contamination of magmas.

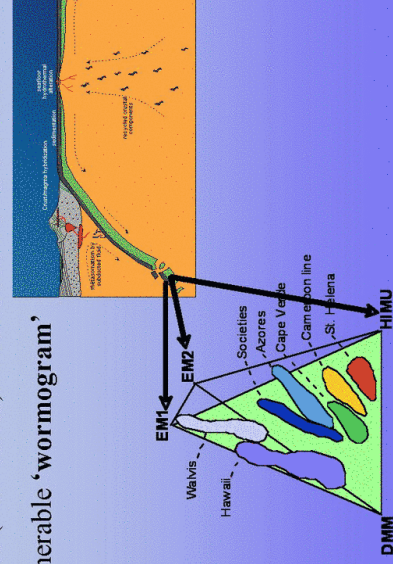


Things this could accomplish

- Subducted crust (and serpentinites?) are sources of **fertility**, and so tied to mantle melting. We would like to know where these things are.
- Subducted crust hosts high concentrations of **heat-producing elements**, and thus its distribution in the mantle is tied to the 'heat flow' problem.
- The total amount of crust subducted into the mantle over all of earth history (~6% of the total) potentially hosts a large fraction of earth's **incompatible lithophile elements** (~10's of %). We should know where it is.

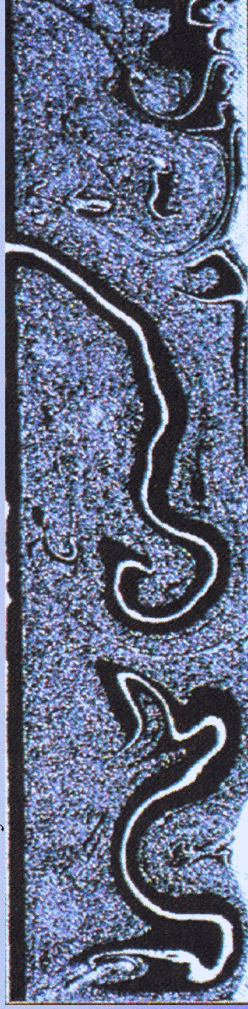
- Untangling the venerable 'wormogram'

problem:



Other things this could accomplish

- Subducted crust might be a major constituent of some ‘special’ layers (D’; transition zone?). We would like to test these ideas when relevant samples can be found.
- Dynamical models could be tested or made concrete using data that ‘tags’ material known to have come from the **upper boundary layer** of the mantle convection system.



Old-school dynamics: Christensen and Hofmann, 1994; distribution of ocean crust (white) and residual depleted mantle (black) after 3.6 Ga of ‘model’ time.

Rules of the road I: Nomenclature

‘Stable isotopes’ are nuclides that do not undergo radioactive decay. Those of interest to us generally are also not products of radioactive decay.

$$\delta^i_{\text{standard}} = \left\{ \frac{R^i_{\text{sample}}}{R^i_{\text{standard}}} - 1 \right\} \times 1000$$

Where i is an isotope of interest (e.g., ^{18}O or D)

$$\text{And } R^i = \frac{[\text{isotope } i]}{[\text{reference isotope}]}$$

\nwarrow Rare, heavy (e.g., D, ^{13}C , ^{18}O)
 \swarrow Common, light (e.g., H, ^{12}C , ^{16}O)

High ‘ δ ’ values are rich in heavy isotopes, and visa versa.

δ values are reported in ‘per mil’ (parts per thousand), or ‰

‘Fractionations’ refer to differences in δ values between two or more materials of interest.

Rules of the road II: Why do stable isotopes fractionate?

- Heavy isotopes move (e.g., diffuse) more slowly than light isotopes



- Irreversible reactions (e.g., photolysis; organic synthesis) involving heavy isotopes are generally slower than those involving light isotopes



- Heavy isotopes gravitate into 'tight', fast-vibrating bonds in systems at or approaching thermodynamic equilibrium.



Isotope exchange as seen by classical thermodynamics

$$-RT \ln K = \Delta G_{\text{rxn}}^{\text{T,P}} = \Delta H_{\text{rxn}}^0 - T \Delta S_{\text{rxn}}^0 + P \Delta V_{\text{rxn}}^0$$

Systems evolve toward the lowest G state

ΔH_{rxn}^0 : Isotopologues with relatively low heats of formation from the elements (i.e., relatively strong bonds) are favored

$T \Delta S_{\text{rxn}}^0$: Random sharing of isotopes among all co-existing species is increasingly favored at higher temperatures (i.e., fractionations $\rightarrow 0$ as $T \rightarrow \infty$)

Competition between ΔH and $T \Delta S$ terms is source of T sensitivity to K. If H, S and V are insensitive to T, K will vary with T^{-1}

$P \Delta V_{\text{rxn}}^0$: Isotopologues with the lowest partial molar volumes are increasingly favored at higher pressure.

This effect long thought to be negligible; actually as important as T for hydrogen isotope fractionations between water or brine and minerals at geological P and T.

$\Delta G_{\text{rxn}}^{\text{T,P}}$ for stable isotope exchange reactions are generally on the order of 10^{-3} kcal/mol, while errors in measuring H, S and V are equivalent to ca. 1-10 kcal/mol. Therefore calorimetry and cell refinements cannot be used to calibrate rxns of interest.

- Turn to:*
- Statistical mechanics
 - Experiments producing nominally equilibrated model systems
 - Empirical calibration using nominally equilibrated natural assemblages

Statistical thermodynamics and the zero point energy

'Classical' spring physics: bond distance is fixed at energy minimum; no isotope effect on system energy

Yes, yes, yes!

Quantum spring physics: bond vibrates even at lowest, 'zero point' energy, with frequency that depends on mass. High mass isotopes access lower ZPE's, and thus are more stable.

SHO $E = (n + 1/2)h\nu$

$^{20}\text{Ne}-^{20}\text{Ne}$
 $^{22}\text{Ne}-^{22}\text{Ne}$

No!

Yes, yes, yes!

Quantum spring physics: bond vibrates even at lowest, 'zero point' energy, with frequency that depends on mass. High mass isotopes access lower ZPE's, and thus are more stable.

$F = -kx$
 $P.E. = 1/2 kx^2$

Digging deeper...

If you 'tweak' a harmonic oscillator, it will vibrate with the frequency:

$$\nu = \frac{1}{2\pi} \left[\frac{k}{\mu} \right]^{1/2}$$

- k is the spring constant (in $\text{Kg}\cdot\text{s}^{-2}$) on the bond. Intra-molecular bonds generally have spring constants of ca. 10^5 to $100 \text{ Kg}\cdot\text{s}^{-2}$. Intermolecular bonds (e.g., van der Waal's forces) generally have spring constants of ca. $1-10 \text{ Kg}\cdot\text{s}^{-2}$. A slinky is $1 \text{ Kg}\cdot\text{s}^{-2}$
- ν is the frequency in s^{-1} ; note $\omega = \nu c$ (i.e., wave numbers in cm^{-1} = frequency in $\text{s}^{-1} \times c$ in cm/s)
- μ is the 'reduced mass':

For dimers and vibrational modes where only 2 atoms move (e.g., CO_2 symmetric stretch)

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

For vibrations involving three or more atoms

$$\frac{\sum m_i m_j}{\sum m_k}$$

for all i-j bonds
for all k atoms
(see CO_2 example, below)

Keep going...almost....there....

Isotopically
'normal' bond

Vibration rate $v = \frac{1}{2\pi} \left[\frac{k}{\mu} \right]^{1/2}$

Energy $E = (n_i + 1/2)h\nu$

Isotopically
'heavy' bond

$v' = \frac{1}{2\pi} \left[\frac{k}{\mu'} \right]^{1/2}$

$E' = (n_i + 1/2)h\nu'$

$\frac{v'}{v} = \left(\frac{\mu}{\mu'} \right)^{1/2}$

$E_i - E_i' = [(n_i + 1/2)h](v - v')$

$ZPE - ZPE' = 1/2 h(v - v')$

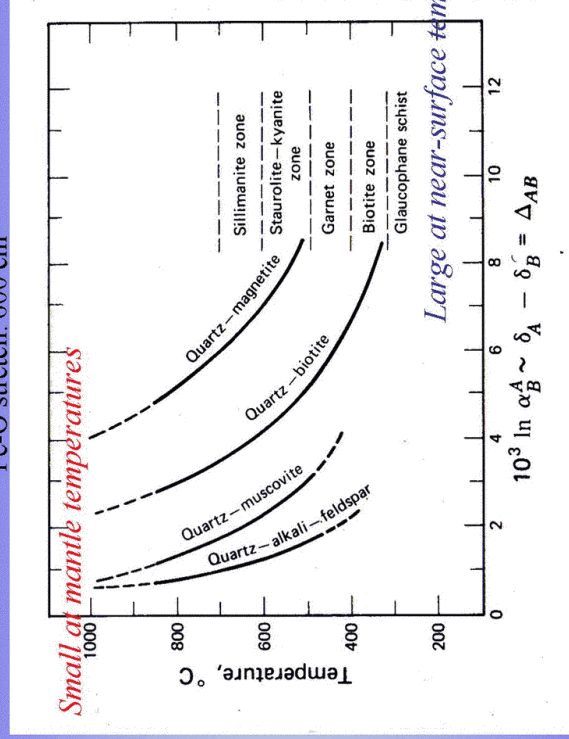
$(v - v') = v \left(1 - \left(\frac{\mu}{\mu'} \right)^{1/2} \right)$

So, in any exchange reaction between two compounds with atoms of similar mass, the heavy isotope will be concentrated in the compound with the higher frequency of molecular vibration.

v: frequency; E: energy; ni: quantum state i; h: plank's constant; ZPE: zero-point energy

