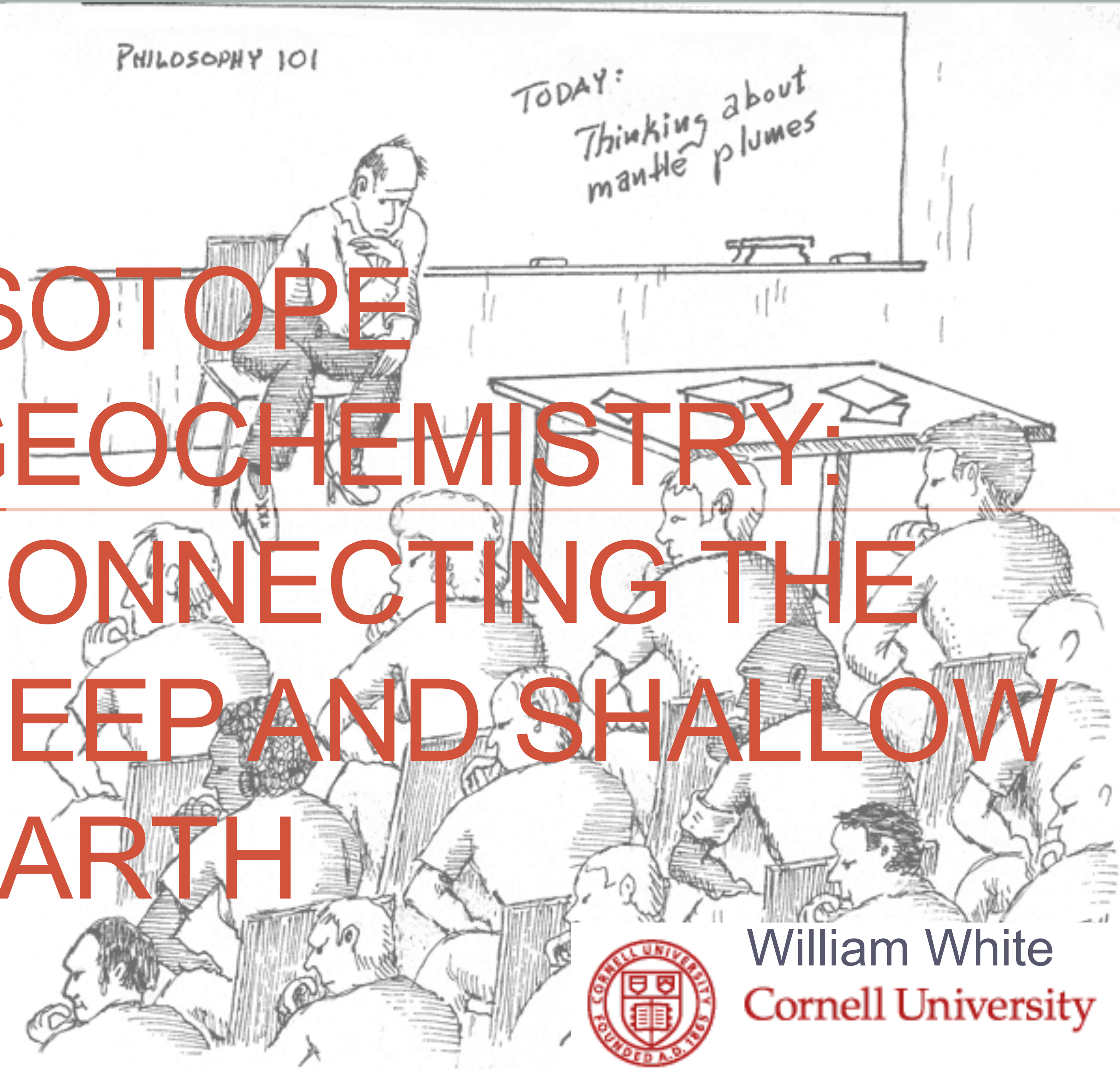
ISOTOPE GEOCHEMISTRY: CONNECTING THE DEEP AND SHALLOW EARTH



William White
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Outline

- A few fundamentals of trace element and radiogenic isotope geochemistry.
- Initializing: Poor constraint’s on Earth’s Composition
- Mantle Radiogenic Isotope Systematics
- Mantle Chemical Evolution: Dominance of Crustal Recycling
- The Noble Gas Perspective: A Primitive Component Too
- Anekantavada
- Top to Bottom and Back Again: Mantle Plumes Complete the Cycle

Differentiation of the Earth

- Based on what we know from meteorites, the Earth's core formed very early (metal-silicate segregation likely occurred in the planetary embryos that accreted to form the Earth.
- An early protocrust may have formed by crystallization of magma oceans (or magma lakes) as the Earth accreted (as it did on Vesta and the Moon), but no vestige of this crust remains.
- While the Earth's core formed early, the present crust has grown by *melting* of the mantle over geologic time (rate through time is debated).
- Partitioning of elements between crust and mantle depends on an element's *compatibility.*

The Partition Coefficient

- Geochemists find it convenient to define a *partition or distribution coefficient* of element i between phases α and β:

$$D_i^{\alpha-\beta} = \frac{C_i^\alpha}{C_i^\beta}$$

- Where one phase is a liquid, the convention is the solid is placed in the denominator:

$$D_i^{s-\ell} = \frac{C_i^s}{C_i^\ell}$$

  - (Metal-silicate partition coefficients relevant to core formation are defined in an exactly analogous way.)
- *Trace element* partitioning depends on how easily an element can substitute for a major element in a crystal lattice site.
- ***This depends mainly on ionic size and charge.***

INCOMPATIBLE ELEMENTS ARE THOSE WITH $D^{S/L} \ll 1$.
COMPATIBLE ELEMENTS ARE THOSE WITH $D^{S/L} \geq 1$.

These terms refer to partitioning *between silicate melts and phases common to mantle rocks (peridotite)*. It is this phase assemblage that dictates whether trace elements are concentrated in the Earth's crust, hence the significance of these terms.

The Rare Earth Elements

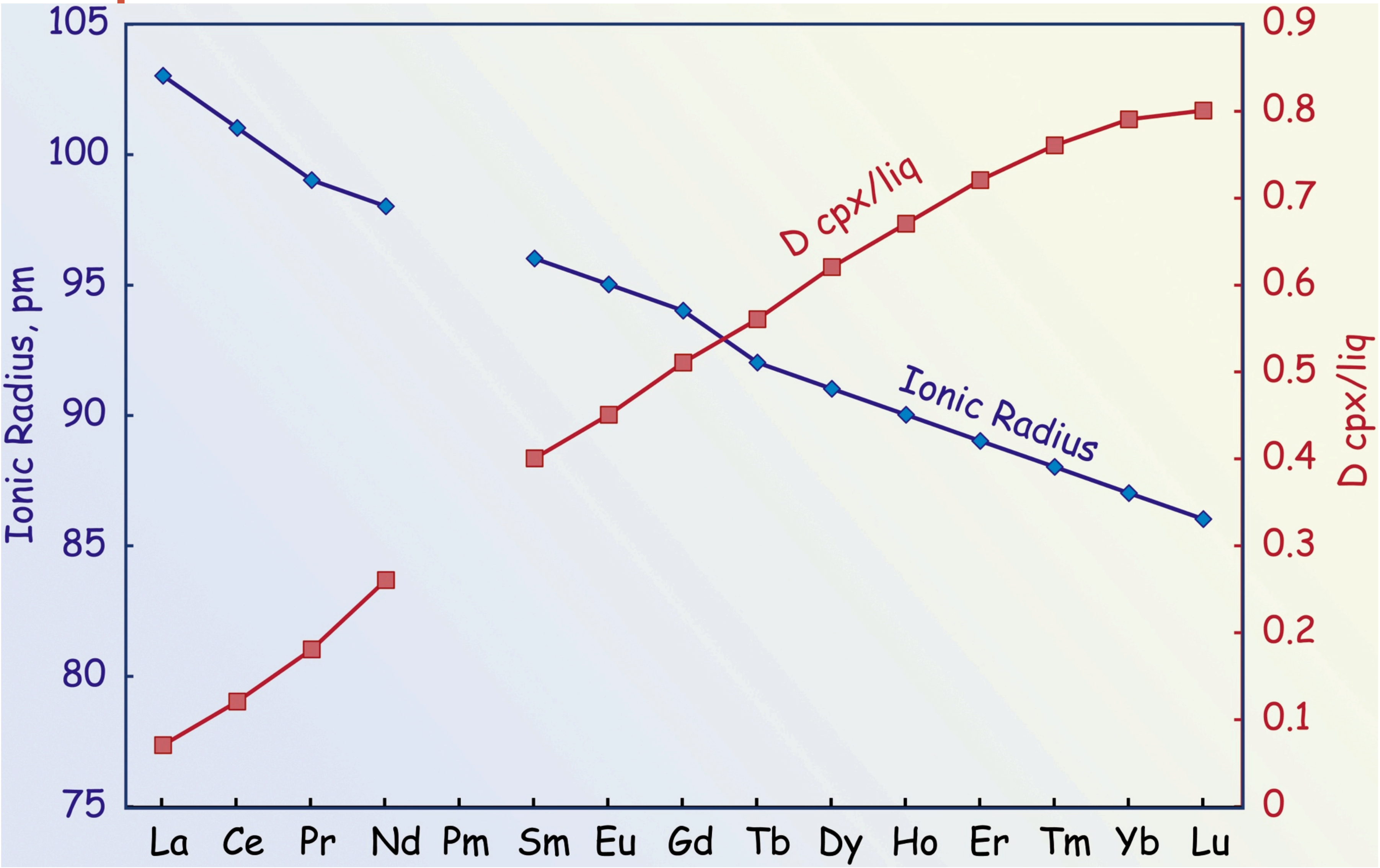
Group

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1																	He 2
2	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
7	Fr 87	Ra 88	Ac 89															

Rare Earths

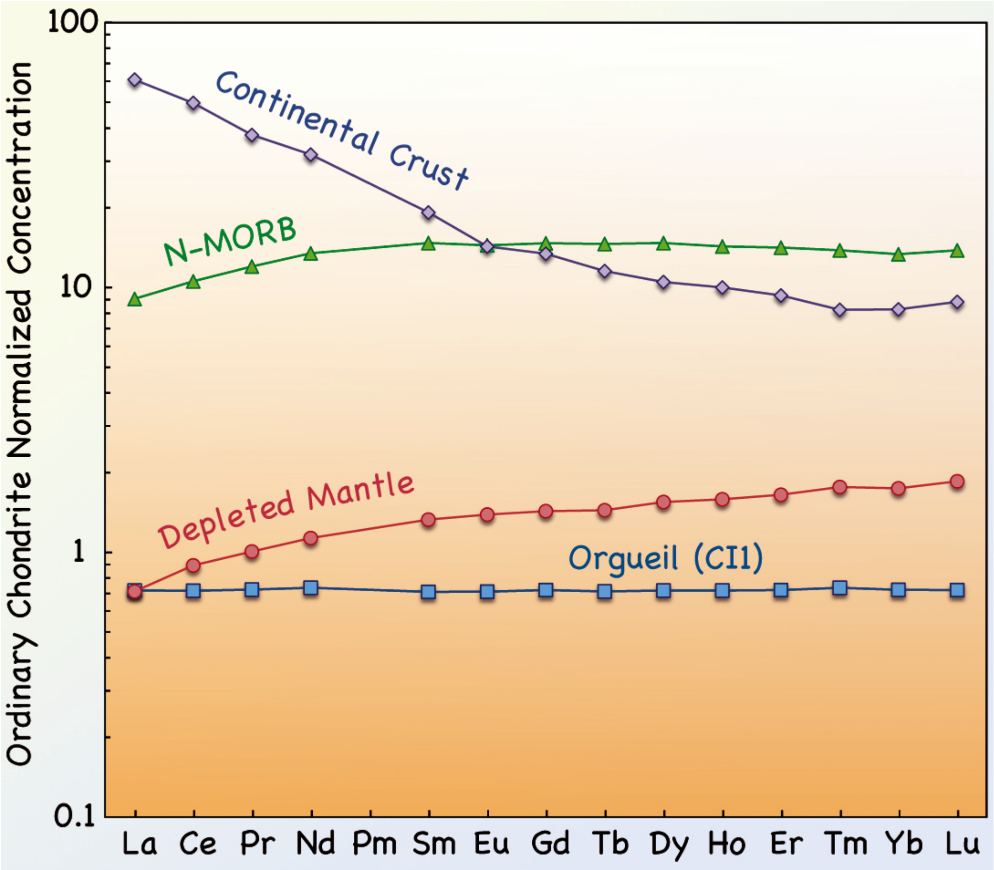
Lantanides (6)	La 57	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
Actinides (7)	Ac 89	Th 90	Pa 91	U 92	Np	Pu									

Importance of Ionic Size

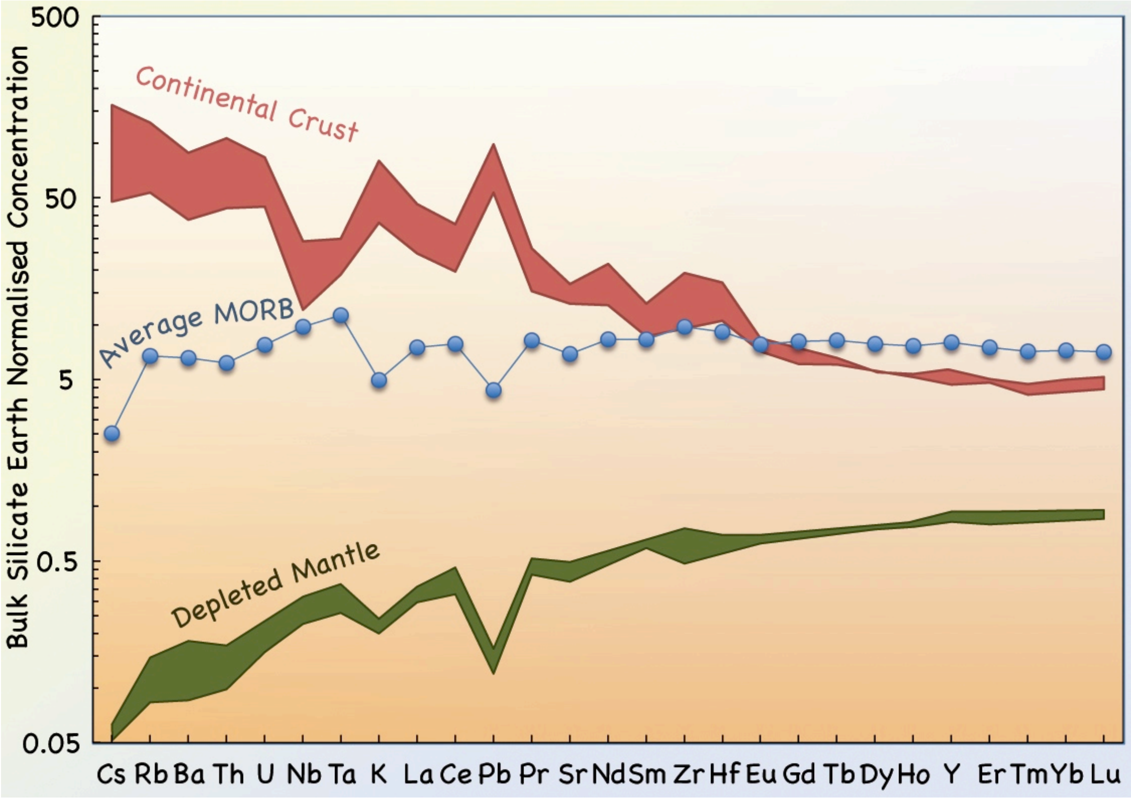


Rare Earth Diagrams

- Relative abundances are calculated by dividing the concentration of each rare earth by a reference concentration, such as chondrites.
  - Rare earths are *refractory* elements, so that their relative abundances are the same in most primitive meteorites - and presumably (to a first approximation) in the Earth.
- Why do we use relative abundances? To smooth out the saw-toothed pattern abundance of cosmic abundances (a result of nuclear stability.
- Abundances in chondritic meteorites are generally used for normalization.

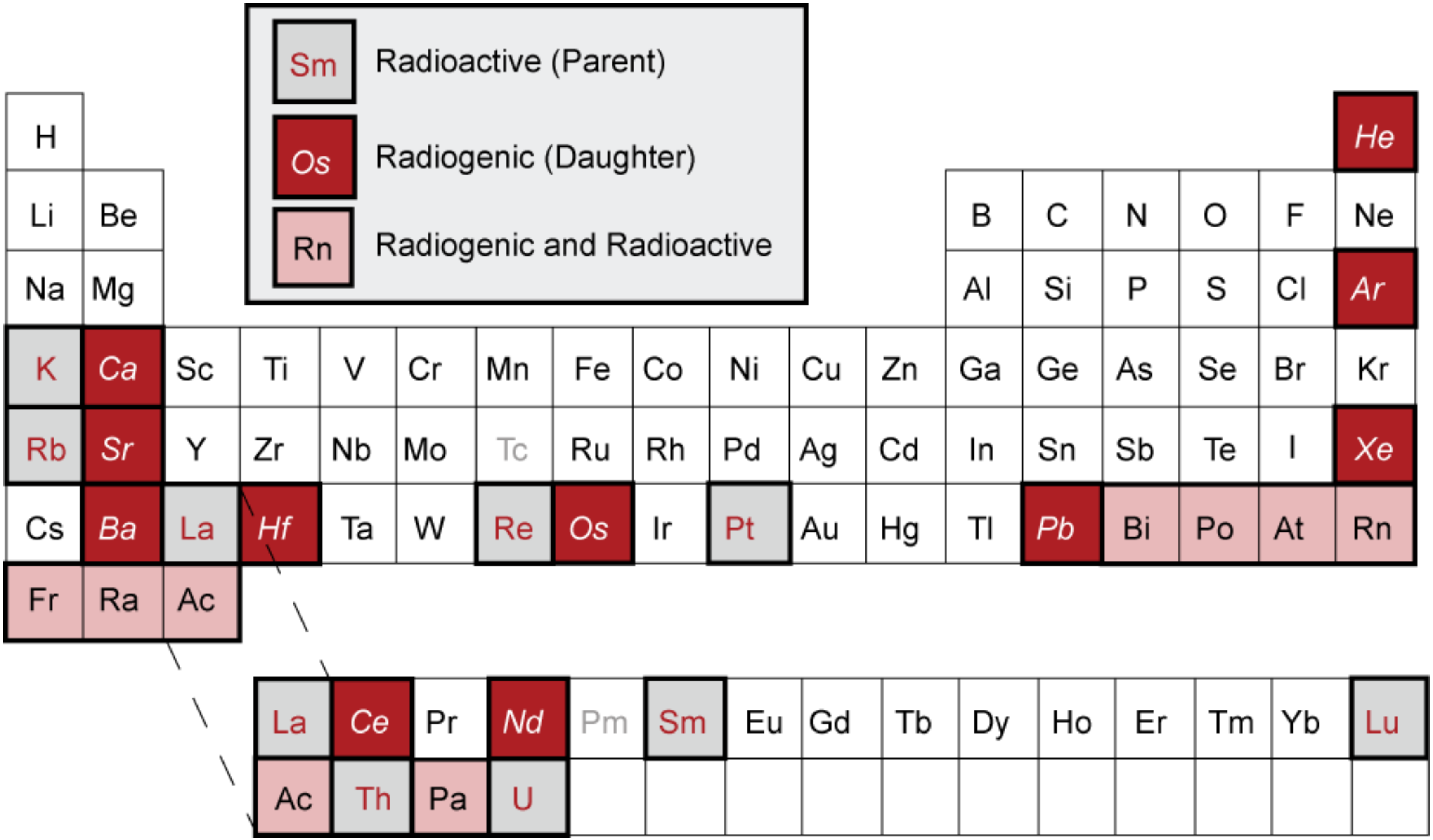


Crust-Mantle Relationships



We can incorporate other elements into the REE diagram by placing them in order of increasing compatibility. This works only so well, and "anomalies" develop because of factors other than ionic size & charge, but these anomalies are diagnostic.

