CO₂-Rich Rejuvenated Stage Lavas on Hawaiian Islands

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Abstract

Sedimentary carbonates are sent to the deep mantle if they are not completely destroyed at subduction zones, and subducted carbonates may contribute to plume volcanism. To better constrain the role of recycled carbonates in Hawaiian volcanism, we report high-precision olivine and whole-rock geochemical compositions of shield and rejuvenated stage lavas from Kauai, Oahu and Maui Islands. The studied rejuvenated stage whole-rocks have low SiO₂ and high CaO concentrations, and are depleted in high field strength elements, such as, Nb and Zr, consistent with a role of carbonated melt. Rejuvenated stage olivines have Ni abundance lower than and CaO and MnO contents similar to those of shield stage at a given Fo. The calculated partition coefficients of Ca (D²⁹⁻melt) and Mn (D⁸⁰⁻melt) between olivine and shield melts are consistent with those of a dry melt system. However, the low D²⁹⁻melt and D⁸⁰⁻melt for rejuvenated lavas can only be explained by a volatile-rich melt system. Based on the observed D²⁹⁻melt and D⁸⁰⁻melt in rejuvenated lavas, and considering the effect of H₂O, our modeling calculation shows that rejuvenated primary magmas contain up to ~10 wt% CO₂, indicating a CO₂-rich mantle source. Using olivine-spinel aluminum exchange thermometry, we show that the rejuvenated primary magma temperatures are similar to those of shield stage. We posit that the CO₂-rich rejuvenated stage lavas with lower olivine Ni than those of shield stage lavas were originated from melting of carbonated peridotites in the plume. The carbonated melts that metasomatized the peridotites were likely derived from subducted ancient carbonate-bearing lithospheric mantle.

1. Introduction

The deep mantle may store most of the Earth's carbon (Dasgupta & Hirschmann, 2010; Dasgupta et al., 2006; Plank & Manning, 2019; Zhang et al., 2017). Plate subduction is considered to be an important factor of carbon enrichment in the deep Earth's interior (Dasgupta & Hirschmann, 2010; Plank & Manning, 2019). Deep-rooted mantle plumes (e.g., Hawaiian plume) are good candidate for the study of deep Earth's carbon cycle (Dixon et al., 2008). Since CO₂ can significantly change the chemistry of mantle-sourced melts, for example, lowering SiO₂ and elevating CaO of melts (Dasgupta et al., 2007a, 2007b; Zhang et al., 2017), it may play an important role in the origin of alkali basalts (Dasgupta et al., 2006, 2007a, 2007b; Dixon et al., 2008; Sisson et al., 2009).

The Emperor-Hawaii seamount chain is a type volcanic chain that may originate from near the core-mantle boundary (French & Romanowicz, 2015; Huang et al., 2011; Montelli et al., 2004; Weis et al., 2011). Shield stage tholeiitic basalts account for the majority (95 vol%) of Hawaiian volcanic rocks, while pre-shield, post-shield and rejuvenated stages account for the rest 5% (Sherrod et al., 2007). The role of an olivine-free lithology, pyroxenite or eclogite, in the petrogenesis of Hawaiian shield lavas is highly debated. Specifically, Hawaiian shield tholeiitic lavas have too high SiO₂ content to be produced by partial melting of garnet peridotite (e.g., Hauri, 1996; Huang et al., 2005; Wagner & Grove, 1998). This led to the suggestion that an eclogite component played a role in producing the high SiO₂ contents in Hawaiian tholeiitic lavas (Hauri, 1996; Huang et al., 2005). Alternatively, the high SiO₂ content may be a result of melt-harzburgite reaction (Wagner & Grove, 1998). Sobolev et al. (2005, 2007) and Herzberg (2006, 2011) noted that the high olivine Ni contents and low CaO and MnO in olivines from Hawaiian shield lavas, as well as low whole rock CaO contents, required a pyroxenite-dominated mantle source for Hawaiian shield lavas. Alternatively, the low CaO and MnO contents, and high SiO₂ content of Hawaiian lavas may be explained if they represent mixtures of partial melts from garnet peridotite and from eclogite (Huang et al., 2007). Matzen et al. (2013, 2017) showed that the high olivine Ni content in Hawaiian shield stage olivines reflect the temperature difference between partial melting beneath the thick lithosphere and olivine crystallization in a shallow magma chamber, and a pyroxenite-dominated mantle source is not required.
Hawaiian rejuvenated stage volcanism occurred 0.5–2 Myr after shield stage and consists of silica-undersaturated alkaline-rich rocks, for example, alkali basalt, hawaiite, nephelinite and melilitite (e.g., Clague & Dalrymple, 1987; Garcia et al., 2010; Phillips et al., 2016). Hawaiian rejuvenated lavas are among the most silica-undersaturated and alkaline-rich in oceanic Islands/seamounts (Chauvel et al., 1997). It remains unclear on the origin of rejuvenated stage low-SiO$_2$ alkali-rich volcanic rocks (Ballmer et al., 2011; Garcia et al., 2010; Hofmann & Farnetani, 2013; Phillips et al., 2016; Reiners & Nelson, 1998). Hawaiian rejuvenated lavas are more depleted in Sr-Nd-Hf isotope compositions than those of shield stage (e.g., Beguelin et al., 2019; Chen & Frey, 1983; DeFelice et al., 2019; Frey et al., 2000; Harrison et al., 2020; Hofmann & Farnetani, 2013; Yang et al., 2003), indicating different mantle sources. Earlier studies suggested an origin of Hawaiian rejuvenated lavas from the underlying metasomatically enriched Pacific lithospheric mantle (Chen & Frey, 1983; Garcia et al., 2010). However, there are increasing studies suggesting the isotopically depleted rejuvenated stage source component is intrinsic of the mantle plume (DeFelice et al., 2019; Harrison et al., 2020; Hofmann & Farnetani, 2013; Ribe & Christensen, 1999).