Some representative oxygen isotope fractionations

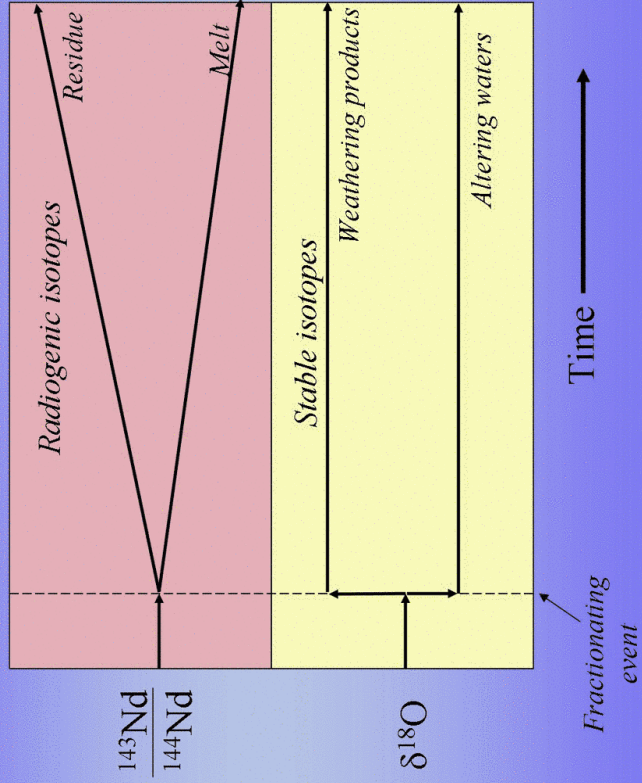
Si-O stretch: 1000 cm⁻¹
Fe-O stretch: 600 cm⁻¹



Small at mantle temperatures

Large at near-surface temperatures

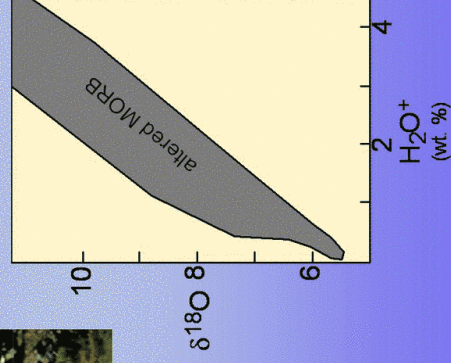
Differences between radiogenic and stable isotopes



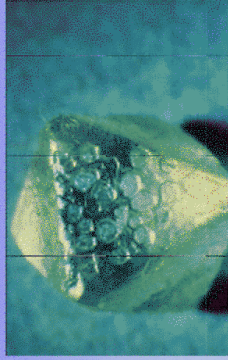
Caveat #1: Lavas and mantle rocks are generally sampled from the earth's surface



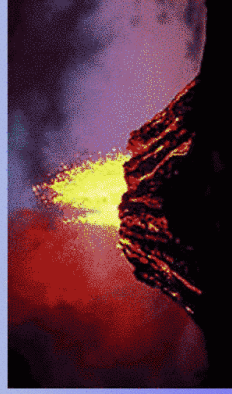
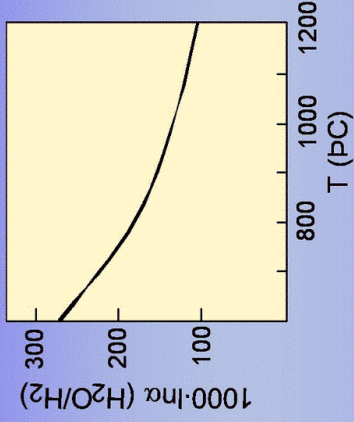
Fresh Pleistocene basalt overlying older, weathered basalt. Snake River Plain, Idaho. Photo from USU petrology website.



Caveat #2: fractionations involving vapors and/or redox reactions can be large at all temperatures.

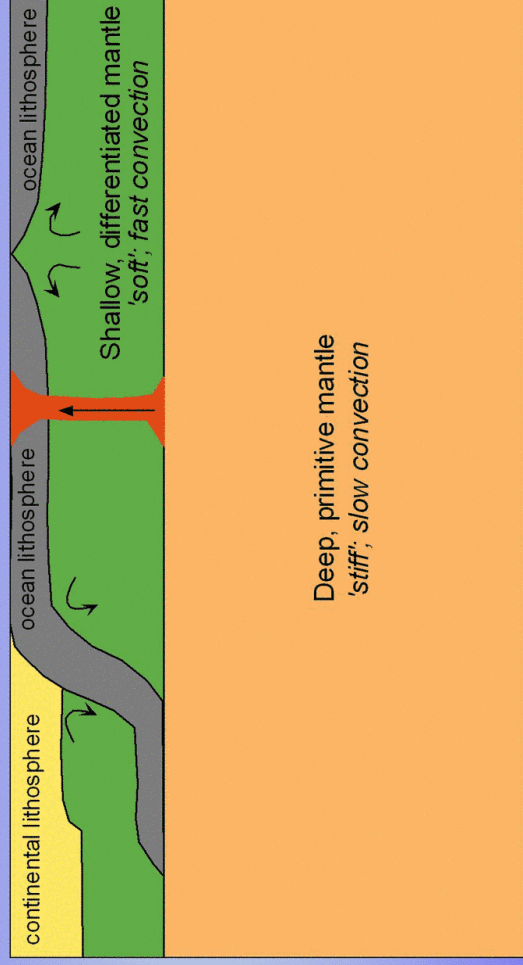


Diamond octagon with hexagonal resorption pits; Argyle W. Australia

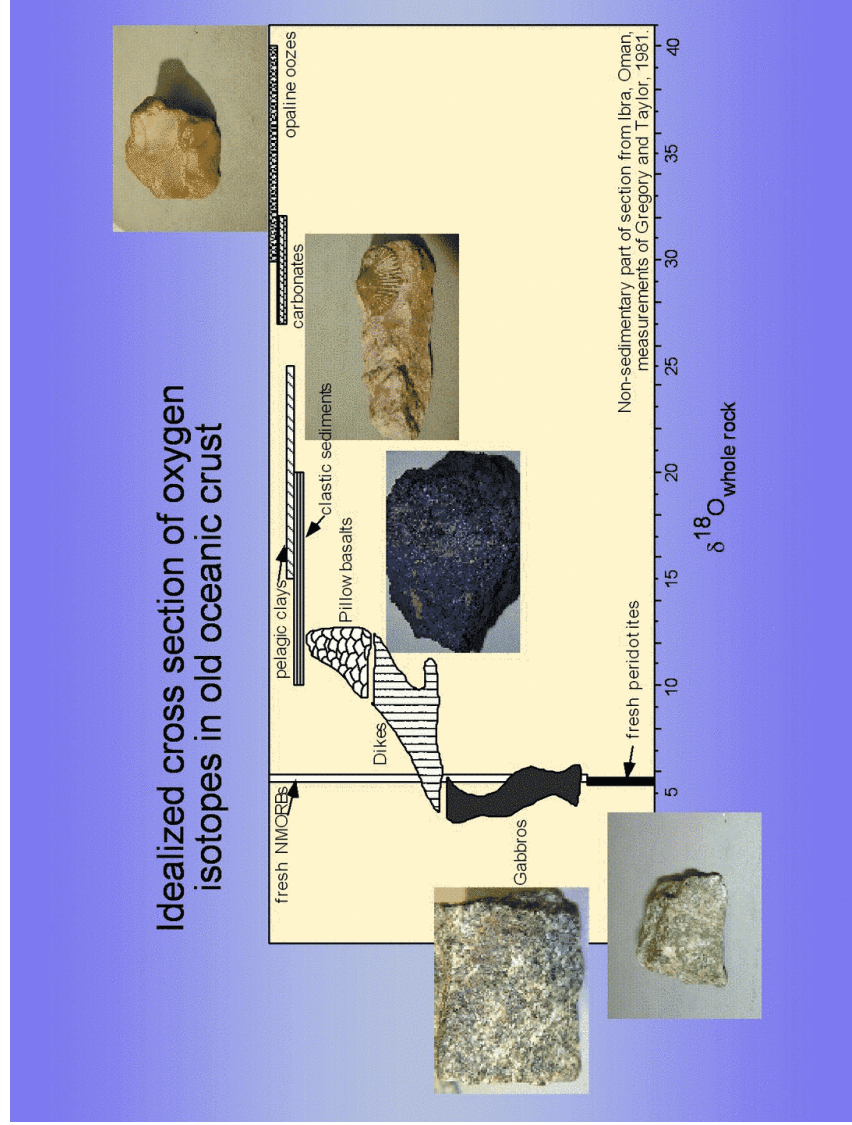
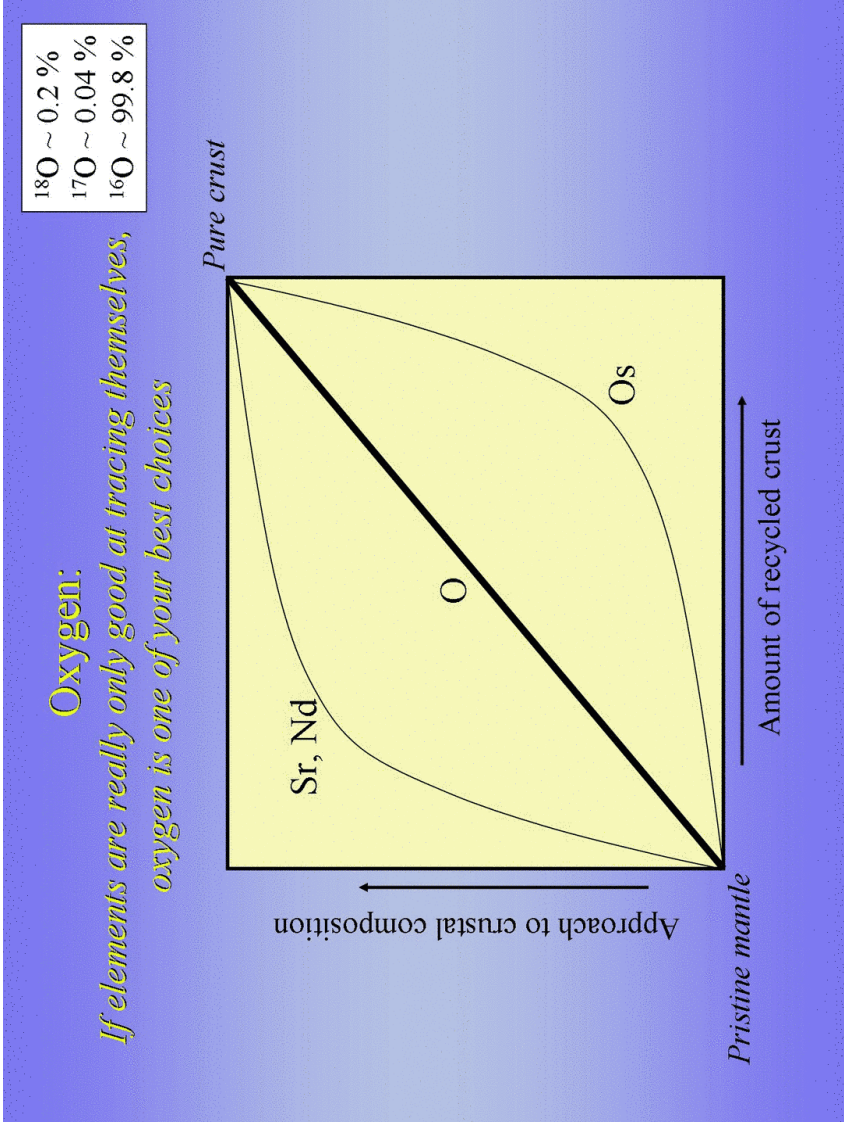