Radiogenic Isotope Geochemistry



Isotopic Evolution

- Basic Equation: $$\frac{d^{147}Sm}{dt} = -\lambda_{147}{}^{147}Sm$$
- From this, we can derive the following equation to describe the evolution of the $^{143}Nd/^{144}Nd$ ratio through time in a closed system, one that neither looses nor gains Sm or Nd:

$$\frac{^{143}Nd}{^{144}Nd} = \left(\frac{^{143}Nd}{^{144}Nd}\right)_0 + \frac{^{147}Sm}{^{144}Nd}(e^{\lambda t} - 1)$$

- Here we see that $^{143}Nd/^{144}Nd$ will be a function of 4 parameters:
  - The time elapsed since the initial time, *t,*
  - The present $^{147}Sm/^{144}Nd$ ratio of the system,
  - The initial $^{143}Nd/^{144}Nd$ of the system (i.e., at time t=0), $(^{143}Nd/^{144}Nd)_0$
  - The decay constant, λ,

Bottom Line

- Radiogenic isotope ratios are *time-integrated* measure of elemental ratios such as Rb/Sr, Sm/Nd, U/Pb, Lu/Hf, and Re/Os.

Some Notations

- Mu

$$\mu_{Nd} = \left(\frac{{}^{142}Nd/{}^{144}Nd_{sample} - {}^{142}Nd/{}^{144}Nd_{terrestrial\,std}}{{}^{142}Nd/{}^{144}Nd_{terrestrial\,std}} \right) \times 10^6$$

- Epsilon

$$\varepsilon_{Nd} = \left(\frac{{}^{143}Nd/{}^{144}Nd_{sample} - {}^{143}Nd/{}^{144}Nd_{CHUR}}{{}^{143}Nd/{}^{144}Nd_{CHUR}} \right) \times 10000$$

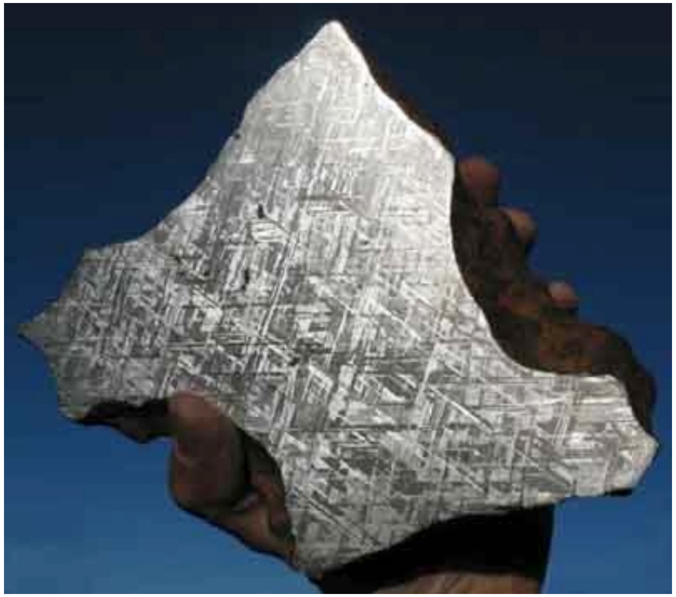
- Delta

$$\delta^{18}O = \left[\frac{{}^{18}O/{}^{16}O_{sample} - {}^{18}O/{}^{16}O_{std}}{{}^{18}O/{}^{16}O_{std}} \right] \times 1000$$

INITIALIZING: WHAT'S THE COMPOSITION OF THE EARTH?

Meteorites

- Differentiated (parts of differentiated planetesimals)
  - Achondrites
  - Irons
  - Stony-Irons
- Chondrites (collections of nebular dust)
  - Carbonaceous (volatile-rich)
  - Ordinary (most common)
  - Enstatite (highly reduced)

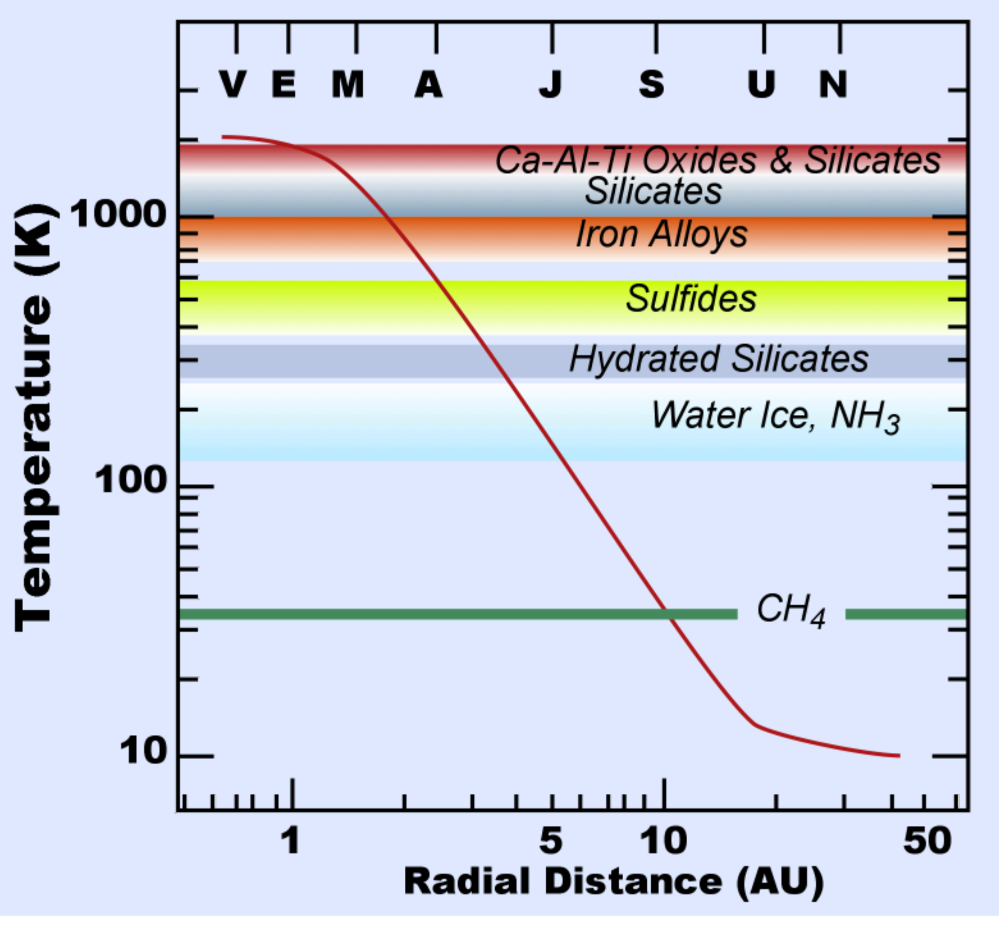


Chondrites

- Although somewhat metamorphosed and altered on parent bodies, chondrites are samples of the solar nebula.
- Compositions vary mainly in:
  - Oxidation state
  - Ratio of metal to silicate
  - ***Ratio of volatile to refractory material.***

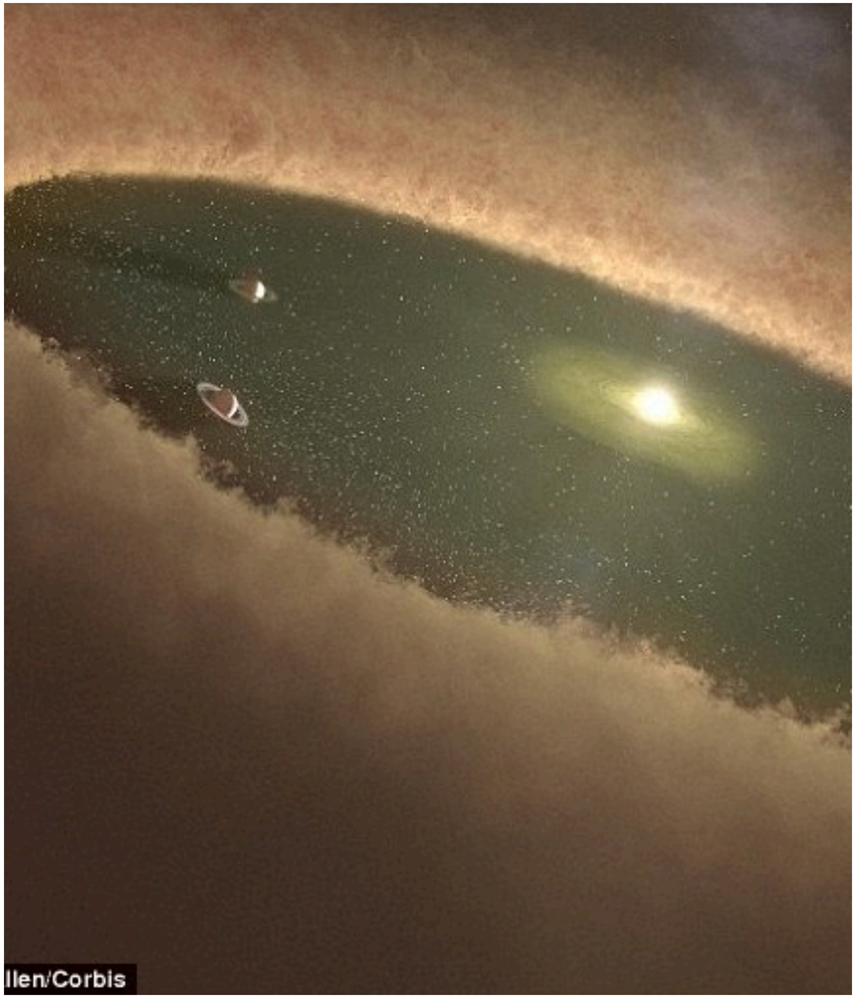
Murchison CM2

Temperatures in Protoplanetary Disk

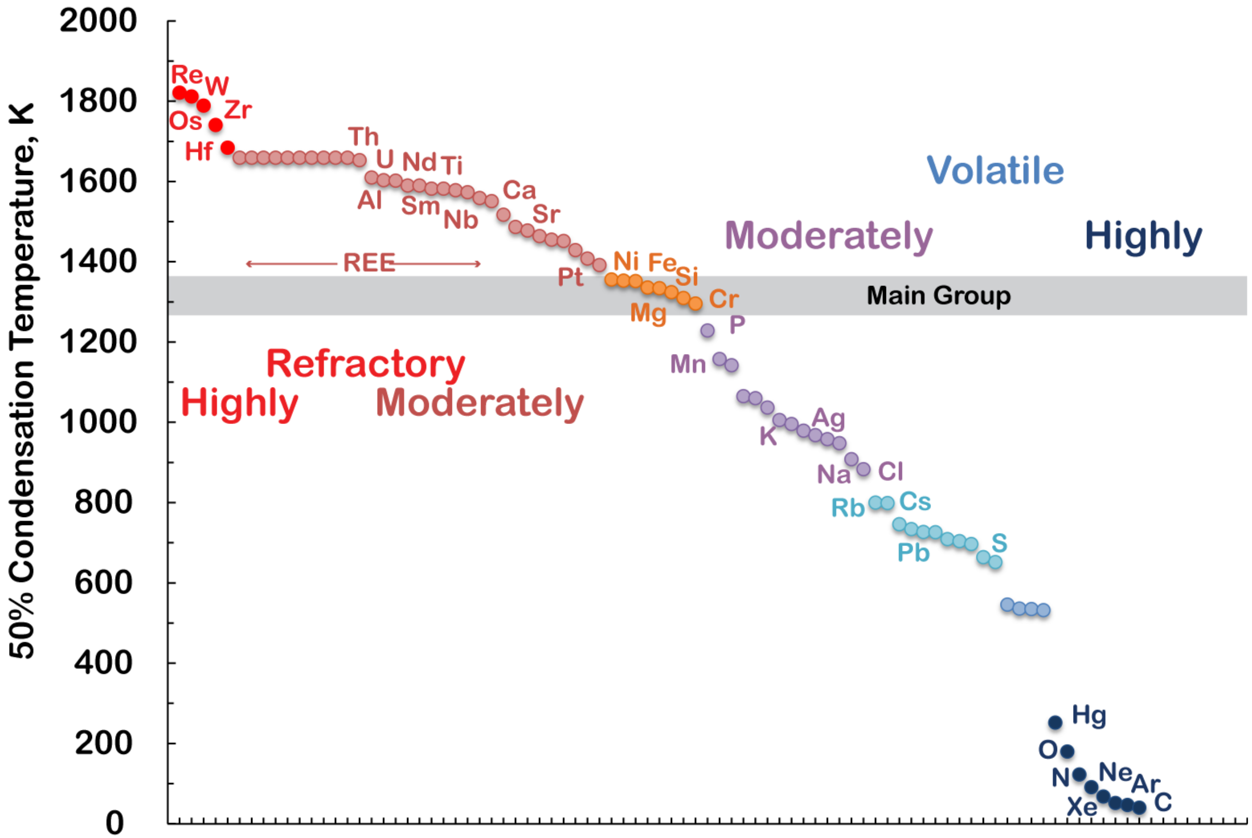


Canonical Model of Terrestrial Planet Formation

- Rocky planetesimals and planetary embryos form quickly in the inner solar system while it is still hot, but growth to full sized planets is slow.
  - Planetary embryos quickly (few Ma at most) melt and differentiate.
- Inner nebula is cleared of gas, and with it the volatile elements.
- Final accretion of terrestrial planets from already differentiated planetary embryos takes much longer.
- Giant planets form beyond the snow line, accrete quickly before nebular gas.
- Implication: ***main difference between terrestrial and nebular (chondritic) composition is just volatility.***



Volatility in the Solar Nebula



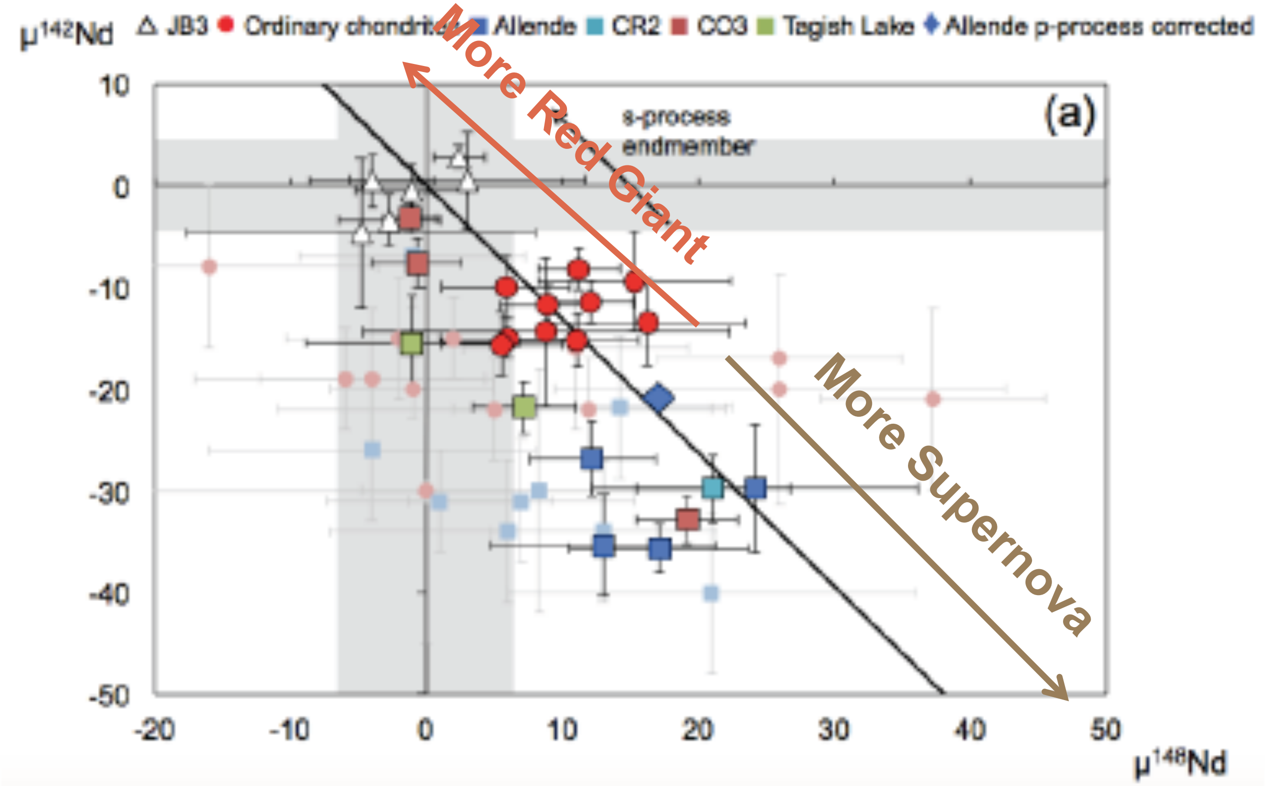
- 50% Condensation temperatures of the elements from a low pressure nebula of solar composition.

