# Geochemical zoning of volcanic chains associated with Pacific hotspots

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Recent Hawaiian volcanism is manifest as two geographically and geochemically distinct groups of volcanoes[1], the Loa trend in the south and the Kea trend in the north[2,3]. The differences between the Loa and Kea lavas are attributed to spatial variations in the geochemical structure of the underlying Hawaiian mantle plume[4–9]. In turn, the Hawaiian plume structure is thought to reflect heterogeneities in its mantle source[7,8]. Here we compile geochemical data[10] from the Hawaiian and two other volcanic ocean island chains—the Samoan and Marquesas—that formed above mantle plumes upwelling beneath the Pacific plate. We find that the volcanoes at both Samoa[11] and the Marquesas[12] show geographic and geochemical trends similar to those observed at Hawaii. Specifically, two subparallel arrays of volcanoes exist at both locations. In each case, the southern trend of volcanoes has higher radiogenic lead isotope ratios, $^{208}Pb^*/^{206}Pb^*$, and lower neodymium isotope ratios, ε_{Nd}, than those of the corresponding northern trend. We suggest that geochemical zoning may be a common feature of mantle plumes beneath the Pacific plate. Furthermore, we find that the pattern repeats between island chains, with the highest $^{208}Pb^*/^{206}Pb^*$ and the lowest ε_{Nd} found at Samoa in the south and the lowest $^{208}Pb^*/^{206}Pb^*$ and the highest ε_{Nd} observed at Hawaii in the north. We infer that isotopically enriched material is preferentially distributed in the lower mantle of the Southern Hemisphere, within the Pacific low seismic velocity zone.

Although considerable variability exists in the geophysical and geochemical characteristics of hotspots, implying variations in their particular origins, a range of evidence strongly suggests that at least some hotspots are caused by mantle plumes rising from a thermal boundary layer (TBL) at the core–mantle boundary (CMB; refs 13–16). This set of hotspots, which include Hawaii, Samoa and the Marquesas, thus provide an important window into the lowermost mantle.

Hawaiian volcanism (<2 Myr) manifests itself as two subparallel, *en echelon* groups of volcanoes, the Loa (southern) and the Kea (northern) trends[1] (Fig. 1). The formation of *en echelon* volcanic trends at Hawaii has been attributed to the patterns of stress within the lithosphere that develop as a result of volcanic loading following a change in the direction of relative motion between the plate and plume[17,18]. Important geochemical differences in lavas from the two Hawaiian volcanic trends have been documented[2–4,9]. Specifically, Abouchami *et al.*[2] showed that at a given $^{206}Pb/^{204}Pb$, Loa trend lavas have higher $^{208}Pb/^{204}Pb$ than Kea trend lavas. This Pb isotopic difference can be expressed using a combined Pb isotopic ratio, $^{208}Pb^*/^{206}Pb^*$, the ratio of radiogenic ingrowth of ^{208}Pb and ^{206}Pb since the formation of the Earth that measures the time-integrated Th/U (ref. 19). At Hawaii, $^{208}Pb^*/^{206}Pb^*$ is correlated with Sr and Nd isotopic ratios[2,3] and La/Nb (ref. 20), and Loa trend lavas have
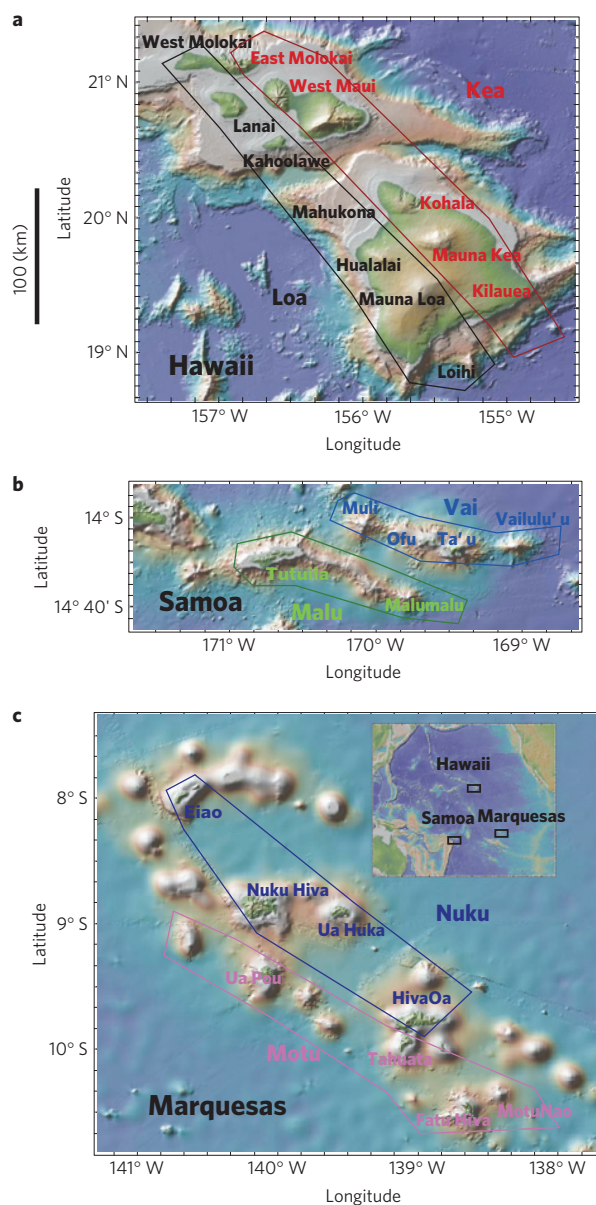
Figure 1 | Maps of Hawaiian, Samoan and Marquesas volcanoes and their positions in the Pacific Ocean.