Silica under-saturated alkali lavas could be explained by involvement of CO$_2$ in the mantle source (Mallik & Dasgupta, 2012, 2013). Several studies have indicated that CO$_2$ played an important role in the origin of Hawaiian lavas (Borisova & Tilhac, 2021; Dixon et al., 2008; Huang et al., 2009, 2011; Sisson et al., 2009). Tucker et al. (2019) showed that the mantle sources of Hawaiian shield stage lavas contain 380–480 ppm CO$_2$ based on measurement of olivine hosted melt inclusions, while the source CO$_2$ contents of rejuvenated lavas were not constrained. Dixon et al. (2008) explained Hawaiian rejuvenated lavas with elevated Ba/Th by carbonatite metasomatism, but the content of CO$_2$ has not been directly constrained. CO$_2$ not only affects magma chemical compositions, but also element partitioning between olivine and melts (Gavrilenko et al., 2016). In this study, we have analyzed high-precision olivine chemistry and whole-rock major and trace elements of Hawaiian rejuvenated stage lavas, aiming to evaluate the role of CO$_2$ in Hawaiian magmatism.

2. Samples

Shield and rejuvenated stage rock samples in this study were collected from Kauai, Oahu and Maui Islands (Figure 1), and the sampling information is shown in Table 1. We have collected 26 rock samples, including 16 rejuvenated stage and 10 shield stage, from these Islands (Figure 1; Table 1). At Kauai Island, there are two sampling sites from the shield stage Waimea volcanics (5.5-4 Ma), and five sites from the rejuvenated stage Koloa volcanics (2.6-0.15 Ma). At Oahu Island, there are two sampling sites from the shield stage Wai‘anae volcanics and one site from the shield stage Ko‘olau volcano (3.0-1.8 Ma); two sampling sites from the rejuvenated stage Honolulu volcanics (0.8-0.1 Ma). At Maui Island, there is one sampling site from the shield stage Wailuku volcanics (2.0-1.3 Ma); two sites from the rejuvenated stage Hana volcanics (0-1.5 Ma) and one site from the rejuvenated stage Kula volcanics (0.93-0.15 Ma). The detailed information on division of volcanics can be referred to Sherrod et al. (2007). Despite the absence of distinct differences in formation age between the Hana and Kula volcanics, we classify the Hana and Kula volcanics as rejuvenated stage because of their low-silica and high alkaline characteristics. The detailed information on sampling can be found in Table 1.

3. Methods and Results

3.1. Methods

The 26 rock samples were analyzed for bulk-rock major and trace elements, and their olivine phenocrysts were analyzed for major and trace elements using in situ high-precision electron probe microanalyzer (EMPMA) technique. Bulk-rock major elements were analyzed using fused glass discs with an Axios sequential X-ray Fluorescence Spectrometer at Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China. Samples were fused at 1050°C using a lithium tetraborate flux (Li$_2$B$_4$O$_7$) in a mixture consisting of 0.5 g of sample and 5 g of lithium tetraborate. Loss on ignition was determined at a temperature of 1000°C in air for 3 hr. Basalt standards BCR-2, BHVO-2 and GSR-3 were analyzed as unknowns and the results are shown in Table S1 in Supporting Information S1. Bulk-rock trace elements were analyzed by a Perkin-Elmer Sciex ELAN DRC-e ICP-MS at the State Key Laboratory of Ore Deposit Geochemistry, IGCAS. The powdered samples (50 mg) were dissolved with HF + HNO$_3$ mixture in high-pressure Teflon Bombs at ~190°C for 48 hr (Qi et al., 2000). Rh was used as an internal standard to monitor sensitivity drift during measurement. How do you measure the trace
Figure 1. Geological setting and sampling locations of this study. The geologic maps are modified based on Sherrod et al. (2007).
element abundances? BCR-2 and BHVO-2 solutions were used to monitor analytical accuracy. The analytical precision was generally better than 10% (2 sigma) based on replication of basalt standards analyses. Quantitative in situ analyses of olivine and spinel major and minor elements were conducted on JXA-8230 EMPA equipped with five wavelength dispersive spectrometers at Institute of Oceanology, Chinese Academy of Sciences. The operating conditions were: 20 kV accelerating voltage, 60 nA beam current, and 1–5 μm beam diameter. For olivine analyses, the counting time was 30 s for Si kα, Mg kα and Fe kα, and 80 s for Mn kα, Ni kα, Ca kα, Cr kα, Al kα. The off peak counting time was 80 s for Mn kα, Ni kα, Ca kα, Cr kα, Al kα. Standards used were olivine (Si, Mg), corundum (Al), MnO (Mn), wollastonite (Ca), NiO (Ni), and apatite (Fe), magnetite (Fe), and Cr₂O₃ (Cr). For spinel analyses, the counting time was 30 s for Si kα, Mg kα, Fe kα, and 80 s for Mn kα, Ni kα, Cr kα, Al kα. The off peak counting time was 20 s for Si kα, Mg kα, Al kα, Mn kα, Ni kα, Cr kα, Ti kα and Fe kα. Standards used were spinel (Al, Mg), quartz (Si), MnO (Mn), rutile (Ti), NiO (Ni), magnetite (Fe) and Cr₂O₃ (Cr). Unknown and standard intensities were corrected for dead time. All data were corrected with the standard ZAF correction procedures. The olivine standard MongOLSh11-2 (Batanova et al., 2019) was replicated during the analyses to monitor the reproducibility and accuracy, and the results are shown in Table S3 in Supporting Information S1.

