

ISOTOPIC COMPOSITION OF LEAD IN OCEANIC BASALT AND ITS IMPLICATION TO MANTLE EVOLUTION

MITSUNOBU TATSUMOTO

U.S. Geological Survey, Denver, Colo. 80225 (USA)

New data are given in this report for (1) Pb isotopic compositions and U, Th, and Pb concentrations of basalts from the island of Hawaii; (2) redetermined Pb isotopic compositions of some abyssal tholeiites; and (3) U, Th, and Pb concentrations of altered and fresh abyssal basalts, and basalt genesis and mantle evolution are discussed. The Th/U ratios of abyssal and Japanese tholeiites are distinctly lower than those of tholeiites and alkali basalts from other areas. It is thought that these low values reflect a part of the mantle depleted in large ionic lithophile elements. Thus a mantle evolution model is presented, in which Th/U ratios of the depleted zone in the mantle have decreased to ~ 2 , and U/Pb ratios have increased, showing an apparent ~ 1.5 -b.y. isochron trend in the $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plot. The Pb isotopic compositions of basalts from the island of Hawaii are distinct for each of the five volcanoes, and within each volcano, Pb's of tholeiites and alkali basalts are similar. An interaction between partially melted material (hot plume?) of the asthenosphere and the lithosphere is suggested to explain the trend in the Pb isotopic compositions of Hawaiian basalts.

1. Introduction

Oceanic basalts are presumably less subject to crustal contamination on the way to the surface from a magma reservoir during an eruption than are continental basalts. Therefore, studies of trace elements and the Pb and Sr isotope geochemistry of oceanic basalts have been of particular interest for determining the chemical characteristics of the upper mantle and the genesis of basalt. The discussions presented in this article are restricted to the applications of variations in Pb isotope abundances and U, Th, and Pb concentrations in oceanic basalts to problems of oceanic basalt genesis and upper mantle evolution. Doe [1] has reviewed the general field of Pb isotope geology. Only some pertinent Sr data are included for comparison to the Pb isotopic data.

The objectives of this paper are (1) to review Pb isotopic compositions of oceanic basalts; (2) to report Pb isotopic data for Hawaiian basalts; (3) to report U, Th, and Pb concentrations of altered and fresh abyssal basalt samples; (4) to outline interpretations of the Pb isotope data regarding basalt genesis; and (5) to discuss a mantle evolution model.

Oceanic volcanic rocks are generally divided into

two major chemical types; tholeiitic (silica-saturated and -oversaturated) and alkalic (silica-undersaturated). Basalts produced at spreading mid-oceanic ridges have been recognized as being tholeiitic (e.g. [2–4]) and have been found to contain low concentrations of large-ionic lithophile (LIL) elements, such as K, U, Th, P, and Ti and of rare earth elements (REE). In contrast, islands and seamounts are commonly encrusted with alkali volcanic rocks which are more enriched in LIL elements than abyssal basalts.

High-pressure studies (e.g. [5–9]) in which the crystal-liquid equilibria of the mineral components pertinent to the mantle's composition were investigated have suggested that these two types of magma are generated by different degrees of partial melting of mantle peridotite at varying depths.

In 1968, Paul Gast published a remarkable paper concerning the calculation of a partial melting model for basalt genesis using trace element data [98]. His work suggested that alkali basalts were produced by small-scale partial melting (3–6%) of the mantle in equilibrium with garnet (i.e., from depths >100 km) and that abyssal ridge basalts were generated by a large degree of partial melting (20–30%) of the mantle peridotites at shallower levels. Although it

was not the first paper in this field, this paper laid the ground-work for all subsequent researches in the field of trace element geochemistry of basalts.

2. Background for lead isotope tracer studies

There are four naturally occurring stable Pb isotopes: ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb . Three of these, ^{206}Pb , ^{207}Pb , and ^{208}Pb , are also the final decay products of the ^{238}U , ^{235}U , and ^{232}Th decay series, respectively. No long-lived parent for ^{204}Pb is known. Therefore, the relative abundances of the three radiogenic isotopes are usually expressed as the ratios of the number of atoms of these three isotopes to the number of ^{204}Pb atoms. The total Pb isotopic ratios are the initial Pb isotopic ratios plus the time-integrated results of the U/Pb and Th/Pb ratios (from time t_0 to present $t = 0$) in a given chemical system:

$$\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_{\text{observed}} = \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_{\text{initial}} + \int_0^{t_0} \frac{^{238}\text{U}(t)}{^{204}\text{Pb}} \lambda_8 e^{\lambda_8 t} dt \quad (1)$$

$$\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_{\text{observed}} = \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_{\text{initial}} + \int_0^{t_0} \frac{^{235}\text{U}(t)}{^{204}\text{Pb}} \lambda_5 e^{\lambda_5 t} dt \quad (2)$$

$$\left(\frac{^{208}\text{Pb}}{^{204}\text{Pb}}\right)_{\text{observed}} = \left(\frac{^{208}\text{Pb}}{^{204}\text{Pb}}\right)_{\text{initial}} + \int_0^{t_0} \frac{^{232}\text{Th}(t)}{^{204}\text{Pb}} \lambda_2 e^{\lambda_2 t} dt \quad (3)$$

where λ_8 , λ_5 , and λ_2 are the decay constants of ^{238}U , ^{235}U , and ^{232}Th , respectively. If we write, as is customary, the ratios of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ as α , β , and γ ; and the ratios $^{238}\text{U}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{238}\text{U}$ at the present day as μ and κ , respectively; knowing the present-day ratio $^{238}\text{U}/^{235}\text{U} = 137.88$ [10] for normal terrestrial materials, the single-stage solutions of equations (1), (2), and (3)

are:

$$\alpha = \alpha_i + \mu(e^{\lambda_8 t} - 1) \quad (4)$$

$$\beta = \beta_i + \frac{\mu}{137.88}(e^{\lambda_5 t} - 1) \quad (5)$$

$$\gamma = \gamma_i + \mu \cdot \kappa(e^{\lambda_2 t} - 1) \quad (6)$$

The half-life of ^{235}U ($T_{1/2} = 7.0381 \times 10^8$ yr; $\lambda_5 = 0.98485 \times 10^{-9} \text{ yr}^{-1}$ [11]) is short in comparison to the age of the earth (4.55×10^9 yr), and now 98.8% of the ^{235}U originally present in the earth has decayed to ^{207}Pb . The half-life of ^{238}U ($T_{1/2} = 4.4683 \times 10^9$ yr; $\lambda_8 = 0.155125 \times 10^{-9} \text{ yr}^{-1}$) is similar to the age of the earth, and the half-life of ^{232}Th ($T_{1/2} = 1.401 \times 10^{10}$ yr; $\lambda_2 = 0.049475 \times 10^{-9} \text{ yr}^{-1}$; [12] is 3 times longer. Thus, if a geological event early in the earth's history (say earlier than 2.5 b.y. ago) changed U/Pb and Th/Pb ratios from those of the original system, subsequent changes in the relative abundance of ^{207}Pb (because ^{235}U was relatively abundant that long ago), are large compared to those of ^{206}Pb and ^{208}Pb . A similar event late in the earth's history would have resulted in little change in the relative abundance of ^{207}Pb but would have resulted in significant changes in the abundances of ^{206}Pb and ^{208}Pb .

Eliminating μ from the two U-Pb systems (^{238}U - ^{206}Pb and ^{235}U - ^{207}Pb) results in the following equation:

$$\frac{\beta - \beta_i}{\alpha - \alpha_i} = \frac{(e^{\lambda_5 t} - 1)}{137.88(e^{\lambda_8 t} - 1)} \quad (7)$$

Thus by knowing only the Pb isotopic composition, we can provide an age interpretation for rocks, or for the source material in some cases. If initial ratios are assumed for a rock a "model age" is obtained, but the slope (Δ) generated by Pb's in a suite of rocks or cogenetic minerals commonly defines the rock formation age:

$$\Delta = \frac{(e^{\lambda_5 t} - 1)}{137.88(e^{\lambda_8 t} - 1)} \quad (8)$$

Owing to the large amount of mass fractionation (preferential volatilization of the lighter isotope than the heavier isotope in a solid-source mass spectrometer) that results from use of the PbS method [13]

in mass spectrometry for Pb isotope abundance measurements, small variations in the ^{207}Pb abundances in common rocks and minerals (unless U-rich minerals are included) were difficult to measure. Techniques to remove the effects of systematic discrimination in the isotopic measurements have been developed by Catanzaro [14] using a triple-filament technique, and by Compston and Oversby [15] using a double-spiking technique. Employment of the former method is limited to high-Pb minerals such as galena. The latter technique can only be applied when the analytical blanks for the Pb isotope ratio measurements are low. Otherwise the mass fractionation errors are propagated resulting in a large error [16].

Because Akishin et al. [17] discovered an effective Pb ion emitter for isotopic measurements by mass spectrometry, which was further improved by Chernyshev and Shannin [18] and Cameron et al. [19], it is now possible to analyze less than 100 ng of Pb with an accuracy of $\pm 0.1\%$ by the silica-gel phosphate method with a similarly reduced blank. The mass fractionations commonly observed in Pb isotope ratio measurements by the silica-gel phosphate method are $0.1 \pm 0.03\%$ per mass unit in a wide filament temperature range between 1200 and 1500°C. Now we can more accurately measure Pb isotope abundance ratios

and define the slope generated by a suite of rocks or cogenetic minerals on a $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram, and more profoundly consider the significance of such an array.

For terrestrial Pb evolution, the single (primary) growth equations [20] are too simple, and at least a two-stage evolution model is required, e.g.:

$$\alpha = \alpha_i + \mu_0(e^{\lambda_8 t_0} - e^{\lambda_8 t_1}) + \mu_1(e^{\lambda_8 t_1} - 1)$$

Physical examples of the two-stage model have been presented for conformable Pb (e.g. [21,22]). For most geological materials the two-stage model is, however, still too simple and episodic multistage [23–25] or continuous differentiation models [26–30,34] are required to interpret the Pb data.

Uranium and Th are LIL elements and are geochemically coherent to K, and both appear to have been concentrated in magmas rather than in residual mafic minerals. Lead also tends to be concentrated in magma but it seems to be less concentrated than U and Th. An example which depicts U, Th, and Pb concentrations, relative to K is shown in Fig. 1. Consequently, the μ value becomes higher in magma than in the residue. Because of this, the Pb isotopic compositions become more radiogenic with time in differentiated rocks or in certain minerals.

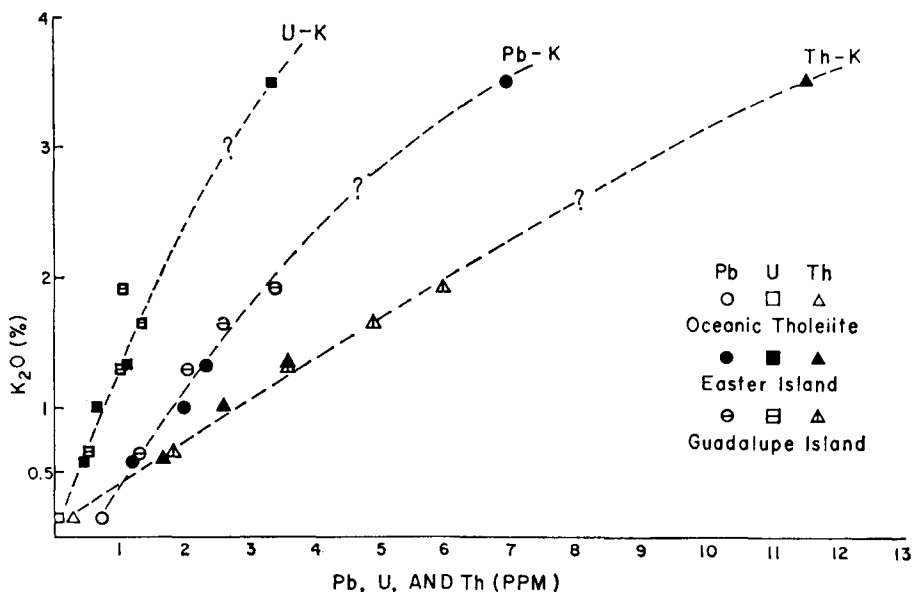


Fig. 1. Relations between concentrations of K_2O and Pb, U, and Th [37]. Plotted are average values of six oceanic tholeiites and the concentrations of alkali basalt suites from Guadalupe and Easter Islands.

It is important to note that thermodynamic considerations and isotopic studies indicate that crystallization differentiation of magmas produces no measurable change in the isotopic abundance ratios of elements as heavy as Pb and Sr. Lead is one of the very mobile elements and the Pb isotopic composition in a magma reservoir is usually considered to be isotopically homogenized. Regardless of the degree of fractional crystallization, the Pb isotopic composition of a basalt at time of crystallization should be the same as that of its parental magma, provided that the magma is not contaminated by foreign material which contains Pb with a different isotopic composition. Rocks with significantly different calculated initial Pb isotopic compositions (corrected for the growth of radiogenic Pb generated by the decay of U and Th after the rock formed, providing the Pb, U and Th concentrations have not changed since the time of crystallization) either are not comagmatic, or are comagmatic but contaminated to different degrees with foreign Pb.

3. Uranium, thorium, and lead concentrations in basalts

Differentiation of Pb and Sr isotopes is not expected in a short-term geological event such as magma formation if isotopic equilibrium was attained during partial melting or crystallization differentiation (isotopic disequilibrium will be discussed later). However, concentrations of U, Th, Pb, Rb, and Sr vary widely as a result of partial melting and, to some extent, crystallization differentiation. These concentration variations provide valuable information regarding processes of magma derivation and the geochemistry of the mantle source regions.

