Haleakala Crater, Maui
Photo Credit: S. Zhou, 2003

Chemical Analysis of Post-erosional Basalts from Maui and Hawaii

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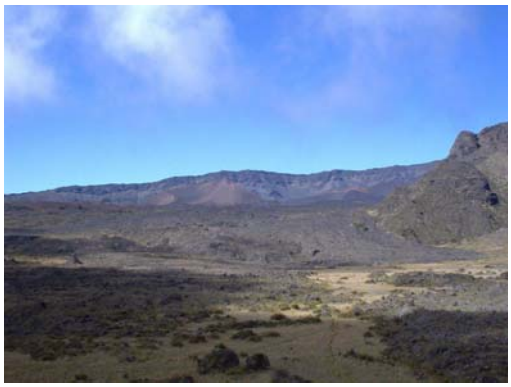

Pictures from Haleakala Crater, Maui
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Abstract:

Geochemical analysis of radiogenic isotope ratios in erupted lavas has long been used as a tool for probing deep inside the Earth. As isotope ratios are unaffected by the immense stresses experienced by materials that are up-welled and erupted on Earth's surface, they can be used to infer not only the compositions of the sources of igneous rocks but also how these sources mixed and melted to form the rocks on the surface. Combined with major and trace element data, hafnium and neodymium isotope ratios can even be used to determine the degree of melting that occurred.

For Hawaii, an ocean island chain, much isotopic work has been done on tholeiitic, shield-building stage lavas, the bulk of the volcanic activity. Relatively little work has been done on post-erosional basalts, which are erupted about two million years after the main shield-building stage ceases. While shield-building lavas have compositions expected for ocean island basalts, whose origin seems to be a deep-seated, stationary plume, post-erosional basalts have a composition more similar to mid-ocean ridge basalts.

In this study, neodymium and hafnium isotopes were analyzed in post-erosional samples from Haleakala Volcano on Maui and Hualalai Volcano on Hawaii. The isotopic data suggests that: 1) the source of Hawaiian post-erosional basalts is much shallower than that of shield-building basalts and 2) the degree of melt is much less than that which produced the shield-building basalts.

Introduction:

Since the acceptance of plate tectonics in the 1960s and the realization that most volcanic activity occurs along plate boundaries, what produces volcanic activity in Hawaii and other ocean island chains sitting in the middle of tectonic plates has been a challenging question for geologists. In 1963 JT Wilson (Wilson, 1963) first postulated that Hawaiian volcanism might be generated by a rising plume of mantle material. Today, geologists generally agree that a deep-seated plume of rising mantle material does seem responsible for generating the Hawaiian island chain. However, the details of the sources of this plume and how the plume interacts with the asthenosphere and lithosphere as it travels to the surface are still somewhat unknown. The recent discovery (Blichert-Toft et al., 1998), for instance, of signatures of old crust and marine sediments in Pb, O, Hf, and

Os isotopes in Hawaiian lavas suggests that when the plume rises it carries along with it old, subducted materials. Certainly, Hawaiian volcanism is much more complicated than current models and theories depict.

In general, the growth of Hawaiian shield volcanoes is fairly well understood. There are four evolutionary stages in the life of a Hawaiian volcano (Stearns, 1940; MacDonald et al., 1983). The first of these, the pre-shield stage, consists of basanitic, alkalic, and tholeiitic basalts and constitutes about 3% of the volume of the volcano (Moore et al., 1982). The second stage, the shield-building stage, consists of voluminous outpourings of tholeiitic basalt and is responsible for the bulk of the volcanic activity, about 94 – 95 % of the volcano volume (Macdonald and Katsura, 1962). The alkalic cap or post-shield stage is a transitional period during which a thin layer of alkalic to trachyte series basalt is deposited, only 0.1 - 3 % of the volcano volume (Macdonald, 1963). The last stage of volcanism, the post-erosional or rejuvenated stage, occurs after a period of quiescence ranging from 0.3 to 2.5 million years, more typically about 2 million years (Best, 2003). During this last stage, which represents less than 1% of the volcano volume (Macdonald, 1968), small, localized eruptions of highly silica-undersaturated lavas are produced.