higher $^{208}Pb^*/^{206}Pb^*$ and lower ε_{Nd} than Kea trend lavas (Fig. 2). This inter-trend difference has been interpreted as reflecting

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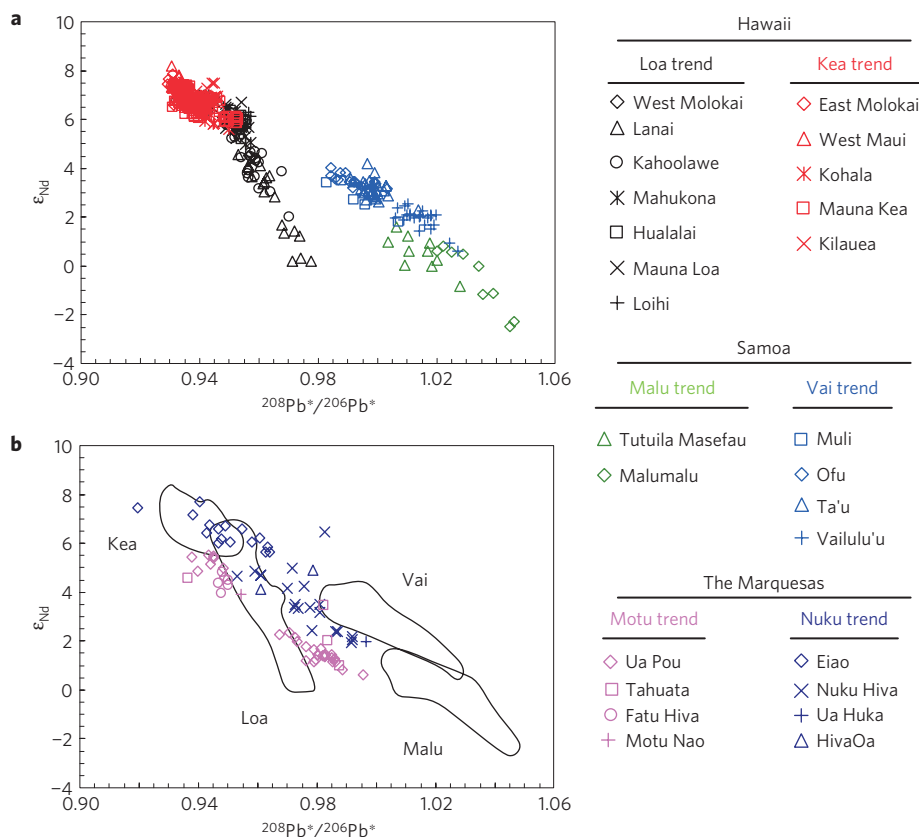
Figure 2 | ^{208}Pb*/^{206}Pb* versus ε_{Nd} for the Pacific hotspot lavas. a, The Hawaiian and Samoan lavas. **b**, The Marquesas lavas compared with the Hawaiian and Samoan lavas. ^{208}Pb*/^{206}Pb* measures the radiogenic ingrowth of ^{208}Pb/^{204}Pb and ^{206}Pb/^{204}Pb since the formation of the Earth, and is defined as [(^{208}Pb/^{204}Pb)$_{sample}$ −(^{208}Pb/^{204}Pb)$_{Earth\ Initial}$]/ [(^{206}Pb/^{204}Pb)$_{sample}$ −(^{206}Pb/^{204}Pb)$_{Earth\ Initial}$], with (^{208}Pb/^{204}Pb)$_{Earth\ Initial}$ = 29.475 and (^{206}Pb/^{204}Pb)$_{Earth\ Initial}$ = 9.307 based on Canyon Diablo Troilite[19]. ε_{Nd} = [(^{143}Nd/^{144}Nd)$_{sample}$/(^{143}Nd/^{144}Nd)$_{CHUR}$ − 1] × 1,000, where (^{143}Nd/^{144}Nd)$_{CHUR}$ = 0.512638 for Nd isotopic measurements normalized to ^{146}Nd/^{144}Nd = 0.7219, and (^{143}Nd/^{144}Nd)$_{CHUR}$ = 0.511836 for Nd isotopic measurements normalized to ^{146}Nd/^{142}Nd = 0.636151. Data sources are in Supplementary Table S1. The analytical uncertainties are in generally smaller than the symbol size.

