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Derivation of Hawaiian rejuvenated magmas from deep carbonated mantle sources: a review of experimental and natural constraints

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ABSTRACT

The role of carbon-rich or carbonatitic melts as an important metasomatizing agent in the Earth's mantle is supported by direct and indirect evidence of their involvement, ranging from the presence of erupted carbonatitic lavas to metasomatic reactions documented in minerals and melt inclusions from mantle xenoliths. Carbonatite metasomatism in hot-spot settings, and more particularly in the mantle sources of rejuvenated Hawaiian lavas, has long been suspected. However, an unequivocal geochemical tracer of carbonated mantle sources in alkaline volcanic suites is still missing. We here examine high-quality major- and trace-element compositions of ~ 400 primitive Hawaiian lavas (MgO = 8.5 - 21 wt%, SiO₂ = 37 - 50 wt%) and associated xenoliths, focusing on those erupted during rejuvenated stages of activity of the Hawaiian hot spot, Pacific Ocean. The rejuvenated-stage alkaline lavas are the most enriched in volatile elements among the four-stage Hawaiian lavas. Our compilation shows that these rejuvenated-stage lavas range from melilite/nephelinite to transitional basalts and are characterized by low-Si and high-Na, -K and -Ca contents, along with the enrichment of REE, Th and Ba relative to K, Hf, Zr, Ti and Nb. Their trace-element systematics argues against derivation from a homogeneous lherzolitic or pyroxenitic source, regardless of the involvement of residual garnet or hydrous phases. Based on a comprehensive review of natural and experimental constraints on partitioning between carbonatites and mantle minerals and numerical simulations of open-system melting, we show that it is rather consistent with carbonatite metasomatism in their source. Variations in SiO₂, CaO, alkali contents and trace-element proxies such as Hf/Sm also specify temporal variations in the depth of melting and/or the respective contribution of lherzolites and pyroxenites in a hybrid (probably asthenospheric) source fluxed by carbonatitic melts. We suggest that this episode took place ≤ 4.2 Ma at temperatures and pressures in excess of 1100°C and 2 GPa. The low-solidus carbonatite melts were likely generated following a time lag which allowed for cooling of the plume and likely derived from an ancient (> 1 Ga),

recycled mantle, or lower mantle, source in the Hawaiian plume, in good agreement with Sr-Nd-Hf-Os isotope systematics and other chemical and mineralogical features of Hawaiian rejuvenated lavas and xenoliths. The identification of a deep carbonated mantle source for Hawaiian rejuvenated volcanic series is also in line with noble gas and light stable isotope systematics and suggests that the interaction between carbonatite melts and peridotites/pyroxenites may be a critical process explaining the compositional variability of many oceanic island magmas.

INTRODUCTION

The presence of significant amounts of carbon in mantle plumes is well established (Trull et al., 1993; Hofmann et al., 2011; Anderson & Poland, 2017; Tucker et al., 2019). Direct and indirect evidence for carbon-rich or carbonatitic melts and fluids has been widely documented in oceanic hot-spot settings (*e.g.*, Salters & Shimizu, 1988; Schmidt & Weidendorfer, 2018 and references therein). Erupted carbonatite melts are, for instance, reported from the Cape Verde and Canary Islands (Allègre et al., 1971; Silva et al., 1981; Barrera et al., 1981; Gerlach et al., 1988; Hoernle et al., 2002). Metasomatic reactions between carbonatitic fluids and mantle rocks are observed in xenoliths from the Solomon (Nixon & Boyd, 1979), Canary, Kerguelen or Fernando de Noronha Islands (*e.g.*, Kogarko et al., 1995; 2001; Schiano et al., 1994) and Hawaii (Wirth & Rocholl 2003). Furthermore, based on the compositions of peridotite minerals and melt inclusions, Hauri et al. (1993), Kogarko et al. (1995), Coltorti et al. (1999), Schiano et al. (1994), Mattielli et al. (1999), Hassler (1999), Grégoire et al. (2000), Kogarko et al. (2001) and Hoernle et al. (2002) inferred that ultramafic xenolith suites affected by carbonatite metasomatism are widespread in oceanic environments (*e.g.* Savai'i, Tubuai, Canary, Fernando de Noronha, Grande Comore and Kerguelen). Carbonatite and CO₂-rich silicate melts play an important role as metasomatizing agents in the mantle lithosphere, as documented by newly formed clinopyroxene (Cpx) (Mattielli et al. 1999;

Grégoire et al., 2000), apatite (Hassler, 1999), phlogopite and amphibole (Grégoire et al., 2000), and melt inclusions (Schiano et al., 1994) in metasomatized peridotites from the Kerguelen Archipelago. In fact, there is ubiquitous evidence of the involvement of carbonatites from mantle xenoliths, implying that carbonated mantle probably plays a major role in the source geochemistry of oceanic hot-spot magmas.

Metasomatism by kimberlites, carbon-rich melts and carbonatites in the mantle sources of rejuvenated Hawaiian lavas has long been suspected (*e.g.*, Salters & Zindler, 1995; Keshav & Sen, 2003; 2004; Wirth & Rocholl, 2003; Sen et al., 2005; Frezzotti & Peccerillo, 2007; Dixon et al., 2008; Hofmann et al., 2011; Hofmann & Farnetani, 2013; Rocholl et al., 2015; Schmidt & Wiedendorfer, 2018 and references therein; Rocholl et al., 2019). Alternative models for the origin of these lavas involve partial melting of garnet (Grt)-bearing lherzolites and pyroxenites leaving residual apatite, phlogopite and titanite/Fe-Ti oxides in a mixed lithosphere-plume source (*e.g.*, Claas and Goldstein; Clague and Frey, 1982; Lassiter et al., 2000; Frey et al., 2000; Sen et al., 2005; Clague et al., 2006; Garcia et al., 2016). In contrast, based on the geochemistry of the primitive Kiekie lavas and glasses from the Niihau island, Dixon et al. (2008) proposed that low-degree partial melting of the Hawaiian plume led to silicate and carbonatite metasomatism along the depleted-mantle plume margins at sub-lithospheric depths.

Compositional heterogeneities of mantle sources consequent to carbonatite metasomatism are generally inferred in intraplate magmas from Hf/rare earth elements (REE) and Zr/Hf variations (*e.g.*, Dupuy et al., 1992; Hauri et al., 1993; Hoernle et al., 2002). However, these variations can be controlled by fractional crystallization of Cpx and Grt and other authors propose that fractionation may also occur during OIB and MORB generation due to increasing bulk partitioning coefficients $D_{Sm} < D_{Hf} < D_{Eu}$ between mantle minerals and basaltic melts (*e.g.*, David et al., 2000). An unequivocal geochemical tracer of carbonated mantle sources in alkaline volcanic suites is thus missing. To constrain the role of carbonatite metasomatism and/or hybrid peridotite/pyroxenite sources in the

generation of the volatile-rich rejuvenated-stage Hawaiian magmas, we here present an extensive dataset of major- and trace-element compositions compiled from the literature since 1982. For that purpose, we particularly focus on high-quality analytical data on incompatible trace-elements compositions of bulk rocks (lavas), glasses and mineral samples and discuss trace-element partitioning between minerals and silicate and carbonatite melts as well as the trace-element compositions of carbonatite magmas, melts and carbonated peridotite xenoliths worldwide. These data along with the decoupled Nd-Hf isotope systematics documented in the Salt Lake Crater (SLC) mantle xenoliths (e.g., Bizimis et al., 2005; 2013 and references therein) are consistent with carbonatite metasomatism derived from a deep, potentially lower-mantle, source containing ancient recycled material (> 1 Ga) within the Hawaiian plume.

2. DATA COMPILATION

2.1 Sample systematics and analytical data selected for this study

Four volcanic stages have been distinguished in the Hawaiian-Emperor volcanic chain (**Fig. 1a,b**): (1) alkalic preshield (3% in volume), (2) tholeiitic shield (98 - 95%), (3) alkalic postshield (<1%) and (4) alkalic rejuvenated stages (<1%) (Clague, 1987a; Sobolev & Nikogosian, 1994). The rejuvenated-stage alkaline lavas are the most enriched in volatile elements but also the most isotopically depleted (and the most homogeneous) with highly radiogenic Nd and Hf and unradiogenic Sr (e.g., Lassiter et al., 2000; Fekiacova et al., 2007; Dixon et al., 2008; Bizimis et al., 2013; Béguelin et al., 2019; Harrison et al., 2020). To constrain the role of carbonatite fluxing and/or hybrid mantle sources in the generation of their parental magmas, we have compiled a dataset of ~ 400 primitive lavas and glasses with $\text{SiO}_2 \leq 50$ wt.% and $\text{MgO} \geq 8.5$ wt.% (**Fig. 2**) from Honolulu (Oahu), Haleakala (Maui), Koloa (Kauai), the submarine Wailau landslide on Molokai,

the North Arch volcanic field off Oahu, lavas from West Maui and Mauna Kea as well as from volcanoes on Molokai, Niihau, Kauai, Oahu, and Kaula and other Hawaiian Islands. The volcanic activity of the selected localities is mostly related to the rejuvenated stage (Clague and Frey, 1982; Frey & Clague, 1983; Chen and Frey, 1985; Clague & Dalrymple, 1988; Maaløe et al., 1992; Chen et al., 1991; Reiners and Nelson, 1998; Frey et al. 2000; Dixon & Clague, 2001; Clague & Moore, 2002; Gaffney et al. 2004; Clague et al., 2006; Dixon et al., 2008; Cousens & Clague, 2015; Phillips et al., 2016) (**Table 1**). The lavas and glasses are classified as ijolites, melilite nephelinites, nepheline melilites, nepheline basanites and alkaline olivine (Ol) basalts, as well as some transitional-type basalts (**Fig. 2; Table 1; Supplementary Dataset 1**). These alkaline to transitional lavas were erupted after an erosion interval of 0.25 - 2.7 My following the shield-stage volcanism (Clague, 1987b; Garcia et al., 2016 and references therein). Petrographic description of these lavas can be found elsewhere (*e.g.*, Clague & Frey, 1982; Garcia et al., 1986; Clague & Dalrymple, 1988).

Analytical data were primarily selected based on the quality of the major- and trace-element analyses, but also aiming for sample representativity and limited or absence of secondary alteration features. Various analytical techniques performed in different laboratories were used, so we preferentially included analyses obtained using neutron activation or inductively coupled plasma mass spectrometry (ICP-MS) for Hf, Ta, Th and REE and X-ray fluorescence for Zr, Nb and Y. Following on previous compilations (*e.g.*, Clague & Frey, 1982; Frey & Clague, 1983; Clague & Dalrymple, 1988; Chen et al., 1991; Frey et al., 2000), we consider that “old” data on Zr, Hf, Nb, Ba, REE, Ta and Th have an analytical precision of ± 15 to 20 %, and up to 25 % only (*e.g.*, Yang et al., 2003) for the Th contents of Frey et al. (2000). In contrast, recent trace-element analyses performed by ICP-MS have 2σ precision of 3-5% (Reiners & Nelson, 1998) and better than 0.5 % for major elements. For instance, major-element compositions acquired by X-ray fluorescence (XRF) and ICP-MS trace-element analyses carried out at the Washington State University GeoAnalytical Laboratory yielded a 2σ precision mostly $< 3\%$ based on repeated analyses of the

BCR-P standard, reaching 6-7 % for incompatible lithophile elements and < 15% for Ni, Sc and Ga (Gaffney et al., 2004; Dixon et al., 2008).

2.2. Compositional features of the Hawaiian rejuvenated-stage lavas

The selected samples are characterized by a wide range of Zr (69-260 ppm), Hf (1.7-6.9 ppm), La (8.5-109 ppm), Sm (3.3-17 ppm) and Lu (0.05-0.61 ppm) abundances (**Fig. 3**). Where missing, Hf concentrations were calculated from Zr contents assuming the average Zr/Hf (43 ± 10) of rejuvenated-stage lavas (as detailed below). This is the case for the database of Reiners and Nelson (1998) on rejuvenated-stage basalts from Kauai, which shows similar trace-element ratios and primitive mantle (PM)-normalized (Sun & McDonough, 1989) patterns compared with other rejuvenated-stage Hawaiian lavas.

Hawaiian lava series are characterized by positive correlations between $(\text{Hf/Sm})_n$ [or $(\text{Zr/Sm})_n$] and $(\text{Ti/Eu})_n$, particularly marked in the rejuvenated-stage lavas (**Fig. 3a**), and negative correlations between $(\text{Hf/Sm})_n$ and $(\text{La/K})_n$; the latter reach particularly high values (up to 10) in lavas from Oahu and Kauai islands (**Fig. 3b**). These observations reflect coherent K, Zr, Hf and Ti depletion relative to REE compared to the PM. Negative correlations between $(\text{Hf/Sm})_n$ and $(\text{Zr/Hf})_n$ are also observed in some of the lavas from Honolulu volcano and Kauai (**Fig. 3c**). The rejuvenated-stage lava series exhibit a clear negative correlation between $(\text{Hf/Sm})_n$ and $(\text{La/Sm})_n$, reflecting coherent light rare earth element (LREE) enrichment and Hf depletion (**Fig. 3e**). Two trends of $(\text{Hf/Sm})_n$ versus $(\text{Nb/Th})_n$ and $(\text{K/Th})_n$ reflect two types of correlations between $(\text{Hf/Sm})_n$ [or $(\text{Zr/Sm})_n$] and $(\text{Nb/Th})_n$ and between $(\text{Hf/Sm})_n$ and $(\text{K/Th})_n$ (**Figs. 3f & g**). In such cases, Hf depletion is accompanied by variable K and Nb depletion. Additionally, $(\text{Ba/Th})_n$, and to a lesser extent $(\text{Ba/K})_n$, vary widely, showing an absence of coherence between K, Ba and Th behaviour, but

the broad negative correlation between $(\text{Ba}/\text{K})_n$ and $(\text{Hf}/\text{Sm})_n$ suggests that the most Hf depleted lavas and glasses tend to be enriched in Ba (**Fig. 3d & h**).

