

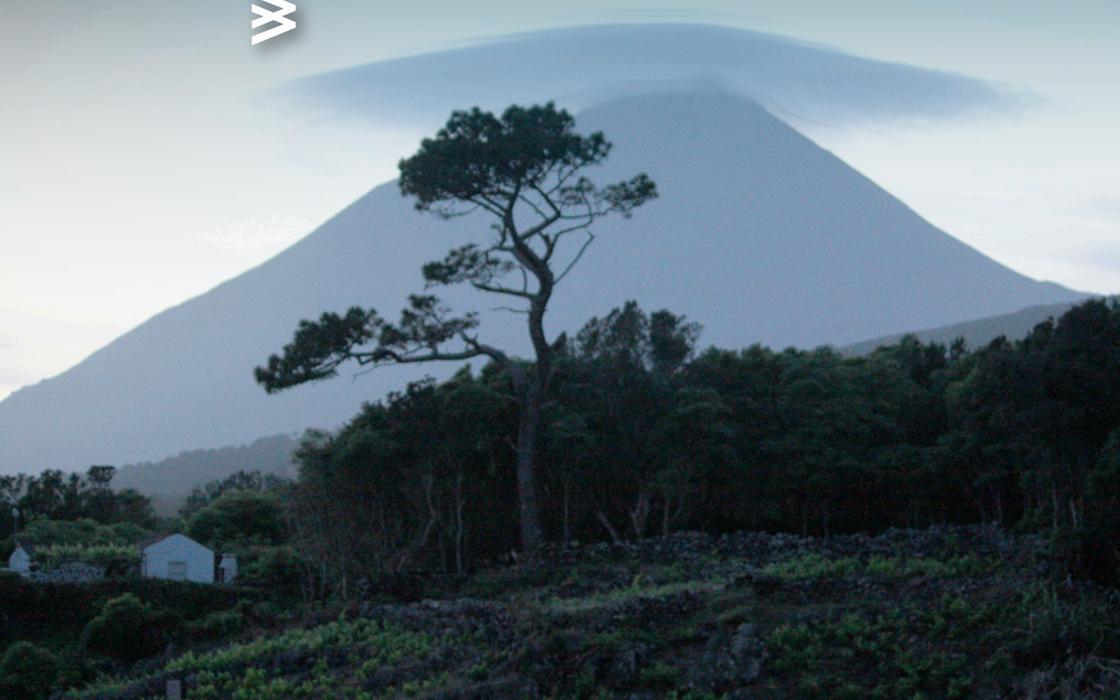
Geochemical Perspectives



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WILLIAM M. WHITE

Probing the Earth's Deep Interior Through Geochemistry



Each issue of *Geochemical Perspectives* presents a single article with an in-depth view on the past, present and future of a field of geochemistry, seen through the eyes of highly respected members of our community. The articles combine research and history of the field's development and the scientist's opinions about future directions. We welcome personal glimpses into the author's scientific life, how ideas were generated and pitfalls along the way. *Perspectives* articles are intended to appeal to the entire geochemical community, not only to experts. They are not reviews or monographs; they go beyond the current state of the art, providing opinions about future directions and impact in the field.

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Lenticular cloud forms over Pico Volcano, Pico Island, Azores.

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CONTENTS

Preface and Acknowledgements	III
Probing the Earth's Deep Interior Through Geochemistry	95
Abstract	95
1. Introduction	97
1.1 A Role for Geochemistry	97
1.2 A Quick Tour of the Periodic Table	98
1.3 Isotopes	102
1.4 Finding a Window into the Unknown	104
2. Island Chains, Hot Spots, and Mantle Plumes	106
2.1 From Hot Spots to Plumes	106
2.2 Geochemistry Gets into the Act	107
2.3 Isotopes Weigh In	109
3. More Isotopes and The Two-Layer Mantle	111
3.1 Hafnium Joins the Fray	113
3.2 Helium and the Noble Gases	115
3.3 Pb Isotopes and the Pb-Paradox	116



4.	The Mantle Zoo	120
4.1	In Vino Veritas: The Three Component Mantle	120
4.2	Then There Were Five	122
5.	MORB and The Upper Mantle	127
5.1	Depletion	128
5.2	Replenishment	129
6.	Oceanic Islands and the Deep Mantle	136
6.1	Nature of the Lower Mantle	136
6.2	The Physics of Mantle Plumes	140
6.3	A Deep Mantle Signal?	146
6.4	Armstrong’s Idea	148
6.5	The Fate of Subducted Slabs	150
6.6	Variations on a Theme	152
6.7	Evidence from Conventional Stable Isotopes	156
6.8	Evidence from Unconventional Stable Isotopes	160
6.9	A Primitive Signal as Well	166
7.	Going Down: Subduction, Subduction Erosion and Crustal Foundering	167
7.1	The Craziest Idea Ever?	169
7.2	The Subduction Zone Filter	171
7.3	Subduction and OIB	176
7.4	Subduction Erosion and Lower Crustal Foundering	180
8.	Composition and Structure of Mantle Plumes	185
8.1	Lithologic Heterogeneity	185
8.2	A Case Study: The Hawaiian Plume	189
8.3	Lateral and Temporal Variations Within the Galápagos and Other Plumes	194
8.4	A Geochemical Map of the Deep Mantle?	201
8.5	The Mystery of Rejuvenescent Volcanism	202
9.	The Emerging Picture	206
9.1	Whither Primitive Mantle?	206
9.2	Heat, Convection, and Plumes	214
9.3	Summing Up	216
	References	221
	Index	247

PREFACE AND ACKNOWLEDGEMENTS

Science is about ideas, ideas about how the Earth works in our field, and how we evaluate ideas, but those ideas come from people. After all, God didn't reveal the laws of motion to Newton from behind a burning bush – Newton guessed; more or less correctly, but he guessed nonetheless. Consequently, ideas have a history and I have tried to tell this story at least partly as an historical narrative. I had the great fortune to be an undergraduate student during the latter part of the plate tectonic revolution in the late 1960's and witness that debate. I began graduate school just as the follow-up debate over mantle plumes was beginning. At that time, the field of mantle geochemistry was in its infancy and I was able to witness and participate in its development. This timing was also advantageous for my career: for one thing, there was not that much to learn as a graduate student because not that much was known! For another, the opportunities for research were virtually endless. There were downsides as well, including relatively primitive instrumentation, and thrashing about in ignorance because, again, not that much was known.

Another major advantage of the fortuitous timing of my career was the opportunity to know and interact with so many of the giants in the field. These include not only my immediate formal mentors, *Jean-Guy Schilling*, *Stan Hart*, *Mitsunobu Tatsumoto*, and *Al Hofmann*, but so many others who were busy developing the field of mantle geochemistry. Two who above all deserve mention, *Claude Allègre* and *Jerry Wasserburg*. Although these two play only supporting roles in my narrative, they very much deserved the honour they shared as the 1986 Crafoord Prize winners. Others include *Dick Armstrong*, who does play a



leading role in this narrative, *Ted Ringwood*, *George Wetherill*, *George Tilton* (who taught me Pb isotopic analysis during his sabbatical at Carnegie), *Tom Aldrich*, *Carl Hedge*, *Shen-Su Sun*, *Keith O’Nions* (“*Sir Keith*”), *Gil Hanson* and *Mike O’Hara* (who is assigned the role of villain in this narrative, but he was right far more often than he was wrong). I was also fortunate to eventually come to know and interact with many of the geophysicists who had invented plate tectonics, including *Jason Morgan*, *Dan McKenzie*, and my Cornell colleagues *Don Turcotte*, *Bryan Isacks*, and *Jack Oliver*. And, of course, I had the privilege of knowing and working with my own generation of mantle geochemists, many of them students of these founders. I dare not list their names for fear of leaving some out, but their work is cited in this narrative.

I was not present for the birth of mantle and isotope geochemistry, so there is a backstory and a history that I did not witness. The birth of mantle geochemistry occurred, in my view, between publication of the first papers in *Geochimica et Cosmochimica Acta* to contain the word “mantle” in the title (by *Royal Marshall* and *Ted Ringwood* in 1957 and 1958, respectively) and *Paul Gast’s* 1960 paper “*Limitations on the Composition of the Upper Mantle*”, which is where my narrative begins. Unfortunately, I never had the opportunity to meet *Paul Gast*. I was sitting in *Jean-Guy Schilling’s* office when he got a call informing him of *Paul Gast’s* death. *Jean-Guy* explained to me at the time that while he and *Gast* had their differences, his premature death was an enormous loss to geochemistry. In his assessment of the composition of the upper mantle, *Gast* relied not only on trace element abundances, but on Sr isotopic compositions as well, thus bringing the power of radiogenic isotope geochemistry into study of the Earth’s mantle. That field too was quite young; its birth marked, perhaps, by a paper on Pb isotopic evolution published in 1947 by *Fritz Houtermans* entitled the “*Das Alter des Urans*” (“The age of uranium”; *Houtermans* had the unfortunate distinction of having been arrested and imprisoned by both the Soviets and the Nazis). That same year, publication of papers by *Harold Urey* and his University of Chicago colleagues *Jacob Bigeleisen* and *Maria Mayer* marks the birth of stable isotope geochemistry.

My other objective in this *Perspective* was to summarise the understanding of mantle evolution and chemistry some fifty years later. Our understanding of mantle evolution is evolving rapidly, so this can only be a status report and certainly some of what I have written will turn out to be wrong or irrelevant. One thing I have learned through my career in science is to never completely believe anything – as *Einstein* remarked, God is subtle; it’s easy to be wrong. Furthermore, this is, of course, my own perspective and there are as many perspectives as workers in the field. I have placed a lot of emphasis on the idea that the mantle is extensively polluted by material of crustal origin, an idea originally proposed by *Dick Armstrong* in 1968, and that this pollution is most apparent in the sources of oceanic island basalts. These ideas now seem widely accepted, although there is much we still do not understand about the process, including how to reconcile this with noble gas evidence of quite primitive components in mantle plumes. The question of the bulk composition of the Earth and the degree to which it deviates from “chondritic” is also controversial. I have emphasised the case for



collisional erosion. In researching this topic I have become convinced that planetary accretion is very much a non-conservative process and that it is naive to believe that planetary compositions merely reflect the compositions of the raw materials from which they were constructed. I am somewhat less convinced that this explains the apparent non-chondritic Sm/Nd ratio of the Earth evidenced by excess ^{142}Nd in terrestrial rocks.

I would like to thank first of all my editor and friend *Janne Blichert-Toft*, who first proposed this project to me, encouraged me over the year it took to complete, and repeatedly read and improved the various drafts. The work also benefited enormously from reviews by *Stan Hart* (who occasionally corrected my history), *Matt Jackson*, and *Tim Elliott*. I am grateful for their efforts.

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PROBING THE EARTH'S DEEP INTERIOR THROUGH GEOCHEMISTRY

ABSTRACT

Basaltic volcanism provides a window into the Earth's mantle. Seeing through this window requires seeing through the processes of magma genesis and evolution that distort the view. Radiogenic isotope ratios, and to a lesser extent incompatible elements and stable isotope ratios, allow us to see through these distortions and infer the nature and evolution of various mantle magma sources. Geochemical studies of mid-ocean ridge basalts (MORB) reveal that the upper mantle was long ago depleted in incompatible elements through previous episodes of melt extraction, likely associated with crust formation. Oceanic island basalts (OIB) are the products of mantle plumes and hence provide us with a view of the deepest parts of the Earth's mantle. These plumes can be divided into several genera, EMI, EM II, and HIMU, most of which contain several species. Little or no mixing is observed between these genera, but all mix with a prevalent mantle component, PREMA, that contributes to many if not all plumes. Although the mantle comprising plumes also show evidence of previous melt extraction events, the more prominent chemical signature is of material anciently recycled from the Earth's surface through subduction of oceanic crust and sediment, subduction erosion, and foundering of lower continental crust. This is most unambiguously



manifest in variations in stable isotope ratios that could only have been produced at or near the surface of the Earth. In addition to a recycled component, many plumes also contain a quite primitive component, manifested primarily in their noble gas isotope ratios. The primitive component seems most closely associated with PREMA.

In contrast to hot spot and mid-ocean ridge volcanism, subduction-related volcanism allows an assessment of the flux *into* the Earth's mantle. It was apparent from early Pb isotope data that sediment was subducted along with oceanic crust, an observation later dramatically confirmed by the discovery of cosmogenic ^{10}Be in subduction zone magmas. Because of this sediment, the flux into the mantle at subduction zones is more incompatible-element enriched than MORB. Although some fraction of this material is extracted into subduction zone magmas, a variety of approaches reveal that the flux into the deep mantle remains incompatible-element enriched. Other studies, particularly geophysical ones, indicate that this subduction flux is substantially augmented by subduction erosion of the overriding plate. Over Earth's history these processes together with continental crustal founding may have delivered a volume of material equal to the present volume of the continents.

The discovery that all modern terrestrial rocks have an excess of ^{142}Nd , which is the decay product of the extinct radionuclide ^{146}Sm , compared to chondrites, reopens the question of the Earth's composition. One important implication is that the concentrations of heat producing elements, U, Th, and K, may be 25% or more lower than previously thought. Another implication is that the depleted source of MORB may constitute a very large fraction of the mantle, perhaps nearly all of it. On the other hand, the heat flow from the core may be substantially greater than previously thought. This implies that the lowermost mantle and the core-mantle boundary layer may play a dominant role in driving mantle convection, and ultimately all geologic processes. Geophysical evidence is revealing that the lowermost mantle is indeed a dynamic and interesting region. The challenge for mantle geochemists is to integrate their observations with those of geophysicists and progress is slowly being made in this respect.



1.1 A Role for Geochemistry

The last 50 years have been an exciting time for earth science. Above all, plate tectonics provide an integrated explanation for the most obvious and dramatic geologic activity on the Earth's surface: crustal deformation, earthquakes, volcanoes, etc. This was the big 'breaking story' and still bitterly controversial when I was an undergraduate at U.C. Berkeley in the late 1960's and remains one of the greatest revolutions and paradigm shifts in the history of science. Plate tectonics, however, is only a part of what we have learned in the last 50 years. In addition, we now have a modest understanding of early solar system history and how the Earth and Moon formed; we know a lot about how the continents have evolved through time; we have a detailed history of the Earth's magnetic field and some understanding of its generation; we know something of when life began and how it diversified, when the atmosphere became oxygenated, something about the Earth's climate history and what controls it, and when and where our own species arose. Few of these problems would appear to be "chemical", but regardless, the contribution of chemistry to most of them is remarkable, some of them documented in other *Geochemical Perspectives* (e.g., Broecker, 2012; Arndt, 2013). Of course, much remains to be learned. The details of the Earth's formation remain obscure, we don't know how life arose, we don't fully understand the role of tectonics in controlling climate, and while we know much about how the existing crust has grown, we remain very ignorant of how much of it might have been destroyed. Add to these the questions we don't even know to ask yet; what former US Defense Secretary *Donald Rumsfeld* famously called "the unknown unknowns". All this means that the next 50 years in science could be as exciting as the last.

I didn't initially recognise the value of geochemistry and I didn't set out to be a geochemist. My interest in the field was first piqued as an undergraduate in *John Verhoogen's* tectonics class when I learned that Sr isotope ratios could be used to discriminate unambiguously between crustal and mantle sources of magmas. I only subsequently realised that it is not quite that simple and unambiguous, since crustal strontium can find its way into magma in a great variety of ways, including recycling through the deep mantle, for example in Samoa (e.g., White and Hofmann, 1982; Jackson *et al.*, 2007). Nevertheless, geochemistry has fascinated me ever since.

In the following pages, I'll try to tell the story of how geochemistry has provided and continues to provide insights into one of the remotest parts of our planet: its deep interior. Of course, geochemistry is only one tool amongst many in this respect and it must work in tandem with other fields, including seismology, geodesy, and geodynamic modelling to try to create a picture of how the Earth's



deep interior works and how it has evolved. This might at first seem a truly remote and academic exercise until one realises that much of what happens at the surface of the Earth is a consequence of what is occurring in the Earth's deep interior. The immediate effect is plate tectonics and associated phenomena, but these in turn have affected the evolution of everything else from atmospheric composition and climate to life. Thus to really understand our planet, we need to understand how its deepest parts work. At this point, what we don't know exceeds what we know: much remains to be learned. To begin with, I'll provide a brief background on the tools geochemists use in this endeavour: trace element distributions and isotope ratios.

1.2 A Quick Tour of the Periodic Table

Chemistry, and the periodic table, can be daunting at first; after all there are 92 'naturally occurring' elements and another nearly two dozen artificially created ones, each with unique properties (I remember being assigned to memorise the periodic table up through iron in freshman chemistry for the midterm exam. I don't think I succeeded). That 92 number itself is a bit fuzzy: two of them, technetium and praseodymium, are present in the Earth in miniscule, nearly undetectable quantities and only because they are continually produced by uranium fission. Another 8 are only present because they are continually created through alpha and beta decay of uranium and thorium, which brings us down to 82. On the other hand, some elements not generally counted among the 'naturally occurring' are produced naturally in supernovae and flung out into the cosmos. At least one, plutonium, was still present when the Earth formed.

There is order in this apparent chaos, and this was *Mendeleev's* great insight: chemical properties vary in a systematic way with atomic weight (or more precisely, atomic number). But we can simplify things even further. Based on how they were distributed in meteorites, Goldschmidt (1937) divided the elements into 4 categories, illustrated in Figure 1.1. *Lithophile* elements are concentrated in silicate and oxide phases of meteorites and in the mantles and crusts of planets and asteroids. *Siderophile* elements are concentrated in metal phases in meteorites and in the cores of planets and asteroids. *Chalcophile* elements are concentrated in sulphide phases in meteorites. Chalcophile elements are for the most part somewhat siderophile as well and thus also concentrate in planetary cores to some degree. *Atmophile* elements are those that generally form gases even at quite low temperature. They are usually underabundant in meteorites and are concentrated in the atmospheres of planets. Because the focus of this *Geochemical Perspective* is on the mantle, we will mainly be interested in the lithophile elements.

Most elements in the periodic table are present in the Earth as trace elements. Just six, O, Mg, Si, Fe, Al, and Ca, make up 99.1 % of the silicate Earth. If we include the core, then only nickel, and perhaps sulphur, need be added to this list. A few more, such as Na, K, Ti, and Mn, are sufficiently concentrated in the crust that geochemists often treat them as major elements. The remaining



elements rarely form their own minerals and instead substitute into crystallographic sites normally occupied by other elements, except when they have become extraordinarily concentrated by geologic accident (pegmatites and limestones, for example). *Goldschmidt* recognised that the distribution of lithophile trace elements between phases depends mainly on their ionic size and charge. In large measure this is because the electronic structure of many of these elements is such that they effectively behave as hard, charged spheres and form predominantly ionic bonds. To put it simply, *Goldschmidt* noted that the greater the difference between ionic size and charge of a trace element and the size and charge of the atom normally occupying a crystallographic site, the less likely that element would be found in that site.

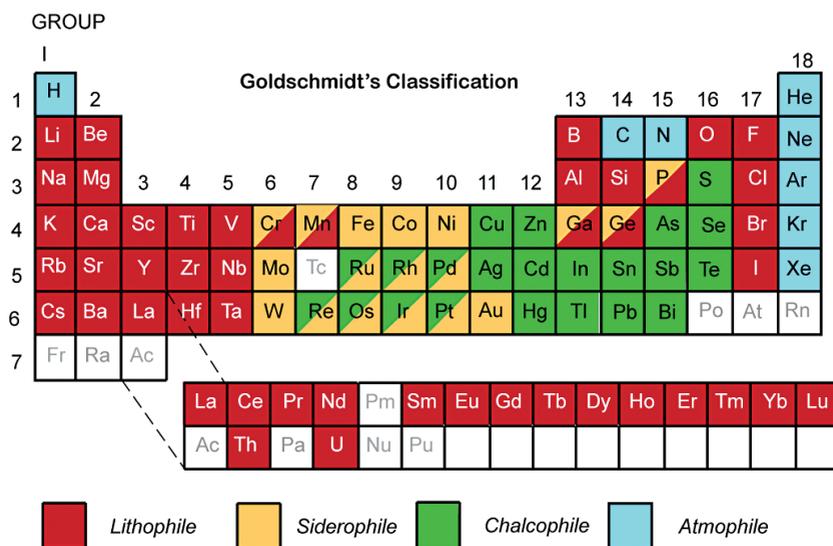


Figure 1.1 Goldschmidt's classification of the Elements.

This gives rise to another classification of elements into “compatible” and “incompatible” ones. *Compatible* elements are those that substitute readily into common minerals, specifically mantle minerals: mainly olivine, pyroxenes, spinel and garnet. Nickel and chromium, which readily substitute into olivine and pyroxene, respectively, are examples of highly compatible elements. *Incompatible* elements are those that don't readily substitute into these minerals. Rubidium, with a charge of +1 and a radius of 166 pm (about twice that of Mg^{2+}) is an example of a highly incompatible element. Being unwelcome in mantle minerals, these elements partition into magma when melting occurs and consequently have become concentrated in the crusts of planets.



The behaviour of an element, i , during melting is conventionally described by a partition coefficient, defined as the equilibrium ratio of concentration, C , in the solid, s , to that in the liquid, l :

$$D_i^{s/l} = \frac{C_i^s}{C_i^l} \quad (1.1)$$

Partition coefficients have generally been determined experimentally or from phenocryst-matrix pairs (e.g., Shimizu, 1974), but can also be predicted theoretically (e.g., Blundy and Wood, 1994). The partition coefficient then provides a measure of incompatibility. The relationship between ionic size and incompatibility is readily demonstrated with the lanthanoid (lathanide) rare earths (hereafter referred to only as 'rare earths'). The radii of these elements, all of which normally have an ionic charge of 3+, shrink with increasing atomic number due to ineffective shielding of nuclear charge by electrons in the f shell. As a consequence, solid/liquid partition coefficients change systematically, for example increasing by an order of magnitude going from lanthanum to lutetium in many minerals (Fig. 1.2). Lanthanum is a highly incompatible element, lutetium not so much.

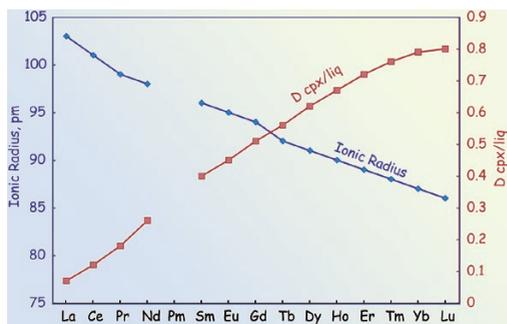


Figure 1.2 Trivalent ionic radii (in picometres) and clinopyroxene-liquid partition coefficients of the lanthanide rare earths. The rare earths become more compatible as ionic radius shrinks.

The distribution of elements between crust and mantle is best illustrated using a rare earth plot (or Coryell-Masuda diagram), in which the concentrations normalised to (*i.e.* divided by) concentrations in chondritic meteorites are plotted vs. atomic number (Fig. 1.3). The continental crust is enriched in light compared to heavy rare earths. In contrast, mid-ocean ridge basalts (MORB) are depleted in the light relative to the heavy rare earths. The mantle giving rise

to MORB, which are the most voluminous magmas on Earth, is inferred to have been depleted in incompatible elements through previous melting episodes and is often referred to as the *depleted mantle (DM)* or the *depleted MORB mantle (DMM)*.

Because much of the variation in mantle chemistry appears to result from extraction of partial melt and subduction of crust formed by those melts, there is a very considerable focus on incompatible elements, particularly the incompatible lithophile elements. These include, in addition to the rare earths, the alkali and alkaline earths (K, Rb, Cs, Sr, Ba), and the high field strength elements (Nb, Zr, Hf, Ta), so called because their incompatibility results from their high ionic charge



(4+ or 5+) rather than size, and the actinide rare earths, U and Th.

Yet another way to classify the elements geochemically (or perhaps more accurately, cosmochemically) is by their 50% condensation temperatures under conditions likely to have prevailed in the solar nebula (e.g., Lodders, 2003). The most abundant metals in the Earth, Mg, Fe, and Si, have 50% condensation temperatures of between 1336 K and 1310 K. Elements whose condensation temperatures are greater than this 'main group' of elements are considered *refractory* elements; those with lower condensation temperatures are classified as volatile elements. These can be further subdivided into lithophile and siderophile. The *refractory lithophile elements*, which include Ca, Al, Ti, Sr, Ba, Nb, Zr, Hf, Ta, U, Th, and the rare earths have the interesting property that

their relative concentrations in chondritic meteorites are nearly constant. Because chondritic meteorites, which are essentially collections of nebular dust (albeit variously processed), are otherwise petrologically and chemically diverse and likely formed in a variety of conditions in different parts of the nebula, this observation leads to the inference that nebular processes were unable to fractionate these elements and, therefore, that the relative abundances of these elements in the nebula was uniform. Since the Earth accreted from these nebular materials, the relative (but not absolute) abundances of these elements should be the same as in chondrites. This assumption forms the basis for conventional estimates of the composition of the silicate Earth (e.g., Jagoutz *et al.*, 1979; Hart and Zindler, 1986; McDonough and Sun, 1995; Palme and O'Neill, 2003), and is commonly referred to as the Bulk Silicate Earth (BSE) composition. Because the crust appears to have formed from the mantle and any chemical exchange between the core and the mantle is assumed to be insignificant, the BSE composition is also the composition of 'primitive mantle'. However, as I'll explain in Section 9, this assumption is now questioned.

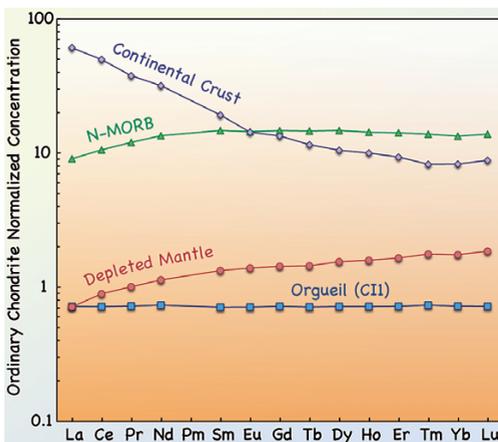


Figure 1.3

A rare earth, or Coryell- Masuda plot in which concentrations are normalised to the average of ordinary chondrites. The CI1 carbonaceous chondrite *Orgueil* has the same relative rare earth concentrations as ordinary chondrites, but lower absolute concentrations due to dilution by low temperature condensate. The continental crust (Rudnick and Gao, 2014) is enriched in light rare earths while typical depleted mid-ocean ridge basalt N-MORB (White and Klein, 2014) shows relative light rare earth depletion. The 'depleted mantle' is the estimated composition of the mantle source of MORB (Salters and Stracke, 2004).



1.3 Isotopes

It gets more complicated: atoms of an element are not necessarily the same; some can have more neutrons than others and consequently many elements have more than one isotope. While complications are rarely welcome, this one turns out to be fortuitous for geochemistry for a couple of reasons. First, although an extra neutron or two plays no direct role in chemical behaviour, the difference in mass leads to slight differences in bond strength as well as to the rate at which an atom can move and diffuse. These effects tend to be small, so that isotope ratio variations are usually reported as deviations in parts per thousand from a standard. For example, the $^{18}\text{O}/^{16}\text{O}$ ratio is reported as:

$$\delta^{18}\text{O} = \left(\frac{^{18}\text{O}/^{16}\text{O}_{\text{sample}}}{^{18}\text{O}/^{16}\text{O}_{\text{SMOW}}} \right) \times 1000 \quad (1.2)$$

where *SMOW* is *Standard Mean Ocean Water*. Stable isotope studies have proved enormously useful for everything from palaeoclimate to palaeontology. However, stable isotope fractionations decrease with the square of increasing temperature and usually become effectively insignificant at mantle temperatures. However, they, particularly oxygen isotope ratios, are useful in mantle studies for precisely that reason. As Taylor and Sheppard (1986) wrote, “igneous rocks whose $\delta^{18}\text{O}$ differ significantly from the primordial value ($\sim +6$) must either have been affected by low temperature processes, or must contain a component that was at one time at the surface of the Earth”. As we’ll find in Section 6.7, this makes oxygen and other stable isotopes extraordinarily useful in tracing recycled surficial material in the mantle.

The isotopic composition of some elements varies for another reason: radioactive decay. The rate of radioactive decay is expressed as:

$$\frac{dN}{dt} = \lambda N \quad (1.3)$$

where N is the number of atoms (or moles) of a radioactive nuclide and λ is the decay constant specific to that nuclide. This is a first order rate equation of the kind seen in kinetics; the difference is that the decay constant is absolutely independent of external influences¹. The value of radioactive decay in geology results from this absolute constancy of the rate constant. It is the entire basis of geochronology and by introducing the element of time, it is the one thing that allows geochemists to understand how things have *evolved*. The decay results in the production of a daughter nuclide, D , whose production over time t is:

$$D = N(e^{\lambda t} - 1) \quad (1.4)$$

1. There is a slight effect of pressure on the rate of electron capture decay, such as the ^{40}K - ^{40}Ar decay and nuclei in excited states can decay more rapidly than when they are in their ground state.



Since some amount of the daughter, D_0 , would have been present at $t = 0$, the total amount is then:

$$D = D_0 + N(e^{\lambda t} - 1) \quad (1.5)$$

Consider the specific case of ^{87}Rb , which beta decays to ^{87}Sr . It is far simpler to deal with ratios of isotopes rather than absolute abundances, which is why we divide equation (1.5) by the abundance of another, non-radiogenic isotope of Sr, which by convention is ^{86}Sr . Equation (1.5) then becomes:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right) = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0 + \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)(e^{\lambda t} - 1) \quad (1.6)$$

With this equation in mind, Gast (1960) summarised the value of radiogenic isotopes in mantle geochemistry as follows:

“In a given chemical system the isotopic abundance of ^{87}Sr is determined by four parameters: the isotopic abundance at a given initial time, the Rb/Sr ratio of the system, the decay constant of ^{87}Rb , and the time elapsed since the initial time. The isotopic composition of a particular sample of strontium, whose history may or may not be known, may be the result of time spent in a number of such systems or environments. In any case the isotopic composition is the time-integrated result of the Rb/Sr ratios in all the past environments. Local differences in the Rb/Sr will, in time, result in local differences in the abundance of ^{87}Sr . Mixing of material during processes will tend to homogenize these local variations. Once homogenization occurs, the isotopic composition is not further affected by these processes.”

In addition to Sr, the early application of radiogenic isotope ratios to mantle geochemistry included Pb isotope ratios, which vary due to decay of U and Th. Subsequently, techniques were developed for the ^{147}Sm - ^{143}Nd , ^{176}Lu - ^{176}Hf , and ^{187}Re - ^{187}Os decays and some work has been done with the ^{138}La - ^{138}Ce , ^{190}Pt - ^{186}Os , and ^{40}K - ^{40}Ca decays. Of course the principles enunciated by *Gast* apply to these other systems as well.

In addition to these elements, the isotopic composition of the noble gases also vary due to radioactive decay: ^4He is, of course, produced by alpha decay (mainly of U and Th), ^{40}Ar by decay of ^{40}K , and the heavy isotopes of Xe are produced by fission of ^{238}U , as are isotopes of Kr (but in lesser amounts). Ne isotopes, particularly ^{21}Ne , although not produced directly by radioactive decay, are produced by secondary nuclear reactions initiated by alpha particles and fission neutrons. All these radioactive parents have very long half-lives, listed in Table 1.1, so that the resulting isotopic variations are quite small, requiring high-precision measurement. Noble gas studies have proved extraordinarily important in mantle geochemistry, but we will not consider them in detail here because they are already the subject of another published *Geochemical Perspectives* (Moreira, 2013).



Table 1.1 Long-Lived Radioactive Decay Systems of Geochemical Interest.

Parent	Decay Mode	λ	Half-life	Daughter	Ratio
^{40}K	β^+ , e.c., β^-	$5.5492 \times 10^{-10}\text{yr}^{-1*}$	$1.25 \times 10^9\text{yr}$	^{40}Ar , ^{40}Ca	$^{40}\text{Ar}/^{36}\text{Ar}$
^{87}Rb	β^-	$1.42 \times 10^{-11}\text{yr}^{-1}$	$4.88 \times 10^{10}\text{yr}$	^{87}Sr	$^{87}\text{Sr}/^{86}\text{Sr}$
^{138}La	β^-	$2.67 \times 10^{-12}\text{yr}^{-1}$	$2.60 \times 10^{11}\text{yr}$	^{138}Ce	$^{138}\text{Ce}/^{142}\text{Ce}$, $^{138}\text{Ce}/^{136}\text{Ce}$
^{147}Sm	α	$6.54 \times 10^{-12}\text{yr}^{-1}$	$1.06 \times 10^{11}\text{yr}$	^{143}Nd	$^{143}\text{Nd}/^{144}\text{Nd}$
^{176}Lu	β^-	$1.867 \times 10^{-11}\text{yr}^{-1\ddagger}$	$3.71 \times 10^{10}\text{y}$	^{176}Hf	$^{176}\text{Hf}/^{177}\text{Hf}$
^{187}Re	β^-	$1.64 \times 10^{-11}\text{yr}^{-1}$	$4.23 \times 10^{10}\text{yr}$	^{187}Os	$^{187}\text{Os}/^{188}\text{Os}$
^{190}Pt	α	$1.54 \times 10^{-12}\text{yr}^{-1}$	$450 \times 10^{11}\text{yr}$	^{186}Os	$^{187}\text{Os}/^{188}\text{Os}$
^{232}Th	α	$4.948 \times 10^{-11}\text{yr}^{-1}$	$1.40 \times 10^{10}\text{yr}$	^{208}Pb , ^4He	$^{208}\text{Pb}/^{204}\text{Pb}$, $^4\text{He}/^3\text{He}$
^{235}U	α	$9.849 \times 10^{-10}\text{yr}^{-1\dagger}$	$7.04 \times 10^8\text{yr}$	^{207}Pb , ^4He	$^{207}\text{Pb}/^{204}\text{Pb}$, $^4\text{He}/^3\text{He}$
^{238}U	α	$1.55125 \times 10^{-10}\text{yr}^{-1}$	$4.47 \times 10^9\text{yr}$	^{206}Pb , ^4He	$^{206}\text{Pb}/^{204}\text{Pb}$, $^4\text{He}/^3\text{He}$

Note: the branching ratio, *i.e.* ratios of decays to ^{40}Ar to total decays of ^{40}K is 0.117. The production of ^4He from ^{147}Sm decay is insignificant compared to that produced by decay of U and Th.

*Value suggested by Renne *et al.* (2010). The conventional value is $5.543 \times 10^{-10}\text{yr}^{-1}$.

‡Value recommended by Söderlund *et al.* (2004).

†Value suggested by Mattinson (2010). The conventional value is $0.98485 \times 10^{-10}\text{yr}^{-1}$.

In addition to long-lived *extant* radionuclides, isotopic variation in some elements results from decay of short-lived *extinct* radionuclides, whose half-lives were nevertheless long enough that they were present in the early Earth: ^{146}Sm , which decays to ^{142}Nd , ^{129}I which decays to ^{129}Xe , and ^{244}Pu , whose fission products include isotopes of Xe. In addition, variation in the isotopic composition of tungsten resulting from the decay of ^{182}Hf has also been observed in some rocks, but it is unclear whether ^{182}Hf , with a half-life of 9 Ma, was still present in the early Earth: the observed variation in $^{182}\text{W}/^{184}\text{W}$ may instead be a consequence of incomplete homogenisation of material that accreted to form the Earth. Of these daughters of extinct radionuclides, isotopic variation in the modern mantle has been observed only in Xe. This absence together with the presence of variations in $^{182}\text{W}/^{184}\text{W}$ and particularly $^{142}\text{Nd}/^{144}\text{Nd}$ preserved in early crustal rocks nevertheless provides important constraints on the subsequent mantle evolution.

1.4 Finding a Window into the Unknown

By 1960, the geologic time scale had been worked out and ages assigned, the age of the Earth was known (and almost as well as we know it now; Patterson, 1956), the geology of the continents had largely been mapped, and the structure



of the oceanic crust was in the process of being sorted out. Seismologists had worked out that the mantle was 2880 km thick, was solid and that there was a change in seismic velocity greater than could be explained by self-compression alone somewhere around 700 km depth. Seismic velocities were consistent with the mantle being composed of something like peridotite, but not much else could be said about the mantle. It was understood that basaltic magmas were almost certainly generated within the mantle rather than the crust and a few people, such as *Paul Gast*, *George Tilton*, and *Carl Hedge*, realised that basalts might provide a geochemical window into the mantle. Gast (1960) reported the first Sr isotopic analyses of mantle-derived materials. The analytical precision was too poor to allow any inferences about how or whether $^{87}\text{Sr}/^{86}\text{Sr}$ might vary in the mantle, but he concluded that *“it appears that the abundance of alkali metals, relative to strontium, barium, and uranium, is and always has been, much lower in the upper mantle than in chondrites”* and *“This depletion may be an indication of a nonchondritic earth composition; it may also result from an earth differentiation in which K, Rb, and Cs were concentrated or retained in the lower mantle.”* Although he was certainly right about the nonchondritic composition of the Earth, it is interesting that 50 years later we have not been able to entirely rule out the possibility that incompatible elements may be concentrated in the lower mantle (Boyett and Carlson, 2006)! Faure and Hurley (1963) also could not resolve any variation in Sr isotope ratios in basalts beyond analytical error, but they did note that $^{87}\text{Sr}/^{86}\text{Sr}$ in basalts was sufficiently lower than that of crustal materials and that hence $^{87}\text{Sr}/^{86}\text{Sr}$ in igneous rocks *“could be used as a criterion for the origin of the material”*, i.e. that $^{87}\text{Sr}/^{86}\text{Sr}$ could be used to distinguish crustal from mantle magma sources (as was to I learn in *Verhoogen’s* class a few years later). Subsequent studies by Gast *et al.* (1964), Lessing and Catanzaro (1964), Tatsumoto *et al.* (1965), Powell *et al.* (1965), and Hedge (1966) had sufficient analytical precision to demonstrate real variation in $^{87}\text{Sr}/^{86}\text{Sr}$ as well as in Pb isotope ratios among basalts so that Hedge (1966) could conclude that *“the upper mantle contains certain inhomogeneities with respect to Rb/Sr which have probably persisted for significant periods of geologic time.”* He also noted that volcanic rocks erupted on *“established continental crust”* had higher $^{87}\text{Sr}/^{86}\text{Sr}$ than did oceanic basalts and he suggested assimilation was the cause. Sometime during those years between 1960 and 1966, the field of mantle isotope geochemistry had been born.

By the end of that decade, enough data had accumulated to reveal that this heterogeneity was not random and that, as Hart (1971) concluded: *“Oceanic-island basalts are derived from a different type of mantle than submarine ridge basalts.”* (We now refer to the former as oceanic island basalts or OIB and the latter as mid-ocean ridge basalts or MORB – the first of the many acronyms coined by *Stan Hart*). An interesting dilemma arose in the case of islands such as Iceland that sat atop mid-ocean ridges. As *Stan* put it in that same paper, *“The mantle which feeds the ridges must pass under the oceanic islands, and yet somehow maintain an identity distinct from that of the mantle which is supplying magma to the oceanic islands.”* The explanation would be proposed that same year, and *Stan’s* work on Iceland and the Reykjanes Ridge would play the key role in its development.



2.1 From Hot Spots to Plumes

Around the same time as mantle isotope geochemistry was developing, ideas and theories about continental drift and sea-floor spreading were being assembled into what would eventually be called plate tectonics. It was a time of fierce and bitter debate (I recall one of my Berkeley professors angrily saying that the proponents of the new theory should be confined to insane asylums). One of the key early papers in this development was that of Wilson (1963), who noted the parallel nature of volcanic island chains in the Pacific and suggested they formed as convection currents in the shallow mantle dragged oceanic floor over a fixed melting region in the deeper mantle. The *hot spot* idea (Wilson did not use the term) well explained Hawaii and other such chains, but required a surface of the solid Earth to be mobile, something not everyone could accept. It would be several more years before the various observations were finally assembled into what we now recognise as plate tectonics (Isacks *et al.*, 1968; Le Pichon, 1968; Morgan, 1968). Alas, some things were left by the way side. While plate tectonics explained most volcanism on the planet and explained the progression of volcanism along oceanic island chains, it did not explain why the volcanoes were there in the first place; in other words it failed to explain why Wilson's hot spots were hot and or even why they were spots; *i.e.* why they were stationary.

The now widely, but not universally (*e.g.*, Anderson, 2000), accepted answer was proposed by Morgan (1971): Wilson's 'hot spots' were the surface manifestation of convection plumes rising from the lower mantle. Morgan described these *mantle plumes* as similar to convection cells in the atmosphere that give rise to thunderstorms. Like air, hot mantle is buoyant and consequently can rise in a more or less vertical column. The idea was initially no less controversial than sea-floor spreading had been a decade earlier. Even for some of the early proponents of continental drift/sea-floor spreading, this was just one step too far. At a 1973 Royal Astronomical Society Meeting on the subject, Keith Runcorn, an early proponent of continental drift told Sir Harold Jeffreys, long a continental drift skeptic, "I don't believe them either, Harold" (Nature, 1973). Furthermore, it was unclear how the idea could be tested – it hardly seemed feasible to seismically image rising columns of hot rock (although they would be some 40 years later). The first evidence came rather quickly. Vogt (1971) reported finding "V-shaped... basement ridges and crustal isochrons suggests asthenosphere flow, at least under the spreading axis, away from the Iceland 'hot spot' (mantle plume)." Two years later, geochemistry would get into the act as well.

Before going further, I should make clear that few if any scientists believe that all intraplate volcanism are products of mantle plumes. As Al Hofmann and Stan Hart (Hofmann and Hart, 2007) made clear in a rather delightful comment



in Science, finding an intraplate volcano that is not a product of plumes does not disprove plume theory. There are many examples of intraplate volcanoes that clearly are not the products of mantle plumes. On the other hand, there are also examples, such as Hawaii, Reunion, Kerguelen, etc. that are far better explained by the plume hypothesis than any alternative. And then there are some 'hot spots', such as the Cook-Australis, whose cause can be legitimately debated. Finally, it is possible that there are different kinds of plumes (Courtillet *et al.*, 2003). I'll discuss some of these issues, but will not attempt to sort out which hot spots are produced by plumes and which are not.

2.2 Geochemistry Gets into the Act

Another issue around this time (and incompletely resolved today) is the question of what controls incompatible trace element concentrations in magmas and the relationship between alkali and tholeiitic basalts. Both types are present in Hawaii, with alkali basalts strongly enriched in incompatible elements compared to tholeiites. Bowen's (1928) recognition of the importance of fractional crystallisation in accounting for the diversity of igneous rock chemistry was one of the truly great landmarks in the evolution of geology, but, as Yoder and Tilley (1962) demonstrated, this could not account for the difference between the alkalic and tholeiitic magma series: the presence of a 'thermal divide' meant that one could not be produced from the other. Early studies of Hawaiian basalts showed that the highly alkalic ones had lower $^{87}\text{Sr}/^{86}\text{Sr}$ than the tholeiitic ones. Lessing and Catanzaro (1964) suggested assimilation of marine sediments by the tholeiites while Powell *et al.* (1965) suggested mantle heterogeneity, but in the opposite sense of what was needed to explain the difference in incompatible elements.

Jean-Guy Schilling (1966; Schilling and Winchester, 1967), my future PhD advisor, argued that degree, or extent, of melting could account for the incompatible element differences between the tholeiites and alkali basalts. Let's consider this in a bit more detail. If the distribution of an element, i , between bulk solid and liquid is expressed as a partition coefficient D_i , as defined in equation (1.1), and the fraction of melt present in an equilibrium partial melt is F , it is readily shown from mass balance that

$$C_i^l = \frac{C_i^o}{D(1-F) + F} \quad (2.1)$$

where the superscript l denotes the liquid and the superscript o denotes the concentration in the bulk system or, equivalently, the original solid. If D is much smaller than F , as it is for a highly incompatible element, then the concentration in the liquid varies inversely with the extent of melting. Thus the difference between alkali basalts and tholeiites in incompatible elements could be explained by alkali basalts being smaller-degree melts than tholeiites. This insight was reiterated in a classic paper by Gast (1968) and although other factors such as mantle



heterogeneity and depth of melting (through effects on the phases present, *D*, and *F*) are also often involved, this remains the main explanation for the differences in incompatible elements between the two magma series.

Having taken up a faculty position at the University of Rhode Island's Graduate School of Oceanography, *Schilling* became interested in ocean floor basalts (what we now call MORB). *Schilling* led a sampling expedition to the Reykjanes Ridge south of Iceland and found that the basalts he recovered became progressively enriched in incompatible elements and went from being light rare earth element (LREE)-depleted to LREE-enriched as Iceland was approached. *Schilling* at first explored what he called 'single mantle source models' as an explanation, but found that they failed. For example, he found that degree of melting would have to decrease by at least a factor of 2 to 4 from the southern Reykjanes Ridge to Iceland, with little change in major element chemistry. Furthermore, seismic studies suggested that the Iceland crust was 2 to 4 times thicker than normal oceanic crust, suggesting greater, not lesser, extents of melting beneath Iceland.

Morgan (1971) had pointed out that his plume model was "compatible with the observation that there is a difference between oceanic island and oceanic ridge basalts" since plumes would bring "relatively primordial material from deep in the mantle". *Stan Hart* and *Jim Powell* had already begun to analyse the Sr isotope ratios in Jean-Guys' Reykjanes Ridge samples and *Stan* pointed out that the isotopes clearly proscribed single source models. *Schilling* (1973a) thus embraced the Morgan plume model to explain the Reykjanes Ridge data. Specifically, he argued that a "primordial hot mantle plume" rose beneath Iceland and either this material or partial melts of it then flowed southward along the Reykjanes Ridge becoming progressively diluted by melts of the "depleted low velocity layer" – what is now variously referred to as "depleted upper mantle" (DUM), "depleted MORB mantle" (DMM), or sometimes just "depleted mantle" (DM).

Jean-Guy Schilling's work was immediately attacked by *Mike O'Hara* (1973). Much of *O'Hara's* criticism centred on *Schilling's* reference to mixing of 'primary' magmas. *Schilling* had used the term in the sense of 'end members' of the mixture, but *O'Hara* interpreted it in the sense it is still commonly used today, namely having ascended and erupted without having experienced fractional crystallisation. *Schilling* had argued that fractional crystallisation could not explain the changing incompatible element chemistry along the Reykjanes Ridge, but had not meant to imply that no fractional crystallisation had occurred, as he explained in his reply (*Schilling*, 1973b). Thus this part of *O'Hara's* criticism was simply a misunderstanding (and I think the word 'primary' has been reserved for the sense in which *O'Hara* used it ever since). This was a sensitive subject for *O'Hara*, who had been arguing against the notion that ocean floor basalts were primary (e.g., *Engel et al.*, 1965; *O'Hara*, 1968). Most would agree with *O'Hara* on this today: MORB have generally experienced a complex evolution before they erupt on the ocean floor. But *O'Hara* undoubtedly placed too much emphasis on fractional crystallisation when he argued that instead of Icelandic basalts being enriched in light rare earths, they had actually been depleted in heavy rare earths by eclogite



fractionation. He went on to dismiss any isotopic evidence of mantle heterogeneity discussed in the following section, suggesting that “*it may be necessary to re-examine the proposition that isotope ratios do not change during fractional crystallization*” (O’Hara, 1973). Here O’Hara was wrong: in the subsequent 40 years, no evidence has emerged to suggest that radiogenic isotope ratios are affected by fractional crystallisation in the absence of assimilation.

2.3 Isotopes Weigh In

Schilling’s paper was quickly followed by papers by Hart *et al.* (1973) with the data mentioned above that demonstrated a progressive increase in $^{87}\text{Sr}/^{86}\text{Sr}$ along the Reykjanes Ridge demonstrating distinct mantle sources beneath Iceland and the southern Reykjanes Ridge. Sun *et al.* (1975) found a similar increase in Pb isotope ratios along the Reykjanes Ridge toward Iceland. Sun *et al.* (1975) did point out that Pb isotope ratios were inconsistent with the Iceland mantle plume being ‘primordial’ in a strict sense as the Pb isotope data required that this mantle had been processed at some point in the past as Gast *et al.* (1964) had pointed out. For most geochemists, this seemed strong evidence for mantle heterogeneity and excited interest in, if perhaps not acceptance of, the mantle plume hypothesis. O’Hara’s skepticism of isotope geochemistry was tenacious, however (O’Hara, 1975). Indeed, I remember still arguing with him about this 6 or 7 years later when I was a post-doc at Carnegie.



Figure 2.1 Azores, Coast of Faial Island.