Data from Lodders, 2003

Refractory Lithophile Elements & Earth Models

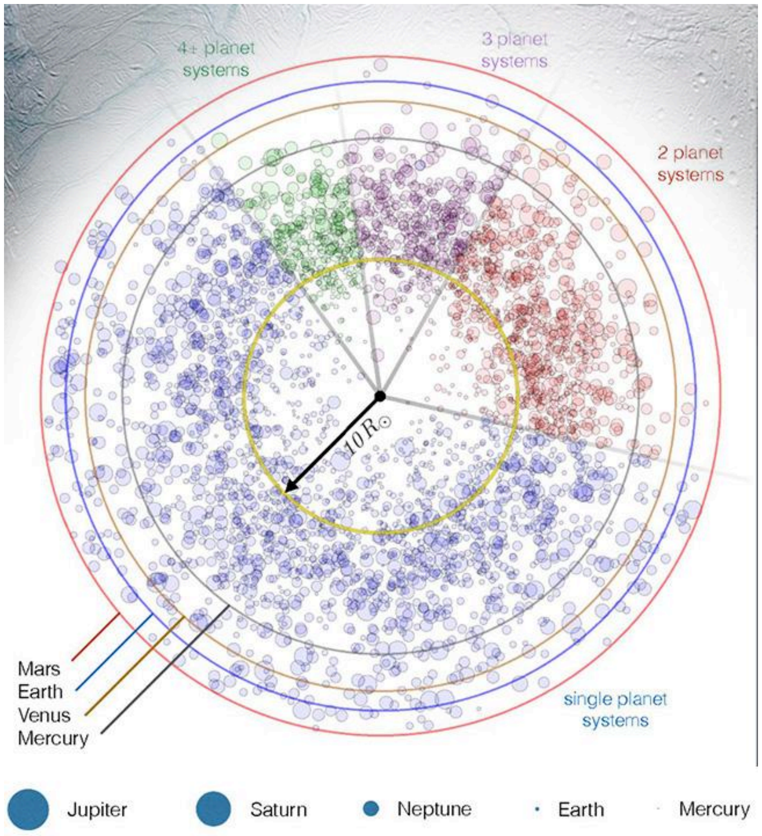
- The *relative* (but not absolute) abundances of refractory lithophile elements (RLE's) are very similar in all chondrite classes.
  - This implies nebular processes did not fractionate refractory elements from one and other.
- Models of Earth's composition rely, to varying degrees, on the assumption that the Earth too has chondritic *relative* abundances of refractory elements.

Complication #1: Heterogeneous Solar Nebula



- Heavy elements synthesized in Red Giants and in Supernova were not thoroughly mixed in the solar nebula

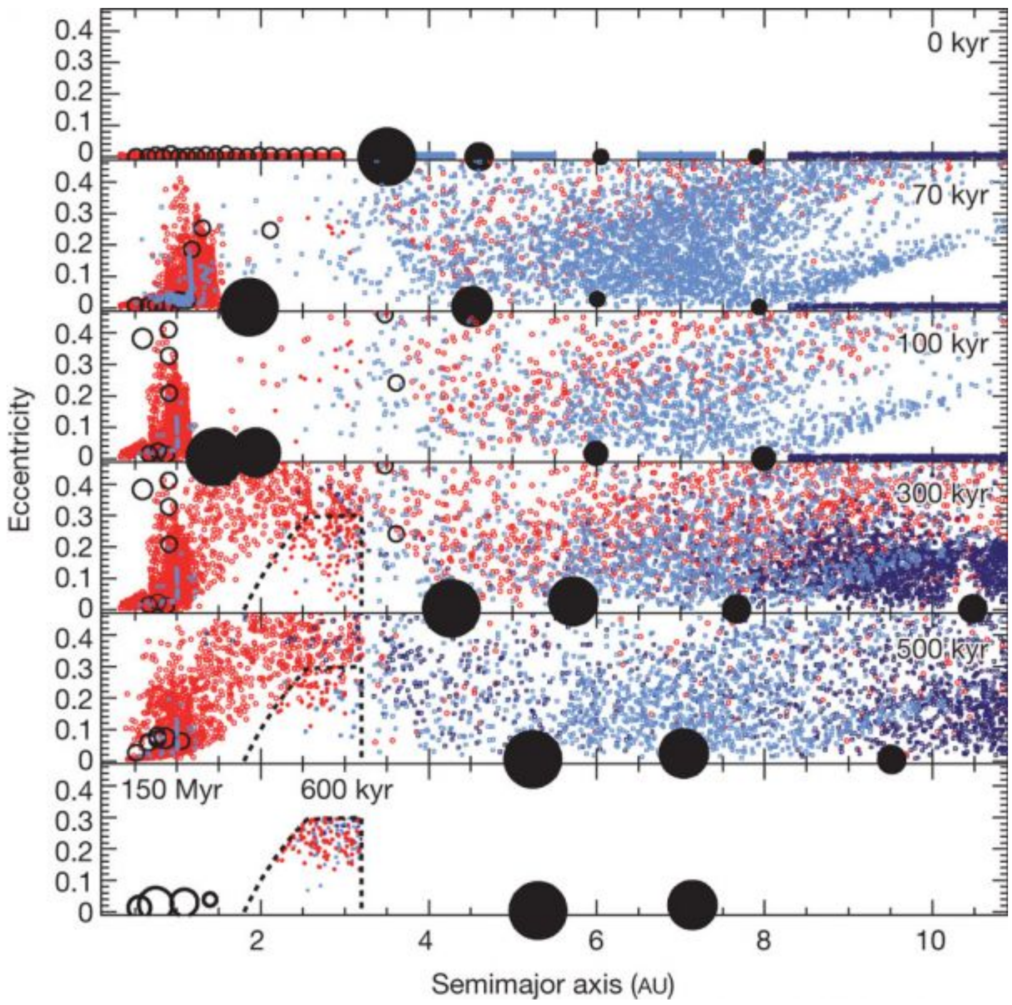
Complication #2: Our Solar System Is Odd



- Most solar systems have “Super-Earth” planets, often several large, inside the orbit of Mercury.
- Our inner solar system is weirdly empty.
- Why?

Grand Tack Model

- In the Grand Tack Model, Jupiter migrated inward from its formation site and subsequently moved outward as a consequence of locking into a 3:2 mean motion resonance with a newly formed Saturn.
- This throws newly formed planetary embryos into highly eccentric orbits.

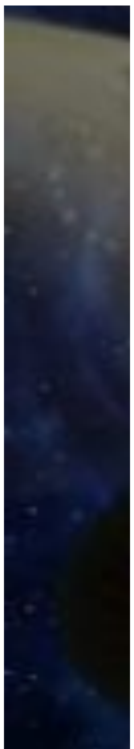


Grand Tack Model

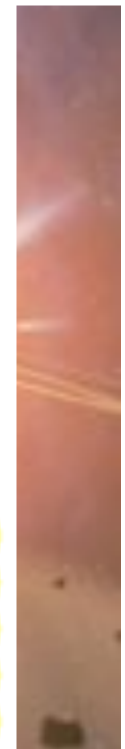
Jupiter's decisive role in the inner Solar System's early evolution

Konstantin Batygin[a,1] and Greg Laughlin[b]

PNAS, 2015



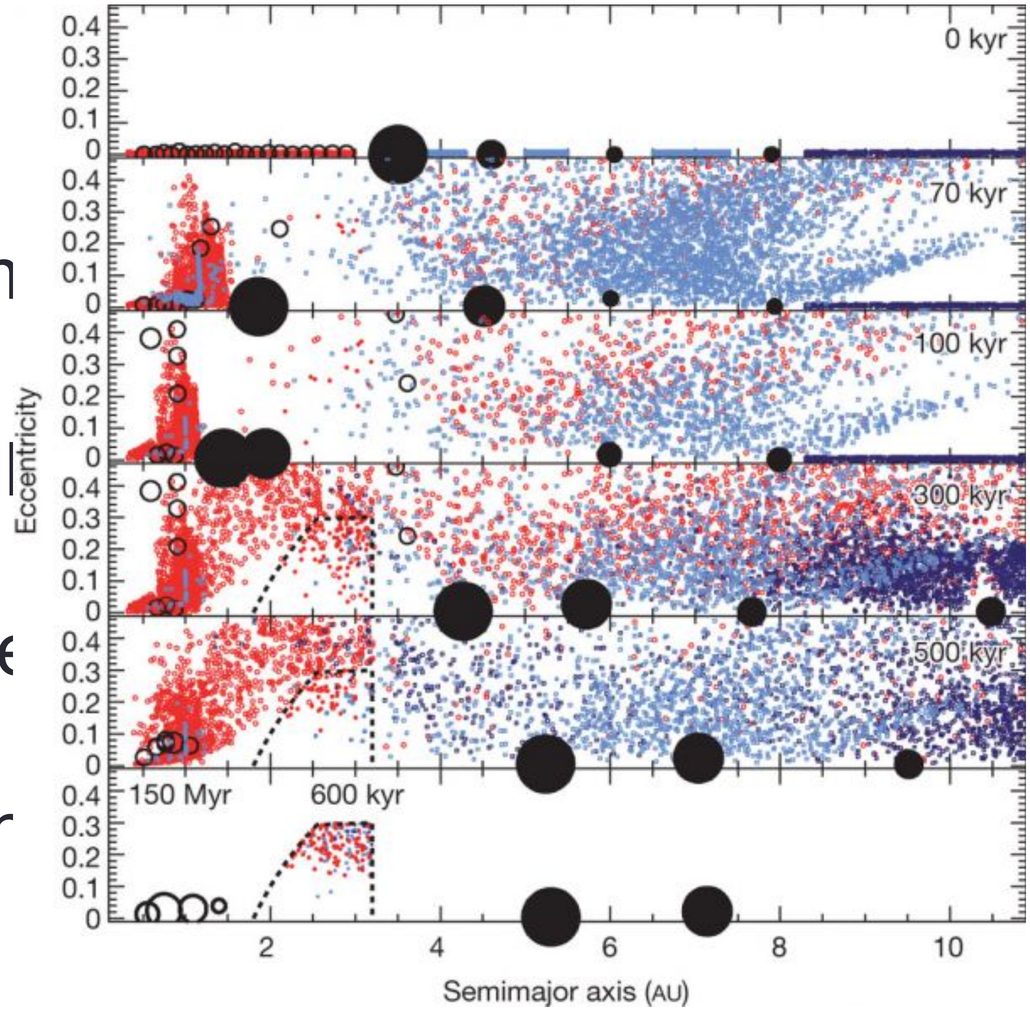
The statistics of extrasolar planetary systems indicate that the default mode of planet formation generates planets with orbital periods shorter than 100 days and masses substantially exceeding that of the Earth. When viewed in this context, the Solar System is unusual. Here, we present simulations which show that a popular formation scenario for Jupiter and Saturn, in which Jupiter migrates inward from $a > 5$ astronomical units (AU) to $a \approx 1.5$ AU before reversing direction, can explain the low overall mass of the Solar System's terrestrial planets, as well as the absence of planets with $a < 0.4$ AU. Jupiter's inward migration entrained $s \gtrsim 10$–100 km planetesimals into low-order mean motion resonances, shepherding and exciting their orbits. The resulting collisional cascade generated a planetesimal disk that, evolving under gas drag, would have driven any preexisting short-period planets into the Sun. In this scenario, the Solar System's terrestrial planets formed from gas-starved mass-depleted debris that remained after the primary period of dynamical evolution.



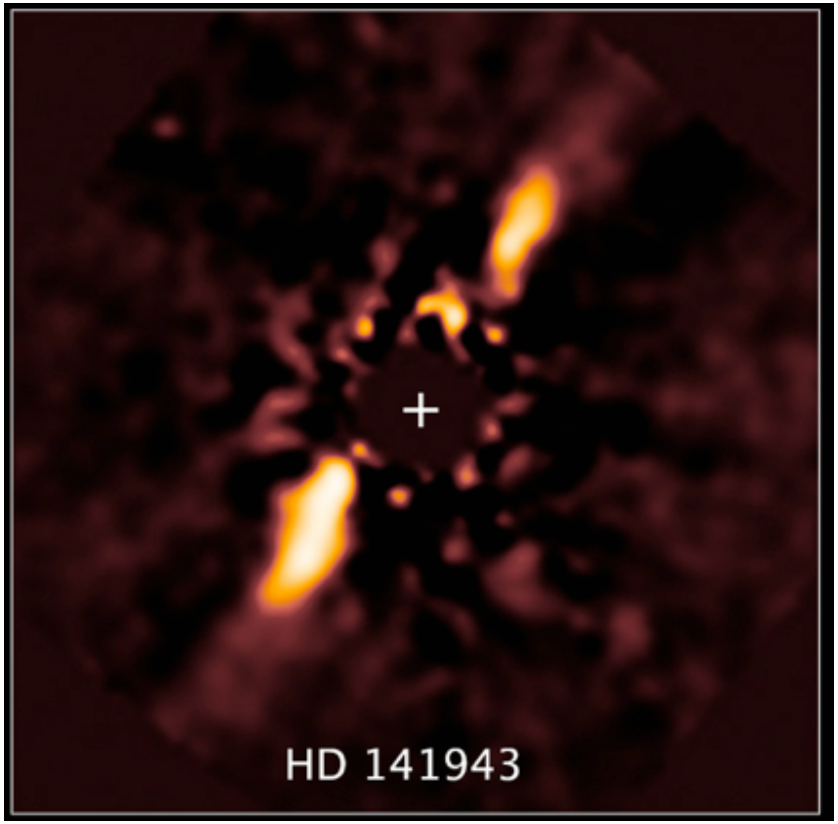
Grand Tack model is surprisingly successful in predicting size and positions of terrestrial planets.

Roman Concrete Model of Terrestrial Planets

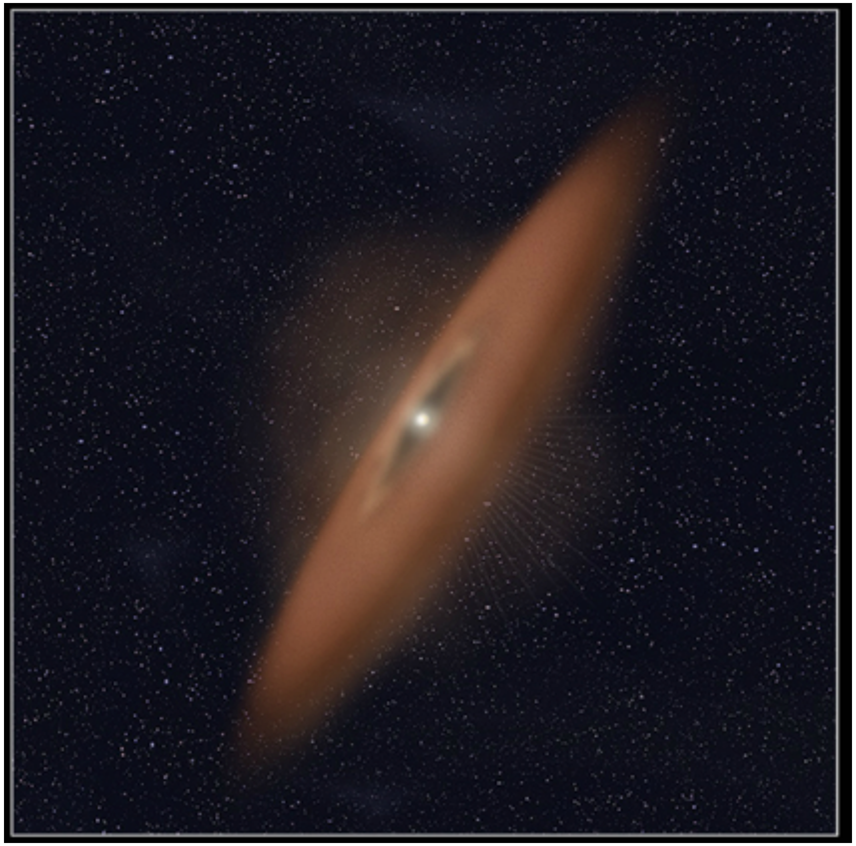
- In the Grand Tack Model, the terrestrial planets are built from this residual debris.
- In short, they are buil from recycled material: much as the Roman's recycled construction debris ir their concrete.



