HAWAIIAN HOTSPOT DYNAMICS AS INFERRED FROM THE HF AND PB ISOTOPE EVOLUTION OF MAUNA KEA VOLCANO

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Abstract

The present work reports the isotopic compositions of Hf and Pb in the first three kilometers of the deep core retrieved by the Hawaii Scientific Drilling Project. The measurements cover all the samples from the standard geochemical reference set. Hafnium isotopic data on glasses from the deep hole and replicates from the pilot hole have also been included in this study. All the measurements are high-precision isotope analyses obtained by multiple collector ICP-MS.

The isotopic properties of Mauna Loa and Mauna Kea samples are very distinctive with both Hf and Pb being less radiogenic in Mauna Loa with respect to Mauna Kea samples. Part of the noise on $^{207}Pb/^{204}Pb$ may reflect an analytical artifact arising from Pb isotope fractionation during separation chemistry. Although the transition between Mauna Kea and Mauna Loa is progressive for ε_{Hf} and $^{208}Pb/^{204}Pb$, a sharp discontinuity is observed for $^{208}Pb*/^{206}Pb*$. There is essentially no correlation between the alkalinity of the samples and their isotopic composition. In detail, the Hf isotope compositions of samples from the pilot hole do not systematically coincide with those of the HSDP-2 core for samples retrieved from a similar depth, suggesting that steep topography existed at the time of emplacement or that a different eruptive sequence was recorded.

The strong correlation between $^{208}Pb*/^{206}Pb*$ and $^{3}He/^{4}He$ (He data from *Kurz et al.,* [this volume]) requires the episodic incorporation of a component that resembles the basalts erupted by either Kilauea or the Loihi eruptive centers (this component is referred to as K/L). The data suggest that some 500 ky ago, Mauna Kea was tapping a mantle source similar to that tapped by Kilauea today. Isotopic variability of Pb and He cannot be accounted for by radiogenic ingrowth in a closed system, but calls for the mixing of components with distinct outgassing histories.

Because apparent hot spot fixity makes more sense if upwelling velocity in the plume conduit is higher than plate velocity, we argue that the geochemical cross section of the plume conduit cannot be considered as time invariant. Because volcanoes seem to collect melt from a source disk ca. 30 km in radius [*Ribe and Christensen*, 1999; *DePaolo et al.*, 2001], vertical variations cannot be neglected as the possible cause of geochemical fluctuations of a volcanic center. The time series of isotopic and concentration data in Mauna Kea samples indicate the

recurrence of geochemical patterns in the melting column. Ignoring the most recent alkalic samples, we find that the dominant fluctuations of Hf and ^{207}Pb/^{204}Pb isotopic pattern recurrence corresponds to a period of 50,000 years contrasting with a dominant period of ca. 18,000 years for La/Yb, Zr/Nb, ^{87}Sr/^{86}Sr, ^{206}Pb/^{204}Pb, ^{207}Pb/^{206}Pb, and ^{208}Pb/^{206}Pb. Once provision is made for the existence of harmonics, the consistency between the isotopic spectrum of the pilot hole and the HDSP-2 core is very good. The input of the K/L component does not seem to be periodic. We use these recurrence intervals in conjunction with the upwelling rate deduced from buoyancy flux and seismic evidence of the maximum dimension of scatterers to constrain the radius of the Hawaiian plume to be in the range of 10-50 km and the upwelling velocity to be in the range of 0.13-3 m/y. Plausible vertical length scales of heterogeneities in the conduit are 6.5-160 km.

Introduction

Although numerous important scientific results were obtained from the geochemistry of the HSDP pilot hole lavas, this relatively short core did not make it possible to use the geochemical analyses, in particular those of radiogenic isotopes, as time series because the time window was not sufficiently broad to be of geophysical significance with respect to hotspot dynamics [e.g., *DePaolo et al.,* 2001]. In the present contribution to the HSDP initiative, we use a comprehensive time series of combined high-resolution, high-precision Hf and Pb isotope data for the continuous 3 km sequence of Mauna Kea lavas to set constraints on the nature of the Mauna Kea mantle sources and how they varied through time. Before reaching Mauna Kea by drilling, *ca* 250 m of lavas from the currently active Mauna Loa volcano had to be traversed, and here we also present the Hf and Pb isotope data for this suite of samples. The petrology and geochemistry of modern Hawaiian lava flows offer a two-dimensional view of the hot spot activity which has been used to infer cross sections of melt extraction [*Ribe and Christensen*, 1999] and mantle heterogeneities in the plume conduit [*DePaolo et al.,* 2001]. One of the most important goals of a high-resolution series of samples covering a significant interval of the lifetime of a volcano is to provide geochemical time series (assuming a reliable time scale for the stratigraphic column) that allow the geochemical

cross sections inferred from the modern eruptions to be tested. The present results for the Mauna Kea and Mauna Loa volcanoes have allowed us to deduce aspects of the chemical and physical structure and the dynamics of the Hawaiian plume beneath Mauna Kea, examine how the plumbing systems of different volcanoes may interact, and make inferences about the relationships of Mauna Kea with its neighboring volcanoes, notably Mauna Loa, Kilauea, and Loihi.

Samples and Analytical Techniques

Hf isotope analyses

We report 155 Hf isotope analyses of 123 different samples from Mauna Loa (19 samples) and Mauna Kea (104 samples) from the second Hawaii Scientific Drilling Project core (HSDP-2) (Table 1). The Hf isotopic compositions were analyzed by MC-ICP-MS (the VG Plasma 54 instrument in Lyon) during the period of January 2000 to April 2001. Hafnium purification and mass spectrometry followed the procedures described in *Blichert-Toft et al.* [1997]. To avoid ambiguity between measured isotopic variations and potential chemistry problems or machine drift during long run sessions (as required by the large number of samples analyzed), samples were routinely randomized for both Hf separation chemistry and mass spectrometric analysis. Furthermore, in order to monitor machine performance, the JMC-475 Hf standard was run systematically in between every second or third sample throughout the entire project. Hf total procedural blanks routinely were less then 25 pg.

The analyzed sample suite spans the entire depth interval from sea level to current coring depth with the deepest sample coming from 3069 mbsl. One hundred and nineteen of these samples are powders from the 119-sample standard geochemical reference set, while four samples are hand-picked glasses from Mauna Kea from the depth interval between 2200 and 2400 mbsl. Based on major element data [*Rhodes and Vollinger*, this volume], this particular depth interval may represent a unique excursion of increased alkalinity in the middle of several kilometers of basalts with a strong tholeiitic character. We considered it important to investigate this feature in more detail by undertaking the additional glass analyses. Nineteen of the samples from the reference suite are from Mauna Loa (sea level

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down to 246 mbsl) and 100 of the samples are from Mauna Kea (between 246 and 3098 mbsl, the coring depth at the time of writing).

In order to verify the external reproducibility for Hf isotopic measurement of 0.35 epsilon units, as indicated by the JMC-475 Hf standard analyses, six samples from Mauna Loa and 20 samples from Mauna Kea were analyzed in duplicate. Some of these samples were chosen for repeat measurement because their in-run errors were greater than the external reproducibility as judged from the analyses of JMC-475. Three additional samples from Mauna Kea were further analyzed in triplicate in order to certify their measured Hf isotopic composition. The excellent reproducibility of all replicate analyses (Table 1) and the consistency of Hf isotopic compositions between consecutive samples, which, as noted above, were not analyzed in successive order, indicate that our error assignment is conservative. In order to further check for potential analytical bias between Hf isotopic measurements for HSDP-1 (the first Hawaii Scientific Drilling Project pilot core) and HSDP-2, four samples from the bottom of HSDP-1 (which overlaps with HSDP-2) were re-analyzed simultaneously with samples from HSDP-2 (Table 1). The results for the HSDP-1 replicates are identical within error to the original analyses carried out by *Blichert-Toft and Albarède* [1999], thus allowing direct comparison between the two cores.

Pb isotope analyses

All the samples measured for Pb isotopic composition were processed in the clean laboratory at Université Libre de Bruxelles. The samples were leached with 6 N HCl, as described in *Weis and Frey* [1991], in order to remove a maximum of secondary alteration products. Lead was subsequently separated by a single passage through an anion-exchange column. Total blanks for the entire procedure were 100-200 pg, which is negligible with respect to the Pb of the samples analyzed (~100-300 ng). The Pb isotopic compositions were measured on the MC-ICP-MS VG Plasma 54 in Lyon from June 2000 to June 2001. Thallium spike was added to all samples and standards to monitor mass fractionation [*White et al.*, 2000]. The total Pb ion beam intensities varied from 0.6 to 8 V, but only results for samples with an intensity exceeding 2 V of total Pb were used in order to have sufficient precision on the isotopic

ratios. Furthermore, because the Tl/Pb ratio appears to be critical to the accuracy of the Pb isotope results, especially for $^{207}Pb/^{204}Pb$, only results for samples with Tl/Pb < 0.5 were retained. Almost all the samples from the standard geochemical reference set were analyzed. Among these, 19 are duplicates and two are triplicates. Nineteen samples are from Mauna Loa and 95 samples are from Mauna Kea. As done for Hf, samples were processed randomly for both Pb separation chemistry and mass spectrometric analysis. Because the NBS 981 standard is run systematically after every two samples as a reference to calculate the sample isotopic ratios, no single value of this standard can be reported that would be an independent test of machine accuracy. However, it has been shown by *White et al.* [2000] that the method used in this study reproduces thermal-ionization Pb isotope results on basaltic samples very accurately. It is worth re-emphasizing here that the current technique does *not* assume that Pb and Tl have similar mass biases, but rather that the biases of these two elements maintain a constant ratio over the time period of a few runs. The good performance of the Plasma 54 was further substantiated by the measurement of multiple NIST 981-NIST 982 mixtures [*B. Nelson and F. Albarède*, unpublished data]: $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ are precise to better than 50 ppm, while $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ typically are precise to within 100 ppm per atomic mass unit.