In what became a career-long project, *Jean-Guy Schilling* continued to investigate plume-ridge interaction, moving his focus southward along the Mid-Atlantic Ridge to the Azores, where he documented similar gradients in La/Sm ratios along the ridge as the Azores was approached (*Schilling, 1975*). *Schilling* had become my thesis advisor about the time he submitted his Iceland paper. I became involved in this next phase, participating in several oceanographic expeditions to dredge samples from the Mid-Atlantic Ridge working south from the Reykjanes Ridges and then down to about 30 °N. I also spent a month collecting samples from the Azores Islands themselves. These are strikingly beautiful islands (Fig. 2.1), although back then they seemed frozen in time: while cars were common, one could also see the occasional ox-drawn cart. One might expect people from that sort of isolated environment to be a bit remote and, well, insular. Instead they were among the most friendly and hospitable people I have ever encountered (among other things, I learned that just about everyone there had a cousin in America). It was good to see that the people had not changed despite the very welcome economic progress when I returned there 35 years later.

When it came to the specifics of a dissertation project, I mentioned my interest in isotope geochemistry to *Schilling*, but, lacking a mass spectrometer at URI, *Schilling* said he didn't think it possible. We discussed instead a possible thesis centred on noble gases perhaps done in collaboration with *Jack Dymond* at Oregon State. A few months later *Schilling* came back to me and said there was a possibility of my doing a pre-doc at Carnegie Institution's Department of Terrestrial Magnetism and analysing Sr isotope ratios under the tutelage of *Stan Hart*. I jumped at the chance. Under *Stan's* guidance I analysed roughly 100 samples (all with a single shot, manually operated mass spectrometer) for Sr isotope ratios and K, Rb, Cs, Sr, and Ba concentrations in four months there. The results showed a clear isotopic anomaly along the ridge in the vicinity of the Azores, more or less as *Schilling's* plume-asthenosphere mixing model predicted (*White et al., 1976*). Figure 2.2 shows the combined results of the two studies. *Schilling* continued his effort to geochemically 'map' the mid-ocean ridge system over the next several decades. Others contributed as well, so that today, much of the mid-ocean ridge system has been so mapped (*e.g., Meyzen et al., 2007*). We'll examine that at a later point.

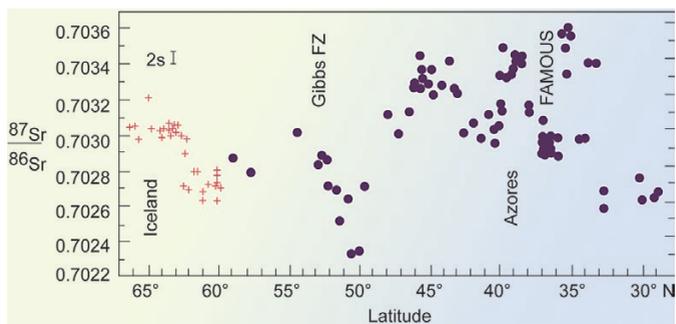


Figure 2.2

Sr isotope ratio variations along the northern Mid-Atlantic Ridge. Data from Hart *et al.* (1973) (red crosses) and White *et al.* (1976) (purple circles).



3. MORE ISOTOPES AND THE TWO-LAYER MANTLE

At the time I was doing my dissertation research, Sr and Pb isotopes were the only tools available for mantle isotope geochemistry, although some inferences about mantle and atmospheric evolution had been made based on argon isotope ratios (e.g., Damon and Kulp, 1958). Since, as expected, stable isotope ratios appeared to be constant within analytical error in the mantle they were of no interest (that eventually changed, as I'll recount in a subsequent section). However, Notsu *et al.* (1973) had used the ^{147}Sm - ^{143}Nd decay system to date a Roberts Victor Mine eclogite and Lugmair (1974) had used it to date the eucritic meteorite *Juvinas*. Since Sm and Nd were rare earths, Schilling was naturally intrigued. He asked me to research the topic in more detail and predict how $^{143}\text{Nd}/^{144}\text{Nd}$ might vary along the northern Mid-Atlantic Ridge and write up the results for him. Lugmair had reported the initial ratio for *Juvinas* and noted that the Columbia River basalt BCR-1 had approximately chondritic $^{143}\text{Nd}/^{144}\text{Nd}$. Based on that, the observed variations in the Sm/Nd ratio and the half-life of ^{147}Sm , I calculated that there should be quite significant variation in $^{143}\text{Nd}/^{144}\text{Nd}$ along the Mid-Atlantic Ridge, ranging from lesser to greater than chondritic values. Shortly after that, DePaolo and Wasserburg (1976a,b) reported $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in MORB and other basalts and the results were, to me at least, surprising since most values were greater than the chondritic value, which was inconsistent with what I had predicted. The Caltech work was quickly followed by similar studies by the Paris (Richard *et al.*, 1976) and Lamont labs (O'Nions *et al.*, 1977).

Sm and Nd are refractory lithophile elements, and it was therefore reasonable to assume, as Don DePaolo and Jerry Wasserburg did, that the Earth as a whole has a chondritic Sm/Nd ratio and therefore a chondritic $^{143}\text{Nd}/^{144}\text{Nd}$. In contrast, while Sr is refractory, Rb is not and we hence did not have an *a priori* way to know the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Earth. There was (and still to some degree is) similar uncertainty about the U/Pb and Th/Pb ratios. This made the Sm-Nd system a particularly powerful tool in understanding mantle evolution. It also inspired the useful system of notation introduced by DePaolo and Wasserburg, namely epsilon, which they defined as

$$\epsilon_{\text{Nd}} = \left(\frac{{}^{143}\text{Nd}/{}^{144}\text{Nd}_{\text{sample}} - {}^{143}\text{Nd}/{}^{144}\text{Nd}_{\text{CHUR}}}{{}^{143}\text{Nd}/{}^{144}\text{Nd}_{\text{CHUR}}} \right) \times 1000 \quad (3.1)$$

where CHUR is an acronym for *Chondritic Uniform Reservoir*. Thus ϵ_{Nd} is the deviation in parts per 10,000 from the chondritic value. Since the Earth as a whole was assumed to have a chondritic Sm/Nd ratio, it should also have $\epsilon_{\text{Nd}} = 0$. Any reservoir evolving with a time-integrated Sm/Nd ratio less than chondritic, such as the continental crust, will have an $\epsilon_{\text{Nd}} < 0$, while an incompatible element-depleted reservoir with time-integrated Sm/Nd greater than chondritic will have an $\epsilon_{\text{Nd}} > 0$. As we shall see, developments in recent years have raised doubts about whether



the Sm/Nd ratio of the Earth is in fact exactly chondritic, but the epsilon notation is nevertheless useful and is applied to Hf isotope ratios in an exactly analogous way. Because the basalts on the Mid-Atlantic Ridge ranged from typical light rare earth-depleted MORB to light rare earth-enriched near Iceland and the Azores, and assuming that these differences had existed for 2 billion years or so, I calculated that the $^{143}\text{Nd}/^{144}\text{Nd}$ should range from less than, to greater than, chondritic. Expressed in terms of ϵ_{Nd} , I expected we would see both positive and negative values along the Mid-Atlantic Ridge. Although *Don DePaolo* and *Jerry Wasserburg* did not report Nd isotope ratios from either Iceland or the Azores, they showed that $^{143}\text{Nd}/^{144}\text{Nd}$ correlated inversely with $^{87}\text{Sr}/^{86}\text{Sr}$ in oceanic basalts (Fig. 3.1) so that it was possible to predict the ϵ_{Nd} of basalts from strontium isotope ratios. This correlation predicted (and subsequent analyses showed) that all basalts from the North Atlantic, including those from Iceland and the Azores, should have positive ϵ_{Nd} , inconsistent with my prediction. This suggested that mantle evolution was complex and that the apparent light rare earth enrichment of mantle plumes

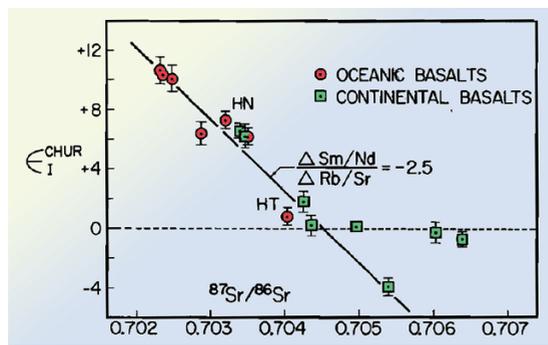


Figure 3.1 The correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} , which came to be known as the “mantle array” as found by DePaolo and Wasserburg (1976b) (modified from DePaolo and Wasserburg, 1976b).

had been preceded by a period of light rare earth depletion. The correlation between $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ came to be known as the “mantle array”. While the correlation was not surprising, there did not seem to be a similar correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and Pb isotope ratios, so it was important and suggested that the evolution of Rb/Sr and Sm/Nd in the mantle was linked. Based on the correlation and the assumption that the bulk Earth had $\epsilon_{\text{Nd}} = 0$, DePaolo and Wasserburg (1976a) inferred a bulk Earth Rb/Sr ratio of 0.029. That value is well below the chondritic value, just as Gast (1960) had predicted.

The correlation appeared to end at $\epsilon_{\text{Nd}} = 0$: no oceanic basalts had ϵ_{Nd} less than 0, although some continental ones did (Fig. 3.1), which *DePaolo* and *Wasserburg* suggested reflected assimilation. This led DePaolo and Wasserburg (1976a) to propose a two-reservoir model for the mantle: a primitive reservoir, which, assuming the Earth had chondritic Sm/Nd, they called CHUR, and a Mid-Ocean Ridge Reservoir (MORR), which we now refer to as DMM or DUM, that they laid out more formally in a subsequent paper (Wasserburg and DePaolo, 1979). Consistent with the suggestions of *Schilling* and *Morgan*, they proposed that plumes tapped this deep primitive reservoir. The basic idea was that, “with



the exception of a few anomalous regions" (DePaolo and Wasserburg, 1976b), the mantle consisted of an upper incompatible element-depleted layer with $\epsilon_{Nd} \approx +10$ and a deep primitive layer ($\epsilon_{Nd} = 0$) in which the relative abundances of refractory lithophile elements were assumed to be chondritic (for reasons I explained in Section 1.2). In the model, those basalts with ϵ_{Nd} between 0 and +10 are derived from a mixture of primitive mantle and DUM.

Based on mass balance involving just these two mantle reservoirs plus continental crust, O'Nions *et al.* (1979), Allègre *et al.* (1979), Jacobsen and Wasserburg (1979), and DePaolo (1980) calculated that the depleted mantle occupied about 35 to 50 % of the mantle. This range encompasses the mass fraction of the seismically defined upper mantle (the mantle above 670 km), inviting the inference that the 670 km discontinuity was a chemical boundary between the upper depleted mantle and the lower primitive mantle. O'Nions *et al.* (1979) also noted that degassing of this fraction of the mantle would account for the radiogenic ^{40}Ar now in the atmosphere assuming a bulk silicate Earth K concentration of around 200 ppm. These models too were based on the assumption that the Sm/Nd ratio and the ϵ_{Nd} of the Earth are chondritic (*i.e.* $\epsilon_{Nd} = 0$). As Don DePaolo (DePaolo, 1980) noted, "if the Sm/Nd ratio of the Earth were different from that assumed by 5 % or more, it could require changes in the conclusions given here and elsewhere", a caveat that appears prophetic in hindsight.

3.1 Hafnium Joins the Fray

After my post-doc at Carnegie, I moved to Denver to work under *Mitsunobu Tatsu-moto*. As I'll explain in Section 7, 'Tats' had been one of the first to explore the geochemical implications of plate tectonics. A few months later, we were joined by a second post-doc, *Jon Patchett*, to whom *Tats* gave the task of developing techniques for analysing Hf isotope ratios and exploring the geochemical implications of the ^{176}Lu - ^{176}Hf decay system. Both Lu and Hf are, like Sm and Nd, refractory lithophile elements and the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio is often reported in epsilon notation (ϵ_{Hf} that is, deviations in parts in 10,000 from the chondritic ratio) in a manner exactly analogous to ϵ_{Nd} . The half-life of ^{176}Lu is only a third as long as that of ^{147}Sm and variation of Lu/Hf in the Earth is greater than that of Sm/Nd, which leads to larger variation of $^{176}\text{Hf}/^{177}\text{Hf}$ than of $^{143}\text{Nd}/^{144}\text{Nd}$. Hence, investigating the geochemistry of the Lu-Hf decay system seemed worthwhile. On the other hand, the chemistry involved in purifying Hf is complex and difficult (undoubtedly one reason why hafnium was the very last stable element in the periodic table to be isolated), as can be the mass spectrometry – as I explain below.

Despite these difficulties, *Jon* succeeded spectacularly and within a year published papers that described the analytical technique, determined the initial $^{176}\text{Hf}/^{177}\text{Hf}$ of the solar system, and documented the $^{176}\text{Hf}/^{177}\text{Hf}$ evolution of the Earth (Patchett and Tatumoto, 1980a,b,c). Among other things, *Jon* and *Tats* showed that $^{176}\text{Hf}/^{177}\text{Hf}$ generally correlated well with $^{143}\text{Nd}/^{144}\text{Nd}$ in oceanic island basalts, but this correlation tended to break down in MORB, with



$^{176}\text{Hf}/^{177}\text{Hf}$ showing more variation than could be expected from the $^{143}\text{Nd}/^{144}\text{Nd}$ variation. The cause is most likely residual garnet during melting (Salters and Hart, 1989), but as *Catherine Chauvel* and *Janne Blichert-Toft* (Chauvel and Blichert-Toft, 2001) argued, it is something inherited from previous depletion episodes in other environments rather than melting beneath ridges. *Catherine* and *Janne* also showed that the excess variation in $^{176}\text{Hf}/^{177}\text{Hf}$ at a given $^{143}\text{Nd}/^{144}\text{Nd}$ was restricted to Indian and Atlantic MORB and argued that the large spread in Indian MORB was likely due to recycling of oceanic crust and sediment; I'll return to that in Section 5.2.

Other than providing samples and unpublished Nd isotope data, I did not participate in the Hf project while I was at the USGS, but I was keen to dive into Hf isotope geochemistry in my new position as a staff scientist in *Al Hofmann's* new Geochemistry Division at the Max Planck Institut in Mainz. *Al* had an additional staff position to fill and *Jon*, with whom I had kept in close touch, was looking for a job as his USGS post-doc was coming to an end, so I lobbied hard for *Jon* with *Al* (reminding *Al* that *Jon* had done a previous post-doc in Germany and spoke fluent German seemed to help). Officially, I wanted help in setting up Hf analytical techniques; unofficially I greatly valued *Jon's* friendship and intellectual stimulation. We had a new dual-collector mass spectrometer, one of the first thermal ionisation multi-collector instruments, with the two Faraday cups fixed for Sr isotope analysis. It occurred to me that the relative mass difference between ^{87}Sr and ^{88}Sr was very nearly the same as between ^{176}Hf and ^{178}Hf , so I thought it might be possible to measure the $^{176}\text{Hf}/^{178}\text{Hf}$ ratio with that instrument and, after correcting for fractionation using the $^{177}\text{Hf}/^{179}\text{Hf}$ ratio, calculate the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio. It worked as I anticipated and I had modified the software and demonstrated high precision measurements of standards by the time *Jon* arrived. He set up the chemistry and we were soon the only lab in the world other than USGS Denver in the Hf business.

Although *Jon* had defined the Hf-Nd mantle array, *Jon's* first love was always the continental crust while mine was the mantle. Our interests intersected in subduction zone volcanism, where both continental crust and mantle heterogeneity are generated, so our first collaboration was to investigate Hf isotope systematics of island arc volcanics (White and Patchett, 1984). We concluded that subducted sediment contributed to island arc lavas (as had others before us) and it seemed to us that marine sediments should be the target of our next collaboration along with *Dalilia Ben Othman*. One of our first discoveries was that the Lu/Hf ratio showed far more dispersion in sediments than did Sm/Nd and we quickly realised that this was due to Hf being concentrated in zircon in continental rocks (Patchett *et al.*, 1984). When these rocks weather, Lu, as well as Sm and Nd, are concentrated in clays and can be carried far from their source, whereas Hf remains in the zircon, which is concentrated in the less easily transported sand fraction. The results at the time seemed inconsistent with the presence of recycled sedimentary material in oceanic island basalts, but Hf isotope ratios eventually provided strong evidence of sediment recycling as I'll discuss in Section 8.1. We also found that Hf and Nd isotope ratios in marine sediments



showed more dispersion than they did in the mantle (White *et al.*, 1986). In an indirect way, this may also be due the ‘zircon effect’, as it reduces the amount of Hf in the dissolved riverine flux to the oceans from continents, resulting in the mantle flux being large in a relative sense. This mantle-derived Hf results in high ϵ_{Hf} compared to ϵ_{Nd} in sediments with a significant hydrogenous (*i.e.* seawater-derived) component, such as red clays and Mn nodules but not in detrital sediments. This leads to a shallower $\epsilon_{\text{Hf}} - \epsilon_{\text{Nd}}$ correlation in these homogeneous sediments than the “mantle array”, – which Albarède *et al.* (1998) called the “seawater array”. Our documentation of this effect was based on rather limited sampling. A collaboration between my former student *Jeff Vervoort* (who learned the art of Hf isotope analysis as a post-doc with *Jon Patchett* rather than from me) and former post-doc *Terry Plank* produced a far more definitive study of Hf isotopes in marine sediments (Vervoort *et al.*, 2011).

The chemistry of purifying Hf is difficult but the mass spectrometry was even worse, at least by thermal ionisation. Hf is extremely refractory and even limited ionisation necessitates a high filament temperature that in turn requires high Re ion currents. The instruments in Mainz could handle this, but many instruments, including the one I obtained when I moved to Cornell in 1986, would arc, making analysis impossible. Consequently for some time only a few labs in the world continued work on Hf isotopes. Subsequently, new mass spectrometry techniques were developed that revitalised the field. *Vincent Salters* and *Alan Zindler* developed a “hot SIMS” technique which involved holding the sample at high temperature (~2000 K) while bombarding it with 15kV Ar⁺ ions to induce ionisation (Salters and Zindler, 1995). While this greatly improved ionisation and allowed for precise analysis of much smaller samples, it also required a very specialised and expensive instrument. The advent of multi-collector inductively coupled plasma mass spectrometers (MC-ICP-MS) in the 1990’s brought the true revolution. The plasma temperatures, ~6000 K, are well above those needed for efficient ionisation of Hf. The plasma instrument, however, brought its own problems, but these were quickly surmounted by *Janne Blichert-Toft* and *Francis Albarède* (1997). Their work opened the door for the Lu-Hf decay system to reach its full potential as a geochemical and geochronological tool.

3.2 Helium and the Noble Gases

The discovery of $^3\text{He}/^4\text{He}$ ratios greater than atmospheric in dredged basalts (Lupton and Craig, 1975) and xenoliths (Tolstikhin *et al.*, 1974) suggested that some fraction of the Earth’s initial inventory of noble gases remained in the mantle (He is lost from the Earth by atmospheric escape and while ^4He is produced by α -decay of U and Th, ^3He is not produced this way, so essentially all ^3He derives from the Earth’s initial inventory). The observation that OIB had generally higher $^3\text{He}/^4\text{He}$ than MORB (Kurz *et al.*, 1982a) was consistent with the idea that OIB were derived from mantle plumes, which in turn sampled a lower primitive mantle. Subsequently, the isotopic compositions of the other noble gases were analysed in MORB and OIB, generally supporting the notion



that OIB were derived from a more primitive mantle source. Since this story is told in detail in another *Geochemical Perspectives* (Moreira, 2013), I'll skip over the details here. That story, however, is integral to this one.

Even in some of the early work by *Mark Kurz* and his colleagues, the story was not so simple. Some islands, Gough in the South Atlantic, for example, had lower $^3\text{He}/^4\text{He}$ than MORB (Kurz *et al.*, 1982a) and MORB from the Mid-Atlantic Ridge in the Azores region had $^3\text{He}/^4\text{He}$ that was lower than elsewhere (Kurz *et al.*, 1982b). While it is possible to explain low $^3\text{He}/^4\text{He}$ ratios as post-eruption radiogenic ingrowth, it was difficult to imagine why this would systematically be the case in one particular island (Gough) or region (the Azores). This suggested the model of a primitive mantle feeding mantle plumes needed modification.

3.3 Pb Isotopes and the Pb-Paradox

Perhaps the biggest objection to the two-layer model as described above came from Pb isotope ratios. As I noted earlier, Sun *et al.* (1975) had pointed out that Pb isotope ratios were inconsistent with the idea that the Icelandic mantle plume consisted of primitive mantle. Before delving into that, we first need to understand a bit about the U-Pb decay system. Three radioactive isotopes, ^{238}U , ^{235}U , and ^{232}Th , decay to, respectively, ^{206}Pb , ^{207}Pb , and ^{208}Pb at different rates. It is the two U isotopes decaying at different rates that makes this system particularly valuable and we'll focus on those first. Figure 3.2 is the conventional $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plot often used by isotope geochemists and it illustrates isotopic evolution in this system. Consider an initially isotopically homogeneous reservoir that differentiates into a series of closed systems that then evolve independently. The isotopic composition of these systems will evolve along curved lines with trajectories that depend on the $^{238}\text{U}/^{204}\text{Pb}$ ratio, known as μ . Figure 3.2 illustrates the evolution of three such systems. The present isotopic composition of these systems will plot along a line, or isochron, whose slope depends on the time, t , elapsed since the differentiation event:

$$\frac{\Delta^{207}\text{Pb}/^{204}\text{Pb}}{\Delta^{206}\text{Pb}/^{204}\text{Pb}} = \frac{^{235}\text{U} \left(e^{\lambda_{235}t} - 1 \right)}{^{238}\text{U} \left(e^{\lambda_{238}t} - 1 \right)} \quad (3.2)$$

Because the decay constants, λ_{235} and λ_{238} , are constants and the $^{235}\text{U}/^{238}\text{U}$ is also constant at any given time², the only variable on the right hand side of this equation is t .

2. Small variations in $^{235}\text{U}/^{238}\text{U}$ resulting from chemical fractionation have been demonstrated. However, these are insignificant for all but the highest precision geochronology and will not concern us here.



An isochron passing through the initial Pb isotopic composition of the solar system (Blichert-Toft *et al.*, 2010) and slope corresponding to an age of 4.567 Ga is known as the *Geochron*. Any system whose initial Pb isotopic composition was the same as that of the solar nebula and which has remained closed for U and Pb over the age of the solar system must plot on the Geochron. We expect the Earth as a whole to be such a system and hence its bulk Pb isotopic composition to plot on the Geochron.

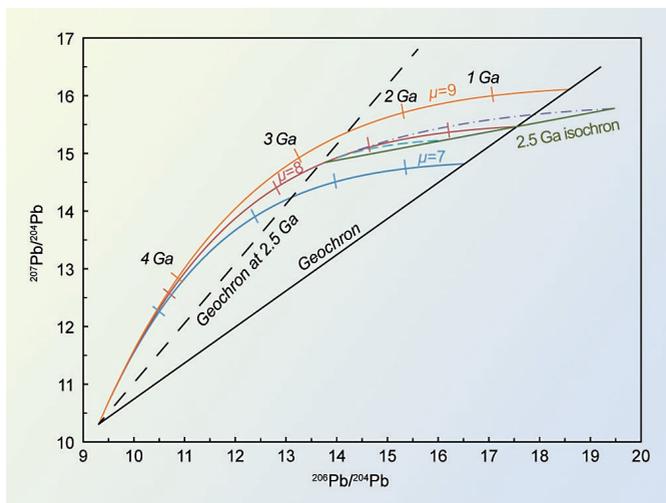


Figure 3.2

Evolution of Pb isotopes through time for three values of μ ($^{238}\text{U}/^{204}\text{Pb}$ as measured today). Any system with initial Pb isotopic composition the same as that of the solar nebula and that has remained closed for 4.567 Ga must plot on the line labelled Geochron. A system with that composition that was disturbed at 2.5 Ga would plot on a 2.5 Ga “secondary” isochron shown. Also shown is the Geochron as it was at 2.5 Ga.

The two dashed evolution curves in Figure 3.2 illustrate open system evolution where μ changes – from 8 to 16 and from 9 to 7 at 2.5 Ga. This illustrates another useful aspect of this plot: systems in which μ has increased in the past evolve to the high $^{206}\text{Pb}/^{204}\text{Pb}$ side of the Geochron, while those in which μ has decreased to evolve to the low side. Also note that the present isotopic compositions of these two systems together with the ‘parental’ one with a constant μ of 8 plot along a secondary isochron whose age corresponds to the time of this differentiation event.

Trying to estimate the Pb isotope composition of the Earth is difficult: unlike the Sm-Nd system there is no reason to think it should be chondritic because Pb is volatile. Furthermore, Pb is chalcophile and somewhat siderophile too, so the core could contain significant amounts of Pb but we have no samples from it to find out. Thus attention focuses on just the silicate Earth, but that is



difficult also, since the mantle and crust are both isotopically heterogeneous and all but the upper crust is incompletely sampled. Nevertheless, it is clear that the Pb isotopic composition of the bulk silicate Earth does not lie on the Geochron as defined above. Figure 3.3 shows Pb isotope ratios in the four main silicate reservoirs of the Earth: the upper and lower crust, the upper mantle, represented by MORB, and the lower mantle, represented by oceanic island basalts, presumably the products of mantle plumes. Of the four, three plot to the right of the Geochron, indicating they experienced a net increase in μ . Only the lower crust plots to the left. The star in the diagram is the average of 10 estimates of the bulk silicate Earth Pb isotopic composition compiled by Halliday (2004), all of which plot significantly to the high $^{206}\text{Pb}/^{204}\text{Pb}$ side of the 4.567 Ga Geochron. Thus the silicate Earth appears to have experienced an increase in μ – the first of several Pb paradoxes.

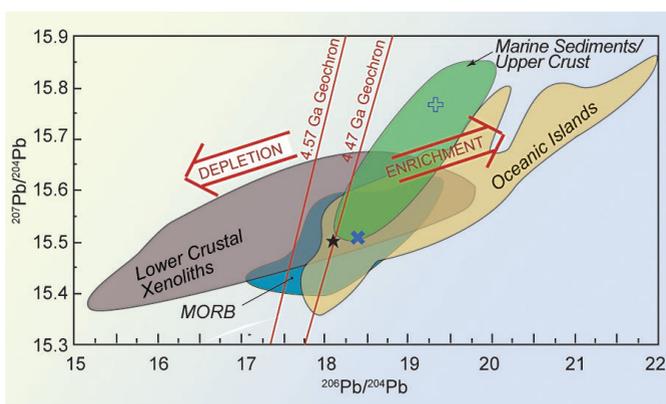


Figure 3.3 Pb isotope ratios in the principal silicate reservoirs of the Earth. \oplus is the average upper crustal composition of Asmeron and Jacobsen (1993), \times is average MORB (White and Klein, 2014), and \star is the average of 10 estimates of bulk silicate Earth Pb isotopic composition compiled by Halliday (2004).

That the silicate Earth experienced an increase in μ is not surprising since the nebular μ value is ~ 0.14 and the silicate Earth value is ~ 8 to 9 (as a result of the siderophile and volatile character of Pb). However, this increase must have occurred substantially, on the order of 100 million years or more, after the start of the solar system in order to shift the Earth's present Pb isotopic composition significantly to the right of the Geochron. *Alex Halliday* (Halliday, 2004) computed a series of models in which the bulk silicate Earth μ progressively increases as accretion of the Earth proceeds and Pb partitions into the growing core or is lost by volatilisation. These models can be approximated by a simple two-stage history. For example, evolution with an average μ of 1.5 for the first 100 Ma and a subsequent μ of ~ 8.75 produces a present day bulk silicate Earth Pb isotopic composition equal to the average of the estimates compiled by *Halliday*. The



corresponding “4.47 Ga” Geochron is shown in Figure 3.3. There is, however, considerable uncertainty in the Pb isotopic composition of the various reservoirs and, hence, the mass balance issue remains incompletely resolved.

Other aspects of Pb isotope geochemistry are also paradoxical. First, we would expect the depleted upper mantle sampled by MORB to have experienced a decrease in μ , because Pb is more enriched in the continental crust than U. Yet both the majority of MORB and the average value plot to the right of the 4.47 Ga Geochron – indicating an increase in μ over the history of this reservoir. Furthermore, average continental crust appears to have slightly lower $^{206}\text{Pb}/^{204}\text{Pb}$ than average MORB and the primary difference between crust and mantle appears to be in the $^{207}\text{Pb}/^{204}\text{Pb}$ ratio. Because the half-life of the parent of ^{207}Pb , ^{235}U , is short, 700 Ma, virtually all ^{207}Pb was produced early in Earth’s history, and hence the difference in μ between crust and mantle must have been established early in Earth’s history. Patterson and Tatsumoto (1964) concluded exactly this based on far fewer data than we have today, and inferred that the “*bulk of the North American continent was formed during the interval 3500-2600 m.y. ago.*”

With that introduction to the mysteries and paradoxes of Pb isotope geochemistry, we can return to the question of why Pb isotope ratios are inconsistent with the idea that mantle plumes consist of primordial material. As Figure 3.3 shows, with a few exceptions, OIB generally have more radiogenic Pb and plot further from the Geochron than MORB. Specifically, Sun *et al.* (1975) found that Pb isotope ratios increased along the Reykjanes Ridge toward Iceland. If the Icelandic plume consisted of primitive material, they should have decreased toward Iceland, trending toward the Geochron. There was also the nagging problem of how to explain the fact that oceanic island basalts, and MORB in the vicinity of oceanic islands, were almost always light rare earth-enriched, yet had positive ϵ_{Nd} , which implies a time-integrated light rare earth-depleted history. It is possible to produce light rare earth-enriched basalts from a light rare earth-depleted mantle, but this required very low, in most cases implausibly low, extents of melting. These paradoxes and contradictions left me, among others, suspecting that mantle evolution was more complex.



4.1 In Vino Veritas: The Three Component Mantle

The early Nd and Hf isotope data correlated well with $^{87}\text{Sr}/^{86}\text{Sr}$ and appeared to terminate at $\epsilon_{\text{Nd}} = 0$ and $\epsilon_{\text{Hf}} = 0$, forming the mantle array in Figure 3.1. This seemed consistent with the idea that the mantle sources of oceanic basalts were mixtures of two components: a depleted reservoir (MORB source) and a primitive, or possibly enriched, reservoir. However, even some of the earliest published Sr and Pb isotope data suggested the situation was more complicated. Along the northern Mid-Atlantic Ridge, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ were correlated and, as I noted earlier, both increased toward Iceland (Hart *et al.*, 1973, Sun *et al.*, 1975). This was more or less expected since, in both cases, the parents (Rb and U) appear to behave more incompatibly than the daughters (Sr and Pb). Yet Gast *et al.* (1964) had reported high $^{87}\text{Sr}/^{86}\text{Sr}$ and low $^{206}\text{Pb}/^{204}\text{Pb}$ in Gough Island lavas and low $^{87}\text{Sr}/^{86}\text{Sr}$ and high $^{206}\text{Pb}/^{204}\text{Pb}$ in Ascension Island (also in the South Atlantic) lavas. So it was clear early on that radiogenic isotope ratios were not always correlated and that a simple two-reservoir model of the mantle was inadequate. When I began my tenure as a post-doc at Carnegie Institution's Department of Terrestrial Magnetism under *Al Hofmann* in 1977 there was still very little Nd isotope data in the literature, so I set out to analyse the Nd isotopic composition of islands known from previous work to have extreme Sr or Pb isotope ratios, such as the French Polynesia, Samoa, St. Helena, and Tristan da Cunha (Hedge, 1966; Sun, 1973; Duncan and Compston, 1976). *Bob Duncan* and *Shen-Su Sun* were kind enough to provide some of their samples. Being in Washington, DC turned out to be convenient as the Smithsonian had an extensive collection of rocks from these exotic places, which the curator kindly allowed me to sample. I also had access to *Norman Watkins'* collections of oceanic island basalts at the University of Rhode Island. (*Watkins* was a palaeomagnetist who had collected oceanic island samples primarily to work out the geomagnetic reversal time scale. *Watkins* sadly died at a young age while I was still a grad student.) I continued to work on this at the U.S.G.S. in Denver and at the Max Planck Institut in Mainz. The results, published in White and Hofmann (1982), showed that the 'mantle array' actually bifurcated at high $^{87}\text{Sr}/^{86}\text{Sr}$ and low ϵ_{Nd} into a low- $^{87}\text{Sr}/^{86}\text{Sr}$ branch defined by Kerguelen and Tristan and a high- $^{87}\text{Sr}/^{86}\text{Sr}$ branch defined by Samoa, the Societies, and the Azores island Saõ Miguel. Furthermore, St. Helena, Ascension, and some samples from the Cook-Austral chain plotted off the Sr-Nd mantle array. It was now clear, even from only Sr and Nd isotope data, that the two-reservoir mantle model was inadequate.

This reality was made even clearer in a work by *Alan Zindler* and others (1982). The basic idea and outline of this 1982 classic paper was developed in an all night session between *Alan*, *Steve Goldstein*, and *Emil Jagoutz*, which followed a party at *Al Hofmann's* house in Nieder-Olm outside Mainz at which copious amounts of wine from the vineyards the house overlooks were consumed.



They showed that the majority of the oceanic basalt Sr, Nd, and Pb isotope data plotted on a plane in $^{87}\text{Sr}/^{86}\text{Sr}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ - ϵ_{Nd} space (Fig. 4.1). This implied that oceanic basalts were mixtures of three components rather than two. The source of mid-ocean ridge basalts, depleted upper mantle, appeared to represent one component, St. Helena another, and Kerguelen, Gough and Tristan da Cunha the third. In general, mixing of components with differing concentration ratios produces curved lines or surfaces in isotope ratio space and only in the special case where concentration ratios are the same will mixing produce lines in two-isotope space or a plane in multi-isotope space (Vollmer, 1976; Langmuir *et al.*, 1978). Thus the planar nature of the data implied that all three components had similar Sr/Nd and Sr/Pb concentration ratios. Another important aspect of this paper was the demonstration that variations in Pb isotope ratios could be related to variations in Sr and Nd isotope ratios, and hence were governed by the same processes, whereas earlier thinking was that Pb isotopes reflected something entirely different, such as core-mantle exchange.

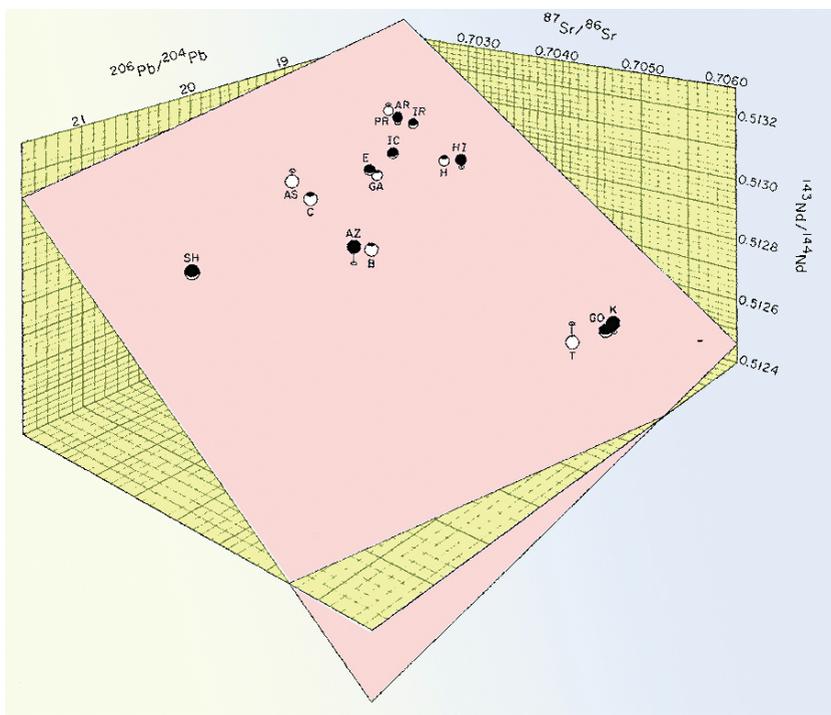


Figure 4.1

The “Mantle Plane” of Zindler *et al.* (1982). Points are averages of oceanic island or mid-ocean ridges. SH: St. Helena, AS: Ascension, C: Canary Islands, AZ: Azores B: Bouvet, E: Easter, GA: Galápagos, IC: Iceland, H: Island of Hawaii, HI: Hawaiian Islands, IR: Indian Ocean, PR: Pacific Ocean, AR: Atlantic Ocean, T: Tristan da Cunha, GO: Gough, K: Kerguelen.



4.2 Then There Were Five

Zindler *et al.* (1982) did not include some key island chains, such as Samoa and the Society Islands, in their ‘mantle plane’ as at the time there were few analyses of all three isotope ratios published on basalts from Samoa and Society Islands. However, I had already begun to acquire Pb isotope data on these samples and they did not plot on the mantle plane. As I acquired more data, it became clear that basalts from these islands, as well as São Miguel, required at least one additional component or mantle reservoir. Alan Zindler and his co-workers had based their 3-component model on average isotopic compositions of islands and island groups. This, I felt, overlooked a key part of the story, as different chains defined different correlations in multi-isotope space. Considering both trends and correlations within island groups as well as the overall variation in the data set, I found I could identify five ‘groups’ (White, 1985), as shown in Figure 4.2. The first of these was MORB, but it also included some islands, such as Iceland, the Galápagos, and Easter Island because the latter fell on the same Pb, Sr, and Nd isotope ratio arrays as MORB, in effect defining the “enriched” end of the MORB array, whereas other islands fell off this array. I called the second group St. Helena, as it was typified by this Atlantic island, but also included nearby Ascension Island and many of the Cook-Austral Islands in the Pacific. These have highly radiogenic Pb, unradiogenic Sr, and plotted to the unradiogenic Sr side of the $^{87}\text{Sr}/^{86}\text{Sr}-\epsilon_{\text{Nd}}$ and low ϵ_{Hf} side of the $\epsilon_{\text{Hf}}-\epsilon_{\text{Nd}}$ mantle arrays. The Kerguelen group included Tristan da Cunha, Gough, and Kerguelen, and is characterised by radiogenic Sr and unradiogenic Nd and Pb as well as relatively high $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios for a given $^{206}\text{Pb}/^{204}\text{Pb}$. This group, together with MORB, effectively defined the original DePaolo and Wasserburg Sr-Nd mantle array. I called the fourth group Society, and it included Samoa as well as the Azores (particularly São Miguel). These too tend to have high $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ for a given $^{206}\text{Pb}/^{204}\text{Pb}$ and generally have higher $^{206}\text{Pb}/^{204}\text{Pb}$ than the Kerguelen group, but lower $^{206}\text{Pb}/^{204}\text{Pb}$ than the St. Helena group. However, the essential distinction between this and the Kerguelen group is Sr-Nd isotope systematics. The Society group exhibits a shallower $^{87}\text{Sr}/^{86}\text{Sr}-^{143}\text{Nd}/^{144}\text{Nd}$ correlation (slope = -0.112) than that for oceanic basalts in general (slope = -0.156). Hawaii did not fit readily into any of the above, so I assigned it to a separate Hawaii group. Its distinctive nature was particularly apparent on plots of $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$, defining a negative correlation on the former and a positive correlation on the latter. Although they plot within the MORB field, they actually define a shallower trend on $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagrams.

In a review paper published the following year, Zindler and Hart (1986) introduced new names for these groups: DMM (MORB), HIMU (St. Helena), EM I (Kerguelen), EM II (Society) and PREMA (Hawaii) and it is these names that have stuck. The defining isotopic characteristics of the first four were essentially the same as mine. Their PREMA, an acronym for ‘Prevalent Mantle’, differed somewhat from my Hawaii group. Alan Zindler and Stan Hart pointed out that many



individual isotopic arrays converged on this isotopic composition, which occupies the centroid of oceanic basalt radiogenic isotope space. Hence they argued that this composition was ubiquitously available in the mantle to mix with the more exotic compositions. This was the first inference of a “common” component of mantle plumes. Others arrived at a similar inference but in different ways (e.g., Farley *et al.*, 1992; Hart *et al.*, 1992; Hanan and Graham, 1996).

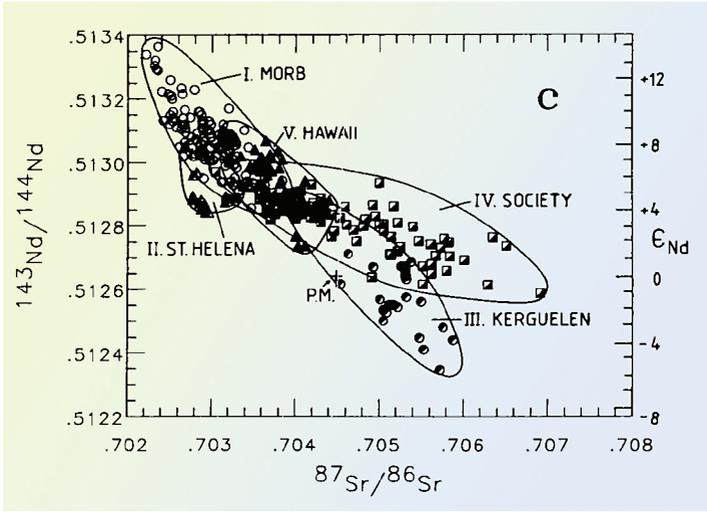


Figure 4.2 The five isotopic groups defined by White (1985).

Zindler and Hart’s interpretation, however, differed from mine in an important way. I argued that that while the 5 groups “*may represent five end-members, or components from which all intermediate compositions can be derived by mixing, it is more likely that each of these groups represents a distinct, internally heterogeneous reservoir or that each group is composed of a number of isotopically, and by inference chemically, similar reservoirs.*” Zindler and Hart, on the other hand, interpreted them as end-member components that then mix to form the variety of arrays observed in multi-isotope space. As new data have accumulated, it has become, I think, clear that the unique component interpretation is problematic. This is illustrated in Figures 4.3 through 4.6, which shows the current data set and the approximate compositions of the Zindler and Hart components.

The first observation is that there is no evidence of mixing between the three ‘enriched’ components, EM I, EM II, and HIMU. Instead, the individual island groups form arrays extending from the central region (PREMA) to more extreme compositions. The second observation is that the various island chains within each group form unique, although similar, correlations. Thus, for example, although the ‘EM I’ island groups generally share common features, they

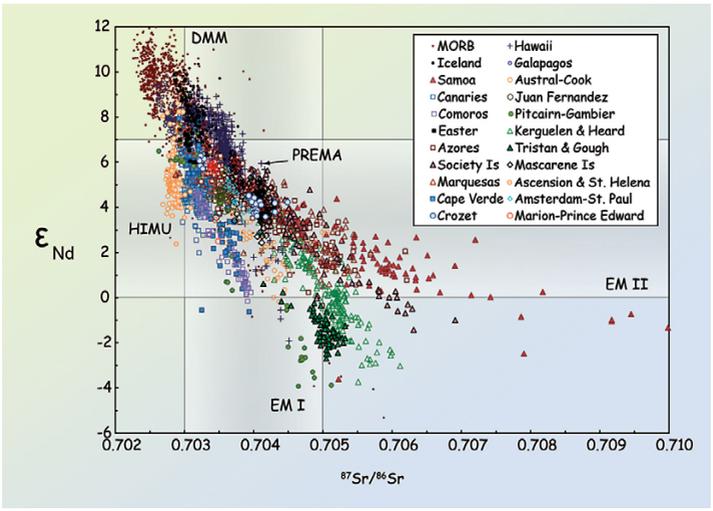


Figure 4.3 Present Sr-Nd isotope data set of oceanic basalts compiled from the GEOROC and PetDB databases. Note that the Samoan data extends to much higher $^{87}\text{Sr}/^{86}\text{Sr}$ (>0.720) than shown. Grey areas show the range of estimates of primitive mantle, or bulk silicate Earth, composition (see Section 9.1).

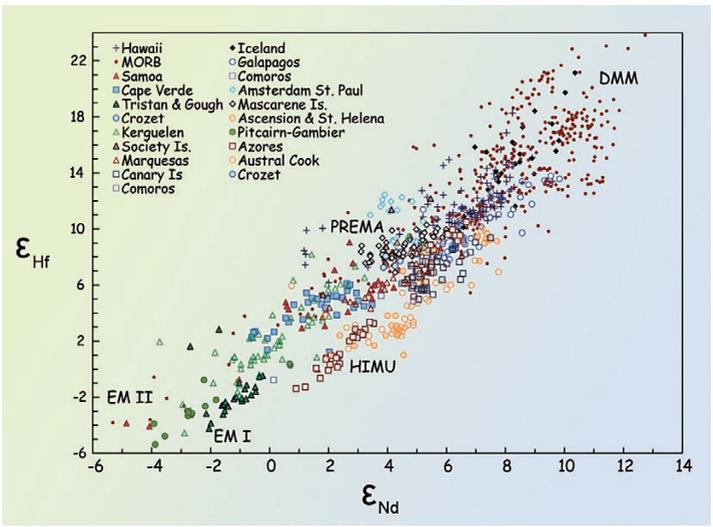


Figure 4.4 Present Hf-Nd isotope data set of oceanic basalts compiled from the GEOROC and PetDB databases.



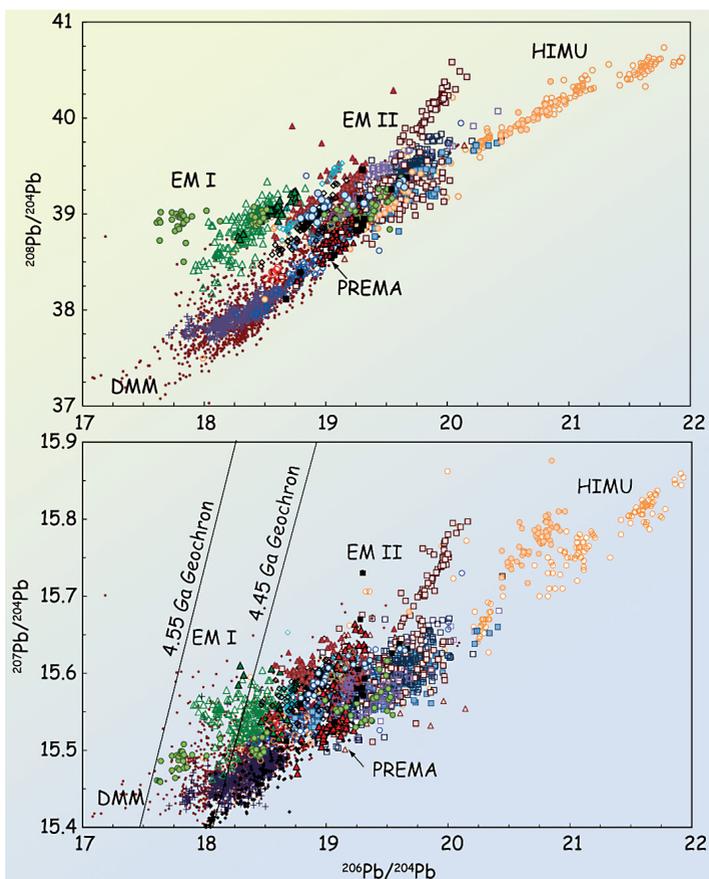


Figure 4.5 Present Pb isotope data set of oceanic basalts. Symbols are the same as in Figure 4.3. Also shown are 4.57 and 4.45 Ga Geochrons. The Pb isotopic composition of the bulk silicate Earth must lie between these two lines.

nonetheless form diverse trends that extrapolate to a variety of $^{206}\text{Pb}/^{204}\text{Pb}$ ratios at low ϵ_{Nd} and high $^{87}\text{Sr}/^{86}\text{Sr}$. The same is true of the EM II group; it defines shallow $^{87}\text{Sr}/^{86}\text{Sr}-\epsilon_{\text{Nd}}$ arrays and has higher $^{206}\text{Pb}/^{204}\text{Pb}$ than EM I but nevertheless defines arrays that extrapolate to a variety of end-member compositions.

HIMU may be an exception in that the HIMU group appears to form a single, but slightly scattered correlation in isotope space that can plausibly be explained by mixing between a modestly heterogeneous, high- $^{206}\text{Pb}/^{204}\text{Pb}$, low- $^{87}\text{Sr}/^{86}\text{Sr}$, and intermediate- ϵ_{Nd} component and a component with a more moderate composition such as PREMA. However, this HIMU component occurs only in lavas from St. Helena, Ascension, and *some* of the Austral Islands. While



some other island groups, such as the Canary Islands and the Easter–Sala y Gomez chain, have elevated $^{206}\text{Pb}/^{204}\text{Pb}$, they lack the other characteristics of HIMU and do not fall on the HIMU trend. The plumes producing the HIMU volcanoes (if indeed they are plume related; the Australs define three time-progressive chains rather than one and some volcanoes are EM I in character rather than HIMU) are small, suggesting HIMU is a rare component of quite limited distribution in the mantle.