Debris disk around the young star HD 141943



Hubble Space Telescope Image



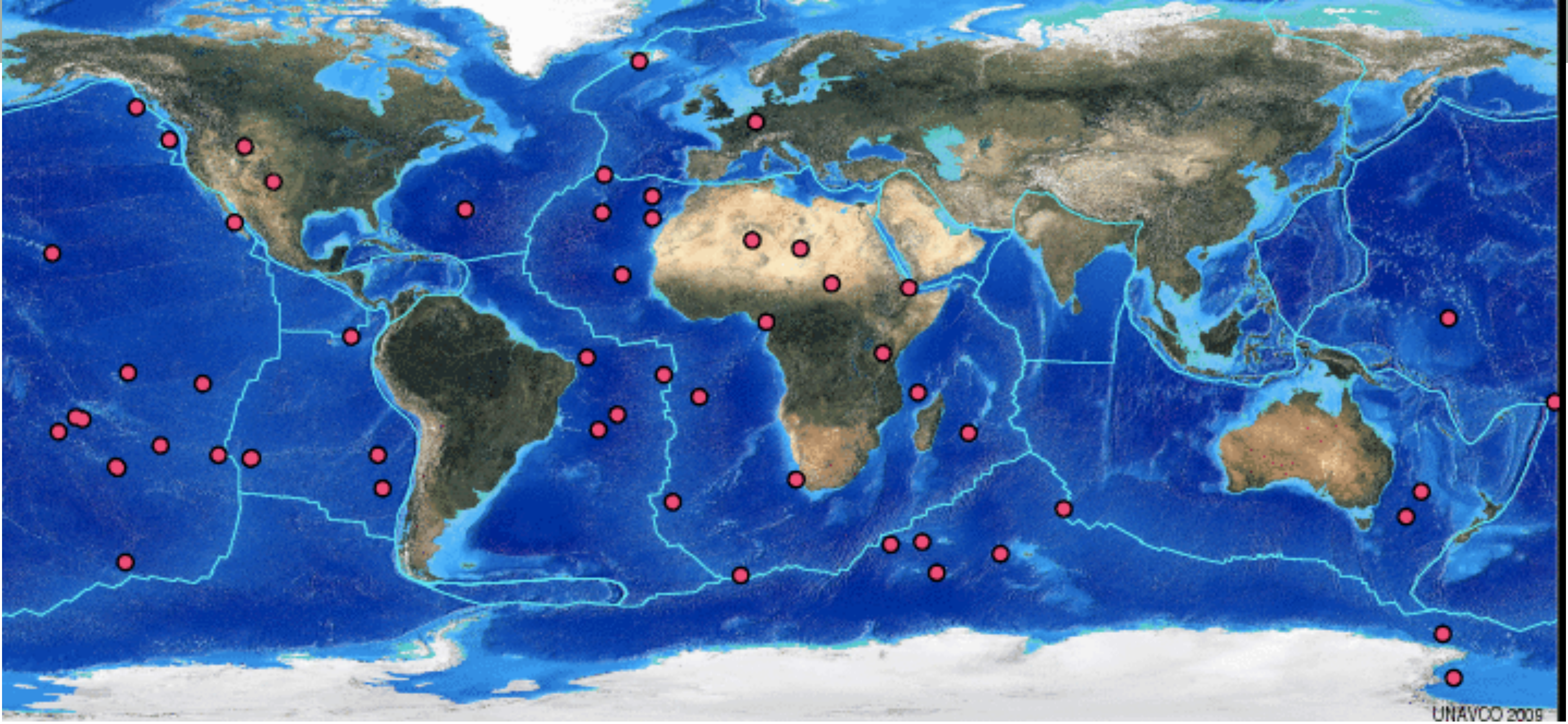
Artist’s Conception

TAKE AWAY

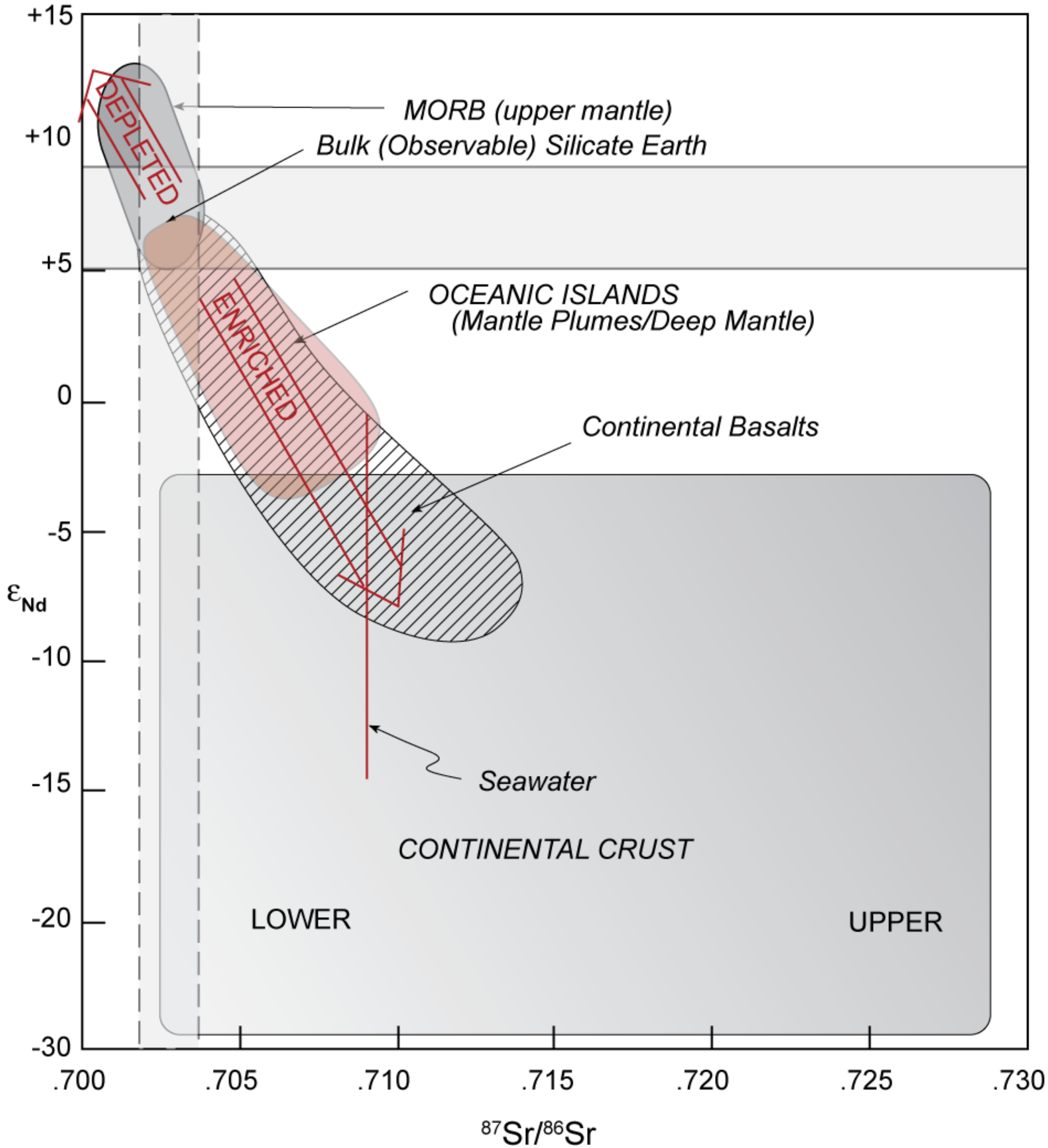
Terrestrial planet composition may not be simply related to raw nebular materials.

This introduces uncertainty in terrestrial evolution models since we do not know how to initialize them.

MANTLE ISOTOPE SYSTEMATICS



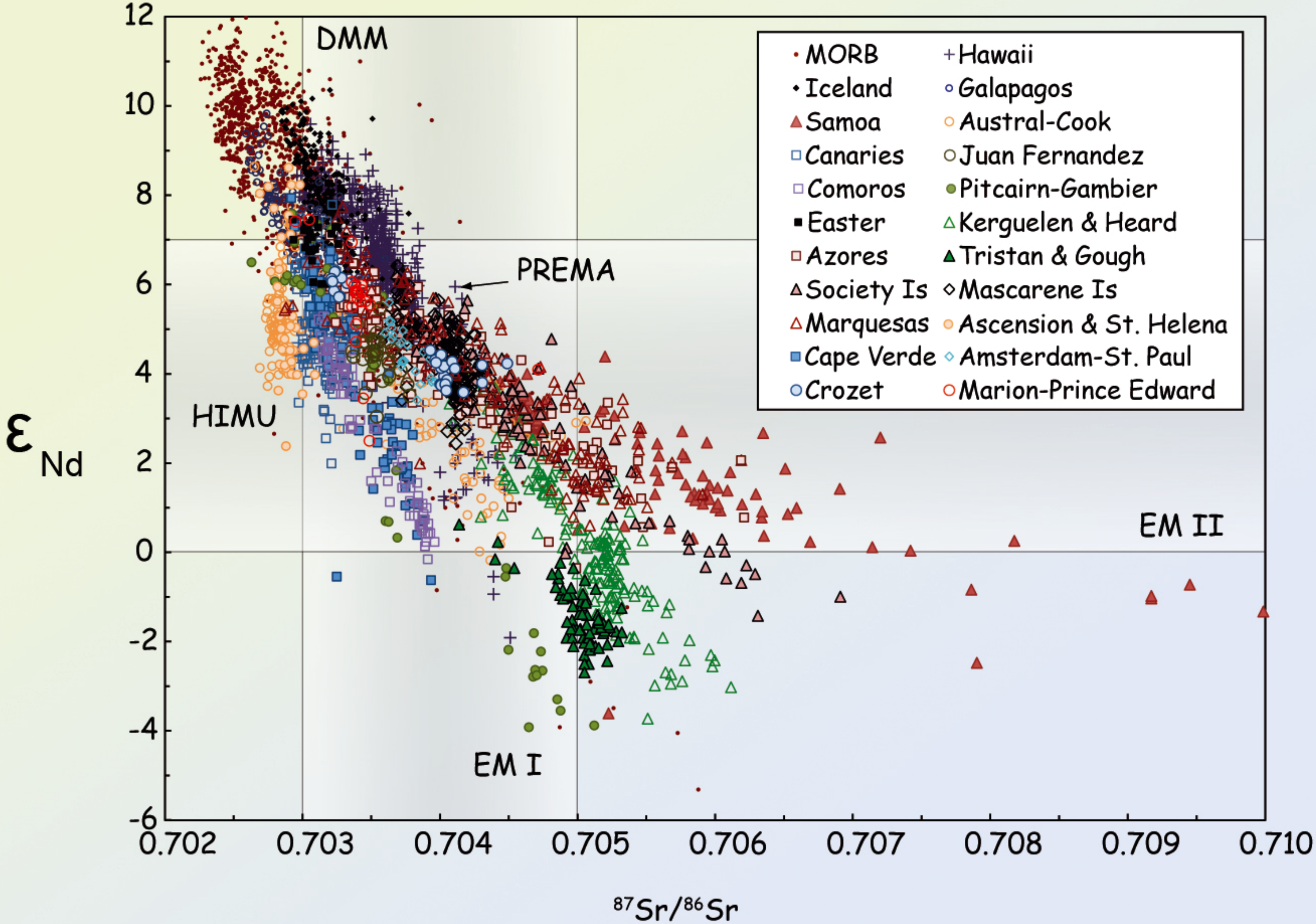
Even in the 1960’s, isotope ratios revealed that the mantle was chemically heterogeneous and that there was a fundamental difference in the source of magmas erupted at mid-ocean ridges (MORB) and oceanic islands (OIB).



+15
+10
+5
0
-5
-10
-15
-20
-30
εNd
.700
.705
.710
.715
.720
.725
.730
87Sr/86Sr
DEPLETED
ENRICHED
MORB (upper mantle)
Bulk (Observable) Silicate Earth
OCEANIC ISLANDS
(Mantle Plumes/Deep Mantle)
Continental Basalts
Seawater
CONTINENTAL CRUST
LOWER
UPPER

MANTLE TAXONOMY

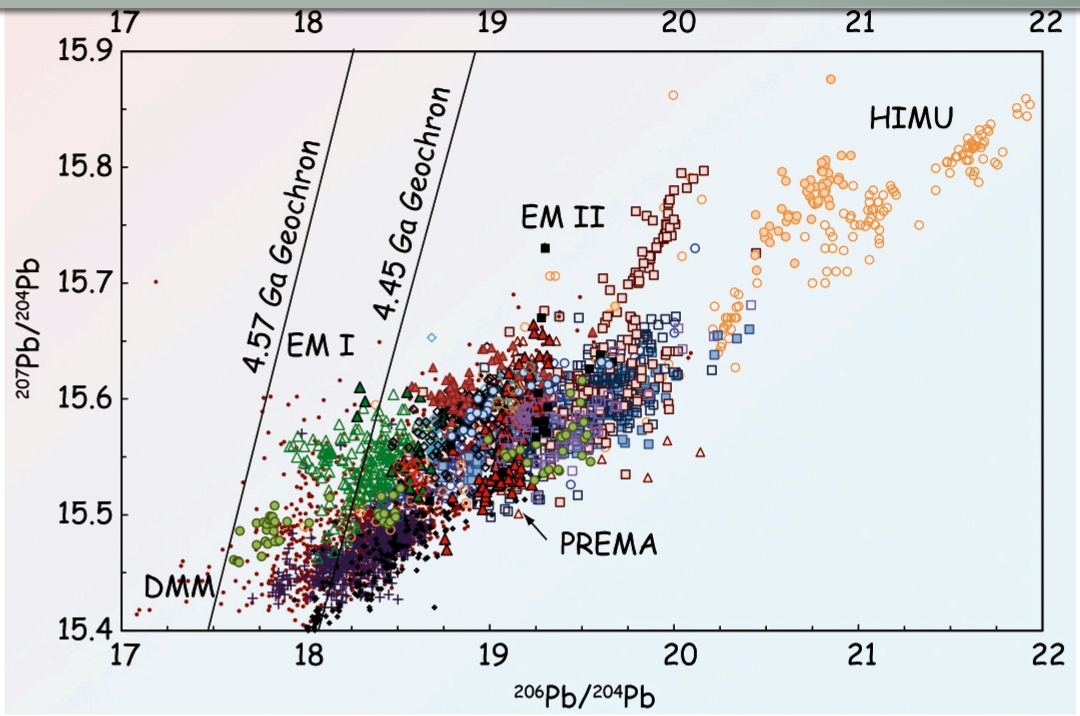
In detail, we find that Oceanic Island Basalts can be divided into a limited number of groups based on radiogenic isotopic composition