geochemical structure within the conduit of the Hawaiian plume, and several models of plume structure have been proposed[2,4–8].

Samoan volcanism also forms two subparallel, *en echelon* volcanic trends, known as the Malu (southern) and Vai (northern) trends[21] (Fig. 1). The separation of the Malu and Vai trends is ~50 km, similar to that between the Loa and Kea trends at Hawaii (Fig. 1). Samoan lavas form a negative ^{208}Pb*/^{206}Pb*– ε_{Nd} array, and as at Hawaii, the southern trend (Malu) lavas have higher ^{208}Pb*/^{206}Pb* and lower ε_{Nd} than the northern trend (Vai) lavas (Fig. 2).

The physical pattern of volcanism at the Marquesas is somewhat less well defined than that at Hawaii or Samoa, owing in part to a lack of high-resolution bathymetric data that would better constrain submarine volcanism in the area (Fig. 1). However, the Marquesas volcanoes show a clear geographic–geochemical correlation[12]. This correlation is very similar to that exhibited at both Hawaii and Samoa. In detail, lavas from the southern (Motu) trend of the Marquesas volcanoes (Ua Pou, Tahuata, Fatu Hiva and Motu Nao) have lower ε_{Nd} at a given ^{208}Pb*/^{206}Pb* than lavas from the northern (Nuku) trend (Eiao, Nuku Hiva, Ua Huka, and Hiva Oa; Figs 1 and 2).

The Hawaiian, Marquesas and Samoan hotspots exhibit strikingly systematic geographic–geochemical variations. At an intra-hotspot scale, lavas from the southern trend at each hotspot (Loa at Hawaii, Malu at Samoa, Motu at the Marquesas) have more enriched (higher ^{208}Pb*/^{206}Pb* and lower ε_{Nd}) isotopic compositions than lavas from the respective northern trends (Kea at