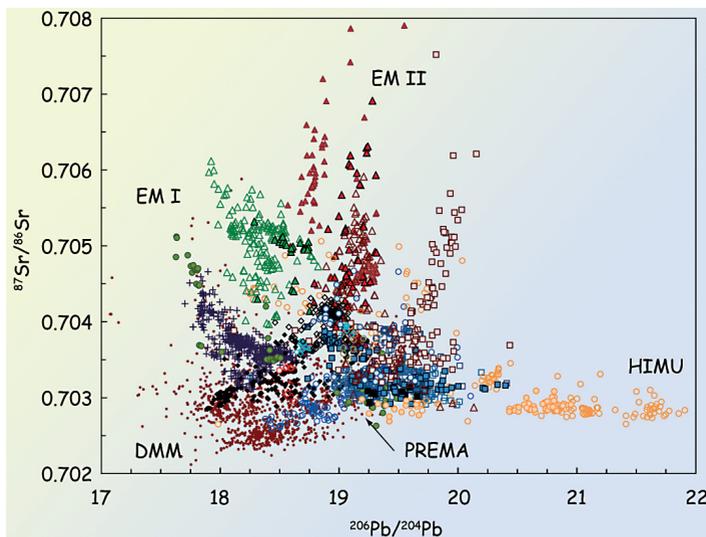


Figure 4.6 Sr-Pb isotope systematics in oceanic basalts. Symbols are the same as in Figure 4.3.

Al Hofmann referred to these isotopic groups as species. While the analogy to biological taxonomy is useful, it would be better to consider them as genera, with each genus consisting of a variety of closely related species that share a common evolution. Interestingly, HIMU may then be analogous to the genus *Homo*, which now consists of a lone species (a recent development, as it turns out). The analogy has its limits, however, in that species of the same genus have evolved from a common ancestor; this need not be the case in mantle compositions. Rather, the species in each isotopic genus have evolved through similar ‘evolutionary pressure’ (in this case, physiochemical processes) in parallel fashion (perhaps analogous to convergent evolution that, for example, leads to strong resemblance of dolphins to fish and brachiopods to bivalves). That there are, apparently, a limited number of isotopic genera is nonetheless significant: it implies a limited number of evolutionary pathways through which heterogeneity has developed in the mantle. The big question is, of course, what are those evolutionary pathways?



My scientific career began with mid-ocean ridge basalts, although at the time they were still widely called ocean-floor, abyssal, or seafloor basalts; *Stan Hart's* (Hart *et al.*, 1972) MORB acronym had not yet caught on. In my second semester of graduate school, *Jean-Guy Schilling* assigned me the task of doing petrographic descriptions and modal analyses of the basalts he had dredged from the Mid-Atlantic Ridge. My initial reaction was dread; despite having taken a full year of mineralogy and a quarter of igneous petrology at UC Berkeley, this was real world research and there was no TA to turn to for help (*Schilling's* background was in engineering and chemistry, so his petrographic skills were, at that point at least, not much better than mine). My panic was entirely unjustified; it turns out MORB are petrographically pretty simple and I was soon working through the collection efficiently. Plagioclase and olivine are the only common phenocrysts; both are fairly easily identified even by a novice, and usually together comprise less than 10% of the rock. I convinced *Schilling* to buy a universal stage to allow me to estimate plagioclase compositions optically. Since we did not have an electron microprobe at the time, this was the only way to obtain compositional information. The rest is glass or groundmass, consisting of very fine plagioclase and clinopyroxene intergrowths, magnetite and occasional skeletal olivine. Chromian spinel microphenocrysts are sometimes present, but they too were easily identified. Even clinopyroxene phenocrysts were rare, but became more common in the vicinity of the Azores. That was perhaps the one significant discovery of my work, which was finally published nearly ten years later in *Schilling's* opus on the northern Mid-Atlantic Ridge (Schilling *et al.*, 1983). As that paper explains, the appearance of clinopyroxene as a phenocryst phase near the Azores reflected changes in the major element composition of magmas in the vicinity of the Azores and, to a lesser degree, Iceland.

That summer, I spent several months as a graduate student aboard the R/V Trident dredging more MORB from the Mid-Atlantic and Kolbeinsey Ridges, with a week of field work in Iceland at the end. I had long wanted to become an oceanographer, partly, I suppose, because of the mysteriousness of the oceans. As I began my career in oceanography, however, I was slowly being seduced by the idea of discovering the secrets of another remote region: the Earth's mantle. For me, oceanography would become only a means to that end.

MORB are the most voluminous volcanic rocks on Earth, despite our never having observed an eruption (the immediate aftermath of eruptions on mid-ocean ridges have, however, been observed several times). The principal force driving plate motion is 'slab pull' (Forsyth and Uyeda, 1975). Thus magmatism at mid-ocean ridges is a passive consequence of plate motion; as plates spread, mantle upwells to fill the gap and the consequent decompression results in melting. The melts rise to form new oceanic crust. Because of this and because MORB compositions are eventually observed almost wherever plates spread,



there is a very broad consensus that MORB sample the uppermost convecting mantle. Although significant compositional variation does occur, some of which can be shown to be regional (I'll return to that below), MORB are remarkably uniform compared to the vast range in magma compositions erupted elsewhere on the planet. As tholeiites, they are relatively large-degree melts, ~8% or more (Langmuir *et al.*, 1993), and have been systematically modified by moderate, but rarely extreme, fractional crystallisation. An additional distinguishing characteristic is a relative depletion in incompatible elements, illustrated for the rare earths in Figure 1.3. Radiogenic isotopic compositions confirm that this is a feature of the source and that the depletion must have occurred long ago. Thus MORB appears to tap a nearly global shallow mantle source depleted in incompatible elements. How has this source evolved?

5.1 Depletion

As mentioned earlier, the continental crust appears to have formed from the mantle through melting and magmatism over time. Specifically, subduction-related magmatism appears to be responsible for formation of the majority of continental crust, as my friend and former colleague *Nick Arndt* details in his *Geochemical Perspectives* (Arndt, 2013). The rate at which the crust has formed, however, remains very much a matter of debate. What we can firmly say is that the process appears to have begun 4.4 billion or more years ago, that very little crust older than 3 billion years has survived, and that the rate of crustal growth has been slower in the Phanerozoic than it was in the Precambrian. Armstrong (1981) pointed out that because continental crust can be destroyed through sediment subduction, we need to distinguish between the rate of addition of new crust and the net rate of crustal growth. Hence it is unclear whether the paucity of Hadean and early Archean continental crust reflect slow crustal growth in the early Earth, or, as *Armstrong* argued, merely that little of that crust has survived. The growth of the continents is considered in detail by Arndt (2013) and I won't delve into this question here but I will return to the question of how much continental crust has been destroyed and recycled into the mantle in Section 7. I'll merely note that crust and mantle evolution are linked through the transfer of incompatible elements from the mantle to the crust: crustal growth necessarily results in depletion of the mantle in these elements.

Figure 5.1 is an 'extended rare earth' or 'spider' diagram produced by ordering incompatible elements as a function of increasing compatibility and normalised to the bulk silicate Earth composition. Here again we see that the 'depleted mantle' is depleted in the same elements that are enriched in the continental crust. Unlike the smooth rare earth patterns of Figure 1.3, however, the crust shows anomalous depletion in Nb and Ta and enrichment in Pb, while the depleted mantle shows the opposite. The same anomalies observed in the continental crust also characterise subduction-related magmas, providing one line of evidence that this has been the principal mechanism by which the continents have formed. To a first approximation, then, the depleted mantle appears to be



the complement of the continental crust. Workman and Hart (2005) concluded that this mantle reservoir had lost roughly 3 % fractional melt. In detail, however, the two are not exactly complementary, hinting at the existence of other mantle reservoirs (Salters and Stracke, 2004; Workman and Hart, 2005). Perhaps this should not be surprising since melting of the depleted mantle produces oceanic crust and rarely contributes directly to continent growth (*e.g.*, Guitreau *et al.*, 2012). There are other reasons, discussed below, to believe that the evolution of the upper mantle has been more complex. Nevertheless, we can conclude that the depleted mantle reservoir has evolved principally through extraction of magma and that much of the incompatible element inventory extracted now resides in continental crust. Radiogenic isotope ratios demonstrate that this depletion must have begun billions of years ago, consistent with most growth of the continental crust having occurred in the Precambrian.

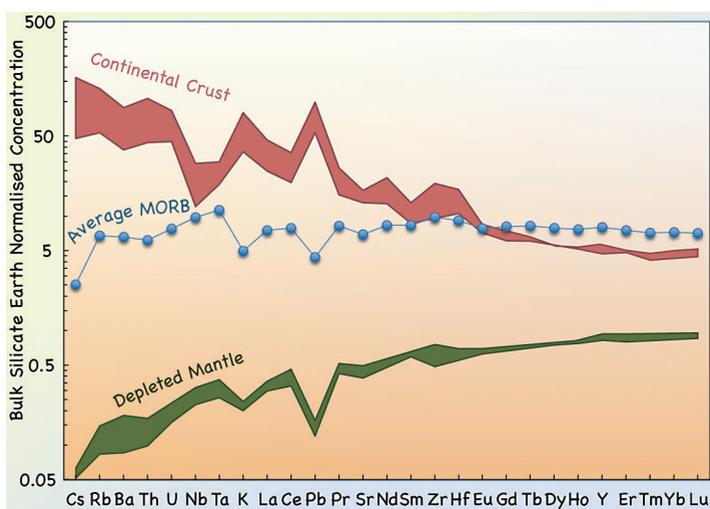


Figure 5.1

Extended rare earth or spider diagram shown the composition of average MORB, the estimated composition of the MORB source or depleted mantle (Salters and Stracke, 2004; Workman and Hart, 2005), and the estimated composition of the continental crust (Taylor and McLennan, 1995; Wedepohl, 1995; Rudnick and Gao, 2014) normalised to the bulk silicate Earth composition of McDonough and Sun (1995).

5.2 Replenishment

Several lines of evidence indicate that depleted mantle could not have evolved solely through extraction of partial melt. First, Galer and O’Nions (1985) considered the ratio of radiogenic ^{208}Pb to radiogenic ^{206}Pb , denoted $^{208}\text{Pb}^*/^{206}\text{Pb}^*$, calculated as:



$$\frac{{}^{208}\text{Pb}^*}{{}^{206}\text{Pb}^*} = \frac{{}^{208}\text{Pb}/{}^{204}\text{Pb} - ({}^{208}\text{Pb}/{}^{204}\text{Pb})_i}{{}^{206}\text{Pb}/{}^{204}\text{Pb} - ({}^{206}\text{Pb}/{}^{204}\text{Pb})_i} \quad (5.1)$$

where the subscript i denotes the initial solar system values measured in the Canyon Diablo meteorite. This ratio is proportional to the time-integrated Th/U ratio, which they denoted κ_{Pb} . They showed that in MORB this time-integrated ratio was much greater than the modern Th/U ratio, denoted κ_{Th} , of the MORB source inferred from Th isotope ratios. They concluded that Pb in the depleted upper mantle must be resupplied from some other reservoir such that the residence time of Pb, and by inference other incompatible elements, in the depleted upper mantle was relatively short. They suggested resupply from primitive lower mantle; that, however, can be fairly easily ruled out and, as I suggested instead (White, 1993), plumes are a more likely source which I'll explore in more detail below. Nevertheless, the point is that the DMM is an *open system*, which both gains and loses elements. As *Galer and O'Nions* explained, this means that concentrations are governed by the relative rates of flows into and out of the reservoir, rather than by any particular process.

The second line of evidence that evolution of the DMM reservoir involves more than melt extraction is oxygen isotope ratios and their correlation with incompatible elements. As I explained earlier, significant fractionation of oxygen isotope ratios occurs only at low temperature; that is, only at or near the Earth's surface. Ito *et al.* (1987) attempted to look for the signature of such surficial material that might have been recycled into the depleted mantle by looking for correlations between radiogenic and oxygen isotope ratios in MORB. That effort essentially failed; the best we could find was *"a weak, but statistically significant correlation ... between $\delta^{18}\text{O}$ and Nd and Pb isotope ratios in Pacific MORB, which warrants further investigation."* A decade or so later, however, *John Eiler* and his collaborators (Eiler *et al.*, 2000), benefiting from improved analytical precision and techniques, found that $\delta^{18}\text{O}$ in fresh MORB glasses correlated positively with K_2O and incompatible element ratios such as La/Sm and K/U. In addition, they found that $\delta^{18}\text{O}$ correlated positively with $\text{K}_2\text{O}/\text{H}_2\text{O}$, which is the opposite of what one would expect if low-temperature secondary alteration were the cause. *John Eiler* and coworkers concluded that *"these correlations are consistent with control of the oxygen isotope and incompatible-element geochemistry of MORBs by a component of recycled crust that is variably distributed throughout their upper mantle sources."* A subsequent study by *Kari Cooper et al.* (2004) confirmed and strengthened these conclusions.

There are differences between MORB in the Pacific, Atlantic, and Indian Oceans. The largest difference is between the Indian MORB and those from elsewhere. *Hedge et al.* (1973) noted a difference in Sr isotope ratios early on. A decade later, *Dupré and Allègre* (1983) confirmed *Hedge's* finding and also showed that Indian MORB had higher ${}^{208}\text{Pb}/{}^{204}\text{Pb}$ and ${}^{207}\text{Pb}/{}^{204}\text{Pb}$ for a given ${}^{206}\text{Pb}/{}^{204}\text{Pb}$ ratio. Furthermore ${}^{206}\text{Pb}/{}^{204}\text{Pb}$ tended to be lower than in Atlantic or Pacific MORB. They also showed that oceanic islands and aseismic ridges in the Indian Ocean shared these same isotopic characteristics. In the following year, *Stan Hart* (1984) argued that this was part of a large-scale Pb and Sr isotopic



anomaly in the mantle, which he called DUPAL in reference to *Dupré* and *Allègre*. *Stan* quantified the anomalous isotopic compositions of this region as follows. First, he noted that Pb isotope ratios from both OIB and MORB in the northern hemisphere defined arrays that he called the “Northern Hemisphere Reference Line” with slopes as follows:

$$^{207}\text{Pb}/^{204}\text{Pb} = 0.1084(^{206}\text{Pb}/^{204}\text{Pb}) + 13.491 \quad (5.2)$$

$$^{208}\text{Pb}/^{204}\text{Pb} = 0.209(^{206}\text{Pb}/^{204}\text{Pb}) + 15.627 \quad (5.3)$$

He then defined the parameters $\Delta 7/4$ and $\Delta 8/4$ as deviations of $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, respectively, from values predicted by these equations times 100. ΔSr was defined as the deviation in parts per 10,000 from $^{87}\text{Sr}/^{86}\text{Sr} = 0.700$. *Hart* defined the DUPAL anomaly as the region where $\Delta 7/4$ and $\Delta 8/4$ exceeded 40, which encompassed southern hemisphere regions of the Indian, Atlantic, and Pacific Oceans. DUPAL anomalies occur in both MORB and OIB in the Indian and Atlantic, but not in the Pacific.

A few years later, *Ito et al.* (1987) noted that there was also a far more subtle difference in Sr-Nd isotope systematics between Pacific and Atlantic MORB, which seemed to define two parallel arrays, but with Atlantic MORB offset by having slightly higher $^{87}\text{Sr}/^{86}\text{Sr}$ than Pacific MORB. Subsequently published data has confirmed this and, recently, *I* and *Emily Klein* (*White and Klein, 2014*) found that the mean $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} of Atlantic and Pacific MORB are different too. These differences are statistically significant at the 2-sigma level, regardless of whether plume-influenced ridge segments are included or not (*i.e.* it is true for both N-MORB and all MORB). These differences suggest that exchange and mixing between regions in the upper mantle underlying these areas are limited.

Another important discovery came when *Emily Klein* (*Klein et al., 1988*) showed that the geochemical boundary between the Indian and Pacific upper mantle was sharp and corresponded to the Australian-Antarctic Discordance (AAD). The AAD is a curious region of the global ridge system characterised by great depth, rough topography, a negative gravity anomaly, fast seismic velocities in the underlying uppermost mantle, and frequent north-south fracture zones that seem to offset the plate boundary almost randomly. Major element chemistry of MORB from this region suggests relatively low-degree, shallow melting consistent with low mantle potential temperatures (*Klein and Langmuir, 1987*). Some of these features led *Weissel and Hayes (1974)* to suggest that the AAD is a region of “*predominantly downward convective flow in the asthenosphere.*” *Klein et al.* (1988) found that the geochemical boundary spanned a single 200 km ridge segment. Subsequently, *Pyle et al.* (1992) were able to show that the boundary was gradational over only 40 km. *Meyzen et al.* (2007) published a summary of isotopic variations along the ridge system that was remarkable both for the extensiveness of the data set and also for the novel way in which the data were presented. Data on MORB are often displayed as a linear function of distance (or alternatively, latitude or longitude), but the entire global system cannot be displayed in this way. *Christine Meyzen* and coworkers chose to plot the data as a function of angular distance, in degrees, along the mid-ocean ridge system from the northernmost



data point on the Gakkel Ridge (Fig. 5.2), although lesser branches of the system such as the Carlsberg Ridge, the Galápagos Spreading Centre, and the Chile Ridge are not included on this plot. Much of the variance is confined to regions around mantle plumes and is a consequence of material from those plumes mixing with asthenosphere beneath the ridge system. There are more on- or near-ridge plumes in the Atlantic and Indian Oceans than in the Pacific and this, together with slower spreading in the Atlantic and Indian, which results in less dilution of plume material, lead to these signals being stronger in those ocean basins. Nevertheless, Meyzen and others identified two additional geochemical boundaries, one between the North and South Atlantic provinces, which occurs near 23 °S and one between the South Atlantic and the Indian provinces, which occurs west of the Andrew Bain Fracture Zone (the Antarctic-Nubian, Somalian triple junction) at 30 °E on the South West Indian Ridge. Unlike the boundary at the AAD, these two boundaries are diffuse.

Figure 5.3 illustrates how isotopic compositions differ in these four provinces. In addition to being shifted to higher $^{87}\text{Sr}/^{86}\text{Sr}$ for a given ϵ_{Nd} , North Atlantic MORB are also shifted to higher ϵ_{Hf} . North Atlantic MORB also tend to have a bit higher $^{208}\text{Pb}/^{204}\text{Pb}$ for a given $^{206}\text{Pb}/^{204}\text{Pb}$ than Pacific MORB. This is also true of S. Atlantic MORB, which overlap considerably with Indian MORB. In addition, this figure shows that variance in the MORB $\epsilon_{\text{Nd}}-\epsilon_{\text{Hf}}$ array (Patchett and Tastumoto, 1980a) is largely due to MORB from the North Atlantic and, to a lesser degree, the Indian provinces, and that North Atlantic MORB tend to have higher ϵ_{Hf} for a given ϵ_{Nd} than MORB from other regions.

The Indian depleted mantle province is the most distinctive of the four and a variety of explanations have been proposed for its unique composition, among them contamination by lower continental crust or subcontinental lithosphere following the breakup of Gondwana. However, assuming that plumes rising from the deep mantle are responsible for oceanic islands such as Réunion and Kerguelen, this does not explain the isotopic similarity of Indian Ocean MORB and OIB noted by Bernard Dupré and Claude Allègre (Dupré and Allègre, 1983). They instead proposed that the upper mantle beneath the Indian Ocean has been, in effect, polluted by mantle plumes: *"If oceanic-island basalts came from the lower mantle, transfer of lower mantle material into the upper mantle must be considered a fact."* They acknowledged that this would also occur beneath other ocean basins, but argued that the distinctive isotopic composition of Indian Ocean OIB imparted that same distinctive signature on the upper mantle beneath the Indian Ocean. Meyzen *et al.* (2007) came to the same conclusion: *"The unmistakable common isotopic flavor of ocean island and mid-ocean ridge basalts from the Indian Ocean domain (region III) suggests a deep mantle origin for the overall Indian signature."* Chauvel and Blichert-Toft (2001) earlier had also reached a similar conclusion.

There are certainly a variety of reasons to think that the depleted mantle is resupplied with its basaltic component and incompatible elements from mantle plumes. First, of course, is Steve Galer's and Keith O'Nions' observation that the residence time of Pb in the depleted mantle is short. Second, plumes must



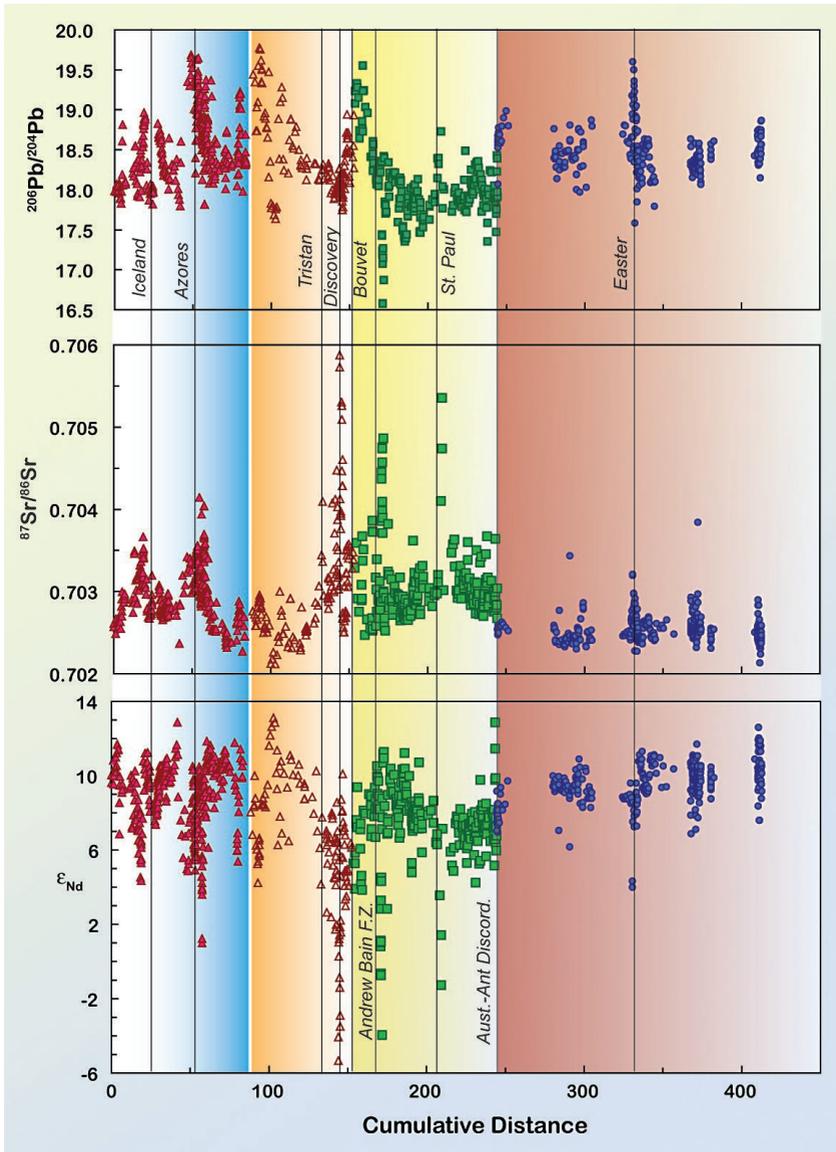


Figure 5.2 Sr, Nd, and Pb isotope ratios in MORB as a function of angular distance along the ridge system from the northernmost sample on the Gakkel Ridge 85.64 °N, 85.05 °E following Meyzen *et al.* (2007) (modified from White and Klein, 2014).



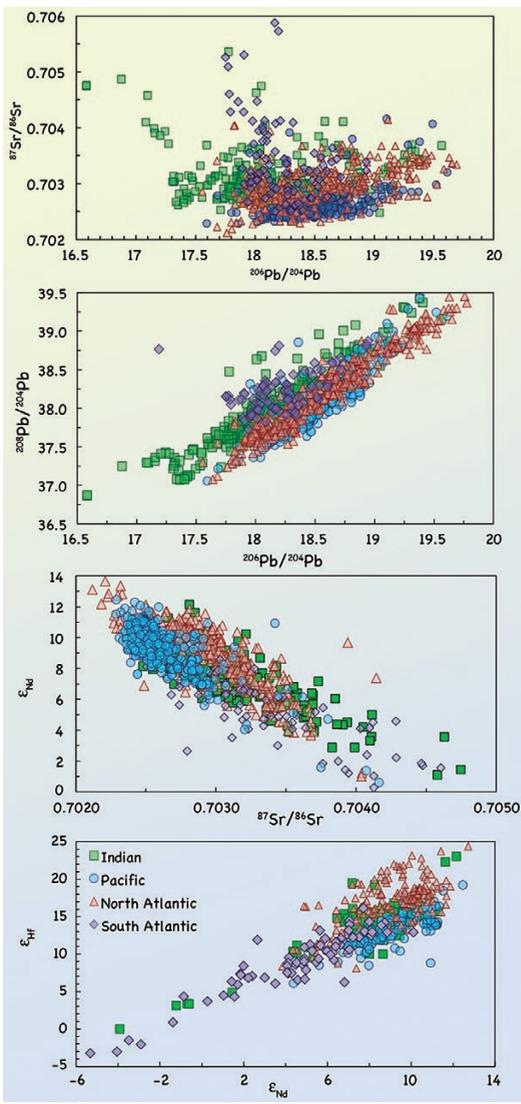


Figure 5.3 Isotope ratios in MORB illustrating the differences between the various upper mantle geochemical provinces. Note: some of the Indian data is hidden behind Atlantic and Pacific data in the lowermost two plots (data from PetDB <http://www.earthchem.org/petdb>).

necessarily intrude into the depleted upper mantle to generate the oceanic island volcanoes we observe. While some of the basaltic fraction and incompatible element inventory is extracted by melting, not all of the plume melts (Farnetani and Richards, 1995) and thus the restite becomes part of the upper mantle. Third, Malamud and Turcotte (1999) showed that known plumes follow a power law, or fractal, size-frequency distribution (*i.e.* big plumes such as Hawaii are rare and smaller plumes are more common), from which they infer the existence of many even smaller plumes. These may not have the thermal buoyancy to rise to the base of the lithosphere and melt extensively enough to generate volcanoes and hence have no surface expression. These smaller plumes then become part of the upper mantle. Finally, relatively incompatible element-enriched basalts, so-called E-MORB, are occasionally found along mid-ocean ridges. While most E-MORB occur in proximity to oceanic islands such as the Azores, they also occur in regions uninfluenced by mantle plumes. Many of these basalts have oceanic island-like incompatible element and isotope ratios, the 45 °N area on the Mid-Atlantic Ridge is a



good example (*e.g.*, White and Schilling, 1978) but there are examples in the other ocean basins as well (*e.g.*, Dosso *et al.*, 1991; Sturm *et al.*, 1999), most dramatically in the Indian Ocean (*e.g.*, Hamelin *et al.*, 1986), demonstrating the presence of at least some OIB source material in the upper mantle.

It is less apparent that the difference between the other three upper mantle geochemical provinces can be explained by the compositions of plumes rising into them. Meyzen *et al.* (2007) suggested that mantle flowing upward and outward from the large low s-wave velocity province (LLSVP) in the lower and mid-mantle, as inferred from seismic anisotropy (Behn *et al.*, 2004), could erode the ancient African continental root “contaminated by old subduction zones or sprinkled with subducted fragments and continental crust.” That may be possible, but the similarity of the isotopic compositions in hot spots in both the Indian and South Atlantic geochemical provinces, with EM I types predominating in both, suggests that the South Atlantic province also inherits its composition from plumes rising into it. There are, however, no systematic differences in Pacific and North Atlantic plume compositions that could explain the subtle differences in MORB.

In summary, what Alan Zindler and Stan Hart referred to as the DMM reservoir occupies much of the convecting upper mantle. It is internally heterogeneous and exhibits subtle regional variations in composition; the boundaries between some of these regions are sharp, others are diffuse. It behaves as an open system, with fluxes both into and out of it. Its evolution is connected to both that of the continental and oceanic crust as well as to the lower mantle, to which we now turn our attention.



As I mentioned earlier, it now seems well established that most, although certainly not all, intraplate volcanism is a consequence of mantle plumes rising from the deep mantle, just as Morgan (1971) proposed. *Morgan* suggested these mantle plumes were analogous to atmospheric convection cells that give rise to thunderstorms. Like air, hot mantle is buoyant and consequently rises in a more or less vertical column. The analogy can be taken one step further: just as rising air in a thunder cell eventually undergoes a phase change as water vapour partially condenses, rising mantle eventually undergoes a phase change and partially melts. While gravity carries the raindrops down, it drives the buoyant melt up. Early laboratory and numerical experiments revealed that plumes most likely arise from a thermal boundary layer (Whitehead and Luther, 1975), but where might such a boundary layer be? It is useful to briefly consider what we've learned about the nature of the deep mantle over the last several decades.

6.1 Nature of the Lower Mantle

At the time of *Morgan's* proposal, very little was known about the deep mantle. Even in the subsequent two decades, scientists, and particularly geochemists thought principally in terms of radial compositional variation in the mantle, *i.e.* the *DePaolo* and *Wasserburg* two-layer mantle. Little thought was given to lateral variation. Perhaps this was because much of what we knew about the deep mantle came from seismology and vertical variations in seismic velocity were obvious while lateral variations were elusive and speculative. That, of course, changed and various fields of geophysics and mineral physics have provided us with a vastly more detailed picture of the mantle. Thus, even though this perspective is a geochemical one, a brief review of the geophysical and mineral physical constraints on the lower mantle is useful. We now define the lower mantle as the region beneath the 670 km seismic discontinuity. An increase in seismic velocity at about this depth had long been recognised, although the exact depth, its sharpness, and cause were not initially understood. Below that depth, radially averaged seismic velocities were, and largely still are, consistent with simple adiabatic self-compression (Birch, 1952) almost to the core-mantle boundary. Based on studies of germane analogues, Ringwood (1966) proposed that the seismic discontinuity was due to a phase change in which silicates transformed from a structure in which silicon was octahedrally, rather than tetrahedrally, coordinated with oxygen. This prediction was ultimately confirmed by high pressure experiments (Liu, 1976). Subsequent studies, such as Ito and Takahashi (1989), confirmed that the transition occurred over a very narrow pressure range matching the depth of the seismic discontinuity, set at 670 km in the Preliminary Earth Reference Model (PREM) of radially average seismic velocity (Dziewonski and Anderson, 1981). Despite the "preliminary" in the name PREM, this model



remains the standard and almost universally employed reference for seismic velocities in the Earth. The principal lower mantle mineral, $(\text{Mg,Fe})\text{SiO}_3$, long referred to simply as Mg-perovskite (due to its structural similarity to CaTiO_3), has recently been identified in shock veins of the Tenham L6 chondrite and named *bridgemanite* in honour of the high pressure experimentalist *Percy Bridgeman*[†]. It is accompanied in the deep mantle by $(\text{Mg,Fe})\text{O}$ and CaSiO_3 phases, which, because they have not yet been found and characterised in nature, continue to be referred to as magnesiowüstite (alternatively ferripericlase) and Ca-perovskite. Although the transformation from ringwoodite (a polymorph of $(\text{Mg,Fe})_2\text{SiO}_4$) to bridgemanite occurs over a very narrow pressure range, tetrahedral majorite garnet persists below 670 km and the complete transformation to octahedrally structured silicates is not complete until a depth of 800 km or so.

Uncertainty remained, and to some degree still does (e.g., Javoy *et al.*, 2010; Kaminsky, 2012), as to whether the 670 km discontinuity might also represent a chemical boundary, although it fairly soon became clear that a compositional change, while possible, was not required by seismic velocities (Jackson, 1983). And even if the discontinuity was not a chemical boundary, uncertainty remained as to whether it might nonetheless be a barrier to chemical transport due to the pressure-temperature (Clapeyron) slope of the phase boundary. The slope proved to be negative, meaning that the phase transition in hot material rising from below or material sinking from above is delayed, making that material more or less dense, respectively, than surrounding rock and consequently impeding transport across the boundary. The issue was eventually resolved by seismic tomography showing that at least some subducting slabs penetrate this boundary (van der Hilst *et al.*, 1991). Fukao *et al.* (1992) found that although “*descending slabs of lithosphere in the Western Pacific tend to stagnate in the transition zone under a subtle control of the 670-km discontinuity*”, these “*stagnant slab materials eventually descend into the lower mantle.*” Based on a more global study, Jordan *et al.* (1993) concluded that “*any stratification induced by phase or chemical changes across the mid-mantle transition zone has a relatively small effect on the large-scale circulation of mantle material.*”

A reduced seismic velocity gradient in the lowermost several hundred km of the mantle, a region known as D', had long been recognised (Bullen, 1949), but as time passed it became clear that an increase in s-wave velocity occurred at the top of this region, although at variable depth. Furthermore, seismic velocities were found to be unusually variable within D' (e.g., Julian and Sangupta, 1973; Lay and Helmberger, 1983), both laterally and vertically. The region is also characterised by an anti-correlation between s-wave and bulk sound velocity (Su and Dziewonski, 1997) and a marked increase in s-wave horizontal anisotropy (Panning and Romanowicz, 2006; Kustowski *et al.*, 2008). These variations appear to require compositional as well as temperature variations within D' (Jellinek and Manga, 2004). Further study of the rich variety of reflected and refracted waves passing through this region and modelling of their waveforms ultimately resulted in recognition of small, thin (<40 km) “ultra-low shear-wave velocity zones” (ULVZ) where s-wave velocities are more than 10% lower than in surrounding



regions directly above the core-mantle boundary. The much smaller reduction in P-wave velocities led Williams and Garnero (1996) to suggest these were regions of partial melting. In part because iron would preferentially partition into them, such high-pressure melts may be as dense or denser than surrounding solid (Stixrude *et al.*, 2009). Alternatively, the ULVZ may be compositionally distinct layers, possibly due to iron enrichment produced by reactions between core and mantle (Lay and Garnero, 2011). Some, and perhaps many, of the anomalous features in D' appear to be due to the transition of bridgemanite to a 'post-perovskite phase', first identified in experiments by Murakami *et al.* (2004). Because the thermal gradient near the core-mantle boundary is expected to be high, with temperatures possibly increasing by as much as 1000 K or more within D' and the Clapeyron slope of the phase change is positive, a "double crossing" of the phase boundary, *i.e.* bridgemanite to post-perovskite and back to bridgemanite, is possible and may explain some of the complexity of D' (Hirose, 2006).

At the same time, the lower mantle above D' was proving interesting as well. This region had long been viewed as seismically homogeneous and boring, but perhaps only because the seismic data set and computational power allowed only a radially symmetric perspective. As the earthquake catalogue became more extensive, digital seismic data became available, and computers became more powerful, evidence of significant lateral variation in seismic velocities began to emerge (*e.g.*, Dziewonski *et al.*, 1977; Masters *et al.*, 1982) and these seem to relate to convection-driven geoid anomalies (Busse, 1983). Dziewonski (1984) found discontinuous regions of anomalously slow velocity beneath South Africa and the south central Pacific. These in turn were surrounded by regions of anomalously fast seismic velocity. Hart (1984) noted an apparent geographic relationship between his "DUPAL anomaly" and the geoid anomalies of Busse (1983). Castillo (1988) showed that these were geographically related to Dziewonski's (1984) slow seismic velocity anomalies (Fig. 6.1). Staudigel *et al.* (1991) noted that the Pacific part of the DUPAL anomaly correlated with unusually shallow seafloor in the region and named it "SOPITA" (South Pacific Isotopic and Thermal Anomaly). In fact, I think these are two isotopically distinct regions of the lower mantle, the difference more or less corresponding to the differences between EM I (DUPAL) and EM II (SOPITA) signatures.

The seismic velocity structure of the lower mantle is now far better defined; as Dziewonski *et al.* (2010) stated "*Global models of mantle shear velocity anomalies have reached maturity*", meaning that they "*have resolved, on the global scale, the dominant large-wavelength anomalies.*" In addition to the correlation with the geoid noted above, the slow velocity anomalies, known as "large low shear-wave velocity provinces" or LLSVP's, correlate positively with the locations of hot spots and negatively with integrated subduction history (Richards and Engebretson, 1992), suggesting they may either control or are controlled by the pattern of mantle flow and plate tectonics. Remarkably, they are almost antipodal and centred near the equatorial plane, leading Dziewonski *et al.* (2010) to suggest they consequently have stabilised the Earth's rotational axis close to the present one for geologically long periods, perhaps the entire history of the Earth. Based on the



position of large igneous provinces through time, Burke (2011) and Condie (1989) argued that these LLSVP's are effectively permanent and stationary. Others argue the location of the LLSVP's is controlled by the descent of cold subducted lithosphere that focuses hot dense material into piles (McNamara and Zhong, 2005).

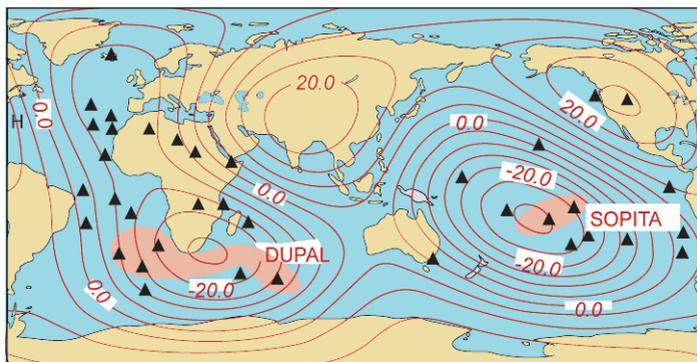


Figure 6.1 Contours of lower mantle p-wave velocity anomalies, hot spots (triangles), and maxima of Pb and Sr isotopic anomalies (red) in OIB in the Indian-South Atlantic (DUPAL) and South Pacific (SOPITA) regions (after Castillo, 1988).

Alternatively known as “superplumes”, the LLSVP’s appear to have sharp boundaries and together cover nearly half of the core mantle boundary (Fig. 6.2). Rather than being located over their centres, hot spots appear to be preferentially located on the margins of these features (Burke *et al.*, 2008), and the ULVZ’s also appear to be preferentially located beneath the margins of the LLSVP’s (McNamara *et al.*, 2010). The South Pacific LLSVP extends at least 400 km above the core-mantle boundary while the African LLSVP extends at least 1000 km above it. Together, they cover a substantial (approaching 50%) fraction of the core-mantle boundary, but represent only a small fraction (<2.5%) of total mantle volume (Hernlund and Houser, 2008). Although variations in mantle seismic velocity have generally been interpreted in terms of temperature (hot equals slow), a number of factors indicate that the LLSVP’s are also compositionally distinct. These include the sharp boundaries of the LLSVP’s, which would be quickly “softened” by thermal diffusion, the very low s-wave velocities combined with moderate decreases in p-wave velocities, and changes in the ratio of s-wave velocity to bulk sound speed. In one scenario, the LLSVP’s are both denser (by 2 to 3%) and hotter than surrounding material that accumulates as convection sweeps denser material toward upwelling regions, consistent with the location relative to subduction and plumes (Garnero and McNamara, 2008). Schubert *et al.* (2004) argued that the LLSVP’s are too large to be thermally buoyant plumes generated at a thermal boundary layer and are instead clusters of smaller plumes that are not resolved seismically. They also pointed out that higher in the mantle the superplumes appear to resolve into multiple upwellings. Davaille *et al.* (2005)

argued that large dome-like thermochemical instabilities could develop in a chemically heterogeneous mantle, depending on the ratio of thermal to chemical buoyancy. In their view these domes then give rise to a half dozen or so smaller plume-like instabilities with an episodicity of 100-200 Ma, which, they argue, is similar to the frequency of large igneous provinces and plumes in the vicinity of the African LLSVP.

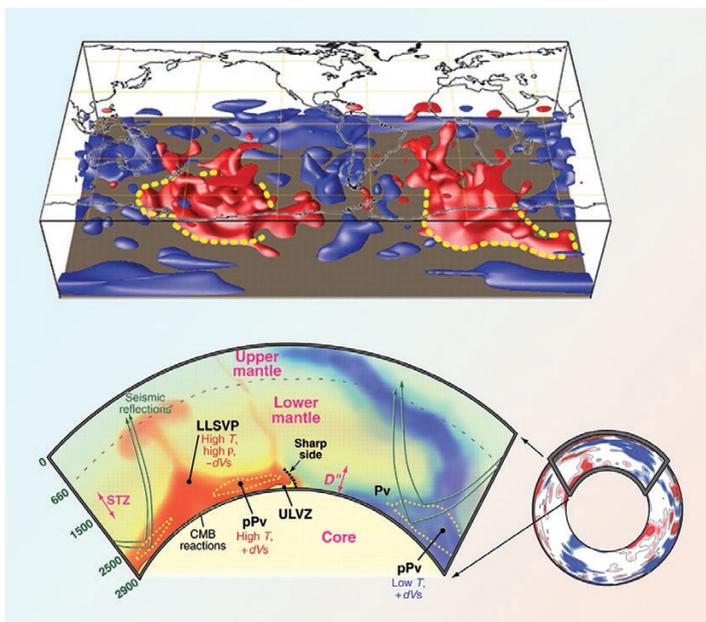


Figure 6.2

Figure 6.2 Seismic structure of the lower mantle. Top figure shows the LLSVP's defined by $>-0.6\%$ velocity decrease relative to PREM in red. They are surrounded by regions of $>0.6\%$ velocity increase relative to PREM shown in blue. Lower figure is a cartoon illustrating some of the features discussed on this section, including the transition to the post-perovskite phase (pPv), ultra-low velocity zones (ULVZ's), and reactions at the core-mantle boundary. The spin transition zone (STZ) is where a change in electron orbital spin may occur in Fe^{2+} and Fe^{3+} and affect density (from Garnero and McNamara, 2008 with permission from The American Association for the Advancement of Science).

6.2 The Physics of Mantle Plumes

The first attempt to evaluate the physical plausibility of Morgan's (1971) mantle plume hypothesis was by (Whitehead and Luther, 1975) who showed that Rayleigh-Taylor instabilities at the base of a fluid could develop into plume-like structures. Many, indeed far too many to review here, subsequent studies



followed, focusing on various aspects of the fluid dynamics of mantle plumes. These confirmed that plumes are most likely to develop as instabilities in a thermal boundary layer (e.g., Olson *et al.*, 1987; Sleep, 1988) with large heads (e.g., Griffiths and Campbell, 1990), but other mechanisms may be possible (Farnetani and Samuel, 2005; e.g., Davies and Bunge, 2006). The large plume heads are thought to be responsible for large igneous provinces, *i.e.* flood basalt provinces such as the Deccan traps or oceanic plateaus such as Ontong-Java, and indeed a number of present plumes, but not all, can be associated with these volcanic outbursts (Richards *et al.*, 1989). As they develop, plumes will entrain material from just above the boundary layer (e.g., Sleep, 1988) and ultimately the mantle through which it rises (e.g., Hauri *et al.*, 1994). As it rises through the mantle, the plume will be deflected by any convective motion within the mantle (the “mantle wind”) and consequently plumes will not be completely stationary (Griffiths and Richards, 1989) and indeed the apparent relative motion between plumes appears to be consistent with mantle convection patterns inferred from seismic velocities and plate motions (Steinberger and O’Connell, 1998). Greater deflection is likely in the uppermost mantle as plumes begin to “feel” lithospheric drag, and this can result in additional entrainment of surrounding mantle (Griffiths and Campbell, 1991a; Ribe and Christensen, 1994). One important geochemical consequence of entrainment is lateral heterogeneity in plumes and the volcanoes they produce (e.g., Hauri *et al.*, 1994; Farnetani *et al.*, 2002; Farnetani and Hofmann, 2009). In the simplest case, this will result in radial zoning, but the pattern can also be more complex (e.g., Griffiths and Campbell, 1991b; Farnetani and Hofmann, 2009) and I’ll discuss this in greater detail in Section 8.2. Another consequence is a strong radial temperature gradient within the plume, with excess temperature decreasing rapidly outside the plume core. This can potentially generate compositional differences in the magmas produced as a consequence of varying degrees of melting. On the other hand, much of the entrained material may not be hot enough to melt (Farnetani and Richards, 1995).

As *Morgan* originally proposed, mantle plumes are thought to be a form of convection driven by thermal buoyancy enhanced by the lower viscosity that accompanies higher temperatures. This rising hot material deflects both the surface and the geoid upward. Davies (1988) and Sleep (1990) used these deflections, known as ‘hot spot swells’, to estimate the buoyancy and thermal fluxes of plumes. Hawaii has by far the largest buoyancy flux, while Kerguelen, the smallest considered by *Sleep*, has a buoyancy flux 30 times smaller. Both *Davies* and *Sleep* concluded that the total heat flux carried by plumes was about 10 % of total terrestrial heat flux and comparable to the estimated flux of heat from the core at that time. This result tended to support the idea that plumes develop from a thermal boundary layer at the base of the mantle, the temperature increase across which might be in excess of 1000 °C. King and Adam (2014) revisited the question of buoyancy fluxes and their estimates tend to be lower than those of *Sleep* and *Davies*, as is their estimated total plume heat flux. At the same time, estimates of heat flow from the core have increased (Pozzo *et al.*, 2012) so that the most recent estimates of plume heat flux are significantly lower than the heat



flux from the core. On the other hand, geodynamic modelling suggests that much of the heat that plumes carry away from the core-mantle boundary layer is likely lost to the surrounding mantle before it reaches the surface (e.g., Leng and Zhong, 2008), mainly as a consequence of the work done by plumes rather than diffusive heat loss.

Neither Davies (1988), Sleep (1990), nor King and Allen (2014) attempted to answer what would seem to be a key question: just how much hotter are plumes? McKenzie (1984) estimated that the Hawaiian plume needed to be some 200 °C hotter than mantle beneath mid-ocean ridges to produce the volume of basalt observed. Klein and Langmuir (1987) showed that MORB chemistry, specifically sodium and iron contents that are sensitive to the degree and depth of melting, correlated with ridge depth such that high extents and greater depths of melting were associated with shallower ridge depths. They concluded that both the Na and Fe variations resulted from variations in mantle temperatures of as much as 250 °C beneath the mid-ocean ridges. The highest temperatures were invariably associated with near hot spots such as Iceland. Wyllie (1988) estimated that the Hawaiian plume was perhaps 300 °C hotter than mantle beneath mid-ocean ridges. A decade later, Herzberg and O'Hara (1998) estimated that the Hawaiian plume was "200 to 250 °C hotter than present day ridges" while Iceland was only 100 to 150 °C hotter. Putirka *et al.* (2007) used a recalibrated olivine geothermometer to calculate melt temperatures and then derive mantle potential temperature. They found the mantle potential temperature beneath mid-ocean ridges is 1454±81 °C and that the potential temperature of the Hawaiian and Samoan plumes are identical at 1722 °C and the Iceland plume has a potential temperature of 1616 °C. These translate into excess temperatures of 268 °C and 162 °C, respectively, in overall good agreement with earlier studies. Niu *et al.* (2011) argued that at least some of the difference between the estimated temperatures between Iceland and Hawaii was due to differences in lithospheric thickness between Iceland and the other hot spots because this thickness controls the depth of last equilibration between mantle and melts. Herzberg *et al.* (2007) found lower potential temperatures for ambient mantle, in the range of 1280-1400 °C, but nevertheless conclude that plumes are typically 200-300 °C hotter. Herzberg and Asimow (2008) estimated mantle excess potential temperatures for a variety of other plumes and found that they fell, with scatter, between those for Hawaii (~200 °C) and Iceland (~100 °C). These estimates are generally in good agreement with studies that use entirely different approaches, such as the width of the geochemical anomaly along ridges (Schilling, 1991) and melt production, excess topography and geoid height (Watson and McKenzie, 1991).

These results weren't without controversy, however, as Green *et al.* (2001) and Falloon *et al.* (2007) found no difference in potential temperatures between the sub-ridge and the sub-Hawaiian mantle. Niu and O'Hara (2008) argued that much of the apparent temperature variation found by Klein and Langmuir (1987) and subsequent studies was actually due to compositional variation. They calculated much smaller temperature variations of ~50 °C. Recently, however, Dalton *et al.* (2014) showed that both MORB chemistry, particularly



fractionation-corrected sodium contents, and ridge depth correlate with upper mantle s-wave velocities beneath ridges. They concluded that this strongly supported earlier findings of mantle temperature variations of 250 °C down to >400 km beneath ridges with the highest temperatures associated with hot spots. In a similar vein, Courtier *et al.* (2007) showed a correlation between petrologic estimates of mantle potential temperature in MORB and OIB and the thickness of the underlying mantle transition zone. The latter is sensitive to temperature because the bridgmanite-ringwoodite transition at roughly 670 km has a negative Clapeyron slope and hence is deflected upward by rising hot mantle, while the olivine-ringwoodite transition at roughly 410 km depth has a positive Clapeyron slope and hence is deflected downward by rising hot mantle.

If plumes develop from a thermal boundary layer that is ~1000 °C hotter than the overlying mantle, why are they only several hundred degrees hotter at the surface? Even considering the heat lost through the work plumes rising through the mantle (Leng and Zhong, 2008) this difference seems too great. Farnetani (1997) suggested the difference required that the basal layer, the source of plumes, be some 5% denser than the overlying mantle, which hinders the incorporation of the hottest, deepest part of a thermal boundary layer into the plume. As we will see, this greater density is consistent with the geochemical evidence that plumes consist in part of recycled crustal material.