Three geochemical groups may be distinguished among Hawaiian late-stage lavas on the primitive mantle (PM)-normalized trace-element diagrams. (1) PM-normalized trace-element patterns of the postshield-stage lavas show no distinctive anomalies for “critical” elements like K, Zr, Hf, Ti, corresponding to $(\text{La}/\text{K})_n$, $(\text{Hf}/\text{Sm})_n$ and $(\text{Ti}/\text{Eu})_n$ ratios close to 1 (**Fig. 4**). Postshield-stage lavas with moderate $(\text{La}/\text{Sm})_n$ show different degrees of Rb and Th depletion relative to LREE. In contrast, two types of rejuvenated-stage series with low $(\text{Hf}/\text{Sm})_n < 1$ may be distinguished based on characteristic anomalies in PM-normalized patterns. Both types variously exhibit K, Zr, Hf and Ti anomalies. (2) On the one hand, PM-normalized trace-element patterns of the Honolulu rejuvenated-stage lavas with low $(\text{Hf}/\text{Sm})_n (< 1)$ and high $(\text{La}/\text{Sm})_n (> 3.3)$ show strongly negative Rb, K, Zr, Hf and Ti and positive Ba anomalies, and variable Th contents (**Fig. 4**). These anomalies are expressed in variably low $(\text{La}/\text{K})_n$, $(\text{Hf}/\text{Sm})_n$, $(\text{Ti}/\text{Eu})_n$ and $(\text{Ba}/\text{Th})_n$ ratios. (3) On the other hand, the Niihau rejuvenated-stage basaltic series is characterized by variable Th depletion relative to Ba and a weak Zr, Hf depletions relative to REE and an absence of pronounced K and Ti depletion.

3. DISCUSSION

The high MgO contents (8.5 - 21 wt.%) of the Hawaiian volcanic series suggest that their compositions are probably not far from that of primary melts and that the effect of fractional crystallization is negligible. Nickel contents (200 - 600 ppm) show broadly positive correlations with MgO contents in most Hawaiian lava series, reflecting some extent of fractional crystallization/accumulation. In contrast, the absence of such correlation for Sc concentrations, which are restricted to 10 – 30 ppm, excludes significant Cpx fractionation (**Figs. A1, A2**). The trace-element fractionation trends observed are thus considered below in terms of variations in

source mineralogy and composition and melting processes before to envisage their geological significance.

3.1. Source mineralogy

3.1.1 An anhydrous garnet lherzolite source?

Partial melting of anhydrous Grt lherzolite/pyroxenite has been invoked in the source of Hawaiian lavas by various workers (Lasiter et al., 2000; Sobolev et al., 2005; 2007; Borghini & Fumagalli, 2020). Experimental data on trace-element partitioning (**Table 2**) in the presence of basaltic/basanite melts show that: (1) K_d^{Hf} and K_d^{Sm} values are similar among mantle minerals, (2) the K_d^{Zr} of Cpx (0.09 - 0.27) are comparable to K_d^{Hf} (0.1 - 0.55) and K_d^{Sm} (0.09 - 0.67); (3) K_d vary with temperature, pressure and melt composition but remain as follows: $K_d^{\text{Zr}} \leq K_d^{\text{Hf}} \approx K_d^{\text{Sm}}$ or $K_d^{\text{Hf}} \leq K_d^{\text{Zr}} \approx K_d^{\text{Sm}}$ in Cpx, Grt and other silicates (**Table 2**). This is, for instance, the case between Grt and basanitic melt (Adam & Green (2006). Corgne & Wood (2004) and Corgne et al. (2012) also demonstrated that Hf is significantly more compatible compared to Sm in majoritic Grt suggesting that Hf depletion relative to Sm would be expected upon fractionation of majorite garnet or derivation of primary alkaline melts from such majorite Grt-bearing mantle source.

We used a batch melting model (**Fig. 3, Fig. A3a-d**) to simulate the trace-element fractionation associated with partial melting of a Grt lherzolite. The results show that Hf/Sm and Ba/Th in partial melts remain constant relative to the source, with a weak Ba fractionation relative to Th (**Fig. A3c**). Most Hawaiian rejuvenated-stage lavas exhibit such fractionation but variable K, Hf, Zr and Ti depletion (*i.e.* low Hf/Sm, Zr/Sm, Ti/Eu and high La/K, Zr/Hf relative to the PM) are observed (**Fig. 3a-h**), which probably excludes the involvement of Grt in an anhydrous lherzolite source and instead requires additional mineral/melt phase(s) and/or REE enrichment by

metasomatism. Similarly, the observed fractionation of Ba from Th, Nb and Ta could not be solely explained by the presence of majoritic Grt, owing to the similarity of its partition coefficients for these elements. The strong variations in $(\text{Ba}/\text{Th})_n$ at nearly constant $(\text{Hf}/\text{Sm})_n$ observed, for instance, in Niihau basaltic series is clearly incompatible with the presence of majoritic Grt in their mantle source.

It is currently considered that partial melting of mantle peridotite is a dynamic process, involving differential flow of melt and residual matrix (*e.g.*, Oliveira et al., 2020, and references therein). However, when trace elements show similar bulk distribution coefficients (*e.g.*, Dy and Yb) between mantle minerals and melts, only limited additional fractionation is expected from dynamic melting models compared to the predictions of batch melting (Eggins, 1992). Dynamic incongruent melting/mineral dissolution can produce noticeable differences only when the partition coefficients of the produced mineral are sufficiently different from those of the reacting minerals (Zou & Reid, 2001). Dynamic melting of anhydrous lherzolitic assemblages is unable to cause any substantial trace-element fractionation in melts (*e.g.*, Hf vs Sm, Zr vs Sm, La vs K, K vs Ba) considering the similarity of their bulk partition coefficients (**Fig. 3a-h**). We conclude that the strong trace-element variations from PM values observed among the alkaline lavas of Hawaii rejuvenated-stage volcanism cannot be explained by simple batch nor dynamic melting models from a homogeneous, anhydrous lherzolite source, whether or not Grt (including majoritic Grt) is present.

3.1.2 Hydrous silicate phases

Trace-element contents of ocean-island basalts may be controlled by the presence of hydrated phases such amphibole (Amp) or phlogopite (Phl) during partial melting (*e.g.*, Clague & Frey, 1982; Class & Goldstein, 1997; Class et al., 1998; Frey et al., 2000; Sen et al., 2005; Clague et al., 2006; Garcia et al., 2016). Both minerals have similar partition coefficients with basaltic melts (Green,

1994; LaTourette et al., 1995; Adam & Green, 2006). Specifically, Hf partition coefficients of Amp and Phl ($K_d^{\text{Hf}} = 0.008 - 0.59$) overlap those for Sm (0.017 - 0.66) and Zr (0.008 - 0.45) (**Table A1**; Adam et al., 1993, Green, 1994, LaTourette et al., 1995, and Adam & Green, 2006). A decrease in melting degree of an Amp- and Phl-bearing mantle source results in similar Hf/Sm and Zr/Sm between melt and residue, and a slightly increasing Zr/Hf ratio in the melt (**Fig. 3c**, **Fig. A3a**). Partial melting in the presence of Amp and Phl are rather fingerprinted by enrichment in K, Nb, Ba and Ti relative to REE (**Table 2**; LaTourette et al., 1995; Brenan et al., 1995; Adam & Green, 2006).

If Amp and Phl were responsible for the K and Ti depletion observed in Hawaiian rejuvenated-stage lavas, they would also exhibit Ba and Nb depletion (*e.g.*, La Tourette et al., 1995) and Th enrichment, which are not observed. If residual Amp were present, for instance, during partial melting of lherzolites, Hf/Sm and Ba/K ratios of the partial melts would show positive correlations, while the opposite situation is observed. Amphibole and Phl also have much lower La partition coefficients than those of K (**Table 2**) so that Hf/Sm and La/K of partial melts are expected to be positively correlated in the presence of such residual phases (**Fig. 3b**; **Fig. A3b**). Strong contrast in Amp and Phl partitioning of K and Ba relative to that of Nb and Th (**Table 2**, *e.g.*, LaTourette et al., 1995; Green, 1994; Adam & Green, 2006) also suggests that, if these phases are present during partial melting of a homogeneous mantle source, K/Th and Ba/Th would vary at nearly constant Hf/Sm or Zr/Sm (**Figs. 3e,g**, **Fig. A3c**). Weakly negative correlations between Hf/Sm and Ti/Eu are also expected (**Fig. 3a**; **Fig. A3d**). In contrast, Hawaiian rejuvenated-stage lava series show clear negative correlations between $(\text{Hf/Sm})_n$ and $(\text{La/K})_n$ (**Fig. 3b**) and positive correlations of $(\text{Hf/Sm})_n$ with $(\text{K/Th})_n$, $(\text{Nb/Th})_n$, and $(\text{Ti/Eu})_n$ (**Figs. 3a,f,g**), ruling out the involvement of Amp and Phl in their source. A different process is therefore needed to explain the coherent K and high-field strength elements (HFSE) depletion and relative Th, Ba and REE enrichment.

Note that Niihau basaltic series is an exception devoid of pronounced K depletion relative to LREE (**Fig. 4**) and characterized by strong variations in $(\text{Nb/Th})_n$, $(\text{Ba/Th})_n$ and $(\text{K/Th})_n$ at nearly constant $(\text{Hf/Sm})_n$ (**Fig. 3f,g,h**). The presence of hydrous phases in the mantle source of these lavas, as well as hydrous silicate fractionation, cannot be excluded, although the absence of pronounced K depletion relative La does not support this hypothesis.

3.2. Carbonatite metasomatism

The trace-element variations observed in the Hawaiian rejuvenated-stage lavas, such as the range of Hf depletion relative to REE, point towards significant variability of their mantle source(s). The contrasting degrees of enrichment of fluid-mobile incompatible elements (LREE, Ba and Th) relative to the less mobile K, Hf, Zr, Ti and Nb specifically points towards metasomatic enrichment in the source of Hawaiian rejuvenated-stage lavas. We concur, in this regard, with Dupuy et al. (1992) who ascribed variations of Hf/Sm, Zr/Hf and Zr/Sm in ocean-island lavas to carbonatite metasomatism of their mantle source. This interpretation also corresponds to the scenario proposed by Dixon et al. (2008), invoking coupled carbonatite-silicate metasomatism in the source of the primitive Kiekie lavas on Niihau, Hawaii. To develop a robust model compatible with all available geochemical and petrologic data on the primitive lavas (and mantle xenoliths) of the Hawaiian series, we first envisage the geochemical consequences of carbonatite metasomatism from (1) the compositions of oceanic and continental carbonatite melts/glasses and lavas, (2) experimentally determined partition coefficients between mantle minerals and carbonatite melts, (3) the compositions of mantle peridotites and pyroxenites affected by carbonatite metasomatism.

3.2.1 Trace-element characteristics of carbonatites

Differentiated carbonatite melts are characterized by high Ba, Th, Sr, LREE contents relative to Rb, K, Zr, Hf, Ti and heavy REE (HREE) (Nelson et al., 1988; Walter et al., 2008). These features may be explained by different extents of trace-element complexation with CO_3^{2-} as well as carbonatite melt equilibration with majoritic Grt-bearing eclogite at high pressure (~ 25 GPa, Corgne & Wood, 2004). Carbonatites also exhibit variable Sr, Ta, Th, Nb and P contents, as well as significant Zr/Hf and Nb/Ta fractionation, potentially explained by fractional crystallization (Nelson et al., 1988; Eggler, 1989; Walter et al., 2008) and the appearance of Zr- and Nb-rich phases. In particular, Zr/Hf range between 5 and 465,000 in continental and oceanic carbonatite series (**Supplementary Data 2**; Nelson et al., 1988, Gerlach et al., 1988, Woolley et al., 1991, Beccaluva et al., 1992 and Tayoda et al., 1994, Hoernle et al., 2002 and Bizimis et al., 2003) and vary widely in carbonated peridotites. For example, Zr/Hf in the carbonated Tanzanian mantle xenoliths vary from 20 to 100 (Rudnick et al., 1993). Since the Zr/Hf ratio in the PM is estimated to be 34 - 36 (Jochum et al., 1989; Weyer et al., 2002), the effect of carbonatite metasomatism (or melting of metasomatised peridotites) in the mantle lithosphere is expected to very significant, potentially resulting in either an increase or a decrease of Zr/Hf relative to the primitive mantle. Additionally, carbonatite melts are enriched in REE, Th and Ba relative to K, Zr, Hf and Ti. Indeed, carbonatite melts with $\text{CO}_2 = 17 - 45$ wt.% and $\text{SiO}_2 < 7$ wt.% are shown to have highly variable, and systematically lower than unity, $(\text{Ti}/\text{Eu})_n = 0.0004 - 0.27$, $(\text{Zr}/\text{Sm})_n = 0.0006 - 1.1$ and $(\text{Hf}/\text{Sm})_n = 0.0006 - 0.9$, $(\text{K}/\text{Th})_n = 0.0003 - 0.9$ (Nelson et al., 1988, Gerlach et al., 1988, Woolley et al., 1991, Beccaluva et al., 1992, Tayoda et al., 1994, Hoernle et al., 2002, Bizimis et al., 2003), contrasting with high $(\text{La}/\text{K})_n$ (2.7 – 4300) and $(\text{Ba}/\text{K})_n$ (5 – 3500) (**Fig. 5**) and highly variable $(\text{Ba}/\text{Th})_n$ (0.02 - 266). In carbonatite melts with higher SiO_2 (7 - 22 wt.%), these ratios are much more restricted: $(\text{Ti}/\text{Eu})_n = 0.2 - 0.3$, $(\text{Zr}/\text{Sm})_n = 0.4 - 0.7$, $(\text{Hf}/\text{Sm})_n = 0.6 - 0.9$, $(\text{La}/\text{K})_n = 3 - 38$ and $(\text{Ba}/\text{K})_n = 4 - 34$.

