Lecture 43

Radiogenic Isotope Geochemistry – applications to igneous systems

Reading - McSween et al., Chapter 14

Today

❶ Distinguishing ancient heterogeneity from modern petrogenesis

❷ Isotopic heterogeneity in the Sr, Nd, Hf and Pb systems and mantle evolution.

Distinguishing chemical signals of ancient mantle heterogeneity from modern petrogenesis

We can harness the chemical and time-dependent characteristics of radiogenic isotope ratios, and compare these to major and trace element compositions, to determine which chemical signatures in a volcanic rock reflect how the rock was formed, and which ones reflect the source it came from.

Many magmas are incompletely homogenized mixtures of liquids of different compositions, arising from the conditions of magma production or source rocks variations.

So to start this discussion, we return to the last topic of lecture 40, which was about tracing mixtures in igneous petrogenesis with radiogenic isotopes and trace elements.

Tracing Mixtures with Radiogenic Isotopes and Trace Elements

Recall that how and when materials are mixed makes a difference in what a mixture looks like for both trace elements and radiogenic isotope ratios.

Isotopic heterogeneity in long-lived systems like Rb-Sr, Sm-Nd, Lu-Hf, U-Pb and Th-Pb is nevertheless attributable to the source rocks (or contamination) because melting and crystallization do not fractinate isotopes like they do trac element ratios.

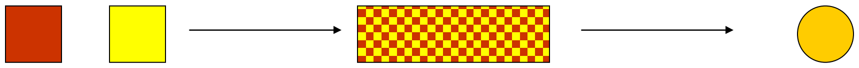
So differences between $^{87}Sr/^{86}Sr_{lava}$ and $(a/b)_{lava}$ help us to categorize...

- the types of mantle heterogeneities that exist,
  - where they came from,
    - when they formed,
      - and what sorts of other trace element signatures they might have.

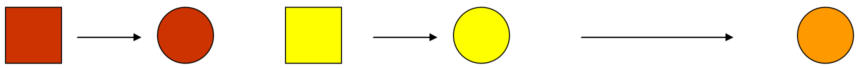
Tracing Mixtures …

Consider three mixing scenarios for two mantle materials 1 & 2:

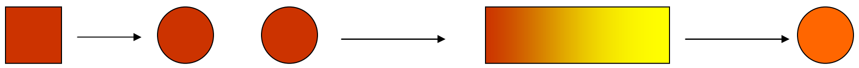
- $solid_1$ + $solid_2$ mixes to make $solid_{12}$. $solid_{12}$ melts to make $melt_{12}$



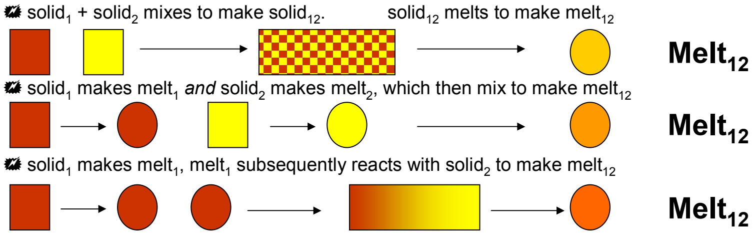
- $solid_1$ makes $melt_1$ *and* $solid_2$ makes $melt_2$, which then mix to make $melt_{12}$



- $solid_1$ makes $melt_1$, $melt_1$ subsequently reacts with $solid_2$ to make $melt_{12}$



Tracing Mixtures …



- solid$_1$ + solid$_2$ mixes to make solid$_{12}$. solid$_{12}$ melts to make melt$_{12}$

Melt$_{12}$

- solid$_1$ makes melt$_1$ *and* solid$_2$ makes melt$_2$, which then mix to make melt$_{12}$

Melt$_{12}$

- solid$_1$ makes melt$_1$, melt$_1$ subsequently reacts with solid$_2$ to make melt$_{12}$

Melt$_{12}$

Melt$_{12}$ will be different in each case because mixtures are made at different points in the melting process.