If plumes are hotter than surrounding mantle then the velocity of seismic waves passing through them should be slowed, which should result in late arrival times for those waves. Using arrival times of many such waves, tomographic techniques should, in principle, be able to reveal slow regions and image mantle plumes. This is more difficult than it might at first seem because the resolution of seismic tomography is limited by (1) the wavelength of the teleseismic waves themselves, (2) the density of crossing ray paths, (3) the density of seismographic stations, (4) limited distribution of earthquakes, and (5) wave diffraction and resulting 'wavefront healing' (Nolet *et al.*, 2007). As a consequence of these factors, resolution is generally not better than 100 km in the upper mantle and not better than 200 km in the lower mantle. Nataf and VanDecar (1993) reported slow seismic velocities at a depth of 700 km beneath Bowie Seamount in the northeast Pacific and suggested this reflected a ~300 °C temperature contrast. Wolfe *et al.* (1997) and Allen *et al.* (2002) were able to detect anomalously slow velocities beneath Iceland down to the limit of their resolution at 400 km depth. On the other hand, while Wolfe *et al.* (2002) were able to image a slow region in the uppermost mantle near Hawaii, it was centred beneath downstream volcanoes on Molokai and Maui and hence they were unable to image a deeper plume beneath the island of Hawaii, where it was expected.

Montelli *et al.* (2004) applied Born theory and finite frequency analysis to low frequency P-waves to improve resolution by overcoming the effects of wave healing to image plumes beneath 30 hot spots. Of these, the anomalies extended through the 670 km seismic discontinuity into the deep mantle in 26 cases. In 8 cases, including Ascension/St. Helena, Azores, Canary, Easter,



Samoa, and Tahiti (Society Is.), the anomalies extended to the base of the mantle or nearly so. Montelli *et al.* (2006) applied the same techniques to s-waves and were able to trace additional plumes into the deepest mantle, but with essentially the same results. This approach, however, has been controversial. While the finite frequency analysis does indeed improve resolution, it also tends to smear anomalies downward, which, of course, could make simple anomalies appear as tube-like plumes (Boschi *et al.*, 2006; Nolet *et al.*, 2007). Boschi *et al.* (2007) used a different approach and found only 12 hotspots that extended into the deep mantle. They also detected a number of “secondary” plumes that appeared to originate from slow/hot regions in the mantle such as the LLSVP’s discussed previously. Most recently, French and Romanowicz (2014) found a number of narrow low velocity anomalies associated with major hotspots using spectral element wave-form tomography to assess whole mantle radial s-wave anisotropy (Fig. 6.3).

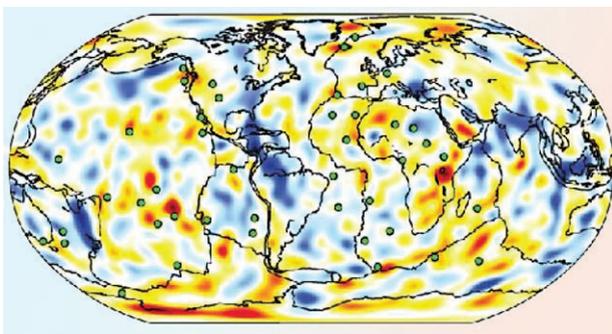


Figure 6.3 S-wave velocity variations at 1000 km depth in the SEMUCB-WM1 tomographic model of French and Romanowicz (2014). Variation is $\pm 2\%$; blue = fast, red = slow. Circles are hot spots from Steinberger (2000), many of which, including Iceland, Hawaii, the Azores, Samoa, and the Society Islands are located near narrow regions of low s-wave velocity in the uppermost lower mantle.

Using a relatively high density network of land-based and ocean-bottom seismometers, Wolfe *et al.* (2009) were able to image the Hawaiian plume using s-waves to depths of 1500 km. The uppermost mantle images show the lowest velocity region elongate in the direction of plate motion then shifting southeastward and becoming narrower at greater depth, in good agreement with geodynamic models such as that of Ribe and Christensen (1994). P-wave tomography confirmed these results (Wolfe *et al.*, 2011) but resolution was not sufficient in either analysis to trace the anomalies into the lower half of the mantle. However, (Cottaar and Romanowicz, 2012) found a particularly large (~900 km diameter) and strong (>20% velocity reduction) thin ULVZ 11° southwest of Hawaii that they speculate could be the root of the Hawaiian plume.



The s- and p-wave images reveal that the Hawaiian plume is partially surrounded by anomalous high velocities in the upper mantle, which Wolfe *et al.* (2011) interpret as downwelling asthenosphere displaced by the plume. There were, however, some curious differences between the p- and s-wave images. The lowest p-wave velocities in the upper mantle tended to be offset to the southwest of the lowest s-wave velocities, although the difference is less when station terms were included in the inversion. Because the recent Hawaiian volcanoes can be divided into two distinct chains, the offset of the lowest velocities relative to the volcanoes may be significant in explaining compositional differences between the chains. I'll return to this in a subsequent section.

Courtillot *et al.* (2003) concluded that only 7 to 10 hot spots of the 49 they considered were products of plumes rising from the core–mantle boundary layer based on five criteria: (1) a long-lived track, (2) a LIP at initiation, (3) a topographic anomaly indicative of a buoyancy flux in excess of 10^3 kg/s, (4) high $^3\text{He}/^4\text{He}$ and $^{20}\text{Ne}/^{22}\text{Ne}$ ratios, and (5) negative shear wave anomalies indicative of hot mantle. Only those hotspots meeting at least 3 or more of these criteria were considered to be 'primary plumes' of likely deep mantle origin. I don't think that the criterion of a primitive noble gas signature is a valid one. Indeed, as I'll show in subsequent sections, the dominant chemical signature observed in OIB is one of material recycled from the Earth's surface. While many OIB do indeed contain a primitive noble gas signature, its origin is problematic as little else in their chemistry hints at a primitive component. I'll return to this problem in the final section. In addition, considerable progress, described above, has been made in identifying seismic anomalies associated with plumes since 2003.

Courtillot *et al.* (2003) classified hot spots that did not meet their plume criteria as "secondary". Some hot spots, such as Reunion, Hawaii, Galápagos, and Tristan have long tracks that can be traced back many tens of millions of years. Others, such as the Society Islands and Marquesas, have particularly short-lived tracks of 5 million years or so. The Australs, located in the same region, represent a particularly intriguing case. Although volcanism there extends back 20 million years, that volcanism defines 3 distinct time-distance trends such that volcanism was repeated on some islands, such as Raivavae, and occurred simultaneously on widely separated islands along the chain (Maury *et al.*, 2013). Courtillot suggested the Australs were secondary hotspots triggered by LSSVP's. The hotspots of French Polynesia are indeed closely associated with the Pacific LLSVP. Notably, the tops of the LLSVP's are seismically indistinct and Schubert *et al.* (2004) suggested that they break-up into clusters of smaller plumes. Indeed, the Society and Austral (McDonald) hotspots seem connected to the Pacific LLSVP through what French *et al.* (2013) describe as "*vertically elongated plume-like conduits*" (Fig. 6.3). Schilling and Noe-Nygaard (1974) long ago suggested that plume flux might vary significantly through time and there is no apparent geodynamic reason why this could not be the case. Thus the French Polynesian chains, particularly the Australs, may result from relatively intermittent upwellings, perhaps from the Pacific LLSVP rather than the base of the mantle. On the other hand, although the subaerial volcanoes of the Cook-Austral chains are



young (<20 Ma), plate reconstructions and geochemistry link them to 3 much older seamount chains in the Western Pacific, suggesting that while these plumes may not be vigorous, they are long-lived (Konter *et al.*, 2008).

6.3 A Deep Mantle Signal?

Most melting in the Earth occurs within the outermost few hundred kilometres. As we saw in the previous section, however, regions of anomalously low s-wave velocities occur within the D' thermal boundary layer, which also likely is a region of very high thermal gradient. This raises the question of whether melting might be occurring in the region (*e.g.*, Williams and Garnero, 1996; Stixrude *et al.*, 2009). Furthermore, given that mantle plumes appear to arise from near the base of the mantle (Montelli *et al.*, 2004, 2006), could some of the heterogeneity evidenced by oceanic island basalts be created by deep mantle melting? Let's address this with some simple models of trace element behaviour in the upper and lower mantle. Although lower mantle trace element partitioning is far less well constrained than for the upper mantle, a number of experimental partitioning studies at deep mantle pressures have been carried out, albeit at lower precision than for upper mantle assemblages, with reasonably consistent results (*e.g.*, Kato *et al.*, 1988; Hirose *et al.*, 2004; Corgne *et al.*, 2005). The exception is the post-perovskite phase in D'', for which no partitioning experiments have been carried out. Phase assemblages are also at least somewhat understood (Hirose *et al.*, 2005; Hirose, 2006).

Figure 6.4 is a spider diagram (also referred to in Section 5.1 as an extended rare earth diagram) comparing the calculated concentrations of incompatible elements in upper and lower mantle melts with those in oceanic island basalts. For the upper mantle, I have assumed a phase assemblage of 50 % olivine, 20 % orthopyroxene, 20 % clinopyroxene, and 10 % garnet and partition coefficients taken from the GERM database and listed in White (2013). In this case, I assume 8 % non-modal batch melting (Schilling, 1971) with garnet and clinopyroxene preferentially entering the melt (equations 7.45 through 7.48 in White, 2013). For the lower mantle, I assume the phase assemblage given by Hirose (2006) of 78 % bridgemanite, 16 % ferripericlase, and 6 % Ca-perovskite and partition coefficients from Hirose *et al.* (2004) and Corgne *et al.* (2005) (where no partition coefficients were available, they were assumed to be 0.002), and simple modal batch melting as described by equation (2.1). The green shaded area shows the range of predicted compositions of upper mantle melts for source compositions ranging from primitive mantle to a hypothetical subducted lithosphere composition consisting of 85 % depleted mantle (Salters and Stracke, 2004), 17.5 % MORB (White and Klein, 2014), and 2.5 % marine sediment (Plank, 2014). The source composition range is the same as for the lower mantle melt. Also shown is the lower mantle 15 % modal melt of MORB with a phase assemblage of 35 % bridgemanite, 23 % Ca-perovskite, 15 % Ca-ferrite Al-bearing phase, and 17 % post-stishovite SiO₂ (Hirose *et al.*, 2005). Partition coefficients for the SiO₂ phase were assumed



to be 0, as were U and Th partition coefficients for the Ca-ferrite phase (U and Th were not detected in this phase by Hirose *et al.*, 2004). A partition coefficient for Pb was unavailable for the Ca-ferrite phase so I assumed a value of 1; the actual value is likely much lower since Hirose *et al.* (2004) did not detect Pb in this phase (although concentrations in the melt were high).

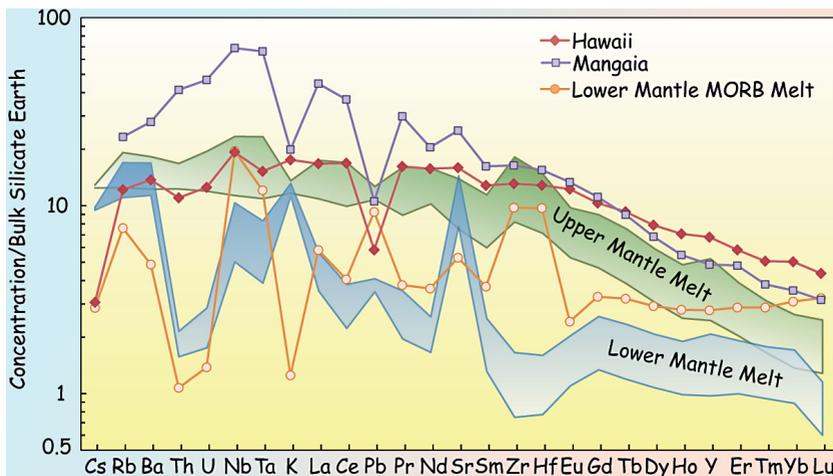


Figure 6.4 Normalised incompatible trace element concentration patterns in a typical Kilauean (Hawaii) basalt and the average of 5 basalts from Mangaia (Austral-Cook Islands) (Hanyu *et al.*, 2011) compared to predicted partial peridotitic and basaltic melts in the upper and lower mantle.

The patterns of upper mantle melts are broadly similar, but not identical, to that of the oceanic island basalts, but lower mantle melts are different. In particular, U, Th, Pb and the rare earths are strongly retained in the Ca-perovskite phase in the lower mantle. Sr, Hf, and Zr also have partition coefficients greater than 1 in Ca-perovskite, but nevertheless much lower than the rare earth partition coefficients, which are 10 or greater for the intermediate and heavy rare earths. Hf and Zr are, on the other hand, strongly retained in bridgemanite. Ta and Nb do not partition strongly into any of the lower mantle minerals. The presence of the Ca-ferrite phase and the low modal abundance of bridgemanite makes melting of a MORB composition distinct from a peridotitic one as the Ca-ferrite phase retains K and Sr.

Hanyu *et al.* (2011) argued that the isotope systematics of the HIMU reservoir were difficult to explain through recycling of oceanic crust and sediment but could be explained if subducted material were to melt in the deep mantle and “migrate laterally and metasomatize the ambient pyrolytic mantle.” However, as Figure 6.4 shows, the incompatible trace element pattern of basalts from Mangaia, the Austral island with the strongest HIMU signature, is quite different from that

expected of a lower mantle melt of either basaltic or peridotitic lithology. It thus seems unlikely that deep mantle melting contributes to the geochemical signature of HIMU basalts.

The melting models illustrated in Figure 6.4 do not completely explore the range of possible melt compositions in the lower mantle: other phase assemblages could produce somewhat different incompatible element patterns. Furthermore, lower mantle melt could be overlooked if it were sufficiently diluted by other material. However, much of the distinctiveness of lower mantle melting is due to retention of elements that are incompatible in the upper mantle in Ca-perovskite, which remains as a stable phase to the base of the mantle (Hirose, 2006). Furthermore, all lower mantle assemblages likely retain U and Th in the solid, resulting in U/K, U/Nb, and U/Pb fractionations different from those observed in oceanic basalts. Additionally, lower mantle minerals tend to fractionate Zr and Hf differently from the middle rare earths, which should lead to variable Hf/Sm ratios and this is not observed. We can conclude from this comparison that while oceanic island basalts may be produced by plumes rising from the lower mantle, they have an upper mantle geochemical ancestry. I should, however, emphasise that this does not rule out melting in the lower mantle – all we can say is that if such melts occur they do not contribute to observed mantle heterogeneity.

6.4 Armstrong's Idea

Most of us can probably remember being taught in primary school that nature wastes little: animal waste, fallen leaves, and dead logs are recycled by soil organisms into nutrients for plants that provide food for animals, etc. The environmental movement urges society to become more like nature and waste less and recycle more. Recycling, in that social sense of actions like separating metals, glass, paper, etc, from 'non-recyclables', came into vogue in the 1980's, but it's origins are earlier and date to the explosion of environmental concern in the 1960's and early 1970's – triggered, perhaps, by *Rachel Carson's* 1962 book *Silent Spring*. It turns out that ecosystems are not the only way in which nature recycles. Another kind of recycling movement also caught on in 1980's and also had its origins in the 1960's – triggered by the work of *Dick Armstrong* (1968). He wrote, "*Contrasting interpretations of existing models of Sr and Pb isotope evolution can be eliminated with a model in which crustal material is recycled through the mantle. In this model the earth's crust and upper mantle (above approximately 500 km depth) are in a steady-state system, and the volumes and bulk compositions of oceanic crust, continental crust, and mantle have been nearly constant for at least the last 2.5 b.y. and probably for most of the Earth's history.*" The paper is remarkable in a number of respects, not the least of which is that it was published before the papers that same year by *Isacks et al.* (1968) and *Le Pichon* (1968) that integrated seafloor spreading and continental drift into the modern theory of plate tectonics. *Armstrong* was way ahead of everyone else in thinking about the implications of plate tectonics for the chemical evolution of the Earth.



As a graduate student, I was intrigued by *Armstrong's* ideas. In trying to interpret my thesis data from the Mid-Atlantic Ridge and the Azores, it seemed to me that neither the Icelandic nor the Azores plume could consist of primitive material or some mixture of primitive material and depleted mantle: their evolution must have been more complex. In addition, using simple melting model calculations, such as equation 2.1, I found that the mantle source of Azores basalts was much like somewhat incompatible element-enriched MORB (what we today might call E-MORB). *Armstrong's* idea seemed the explanation: what if the Azores plume consisted, in part, of recycled oceanic crust with perhaps some subducted sediment to provide a bit more incompatible-element enrichment? What if, instead of subducted oceanic crust and sediment being homogenised back into the upper mantle as *Armstrong* seemed to imply, it remained sequestered somewhere in the deep mantle until its higher heat-producing element concentrations made it buoyant? I wrote those ideas up in the draft of my thesis. When *Schilling* read it, however, he suggested it was too speculative and that I drop it. I was too close to finishing to engage in another battle with my advisor at that point. Furthermore, I was only a grad student: what did I know? So I deleted that from my thesis, but held on to the hand-written draft, intending to write up the idea and publish it later.

Afraid of being 'scooped', I discussed the idea with few other people. I am not sure whether *Al Hofmann* came to the idea independently or through discussions with me. I do remember a telephone conversation with him during my post-doc at USGS in Denver. *Al* asked if he had told me of his new idea (plumes from recycled crust) that he was writing up for that year's Carnegie Annual Report. I replied that the idea wasn't new – I had written it up several years earlier in my thesis and I sent him copies of my handwritten draft. He graciously added my name to a brief report in the Carnegie Yearbook (*Hofmann and White, 1980*). When I joined him in the newly established Geochemistry Division at the Max Planck Institut für Chemie in Mainz, we continued to work on the idea and the result was the *Hofmann and White (1982)* paper. By that time, however, we had already been scooped – twice. Although it wasn't the main thrust of the paper, *Hawkesworth et al. (1979)* proposed the idea as an explanation for their Sr and Nd isotope data from the Azores, and it was the main thrust of the *Chase (1981)* paper (*Clem Chase* was one of the few people that I do remember talking to about the recycling idea; as he was a geophysicist, I thought it was safe).

One of the reasons I had held off writing up the recycling idea was that I wanted more evidence. Sr and Nd isotope data on oceanic island basalts that I had acquired at Carnegie, USGS, and MPI appeared to provide it. In particular, extreme isotopic compositions from Samoa, the Society Islands, Tristan da Cunha, and Kerguelen seemed best explained by the recycling hypothesis; they certainly could not be explained by primitive mantle–depleted mantle mixing, which was then in vogue. At the time, the Sr–Nd isotope mantle array appeared to bifurcate into two trends: one through Tristan and Kerguelen (what we now call EM I), the other through the Society Islands, Samoa, and the Azores (what we



now call EM II). In White and Hofmann (1982), we suggested the latter resulted from sediment-dominated subducted material, while the former resulted from subduction of oceanic crust without sediment.

6.5 The Fate of Subducted Slabs

The recycling hypothesis has several variants. Hofmann and White (1982) emphasised oceanic crustal recycling. There is, of course, overwhelming evidence that oceanic crust is recycled into the mantle. After billions of years of oceanic crust production, only slivers are preserved on the surface. But what happens to it once it disappears from the surface? The first clue is density. Subduction occurs because oceanic lithosphere cools and becomes dense. In addition to thermally driven density changes, however, intrinsic density differences (that is, density differences between materials at the same temperature) also play a role. Interestingly, when the mantle melts at low pressure, both the crystallised melt and the residual harzburgite have lower density than the original peridotite (density is not a conservative property). However, when the basaltic oceanic crust subducts beyond 60 km depth or so, a garnet-rich lithology forms and the crust becomes intrinsically denser than peridotite. This intrinsic density difference, which remains throughout the upper mantle, helps to drive subduction.

Near the base of the upper mantle at 670 km, things become a bit more complicated. Ringwood (1982) suggested that oceanic crust and lithosphere could not penetrate the 670 km phase boundary. This is because the transformation from ringwoodite to bridgemanite has a negative pressure-temperature Clapeyron slope as noted earlier. In effect, this means that cold descending material will transform later, and hence will be less dense than surrounding mantle just below 670 km. Further, basaltic compositions transform to a phase assemblage relatively rich in Ca-perovskite and the transformation to this phase occurs at greater depth than the ringwoodite-bridgemanite transformation, making basaltic material relatively buoyant in the region of the phase transformation. Because of this, Ringwood argued that oceanic lithosphere piled up as “mega-liths” in the transition zone. In a variation on the Hofmann and White model, he argued that over 1 to 2 billion years the oceanic crust heat ups and melts. The melts ‘fertilise’ the harzburgite, which becomes buoyant and rises as ‘diapirs’ producing oceanic island volcanoes.

Subsequent mineral physics studies found that the delay in the transformation to octahedral structure in a basaltic composition is smaller than proposed by Irifune and Ringwood (1993). For example, Hirose *et al.* (1999) found that the transformation in basaltic lithology is complete by around 27 GPa, corresponding to a depth of 720 km. Furthermore, they found that the Clapeyron slope for the majorite–Ca-perovskite transformation is positive, and because this phase is more abundant in basaltic lithologies than bridgemanite, the overall pressure-temperature Clapeyron slope is positive for basalt, which promotes rather



than inhibits its transport across the boundary (Hirose *et al.*, 1999). Below about 720 km, basalt remains denser than peridotite to the base of the mantle (Hirose *et al.*, 1999).

Seismic tomography provides additional insight into the fate of slabs. Some slabs, such as the Farallon plate beneath North America, clearly appear to penetrate into the deep mantle, and arguably to the base of the mantle (Fig. 6.5). In other regions, such as in the Japan-Kurile subduction zone, the slab appears to deflect at the 670 km discontinuity. Thus Ringwood was apparently at least partly right. On the other hand, no evidence of his “megaliths” near the boundary has been found and the consensus seems to be that a “stagnant slab is a temporary feature and is, eventually, likely to fall well into the lower mantle as a slab avalanche” (e.g., Fukao *et al.*, 1992, 2009). There is also evidence that slabs accumulate at the base of the mantle, forming “slab graveyards” associated with fast seismic and negative geoid anomalies (Richards and Engebretson, 1992; e.g., Konishi *et al.*, 2009; Spasojevic *et al.*, 2010) that surround the LLSVP’s discussed earlier.

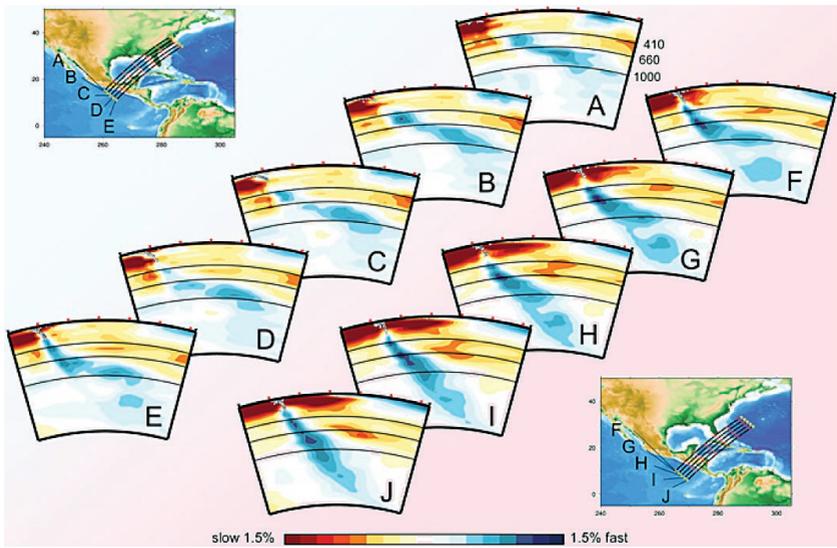


Figure 6.5 Seismic tomographic image showing the Farallon slab, defined by fast s-wave velocities, descending into the lower mantle beneath North America (from Fukao and Obayashi, 2013 with permission from John Wiley and Sons).

Thus oceanic crust is subducted into the deep mantle and appears to accumulate at its base, consistent with the *Hofmann and White* model. These slabs, however, consist of the crust plus ~100 km mantle lithosphere that is largely the melting residue of oceanic crust production. To a first approximation then, the entire lithosphere, crust plus residual mantle, has the same composition as the mantle source of MORB. The *Hofmann and White* model would seem to

require that the crust somehow separates from the underlying residual mantle and concentrates in specific regions. Computer simulations by Tackley (2011) indicate that this may indeed occur within the core-mantle thermal boundary layer. The greater density of the basalt relative to the underlying harzburgite results in rotation of the slab and its landing upside down at the base of the mantle. Heating from the boundary layer then causes the harzburgite to rise, leaving the denser basalt imbedded in the thermal boundary layer.

Tackley (2011) found that this separation is not complete and could be anywhere between 25 and 70 % efficient, depending on the density in the thermal boundary layer. That may well be sufficient to ultimately explain the enrichment observed in plumes. Furthermore, *Hofmann* and *White* noted that an ultramafic component in plumes is necessary to account for the nickel contents of OIB, which are similar to those of MORB. In addition, temperatures necessary to make plumes buoyant and overcome the intrinsic density difference between basalt and peridotite would be extraordinarily high if plumes consisted only of recycled oceanic crust as Niu and O'Hara (2003) pointed out. However, if they consist of 50 % or less recycled crust, plumes would become buoyant with temperature excesses in the range of 200-300 °C (White, 2010), which is within the range of apparent temperature excesses of plumes (Sleep, 1990; *e.g.*, Putirka, 2005).

An alternative possibility is that the oceanic crust and sediment do not separate from the harzburgite, or separate incompletely, and that oceanic island basalts are derived from melting of veins or pods of this material with very little contribution from surrounding depleted mantle peridotite, which is possible because of the lower solidus temperature of the former (Hirschmann *et al.*, 2003). Another possible variant of this model is one in which the recycled crust melts and is then consumed by reaction with surrounding peridotite, which then melts to produce OIB upon further decompression in the rising plume (Sobolev *et al.*, 2005). I'll return to this topic in Section 8.1.

6.6 Variations on a Theme

McKenzie and O'Nions (1983), noting the similarity of Sr-Nd isotope systematics in oceanic island basalts and peridotite xenoliths from the continents, particularly the negative ϵ_{Nd} observed in both, suggested that the continental lithosphere might under some circumstances detach from the overlying crust and sink into the deep mantle and be incorporated in mantle plumes. The incompatible element-enrichment of the mantle lithosphere appears to occur as a result of small degree melts from the underlying asthenosphere or fluids from subducting lithosphere rising into it and reacting with it, a process referred to as 'mantle metasomatism' (*e.g.*, Menzies and Hawkesworth, 1987). As McKenzie and O'Nions noted, there is some geophysical evidence that lithospheric detachment occurs when it is overthickened in compressional zones such as the Himalayas. One problem with this hypothesis is that, although occasionally incompatible element enriched, the subcontinental lithosphere appears to have been extensively stripped of its



basaltic component and is intrinsically less dense than more fertile peridotite. Its low temperature might be sufficient to initially overcome this buoyancy and allow it to sink, but it is unclear how deep it could sink before rising temperature makes it buoyant again.

A second difficulty is geochemical. As *McKenzie* and *O’Nions* noted, the Sr, Nd, and Pb isotopic systematics observed in subcontinental lithospheric mantle are similar to those observed in OIB. However, Os isotope systematics and Os-Nd isotopic relationships appear to be different. ^{187}Os is produced by decay of ^{187}Re with a half-life of 43 billion years. Both Os and Re are siderophile elements and highly depleted in the silicate part of the Earth. In the silicate Earth, Os behaves as a highly compatible element and is concentrated in the mantle, while Re behaves as a moderately incompatible element and is somewhat concentrated in the crust (see review by Day, 2013). As a result of this differing behaviour, Re/Os and $^{187}\text{Os}/^{188}\text{Os}$ ratios show a very large range of variation, with quite high ratios in the crust and slightly sub-chondritic ratios in much of the mantle. Indeed, Os isotope ratios are so variable that they are expressed in percentages, rather than parts per 10,000 deviations from the chondritic or “primitive upper mantle” (PUM) value of 0.1296 (*Meisel et al.*, 2001):

$$\gamma_{\text{Os}} = \left(\frac{^{187}\text{Os}/^{188}\text{Os}_{\text{sample}} - ^{187}\text{Os}/^{188}\text{Os}_{\text{PUM}}}{^{187}\text{Os}/^{188}\text{Os}_{\text{PUM}}} \right) \times 100 \quad (6.1)$$

Most mantle peridotites have negative γ_{Os} values as a consequence of Re depletion from previous episodes of melting. Consistent with this, peridotite xenoliths from non-cratonic subcontinental lithosphere, such as Morocco, or oceanic lithosphere, such as Hawaii, also have positive ϵ_{Nd} (*Bizimis et al.*, 2007; *Wittig et al.*, 2010). In contrast, peridotite xenoliths from the lithosphere beneath continental cratons often have quite low ϵ_{Nd} (Fig. 6.6) despite strongly negative γ_{Os} . The low ϵ_{Nd} suggests incompatible element enrichment as a consequence of metasomatism that apparently did not affect the Re-Os system. The explanation appears to be that neither Re nor Os are transported effectively by metasomatic fluids (e.g., *Carlson and Irving*, 1994). Regardless of why, this combination of low γ_{Os} and low ϵ_{Nd} is not observed in OIB, excluding metasomatised subcratonic lithosphere as the “enriched” component in mantle plumes. The OIB field does overlap the field of non-cratonic and oceanic lithospheric peridotites, but at the high ϵ_{Nd} and low γ_{Os} end of the range. Such material could well be present in plumes, and indeed it may be required to explain some of the quite low γ_{Os} observed in some OIB from Iceland, Jan Mayen, and the Azores (e.g., *Debaille et al.*, 2009; *Day*, 2013), but it cannot explain the low ϵ_{Nd} and high γ_{Os} values observed in other OIB.

On the other hand, $\gamma_{\text{Os}}-\epsilon_{\text{Nd}}$ systematics in some OIB seem at least qualitatively consistent with their sources being mixtures of a mantle component, such as suboceanic lithosphere or depleted or primitive mantle, and a crustal component, either oceanic or continental, once assimilation is taken into account. As *Reisberg et al.* (1993) noted, low Os isotopic compositions in basalts, particularly those with concentrations less than 30 ppt or so, leave them susceptible



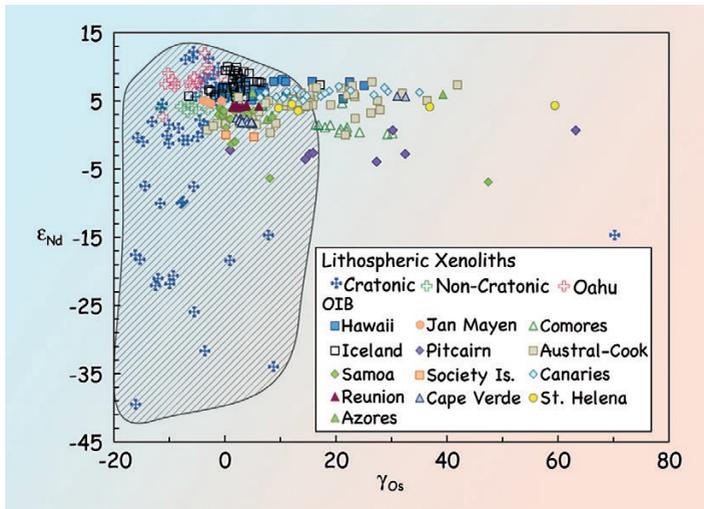


Figure 6.6 ϵ_{Nd} vs. γ_{Os} in oceanic island basalts and lithospheric peridotites. Lithospheric peridotites plot within the crosshatched field with the exception of one peridotite xenolith from Wyoming. The ϵ_{Nd} - γ_{Os} systematics of cratonic lithospheric peridotites essentially rules out their contributing significantly to OIB sources.

to Os contamination by oceanic crust and sediment. Ferromanganese crusts and nodules have particularly high Os concentrations (up to several ppb) and assimilation of even quite small amounts of this material could significantly increase γ_{Os} in the magma (Reisberg *et al.*, 2008). Furthermore, Re/Os ratios in fresh MORB are high, but uptake of Re during hydrothermal alteration of the crust further increases this ratio, which leads to rapid evolution of the $^{187}Os/^{188}Os$ ratio in the oceanic crust (Peucker-Ehrenbrink *et al.*, 2003; Reisberg *et al.*, 2008; Peucker-Ehrenbrink *et al.*, 2012). Finally, there is a well-documented inverse correlation between Os concentrations and $^{187}Os/^{188}Os$ in OIB, which strongly suggests that assimilation is indeed a significant process (*e.g.*, Reisberg *et al.*, 1993; Day, 2013). Because the mantle component in these mixtures has a much higher Os/Nd ratio than the crustal component, mixing arrays between these will be highly curved. Figure 6.7 provides a more detailed view of the OIB data set and illustrates several hypothetical mixing curves with a variety of end member isotopic compositions and Os and Nd concentrations that could plausibly explain trends observed in the Society Island, Samoa, the Comoros, Cape Verde, and Pitcairn data. Samples that fall off these trends likely have assimilated ocean crust through which they rose, as Jackson and Shirey (2011) found for Samoa. Clearly, a mixing model involving a more radiogenic ϵ_{Nd} end-member could explain the Australs as well. Such simple two-component mixing models are less successful if other isotopes are included. If, as has been suggested, the HIMU reservoir results from recycling of Pb-depleted ancient oceanic crust (*e.g.*, Chauvel *et al.*, 1992), one

would expect the radiogenic Pb that characterises this reservoir to be associated with radiogenic Os. However, as Hanyu *et al.* (2011) pointed out, there is little or no correlation between γ_{Os} and Pb isotope ratios in Australs and, if anything, the most radiogenic Pb is associated with relatively unradiogenic Os. They instead suggested secondary melting in the deep mantle as a possible explanation, but as discussed in Section 6.2, the incompatible element pattern in Austral basalts seems inconsistent with this. Something similar occurring in the upper mantle, *e.g.*, the multi-stage melting hypothesis of Sobolev *et al.* (2005), might result in the recycled Os being overwhelmed by peridotitic Os, effectively masking original isotopic relationships (Day, 2013).

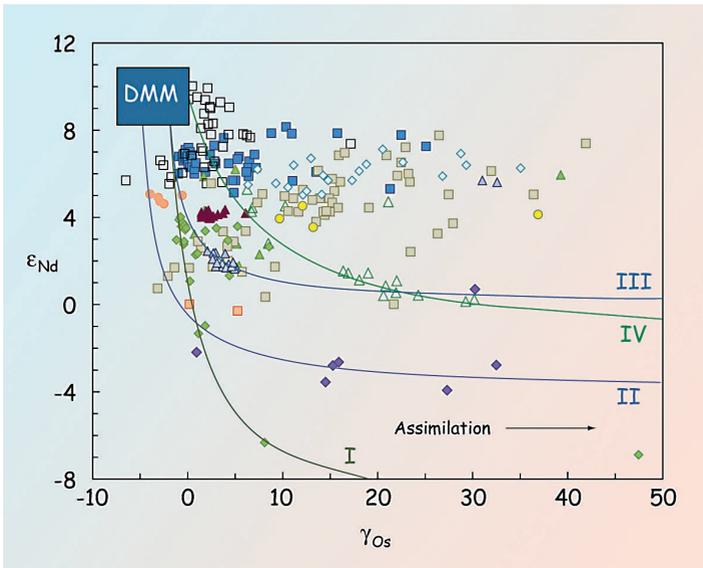


Figure 6.7

γ_{Os} - ϵ_{Nd} systematics in oceanic island basalts and 4 hypothetical models of mixing between a mantle peridotitic component and a crustal component. Symbols are the same as in Figure 6.6. Model I: “sediment-depleted mantle”; Model II: “continental crust-depleted mantle”; Model III: “continental crust-upper mantle”; Model IV: “2.5 Ga subducted oceanic crust-depleted mantle”. Mantle end-member has ϵ_{Nd} of +10 in models I through III and +9 in model IV. Crustal end-member has γ_{Os} of +1830, 1500, 1700, and 2000 and ϵ_{Nd} of -10, -4, -2, and 0 in models I through IV, respectively. Crust/mantle end member concentration ratios are $Nd_C/Nd_M = 38.7, 23.8, 23.8,$ and 12.6 and $Os_C/Os_M = 0.05, 0.027, 0.091,$ and 0.015 for models I through IV respectively.

The most recent variation on the recycling theme was proposed by Niu and O’Hara (2003) who proposed that it was the deep oceanic mantle lithosphere that carried the incompatible element-enriched signature. Workman *et al.* (2004) proposed essentially the same thing to explain isotopic compositions and



trace element patterns in Samoan volcanics. Three years later, the latter authors reversed course and returned to the crustal-derived sediment recycling hypothesis I proposed (White and Hofmann, 1982) as a consequence of the extremely radiogenic Sr discovered in lavas from Samoan seamounts (Jackson *et al.*, 2007), but this idea nevertheless deserves some consideration. Workman *et al.* (2004) noted that the pattern of incompatible elements in Samoan lavas lacked the depletions in high field strength elements, Nb, Ta, Hf, Zr, and Ti, as well as the Pb enrichment typically observed in marine sediments. The idea is similar to that of McKenzie and O'Nions in that small-degree melts from the asthenosphere percolate into the oceanic lithosphere. Specifically, Workman *et al.* found that a lithosphere metasomatised by a 0.5% melt matched their calculated Samoan source well. According to them, about 1% of the oceanic lithosphere would be metasomatised in this way. There is evidence that the oceanic lithosphere can be metasomatically enriched (Hauri *et al.*, 1993). The idea also has the advantage that oceanic lithosphere clearly is recycled into the deeper mantle. The problem is that such metasomatism likely affects, as the model proposes, only a small fraction of the oceanic lithosphere, which remains overall incompatible element-depleted as a consequence of oceanic crust generation and there is no obvious way to concentrate these scarce enriched parts.

6.7 Evidence from Conventional Stable Isotopes

As we have seen, radiogenic and trace element evidence strongly constrain observed mantle heterogeneity to have developed in the outer part of the Earth: above the 670 km discontinuity. These data are more equivocal as to whether material at the Earth's surface has played a role. Stable isotopes can answer this question. The reason is, as noted earlier, that fractionation of isotopes between different species decreases with the square root of temperature and becomes nearly negligible in most cases at mantle temperatures. Oxygen isotope fractionations of greater than one per mille or so occur only when rock interacts with water at or near the surface of the Earth; hence oxygen isotopes are potential tracers of material that was once at the surface of the Earth. In addition, unique mass-independent fractionation of sulphur isotopes occurs only in the atmosphere, so those too provide tracers of surficial material in the mantle. Lithium, carbon, boron, nitrogen, magnesium, sulphur, chlorine, and iron isotopes also suggest that surficial material has found its way into the mantle.

Oxygen isotopes significantly different from the mantle value were found in subduction-related volcanics, suggesting sediment is being subducted to depths of 100 km or more (*e.g.*, Magaritz *et al.*, 1978). Furthermore, oxygen isotope ratios that are both well above and well below the mantle value ($\sim\pm 5.5\text{‰}$) have been found in eclogite xenoliths from kimberlites (*e.g.*, MacGregor and Manton, 1986; Pernet-Fisher *et al.*, 2014; Smart *et al.*, 2014). Eclogitic diamonds also show highly variable carbon (Mattey, 1987) and nitrogen (Marty and Dauphas, 2003) isotopic compositions. These variations strongly suggest that the eclogitic precursors



originated at or near the surface, most likely as oceanic crust, and had been carried into the upper mantle in ancient subduction zones and stranded in the subcontinental lithosphere. Walter *et al.* (2011) reported $\delta^{13}\text{C}$ between -15‰ and -24‰ in several diamonds that contain inclusions matching the compositions of basaltic phases in the lower mantle. Such carbon isotopic compositions strongly suggest an origin as biologically produced organic matter, which had apparently been subducted into the deep mantle and subsequently returned to the shallow mantle in the Cretaceous by a mantle plume rising beneath Brazil.

Perhaps the most dramatic discovery linking diamonds to the Earth's surface was mass-independent fractionation of sulphur in diamond sulphide inclusions (Farquhar *et al.*, 2002). Most isotopic fractionation is mass dependent, which is to say that the extent of the fractionation depends on the difference in mass between the two isotopes; thus, for example, the variation of the $^{33}\text{S}/^{34}\text{S}$ ratio is about half that of the $^{34}\text{S}/^{32}\text{S}$ ratio. Mass independent fractionation (MIF) refers to fractionation where this relationship does not hold and $\Delta^{33}\text{S}$, the per mille deviation from predicted mass-dependent fractionation, is a measure of this effect.

Mass-independent oxygen isotope fractionation is observed in the modern stratosphere and ultraviolet mass independent sulphur isotope fractionation of sulphur species has been demonstrated in laboratory experiments (see review of Thiemens, 2006). MIF sulphur is common in sedimentary and hydrothermal sulphides and sulphates in rocks older than 2.3 Ga, but disappears completely by 2.0 Ga (Farquhar *et al.*, 2000; Farquhar and Wing, 2003). There is a host of other evidence suggesting that significant amount of atmospheric oxygen first developed just prior to 2.3 Ga (reviewed in Kasting and Catling, 2003). Farquhar and Wing reasoned that in the absence of oxygen and ozone, ultraviolet radiation could penetrate through the whole atmosphere and fractionate atmospheric sulphur, but the development of stratospheric ozone around 2.3 Ga severely limited the penetration of ultraviolet radiation into the troposphere, ending mass-independent fractionation of sulphur. Thus the diamonds analysed by Farquhar *et al.* (2002) apparently contain sulphur that had cycled through the atmosphere in the Archean or earliest Proterozoic and was subsequently subducted and stored in the subcontinental lithosphere.

Stable isotope ratios in diamonds and eclogites thus clearly confirm the subduction of crustal material into the shallow mantle, but is there evidence that it can be carried into the deep mantle? Eiler *et al.* (1997) found significant oxygen isotope variations in some oceanic island basalts. Unlike the Ito *et al.* (1987) study of oxygen isotopes in MORB described earlier, Eiler *et al.* analysed oxygen in individual olivine phenocrysts, which has the advantage of avoiding weathering effects. There is about a 0.5 ‰ fractionation of $\delta^{18}\text{O}$ between olivine and basaltic liquid, so that mantle olivine has $\delta^{18}\text{O}_{\text{SMOW}} \approx +5.2\text{‰}$ compared to the average MORB value of $\approx +5.7\text{‰}$. Eiler *et al.* reported $\delta^{18}\text{O}_{\text{SMOW}}$ values as high as 6.1 ‰ in basalts from the Society Islands. Basalts from these islands have particularly high $^{87}\text{Sr}/^{86}\text{Sr}$ and low ϵ_{Nd} and were the ones that White and Hofmann (1982) argued provided the best case for recycled crustal material.



Sedimentary materials typically have high $\delta^{18}\text{O}_{\text{SMOW}}$, as high as +20 ‰ in shales or +30 ‰ in limestones. Assuming a $\delta^{18}\text{O}_{\text{SMOW}}$ of +15 ‰, Eiler *et al.* calculated that the mantle source of Society Islands lavas contained up to 5% of a sedimentary component. Elevated $\delta^{18}\text{O}$ also occurs in Samoan peridotite xenoliths and Eiler *et al.* suggested that they too could contain a recycled sedimentary component. Subsequently, Workman *et al.* (2008) reported variations of $\delta^{18}\text{O}$ in olivines in Samoan lavas that correlated positively with $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ and incompatible element ratios, confirming the presence of recycled material in the source of Samoan lavas (Fig. 6.8).

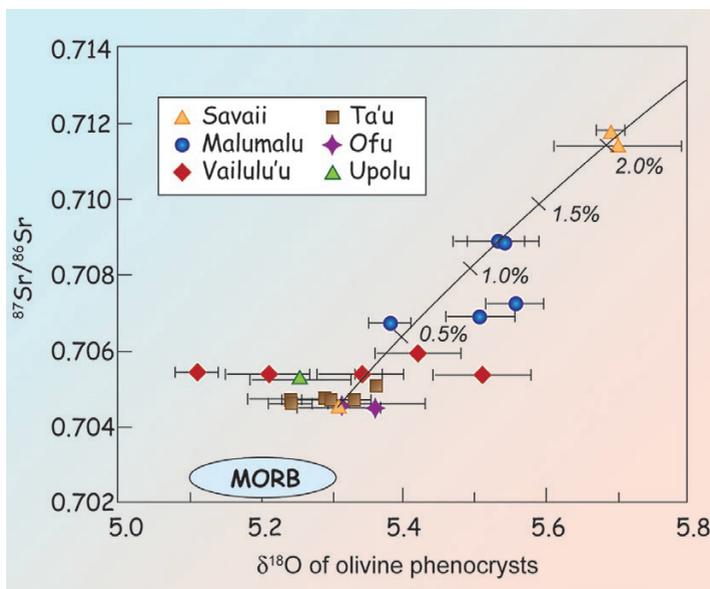


Figure 6.8 $^{87}\text{Sr}/^{86}\text{Sr}$ in Samoan lavas plotted against oxygen isotope ratios measure in olivine phenocrysts. Line shows a mixing model between clastic sediment addition ($\delta^{18}\text{O} = 25$ ‰, $\text{Sr} = 250$ ppm, $^{87}\text{Sr}/^{86}\text{Sr} = 0.75$) to the least enriched Samoan mantle component in Ta'u lavas (data from Workman *et al.*, 2008).

Eiler *et al.* (1997) also found that some basalts from other island chains, particularly those with the HIMU isotopic signature, had low $\delta^{18}\text{O}_{\text{SMOW}}$. Low $\delta^{18}\text{O}_{\text{SMOW}}$ can be produced by hydrothermal interaction between water and rock, and Eiler *et al.* suggested that the low values reflected assimilation of hydrothermally altered material in the volcanic edifice. However, the remarkable discovery of MIF sulphur in olivine sulphide inclusions from one of these islands, Mangaia of the Cook-Austral chain (Cabral *et al.*, 2013), suggests that these low $\delta^{18}\text{O}$ values reflect the presence of very ancient recycled hydrothermally altered oceanic crust rather than modern assimilation.



Cabral *et al.*'s discovery is one of the most remarkable ones in mantle geochemistry because it both unequivocally demonstrates the presence of recycled surficial material in the mantle and constrains the age of this material to be 2.3 billion years or older. As I explained earlier, such MIF sulphur appears to have been exclusively produced by photolysis when ultraviolet radiation could penetrate deeply into the atmosphere prior to the Great Oxidation Event. Unlike carbon, nitrogen, and sulphur evidence for surficial material in diamonds, the sulphur in Mangaia olivines could not have been stored in the subcontinental lithosphere and must have come from the convecting mantle, most likely the deep mantle.

Mass independent sulphur fractionation in the early Earth produced oxidised sulphur with negative $\Delta^{33}\text{S}$ anomalies and reduced sulphur with positive $\Delta^{33}\text{S}$ anomalies. Cabral *et al.*'s data are shown in Figure 6.9. They (with one exception) exhibit negative $\Delta^{33}\text{S}$ anomalies, which are characteristic of Archean barites and hydrothermal sulphides (Farquhar and Wing, 2003), in contrast to sulphides in diamonds, which exhibit positive $\Delta^{33}\text{S}$ anomalies. This led Cabral *et al.* to argue that anciently subducted hydrothermally altered oceanic crust was the carrier of the mass independently fractionated sulphur.

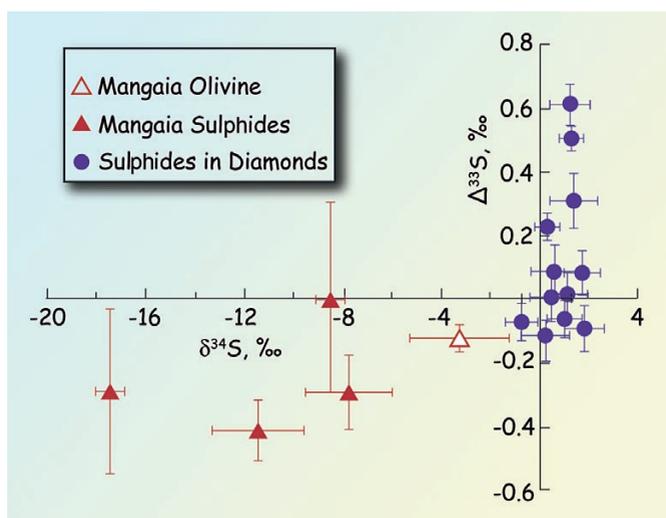


Figure 6.9 Sulphur isotope ratios in sulphide inclusions in olivines (triangles) from Mangaia, Austral-Cook Islands (Cabral *et al.*, 2013) and in diamonds (circles) from the Orapa kimberlite pipe in Botswana (Farquhar *et al.*, 2002).