| Site | Sample ID | Island name | Latitude (°N) | Longitude (°W) | Volcanics | Volcanic stage | Age   |
|------|-----------|-------------|---------------|----------------|-----------|----------------|-------|
| K1   | K1-1      | Kauai       | 21°59′43.88″  | 159°21′27.28′ | Waimea Shield | 5.5-4 Ma       |
| K4   | K4-2      | Kauai       | 21°55′48.47″  | 159°29′47.85′ | Koloa Rejuvenated | 2.6-0.15 Ma   |
| K5   | K5-3      | Kauai       | 21°55′18.19′  | 159°33′03.96′ | Waimea Shield | 5.5-4 Ma       |
| K7   | K7-1      | Kauai       | 21°54′3.11″   | 159°35′50.05′ | Koloa Rejuvenated | 2.6-0.15 Ma   |
| K11  | K11-2     | Kauai       | 21°53′7.66″   | 159°29′39.94′ | Koloa Rejuvenated | 2.6-0.15 Ma   |
| K13  | K13-1     | Kauai       | 22°03′10.3″   | 159°20′00.75′ | Waimea Shield | 5.5-4 Ma       |
| K14  | K14-1     | Kauai       | 22°13′13.64″  | 159°23′08.43′ | Koloa Rejuvenated | 2.6-0.15 Ma   |
| K15  | K15-1     | Kauai       | 22°12′14.03″  | 159°20′05.52′ | Koloa Rejuvenated | 2.6-0.15 Ma   |
| O1   | O1-1      | Oahu        | 21°16′36.02″  | 157°41′12.62′ | Honolulu Rejuvenated | 2.6-0.15 Ma   |
| O2   | O2-2      | Oahu        | 21°17′13.13″  | 157°40′7.12′  | Honolulu Rejuvenated | 2.6-0.15 Ma   |
| O3   | O3-2      | Oahu        | 21°18′48.91″  | 157°39′37.77′ | Honolulu Rejuvenated | 0.8-<0.1 Ma   |
| O7   | O7-1      | Oahu        | 21°20′29.21″  | 157°52′4.72′  | Honolulu Rejuvenated | 0.8-<0.1 Ma   |
| O7   | O7-2      | Oahu        | 21°20′29.21″  | 157°52′4.72′  | Honolulu Rejuvenated | 0.8-0.1 Ma    |
| O7   | O7-3      | Oahu        | 21°20′29.21″  | 157°52′4.72′  | Honolulu Rejuvenated | 0.8-0.1 Ma    |
| O8   | O8-1      | Oahu        | 21°18′0.18″   | 157°52′26.23′ | Ko‘olau Shield | 3.0-1.8 Ma     |
| O15  | O15-3     | Oahu        | 21°27′37.21″  | 158°12′51.35′ | Wa’ialae Shield | 4.0-2.9 Ma     |
| O15  | O15-5     | Oahu        | 21°27′37.21″  | 158°12′51.35′ | Wa’ialae Shield | 4.0-2.9 Ma     |
| O16  | O16-1     | Oahu        | 21°23′51.02″  | 158°10′8.13′  | Wa’ialae Shield | 4.0-2.9 Ma     |
| M2   | M2-1      | Maui        | 20°38′22.00″  | 156°26′51.48′ | Hana Rejuvenated | 13-50 Kyr      |
| M7   | M7-2      | Maui        | 20°36′45.87″  | 156°25′54.89′ | Hana Rejuvenated | 0-1.5 Kyr      |
| M8   | M8-2      | Maui        | 20°36′23.40″  | 156°25′34.20′ | Hana Rejuvenated | 0-1.5 Kyr      |
| M15  | M15-1     | Maui        | 20°46′13.99″  | 156°27′34.51′ | Kula Rejuvenated | 0.93-0.15 Ma   |
| M16  | M16-3     | Maui        | 20°46′38.32″  | 156°31′23.88′ | Wailuku Shield | 2.0-1.3 Ma     |
| M17  | M17-1     | Maui        | 20°47′20.61″  | 156°33′27.89′ | Wailuku Shield | 2.0-1.3 Ma     |
| M17  | M17-2     | Maui        | 20°47′20.61″  | 156°33′27.89′ | Wailuku Shield | 2.0-1.3 Ma     |
| M28  | M28-1     | Maui        | 20°37′30.05″  | 156°12′37.34′ | Kula Post-shield/Rejuvenated | 0.93-0.15 Ma   |

Note. Division and ages of volcanics are based on Sherrod et al. (2007).
3.2. Results

3.2.1. Whole-Rock Major and Trace Elements

Whole-rock major and trace element compositions are shown in Data Set S1. As shown in the plot of TAS versus SiO$_2$, (Figure S1 in Supporting Information S1), shield stage lavas are tholeiitic basalts with two plotting close to the division line between alkali basalt and tholeiitic basalts. Shield stage lavas have SiO$_2$ between 46.4 and 50.0 wt%, MgO between 11.5 and 23.4 wt%, CaO between 5.1 and 10.7 wt%, Na$_2$O between 1.44 and 2.51 wt%, and P$_2$O$_5$ between 0.18 and 0.35 wt%. Shield stage lavas show slight enrichment of light over heavy rare earth elements (REEs) and slight enrichment of Ba. Rejuvenated stage lavas are all rich in alkaline elements and can be classified into foidite, basanite and alkali basalts (Figure S1 in Supporting Information S1), of which the three foidite samples from Site O7 (Honolulu volcanics) have the highest alkaline (Na$_2$O + K$_2$O) and P$_2$O$_5$ and the lowest SiO$_2$ contents (Figure 2). Except for Site O7 foidite samples, the other rejuvenated stage samples have SiO$_2$ between 37.7 and 45.3 wt%, MgO between 7.15 and 15.1 wt%, CaO between 9.4 and 13.3 wt%, Na$_2$O between 2.4 and 3.8 wt%, and P$_2$O$_5$ between 0.33 and 0.92 wt%.

These rejuvenated stage lavas are strongly enriched in light rare earth elements (LREEs) and large ion lithophile elements (LILEs) (Figure 3) compared with shield stage lavas. These rejuvenated stage lavas also have positive anomalies of Ba and negative anomalies of Zr-Hf (Figure 3). Site O7 foidite lavas have the strongest enrichment of LILEs and Th-U and the strongest negative anomalies of high field strength elements (HFSEs, e.g.,...
These rejuvenated stage lavas show systematically lower SiO$_2$ and Al$_2$O$_3$ and higher total iron and CaO/Al$_2$O$_3$ compared to shield stage lavas (Figure 2, Figure S2 in Supporting Information S1). Rejuvenated stage lavas also have systematically lower Ni than those of shield stage for a given MgO content (Figure 2b). Moreover, rejuvenated stage lavas have overall higher CaO and MnO contents than those of shield stage for a given MgO content (Figures 2b and 2d).