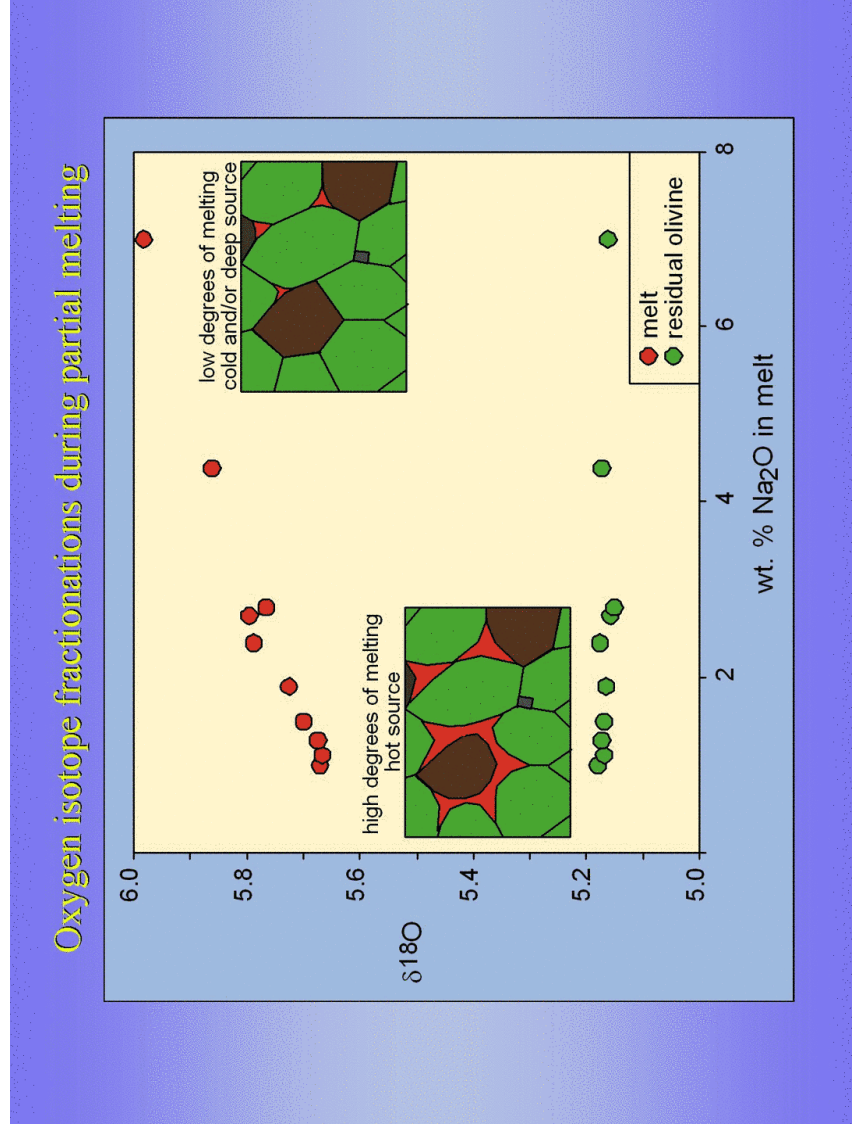
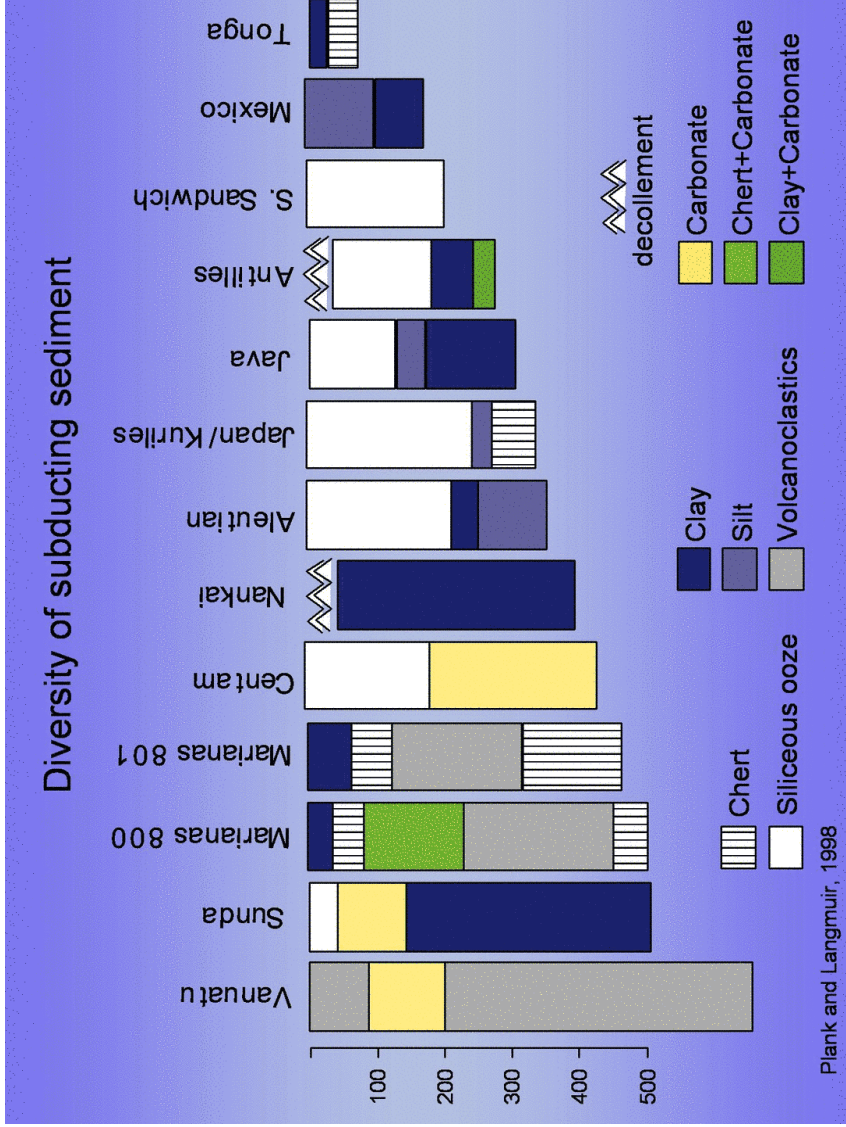
Fire fountain; Kilauea east rift zone

Caveat #3: Possibility of exotic reservoirs in earth interior that have nothing to do with subduction (i.e., 'primordial' volatiles).