Labidi *et al.* (2013) reported new high precision sulphur isotope data for MORB and showed that $\delta^{34}\text{S}_{\text{CDT}}$ in MORB is negative, in contrast to previous work that indicated that mantle $\delta^{34}\text{S}_{\text{CDT}}$ was close to the chondritic value of ~ 0 ‰. More significantly, they found that $\delta^{34}\text{S}$ in MORB from the South Atlantic



correlates positively with $^{87}\text{Sr}/^{86}\text{Sr}$ and negatively with $^{143}\text{Nd}/^{144}\text{Nd}$ (Fig. 6.10). They interpreted these correlations as evidence of mixing between a DMM component with $\delta^{34}\text{S}_{\text{CDT}} \approx 1.5$ ‰ and an ‘enriched’ component associated with the Discovery and Shona mantle plumes. They argue the data are most consistent with the enriched component being recycled sediment with $\delta^{34}\text{S}_{\text{CDT}} \approx +10$ ‰. They found no evidence of mass-independent fractionation ($\Delta^{33}\text{S}$ and $\Delta^{36}\text{S} = 0$ within error), which implies that the recycled component is of Proterozoic or younger age. Subsequently, Labidi *et al.* (2015) reported $\delta^{34}\text{S}$ values ranging from +0.11 ‰ to +2.79 ‰ in the reduced sulphur fraction of Samoan lavas (the subordinate sulphate fraction had higher $\delta^{34}\text{S}$). Furthermore, $\delta^{34}\text{S}$ in the reduced sulphur correlated with $^{87}\text{Sr}/^{86}\text{Sr}$ in glasses (Fig. 6.10). They argued the correlation “requires the EM-2 endmember to be relatively S-rich, and only sediments can account for these isotopic characteristics.”

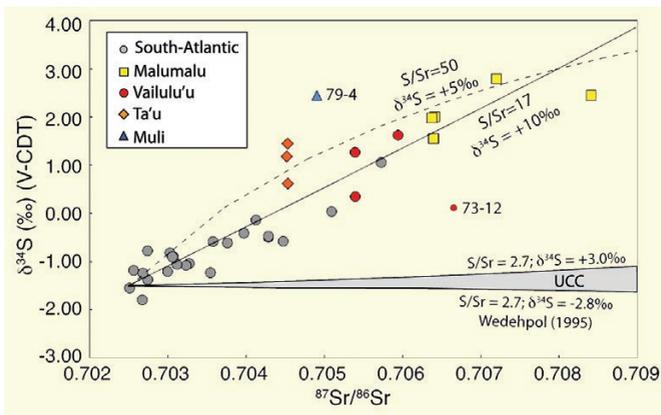


Figure 6.10 $\delta^{34}\text{S}_{\text{CDT}}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ in lavas from Samoan volcanoes (Malumalu, Vailulu'u, Ta'u, and Muli) and MORB from the South Atlantic. Also shown are mixing curves between a mantle component and potential sedimentary or upper crustal end-members with distinct $\delta^{34}\text{S}$ and S/Sr ratios (modified from Labidi *et al.*, 2015).

6.8 Evidence from Unconventional Stable Isotopes

Over the last couple of decades stable isotope geochemistry has greatly expanded beyond the traditional list of H, O, C, N, and S to include other light elements such as lithium and boron as well as heavier metals such as Mg, Cl, Ca, Fe, and U. Fractionation of the latter are small, a few per mille at most, but because the relative mass differences between isotopes are large, fractionations of tens of per mille are observed for Li and B. Just as is the case for the ‘traditional’ stable isotopes, fractionation decreases with the square of temperature and become



small or negligible in most cases at mantle temperatures. Thus significant variation in the isotopic composition of these elements in mantle-derived rocks has most likely originated in a near-surface environment in most cases.

Additional support for the antiquity of OIB sources has recently been reported by Andersen *et al.* (2015) who found that $^{238}\text{U}/^{235}\text{U}$ in MORB and OIB differ, with OIB values similar to bulk Earth values, and MORB values slightly ^{238}U enriched. Uranium isotope fractionation results almost exclusively from redox reactions at low temperature – reactions that only became possible when atmospheric and marine oxygen levels rose sufficiently to oxidise U^{4+} to U^{6+} in the Palaeoproterozoic (although the Earth's atmosphere first became oxidising around 2.4 Ga, levels remained sufficiently low through most of the Proterozoic that the deep ocean remained anoxic). They argue that isotopically fractionated U recycled from the surface during the Phanerozoic has extensively polluted the upper mantle, while OIB sources contain Precambrian recycled material with unfractionated uranium.

The $^7\text{Li}/^6\text{Li}$ ratio, usually expressed as $\delta^7\text{Li}$, *i.e.* per mille deviations from a laboratory standard, shows a range of variation in terrestrial materials of over 50 ‰, or 5 %. For background, the continental crust appears to have average $\delta^7\text{Li}$ of +1.2 ‰ (Teng *et al.*, 2009), modern seawater has a uniform composition at $\delta^7\text{Li} = +31$ ‰ (*e.g.*, Jeffcoate *et al.*, 2004), but seawater $\delta^7\text{Li}$ has increased by about 7 ‰ over the Cenozoic (Misra and Froelich, 2012). Fresh mantle peridotite has $\delta^7\text{Li} = +3.5 \pm 0.5$ ‰, similar to carbonaceous and ordinary chondrites (2.96 ± 0.77 ‰) (Pogge von Strandmann *et al.*, 2011). This value presumably represents the bulk silicate Earth or primitive mantle value. $\delta^7\text{Li}$ values in MORB, $+3.7 \pm 1$ ‰ (± 1 sigma), are similar. In the marine environment, low temperature alteration appears to involve primarily uptake of Li from seawater and a consequent increase in both Li concentration and $\delta^7\text{Li}$, with altered MORB having an average $\delta^7\text{Li}$ of +11.3 ‰ (Elliott *et al.*, 2006). In contrast, hydrothermal metamorphism extracts Li from basalt, with ^7Li extracted more readily than ^6Li , so that both Li concentration and $\delta^7\text{Li}$ decrease in the process (Chan *et al.*, 2002). The net effect of low and high temperature seawater interaction is not entirely clear, but appears to result in a decrease in Li concentration and $\delta^7\text{Li}$ of the oceanic crust (Misra and Froelich, 2012). $\delta^7\text{Li}$ of clastic sediment tends to be lighter (-3 to $+5$ ‰) than that of biogenic sediment ($+6$ to $+15$ ‰) so that subducting sediment varies among subduction zones from about -1 to $+9$ ‰ (Plank, 2014).

Thus subducting lithosphere can potentially have both higher and lower $\delta^7\text{Li}$ than primitive mantle. Subduction-related basalts have $\delta^7\text{Li} = +4.05 \pm 1.5$ ‰, just slightly, but not significantly, higher than MORB.

Li is a quite reactive, mobile element and its concentration and isotopic composition is readily changed during weathering and metamorphism. And although equilibrium fractionations appear to be small during melting and crystallisation (Tomascak *et al.*, 1999), the small size and mass of the Li ion result in large kinetic fractionations during diffusion which could lead to second order effects (Teng *et al.*, 2006; Gallagher and Elliott, 2009). In addition, assimilation



of altered oceanic crust or sediment could affect $\delta^7\text{Li}$ in oceanic basalts, and Genske *et al.* (2014) have argued that such a process accounts for highly variable Li and B isotopic compositions observed in the western Azores islands of Corvo and Flores. Thus some caution is necessary in interpreting Li isotope ratios in oceanic basalts. In the following I have excluded samples where weathering or assimilation effects are suspected.

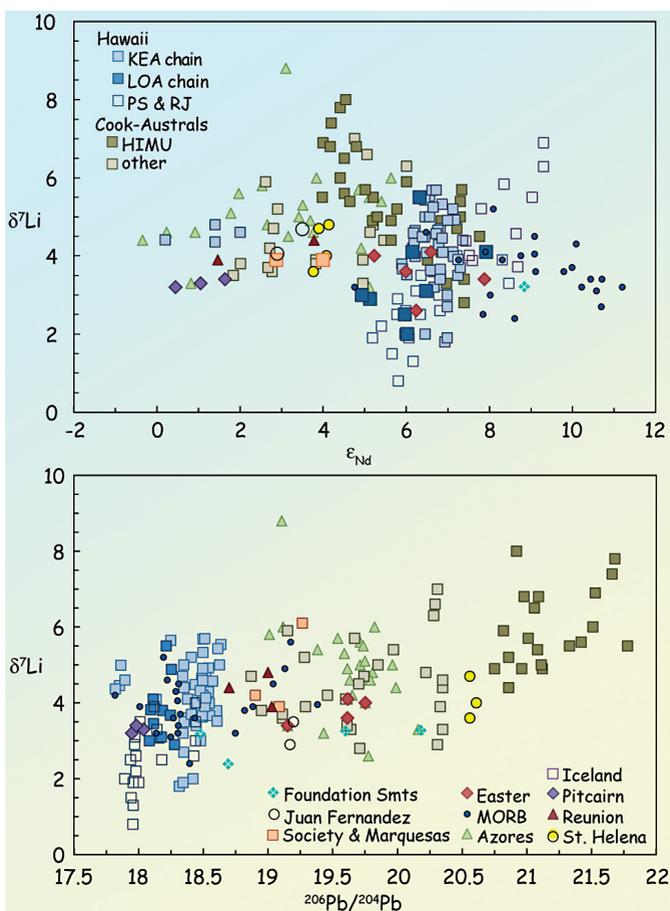


Figure 6.11 Li, Pb, and Nd isotope ratios in oceanic basalts.

Figure 6.11 shows $\delta^7\text{Li}$ in oceanic basalts as a function of $^{206}\text{Pb}/^{204}\text{Pb}$ and ϵ_{Nd} . Values both below and above the primitive mantle value occur and there is a trend of increasing $\delta^7\text{Li}$ with increasing $^{206}\text{Pb}/^{204}\text{Pb}$ and decreasing ϵ_{Nd} , which it is statistically significant. Elliott *et al.* (2006) reported a correlation between



$\delta^7\text{Li}$ and ϵ_{Nd} in East Pacific Rise MORB; a similar trend can be seen for MORB in Figure 6.11, but the correlation between $\delta^7\text{Li}$ and ϵ_{Nd} (or either $^{87}\text{Sr}/^{86}\text{Sr}$ or $^{206}\text{Pb}/^{204}\text{Pb}$) in MORB is not statistically significant. Hawaiian basalts show a particularly large range in $\delta^7\text{Li}$, which correlates significantly with $^{206}\text{Pb}/^{204}\text{Pb}$ but not ϵ_{Nd} . Volcanoes of the Loa trend have, on average, lower $\delta^7\text{Li}$ than volcanoes of the Kea trend and the post-shield and rejuvenescent stage lavas have systematically lower $\delta^7\text{Li}$ than both Loa and Kea shield lavas (Harrison *et al.*, 2015). There are considerable data from the Austral-Cook Islands and, as Chan *et al.* (2009) noted, the $\delta^7\text{Li}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ correlation exists in this data set alone. Chan *et al.* also analysed olivine compositions in Cook-Austral samples and found some examples of disequilibrium, which they attributed to post-eruptive alteration (those samples and others where secondary effects are suspected were excluded from Fig. 6.11). They nevertheless concluded that “the heavy $\delta^7\text{Li}$ values in HIMU olivines are a source characteristic” and that these “lavas derive from a source containing recycled dehydrated oceanic crust, and that the “heavy” Li-isotope signature of altered oceanic crust is partially preserved during passage through the subduction factory”. In contrast to the isotopically heavy lithium observed in HIMU lavas, EM I and EM II type lavas from Pitcairn, the Koolau Series of Oahu, the Societies, Marquesas, and Azores tend to exhibit decreasing ^7Li with decreasing ϵ_{Nd} , suggesting the presence of a continental or marine sedimentary component. Krienitz *et al.* (2012) concluded that “The Li contents and isotope characteristics of HIMU-type lavas are consistent with recycling of altered and dehydrated oceanic crust, whereas those of the EM1-type lavas can be attributed to sediment recycling.” While it is certainly speculative at this point to associate specific Li isotopic compositions in OIB with specific crustal components, the Li isotope data nonetheless provide evidence that the mantle has been extensively polluted by material from the surface of the Earth.

Boron isotope ratios, like lithium, show wide variation at the surface of the Earth, with a range in the $^{11}\text{B}/^{10}\text{B}$ ratio, usually expressed as $\delta^{11}\text{B}$, of about 70 ‰. Seawater, with $\delta^{11}\text{B} = +39.6$ ‰, represents one end of this range. Most marine sediments have positive $\delta^{11}\text{B}$ while continental rocks, sediments, and hydrothermal solutions generally have negative $\delta^{11}\text{B}$. If this material is subducted into the deep mantle, it should result in boron isotopic heterogeneity of the mantle. Indeed, subduction-related basalts show a clear and systematic offset to more positive $\delta^{11}\text{B}$ values compared to mid-ocean ridge and intraplate basalts, clearly indicating that surficial boron is subducted into the mantle.

There are, however, relatively few data on OIB and MORB. This may in part be because, as Brounce *et al.* (2012) point out, “due to the very low concentrations of B in mantle-derived melts and the strong isotopic contrast between the mantle and surface materials”. Because of the latter boron isotope ratios may have more “potential for tracing alteration and assimilation in basaltic systems” than in identifying recycled material in the mantle. In particular, boron is present at relatively high concentrations in seawater. While MORB are uniform in isotopic composition compared to other basalts, they nevertheless show a surprisingly large range in boron isotopic composition ($\delta^{11}\text{B}$ -10.5 ‰ to +2.06 ‰). This likely reflects assimilation of hydrothermally altered oceanic crust in amounts too small to affect most other chemical and isotopic parameters (Chaussidon and Marty, 1995; Gannoun *et al.*, 2007).



Combined boron, lithium, and oxygen isotope data also suggest that assimilation of altered oceanic crust has occurred in the eastern Azores islands of Corvo and Flores (Genske *et al.*, 2014), but because of the similarity of composition, this has little or no effect on radiogenic isotope ratios.

Disequilibrium between melt inclusions and fresh glass in some Icelandic lavas, notably those from the 1783 Laki eruption, provides evidence in support of this view (Gurenko and Chaussidon, 1997; Brounce *et al.*, 2012). One of the consequent difficulties is ascertaining the boron isotopic composition of depleted and primitive mantle. Based principally on mass balance, Chaussidon and Marty (1995) estimated the boron isotopic composition of both to be about -10 ‰. Iceland and the Galápagos mantle appear to have $\delta^{11}\text{B}$ close to this value, but values are systematically higher, 7 ‰ to -3 ‰ in unaltered Azores and Hawaii samples (Tanaka and Nakamura, 2005; Turner *et al.*, 2007). Overall, $\delta^{11}\text{B}$ correlates significantly at the 99 % level with $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} in OIB. The correlation with $^{87}\text{Sr}/^{86}\text{Sr}$, however, is opposite what Yamaoka *et al.* (2012) observe in the Oman ophiolite. In Oman, $\delta^{11}\text{B}$ of the oceanic crust increased in both low-temperature and high-temperature hydrothermally altered sections with the latter having generally higher $\delta^{11}\text{B}$ and lower $^{87}\text{Sr}/^{86}\text{Sr}$. However, marine sediments generally have positive $\delta^{11}\text{B}$ and have high $^{87}\text{Sr}/^{86}\text{Sr}$, so the correlation could reflect sediment recycling. On the other hand, it appears that boron is nearly quantitatively extracted from subducting sediment in subduction zones (Ryan and Chauvel, 2014). It seems that on balance boron isotopes provide some evidence of recycled surficial materials in the mantle, but assimilation of altered rocks in the crust by rising magmas partially obscure the picture.

Mg, Fe, and Cl isotopes may also provide evidence of recycling of surficial material into the mantle, but this remains tentative at best at this stage. The $^{26}\text{Mg}/^{24}\text{Mg}$ ratio is generally expressed as $\delta^{26}\text{Mg}$ in per mille deviations from the DMS3 standard. Iron isotope ratios, either $^{56}\text{Fe}/^{54}\text{Fe}$ or $^{57}\text{Fe}/^{54}\text{Fe}$ are generally expressed as $\delta^{56}\text{Fe}$ or $\delta^{57}\text{Fe}$ in per mille variations from the IRMM-14 standard. Because all Fe isotope fractionations observed to date are mass-dependent, $\delta^{56}\text{Fe} = \delta^{57}\text{Fe} \times 0.67$. Both $\delta^{26}\text{Mg}$ and $\delta^{56}\text{Fe}$ exhibit small but significant variations in oceanic basalts and basalts from the Society Islands are on average higher than in both Hawaii and MORB (Teng *et al.*, 2010; Teng *et al.*, 2013) and the difference is statistically significant ($\delta^{26}\text{Mg}$: Society Is.: = -0.29 ± 0.3 ‰, Hawaii = 0.24 ± 0.03 ‰, MORB = -0.25 ± 0.03 ‰; $\delta^{56}\text{Fe}_{\text{IRMM-14}}$: Society = $+0.14 \pm 0.02$ ‰, Hawaii = $+0.10 \pm 0.04$ ‰, MORB = $+0.10 \pm 0.02$ ‰). Furthermore, Mg and Fe isotopes in these basalts appear to be anti-correlated. Some fractionation of both Mg and Fe isotope ratios occurs during partial melting and fractional crystallisation, but these fractionations cannot readily explain the above differences.

Some of the Fe isotope variation may be due to small (0.15 to 0.2 ‰) but significant fractionation that occurs between pyroxene and olivine due to differences in bonding environment (Williams and Bizimis, 2014). Williams and Bizimis found that iron in garnet pyroxenites from Hawaii is on average isotopically heavy ($\delta^{57}\text{Fe}_{\text{IRMM-14}} = +0.10$ to $+0.27$ ‰) compared to depleted peridotites (-0.34 to $+0.14$ ‰), primitive mantle ($\sim +0.14$ ‰), and MORB ($\sim +0.16$ ‰). They also found that $\delta^{57}\text{Fe}$ inversely correlates with several indicators of melt depletion



in Oahu peridotites and pyroxenites as well as ϵ_{Hf} (Fig. 6.12). They suggested that the isotopically heavy iron observed in some OIB, notably the Society and Austral Islands, is due to the presence of pyroxenites, perhaps derived from recycled oceanic crust and sediment in the sources of these islands. The isotopically light Fe in depleted peridotites was particularly problematic in their view and appeared to require multiple episodes of melt depletion.

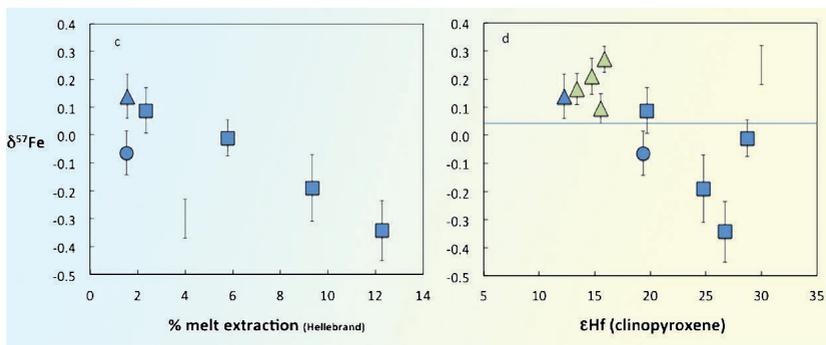


Figure 6.12 $\delta^{57}\text{Fe}$ as a function of calculated melt depletion and ϵ_{Hf} in Hawaiian peridotite (blue) and pyroxenite (green) xenoliths (modified from Williams and Bizimis, 2014).

The largest fractionations in Fe isotopes occur as a consequence of redox reactions at low temperature, in which Fe^{3+} can be several per mille heavier than Fe^{2+} (e.g., Johnson *et al.*, 2008). Cottrell and Kelley (2014) reported that when corrected for low-pressure fractional crystallisation, basalts from Samoa, Hawaii, Pitcairn and the Society Islands all have higher $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios than MORB, implying the former are derived from more oxidised mantle sources. Furthermore, they found that $\text{Fe}^{3+}/\Sigma\text{Fe}$ correlated with $^{87}\text{Sr}/^{86}\text{Sr}$. They inferred that “a variety of processes, including recycling of surface-derived materials, generate redox heterogeneities in the mantle that persist and influence OIB petrogenesis.” One can’t help but speculate that the more oxidised state of these OIB might also partly explain the heavier Fe isotope ratios observed in them. Certainly this is a subject that deserves further research.

Variation of chlorine isotope ratios in oceanic basalts also suggests the presence of recycled surficial material in the deep mantle. However, contamination issues are particularly acute in this case, given the high concentration of chlorine in seawater. Chlorine is also present in rainwater, particularly near the ocean, so the contamination potential extends to subaerial as well as submarine basalts. Seawater has $\delta^{37}\text{Cl}$ of 0 ‰ (by definition) and low-Cl MORB have $\delta^{37}\text{Cl}$ of -3 ‰ to ~0 ‰. Higher ratios are present in high-Cl MORB and Bonifacie *et al.* (2008) showed that they correlate with Cl content. The most likely explanation is assimilation of Cl-rich brines or hydrothermally altered rocks within the oceanic crust. The sparse data on $\delta^{37}\text{Cl}$ in OIB suggests they have generally higher values



than MORB, with $\delta^{37}\text{Cl}$ ranging from -1.5‰ to $+3\text{‰}$. There is also a statistically significant correlation between $\delta^{37}\text{Cl}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in oceanic basalts overall and a systematic variation among island chains, with values similar to MORB in St. Helena and the highest values occurring in the Society Islands (John *et al.*, 2010). Other than high-temperature fumaroles, where large fractionations can occur in association with Rayleigh distillation and condensation of hydrothermal fluids, the isotopically heaviest Cl is observed in serpentinised peridotite, and it may be recycling of this material that imparts the heavy Cl signature to some OIB. It may be premature to conclude that we are seeing a recycled signal in Cl isotope ratios, but further work on this is certainly warranted.

6.9 A Primitive Signal as Well

Although a recycled signature seems present in many, if not all, mantle plumes, many also contain a remarkably primitive noble gas signature. Noble gases are the subject of another *Geochemical Perspectives* (Moreira, 2013), but they place such important constraints on mantle evolution that brief mention here is necessary. A primitive noble gas signature is most commonly manifested in elevated $^3\text{He}/^4\text{He}$ ratios as described in Section 3.1. It is, however, somewhat equivocal in demonstrating a truly 'primitive' signal. Because Earth's initial He concentration and the U-Th/He ratio are poorly constrained, so is the evolution of $^3\text{He}/^4\text{He}$ in the Earth through time. Thus high $^3\text{He}/^4\text{He}$ ratios merely require a contribution from a somewhat less degassed reservoir, although one that has likely been isolated from the convecting mantle for at least 3 Ga (Porcelli and Elliott, 2008). However, other noble gas isotope ratios, including those of neon and argon, but particularly those of xenon, imply that some plumes contain a very primitive component indeed and one that has been isolated for all or nearly all of Earth's history. Xenon isotopic composition varies because of decay of two extinct radionuclides: ^{129}I , which decays to ^{129}Xe with a 15.7 million year half-life and ^{244}Pu , which has a 82 million year half-life and whose principal fission products include the heavy Xe isotopes (Xe isotopic composition also varies due to mass-dependent fractionation and fission of ^{238}U). $^{129}\text{Xe}/^{130}\text{Xe}$ ratios in OIB are higher than in the atmosphere and are higher still in MORB (Staudacher and Allègre, 1982; Mukhopadhyay, 2012). These differences, as well as those in heavy fissionogenic Xe isotopes, must have been established within the first 100 million years of Earth's history and require the Iceland plume source, and perhaps others, to be less degassed than the MORB source and any subsequent mixing between them and the atmosphere over the next nearly 4.5 billion years to have been limited (Mukhopadhyay, 2012). Furthermore, the MORB and OIB reservoirs appear to have distinctly different ratios of non-radiogenic He to Ne (*i.e.* $^3\text{He}/^{22}\text{Ne}$) inherited from the earliest part of Earth's history (Tucker and Mukhopadhyay, 2014). This primitive signal appears to be confined to noble gases. Exactly how some plumes sample both a recycled and an extremely primitive signature is one of the more vexing and fascinating problems in mantle geochemistry and I'll return to this topic in Section 9.3.



7.

GOING DOWN: SUBDUCTION, SUBDUCTION EROSION AND CRUSTAL FOUNDERING

Return of oceanic crust to the mantle through subduction was explicitly part of plate tectonic theory (Isacks *et al.*, 1968; Le Pichon, 1968), but it took longer for the idea that sediment, and therefore indirectly continental crust, could also be subducted into the mantle. Here again, *Dick Armstrong* along with *Mitsunobu Tatsumoto* were ahead of the crowd. Tatsumoto (1969) wrote that “a mixture of one to two percent of oceanic sediment with abyssal tholeiite can roughly make a balance sheet for the Pb, U, and Th concentrations in the Japanese tholeiite.” Armstrong (1971), comparing Pb isotope ratios in marine sediments and in subduction related volcanics from the Lesser Antilles and New Zealand, concluded “recycling of crustal material through the mantle seems the best explanation for the Pb isotopic similarity of volcanic arc magmas and oceanic sediments.” Based on incompatible element ratios, Jakeš and Gill (1970) also suggested that subducted sediment contributed to island arc lavas.

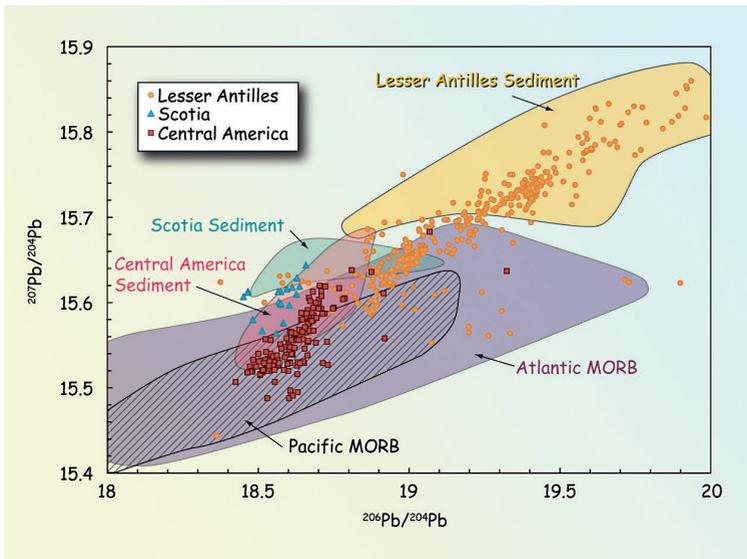


Figure 7.1

Pb isotope ratios in volcanics from three subduction zones compared with sediments on the adjacent subducting plate (data from GEOROC <http://georoc.mpch-mainz.gwdg.de/georoc/> and SedDB <http://www.earthchem.org/seddb>).

Figure 7.1 makes *Armstrong's* point with an updated data set for three very different subduction zones: the South Shetland/Scotia arc, the Lesser Antilles arc, and the central and northern Central American arc. Pb isotopic compositions in volcanics from the three arcs are quite distinct, but in each case, in *Armstrong's*



(1971) words, “close correlation exists between average $^{206}\text{Pb}/^{204}\text{Pb}$ for each arc and for ocean floor sediments in front of the respective arcs.” The Lesser Antilles, a focus of Armstrong’s original work, provides particularly strong evidence of the influence of subducting sediment on arc lava compositions. Because of the proximity to the South American continent and particularly the mouth of the Orinoco River, there is a strong north-south gradient in the isotopic composition of sediments in front of the arc (White *et al.*, 1985) that is matched by a north-south gradient in the isotopic compositions of arc lavas (White and Dupré, 1986; Carpentier *et al.*, 2008). Strengthening the case for the role of subducted sediment, Plank and Langmuir (1993) demonstrated a correlation between the sediment subduction flux of incompatible elements and the concentrations of those elements in lavas of the respective island arc.

Of course, *Tatsumoto’s* simple mixing hypothesis is an oversimplification, and Pb isotopes in arc lavas often reflect additional complexities. For example, there is good evidence for crustal assimilation in a few volcanoes in the Lesser Antilles and Central America (*e.g.*, Davidson, 1985; Cigolini, 1998). In the southern Central American arc (data not shown in Fig. 7.1), there is additional complexity due to the presence of Galápagos plume-related mantle beneath the region (Patino *et al.*, 2000; *e.g.*, Gazel *et al.*, 2011). Finally, the source of island arc magmas is not simply a mixture of subducting sediment, basalt, and mantle, although one can see physical mixtures of these materials in subduction complexes such as the Catalina schist (Bebout and Barton, 1989). The Franciscan Formation exposed in Big Sur along California Route 1 is another example. The road is full of twists and turns as if follows the steep coast and the scenery is spectacular, so it can be hard to pay attention to the rocks. But if you look, you will see serpentinised peridotite just around the bend from a mélange of pillow basalt and sediment. That aside, we now understand that arc basalts are produced by melting of a mantle wedge modified by fluids and melts derived from the subducting lithosphere, as Jakeš and Gill (1970) had presciently realised.

This point is made by Figure 7.2, which compares incompatible element abundances in MORB and global average subducting sediment (GLOSS, Plank, 2014) to an island arc tholeiitic basalt from Vanuatu, and an island arc andesite from the Aleutians. Compared to a mixture of MORB and a few percent sediment, island arc volcanics (IAV) are enriched in Ba, U, K, Sr, and Pb but depleted in Th, Nb and Ta, even after considering plausible melting and fractional crystallisation effects. Generally those elements most strongly enriched in IAV are “fluid-mobile”, *i.e.* relatively soluble in hydrous solution, while those not enriched or depleted, are highly insoluble. Magma generation in subduction zones is complex, arguably much more so than in other tectonic environments. A detailed examination would take us too far afield from the focus here, which is what goes down, so the reader is referred to reviews such as those of Stern (2002), Tatsumi (2005) and Grove *et al.* (2006).



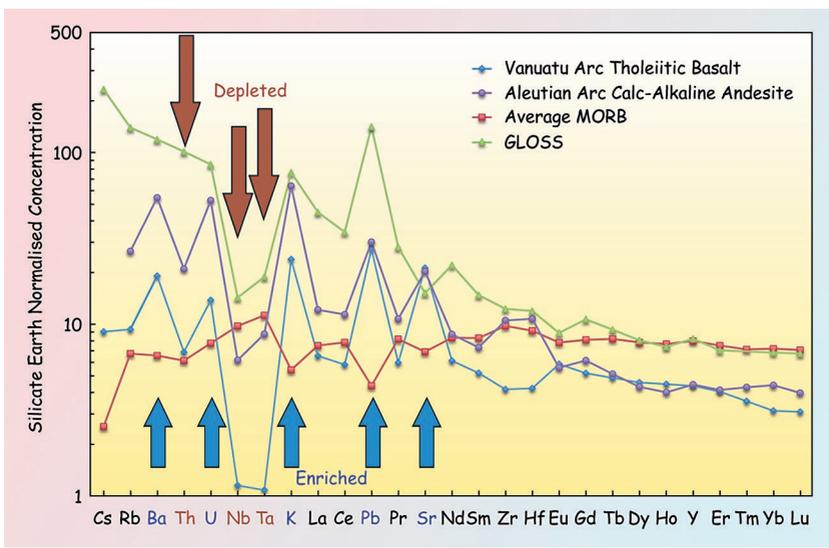


Figure 7.2 Incompatible element abundances in island arc volcanics compared to MORB and average subducting sediment. Fluid-mobile elements, notably Ba, U, K, Pb, and Sr, are more enriched in IAV than can be explained by sediment-ocean crust-mantle mixing while other elements, notably Th, Nb, and Ta are depleted compared to such a mixture. Vanuatu basalts from Peate *et al.* (1997), Aleutian andesite from unpublished data of Tibbets, Kay, and White, GLOSS from Plank (2014) and MORB from White and Klein (2014).

7.1 The Craziest Idea Ever?

While there is little doubt today that subducting sediment contributes Pb to arc lavas, that was not always so. The development of accretionary prisms in some subduction zones, such as Japan, Oregon, and the Lesser Antilles, implied that sediment was too soft to be subducted and was simply scraped off. *Dave Scholl* and others (Scholl *et al.*, 1980) pointed out that while accretionary prisms were indeed forming adjacent to some subduction zones, in others, such as the Marianas, no sediment was accumulating and in still others, such as the Chilean margin, not only was no sediment accumulating, the forearc itself appeared to be eroding – a topic I’ll return to below. Nevertheless, the debate over whether sediment was actually subducted and the degree it contributed to arc magmatism continued (*e.g.*, Karig and Kay, 1981; Stern, 1982; Whitford and Jezek, 1982). During some of those years, I was a post-doc at the Department of Terrestrial Magnetism (DTM) of the Carnegie Institution of Washington. As often happens to research institutions, DTM’s focus had shifted over the years. It was initially set up in 1904 to map the Earth’s magnetic field and variations thereof, but it’s mission began to



evolve when the ship built for the purpose, the Carnegie, burned in Apia, Upolu, Samoa, in 1929. One of the subsequent areas of research was nuclear physics, and Van der Graaff and cyclotron accelerators had been built for that purpose (the Van der Graaff had been artfully disguised as an astronomical observatory so as not to upset the neighbours). By the time I arrived, however, the forefront of research in nuclear physics had long since moved on to much higher energies than these accelerators could produce and that area of research had largely been abandoned, with a single nuclear physicist, *Lou Brown*, remaining on the staff. *Fouad Tera*, formerly principal Pb isotope geochemist and general all around chemical magician in *Jerry Wasserburg's* 'Lunatic Asylum' at Cal Tech, had just been hired to replace *Stan Hart* as a staff scientist in geochemistry. In addition to geochemistry, geophysics, planetary science, and astrophysics were, and remain, areas of research focus at DTM. There was considerable interest in subduction zones, the Andes in particular, among both the geochemists and geophysicists, and indeed one of the seismologists, *Dave James*, became a full time geochemist for a while, before being once again seduced by the Dark Side of the Force and returning to his very successful career in seismology. My officemate at the time was *Dave Whitford*, who was studying arc volcanism in Indonesia and was very much interested in the question of the role played by subducted sediment in arc volcanism. This odd array of scientific talent led to several interesting collaborations. One, between *Whitford* and *James* and another post-doc at the time, *Mordecai Magaritz*, led to pioneering work using oxygen isotopes in arc lavas as a measure of the crustal contribution (Magaritz *et al.*, 1978). A collaboration between *Brown*, *Tera*, *Whitford*, and another DTM post-doc, *Sundar Rajan*, a planetary scientist, while innovative, was less successful: they attempted to measure Li isotopic compositions in meteorites and terrestrial rocks using the Van der Graaff accelerator by analysing the energy spectra of ${}^6\text{Li}({}^2\text{H}, \alpha){}^4\text{He}$ and ${}^7\text{Li}({}^2\text{H}, \alpha){}^5\text{He}(\text{n}){}^4\text{He}$ reactions (Brown *et al.*, 1977, 1978). The one percent precision they achieved was impressive, but ultimately insufficient to be truly useful.

It was, however, another idea, first suggested by *Sundar Rajan* as I recall, that eventually provided nearly indisputable evidence that sediment was indeed being subducted and finding its way into arc magmas. *Sundar*, who had worked on cosmogenic nuclides in meteorites, suggested looking for evidence of ${}^{10}\text{Be}$ in arc lavas as a way to demonstrate a subducted sedimentary component. ${}^{10}\text{Be}$ is created in extremely small quantities by cosmic ray spallation reactions on nitrogen and oxygen in the atmosphere. It is quickly washed out by rain and adsorbed on soil and sedimentary particles and decays to ${}^{10}\text{B}$ with a half-life of 1.5 million years. Since cosmic rays don't penetrate the solid Earth to depths of much more than a metre, none should be present in the Earth's interior. Hence if found in lavas and contamination could be ruled out, it would be possible to demonstrate that the source of those lavas contained a component that had been at the surface of the Earth as recently as a few million years earlier. Back of the envelope calculations suggested that the amount one might expect in arc lavas would be something on the order of 10^7 atoms per gram (Brown *et al.*, 1980), extraordinarily small quantities. *Dave Whitford* and I frankly thought the idea of detecting such quantities in arc lavas was ludicrous – the craziest idea we had



ever heard. We ribbed *Sundar* unmercifully about it. However, *Fouad Tera* saw it as a challenge and *Lou Brown* saw it as reason to once again fire up the Van der Graaff and do some new science. *Dave Whitford*, *Sundar Rajan*, and I all left DTM while the project was still at the discussion stage, but within a year or so, *Fouad Tera* had worked out the chemical techniques to extract Be with 70 % yield out of 450 g of lava (*Brown et al.*, 1980). I visited DTM a few years later when the operation was in full swing – *Fouad* had built 2-metre high ion exchange columns and the eluant fractions were collected in buckets! The Van der Graaff, however, had quickly proved unsuitable, so the DTM group formed a collaboration with *Roy Middleton* and other physicists using the accelerator mass spectrometer at the University of Pennsylvania, which proved quite suitable to the task. *Julie Morris* subsequently joined the team as a post-doc. They found concentrations of ^{10}Be as high as 2×10^7 atoms of $^{10}\text{Be}/\text{g}$ (in excellent agreement with their initial predictions). They were careful to rule out contamination and in the context of their study “fresh” took on a whole new meaning; namely that samples had been collected while still hot! They also carefully demonstrated the absence of ^{10}Be in non-arc lavas. As is usually the case in science, there was some initial scepticism, but it soon evaporated and the results essentially ended the question of whether sediment is subducted (*Brown et al.*, 1982; *Tera et al.*, 1986; *Morris and Tera*, 1989). Although *Dave Whitford* and I had been so embarrassingly wrong about the prospects of success of the project (and I’m not sure we ever have gotten all the egg off our faces), we both found the results thrilling. It was evidence that *Armstrong*, *Tatsumoto*, and *Scholl* had been right all along.

7.2 The Subduction Zone Filter

The presence of subducted oceanic crust and sediment in arc magmas raises the question of how much survives the subduction zone filter to be carried into the deep mantle. Furthermore, as noted earlier, production of arc magma is more complex than simply mixing subducting material with mantle and melting it. As oceanic crust subducts, increasing heat and pressure result in release of water and elements dissolved in it to the overlying plate. The process begins with expulsion of pore water, which has little effect on trace element concentrations for all but the most fluid-mobile elements such as Cs, As and B (*Bebout*, 2014). Subsequent low temperature reactions such as carbonate dissolution and the transformation of opal to quartz and clays to micas release additional water, which contributes to seeps and mud volcanoes in the forearc. This process also has minimal effect on the trace element budget of the subducting slab (*Bebout*, 2014; *Ryan and Chauvel*, 2014). Eventually, however, increasing temperature and pressure result in dehydration reactions releasing fluids that transport significant amounts of fluid-mobile elements into the overlying mantle wedge. Finally, enrichment in insoluble elements such as the light rare earths observed in some arc lavas appeared to require partial melting of sediments (*e.g.*, *Elliott et al.*, 1997; *Hawkesworth et al.*, 1997; *Johnson and Plank*, 1999). That seemed somewhat surprising in view of the predicted temperatures of subducting slabs at relevant depths beneath arcs, which were generally thought to be below the solidus, even for sediments (*e.g.*, *Peacock*,



1996). More recent work with improved convection models indicate temperatures in the range of 750 to 900 °C on top of the slab (Syracuse *et al.*, 2010), sufficient for hydrous melting, although slab interiors are cool.

A variety of approaches have been taken to assess these chemical changes in the subducting slab. The first of these is experimental. Open system experiments on natural basaltic amphibolite by Kogiso *et al.* (1997) indicated dramatic losses of Rb, Sr, Ba, and Pb, as well as significant losses of U, Th, and the light rare earths during dehydration at 900 °C and 5.5 GPa. Ta, Nb, and the heavy rare earths appeared to be quantitatively retained, presumably in rutile and garnet, while Li and Be showed only very limited mobility. Sediment dehydration and melting experiments at lower pressure (2 to 4 GPa) and a range of temperatures (600–1000 °C) suggested much more complex behaviour (Johnson and Plank, 1999). Below the solidus, which ranged from 775 °C at 2 GPa to 1025 °C at 4 GPa, Johnson and Plank found that only Sr, Ba, and Pb partitioned preferentially into the fluid phase, in part because of the presence of phengite, which strongly retains the alkalis. There was greater mobility above the solidus, particularly for Th and the alkalis, but mobility of the light rare earths was limited, although notably greater than that of Ta, Nb, and the heavy rare earths.

One of the difficulties in interpreting experiments such as these, beyond the difficulty of trapping and analysing the fluid phase, is that hydrous fluids and silicate melts become indistinguishable above the second critical endpoint; *i.e.* the point where there is complete miscibility between water and silicate melt (*e.g.*, Manning, 2004; Hermann *et al.*, 2006). This second critical endpoint is located around 2.5 GPa and 750 °C in sedimentary rocks, but occurs at much higher pressure, roughly 5 to 6 GPa in basaltic compositions (Kessel *et al.*, 2005b). Thus both the experiments of Kogiso *et al.* and Johnson and Plank would have been near or above the critical point. Kessel *et al.* (2005a) performed a particularly enlightening series of experiments on basalt at 4 and 6 GPa at temperatures ranging from 700 °C to 1200 °C. At low temperatures, hydrous fluids are quite dilute, but become more concentrated with increasing temperature as the second critical end point is approached. At 4 GPa and 700 °C, below the critical point, only B, Rb, Cs, and Pb are partitioned into the hydrous fluid, but the concentrations of all incompatible elements increased with increasing temperature such that at 1000 °C all except Y and the rare earths heavier than Eu had fluid/solid partition coefficients greater than 1. Nevertheless, while absolute abundances changed, the overall pattern of fluid–solid partitioning remained similar. At 6 GPa, above the critical point, even at the lowest temperature, 800 °C, all elements except the middle and heavy rare earths, Nb, Ta, Hf, and Zr had hydrous melt/solid partition coefficients greater than 1. At 1200 °C, only the rare earths heavier than Dy had hydrous melt/solid partition coefficients less than 1, and again the overall pattern of partitioning remained similar.

One can draw several conclusions from these studies. First, the enrichment of elements in arc magmas compared to magmas from other tectonic environments does indeed appear to result from loss of these elements from the subducting slab. Second, incompatible element behaviour during dehydration and



melting is complex and a strong function of both temperature and pressure. Third, the nature of the solid residual phases, including accessory phases, are important in governing individual elemental behaviour and elemental ratios in fluids and melts (e.g., Hermann and Rubatto, 2009). For example, alkalis are retained when phengite is present and garnet retains the heavy rare earths over a wide range of conditions. Rutile controls the distribution of Nb and Ta and Nb/Ta ratios while allanite controls distribution of the light rare earths and Th and ratios such as Th/U and Th/La (Klimm *et al.*, 2008).

The second approach has been to examine the composition of subduction zone metamorphic rocks stranded in the crust, including high-pressure (HP) alpine peridotites, eclogite and blueschist facies rocks and ultra-high-pressure (UHP) metamorphic rocks. Reid *et al.* (1989) found that metapelites present as xenoliths in the Kilbourne Hole, New Mexico maar and likely emplaced in the lower crust in a Neoproterozoic subduction zone had incompatible element abundances similar to unmetamorphosed sediments except for depletions in Cs and U. In the Raspas eclogite-blueschist-amphibolite complex of Ecuador, Arculus *et al.* (1999) concluded that the metabasalts and gabbros had experienced extensive (>50%) loss of Rb, Ba, and Sr, while most other elements, including U, were immobile and Pb exhibited significant enrichment (derived from surrounding metapelites?). Becker *et al.* (2000) found that ratios of K and Ba to Nb and Th in a variety of European blueschist and eclogites facies metabasalts were several orders of magnitude lower than in fresh or altered MORB, suggesting high rates of loss of K and Ba, as well as Rb, during subduction dehydration. Other elements, including the normally less mobile ones as well as U, Pb and Sr did not show systematic depletion and Becker *et al.* (2000) concluded that losses of these elements were less than 10 to 20%. In high-pressure and ultra-high pressure metasediments, incompatible element loss appears limited but variable. Detailed analysis of blueschist to eclogite facies metamorphic rocks by Spandler *et al.* (2003) confirms that nominally mobile elements such as U, Pb, and Sr can be substantially retained to high metamorphic grade and suggests why: they are accommodated in newly formed minerals such as zoisite and allanite. Xiao *et al.* (2012) examined blueschist and eclogite facies metamorphic rocks from the western Tianshan ultrahigh-pressure metamorphic belt of northwest China. They found that high field strength and rare earth elements, Th, and U were relatively immobile and Pb and Sr were mobile in both metabasalts and metasediments. K, Rb, Cs, and Ba were mobile in metabasalts but immobile in metasediments because of the persistence of white mica throughout metamorphism. Thus studies of subduction-related metamorphic rocks reveals some variation in behaviour, with K, Rb, Cs, and Ba being mobile in most cases, variable mobility of Sr and Pb, and U, Th, and the high field strength and rare earth elements being immobile.

Complicating interpretation of these results, however, is variability of incompatible element concentrations in MORB and the oceanic crust (partly a simple consequence of fractional crystallisation). In addition, the oceanic crust undergoes a variety of reactions with seawater, adding to this variability, particularly for the so-called large-ion-lithophile elements (LILE), K, Rb, Sr, and Ba (e.g.,



Staudigel, 2014). Finally, the absolute concentrations of these elements in the metamorphic rocks are also highly variable with K, Rb, and Ba concentrations both lower and higher than in fresh MORB. Higher concentrations might be explained by gain from closely associated metasediments, with which the mafic protoliths are often complexly intermixed (Bebout, 1995). The complexity is such that Bebout (2014) stated that, “any addition or subtraction of LILE due to the passage of fluids during HP/UHP metamorphism is obscured by this overlap with the trends for seafloor alteration”. Similarly, Nb/U ratios in such rocks largely overlap the range observed in altered oceanic crust and Pb concentrations and Pb/Ce are generally higher, masking evidence of systematic U or Pb loss during subduction metamorphism. Nevertheless, these observations are broadly consistent with both the experimental work described above and the observed enrichment of arc lavas in fluid-mobile over fluid-immobile elements.

Yet another approach is to examine variations in elemental abundances and ratios across island arcs. Ratios such as B/Be, Pb/Ce and Cs/Th decline progressively from the arc-front to back-arc volcanoes, suggesting preferential extraction of B, Pb, and Cs, consistent with experimental approaches described earlier (Ryan and Chauvel, 2014). Other ratios and some element abundances show more complex cross-arc patterns, in part perhaps due to their being released from the slab through melting rather than dehydration and in part due to a general decrease in melting percentage from the volcanic front to the back-arc. Based on this and studies of metamorphic rocks as described above, Ryan and Chauvel (2014) concluded that the extraction efficiency from the down-going slab was $B > As, Cs > Sb > Pb > Rb > Ba, Sr, Be, \sim U > Th$.

The final approach is mass balance: estimating the flux of elements delivered to the subduction zone, estimating the flux of elements lost from the slab in the subduction zone, and calculating what remains in the slab to be carried into the deep mantle. Perhaps the first attempt to look at mass balance in subduction zones was that of my Cornell colleagues *Dan Karig* and *Bob Kay* (Kay, 1980; Karig and Kay, 1981). They were not specifically interested in the flux from the residual slab to the deep mantle, but they did conclude that “about 50 m of sediment and 700 m of altered oceanic crust are sufficient to furnish all the required K” in the Marianas volcanic flux. Since this is only a fraction of the sediment and ocean crust subducted, their simple calculation implied that significant amounts of K remain in the residual slab to be carried into the mantle. Kelley *et al.* (2005) examined the mass balance for U, Th, and Pb in the Marianas. They assumed all Th above MORB levels was derived from subducted sediment and that sedimentary contributions of Pb and U were proportional to U/Pb and Th/U ratios in the sediment. Excesses of Pb and U above the calculated sedimentary contribution in the arc and back-arc lavas were assumed to be derived from altered oceanic crust. They concluded that 44 to 75 % of Pb and less than 10 % of U were lost from altered oceanic crust as it passed under the arc and another 10 to 43 % of Pb and 19-40 % of U was lost in the back-arc. This results in an 8-fold increase in the U/Pb ratio of the altered oceanic crust. Since seafloor alteration of oceanic crust produces a 4-fold increase in U/Pb, they concluded that the plate tectonic



cycle significantly increases both U/Pb and Th/U of the mantle. Their calculations, however, explicitly ignored the contribution of sediment subduction on mantle evolution.

My former student Kate Porter and I considered the total mass balance for 19 incompatible elements in 8 intra-oceanic arcs (Porter and White, 2009). In contrast to Kelley *et al.* (2005) we considered only the whole subduction package with no attempt to distinguish between sedimentary and oceanic crust contributions. The flux of the subducting oceanic crust was based on average MORB after correcting for fractional crystallisation (MORB are more evolved than the oceanic crust as a whole) and the effects of seawater interaction (Staudigel *et al.*, 1996; Bach *et al.*, 2003; Kelley *et al.*, 2003). Sediment fluxes were from Plank and Langmuir (1998), except for the Lesser Antilles, which were from Carpentier *et al.* (2008). Applying regression and thermodynamic modelling (*i.e.* pMelts; Ghiorso *et al.*, 2002) to data retrieved from GEOROC, we calculated average primitive magmas for each arc. We assumed the unmodified mantle wedge was the same as the MORB source and that the degree of melting was on average the same as beneath mid-ocean ridges. Because Yb, as a heavy rare earth, was among the least mobile of the elements we considered, we assumed that any excess of the element/Yb concentration ratio over that ratio in MORB reflected the contribution from the subducting slab. The flux into the arc was then just this excess times the magmatic flux. Implicit assumptions are that the mantle wedge is compositionally identical to the MORB source, that the melting process is similar to MORB generation, and that there is no net flux to the mantle wedge, *i.e.* everything lost from the subducting slab emerges in arc magmas. While these assumptions have considerable uncertainty, the uncertainties in the subduction mass flux and the arc magmatic flux are more significant. Figure 7.3 shows our calculated residual slab compositions. We found that “Almost all of the subducted Nb, Ta, and intermediate and heavy rare earths survive into the deep mantle, as do most of the light rare earths. On average, 73 % of Th and Pb, 74 % of K, 79 % of U, 80 % of Rb, 80 % of Sr, and 82 % of Ba survive into the deep mantle.” However, the uncertainties were considerable. For example, the weighted average of the fraction of Pb and Th surviving into the deep mantle might be as much as 87 % and 91 % or as little as 38 % and 55 %, respectively. Results also varied from arc to arc. In the Marianas, for example, we calculated that between 17 % and 83 % of the Pb was extracted with a best estimate of 38 %, overlapping the estimate of Kelley *et al.* (2005). We explicitly did not consider losses in the back-arc, so that our estimates of recycled fractions might be somewhat too high for arcs with active back-arc spreading, such as Tonga-Kermadec, Izu, and the Marianas.