Hawaii, Vai at Samoa, Nuku at the Marquesas). At an inter-hotspot scale, the Samoan, Marquesas and Hawaiian hotspots as a whole exhibit trends in isotopic composition that are at least qualitatively consistent with the individual intra-hotspot trends. In particular, ^{208}Pb*/^{206}Pb* increases and ε_{Nd} decreases from north to south in the order of Hawaii–Marquesas–Samoa (Figs 2 and 3). Moving from north to south, these variations imply an increase in the relative proportion of a high-^{208}Pb*/^{206}Pb* and low-ε_{Nd} component at the TBL where these plumes originate (Fig. 3). The high-^{208}Pb*/^{206}Pb* and low-ε_{Nd} isotopic signature at Samoa is likely to reflect a recycled, ancient continental crustal component[11]. At Hawaii, although other interpretations exist[22], the high-^{208}Pb*/^{206}Pb* and low-ε_{Nd} isotopic signature is arguably best explained as reflecting a recycled, ancient oceanic crustal component, including sediments[20,23]. Consequently, we suggest that the high-^{208}Pb*/^{206}Pb* and low-ε_{Nd} components exhibited at Hawaii, Marquesas and Samoa are related to the DUPAL anomaly, a globe-encircling region of isotopic enrichment (high ^{208}Pb*/^{206}Pb*) at the base of the southern hemispheric mantle that is believed to be a heterogeneous assemblage of ancient recycled crustal materials[24]. This is not to say that the Hawaiian, Marquesas and Samoan lavas sample the same high-^{208}Pb*/^{206}Pb* and low-ε_{Nd} component. Rather, the enriched components at these three hotspots have the same isotopic characteristics (high-^{208}Pb*/^{206}Pb* and low-ε_{Nd}), which, together, can be best explained as recycled ancient crustal components.
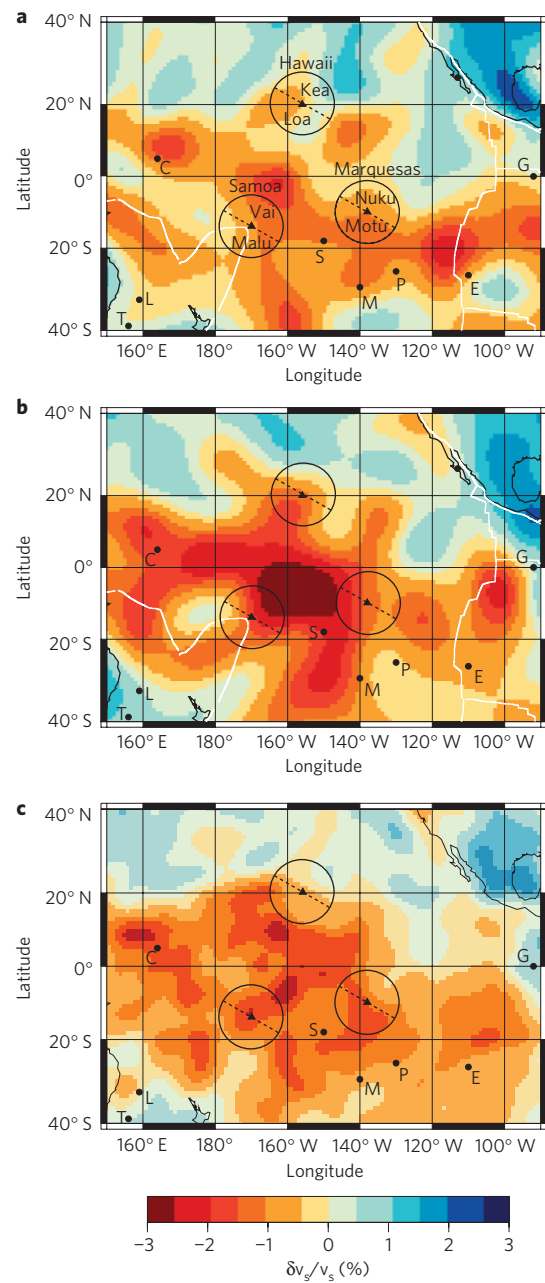
The surface distribution of hotspot lavas characterized by the DUPAL anomaly has been shown to be correlated with the large
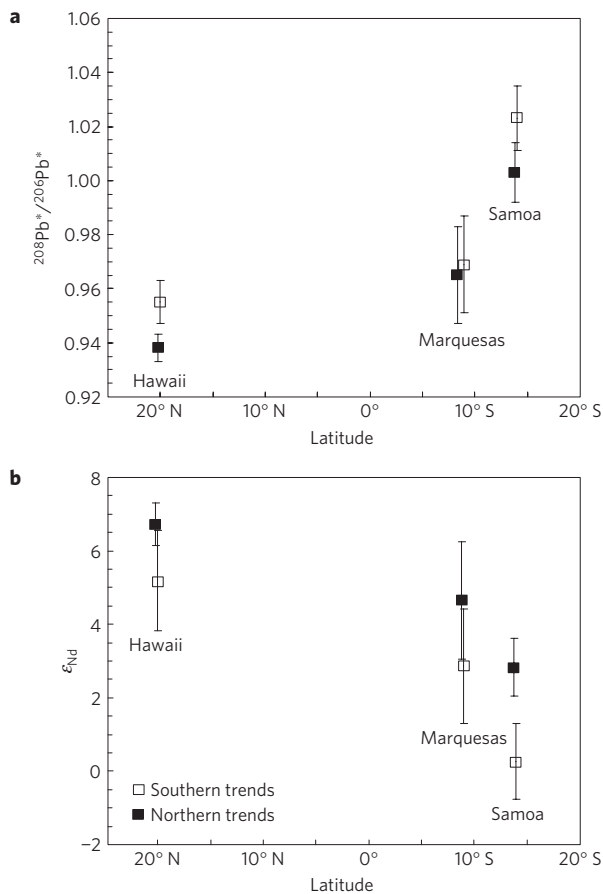
Figure 3 | Geochemical variation of the Hawaiian, Samoan and Marquesas lavas with latitude. a, Average $^{208}Pb*/^{206}Pb*$ versus latitude. **b**, Average ε_{Nd} versus latitude. The bars denote one standard deviation around the averages of the isotopic compositions of lavas from each trends: Kea (179 samples), Loa (100), Vai (63), Malu (19), Nuku (39) and Motu (40) (Supplementary Table S1). Open squares are for southern trends and filled squares for northern trends.