The strong depletion of LIL elements in abyssal tholeiites is one of the most important characteristics of these rocks. It has been ascribed to their derivation from a mantle source which was depleted in LIL elements by previous magma extraction (e.g. [32,35–37,98]. In this paper I would like to discuss only U, Th, and Pb relations because characteristics of other LIL elements in abyssal basalts may be obtained from other chapters in this volume.

The Th, U, and Pb data of oceanic basalts are plotted on a $^{232}\text{Th}/^{238}\text{U}$ vs. $^{238}\text{U}/^{204}\text{Pb}$ diagram in

Fig. 2 and Th/U values in basalts from various tectonic environments are also listed in Table 1. The diagram clearly demonstrates that abyssal tholeiites have unusually low Th/U ratios ranging from 0.65 to 3.0 (except for one sample which was collected very close to Iceland and which has a ratio of 3.3), while alkali basalts have generally high Th/U ratios of greater than 3.3. Tholeiites from Hawaii, Iceland, and Oregon have intermediate characters. Tholeiites from Japan show low Th/U values similar to those of abyssal tholeiites. These low Th/U ratios which are distinctly characteristic of abyssal (and Japanese) tholeiites must be explained by mantle mineralogy, partial melting and crystallization differentiation of magmas.

As O'Hara [33] emphasized, erupted magmas are not primary, owing to fractional crystallization of the primary magma and separation of crystals on the way to the surface. It is considered, however, that the abundance ratios of two LIL elements which have similar solid/liquid distribution coefficients would not be significantly changed in the liquid phase by separation of crystals (e.g. clinopyroxene, olivine) from those abundance ratios in the primary magma. Applying this assumption and considering a large degree of partial melting, I demonstrated that the $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{238}\text{U}/^{204}\text{Pb}$ relationships among oceanic tholeiites

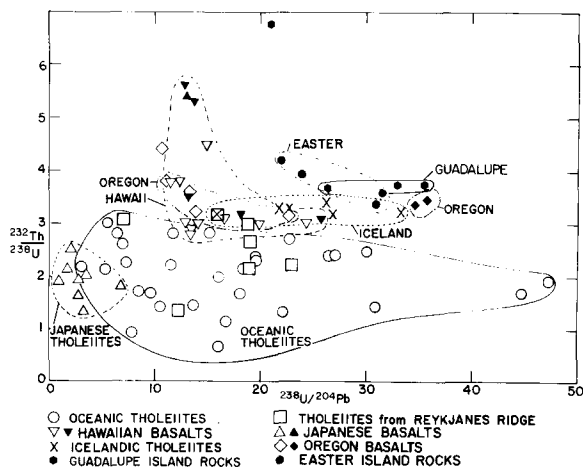


Fig. 2. $^{232}\text{Th}/^{238}\text{U}$ vs. $^{238}\text{U}/^{204}\text{Pb}$ diagram for basalts from oceanic regions. Data plotted are from abyssal tholeiites [25,37,55,81] and basalts from Hawaii (this paper, M. Tatsumoto, unpublished data), Iceland [66], Japan [50] and Oregon [108]. Open symbols are for tholeiitic basalts and solid symbols are for alkali basalts.

TABLE 1

Th/U ratios in basalts from oceanic regions

Tectonic regions		Th/U	References
1. Mid-oceanic ridges	Mid-Atlantic	0.9 – 3.3	[37,81]
	East Pacific	0.65–2.8	[25,37,55]
2. Seamounts	East Pacific	0.53–4.9 *	[25]
3. Intra-oceanic islands	Hawaii	2.8 – 6.6 *	[38], this paper
	Iceland	3.0 – 3.3	[66]
	Easter	3.4 – 4.2 *	[37]
	Guadalupe	3.7 – 6.8 *	[37]
4. Orogenic belts	Oregon	3	[108]
	Japan	1.3 – 7 *	[38,50]

* Includes alkalic volcanics.

yields a relatively old differentiation age (>1.2 b.y.) for the parental upper mantle [37]. This confirms a rather old (>1.5 b.y.) model mantle differentiation age estimated from Pb isotopes alone [37,38]. However, this method of obtaining the differentiation age from $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{238}\text{U}/^{204}\text{Pb}$ (μ) relationships is not *rigorously* correct, if one argues that a *small* amount of U-Pb fractionation takes place during partial melting crystallization differentiation.

Let us exercise a simple calculation to see how μ changes with partial melting. Unfortunately the solid-liquid distribution coefficients for Pb are not well known for pertinent minerals in the upper mantle, but considering μ variations in basalts one may estimate the Pb distribution coefficients to be about 20 times higher than those of U. Uranium has a solid/liquid distribution of 0.001–0.002 between diopside and melt [31]. Thus in this type of system ~ 99.5 – 99.8% of the U and ~ 91.5 – 95.5% of the Pb would be in the liquid phase, resulting in only 4–9% fractionation in the U/Pb ratio from that of the parental material, assuming a 30% equilibrium melt. However, the U/Pb ratio in the diopside would be fractionated on the order of 90–95% from that of the parental material. In other words, if the μ of the parental material were 8.0 then the μ of the liquid would be ~ 8.3 – 8.7 but the μ of the diopside would be ~ 0.5 – 1.4 .

The distinct Th/U ratios displayed by abyssal tholeiites and alkali basalts provide useful criteria for distinguishing them from one another. This charac-

teristic feature must also be explained by partial melting of mineral constituents of the basalt source region in the mantle. Uranium and Th concentrations determined by isotope dilution are listed in Table 2 for olivine, enstatite, diopside, and spinel separated from nodules in alkali basalt of Boss Mountain, British Columbia, Canada. The spinel and diopside contain about 10 and 30 times more U, respectively, than does either the olivine or the enstatite, while the Th concentrations in the former two minerals are only 2–3 times higher than those in the latter two minerals. The Th/U ratios in the spinel and diopside are only 0.4 and 0.8, respectively, in contrast to that of augite in an alkali olivine basalt from Takashima which is 4.7. Because spinel is not abundant in peridotite, I presume clinopyroxene is probably the major phase involved in partitioning between U and Th in the generation of abyssal tholeiites. However, we have pertinent data only for alkali basalts but not for abyssal tholeiites.

There are several papers (e.g. [40–42]) which report U concentrations of peridotite minerals determined by the fission track method. The U concentrations of peridotite may provide a true estimate of the U concentration in the upper mantle if peridotites represent primary mantle material. It is more likely, though, that the U concentration of peridotite provides a lower limit to the U concentration in the upper mantle, because peridotites probably represent either crystal cumulates, or residues after partial melting. For example, the U concentrations in minerals of

TABLE 2
U and Th concentrations (ppb) in coexisting mineral phases

Rocks	Peridotite inclusion ¹ (British Columbia, Canada)			Alkali olivine basalt ² (Takashima, Japan)			Peridotite inclusion ³ (Nunivak Is., Alaska)			Lherzolites, Victoria ⁴ (Victoria, Australia)		
	Th	U	Th/U	Th	U	Th/U	U	U	U	classification	U	Kd
Olivine	6.55	1.48	4.33	—	—	—	13	15	0.2—		0.7	
Orthopyroxene	5.00	1.29	3.88	—	—	—	9	19	0.5—		5	
Clinopyroxene	17.8	40.7	0.44	55.5	11.8	4.70	55	17	6—	(I)	370	
									13—	(Ia)	47	0.1—0.01
Spinel	10.7	13.3	0.81	—	—	—	150	<10	12—	(II)	16	0.004—0.01
Phlogopite	—	—	—	—	—	—	130	—	0.2—		0.7	
Hornblende	—	—	—	—	—	—	300	—	0.5			
Apatite	—	—	—	—	—	—	—	—	0.5			
									35,000	(I)		
									5,800	(II)		

¹ M. Tatsumoto and T.N. Irvine, unpublished; determined by isotope dilution method for minerals separated from inclusions in alkali basalt.

² Onuma et al. [111]; by neutron activation analysis.

³ Haines and Zartman [42]; by fission track counting method.

⁴ Kleeman et al. [40]; by fission track counting method; I, primary phases; Ia, modified primary phases (retaining the same optic orientation as I); II, recrystallized phases; Kd, partition coefficients.

two peridotites, one from Nunivak Island and the other from Hawaii, are listed in Table 2. The U distribution in the peridotite from Nunivak Island appears to be similar to that observed in nodules of alkali basalt from British Columbia (Table 2) but the Hawaiian sample contains clinopyroxene and spinel which have distinctly low U concentrations. Because the intergranular part of the Hawaiian peridotite contains an excessive amount of U, Haines and Zartman [42] concluded that the U distribution in the Hawaiian peridotite minerals has already been disturbed by partial melting. These low U concentrations in pyroxene have also been observed by Kleeman et al. [40] in Victorian peridotite. They found that primary clinopyroxene contains 300 ppb U, but secondary clinopyroxene, crystallizing in equilibrium with glass formed by partial melting of the peridotite, has a much lower U abundance.

The solid/liquid distribution coefficients of U and Th between diopside and melt have been studied by Seitz [31] by high-pressure experiments at pressures up to 25 kbars using fission track counting methods. He found that although the solid/liquid distribution coefficients of U (0.001–0.002) and Th (0.006–0.017) between diopside and liquid were both small, U was transferred to the liquid more efficiently than was Th, resulting in a Th/U ratio in the liquid which is similar to that of primary magma, but a high Th/U ratio in the residual clinopyroxene. He further found that there is no detectable difference in U and Th partitioning between atmospheric pressure and 25 kbars.

We further investigated Th and U partition coefficients by a high-pressure experiment using an olivine tholeiite from a Kilauea volcano 1921 eruption [44]. The tholeiite was melted at 1400°C, then allowed to equilibrate under water-free conditions at 14 kbars and 1200°C, for 4 hours. Clinopyroxene and glass (~80% pure) fractions were separated by using heavy liquids and the former was further purified to >95% purity by a chemical differential dissolution technique [45]. The U and Th concentrations were determined in the glass and clinopyroxene by isotope dilution. The partition coefficients for U and Th obtained were calculated to be 0.014 and 0.021, respectively, and Th/U ratios were 3.21 and 2.07 for clinopyroxene and glass, respectively. Although the U and Th partition coefficients are about 3–7 times higher than

those reported by Seitz [31] probably indicating our separates were less pure, the results agree with Seitz's by clearly indicating that the Th/U ratio is lower in the liquid than in the clinopyroxene as a result of partial melting. If these results of high-pressure experiments are applicable to the upper mantle clinopyroxene, then U and Th concentrations in the residual pyroxene should be very small and the Th/U ratio should be larger than that of the primary mantle (~3.8), since magma has been extracted from the upper mantle in the geologic past. On the contrary, Pb isotopic compositions of abyssal basalts indicate that lower Th/U ratios must have persisted in the basalt source region for over the last 1 b.y. It appears difficult to produce the low Th/U ratios found in abyssal tholeiites from mantle peridotite by ~30% partial melting if the Th/U ratios in abyssal tholeiites are mainly controlled by clinopyroxene. Because water content and oxygen fugacity differ between natural and experimental materials and because U is in the +4 and +6 states whereas Th is always in the +4 state [31,37], the results of the high-pressure experiments might not be applicable to natural systems. However, the apparent difficulties in producing low Th/U ratios may be due to my wrong assumption that clinopyroxene is the main control of the Th/U ratio in oceanic tholeiites. Other minerals such as phlogopite and amphibole may be more important minerals in controlling the Th/U ratios in tholeiites. Due to a lack of reliable data for Th and U, and also to a lack of Pb partition coefficients in appropriate mineral phases, further discussion would not, at present, be very fruitful.

It is interesting to note that the Th/U ratios in Japanese tholeiites are distinctly low compared not only to tholeiites from Hawaii and Iceland, but also to tholeiites from the Oregon Coast, where the oceanic lithosphere is also being subducted under the continent as it is along the Japanese arc. I have suggested that the Pb in Japanese tholeiites may have originated from the remelt of an oceanic underthrusting plate [46] involving 1–2% of oceanic sediments. Oversby and Ewart [47] strongly objected to this proposal mainly on the grounds of their U-Pb systematics study of Tonga-Kermadec volcanics. Meijer [48], however, suggested, on the basis of his Pb and Sr isotope study of Mariana arc volcanics, that the rocks were derived, at least in part, from altered

Pacific lithosphere subducted beneath the Mariana arc, but involving not more than 1% oceanic sediment. If we use the low Th/U ratio as a distinct characteristic for the oceanic lithosphere, it may be interesting to note that, in Meijer's limited analyses, two Mariana andesites show comparably low Th/U ratios but the other Mariana andesite has a higher Th/U ratio. In any case, there may be a distinct difference between the tectonic environments of the Japanese arc and the other arcs. If the hot plate, the Kula-Pacific Ridge [49], was thrust under the Japanese arc, the low Th/U ratios could be explained as characteristic of tholeiites from a spreading center and the low U/Pb ratios as being influenced by Pb contamination from crustal sedimentary rocks or from a small amount of abyssal sediment being carried down with the underthrusting lithosphere [50].

4. Seawater alteration

The low Th/U ratios appear to be a primary feature of abyssal tholeiites and are not caused by alteration and contamination by seawater and sediments.

Uranium, Th, and Pb concentrations have been determined for altered outer zones and unaltered interiors of abyssal basalts (see Hart [51], for sample description). The results are shown in Table 3. Most samples show significant decreases (10–50%) in Pb concentrations and small but still distinct decreases (10–30%) in U concentrations, from the unaltered to altered zones, respectively. Exceptions are PV 618 (for Pb) and Ad2 (for U); in these samples the concentrations do not significantly change. On the other hand, Th concentrations in most samples either increased or remained unchanged in the altered zones (PV 618 again is an exception). As a result, $^{238}\text{U}/^{204}\text{Pb}$ and Th/U ratios of most samples increase in the altered portion in relation to those ratios in the fresh portion.