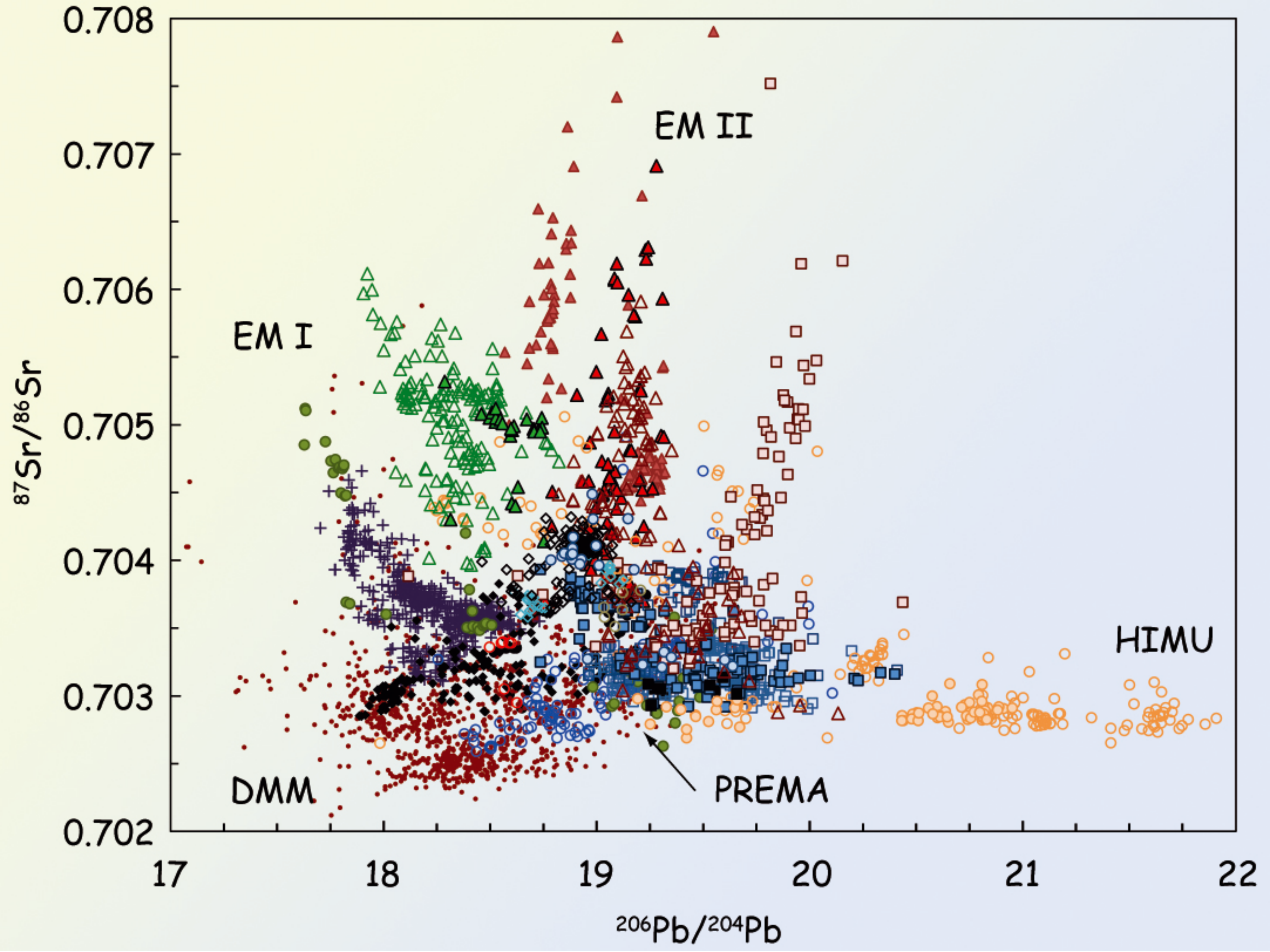


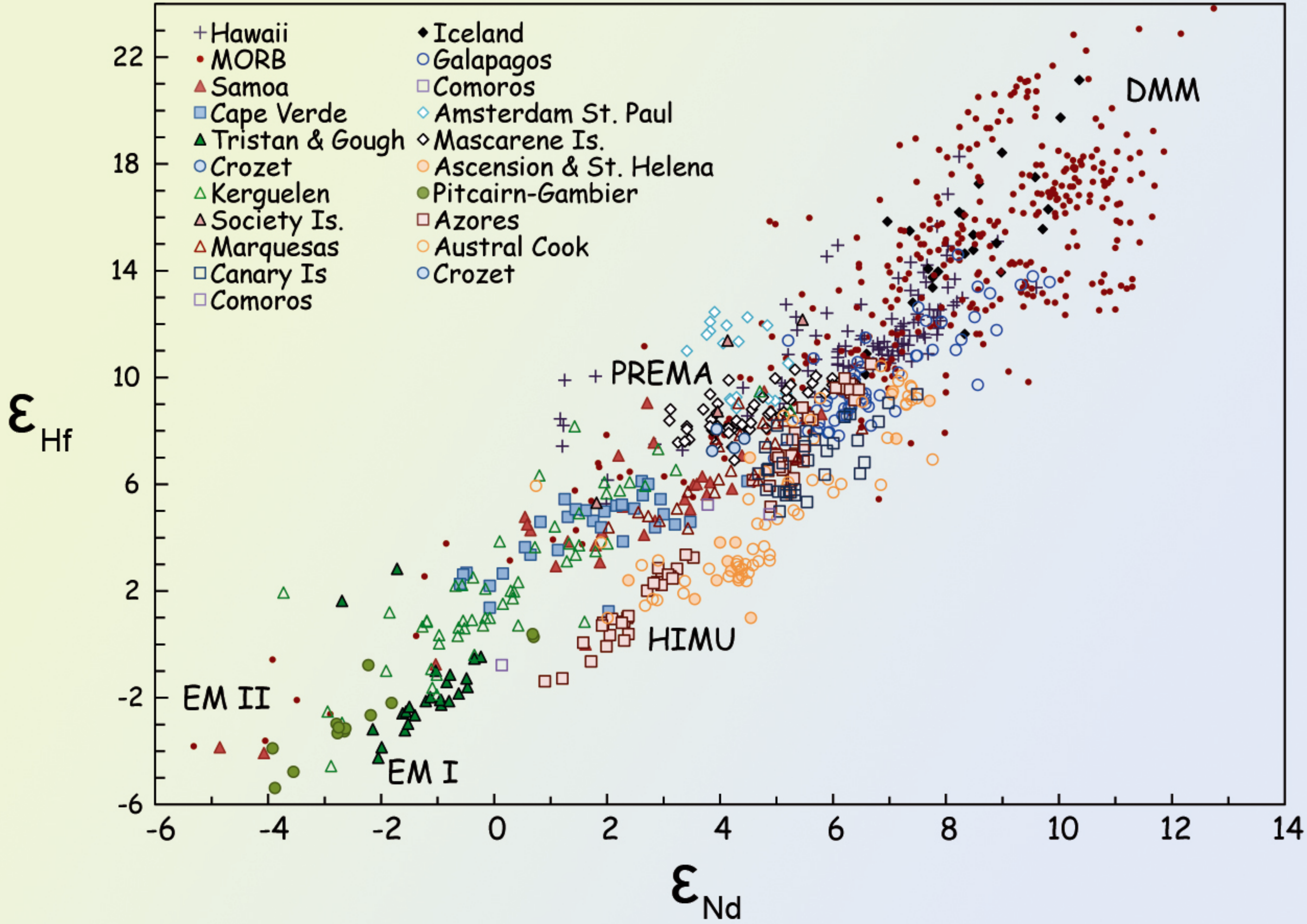
12
10
8
6
4
2
0
-2
-4
-6
DMM
PREMA
HIMU
EM II
EM I
ε Nd
0.702
0.703
0.704
0.705
0.706
0.707
0.708
0.709
0.710
87Sr/86Sr
MORB
Iceland
Samoa
Canaries
Comoros
Easter
Azores
Society Is
Marquesas
Cape Verde
Crozet
Hawaii
Galapagos
Austral-Cook
Juan Fernandez
Pitcairn-Gambier
Kerguelen & Heard
Tristan & Gough
Mascarene Is
Ascension & St. Helena
Amsterdam-St. Paul
Marion-Prince Edward

The Lead Paradox:

If OIB are more primitive, why are they more displaced from "primordial Pb" – Pb isotopes plotting on the "Geochron" than MORB?

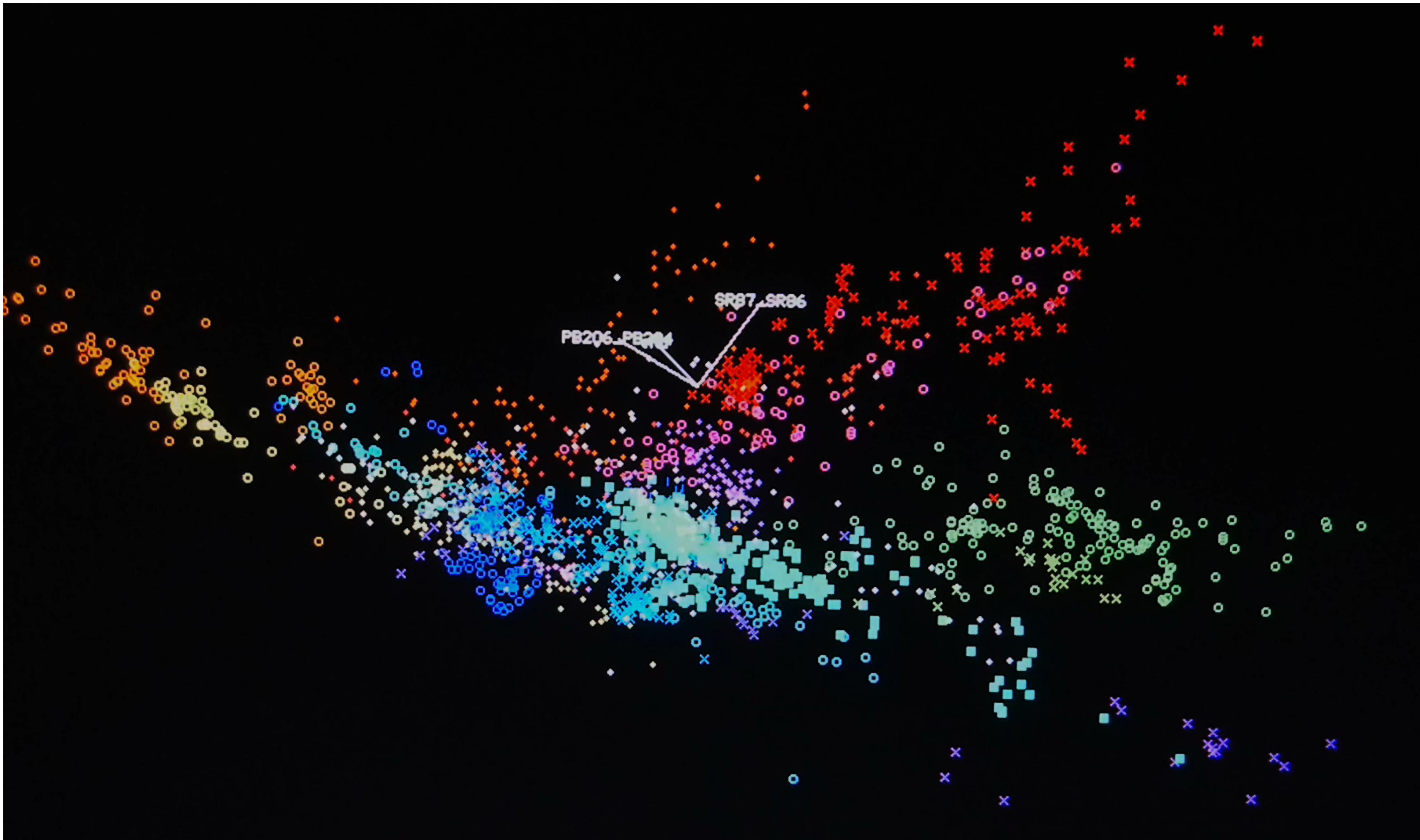



0.708
0.707
0.706
0.705
0.704
0.703
0.702
$^{87}Sr/^{86}Sr$
EM II
EM I
HIMU
DMM
PREMA
17
18
19
20
21
22
$^{206}Pb/^{204}Pb$



Hawaii
MORB
Samoa
Cape Verde
Tristan & Gough
Crozet
Kerguelen
Society Is.
Marquesas
Canary Is
Comoros
Iceland
Galapagos
Comoros
Amsterdam St. Paul
Mascarene Is.
Ascension & St. Helena
Pitcairn-Gambier
Azores
Austral Cook
Crozet
DMM
PREMA
HIMU
EM II
EM I
ε_{Hf}
ε_{Nd}
22
18
14
10
6
2
-2
-6
-6
-4
-2
0
2
4
6
8
10
12
14

Many Species, Fewer Genera



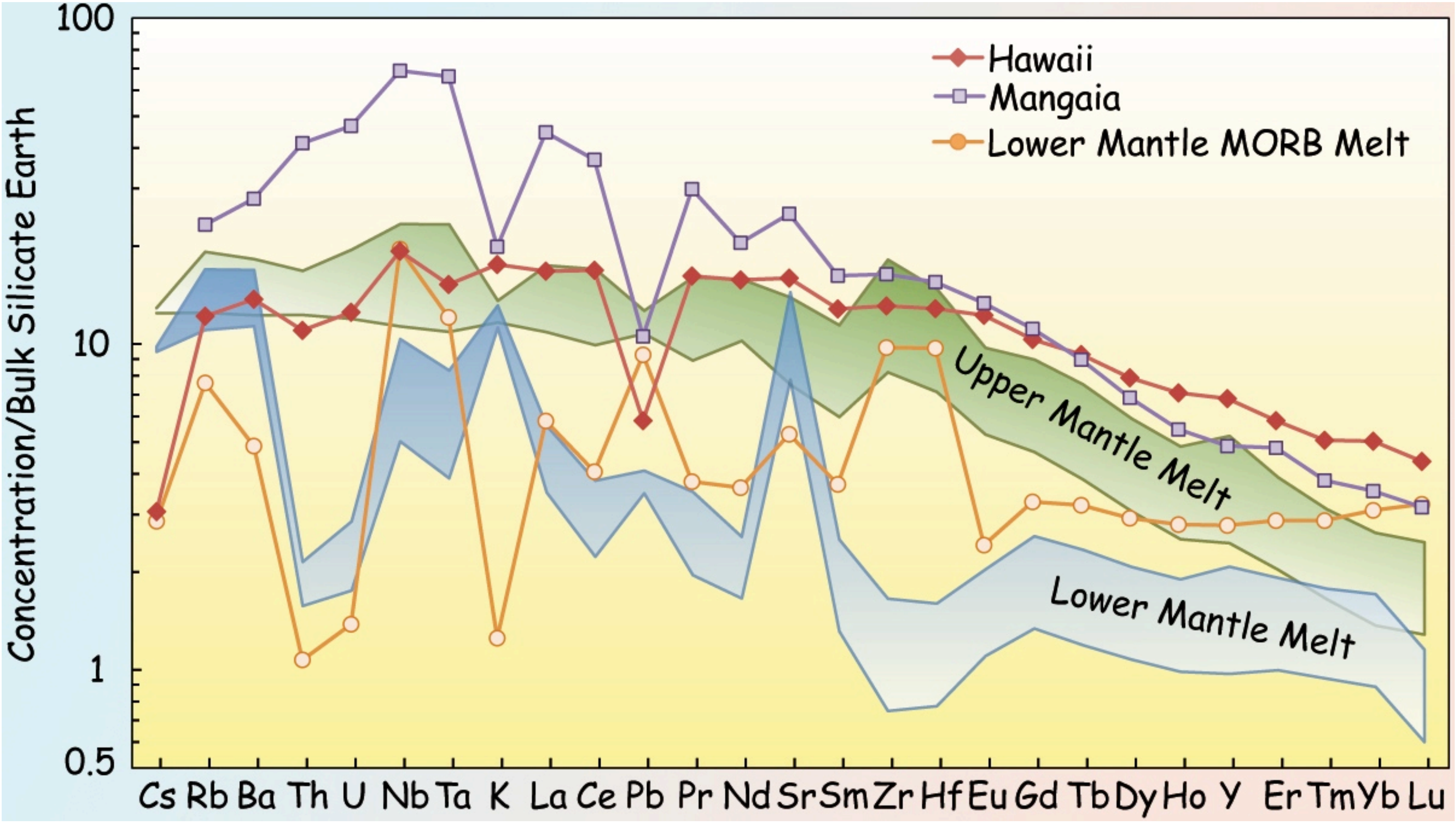
Key Points About Mantle Taxonomy

- Each hotspot is to some degree unique.
  - In many cases, e.g., Hawaii, Galapagos, etc., several distinct and unique isotope trends can be identified.
- Hot spots nonetheless can be divided into a limited number of compositional groups.
- These groups are thus analogous to *genera* rather than *species.*
  - *The species of each genera have evolved in similar ways.*
- Isotopic trends or correlations in these groups tend to converge on a central composition– variously called PREMA, FOZO, “C”, PHEM.
- Other than with PREMA (or rarely MORB), there is little mixing between the isotopic genera.

THE BIG QUESTION

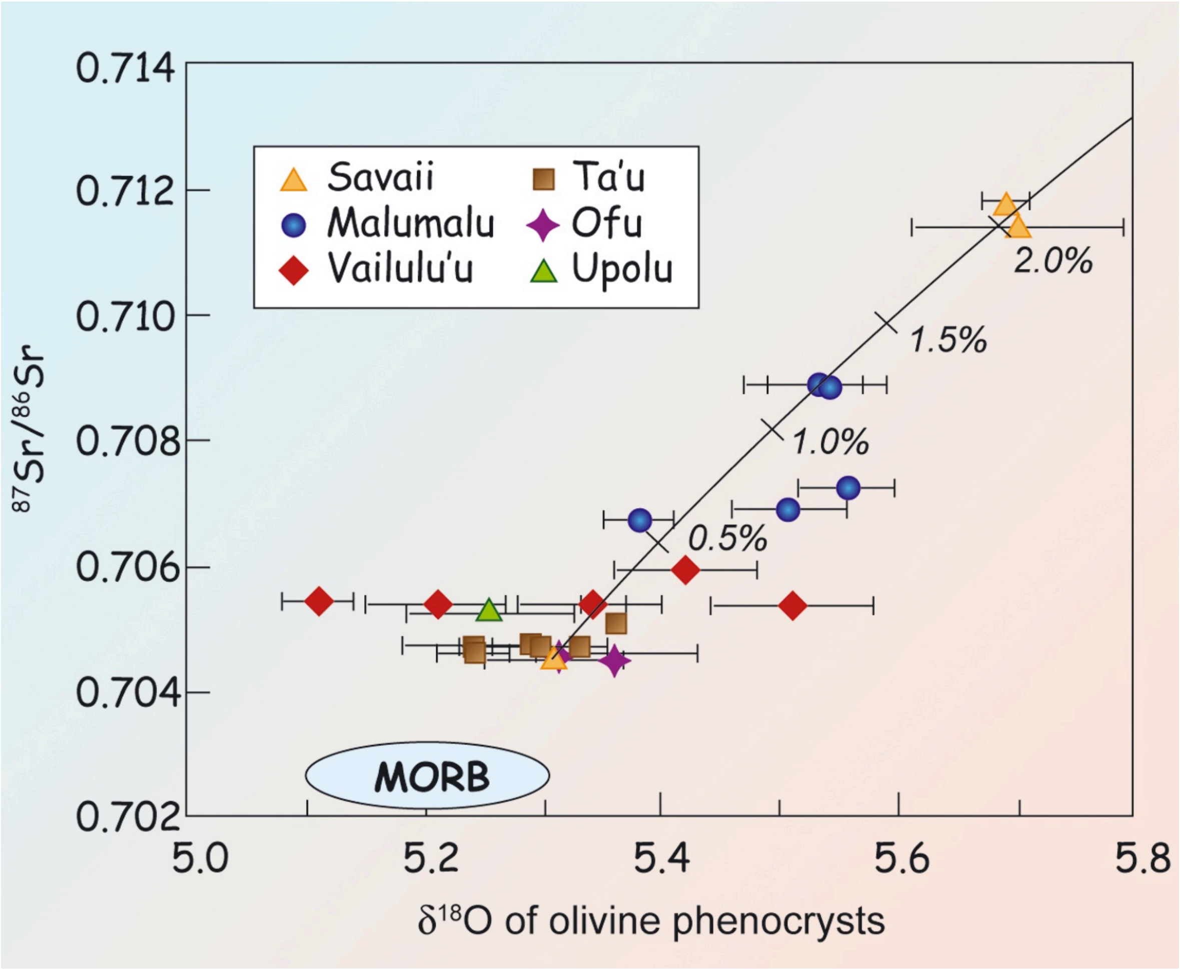
What are radiogenic isotopes tell us about mantle evolution?