The Pb isotope results and a comparison with triple-spike Pb isotope data [*Eisele et al.*, this volume] on a subset of samples from the Mauna Kea section of the deep core (HSDP-2) is presented in Figure 1. Except for $^{207}Pb/^{204}Pb$, for which the Plasma 54 data are clearly significantly more noisy than the triple-spike data, the agreement between the MC-ICP-MS and the triple-spike values is remarkable, especially when taking into account the downcore isotopic variations. The cause for the noise on the $^{207}Pb/^{204}Pb$ measurements by MC-ICP-MS is not yet understood. Although matrix left after elution may alter mass fractionation to some extent, it is our experience that Pb isotope measurements on solutions with a relatively heavy matrix reproduce well within the stated errors. Memory should not be a significant issue since the Plasma 54 of Lyon never sees any ^{204}Pb or ^{207}Pb spike, while the $^{207}Pb/^{204}Pb$ ratios of the bracketing standard (NIST 981) and the samples are nearly identical. *Eisele et al.* [this volume] observe a lack of reproducibility of $^{207}Pb/^{204}Pb$ measurements on some subaerial

basalts from the HSDP pilot core and ascribe it to contamination by particles transported with groundwater. Because our leaching procedure is less severe than the procedure used in Mainz, we may be seeing a similar effect. A last option is that our HCl-based chemistry fractionates Pb isotopes on anion-exchange resin. Such a process has been previously documented for Zn, Cu [*Maréchal et al.,* 1999; *Maréchal and Albarède,* 2002] and Fe [*Anbar et al,* 2000] and has been tested here for Pb by eluting a few micrograms of NIST 981 on an anion-exchange column. The surprising result of this experiment (mass fractionation on $^{207}Pb/^{204}Pb$ in excess of 2000 ppm across the elution peak) is described in Appendix A. A similar experiment with a similar outcome was described by *Baker et al.* [2002]. Unfortunately, it has not been possible to assess the yield of our Pb purification chemistry for the HSDP-2 samples, which were all run prior to this experiment. However, the observation that the Pb isotope partition coefficients between the anion-exchange resin and HCl may change by as little as 40 ppm per mass unit from ^{204}Pb to ^{208}Pb may account for some of the noise observed in our HSDP-2 data. Natural variations in $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ are an order of magnitude larger than the $^{207}Pb/^{204}Pb$ variations: the impact of potential analytical artifacts is therefore less critical on the first two ratios.

Results

Hf isotopes

Hf isotopic compositions for Mauna Loa lavas from the deep core (HSDP-2) have $^{176}Hf/^{177}Hf$ that varies from 0.283051 to 0.283115, corresponding to ε_{Hf} = +9.9 - +12.1 (Table 1; Figure 2). This is similar to, though slightly more variable than observed for Mauna Loa lavas from the pilot core (HSDP-1) (ε_{Hf} = +10.5 - +11.6; *Blichert-Toft and Albarède* [1999]). Samples from the top of the Mauna Loa section are the least radiogenic, with successive samples becoming progressively more radiogenic with depth except for a small wiggle at about 125 mbsl and an abrupt excursion to less radiogenic values at about 200 mbsl. Samples following this excursion gradually become more radiogenic during the remaining 50 m leading to the contact with Mauna Kea (Figure 2). The range of $^{176}Hf/^{177}Hf$ for the HSDP-2 Mauna Kea section (0.283087-0.283152 or ε_{Hf} = +11.1 - +13.4) likewise is indistinguishable

from that of the HSDP-1 Mauna Kea section (ε_{Hf} = +11.4 - +13.1; *Blichert-Toft and Albarède* [1999]). However, between 500 and 750 mbsl, Hf in HSDP-2 is offset systematically with about 0.5 epsilon units towards more radiogenic values relative to HSDP-1 (Figure 3b). The discrepancy in Hf isotopic composition for this part of the overlapping depth interval between the two cores cannot be due to an analytical artifact as the four duplicate analyses from HSDP-1 analyzed together with the new samples from HSDP-2 came out identical within error to the first set of analyses by *Blichert-Toft and Albarède* [1999] (Table 1). It would of course have been preferable to duplicate the Hf isotope measurements in the section where the two cores are isotopically distinct. We consider, however, that the reproducibility of HSDP pilot core data acquired on the same samples three years apart and the overall consistency of the multiple replicates of HSDP-2 analyses make it unlikely that an analytical bias may account for the Hf isotope discrepancy between the two cores. Despite the two holes having been drilled just a few kilometers apart and the similarity of one particular alkaline flow in each core (SR131 and R177 as pointed out by *Huang and Frey* [this volume]), it seems clear that stratigraphic correlations cannot be retrieved from the depth in the core alone.

As observed previously for the pilot core [*Blichert-Toft and Albarède*, 1999], Hf isotope compositions of Mauna Kea lavas in the HSDP-2 core ($\varepsilon_{Hf} \sim$ +12.3 ± 0.9) are overall more radiogenic than those of Mauna Loa lavas ($\varepsilon_{Hf} \sim$ +11.0 ± 0.9) (Figure 2). While the transition from Mauna Kea to Mauna Loa lavas in the pilot core is abrupt with a drop of about one ε_{Hf} unit [*Blichert-Toft and Albarède*, 1999], it is preceded in the HSDP-2 core by a conspicuous gradual decrease of almost two ε_{Hf} units over the top 200 meters of Mauna Kea flows (Figure 2). Hafnium in the flows between 500 and 1500 mbsl generally seems to be more radiogenic than in the flows at the bottom of the core. Hf isotope compositions oscillate with only few observed breaks that exceed error bars (Figure 3b). The hyaloclastite sample SR0705-0.15 (at 1823.2 mbsl), analyzed in triplicate to verify its aberrant (with respect to neighboring samples) isotopic composition, is clearly anomalous (Figure 2) and will not be discussed further. The four hand-picked glasses from the depth interval of 2200 to 2400 mbsl were leached and also analyzed for their Hf isotopic compositions. Their ε_{Hf} values are indistinguishable within error from those of the corresponding whole-rock powders from the

standard geochemical reference set (Figure 2). The glasses define a distinct trend of increasingly radiogenic $^{176}Hf/^{177}Hf$ (or increasing ε_{Hf}) with decreasing depth that overlaps the identical trend defined by the whole-rock powders.

Pb isotopes

Lead isotopic compositions for the Mauna Loa part of the deep core (HSDP-2) vary between 18.061 and 18.250 for $^{206}Pb/^{204}Pb$ and 37.804 and 37.995 for $^{208}Pb/^{204}Pb$ (Table 1; Figure 1). Whereas $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ do not show systematic variability downcore, $^{208}Pb/^{204}Pb$ increases more or less systematically between 9.5 and 242 mbsl, the latter depth defining the contact with Mauna Kea. For the Mauna Kea section of HSDP-2, $^{206}Pb/^{204}Pb$ varies between 18.408 and 18.670 and $^{208}Pb/^{204}Pb$ between 37.933 and 38.248. In a $^{208}Pb/^{204}Pb$ (and $^{207}Pb/^{204}Pb$) *vs.* $^{206}Pb/^{204}Pb$ plot, there is no overlap between the Mauna Loa and Mauna Kea data (Figure 4). The lavas in the upper part of the Mauna Kea section are characterized by slightly less radiogenic Pb isotopic compositions than typical for deeper Mauna Kea lavas and cluster in the least radiogenic part of the Mauna Kea field in a Pb-Pb diagram.

While $^{208}Pb/^{204}Pb$, like $^{176}Hf/^{177}Hf$, displays some continuity between Mauna Kea and Mauna Loa samples the transition between the two volcanoes for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb^*/^{206}Pb^*$ is marked by a sharp discontinuity (Figure 1). Relative to Mauna Loa, Mauna Kea is characterized by more radiogenic Pb and a lower source Th/U ($^{208}Pb^*/^{206}Pb^*$) ratio, the latter showing an overall increase with depth. Nine samples from mid-depth, notably from the interval 1973.8 to 2123.7 mbsl and from 2321.6, 2467.3, 2503.5, and 2654.1 mbsl, which all have a less negative alkalinity than the bulk of Mauna Kea lavas (Figure 3a), have distinctly higher $^{208}Pb^*/^{206}Pb^*$ ratios. For reasons to be explained in the Discussion, we will hereafter refer to these samples as the K/L group. As mentioned above, in a $^{207}Pb/^{204}Pb$ *vs.* $^{206}Pb/^{204}Pb$ plot (Figure 4b), the difference between Mauna Kea and Mauna Loa stands out, but in contrast with the results of *Abouchami et al.* [2000] on the pilot core, no fine structure can be defined within the data. We ascribe this to the larger errors on $^{207}Pb/^{204}Pb$ associated with the thallium-spike method used here with respect to the triple-spike method employed by *Abouchami et al.* [2000]. Another reason may be a variable efficiency of Pb contamination

removal by acid leaching (see *Eisele et al.* [this volume]). As also remarked above, the same contrast between Mauna Kea and Mauna Loa shows up in a $^{208}Pb/^{204}Pb$ *vs.* $^{206}Pb/^{204}Pb$ plot with the more alkaline K/L Mauna Kea samples plotting with unusually high $^{208}Pb/^{204}Pb$ for a given $^{206}Pb/^{204}Pb$ (Figure 4a). Despite the potential analytical limitations on $^{207}Pb/^{204}Pb$, we used a 3-D rotated Pb projection to attempt to demonstrate that most Mauna Kea data fall within a plane, whereas the more alkaline K/L samples plot distinctly above this plane (Figure 5).