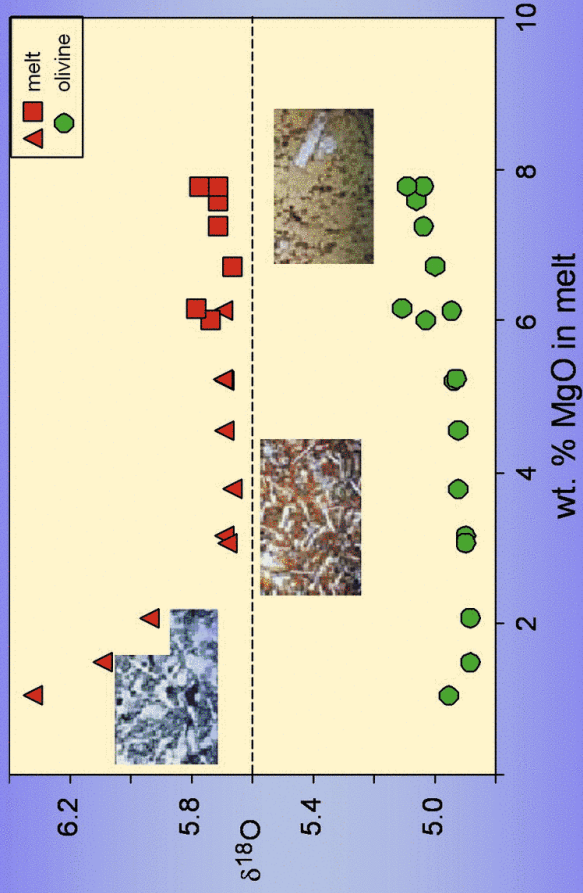


Deep, primitive mantle
'stiff': slow convection



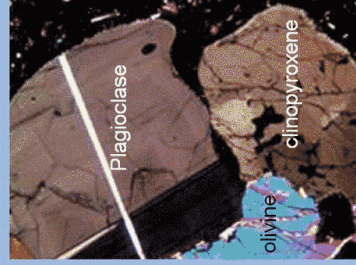


Crystallization-differentiation of basalt

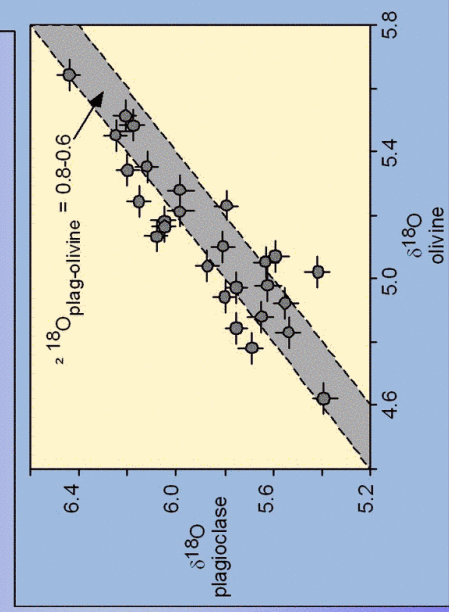


Based on melt compositions of Juster and Grove; Tormey et al.

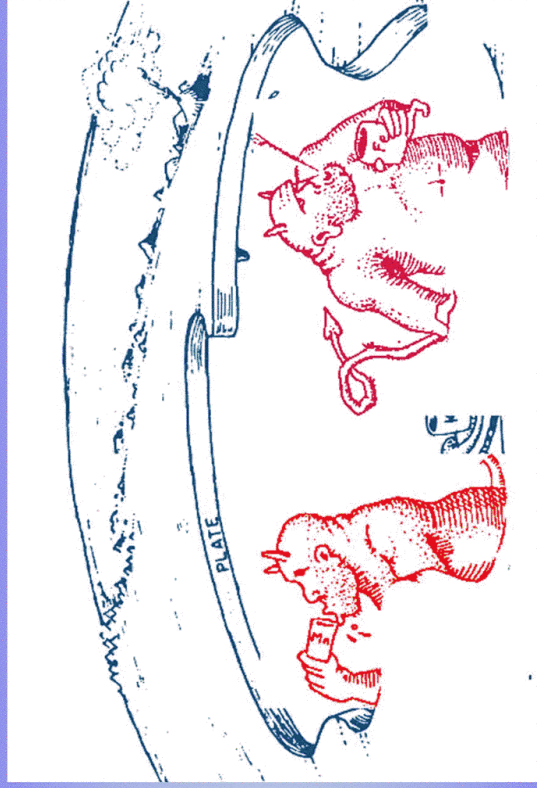
Using high-temperature fractionations to our advantage



Tests for intra-lava equilibrium:
 Central American arc-related basalts

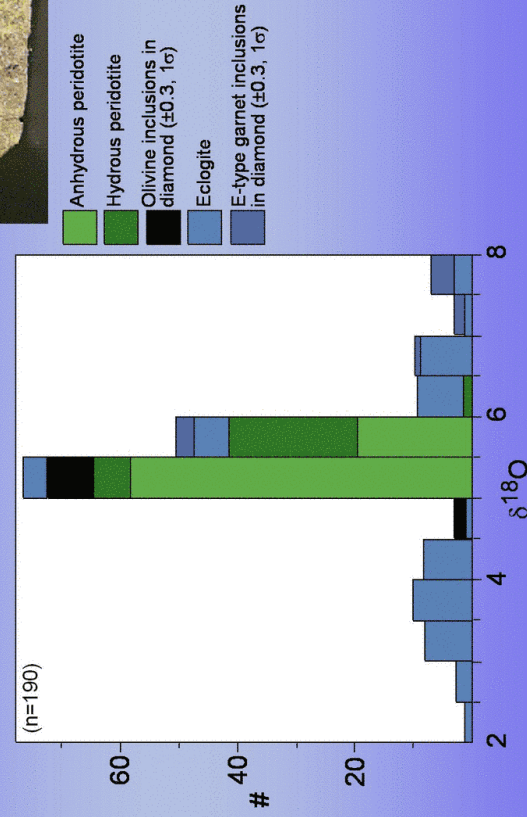
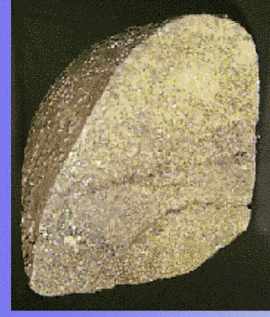


Off to the deep earth interior...



Holden and Vogt, 1977

Chunks of ancient, subducted ocean crust in the sub-continental mantle

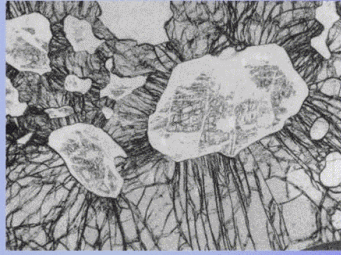


Garlick et al., 1971; Matthey et al., various.

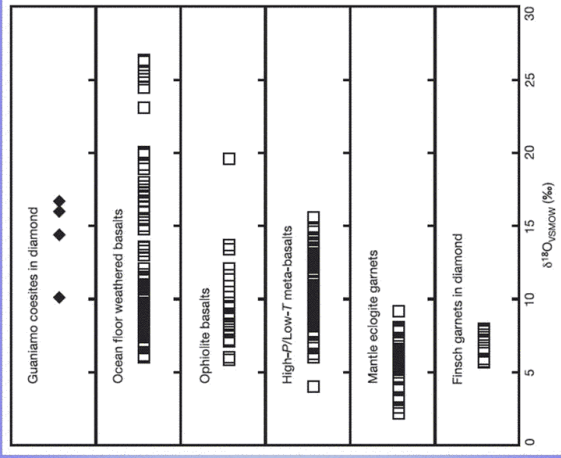
Pieces of subducted sediment or weathered basalt

Table 1 Oxygen isotope values of coesite inclusions in Guantamo diamonds

Diamond	Inclusion	$\delta^{18}\text{O}_{\text{vescov}}$ (‰)
13-127-16	3	15.0
13-127-16	3 (repeat)	16.4
13-127-16	4	16.9
13-127-X	1	10.2