Heterogeneity Not Produced in Lower Mantle



STABLE ISOTOPE GEOCHEMISTRY REINFORCES THIS INFERENCE

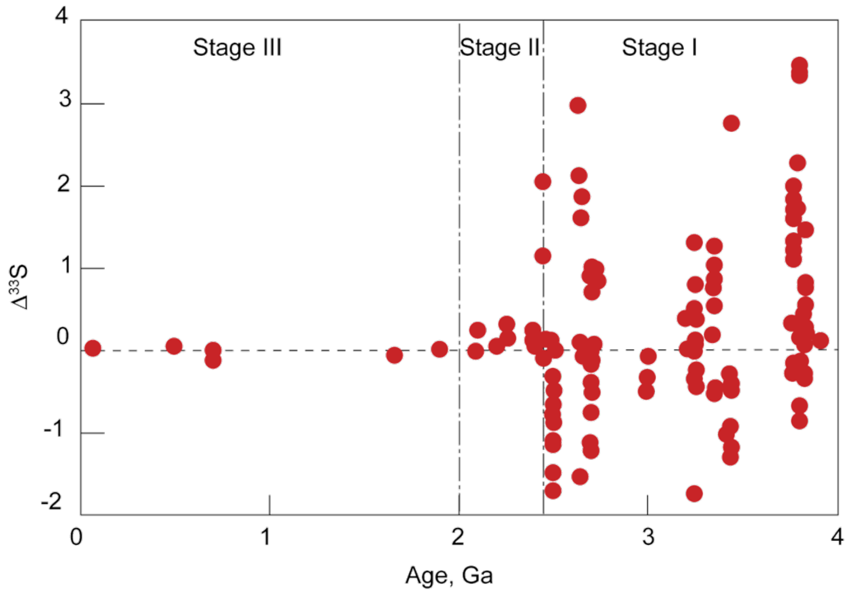
$\delta^{18}O$ in Samoan (EM II) Lavas



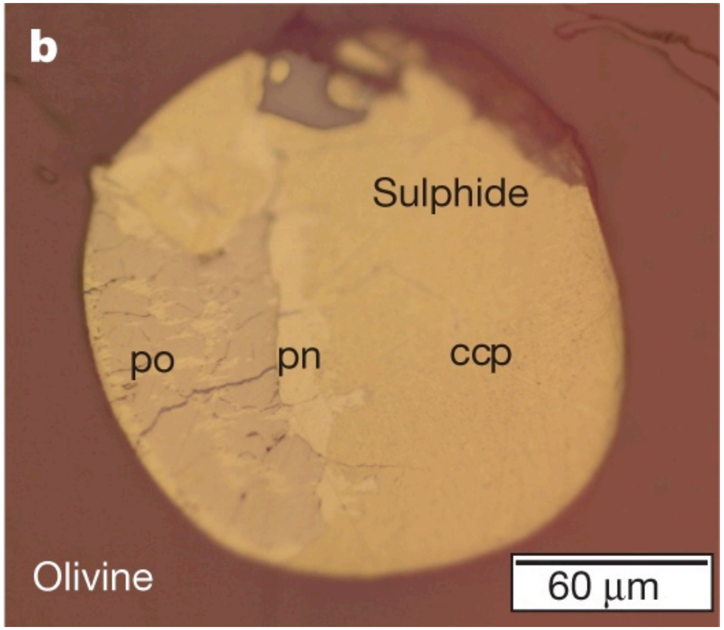
Workman et al. (2008)

MIF Sulfur

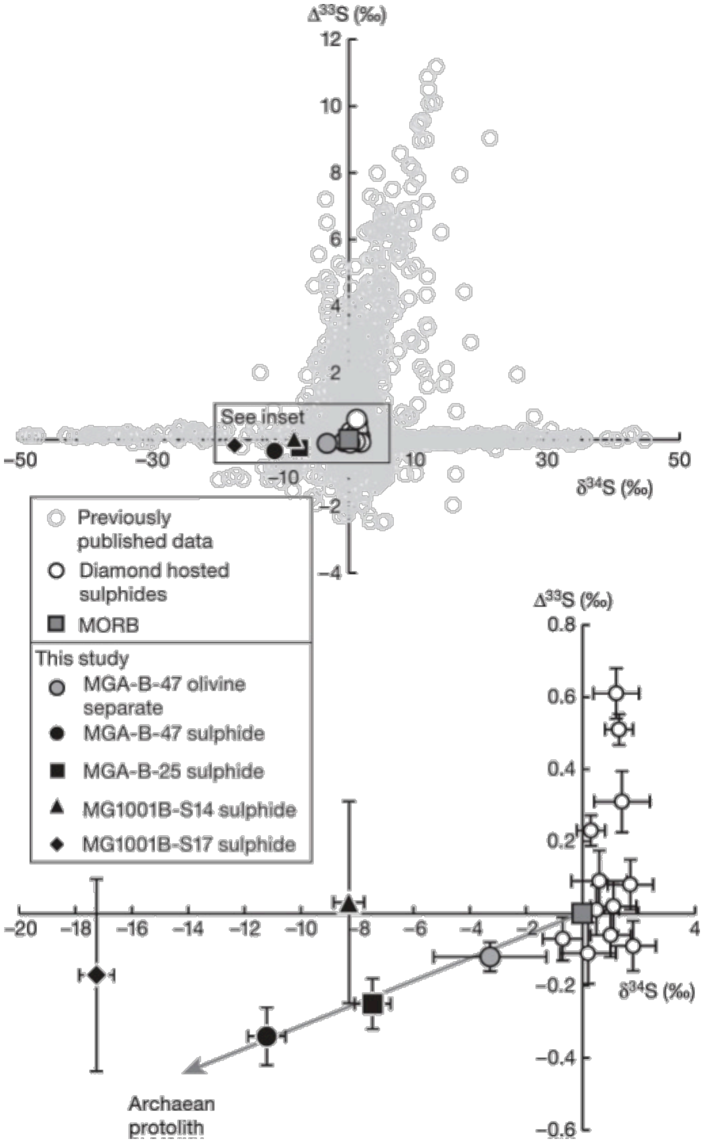
- Mass Independent Fractionation (MIF) is a rare phenomenon that generally involves photodissociation. It occurs in the modern stratosphere.
- Mass independent fractionation of sulfur is restricted to time before 2.3 Ga when UV radiation could penetrate an oxygen- and ozone-free atmosphere.



‘MIF’ Sulfur in Mangaia (Australs) Olivine Sulfide Inclusion Lava

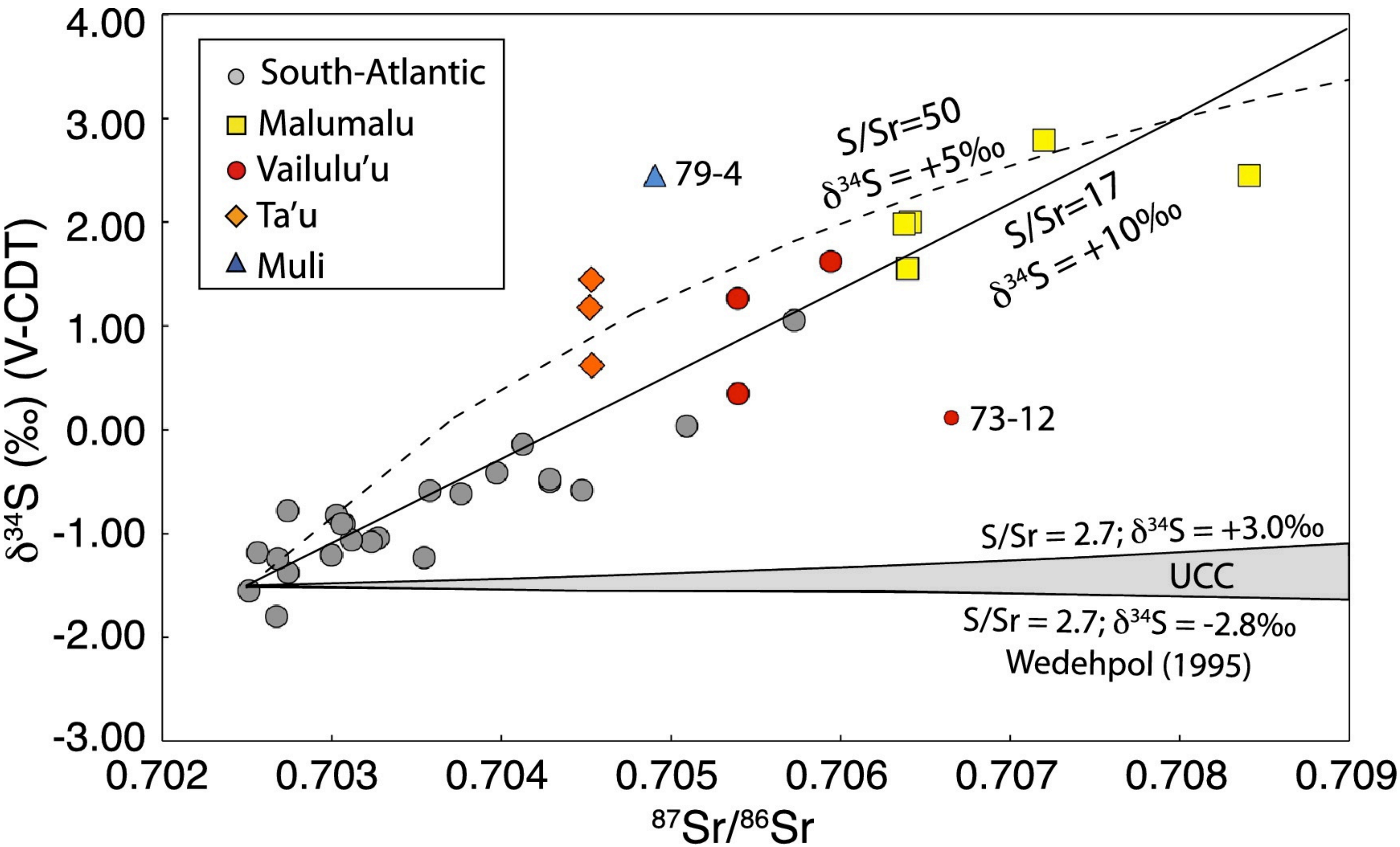


Reflected-light photomicrographs of sulphide inclusions.



From: Cabral *et al*. *Nature* (2013)

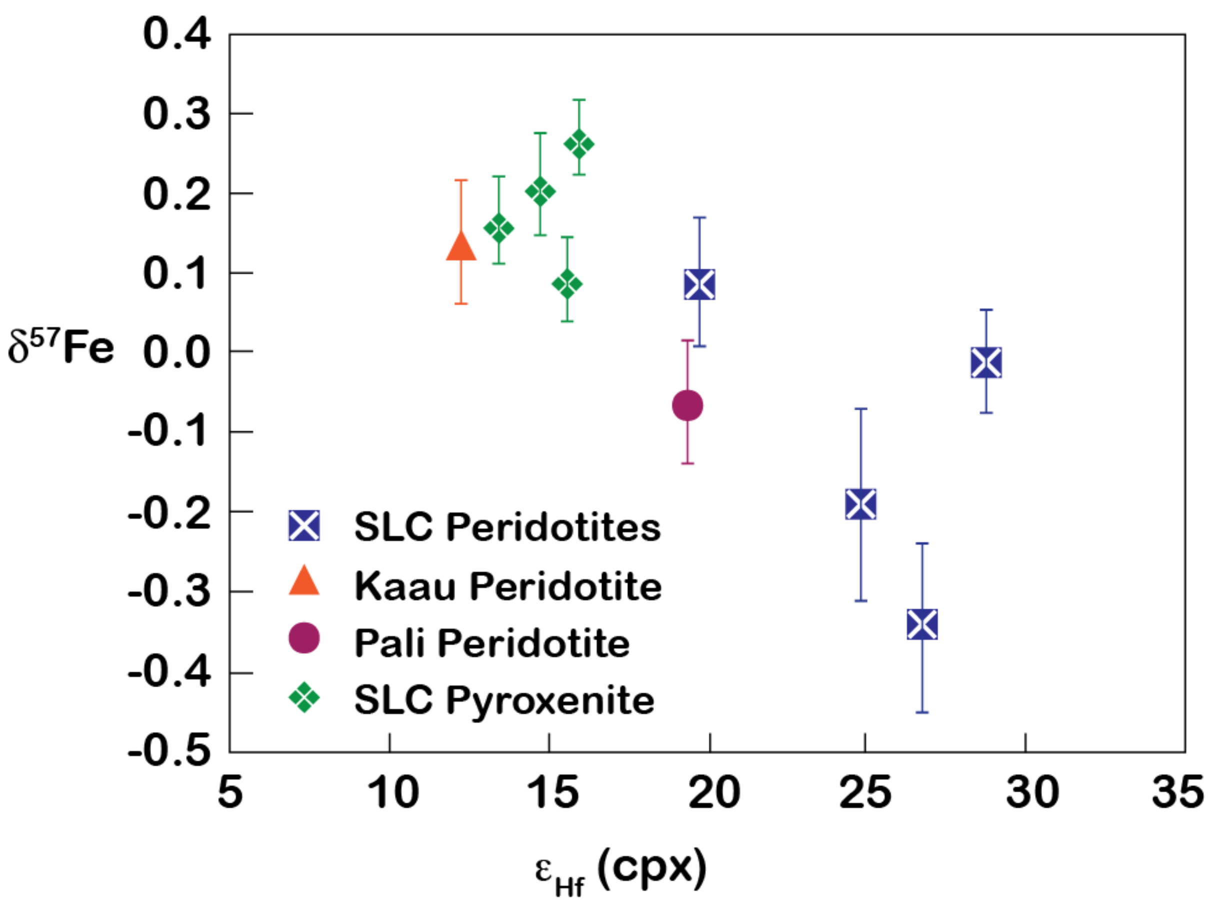
Sulfur Isotope Variations in Samoa



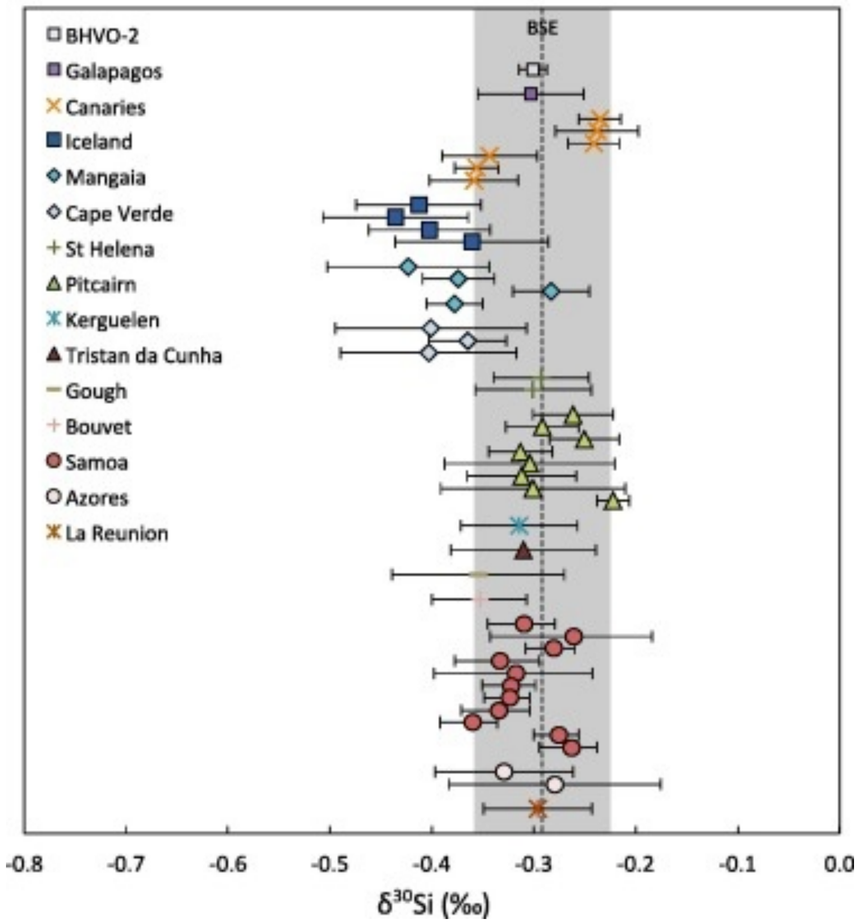
Labidi et al., 2015

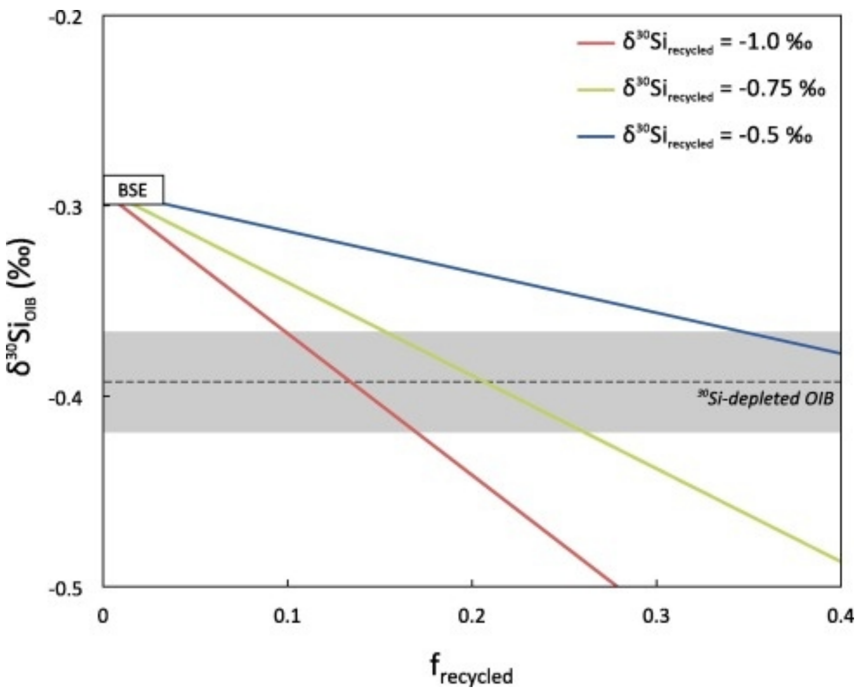
Iron Isotopes

- δ^{57}Fe in Hawaiian xenoliths inversely correlates with several indicators of melt depletion in Oahu peridotites and pyroxenites as well as ε_{Hf}
- Isotopically heavy iron observed in Hawaii, Society and Austral Islands, due to the presence of pyroxenites, perhaps derived from recycled oceanic crust in the sources of these islands. (Williams & Bizimis, 2014).