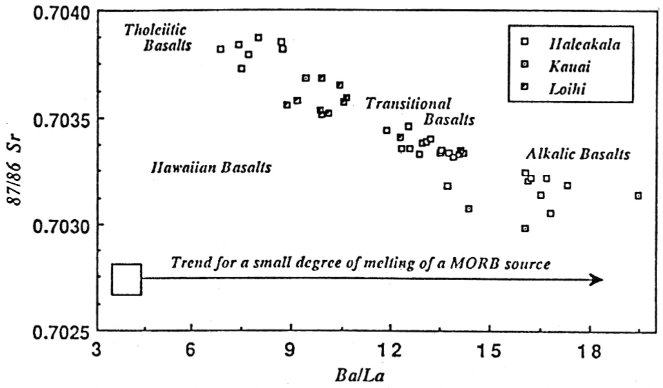
So, the *concentrations* of the chemical elements we are monitoring cause different mixing parameters (R) in each case.

We use isotopes and trace elements together to “back out” likely end member compositions and the extent of source heterogeneity versus petrogenetic heterogeneity upon magma formation and evolution.

Let’s go through an example.

Using Mixtures to Trace Processes

Here are data for $^{87}Sr/^{86}Sr$ and Ba/La, a ratio of two highly incompatible trace elements, in lavas from three Hawaiian volcanoes.



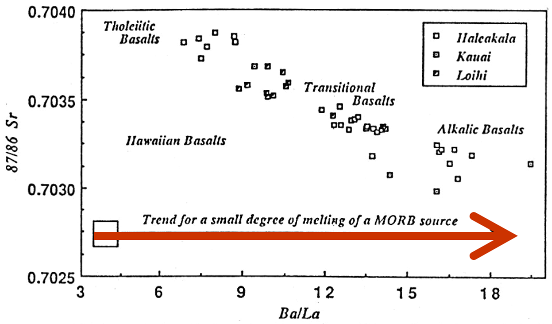
Sun & McDonough Fig 148., from Saunders & Norry, "Magmatism in Ocean Basins"

These data suggest *mixing* of materials with different isotopic and trace element compositions. Sr/La in each end-member appears similar, as the data array is roughly linear (r≈1). But when and how did such mixing occur?

Using Mixtures to trace processes

🛠 If all the Ba/La dispersion were from melting alone, we would expect a horizontal array (no relationship to $^{87}Sr/^{86}Sr$)

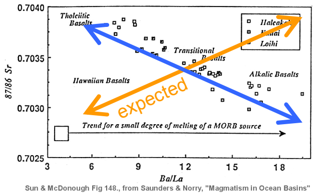
Thus, heterogeneities in the Hawaiian mantle are required. We need two end-members: a “tholeiitic-source” mantle and an “alkalic-source” mantle.



Sun & McDonough Fig 148., from Saunders & Norry, "Magmatism in Ocean Basins"

Using Mixtures to trace processes

🛠 Recall that $^{87}Sr/^{86}Sr$ reflects *time-averaged* Rb/Sr.



Sun & McDonough Fig 148., from Saunders & Norry, "Magmatism in Ocean Basins"

Could some ancient event have separated a homogeneous parcel of mantle into two reservoirs with different Rb/Sr and Ba/La, and then these reservoirs subsequently melted and mixed?

This is unlikely. Time-averaged Rb/Sr (as $^{87}Sr/^{86}Sr$) is inversely correlated with Ba/La here, but typical solid-melt D values require a positive correlation if the data array were caused by a single ancient event.

$K_d^{Rb} \sim 0.02$ $K_d^{Sr} \sim 0.05$	$K_d^{Rb} / K_d^{Sr} \sim 0.4$
$K_d^{Ba} \sim 0.02$ $K_d^{La} \sim 0.08$	$K_d^{Ba} / K_d^{La} \sim 0.25$

In mantle melts, Rb/Sr and Ba/La *should both increase* relative to the source rock. That’s not what we see.

Using Mixtures to trace processes

But can we disprove this hypothesis quantitatively?

If the heterogeneity in the Hawaiian mantle was produced by a single ancient melting (and melt-extraction) event, we would expect to see roughly 1.6 times more variation in Rb/Sr than in Ba/La

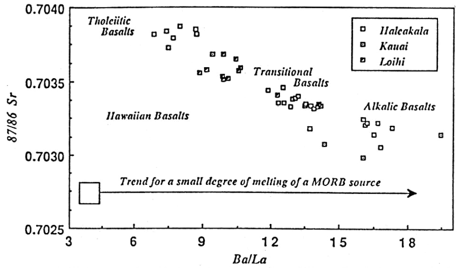
Let's first see if all the trace element and isotopic heterogeneity could be ancient.