Recently the Pb concentrations of deep-sea water have been redetermined using improved water sampling and isotope dilution techniques. The Pb concentrations were found to be extremely low (~ 0.002 ppb; C.C. Patterson, oral communication, 1976) but those of slowly precipitated abyssal sediments are as high as ~ 75 ppm. As will be shown later in Fig. 9,

TABLE 3

Comparison of U, Th, and Pb concentrations (ppm) in altered and fresh abyssal tholeiite *

Sample No.	Description	Pb	U	Th	$^{238}\text{U}/^{204}\text{Pb}$	$^{232}\text{Th}/^{238}\text{U}$
<i>Mid-Atlantic Ridge</i>						
AD2-1	altered	0.80	0.073	0.126	5.72	1.79
AD2-1	fresh	0.95	0.072	0.128	4.75	1.85
(AD2-1)	(1), (2) **	(1.29)	(0.16)	(0.15)	(7.9)	(0.9)
AD3-3	altered	0.56	0.092	0.286	10.1	3.21
AD3-3	fresh	0.91	0.118	0.241	8.0	2.11
(AD3-3)	(1), (2)	(1.15)	(0.10)	(0.29)	(5.6)	(3.0)
AD5-5	altered	0.77	0.119	0.092	9.92	0.80
AD5-5	fresh	0.85	0.132	0.076	9.91	0.59
AD5-11	(1)	(0.56)	(0.09)	(0.13)	(10.5)	(1.4)
AD5-18	altered	0.40	0.051	0.152	8.2	3.07
AD5-18	middle	0.45	0.045	0.072	6.3	1.66
AD5-18	fresh	0.79	0.075	0.108	6.1	1.49
<i>Galapagos Rise</i>						
PV 618	altered	0.69	0.139	0.319	12.7	2.37
PV 618	fresh	0.71	0.153	0.356	13.7	2.40

* Samples are by courtesy of S.R. Hart except as noted. For detailed sample description, see Hart [51].

** (1) Samples by courtesy of A.E.J. Engel. The Pb, U, and Th concentrations were reported in Tatsumoto [37].

(2) It is unknown why the concentrations are different in the same-numbered "fresh" samples from Hart and Engel. It may be that the two samples came from different portions of a pillow and they have, in fact, undergone different degrees of alteration.

the isotopic compositions of Pb in seawater and in most abyssal sediments [48,52–54] except metalliferous sediments near the East Pacific Rise [43,55] whose Pb is considered to have originated from volcanic emanations from the ridge, are distinctly different from the Pb isotopic trend of abyssal tholeiites. Thus, it is concluded that the deep-sea weathering processes of Pb exchange with seawater or sediments are not controlling factors for the low Th/U ratios and differences in Pb isotopic abundances found in abyssal tholeiites. These distinct differences can only be related to the basalt sources or to some petrogenetic process.

5. Lead in basalts from the island of Hawaii

Comparing Pb data of volcanic rocks from the island of Hawaii and from Iceland may be of interest, as each originates from one of Morgan's [56] "hot spots," and because the Th/U ratios in volcanic rocks from both localities are indistinguishable (Fig. 2).

The island of Hawaii is located at the southeasternmost end of the Hawaiian Archipelago, which consists of more than fifty huge undersea volcanoes and volcanic islands extending over 3000 km. The volcanoes of the Hawaiian Islands become progressively younger to the southeast from 6 m.y. old at Kauai to the presently active volcanoes [57,58]. The island of Hawaii is the youngest and is comprised of five volcanoes, Kohala, Mauna Kea, Hualalai, and the presently active volcanoes of Mauna Loa and Kilauea (e.g. [59,60]).

The Pb isotopic compositions and concentrations of Pb, U, and Th for basalts from the island of Hawaii are listed in Table 4. The Pb isotopic compositions are depicted on a $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram in Fig. 3. For comparison, Pb isotopic compositions (Table 5) of oceanic tholeiites [37], redetermined by the silica-gel phosphate method, are also plotted in Fig. 3. The Hawaiian basalt are further compared with all abyssal basalt data so far reported on $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ in Fig. 4. The $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ trend of Hawaiian rocks is not distinguishable from the trend of oceanic tholeiites. Because the Th/U ratios of 2.8–5.3 for Hawaiian rocks are distinctly higher than those found for abyssal tholeiites (0.5 ~ 3.0), one would expect to observe larger $^{208}\text{Pb}/^{204}\text{Pb}$ ratios in

Hawaiian rocks than in abyssal basalts, if the basalt source region of Hawaii differentiated at a significantly early time, as suggested by the $^{207}\text{Pb}/^{206}\text{Pb}$ trend. The $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of Hawaiian basalts with less radiogenic Pb (i.e., lower $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, Fig. 4) are indeed larger than those of abyssal basalts with comparable $^{206}\text{Pb}/^{204}\text{Pb}$ ratios indicating that a higher Th/U ratio must have persisted in the Hawaiian subcrust for a long time (~1 b.y.). The $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of Hawaiian basalts with more radiogenic Pb (Fig. 4) are, however, not distinctly different from those of abyssal basalts with comparable $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. This is one of the reasons which causes me to propose a mixing model for Hawaiian basalt Pb variations.

The results of Pb study on Hawaiian rocks are summarized as follows:

(1) Hawaiian data on the $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram all fall to the right of the primary zero isochron and form a trend whose slope is equivalent to 0.94 b.y.

(2) The Pb isotopic compositions of the five volcanoes are distinctly different from one another.

(3) Within each volcano, Pb isotopic compositions vary measurably among different lava flows, and the variations are not linearly correlated with the eruption age sequence. This feature is in contrast to O'Nions and Pankhurst's [61] results for Si isotopic compositions in Icelandic volcanic rocks. They observed a constant variation with the older rocks being more radiogenic than the younger rocks.

(4) Lead in alkali basalts which were erupted during the latter stage of volcanism in Hawaiian volcanoes shows Pb isotopic compositions which are similar to, or within the variation of, the Pb isotopic compositions found for tholeiites from each volcano. This suggests a very close relationship between the tholeiite and alkali basalt sources of each volcano. This result is consistent with a hypothesis that the late-stage alkalic lava is a fractionated product of tholeiitic lava [62–64]. In the case of Hawaiian eruptions the alkali basalts and tholeiites of each volcano appear to originate from the same source or closely related sources, and they could not have come from different depths in the heterogeneous mantle.

These features will have to be considered with regard to geophysical and geological evidence or theories in order to determine the nature of magma-

TABLE 4

The isotopic composition of Pb and concentrations (ppm) of Pb, U, and Th in volcanic rocks from Hawaii Island

Sample No. *	Description	Pb	U	Th	Atomic ratio				
					$\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{207}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{208}\text{U}}{^{204}\text{Pb}}$	$\frac{^{238}\text{U}}{^{204}\text{Pb}}$	$\frac{^{232}\text{Th}}{^{238}\text{U}}$
<i>Kohala</i>									
C-53	tholeiite, lower member	1.02	0.18	0.67	18.136	15.457	37.760	11.5	3.8
C-62	tholeiite, lower member	0.79	0.15	0.56	18.155	15.456	37.783	12.4	3.8
					18.156	15.463	37.831		
C-66	tholeiite, lower member	0.75	0.21	0.62	18.267	15.474	37.916	17.6	3.1
					18.268	15.471	37.897		
C-70	alkalic olivine basalt, upper member	2.14	0.87	2.60	18.211	15.458	37.828	25.8	3.1
<i>Mauna Kea</i>									
C-78	alkalic olivine basalt, lower member of Hamakua series	1.39	0.29	1.50	18.421	15.474	38.003	13.6	5.3
C-74	tholeiite, intermediate upper member of Hamakua series	1.15	0.26	1.14	18.401	15.476	37.923	14.8	4.5
<i>Hualalai</i>									
1801	alkali basalt, 1801 Kaupulchu flows	2.55	0.52	1.79	17.918	15.439	37.686	13.2	3.5
					17.903	15.429	37.747		
<i>Mauna Loa</i>									
1907	tholeiite, 1907 lava flow from the southwest rift	0.98	0.21	0.56	18.173	15.469	37.898	13.4	2.8
					18.155	15.447	37.833		
1926	tholeiite, 1926 lava flow from the southwest rift	0.83	0.20	0.56	18.113	15.458	37.817	15.2	2.9
					18.118	15.459	37.829		
1950	tholeiite, 1950 lava flow from the southwest rift	0.84	0.19	0.55	18.089	15.449	37.824	14.1	3.0
<i>Kilauea</i>									
1921	tholeiite, 1921 overflow from Halemaumau	1.75	0.45	1.34	18.647	15.491	38.192	16.5	3.1
1955	tholeiite, the earliest 1955 main flow from the east rift	1.83	0.57	1.69	18.485	15.475	38.108	20.0	3.0
					18.491	15.473	38.111		
1960	tholeiite, 1960 eruption from the east rift	1.32	0.51	1.49	18.533	15.486	38.155	24.4	3.0
					18.526	15.481	38.150		
1963	tholeiite, 1963 lava lake in Alae crater	2.03	0.41	1.23	18.541	15.481	38.155	13.0	3.1
					18.542	15.487	38.173		

* C-series samples are splits from Macdonald and Katsura [64]. Historic flows were collected by H.A. Powers.

forming events and the mantle chemistry under Hawaii. Others have concluded from previous Pb isotopic studies (e.g. [25,37,38,65,66]) that the mantle is heterogeneous when isotopically distinct Pb was found. Is this also correct for Hawaiian volcanics since the Pb isotopic compositions are distinct for each volcano?

The regularity in the Pb isotopic compositions of Hawaiian volcanics shown in Fig. 3 may be divided

into two groups. The group which has less radiogenic Pb consists of Hualalai and Mauna Loa, and the other group which has more radiogenic Pb, consists of Kohala, Mauna Kea, and Kilauea. Within each group the northern volcano tends to be less radiogenic. This grouping agrees with the two locus lines of Loa and Kea (e.g. [58]), and trends in each group coincide with the volcano age sequence. It is interesting to note that this grouping is also applicable to other

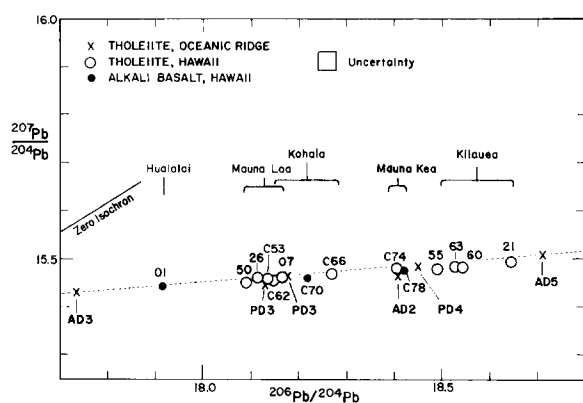


Fig. 3. $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram of basalts from the island of Hawaii. Shown for comparison are re-determined values of abyssal tholeiites indicated by an "X". The Pb from each volcano has a distinct isotopic composition.

islands of the Hawaiian Islands; Pb from Maui belongs to the Kea group and Pb from Kauai and Oahu are in the range observed for the Loa group [67]. Furthermore, Hawaiian data plotted on a $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram form a trend whose slope is equivalent to a 0.94 ± 0.42 b.y. age (Figs. 3 and 4A). This Hawaiian basalt trend cannot be distinguished from the Pb trend of the abyssal tholeiites [25,68], although the $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of Hawaiian basalts are distinctly different. Sun and Jahn [66] also found a similar trend for Icelandic rocks. Their Pb data form an apparent 1.5 ± 0.5 b.y. trend. A similar trend was also reported by Oversby and Gast [69] for volcanic

rock Pb's from Tristan de Cunha, St. Helena, Ascension, and Gough, although their data were not precise enough to discuss this slope [68,70].

Has this " ~ 1.5 -b.y." trend been created by mantle fractionation resulting in an increased U/Pb ratio in the source regions of these basalts at a discrete time or for a prolonged time in the past? Or is it a mixing line of two extremes, such as material from a mantle plume [56] and the low-velocity zone, as Schilling [71] suggested for basalts from the Iceland-Reykjanes Ridge?

On a small scale, there must be some other mechanism to produce the individual Loa and the Kea Pb trends, although Pb's from all oceanic regions appear to fall on the same trend. I prefer a two-source mixing model to explain the " 1.5 -b.y." trend. However, for Hawaii I propose that the two sources are not the mantle plume and the low-velocity zone as Schilling [71] proposed for Reykjanes Ridge basalts, but rather the mantle and the lithosphere. It is difficult to construct this small scale Pb trend if two phases were mixed in the mantle (asthenosphere) and rose up through the lithosphere to form volcanoes, because it is quite probable that Pb would have been more or less isotopically homogenized in the mixture. The "hot spot" or "plume" hypotheses [56,72,73], the "propagating fracture" hypothesis [74–76], and the "shear-melting" hypothesis [77] all could involve lithosphere and mantle mixing at the melting spots.