### 3.2.2. In Situ Olivine and Spinel Chemistry

Olivine phenocrysts and olivine-spinel pairs have been analyzed for high-precision major and trace element compositions by EMPA, and the results are shown in Data Sets S2 and S3, respectively. The volcanic rock samples of shield and rejuvenated stages in this study have similar ranges in Fo (molar Mg/(Mg + Fe) × 100%) (Figure 4). For shield stage volcanic rocks, the highest Fo of olivines are 86.8, 89.1, 88.5, and 87.4 for Waimea, Wai'anae, Ko'olau and Wailuku volcanics, respectively; while for rejuvenated stage volcanic rocks, the highest Fo of olivines are 87.5, 86.9, 87.3, and 84.1 for Koloa, Honolulu, Hana, and Kula, respectively. As shown in Figure 4, at a given Fo, shield stage volcanic rocks have olivine Ni contents distinctly higher and Mn-Ca contents lower than those of global MORBs. The olivines of rejuvenated stage lavas also have Ni contents systematically higher than those of global MORBs but lower than those of shield stage lavas for a given Fo. Despite the distinct

**Figure 3.** Trace element patterns for the volcanic rock samples from Hawaiian Islands. Data are normalized to the primitive mantle data of McDonough and Sun (1995). The typical carbonatite (Sample #: 85LB25, the carbonatite lava) for comparison from Hoernle et al. (2002).
compositions of olivine Ni between shield stage and rejuvenated stage lavas, their olivine Ca and Mn contents are comparable for a given Fo (Figure 4). The olivines with the highest Fo for both shield and rejuvenated stages have similarly Mn and Ca contents, which are lower than those of MORBs.

4. Discussion

4.1. Implication of Whole-Rock Geochemistry on the Role of CO2

It has been suggested that shield stage lavas characterized by depletion of CaO and enrichment of SiO2 cannot be explained by melting of peridotites (Dasgupta et al., 2010; Hauri, 1996; Herzberg, 2006; Herzberg & Asimow, 2008; Huang et al., 2005; Wagner & Grove, 1998), but can be explained by partial melting of mixed pyroxenite (recycled oceanic crust) and peridotite (e.g., Herzberg, 2011; Herzberg & Asimow, 2008; Huang et al., 2007; Mallik & Dasgupta, 2012; Sobolev et al., 2005, 2007). Rejuvenated stage lavas are usually silica-under saturated and enriched in CaO that are distinct from shield stage volcanism (Figure 2). The enrichment of LREEs and LILCs in rejuvenated lavas (Figure 3) could be explained by low degree of melting in the mantle source and a geochemically enriched mantle source. However, the high CaO and SiO2-poor nature of rejuvenated stage lavas cannot be explained by melting of dry pyroxenite (e.g., Mallik & Dasgupta, 2013) or peridotite (e.g., Dasgupta et al., 2010) at any temperature and pressure. Results of high pressure/temperature experiments indicate that, with the presence of CO2, partial melts of either peridotite or pyroxenite/eclogite have high CaO and low SiO2 contents (e.g., Dasgupta et al., 2007b; Mallik & Dasgupta, 2013).

Plate subduction is an effective way to introduce sedimentary carbonate into deep mantle (e.g., Plank & Manning, 2019; Thomson et al., 2016; Zhang & Smith-Duque, 2014). If recycled oceanic crust is involved in the Hawaiian mantle plume, sedimentary carbonates may have played a role during mantle melting, especially at low degrees of melting. Based on the results of melting experiment (e.g., Mallik & Dasgupta, 2013), melting of carbonate-bearing MORB can only produce melts with MgO of <8 wt%, which cannot explain Hawaiian rejuvenated stage lavas with MgO of >10 wt%. Partial melts of carbonated pyroxenite and peridotite mixture and carbonated peridotite have both high MgO and CaO contents, as well as low SiO2 content (e.g., Mallik & Dasgupta, 2013). Carbonatitic melts typically have high contents of CaO, MnO, Ba, and REEs, and are depleted in HFSEs, (such as Nb-Ta-Zr-Hf-Ti) (e.g., Dalou et al., 2009; Dixon et al., 2008; Hoernle et al., 2002; Jones et al., 2013). We find that Site O7 samples from the Honolulu volcanics on Oahu Island, in addition to their anomalously high CaO-MnO and extremely low SiO2, have highly enriched LREEs and relative depletion in Nb-Ta-Zr-Hf-Ti (Figure 3). These observations could be explained by melting a carbonated mantle source.

4.2. Role of CO2 Indicated by Olivine Ca-Mn

Hawaiian rejuvenated stage volcanic rocks have higher CaO and MnO contents for a given MgO content than shield stage lavas (Figure 2), while their olivine Ca and Mn contents overlap at a given olivine Fo (Figure 4), reflecting a difference in partitioning of Ca-Mn between olivine/melt during the two volcanic stages. To better understand the partitioning of Ca-Mn between olivine/melt in Hawaiian lavas, we have calculated the partition coefficients of Ca and Mn between olivine/melt (Data Set S4). Hawaiian lavas
in this study, both shield and rejuvenated stages, have variable amount of olivine accumulation, and the samples with clinopyroxene accumulation are excluded. A mineral-melt pair in equilibrium is required before calculation of partition coefficient. Although primary melt composition can be calculated by assuming a Fo of ∼91, the exact Ca content of the equilibrium primary olivine is not known. Most of the rejuvenated stage lavas have variable degrees of olivine accumulations, thus, a way to obtain olivine-melt pairs in equilibrium is to remove the accumulated olivines. Thus, in this way, we can obtain the exact Ca composition of olivine in equilibrium. Ten to twenty olivine grains with the highest Fo and their average chemical compositions were used as the final equilibrium olivine (Data Set S4). These final equilibrium olivines have Fo of 84–87 for rejuvenated stage lavas and 83–89 for shield stage lavas. We have removed this average olivine composition step-by-step from the melt until the resulted melt was in equilibrium with the average olivine based on PRIMelt3 program (Herzberg & Asimow, 2015), in which a melt Fe\(^{2+}\)/Fe\(_{tot}\) is specified. The resulted equilibrium melt compositions are shown in Data Set S4. The equilibrium melts calculated for rejuvenated stages lavas have MgO of 8–12 wt%, while the equilibrium melts of shield stage have MgO of 10–14 wt%. It is clear that the calculated melts are not primary melts but evolved melts in equilibrium with the average olivines. We have calculated the partition coefficients of Ca and Mn between olivine/melt based on these olivine-melt pairs, which are shown in Data Set S5 and plotted in Figure 5. The calculated olivine/melt partition coefficients of Ca and Mn for rejuvenated stage samples are overall lower than those for shield stage for a given olivine Fo and melt MgO content, despite these evolved melts have degassed to certain degrees.