Discussion

Interaction between Mauna Kea basalts and the Pacific lithosphere

The field of combined Hf and Pb isotope compositions for the HSDP-2 samples is very similar to that of the pilot hole and we will not repeat here the discussion presented elsewhere for Hf [*Blichert-Toft and Albarède,* 1999; *Blichert-Toft et al.,* 1999; *Huang and Frey*, this volume] and Pb [*Abouchami et al.*, 2000]. We note, however, that the present Pb and Hf isotope compositions plot on the general hyperbolic array that *Blichert-Toft et al.* [1999] used to infer that the East Pacific plate is not involved as a significant component in Hawaiian basalts (Figure 6). This point is discussed in *Wang et al.* [this volume] who emphasize that the ε_{Hf} of Pacific MORB and Mauna Kea basalts overlap. The histogram shown as an inset in Figure 6 does indeed show *some* overlap and it may be argued that *some* Mauna Kea basalts may have incorporated particularly infrequent E-type (enriched) lithospheric material, e.g., similar to MORB from the Siqueiros fracture zone [*Sims et al.,* in press]. As a whole, however, the Pacific plate remains a very unlikely depleted end-member of Hawaiian basalts.

The transition between Mauna Loa and Mauna Kea

Although Hf and Pb isotopic data allow a clear distinction to be made between lavas from Mauna Loa and Mauna Kea, there is a tendency for the uppermost 200 meters of Mauna Kea lavas to show isotopic compositions intermediate to those of the two volcanoes (Figures 1-3). The series of $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios are virtually continuous across the transition, while the series of $^{206}Pb/^{204}Pb$ ratios shows a gap but no discontinuity of the trend. In contrast,

the $^{208}Pb^*/^{206}Pb^*$ ratios show both a gap and an abrupt discontinuity of the trend. Only the most recent (topmost) of these transitional lavas are alkaline (Figure 3a), which confirms the observation from the pilot core that there is no *overall* correlation between alkalinity and Hf (or Pb) isotopic composition [*Blichert-Toft and Albarède*, 1999]. Hafnium in the most alkaline samples from the uppermost Mauna Kea flows in the HSDP-2 core is substantially less radiogenic than in the alkaline samples from the same depth interval in the pilot hole [*Blichert-Toft and Albarede*, 1999] (Figure 3b). Were it not for $^{208}Pb^*/^{206}Pb^*$, the HSDP-2 core Hf and Pb isotope data would support a transitional regime between Mauna Kea and Mauna Loa indicative of a mixed source of interacting batches of magmas, probably reflecting the gradual invasion of the plumbing system of Mauna Kea by that of Mauna Loa. This observation contrasts with the sharp discontinuity between the two volcanoes observed in the Hf and Pb isotope data from the pilot hole [*Blichert-Toft and Albarède*, 1999; *Abouchami et al.,* 2000]. The distinctive properties of the two cores are further illustrated by the significantly more radiogenic character of Hf in the lava flows of the HSDP-2 core between 500 and 750 mbsl relative to those of the pilot core. These discrepancies suggest that, at equivalent depths, the two drill holes did not sample the exact same lava piles, indicating either a lateral shift in stratigraphy between the two cores over the *ca* 2 km that separate them or the accumulation of different lava flow sequences at the two locations, perhaps caused by steep topography at the time of eruption. In contrast, Mauna Loa lavas have identical ε_{Hf} *vs.* depth relationships in the two cores. As for Pb isotopes, no samples from the pilot hole were analyzed by MC-ICP-MS, thus preventing direct comparison between the two cores. However, the agreement between the Pb isotopic compositions obtained for HSDP-2 in the present study by MC-ICP-MS and those obtained by triple spike for the HSDP-1 core [*Abouchami et al.*, 2000] is good.

Mauna Kea source heterogeneity

In order to evaluate which isotopic properties may be correlated, we first ran our own Hf and Pb isotope data together with the Sr and Nd isotope data produced by *Bryce et al.* [this volume] and the He isotope data produced by *Kurz et al.* [this volume] on the same samples

through a Principal Component Analysis (PCA) software. PCA is a method used to identify the orthogonal directions of maximum variability and is described in a number of different textbooks [e.g., *Johnson and Winchern*, 1992; *Albarède*, 1995; *Reyment and Jöreskog*, 1996]. The three components obtained for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$, respectively, account for 46.3, 24.2, and 13.0 percent of the variability. There is hardly any correlation between the Pb isotopic ratios and other isotope compositions, since, as demonstrated by *Blichert-Toft et al.* [1999], such mixing relationships are strongly non-linear. One exception stands out, however: $^{208}Pb*/^{204}Pb*$ and $^3He/^4He$ plot next to each other in the space of the first three components (Figure 7) which indicates that they are strongly correlated [*Eiler et al.*, 1998]. We surmise that the odd position of $^{87}Sr/^{86}Sr$ along the axis of the third component may signal the occasional presence of a seawater component, either as a contaminant in the lava pile or as a real mantle component. The position of the ε_{Hf} and $^{206}Pb/^{204}Pb$ axes in the plane of the first two components confirms that, although three components are necessary to describe the overall isotopic variability of Hawaiian basalts, two components seem to be enough to describe the relationship between ε_{Hf} and $^{206}Pb/^{204}Pb$ [*Blichert-Toft et al.*, 1999].

The systematics of Pb isotopic compositions, particularly in $^{208}Pb/^{204}Pb$-$^{206}Pb/^{204}Pb$ space (Figure 4a), require that more than two components be involved in the Mauna Kea lavas. As indicated in the Results section, the mid-depth K/L samples as a group and the rest of the Mauna Kea samples have different Pb isotopic compositions. The K/L samples, which *Rhodes and Vollinger* [this volume] refer to as type-3 basalts, are readily identified by their high values of $^{208}Pb/^{204}Pb$ for a given value of $^{206}Pb/^{204}Pb$, but also stand out by their less negative alkalinity, high Ca, Ti, and Nb contents, and low silica (Figure 8). Although *Rhodes and Vollinger* [this volume] found these lavas very similar to Loihi basalts, *Frey and Rhodes* [1993] list these features as characteristic of lavas from Kilauea with respect to Mauna Loa. The $^3He/^4He$ ratios of the Mauna Kea samples reach values of up to 25 [*Kurz et al.*, this volume] which would be more diagnostic of Loihi basalts if it was not because $^3He/^4He$ values in excess of 20 are also known from Kilauea [*Kurz et al.*, 1996]. More extensive sampling of Kilauea may turn up even less radiogenic He. The Sr, Nd [*Garcia et al.*, 1995], and Hf [*Blichert-Toft et al.*, 1999] (Figure 6) isotope compositions of the two volcanoes are

not distinguishable from each other. The isotopic ratio for which the overlap between Loihi and Kilauea data is minimal is $^{208}Pb*/^{204}Pb*$, with Loihi values being higher. However, evidence from conventional TIMS data [*Staudigel et al*., 1984; *Garcia et al.,* 1993, 1995] that these two volcanoes do not overlap in Pb isotope space is not very strong and a better case must await full publication of high-precision triple-spike Pb isotope data [*Abouchami et al.,* 2000] . By referring to a K/L component, it is not our intention to suggest that a common Kilauea-Loihi component exists which lumps together the properties of these two distinct volcanoes but rather that, based on the available data, one volcano may be as appropriate a reference as the other. With respect to the chronological relationships discussed below, we simply point out here that assigning the K/L (type-3) basalts to a Loihi stage in the evolution of the Mauna Kea volcano requires strengthening of existing arguments.

$^{3}He/^{4}He$ usually is observed to be decoupled from non-volatile isotopic systems (e.g., *Valbracht et al.,* [1996]) but *Eiler et al*. [1998] demonstrated that, in Hawaiian basalts, there is a strong correlation between $^{3}He/^{4}He$ and some combination of Pb isotopic ratios that we wish to elaborate further on here. As expected from the Principal Component Analysis results, there is a strikingly positive correlation between $^{3}He/^{4}He$ and $^{208}Pb^{*}/^{206}Pb^{*}$ for Mauna Kea (Figure 8a). The K/L samples represent the high-$^{3}He/^{4}He$ and high-$^{208}Pb^{*}/^{206}Pb^{*}$ end-member of this correlation. It can be shown by writing the equation for radiogenic ingrowth that this correlation is not due to mere radiogenic ingrowth of ^{4}He in a closed system:

$$\left(\frac{^{4}He}{^{3}He}\right)_{0} = \left(\frac{^{4}He}{^{3}He}\right)_{T_0} + 8\left(\frac{^{238}U}{^{3}He}\right)_{0}\left(e^{\lambda_{238U}T_0} - 1\right)$$
$$+ 7\left(\frac{^{235}U}{^{3}He}\right)_{0}\left(e^{\lambda_{235U}T_0} - 1\right) + 6\left(\frac{^{232}Th}{^{3}He}\right)_{0}\left(e^{\lambda_{232Th}T_0} - 1\right)$$

in which the subscript 0 refers to modern values, T_0 is the age of the Earth and λ_i stands for the decay constant for the nuclide i. Likewise, the radiogenic ingrowth of the $^{208}Pb^{*}/^{206}Pb^{*}$ ratio is given by

$$\left(\frac{^{208}Pb^{*}}{^{206}Pb^{*}}\right)_{0} = \left(\frac{^{232}Th}{^{238}U}\right)_{0}\frac{e^{\lambda_{232Th}T_0} - 1}{e^{\lambda_{238U}T_0} - 1}$$