Morgan's plume hypothesis proposed that the volcanoes are the surface expression of hot plumes

TABLE 5

Redetermined lead isotopic composition * of oceanic tholeiites by SiO_2 gel-phosphate method

Sample No.	Location references	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
<i>Mid-Atlantic Ridge</i>				
AD2-1	[2]	18.404	15.463	37.847
AD3-2	[2]	17.736	15.433	37.175
AD3-3	[2]	17.734	15.428	37.154
AD5-5	[2]	18.709	15.508	38.160
<i>East-Pacific Rise</i>				
PD1-P	[3]	18.128	15.451	37.653
PD3-A	[3]	18.170	15.452	37.757
PP4-G	[3]	18.449	15.482	37.900

* Lead isotopic data were previously determined by PbS method [37].

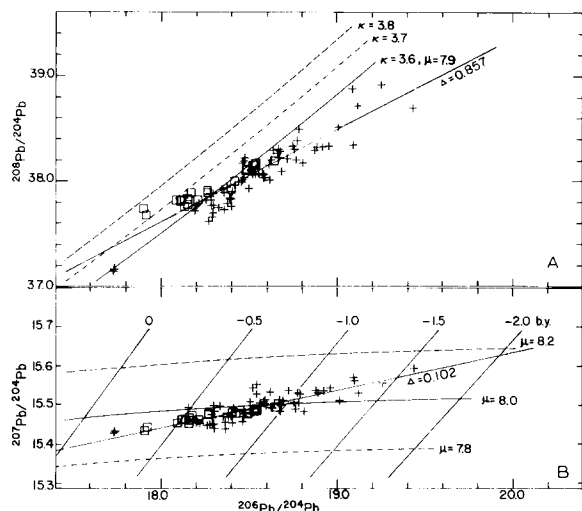


Fig. 4. $^{207}\text{Pb}/^{204}\text{Pb}$ (lower) and $^{208}\text{Pb}/^{204}\text{Pb}$ (upper) vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram. Single-stage growth curves since the earth's formation with $\mu = 7.8, 8.0$ and 8.2 and the model ages for $0, -0.5, -1.0, -1.5$ and -2.0 b.y. are drawn for references in the lower diagram and single-stage growth curves with $\kappa = 3.6, 3.7$, and 3.8 for $\mu = 7.9$ are drawn in the upper diagram. The array of the abyssal tholeiite and Hawaiian basalt data as a whole yield a slope of 0.102 ± 0.012 (2σ), which corresponds to an isochron age of 1.66 ± 0.20 b.y. in the lower diagram, and a slope of 0.857 ± 0.030 in the upper diagram. The Hawaiian basalts alone (squares) yield a slope of 0.0704 ± 0.0316 (2σ) in the lower diagram which is indistinguishable from that of the abyssal tholeiites (crosses; slope = 0.1079 ± 0.0138 , 2σ). However, in the upper diagram the Hawaiian basalt array has a slope of 0.736 ± 0.028 , which appears to be distinctly different from that of the abyssal basalts (0.957 ± 0.068). This distinct difference suggests that Pb in some Hawaiian basalts was generated in a higher Th/U environment, and appears to contradict the concept of a two-stage model in which mixing occurred between a previously (1.7 b.y.) segregated relatively radiogenic and unradiogenic phases. The plotting is from the "Lead isotope data bank" [109] and data are from Sun et al. [81], Doe and Stacey [110], Church and Tatsumoto [25], Unruh and Tatsumoto [55] and this paper.

which originate deep within the mantle. The narrow (about 150 km in diameter), high-velocity (2 m yr^{-1}) stream rising from the lower part of the mantle is "plastered" [78] at the lithosphere-asthenosphere interface. The "plastered" material then rises through a vent and forms volcanoes. Morgan [73] argued that the cycle time of mantle overturn may be 1.8 b.y., referring to the 1.8 -b.y. isochron Pb age obtained by Oversby and Gast [69] for Tristan de Chunha and St.

Helena rocks. A hot plume which approached the surface 1.8 b.y. ago returned at a low velocity to the mantle over a large area, as dispersing "streams". In this case, each "stream" must have kept its U/Pb ratio and Pb isotopic characteristics until the stream recycled back to the surface. If six convecting cells which have had distinct Pb isotopic identities in the Atlantic basin have nearly the same recycling time of ~ 1.8 b.y., then it is conceivable that the Pb isotopic compositions of Atlantic islands may define the true convection cycle age. The 1.8 -b.y. age would be valid only if one of the following two conditions is met: (1) there was little or no mixing between the rising plume (originating in the mesosphere?) and the asthenosphere during the formation of the Atlantic Islands, or (2) if there has been substantial mixing, the asthenosphere-mesosphere differentiation age (not necessarily related to the convection cycle age) must be about 1.8 b.y. (a two-stage Pb evolution model is valid). It is still debatable whether or not the 1.8 -b.y. differentiation age is real [79] as discussed later in this paper.

Even if the above model is valid for Atlantic basalts, it is difficult to imagine that the Pb isotopic identities of five separate volcanoes could have been individually retained in a single hot plume, if there is one, under the Hawaiian Islands. On the other hand, if the isotopic identity was kept in each individual blob, it is difficult to explain the two trends of Lao and Kea.

Because the five Hawaiian volcanoes which have individual Pb identities appear to be divided into two groups, I propose a lithosphere and plume mixing model; the hot plume (or plastered zone) under the Hawaiian Islands has (at present and for the last 6 m.y.) split in the lithosphere into two streams which produce magma reservoirs that contain different proportions of plume and remelted lithospheric material. The lithosphere created at the East Pacific Rise has a high U/Pb ratio resulting in a large $^{206}\text{Pb}/^{204}\text{Pb}$ increase (this also causes the shallower ~ 1 -b.y. trend for Hawaiian Pb compared to the 1.7 -b.y. trend of abyssal basalts). If the plume material is less radiogenic (low $^{206}\text{Pb}/^{204}\text{Pb}$ but high $^{208}\text{Pb}/^{204}\text{Pb}$) than the tholeiitic lithosphere, then the larger "stream" from the plume would be related to the Loa group, and the smaller to the Kea group. The individual Pb characteristics of each volcano would be related to

the amount of mixing between a “stream” and the lithosphere, during the formation of the magma reservoir for each volcano. That is, in a larger magma reservoir, there would probably be less dilution of plume material by lithospheric material, and hence the Pb isotopic composition in a larger reservoir would be less radiogenic than in a smaller reservoir. Movements of the oceanic plate over the “hot spot” causes the homogeneous magma chamber to be sealed off from the stream [76]. The isolated magma chamber then differentiates and produces a volcano whose flows become progressively less silica-saturated producing alkali basalts and nepheline as the last stage. I prefer the interpretation that the small variations in the Pb isotopic compositions within a given volcano are created in the magma conduit by assimilation of Pb. It is also feasible that two “streams” or blobs arose under the islands of Hawaii and created the two trends of Loa and Kea. In this case, mixing of a stream with the lithosphere would also be necessary to create the isotopic identity for each volcano.

If this type of two component mixing is correct, the Pb isotope identities of Hawaiian rocks can also be explained either by the propagating fracture hypothesis or by the shear-melting hypothesis. Shaw [77] observed that the volume rate of eruption of Hawaiian volcanoes progressively increases from northwest to southeast, with Kilauea having the largest flow rate. It is conceivable that there is a correlation between the radiogenicity of the Pb from each volcano and the size of the volcano (and presumably its magma chamber), with Kilauea being the most radiogenic among Hawaiian volcanic rocks, if remelting of the lithosphere has increased with time.

It is important to note at this stage that my evolution model, which will be explained in detail later, is completely opposite to Schilling's ([71]; also refer to Brooks et al. [79]) as schematically illustrated in Fig. 5. I envision that LIL elements were concentrated upward during the primary differentiation of the earth and that the Hawaiian plume or blob is generated in this fertile asthenosphere (inner part of the convection cell, see Fig. 10). The main reason for reversing Schilling's model is that his model would require tremendous amounts of LIL-depleted material from the low-velocity zone to be mixed into the rising material from the mesosphere, which had much richer LIL contents, in order to produce the LIL-

SCHILLING, 1973

THIS PAPER

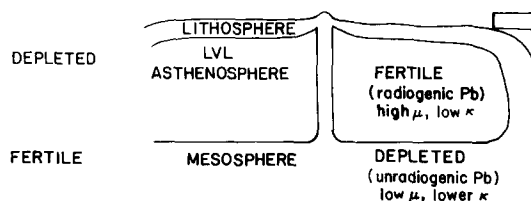


Fig. 5. Schematic comparison between the basic ideas of Schilling [71] and this paper. The models are diametrically opposed in terms of the inferred compositions of the asthenosphere and the mesosphere. In this paper, it is interpreted that depleted material (unradiogenic Pb with low $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios) rises at the oceanic ridges whereas fertile material (radiogenic Pb with high $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios) rises at “hot spots”.

depleted characteristics and the non-radiogenic Pb and Sr isotopic characteristics of the Reykjanes Ridge tholeiites.

6. Thorium-uranium-lead systematics of basalts from Reykjanes Ridge

Schilling [71] observed geochemical gradients, particularly in the La/Sm ratio, in basalts along the Reykjanes Ridge. Invoking the mantle plume hypothesis [56,72], he proposed a mixing model of two mantle sources, a mantle plume rising beneath Iceland and a trace-element-depleted low-velocity layer (LVL; Fig. 5) beneath the Reykjanes Ridge. Mixing between these sources caused the observed gradients in the minor and trace element chemistry of the Reykjanes Ridge basalts.

Results from Sr [80] and Pb [81] isotope studies generally supported the binary mixing model presented by Schilling, although minor complications were observed. The radiogenic character of Pb isotopic compositions in basalts along the ridge apparently increases linearly toward Iceland. Uranium, Th, and Pb contents as well as Th/U and U/Pb ratios also increase toward Iceland. These relations are depicted in Fig. 6. Lead isotopes and Th/U ratios show a good linear relation with La/Sm ratios. Relations between the Pb isotopic ratios and the inverse of the Pb concentrations plotted in the manner of Lancelot and Allègre [82] also show a linear relationship. Sun et al.

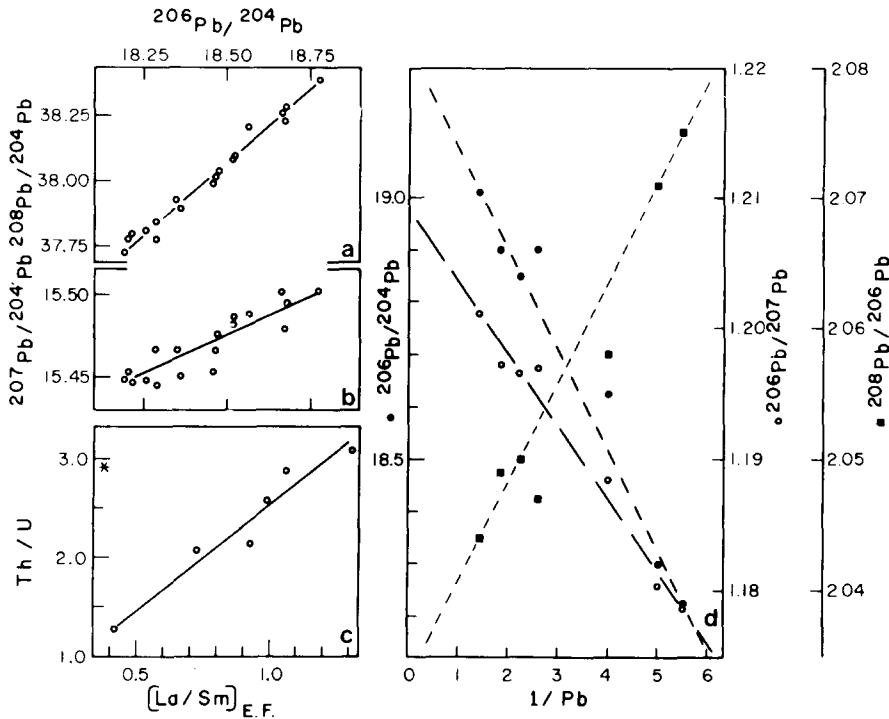


Fig. 6. Relations between Pb isotopic composition vs. $1/\text{Pb}$ (ppm) and Th/U vs. $[\text{La}/\text{Sm}]_{\text{E.F.}}$ of tholeiites from Reykjanes Ridge to Iceland [81]. The Pb isotopic compositions, Th/U and La/Sm ratios increase almost linearly toward Iceland.

[81] had previously concluded that all these features appear to be supporting evidences for the binary mixing model.

The Reykjanes Ridge data are now plotted on a $^{232}\text{Th}/^{204}\text{Pb}$ (atomic ratio) vs. Th concentration (ppm) diagram in Fig. 7, and a $^{238}\text{U}/^{204}\text{Pb}$ vs. U concentration diagram in Fig. 8. These are diagrams of

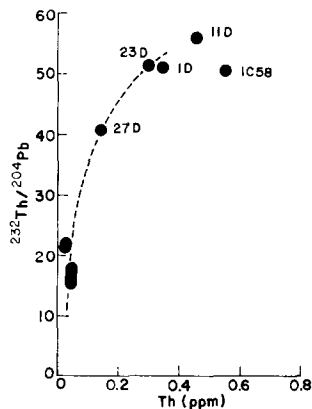


Fig. 7. Relationship between $^{232}\text{Th}/^{204}\text{Pb}$ and Th concentration for tholeiites from Reykjanes Ridge to Iceland. Tholeiite data from the Gibbs fracture zone to 200 km south of Iceland fall on a mixing line indicated by the dashed line, but tholeiites within 200 km from Iceland do not fall on the mixing line.