There are several observations indicating that CO\(_2\) has played an essential role in the activities of Hawaiian mantle plume. Sisson et al. (2009) argued that a carbonated garnet lherzolite source is required to produce the pre-shield basanite-nepheline lavas at Kilauea. Barsanti et al. (2009) showed that a suite of magmas of recent

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**Figure 5.** Plots of \(D_{Ca}\) (Ol/melt) versus (a) Fo and (b) melt MgO, and \(D_{Mn}\) (Ol/melt) versus (c) olivine Mg number (Fo) and (d) melt MgO. Source of literature data for comparison: data for \(D_{Mn}\) (Mallik & Dasgupta, 2012, 2013; Matzen et al., 2017), data for \(D_{Ca}\) (Dasgupta et al., 2007b; Kogiso et al., 1998; Mallik & Dasgupta, 2012, 2013; Matzen et al., 2017; Robinson et al., 1998).
(1842–1844) Kilauea eruption contain 2–6 wt% CO₂, and attributed the high CO₂ contents to enrichment by magma degassing at low pressures. Based on the CO₂ emission rate and volcanic magma supply rate at Kilauea, Anderson and Poland (2017) estimated 1 wt% CO₂ in the parental magma supplying Kilauea, which translates to 263 ppm C in their mantle source. This is consistent with the result of a recent work using melt inclusions. Tucker et al. (2019) showed that parental magmas of Hawaiian volcanos (Hualalai, Kilauea, Koolau, Loihi, and Mauna Loa) have 0.39–1.0 wt% CO₂, and their mantle sources contain 380–480 ppm CO₂ that are at least a factor of ~4 more than the MORB mantle. The negatively correlated Rb/Sr and ⁸⁷Sr/⁸⁶Sr in shield stage Mahukona lavas (Huang et al., 2009) and the light Ca isotope compositions in most shield stage Hawaiian lavas (Huang et al., 2011) may reflect a role of sedimentary carbonates in the Hawaiian mantle plume. Wirth and Rocholl (2003) reported nanocrystalline diamond in pyroxenite xenolith of Oahu Island, which may crystallize from rejuvenated stage magmas. Dixon et al. (2008) argued for a role of carbonatite metasomatism in the petrogenesis of Hawaiian rejuvenated stage lavas, requiring a CO₂ rich mantle source during the rejuvenated stage volcanism.

As shown in Figure 2, partial melts of carbonated pyroxenites and carbonated peridotites have higher contents of CaO and MnO compared to those from CO₂-free peridotites and pyroxenites. Garnet, Clinopyroxene (Cpx) and orthopyroxene (Opx) are important hosts for Ca and Mn during the mantle melting processes. The Cpx/melt partition coefficient of Mn (1.06–1.16) is lower than that between garnet/melt (1–4.8), but higher than that between Opx/melt (0.66–1.05) (Herzberg et al., 2013; Le Roux et al., 2011; Shea & Foley, 2019). The presence of CO₂ in the mantle source would increase the stability of Opx relative to Cpx and garnet, thus, the carbonated melts are enriched in Ca and Mn. This is supported by the observation that natural carbonatites usually are enriched in Ca and Mn (e.g., Hoernle et al., 2002). To further investigate the effect of CO₂ on the partitioning of Ca-Mn in olivine, we have selected the results of a suite of high-quality experiments with resulted melts similar in composition to this study for comparison.

Dasgupta et al. (2007b) conducted partial melting experiments on “peridotite + CO₂” and Mallik and Dasgupta (2013) conducted melting experiment on “eclogite + peridotite + CO₂.” These two studies obtained carbonated silicate melts with SiO₂ of 30–48 wt% and CaO of 7–25 wt%, which are comparable to the geochemistry of rejuvenated stage lavas. We also compared the Ca partition coefficients for Hawaiian lavas with the results of experiments that produced olivines equilibrium with dry silicate melts (Kogiso et al., 1998; Mallik & Dasgupta, 2012; Matzen et al., 2013, 2017; Robinson et al., 1998). These experiments either produced silicate melts in equilibrium with olivine based on melting of peridotite (Robinson et al., 1998) and mixed peridotite + eclogite (Kogiso et al., 1998; Mallik & Dasgupta, 2012), or modeled crystallization of olivine from MORB-like melts (Matzen et al., 2013, 2017). These experiments all produced dry silicate melts with SiO₂ of 45–53 wt% and CaO of 6–11 wt% that are similar to shield stage lavas and olivines with high precision Ca contents. We calculated the partition coefficient of Ca between olivine/melt based on the above experiment studies, and the results are plotted in Figure 5.

To understand the effect of CO₂ on partitioning of Mn between olivine and melt, we have compared our results with Mallik and Dasgupta (2013) (melting of eclogite + peridotite + CO₂), Mallik and Dasgupta (2012) (melting of peridotite + eclogite), and Dasgupta et al. (2007b) (melting of peridotite). The calculated partition coefficient of Mn for olivine-carbonated melt and olivine-dry silicate melt are shown in Figure 5. As shown in Figure 5, the experimental partition coefficients of Ca-Mn between olivine and carbonated silicate melt are overall lower than those between olivine and dry silicate melt for a given Fo and MgO content of melt. Rejuvenated stage foidite samples have the lowest DCaₘₐₜ and DMnₘₐₜ for a given Fo and magma MgO, while thebasanites and alkali basalts have D⁰⁻melt and D¹⁻melt intermediate between foidites and shield stage lavas (Figure 5). DCa₀⁻melt and DMn₀⁻melt from the olivine-dry silicate melt pairs are similar to those of shield stage lavas, while the partition coefficients of Ca-Mn calculated from the olivine/carbonated silicate melt are comparable to those of rejuvenated stage (Figure 5). We suggest that the lower DCa₀⁻melt and DMn₀⁻melt of rejuvenated stage lavas relative to shield stage lavas are consistent with the role of CO₂ during the mantle melting.