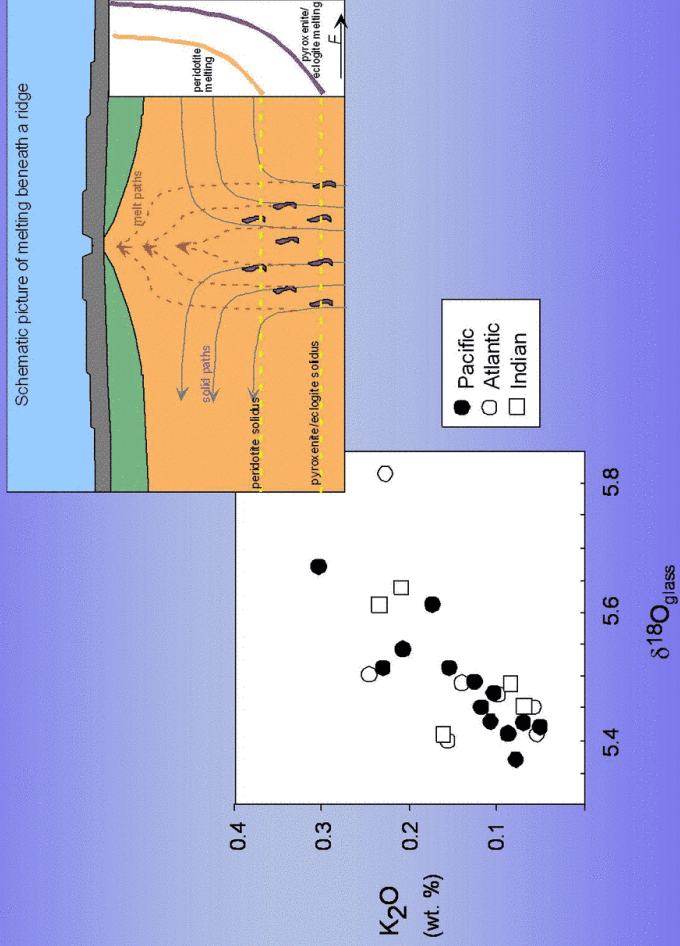


Coesite in an eclogite garnet, Dora Maira



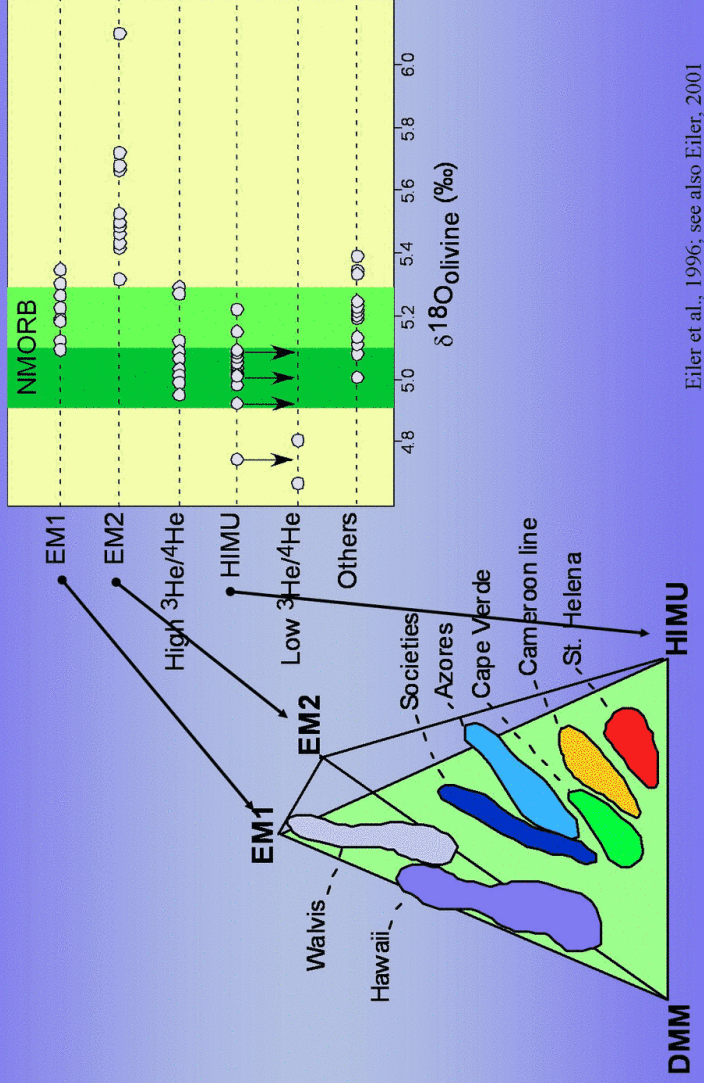
Schultze et al., 2004

Evidence for recycling of upper ocean crust into the sources of mid-ocean-ridge basalts

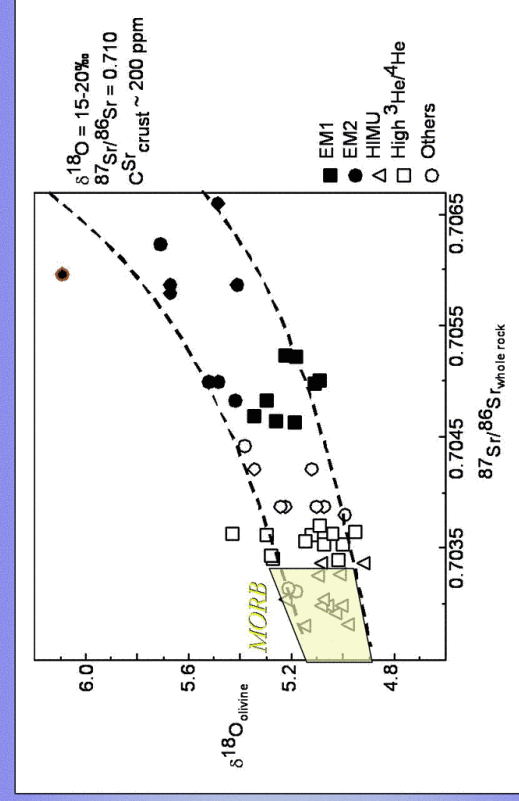


Eiler et al., 2000; see also Cooper et al., 2004

Turning to the sources of ocean-island basalts

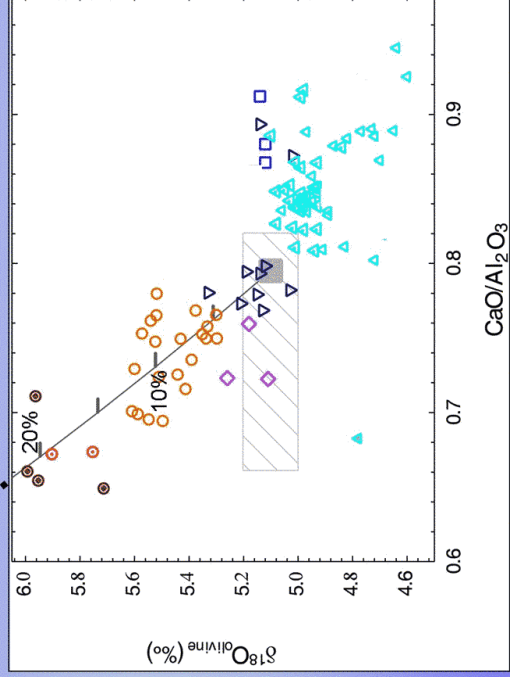


The continuum of crustal abundances in mantle sources



An example of detailed petrogenetic inferences based on oxygen isotopes: Koolau Hawaii

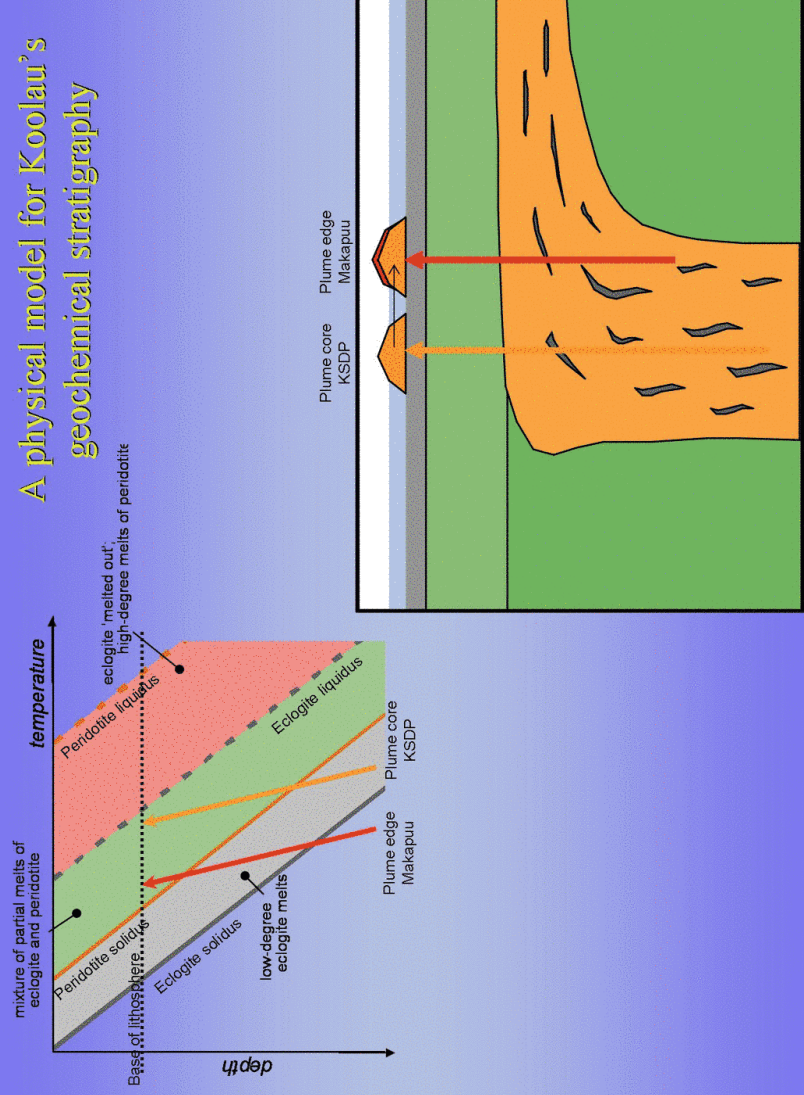
Eclogite melt



Eclogite melt	
SiO ₂	60.0
FeO ^T	5.7
CaO	4.1
Al ₂ O ₃	12.9
K ₂ O	1.4
δ ¹⁸ O	9.9

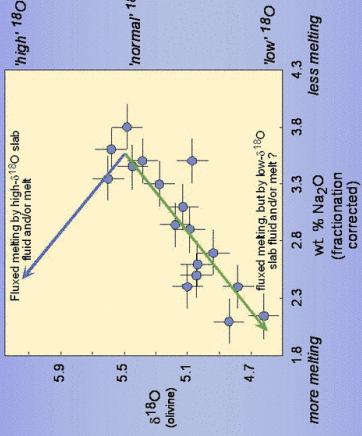
Wang et al., 2006, see Workman et al., 2006 for another example from Samoa; Cooper et al., 2004 for an example for MORB

A physical model for Koolau's geochemical stratigraphy

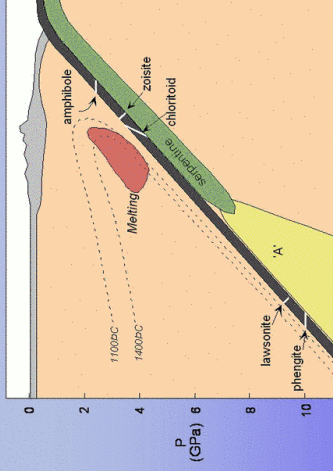


Low- $\delta^{18}\text{O}$ components are in the ocean lithosphere, represented in our eclogite xenolith collections, and influence the sources of arc lavas; surely we should see them in the sources of MORB and OIB

Oxygen-isotope evidence for fluid from serpentinite or gabbro?