Upon elimination of the Th/U ratio, the last two equations can be combined as:

$$\left(\frac{^4\text{He}}{^3\text{He}}\right)_0 = \left(\frac{^4\text{He}}{^3\text{He}}\right)_{T_0} + \left(\frac{^{238}\text{U}}{^3\text{He}}\right)_0 \left(e^{\lambda_{238\text{U}} T_0} - 1\right)$$
$$\left[8 + \frac{7}{(^{238}\text{U}/^{235}\text{U})_0} \frac{e^{\lambda_{235\text{U}} T_0} - 1}{e^{\lambda_{238\text{U}} T_0} - 1} + 6 \left(\frac{^{208}\text{Pb}^*}{^{206}\text{Pb}^*}\right)_0\right]$$

This relationship indicates that radiogenic ingrowth in a closed system with a broadly uniform $^{238}\text{U}/^3\text{He}$ ratio but a variable Th/U ratio would lead to a *negative* correlation between $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ and $^3\text{He}/^4\text{He}$, which is the opposite of what we observe for the Mauna Kea data (Figure 8a). The trend observed in this figure shows that it is not the variation of the Th/U ratios in the source that creates the observed correlation but mixing between two mantle components with a distinct fractionation/outgassing history: the relatively undegassed K/L component with high $^3\text{He}/^4\text{He}$ (low integrated $^{238}\text{U}/^3\text{He}$) happened to have a high source Th/U while the relatively degassed component with a "normal" (7-15) $^3\text{He}/^4\text{He}$ (higher integrated $^{238}\text{U}/^3\text{He}$) happened to have a lower Th/U ratio. We are therefore not observing a real correlation between $^3\text{He}/^4\text{He}$ and the U-Th-Pb isotopic system [*Eiler et al.,* 1998]) but rather a simple mixing relationship between the $^3\text{He}/^4\text{He}$ and the U/He ratios of two variably outgassed mantle components with different Th/U ratios. In other words, the conundrum of He isotope decoupling from non-volatile systems is yet to be resolved. This decoupling, which may reflect the decoupled dynamics of volatiles and magmas [*Valbracht et al.,* 1996], probably explains why $^3\text{He}/^4\text{He}$ is so variable in the HSDP-2 samples whereas their ε_{Hf} is relatively constant.

The bulk of Mauna Kea samples do not separate into two distinct groups, but rather form a trend that shows that each Mauna Kea sample contains different proportions of a Kilauea-like mantle source (as an example we have singled out the "intermediate Mauna Kea" group as shown in Figure 8). The Kilauea "flavor" is dominant in the nine K/L samples that, according to the age model of *DePaolo et al.* [this volume], should be 496-532 ka old. Kilauea is the youngest aerial Hawaiian volcano. The oldest dated Kilauea sample is only 341 ka [*Quane et al.*, 2000], but, from the growth model established on Mauna Kea, *DePaolo and Stolper* [1996] inferred that Kilauea is probably as old as 600 ka. Because essentially all mid-

depth Kea samples contain some proportion of the K/L component, it is unlikely that the HSDP-2 core inadvertently sampled isolated Kilauea lava flows. Rather, some 500 ky ago, Mauna Kea was tapping a mantle source similar to the source Kilauea is tapping today.

Time series analysis

With reliable age information, a relatively long core, such as the HSDP-2 core, becomes a prime source of information for the length scales of heterogeneities in the mantle and the time scales of melting processes. One limitation, however, is the possible presence of hiatuses in the volcanic activity at the location of the drill core. The survival time of volcano surfaces (resurfacing time) is, however, known to be a Poisson process. It has been demonstrated that the ages of Hawaiian surface elements are exponentially distributed with, for Kilauea, a mean resurfacing time of about 500 years [*Holcomb*, 1987], an estimate that also seems to hold for Mauna Loa [*Kauahikaua et al.*, 1995]. The HSDP-2 core counts about 1000 flow units, most of which erupted over a period of about 350 ky, suggesting an average resurfacing time of 350 years, i.e., not very different from estimates for other volcanoes. Assuming time-invariant resurfacing with an exponential distribution of resurfacing times, the number of lava flows within a given time interval Δt is Poisson-distributed with, for Mauna Kea, a mean value of $\Delta t/350$ and a standard deviation of $(\Delta t/350)^{1/2}$. An estimate of the maximum error on age assignment at the one sigma level for the entire core is therefore on the order of $(1000)^{1/2}*350 \approx 10,000$ years, an uncertainty smaller than that associated with K-Ar ages. Consequently, although basalt production by Mauna Kea probably declined over its lifetime, we can argue that random hiatuses are unlikely to introduce a major bias in the time analysis of the geochemical data.

The ages in the stratigraphic column have been established by fitting the existing Ar-Ar dates [*Sharp et al.,* this volume], which are few and have relatively large error bars. Because the samples are irregularly spaced downcore, we cannot use standard FFT (Fast Fourier Transform) techniques, as interpolation is known to produce spurious peaks. Instead, we used the method of periodograms specifically designed for unevenly spaced data [*Lomb,*

1976; *Scargle, 1982; Albarède,* 1995*; Abouchami et al.*, 2000] and which is nothing more but a fit of the data by a periodic function of prescribed frequency. For the purpose of not creating spurious peaks at very low frequencies, an appropriate background (i.e., the secular trend) must first be removed. This background was evaluated here by smoothing the data with a Gaussian filter, which is a running mean with weights normally distributed around the point to be smoothed (Figure 9). The standard deviation of 50,000 years chosen here for this filter ensures there is no significant bias in the high-frequency range. Other values of the standard deviation were tested with no or only very little consequence to the well-constrained part of the spectrum, but our option was that peaks beyond 50,000 years are insufficiently constrained within the considered time window and were therefore ascribed to the secular trend. Once normalized to the standard deviation of the analyzed variable, the peak heights can be associated with significance levels allowing for the probability that the peak is not a false alarm to be estimated [*Scargle*, 1982].

Tables 2 and 3 presents the results of the periodogram analysis before and after removal of the secular trend for the isotopic compositions of Hf, Pb, Nd, Sr (Nd and Sr data from *Bryce et al.,* [this volume]), and He (from *Kurz et al.,* [this volume]), for the incompatible element ratios La/Yb (from *Huang and Frey,* [this volume]), Zr/Nb and for alkalinity (both from *Rhodes and Vollinger* [this volume]) in Mauna Kea flows. The results for Pb and Hf isotopic data after removal of the secular trend are shown in Figure 10. These results report the frequency at the peak, the power (height of the peak), the period (one over the frequency), and the confidence level. Only peaks with confidence levels in excess of 50 percent have been considered. As it is clear that some of the peaks are harmonics of lower frequency (longer period) fluctuations, we plotted the base-two logarithm of the peak heights obtained after applying the Gaussian filter (Figure 11). In this base, two peaks differing by one unit are harmonics of each other (multiplication by two). The strongest peaks characterizing the trace element ratios and alkalinity signal are less significant than those characterizing the isotopic ratios, which strongly suggests that melting blurs the signal of source heterogeneity. Two families of peaks emerge that differ by a factor of four and therefore are double harmonics of each other. These two groups of peaks (one at 4,500-5,000

years, the other at 17,000-19,000 years) may not represent fundamental periods but the HSDP-2 core is currently too short to allow for the identification of potentially longer periods. These two groups involve the incompatible element ratios La/Yb and Zr/Nb, ^{87}Sr/^{86}Sr, ^{206}Pb/^{204}Pb, ^{207}Pb/^{206}Pb, ^{208}Pb/^{206}Pb and at a lower confidence level ^{176}Hf/^{177}Hf. In addition to the stable 19,000 years period, the unfiltered data show strong 10 ky peaks consistent with the ^{206}Pb/^{204}Pb peak found by *Abouchami et al.* [2000] on the pilot core and by *Eisele et al.* [this volume] for the HSDP-2 samples, but this feature appears to be an intermediate harmonics that disappears after removal of the secular trend. Slower and very significant fluctuations are observed for ^{207}Pb/^{204}Pb (48,000 years), probably in phase and harmonic relationships with those of Hf (50,500 and 115,000 years) and reproduce the strong peak observed at 48,000 years by Abouchami et al. [2000] on the pilot core. The ^{208}Pb*/^{206}Pb* peak has a low confidence level (0.59) and its position moves from 714,000 to 96,000 upon removal of the secular component (Tables 2 and 3). Neither ^{3}He/^{4}He nor ε_{Nd} variations seem to have a periodic component in that time window. Input of the K/L component does not seem to be a periodically recurring phenomenon.

The size of mantle heterogeneities

With rare exceptions [*Nataf and VanDecar*, 1993], plume conduits away from ridge axes are too thin to be observed by seismic waves. It is usually assessed that an upper limit of the conduit diameter is the Fresnel zone of body seismic waves, i.e., the interval between two objects that scattering at the P and S wavelengths does not allow to separate. It is therefore assumed that plume conduits must be narrower than this wavelength, i.e., on the order of a few tens of kilometers, a diameter confirmed by geodynamic modeling [*Loper and Stacey,* 1983*; Olson et al.,* 1993].