The relationships of D⁰⁻melt versus magma MgO for the shield and rejuvenated lavas in this study are compared with those resulted from experimental studies in Figure 6a. As shown in Figure 6a, the DCa₀⁻melt for the dry silicate melt system first slightly decreases and then increases with decreasing MgO based on Gavrilenko et al. (2016). The calculated D⁰⁻melt for shield stage lavas basically follow the trend in D⁰⁻melt versus MgO for the dry silicate melts (Figure 6a). Similar to the experimentally derived D⁰⁻melt for carbonated silicate melt system, the D⁰⁻melt calculated for rejuvenated stage lavas are well below the curve for the dry silicate melts. We have calculated the
difference in $D_{\text{Ca}}$ ($\Delta D_{\text{Ca}}^{\text{melt}}$) between our calculated melts and experimental volatile-free melts, and the results are shown in Data Set S5. The foidites with the lowest SiO$_2$ tend to have the lowest $D_{\text{Ca}}^{\text{melt}}$ and $D_{\text{Mn}}^{\text{melt}}$ for a given olivine Fo and melt MgO content (Figure 5), while the basanites and alkali basalts are intermediate between foidites and shield stage lavas (Figure 5). The overall high $\Delta D_{\text{Ca}}^{\text{melt}}$ for rejuvenated stage lavas relative to shield stage lavas (Figure 6c) is consistent with the role of CO$_2$ in the mantle source, which significantly decreases SiO$_2$ in melt. Another role of CO$_2$ is to cause negative anomalies of HFSEs (e.g., decreases in $Zr$/Sm; $N$, normalized to primitive mantle; $Zr_N^*$, calculated as $\sqrt{Nd_N \times Sm_N}$), because REEs are enriched relative to HFSEs in carbonated melts (Zhang et al., 2017). As shown in Figure 6d, the relatively low $Zr$/Zr$^*$ (0.3–0.8) and elevated $\Delta D_{\text{Ca}}^{\text{melt}}$ for rejuvenated stage lavas relative to shield stage further indicates the role of CO$_2$ in mantle melting. It should be noted that the Honolulu foidites with the lowest SiO$_2$, and $D_{\text{Ca}}^{\text{melt}}$ and $D_{\text{Mn}}^{\text{melt}}$ have the strongest negative anomalies of Nb and Zr (Figures 3, Figure 6d). This suggests that rejuvenated stage foidites were subjected to the strongest influence of CO$_2$ during mantle melting.

Gavrilenko et al. (2016) gave an equation of CO$_2$ (wt.%) = $270 \times \Delta D_{\text{Ca}} - 3330 \times \Delta D_{\text{Mn}} + 1.8 \times 10^6 \times \Delta D_{\text{Ca}}^{3}$ to calculate melt CO$_2$ content based on the correlation of CO$_2$ with the difference ($\Delta D_{\text{Ca}}$) in the $D_{\text{Ca}}$ values of carbonated melts and volatile-free melts. Since both H$_2$O and CO$_2$ can lower $D_{\text{Ca}}^{\text{melt}}$ (Gavrilenko et al., 2016), the effect of H$_2$O should also be considered to estimate magma CO$_2$ content based on $D_{\text{Ca}}^{\text{melt}}$. As shown in Dixon et al. (1997), the alkali basaltic to nephelinitic lavas from the North Arch Volcanic Field, Hawaii, can have H$_2$O up to 1.9 wt% and CO$_2$ up to 5.4 wt% based on analyses of batch glass and vesicles. Dixon et al. (2008) estimated 350 ppm H$_2$O in the Hawaii plume mantle, which is ~5 factors higher than the depleted MORB mantle. Dixon et al. (2008) estimated a bulk partition coefficient of ~0.01 for H$_2$O in the Hawaiian mantle. Hawaiian rejuvenated lavas are usually considered to have partial melting extents of <5%, thus, we have calculated rejuvenated magma H$_2$O contents based on a bulk partition coefficient of 0.01 for H$_2$O and batch melting degrees of 2% and 4%, and our calculation results in H$_2$O contents of 1.17 wt% and 0.71 wt%, respectively. Shield stage magma H$_2$O is calculated by assuming a batch melting degree of 20% in Hawaiian mantle source, and a magma H$_2$O content of 0.17 wt% is obtained. For comparison, Hauri (2002) reported a H$_2$O content of 0.17 wt% is obtained. For comparison, Hauri (2002) reported a H$_2$O content of 0.03 to 0.84 wt% in melt inclusions from five shield stage lavas from Hawaii. We estimated the influence of H$_2$O on $D_{\text{Ca}}^{\text{melt}}$ ($\Delta D_{\text{Ca}}$ at a given H$_2$O content) based on Gavrilenko et al. (2016). Then, we calculated the difference between $\Delta D_{\text{Ca}}^{\text{melt}}$ and $\Delta D_{\text{Ca}}$ at a given H$_2$O content, which is used to calculate the content of CO$_2$ based on the equation of Gavrilenko et al. (2016). The calculated results of CO$_2$ are shown in Data Set S5.

The mantle-derived primary magmas usually crystallize olivines with Fo up to ~91, which are higher than the olivine phenocrysts in this study (Figure 4). Thus, the result using the above method only represents the CO$_2$ concentration of evolved magmas, rather than primary magmas. The primary magma composition can be obtained by addition of equilibrium olivines to melt, however, the Ca contents of high Fo (>90) olivines in equilibrium with primary magmas are not known. Therefore, we cannot obtain the primary magma CO$_2$ content directly based on the equation of Gavrilenko et al. (2016). To obtain primary magma CO$_2$ content, we assume that magmas have not significantly degassed during fractionation. Then, the equilibrium olivines were added step by step to melts until the melts are in equilibrium with olivine with Fo of 91 based on PREMELT3 MEGA.XLSM of Herzberg and Asimow (2015), the resulted primary magma compositions and fraction of olivine added are shown in Data
Set S5. The primary magma CO₂ contents were obtained after correction to fraction of olivine added to melts. The calculation procedure and results are shown in Data Set S5. The CO₂ contents of the calculated shield stage primary magmas are close to zero. The calculated primary magma CO₂ for rejuvenated stage are up to 5.6 wt% and 8.3 wt% for batch melting degrees of 2% and 4%, respectively (Data Set S5).