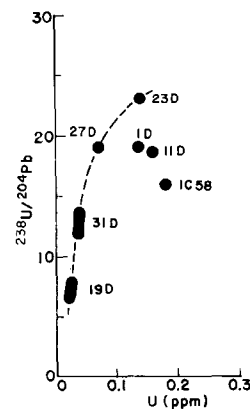


Fig. 8. Relationship between $^{238}\text{U}/^{204}\text{Pb}$ and U concentration of tholeiites from Reykjanes Ridge to Iceland. Data for tholeiites from within 200 km of Iceland do not fall on the mixing line (dashed line).

A/B vs. A and provide a parabola for binary mixing. The usefulness of this type of diagram has been suggested by Treuil [83] especially for a pair of elements, one of which is strongly concentrated in the liquid phase (for example, U or Th), and the other of which is less strongly concentrated in the liquid phase (Pb) during the partial melting of a mantle peridotite. In these types of diagrams, data which form a curve are indicative of binary mixing whereas a straight line indicates a single source involving partial melting and fractional crystallization [83]. Basalts which erupted from the Gibbs fracture zone to 200 km south of Iceland appear to follow a mixing curve, whereas basalts within 200 km of Iceland do not. This probably means that the geochemical gradient along Reykjanes Ridge is not a result of simply two-source mixing, but that other events such as fractional crystallization (although Pb or Sr isotopic composition do not change by fractional crystallization), or the kind of lithosphere assimilation discussed for Pb in Hawaiian rocks are also prevailing phenomena near Iceland.

A similar phenomenon was also observed by Hart et al. [80] for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. One group of samples from Iceland to 200 km south along the ridge, shows an average value of 0.70304, while another group of ridge-type tholeiites from more than 400 km south of Reykjanes Peninsula has an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of about 0.7027. Furthermore, there is an irregular transition between groups. The transition zone was interpreted by Hart et al. [80] as due to interfingering of the two mantle sources and that this interfingering is directly related to topographic relief. In the transition zone, Pb isotopic compositions in basalts from ~250 km to ~350 km south of Iceland are almost identical, and also do not show an exact linear gradient. These results on Sr and Pb isotopic compositions suggest a complex mixing of material on a 100-km scale rather than a simple linear mixing of two end-members.

On the other hand, Welke et al. [84] and Sun and Jahn [66] found a significant difference in Pb isotopic compositions of rocks on Iceland. Lead from the northern neovolcanic zone (Group I) is less radiogenic than that of the southwestern part of the island (Group II). This difference further suggests that these basalts were not simply derived from a single source, such as an isotopically homogeneous plume rising under Iceland, but from a heterogeneous plume; or that other factors, such as asthenosphere or litho-

sphere mixing, are involved in the genesis of the basalts. O'Nions and Pankhurst [61] also reported that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in basalts from Iceland and the Mid-Atlantic Ridge could not be explained by Schilling's binary mixing model. They proposed an isotope disequilibrium partial melting mechanism to explain their Sr isotope results, although they later retracted their proposal [85]. Disequilibrium partial melting will be discussed later.

7. Lead isotopic compositions in abyssal basalts

The Pb isotopic data of abyssal basalts are plotted on the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram in Fig. 9.

Data plotted in Fig. 9 for oceanic basalts are from Reykjanes Ridge [81], Juan de Fuca-Gorda Ridge and East Pacific seamounts [25], Nazca plate (DSDP Leg 34 [55]) and Easter Island ([37]; corrected for SiO_2 -phosphate value from data obtained by H_2S [86]). For comparison, values are also plotted for East Pacific seawater inferred from the average value of Mn nodules ([52], corrected to our scale; [87]) and for East Pacific abyssal sediments (DSDP Leg 34 [55]; metalliferous sediment [43]). In the figure, isochrons and growth curves ($\mu_0 = 7.8$ and 8.0, and $\mu_0 = 7.9$ and $\kappa_0 = 3.7$) of a closed system for the earth, starting with meteorite primordial Pb 4.57 b.y. ago, are drawn as a convenient frame of reference.

All data fall in the area corresponding to negative (future) single-stage model Pb ages and there is a wide variation in the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of the data. These observations indicate that the mantle has been an open system in which concentrations of U and Th increased relative to Pb in the basalt source regions in the mantle for a considerable period of time, and that the basalts have been derived from an isotopically heterogeneous mantle. Furthermore, U must have accumulated more effectively than Pb during recent times ($\mu = ^{238}\text{U}/^{204}\text{Pb}$ ratio has increased), since a late μ increase causes ^{206}Pb to accumulate faster than ^{207}Pb (data points displace to the right or the "younger" side) whereas a μ increase early in the earth's history would cause ^{207}Pb to accumulate appreciably. The data in Fig. 9 yield a relatively good linear array which corresponds to an *apparent* 1.7-b.y. secondary isochron.

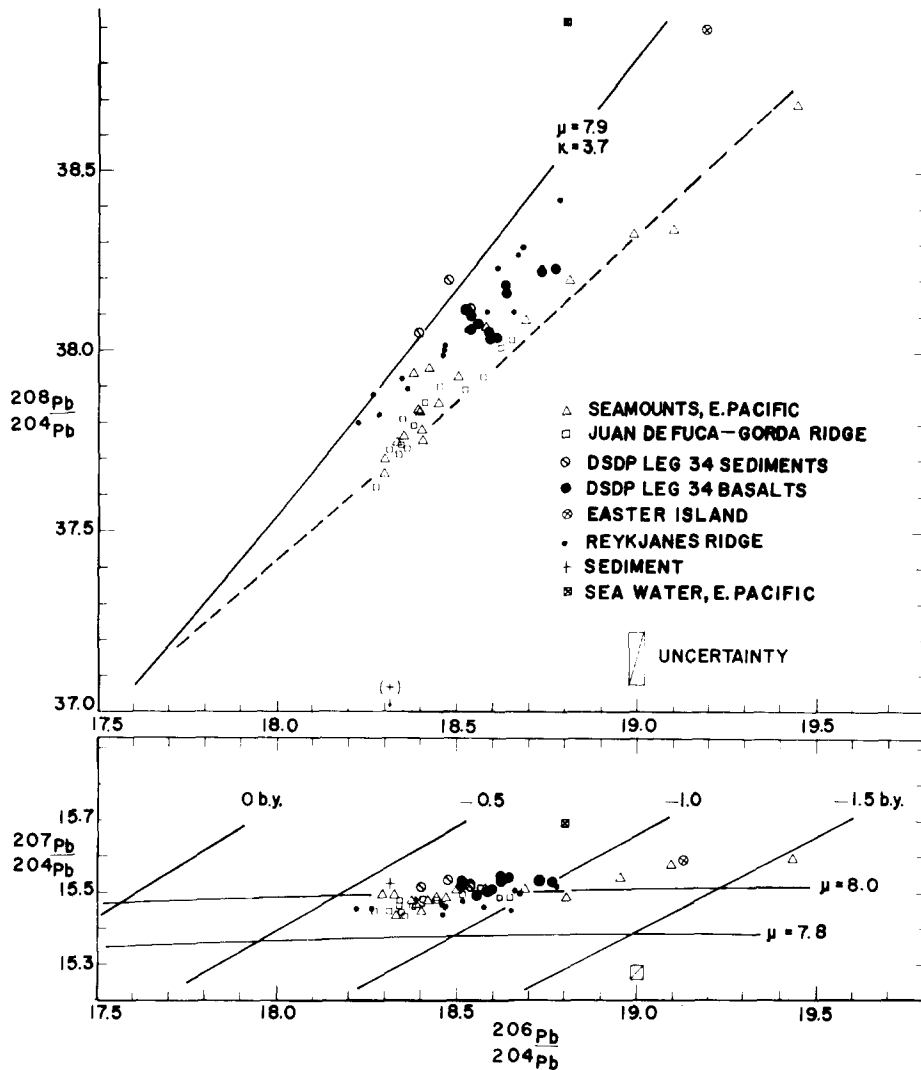


Fig. 9. $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram of oceanic basalts from the Reykjanes Ridge [81], Juan de Fuca-Gorda Ridge [25], Nazca plate (DSDP Leg 34 samples [55]), and Easter Island [37]. Shown for comparison are seawater [53], a metalliferous sediment ([43]; the $^{208}\text{Pb}/^{204}\text{Pb}$ value appeared to be misprinted), and Nazca plate sediments [55].

Earlier efforts (e.g. [26,28,29,35,37,38,88,89, 115]) have shown that the closed-system model is inappropriate for the growth of Pb and Sr isotopes in the earth's mantle. The variations in the Pb and Sr isotopic compositions in oceanic volcanic rocks are commonly interpreted as being due to isotopic heterogeneity of the mantle on a scale of 100–1000 km considering distances between oceanic volcanic islands which each have distinct but uniform Pb and Sr iso-

topic compositions. It is obvious that extraction of a partial melt from the mantle, leaving a solid residue, could create random inhomogeneities in the mantle. Based on the previous discussion about Hawaii, a scale of ~ 50 km might be a more appropriate size for a homogeneous mantle domain, if lithosphere assimilation is not considered.

However, I see a clear trend among oceanic lead, as exemplified by the linear array in Fig. 9, and not a

random scatter. Thus, I believe that any basalt-genesis or mantle-evolution model must take this trend into account, and should not be dependent on *random* mantle heterogeneity.

8. Disequilibrium partial melting

One may argue that the Pb identity could be kept in a small domain, for example, within mineral components or even on a small regional scale, and isotopic disequilibrium partial melting could create the apparent 1.7-b.y. trend observed in Fig. 9 (e.g. [25,61]). Based on available kinetic data, Hofmann and Hart [90] challenged O'Nions and Pankhurst's proposal of isotopic disequilibrium partial melting of a homogeneous mantle to explain the Sr isotope trend in basalts from near Iceland. Diffusion coefficients are available for Ar, Ca, Sr, Al, Fe-Mg interdiffusion, and U in various mantle minerals [90, fig. 48]. From these data, Hofmann and Hart estimated a lower limit to the diffusion rate of about $D = 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ for cation exchange at 1000°C which would be the lower temperature limit for the partially melting mantle. Using this D value, the diffusion distance is only $\sim 60 \text{ cm}$ in 1 b.y.

The U diffusion coefficient is conceivably as low as $\sim 10^{-13}$ to $10^{-14} \text{ cm}^2 \text{ s}^{-1}$ at 1000°C , extrapolated from the data for 1240°C [39], and thus U reaches equilibrium within 1–10 m.y. at 1000°C in a clinopyroxene crystal 1 cm in diameter. Pb is a volatile element and is geochemically mobile. Furthermore, radiogenic Pb does not fit in the crystal lattice in the site previously occupied by U and may also be moved by the recoil energy of α decay. Thus, I presume that the Pb diffusion coefficient is 10 or 100 times higher than that of U. However, even with a higher diffusion coefficient Pb could move no more than 1 m in 1 m.y. at 1000°C and thus the Pb isotopes could not equilibrate to any great extent in a few million years. In the partially molten low-velocity zone or in a hot plume the equilibration time must, however, be several orders of magnitude faster than that stated above since the melt acts as a short circuit between solids [90]. Using a diffusion coefficient as high as $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for a partially molten mantle, isotope equilibration could be reached on a scale of only $\sim 3 \text{ km}^2$ in 1 b.y. With a relatively faster magma segregation

rate compared to a slow isotopic re-equilibration rate, Church and Tatsumoto [25] demonstrated that U and Th enrichment compared to ^{204}Pb in the interstitial phase of the mantle can produce the Pb isotope array observed in abyssal basalts from Juan de Fuca-Gorda Ridge. With this slow diffusion rate, one may argue that isotopic homogeneity is not obtained within a single plume or blob. However, the similarity in the Pb isotopic compositions in abyssal basalts which erupted over an $\sim 25 \text{ m.y.}$ interval on the Nazca plate, when corrected for in-situ U decay [55], suggests to me that isotopic homogeneity can almost be obtained in a single plume. Thus there must also be stirring and mixing of the partially molten material during its diapiric ascent in order to achieve a regional isotopic constancy.

Due to its presumably high diffusion coefficient, it is conceivable that Pb may also be assimilated into the magma from the wall rock of veins and conduits by a zone refining process [6,91]. This certainly appears to be the case for Hawaiian basalt Pb.

9. Mantle evolution model

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of tholeiites from the Juan de Fuca-Gorda Rise determined by Hedge and Peterman [35] range from 0.7024 to 0.7031 (one value of 0.7012 was rejected; [92]) and average 0.7026. This average value is similar to values of 0.7023 to 0.7028 found for abyssal tholeiites from the Atlantic and Pacific [36], 0.7027 for Reykjanes Ridge tholeiites reported by Hart et al. [80], and 0.7026 for Red Sea tholeiites determined by C.E. Hedge (oral communication, 1974). Only mid-Indian Ocean Ridge tholeiites have higher values (0.7032–0.7043) than tholeiites from other oceans [93]. I speculate that the tholeiites from the mid-Indian Ocean Ridge have higher $^{87}\text{Sr}/^{86}\text{Sr}$ values than those from the mid-Atlantic and the mid-Pacific tholeiites because they are from the triple junction of an inverted "Y" in the center of the Indian Ocean. If Pb isotopes were measured for these tholeiites, they should be more radiogenic than those of "usual" abyssal basalts. "Normal" Indian Ocean Ridge basalts, then, probably have a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of about 0.7027 – the value Hart [36] documented for the Carlsberg Ridge tholeiite. The Carlsberg Ridge is a slow spreading northern

extension of the mid-Indian Ocean Ridge system. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of normal abyssal tholeiites are lower than those in oceanic island basalts, which vary mostly from 0.7030 to 0.7045 [35,65,94,95]. Peterman and Hedge [112] clearly illustrated that the $^{87}\text{Sr}/^{86}\text{Sr}$ values in oceanic basalts correlate with basalt composition in terms of the ratios of alkali elements. They suggested that if Rb and K are depleted relative to Sr by volcanism occurring throughout geologic time, then many island basalts represent the least depleted portions of the mantle.