Chauvel *et al.* (2009) used an isotope mass balance approach to calculate that >85 % of Hf and Nd in sediments subducted beneath the Izu-Bonin-Mariana arc survives into the deep mantle. For that same subduction zone, Ryan and Chauvel (2014) calculated that less than 60 % of sedimentary Pb survives. By their calculations, somewhat greater amounts of Nd and Hf are extracted in the Lesser Antilles, so that only 80 % of the Nd and Hf survives in the northern Lesser Antilles and only 65 % in the southern Lesser Antilles, with 40-80 % of the Pb surviving in the northern arc and 33-65 % surviving in the southern arc.



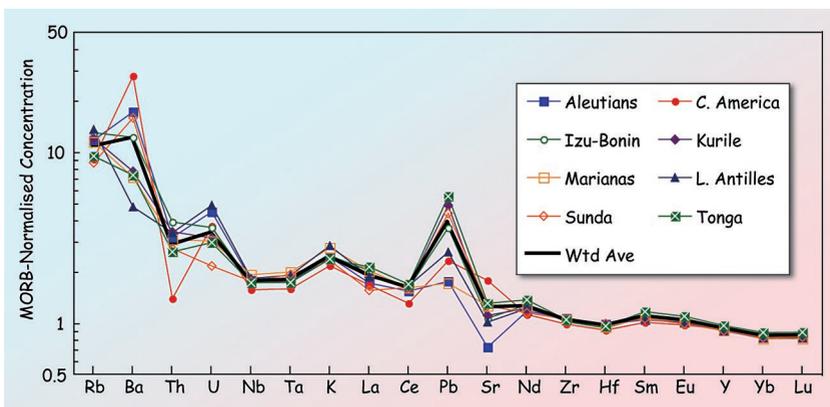


Figure 7.3 Calculated MORB-normalised compositions of subducting oceanic crust plus sediment after passing through the subduction zone filter (from Porter and White, 2009 with permission from John Wiley and Sons).

It is somewhat difficult to compare these three sets of estimates in that Kelley *et al.* (2005) considered only the oceanic crust, Chauvel *et al.* (2009) and Ryan and Chauvel (2014) considered only the sedimentary component, and Porter and White (2009) considered only the whole package. Nevertheless, the results seem consistent within the uncertainties: significant fractions of fluid-mobile elements such as K, Rb, U, and Pb are extracted in the subduction zone while most of the fluid-immobile elements survive to be carried into the deep mantle.

7.3 Subduction and OIB

The next questions are whether the subducting slab, as modified by the subduction filter, can be matched to the compositions of oceanic island basalts and what are the long-term consequences for mantle compositional evolution? Specifically, OIB have lower ϵ_{Nd} and ϵ_{Hf} than MORB and, except for HIMU islands, higher $^{87}Sr/^{86}Sr$, which in turn implies lower Sm/Nd and Lu/Hf and higher Rb/Sr than depleted mantle. Pb isotope ratios in OIB are on average somewhat higher than in MORB, but they extensively overlap the MORB range and can be lower (EM I) or substantially higher (EM II and HIMU). However, $^{208}Pb^*/^{206}Pb^*$ ratios, which as we noted earlier are proportional to the time-integrated Th/U ratio, are higher in OIB. How would recycled crust and sediment evolve after subduction zone processing? In addition, MORB and most OIB have similar ratios of Nb/U and Pb/Ce, yet these ratios are markedly different from values typical of continental crust (Hofmann *et al.*, 1986) and, particularly, marine sediment. In addition, basalt-seawater reactions drive Nb/U ratios in the oceanic crust down so that



Nb/U and Pb/Ce ratios of the flux into the subduction zone are respectively lower and higher than mantle values, including those in most OIB. Subduction zone processing drives these ratios up and down, respectively, but by how much?

Kelley *et al.* (2005) found that subduction zones “remove enough Pb and U from the slab to enable it to evolve rapidly (~0.5 Ga) to sources suitable to explain the $^{208}\text{Pb}/^{206}\text{Pb}$ isotopic array of OIB.” On the other hand, they found that so much Pb was removed that over geologic time the mantle should be driven to Pb/Ce ratios far lower than those observed. They pointed out, however, that the sedimentary flux, which they did not consider, could balance this deficit.

As I pointed out in Section 3.1, while ϵ_{Hf} and ϵ_{Nd} are strongly correlated in oceanic basalts (Fig. 4.4), they show more dispersion in sediments. Chauvel *et al.* (2008) considered the impact of subduction recycling on the evolution of Hf and Nd isotope ratios in the mantle. Their approach was to use a Monte Carlo simulation of recycling variable fractions of oceanic crust and sediment over the past 3 billion years. They concluded that recycling of oceanic crust alone could not reproduce the Hf-Nd mantle array. On the other hand, Hf-Nd isotopic systematics of OIB could be reproduced “by involving 20–30% recycled basalt and associated sediments” of an appropriate mixture of terrigenous and hydrogenous compositions and 0–15% recycled material in MORB.

Ryan and Chauvel (2014) extended this analysis to Pb isotope ratios (Fig. 7.4) and found that “the overall position of the density field in Pb isotopic space corresponds roughly to the measurements”. There is, however, a clear misfit between their model and actual oceanic basalt data on a $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ plot, with the data plotting along a lower slope than the model simulations. They stated, “A better fit might be obtained if the basaltic crust recycled through time had had a lower U/Pb ratio because ancient basalts would have much lower $^{207}\text{Pb}/^{204}\text{Pb}$ ratios.” In other words, to fit their recycling model, oceanic crust recycled into the mantle prior to 1 to 2 Ga would need to have lower U/Pb than that of more recently recycled oceanic crust.

In fact, subducted Archean and Proterozoic oceanic crust very likely did have lower U/Pb ratios than Phanerozoic oceanic crust. Uranium behaviour depends strongly on oxidation state: in its oxidised U^{6+} state, it forms the oxyanion UO_2^{2-} , which is highly soluble and consequently U is mobile at the surface of the modern Earth and its concentration high in seawater. In its U^{4+} reduced form, U solubility is similar to that of Th (which is to say quite low). In modern hydrothermal systems, seawater is reduced in seafloor hydrothermal systems to U^{4+} and fixed in the oceanic crust. It is now reasonably well established that atmospheric oxygen levels in the Archean were very low. Indeed, one key piece of evidence is the existence of detrital uraninite (UO_2) in Archean and early Proterozoic sediments (Holland, 1984). The concentration of U in Archean seawater was therefore undoubtedly low, and hydrothermal processes would not have enriched U in Archean oceanic crust. The nature of the Proterozoic U cycle is less certain. There is clear evidence that weathering began to release U to solution and that the surface ocean became oxidising around the time of the Great Oxidation



Event at about 2.3 Ga. However, oxygenation of ocean deep water appears to have remained limited at least until the late Palaeoproterozoic (*e.g.*, Canfield, 1998; Holland, 2006) and U concentrations in seawater were likely low until then (Partin *et al.*, 2010). Consequently, Proterozoic oceanic crust may not have experienced U enrichment, and U isotopic data of Andersen *et al.* (2015) discussed in Section 6.7 suggest just that. Thus the apparent failure of Ryan and Chauvel's model might actually be a success.

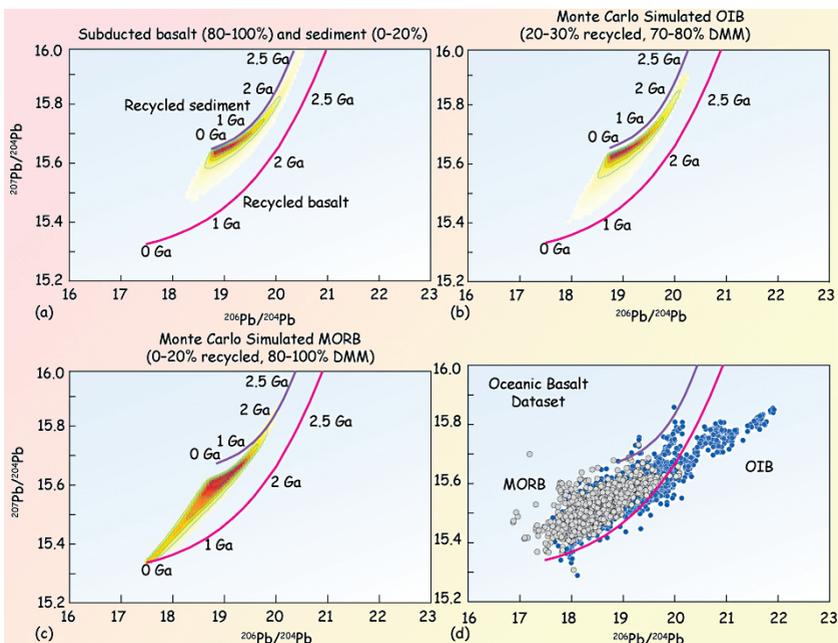


Figure 7.4 Calculated Pb isotopic compositions of material recycled into the mantle over Earth history (a through c) compared to MORB and OIB data (d) (modified from Ryan and Chauvel, 2014).

Porter and White (2009) also examined how radiogenic isotope ratios in recycled oceanic crust and sediment would evolve through time. Based on the $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ slope of the oceanic basalt data, we assumed that the average age of recycled material now contributing to OIB was 1.8 Ga: the “cycle time”. We calculated average crustal and depleted mantle isotopic compositions for that age and assigned best-estimate values to the sedimentary and oceanic crustal components at the time of subduction. We used the calculated parent/daughter ratios in the residual slabs for each of the 8 arcs we examined to calculate present-day Sr, Nd, and Pb isotopic compositions (Fig. 7.5). We found that these slabs would evolve to a wide range of present-day Pb isotopic compositions, from $^{206}\text{Pb}/^{204}\text{Pb}$ of ~17 to ~23, encompassing essentially the entire range of oceanic



basalts. $^{87}\text{Sr}/^{86}\text{Sr}$ also showed a wide range, from ~ 0.704 to ~ 0.709 (and both higher and lower values if uncertainties were included). However, Sm/Nd ratios of residual slabs in the 8 modern arcs are such that, had they been subducted at 1.8 Ga, none would evolve to present-day ϵ_{Nd} lower than +2.5. It thus would seem difficult to explain the low ϵ_{Nd} observed in some OIB, particularly those from EM I islands such as Pitcairn, Kerguelen, and Tristan da Cunha through subduction recycling.

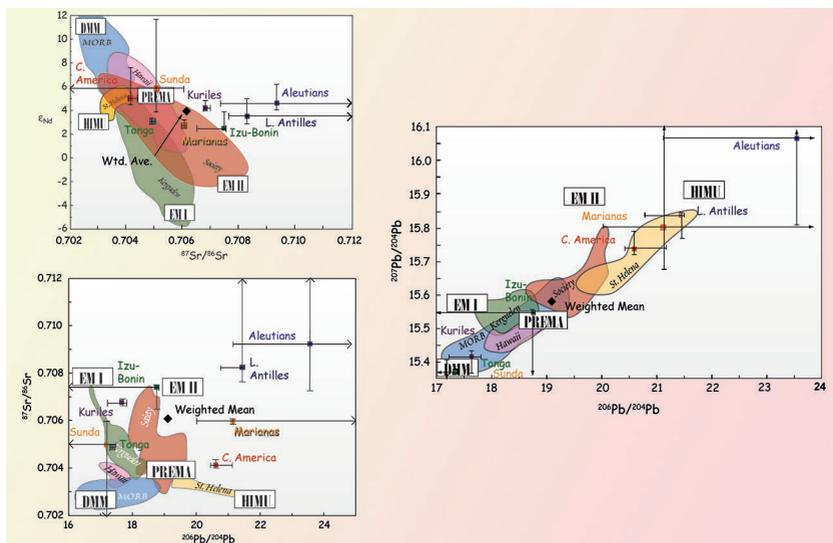


Figure 7.5 Predicted present isotopic compositions of 8 modern residual slabs had they been subducted at 1.8 Ga (from Porter and White, 2009 with permission from John Wiley and Sons).

The discovery of Archean MIF sulphur in a Mangaia lava (Cabral *et al.*, 2013) suggests that our assumption of a 1.8 Ga cycle time may be too short, perhaps due to the short residence time of Pb in mantle reservoirs (Albarède, 2001). Using instead a 3 Ga age for the cycle time, recycled slabs with compositions similar to modern ones could evolve to ϵ_{Nd} as low as -1.5, which is still not as low as observed in some OIB. Lower values are of course possible by assuming less depleted oceanic crust or more enriched or greater amounts of sediment. A longer cycle time has a greater effect on predicted $^{87}\text{Sr}/^{86}\text{Sr}$, with values as high as 0.714 (and greater when uncertainties are taken into account).

The calculated residual slab compositions of Porter and White (2009) also did not match OIB particularly well in other ways. The flux into subduction zones has higher Pb/Ce and lower Nb/U than typical mantle values as a consequence of non-mantle ratios in sediment and altered oceanic crust. We found that the effect of the subduction zone filter was generally to lower Pb/Ce and raise Nb/U



(due to preferential loss of Pb and U) but in most subduction zones the effect was not great enough to bring these ratios within the mantle range. This was truer for the Nb/U ratio than Pb/Ce. One possible explanation is again that Archean, and probably Proterozoic, altered oceanic crust would not have been as enriched in U as is modern crust.

The *Porter* and *White* study predicted that ancient subducted crust and sediment is more likely to evolve to isotopic compositions similar to those observed in EM II islands such as the Society Islands and Samoa, with very radiogenic Sr and only moderately unradiogenic Nd than to those of other islands. Indeed, basalts from EM II islands have more continental-like Pb/Ce and U/Nb ratios and these correlate with isotopic compositions (White and Duncan, 1996; Jackson *et al.*, 2007). Assuming the subduction process operated similarly to modern subduction zones, intermediate isotopic compositions, such as those similar to PREMA, FOZO or “C”, are also consistent with isotopic compositions of ancient residual slabs after several billion years of isotopic evolution. The HIMU- and EM I-type compositions appear to be more difficult to explain. Nevertheless, the presence of MIF sulphur in a HIMU lava from Mangaia appears to provide unequivocal evidence of a surficial component, most likely oceanic crust, in HIMU lavas, apparently confirming the interpretation of Chauvel *et al.* (1992). It is also worth noting that isotopic compositions observed in Samoa are more extreme than predicted by Porter and White (indeed, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios exceed the value of average modern upper continental crust), and there can be little doubt that this signature is derived from crustal recycling. The *Porter* and *White* approach was, however, arguably overly uniformitarian: we assumed that the ancient Earth operated the same as the modern Earth. The lesson may be that *Lyell's* uniformitarianism has its limits; there is certainly abundant evidence that the Earth has operated differently in the past (*e.g.*, Arndt and Davaille, 2013). Nor did we fully take account of the variability in the materials and processes involved. Finally, there are other mechanisms, explored below, by which continental material can be exported to the mantle. Thus it would be premature to rule out the possibility that some anciently subducted slabs could evolve to EM I-type compositions today.

7.4 Subduction Erosion and Lower Crustal Foundering

In 1980, *Dave Scholl* and other geologists from the USGS Menlo Park group proposed that in some subduction zones the subducting plate was actually tectonically removing the upper plate, a process they called *subduction erosion* (Scholl *et al.*, 1980), and in this way delivering continental crust to the mantle. This claim was based on evidence such as migration of magmatic arcs away from the trench axis and truncation of geologic trench features on the overriding plate. Subsequent studies documented additional evidence. This includes crystalline basement in the landward trench wall, tilting and subsiding erosional surfaces on the overriding plate (*e.g.*, Scholl and von Huene, 2007), the presence of ‘ghost’ detrital zircons, *i.e.* zircons in Japanese sandstones derived from Palaeozoic and Mesozoic intrusions no longer present in the islands (Isozaki *et al.*, 2010), and the



paucity of pre-Neoproterozoic blueschist facies rocks (Stern, 2011). The evidence is sufficient enough that Scholl and von Huene (2007) inferred that subduction erosion occurs in all subduction zones, even at so-called “accreting margins”, although rates are much lower in the latter and Clift *et al.* (2009) wrote “*there is now a consensus that this process is even more important than subduction accretion in the evolution of active plate margins.*”

The importance of this process is now widely recognised among geophysicists and geologists interested in the growth of continents and subduction zone processes (*e.g.*, Clift *et al.*, 2009; Stern and Scholl, 2010; Stern, 2011). Estimates of the rates of subduction erosion are difficult to make and are additionally complicated by the temporal variability of the process, which increases during collisions with ridges and seamounts on the under-riding plate. Nevertheless, current estimates of the global rate of subduction erosion agree within 25 % (Table 7.1). Stern (2011) and Stern and Scholl (2010) argue that the continental mass loss due to subduction erosion exceeds that due to sediment subduction while Clift *et al.* (2009) estimate that subduction erosion losses are 80 % of sediment subduction losses. All three papers argue that, consequently, subduction zones are regions of net continent destruction (Fig. 7.6). In the analysis of Clift *et al.* (2009), additions from plume volcanism and oceanic plateau accretion are assumed sufficient to balance losses in subduction zones, resulting in a steady-state crustal mass. Stern (2011) concluded that “continental crust is probably slowly shrinking” and Stern

Table 7.1 Crustal Additions and Losses (AU) †.

		Stern and Scholl (2010)	Clift <i>et al.</i> (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 oceanic crust		0.4	0.4
	Continent subduction	0.3	0.43	0.4
	Crustal foundering		1.1	1.1
Total Losses		>3.2	4.93	5.25

† Armstrong Units = 1 km³/yr (Kay and Kay, 2008).



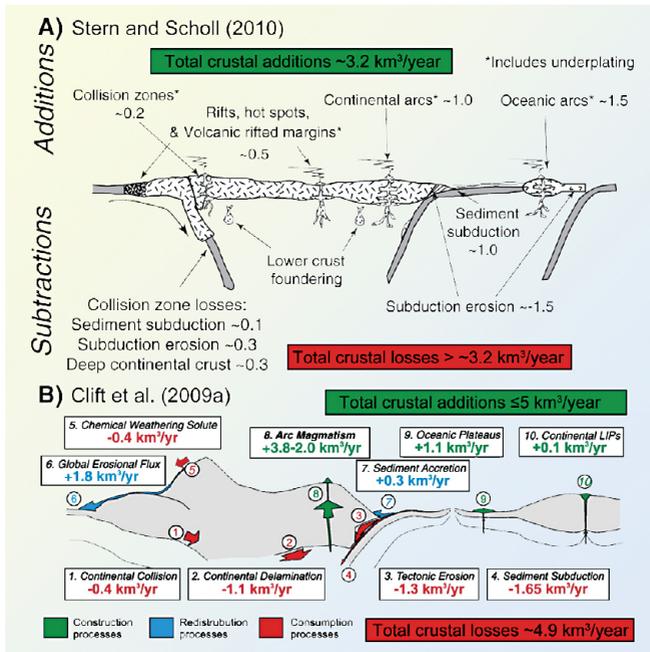


Figure 7.6 Summary of continental crustal additions and losses of Stern and Scholl (2010) and Clift et al. (2009) in Armstrong Units (AU) from Stern (2011). The latter's revised estimate of subduction erosion (1.65 AU) raise total estimated crustal losses to 5.25 AU.

and Scholl (2009) argued that “These conclusions challenge the widely held view that continental crust volume has increased over time due to plate tectonic activity; it is just as likely that this volume has decreased.”

Although much of the evidence for subduction erosion comes from geophysical observations, there is geochemical evidence as well, reviewed extensively by Stern (2011). For example, in the Chilean Andes adjacent the Juan Fernández Ridge, temporal Pb, Sr, and Nd isotopic magmatic evolution correlates with periods of magmatic arc retreat and tectonic deformation (Kay et al., 2005). While the more “crustal” isotopic signature of magmas during these periods could be explained by assimilation, the amount of assimilated crust required (up to 50 %) is unreasonable in view of the relatively primitive magmatic compositions. A lack of correlation of isotope ratios with SiO₂ content also argues against a dominant role for assimilation (Stern et al., 2011), although some crustal assimilation does occur (Kay et al., 2005). Instead, Kay et al. (2005) concluded that “The magmatic changes require differences in magma source regions” which they attributed to a “combination of melting the base of thickened lower crust and crust entering the mantle through subduction erosion” driven by collision of the Juan Fernández



Ridge with the South American plate. In Costa Rica, accreted ophiolites on the Nicoya Peninsula and elsewhere appear to be related to the early stages of the Galápagos mantle plume and a Galápagos plume isotopic signature is observed in the arc magmas (Hoernle *et al.*, 2002). Goss and Kay (2006) noted that eruption of adakitic magmas with steep REE patterns coincided with the collision of the Cocos Ridge around 4 million years ago. Additionally, the inception of slab shallowing in the region and a variety of geophysical evidence suggest high rates of Neogene subduction erosion in the region at that time. Based on these observations, Goss and Kay (2006) argued that these magmas inherited their Galápagos-like isotopic signatures through subduction erosion of the ophiolite complexes from the forearc.

Lower crustal foundering (often called “delamination”, less accurately I believe) is another important mechanism of crustal loss. This includes both the apparently common loss of dense young mafic arc lower crust (*e.g.*, Behn *et al.*, 2007; Tatsumi *et al.*, 2008) and loss of older, mature continental crust that occurs when the lower crust transforms to eclogite and becomes denser than the underlying mantle (Kay and Kay, 1993). In addition to seismic imaging (Gurría and Mezcuá, 2000), evidence includes eruption of strongly LREE-enriched andesitic and dacitic magmas, sometimes with lower crustal isotopic signatures and old xenocrystic zircons (Clift *et al.*, 2009). Magmatism is often accompanied or followed by topographic uplift as the dense continental root is lost. Examples include the North China Craton, the Western US, the Western Mediterranean, and the Andes. Quantifying the rate of loss is difficult, however. Clift *et al.* (2009) estimate the rate at 1.1 Armstrong Units over the last 120 Ma.

The magnitude of the subduction erosion and foundering fluxes has profound implications for evolution of both the crust and the mantle. Growth of the continental crust through time remains one of the most important and debated questions in geology. While it is clear that material has been added to the crust through time, the net rate of growth of the continental mass depends on the balance between additions and losses, as Armstrong (1968) pointed out. He argued that as a result the volume of continental crust has been “*nearly constant for at least the last 2.5 b.y. and probably most of Earth’s history.*” This has often been considered an extreme view and others have argued for net continental growth that decreased through time (*e.g.*, O’Nions *et al.*, 1979; Schubert and Reymer, 1985). It is now clear that new additions to continents have come in pulses (Condie and Aster, 2010). While some argue that these pulses represent enhanced rates of magmatism (*e.g.*, Arndt, 2013), others have argued that the peaks represent peaks in enhanced preservation during supercontinent assembly (*e.g.*, Hawkesworth *et al.*, 2010). The prodigious rates of continent destruction listed in Table 7.1 demonstrating that subduction zones are most often areas of net continental loss tend to support the latter interpretation. Hawkesworth *et al.* (2010) adopted Armstrong’s view, arguing that “*the present volume of the continental crust was established 2–3 Ga ago.*”

Regardless of whether or not the continents have grown through time, the rates of continental loss in Table 7.1 and Figure 7.6 suggest that the flux of continental crust to the mantle is much larger than sediment subduction flux



alone. Some of the material removed by subduction erosion finds its way into arc magmas, but 80 to 90 % is exported to the deep mantle (Clift *et al.*, 2009; Stern, 2011). Clift *et al.* (2009) pointed out that their estimated rates of crustal destruction would result in recycling of an entire crustal mass in 1.8 Ga; Stern (2011) argued that the recycling rates are even higher. Tatsumi *et al.* (2014) suggested that the volume of mafic lower arc crust lost through foundering over geologic time ($2.3\text{--}3.8 \times 10^{10} \text{ km}^3$) exceeds the total present volume of the continental crust ($\sim 9 \times 10^9 \text{ km}^3$) and is comparable to the total amount of subducted oceanic crust ($\sim 7 \times 10^{10} \text{ km}^3$ assuming steady-state production). They speculated that this material, which they term 'anti-continent', sinks to the base of the mantle forming D'', whose volume is comparable.

Given the magnitude of the fluxes involved, the role of subduction erosion and crustal foundering has received relatively little consideration from mantle geochemists, although a few studies have considered it. Sediment subduction preferentially recycles upper continental crust; lower crustal foundering and subduction erosion represent the only plausible mechanisms for recycling lower crust into the mantle. Because lower crustal Pb is significantly less radiogenic on average than upper crustal Pb (Rudnick and Goldstein, 1990), my former student *Debajyoti Paul* and I found that we could model mantle Pb isotopic evolution only if lower as well as upper crust was recycled into the mantle (Paul *et al.*, 2002). Willbold and Stracke (2006) pointed out that variability and differences occur in trace element ratios, such as Nb/Rb, Rb/La, Ce/Pb and Nb/La, between HIMU, EM I, and EM II basalts that were not readily explained by marine sediment recycling, whose incompatible element ratio distribution is unimodal. They argued that this variability required recycling of lower as well as upper continental crust with the former accomplished through subduction erosion. Willbold and Stracke (2010) expanded on this theme, and argued that EM I basalts tend to have positive Eu anomalies (Eu/Eu*), while EM II tend to have negative ones. Intracrustal melting leaves a lower crustal plagioclase-bearing residuum with positive Eu anomalies and an upper crust with negative ones. They pointed out that this difference correlated with differences in Pb isotope ratios between EM I and EM II basalts, with EM I being less radiogenic (White, 1985) and interpreted these observations as implicating lower continental crust recycled through subduction erosion and crustal foundering as a dominant component of EM I plumes. Finally, *Kate Porter* and I cautioned that our analysis had ignored subduction erosion and that this might explain why some OIB have more enriched isotopic signatures than could be explained by ocean crust and sediment recycling alone (Porter and White 2009).

Table 7.1 demonstrates that the continental flux into the mantle due to subduction erosion and lower crustal foundering likely exceeds that due to sediment subduction. Because the former involves material not exposed for sampling, quantifying elemental and isotopic fluxes is far more difficult than quantifying fluxes associated with sediment subduction. Nevertheless, geochemists will have to find ways of doing this in the future if we expect to fully understand crust-mantle chemical evolution.



8.1 Lithologic Heterogeneity

The mantle consists of peridotite. That took a while to establish (Ringwood, 1975), and once it had been, there was a tendency to view it as consisting solely of peridotite. That view was always perhaps a bit simplistic as the mantle xenolith population contains a small but significant fraction of mafic materials such as eclogite and pyroxenite. A recognition has subsequently emerged that mafic, *i.e.* basaltic, materials are widespread, if not ubiquitous, and could play a critical role in basalt generation and influence isotopic and trace element compositions as well. Perhaps the first works to point out the potential geochemical significance of lithological heterogeneity were those of Hanson (1977) and Zindler *et al.* (1979). Allègre and Turcotte (1986) pointed out that continuous production and subduction of oceanic crust over billions of years was likely to produce a “marble cake” mantle with ubiquitous stringers of mafic material embedded in an ultramafic matrix. Indeed, recent numerical simulations suggests 97% of the mantle has been processed through the oceanic crust cycle (Huang and Davies, 2007). Hofmann and White (1982) proposed that mantle plumes were particularly rich in this basaltic material (although we argued plumes were unlikely to be exclusively composed of basalt). This raises the question of whether there is evidence, beyond incompatible element and isotopic signatures, of an enhanced mafic component in mantle plumes.

Over the past decade or two, geochemists and petrologists have begun to address this question. A number of studies have explored it experimentally (Hirschmann and Stolper, 1996; Hirschmann *et al.*, 2003; Pertermann and Hirschmann, 2003; Kogiso *et al.*, 2004; Pertermann *et al.*, 2004). Other studies have examined major and compatible trace element abundances in OIB; *e.g.*, Hauri (1996) found that the major oxides SiO₂, FeO, CaO, TiO₂, and Na₂O correlated with Nd, Sr and Os isotope ratios in Hawaiian lavas and concluded that “these correlations indicate the presence of a component beneath Hawaii ... that is most probably recycled oceanic crust distributed within the Hawaiian plume as segregations of quartz-bearing garnet pyroxenite or eclogite”. Reiners (2002) argued that “temporal-compositional trends in the form of decreasing incompatible elements and MgO, with increasing SiO₂, as the eruption proceeds ... reflect sequential eruption of melt from increasing depths in mantle melting regions that are compositionally zoned because of different solidii and melt productivities of distinct peridotite and pyroxenite lithologic domains.” Jackson and Dasgupta (2008) considered 18 oceanic hotspots and found that HIMU hotspots have high CaO/Al₂O₃, FeO_T, and TiO₂ and low SiO₂ and Al₂O₃. EM I and EM II exhibit higher K₂O concentrations and K₂O/TiO₂ ratios than HIMU lavas and EM I lavas exhibit the lowest CaO/Al₂O₃. Dasgupta *et al.* (2010) calculated parental magma compositions (X_{OIB}^{73}) that



is the concentration corrected for fractional crystallisation to a $Mg/(Mg+Fe^{2+})$ atomic ratio of 0.73) for basalts from 31 oceanic island groups and concluded that “Comparison between X_{OIB}^{73} and experimental partial melts of fertile peridotite indicates that at least two additional melt components need to be derived from OIB source regions. ... We suggest that carbonated eclogite and volatile-free, silica-excess eclogite are the two most likely candidates, which in conjunction with fertile mantle peridotite, give rise to the two primitive OIB end members.” Le Roux *et al.* (2010) examined Zn/Fe ratios in OIB and concluded that “high Zn/Fe ratios of some OIB cannot be explained by peridotite melting alone, but instead require the presence of high Zn/Fe lithologies... such as eclogites and garnet pyroxenites.” Based on a study of first-row transition element (FRTE) partitioning, Davis *et al.* (2013) came to the conclusion that Zn/Fe was not a particularly sensitive indicator of source lithology, but nevertheless concluded that “When taking into account several FRTE ratios simultaneously, few OIB appear to be consistent with derivation solely from a reduced peridotitic source.” Prytulak and Elliott (2007) concluded that OIB “Ti contents are generally too high to be derived from melting of a peridotitic mantle” and “of the enriched components commonly invoked to explain the range in OIB radiogenic isotopic signatures, only the addition of small amounts (~ 1–10%) of recycled mafic crust is compatible with all geochemical constraints.” On the other hand, Stracke *et al.* (1999) argued against the existence of garnet-pyroxenite or eclogite in the Hawaiian source on the basis of combined Hf-Nd-Th isotope and trace element systematics.

A particularly interesting, provocative, and consequently controversial, idea was proposed by Sobolev *et al.* (2005), who argued on the basis of concentrations of Ni in olivine and SiO_2 that the Hawaiian source is olivine-free. They suggested that eclogite, which originates as recycled oceanic crust, composes up to 30% of the Hawaiian plume. As a consequence of its much lower solidus, the eclogite melts at greater depth than peridotite. This melt then reacts with surrounding peridotite to form pyroxenite, which subsequently melts at shallower depth (Fig. 8.1). Sobolev *et al.* (2007) argued that recycled oceanic crust in the form of eclogite stringers, and consequently this two-stage melting process, is pervasive in the mantle; according to them even MORB are composed of 10 to 30% pyroxenite-derived melts. Based on his study of the major element chemistry of basalts from the Hawaiian Scientific Drilling Project, Herzberg (2006) concluded that compositions were “consistent with previous suggestions that pyroxenite occurs in a host peridotite, and both contribute to melt production.” Again in 2011, he concluded that “olivine phenocrysts in shield-building lavas on Hawaii are higher in Ni and Fe/Mn, and lower in Mn and Ca than those expected to crystallize from melts of a normal peridotite source, and point to the importance of pyroxenite as proposed by Sobolev and co-workers” (Herzberg, 2011). On the other hand, based on experiments on eclogitic melts, Wang and Gaetani (2008) argued that the Sobolev *et al.* model may be overly complex as “mixing of reacted eclogite partial melt with primitive basalt is capable of producing the positive correlation between melt SiO_2 content and olivine Ni content observed in some Hawaiian lavas.” They concluded that “the proportion of eclogite in the Hawaiian plume is less than has been estimated in recent studies.” Niu *et al.* (2011) reached a similar conclusion.



Not everyone agrees with this scenario. Comparing primitive Hawaiian lavas with primitive MORB from the Siqueiros Fracture Zone, Putirka *et al.* (2011) argued that both can be derived from peridotites and that differences in major element chemistry between the two could be explained by higher pressure melting of a more enriched source in Hawaii. The latter, they conceded, may well result from an admixture of recycled oceanic crust, but that after mixing the result was merely fertile peridotite. Comparing Hawaiian basalt compositions to a model derived from their phase equilibrium experiments, Grove *et al.* (2013) found that “*Magnas with major element compositional characteristics of pyroxenite melts are truly the rare exception in Hawaii, and only 3 emerge from this analysis of major element characteristics.*” They had, however, not considered nickel or other transition metals, which form some of the strongest evidence of a non-peridotite component, and concluded that, “*From this major element evidence, it appears that we must identify processes that can reconcile both the major and trace element signatures of Hawaiian lavas.*” Based on Ni partition experiments Matzen *et al.* (2013) argued that the high Ni content of Hawaiian olivines reflected the strong inverse temperature dependence of Ni partitioning between olivine and silicate melts. Melting of peridotite at high temperatures, and consequently low olivine-liquid partition coefficients, produces Ni-rich parental magmas. Subsequently lower temperature crystallisation then produces olivines

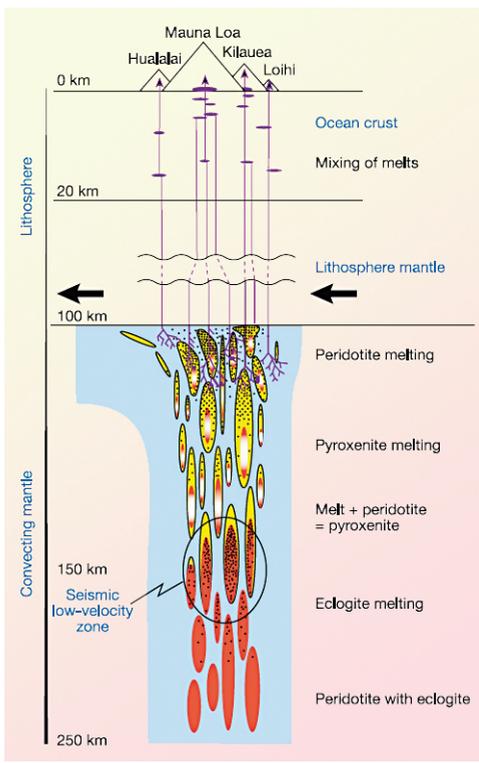


Figure 8.1

Multi-stage melting model of the Hawaiian plume of Sobolev *et al.* (2005). Red: eclogite representing recycled oceanic crust; blue: peridotite; yellow: reaction (secondary) pyroxenite produced by infiltration of eclogite-derived melt into peridotite; white and red, eclogitic restite; black dots: melts; violet: magma pathways, conduits and small magma chambers. Eclogitic melts produced at high pressure are consumed by reaction with peridotite to produce secondary pyroxenite, which subsequently melts along with peridotite to produce Hawaiian magmas (from Sobolev *et al.*, 2005 with permission from Nature Publishing Group).

with “significantly higher NiO contents than those in the residual source from which the melt was extracted.” Thus while a strong case can be made that mantle plumes are mixtures of peridotite and recycled crustal components that to some degree survive as discrete lithologic entities within plumes, the relative amount of this mafic component present is still disputed.

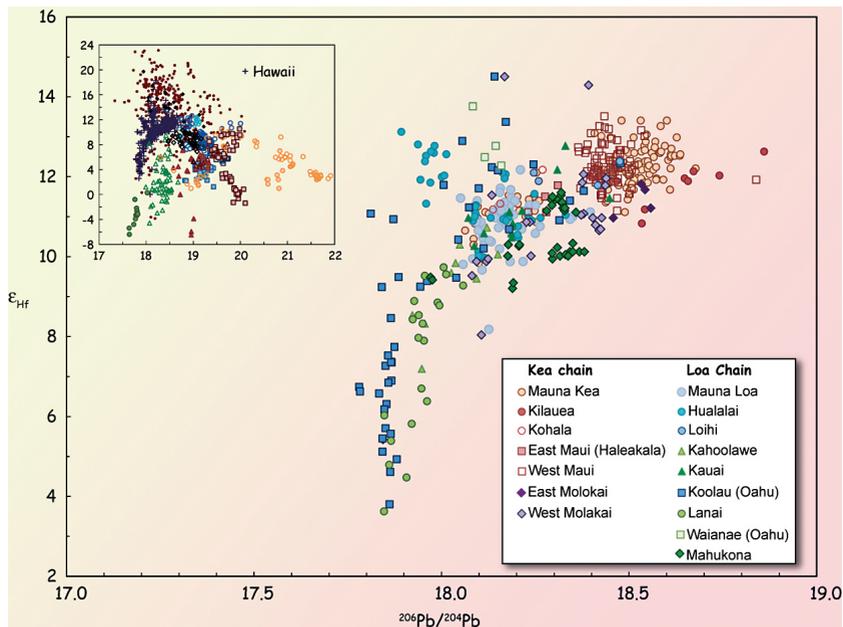


Figure 8.2 $\epsilon_{\text{Hf}}-^{206}\text{Pb}/^{204}\text{Pb}$ in Hawaiian shield and post-shield phase basalts (data from Georoc database georoc.mpch-mainz.gwdg.de/georoc/).

Hafnium-neodymium-lead isotopic relationships in Hawaiian lavas strongly suggest that in addition to a recycled basaltic component, a recycled sedimentary component is also present in the Hawaiian plume (Blichert-Toft *et al.*, 1999). As I described in Section 3.1, the usual strong correlation between ϵ_{Hf} and ϵ_{Nd} breaks down in marine sediments, with terrigenous sediments plotting below the igneous $\epsilon_{\text{Hf}}-\epsilon_{\text{Nd}}$ array and hydrogenous pelagic clays and Mn nodules plotting above it. *Janne Blichert-Toft* and others found that Hawaiian basalts tended to form shallow $\epsilon_{\text{Hf}}-\epsilon_{\text{Nd}}$ correlations. Even more dramatic was their discovery of the strongly curved $\epsilon_{\text{Hf}}-^{206}\text{Pb}/^{204}\text{Pb}$ array in Hawaiian basalts (Fig. 8.2) strongly suggestive of two-component mixing between a typical mantle component, which they labelled *Kea* and one with unradiogenic Pb and a low Hf/Pb concentration ratio, which they labelled *Koolau*. Blichert-Toft *et al.* (1999) argued that the latter component had the isotopic characteristics expected of ancient recycled hydrogenous sediment. Subsequently published data has complicated the picture



somewhat and revealed the presence of additional components, perhaps most notably one with relatively high ϵ_{Hf} , called the *Depleted Makapuu Component* by Tanaka *et al.* (2008) and Hanano *et al.* (2010) that is particularly apparent in Hualalai lavas in Figure 8.2.

8.2 A Case Study: The Hawaiian Plume

The geochemistry of plume-derived OIB varies. Much of this can be attributed to variability in processes of magma genesis and evolution – such as variable extent of melting and fractional crystallisation. Isotopic variations, as well as much of the variation in incompatible element ratios, rarely can be so attributed, however. Rather, this variability reflects intrinsic heterogeneity in the source region. Much of this appears to be random, but some is certainly not. The first demonstration of systematic isotopic variation was perhaps the work of Tatsumoto (1978), who showed that on the island of Hawaii the two volcanic chains defined by Jackson *et al.* (1972) had systematically different Pb isotopic compositions, with the Loa chain (Mauna Loa and Hualalai) having less radiogenic Pb than the Kea chain (Kilauea, Mauna Kea, and Kohala). Stille *et al.* (1986) showed that the distinction extended to Sr, Nd, and Hf isotope systematics as well, with the Loa chain having the more enriched isotopic signatures, and extended back 3 million years. Koolau volcano of Oahu appears to mark the first appearance of the Loa isotopic signal; prior to that almost all Hawaiian-Emperor volcanoes appear to have been produced from Kea-type mantle (Tanaka *et al.*, 2008). Higher precision Pb isotope analyses (*e.g.*, Abouchami *et al.*, 2005) reaffirmed the general Loa-Kea distinction (Fig. 8.3). As Abouchami *et al.* emphasise, however, individual volcanoes define distinct Pb isotopic trends within this general framework.

Hawaiian volcanoes, or at least many of them, appear to evolve through time in a systematic way (Macdonald, 1968; Clague and Dalrymple, 1987). During the early stage, sometimes called the *pre-shield* or *Loihi* stage, basalts are typically alkalic, heterogeneous, and somewhat incompatible element-enriched compared to the *shield* stage that follows. The vast bulk of the volcano, >95 %, is built during the shield stage during which relatively homogeneous tholeiitic basalt is erupted in large volumes; Kilauea is in the early part of its shield stage while Mauna Loa is approaching the end of its shield stage. This is followed by the *post-shield alkalic* stage, characterised by infrequent eruptions of small volumes of more incompatible element-enriched alkali basalt; Hualalai, Mauna Kea, and Haleakala (East Maui) are presently in the post-shield stage. Somewhat paradoxically, the isotope ratios of the post-shield lavas typically indicate a less incompatible element-enriched source. This is often followed after a hiatus of a half to several million years by what MacDonald called the post-erosional stage, now referred to as the *rejuvenescent* stage. This stage is characterised by infrequent eruptions of small volumes of highly alkalic basalts with a distinctly more depleted isotopic signature. The Honolulu volcanics of Oahu represent this stage of Waianae Volcano.



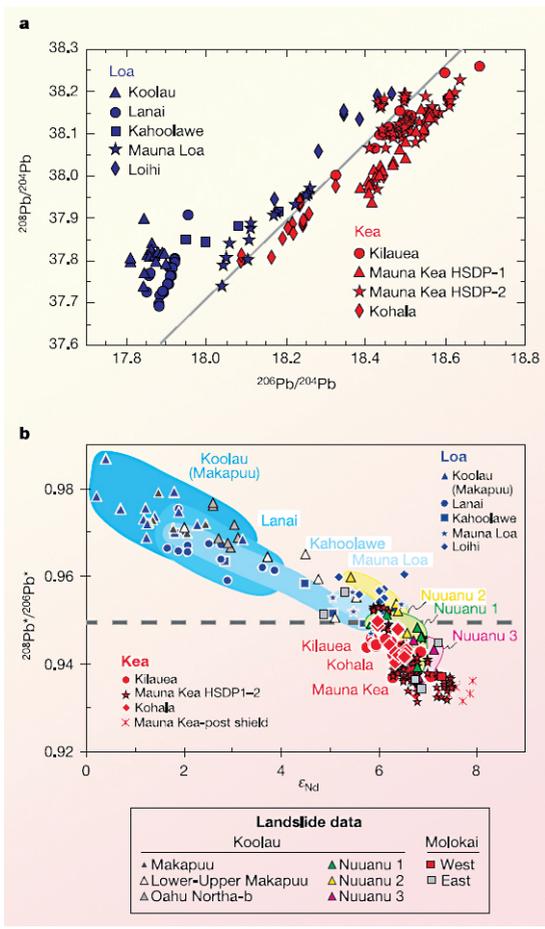


Figure 8.3 Pb and Nd isotope ratios in Hawaiian basalts. Kea trend volcanoes have lower $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ and higher ϵ_{Nd} than Loa trend volcanoes (from Abouchami, 2005 with permission from Nature Publishing Group).

proposed a steady-state concentrically zoned Hawaiian plume, with a lower mantle-derived plume core with high $^3\text{He}/^4\text{He}$ and enriched radiogenic isotopic signatures surrounded by a rim of less primitive He and less enriched radiogenic isotopic signatures. In the model, individual volcanoes sample a 50-60 km wide strip as they pass over this plume and much of the temporal and spatial variations in the composition of the volcanoes result from this motion over the

The Hawaiian Scientific Drilling Project (HSDP), which penetrated 250 m of Mauna Loa lavas and subsequently over 3 km of Mauna Kea lavas, provided a remarkable temporal record of these volcanoes. And because the volcanoes transect the plume over time, it also provides a geographic perspective of the plume itself. Analyses revealed systematic changes in isotopic and elemental composition in the Mauna Loa and upper part of the Mauna Kea sections, most apparently in Pb and He isotopic compositions, which evolved towards more “depleted” and degassed compositions with time (e.g., Abouchami *et al.*, 2000; Blichert-Toft *et al.*, 2003; Eisele *et al.*, 2003; Kurz *et al.*, 2004). Lavas from the deeper part of the Mauna Kea section have a generally more enriched isotopic signature, but also exhibit considerable temporal variability.

Based on results from the shallower pilot hole, DePaolo *et al.* (2001)



plume. Bryce *et al.* (2005) refined this model using the fuller data set from HSDP2, which extended to 3 km depth. In their model, the radius of the thermal anomaly (~300 °C) is roughly 260 km in diameter, but almost all the melt is derived from an inner melting zone that is only a third this width. The most enriched isotopic signatures come from a plume “core” that is only 30 km wide (Fig. 8.4). As it reaches the bottom of the lithosphere, much of the plume is deflected in the direction of plate motion (Ribe and Christensen, 1994) producing a tail pointed downstream. A key additional feature of this model is that the difference between the Kea and Loa chains results from the Loa volcanoes developing close to the centre of the plume, while the Kea volcanoes are offset

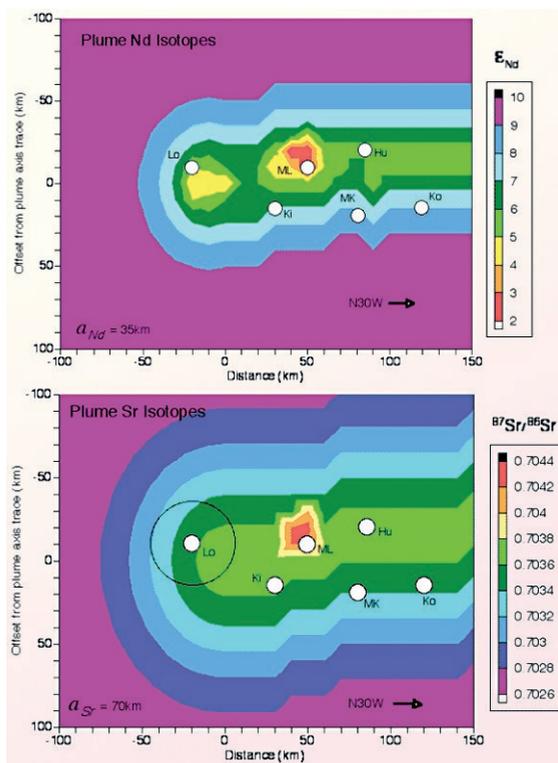


Figure 8.4 Zoned, heterogeneous plume Hawaiian model of Bryce *et al.* (2005). Lo: Loihi, Ki: Kilauea, ML: Mauna Loa, MK: Mauna Kea, Hu: Hualalai, Ko: Kohala (from Bryce *et al.*, 2005 with permission from John Wiley and Sons).

from the centre. Higher frequency variations, however, require the plume to be heterogeneous, with much of the heterogeneity concentrated in the plume core (Fig. 8.3). They argued that the differences between the Loa and Kea trends noted above could also be explained by the radial model with differences between the Loa and Kea chains explained by the offset of the latter relative to the plume core. Based on He isotope ratios, Kurz *et al.* (2004) inferred a somewhat larger size for the plume core, but like Bryce *et al.* (2005), concluded that “Mauna Kea has never been directly over the high $^3\text{He}/^4\text{He}$ plume center”. Importantly, Kurz *et al.* (2004) found that high $^3\text{He}/^4\text{He}$ ratios in Mauna Loa were associated with “enriched” Sr, Nd, and Pb isotopic signatures and concluded that “The He-Sr-Nd relations within HSDP2 Mauna Kea are not consistent with helium being more compatible than Th and U during silicate melting” as proposed by Parman *et al.* (2005).