3.2.2 Partitioning between mantle minerals and carbonatite melts

Several experimental investigations have been performed to determine the partition coefficients between mantle minerals and carbonatite melts. Green and Wallace (1988) inferred that the reaction of primary carbonatite melt with spinel (Spl) lherzolite produces an increase in large-ion lithophile elements (LILE) without any significant decrease in $Mg/(Mg+Fe)$. Brenan and Watson (1991) showed that interaction of carbonatite melt with a depleted lherzolite may markedly particularly raise the levels of LILE in Cpx. Based on experimentally determined trace-element partitioning between Cpx and carbonatite melt, Klemme et al. (1995) found that the most sensitive indicator of carbonatite metasomatism appeared to be low Ti/Eu in the metasomatised peridotite. Over a wider range of pressure conditions, Sweeney et al. (1995) and Dasgupta et al. (2009) concluded that carbonatite metasomatism results in Ti depletion and increase in LREE/HREE, LREE/Hf and LREE/Ti in mantle minerals. Similarly, Dalou et al. (2009) investigated trace-element partitioning between majoritic Grt and carbonatite melt at 20 GPa, demonstrating that natural magnesio- and calcio-carbonatite melts are strongly depleted in Hf relative to Sm at high-pressure; however, no data for Ti were reported by these authors.

3.2.3 Metasomatized peridotites

From all the available data on metasomatised peridotite xenoliths, we preferred to make use of high-quality ICP-MS data on trace element concentrations including Hf, Zr, REE, Th, Nb, Ta. Based on such data, Hauri et al. (1993) and Coltorti et al. (1999) showed that peridotite xenoliths from the islands of Savai'i, Tubuai and Grande Comore have been affected by carbonatite melts (**Supplementary Dataset 2**). These peridotite xenoliths show high REE abundances relative to Zr and Ti. Ionov et al. (1993) performed a detailed investigation of Spitsbergen peridotite xenoliths containing primary carbonate aggregates and quenched dolomite melts. These metasomatised

peridotites showed marked enrichment in LREE, Sr, Ba and depletion in Zr, Hf, Nb and Ta. In their investigation of the peridotite xenoliths from western Victoria, Yaxley et al. (1991) described apatite-bearing wehrlites and lherzolites, concluding that interaction between mantle peridotites and carbonatite melt results in LILE and CaO enrichment of the peridotites (Yaxley et al., 1991). Similar features have been described by Rudnick et al. (1993) in carbonated Tanzanian peridotite xenoliths. The main geochemical characteristics of such metasomatized xenoliths are LREE enrichment and strong Ti depletion (**Fig. 5**), with low $(\text{Ti}/\text{Eu})_n = 0.02 - 0.4$, $(\text{Hf}/\text{Sm})_n = 0.1 - 0.7$, $(\text{Zr}/\text{Sm})_n = 0.12 - 1.5$, $(\text{K}/\text{Th})_n = 0.04 - 1.3$, $(\text{Nb}/\text{Th})_n = 0.27 - 1.0$ and high $(\text{La}/\text{K})_n = 1.8 - 54$ and $(\text{Ba}/\text{K})_n = 1.2 - 15.8$ and variable $(\text{Ba}/\text{Th})_n = 0.05 - 2.3$ (Ionov et al., 1993, Rudnick et al., 1993, Yaxley et al., 1991), also reflecting variable K, Hf, Zr and Nb depletion relative to adjacent REE, Th and Ba. Rb/Sr and Sm/Nd ratios also decrease during metasomatic processes involving carbonatitic fluids/melts (**Fig. 5**), which results in time in reduced radiogenic ingrowth of Sr and Nd isotope ratios in the mantle source (Meen et al., 1989).

3.3. Carbonated sources in the Hawaiian mantle

As discussed above, carbonatite metasomatism is fingerprinted by high La/K, Ba/K and low Hf/Sm, Zr/Sm, and Ti/Eu. These signatures are not only consistent with the compositional variability of Hawaiian rejuvenated volcanic series studied, but they also only weakly depend on the degree of melting of the peridotite or pyroxenite protolith. We argue below that the primitive lavas erupted during Hawaiian rejuvenated-stage volcanism were derived from a heterogeneous mantle variously affected by carbonatitic metasomatism.

3.3.1 Numerical modelling

We performed numerical modelling to simulate the impact of carbonatite melt metasomatism on the source of the rejuvenated-stage lavas. We here focus exclusively on trace-element ratios because consistently simulating major-element compositions in such a complex (*i.e.* polybaric, open-system heterogeneous source) scenario is not only challenging (*e.g.* Oliveira *et al.*, 2020), but it would also require making assumptions that are beyond the scope of this work. Similarly, radiogenic-isotope compositions are not considered here but discussed qualitatively in a separate section; they have been addressed in more detail by Béguelin *et al.* (2019) and Harrison *et al.* (2020).

For the purpose of this discussion, different modelling approaches were envisageable. The simplest one consisted in mixing models where carbonatitic component is added to a source then used to generate lavas *via* batch/fractional melting formulations. In contrast, we formulated the hypothesis that the carbonatitic metasomatism was coeval with and related to the partial melting and used a flux melting model. This approach is fairly similar from a trace-element perspective to combined mixing/melting models but it provides a better fit to several key trace-element proxies (as demonstrated below), supporting the idea of flux melting. The model used is the open-system melting (OSM-4) of Ozawa (2001), which consists in an analytical expression of the mass-conservation equations of 1D steady-state melting (*e.g.* Iwamori, 1994) where melting degree (F) is related to the influx rate (β). The system first operates as batch melting (Shaw, 1970) until a critical porosity (α_c) is reached, from which point the system is opened to fluxing, maintaining a constant melt separation rate (γ). We used a PM source (Sun and McDonough, 1989), which might not be ideal from an isotopic perspective (*e.g.* Yang *et al.*, 2003) but is perfectly appropriate as far as trace-element ratios are concerned. The fluxing agent is a carbonatite melt whose composition was taken as that of representative sample 82LB35 from Hoernle *et al.* (2002). Three different scenarios were tested, assuming a Grt lherzolite source mineralogy with low influx rate ($\beta = 0.01$; Model 1), the same source with a higher influx rate ($\beta = 1$; Model 2) and a Grt pyroxenite source (Model 3) with

the same influx rate as in Model 1. Other model inputs and parameters and corresponding assumptions are detailed in **Supplementary Models**.

The results show that the trace-element compositions of the Hawaiian rejuvenated-stage lavas are particularly comparable to the instantaneous melts derived from the carbonated lherzolite and pyroxenite sources (Models 2 and 3). Variable K, Hf, Zr, Ti depletions relative to the REE, are well accounted for by high carbonatite melt fluxing (**Figs. 3a-h**). Model 2 indeed reproduces the variations in K/Th, Nb/Th and Ba/Th observed in most rejuvenated-stage lavas. Variations in La/K and Ti/Eu vs Hf/Sm are also well reproduced by the high-flux model but they are also compatible with the results of low-flux Models 1 and 3. We note, however, that the involvement of a Zr-rich phase is required to reproduce the Zr-Hf fractionation observed (as illustrated by Model 1^{*}; **Fig. 3c**), whereas the observed (La/Sm)_n vs (Hf/Sm)_n is best reproduced by using a slightly lower La content in the fluxing agent (Model 1^{***}) (**Fig. 3e**). The modelled (Nb/Th)_n are also sensitive to the critical porosity (α_c) used (*i.e.* the melting degree from which melt is efficiently extracted) as illustrated by Model 1^{**} (**Fig. 3g**).

3.3.2 Petrological constraints

Experimental studies show that carbonatite melts can occur within the mantle lithosphere but may also be stable in the deeper asthenospheric mantle. The experimental work of Green and Wallace (1988) defines a distinctive window in the oceanic or young continental lithosphere's geotherm, where sodic-dolomitic carbonatite melts derived from fertile lherzolites may cause mantle metasomatism at 930 - 1080°C and pressures lower than 3.1 GPa. Falloon and Green (1989) and Baker and Wyllie (1992) concluded that at pressures > 2.1-2.2 GPa, near-solidus melts derived from peridotite + CO₂ ± H₂O below 1050°C are dolomitic (Mg-rich carbonatite) melts. Dalton and Wood (1993) experimentally determined that near-solidus melts derived from depleted natural lherzolite at

> 2.5 GPa are carbonatites with low alkali contents similar to natural magnesio-carbonatites. Sweeney (1994) demonstrated that dolomitic melts can be in equilibrium with a peridotitic mantle at 2.0-5.0 GPa and 950-1200°C. If melt segregation and aggregation operate under such conditions, these melts may move rapidly to the surface yielding primary sodic-dolomitic carbonatite magmas or fractionated natrocarbonatite derivatives (Green and Wallace, 1988; Sweeney, 1994). However, if the carbonatite melts infiltrate a lherzolite at < 2.0 GPa and 950-1050°C, decarbonation reactions will take place and release CO₂ (Green & Wallace, 1988; Harmer & Gittins, 1998). Experimental studies and data compilations also show that eclogite-derived, calcic carbonatite melts may be stable above 2 GPa in the asthenosphere (Hammouda, 2003; Thomson et al., 2016).

Hawaiian mantle xenoliths also provide evidence for the influence of carbonatite metasomatism on the oceanic mantle. For instance, mantle minerals from anhydrous Spl lherzolites of SLC, Honolulu, Hawaii contain inclusions of a dense supercritical CO₂ fluid phase (1.16 g/cm³; De Vivo et al., 1988) and LREE-enriched Cpx (Salters & Zindler, 1995). Pyroxenite xenoliths from the SLC also consist of newly formed LREE-enriched containing superdense CO₂ (1.21 g/cm³) and apatite (Frezzotti et al., 1992; Sen et al., 1993). The estimated pressures of fluid-inclusion entrapment in the SLC peridotite minerals are lower than 2.0 GPa (Frezzotti et al., 1992). At these pressures, carbonatite metasomatism results in LILE and P enrichment and conversion of Spl lherzolite to apatite-bearing wehrlite containing Ol and diopside (Green & Wallace, 1988). Clinopyroxene- and Grt-bearing peridotites in equilibrium with carbonatite melts would have low (Hf/Sm)_n, (Zr/Sm)_n and (Ti/Eu)_n, combined with high LREE/HREE ratios (Dasgupta et al., 2009). As pointed out by Salters and Zindler (1995), the low Hf/Sm and Ti/Eu in Cpx of the anhydrous Spl lherzolites and low (Hf/Sm)_n, (Zr/Sm)_n and (Ti/Eu)_n (down to 0.71, 0.43 and 0.7, respectively) measured in type-I and -II pyroxenites from SLC (Frey, 1980) are consistent with such reaction involving carbonatite melts. In fact, there is also clear evidence for incongruent dissolution of orthopyroxene during carbonation reactions in the SLC xenoliths (Rocholl et al., 2019).

To account for the metasomatism documented in Hawaiian mantle xenoliths, we argue that low-degree (carbonatitic) melts with a $\text{CO}_2 > 40$ wt.% and low H_2O content (1 – 2 wt.%) are far more effective as metasomatizing agents (Green & Wallace, 1988) than the silicate melts involved in the coupled silicate-carbonatite metasomatism model proposed by Dixon et al. (2008). Despite some evidence of pargasite megacrysts equilibrated with a carbonatitic melt (*e.g.*, Harmer & Gittins, 1998), high CO_2 and low H_2O activity during the metasomatism would result in partial dehydration reactions and the dissolution of hydrous minerals (*e.g.*, Ashley et al., 2020). This leads us to suggest that the Amp-bearing or Phl-bearing veins relate to more recent hydrous silicate metasomatism in the Hawaiian mantle. This conclusion is in accordance with Keshav et al. (2007), who considered that Phl from the SLC xenoliths are not related to the formation of the host xenoliths. The water contents in anhydrous minerals of the SLC xenoliths (although relatively high) are also consistent with CO_2 -rich nephelinite melts adding limited amounts of water to plume mantle (Peslier & Bizimis, 2015).

3.3.3 Temporal evolution: pyroxenite- vs peridotite-dominated source

Isotopic investigations of Hawaiian primitive alkaline lavas suggest that they derived from a mixed lherzolite/pyroxenite (*e.g.*, Lassiter et al., 2000) or predominantly pyroxenitic source (Garcia et al., 2016). Such pyroxenite veins may have formed due to high-temperature crystallization of plume-derived primitive (Mg-rich) basaltic melts at pressures of ~ 1.0 GPa and temperature of $\sim 1300^\circ\text{C}$ (*e.g.*, Borisova et al., 2017). To highlight potential changes in the source of the rejuvenated melts, we show in **Figures 6a-c** positive correlations of $(\text{Hf}/\text{Sm})_n$ with SiO_2 and negative correlations with alkalinity ($\text{K}_2\text{O}+\text{Na}_2\text{O}$), and CaO in the Hawaiian volcanics. According to Lassiter et al. (2000) and Garcia and Presti (1987), melting of pyroxenite veins yield high- SiO_2 (42 - 47 wt.%), Al_2O_3 (10 - 14 wt.%) and low-CaO (10 - 12 wt.%) melts, equivalent to the Hawaiian transitional basalts (**Fig. 6**).