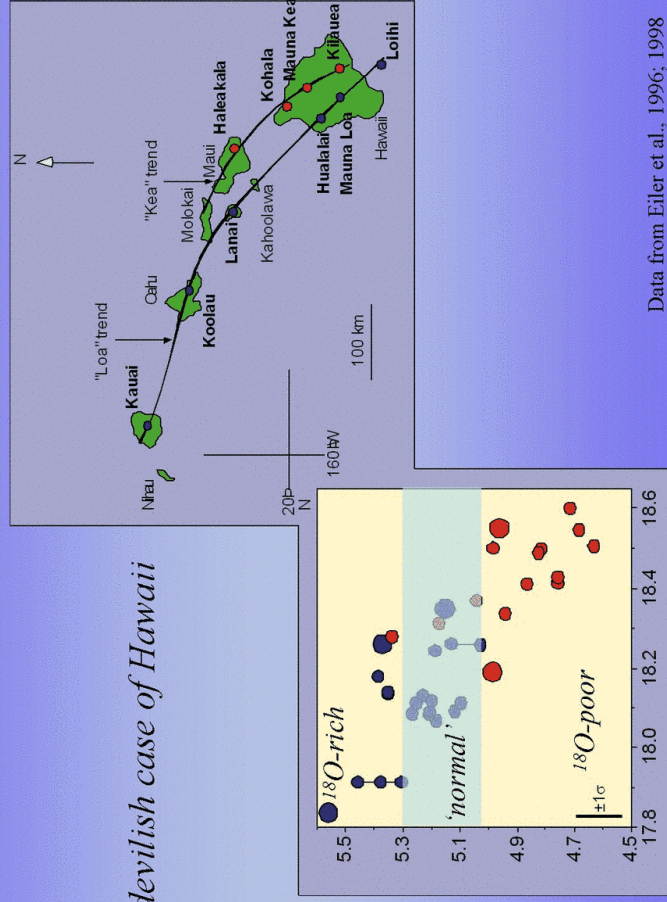
Stability limits of hydrous minerals and the zone of melting beneath convergent margins



Schmidt and Poli, 1988

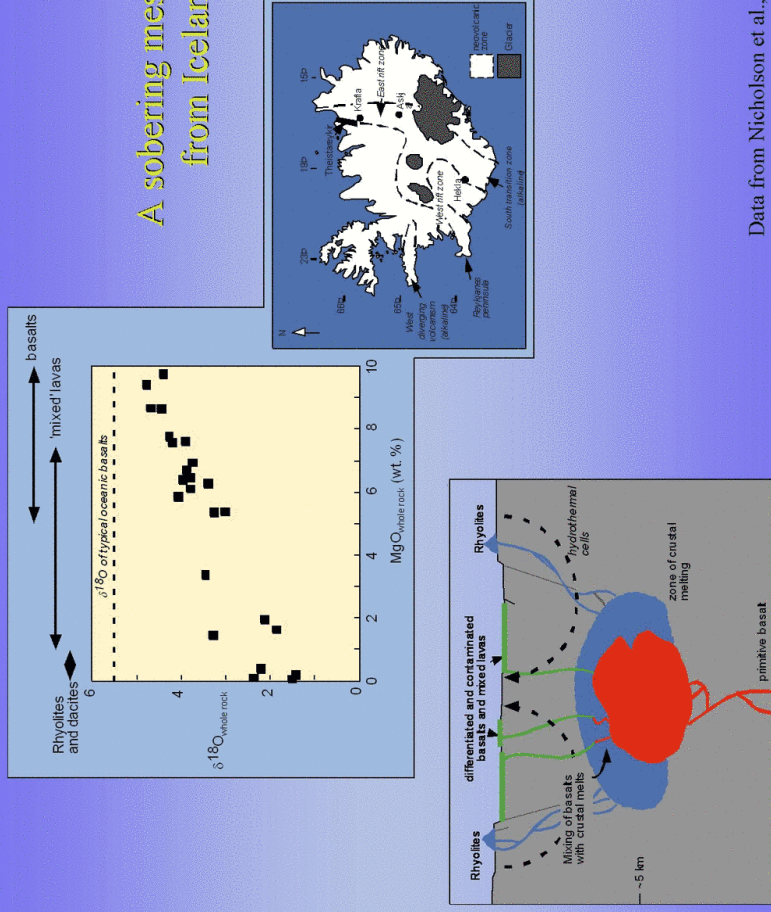
Subducted low- $\delta^{18}\text{O}$ components (i.e., recycled gabbros and serpentinites) in the sources of Hawaiian lavas?

The devilish case of Hawaii



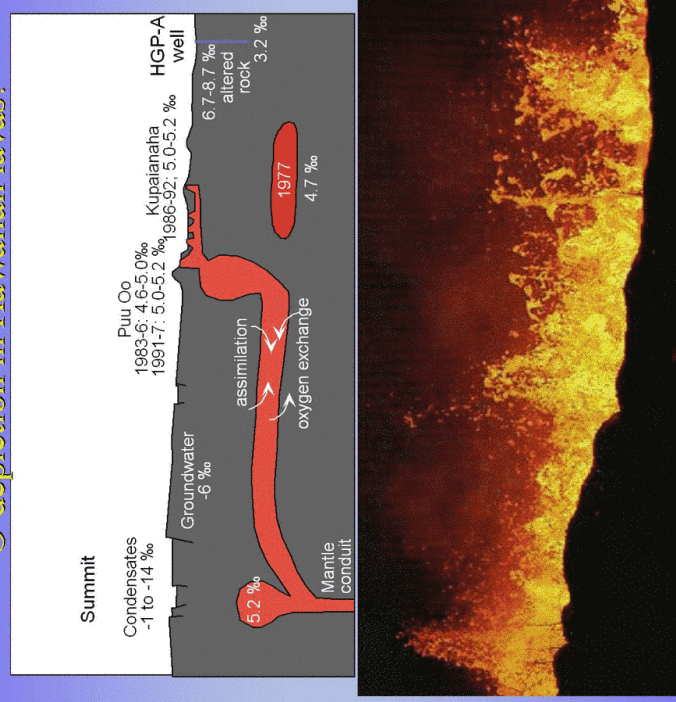
Data from Eiler et al., 1996; 1998

A sobering message from Iceland



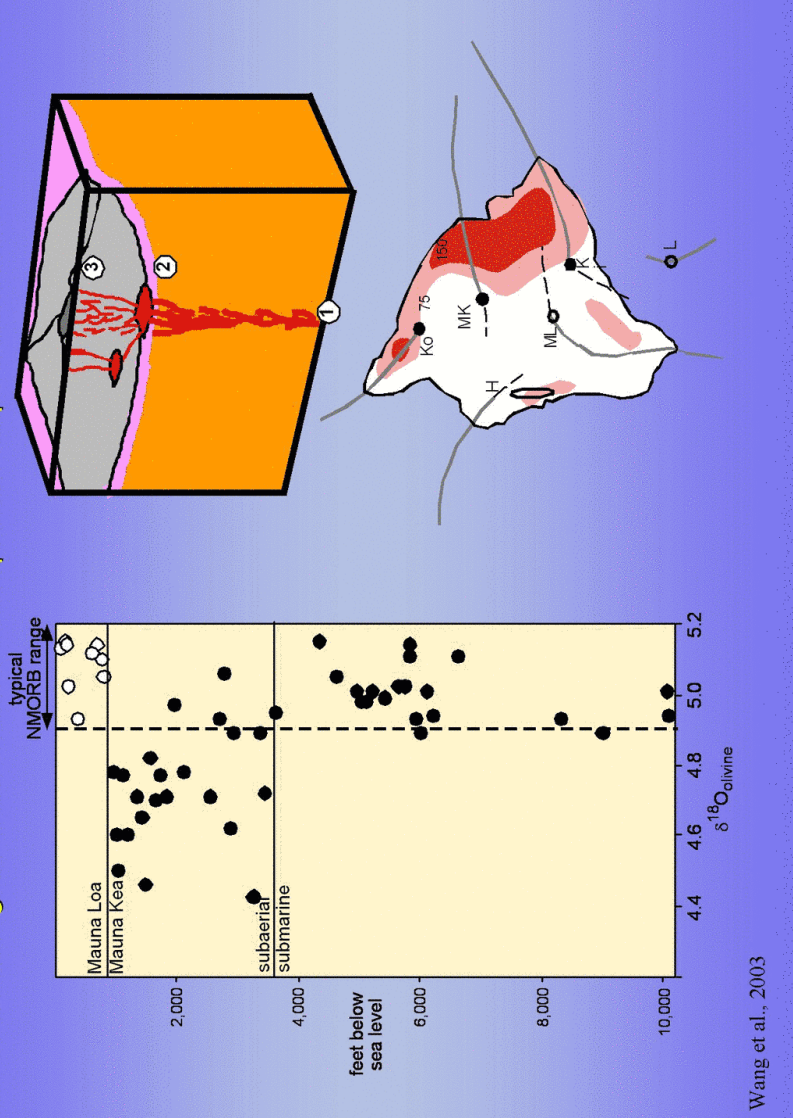
Data from Nicholson et al., 1991

Is Kilauea's east rift zone the Rosetta stone for understanding ^{18}O -depletion in Hawaiian lavas?