The shape and volume of the mantle source in the plume conduits that Hawaiian volcanoes actually tap is unclear. Consequently, the shape of isotopic heterogeneities becomes relevant to the interpretation of their record in volcanic time series. *Ribe and Christensen* [1999] assumed that melt is extracted vertically at steady-state and considered that, when moving across the plume conduit over their lifetime (approximately 1 My), Hawaiian

volcanoes tap a disk-shaped volume centered on the summit. They estimated the instantaneous eruption rate Q_e as the integral of the melt supply rate $q\,(x,y)$ of the plume conduit over the area of a disk of radius r as:

$$Q_e\left(t\right) = \frac{1}{\rho_c} \int_{C(r)} q\left(x + Vt, y\right) dx\, dy$$

where x is the coordinate on the lithosphere along the volcanic chain axis, y the transverse coordinate, V the plate velocity, and ρ_c the basalt density. They determined that a value of $r = 33.6$ km accounts for the typical volume of a single volcano. We can likewise determine the instantaneous concentration of a particular element in the erupted lava as:

$$C_e\left(t\right) = \frac{1}{\rho_c Q_e\left(t\right)} \int_{C(r)} q\left(x + Vt, y\right) C\left(x + Vt, y\right) dx\, dy$$

This complex formula expresses the rather trivial statement that a basalt has the composition of its constitutive melt packets weighted by their respective sizes. The model used by *DePaolo et al.* [2001] uses a geometry similar to that of *Ribe and Christensen* [1999] and a steady-state melting column to constrain the melt supply rate $q(x,y)$ and then inverts the set of geochemical data on Hawaiian volcanoes to produce $C(x,y)$ maps and their isotopic analogs. Both *Ribe and Christensen* [1999] and *DePaolo et al.* [2001] therefore assume that the geochemical cross section of the plume conduit is time invariant. A similar assumption was used by *Eisele et al.* [this volume] to model their time-series of Pb isotopes: these authors view heterogeneities as very long filaments stretched parallel to the plume axis such that fluctuating isotopic compositions exclusively reflect the density of filaments across the plume conduit.

However, whether volcanic successions record a horizontal compositional gradient across the plume conduit at the successive locations of the volcano summit or vertical heterogeneities in the plume conduit is arguable (Figure 12). If we ignore the upward broadening of the plume conduit, the equation for advective transport in two dimensions can be formulated as

$$\frac{\partial C}{\partial t} = -V \frac{\partial C}{\partial x} - v_z \frac{\partial C}{\partial z}$$

18

where v_z is the upwelling velocity. For a hot spot the strength of Hawaii, modeling predicts centerline vertical velocities of about 1 m/y [*Loper and Stacey*, 1983; *Olson et al.*, 1993; *Schubert et al.*, 2001], which indicates that the vertical component of heterogeneity gradients cannot be neglected with respect to the radial components. Two factors will therefore contribute to increase the relative importance of the second term on the right-hand side of the above equation with respect to the first term: (i) the plate velocity V is likely to be smaller than the upwelling velocity v_z, and (ii) cross sectional heterogeneities (as measured by $\partial C/\partial x$) will be horizontally averaged by magma extraction.

The size and shape distribution of heterogeneities is largely unknown since numerical experiments of continuum mechanics, such as those used by *Farnetani and Richards* [1995], *Ribe and Christensen* [1999], and *Farnetani et al.* [2002] must mesh the mantle using elements with a dimension still fairly coarse (10-20 km) with respect to the radius of the conduit and the source disk. Stretching in plume conduits is, however, potentially significant, although far less important than in plume heads [*Farnetani et al.,* 2002]. With stretching simply reflecting velocity gradients, its effect on bulk compositions is minimized by the mere fact that the very slow outer conduit layers will have a very small contribution to the overall material budget of the plume. The reason why heterogeneities stretched along the conduit walls are unlikely to contribute significantly to the magma budget is the same as that accounting for the apparent lack of entrained upper mantle in the source of hot spot basalts [*Farnetani and Richards*, 1995; *Ribe and Christensen,* 1999]: temperature dependence of viscosity in a strong temperature gradient confines plume flow to a well-defined high-velocity conduit with a rather sharp, efficiently 'lubricated' edge, and with piston flow as the best analogue. We do not claim here that the plume-conduit cross section is geochemically homogeneous ('striped' plume), and the very existence of contrasting Kea and Loa trends is there to illustrate it. However, ignoring the vertical component of heterogeneities along the conduit is bound to result in inadequate description of the plume.

If the observed peaks in our periodograms (Figure 11) are fundamental and not harmonic modes of much slower fluctuations, they may be taken as indicating that the

diameter of the mantle plume is at least on the order of a few kilometers to a few tens of kilometers. *Davies* [1988; 1999] and *Sleep* [1990] argued that the Hawaiian swell, i.e., the area of shallower seafloor depth around the hotspot, is due to upwelling of hot and therefore light material. In contrast, *Phipps Morgan* et al. [1995] argued that a large part of the buoyancy flux may be due to the depletion of the upwelling material. From the geometry of the Hawaiian swell and the assumption that the excess buoyancy is entirely of thermal origin, the flux of plume material Q_p was inferred to range from 7.5 km^3/y [*Davies*, 1988] to 9.5 km^3/y [*Sleep*, 1990], which *Ribe and Christensen* [1999] reduced to less than 4 km^3/y. The magma production of the recent Hawaiian volcanoes is of about 0.1-0.2 km^3/y [*Swanson*, 1972; *Clague and Dalrymple*, 1987; *Moore*, 1987; *Watts and ten Brink*, 1989] but may drop to a mean value of 0.03 km^3/y or less when integrated over the entire volcanic chain [*Clague and Dalrymple*, 1987; *Davies*, 1999]. Such a value corresponds to 1-5 percent of the hotspot upwelling rate, a number consistent with the degrees of melting inferred from petrological and geochemical arguments.

For isotopic fluctuations modulated by plume flux, it is possible to evaluate the amount of plume material upwelling between two surges of a particular component and elaborate on characteristic length scales associated with isotopic heterogeneities. Hafnium isotope and ^{207}Pb/^{204}Pb fluctuations come in 'cycles' of $T = 50,500$ years and therefore, using *Ribe and Christensen's* [1999] value of 4 km^3/y, are associated with packets of mantle with a volume $\Delta V = Q_p\,T$ (Figure 13) of about 202,000 km^3. The range of plume conduit radii and upwelling velocities must be consistent with continuum mechanics constraints [*Schubert et al.*, 2001]. If we assume a maximum radius R of the hotspot conduit of about 50 km (as suggested by the width of the Fresnel zone of P and S waves), the layers with a same mean isotope composition must be separated by an interval $\Delta l = \Delta V /4\pi R^2$ of about 6.5 km and the upwelling velocity $v_z = \Delta l /T$ must be 13 cm/y. Such a low velocity is equivalent to the plate velocity and therefore is at odds with the apparent fixity (or near fixity) of the Hawaiian hot spot over most of the Cenozoic. With a conduit radius $R = 10$ km, the separation Δl would increase to 160 km and the upwelling velocity v_z to 3 m/y, a value more consistent with the

hot spot remaining fixed in the upper mantle circulation. All these results are contingent on the assumption that we successfully identified the fundamental mode and not the harmonics: if, as suggested by *Eisele et al.* [this volume], the strongest Pb isotope period is 100 ky rather than 50 ky, the length scale of heterogeneities should be modified accordingly. Only future deepening of the HSDP-2 drill hole may resolve this ambiguity.

Appendix A: Evidence for Pb isotope fractionation on anion-exchange columns in HCl medium

This experiment was designed to elucidate whether incomplete yields of Pb elutions can account for significant isotope fractionation during chemical processing of samples. Twenty micrograms of NIST 981 Pb standard were evaporated, loaded in 2.5 N HCl on 1ml AG1-X8 200-400 mesh anion-exchange resin, and then eluted with the same acid. The ^{208}Pb signal and the Pb isotopic composition of each fraction were measured on the Plasma 54. We found that ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb were fractionated by several permil across the elution peak (Figure 14) and that isotopic fractionation was mass dependent (Figure 15). We used the same procedure, essentially a fit of the elution curve of each isotope by an error function, as in *Maréchal and Albarède* [2002], to retrieve the partition coefficient of each isotope. We found that a partition coefficient of 30, which is consistent with the classical results of *Kraus and Nelson* [1956], and a variation of the partition coefficients of 40 ppm per mass unit account extremely well for the observed results. We then integrated the isotopic ratios of the individual fractions collected up to a certain yield (Figure 16) in order to evaluate the potential isotopic bias introduced by incomplete recovery of sample Pb.

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Figure Captions

Figure 1. Downhole Pb isotopic variations for HSDP-2 as measured by the thallium-spike method using MC-ICP-MS (Plasma 54). Except for ^{207}Pb/^{204}Pb, the analytical uncertainties are smaller than the size of the symbols. Overall good overlap and comparable downcore variations with the triple-spike TIMS data from *Eisele et al.* [this volume] (open circles) are demonstrated between the two data sets with the exception of ^{207}Pb/^{204}Pb. ^{208}Pb*/^{206}Pb* ratios were calculated by removing primordial lead from the ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios.

Figure 2. Variations in ε_{Hf} with depth for Mauna Loa (ML) and Mauna Kea (MK) HSDP-2 lavas. Replicate analyses as listed in Table 1 are all shown individually.

Figure 3. Compared variations in alkalinity (a) and ε_{Hf} (b) with depth for Mauna Loa and Mauna Kea HSDP-2 lavas. Replicate analyses plotted as single mean values. Alkalinity from *Rhodes and Vollinger* [this volume]. The K/L group of mid-depth Mauna Kea defined on the basis of its Pb isotopic composition (see text for explanation) is shown with a bull's-eye symbol. Breaks in Hf isotopic composition that exceed error bars (five in total) are shown with open symbols in panel b. Panel b also traces with solid lines the Hf isotopic variation in the HSDP pilot hole [*Blichert-Toft and Albarède*, 1999] for purpose of comparison between the two cores. Between 500 and 750 mbsl, ε_{Hf} in HSDP-2 is higher by about 0.5 epsilon units relative to the pilot hole. Another difference between the two cores in the Mauna Kea section is observed in the depth interval leading up to the contact with Mauna Loa, where HSDP-2 displays Hf isotopic compositions intermediate between those of Mauna Kea and Mauna Loa, whereas, in the pilot hole, Hf becomes very radiogenic and shows a sharp discontinuity with respect to Mauna Loa. By contrast, the Mauna Loa Hf isotopic signatures are identical for the pilot core and the HSDP-2 core.