Silicon Isotopes

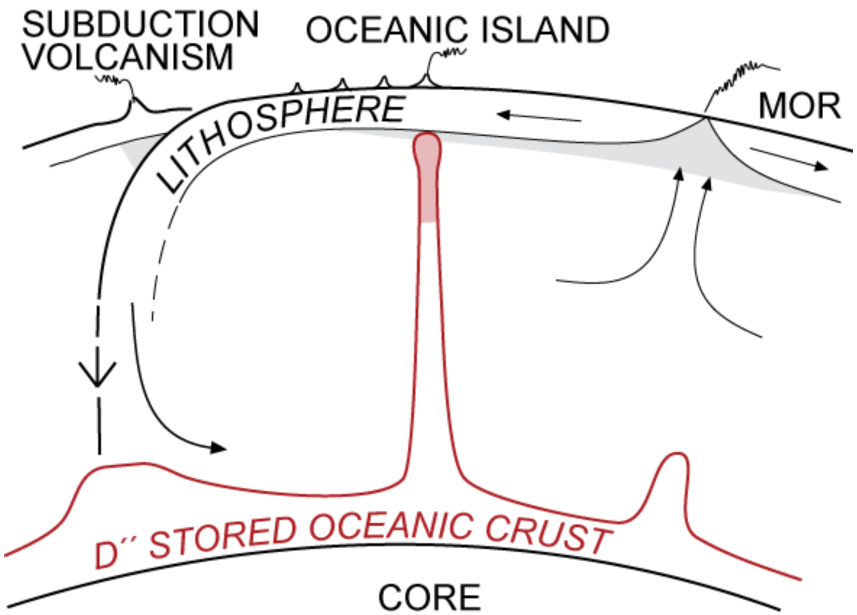




Pringle et al. Geochim. Cosmchim Acta, 2016

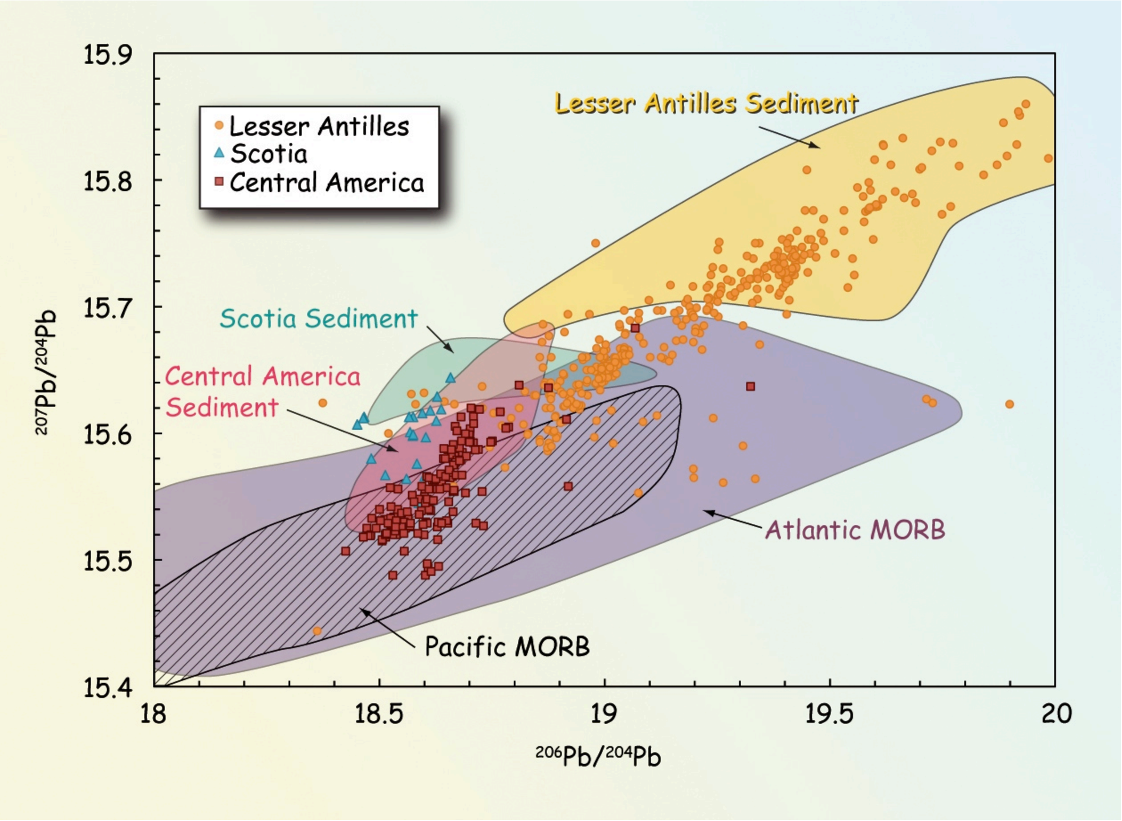
Mantle Evolution

- Conclusion:
  - Mantle heterogeneity is a consequence of processes occurring in the crust or upper mantle.
- Although plumes rise from the deep mantle, rock in them acquired its chemical properties in the upper mantle.
- How?
  - Subduction
  - Subduction erosion
  - Lower crustal floundering



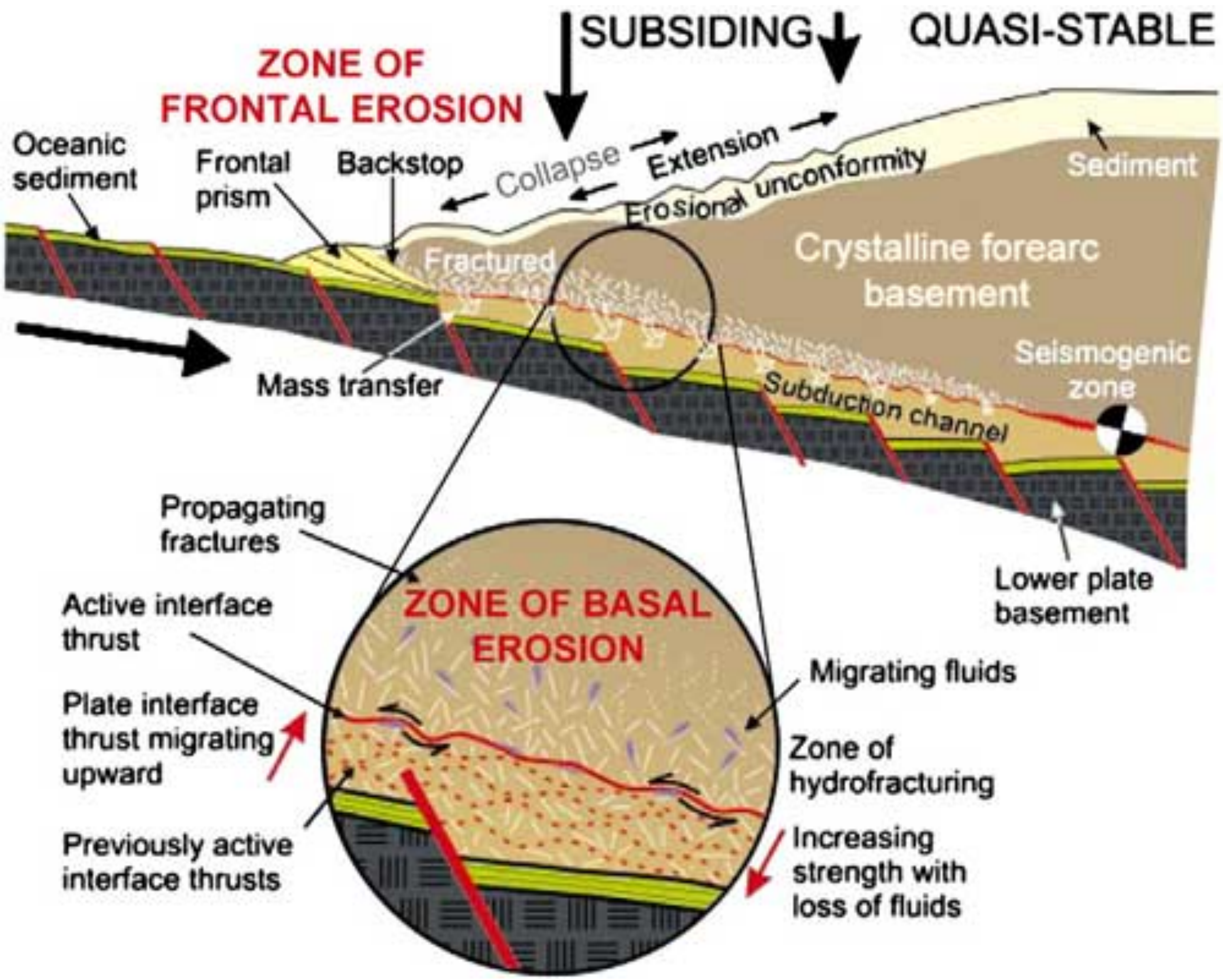
Hofmann & White '82

Sediment Subduction and Crustal Recycling



- Armstrong (1971) pointed out the similarity of Pb isotopes in island arcs to those of sediments outboard from those arcs and argued that sediment subduction was a way to return continental crust to the mantle.

Subduction Erosion



Crustal Additions and Losses

Armstrong Units†		Stern & Scholl (2010)	Clift et al (2009)	Stern (2011)
Subduction Zone Additions				
	Intra-oceanic arcs	1.5		
	Continental arcs	1		
	Total	2.5	3.8	
Other Additions				
	Intraplate magmatism	0.7	0.03	
	Oceanic plateau accretion		1.1	
Total Additions		**3.2**	**4.93**	**–**
Losses in subduction zones				
	Sediment subduction	1.1	1.65	1.65
	Subduction erosion	**1.8**	**1.35**	**1.7**
	Dissolved in o. crust		0.4	0.4
	Continent subduction	0.3	0.43	0.4
	Crustal Foundering		1.1	1.1
Total Losses		**>3.2 AU**	**4.93 AU**	**5.25 AU**

† Armstrong Units = 1 km^3/yr (Kay and Kay, 2008).

BOTTOM LINE

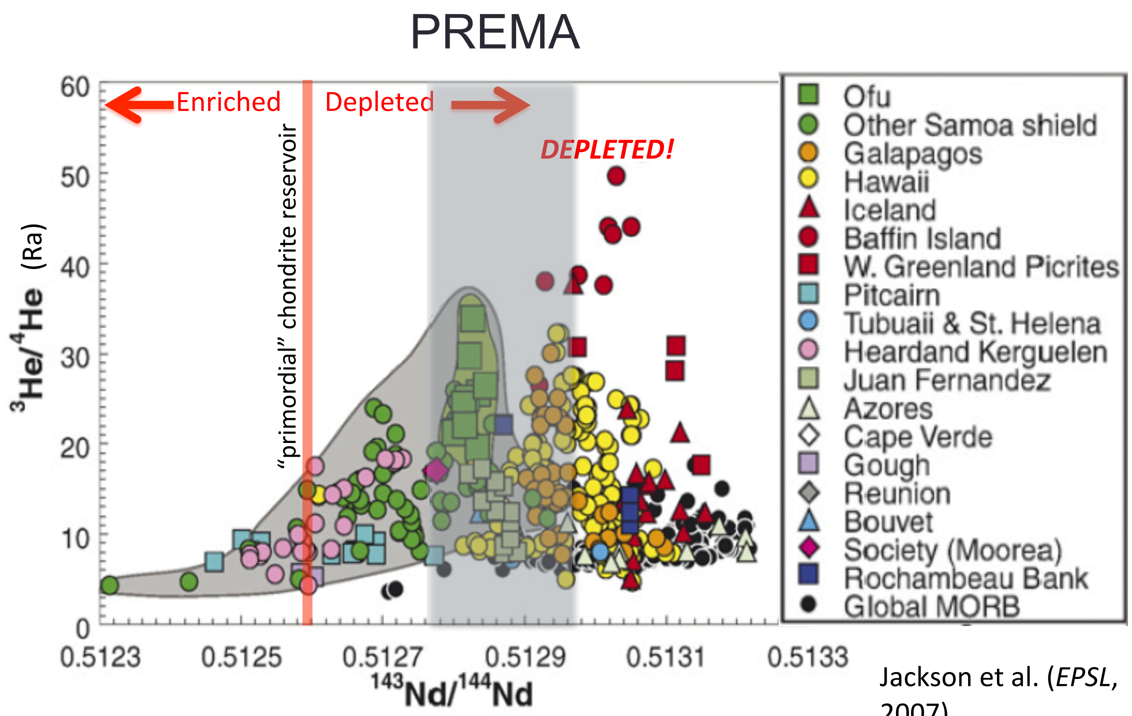
The crust-to-mantle flux from sediment subduction, subduction erosion and continental foundering is large. The contribution of the latter two is difficult to geochemically assess, but may exceed the sediment subduction flux.

NOBLE GASES TELL A DIFFERENT STORY

An ancient primitive component?

$^3He/^4He$

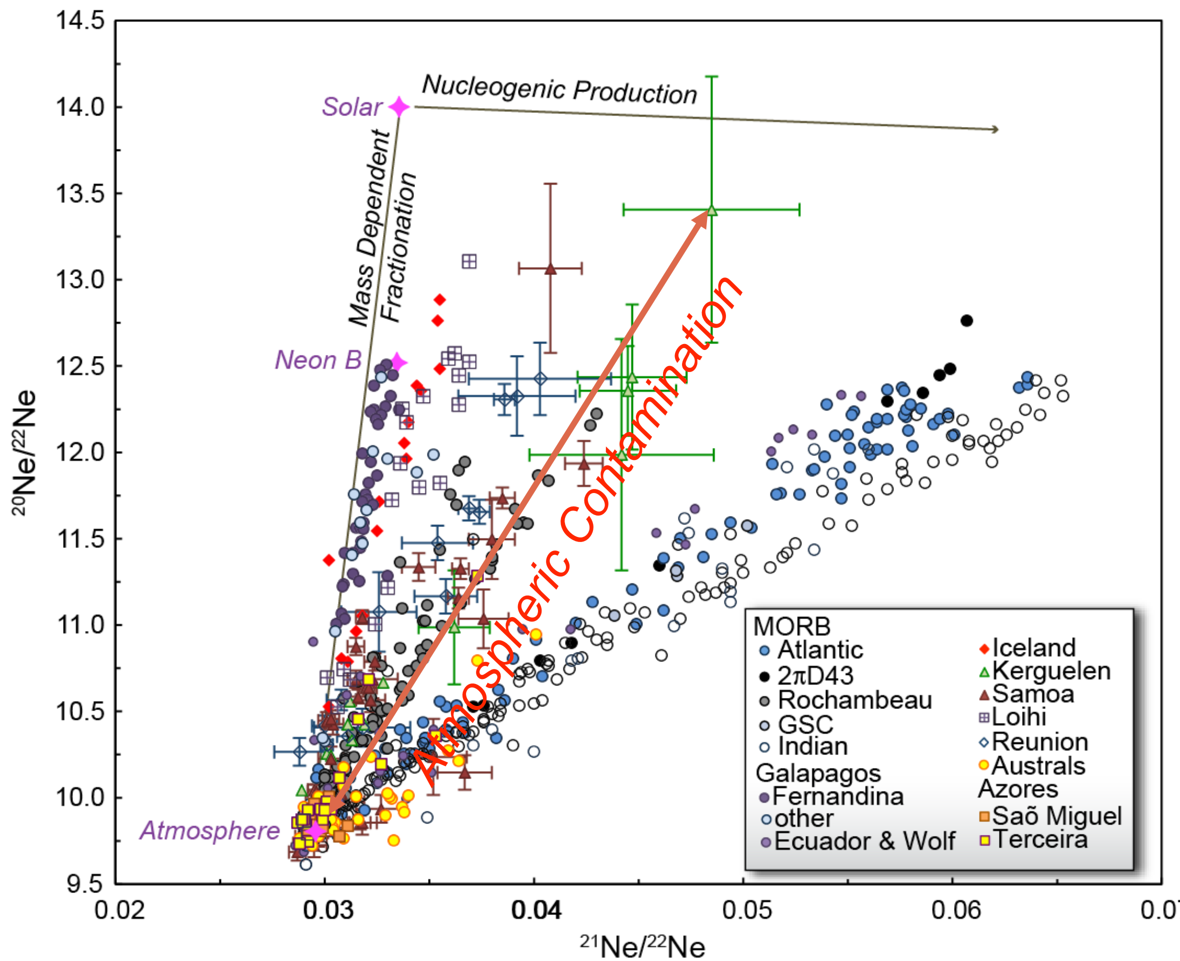
- ^4He produced by alpha decay; ^3He is primordial and not conserved in the Earth.
- Highest $^3He/^4He$ associated with *intermediate* radiogenic isotopic compositions:
  - PREMA, FOZO, etc.



Jackson et al. (*EPSL*, 2007)

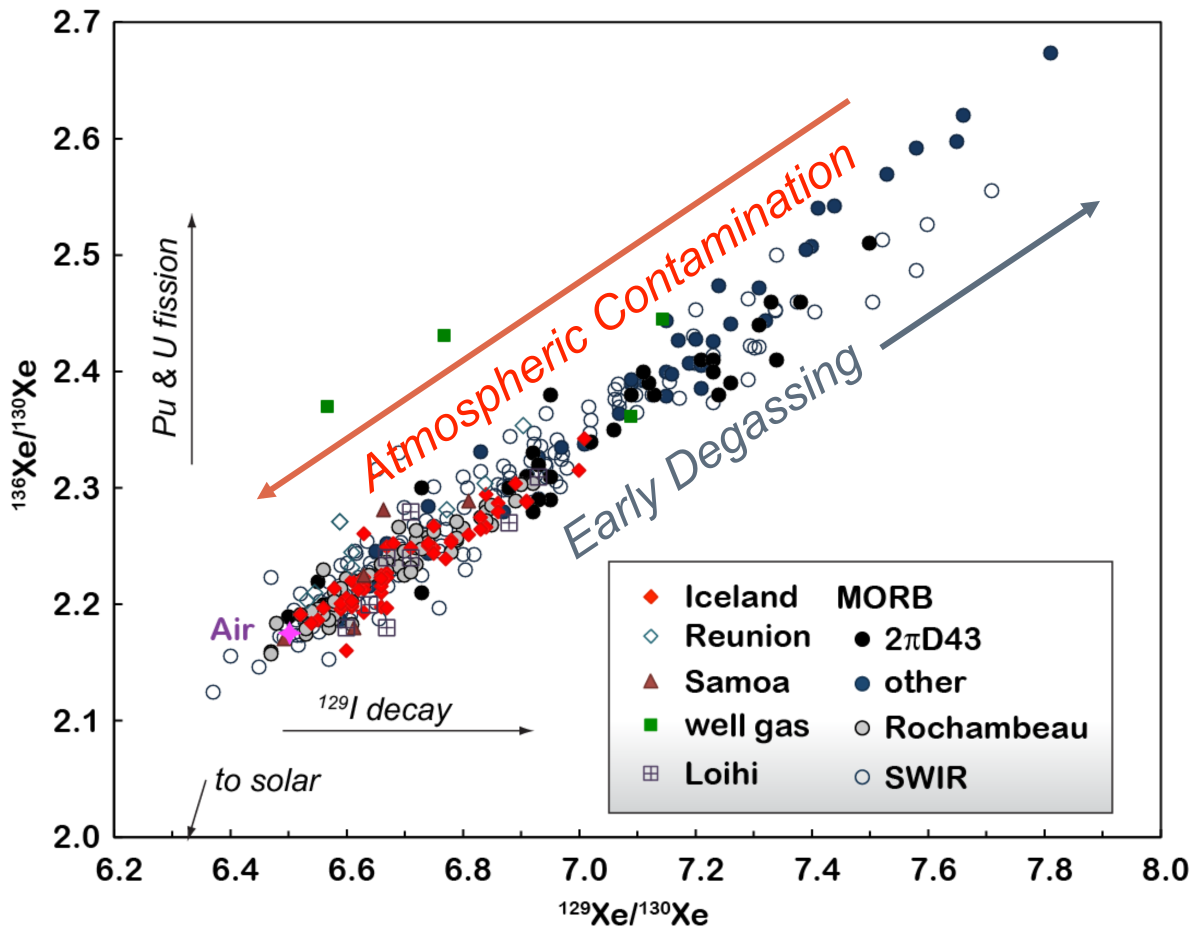
Neon Isotopes

- Atmospheric $^{20}Ne/^{22}Ne$ is mass dependently fractionated relative to meteoritic and solar (catastrophic atmospheric loss?).
- $^{21}Ne/^{22}Ne$ varies due to *nucleogenic* production associated with U and Th decay. Hence related to U/Ne ratio.
- Each hotspot (and MORB) define unique mixing (contamination) line between atmospheric and mantle Ne (mantle value ≥ highest $^{20}Ne/^{22}Ne$).