The source of the post-erosional lavas remains one of the most puzzling questions regarding Hawaiian volcanism. Post-erosional lavas are found on almost all the major Hawaiian islands, including Niihau (Kiekei Basalt), Kauai (Koloa Volcanics), Oahu (Koolau Volcano), Maui (Haleakala Volcano), and Hawaii (Hualalai Volcano). In addition, submarine lavas along the Hawaiian Arch off the coast of Oahu are compositionally similar to post-erosional basalts (Yang et al., 2002). While relatively

little isotopic work has been done on post-erosional basalts, the studies that have been done show that post-erosional basalts are unusually enriched in incompatible elements. In particular, post-erosionals have low ^{87}Sr / ^{86}Sr and high ^{143}Nd / ^{144}Nd relative to bulk earth ratios and the shield-building basalts (Yang et al., 2002).

One way to explain the chemical composition of the post-erosionals is that their source, unlike the shield-building basalts, includes a significant amount of the depleted upper mantle, which is mixed with material from the Hawaiian plume (Lassiter et al., 2000). Exactly what sources are mixing and what triggers the eruption of post-erosional lavas after up to 2.5 million years of volcanic quiescence (Lassiter et al., 2000) is still largely a mystery.

The goal of this study is to gather further isotopic data on Hawaiian post-erosional basalts in order to learn more about their sources and the degree of melt which produced them. To do this, Nd and Hf isotopes were analyzed in post-erosional basalts from Haleakala Volcano on Maui and Hualalai Volcano on Hawaii. Ultimately, this data will be combined with Th data currently being collected by Dr. Kenneth Sims of Woods Hole Oceanographic Institute so that rate of melting can be determined. In the end, this data will be used to develop new theories and models having to do with why the post-erosional basalts are erupted and how their eruption fits in with current Hawaiian plume theories and models.

Samples:

Twelve powdered samples were analyzed for hafnium and neodymium isotopes. Seven of these samples are from Haleakala Volcano on East Maui and five are from Hualalai Volcano, near Mauna Loa on Hawaii. All twelve samples are from post-erosional flows. The samples were collected by Dr. Kenneth Sims of Woods Hole Oceanographic Institute.

Methods:

All of the chemical analysis was done in the Geochemistry Laboratory in the National High Magnetic Field Laboratory at Florida State University. Sample dissolution and column work was done in the Class 100 clean lab there.

Dissolution Process:

About 0.1 gram of each sample was dissolved using HF-HCl digestion. The samples were first dissolved in 3:1 HF: HNO_3. HF removes silicates, the bulk of the rock sample. The samples were then dried down and re-dissolved in 3-4 ml of 6 N HCl. The beakers were then capped and heated on a hotplate at about 150 – 175 degrees Celsius until dry. This 6 N HCl step was repeated two more times or until a clear solution was obtained, indicating that the basalts were fully dissolved. HCl converts the fluorides to chlorides, a necessary step before samples can be loaded onto columns. After the samples were fully dissolved, they were separated and prepared for columns.

Hafnium Columns:

90% of each sample was run through Ln-spec resin columns to extract Hf. Before loading the columns, ascorbic acid was added to each sample to convert Fe^{+3} to Fe^{+2} to

decrease the compatibility of Fe in the resin. Also, the Hf columns were run twice to ensure that Zr was fully removed.

Rare Earth Element Columns:

10% of each sample was run through Rare Earth Element columns to extract Nd. Each REE column consists of a 0.5 cm diameter, 19 cm tall volume of Dowex AG50X-8, 200-400 mesh cation exchange resin obtained from Bio-Rad laboratories.

Neodymium Columns:

As Nd cannot be collected directly from the REE columns, an additional column step was used to collect Nd. Each Nd column consists of a 0.5 cm diameter, 10 cm tall volume of Teflon powder HDEHP, 10:1 in an acetone slurry. This column material is capped with 0.5 cm of Dowex AG1-X8, 200-400 mesh anion resin to prevent Teflon flotation.

REE Columns
Photo Credit: E. Mervine, 2003

Loading Hf Columns
Photo Credit: M. Bizimus, 2003

Mass Spectrometry:

For analysis in the mass spectrometers, neodymium samples were loaded on rhenium filaments and analyzed in a Finnigan Mat 262 Thermal Ionization Mass Spectrometer (TIMS). The hafnium samples were also loaded on rhenium filaments and analyzed on a VG Isolab 54 Hot Secondary Ionization Mass Spectrometer (SIMS). Both mass spectrometers are located in the Geochemistry Department in the National High Magnetic Field Laboratory at Florida State University.