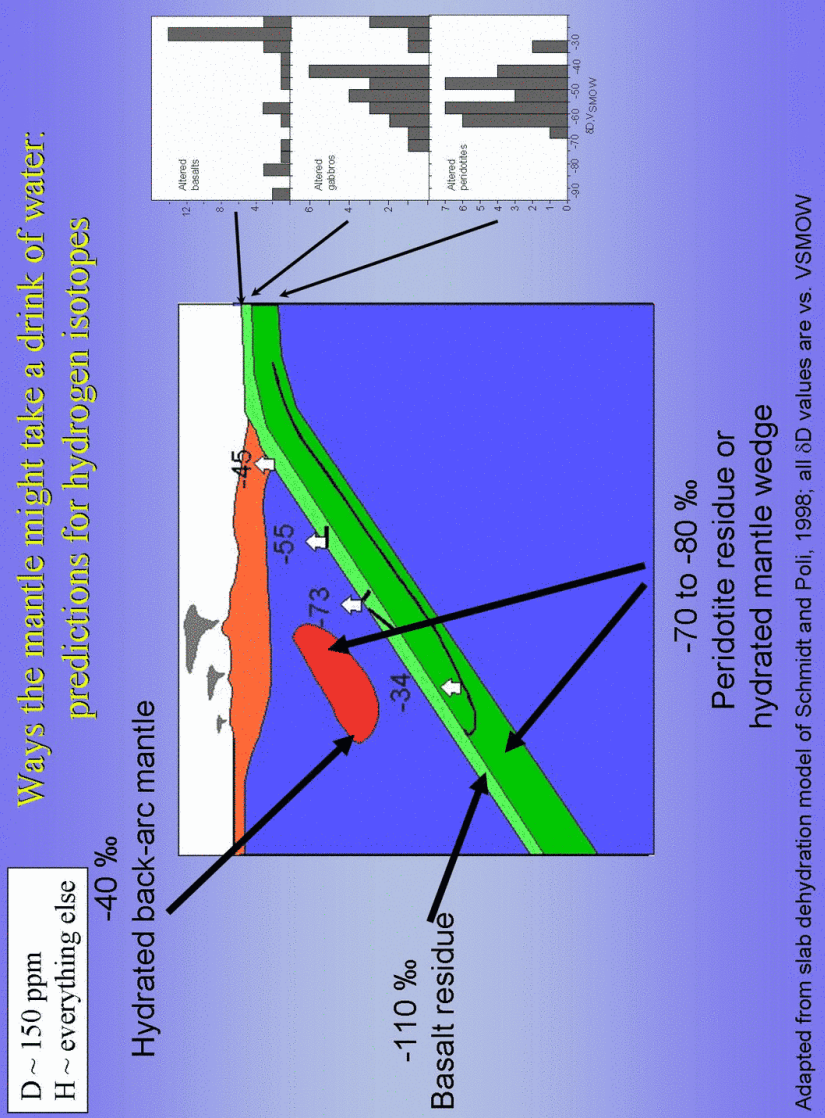


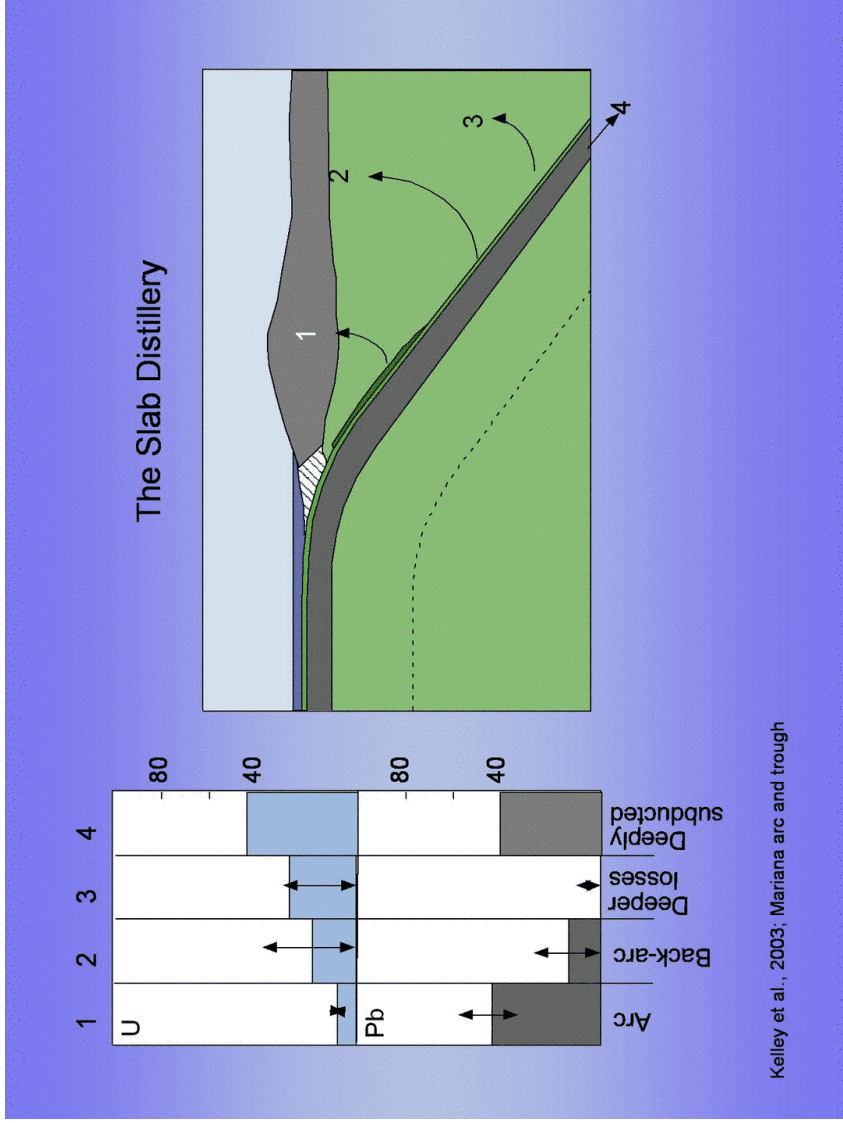
Garcia et al., 1998

Volcanological control of the ^{18}O -depleted component of Hawaiian lavas?



Ways the mantle might take a drink of water:
predictions for hydrogen isotopes

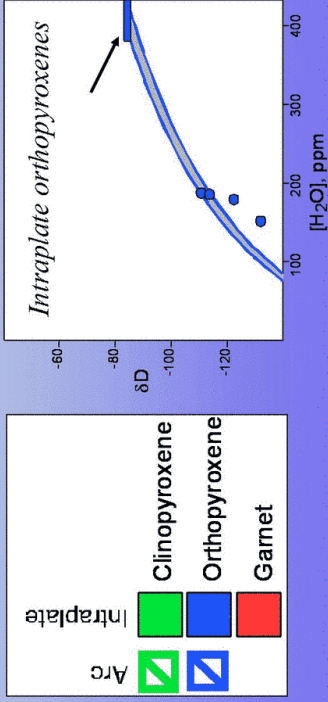
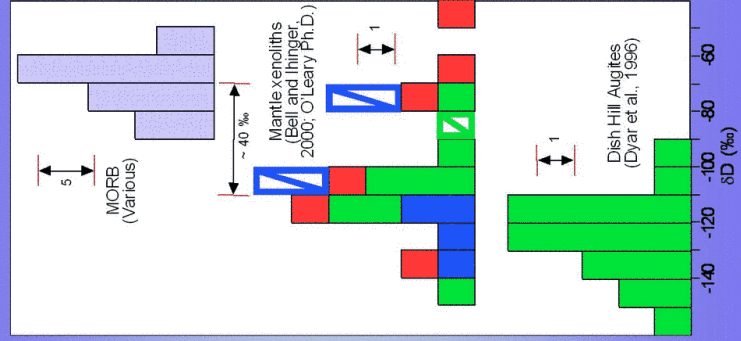




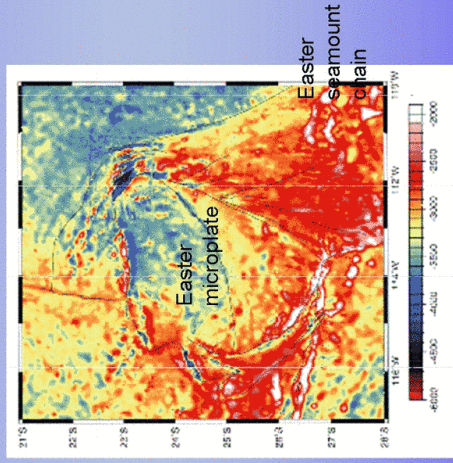
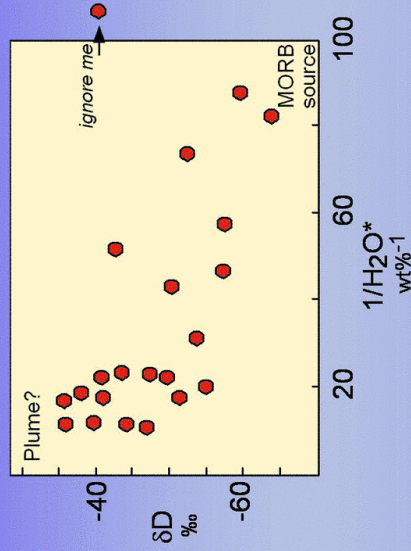
Attempts to establish the 'normal' background peridotite lead to madness

Nominally anhydrous minerals are D-poor because...