Despite the absence of experimental data on the partial melting of carbonated pyroxenites (as emphasized by Lambart et al., 2016), we speculate that this process could be involved in the petrogenesis of the high-(Hf/Sm)_n lavas in Hawaii, which exhibit such major-element compositions. Most of the preshield and postshield high-SiO₂ melts with low alkalinity, (La/Sm)_n and CaO contents are indeed consistent with the higher degrees of melting of mafic pyroxenite veins (Reiners and Nelson, 1998; Lassiter et al., 2000). Higher temperatures along with the lower solidi and greater melt productivity of pyroxenites (*e.g.*, Hirschmann & Stolper, 1996; Yang et al., 1998; Lambart et al., 2016) could have contributed to high productivity observed in Hawaiian preshield-, shield- and postshield-stage volcanism (Clague, 1987).

In contrast, under relatively low-temperature conditions, carbonatite melt addition to a deep asthenospheric lherzolite source results in the generation of SiO₂-poor melts (Hirose, 1997; Dasgupta et al., 2004), suggesting that most rejuvenated-stage lavas may be derived from variable degrees of carbonated flux melting of a mixed lherzolite/pyroxenite source. Furthermore, the reaction between carbonatite melts and Spl lherzolite is known to produce an increase in Ca/Al and Na/Ca, along with an enrichment in LILE and REE in the carbonated lherzolite (Green & Wallace, 1988). Decreasing degrees of partial melting of a deeper mantle source also result in higher alkalinity and LREE enrichment in the melts (**Fig. 3**). Low Hf/Sm and high K₂O+Na₂O is consistent with the idea of flux melting, where stronger carbonatitic fluxing may have promoted deeper melting. Therefore, the higher CaO contents, (La/Sm)_n ratios and higher alkalinity of the SiO₂-poor melts characteristic of the rejuvenated-stage series may be explained by increasing carbonated metasomatism of a deeper (but still hybrid) source. We conclude that the LREE enrichment and relative Hf depletion observed in rejuvenated-stage Hawaiian series is due to the combined effect of variations in the depth of partial melting and fluxing (**Figs. 3e, 4, 6**). On the one hand, deep carbonated Grt lherzolites were the source of SiO₂-poor (< 42 wt.%), CaO-rich melts with high La/Sm and low Hf/Sm observed in most rejuvenated alkaline lavas of Honolulu, Koloa and other

volcanoes of the Hawaiian Islands. On the other hand, shallow carbonated lherzolites/pyroxenites may be the source of SiO₂-richer (CaO-poor, low-La/Sm) basaltic melts (**Fig. 6**). Different degrees of carbonatite flux melting would also provide a simple explanation for the double trends observed in **Figs. 3h** and the isotopic similarity of Niihau and Oahu lava series (NOK group; Béguelin et al., 2019) without requiring the involvement of silicate and carbonatitic metasomatic agents as suggested by Dixon et al. (2008).

3.4. Deep carbonated sources in the Hawaiian plume

We consider that Hawaiian rejuvenated-stage lava series are derived from a deep source, mainly asthenospheric, in a region where the lithosphere has a maximal thickness of 75 - 90 km (*e.g.*, Gurriet, 1987; Liu & Chase 1991; Lassiter et al., 2000; Schmidt & Weidendorfer, 2018). The ≤ 4.2 -Ma, rejuvenated-stage lavas are characterized by depleted radiogenic isotopes (*e.g.*, lower ⁸⁷Sr/⁸⁶Sr, higher ¹⁴³Nd/¹⁴⁴Nd and ¹⁷⁶Hf/¹⁷⁷Hf) compared to shield-stage basalts (Stille et al., 1983; Frey et al., 2000; Frey et al., 2005; Fekiacova et al., 2007; Garcia et al., 2010; Béguelin et al., 2019; Harrison et al., 2020). Available Sr-Hf-Nd-Os isotope systematics of the rejuvenated-stage lavas and associated mantle xenoliths suggest the presence in the Hawaiian plume of a depleted component that is distinct from the Pacific MORB asthenospheric source (Bizimis et al., 2005; 2007; 2013; Harrison et al. (2020). Additionally, Béguelin et al. (2019) argued for multiple depleted components in the source of the rejuvenated lavas assuming a unique shield-like (Kalihi) plume component in their mixing models while other alternatives are certainly possible in Hf-Nd isotopic space. Our results are not incompatible with these inferences and we envisage that the most isotopically depleted component may reflect the derivation of the carbonatite melts from an old (> 1 Ga) and depleted material with highly radiogenic Hf-isotope compositions, possibly representing long-lived recycled lithospheric mantle within the Hawaiian plume. In such case, provided that they affect the overlying

asthenospheric mantle (e.g., Thompson et al., 2016), the carbonatite melts would be highly mobile (due to low viscosity and ability to wet silicate minerals) and may percolate from the mantle transition zone to the base of the upper mantle at about 2 GPa pressure (e.g., Hofmann et al., 2011).

Alternatively, high carbon solubility in the core (e.g., Dasgupta & Walker, 2008) could result in production of the carbonatite melts in the lower mantle (Dobretsov & Shatskiy, 2012) following core-mantle interactions (e.g., Rizo et al., 2019), which could be envisaged as the deepest plume source of the rejuvenated lavas. Lower mantle source which is likely intrinsic to the Hawaiian mantle plume was also suggested by Harrison et al. (2020) based on the depleted Sr-Nd-Hf isotopic source of the Hawaiian rejuvenated lavas as well as the Ca-rich Hawaiian shield-stage basalts (DeFelice et al., 2019). Because carbonatite melts are stable in the mantle deeper than ~90 km (e.g., Dobretsov & Shatskiy, 2012 and references therein), the impact of their percolation from the deep mantle/core would include a drastic fractionation of Lu/Hf in the carbonated mantle, potentially contributing to the decoupling of Nd-Hf isotope systematics. The strong Hf/Sm fractionation associated with REE fractionation relative to Hf is observed over only a limited range of Sm/Nd fractionation in the carbonated mantle and carbonatite magmas (**Fig. 5**). Salt Lake Crater xenoliths, and other Hawaiian mantle xenolith series, exhibit such strongly decoupled Nd-Hf isotopes towards extremely radiogenic Hf (e.g., Bizimis et al., 2005; 2013 and references therein). This well-known isotopic feature reflects the time integration of Hf fractionation relative to REE and, as such, may result from long-term (≥ 1 Ga) recycling of depleted mantle components (e.g., Harrison et al., 2020 and references therein) but are also not incompatible with ancient core-mantle interaction recorded in the lower mantle.

Recycling of ancient sediments in the Hawaiian plume (Huang et al., 2011) could also be the source of carbon, however, their isotopically enriched source is not observed in the Hawaiian rejuvenated lavas (Béguelin et al., 2019). Furthermore, most studies on the SLC xenoliths from Oahu highlight several important geochemical and petrological features suggesting the existence of

a deep (non-lithospheric) mantle source for the Hawaiian carbonatite melts (Sen et al., 1993; Keshav & Sen 2001; 2003; Wirth & Rocholl, 2003; Keshav & Sen, 2004; Keshav et al., 2005; Bizimis et al., 2005; Frezzotti & Peccerillo, 2007; Bizimis & Peslier, 2015). Additionally, the southwestern (Kaula, Niihau, Oahu) group of the rejuvenated lavas demonstrates similarity of the Hf-isotope compositions to those of the Oahu xenoliths (Béguelin et al., 2019).

- The Oahu xenoliths include high-pressure cumulates related to polybaric magma fractionation at depths ≥ 100 km (Keshav & Sen, 2003; 2004; Keshav et al., 2007) and bear evidence of the deepest majorite Grt reported from oceanic pyroxenites (*e.g.*, Keshav & Sen, 2001), with equilibration pressure of 6 – 9 GPa (*i.e.*, ~ 300 -km depth); the carbonatite melts may be generated even deeper (Thompson et al., 2016).
- The occurrence of pyroxene-hosted nano-diamonds inclusions in the garnet pyroxenite xenoliths (Frezzotti & Peccerillo, 2007; Wirth & Rocholl, 2003) strongly suggests a deep source for the primary carbonatite melts in the Hawaiian hot spot. The fact that some of the diamonds are found in basaltic glasses (Wirth & Rocholl, 2003) implies diamond genesis at 6 GPa pressure and 1300°C where carbonatite and basaltic melts are immiscible (Hammouda, 2003).
- The mineralogy and trace-element characteristics of the SLC pyroxenite xenolith series suggests kimberlite veining (Keshav & Sen, 2003) and/or carbonatite metasomatism, although some pyroxenites may relate to a different, lithospheric stage involving nephelinite melt–mantle (Sen et al., 2011), as suggested by Os-isotope compositions.
- Carbonatite-type melts are documented in the SLC lavas (Rocholl et al. 2015; 2019). Their carbonatite nature is consistent with the evidence for immiscible “kimberlite melts” or carbonate-rich fluids/melts found by Keshav and Sen (2003), Wirth and Rocholl (2003), Sen et al. (2005) and Frezzotti & Peccerillo (2007).

- The source of H₂O and CO₂ in the Hawaiian glasses, lavas and SLC pyroxenites (Dixon et al., 1997; Dixon & Clague, 2001; Bizimis & Peslier, 2015) may also ultimately derive from H₂O-bearing carbonatite melts. According to experimental models of Hammouda (2003) and Thomson et al. (2016), primary carbonatite melts can form from relatively low-temperature partial melting of recycled eclogitic material (assuming the presence of excess carbon) within the mantle transition zone where they may crystallize liquidus minerals such as diamonds due to carbonatite melt-peridotite reactions.

Based on the above considerations, our model proposes that the carbonated and ancient (> 1 Ga) recycled mantle or lower mantle source is involved in the Hawaiian plume. The process summarized in **Figure 7** occurred *via* low-solidus carbonatite melts produced from a deep (≥ 9 GPa) plume source, as inferred from the SLC garnet pyroxenite xenoliths, owing to the time lag after the post-shield stage (as it allows for the cooling of the plume). Subsequent metasomatic interactions in the asthenosphere occurred as these highly mobile carbon-rich melts rose within the plume at > 1100°C and > 2 GPa. This carbonatitic melt fluxing led to melting of the hybrid (lherzolite/pyroxenite) source which produced the ≤ 4.2 Ma Hawaiian rejuvenated-stage magmas. Our model also specifically explains why the Niihau and Oahu rejuvenated series are isotopically similar as part of the southwestern (Kaula, Niihau, Oahu) NOK group (Béguelin et al., 2019), but belong to different trace-element groups. This model is in line with existing Sr-Nd-Hf isotopic source of the Hawaiian rejuvenated lavas (Béguelin et al., 2019; Harrison et al., 2020), noble gas (Hanyu et al., 2005) and light stable isotope (Dixon et al., 2017) systematics of the Hawaiian hot spot, supporting the idea that the transfer of carbonatite melts to peridotite/pyroxenite may account for the geochemical characteristics of the oceanic island magmatism. Our model is also in line with model of Hofmann and Farnetani (2013) involving the thermal boundary layer as the principal source of the rejuvenated melting at the bottom of the mantle where heat is transported predominantly by conduction from the core into the mantle.

Our model supports the idea about heterogeneity of the Hawaiian plume (e.g., Harrison et al., 2020).

4. CONCLUSIONS

We showed that primitive alkaline to transitional lavas series erupted during the recent (≤ 4.2 Ma) rejuvenated stages of volcanic activity on the Hawaiian Islands are characterized by REE, Th and Ba enrichments relative to K, Zr, Hf, and Ti, incompatible with their derivation from an homogeneous mantle source. These characteristics are rather consistent with a hybrid (lherzolite-pyroxenite) asthenospheric source fluxed by carbonatitic melts as the latter, highly mobile, rose within the plume at $> 1100^\circ\text{C}$ and > 2 GPa while the variability in their major- and trace-element contents specify temporal variations in thermal regime, pyroxenite contribution and the extent of carbonatite metasomatism. We inferred that the carbonatite melts were produced from low-solidus partial melting of deep sources (≥ 9 GPa) following the cooling of the plume after the postshield stage. Our observations along with existing Sr-Nd-Hf-Os isotope (e.g., Béguelin et al., 2019; Harrison et al., 2020), noble gas (Hanyu et al., 2005) and light stable isotope (Dixon et al., 2017) systematics of the Hawaiian lava and xenolith series suggest that carbonated sources in the Hawaiian mantle plume may be represented by an ancient (> 1 Ga) recycled depleted mantle and/or lower mantle component that had recorded core-mantle interactions. This scenario is in line with that of Hofmann and Farnetani (2013) involving the thermal boundary layer as the principal source of the rejuvenated melting at the bottom of the mantle where heat is transported predominantly by conduction from the core into the mantle. Our model further confirms the heterogeneity of the Hawaiian plume (e.g., Harrison et al., 2020) and supports the idea that the transfer of carbonatite melts and the involvement of mixed lithologies account for the geochemical characteristics of oceanic-island magmatism. Further investigations of the rejuvenated-stage Hawaiian magmatism coupled with

seismic topography and geodynamic modeling are now important to further constrain such interaction processes and contribute to a better understanding of plume and core-mantle dynamics.

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Author contributions: A.Y.B.: data compilation, conceptualization; investigation; methodology; project administration; writing. R.T.: OSM modeling, conceptualization; writing.

Supplementary Material:

Supplementary Dataset1 represents all major and trace element data available for the primitive (MgO = 8.5 - 21 wt%) Hawaiian (mostly rejuvenated-stage) lava series.