The $^{87}\text{Sr}/^{86}\text{Sr}$ values of abyssal tholeiites show little variance and average about 0.7026 as discussed above, whereas the oceanic island basalts are generally more radiogenic. On the other hand, Pb isotopes of both island basalts and abyssal basalts lie on or nearly on the same array (the ~ 1.7 -b.y. "isochron") in the $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plot, even though the Pb isotopic compositions in basalts differ from suite to suite suggesting a heterogeneous mantle.

The general opinion of petrologists is that tholeiites and alkali basalts originate from independent primary magmas in the mantle (e.g. [5–9, 97]). Also the distinct differences in REE concentrations in alkali basalts and tholeiites suggest independent origins [96,114].

By partial melting calculations, Gast [98] demonstrated that differences in concentrations of LIL elements between alkali basalts and tholeiites can be explained by a smaller degree of partial melting in the mantle for alkali basalts and a larger degree of melting for abyssal tholeiites. Following the thermal model of Oxburgh and Turcotte [99], Gast [98] proposed that ridge tholeiites are derived by extensive partial melting in the axis zone of an ascending plume, whereas alkali basalts are derived by a small degree of partial melting at a deeper site away from the axis of the ascending plume.

Kay et al. [100] and Kay and Gast [101] further refined their model using mineral/melt distribution coefficients to explain distributions of REE and other LIL elements in alkali basalts and nephelinites. They proposed that alkali basalts and nephelinites are derived by about 1–3% partial melting in a convecting cell located within a low-velocity region at the top of the asthenosphere. They suggested that ridge-basalt magmas are segregated from ascending plumes at shallower depths (~ 25 km) in a cell which is about 1500

km deep and about 2000 km wide and which has been depleted in LIL elements by previous partial melting episodes.

As stated above, Schilling [71] proposed a binary mantle mixing model which is diametrically opposed to Gast's, to explain variations in rare earth and minor element concentrations in basalts dredged from Reykjanes Ridge and its extension to the neovolcanic zone of Iceland. In his model, the *primordial* hot mantle plume undepleted in LIL elements rises beneath Iceland from the mesosphere [56] and mixes with depleted material in the partially molten low-velocity zone along the ridge. The mantle plume is diverted along the spreading axis so that the LIL element concentrations monotonically decrease along the ridge axis from Iceland.

Sun and Hanson [102] have suggested a model in which the ridge tholeiites originate from ascending material within a convecting cell in the low-velocity zone, whereas the alkali basalts are derived from the mantle plumes which originate deeper than the convection cells. Their argument was based on the facts that garnet is not a stable phase at the depth of the low-velocity zone, and that most alkali basalts show rather similar bulk chemical compositions. Sun and Hanson's suggestion that mantle plumes are the source of alkali basalt is consistent with Schilling's [71] interpretation. However, one may have difficulty in understanding how a hot plume can be created in the once cooled (solidified?) deeper mantle and reach the surface through the center of a convecting cell or through a plate underthrusting a continent while maintaining its isotopic identity, if Sun and Hanson's [102] model is accepted. Furthermore, it is inconceivable that a potentially denser fertile material would rise to the top of a less dense infertile material [103].

From the preceding discussion, there appears to be two types of magmas which are partially mixed together along the Reykjanes Ridge. However as O'Hara [33] argued, there is no difficulty in explaining the petrological, geophysical or geochemical data of Reykjanes Ridge, whether one uses Schilling's [71] hypothesis, or the exact inverse (tholeiitic plume) of Schilling's hypothesis. The Pb and Sr isotopic data alone admittedly do not prove or disprove either Schilling's hypothesis or its inverse; however, I would like to present a model for mantle evolution to

summarize our accumulated Pb and Sr isotopic data. This model is in opposition to the currently popular models of Schilling [71], Sun and Hanson [102] and Brooks et al. [79] in the basic idea that *depleted* material comes up from the *mesosphere* to oceanic ridges.

Gast et al. [65] and Tatsumoto [37,38] have suggested that the controlling factors in differing Pb and Sr isotopic compositions in basalts are heterogeneities in mantle chemistry, mineralogy, and the differentiation history of the mantle. The scale of the mantle homogeneity has usually been expressed as “regional scale”. Basalts from seamounts and islands near ridges usually show a more alkalic nature and more radiogenic Sr and Pb isotopic compositions (e.g. [25,68]). I tentatively suggest that the scale of the regional homogeneity would be on the order of 50–100 km referring to Pb in Hawaiian volcanoes.

One must, however, consider the general pattern of Sr and Pb isotopes that emerges: (1) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of all abyssal basalts fall into a very narrow range (0.7026 ± 0.0006); (2) Pb data from all abyssal tholeiites as well as from island basalts plotted on $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ appear to define an ~ 1.7 -b.y. isochron; and (3) Rb-Sr data plotted on a Rb-Sr evolution diagram show a “differentiation age” of approximately 1.5 b.y. A model for mantle evolution should be consistent with these features as well as with geophysical and petrological data.

The restricted Pb and Sr isotopic compositions indicate that the earth was molten and chemically well homogenized prior to the primary differentiation. The simplest model is a two-stage evolution model in which the primary differentiation was prolonged and the source region of basalt in the mantle differentiated about 1.7 ± 0.5 b.y. ago, referring to the 1.7-b.y. secondary isochron defined by the Pb data array. This model, however, is too simple and may not satisfactorily explain many features of dynamic earth evolution, even though it has been used frequently to show gross μ changes in a system (e.g. [69]). For example, the average μ (7.9) inferred for the mantle from the basalt Pb data is lower than that ($\mu \sim 8.2$) of the crust, inferred from conformable ores [22], but the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of oceanic basalts are larger than those of the crustal lead indicating a μ increase in the mantle since ~ 2 b.y. ago. It therefore seems most likely that the μ of the man-

tle was once lower than the original mantle μ value, probably as a result of protocrust and mantle differentiation from an isotopically homogenized mantle. Lead data from both oceanic basalts and orebodies plot to the right of the zero isochron on even the two-stage growth curves, thus indicating a primary μ increase in the mantle by the core segregation. This means that Pb evolution in the mantle should be discussed in terms of *at least* a three-stage model, but a dynamic model in which a continuous change in μ (and also the Th/U ratios) is incorporated seems to be even more appropriate [26–28, 34]. The episodic multistage models (e.g. [23,25]) or continuous evolution models, however, cannot provide parameters with rigorous scientific meaning, because parameters of Pb evolution involving more than three stages cannot be uniquely defined and the model becomes more a reflection of one’s prejudice than of concrete scientific deduction.

9.1. Model

A model which is most acceptable to me is one in which the earth was initially molten (mostly from accretional energy). The core probably was segregated first. Convection in very large, deep cells was taking place in the protomantle. As a result of the convection and surface cooling a protocontinent was formed as a “slag” on the surface. This protocontinent was enriched in LIL elements and the first few hundred kilometers beneath the slag were depleted in LIL elements relative to the rest of the “less depleted” mantle (Fig. 10A). The cell continued to convect and the depleted layer became the outer zone of the cell while the inner part of the cell was not as depleted in LIL elements (Fig. 10B). Of course there was mixing between the depleted and “less depleted” layers but I am assuming that there was not total homogenization. As the mantle cooled by heat loss due mainly to conduction (i.e., volcanism) and decline of radioactive decay, the convection cell became shallower and eventually split into two cells (Fig. 10C). The array of smaller cells was effective in creating a lateral differential force of sufficient strength to split and separate the protocontinent [104]. The center of the original cell (Fig. 10B) now rose as a hot plume between the new cells creating a “hot spot” at the surface of the mantle. As I suggested for the Hawaiian

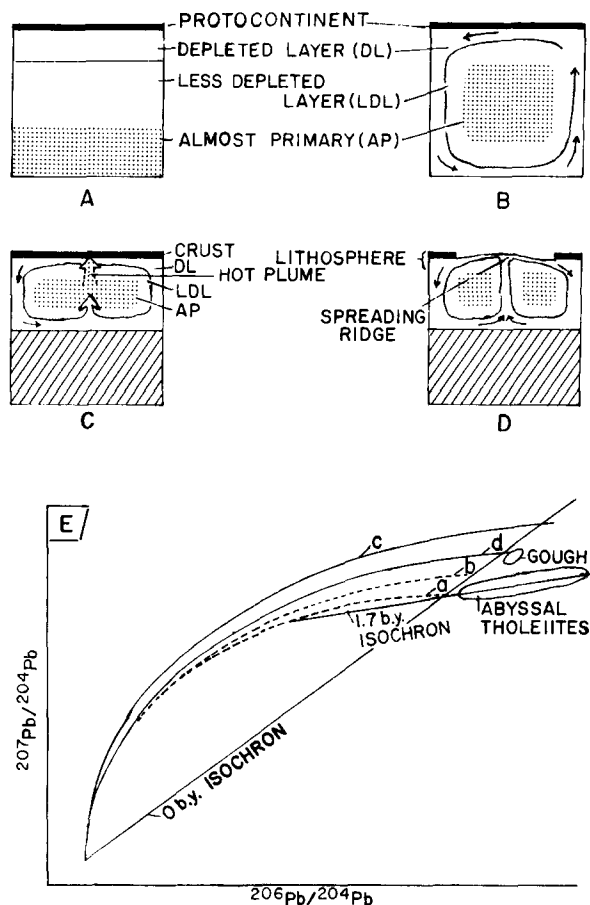


Fig. 10. Mantle evolution model. A. Primary differentiation; protocontinent (lithosphere) formed at surface and a depleted layer (DL) below it. The deeper layer was less depleted (LDL) underlying an almost primary layer (AP). B. The cell continued to convect and the DL layer became the outer layer of the cell while the LDL layer became the inner part. C. As the mantle cooled, the convection cell became shallower and eventually split into two cells. At this stage, the LDL layer rose up as a hot plume. As convection continued the DL layer eventually merged into the plume. D. Schematic diagram for mantle convection and mantle sources for tholeiites and alkali basalts. E. Schematic explanation for Pb growth; *a* = depleted layer; *b* = less depleted layer; *c* = protocontinent; and *d* = almost primary.

plume, this hot plume was not initially as depleted in LIL elements as the borders of the two new cells (Fig. 10C). Hawaii may be at this stage. The portion of the depleted layer which convected down was partially remelted at the bottom of the less depleted layer due either to heat generated from the core or to frictional

heat generated at the base of the cell. Owing to specific gravity differences and thermal convection, this layer eventually cycled into the plume and rose to the surface (Fig. 10D). As time passed the "hot spots" began to propagate in a line perpendicular to the direction of spreading, creating an oceanic ridge. I believe this to be a plausible explanation for the present Mid-Atlantic Ridge. The depleted outer layer then mixed with the less depleted material in the original plume and further mixed with the previously extruded (less depleted) material at the lithosphere-asthenosphere interface and was then extruded along the ridge. This would be the feature of Iceland-Reykjanes Ridge. Thus, a gradient in LIL element distribution was achieved between original "hot spots". O'Nions and Pankhurst [85] observed $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from typical oceanic tholeiite values of 0.7029 to typical alkali basalt values of 0.7034 in basalts from around Iceland. White et al. [105] observed nearly the same picture in basalts from around the Azores. In both cases Sr in the basalts became less radiogenic the further the samples were from the original hot spot.

9.2. Lead isotope evolution

Mantle evolution is probably a continuous process, and the U/Pb and Th/U ratios as well as other trace element abundances probably did not change episodically. However, for simplicity, I would like to approximate an episodic mantle evolution and explain the observed Pb isotope array in oceanic basalts according to the above mentioned model.

The earth's global differentiation started at 4.57 b.y. ago (e.g. [16,106]). The μ of the protomantle rapidly increased to ~ 7.8 from the μ of whole earth (arbitrarily set to 5) as the core segregated and the "scum" (protocrust; *c* in Fig. 10E) would have had a μ value of ~ 12 [53]. Due to protocrust differentiation (Fig. 10A, B), the U/Pb ratio in the depleted layer of the mantle immediately below the crust would have decreased from the original mantle value ($\mu \approx 7.8$) to $\mu \approx 7.5$ (these μ values are only approximation based on a five-stage model calculation). The less depleted and almost "primary" zone of the deep mantle would have had a μ of 7.8. The μ 's in the depleted zone (*a* in Fig. 10E), and the less-depleted zone (*b* in Fig. 10E) have progressively increased

since the primary differentiation time, as a result of differentiation (formation of the solidified layer in the deep mantle).

The μ increase in the depleted zone would be much greater than that in the less depleted zone. I presume that the 1.7-b.y. trend observed for abyssal basalts on a $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram was created, as we discussed [25], only in the depleted zone which ascends to the ridges by mixing of interstitial material (melt) with a residual phase, but not by mixing between material from the depleted (mesosphere) and the less depleted (asthenosphere) layers. The 1.7-b.y. trend is the result of random mixing of the melt containing radiogenic Pb with less radiogenic Pb of residual phases at the ridges. At the spreading center where the ascending rate is fast, Pb becomes less radiogenic due to a larger degree of partial melting, whereas a smaller degree of partial melting would produce more radiogenic Pb as seen for seamount basalts which are probably created from "stray" small diapirs along ridge. When material less depleted and high in Th/U from the asthenosphere was mixed with material from the mesosphere (depleted and low in Th/U), a different trend can be observed from the trend of mesosphere material only. This trend is what we observe for Hawaiian basalts. Brooks et al. [79] emphasized that the 1.7-b.y. trend age corresponds to a "mantle isochron" representing a real mantle differentiation event. However, the trend could also be

considered an average age for cumulative results of progressive mantle differentiation which started ~ 4.5 b.y. ago. As shown above, a Pb trend between depleted and less depleted zones is generally different from the 1.7-b.y. trend.