Other studies focused on the shorter term variability within the Mauna Kea record and applied time-series analysis in an attempt to constrain the scale of heterogeneities with the plume. Blichert-Toft *et al.* (2003), Eisele *et al.* (2003) and Kurz *et al.* (2005) sought to identify periodic variations in the HDSP data set that might constrain the length scales of heterogeneity within the plume and found periods ranging from 10,000 to 100,000 years, but none of these showed up in all the analyses. A subsequent frequency analysis by Blichert-Toft and Albarède (2009) found the spectra to be “white” with no statistically significant peaks, suggesting the heterogeneity within the Mauna Kea magma feeding zone is largely random. Curiously, some lavas within the Mauna Kea sequence exhibit isotopic compositions similar to Kilauea, the youngest Kea volcano, and also to Loihi, the youngest Loa volcano (*e.g.*, Blichert-Toft and Albarède, 2009). The latter in particular suggest the possibility that some of the samples are products of a volcano other than Mauna Kea, including, perhaps, a “lost volcano” of Loa chain affinity that was subsequently buried by lavas of other volcanoes (Stolper *et al.*, 2004; Blichert-Toft and Albarède, 2009).

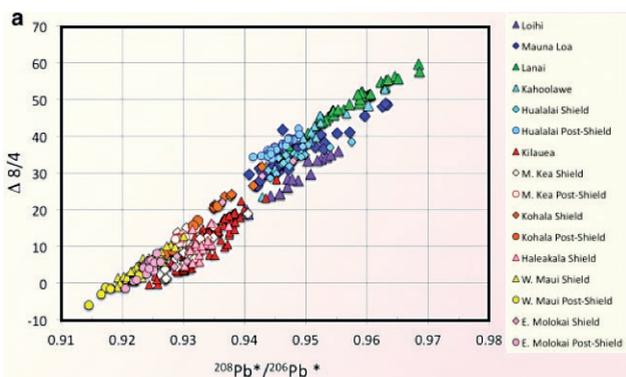


Figure 8.5

Pb isotopes in Hawaiian shield lavas. $\Delta 8/4$ is calculated from $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ as in equations 5.2 and 5.3 and $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ is the ratio of thorogenic to uranogenic Pb calculated as in equation 5.1. Cool colours (blues and greens) are from the Loa chain; warm colours from the Kea chain (from Hofmann and Farnetani, 2013 with permission from John Wiley and Sons).

The nature of the Loa-Kea distinction is a matter of debate. In the radially zoned plume model of DePaolo *et al.* (2001), much of the difference can be explained by the Loa chain being located over the more incompatible element-enriched and higher $^3\text{He}/^4\text{He}$ core of the plume while the Kea chain samples the less enriched margin but the model also includes some heterogeneity within the plume core. Abouchami *et al.* (2005) argued that “two trends have very little compositional overlap and instead reveal bilateral, non-concentric plume zones, probably derived from the plume source in the mantle.” This difference is most apparent in the relative abundance of ^{208}Pb (Fig. 8.5). Nevertheless, Blichert-Toft and Albarède (2009) found that Pb isotopic compositions of all lavas sampled by



HSDP, including both Mauna Kea and Mauna Loa sections, could be explained as mixtures of just 3 components (Fig. 8.6). One of these appears to be common to both chains and a Loa component appears to be present in Kea magmas. Their interpretation melds the concentrically zoned plume of DePaolo *et al.* (2001) with the filament-like heterogeneities proposed by Abouchami *et al.* (2005). Geodynamic modelling by Farnetani and Hofmann (2009, 2010) revealed that compositional heterogeneities entrained by the plume are likely to be stretched very considerably but that lateral variations in the thermal boundary layer source of the plume will be preserved as the plume rises. Thus, in this interpretation the Loa-Kea distinction ultimately results from heterogeneities at the base of the mantle. All of the interpretations are similar and merely variations on a theme.

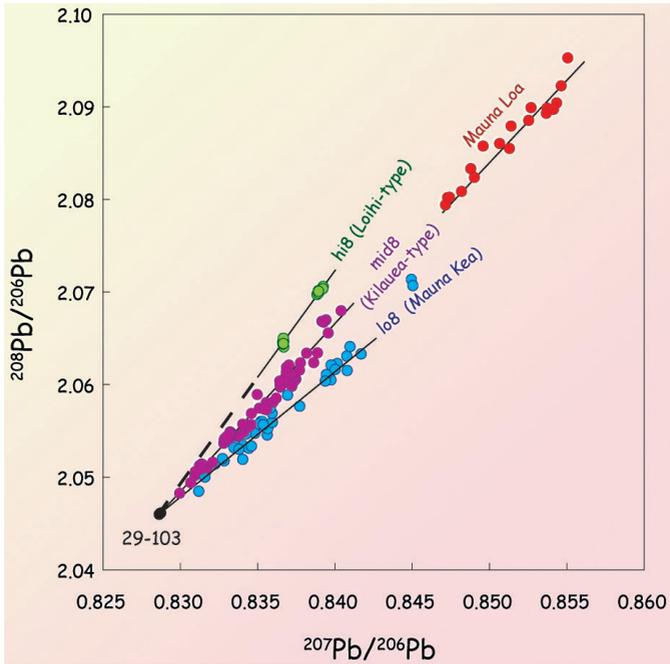


Figure 8.6 Pb isotope ratios from the HSDP. All samples except those in red labelled *Mauna Loa* are from the Mauna Kea section of the core (modified from Blichert-Toft and Albarède, 2009).

A quite different interpretation, however, was proposed by Bianco *et al.* (2008, 2011) based on the hypothesis of Ito and Mahoney (2005, 2006). They proposed that the Hawaiian plume consists of small blobs or veins of one or more enriched components uniformly dispersed in depleted components, which in turn are dispersed in dry, depleted peridotite. The enriched components have lower solidi than the peridotite and begin melting at greater depth. As a consequence,



these enriched components contributed a proportionally greater fraction of magma in the initial stages of volcanic evolution. As the material in the plume continues to rise the depleted peridotite contributes a progressively greater fraction of magma. This explains the trend through time toward lower $^3\text{He}/^4\text{He}$ and higher ϵ_{Nd} observed in Mauna Kea lavas from the HSDP core as well as in other volcanoes. In this model, as in the DePaolo *et al.* (2001) zoned plume model, the isotopic differences between the Loa and Kea chains are a consequence of their location relative to the centre of the plume. Because Loa chain volcanoes pass over the centre of the plume, the deep melting enriched component contributes proportionally more to their magmas, particularly during the main stage of growth. However, the model also predicts a return to very low ϵ_{Nd} at the end of the volcano's life cycle, which is not observed. Bianco *et al.* (2011) conceded that this model does not explain the systematic differences in Pb isotope ratios and suggested it reflects spatial variability in the relative proportions of the various components. In that case, the model differs from that of Farnetani and Hofmann (2009, 2010) perhaps only in the scale of the heterogeneities; there is little question or debate as to the existence of small scale heterogeneity in the mantle (Hofmann and Farnetani, 2013). I'll return to this topic in Section 9 and to the distribution of heterogeneity in the mantle in Section 8.3.

8.3 Lateral and Temporal Variations Within the Galápagos and Other Plumes

The Galápagos provides another example of lateral variations in mantle plume composition and a striking contrast to that of Hawaii. To begin with, the volcanoes do not form age progressive chains, but rather seem arranged in a tectonically controlled rectilinear pattern first recognised by Darwin (1846). Some 18 major and a number of minor subaerial volcanic centres, at least 13 of which have been active in the Holocene, emerge from a broad submarine platform. The tectonic setting is relatively unique in that the archipelago is located on relatively young lithosphere near a mid-ocean ridge, the Galápagos Spreading Center or GSC. However, unlike other near- or on-ridge hot spots, the absolute motion of the Nazca Plate, upon which the Galápagos archipelago is built, is nearly parallel to, rather than away from, the spreading centre, although prior to 5 Ma the hot spot was apparently ridge-centred. A westerly increase in the age of the oldest volcanism and two aseismic ridges, the Cocos and the Carnegie Ridges extending in the direction of Cocos and Nazca plate motions, is consistent with volcanism above a fixed long-lived mantle plume. Indeed, its hot initial plume-head phase in the Cretaceous appears to be responsible for the excessively thick crust of the Caribbean plate as well as the komatiites of Gorgona Island, Colombia (Aitken and Echeverria, 1984; Duncan and Hargraves, 1984; Hoernle *et al.*, 2002; Herzberg and Gazel, 2009).

I first visited the Galápagos during *Jean-Guy Schilling's* 1974 expedition to dredge the GSC, but only began active study of the islands a few years later as a post-doc at Carnegie. *Al Hofmann* and I were interested in the question of



whether there were any systematic isotopic differences between tholeiitic and alkali basalts from oceanic islands. We knew from the classic work of McBirney and Williams (1969) that both types of basalts were present in the Galápagos, so I visited the University of Oregon to obtain samples from *McBirney* (“*Mac*” as he is known by his colleagues and students). We found no systematic relationship between Sr and Nd isotope ratios and major element chemistry, but we did find an interesting geographic pattern, which *Al* was the first to spot: the most depleted isotopic signatures were found in the centre of the archipelago and the most enriched ones around the periphery (White and Hofmann, 1978). This was, of course, just the opposite of what we might expect if a mantle plume mixed with surrounding asthenosphere as it appears to do in Iceland (Schilling, 1973a; Hart *et al.*, 1973) and elsewhere.

Mac also continued to work on the Galápagos, sending a whole generation of graduate students to study individual islands. I continued working on the Galápagos through my years at Max Planck, among other things analysing samples his students collected. The additional data served only to better define the same enigmatic ‘horseshoe-like’ pattern we had initially recognised. When I moved from Max Planck to Oregon State in 1985, I began collaboration with *Mac* and *Bob Duncan* to continue working on the Galápagos. Our sample collecting expedition in December 1986 (which, because of bureaucratic delays in obtaining sampling permits, dragged on to early 1987, to the dismay of my family), included a climb to the summit of Volcan Darwin. Aa lava, which covers the flank, does not make for easy hiking: my boots were so torn to shreds after four days on that volcano that I didn’t bother bringing them home with me. A later expedition attempted to reconstruct the evolution of Volcan Ecuador, which had undergone sector collapse some 60,000 to 100,000 years ago (Geist *et al.*, 2002), in collaboration with *Denny Geist*, *Karen Harpp*, and *Francis Albarède* using the team of climbers that *Francis* had successfully employed to reveal the history of Piton de la Fournaise on Reunion (Albarède *et al.*, 1997).

The problem we hoped to address – the lack of information on the evolution of Galápagos volcanoes through time – is a consequence of the climate in the Galápagos. Despite lying astride the equator (which, incidentally, is how Volcan Ecuador got its name), the Galápagos are remarkably arid as a consequence of Pacific equatorial upwelling of cold deep water. As a result, erosion rates are extremely low, and there is little exposure of older rocks. The cliffs exposed in the collapse of Volcan Ecuador provided access to older lavas of a still active volcano and *Francis’* team of climbers helped us access them. Nevertheless, the sun combined with equatorial heat can be brutal in the Galápagos, and a wide-brimmed hat is a necessity (even with a hat, I came close to heat stroke at one point and was forced to rest for a while in the only shade I could find – that of a prickly pear cactus). *Francis*, however, had not brought a hat (despite my insisting he do so). Always resourceful, *Francis* put his umbrella (an otherwise completely useless accessory) to use as a parasol. I’ll never forget the images of him walking through the desert with an umbrella (Fig. 8.7) as well as of him scrambling up the cliff at the top of the volcano off of which he had just fallen.





Figure 8.7 Francis Albarède doing field work in the Galápagos.

plumes. However, Richards and Griffiths (1989) had shown that a plume deflected by lithospheric motion could thermally entrain asthenosphere into its centre in a rather similar manner and we argued this could explain the geochemical pattern we saw (White *et al.*, 1993). Analyses of our samples from the seamounts by my then student *Karen Harpp* confirmed that the horseshoe did not close (Harpp and White, 2001) (Fig. 8.8).

Mixing between a mantle plume and incompatible element-depleted asthenosphere explained much of the compositional variation in the Galápagos, but more detailed examination and principle component analysis revealed that three enriched components, which *Karen* named WD (for the island Wolf and Darwin), PLUME, and FLO (for the island of Floreana), were involved in addition to the depleted component, DUM (Fig. 8.9). These are geographically distributed and show up principally in the northern, central, southern and eastern sections, respectively, of the archipelago. Based on analyses from seamounts of the Cocos Ridge, this spatial zonation appears to have persisted for at least 14 Ma (Hoernle *et al.*, 2000). Hoernle *et al.* (2000) suggested the depleted component is intrinsic to the plume.

The first decent idea we had to explain the pattern of enriched and depleted isotopic signatures was proposed by *Denny Geist*, who had been a *McBirney* student. Geist *et al.* (1988) proposed a model of entrainment of asthenosphere into the centre of the plume with the original plume material concentrated in a torus-like ring based on lab and numerical experiments of *Ross Griffiths* (1986). The data we had, however, showed only half a torus: a horseshoe-like pattern open to the east, but then we did not have samples from that open eastern side. To see if it closed, *Mac*, *Bob Duncan*, *Mark Richards* and I proposed an oceanographic expedition to dredge seamounts that we knew existed in the area. In the meantime, it became clear that the *Griffiths* torus was relevant only to starting



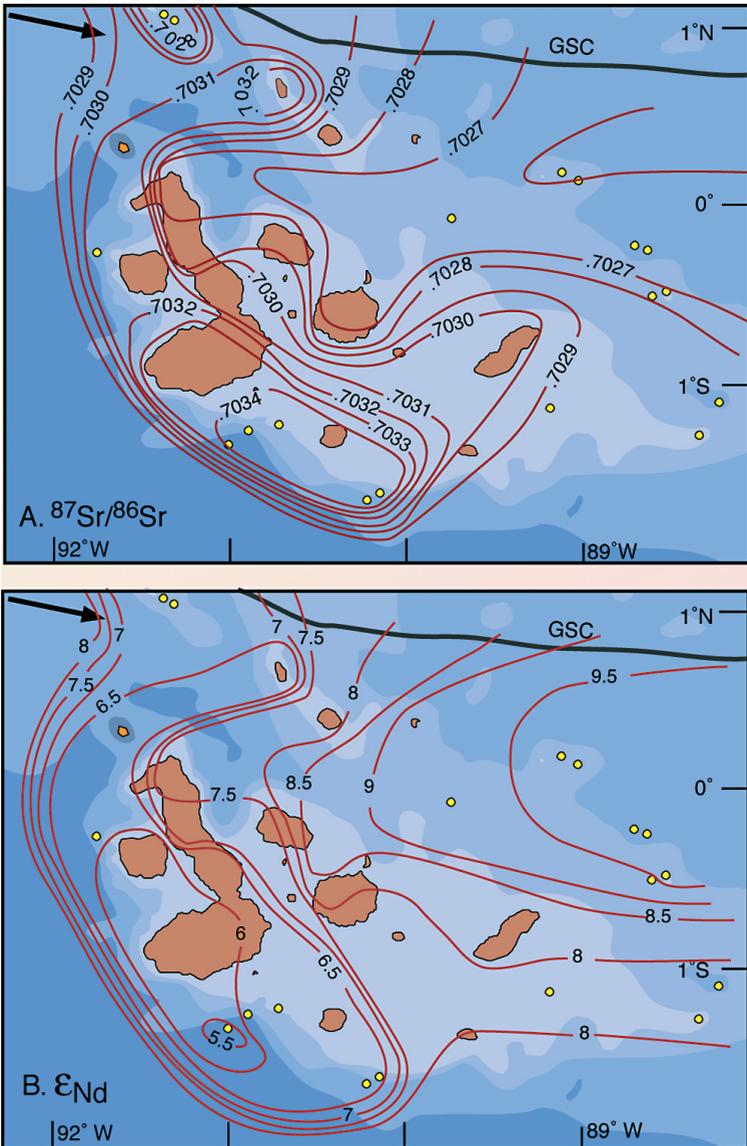


Figure 8.8 Contours of $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} in lavas from the Galápagos and GSC. Yellow dots show the location of dredged samples (from Harpp and White, 2001 with permission from John Wiley and Sons).



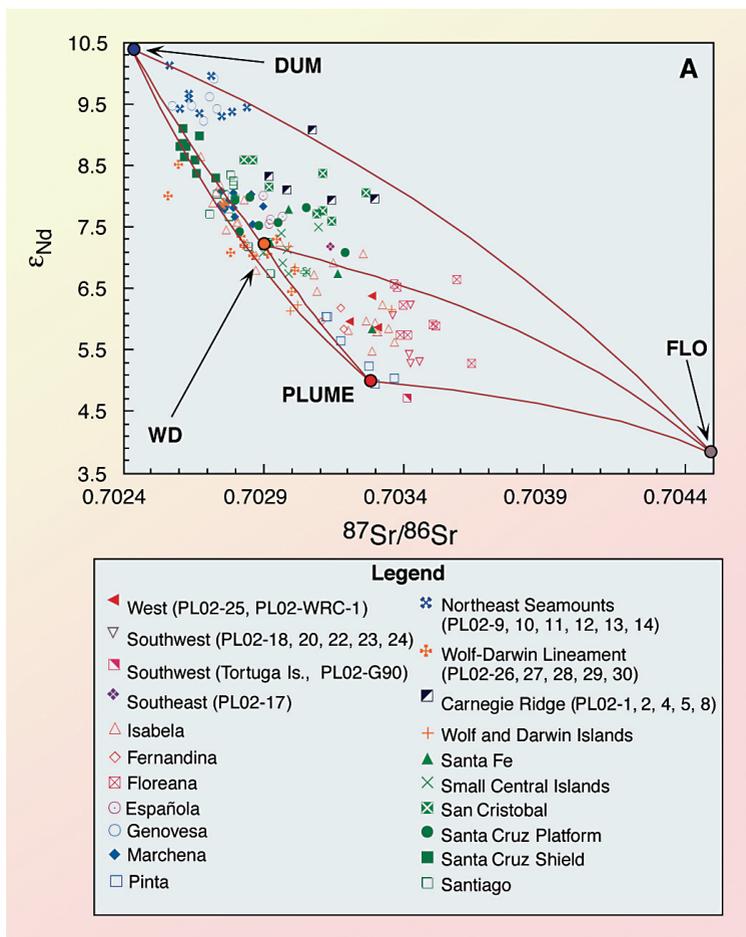


Figure 8.9 $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} in Galápagos lavas and inferred compositional end-members. The WD component differs primarily in $^{208}\text{Pb}/^{204}\text{Pb}$ (from Harpp and White, 2001 with permission from John Wiley and Sons).

Vidito *et al.* (2013) attempted to assess the relative fractions of peridotite and pyroxene sources in Galápagos magmas and found that overall the peridotite dominates, although in a few cases, most notably Darwin volcano and Santiago, pyroxenite dominates. Intriguingly, there appears to be little or no relationship between isotopic signature and source lithology, with variable pyroxenite contributions to lavas with both the most enriched and depleted compositions. They suggested, following Gurenko *et al.* (2010), that older (> 2 Ga) recycled crustal material could be so thoroughly stretched and mixed into mantle peridotite that



it no longer retained its lithologic identity. In contrast, more recently recycled material would retain a 'marble-cake'-like structure of stringers and pods of recycled crust in a peridotite matrix.

White *et al.* (1993) proposed that the plume was bent to the east and south-east by lithospheric drag of the Nazca Plate, which places Fernandina at the leading edge of the plume. Fernandina lavas have the highest $^3\text{He}/^4\text{He}$ in the archipelago, and Kurz and Geist (1999) argued this was consistent with progressive degassing of the bent plume. In this model one would expect the highest temperatures and largest melt fractions at Fernandina. However, when Herzberg and Gazel (2009) determined mantle potential temperatures for Galápagos volcanoes they found the highest temperature (1500 °C) for Cerro Azul, southeast of Fernandina. Santiago and Santa Cruz, which have relatively depleted isotopic signatures and are located well to the east, had potential temperatures of 1485 °C to 1480 °C, indistinguishable from that of Fernandina (1485 °C). The lowest temperature (1460 °C) occurs beneath Floreana, which is consistent with small melt fractions generated at shallow depth inferred by White *et al.* (1993) and Harpp *et al.* (2014). Handley *et al.* (2011) found that the smallest ^{230}Th - ^{238}U disequilibrium occurs in lavas from Wolf Volcano, which has a depleted isotopic signature and is located northeast of Fernandina. ^{230}Th - ^{238}U disequilibrium reflects time-dependent Th-U fractionation in the melting column. In the simplest models ^{230}Th - ^{238}U disequilibrium decreases with extent of melting; this suggests larger melt fractions beneath Wolf than Fernandina. Finally, surface wave tomography of Villagómez *et al.* (2007), although providing at best only a hazy image of the uppermost (130 km) mantle, suggests that the plume is deflected to the north, not to the east as White *et al.* (1993) had assumed. Northward deflection of the plume is consistent with isotopic variations along the GSC, where the maximum plume signal is observed near 91° to 92°W (*e.g.*, Verma *et al.*, 1983; Schilling *et al.*, 2003), almost due north of the youngest volcanoes of Fernandina and Isabela Islands. This suggests that the spreading centre serves as a "sink", drawing plume flow toward it, just as Schilling (1985) had suggested, and that "*plume buoyancy forces dominate over plate drag forces*" (Villagómez *et al.* 2007).

The current evidence thus indicates that the Galápagos mantle plume is entrained by asthenospheric flow northward toward the GSC rather than to the east as White *et al.* proposed. Hoernle *et al.* (2000) had proposed that "the plume is draining two or three chemically distinct regions at its boundary layer source" and that the depleted component is intrinsic to the plume and dispersed throughout it. They suggested it becomes dominant only as enriched components, "for example in the form of enriched pyroxenitic layers", are melted out. If, however, plume material is flowing to the north rather than the east, there is no apparent progressive loss of an enriched signature (with the possible exception of $^3\text{He}/^4\text{He}$). Also, pyroxenite is apparently not restricted only to enriched components of the plume (Vidito *et al.*, 2013). This, together with evidence that the depleted component is generated at temperatures, depths, and melt fractions similar to the enriched components (White *et al.*, 1993; Herzberg and Gazel, 2009; Gibson and Geist, 2010; Handley *et al.*, 2011) and its restricted geographic occurrence, suggests



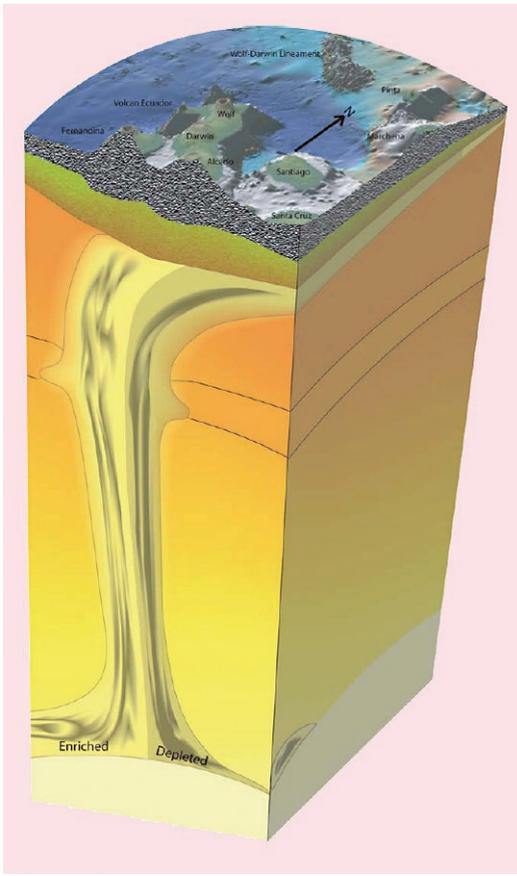


Figure 8.10 Cartoon of the Galápagos mantle plume drawing in both enriched and depleted components from the thermal boundary layer (from Vidito *et al.*, 2013 with permission from John Wiley and Sons).

the depleted component originates from a distinct region in the thermal boundary layer as Vidito *et al.* (2013) argue (Fig. 8.10). The Galápagos plume thus appears to be similar to that of Hawaii, drawing in a variety of compositionally distinct material from the thermal boundary layer that results in an azimuthally zoned plume as Farnetani and Hofmann (2009) envision. What is particularly significant, however, is that the Galápagos depleted component appears to be identical to the upper mantle MORB source. The inference that it is intrinsic to the plume indicates that the depleted mantle reservoir (DMM) is not restricted to the upper mantle but is present in some parts of the deepest mantle as well.

Hawaii and the Galápagos are the best-documented examples of lateral zonation in oceanic island chains, but are not the only ones. There is also evidence of dual tracks with distinct isotopic compositions persisting in the Marquesas (Desonie *et al.*,

1993; Chauvel *et al.*, 2012) and the Society Islands (Payne *et al.*, 2013) for the entire history of the hot spot tracks, 5 and 4 million years, respectively. Two tracks have been identified in Samoa (Workman *et al.*, 2004; Huang *et al.*, 2011; Jackson *et al.*, 2014), but the northern *Vai* chain appeared only about 2.1 million years ago. The Easter–Sala y Gomez chain appears to be another example of a dual track extending back perhaps 30 million years (Ray *et al.*, 2012; Harpp *et al.*, 2014). Tristan da Cunha and Gough are yet other, but somewhat different examples. These two volcanoes are separated by 400 km and could be considered



separate hot spots. They are isotopically similar, but not identical. Interestingly, their hot spot tracks in the Walvis Ridge tend to converge with increasing age but the distinctive geochemistry of the two tracks is maintained for 70 million years (Rohde *et al.*, 2013). Curiously, in most of these cases, Pb isotopes provide the best discriminant between the two tracks. There is some evidence for lateral heterogeneity in the Azores plume as well (Beier *et al.*, 2010). Not all hot spot tracks display systematic lateral heterogeneity through time, however; for example, lateral heterogeneity has not been found in Reunion, Louisville, or Iceland.

8.4 A Geochemical Map of the Deep Mantle?

The radially heterogeneous but azimuthally homogeneous model of the mantle that dominated thinking in the late 20th century must now be abandoned. We have seen that OIB and the plumes that produce them comprise a diverse array of isotopic compositions. There is a broad consensus that many of these plumes originate in the thermal boundary layer at the base of the mantle, thought to coincide with the seismically defined D'' region described in Section 6.1. One of the defining characteristics of this region is strong lateral and vertical heterogeneity in seismic properties, most notably manifested by the two LLSVP's and the ULVZ's that seem to be associated with them. The obvious question is whether and how the geochemical and geophysical observations of heterogeneity are related. The first step in this direction was perhaps Hart (1984) pointing out that his isotopically defined DUPAL anomaly coincided with features in the degree-2 geoid pattern of the Earth. I suggested earlier that it would be better to consider two distinct isotopic anomalies, DUPAL and SOPITA, each of which more or less coincides with an LLSVP. As noted earlier, mantle plumes seem to be preferentially located on the margins of these LLSVP's.

Farnetani *et al.* (2012) showed that simple lateral compositional variation in the plume source region could map into more complex lateral and radial variation within the plume and generate the pattern of spatial and temporal variation seen in Hawaiian volcanoes. Thus the spatial heterogeneity in plumes described in the previous section may reflect heterogeneity in the plume source region at or near the base of the mantle. Weis *et al.* (2011) noted that *"the Hawaiian mantle plume, when projected into the deep mantle, overlies the boundary between typical Pacific lower mantle"* and the Pacific LLSVP on the Loa side of the plume. They concluded *"that the geochemical differences between the Kea and Loa trends reflect preferential sampling of these two distinct sources of deep mantle material"* and furthermore that the Tristan da Cunha and Kerguelen plumes similarly sampled diverse material at the margin of the African LLSVP. Comparing variations in several zoned plumes in the Pacific, Huang *et al.* (2011) argued that these zonations reflect a systematic variation in isotopic composition, particularly in $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ (a proxy for the time-averaged Th/U ratio; equation 5.1) of the lowermost mantle. Weis *et al.* (2011) noted that the Hawaiian plume is located near the northern edge of the Pacific LLSVP and proposed that the southern, or Loa, Hawaiian component



was derived from it. Huang *et al.* (2011), noting similar zonation in the Samoan and Marquesas chains, wrote that these zonations “reflect their respective positions relative to the Pacific superplume” and “that isotopically enriched material is preferentially distributed in the lower mantle of the Southern Hemisphere, within the Pacific low seismic velocity zone.” Harpp *et al.* (2014) argued that lateral variation in the Galápagos and Easter–Sala y Gomez plumes could also be related to their location relative to the Pacific LLSVP. Some caution is necessary, however, in mapping surface geochemistry onto the core–mantle boundary because mantle plumes, just like smoke plumes in the atmosphere, can “bend in the wind” (Steinberger and O’Connell, 1998).

8.5 The Mystery of Rejuvenescent Volcanism

Many oceanic volcanoes experience what one might call reawakening following a hiatus of hundreds of thousands to several million years. The classic example of such rejuvenescent volcanism is, of course, Hawaii (Sterns, 1940; MacDonald and Katsura, 1964; Clague and Dalrymple, 1987). Hawaiian rejuvenescent magmatism is characterised by eruption of small volumes of highly alkalic magmas and occurs on many, but not all, volcanoes. Importantly, while they are generally more incompatible element-enriched than shield stage lavas, the isotopic signature is usually more depleted than the shield stage (*e.g.*, Roden *et al.*, 1984). Rejuvenescent volcanism has so far been identified on only a single volcano each in the Marquesas and Society Islands, but both examples follow the Hawaiian pattern in that the lavas are more alkalic with more depleted isotopic characteristics than the shield stage (Brousse *et al.*, 1986; White and Duncan, 1996; Guillou *et al.*, 2014). Madeira may be just entering a rejuvenescent phase with the eruption of several Holocene lavas that follow this same pattern (Geldmacher *et al.*, 2000).

Mauritius, the penultimate island of the Reunion hotspot track, provides another example and was the subject of PhD dissertations by my former students Jacob Moore and Debajyoti Paul. Here too the rejuvenescent phase follows a long hiatus (>1 million years) and the isotopic signatures of the rejuvenescent phase are more depleted than those of the shield-building phase. Rejuvenescent phase lavas, which erupted from chains of vents aligned diagonally across the centre of the island, cover more than 75 % of the surface of the island. The many drill cores (bored for water supply) reveal that these lavas fill ancient calderas in the island interior to depths of more than 200 m. Nevertheless, Moore *et al.* (2011) calculated that they represent only ~0.05 % of the volume of the volcano, comparable to the fractional volume (0.1 %) of the rejuvenescent phase lavas on Kaua’i calculated by Garcia *et al.* (2010). There are important differences, however. Rejuvenescent lavas are only slightly less silica saturated and, in contrast to Hawaii, are slightly less incompatible element-enriched than shield stage lavas (*e.g.*, Paul *et al.*, 2005; Moore *et al.*, 2011). Furthermore, the rejuvenescent phase has been extraordinarily long (~3.5 million years) and is interrupted by a hiatus of ~600,000 years separating the so-called Intermediate and Younger Series.



Canary volcanoes also experience a rejuvenescent phase but it differs from both Hawaii and Mauritius in that rejuvenescent lavas range in composition from tholeiites to basanites, as do the shield stage lavas, with no systematic compositional distinction between phases (Carracedo *et al.*, 1998). Some of the complexity of volcanic evolution in the Canaries may be due to features of its tectonic setting, including the slow motion of the volcanoes relative to the plume (2 cm/yr), old oceanic crust with a thick sedimentary pile, and proximity to continental lithosphere.

Samoa provides yet another example of rejuvenescent volcanism that also differs from the Hawaiian example. As in Hawaii, rejuvenescent lavas usually are more alkalic than shield stage lavas and, on average, are more incompatible element-enriched. Isotopic compositions differ systematically, mainly in having lower $^{206}\text{Pb}/^{204}\text{Pb}$ but unlike Hawaii, they do not have more depleted Sr and Nd isotopic signatures (Wright and White, 1987; Konter and Jackson, 2012). Rejuvenescent lavas are found on the three westernmost and oldest islands in the chain: Tutuila, Upolu, and Savai'i. Volumes on the younger two islands are quite restricted, but rejuvenescent lavas cover nearly the entire surface of Savai'i. The absence of borehole samples results in considerable uncertainty in the volume, which Konter and Jackson (2012) estimate to be between 0.22 % and 1.8 % of the volume of the volcano. At a minimum, this would be twice the volume fraction on Kaua'i and four times the volume fraction on Mauritius.

Rejuvenescent volcanism presents two difficult questions: why does volcanism renew after a long hiatus when the volcano has moved well off the plume and, given that isotopic compositions indicate a source different from shield phase lavas, what is melting? On the other hand, the silica undersaturated and incompatible element-enriched nature of these lavas in the Hawaiian and similar examples is fairly readily explained as a consequence of much smaller extents of melting, consistent with the small eruptive volumes (Chen and Frey, 1983; Roden *et al.*, 1984).

Let's first consider cause. In the Ribe and Christensen (1999) model of the Hawaiian plume, a weak secondary region of decompression melting occurs 300-500 km downstream from the primary melting zone as a consequence of buoyant lateral spreading. However, Jull and Ribe (2002) subsequently found that the existence of this secondary melting zone was sensitive to boundary conditions. Other numerical models of the Hawaiian plume show a zone of small melt fractions extending well downstream of the plume but it is continuous, unlike the Ribe and Christensen model (Phipps-Morgan and Parmentier, 1998; *e.g.*, Hofmann and Farnetani, 2013). Thus plume dynamics may be able to explain the rejuvenescent volcanism, but not the hiatus that precedes it. Ten Brink and Brocher (1987) suggested that loading of the lithosphere by volcanic growth eventually results in compressive stresses that shut off access of magma to the surface. Further downstream, a bulge or arch develops in response to this loading, relieve horizontal compressive stresses and allowing magma to reach the surface. In combination, a long melting tail and lithospheric flexure could explain



both the volcanism and the hiatus (e.g., Paul *et al.*, 2005; Garcia *et al.*, 2010). Bianco *et al.* (2005) extended the flexure model, arguing that sufficient upwelling occurs in the asthenosphere as the lithosphere arches upward to generate the small melt fractions that characterise the rejuvenescent magmas. In detail, however, predictions of both the timing of flexure-induced rejuvenescent magmatism and volumes of melt fractions in both the melting tail and flexural models fail to match observations (Garcia *et al.*, 2010; Hofmann and Farnetani, 2013). A third explanation is thermal erosion and melting of the lithosphere by the hot plume (Liu and Chase, 1991).

A variety of models have also been proposed to explain the difference in isotopic compositions. Chen and Frey (1983) proposed that the change in isotopic composition results from assimilation of lithosphere composed of depleted upper mantle as the melting rate wanes and lithosphere warms. While this model can, perhaps, explain Sr and Nd isotopic systematics, it fails to explain combined Pb, Sr, and Nd systematics (and hence also correlated Hf isotopes), both in Hawaii (Roden *et al.*, 1984) and elsewhere (White, 2010). An alternative proposed by White and Duncan (1996) for the Society Islands and Fekiacova *et al.* (2007) for Hawaii is that rejuvenescent magmas are generated by melting of the sheath of more depleted material entrained by the plume as it rises through the deep mantle. In the Bianco *et al.* (2005) model, the plume consists of a mixture of pods and lenses of pyroxenite and/or incompatible element-enriched peridotite distributed more or less uniformly in a matrix of depleted peridotite, the latter with a higher solidus temperature than the two former. Shield stage magmas are generated largely by melting the enriched components at depth in the vertical rising stem of the plume, which become exhausted or nearly so at the end of the post-shield stage. The depleted component, which contributed only a limited fraction of shield phase magma production, then becomes the dominant contributor to the rejuvenescent phase. However, as Hanano *et al.* (2010) point out, the depleted component that appears to contribute to Hawaiian shield stage magmas is distinct from that in the rejuvenescent magmas and the heterogeneous plume model is inconsistent with widely varying La/Yb ratios, indicative of widely varying melt fractions, at the nearly constant ϵ_{Nd} observed in rejuvenescent magmas (Hofmann and Farnetani, 2013).

Yet a different model was proposed by Yang *et al.* (2003) for Hawaii and Moore *et al.* (2011) for Mauritius. In this model, the initial small-degree melts of the leading edge of the plume fail to penetrate to the surface and instead react with the lithosphere, creating a hybrid pyroxenite source. As the lithosphere transits the plume, it is slowly heated such that it exceeds the pyroxenite solidus in the lower lithosphere after several million years (Moore *et al.*, 2011), thereby generating the rejuvenescent magmas. That model might be appropriate for Mauritius because, unlike Hawaii, the rejuvenescent source can be plausibly explained as a mixture of plume material and depleted mantle (*i.e.* MORB source). In summary, although there is some convergence of ideas, the causes and sources of rejuvenescent magmatism associated with these plumes remain contentious.



Samoa, on the other hand, is unique both in its tectonic setting and in that a consensus does seem to exist as to the cause of rejuvenescent volcanism. Samoa is located just north of the terminus of the Tonga subduction zone and the Pacific plate is effectively torn as the southern part subducts and the northern part carries Samoa further to the west. Hawkins and Natland (1975) and (Natland, 1980) suggested that the voluminous rejuvenescent magmas are generated as a consequence of flexure of the Pacific plate and shear heating in this unique tectonic environment. The plate flexure interpretation was also adopted by Wright and White (1987). More recently, Konter and Jackson (2012) quantitatively modelled melt generation driven by flexural uplift, which they suggest is on the order of a km, ten times that resulting from plate loading in Hawaii, and concluded that *“flexural upwarping of the Pacific Plate is indeed quantitatively consistent with more rejuvenated-stage melt production in Samoa.”* Unlike almost all other examples of rejuvenescent volcanism, Samoan rejuvenescent lavas carry a strongly enriched isotopic signature. Inverse $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ correlations strongly suggest that the rejuvenescent lavas are generated from a mixture of Samoan plume material and an exotic component with EM I characteristics (Wright and White, 1987). Konter and Jackson (2012) concluded that a third, MORB-like component was also involved. They argued that the rejuvenated component was Pacific plate lithosphere, with an initially MORB-like isotopic composition that had been metasomatised by melts from the Raratonga hot spot some 15 million years earlier.



9.1 Whither Primitive Mantle?

The DePaolo and Wasserburg (1976a,b) model of a two-layered mantle consisting of a depleted upper layer overlying a lower primitive one, described in Section 3, seemed to be supported by mass balance calculations indicating that the incompatible element inventory of the continents could be derived from a third or so of the mantle. The key assumption in these calculations, that the Earth had a chondritic Sm/Nd ratio and therefore chondritic $^{143}\text{Nd}/^{144}\text{Nd}$, seemed beyond question. The chondritic assumption was extended to all *refractory lithophile elements* (RLE's) – lithophile elements with high nebular condensation temperatures (Section 1.2) – and provided the basis for detailed calculation of the composition of the silicate Earth. The work of McDonough and Sun (1995) is the best known example, but others had and subsequently did derive essentially similar compositions (e.g., Jagoutz *et al.*, 1979; Hart and Zindler, 1986; Palme and O'Neill, 2003), reflecting a broad consensus. I recall a conversation with a planetary science colleague of mine at Cornell, *Joe Ververka*, 20 years or so ago in which I stated that we (geochemists) knew the composition of the Earth fairly well. He laughed.

Despite its supposedly constituting two-thirds of the mass of the mantle, “primitive mantle” proved to be oddly rare and elusive. No magmatic rock with all the chemical characteristics of derivation from primitive mantle had, or ever has, been reported. “Primitive” signatures are, of course, found in the isotopic compositions of helium and other noble gases. However, the most primitive noble gas signatures are associated with positive ϵ_{Nd} values indicative of an incompatible element-depleted history rather than the assumed primitive mantle ϵ_{Nd} value of 0. The absence of a primitive mantle signature became all the more bothersome when seismic tomography showed slabs sinking into the deep mantle, implying whole-mantle rather than layered-mantle convection.

It was a second long-lived isotope of samarium, ^{146}Sm , which alpha-decays to ^{142}Nd , that forced geochemists to reconsider the Earth's, and hence primitive mantle's, composition. I should note that “long-lived” is a relative term: the half-life of ^{146}Sm is 103 million years, three orders of magnitude shorter than the 106 billion year half-life of ^{147}Sm , according to Meissner *et al.* (1987) and it is now extinct.³ While Kinoshita *et al.* (2012) reported a revised value of the half-life to be 68 million years, Marks *et al.* (2014) found that the initial $^{146}\text{Sm}/^{144}\text{Sm}$ of an Allende calcium-aluminum inclusion was consistent with the 103 Ma half-life and not the revised value.) Lugmair and Marti (1977) confirmed the existence of

3. Not quite. A quick calculation reveals that there should be something close to 10^{26} atoms of ^{146}Sm remaining in the Earth. That might sound like a lot, but it works out to be less than 1 atom per gram of rock.



^{146}Sm in meteorites and Harper and Jacobsen (1992) found evidence that it was still present in the early Earth in the form of elevated $^{142}\text{Nd}/^{144}\text{Nd}$ ratios in the 3.8 Ga Isua Greenstone Belt. This was viewed with considerable scepticism for a decade until Boyet *et al.* (2003) and Caro *et al.* (2003) replicated these results and they were accepted. The very important implication was that the Earth had begun to differentiate very early, while significant amounts of ^{146}Sm remained.

If the Earth indeed has a chondritic Sm/Nd ratio, then the Earth's $^{142}\text{Nd}/^{144}\text{Nd}$ should also be chondritic. Harper and Jacobsen (1992), Boyet *et al.* (2003) and Caro *et al.* (2003) all assumed it did. Caro *et al.* (2003) showed that the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio in MORB was uniform and identical to laboratory standards. The trouble was that no one had actually measured the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio of chondrites with sufficient precision to determine whether the chondritic value matched the terrestrial one. So it came as something of a shock then when Boyet and Carlson (2005) showed that chondrites in fact had lower $^{142}\text{Nd}/^{144}\text{Nd}$ than terrestrial rocks, with the Isua values being even more displaced from chondrites than initially thought. Like Caro *et al.* (2003), Boyet and Carlson found no resolvable variation in modern terrestrial rocks, a result confirmed by a variety of subsequent studies (*e.g.*, Boyet and Carlson, 2006; Caro *et al.*, 2006; Andreassen *et al.*, 2008; Murphy *et al.*, 2010; Jackson and Carlson, 2012). Two alternatives emerge: either the Earth does not have chondritic Sm/Nd and by implication does not have a chondritic inventory of refractory lithophile elements or its very early differentiation was such that the entire continental crust and all of the mantle sampled by volcanism is derived from an incompatible element-depleted, super-chondritic Sm/Nd reservoir and that a complementary sub-chondritic Sm/Nd reservoir has not been sampled.

Boyet and Carlson (2005) argued for the latter, proposing that an 'early enriched reservoir' (EER) formed as a result of fractional crystallisation of a magma ocean much as the lunar KREEP reservoir and, being iron-rich, sank into the deep mantle where it has subsequently remained. In this model the Earth is indeed chondritic but the *accessible* or *observable* part, the complementary early-depleted reservoir (EDR) that subsequently gives rise of to the continents and all mantle-derived magmas, is not. The fate of the EER is unclear, but one speculative possibility is that it is contained within the LLVSP's discussed in Section 6.1. They appear to be hot and dense, consistent with such a reservoir being rich in iron and heat producing elements, and Burke (2011) has argued that these features are both permanent and stationary.⁴

Because of the short half-life of ^{146}Sm , this hypothesised differentiation event must have happened very early, within at most a couple tens of millions of years of the start of the Solar System. Delaying it by even as much

4. Wohlers and Wood (2015) have recently proposed yet another alternative: if the Earth accreted a reduced, sulphur-rich body similar to Mercury or the enstatite chondrite parent body, some rare earths, as well as U, could be partitioned into the core, with Nd partitioning into the core in preference to Sm sufficiently to increase the Sm/Nd ratio of the silicate Earth sufficiently to explain the excess ^{142}Nd .



as 30 million years would require the EDR to have ϵ_{Nd} greater than the average MORB value of around +9 (Boyet and Carlson, 2005) or more if the half-life is 68 Ma. Another important observation is that the lunar $^{142}\text{Nd}/^{144}\text{Nd}$ ratio appears to be identical to the terrestrial one (Boyet and Carlson, 2007; Caro, 2010). This implies that the differentiation that created the EER preceded the Moon-forming impact, requiring that the EER somehow survived that event. Furthermore, something between a third and a half of the Earth's inventory of the heat producing elements, U, Th, and K would have to be sequestered in the EER, which means it would eventually become quite buoyant and difficult to keep hidden and undetected for 4.5 Ga at the bottom of the mantle. If the LLSVP's do consist of the EER, they apparently do not contribute to mantle plumes. Murphy *et al.* (2010) calculated that even a small contribution (<0.1%) from the hypothesised EER should produce a measurable anomaly in $^{142}\text{Nd}/^{144}\text{Nd}$. While $^{142}\text{Nd}/^{144}\text{Nd}$ is variable in Archean rocks, this variability dwindles and ends by the late Archean (Debaille *et al.*, 2013), Murphy *et al.* confirmed that no variation in this ratio is discernable in any OIB. Thus it is worthwhile exploring alternative hypotheses.

Two alternatives have been proposed. The first of these evolves out of the observation that chondrites have variable *initial* $^{142}\text{Nd}/^{144}\text{Nd}$. These isotopic variations are correlated with others implying they result from incomplete mixing between the nucleosynthetic products of slow neutron capture (s-process) in red giant stars and those of rapid neutron capture (r-process) and proton capture (p-process) in supernovae (*e.g.*, Carlson *et al.*, 2007; Gannoun *et al.*, 2011; Qin *et al.*, 2011; Boyet and Gannoun, 2013). Furthermore, $^{142}\text{Nd}/^{144}\text{Nd}$ ratios vary between chondrite classes. Ordinary chondrites, usually assumed to be the best compositional model for the Earth, have initial $^{142}\text{Nd}/^{144}\text{Nd}$ that averages 19 ppm or 0.19 epsilon units lower than modern terrestrial samples, but the average difference is about 35 ppm in carbonaceous chondrites and only about 10 ppm in enstatite chondrites (Gannoun *et al.*, 2011), with the $^{142}\text{Nd}/^{144}\text{Nd}$ range in enstatite chondrites overlapping the terrestrial value. Consequently, it is possible that the $^{142}\text{Nd}/^{144}\text{Nd}$ difference between the Earth and chondrites is simply a result of solar system isotopic heterogeneity and that the Sm/Nd ratio of the Earth is chondritic after all. This idea gains additional credibility because the oxygen isotopic composition of the Earth matches that of enstatite chondrites, but not other chondrite classes (Clayton *et al.*, 1976), and indeed *Marc Javoy* has argued that enstatite chondrites provide a better compositional model for the Earth than ordinary chondrites (Javoy, 1995; Javoy *et al.*, 2010; Kaminski and Javoy, 2013). There are, however, difficulties with the enstatite chondrite model. First, one would expect accretion of a fully fledged planet to average out the heterogeneities observed in chondrites, all of which are derived from planetesimals (*e.g.*, Carlson *et al.*, 2014). Hence it is the mean values rather than the range observed in individual specimens that is important. Second, building the Earth from enstatite chondrites would require a substantial fraction of the mantle to be richer in Si and Fe and poorer in Al and Ca than the observable upper mantle and there is little evidence of such layering (Section 6.1) and while the LLSVP's appear to be compositionally distinct, their volume is much too small to explain the discrepancy. Third, the



Si isotope composition of enstatite chondrites differs dramatically from that of the Earth, only a small part of which can be explained by metal-silicate isotopic fractionation during core formation (Fitoussi and Bourdon, 2012).

The second alternative posits that the Earth indeed has a non-chondritic Sm/Nd ratio and RLE inventory as a consequence of the accretion process itself (Caro *et al.*, 2008; O'Neill and Palme, 2008). Planets form through “oligarchic growth”, a process in which small bodies collide and merge to form progressively larger bodies: planetesimals, planetary embryos, and eventually planets. As these bodies grow, collisions become progressively more energetic, and eventually result in partial melting and formation of basaltic protocrusts enriched in incompatible elements on planetary embryos (examples of these crusts are preserved on small bodies such as Vesta and the Moon). The accretion process is, however, inefficient (*e.g.*, Agnor and Asphaug, 2004; Stewart and Leinhardt, 2012). Collisions between planetary embryos result not just in mergers, but also in disruptions, partial accretion, or partial erosion depending on the mass ratio of the objects, the ratio of impact velocity to escape velocity, and impact angle. In modelling the process, Stewart and Leinhardt (2012) found that “*For final planets with masses $>0.7 M_{\text{Earth}}$, 60% are enriched in their core-to-mantle mass fraction by $>10\%$ compared to the initial embryo composition. Fragmentation during planet formation produces significant debris ($\sim 15\%$ of the final mass) and occurs primarily by erosion of the smaller body in partial accretion and hit-and-run events. In partial accretion events, the target body grows by preferentially accreting the iron core of the projectile and the escaping fragments are derived primarily from the silicate mantles of both bodies.*” These models do not have sufficient resolution to explore the fate of the crusts of these bodies, but it seems reasonable to infer that they would be even more readily lost than mantles.