Running the TIMS Machine
Photo Credit: M. Bizimus, 2003

Making Rhenium Filaments
Photo Credit: M. McDowell, 2003

Results:

Of twelve original samples, Nd and Hf data were obtained for ten. For sample HU-3, only Nd data was obtained as the Hf portion was lost in clean lab chemistry. For sample HK-23, only Hf data was obtained as the Nd portion was lost during the mass spectrometry process. The ^{143}Nd / ^{144}Nd ratios for HU (Hualalai) samples ranged from 0.512919 (HU-5) to 0.512926 (HU-2). HK (Haleakala) samples had ^{143}Nd / ^{144}Nd ratios ranging from 0.512977 (HK-19) to 0.513037 (HK-30). For ^{176}Hf / ^{177}Hf HU samples ranged from 0.283114 (HU-1) to 0.283171 (HU-4) while HK samples ranged from

0.283222 (HK-19) to 0.283165 (HK-16). Table 1 contains the isotope ratios and associated 2 sigma errors (uncertainty in last two digits of ratio).

Table 1: Isotope Ratios

	Nd: 143/144		Hf: 176 / 177	
Sample:	Ratio:	2 Sigma Error:	Ratio:	2 Sigma Error:
HU-1	0.512924	+/-7	0.283114	+/- 6
HU-2	0.512926	+/-5	0.283157	+/- 8
HU-3	0.512924	+/-7	Sample Lost	
HU-4	0.512924	+/-9	0.283171	+/-7
HU-5	0.512919	+/-7	0.283144	+/- 9
HK-16	0.513022	+/-7	0.283165	+/- 6
HK-18	0.513012	+/- 14	0.283211	+/-8
HK-19	0.512977	+/- 15	0.283222	+/- 15
HK-22	0.513034	+/-7	0.283209	+/- 7
HK-23	Sample Lost		0.283169	+/- 4
HK-28	0.513028	+/- 7	0.283215	+/- 11
HK-30	0.513037	+/- 6	0.283185	+/- 6
Standards:				
LaJolla-1	0.511847	+/-6		
LaJolla-1 (2nd Run)	0.511833	+/-5		
LaJolla-2	0.511840	+/-6		
LaJolla-3	0.511843	+/-6		
JMC 475-1			0.28220	+/-9

Note: HU = Hualalai Sample, HK= Haleakala Sample

Discussion: Shallow Source:

The Hf and Nd ratios found in post-erosional basalts from Hualalai and Haleakala are much higher than those generally found for ocean island basalts. Figure 1 is a compilation of Hf and Nd values found worldwide for oceanic basalts as well as for Indian, Atlantic, and Pacific mid-ocean ridge basalts. The data was compiled from a large number of studies and is a good representation of the general span of isotope ratios in MORBs and OIBs.