$K_D^{Rb}/K_D^{Sr} = 0.40$ and $K_D^{Ba}/K_D^{La} = 0.25$

If the heterogeneity in the mantle was produced by a simple melting and melt extraction event in the past, one would expect roughly 0.40/0.25 = 1.6 times the variation in Ba/La as in Rb/Sr since

Using Mixtures to trace processes

Estimating the data trend in this figure shows that it runs



Sun & McDonough Fig 148., from Saunders & Norry, "Magmatism in Ocean Basins"

from: $^{87}Sr/^{86}Sr = 0.7038$ Ba/La = 8

to: $^{87}Sr/^{86}Sr = 0.7032$ Ba/La=16

So Ba/La varies by 2x

and, using our K_D relationship from above, we can predict that Rb/Sr should have varied by 2/1.6 = 1.25 x during the melting event.

Using Mixtures to trace processes

Let's now assume a typical Rb/Sr = 0.03 g/g for mantle producing oceanic tholeiites and an arbitrary $^{87}Sr/^{86}Sr_{initial}$ = 0.7000 for some time in the past.

Convert the Rb/Sr weight ratio to a mole ratio of $^{87}Rb/^{86}Sr$:

$$0.03 \times \frac{\text{mol Rb}}{85.47 \text{ g Rb}} \times \frac{87.62 \text{ g Sr}}{\text{mol Sr}} \times \frac{0.2783 \text{ mol } ^{87}\text{Rb}}{\text{Mol Rb}} \times \frac{1 \text{ mol Sr}}{0.0986 \text{ mol } ^{86}\text{Sr}}$$

$^{87}Rb/^{86}Sr$ = 0.0.0868 mol/mol for the "tholeiitic" mantle

And using our estimated Rb/Sr variation from above, the "alkalic mantle" should have

$^{87}Rb/^{86}Sr$ = 0.0868 x 1.25 = 0.1085 mol/mol

Using Mixtures to trace processes

Next we estimate the time required to evolve the $^{87}Sr/^{86}Sr$ we observe today from these Rb/Sr and the initial arbitrary isotopic composition:

$$(^{87}Sr/^{86}Sr)_{today} = (^{87}Sr/^{86}Sr)_{initial} + (^{87}Rb/^{86}Sr)_{today}(e^{\lambda t} - 1)$$

Tho: $0.7038 = 0.7000 + 0.0868 * (e^{\lambda t} - 1)$

Alk: $0.7032 = 0.7000 + 0.1085 * (e^{\lambda t} - 1)$

Subtracting: $0.0006 = -0.0217 \cdot (e^{\lambda t} - 1)$

$e^{\lambda t} = 0.9969$ → **$t = -2.01 \times 10^9$ yr!!**

If a single volume of mantle was fractionated in the past into two reservoirs that then evolved separately until they recently melted beneath Hawaii, ***t*** would have to be positive. But it's clearly not, so our scenario is wrong.

Instead, initial $^{87}Sr/^{86}Sr$ values (and probably Rb/Sr and Ba/La) must have been different in these two mantle end-members.

Using Mixtures to trace processes

We can also examine this problem a different way. Let's see how different $^{87}Sr/^{86}Sr$ would have to be at constant time since fractionation to explain the $^{87}Sr/^{86}Sr$ difference we see today:

In this case, the $e^{-\lambda t}$-1 term in each of the above equations is the same, so that:

Tho: $0.7038 = {}^{87}Sr/{}^{86}Sr_i^{\,Tho} + 0.0868*(e^{-\lambda t}-1)$

Alk: $0.7032 = {}^{87}Sr/{}^{86}Sr_i^{\,Alk} + 0.1085*(e^{-\lambda t}-1)$

rearranging then and substituting one equation into the other...

$^{87}Sr/^{86}Sr_i^{\,Tho} - {}^{87}Sr/^{86}Sr_i^{\,Alk} = 0.1766$

this implies $^{87}Sr/^{86}Sr_i^{\,Tho} > {}^{87}Sr/^{86}Sr_i^{\,Alk}$

i.e., if $^{87}Sr/^{86}Sr_i^{\,Tho} = 0.7000$, then $^{87}Sr/^{86}Sr_i^{\,Alk} = 0.5234$

meaning the tholeiitic source would be initially have been *more radiogenic* than the alkalic one.

Using Mixtures to trace processes

A tholeiitic source that is *more radiogenic* than the alkalic one is *inconsistent* with the Kds of the elements.