There is now a variety of evidence supporting this accretional inefficiency, including:

- At least some fraction of chondrules, which are so abundant in primitive meteorites, are likely melt droplets produced in these collisions (Libourel and Krot, 2007; Asphaug *et al.*, 2011; Libourel and Chaussidon, 2011; Johnson *et al.*, 2015; Morris *et al.*, 2015), again indicating inefficient accretion.
- Debris rings have been observed around young stars (*e.g.*, Gorlova *et al.*, 2004; Rhee *et al.*, 2008; Melis *et al.*, 2010) such as HD 141943 (Fig. 9.1). These debris rings, which are distinct from nebular protoplanetary disks, appear to be short-lived products of collisions and Rhee *et al.* (2008) concluded that a significant fraction of this dust undergoes relatively rapid ($\sim 10^5$ yrs) reduction in grain size and is either blown out of the system by stellar winds or spirals into the star through Poynting–Robertson drag (a consequence of radiation pressure tangential to the grain).





Image Credit: NASA/ESA, R. Soummer, Ann Field (STScI).

Figure 9.1

Upper panel is a Hubble Space Telescope image of the debris disk around the young star HD 141943 and the lower panel shows an artist's conception of it. The debris disk was first discovered using the Spitzer infrared space telescope and is thought to arise as a result of collisions between planetesimals (Hillenbrand *et al.*, 2008).

- The Earth and its sister terrestrial planets have higher bulk Fe/Mg ratios than the Sun and most chondrite classes (including the CI chondrites), consistent with mantle stripping and consequent enhancement of the ratio of core to mantle observed in the simulations of Stewart and Leinhardt (2012) and Bonsor *et al.* (2015).
- Mercury represents the most extreme example of the iron enrichment, with a core constituting about 70% of its mass. Asphaug and Reufer (2014) found that multiple hit and run collisions could have stripped much of Mercury's mantle while retaining a relatively high volatile element content consistent with MESSENGER mission observations.
- Compositional groups of iron meteorites provide evidence of at least 60 disrupted differentiated planetesimals, but far fewer olivine-dominated asteroids or meteorites, suggesting the silicate mantles of those disrupted bodies have been, in the words of Burbine *et al.* (1996), "battered to bits" and lost either to the Sun or interstellar space.
- Based on the results of NASA's DAWN mission and compositions of



Vesta-derived HED achondrites, Consolmagno *et al.* (2015) argue that Vesta is unlikely to be an intact protoplanet; instead “*Vesta either formed from source material with non-chondritic composition or underwent after its formation a radical physical alteration, possibly caused by collisional processes, that affected its global composition and interior structure.*”

O’Neill and Palme (2008) postulated that the Earth lost about 10% of its mass through this process of *collisional erosion*. One consequence of this is the high terrestrial Fe/Mg ratio mentioned earlier. A second consequence is relatively low abundances of moderately volatile elements such as Mn, as these elements are vapourised in energetic collisions. The third consequence is depletion in incompatible elements as these become concentrated in the protocrust that is particularly prone to loss during collisions. Assuming the difference between the Earth’s $^{142}\text{Nd}/^{144}\text{Nd}$ ratio and that in ordinary chondrites is due to a difference in Sm/Nd ratio, the terrestrial Sm/Nd ratio must be 6% higher than chondritic. O’Neill and Palme (2008) used this and the Earth’s elevated Fe/Mg ratio to calculate that roughly 2.6% of the silicate portions of the planetary embryos that formed the Earth was lost through collisional erosion. That small fraction, however, comprised half the mass of the protocrusts of those bodies and consequently resulted in strong depletion in highly incompatible elements. O’Neill and Palme (2008) estimated that highly incompatible elements such as Rb, U, and Th were depleted by nearly 50% compared to conventional estimates such as that of McDonough and Sun (1995). Others have calculated somewhat lower, but still very significant depletions. Jackson and Jellinek (2013) calculated concentrations for the most incompatible elements, including Th and U, that are a little more than 30% lower than the *McDonough* and *Sun* values (Fig. 9.2). Using a somewhat different approach, I calculated values that are as much as 20% lower than the *McDonough* and *Sun* values and are very similar to the concentrations of the most incompatible elements estimated by Lyubetskaya and Korenaga (2007) using yet a different approach (White, 2013).

The collisional erosional hypothesis is consistent with the Moon and Earth having the same Sm/Nd and $^{142}\text{Nd}/^{144}\text{Nd}$ ratios, as the erosion happens primarily during the planetesimal-planetary embryo stage. By the time of the Moon-forming impact, the Sm/Nd ratio would already have been fixed. Furthermore, there is evidence, admittedly equivocal because it is based only on the Shergottite subgroup of SNC meteorites, that Mars also has superchondritic Sm/Nd, implying that the accretional history of the Earth was not unique (Caro *et al.*, 2008). Such a predominance of planets with superchondritic Sm/Nd is consistent with the modelling studies of Stewart and Leinhardt (2012).

The high terrestrial Sm/Nd ratio has important implications. If the Earth has the same *initial* $^{142}\text{Nd}/^{144}\text{Nd}$ as ordinary chondrites, it implies a $^{147}\text{Sm}/^{144}\text{Sm}$ ratio and ϵ_{Nd} for the silicate Earth of 0.2082 and +7, respectively. Using the correlation between ϵ_{Nd} , $^{87}\text{Sr}/^{86}\text{Sr}$, and ϵ_{Hf} in oceanic basalts, Caro and Bourdon (2010) estimated the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ ratios of the silicate Earth as 0.703 and 0.061, respectively, and the ϵ_{Hf} and $^{176}\text{Lu}/^{177}\text{Hf}$ as +12 and 0.0375, respectively. If we



assume instead that the Earth's initial $^{142}\text{Nd}/^{144}\text{Nd}$ was that of enstatite chondrites, then the $^{147}\text{Sm}/^{144}\text{Sm}$ ratio and ϵ_{Nd} for the silicate Earth become 0.2024 and +3.6, respectively (White, 2013). The corresponding $^{87}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Rb}/^{86}\text{Sr}$, and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios and ϵ_{Hf} are 0.7040, 0.0764, 0.03535, and +6.4, respectively. Either way, the implications are significant. For one thing, this level of incompatible element depletion produces a 25-50 % reduction in Th, U and K and implies that terrestrial heat production is 25 to 50 % lower than in the chondritic model and hence that far more of the Earth's heat loss is a result of secular cooling. This has important geodynamic consequences and I'll briefly explore them in the following section. It also means that a much larger fraction of the mantle must have been depleted to form the continental crust (Boyet and Carlson, 2006; Caro and Bourdon, 2010). The exact value of that fraction depends on the values of the initial $^{142}\text{Nd}/^{144}\text{Nd}$, the depleted mantle ϵ_{Nd} , and the Sm/Nd ratio and age of the continents (Allègre *et al.*, 1983a,b; *e.g.*, DePaolo, 1988), but ranges from 40 to 50 % if the Earth had an initial $^{142}\text{Nd}/^{144}\text{Nd}$ equal to the average of enstatite chondrites (White, 2013) to nearly 100 % if the Earth's initial $^{142}\text{Nd}/^{144}\text{Nd}$ was equal to the average of ordinary chondrites (Boyet and Carlson, 2006).

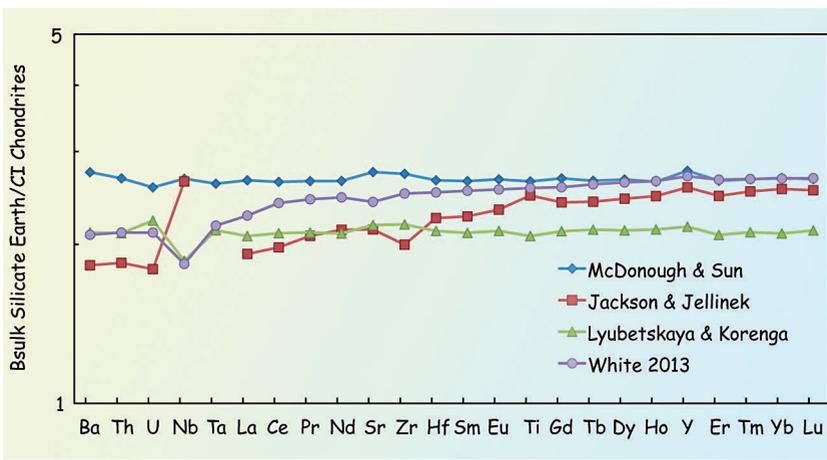


Figure 9.2 Comparison of estimates of the abundance of refractory lithophile trace elements in the Earth.

I should emphasise that the three hypotheses proposed to explain the Earth's super-chondritic $^{142}\text{Nd}/^{144}\text{Nd}$ are not mutually exclusive. As the above discussion implies, some of the $^{142}\text{Nd}/^{144}\text{Nd}$ difference may indeed be due to nebular isotopic heterogeneity. It seems unlikely, however, that all of it can be so explained. Dynamic models imply that collisional erosion of the silicate parts of protoplanets, and particularly of their protocrusts, is likely. It is possible, however, that this too explains only part of the difference and that an incompatible element-enriched reservoir is sequestered somewhere in the deep mantle,



perhaps in the LLSVP's. However, regardless of whether the cause be collisional erosion or early differentiation, it is likely that the *observable* Earth, the continents and the mantle giving rise to all volcanism since the Archean, is depleted in the most incompatible elements compared to chondrites.

This brings us back to the question posed at the beginning of this section and the two dilemmas I mentioned earlier, as well as a third. The first of these is the conflict described in Section 3 between the light rare earth-enriched lavas (particularly in my thesis area of the Azores and adjacent Mid-Atlantic Ridge) and the positive ϵ_{Nd} reported by DePaolo and Wasserburg (1976a,b), which implied a long light rare earth-depleted history of their mantle source. Of course, the melting process tends to enrich the light rare earths in magmas relative to the heavier rare earths, but it is nevertheless difficult to produce light rare earth-enriched magmas from a light rare earth-depleted mantle at all but the lowest melt fractions. This is more easily reconciled if that depleted history began with the formation of the Earth and was followed by subsequent light rare earth enrichment, for example through subduction recycling, which would be the case for a BSE $\epsilon_{Nd} > 3$.

The second dilemma is the absence of primitive mantle, or at least primitive mantle having $\epsilon_{Nd} = 0$. Mass balance calculations based on a higher Sm/Nd, and therefore a higher ϵ_{Nd} for the Earth indicate that much and perhaps most of the mantle has been depleted by continent formation, which would explain the rarity of primitive mantle. Intriguingly, the revised values for the BSE, or at least the observable part of it, ($\epsilon_{Nd} \sim 3-7$), encompass the range of the most common isotope ratios measured in oceanic island basalts, and correspond well with isotope ratios associated with the highest $^3\text{He}/^4\text{He}$ ratios, as Caro and Bourdon (2010) pointed out. This is the mantle reservoir I have been calling PREMA (which in my view is synonymous with 'FOZO', 'C', and 'PHEM'). However, there is no correlation between $^3\text{He}/^4\text{He}$ and ϵ_{Nd} in OIB, and Pb isotope and trace element ratios indicate that PREMA is unlikely to be truly primitive mantle. Although some plume-derived lavas, such as the Baffin Island basalts, produced by the Iceland mantle plume 60 million years ago, have isotopic compositions approximating those expected of high Sm/Nd primitive mantle (Jackson *et al.*, 2010), their incompatible element compositions, most notably Nb/U, are inconsistent with primitive mantle compositions. This is not to say that they could not contain a primitive component highly diluted by other components. Indeed, the very high $^3\text{He}/^4\text{He}$ ratios in some of these basalts suggest the presence of a near-primitive component. Furthermore, there is very strong evidence from xenon isotopes in much younger Icelandic basalts that the Iceland plume does contain primitive or near-primitive components (Mukhopadhyay, 2012).

The third dilemma is the problem of the missing argon. Allègre *et al.* (1996) pointed out that assuming a K concentration of ~250 ppm derived from the assumption of chondritic relative abundances of the RLE's and a K/U ratio of 12,700, only about half of the ^{40}Ar produced by radioactive decay of ^{40}K resides in the atmosphere. After accounting for the amount likely to be in the continental



crust or the depleted mantle reservoir, they concluded that 25 % or more of the Earth's ^{40}Ar inventory was stored in an undegassed or primitive deep mantle. However, using K abundances estimated by Lyubetskaya and Korenaga (2007), (White, 2013), or Jackson and Jellinek (2013), all or nearly all of the Earth's ^{40}Ar can be accounted for by the atmospheric, crustal, and depleted mantle reservoirs.

The answer to the question of “whither primitive mantle?” thus appears to be that it was not what we thought it was, and in any case has not survived.

9.2 Heat, Convection, and Plumes

Harold Urey (1951, 1955) was one of the first to ponder the balance between the Earth's heat loss and heat production; the ratio of heat loss to production has subsequently been named the *Urey ratio*. In his 1955 paper, he adopted the assumption that the two were equal and concluded that the concentrations of heat producing elements, K, Th, and U, were lower than in chondrites and suggested one reason might be “the depletion of these elements in the Earth, the Moon, and Mars during their formation” (foreshadowing the collisional erosion hypothesis?). Urey, however, was working from the poor-quality data available at the time and the chondritic concentrations he used were significantly too high; terrestrial U and Th (but not K) concentrations are higher than carbonaceous chondritic values (even in the eroded Earth model compositions discussed in the previous section).

Fast-forward 40 or some years and the idea that the Urey ratio = 1 had long since been abandoned by geochemists. Heat production in the compositional models of Hart and Zindler (1986), McDonough and Sun (1995), and Palme and O'Neill (2003) range from 19.7 to 20.3 terawatts (TW). Assuming a terrestrial surface heat loss of 47 TW (Davies and Davies, 2010), these correspond to a Urey ratio of 0.42 to 0.43 (*i.e.* 19.7 TW/47 TW). These are significantly lower than values near 0.70 often used in geodynamic models (*e.g.*, Davies, 1980; Schubert *et al.*, 1980). Of this heat, some 5.6 to 8.5 TW is produced in the continental crust (Huang *et al.*, 2013). Using Huang *et al.*'s preferred value of 6.8 TW for crustal production leaves a mantle production of about 13 TW. After accounting for both heat production and secular cooling of the continental lithosphere this leaves a *convective heat flux* (*i.e.* heat flowing out of the mantle) of approximately 36.5 ± 4.5 TW (Korenaga, 2008) and hence an *apparent* “mantle Urey ratio” (ratio of the convective heat flux to the terrestrial heat production corrected for the continental heat production – I say apparent because it includes heat flowing out of the core, but there is no heat production in the core) of about 0.40. The compositional models of Jackson and Jellinek (2013) and Lyubetskaya and Korenaga (2007) reduce heat production to 14 to 16 TW and the Urey ratio to 0.29 to 0.34. More dramatically, mantle heat production drops to 5 to 7 TW and the apparent mantle Urey ratio decreases to 0.20 to 0.28. Thus in these compositional models the mantle and core are losing heat 4 to 5 times more rapidly than it is being produced. If an EER reservoir exists in the deep mantle, it is responsible for an amount of heat roughly equal to the 5 to 7 TW produced in the entire rest of



the mantle. We should note that the depleted mantle compositions of Salters and Stracke (2004) and Workman and Hart (2005) would correspond to a heat productions of 4.2 and 2.2 TW, respectively, if it were to occupy the entire mantle. This is still below the 5 to 7 TW heat production derived from the *Luybetskya* and *Korenaga* and *Jackson* and *Jellinick* compositions, implying reservoirs less depleted than DMM must exist in the mantle.

This reduced heat production has important geodynamic implications and, because it implies greater secular cooling than previously thought, implications for the history of the planet as well. Some of these were considered by *Korenaga* (2008). He assumes a heat flux from the core of 4.5 TW, implying an *internal heating ratio*, (which he calculated as the difference between heat flowing out of the mantle to heat flowing in from the core divided by the heat flowing out) of 0.87, which in turn implies that the mantle is largely internally heated. However, while estimates of mantle heat production have dropped, estimates of heat flow from the core have increased. Based on a revised estimate of conductivity of appropriate iron alloys under core conditions, *Pozzo et al.* (2012) estimate that the amount of heat flowing out of the core is 15 to 16 TW. Using a value of 15 TW decreases the internal heat ratio to 0.59. Thus while internal heat dominates, some 40 % of the convective heat flux derives from the core. The true mantle Urey ratio, *i.e.* the ratio of mantle heat production to heat flowing out of the mantle less core heat flow ranges from 0.32 to 0.42 for the *Jackson* and *Jellinick* and *Luybetskya* and *Korenaga* compositional models and compares with a value of 0.60 for the *McDonough* and *Sun* compositional model. An increased heat flux across the core mantle boundary from 5 to 15 TW has enormous implications for the core-mantle boundary as a thermal boundary layer. Exploring the full geodynamic implications of this is well beyond the scope of this paper, but it does suggest that plumes play a greater role in mantle convection and everything related to it, including plate tectonics and continent evolution, than previously thought.

King and *Adam* (2014) recently revisited the question of hot spot swells (the broad topographic anomalies associated with hot spots) and the plume flux. The total heat flux they derive, about 2 TW, is similar to that calculated by *Davies* (1988) and *Sleep* (1990), but they find that all these estimates have very considerable uncertainty. They also found that the largest hot spot swells occur in the Pacific, whereas they would expect them to occur over the slowest spreading plates. They conclude that *"Either something is missing in our understanding of buoyant mantle interacting with stagnant or mobile plates or convection in the Pacific is significantly more vigorous than under the Atlantic hemisphere."* Turning this around, one might ask whether a greater plume flux in the Pacific may be driving its more vigorous convection. As *King* and *Adam* also noted, *Malamud* and *Turcotte* (1999) suggested that the size of plumes should follow a fractal distribution, implying there may be many (~5000) plumes too small to have a surface expression. Thus these measurements of buoyancy flux may underestimate the contribution of plumes to mantle convection. Interestingly, in his original proposal,



Morgan (1971) claimed that plumes drive plate tectonics. Although the plume hypothesis has been largely accepted, the idea that plumes drive plate tectonics was largely discarded. It may be that Morgan was more right than we realised.

9.3 Summing Up

Morgan's proposal to explain *Wilson's* 'hot spots' was certainly speculative at the time, with the principal evidence supporting it being simply the fixed nature of these hot spots and the observed difference in composition of the related basalts from those erupted along mid-ocean ridges. In the last 45 years, however, the evidence I described in the preceding sections that thermally buoyant plumes rising from the deep mantle are indeed the cause of these hot spots has become overwhelming. The core-mantle boundary area is likely to be the source region of most of these plumes. Geodynamics, seismology and mineral physics described in the preceding sections and in greater detail by (Tackley, 2012) are producing an increasingly coherent picture of this dynamic region. The problem is then to integrate geochemical observations into this picture.

Let's begin by briefly reviewing the relevant geochemical observations. First, both isotopic and trace element abundances show that while MORB are derived from a relatively uniform ancient incompatible element-depleted reservoir, mantle plumes sample diverse reservoirs that are less depleted and in many cases are incompatible element-enriched relative to the bulk Earth. While each hot spot is in some ways geochemically unique, they can be divided into 4 isotopic 'genera' (White, 1985; Zindler and Hart, 1986). Three of these, HIMU, EM I, and EM II, include distinct extreme isotopic compositions that can also be related to distinct trace element compositions (*e.g.*, Weaver, 1991; Willbold and Stracke, 2006). There is little or no evidence of mixing between these three; instead, correlations in isotope ratios suggest that material from these reservoirs almost invariably mixes with and is diluted by material from a fourth reservoir, originally called (Figs. 4.3 through 4.6) PREMA by Zindler and Hart (1986) but subsequently reinvented as FOZO (Hart *et al.*, 1992), C (Hanan and Graham, 1996), and PHEM (Farley *et al.*, 1992). In addition to being present in HIMU, EM I, and EM II, PREMA appears to be the sole ingredient in several other plumes, and hence deserves its name of 'prevalent mantle'. In contrast, the mid-ocean ridge source, DMM, rarely contributes to plume-related volcanism, the Galápagos being an exception, but it does mix with plume-derived components along ridges proximate to plumes.

The predominant chemical signal in mantle plumes is of material recycled from near or at the Earth's surface, as is manifested through a great variety of chemical and isotopic indicators. This has most likely been accomplished through subduction of oceanic crust and in that respect it is hardly surprising that something between 0.1 and 0.5 mantle volumes of oceanic crust have been produced over geologic history (Tackley, 2012). In the modern Earth, subducted oceanic crust is always accompanied by sediment, which is primarily derived from



the continents, contributing additional incompatible element enrichment and a “continental” flavour to mantle plumes. While sediment is primarily derived from the upper crust, subduction erosion and continental foundering may feed lower continental crust into the deep mantle and this appears to be present in some plumes, particularly those of the EM I genus (Willbold and Stracke, 2010). Again, this should not be surprising as the volume of continental crust carried into the mantle through subduction erosion may exceed the volume of subducted sediment (*e.g.*, Clift *et al.*, 2009). The research reviewed in Section 7.3 indicates that the total volume delivered to the mantle over geologic time by these processes, along with crustal foundering, may well exceed that of the present continental crust (*e.g.*, Stern, 2011, Tatsumi *et al.*, 2014), as Armstrong (1968) had long ago argued. Metasomatised oceanic lithosphere may also contribute incompatible element-enriched material to the deep mantle (*e.g.*, Niu and O’Hara, 2003; Workman *et al.*, 2004).

Although the dominant incompatible element and Sr, Nd, Hf, Pb, and Os isotopic signatures in mantle plumes are of recycled surface material, it is the high concentrations of these elements that accounts for this dominance; recycled material likely composes only a minor fraction of plumes. Many plumes also seem to contain a very primitive noble gas component that appears to have been isolated from much of the mantle for nearly all of geologic time (*e.g.*, Moreira, 2013). This material too likely comprises only a small fraction of plumes. The signal is apparent because the remainder of the material in plumes is highly degassed and hence noble gas-depleted. Otherwise, there is no identifiable component in plumes whose origin could plausibly be ascribed to early Earth differentiation, such as fractional crystallisation of a basal magma ocean as suggested by Labrosse *et al.* (2007) or any subsequent solid-melt fractionation in the deep mantle.

Turning to the geophysical observations, the lowermost mantle, comprising D” and the basal thermal boundary layer, appears from seismic observations to be extremely heterogeneous, perhaps as much so as the top thermal boundary layer, the lithosphere. The dominant features are the two approximately antipodal LLSVP’s, one beneath Africa, one beneath the Pacific. These hot, dense regions cover nearly half of the base of the mantle and rise as high as 1000 km above it. They appear to have quite sharp sides, but the tops are indistinct, perhaps breaking up into secondary mantle plumes. Most hot spots, however, are concentrated above the margins of the LLSVP’s, with the ULVZ’s concentrated beneath the margins. Judging from the distribution of large igneous provinces, LLSVP’s appear to have remained approximately stationary for at least the last several hundred million years. The LLSVP’s are surrounded by seismically fast regions that are generally interpreted as slab graveyards, in part because they tend to underlie subduction zones. Seismic anisotropy suggests flow from the cold slab graveyards toward the hot LLSVP’s.

While there is a broad consensus that the LLSVP’s are hot and likely buoyant and dense, likely iron-rich, their origin is unclear. One hypothesis posits that they are primordial, either iron-rich segregations produced by fractional



crystallisation of a basal magma ocean (e.g., Labrosse *et al.*, 2007) or the remains of an iron-rich basaltic crust formed at the top of the moon-forming impact magma ocean and subsequently subducted (e.g., Boyet and Carlson, 2005). An alternative hypothesis is that they are accumulations of oceanic crust produced over geologic time by convection that tends to focus this material into 'thermochemical piles' away from downwelling slabs (e.g., McNamara and Zhong, 2005).

If indeed the LLSVP's are reservoirs of primordial material, then the lower-most mantle may have just the combination of ingredients that we see manifested in mantle plume-derived OIB. In the geodynamic model of Li *et al.* (2014), subduction and convection sweep an initial, dense (2-3% denser), primitive layer at the base of the mantle into 'thermochemical piles', *i.e.* LLSVP's. Thermal plumes form on top of the piles and entrain a few percent of both subducted oceanic crust and primitive material from the thermochemical piles (Fig. 9.3). Some subducted oceanic crust is also episodically flushed into the more primitive reservoir and is stretched and stirred into it because of internal convection in the pile. The fraction of oceanic crust in the piles eventually reaches 1% to more than 15%, depending on viscosity and buoyancy contrasts. The fraction of primitive material in the thermochemical piles diminishes over time, but only slowly. The plumes that form in the model consist of a mixture of ambient deep mantle, relatively recently subducted oceanic crust, primitive material and older oceanic crust from the thermochemical piles. This combination of characteristics may well explain the geochemistry of some plumes, such as Iceland. As Li *et al.* note, "*plumes sampling geographically different parts of the LLSVPs could have different compositions.*" The model is only 2-D and makes assumptions about density and temperature and depth dependence of viscosity that may or may not be valid (although some assumptions are varied in different model runs). Nevertheless, it appears to explain some of the observations about mantle plumes.

If indeed LLSVP's are evolving thermochemical piles similar to those modelled by Li *et al.* and if, as much evidence suggests, they are closely associated with mantle plumes, then it is tempting to associate the PREMA component with the thermochemical piles for several reasons: (1) PREMA is most closely associated with the primitive noble gas signature, (2) PREMA otherwise seems to consist primarily of non-primitive material, (3) PREMA appears to be present in many plumes, and (4) in many respects PREMA appears to just be the *mélange* of other plume flavours that the Li *et al.* model implies. The HIMU, EM I, and EM II signatures could then be related to the variety of surficial material carried into the deep mantle through subduction and related processes without being incorporated in the thermochemical piles.

Thus over the past four decades we have made considerable and encouraging progress in understanding the mantle, both deep and shallow, and how basalts erupted on the surface relate to it. I am particularly encouraged by the way that geochemical and geophysical views of the mantle are converging. If you had attended interdisciplinary meetings on the deep mantle a few decades ago you could be forgiven for thinking that geophysicists and geochemists were



sometimes talking about different planets. Nevertheless, many, many questions remain. With respect to the above model, one could ask that given the unique and ancient nature of the HIMU flavour (Cabral *et al.*, 2013), and its distinct lack of a primitive noble gas component, how has it survived for over 2 Ga in the deep mantle without being swept into the thermochemical piles? Why is it found only in two widely separated mantle plumes (the Australs and St. Helena-Ascension)? More generally, why is there so little geographic coherence in mantle plume geochemical ‘flavours’? Why are there so few isotopic ‘genera’ of plumes (even admitting to many species)? Oceanic crust is at best only modestly enriched in incompatible elements. If it is primarily oceanic crust that is subducted and contributes to plumes, why are plumes most often significantly incompatible element-enriched? If this is due to large volumes of continental crust also carried into the mantle, how has the mantle and continental crust maintained their distinctive compositions, particularly with respect to ratios such as Nb/U and Pb/Ce (*e.g.*, Hofmann, 1986; Hofmann *et al.*, 1986; Hofmann, 1997)? Is a continuous convection model, such as that used by Li *et al.* (2014) appropriate, or is mantle convection very much non-steady-state? For example, does subducted oceanic crust feed continuously into the deep mantle or does it penetrate the 670 km discontinuity only in occasional cascades (*e.g.*, Maruyama *et al.*, 2007)? Could such cascades account for the limited geochemical variety of plumes? How does supercontinent assembly and breakup affect mantle convection patterns and *visa versa*?

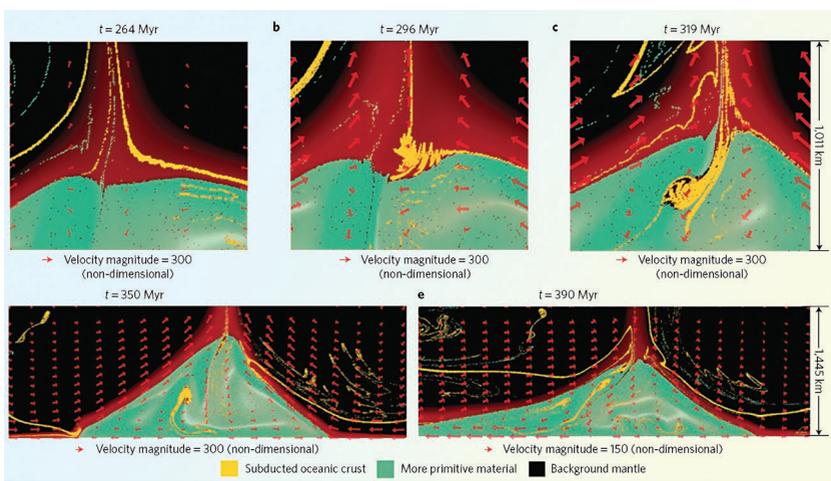


Figure 9.3

Numerical model of the base of the mantle of Li *et al.* (2014) at different times during its evolution. Green, yellow and black colours represent composition with partially transparent temperature field (red) superimposed only for non-dimensional temperatures greater than 0.5. Panels a through c show zoomed in views of the top of the piles, panels d and e zoomed out views (from Li *et al.*, 2014 with permission from Nature Publishing Group).



Some of the most important questions relate to interaction between the mantle and the Earth's surface. *Norm Sleep* and others (Sleep *et al.*, 2012) have argued that the “*Earth’s mantle has been modified by the ubiquitous influence of life on recycled lithosphere*”. One cannot help but ask how has the Earth’s mantle modulated the Earth’s surface and life? One of the most significant changes on the Earth’s surface was the rise of atmospheric oxygen, first at roughly 2.3 to 2.4 Ga in the Great Oxidation Event (GOE), followed by a second rise in the late Proterozoic. The timing of the GOE is reasonably well established, but its cause is not. While atmospheric oxygen is unquestionably a result of oxygenic photosynthesis, which seems to have begun hundreds of millions of years before the GOE, the underlying question is what delayed the rise in oxygen until then (Kasting, 2013)? Curiously, this event coincides with changes in the composition of igneous rocks to less mafic compositions that suggest a significant change in mantle temperature and/or mantle convection at around the Archean-Proterozoic boundary⁵ (e.g., Condie and O’Neill, 2010; Keller and Schoene, 2012). Thus several proposals to explain the timing of the GOE involve changes in mantle-related processes. Volcanic gases are reducing and consume atmospheric oxygen; thus, atmospheric oxygen levels can rise only when photosynthesis and carbon burial produce sufficient oxygen to oxidise them. This observation has led to a widespread suspicion that a change in the oxidation state of volcanic gases or the rate of volcanism somehow controlled the timing of atmospheric oxygen rise. This could reflect a change in oxidation state in the Earth’s interior (e.g., Kasting *et al.*, 1993; Kump *et al.*, 2001) or might reflect other changes, such as the rate of volcanism or the depth at which magmas stagnate and degas (e.g., Kump and Barley, 2007; Condie *et al.*, 2009; Gaillard *et al.*, 2011). Alternatively, Holland (2009) proposed that a progressive increase in subducted carbon and sulphur material coupled with a near-constancy of its water content and H₂/H₂O ratio must lead to a progressive increase in the CO₂/H₂ and SO₂/H₂ ratio, and hence the oxidation state, of volcanic gases released to the atmosphere. It is interesting in this respect that the study of Cottrell and Kelly (2014) showing that OIB are more oxidised than MORB demonstrates that the mantle has indeed become more oxidised as a consequence of subduction. After this initial rise, atmospheric and marine oxygen levels varied but remained relatively low, probably too low to support metazoan life, until roughly 660 to 550 Ma, around the end of the Neoproterozoic extreme glaciations (Scott *et al.*, 2008). Was the mantle involved in these events and the consequent evolution of metazoan life?

No doubt, answers to these and other questions will continue to slowly emerge and I look forward to hearing them.

5. The Archean-Proterozoic boundary is arbitrarily defined at 2.5 Ga. It seems to me that it is now time to redefine it based on actual geologic events. Its definition should be changed to coincide with the GOE, perhaps specifically with the Huronian Glaciation, a global event closely associated with, and likely a consequence of, the GOE.



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INDEX

Symbols

- $^3\text{He}/^4\text{He}$ 115, 116, 145, 166, 190-192, 194, 199, 213, 232, 238, 239
- ^4He 103, 104, 115, 170, 190-192, 194, 199, 213, 232, 238, 239
- ^{10}Be 96, 170, 171, 224, 237, 244
- ^{40}Ar 102-104, 113, 213, 214
- $^{87}\text{Sr}/^{86}\text{Sr}$ 104, 105, 107, 109, 111, 112, 120-122, 124, 125, 131, 132, 157, 158, 160, 163-166, 176, 179, 180, 197, 198, 211, 212, 231, 236, 238
- $^{142}\text{Nd}/^{144}\text{Nd}$ 104, 207, 208, 211, 212, 224, 233, 237
- $^{143}\text{Nd}/^{144}\text{Nd}$ 104, 111-114, 122, 160, 206, 231, 238
- ^{146}Sm 96, 104, 206, 207, 223, 224, 228, 230, 234, 236
- $^{176}\text{Hf}/^{177}\text{Hf}$ 104, 113, 114, 241
- $^{182}\text{W}/^{184}\text{W}$ 104
- $^{187}\text{Os}/^{188}\text{Os}$ 104, 153, 154
- $^{206}\text{Pb}/^{204}\text{Pb}$ 104, 116-122, 125, 126, 130-132, 162, 163, 168, 177, 178, 188, 192, 203, 205
- $^{207}\text{Pb}/^{204}\text{Pb}$ 104, 116, 119, 122, 130, 131, 158, 177, 178, 205
- $^{208}\text{Pb}/^{204}\text{Pb}$ 104, 122, 130-132, 192, 198, 205
- $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ 129, 176, 192, 201
- $^{238}\text{U}/^{235}\text{U}$ 161
- 670 km discontinuity 113, 137, 151, 156, 219
- $\Delta 7/4$ 131
- $\Delta 8/4$ 131, 192
- $\Delta 33\text{S}$ 157, 159, 160
- $\delta 7\text{Li}$ 161-163
- $\delta 18\text{O}$ 158
- $\delta 57\text{Fe}$ 164, 165
- ϵHf 113, 115, 120, 122, 132, 165, 176, 177, 188, 189, 211, 212
- ϵNd 132
- μ 116-119

A

- accretion V, 118, 181, 208, 209, 221, 222, 230, 237
- Albarède, Francis 115, 179, 192, 193, 195, 221, 223, 230
- alkali basalts 107, 195



Armstrong, Dick III, IV, 128, 148, 149, 167, 168, 171, 183, 217, 222, 234
Arndt, Nick 97, 128, 180, 183, 222, 225, 228, 242
Ascension 120-122, 125, 143, 219, 229
atmophile 98
Australian-Antarctic Discordance (AAD) 131
Azores 109, 110, 112, 116, 120-122, 127, 134, 143, 144, 149, 153, 162-164, 201, 213, 222, 229, 231, 241, 245

B

Blichert-Toft, Janne V, 114, 115, 117, 132, 188, 190, 192, 193, 221, 223, 225, 229, 230, 235, 237, 238, 241
bridgemanite 137, 138, 143, 146, 147, 150
Brown, Lou 170, 171, 224, 244
BSE (Bulk Silicate Earth) 101, 213
buoyancy flux 141, 145, 215

C

Ca-perovskite 137, 146-148, 150
chalcophile 98, 117
Chauvel, Catherine 114, 132, 154, 164, 171, 174-178, 180, 200, 224, 225, 229, 236, 241
chondrites 96, 101, 105, 161, 207-214, 223, 228, 239, 244
CHUR (chondritic uniform reservoir) 111, 112
collisional erosion V, 211-214, 238
compatible elements 99
continental crust 95, 100, 105, 111, 113, 114, 119, 128, 129, 132, 135, 148, 155, 161, 167, 176, 180-184, 207, 212, 213, 217, 219, 222, 225, 230, 231, 233, 240, 242, 243, 245
Cook-Australis (or Austral Islands) 107
core 96, 98, 101, 117, 118, 121, 136, 138-142, 145, 152, 190-194, 202, 207, 209, 210, 214-216, 224, 227, 231, 234, 236, 238, 239, 243
core-mantle boundary 136, 138, 139
crustal foundering 167, 180, 181, 183, 184, 217
crustal recycling 150, 180, 222, 233, 238, 241, 243

D

D'' 137, 138, 146, 184, 201, 217, 238
debris rings 209
decay constant 102, 103
dehydration 172-174, 222, 233, 234
DePaolo, Don 111-113, 122, 136, 190, 192-194, 206, 212, 213, 224, 226, 230, 245
depleted mantle 100, 129, 146, 204
DMM 100, 108, 112, 122, 130, 135, 160, 200, 215, 216, 246
Duncan, Bob 120, 180, 194-196, 202, 204, 226, 237, 240, 245
DUPAL 131, 138, 139, 201, 225, 230

E

eclogite 108, 111, 156, 173, 183, 185, 186, 234, 238, 239, 242, 244
EDR (early depleted reservoir) 207, 208
EER (early enriched reservoir) 207, 208, 214
EM I 122, 123, 125, 126, 135, 138, 149, 163, 176, 179, 180, 184, 185, 205, 216-218
EM II 95, 122, 123, 125, 138, 150, 163, 176, 180, 184, 185, 216, 218
enstatite chondrites 208, 209, 212, 223, 228

F

ferripericlase (magnesiowüstite) 137, 146
fluid-mobile elements 169, 171, 176
FOZO 180, 213, 216
fractional crystallisation 107-109, 128, 164, 165, 168, 173, 175, 186, 189, 207, 217
French Polynesia 120, 145

G

Gakkal Ridge 132
Galápagos 121, 122, 132, 145, 164, 168, 183, 194-200, 202, 216, 229, 230, 232, 235, 237, 241, 244, 245
Galápagos Spreading Centre (GSC) 132
Gast, Paul IV, 103, 105, 107, 109, 112, 120, 228
Geist 235
Geist, Denny 195, 196, 199, 229, 244
geochron 117, 118, 119
Gough Island 120
Great Oxidation Event 159, 177, 220



H

- Harpp, Karen 195-200, 202, 229, 230, 244
Hart, Stan III, V, 101, 105, 106, 108-110, 114, 120, 122, 123, 127, 129-131, 135, 138, 170, 195, 201, 206, 214-216, 221, 222, 225-227, 230, 232, 233, 235, 238-240, 245, 246
Hawaii 106, 107, 121, 122, 134, 141-145, 147, 153, 164, 165, 185-187, 189, 194, 200, 202-205, 225, 228, 239, 240, 242, 246
Hedge, Carl IV, 105, 120, 130, 229, 231, 243
HIMU 95, 122, 123, 125, 126, 147, 148, 154, 158, 163, 176, 180, 184, 185, 216, 218, 219, 225, 230, 233
Hofmann, Al III, 97, 106, 114, 120, 126, 141, 149-152, 156, 157, 176, 185, 192-195, 200, 203, 204, 219, 221, 222, 225, 227, 228, 232, 238, 242, 245
hot spot 96, 106, 141, 194, 200, 201, 205, 215, 216, 223, 246

I

- Iceland 105, 106, 108-110, 112, 119-122, 127, 142-144, 153, 164, 166, 195, 201, 213, 218, 222, 226, 230, 238, 239, 241, 244, 246
incompatible elements 95, 99, 100, 105, 107, 108, 128, 130, 132, 146, 156, 168, 172, 175, 185, 209, 211, 213, 219
insoluble elements 171
island arc volcanics (IAV) 168

J

- James, Dave 170, 236

K

- Karig, Dan 169, 174, 230, 234
Kay, Bob 169, 174, 181, 182, 183, 229, 234
Kerguelen 107, 120-122, 132, 141, 149, 179, 201
K/U 130, 213

L

- La/Sm 110, 130
Lesser Antilles 167-169, 175, 224, 226, 245

- LIPs (large igneous provinces) 139-141, 217
lithophile 98-101, 111, 113, 173, 206, 207, 212
LLSVP's (large low shear-wave velocity provinces) 138-140, 144, 145, 151, 201, 208, 213, 217, 218

M

- major elements 98, 233
Mangaia 147, 158, 159, 179, 180
mantle array 112, 114, 115, 120, 122, 149, 177, 225, 235
mantle plume 106, 108, 109, 116, 140, 157, 183, 194-196, 199, 201, 213, 218, 219, 221, 223, 227, 229, 230, 237, 241, 243, 245
Marquesas 145, 163, 200, 202, 225, 226, 229
Mauritius 202-204, 237, 238
McBirney, Alex (Mac) 195, 196, 229, 237, 245
Mid-Atlantic Ridge 110-112, 116, 120, 127, 134, 149, 213, 225, 227, 241, 245
MIF sulphur 157-159, 179, 180
Moore, Jacob 202, 204, 237
MORB (mid-ocean ridge basalts) 95, 96, 100, 105, 108, 111-120, 122, 127-133, 135, 142, 143, 146, 147, 149, 151, 152, 154, 157, 159-161, 163-166, 168, 169, 173-178, 186, 187, 200, 204, 205, 207, 208, 216, 220, 227, 231, 232, 235, 239, 241, 245, 246
Morgan, Jason IV, 106, 108, 112, 136, 140, 141, 203, 216, 222, 225, 232, 235, 237

N

- Nb/U 174, 176, 177, 179, 180, 213, 219

O

- oceanic crust 95, 96, 105, 108, 114, 127, 129, 135, 147-152, 154-159, 161-165, 167, 171, 173-181, 184-187, 203, 216, 218, 219, 222, 225, 232, 234, 236, 239, 240, 242, 244, 245
O'Hara, Mike IV, 108, 109, 142, 152, 155, 217, 231, 238



OIB (oceanic island basalts) 95, 105,
115, 116, 119, 131, 132, 139, 143, 145,
152-154, 161, 163-166, 176, 177-179,
184-186, 189, 201, 208, 213, 218, 220,
238

P

partial melting 138, 164, 171, 209, 226,
229, 231, 239

partition coefficient 100, 107, 147

Patchett, Jon 113-115, 132, 238, 245

Paul, Debajyoti IV, 105, 184, 202, 204, 234,
237, 238

Pb/Ce 174, 176, 177, 179, 180, 219

Pb isotope ratios 103, 105, 109, 112, 116,
118-121, 130, 131, 133, 155, 167, 176,
177, 184, 193, 194

peridotite 105, 150-154, 158, 161, 165, 166,
168, 185-188, 193, 194, 198, 199, 204,
223, 226, 246

PHEM 213, 216

Pitcairn 154, 163, 165, 179

Plank, Terry 115, 146, 161, 168, 169, 171,
172, 175, 222, 225, 227, 233-235, 239,
242, 244

plate tectonics IV, 97, 98, 106, 113, 138,
148, 215, 216, 224, 233, 236

PREMA 95, 96, 122, 123, 125, 180, 213,
216, 218

primitive mantle 101, 113, 115, 116, 124,
146, 149, 153, 161, 162, 164, 206, 213,
214, 236

pyroxenite 165, 185-187, 198, 199, 204,
229, 231, 239, 243

R

Rajan, Sundar 170, 171, 224

rare earth plot 100

refractory elements 101

Reunion 107, 145, 195, 201, 202

Reykjanes Ridge 105, 108, 109, 119, 230,
241, 243

ringwoodite 137, 143, 150

Ringwood, Ted IV, 136, 150, 151, 185, 232,
234, 240

RLE's (refractory lithophile elements) 206,
213

S

Samoa 97, 120, 122, 144, 149, 154, 165,
170, 180, 200, 203, 205, 235, 246

Schilling, Jean-Guy III, IV, 107-112, 127,
135, 142, 145, 146, 149, 194, 195, 199,
227, 230, 235, 241, 243-245

Scholl, Dave 169, 171, 180-182, 239, 241,
242

seawater array 115

sediment subduction 128, 168, 175, 181,
183, 184, 237, 245

siderophile 98, 101, 117, 118, 153, 226

Society Islands 122, 145, 149, 157, 158,
164-166, 180, 200, 202, 204, 239, 245

SOPITA 138, 139, 201

spider diagram 129, 146

St. Helena 120-122, 125, 143, 166, 219

subcontinental lithosphere 132, 152, 153,
157, 159, 226

subduction 95, 96, 100, 114, 128, 135, 138,
139, 150, 151, 156, 157, 161, 163, 164,
167-171, 173-185, 205, 213, 216-218,
220, 222, 224, 225, 227, 229, 231, 232,
234, 236, 237, 239-243, 245, 246

subduction erosion 95, 96, 167, 180-184,
217, 229, 234

T

Tatsumoto, Mitsunobu (Tats) III, 105, 113,
119, 167, 168, 171, 189, 238, 242, 243

Tera, Fouad 170, 171, 224, 237, 244

thermal boundary layer 136, 139, 141, 143,
146, 152, 193, 200, 201, 215, 217

tholeiites 107, 128, 203, 221

Tilton, George IV, 105, 229

trace elements 98, 99, 212, 225, 233, 239,
242

Tristan (da Cunha) 120-122, 145, 149, 179,
200, 201, 240

U

ULVZ's (ultra-low shear-wave velocity
zones) 139, 140, 201, 217

Urey, Harold IV, 214, 244

Urey ratio 214, 215, 235

V

Verhoogen, John 97, 105

Vervoort, Jeff 115, 221, 244



W

Wasserburg, Jerry III, 111-113, 122, 136,
170, 206, 213, 226, 233, 245
Whitford, Dave 169-171, 224, 236, 245

X

xenon isotopes 213

Z

Zindler, Alan 101, 115, 120-123, 135, 185,
206, 214, 216, 227, 230, 234, 240, 242,
246
zircon effect 115



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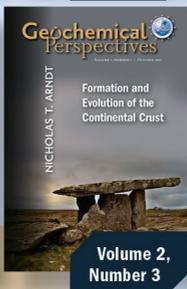
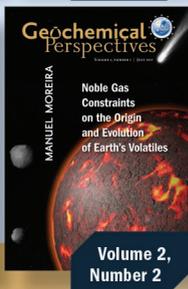
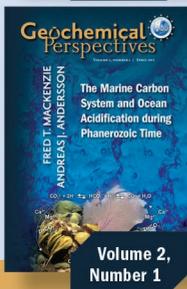
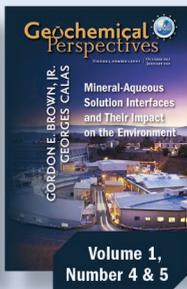
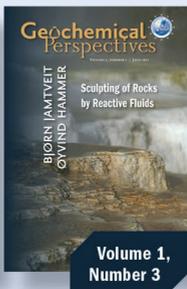
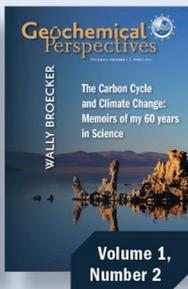
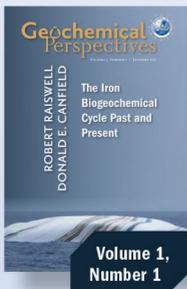
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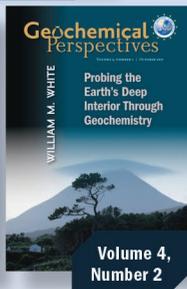
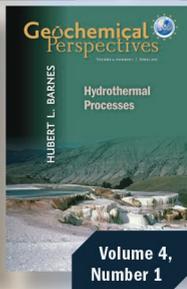
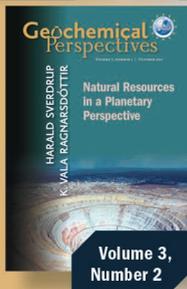
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WILLIAM M. WHITE completed a B.A. in geology at the University of California, Berkeley in 1971 and a PhD in oceanography under Jean-Guy Schilling at University of Rhode Island's Graduate School of Oceanography in 1977. During the course of his dissertation work on the geochemistry of the Azores and the Mid-Atlantic Ridge, he learned the art of isotope geochemistry from Stan Hart as a pre-doctoral fellow at Carnegie Institution of Washington's Department of Terrestrial Magnetism (DTM). He returned to DTM as a post-doctoral fellow from 1977 to 1979. He was a post-doctoral fellow at the USGS in Denver, Colorado from 1979 to 1980 when he joined Al Hofmann's new Abteilung Geochemie at the Max Planck Institut in Mainz, Germany as a staff scientist. In 1985, he moved to the College of Oceanography at Oregon State University and in 1986 to Cornell University where he remains as a professor of earth and atmospheric sciences. In 1995, he spent a 7 month sabbatical in France as a visiting professor at the Ecole Normale Supérieure de Lyon and the Université de Rennes. Returning to old haunts, he was a Merle Tuve Senior Fellow at DTM in 2002.

In the late 1990's, he and a gang of five other geochemists saw the need for an electronic cross-disciplinary journal where all data could be published. They convinced the AGU and the Geochemical Society to jointly publish the journal, *Geochemistry, Geophysics, Geosystems*, one of the first all-electronic scientific journals. White then served as editor from 1999 to 2005.

White currently teaches courses in geochemistry, isotope geochemistry, and introductory earth science. He is the author of two textbooks, *Geochemistry* and *Isotope Geochemistry*. He is a Fellow of the AGU as well as the Geochemical Society and European Association of Geochemistry, and has been named a highly cited author by ISI. He has four grown children with families of their own scattered from Colorado to Massachusetts. When he is not doing geochemistry, he enjoys golf, motorcycling, gardening, and furniture making.