We have compared our primary magma CO₂ contents with those calculated based on a constant CO₂/Ba ratio. Because CO₂ is similar to Ba in incompatibility during mantle melting (e.g., Anderson & Poland, 2017; Miller et al., 2019), the primary magma CO₂ content can be estimated if the mantle source CO₂/Ba ratio can be determined. As suggested by previous studies the Hawaiian mantle has a CO₂/Ba ratio of ∼86 (Anderson & Poland, 2017). The calculated primary magma CO₂ contents through this method is also shown in Data Set S5. The calculated primary magma CO₂ contents are 0.45–3.15 wt% for the shield stage, while the primary magma CO₂ contents are 2.8–10 wt% for rejuvenated stage. We have plotted the primary magma CO₂ contents for anhydrous melting and a melting degree of 4% in this study with those based on the constant CO₂/Ba of 86 in Figure 7. As shown in Figure 7, the foidite samples tend to have the highest primary magma CO₂ contents, while the basanites and alkali basalts are similarly low relative to the foidite samples. The results of anhydrous melting are overall close to those based on assuming a constant CO₂/Ba ratio, however, the results of hydrous melting, melting degree of 4%, for rejuvenated stage are generally lower than those based on assuming a constant CO₂/Ba ratio. Since the latter method is independent of uncertainties in magma degassing and melting degrees, the lower primary magma CO₂ contents could have been caused by these uncertainties. Despite discrepancy between the two methods, they are overall consistent in resulting in primary magma CO₂ contents up to ∼10 wt% for rejuvenated stage lavas and low CO₂ contents for shield stage lavas, suggesting rejuvenated stage lavas have a similar source CO₂ to the plume mantle. However, as a constant CO₂/Ba ratio of Hawaiian mantle source is not verified for shield and rejuvenated stage lavas, our work provides an independent constraint on CO₂ enrichment in Hawaiian rejuvenated lavas.

4.3. Olivine Ni: Effects of Source Versus Temperature

There are different views on the origin of Hawaiian rejuvenated stage volcanism, either from the shallow metasomatized mantle lithosphere (Chen & Frey, 1983; Garcia et al., 2010; Yang et al., 2003), the deep mantle plume component (DeFelice et al., 2019; Dixon et al., 2008; Frey et al., 2005; Harrison et al., 2020; Hofmann & Farnetani, 2013; Sisson et al., 2009), or both (Beguelin et al., 2019). The deep plume origin for rejuvenated stage melts is supported by their distinct isotopic compositions from the Pacific MORBs (Figure S3 in Supporting Information S1). Despite enrichment of LILEs and LREEs in rejuvenated stage lavas, they generally have
more depleted isotopic compositions compared to shield stage lavas (Beguelin et al., 2019; DeFelice et al., 2019; Harrison et al., 2020; Hofmann & Farnetani, 2013; Yang et al., 2003). As shown in Figure S3 in Supporting Information S1, such a depleted signature cannot be explained by involvement of Pacific-type depleted upper mantle, but likely to have been derived from an intrinsic mantle plume component. However, it remains unclear how the low-degree melts of rejuvenated stage preferentially sample the isotopically depleted component in the mantle plume (Beguelin et al., 2019; Bianco et al., 2008; DeFelice et al., 2019; Ribe & Christensen, 1999). For example, it was suggested that rejuvenated stage lavas originated from a deep isotopically depleted zone separated from the primary melting zone that formed shield stage lavas (Ribe & Christensen, 1999), or from a depleted periphery of a zoned mantle plume (Bianco et al., 2008).

As shown in Figure 4a, the olivine Ni contents of rejuvenated stage lavas are overall lower than those of shield stage, but higher than the global MORBs for a given olivine Fo. In contrast, rejuvenated stage lavas have whole-rock Ni lower than shield stage lavas for a given MgO content (Figure 2c). Increasing magma total alkaline (Na₂O + K₂O) increases the partition coefficient of Ni in olivine when total alkaline >8 wt% ( Förster et al., 2018). Most of our studied rocks have K₂O + Na₂O contents significantly lower than 8 wt%, hence, notable difference in D_{Ni}^{Ol-melt} between shield and rejuvenated stage lavas is unexpected. As we discussed above, CO₂ played a key role in the origin of rejuvenated stage magmatism. However, Girnis et al. (2013) showed that CO₂ have negligible influence on the partitioning of Ni between olivine/melt. As such, we suggest the relatively lower olivine Ni contents of the rejuvenated stage compared with the shield stage reflect a lower Ni content in their parental magmas, as indicated by whole-rock Ni contents (Figure 2c).

Melting temperature/pressure, source lithology, and source Ni content could influence primary magma Ni content (Matzen et al., 2013; Putirka et al., 2011; Sobolev et al., 2005, 2007). Partial melts of eclogite/pyroxenite react with peridotite in the Hawaii mantle plume to convert olivines to Opx and to form stage-2 pyroxenite with a lower proportion of (or no) olivine in the source (Sobolev et al., 2005, 2007). Thus, the mantle source with a lowered olivine proportion would generate primary melts with elevated Ni (Sobolev et al., 2005). As indicated by Matzen et al. (2013, 2017), D_{Ni}^{Opx-melt} increases with decreasing temperature and pressure, thus, elevated source temperatures and pressures would result in an increase of olivine Ni in Hawaiian shield lavas. In addition to the stage-2 pyroxenite in the mantle source, the higher olivine Ni of Hawaiian shield stage lavas may at least partly have been caused by higher melting temperatures and pressures (e.g., Matzen et al., 2013). Thus, evaluation of difference in primary magma temperatures among the shield stage lavas, rejuvenated stage lavas and normal MORBs would help understand the origin of their Fo-Ni systematics (Figure 4a).

In this study, we have calculated the magma temperatures of shield and rejuvenated stages based on the olivine-spinel aluminum exchange thermometry. This thermometry is advantageous over the olivine-liquid thermometry since it is independent of equilibrium pressure and melt compositions. Details on the use of the olivine-spinel aluminum exchange thermometry are referred to Wan et al. (2008) and Coogan et al. (2014). We selected the volcanic rock samples from the rejuvenated and shield stages that contain the highest olivine Fo. We used the equation given by Coogan et al. (2014) \( T(K) = 10,000/(0.575 + 0.884Cr# - 0.897\ln(Al_2O_3_{Ol}/Al_2O_3_{Sp})) \), which has extended the use of this thermometry to a relatively oxidizing environment. The data of olivine-spinel are filtered based on the requirements of Coogan et al. (2014), that is, Cr# between 0% and 69%, and Fe³+/Total FeO < 35%. The calculated results are shown in Data Set S3 and plotted in Figure 8a. As shown in Figure 8a, shield stage olivines with the highest Fo (~89) tend to have the highest crystallization temperatures. Rejuvenated stage olivines have statistically lower crystallization temperatures and Fo than those of shield stage as shown in Figures 8c and 8d. The slightly lower olivine crystallization temperatures of rejuvenated stage lavas could also be indicated by their slightly higher olivine Al₂O₃ (Figure S4 in Supporting Information S1) (Coogan et al., 2014). However, the lavas of both shield and rejuvenated stages approximately follow the trend of melt temperature versus equilibrium olivine Fo of the Icelandic primary magmas as shown in Herzberg and Asimov (2015). Thus, for the given highest olivine Fo (e.g., ~91), broadly similar primary magma temperatures for the shield and rejuvenated stage lavas are expected (Figure 8). As shown in Figure 8a, at the highest Fo of up to 91, the MORB olivines tend to have lower temperatures compared with those of Hawaiian olivines. This indicates that the Hawaiian primary magmas, both shield and rejuvenated stages, crystallized high Fo olivines at higher temperatures than those of normal MORBs.