Supplementary Dataset2 represents carbonated peridotite data; carbonatite magma data; pyroxenite and Salt Lake Crater pyroxenite data.

Supplementary Models represents (a) OSM model, OSM parameters, OSM outputs and (b) modal batch melting model parameters and calculations.

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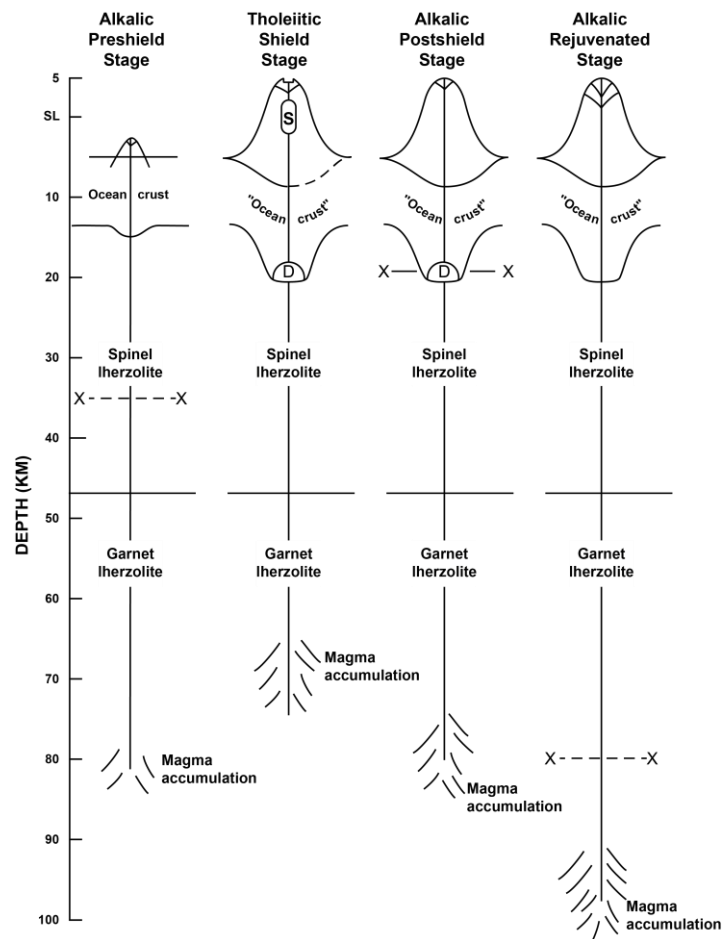
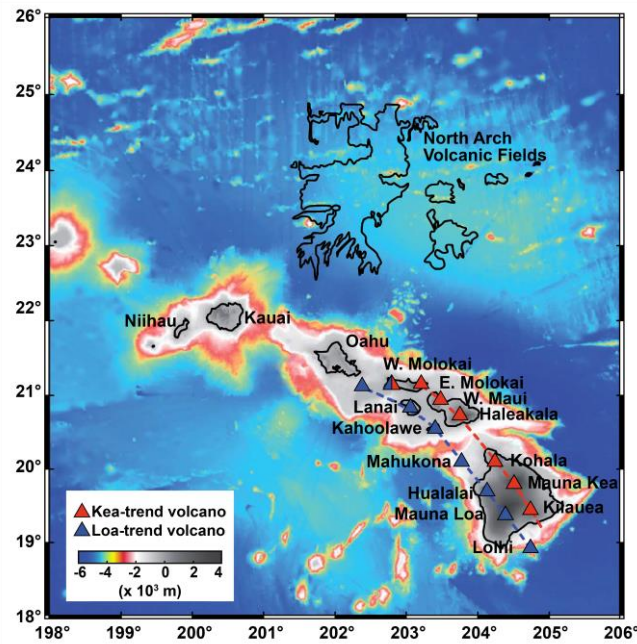


Figure 1 (a). Map showing the locations of the Hawaii, Maui, Molokai, Oahu, Kauai, Niihau Islands and of the North Arch Volcanic Field. The Kea and Loa-trends are also indicated. Modified after Hofmann and Farnetani (2013). **(b)** Schematic representation of the main petrological aspects of the four stages of Hawaiian volcanism (see text for further detail). Modified after Clague (1987).

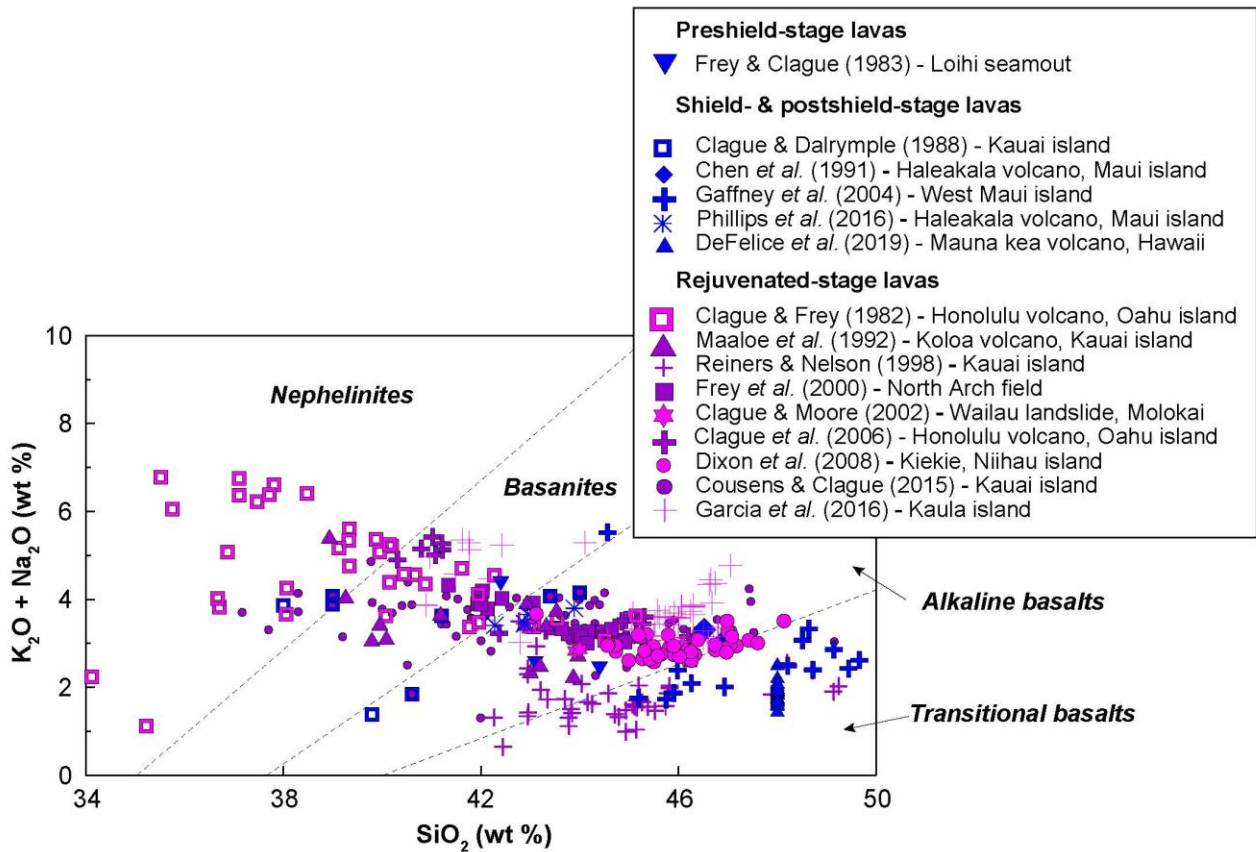


Figure 2. K_2O+Na_2O vs SiO_2 contents classification diagram for Hawaiian island lava series (nephelinites, basanites, alkaline Ol basalts and transitional basalts). The classification is after Cox *et al.* (1979). The compositional database includes analyses of volcanic rocks from Honolulu (Oahu), Haleakala (Maui), Koloa (Kauai), the submarine Wailau landslide on Molokai, the North Arch volcanic field of Oahu, as well as lavas from West Maui and Mauna Kea, and also from volcanoes on Molokai, Niihau, Kauai and other Hawaiian Islands. For the high-Ca basalts from Mauna Kea, Hawaii island, 48 wt% SiO_2 is assumed. The volcanic series plotted here are related to the rejuvenated- and postshield-stages of volcanic activity (Clague and Frey, 1982; Frey & Clague, 1983; Clague & Dalrymple, 1988; Maaløe *et al.*, 1992; Chen *et al.*, 1991; Reiners and Nelson, 1998; Frey *et al.* 2000; Clague & Moore, 2002; Yang *et al.*, 2003; Gaffney *et al.* 2004; Clague *et al.*, 2006; Dixon *et al.*, 2008; Cousens and Clague, 2015; Phillips *et al.*, 2016; Garcia *et al.*, 2016). The data source is given in **Table 1** and summarized in **Supplementary Dataset 1**.

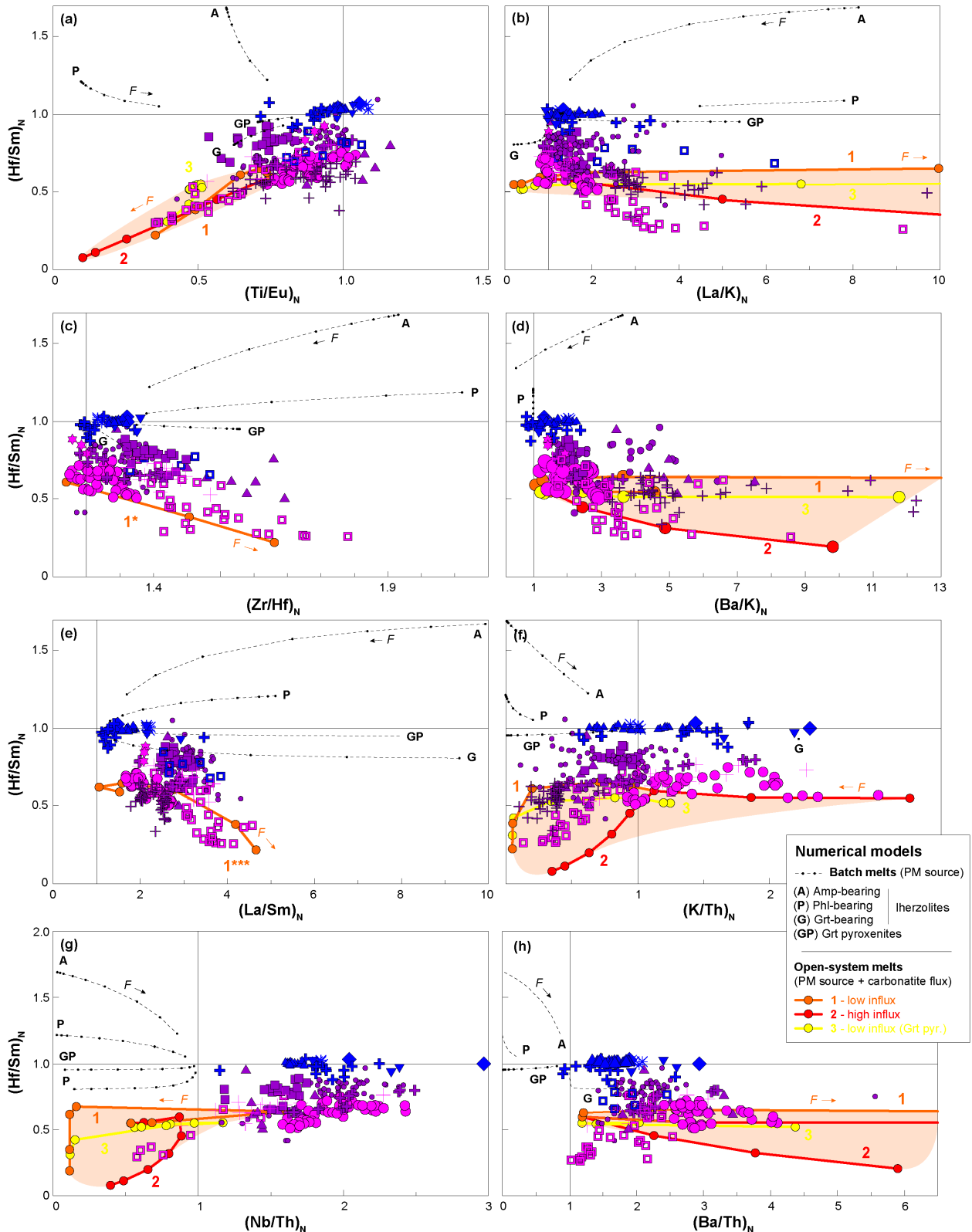


Figure 3. Primitive-mantle-normalized trace-element ratios of the alkaline Hawaiian island volcanic series: $(\text{Hf}/\text{Sm})_n$ vs (a) $(\text{Ti}/\text{Eu})_n$; (b) $(\text{La}/\text{K})_n$; (c) $(\text{Zr}/\text{Hf})_n$; (d) $(\text{Ba}/\text{K})_n$; (e) $(\text{La}/\text{Sm})_n$; (f) $(\text{K}/\text{Th})_n$; (g) $(\text{Nb}/\text{Th})_n$; (h) $(\text{Ba}/\text{Th})_n$. The dataset used here is given in **Supplementary Dataset 1** and **Table 1**. Purple and magenta symbols indicate rejuvenated stage lavas and glasses. Blue symbols correspond to the preshield-stage lavas, postshield stage samples; note that one series of primitive Ca-rich basalts from the shield stage (DeFelice et al., 2019) is also shown. Black dashed lines are trace-

element ratios calculated in partial melts derived from Grt lherzolite (G), Amp (amphibole)-bearing (A), Phl(phlogopite)-bearing (P) lherzolites and garnet pyroxenites (GP). Continuous lines in yellow, orange and red are the instantaneous melt compositions calculated from OSM models simulating carbonatitic flux melting (Models 1, 2 and 3). Arrows along the curves indicate the increasing degree of melting (F) for both types of models. See text and **Appendix** for more details on the batch modelling parameters. Primitive-mantle composition after Sun and McDonough (1989). Other symbols as in **Fig. 1**.