Figure 4. $^{208}Pb/^{204}Pb$ (a) and $^{207}Pb/^{204}Pb$ (b) *vs.* $^{206}Pb/^{204}Pb$ for Mauna Loa and Mauna Kea HSDP-2 lavas. Note the distinct Pb isotopic compositions of Mauna Kea and Mauna Loa volcanoes in both Pb-Pb plots and of the K/L group in $^{208}Pb/^{204}Pb$-$^{206}Pb/^{204}Pb$ space.

Figure 5. 3-D rotated projection of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ shown in two different frozen positions that together illustrate the plane defined by the bulk of Mauna Kea samples and the displacement above this plane of the more alkaline K/L group. We have for better legibility identified intermediate Mauna Kea samples as transitional to the K/L group.

Figure 6. Position of the new Pb and Hf isotopic data on the Hawaiian basalts' mixing hyperbola of *Blichert-Toft et al.* [1999]. Although in general Hawaiian basalts require more than two components to account for their geochemical variations, the Hf-Pb correlation is exceptionally good and well curved. The end-members are best represented by the Koolau and Kilauea basalts. The hyperbolic array allows the ε_{Hf} of the Kilauea end-member and the $^{206}Pb/^{204}Pb$ of the Koolau end-member to be well constrained. Inset: histogram of ε_{Hf} of Pacific MORB [*Chauvel and Blichert-Toft,* 2001; *Sims et al.*, in press; *Blichert-Toft,* unpublished data] and Mauna Kea (this work) which shows that, although E-MORB are undoubtedly present occasionally along the East Pacific Rise, the Pacific lithosphere as a whole remains an unlikely end-member of Hawaiian basalts.

Figure 7. Principal component analysis of isotopic compositions in Mauna Kea basalts. Data from this work for Pb and Hf, from *Bryce et al.* [this volume] for Sr and Nd, and from *Kurz et al.* [this volume] for He. Two components account for more than 70% of the isotopic variability and three components for 84%. The ε_{Hf} and $^{206}Pb/^{204}Pb$ axes essentially lie in the plane of the first two components, which justifies the binary mixing shown in Figure 6. Note also that He and $^{208}Pb*/^{206}Pb*$ are the only coherent systems. This does not reflect a consistency of the U-Th-Pb system with the U-Th-He system (see text) but rather the existence of two separate components with distinct degassing histories.

Figure 8. ^{3}He/^{4}He vs. ^{208}Pb*/^{206}Pb* (a), Nb/Y vs. Zr/Y (b), SiO$_2$ vs. MgO (c), and TiO$_2$ vs. SiO$_2$ (d) for Mauna Loa and Mauna Kea HSDP-2 lavas. Note in particular the positive correlation between ^{3}He/^{4}He and ^{208}Pb*/^{206}Pb*. He isotope data from *Kurz et al.* [this volume] and major and trace element data from *Rhodes and Vollinger* [this volume].

Figure 9. Principle of secular trend removal (example shown is for Hf isotopes). A running average with Gaussian weights is calculated for each point. In the present case (solid line in the upper panel), we used a standard deviation of 50,000 years. The top panel shows the residues after removal of the secular trend. This procedure tends to remove the low frequencies for which the periodic character cannot safely be established.

Figure 10. Periodograms of the Hf and Pb isotopic signal after removal of a secular trend by running a Gaussian filter with a 50,000 years standard deviation. The peaks are labeled with the period (frequency $^{-1}$) and, in parentheses, the significance level (levels smaller than 50% are not shown).

Figure 11. Peaks of the periodograms for isotopic ratios, two critical incompatible element ratios, and alkalinity ordered by increasing period. A secular trend with a period of 50,000 yeras was removed (Tables 2 and 3). The vertical scale is the base-two logarithm of the period in ka so that harmonics of the same fundamental period differ by exactly one unit. It is highly likely that the groups at 4800 ka and the group at 19 ka are in a harmonic relationship. The intermediate harmonics at ca. 10,000 a is present in the unfiltered data (see also *Abouchami et al.,* [2000]). The 50 ka group is present in both the filtered and unfiltered data (see Tables 2 and 3 and *Abouchami et al.,* [2000]). It is highly significant but longer periods are only marginally sampled.

Figure 12. Relationship between upwelling in the hotspot conduit, plate velocity, and source sampling by melting and eruptions. Models such as those used by *Ribe and Christensen* [1999] and *DePaolo et al.* [2001] assume a time-invariant geochemical cross section of the

conduit (left). A disk represents the surface over which melt is collected by the activity of a single volcano. In such a case, time series reveal the horizontal geochemical gradients across the conduit integrated over the collected area. For high upwelling rates, however, the vertical component of heterogeneities cannot be neglected (right). Although the actual situation may be a combination of the two models, the vertical component of plume heterogeneity is likely to be very significant.

Figure 13. Cartoon illustrating the relationship between the hotspot conduit and the volcanic islands. R is the radius of the conduit, v_z is the upwelling velocity. Δl is the height of the mantle column and ΔV is the volume of mantle rising in the conduit during the time corresponding to the recurrence of isotopic patterns.

Figure 14. Elution of NIST 981 Pb standard through an anion-exchange resin AG1-X8 (200-400 mesh) in 2.5 N HCl medium. Left: elution data for ^{208}Pb (open symbols) and fit by a Gaussian curve [*Maréchal and Albarède*, 2002]. Right: deviation of the ^{208}Pb/^{204}Pb ratio in each fraction with respect to the mean value. Solid line: fit using a resin/solution Pb partition coefficient of 30 and a difference of 40 ppm per mass unit of the partition coefficients between the two isotopes.

Figure 15. Mass dependence of the mass fractionation upon elution of Pb on AG1-X8 resin in 2.5 N HCl medium. Numbers refer to the order of eluted fractions. The observed slope (1.44) is only slightly higher than the theoretical slope of ln (208/204)/ln(207/204) = 1.33.

Figure 16. Potential mass fractionation resulting from incomplete yield of Pb extraction chemistry.

Table 1. Hf and Pb isotope compositions of Mauna Loa and Mauna Kea samples from the HSDP-2 core.

Sample name	mbsl	^{176}Hf/^{177}Hf	ε_{Hf}	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb
Mauna Loa						
SR0008-2.70	9.5	0.283051 ± 6	9.9	18.0923	15.4621	37.8526
		0.283059 ± 7	10.1	18.0978	15.4673	37.8667
SR0023-2.90	34.0	0.283058 ± 8	10.1	18.0841	15.4701	37.9204
		0.283064 ± 7	10.3	18.0728	15.4463	37.8387
SR0031-0.50	45.5	0.283077 ± 9	10.8	18.0948	15.4592	37.8257
		0.283083 ± 7	11.0			
SR0036-1.22	53.5	0.283086 ± 7	11.1	18.1248	15.4827	37.9123
		0.283085 ± 8	11.1	18.1174	15.4580	37.8290
SR0040-1.07	59.5	0.283070 ± 9	10.5	18.1152	15.4698	37.8704
		0.283087 ± 7	11.1	18.1262	15.4683	37.8483
SR0046-1.15	68.7	0.283091 ± 6	11.3	18.0831	15.4498	37.8039
				18.0950	15.4514	37.7984
SR0057-3.00	85.9	0.283087 ± 6	11.1	18.1662	15.4647	37.8855
SR0061-0.00	91.2	0.283087 ± 7	11.1	18.1332	15.4591	37.8716
SR0066-0.00	98.8	0.283096 ± 8	11.5	18.2433	15.4742	37.9572
				18.2316	15.4635	37.9419
SR0080-0.35	125.4	0.283084 ± 6	11.0	18.2230	15.4644	37.9462
SR0083-7.85	137.0	0.283088 ± 7	11.2	18.2063	15.4575	37.9125
SR0089-1.15	149.9	0.283087 ± 7	11.1	18.1591	15.4605	37.9147
SR0093-6.55	163.3	0.283088 ± 5	11.2	18.2469	15.4603	37.9569
SR0098-2.00	177.8	0.283108 ± 6	11.9	18.2516	15.4666	37.9674
		0.283115 ± 10	12.1			
SR0104-4.95	197.4	0.283074 ± 6	10.7	18.0803	15.4812	37.9174
				18.0614	15.4565	37.8375
SR0109-0.65	209.1	0.283067 ± 5	10.4	18.1263	15.4561	37.8824
SR0113-6.20	222.5	0.283092 ± 5	11.3	18.1798	15.4647	37.9237
SR0117-4.00	233.7	0.283078 ± 6	10.8	18.2166	15.4765	37.9954
SR0120-1.00	242.0	0.283080 ± 8	10.9	18.2505	15.4564	37.9407
				18.2357	15.4531	37.9291
Mauna Kea						
SR0121-4.40	246.2	0.283103 ± 5	11.7	18.4111	15.4825	37.9959
		0.283112 ± 10	12.0	18.4179	15.4822	37.9853
SR0124-3.90	252.9	0.283100 ± 5	11.6	18.4081	15.4774	37.9487
SR0125-6.25	256.5	0.283097 ± 5	11.5	18.4076	15.4936	38.0349
				18.4329	15.4888	38.0079
SR0127-4.75	261.7	0.283104 ± 4	11.7	18.4310	15.4849	38.0095
SR0129-5.20	267.5	0.283126 ± 7	12.5	18.4362	15.4794	37.9970
		0.283126 ± 7	12.5			
SR0131-6.92	274.4	0.283125 ± 5	12.5	18.4413	15.4863	38.0281
		0.283123 ± 8	12.4			
SR0133-8.20	281.3	0.283121 ± 5	12.3	18.4301	15.4834	37.9918
SR0137-5.98	293.0	0.283109 ± 5	11.9	18.4339	15.4794	37.9807
				18.4343	15.4779	37.9664
SR0141-7.90	305.8	0.283114 ± 5	12.1	18.4465	15.4832	38.0129
SR0148-8.50	326.7	0.283120 ± 6	12.3	18.3848	15.4744	37.9334