If the two sources were the same age, they have experienced a relative Rb/Sr ratio (alkalic/tho) = 0.7478, or

about 37% of the relative Ba/La ratio (alkalic/tho) = 2.

Thus, we conclude that the Ba/La vs. $^{87}Sr/^{86}Sr$ data trend for Hawaiian lavas...

cannot be explained by mixing of materials that were formed during a single event at <u>any</u> time in the past, since…

- we seem to need either *different amounts of time* after a fractionation event from a material with one initial $^{87}Sr/^{86}Sr$ -or-
- *different ratios of K_ds during fractionation* between Rb/Sr and Ba/La after a fixed amount of time since the hypothesized fractionation event.

Using Mixtures to trace processes

Then what's the explanation? The isotopic data demonstrate clearly that we have two mantle end-members. However, recent petrogenesis must also have played a key role in producing the observed Ba/La and Rb/Sr compositions.

🛠 The negative correlation between Ba/La and $^{87}Sr/^{86}Sr$ suggests that the **alkalic Hawaiian basalts** are derived from smaller fractions of partial melting — **smaller F** (i.e., yielding melts with higher Ba/La) — of a part of the mantle beneath the islands that has **greater long-term incompatible-element depletion** (as seen in lower $^{87}Sr/^{86}Sr$) compared to **the part of the mantle from which the tholeiites are mainly derived**.

🛠 This is but one example of a growing body of evidence for tapping of multiple mantle sources under varying conditions of melting at a single hotspot.

Using Mixtures to trace processes

Mixing like this is not just restricted to hotspots like Hawaii. These are recent Nd-Pb isotope data for *non-hotspot MORB* from the Rano Rahi Seamounts on the E. Pacific Rise. The data are explained by two-end-member melting and mixing at a range of F values.

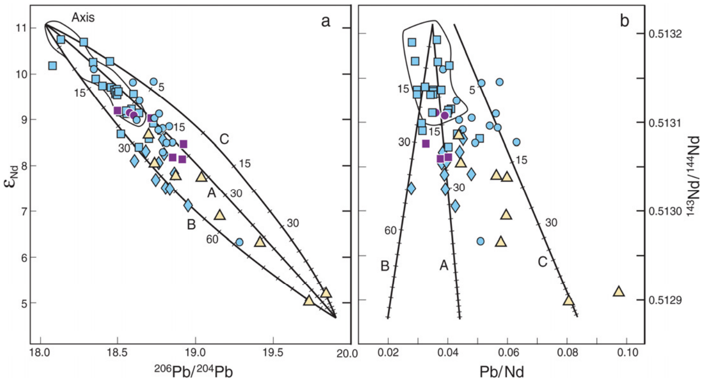


Figure 12. (a) ε_{Nd} vs. $^{206}Pb/^{204}Pb$. Model mixing curves illustrate source mixing (curve A), mixing of a 5% aggregate fractional melt [*Shaw,* 1970] of the high-ε_{Nd} end-member and a 1% melt of the low-ε_{Nd} *C*-type end-member (curve C), and source mixing in which the *C*-type end-member has previously lost a 2% fractional melt (curve B). (b) ε_{Nd} vs. Pb/Nd concentration ratio; the mixing lines correspond to the curves in panel (a). In both panels, tick marks indicate the proportion of material from the *C*-type end-member. Assumed distribution coefficients are from *Workman and Hart* [2005], as are the Nd and Pb concentrations of the high-ε_{Nd} source (0.58 ppm, 0.02 ppm, respectively). The *C*-type source is assumed to have the Nd concentration (1.73 ppm) of the model enriched mantle peridotite of *Ito and Mahoney* [2005] but one-third less Pb (0.076 ppm). **Hall et al. (2006)**

Note that mixing arrays in Pb/Nd vs. ε_{Nd} space are straight lines (Nd is in the denominator of each axis).

Radiogenic Isotopes and Mantle Composition

If we compare isotopic data for volcanoes in different tectonic settings, we find different ranges of Sr, Nd, Pb and Hf isotope values.