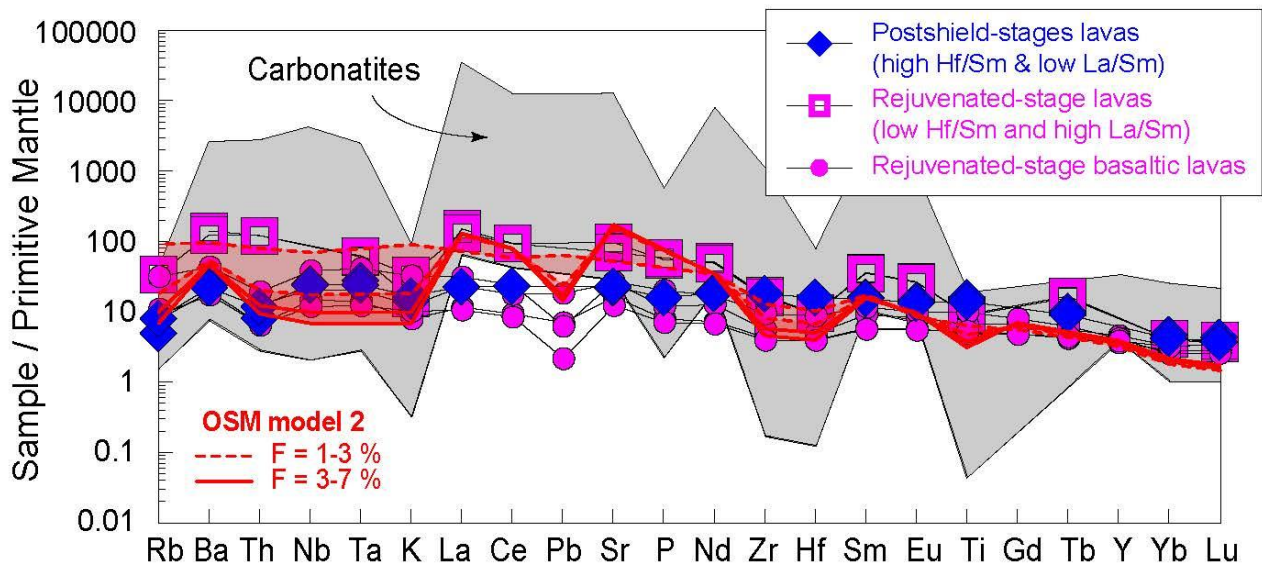


Figure 4. Primitive-mantle-normalized trace-element patterns of Hawaiian (1) postshield-stage lava samples (Ho-12 and Ho-14) with high $(\text{Hf}/\text{Sm})_n$ and low $(\text{La}/\text{Sm})_n$ and (2) rejuvenated-stage lava samples (69KAL1 and 69KAL2) with low $(\text{Hf}/\text{Sm})_n$ and high $(\text{La}/\text{Sm})_n$; (3) rejuvenated-stage basaltic lavas (70Nii-10, 69Nii-9; T318-R19; T318-R2). Data sources are Clague & Frey (1982), Chen et al. (1991) and Dixon et al. (2008). Instantaneous melt compositions calculated from OSM (Model 2) simulating carbonatitic flux melting are shown for comparison. Bulk compositional field of extrusive carbonatite magmas and carbonatite melts are from Nelson et al. (1988), Woolley et al. (1991), Beccaluva et al. (1992), and Tayoda et al. (1994). Primitive mantle composition is after Sun and McDonough (1989).

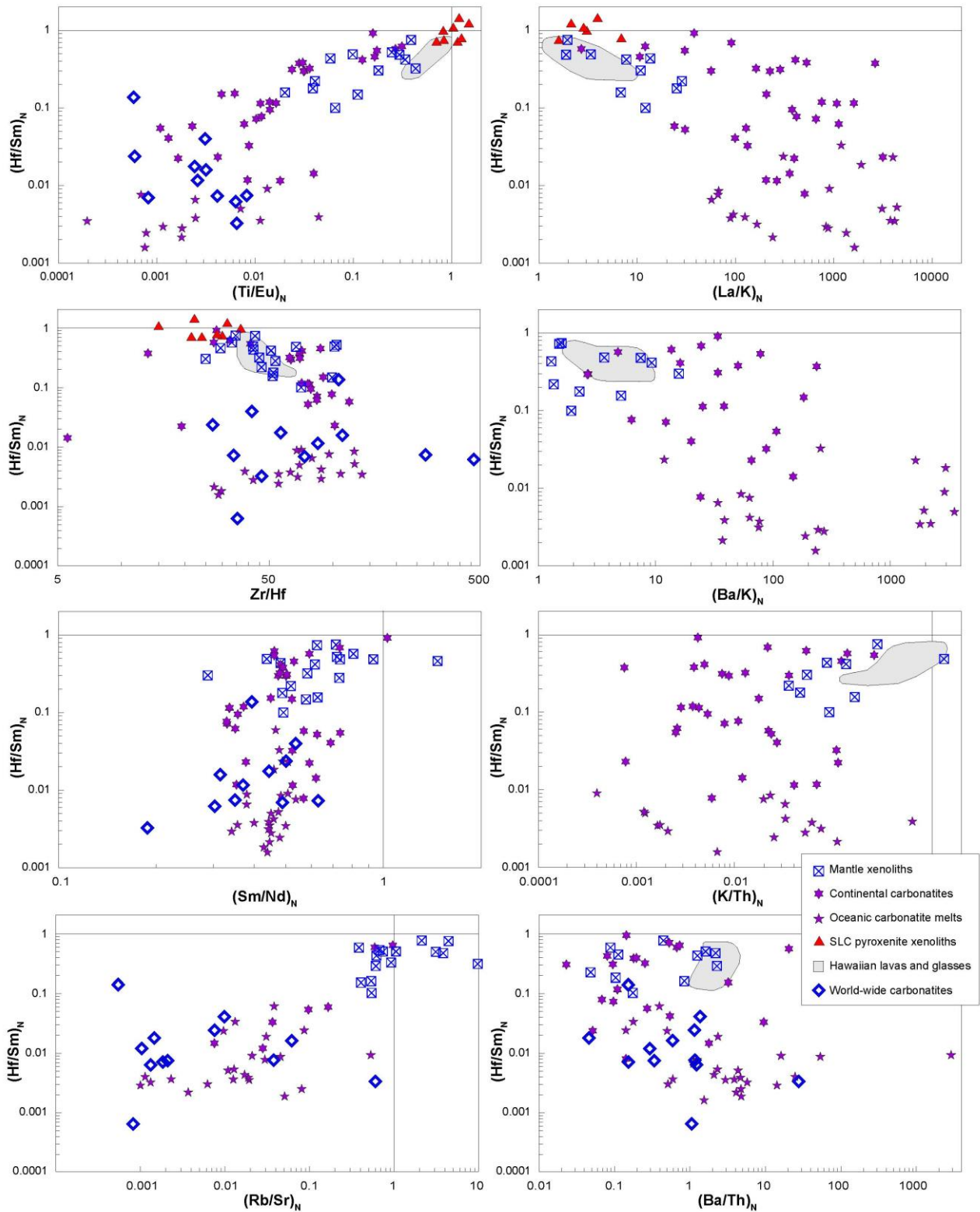


Figure 5. Primitive-mantle-normalize trace-element ratios in mantle xenoliths and in carbonatite melt/magma: $(\text{Hf}/\text{Sm})_N$ vs (a) $(\text{Ti}/\text{Eu})_N$; (b) $(\text{La}/\text{K})_N$; (c) Zr/Hf ; (d) $(\text{K}/\text{Th})_N$; (e) $(\text{Ba}/\text{K})_N$; (f) $(\text{Ba}/\text{Th})_N$; (g) $(\text{Sm}/\text{Nd})_N$; (h) $(\text{Rb}/\text{Sr})_N$. Composition of mantle xenoliths affected by carbonatite metasomatism; composition of continental carbonatites; oceanic carbonatite melts; pyroxenite xenoliths from SLC, Hawaiian Islands; rejuvenated-stage Hawaiian lavas and glasses; world-wide carbonatite composition are plotted. Compositions of mantle peridotites affected by carbonatite metasomatism are from Rudnick et al., 1993; Ionon et al., 1993; Yaxley et al., 1991. Extrusive carbonatite magma

and melt compositions are from Nelson et al. (1988), Gerlach et al. (1988), Woolley et al. (1991), Beccaluva et al. (1992), Tayoda et al. (1994), Hoernle et al., (2002) and Bizimis et al (2003). Compositions of pyroxenite xenoliths are from Frey et al. (1980). The data sources are given in **Supplementary Datasets 1, 2 and Table 1**. Primitive-mantle composition after Sun and McDonough (1989).

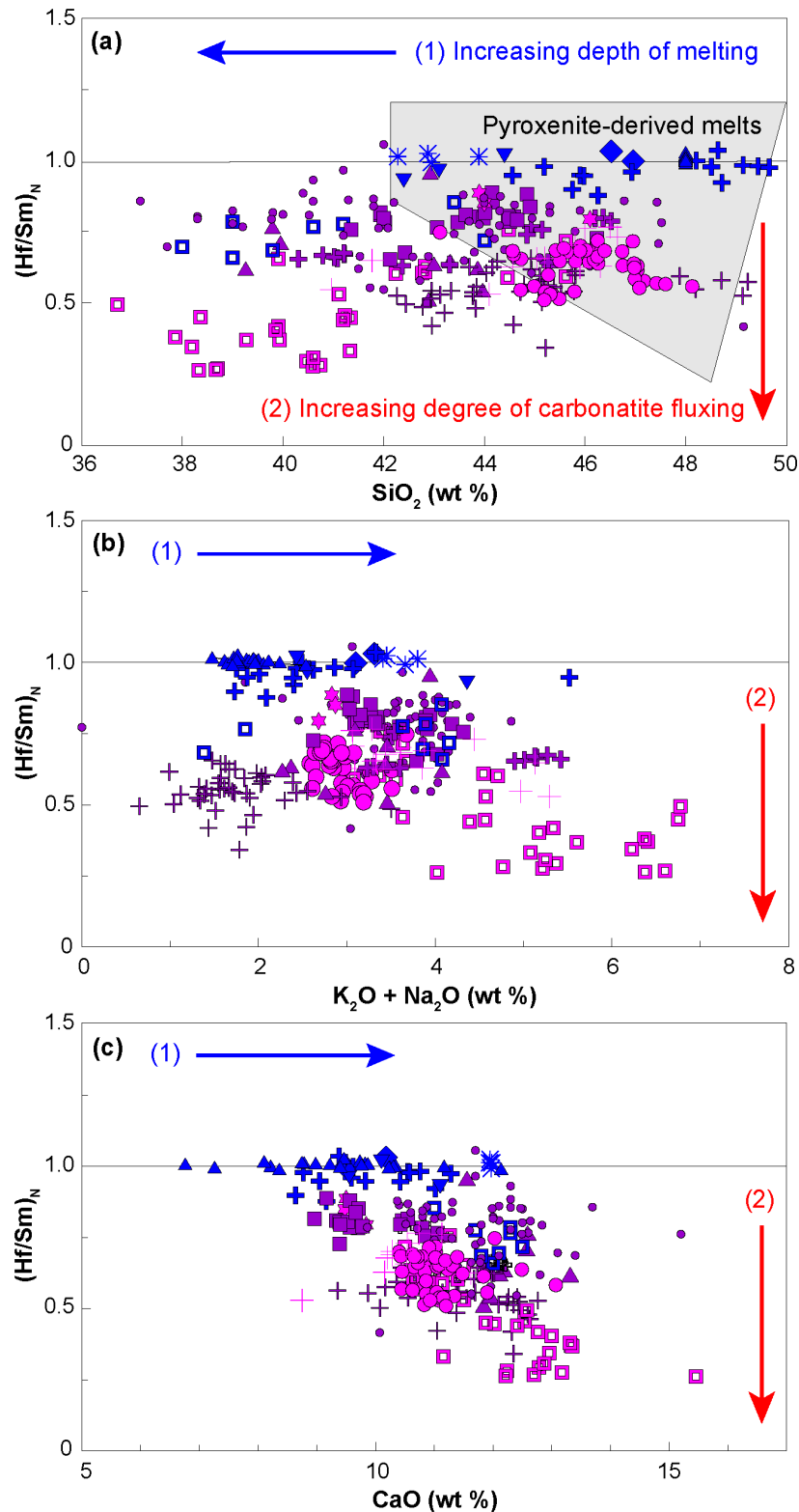


Figure 6. (a) $(\text{Hf}/\text{Sm})_N$ vs SiO_2 ; (b) $(\text{Hf}/\text{Sm})_N$ vs $\text{K}_2\text{O}+\text{Na}_2\text{O}$ (c) $(\text{Hf}/\text{Sm})_N$ vs CaO in the compiled Hawaiian lava series (**Supplementary Dataset 1**). The potential effect of changes in the depth of melting and the extent of carbonatite metatammatism are shown by the arrows, among other controlling factors discussed in the text. The grey-shaded field indicates likely compositions of melts derived from pyroxenite veins in the Hawaiian mantle. Other symbols as in **Fig. 2**. Primitive-mantle composition after Sun and McDonough (1989).