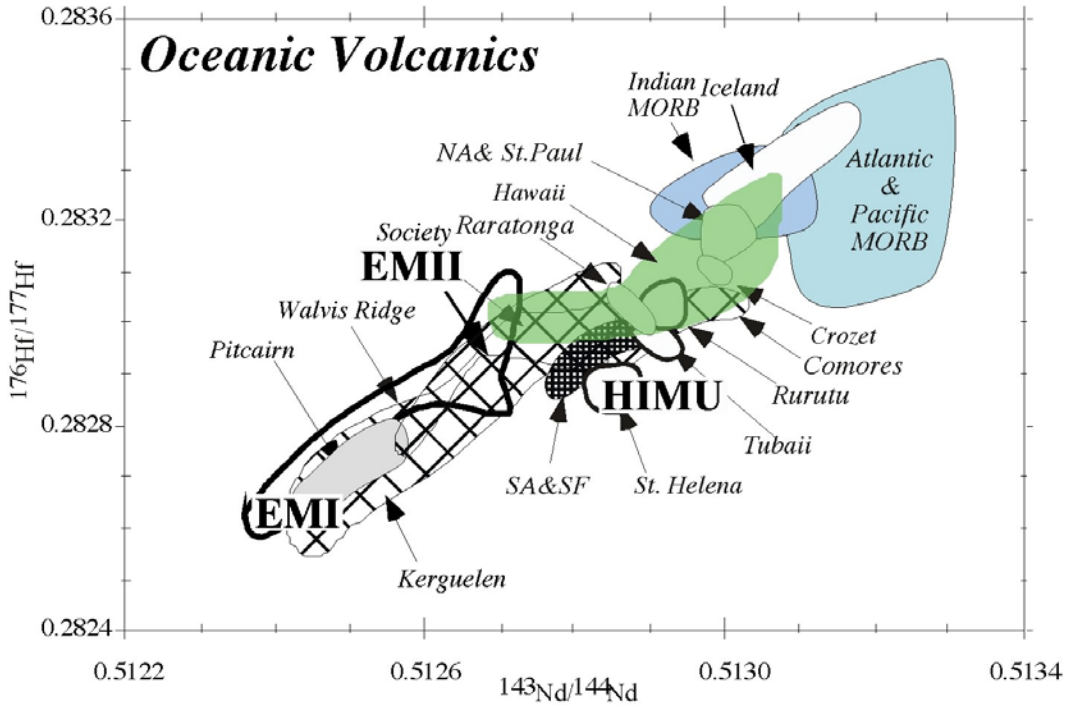

Figure 1: Typical Hf-Nd isotopic compositions of MORBs (mid-ocean ridge basalts) and OIBs (Ocean Island Basalts). As shown on the diagram, there is a direct correlation between Hf and Nd isotope ratios, so that a sample with a high $^{176}Hf / ^{177}Hf$ ratio will also have a high $^{143}Nd / ^{144}Nd$ ratio. EMII and EMI represent end-member or extreme values. HIMU is another end-member where MU = $^{230}U / ^{204}Pb$. Figure is adapted from a figure provided by Dr. Vincent Salters.

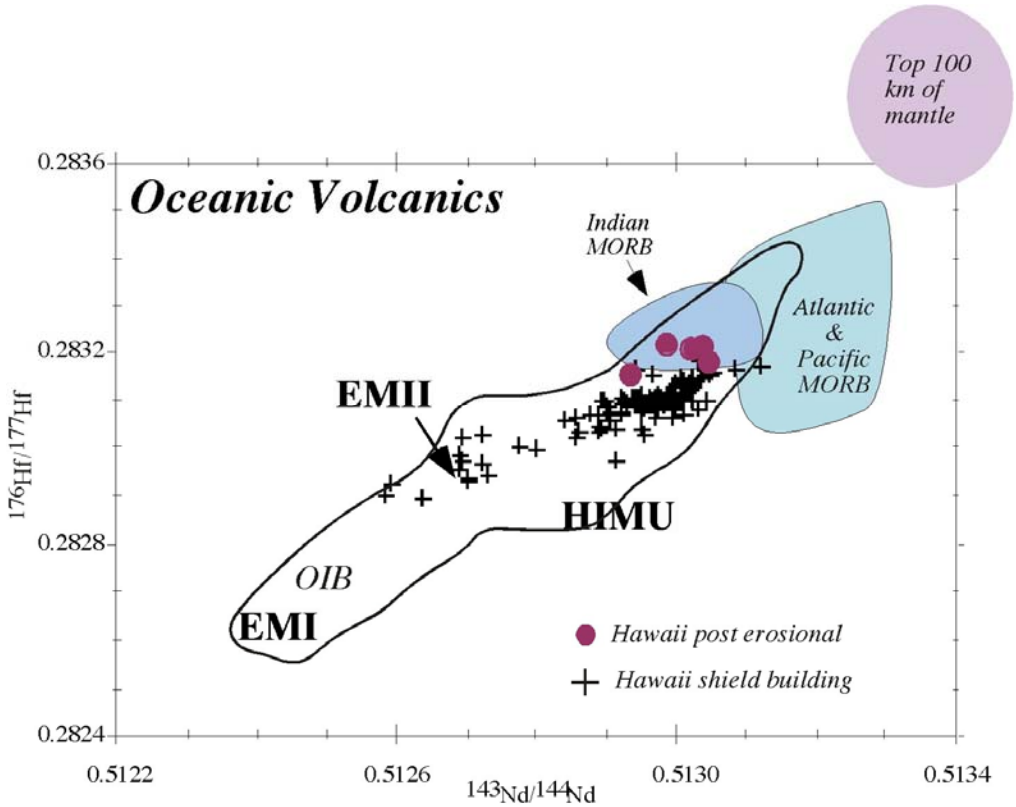

Figure 2: Comparison of Hf-Nd isotopic compositions of Hawaiian post-erosional basalts and Hawaii shield-building basalts.