Xenon Isotopes

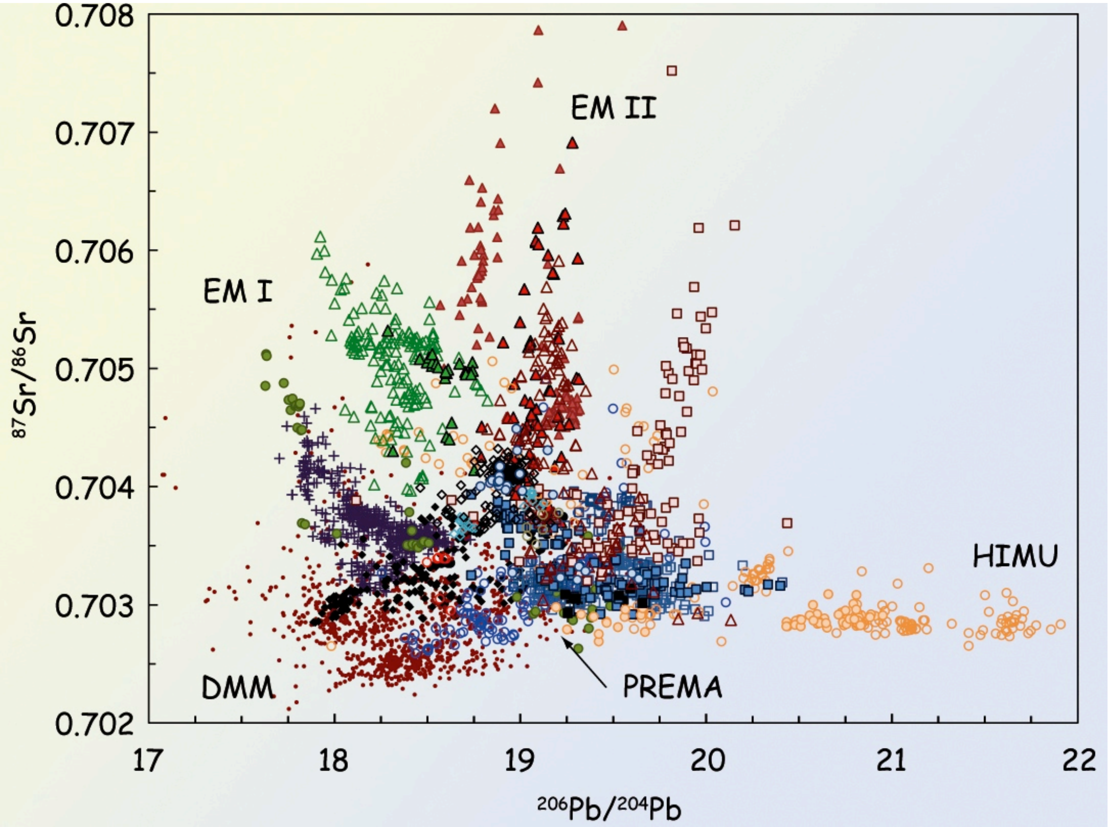
- ^{129}Xe produced by β decay of ^{129}I ($t_{1/2}$ ≈ 16 Ma) and fusion of ^{238}U ($t_{1/2}$ ≈ Ga) and ^{244}Pu ($t_{1/2}$ ≈ 82 Ma).
- As for Ne, atmospheric contamination is pervasive.
- OIB, most notably Iceland, contain a component, that experienced less degassing than the MORB source during an event that occurred within the first ~100 Ma of Earth/Solar System history.



How Much of a Primordial Component?

- Constraints on rare gas abundances in the mantle are weak.
    - Concentration measurements on basalts are almost meaningless.
- Degassing in the early Earth and by subsequent volcanism could produce variation in rare gas abundances of many orders of a magnitude.

What is PREMA?



- Recall that PREMA (PREvalent MAntle; Zindler & Hart, '86) is the centroid of mantle isotopic systematics.
- PREMA cannot be *primitive mantle*, but it could contain some fraction of it (depending on chosen primitive mantle composition).
- PREMA is a region of isotopic composition space, not a point (heterogeneous by nature).
- Most hotspots have arrays extending toward PREMA, suggesting mixing.
- PREMA is perhaps a mixture of *least modified mantle* adulterated with recycled components.

Plume Flavors

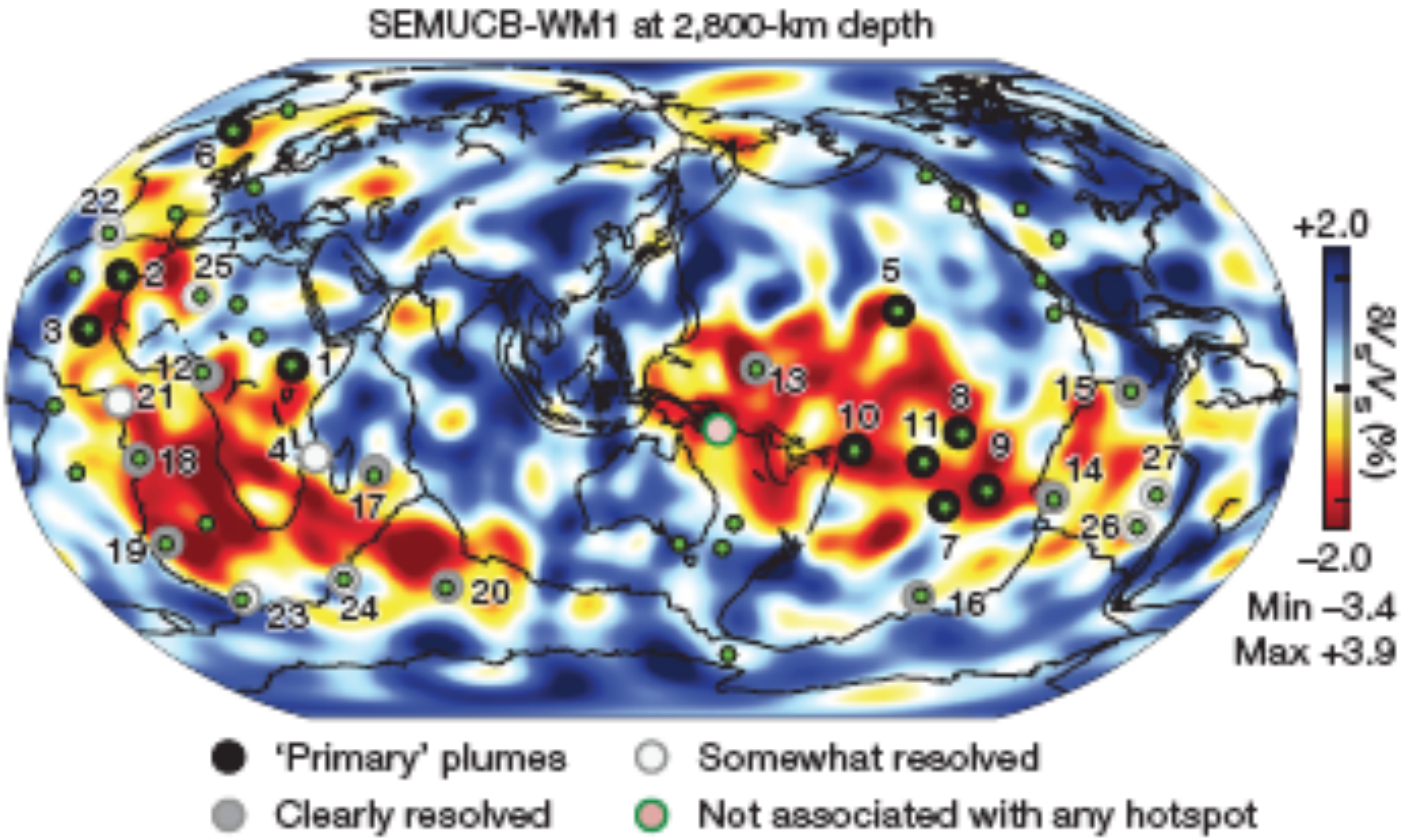
- Since PREMA (broadly defined) seems to be a component of most OIB sources, we should perhaps think of it as the ice cream and HIMU, EMII, etc. the flavoring.


衆瞽探象之圖

According to the Jainist concept of Anekantavada, the truth depends on one’s point of view, and no single point of view comprises the complete truth. These views are not wrong, merely incomplete. The task then is to assemble these various views to produce a more complete picture of the mantle.

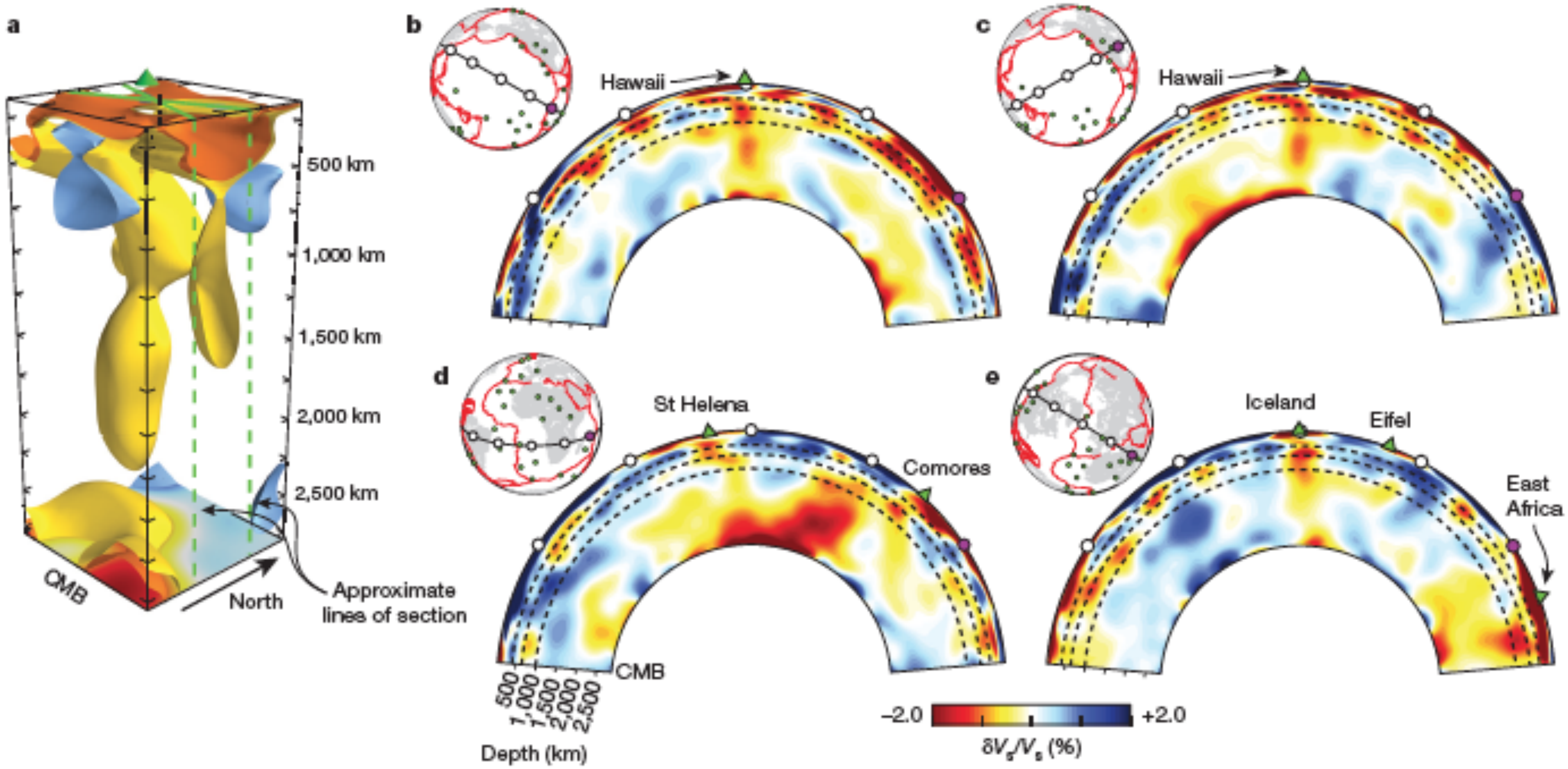
SO WHAT’S PICTURE?

OIB, Plumes, and LLSVP's



French & Romanowicz (2015)

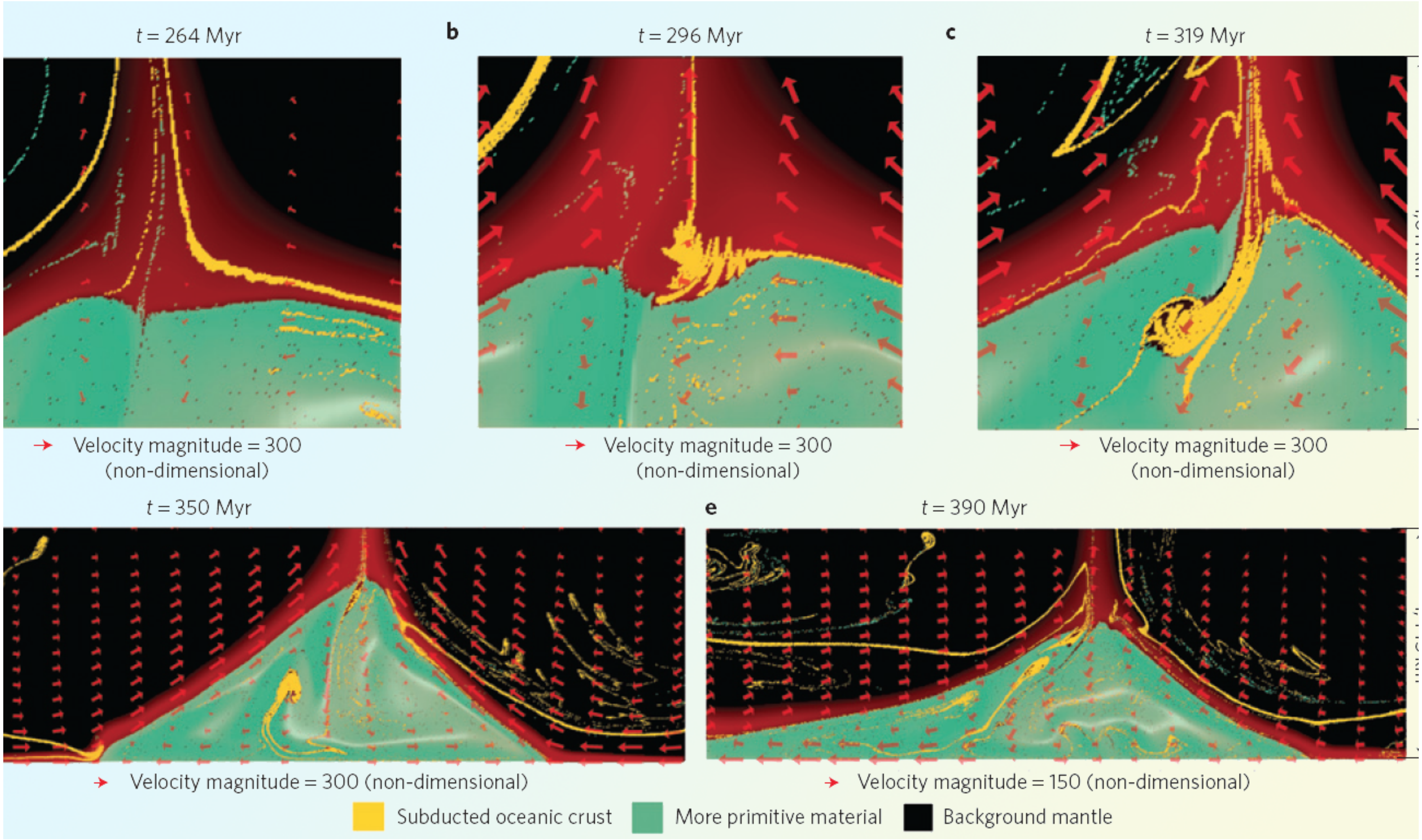
Oceanic Island Basalts are erupted at hot spots located above LLSVP's.



French & Romanowicz (2015)

Mantle Plumes connect LLSVP's to hot spots

Li et al. *Nature Geoscience*, 2014



Favored Model

- LLSVP's may be messy storage vaults for dregs at the bottom of the mantle. They preserve ancient near-primitive material, but it is diluted by dense subducted

Regardless of the specific model we chose, the most important conclusion we reach from combining geochemistry and geophysics is that ***the shallow and deep Earth communicate and their evolutions are intimately connected.***