SR0157-6.25	353.0	0.283115 ± 6	12.1	18.4432	15.4809	37.9999
SR0167-5.90	378.4	0.283124 ± 5	12.4	18.5383	15.4918	38.0950
				18.5148	15.4749	38.0448
				18.5257	15.4763	38.0499
SR0175-5.25	398.1	0.283120 ± 6	12.3	18.5613	15.4809	38.0864
		0.283119 ± 7	12.3			
SR0184-2.80	421.2	0.283152 ± 6	13.4	18.4785	15.4793	38.0148
SR0193-0.00	443.6	0.283143 ± 8	13.1	18.5331	15.4874	38.0899
SR0205-1.30	467.8	0.283142 ± 8	13.1	18.5456	15.4859	38.1218
SR0212-8.20	490.9	0.283152 ± 8	13.4	18.5606	15.5042	38.1380
				18.5995	15.5036	38.1561
SR0222-2.00	516.2	0.283126 ± 9	12.5	18.5597	15.4957	38.1622
SR0232-8.50	542.1	0.283112 ± 9	12.0	18.5521	15.4870	38.0975
		0.283120 ± 10	12.3			
SR0240-3.30	563.5	0.283148 ± 8	13.3	18.5830	15.4947	38.1510
SR0256-0.95	589.0	0.283123 ± 7	12.4	18.5232	15.4846	38.0821
SR0267-6.85	615.8	0.283134 ± 10	12.8	18.5512	15.5000	38.1292
				18.5485	15.4875	38.1029
SR0276-7.85	636.0	0.283130 ± 7	12.7	18.5315	15.4821	38.0940
SR0284-1.75	658.3	0.283131 ± 7	12.7	18.6343	15.4888	38.1720
		0.283127 ± 10	12.6			
SR0294-7.65	678.6	0.283129 ± 7	12.6	18.5815	15.4917	38.1745
SR0300-6.50	695.9	0.283137 ± 7	12.9	18.5688	15.4873	38.1300
SR0311-4.40	724.1	0.283131 ± 7	12.7	18.5409	15.4992	38.1366
SR0328-3.10	759.8	0.283116 ± 8	12.2	18.5164	15.4792	38.0978
SR0340-1.00	793.6	0.283127 ± 6	12.6	18.6117	15.5007	38.1867
SR0346-5.60	812.7	0.283121 ± 8	12.3	18.5245	15.4799	38.1013
SR0354-7.75	833.9	0.283118 ± 10	12.2	18.4280	15.4761	38.0854
SR0372-2.80	871.2	0.283115 ± 6	12.1	18.4967	15.4806	38.0822
SR0379-3.00	888.4	0.283109 ± 5	11.9	18.4560	15.4801	38.0769
SR0392-4.30	921.8	0.283120 ± 7	12.3	18.4979	15.4818	38.0929
				18.4971	15.4912	38.1095
SR0401-2.85	948.9	0.283115 ± 8	12.1	18.4908	15.4857	38.1022
SR0413-3.10	984.2	0.283137 ± 6	12.9	18.4872	15.4936	38.1349
SR0423-3.65	1012.4	0.283129 ± 7	12.6	18.5806	15.4867	38.1432
SR0432-8.50	1037.7	0.283111 ± 7	12.0	18.5307	15.4836	38.1374
SR0441-9.10	1061.2	0.283121 ± 8	12.3	18.4716	15.4825	38.1142
SR0450-3.55	1083.7	0.283117 ± 7	12.2	18.5073	15.4788	38.0710
SR0455-7.40	1098.2	0.283137 ± 9	12.9	18.5431	15.4893	38.1249
SR0472-1.00	1123.2	0.283123 ± 9	12.4	18.4646	15.4846	38.0761
				18.4590	15.4805	38.0738
SR0490-1.50	1229.6	0.283131 ± 7	12.7	18.4918	15.4841	38.1026
SR0502-4.85	1265.2	0.283123 ± 8	12.4	18.5486	15.4778	38.1009
SR0518-0.80	1311.9	0.283120 ± 8	12.3	18.4728	15.4688	38.0615
SR0531-4.40	1352.6	0.283117 ± 8	12.2	18.4417	15.4805	38.1187
SR0545-8.35	1395.0	0.283123 ± 8	12.4	18.4453	15.4808	38.1190
SR0548-8.00	1404.1	0.283118 ± 7	12.2	18.4968	15.4851	38.1105
SR0560-7.50	1435.4	0.283140 ± 8	13.0	18.4491	15.4839	38.1293
SR0574-1.90	1474.7	0.283127 ± 8	12.6	18.6213	15.4880	38.1871
SR0582-10.00	1497.7	0.283140 ± 7	13.0	18.6259	15.4905	38.1946
SR0594-8.70	1521.4	0.283132 ± 10	12.7	18.6116	15.4773	38.1542
SR0603-8.90	1548.2	0.283152 ± 8	13.4	18.5296	15.4908	38.1358
SR0604-2.50	1549.3	0.283140 ± 8	13.0	18.5107	15.4797	38.1008

SR0622-7.10	1581.2	0.283129 ± 7	12.6	18.5595	15.4871	38.1476
SR0630-6.20	1605.0	0.283119 ± 6	12.3	18.5710	15.4984	38.1642
SR0641-1.00	1636.3	0.283114 ± 6	12.1	18.4958	15.4943	38.1301
SR0655-4.00	1678.7	0.283123 ± 9	12.4			
SR0664-5.10	1705.5	0.283108 ± 6	11.9	18.5485	15.4923	38.1358
SR0675-6.90	1739.3	0.283115 ± 8	12.1	18.4422	15.4775	38.1174
SR0683-5.75	1763.2	0.283120 ± 8	12.3			
SR0694-9.00	1794.8	0.283134 ± 9	12.8	18.5944	15.4980	38.1775
SR0705-0.15	1823.2	0.283104 ± 10	11.7	18.4876	15.4756	38.0859
		0.283090 ± 6	11.2			
		0.283087 ± 6	11.1			
SR0709-13.35	1852.0	0.283129 ± 16	12.6	18.5846	15.4889	38.1642
		0.283130 ± 9	12.7			
SR0714-11.55	1883.6	0.283111 ± 10	12.0	18.5842	15.4951	38.1807
SR0720-18.25	1921.6	0.283112 ± 16	12.0			
		0.283107 ± 8	11.8			
SR0723-13.70	1933.8	0.283129 ± 8	12.6	18.5306	15.4892	38.1467
SR0732-1.10	1973.8	0.283103 ± 9	11.7	18.4544	15.4813	38.2007
SR0741-7.90	2009.8	0.283105 ± 11	11.8	18.4569	15.4833	38.1994
		0.283107 ± 5	11.8			
SR0750-12.45	2062.7	0.283102 ± 14	11.7	18.4539	15.4840	38.1903
		0.283095 ± 8	11.4	18.4542	15.4846	38.2035
SR0756-13.25	2098.6	0.283094 ± 20	11.4	18.4304	15.4746	38.1671
		0.283098 ± 10	11.5			
SR0762-4.60	2123.7	0.283108 ± 11	11.9	18.4486	15.4810	38.1835
		0.283105 ± 5	11.8			
SR0768-11.20	2157.4	0.283108 ± 8	11.9	18.5411	15.4841	38.1475
SR0776-17.70	2209.5	0.283119 ± 6	12.3	18.5213	15.4836	38.1237
SR0778-3.20	2218.2	0.283117 ± 5	12.2	18.5386	15.4888	38.1400
SR0780-20.80#	2236.7	0.283115 ± 6	12.1			
SR0791-9.50	2280.2	0.283116 ± 10	12.2	18.4897	15.4703	38.1638
		0.283113 ± 5	12.1			
SR0792-6.20#	2285.2	0.283104 ± 6	11.7			
SR0796-6.70	2300.2	0.283116 ± 8	12.2			
SR0800-13.20	2321.6	0.283113 ± 11	12.1	18.5128	15.4895	38.2212
		0.283110 ± 6	12.0			
SR0807-3.70#	2340.7	0.283102 ± 6	11.7			
SR0814-14.40	2357.0	0.283111 ± 7	12.0			
		0.283104 ± 7	11.7			
SR0822-3.40#	2383.2	0.283099 ± 6	11.6			
SR0826-20.60	2414.1	0.283096 ± 9	11.5			
		0.283099 ± 7	11.6			
SR0836-5.80	2467.3	0.283113 ± 10	12.1	18.4991	15.4892	38.2087
SR0842-2.35	2503.5	0.283106 ± 9	11.8	18.4766	15.4980	38.1988
SR0846-2.80	2525.4	0.283133 ± 11	12.8	18.5675	15.4912	38.1635
		0.283124 ± 6	12.4			
		0.283113 ± 7	12.1			
SR0850-5.95	2550.9	0.283115 ± 8	12.1	18.6762	15.4986	38.2483
		0.283118 ± 5	12.2	18.6697	15.4956	38.2411
				18.6653	15.4928	38.2366
SR0855-0.10	2581.8	0.283128 ± 8	12.6	18.6438	15.4968	38.2395
SR0860-8.10	2615.0	0.283118 ± 9	12.2	18.5042	15.4851	38.1511
SR0871-13.00	2654.1	0.283116 ± 11	12.2	18.4512	15.4816	38.1928