- Exchange with meteoric water? (e.g., Dyar et al., 1996 for Dish Hill)
- Residues of melting a MORB-like source? (Bell and Ihinger, 2000)
- Water derived from residues of dehydrated slabs? (e.g., Hauri, 2002 for Koolau inclusions)
- Fractionation during ascent? (e.g., Xia et al., 2004; O'Leary et al., 2006)



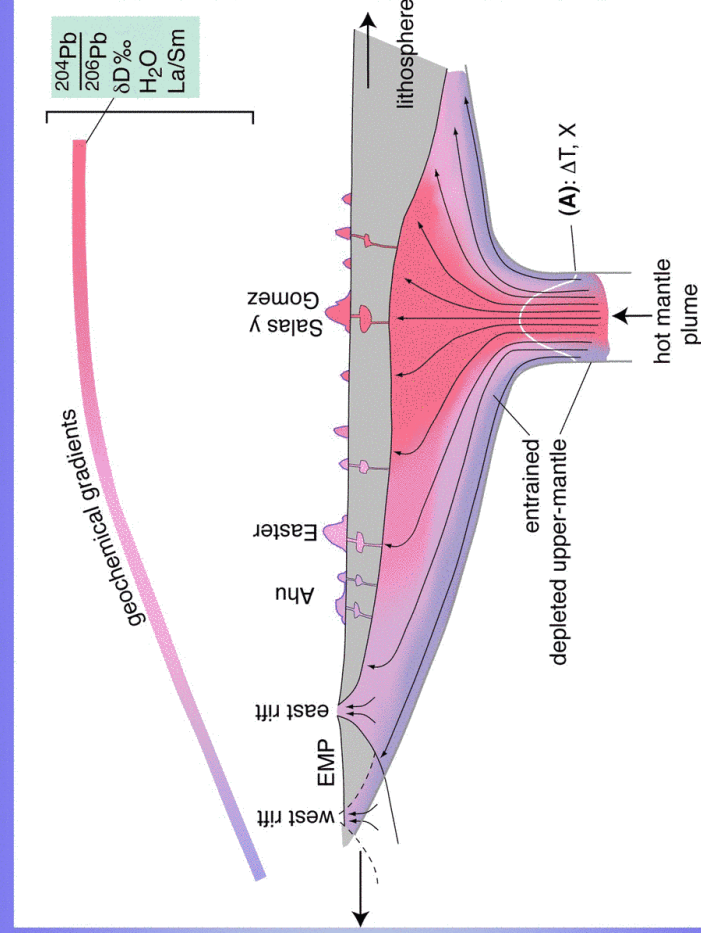
But hydrogen isotopes seem to say... something:
The Easter/Salas y Gomez 'plume'



* water abundance corrected for inferred effects of fractional crystallization and partial melting

Kingsley et al., 2002

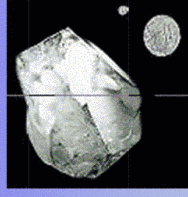
An interpretation of hydrogen in the Easter/Salas y Gomez 'plume'



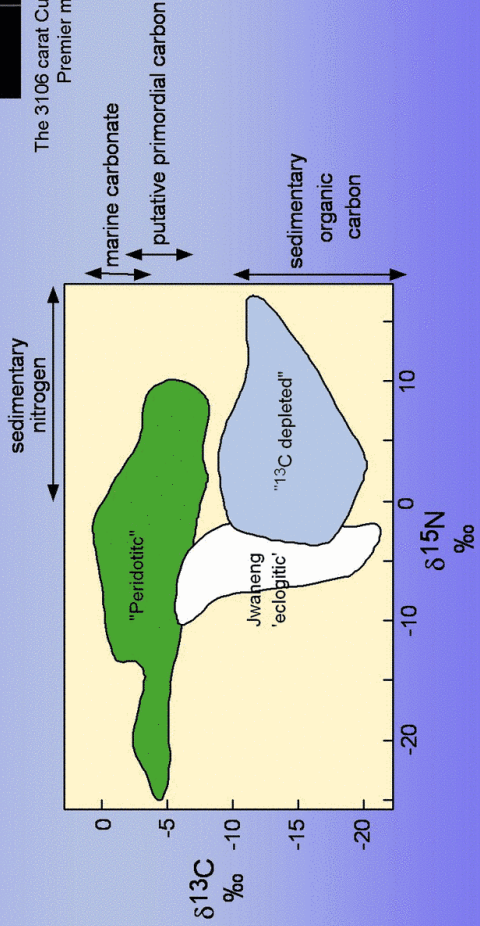
Kingsley et al., 2002

Carbon and nitrogen isotopes in mantle diamonds:
Signatures of the biosphere in the mantle?

$^{13}\text{C} \sim 1\%$
 $^{12}\text{C} \sim 99\%$
 $^{15}\text{N} \sim 0.3\%$
 $^{14}\text{N} \sim 99.7\%$

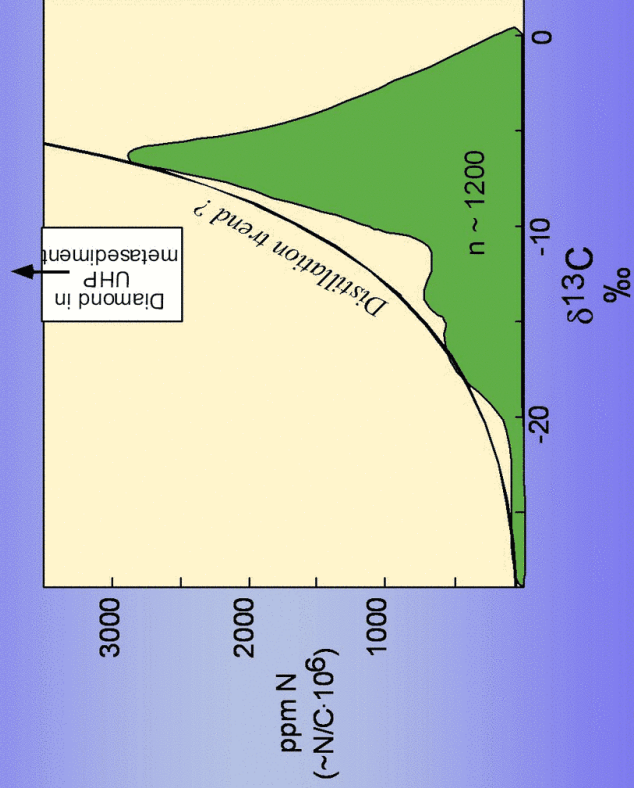


The 3106 carat Cullinan diamond;
Premier mine, SA



Cartigny et al., 1998

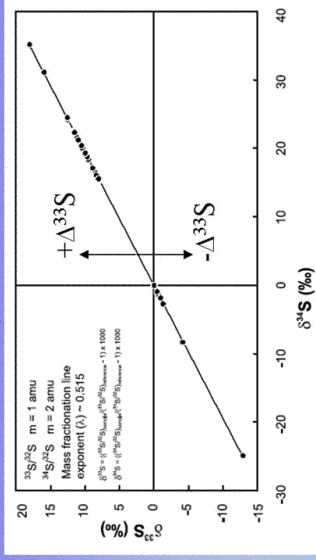
Or maybe not...



Cartigny et al., 2001

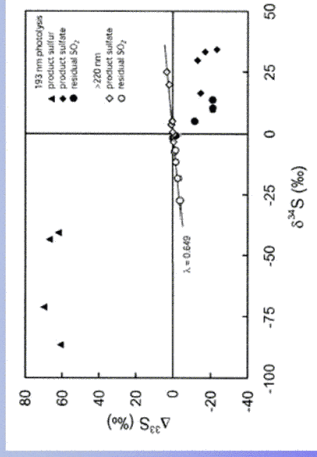
The wacky case of 'mass-independent' sulfur isotope signatures

'normal' fractionations



$^{36}\text{S} \sim 0.02\%$
 $^{34}\text{S} \sim 4.2\%$
 $^{33}\text{S} \sim 0.75\%$
 $^{32}\text{S} \sim 95\%$

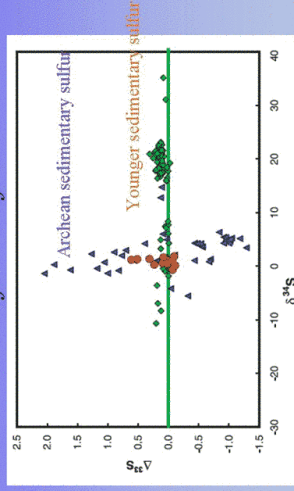
Photochemical fractionations



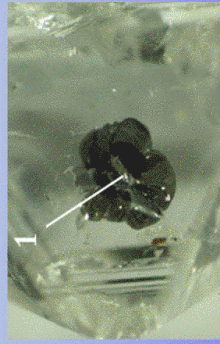
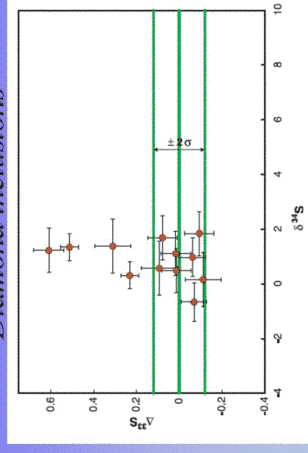
Farquhar and Wing, 2003

The case for recycled Archean sedimentary sulfide

The reference frame



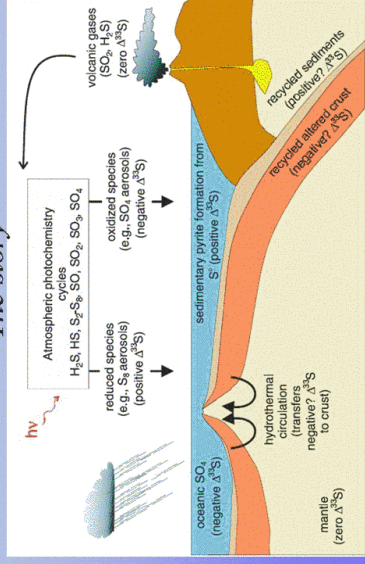
Diamond inclusions



A sulfide inclusion in a mantle diamond

Farquhar et al., 2002

The story



Concluding remarks

- Stable isotopes can identify portions of the mantle that contain abundant recycled crust or that have been modified in a mantle wedge, and under some conditions can quantify the amounts of those materials.
- Such data can help define the mantle's circulation
- This potential is only realized when the relevant chemical and isotopic fractionations are well understood and the data is uncompromised by near-surface processes. Most possible isotopic system are not there yet.
- An overview of the last decade's results suggests ca. 0.1-1.0% abundances of recycled upper crust are widely distributed in the sources of terrestrial basalts, ca. 1-3 % abundances occur in a significant fraction of OIB sources, and high concentrations (ca. 10 %) are restricted to rare OIB sources (Koolau and Samoa for sure; Iceland debated).