Typical isotopic values for Hawaii are shown in light green on Figure 1. Most Hawaiian basalts lie well below MORB values. The overlap between Hawaiian OIBs and Indian MORBs mostly represents isotopic data collected from post-erosional basalts.

Figure 2 plots the data collected from this study (purple dots) against data from shield-building basalts (black crosses) collected by Dr. Vincent Salters as part of another study. The post-erosionals plot much higher than the shield-building basalts and lie somewhere in-between typical values for OIBs and MORBs.

The most likely explanation for the composition of the post-erosionals is that they have a higher component of the top 100 km of mantle in them (a shallower source) than the shield-building basalts. Post-erosional basalts probably represent some sort of mixing between the upper, depleted mantle and the deeper plume that is the main source for the shield-building tholeiites.

Low Degree of Melt:

In addition to having a shallower source than shield-building basalts, post-erosional basalts also seem to be generated by a smaller degree of melt than shield-building basalts. Figure 3 plots the post-erosionals in this study (purple dots) on a melting diagram and compares the post-erosionals to other OIBs as well as MORBs.

δ (Sm/Nd) and δ (Lu/ Hf) are the fractional differences between parent/daughter ratios in the basalts (rocks on the surface) and in their source (Salters, 1989). The parent / daughter pairs are as follows: ^{147}Sm decays to ^{143}Nd and ^{176}Lu decays to ^{176}Hf. δ(Sm/Nd) is calculated according to the following formula (Salters, 1989):

$$\delta_{Sm/Nd} = ((\ Sm\ /\ Nd\ )_{2Gry} - (Sm\ /\ Nd)_m\ /\ (Sm\ /\ Nd)_{2Gry})$$

where $(Sm / Nd)_{2Gry}$ is the calculated Sm / Nd in a 2 billion-year-old source based on the measured present-day $^{143}Nd / ^{144}Nd$ in a basalt. $(Sm / Nd)_m$ is the measured Sm / Nd in a basalt. For δ (Lu/ Hf), the calculation (Salters, 1989) is essentially the same:

$$\delta_{Lu/Hf} = ((Lu / Hf)_{2Gry} - (Lu / Hf)_m / (Lu / Hf)_{2Gry})$$

The greater the difference between the basalts and their source, the less degree of melting occurred to produce the rocks on the surface. Theoretically, 100% melt would produce isotopic compositions on the surface identical to those in the original source. Any melt less than 100% produces a difference in isotopic composition between the original source and the erupted lavas. For basalts, percentages of melt tend to lie somewhere between 1% and 25% with 25% being an extremely large degree of melt (Salters, 1989).