SR0891-15.10	2730.2	0.283117 ± 11	12.2	18.5754	15.4940	38.1846
		0.283113 ± 6	12.1			
SR0896-2.40	2759.3	0.283108 ± 5	11.9	18.5083	15.4892	38.1430
SR0899-2.45	2770.9	0.283106 ± 12	11.8	18.5065	15.4889	38.1435
		0.283107 ± 6	11.8			
SR0907-1.65	2789.9	0.283103 ± 8	11.7	18.5111	15.4963	38.1538
SR0913-2.40	2825.8	0.283118 ± 9	12.2	18.5482	15.4881	38.1818
SR0916-1.15	2837.6	0.283126 ± 9	12.5	18.6044	15.4909	38.1760
SR0930-15.85	2919.5	0.283120 ± 14	12.3	18.5124	15.4890	38.1316
		0.283117 ± 10	12.2			
		0.283109 ± 8	11.9			
SR0939-18.10	2961.0	0.283124 ± 9	12.4	18.6031	15.4836	38.1642
SR0940-18.35	2967.8	0.283102 ± 8	11.7	18.4999	15.4777	38.1908
SR0954-8.00	3009.2	0.283118 ± 15	12.2	18.6272	15.5093	38.2191
		0.283118 ± 11	12.2	18.5967	15.4810	38.1506
				18.6060	15.4821	38.1556
SR0956-18.35	3019.0	0.283122 ± 8	12.4	18.4920	15.4764	38.1269
SR0964-4.30	3058.0	0.283121 ± 8	12.3			
SR0967-2.75	3068.9	0.283104 ± 9	11.7	18.4960	15.4847	38.1082
				18.4899	15.4826	38.1075

HSDP pilot hole: Mauna Kea replicates*

R431-3.70 A	954.9	0.283118 ± 12	12.2 (11.8)*			
R442-2.10 A	983.9	0.283109 ± 8	11.9 (12.2)*			
R446-2.40 A	994.7	0.283120 ± 7	12.3 (12.3)*			
R463-6.00 A	1043.7	0.283102 ± 10	11.7 (11.7)*			

mbsl = meters below sea level.

Hf and Pb isotopic compositions measured by MC-ICP-MS (VG Plasma 54).

^{176}Hf/^{177}Hf normalized for mass fractionation to ^{179}Hf/^{177}Hf = 0.7325. ^{176}Hf/^{177}Hf of JMC-475 Hf standard = 0.28216 ± 0.00001 (i.e., two-sigma external reproducibility = 0.0035% or 35 ppm as also seen from the sample replicate analyses). Hf standard run every second or third sample.

Uncertainties reported on Hf measured isotope ratios are in-run $2\sigma/\sqrt{n}$ analytical errors in last decimal place, where n is the number of measured isotopic ratios.

NBS 981 Pb standard run after every two samples. The 2 sigma standard error on NBS 981 on a typical day of analysis was 142, 120 and 125 ppm , respectively, for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb. Average individual errors on Pb isotopic analyses (two standard deviations) were 0.0048 for ^{205}Tl/^{203}Tl, 0.0204 for ^{208}Pb/^{204}Pb, 0.0186 for ^{207}Pb/^{204}Pb, and 0.0190 for ^{206}Pb/^{204}Pb. Reproducibility of replicate analyses, including leaching, was 0.6 permil (relative difference) or 0.025 for ^{208}Pb/^{204}Pb, 0.008 for ^{207}Pb/^{204}Pb, and 0.010 for ^{206}Pb/^{204}Pb.

Hand-picked glass as opposed to the rest of the samples which are powders from the standard geochemical reference sample set.

* Original analyses published in *Blichert-Toft and Albarède* [1999]. Numbers in parentheses correspond to original values.

Table 2: Most significant peaks of the Lomb periodograms *before* removal of the secular trend.

Ratio	Freqency (ka^{-1})	Power	Period T (ka)	Confidence level	Log$_2$ T	Data Source
La/Yb	0.2241	6.8	4.46	0.873	2.16	[1]
La/Yb	0.2208	6.8	4.53	0.879	2.18	[1]
ε_{Hf}	0.2130	5.4	4.69	0.574	2.23	[2]
^{87}Sr/^{86}Sr	0.2027	6.5	4.93	0.849	2.30	[3]
^{87}Sr/^{86}Sr	0.1994	6.4	5.02	0.825	2.33	[3]
^{87}Sr/^{86}Sr	0.1247	5.4	8.02	0.602	3.00	[3]
Zr/Nb	0.1202	5.6	8.32	0.635	3.06	[4]
^{206}Pb/^{204}Pb	0.0998	6.8	10.0	0.879	3.32	[2]
^{207}Pb/^{206}Pb	0.0998	6.9	10.0	0.896	3.32	[2]
^{207}Pb*/^{206}Pb*	0.0997	7.0	10.0	0.900	3.33	[2]
La/Yb	0.0935	5.6	10.7	0.658	3.42	[1]
Zr/Nb	0.0933	6.3	10.7	0.803	3.42	[4]
^{208}Pb/^{206}Pb	0.0522	5.4	19.2	0.618	4.26	[2]
^{206}Pb/^{204}Pb	0.0521	5.6	19.2	0.651	4.26	[2]
^{207}Pb/^{206}Pb	0.0520	6.4	19.2	0.823	4.27	[2]
^{207}Pb*/^{206}Pb*	0.0519	6.9	19.3	0.892	4.27	[2]
^{207}Pb/^{204}Pb	0.0208	9.1	48.1	0.988	5.59	[2]
ε_{Hf}	0.0198	6.0	50.5	0.741	5.66	[2]
ε_{Hf}	0.0087	7.8	114.9	0.951	6.84	[2]
ε_{Nd}	0.0083	5.1	120.5	0.526	6.91	[2]
Zr/Nb	0.0066	9.4	151.5	0.990	7.24	[4]
^{208}Pb/^{204}Pb	0.0052	11.6	192.3	0.999	7.59	[2]
Zr/Nb	0.0025	6.8	400	0.874	8.64	[4]
ε_{Hf}	0.0023	12.1	435	0.999	8.76	[2]
^{208}Pb*/^{206}Pb*	0.0014	16.0	714	1.000	9.48	[2]
^{3}He/^{4}He	0.0009	15.3	1111	1.000	10.12	[5]
ε_{Nd}	0.0001	9.6	10000	0.993	13.29	[2]
^{208}Pb/^{204}Pb	0.0001	27.8	10000	1.000	13.29	[2]
^{207}Pb/^{206}Pb	0.0001	5.3	10000	0.578	13.29	[2]
^{207}Pb*/^{206}Pb*	0.0001	5.4	10000	0.605	13.29	[2]
alkalinity	0.0001	10.5	10000	0.997	13.29	[4]
La/Yb	0.0001	22.5	10000	1.000	13.29	[1]

[1] *Huang and Frey* [this volume] [2] this work [3] *Bryce et al.* [this volume] [4] *Rhodes and Vollinger* [this volume] [5] *Kurz et al.* [this volume]

Table 3: Most significant peaks of the Lomb periodograms *after* removal of the secular trend by running a Gaussian filter with a standard deviation of 50,000 years. See Table 2 for the source of data.

Ratio	Freqency (ka^{-1})	Power	Period T (ka)	Confidence level	Log$_2$ T
La/Yb	0.2276	5.41	4.39	0.590	2.13
La/Yb	0.2210	6.28	4.52	0.803	2.18
ε_{Hf}	0.2131	5.60	4.69	0.644	2.23
$^{87}Sr/^{86}Sr$	0.2026	6.87	4.94	0.888	2.30
$^{87}Sr/^{86}Sr$	0.1995	7.69	5.01	0.949	2.32
$^{208}Pb/^{206}Pb$	0.1598	5.26	6.26	0.559	2.65
$^{207}Pb/^{206}Pb$	0.0632	5.11	15.82	0.507	3.98
La/Yb	0.0587	5.74	17.04	0.686	4.09
Zr/Nb	0.0585	5.96	17.09	0.737	4.10
$^{206}Pb/^{204}Pb$	0.0528	6.73	18.94	0.875	4.24
$^{207}Pb/^{206}Pb$	0.0526	7.58	19.01	0.944	4.25
$^{207}Pb*/^{206}Pb*$	0.0524	8.14	19.08	0.968	4.25
$^{208}Pb/^{206}Pb$	0.0523	6.60	19.12	0.859	4.26
alkalinity	0.0462	5.62	21.65	0.650	4.44
$^{207}Pb/^{204}Pb$	0.0208	9.93	48.08	0.995	5.59
ε_{Hf}	0.0198	6.38	50.51	0.818	5.66
alkalinity	0.0174	5.73	57.47	0.680	5.84
ε_{Hf}	0.0129	5.40	77.52	0.585	6.28
$^{208}Pb*/^{206}Pb*$	0.0104	5.37	96.15	0.593	6.59
ε_{Hf}	0.0087	8.20	114.9	0.968	6.84
Zr/Nb	0.0068	6.63	147.1	0.855	7.20
$^{208}Pb/^{204}Pb$	0.0064	9.88	156.3	0.994	7.29