The μ of the almost "primary" mantle also has progressively slightly increased (d in Fig. 10E). The Th/U ratio (κ) in the primary convection cell increased during the mantle-protocrust differentiation ($\kappa \approx 4.2\text{--}4.5$) from the original value of $\sim 3.8\text{--}4.0$. This Th/U ratio of the mantle then has been decreasing to ~ 2.0 as the U/Pb ratio has been increasing. Once one accepts this model, the apparent 1.7-b.y. isochron then is just an "average value" from progressive differentiation, and has no real age significance.

This model also could account for alkali basalt eruptions during the initial stages of plate spreading, as is exemplified by the current East Africa Rift system (e.g. [107]).

Sun's [68] Pb isotope study on volcanic rocks from many oceanic islands (Fig. 11) shows that there are some exceptions (such as Gough and Reunion) which deviate from the 1.7-b.y. general trend of oceanic basalts. This indicates that certainly not all of the oceanic Pb data can be explained by the simple mixing model discussed above, and a more complicated model such as two scales of convection in the mantle [113] may be needed. In any case, either the Pb from Gough and Reunion have been generated

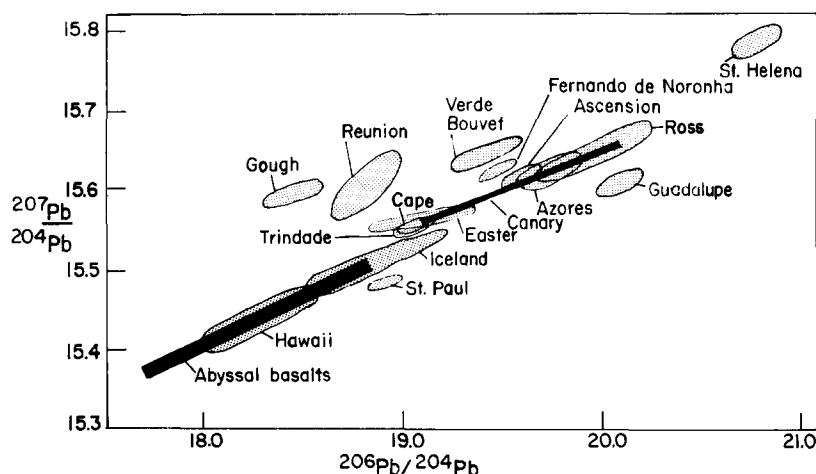


Fig. 11. $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram for abyssal tholeiites and rocks from oceanic islands. Data for abyssal tholeiites are from this paper, Sun et al. [81], Church and Tatsumoto [25] and Unruh and Tatsumoto [55]; data for Hawaiian volcanic rocks are from this paper; and others are from S.S. Sun (unpublished: see also Sun et al. [81, fig. 5]).

in a higher μ mantle system (d in Fig. 10E) which differentiated at an earlier time in the earth's history than those for other oceanic basalts, or they have been generated by mixing the mantle material (a or b in Fig. 10E) with the left-over crust from continental spreading.

The mantle evolution model presented above is based primarily on observed Pb and Sr data, and has been presented solely to explain the apparent 1.7-b.y. Pb trend and the observed variabilities in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. This model should await for geological and geophysical tests for validity.

10. Conclusions

(1) U-Th-Pb systematics of oceanic basalts indicate that the upper mantle has been progressively differentiating since early in the earth's history. The trace element chemistry of the basalts suggests that abyssal tholeiites originate from the depleted mantle, and alkali basalts are from the "less depleted" mantle (however, Hawaiian alkali basalts and tholeiites are probably generated from the same source).

(2) The $^{238}\text{Pb}/^{204}\text{Pb}$ (μ) and $^{232}\text{Th}/^{238}\text{U}$ (κ) ratios have been progressively changing because of mantle differentiation (probably crystal sinking), and because convection cells have been getting smaller. Such changes must be more effective in the depleted zone and the present μ and κ values for the abyssal tholeiite source regions may be in the range of ~ 15 and ~ 2 respectively. The distinctly low κ values (0.5–3.0) for abyssal tholeiites have been produced by $\sim 30\%$ partial melting of differentiated mantle material.

(3) Models which involve small changes in the κ ratio (for example, from 4.0 to 3.7) during the earth's history (e.g. [25]) are not consistent with a large degree of partial melting for the production of tholeiite. The high κ ratios observed in alkali basalts reflect either a κ increase during a small amount of partial melting or a high- κ source material.

(4) The Pb isotopic compositions of basalts from the island of Hawaii are distinct for each volcano. Lead from the volcanoes of the Kea group is more radiogenic than that from volcanoes of the Loa group. There are no distinct differences in Pb isotopic composition between tholeiites and alkali basalts

within each volcano of Hawaii. The Th/U ratios in Hawaiian volcanics are not so low as those for abyssal tholeiites. It is concluded that these features probably have been produced by the mixing of two components: partially melted material from the asthenosphere (mantle plume?) and the lithosphere.

(5) Distinctly low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (~ 0.7027) for abyssal tholeiites, and the 1.7-b.y. isochron trend of most oceanic basalts in a $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ plot, suggest a mantle evolution model in which the μ ratio in the depleted mantle has progressively increased and the κ ratios have progressively decreased, whereas μ and κ values in the less depleted mantle have not greatly changed. The mantle material rising on oceanic ridges is from the depleted mantle. When a mantle convection cell becomes small and splits into two cells, mixing of the depleted and undepleted mantle occur. Such an expression is observed along the Reykjanes Ridge to Iceland.

Acknowledgements

J.D. Obradovich and D.M. Unruh, U.S. Geological Survey, read the original manuscript and provided a stimulating discussion. I am grateful for generous samples supplied by Drs. G.A. Macdonald, University of Hawaii; H.A. Powers, U.S. Geological Survey; and S.R. Hart, Massachusetts Institute of Technology. I have also benefited from manuscript reviews by Drs. C.J. Allègre, University of Paris; B.R. Doe, U.S. Geological Survey; and S.R. Hart.

References

- 1 B.R. Doe, *Lead Isotopes, Minerals, Rocks and Inorganic Materials Series*, 2 (Springer-Verlag, New York, N.Y., 1970).
- 2 A.E.J. Engel and C.G. Engel, Composition of basalts from the Mid-Atlantic Ridge, *Science* 144 (1964) 1330.
- 3 A.E.J. Engel and C.G. Engel, Igneous rocks of the East Pacific Rise, *Science* 146 (1964) 447.
- 4 A.E.J. Engel, C.G. Engel and R.G. Havens, Chemical characteristics of oceanic basalts and the upper mantle, *Bull. Geol. Soc. Am.* 76 (1965) 719.
- 5 I. Kushiro, The liquidus relations in the systems forsterite-CaAl₂SiO₆-silica and forsterite-nepheline-silica at high pressures, *Carnegie Inst. Washington Yearb.* 64 (1965) 103.

- 6 I. Kushiro, Compositions of magmas formed by partial zone melting of the earth's upper mantle, *J. Geophys. Res.* 73 (1968) 619.
- 7 D.H. Green and A.E. Ringwood, The genesis of basaltic magmas, *Contrib. Mineral. Petrol.* 15 (1967) 103.
- 8 I.D. MacGregor, The effect of pressure on the minimum melting composition in the system $\text{MgO-SiO}_2\text{-TiO}_2$, *Carnegie Inst. Washington Yearb.* 64 (1965) 135.
- 9 I.D. MacGregor, Mafic and ultramafic inclusions as indicators of the depth of origin basaltic magmas, *J. Geophys. Res.* 73 (1968) 3737.
- 10 W.R. Shields, in: *Handbook of Chemistry and Physics*, R.C. Weast and S.M. Selby, eds. (Chemical Rubber, Cleveland, Ohio, 1973).
- 11 A.H. Jaffey, K.F. Flynn, L.E. Glendenin, W.C. Bentley and A.M. Essling, Precision measurement of half-lives and specific activities of ^{235}U and ^{238}U , *Phys. Rev. C* 4 (1971) 1889.
- 12 L.J. LeRoux and L.E. Glendenin, Half-life of thorium-232, *Proc. Natl. Meet. on Nuclear Energy*, Pretoria, S. Africa (1963) 83.
- 13 G.R. Tilton, C.C. Patterson, H. Brown, M. Inghram, R. Hayden, D. Hess and E. Larsen, Jr., Isotopic composition and distribution of lead, uranium, and thorium in a Precambrian granite, *Geol. Soc. Am. Bull.* 66 (1955) 1131.
- 14 E.J. Catanzaro, Absolute abundance ratios of three common lead reference samples, *Earth Planet. Sci. Lett.* 3 (1968) 343.
- 15 W. Compston and V.M. Oversby, Lead isotope analyses using a double spike, *J. Geophys. Res.* 74 (1969) 4338.
- 16 M. Tatsumoto, R.J. Knight and C.J. Allègre, Time differences in the formation of meteorites as determined from the ratio of lead-207 to lead-206, *Science* 180 (1973) 1279.
- 17 P.A. Akishin, O.T. Nikitin and G.M. Panchenkov, A new effective ionic emitter for the isotopic analysis of lead, *Geokhimiya* 5 (1957) 425.
- 18 I.V. Chernyshev and L.L. Shannin, Determination of microquantities of lead and uranium by the isotope dilution method, in: *Metodam opredeleniya absolutnogo vosrata mineralov i gornykh porod*, 3d, Seninara, Leningrad, Nauchuo-Issled. Geol. Inst., Leningrad (1967).
- 19 A.E. Cameron, D.H. Smith and R.L. Waler, Mass spectrometry of nanogram-size samples of lead, *Anal. Chem.* 41 (1969) 525.
- 20 R.L. Stanton and R.D. Russell, Anomalous leads and the emplacement of lead sulphide ores, *Econ. Geol.* 54 (1959) 588.
- 21 E.R. Kanasevich, Approximate age of tectonic activity using anomalous lead isotopes, *Geophys. J. R. Astron. Soc.* 7 (1962) 158.
- 22 J.S. Stacey and J.D. Kramers, Approximation of terrestrial lead isotope evolution by a two-stage model, *Earth Planet. Sci. Lett.* 26 (1975) 207.
- 23 R.D. Russell, Evolutionary model for lead isotopes in conformable ores and in ocean volcanics, *Rev. Geophys. Space Phys.* 10 (1972) 529.
- 24 R.L. Armstrong and S.M. Hein, Computer simulation of Pb and Sr isotope evolution of the earth's crust and upper mantle, *Geochim. Cosmochim. Acta* 37 (1973) 1.
- 25 S.E. Church and M. Tatsumoto, Lead isotopic relations in oceanic ridge basalts from the Juan de Fuca-Gorda Ridge area, N.E. Pacific Ocean, *Contrib. Mineral. Petrol.* 53 (1975) 253.
- 26 C.C. Patterson and M. Tatsumoto, The significance of lead isotopes in detrital feldspar with respect to chemical differentiation with the earth's mantle, *Geochim. Cosmochim. Acta* 28 (1964) 1.
- 27 G.J. Wasserburg, Geochronology and isotopic data bearing on development of the continental crust, in: *Advances in Earth Science* (MIT Press, Cambridge, Mass., 1966) 431.
- 28 P.W. Gast, Isotope geochemistry of volcanic rocks, in: *Basalt*, 1, H. Hess and A. Poldervaart, eds. (Interscience, New York, N.Y., 1967) 325.
- 29 C.J. Allègre, Comportement des systèmes U-Th-Pb dans le manteau supérieur et modèle d'évolution de ce dernier au cours des temps géologiques, *Earth Planet. Sci. Lett.* 5 (1968) 261.
- 30 R.L. Armstrong, A model for Sr and Pb isotope evolution in a dynamic earth, *Rev. Geophys.* 6 (1968) 175.
- 31 M.G. Seitz, Uranium and thorium partitioning in diopside-melt and whitlockite-melt systems, *Carnegie Inst. Washington Yearb.* 72 (1973) 581.
- 32 M. Tatsumoto, C.E. Hedge and A.E.J. Engel, Potassium, rubidium, strontium, thorium, uranium, and the ratio of strontium-87 to strontium-86 in oceanic tholeiitic basalts, *Science* 150 (1965) 886.
- 33 M.J. O'Hara, Non-primary magmas and dubious mantle plume beneath Iceland, *Nature* 243 (1973) 507.
- 34 A.K. Sinha and G.R. Tilton, Isotopic evolution of common lead, *Geochim. Cosmochim. Acta* 37 (1973) 1823.
- 35 C.E. Hedge and Z.E. Peterman, The strontium isotopic composition of basalts from the Gorda and Juan de Fuca Rises, northeastern Pacific Ocean, *Contrib. Mineral. Petrol.* 27 (1970) 114.
- 36 S.R. Hart, K. Rb, Cs, Sr and Ba contents and Sr isotope ratios of ocean floor basalts, *Philos. Trans. R. Soc. Lond., Ser. A*, 268 (1971) 573.
- 37 M. Tatsumoto, Genetic relations of oceanic basalts as indicated by lead isotopes, *Science* 153 (1966) 1094.
- 38 M. Tatsumoto, Isotopic composition of lead in volcanic rocks from Hawaii, Iwo-Jima, and Japan, *J. Geophys. Res.* 71 (1966) 1721.
- 39 M.G. Seitz, Uranium and thorium diffusion in diopside and fluorapatite, *Carnegie Inst. Washington Yearb.* 72 (1973) 586.
- 40 J.D. Kleemann, D.H. Green and J.F. Lovering, Uranium distribution in ultramafic inclusions from Victorian basalts, *Earth Planet. Sci. Lett.* 5 (1969) 449.
- 41 A. Nishimura, Partition of uranium between peridotite nodules and host basalt, *Chem. Geol.* 10 (1972) 211.
- 42 E.L. Haines and R.E. Zartman, Uranium concentration and distribution in six peridotite inclusions of probable mantle origin, *Earth Planet. Sci. Lett.* 20 (1973) 45.