Since Hawaiian shield and rejuvenated stage lavas show different Sr-Nd-Hf isotopic compositions (Figure S3 in Supporting Information S1; DeFelice et al., 2019; Hofmann & Farnetani, 2013; Yang et al., 2003), the overall...
lower olivine Ni contents of rejuvenated stage lavas relative to those of shield stage may reflect a mantle source effect. As shown in Figure 8, high Fo olivines from both shield and rejuvenated stage lavas have similar crystallization temperatures. The effect of melting-crystallization temperature difference (Matzen et al., 2013) may have not contributed significantly to the observed olivine Ni difference.

The mantle source of Hawaiian shield stage lavas is considered to contain eclogites that were most likely derived from ancient recycled oceanic crust. Subducted altered oceanic crust, as an important carrier of secondary carbonates (Zhang & Smith-Duque, 2014), may constitute a source of CO2 in the Hawaiian mantle plume. Thus, it is possible that CO2-bearing mixed eclogite/peridotite exists in the Hawaiian mantle plume. However, because the plume mantle source has melted to high degrees to form shield stage lavas, most of CO2 would be extracted from the source mantle after high degrees of melting. As CO2 is highly incompatible during mantle melting (e.g., Dixon et al., 2008), the resulted refractory residual mantle after extraction of shield stage lavas would be difficult to produce carbonated melts. Because Hawaiian rejuvenated stage lavas were formed 0.5–2 Myr after shield stage and ∼100 km from the plume axis, it is possible that the rejuvenated lavas were sourced from the edge of the mantle plume, where mantle upwelling and decompression rate are lower than the plume axis (Figure 9).

As indicated by this study, the rejuvenated stage lavas were most likely sourced from carbonated peridotites that are intrinsic to the Hawaiian mantle plume. Thus, the mantle plume peridotites may have experienced metasomatism of low degree carbonated melts. This is consistent with the enriched trace element patterns and negative anomalies of HFSEs in rejuvenated lavas (Figure 3). However, the distinct Sr-Nd-Hf isotopic compositions between rejuvenated and shield stage lavas indicate that such carbonated melts were unlikely derived from a CO2-bearing eclogite/pyroxenite (carbonate-bearing recycled oceanic crust) feeding shield stage lavas. A possible source for the carbonated melts in the mantle plume is subducted lithospheric mantle (e.g., Kelemen & Manning, 2015). Although carbonate precipitation is generally considered to occur mainly in the oceanic crust during seafloor alteration, it would also occur in shallow lithospheric mantle of the bending plate before subduction (Kelemen & Manning, 2015), and in the exposed abyssal peridotites as represented by slow-to ultraslow spreading ridge settings (e.g., Dick et al., 2000; Schroeder et al., 2002). These carbonate-bearing subducted peridotites may constitute the source required by Hawaiian rejuvenated stage lavas. As shown in Figure 9, the low degree carbonated melts of such carbonate-bearing peridotites near the plume edge can metasomatize the mantle plume peridotites. Thus, along with the upwelling of mantle plume, such carbonated peridotites would decompress and melt, which may explain the CO2-rich rejuvenated stage lavas.

Figure 8. Al-in-olivine crystallization temperature as a function of olivine Fo (a) and histogram for comparing Hawaii rejuvenated and shield stage crystallization temperature (b–c). Data of MORB temperature for comparison are from Coogan et al. (2014). The solid lines for Iceland OIB and Siqueiros MORB are calculated by PREMELT3 MEGA.XLSM based on Herzberg and Asimow (2015).
5. Conclusions

The origin of Hawaiian rejuvenated stage magmatism remains a subject of debate. In this study, we have analyzed the whole-rock major and trace elements, in situ high-precision geochemistry of olivines and olivine-spinel pairs of Hawaiian rejuvenated and shield stage lavas. Unlike shield stage, rejuvenated stage lavas with anomalously high CaO and low SiO₂ and negative anomalies of HFSEs, which could be explained by the influence of CO₂ in the source. It is notable that the olivine Ni contents of rejuvenated stage lavas are systematically lower than those of shield stage, but higher than normal MORBs for a given olivine Fo. While rejuvenated stage lavas have whole-rock CaO and MnO higher than shield stage, their olivine Ca and Mn contents are similar to each other for a given Fo. Our study results in that $D^\text{Ca-melt}_{\text{Ol}}$ and $D^\text{Mn-melt}_{\text{Ol}}$ for rejuvenated stage lavas are systematically lower than those of shield stage, which we suggest is caused by the influence of CO₂. Our calculation based on the reduced $D^\text{Ca-melt}_{\text{Ol}}$ relative to dry basaltic melts indicates that rejuvenated stage primary melts were rich in CO₂, while shield stage melts were relatively dry (low volatile contents). The temperatures of primary magmas of rejuvenated stage are similar to the shield stage, but systematically higher than normal primary MORB magmas. The relatively low olivine Ni of rejuvenated lavas compared to shield stage can be attributed to the mantle source lithology dominated by peridotites, rather than stage-2 pyroxenite in shield stage mantle source. It is suggested that rejuvenated stage lavas were originated from the melting of carbonated peridotites in the Hawaiian mantle plume.

Data Availability Statement

The data used in this paper are included in the text, figures and supplementary information, which are archived externally in Mendeley Data, V1, (https://doi.org/10.17632/r7zrhy6sv.1).
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