Histograms of isotopic data show that on a *time-averaged basis, some parts of the mantle are depleted and some are enriched relative to the estimated primitive-mantle values.*

Putting the different types of data together in *multi-isotope space*, we find that…

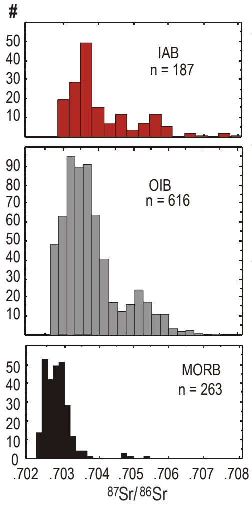


Figure 11.16. Comparison of Pb isotope ratios in MORB, OIB, and IAB.

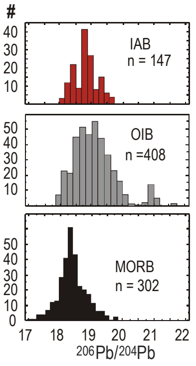


Figure 11.14 Comparison of ^{87}Sr/^{86}Sr ratios in mid-ocean ridge basalts (MORB), oceanic island basalts (OIB) and island arc basalts (IAB).

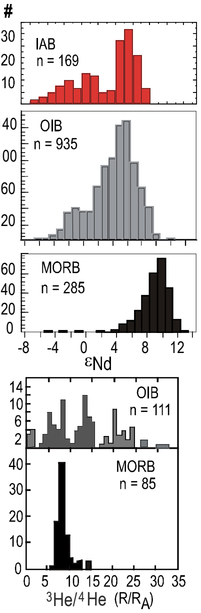


Figure 11.15. Comparison of ε_{Nd} and ^{3}He/^{4}He in mid-ocean ridge basalts(MORB), oceanic island basalts (OIB) and island arc basalts (IAB).

all figures modified from White, "Geochemistry"

Radiogenic Isotopes and Mantle Evolution

…there seem to be **five general types of mantle**, three of which have different levels of relative long-term enrichment.

In addition to the MORB-source end-member, at least three possible "enriched" end-member components are identified in three-dimensional Sr-Nd-Pb isotopic space.

These three components indicate long-term enrichment in different incompatible elements: HIMU (high μ), EM1 and EM2. A fifth type of mantle, "C" or "FOZO", may represent slightly depleted primitive mantle.

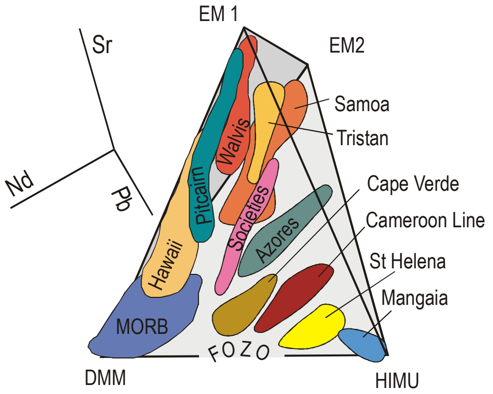


Figure 11.30. Three dimension plot of ^{87}Sr/^{86}Sr, ^{143}Nd/^{144}Nd, & ^{206}Pb/^{204}Pb. Most oceanic basalt data plot within a tetrahedron defined by the composition of EMI, EMII, HIMU, and DMM components. Oceanic islands and island chains tend to form elongate isotopic arrays, many of which seem to point toward a focal zone (FOZO) at the base of the tetrahedron. Adapted from Hart et al. (1992). *modified from White, "Geochemistry"*

Radiogenic Isotopes and Mantle Evolution

One common idea among mantle geochemists is that *some of these components of long-term* ***enriched mantle represent*** *different portions of the material that's injected into the mantle at subduction zones* (altered oceanic crust, marine sediments, oceanic mantle lithosphere).

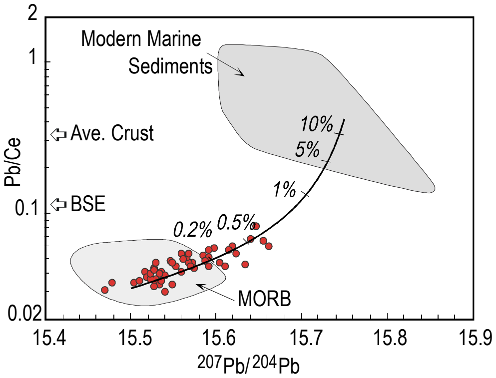


Figure 11.29. Pb/Ce and $^{207}Pb/^{204}Pb$ in basalts from the Society Islands. A mixing line between depleted mantle and sediment passes through the data. Estimated Pb/Ce ratios of average continental crust and bulk silicate Earth (BSE) are also shown. *modified from White, "Geochemistry"*