- 43 E.J. Dasch, J.R. Dymond and G.R. Health, Isotopic analysis of metalliferous sediment from the east Pacific Rise, *Earth Planet. Sci. Lett.* 13 (1971) 175.
- 44 T.R. Wildeman, I. Kushiro and M. Tatsumoto, The partitioning of rare earth elements between clinopyroxene and liquid at 14 kilobars, *Geol. Soc. Am. Abstr. Progr.* 7 (1975) 1318 (abstract).
- 45 N. Shimizu, An experimental study of the partitioning of K, Rb, Cs, Sr and Ba between clinopyroxene and liquid at high pressures, *Geochim. Cosmochim. Acta* 38 (1974) 1789.
- 46 M. Tatsumoto, Lead isotopes in volcanic rocks and possible ocean floor thrusting beneath island arcs, *Earth Planet. Sci. Lett.* 6 (1969) 369.
- 47 V.M. Oversby and A. Ewart, Lead isotopic compositions of Tonga-Kermadec volcanics and their petrogenetic significance, *Contrib. Mineral. Petrol.* 37 (1972) 181.
- 48 A. Meijer, Pb and Sr isotopic data bearing on the origin of volcanic rocks from the Mariana island-arc system, *Geol. Soc. Am. Bull.* 87 (1976) 1358.
- 49 S. Uyeda and A. Miyashiro, Plate tectonics and the Japanese islands: a synthesis, *Geol. Soc. Am. Bull.* 85 (1974) 1159.
- 50 M. Tatsumoto and R.J. Knight, Isotopic composition of lead in volcanic rocks from central Honshu – with regard to basalt genesis, *Geochem. J.* 3 (1969) 53.
- 51 S.R. Hart, K, Rb, Cs contents and K/Rb, K/Cs ratios of fresh and altered submarine basalts, *Earth Planet. Sci. Lett.* 6 (1969) 295.
- 52 T.J. Chow and C.C. Patterson, Lead isotopes in manganese nodules, *Geochim. Cosmochim. Acta* 17 (1959) 21.
- 53 T.J. Chow and C.C. Patterson, The occurrence and significance of lead isotopes in pelagic sediments, *Geochim. Cosmochim. Acta* 26 (1962) 263.
- 54 S.E. Church, The Cascade Mountains revisited: a reevaluation in light of new lead isotopic data, *Earth Planet. Sci. Lett.* 29 (1976) 175.
- 55 D.M. Unruh and M. Tatsumoto, Lead isotopic composition and uranium, thorium, and lead concentrations in sediments and basalts from the Nazca Plate, in: *Initial Report of the Deep Sea Drilling Project 34* (U.S. Government Printing Office, Washington, D.C., 1976) 431.
- 56 W.J. Morgan, Convection plumes in the lower mantle, *Nature* 230 (1971) 42.
- 57 I. McDougall, Potassium-argon ages from lavas of the Hawaiian Islands, *Geol. Soc. Am. Bull.* 75 (1964) 107.
- 58 E.D. Jackson, E.A. Silver and G.B. Dalrymple, Hawaiian-Emperor chain and its relation to Cenozoic circum-Pacific tectonics, *Geol. Soc. Am. Bull.* 83 (1972) 601.
- 59 H.T. Stearns and G.A. Macdonald, Geology and ground-water resources of the Island of Hawaii, *Hawaii Div. Hydrogr. Bull.* 9 (1946) 363.
- 60 G.A. Macdonald, Hawaiian petrographic province, *Geol. Soc. Am. Bull.* 60 (1949) 1541.
- 61 R.K. O'Nions and R.J. Pankhurst, Petrogenic significance of isotope and trace element variations in volcanic rocks from the mid-Atlantic, *J. Petrol.* 15 (1974) 603.
- 62 H.A. Powers, Differentiation of Hawaiian lavas, *Am. J. Sci.*, 5th Ser., 30 (1935) 57.
- 63 H.A. Powers, Composition and origin of basaltic magma of the Hawaiian Islands, *Geochim. Cosmochim. Acta* 7 (1955) 77.
- 64 G.A. Macdonald and T. Katsura, Chemical composition of Hawaiian lavas, *J. Petrol.* 5 (1964) 82.
- 65 P.W. Gast, G.R. Tilton and C.E. Hedge, Isotopic composition of lead and strontium from Ascension and Gough Island, *Science* 145 (1964) 1181.
- 66 S.S. Sun and B.M. Jahn, Lead and strontium isotopes in post-glacial basalts from Iceland, *Nature* 255 (1975) 427.
- 67 M. Tatsumoto and R.J. Knight, Isotopic composition of lead in volcanic rocks from Hawaii, *Progr. Annu. Meet.*, *Geol. Soc. Am.* (1966) 218 (abstract).
- 68 S.S. Sun, Lead isotopic studies of young volcanic rocks from oceanic islands, mid-oceanic ridges and island arcs, Ph.D. Dissertation, Columbia Univ., New York, N.Y. (1973).
- 69 V.M. Oversby and P.W. Gast, Isotopic composition of lead from oceanic islands, *J. Geophys. Res.* 75 (1970) 2097.
- 70 V.M. Oversby, Redetermination of lead isotopic composition in Canyon Diablo troilite, *Geochim. Cosmochim. Acta* 37 (1973) 2693.
- 71 J.G. Schilling, Iceland mantle plume: geochemical study of the Reykjanes Ridge, *Nature* 242 (1973) 565.
- 72 J.T. Wilson, Hypothesis of earth's behavior, *Nature* 198 (1963) 86.
- 73 W.J. Morgan, Deep mantle convection plumes and plate motions, *Am. Assoc. Pet. Geol. Bull.* 56 (1972) 203.
- 74 F. Beltz, Jr. and H.H. Hess, The floor of the North Pacific Ocean, *Geogr. Rev.* 32 (1942) 99.
- 75 E.D. Jackson and T.L. Wright, Xenoliths in the Honolulu volcanic series, Hawaii, *J. Petrol.* 11 (1970) 405.
- 76 I. McDougall, Volcanic island chains and sea floor spreading, *Nature* 231 (1971) 141.
- 77 H.R. Shaw, Mantle convection and volcanic periodicity in the Pacific: evidence from Hawaii, *Geol. Soc. Am. Bull.* 84 (1973) 1505.
- 78 G.B. Dalrymple, E.A. Silver and E.D. Jackson, Origin of the Hawaiian Islands, *Am. Sci.* 61 (1973) 294.
- 79 C. Brooks, S.R. Hart, A. Hoffmann and D.E. James, Rb-Sr mantle isochrons from oceanic regions, *Earth Planet. Sci. Lett.* 32 (1976) 51.
- 80 S.R. Hart, J.G. Schilling and J.L. Powell, Basalts from Iceland and along the Reykjanes Ridge: Sr-isotope geochemistry, *Nature Phys. Sci.* 246 (1973) 104.
- 81 S.S. Sun, M. Tatsumoto and J.G. Schilling, Mantle mixing along the Reykjanes Ridge axis: lead isotope evidence, *Science* 190 (1975) 143.
- 82 J.R. Lancelot and C.J. Allègre, Origin of carbonatitic magma in the light of the Pb-U-Th isotope system, *Earth Planet. Sci. Lett.* 22 (1974) 233.
- 83 M. Treuil, Critères pétrologiques géochimiques et structuraux de la genèse et de la différenciation des magmas basaltiques: exemple de Lafor, Dr.S. Thesis, Université de Paris-Sud, Centre Dorsay (1973).

- 84 H. Welke, S. Moorbath, G.L. Cumming and H. Sigurdsson, Lead isotope studies on igneous rocks from Iceland, *Earth Planet. Sci. Lett.* 4 (1968) 221.
- 85 R.K. O'Nions and R.J. Pankhurst, Nature and development of basalt magma sources beneath Iceland and the Reykjanes Ridge, *J. Petrol.* 17 (1976) 315.
- 86 M. Tatsumoto, R.J. Knight and M.A. Delevaux, Uranium, thorium and lead concentrations in three silicate standards and a method of lead isotopic analysis, *U.S. Geol. Surv. Prof. Paper* 800D (1972) 111.
- 87 P.H. Reynolds and E.J. Dasch, Lead isotopes in marine manganese nodules and ore-lead growth curve, *J. Geophys. Res.* 76 (1971) 5124.
- 88 P.M. Hurley, Absolute abundance and distribution of Rb, K and Sr in the earth, *Geochim. Cosmochim. Acta* 32 (1968) 273.
- 89 P.M. Hurley, Correction to absolute abundance and distribution of Rb, K, Sr in the earth, *Geochim. Cosmochim. Acta* 32 (1968) 1025.
- 90 A.W. Hofmann and S.R. Hart, An assessment of local and regional isotopic equilibrium in partially molten mantle, *Carnegie Inst. Washington Yearb.* 74 (1975) 195.
- 91 P.G. Harris, Zone refining and the origin of potassic basalt, *Geochim. Cosmochim. Acta* 12 (1957) 195.
- 92 S.R. Hart, LIL-element geochemistry, Leg 34 basalts, in: *Initial Reports of the Deep Sea Drilling Project 34* (U.S. Government Printing Office, Washington, D.C., 1976) 283.
- 93 K.V. Subbarao and C.E. Hedge, K, Rb, Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ in rocks from the mid-Indian oceanic ridge, *Earth Planet. Sci. Lett.* 18 (1973) 223.
- 94 J.L. Powell and S.E. DeLong, Isotopic composition of strontium in volcanic rocks from Oahu, *Science* 153 (1966) 1239.
- 95 A.G. Bence, The differentiation history of the earth by rubidium-strontium isotopic relationships, *Mass. Inst. Technol., 14th Annu. Progr. Rep., Dep. Geol. Geophys.* (1966) 35.
- 96 L.A. Haskin and F.A. Frey, Dispersed and not-so-rare earths, *Science* 152 (1966) 299.
- 97 H. Kuno, Differentiation of basalt magma, in: *Basalt: The Poldervaart Treatise on Rocks of Basaltic Composition* (Interscience, New York, N.Y., 1968) 623.
- 98 P.W. Gast, Trace element fractionation and the origin of tholeiitic and alkaline magma types, *Geochim. Cosmochim. Acta* 32 (1968) 1057.
- 99 E.R. Oxburgh and D.L. Turcotte, Mid-ocean ridges and geothermal distribution during mantle convection, *J. Geophys. Res.* 73 (1968) 2643.
- 100 R.W. Kay, N.J. Hubbard and P.W. Gast, Chemical characteristics and origin of oceanic ridge volcanic rocks, *J. Geophys. Res.* 75 (1970) 1585.
- 101 R.W. Kay and P.W. Gast, The rare earth content and origin of alkali-rich basalts, *J. Geol.* 81 (1973) 653.
- 102 S.S. Sun and G. Hanson, Evolution of the mantle, *Geology* 3 (1975) 297.
- 103 M.J. O'Hara, Is there an Icelandic mantle plume?, *Nature* 253 (1975) 708.
- 104 F.M. Richter, Dynamical models for sea floor spreading, *Rev. Geophys. Space Phys.* 11 (1973) 223.
- 105 W.M. White, S.R. Hart and J.G. Schilling, Geochemistry of the Azores and the Mid-Atlantic Ridge: 29°N to 60°N, *Carnegie Inst. Washington Yearb.* 74 (1975) 224.
- 106 C.C. Patterson, Age of meteorites and the earth, *Geochim. Cosmochim. Acta* 10 (1956) 230.
- 107 B.C. King, Volcanicity and rift tectonics in East Africa, in: *African Magmatism and Tectonics*, T.N. Clifford and I.G. Gass, eds. (Hafner, Darien, 1970) 263.
- 108 M. Tatsumoto and P.D. Snavely, Isotopic composition of lead in rocks of the Coast Range, Oregon and Washington, *J. Geophys. Res.* 74 (1969) 1087.
- 109 B.R. Doe, Lead isotope data bank: 2,624 samples and analyses cited, *U.S. Geol. Surv., Open-File Rep.* (1976) 76.
- 110 B.R. Doe and J.S. Stacey, The application of lead isotopes to the problems of ore genesis and ore prospect evaluation: a review, *Econ. Geol.* 69 (1974) 757.
- 111 N. Onuma, H. Higuchi, H. Wakita and H. Nagasawa, Trace element partition between two pyroxenes and the host lava, *Earth Planet. Sci. Lett.* 5 (1968) 47.
- 112 Z.E. Peterman and C.E. Hedge, Related strontium isotopic and chemical variations in oceanic basalts, *Geol. Soc. Am. Bull.* 82 (1971) 493.
- 113 F.M. Richter and B. Parsons, On the interaction of two scales of convection in the mantle, *J. Geophys. Res.* 80 (1975) 2529.
- 114 J.G. Schilling and J.W. Winchester, Rare earths in Hawaiian basalts, *Science* 153 (1966) 867.
- 115 J.A. Cooper and J.R. Richards, Lead isotopes and volcanic magmas, *Earth Planet. Sci. Lett.* 1 (1966) 259.