Figure 4 | Samoa, the Marquesas and Hawaii superimposed on maps of seismic shear wave velocity anomalies at 2,800 km depth. Three different shear wave velocity models are shown: **a**, SAW642AN (ref. 29); **b**, S362ANI (ref. 30); and **c**, S40RTS (ref. 31). The location of active volcanism associated with each hotspot is shown as a black triangle. The corresponding region of the TBL at the base of the mantle sampled by each plume (that is, its footprint) is indicated by the circle around each triangle. These circles correspond to a region with a diameter of approximately 1,000 km (ref. 7). The dashed line bisects the circular footprint of each plume to delineate the two distinct regions of the boundary layer sampled by individual volcanic trends at each hotspot (as labelled), consistent with an azimuthal heterogeneity model[7]. At Hawaii and the Marquesas, the region sampled by the southern trend has significantly lower seismic velocities than the region sampled by the northern trend. At Samoa, differences between the two regions are less pronounced. The surface locations of other hotspot volcanism in the vicinity of the Pacific superswell are shown as small black circles for reference and labelled as follows: C—Caroline, E— Easter, G—Galapagos, L—Lord Howe, M—Macdonald, P—Pitcairn, S—Society, T—Tasmanids.

regions of low seismic velocity in the lowermost mantle, commonly called superplumes[25,26]. The three hotspots considered here all overlie the region of low seismic velocity known as the Pacific superplume (Fig. 4). We propose that the observed inter- and intra-hotspot geochemical differences (Figs 2 and 3) at Hawaii, the Marquesas and Samoa reflect their respective positions relative to the Pacific superplume.

Numerical geodynamic modelling studies have demonstrated that compositional heterogeneities embedded within the TBL remain physically distinct, as elongated filaments, as they are drawn in laterally from distances of as much as ∼1,000 km to ascend through the plume conduit[7,8,27]. These studies also suggest that the spatial distribution of heterogeneities within the TBL is preserved in some way within the plume conduit itself. For example, the presence of horizontal layers in the TBL results in a concentrically zoned plume conduit, whereas heterogeneity arrayed azimuthally in the TBL in the vicinity of the plume conduit retains its relative distribution within the plume conduit, resulting in azimuthal zoning of the plume conduit that echoes the TBL (Fig. 8 of Farnetani and Hofmann[7]). At an inter-hotspot scale, the Hawaiian and Marquesas plume conduits are both situated at the edge of the Pacific superplume, whereas the Samoan plume conduit lies closer to its centre (Fig. 4). Assuming the low velocity anomaly is associated with enriched mantle, that is, the DUPAL anomaly[25], then the Hawaiian plume would sample the least amount of

enriched mantle overall whereas the Samoan plume would sample the greatest relative proportion of enriched mantle, with the Marquesas falling somewhere in between. This interpretation is thus consistent with the overall trend of isotopic enrichment from Hawaii to the Marquesas to Samoa (Fig. 3).