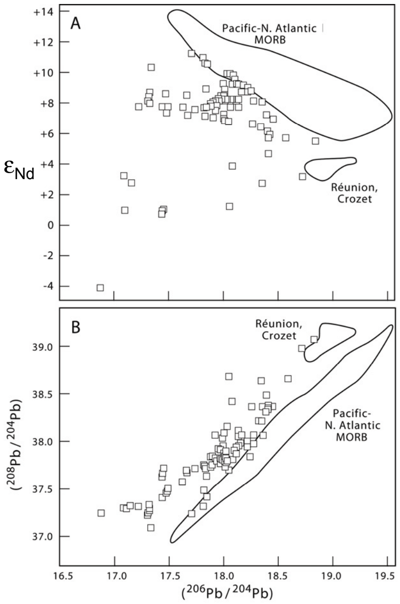
Part of the evidence that recycled material is present in hotspot and other oceanic island sources (here the Society Islands) comes from combined isotopic and trace element data, such as Pb/Ce.

Radiogenic Isotopes and Mantle Evolution

An additional type of "enriched" mantle may result from *continental lithospheric mantle and/or lower crust that gets detached from the lithosphere*, and is left behind in the convecting mantle, where it gradually mixes in. This material may show up in young ocean basins, such as the Indian Ocean.

Indeed, Indian MORB are distinctly different in their Pb-Nd-Sr-Hf isotope composition from Pacific and North Atlantic MORB, in a manner that is consistent with this scenario.

Indian Ocean MORB



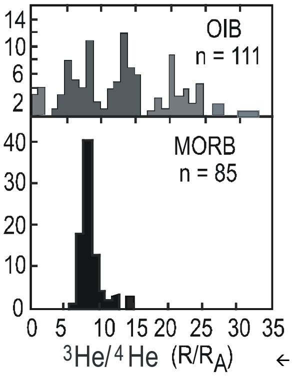
From Mahoney et al. (1998)

Radiogenic Isotopes in Mantle Evolution

What about primitive mantle? Is there any left? Some geochemists believe that there is still a reservoir of “left-over” primitive mantle, based largely on the high amount of ^{3}He in the mantle sources of many oceanic basalts, especially *some hotspot-type OIB*.

^{3}He is primordial and non-radiogenic, unlike ^{4}He.

Mantle-derived rocks with high ratios of ^{3}He to ^{4}He suggest source regions that are *relatively un-degassed* — and thus maybe more or less primitive.



← R_A is the atmospheric ratio.

Figure 11.15. Comparison of ε_{Nd} and ^{3}He/^{4}He in mid-oceanic island basalts (OIB) and island arc basalts (IAB).

Radiogenic Isotopes in Mantle Evolution

Where are all these end-member materials located, and how do they move about in a convecting mantle? This is still a subject of great debate. Both whole-mantle and two-layer convection models for the mantle are consistent with some, but not all, geochemical observations.

2 Competeing Models for disposition of primitive, depleted, and enriched materials in the mantle involve part- and whole- mantle convection

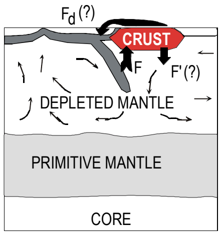


Figure 11.21. The three reservoir model of the mantle. The depleted mantle is the source of MORB and has ε_{Nd} = +10, the lower mantle is primitive and has bulk Earth characteristics, e.g., ε_{Nd} = 0.

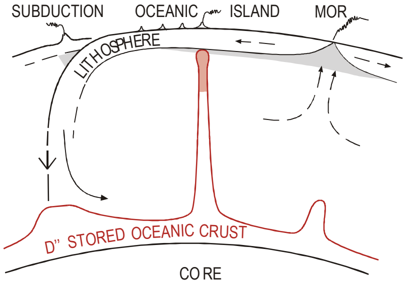


Figure 11.28. Cartoon illustrating the oceanic crustal recycling model of Hofmann and White (1982). Oceanic crust is transformed into eclogite and post-eclogite assemblages upon subduction. It separates from the less dense underlying lithosphere and sinks to the deep mantle where it accumulates. Eventually, it becomes sufficiently hot to form plumes thatrise to the surface, producing oceanic island volcanism. After Hofmann & White (1982).

both figures modified from White, “Geochemistry”