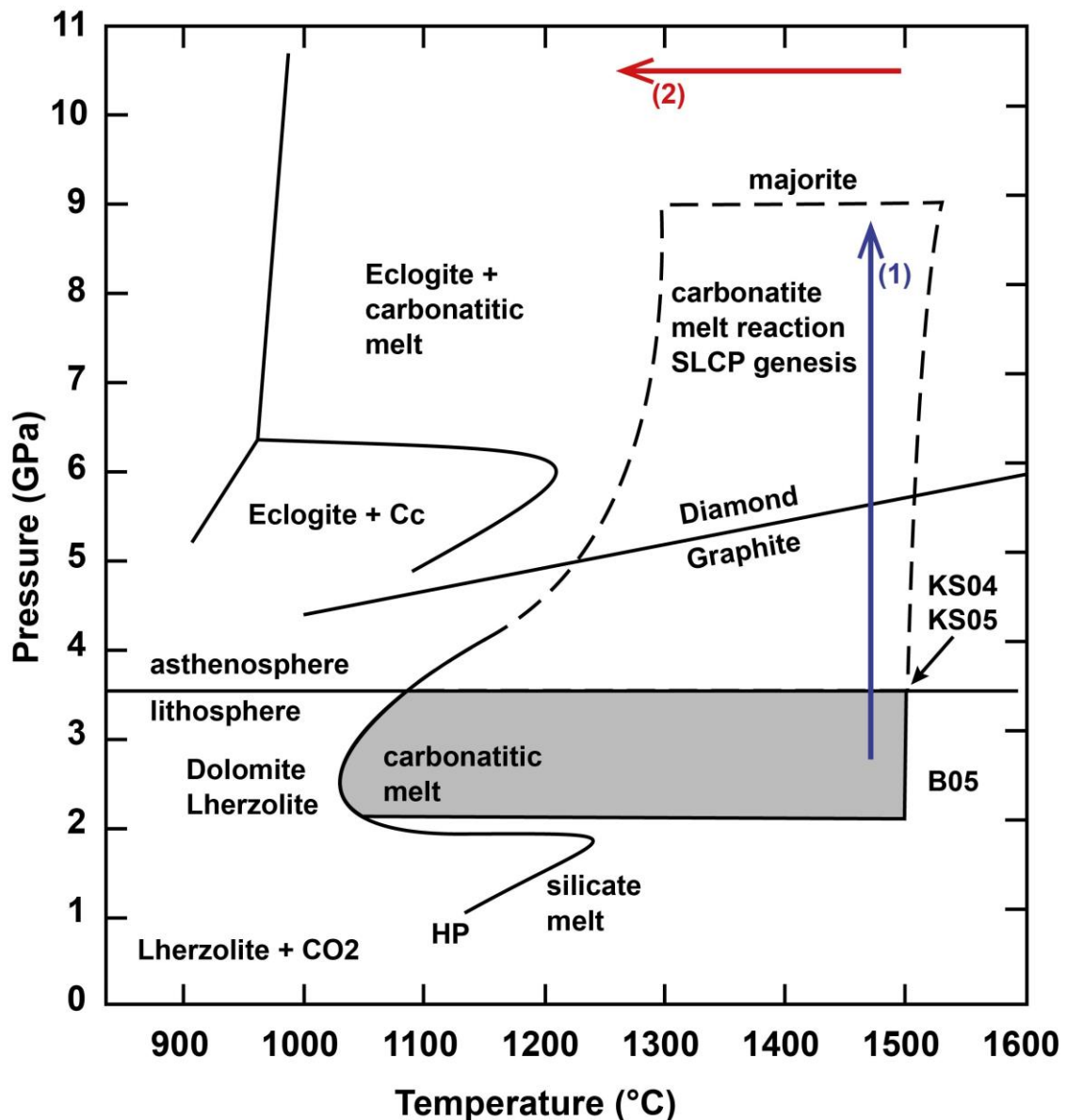


Figure 7. Pressure-temperature diagram showing stability fields relevant to carbonated mantle melting in the Hawaiian plume. Our model suggests that (1) carbonatites were generated after cooling of the Hawaiian plume during low-degree partial melting of a recycled (lower) mantle source at depth of up to 9 GPa, as potentially documented by the SLC pyroxenite xenoliths; (2) these carbonatite melts led to flux melting of a hybrid pyroxenite-lherzolite mantle source at $> 1100^{\circ}\text{C}$ and > 2 GPa producing primitive, rejuvenated-satge Hawaiian lavas. HP: Hawaiian pyrolite; Cc: calcite. B05 refers to Bizimis et al (2005) and KS04 and KS05 to Keshlav & Sen (2004; 2005). Adapted from Hammouda (2003). The potential effect of changes in the depth of melting and the extent of carbonatite metatmatism are shown by two arrows. Two arrows demonstrate: (1) increasing depths of partial melting and (2) increasing degrees of carbonatite fluxing.

Table 1. Location, age and characteristics of the selected Hawaiian lavas and glasses

Volcanic stage	Location	Type of samples	Age	Reference
Post-erosional or rejuvenated*	Honolulu volcano, Oahu island	nepheline melilitite; nephelinite with rare melilitite; basanite; alkali Ol basalt	< 0.58 Ma	Clague & Frey, 1982
Preshield**	Loihi	basanite and alkali basalt	5 ± 4 to 102 ± 13 ka	Frey & Clague, 1983
Postshield and rejuvenated	Kauai island	alkalic basalt, basanite, nephelinite, and nepheline melilitite	between 3.7 and 0.52 Ma	Clague & Dalrymple 1988
Postshield***	Haleakala volcano, Maui island	alkalic basalts	0.5 – 0.1 Ma	Chen et al. 1991
Post-erosional or rejuvenated	Koloa volcano, Kauai island	melilitite; nephelinite; basanite; alkali Ol basalt	a peak in the activity at 1.2 Ma	Maaloe et al. 1992
Rejuvenated	Kauai island	basanites, alkali basalts	from about 3.5 to 0.5 Ma	Reiners & Nelson 1998
Rejuvenated	North Arch volcanic field	alkalic basalt to nephelinite	1.15 – 0.5 Ma	Frey et al., 2000
Rejuvenated	submarine Wailau landslide, Molokai	basanites and alkaline basalts	between 1.5 and 1.4 Ma	Clague & Moore, 2002
Rejuvenated	Hawaiian North Arch and Honolulu Volcanics	melilitite; nephelinite; basanite; alkali basalt	< 0.5 to 1.5 Ma	Yang et al., 2003
Postshield and rejuvenated	West Maui	Ol basalts	0.6 – 0.4 Ma	Gaffney et al. 2004
Rejuvenated*	Honolulu volcano, Oahu island	alkalic basalt to nephelinite	< 0.58 Ma	Clague et al. 2006
Rejuvenated	Kiekie basalt, Niihau island	basalt glasses	3.5 – 0.35 Ma	Dixon et al., 2008
Rejuvenated	Kaula island	nephelinites and associated xenoliths	4.22 ± 0.22? Ma	Bizimis et al., 2013
Rejuvenated	Kauai island	transitional basalt to nephelinite	2.3 – 0.3 Ma	Cousens & Clague, 2015
Postshield***	Haleakala, Maui island	basanites	< 0.15 Ma	Phillips et al., 2016
Shield	Hawaii island	basalts	-	DeFelice et al. 2019

Rejuvenated	Kaula Island	alkalic basalt to basanite	< 1.95 Ma	Garcia et al., 2016
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* Lanphere and Dalrymple (1980); ** Guillou et al. (1997); *** Sherrod et al. (2003).

Table 2. Partition coefficients used in melting models

	OI		Opx	Cpx	Spl	Grt	Amp	Phl
Zr	0.0005 KE ^a 0.0003 FJ <u>0.01 P</u>	0.0025 R	0.014 KE 0.027 R 0.032 GR 0.0099 AGR <u>0.01 P</u>	0.089 S <u>0.1234 HD</u> 0.1280 J 0.164 H 0.18 R 0.27 BL	0.001 R <u>0.07 KE</u>	0.27 J <u>0.3 KE</u> 2.12 H 0.47 AGR	<u>0.127 L</u> 0.23 BR 0.18-0.33 A	<u>0.017 L</u> 0.13 A 0.23 BR 0.008 GR
Hf	0.0028 R 0.001-0.004 D 0.0008 FJ <u>0.005 P</u>		0.025 R 0.04 D 0.017 AGR 0.06 GR <u>0.01 P</u>	0.10-0.20 T 0.179 S 0.19 F 0.23 J <u>0.256 HD</u> 0.29 H 0.3 R 0.34 - 0.38 W 0.36 - 0.46 D 0.55 BL 0.13 E	<u>0.001 R</u> 0.003 E	0.24 J 0.62 T 1.22 H <u>0.32 P</u>	<u>0.33 L</u> 0.45 BR	<u>0.19 L</u> 0.45 BR 0.091 GR

Table 2 (continued):

	Ol	Opx	Cpx	Spl	Grt	Amp	Phl
Sm	0.0007 KE 0.0025 R <u>0.001 P</u>	0.014 R 0.02 KE 0.011 AGR 0.015 GR <u>0.01 P</u>	0.086-0.22 T 0.201 S 0.281 J <u>0.291 HD</u> 0.33 H 0.35 F 0.4 R 0.67 BL 0.31 E 0.21 GR	<u>0.0006 KE</u> 0.0006 R	0.23 T 0.25 J 0.5 KE 0.101 GR <u>0.217 P</u>	<u>0.66 BR</u>	<u>0.27 G</u> 0.66 BR 0.017 GR
La	7E-06 KE 4.5E-04 R <u>0.0005 D</u>	0.0005 KE 0.0025 R <u>0.004 D</u>	0.03 S 0.04-0.28 AG 0.0536 HD 0.06 R 0.089 BL <u>0.015 D</u>	0.0001 R <u>0.0006 KE</u>	0.001 KE 0.0016 J <u>0.007 L</u>	<u>0.055 L</u>	<u>0.06 G</u>
K	<u>1E-09 KE</u>	<u>1E-05 KE</u>	<u>0.0072 HD</u>	<u>0 KE</u>	<u>1E-05 KE</u>	<u>0.58 L</u>	<u>3.67 L</u>
Ba	1E-09 KE * <u>5E-06 D</u>	1E-05 KE <u>6E-06 D</u>	0.00068 HD <u>4E-04 D</u>	<u>0 KE</u>	1E-05 KE <u>7E-05 D</u>	<u>0.16 L</u>	<u>3.68 L</u>
Th	7E-06-1E-05 B 1.3E-04 R <u>5E-06 D</u>	2E-05-3E-05 B <u>12.5E-05 R</u>	<u>1.5E-05 R</u> 1.3E-03- 2.1E-03 B 0.0070 T 0.0086 F 0.014 H	<u>1E-05 R</u> 0.0014 H 0.0036 T	<u>2.1E-03 B</u>	<u>0.0039 L</u> 0.017 BR	<u>0.0014 L</u>
Nb	<u>0.0001 KE</u> 0.0017 R	0.0025 R <u>0.003 KE</u>	0.003 S <u>0.0077 HD</u> 0.008 R 0.020 BL	<u>0.01 KE</u> 0.07 R	0.0042 J <u>0.01 KE</u>	<u>0.159 L</u> 0.20 BR	<u>0.088 L</u>
Ti	<u>0.015 KE</u>	<u>0.14 KE</u>	0.273 S 0.347 J 0.35-0.43 D <u>0.384 HD</u>	<u>0.15 KE</u>	0.28 J <u>0.6 KE</u>	0.95 A <u>1.29 L</u>	0.98 A <u>1.77 L</u>
Eu	9.5E-04 KE 0.0029 R <u>0.002 P</u>	0.0185 R 0.03 KE <u>0.01 P</u>	0.35 HD 0.38 BL <u>0.47 P</u> 0.46 R	<u>6E-04 KE</u> 9E-04 R	<u>1 KE</u> 0.4 P	<u>0.88 IF</u>	<u>0.029 IF</u>
Nd	<u>0.00042 D</u>	<u>0.012 D</u>	<u>0.088 D</u>	<u>0.0006 **</u>	<u>0.064 D</u>		
Ce	<u>0.0005 D</u>	<u>0.004 D</u>	<u>0.038 D</u>	<u>0.0006 **</u>	<u>0.017 D</u>		
Tb	<u>0.006 D</u>	<u>0.0325 D</u>	<u>0.165 D</u>	<u>0.0015 **</u>	<u>1.6 D</u>		
Yb	<u>0.03 D</u>	<u>0.08 D</u>	<u>0.25 D</u>	<u>0.0045 **</u>	<u>4.0 D</u>		

^a Partition coefficients ($K_d = C_i^{\text{mineral}} / C_i^{\text{melt}}$) between the main mantle minerals and basaltic or basanitic melts according to A - Adam et al. (1993); AG - Adam and Green (1994); AGR - Adam and Green (2006); B - Beattie (1993); BL - Blundy et al. (1998); BR - Brenan et al. (1995); D - Dunn (1987); E - Elkins et al. (2008); F - Falloon et al. (1988); FJ - Foley and Jenner (2004); GA - Gaetani et al. (2003); G - Green (1994); GR - Green et al. (2000); H - Hauri et al. (1994); HD - Hart and Dunn (1993); Irving and Frey (1984); J - Johnson (1994); KE - Kelemen et al. (1993); L -

LaTourette et al. (1995); R – Remaidi (1993); S - Skulski et al. (1994); T – Takahashi (1986); W - Watson et al. (1987); D – Dixon et al. (2008) and P - Pilet (2015). Underlined values were used for the calculations. Ol, Opx, Cpx, Spl, Grt, Amph Phl denotes olivine, orthopyroxene, clinopyroxene, spinel, garnet, amphibole, phlogopite.