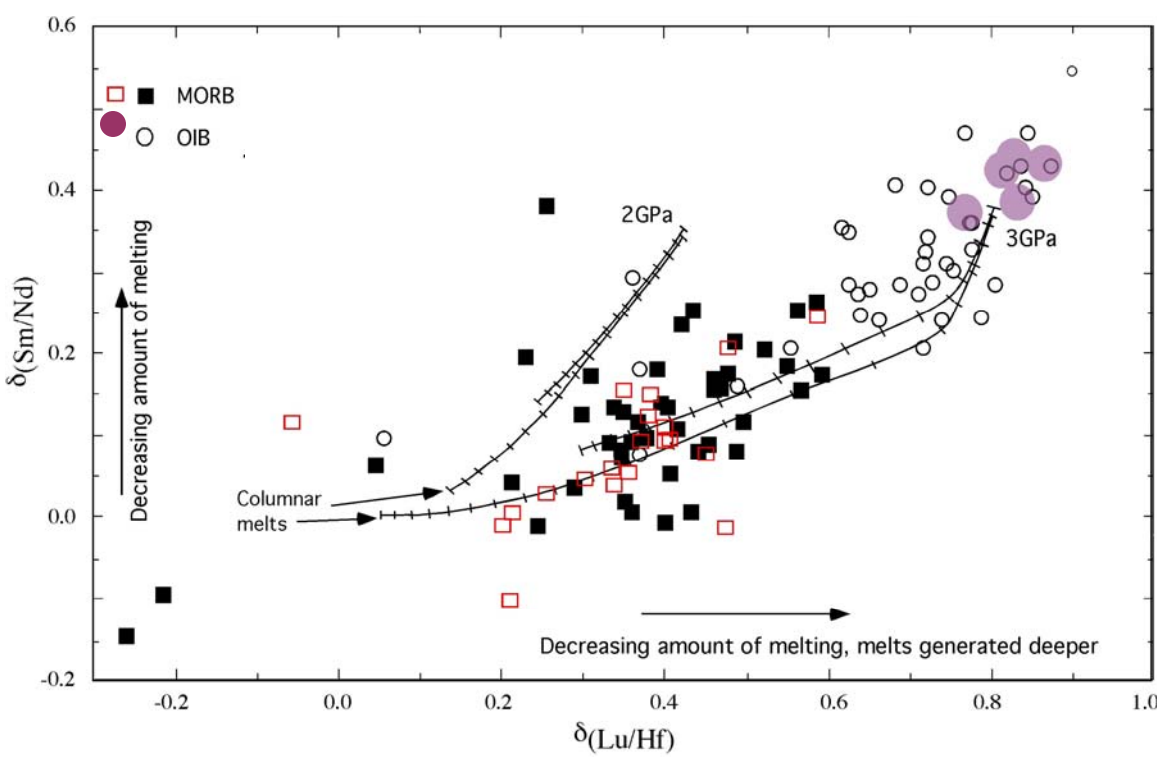

Figure 3: Degree of melt

Figure 3 shows that the post-erosional basalts in this study were produced by smaller degrees of melting and have a greater proportion of garnet in the source, indicating that the melts were generated deeper. Keep in mind, however, that all of the samples on the figure have shallow sources compared with shield-building OIBs. The black circles represent typical OIB (not post-erosional) values and the squares represent typical MORB values. The black circles and red and black squares are data from previous basalt studies done by Dr. Salters. Clearly, the Hualalai and Haleakala post-erosional basalts represent a much smaller degree of melting than typical OIBs or typical MORBs. The black lines represent different percentages of melt in the garnet stability field and are based on a melting model developed by Dr. Salters. One set of lines represents 2 GPa of pressure while the other set represents 3 GPa of pressure.

Summary:

Hawaiian post-erosional basalts clearly have different chemical compositions and were produced in different ways than Hawaiian shield-building basalts. In particular, the source of post-erosionals seems to be much shallower than the source of shield-building basalts. Also, the degree of melt that produced post-erosionals seems to be much less than the degree of melt that produced the shield-building basalts. Chemically and behaviorally, post-erosional basalts seem to lie somewhere in-between OIBs and MORBs.

Future Work:

As relative little chemical analysis of post-erosional basalts from Hawaii has been done, more data needs to be collected. As not all of the HK and HU samples collected by Dr. Kenneth Sims have yet been analyzed for Hf and Nd, plans are in place to analyze at

least six more samples, which are currently dissolved and ready for columns. Dr. Sims is currently collecting Th data from the same HU and HK samples in this study. The combined Hf-Nd-Th isotope data will provide information about not only the degree of melt but also the rate at which the source materials melted. Collecting and analyzing Hawaiian post-erosional samples from volcanic locations aside from Hualalai and Haleakala is, in general, a good idea for future research.

Once isotopic data has been gathered, the next step is to develop this data into likely theories and models having to do with post-erosional basalts and Hawaiian volcanism in general. Why Hawaiian volcanoes suddenly produce post-erosionals, lavas with a noticeably different chemical composition than the lavas which form most of the volcanoes, after a mysterious gap in volcanic activity is an intriguing question and one that, certainly, merits detailed study and analysis.

Acknowledgements:

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