At an intra-hotspot scale, the distributions of geochemical heterogeneity at the base of the Hawaiian and Marquesas plume conduits, as defined by seismic velocity anomalies, are azimuthally arrayed (Fig. 4), similar to that in Fig. 8c of Farnetani and Hofmann[7]. In particular, the southern half of the base of the plume conduit lies within the region of low seismic velocity associated with the Pacific superplume whereas the northern half does not (Fig. 4). The distribution of heterogeneity in the TBL would result in bilaterally zoned plume conduits at both Hawaii and the Marquesas (Fig. 8c,d of Farnetani and Hofmann[7]), with the southern halves of the Hawaiian and Marquesas plume conduits containing greater percentages of mantle derived from the region of low seismic velocity (that is, the enriched, high $^{208}Pb^*/^{206}Pb^*$ and low ε_{Nd}, mantle component) than the northern halves (Figs 2, 4). Such a bilaterally zoned plume model has previously been proposed for the Hawaiian plume[2], although the Pacific superplume was not identified as the source of the zoning.

At Samoa, the picture is somewhat more complicated. As shown in Fig. 4, the northern half of the plume conduit samples a region of lower seismic velocity than does the southern half. As before, assuming low seismic velocities correspond to the enriched mantle component, this would be expected to result in an azimuthally zoned plume conduit in which the northern (Vai) trend lavas have a more enriched (higher $^{208}Pb^*/^{206}Pb^*$ and lower ε_{Nd}) isotopic signature than the southern (Malu) trend lavas. However, this is the opposite of the observed intra-hotspot geochemical difference at Samoa (Fig. 2). This disparity might be explained by a number of factors. First, we note that Samoa is extremely close to the Tongan subduction zone (Fig. 4), and the Samoan plume conduit is likely to be strongly tilted by the mantle flow induced by the subducting slab[28]. Consequently, the base of the Samoan plume conduit may be significantly offset from the assumed simple vertical projection from the Samoan volcanoes. Second, the Samoan plume is well removed from the edge of the Pacific superplume; therefore, the geochemical zoning of the Samoan plume conduit is probably controlled by the detailed structure of heterogeneity within the Pacific superplume, rather than by the contrast between superplume and non-superplume mantle. Such heterogeneity within the superplume might not be well resolvable seismically. Finally, unlike at Hawaii or the Marquesas, there is considerable disagreement between seismic models as to the exact pattern of seismic velocity anomalies at the base of the mantle beneath Samoa, suggesting that further refinement of the seismic models is necessary in this region[29–31] (Fig. 4).

Isotopic heterogeneities in lavas from different hotspots may offer the best opportunity for mapping the distribution of compositional heterogeneity in the lower mantle at a large scale[24,25]. Geodynamic modelling demonstrates that the distribution of such heterogeneities within the boundary layer giving rise to a mantle plume results in characteristic spatial patterns of heterogeneity within the plume conduit[7,8,27]. Hotspots with *en echelon* volcanoes (for example, Hawaii, Samoa, the Marquesas) present opportunities to probe the spatial structure of plume conduits, and thereby map the distribution of heterogeneity in the lowermost mantle in fine detail. Numerous hotspots exhibit *en echelon* or otherwise spatially complex volcanism[32,33]. However, geochemical and bathymetric data for other Pacific hotspots are relatively sparse at present. Nonetheless, further detailed analyses of intra- and inter-hotspot geochemical variations at these additional locations may allow for a more comprehensive and detailed mapping of heterogeneities in the TBL, shedding light on the cause of seismic velocity anomalies at the base of the mantle and the characteristics of convection and mixing in the lowermost mantle.

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Author contributions

All three authors conceived the model, wrote the paper, prepared the figures, and contributed intellectually to the paper.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at http://www.nature.com/reprints. Correspondence and requests for materials should be addressed to S.H.