* K_d^{Ba} values for phlogopite are considered as equal to those of K_d^K . ** - suggested values.

APPENDIX

Estimation of trace-element ratios in partial melts relative to those of amphibole-bearing (A), phlogopite-bearing (P), and garnet (G) lherzolites and garnet pyroxenite (GP) sources

The values of X/Y fractionation in a partial melt relative to X/Y in the mantle source (**Fig. 2**) are calculated using the modal batch melting equation of Shaw (1970) (see Supplementary Models):

$$([X]_{\text{melt}}/[Y]_{\text{melt}}) / ([X]_{\text{source}}/[Y]_{\text{source}}) = [D_o^Y + f(1-D_o^Y)] / [D_o^X + f(1-D_o^X)]$$

where f is degree of melting of the mantle source, D_o corresponds to the bulk distribution coefficients, $[X]$ and $[Y]$ are concentrations of X and Y in the elemental ratio of X and Y .

D_o for A and P lherzolites are calculated using K_d for Ol, Opx, Cpx, Amph and Phl (**Table 2**) and mineral compositions of A and P lherzolites taken from McKenzie and O'Nions (1991): 59.9% Ol, 24.4% Opx, 3.8% Cpx, 11.6 % Amp (Phl). D_o for G lherzolite are calculated using K_d for Ol, Opx, Cpx and Grt (**Table 2**), mineral compositions of lherzolites taken from McKenzie and O'Nions (1991): G (59.8% Ol, 21.1% Opx, 7.6% Cpx and 11.5% Grt). D_o for garnet pyroxenite (GP) are calculated using K_d for Opx, Cpx, Grt (**Table 2**) and the following mineral compositions: 46.5% Opx, 46.5% Cpx, 7% Grt (see Supplementary Models).

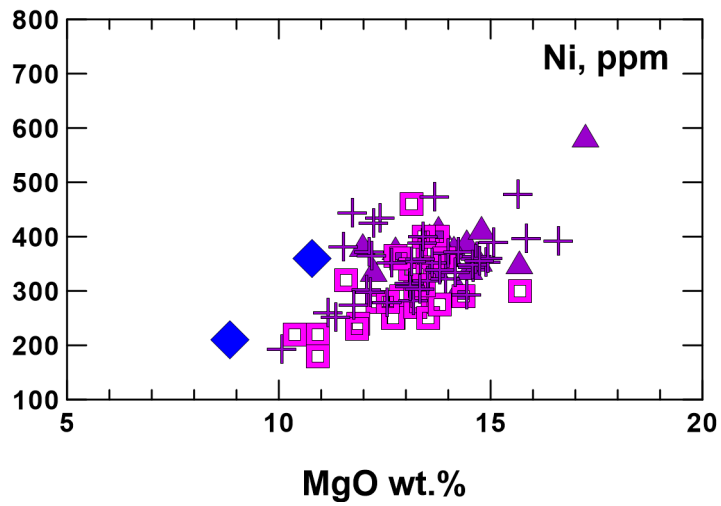


Figure A1. Ni (in ppm) vs MgO (wt.%) contents in the Hawaiian alkaline lavas included in this study. Data sources as in **Figure 2**.

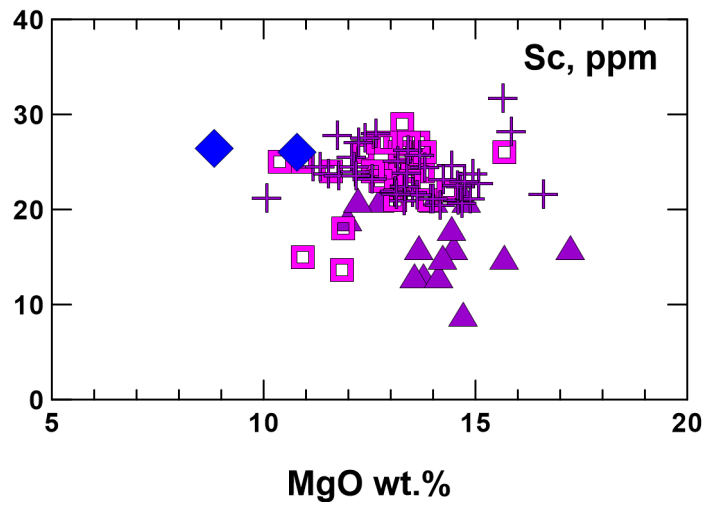


Figure A2. Sc (in ppm) vs MgO (wt.%) contents in the Hawaiian alkaline lavas included in this study. Data sources as in **Figure 2**.

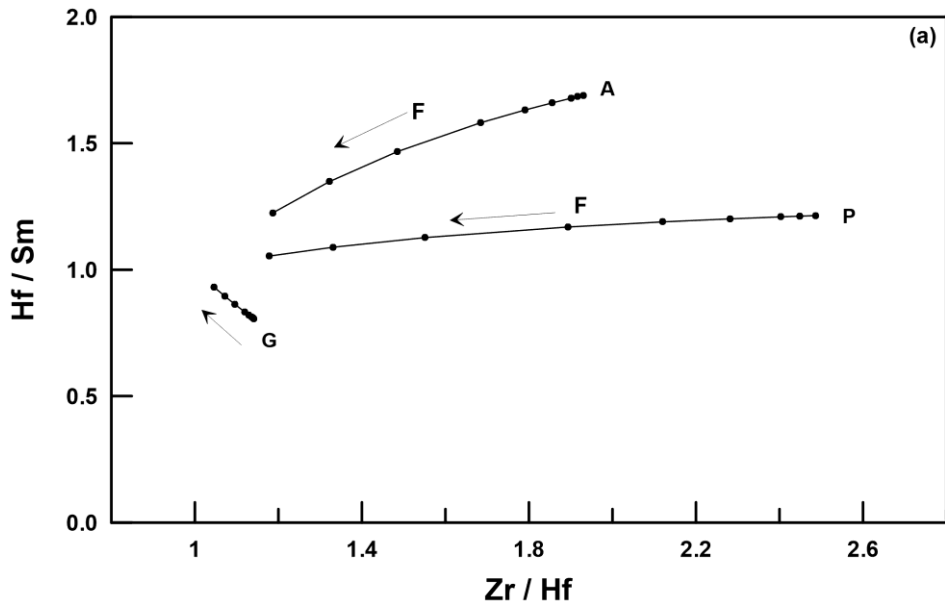


Figure A3(a). Modeling of Hf/Sm vs Zr/Hf behavior during batch modal melting of uncarbonated garnet, amphibole and phlogopite lherzolites. A – amphibole lherzolite, P – phlogopite lherzolite and G – garnet lherzolite. Arrows indicate the increasing degree of melting (F).

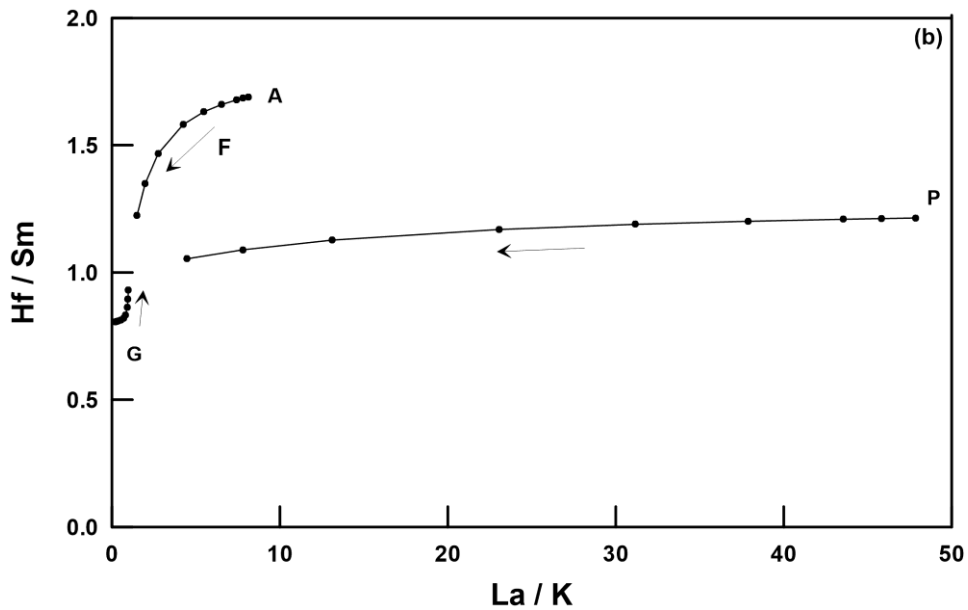


Figure A3(b). Modeling of Hf/Sm vs La/K behavior during batch modal melting of uncarbonated garnet, amphibole and phlogopite lherzolites. A – amphibole lherzolite, P – phlogopite lherzolite and G – garnet lherzolite. Arrows indicate the increasing degree of melting (F).

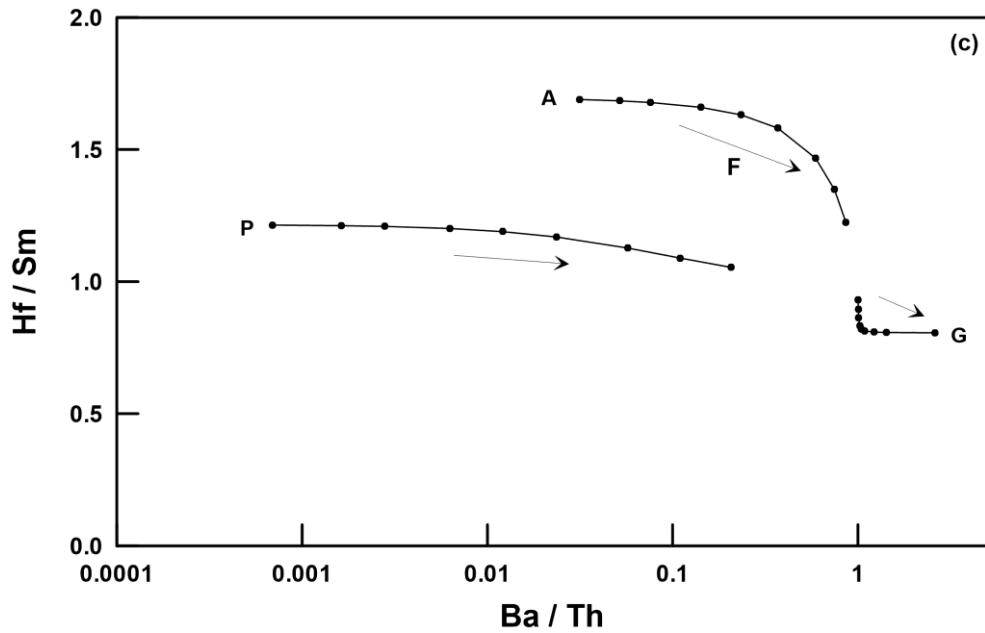


Figure A3(c). Modeling of Hf/Sm vs Ba/Th behavior during batch modal melting of uncarbonated garnet, amphibole and phlogopite lherzolites. A – amphibole lherzolite, P – phlogopite lherzolite and G – garnet lherzolite. Arrows indicate the increasing degree of melting (F).

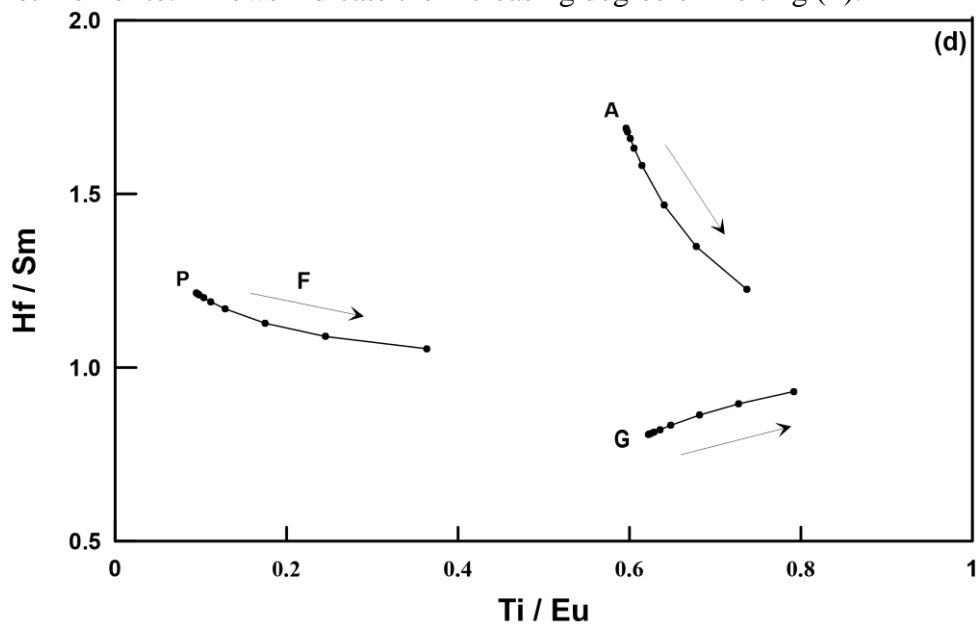


Figure A3(d). Modeling of Hf/Sm vs Ti/Eu behavior during batch modal melting of uncarbonated garnet, amphibole and phlogopite lherzolites. A – amphibole lherzolite, P – phlogopite lherzolite and G – garnet lherzolite. Arrows indicate the increasing degree of melting (F).