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Key Points:

- Andesite with variable CO₂ is reacted experimentally with fertile peridotite
- Reacted alkalic melts increase in Si undersaturation with increasing CO₂
- Eclogite melt, CO₂, and peridotite melt proportions in OIB sources determined

Supporting Information:

- OIB data with references
- Text
- Readme

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Effect of variable CO₂ on eclogite-derived andesite and lherzolite reaction at 3 GPa—Implications for mantle source characteristics of alkalic ocean island basalts

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Abstract We have performed reaction experiments between 1, 4, and 5 wt % CO₂-bearing MORB-eclogite (recycled oceanic crust)-derived low-degree andesitic partial melt and fertile peridotite at 1375°C, 3 GPa for infiltrating melt fractions of 25% and 33% by weight. We observe that the reacted melts are alkalic with degree of alkalinity or Si undersaturation increasing with increasing CO₂ content in reacting melt. Consequently, an andesite evolves through basanite to nephelinite owing to greater drawdown of SiO₂ from melt and enhanced precipitation of orthopyroxene in residue. We have developed an empirical model to predict reacted melt composition as a function of reacting andesite fraction and source CO₂ concentration. Using our model, we have quantified the mutual proportions of equilibrated melt from andesite-peridotite (+ CO₂) hybridization and subsequent peridotite (± CO₂)-derived melt required to produce the major element composition of various ocean island basalts. Our model can thus be applied to characterize the source of ocean islands from primary alkalic lava composition. Accordingly, we determined that average HIMU source requires 24 wt % of MORB-eclogite-derived melt relative to peridotite containing 2 wt % CO₂ and subsequent contribution of 45% of volatile-free peridotite partial melt. We demonstrate that mantle hybridization by eclogite melt-peridotite (± CO₂) reaction in the system can produce high MgO (>15 wt %) basaltic melts at mantle potential temperature (*T_p*) of 1350°C. Therefore, currently used thermometers to estimate *T_p* using MgO content of primary alkalic melts need to be revised, with corrections for melt-rock reaction in a heterogeneous mantle as well as presence of CO₂.

1. Introduction

Alkalic magmas ranging from basanites to nephelinites and melilitites occur commonly in intraplate oceanic and continental settings. It is known for decades that low-degree melting of fertile peridotite gives rise to alkalic magmas [Kushiro, 1975; Hirose and Kushiro, 1993] but many of the major and minor elemental attributes of natural alkalic basalts and basanites, such as high TiO₂, CaO, somewhat lower SiO₂ and Al₂O₃ remained unexplained by small extent of fusion of peridotite alone as pointed out by many previous studies [e.g., Kogiso et al., 1998; Dasgupta et al., 2010]. Furthermore, most of the natural nephelinitic and melilititic magmas remained enigmatic based on the significant difference between their major element chemistry (e.g., low SiO₂, Al₂O₃, CaO/Al₂O₃) and experimental partial melts of volatile-free lherzolite. The role of small quantities of CO₂ or carbonates (<1 wt%) has been recognized in generating silica-poor, strongly alkalic magmas such as kimberlites, melilitites, and nephelinites from peridotite [Wyllie and Huang, 1976; Brey and Green, 1975, 1977; Spera, 1981; Hirose, 1997; Dasgupta et al., 2007, 2013]. TiO₂ and FeO* contents in natural magmas still require involvement of mafic lithologies such as eclogites/pyroxenites either as discrete lithologies or as a distal reactant in a largely peridotitic mantle source [Prytulak and Elliott, 2007; Dasgupta et al., 2006; Gerbode and Dasgupta, 2010; Mallik and Dasgupta, 2012, 2013].

One of the key petrologic arguments against the role of subducted oceanic crust in silica-poor magma generation was that direct partial melting of mid-ocean ridge basalt (MORB)-eclogite at mantle depths produces silica-rich, magnesium-poor dacitic to basaltic magmas [Yaxley and Green, 1998; Pertermann and Hirschmann, 2003; Spandler et al., 2008] that cannot be parental to silica-poor, alkalic basalts. However, Mallik and Dasgupta [2012] showed that if partial reactive crystallization of eclogite-derived low-degree andesitic partial melt in a peridotite matrix or against a peridotite wall rock is taken into consideration, the derivative liquid can be alkalic. Moreover, while at an intermediate andesite:peridotite ratio, the resulting magma becomes basanitic, at a similar melt:rock ratio but in the presence of small amount of dissolved CO₂, the

Table 1. Composition of Peridotite and Starting Melts Used in This Study^a

	Peridotite		Starting Melts				
	KLB-1ox ^b	MixKLB-1 ^c	G2PM1 ^c	BAC1	BAC2.6 ^b	BAC4	BAC5
SiO ₂	44.82	44.54	56.3 (8)	56.31	56.46	56.32	56.40
TiO ₂	0.15	0.21	5.65 (8)	5.65	5.66	5.65	5.66
Al ₂ O ₃	3.51	3.70	15.6 (4)	15.56	15.61	15.57	15.59
Cr ₂ O ₃	0.32	0.23	0.01 (1)	0.01	0.01	0.01	0.01
FeO*	8.19	8.08	8.2 (3)	8.15	8.17	8.16	8.16
MnO	0.12	0.14	0.08 (2)	0.10	0.09	0.10	0.10
MgO	39.50	39.30	2.5 (1)	2.51	2.51	2.51	2.52
CaO	3.07	3.52	7.5 (2)	7.47	7.50	7.46	7.34
Na ₂ O	0.30	0.29	4.02 (9)	4.02	3.76	4.02	4.03
K ₂ O	0.02	0.01	0.21 (1)	0.21	0.21	0.21	0.21
Mg#	89.58	89.66	35.4 (9)	35.43	35.42	35.42	35.47
CO ₂	-	-	-	1.00	2.60	3.98	4.90
Sum	100.00	100.02	99.99	100.00	100.00	100.00	100.00

^aMajor element compositions of BAC1, BAC2.6, BAC4, BAC5 (volatile-free basis) and CO₂ concentrations of the same are based on proportions of oxides and carbonates mixed in the starting compositions. All oxides concentrations are in weight percent. FeO*, all Fe assumed to be FeO. Mg# = $100 \times [\text{MgO}] / ([\text{MgO}] + [\text{FeO}])$, where [MgO] and [FeO] are molar MgO and FeO, respectively.

^bCompositions as reported in *Mallik and Dasgupta* [2013].

^cCompositions as reported in *Mallik and Dasgupta* [2012].

derivative liquid becomes nephelinitic [Mallik and Dasgupta, 2013]. The study of Mallik and Dasgupta [2013] demonstrated that with the presence of only 0.65–0.86 wt % bulk CO₂, a basaltic andesite upon reaction with peridotite at intermediate melt-rock ratios (reacting melt fraction of 25 and 33 wt %) produces nephelinitic melts. These authors demonstrated that the transition from a siliceous melt to a nephelinitic melt can occur owing to reactive crystallization of an initial andesitic melt to form orthopyroxene and enhance orthopyroxene stability at the expense of olivine and clinopyroxene at the liquidus of basalt under the influence of CO₂. Mallik and Dasgupta [2013] also observed an increase in modal proportion of garnet in the residue for the carbonated melt-rock system, which led to diminished Al₂O₃ content of the reacted melt compared to CO₂-free systems. The observed differences between the carbonate-free and carbonate-bearing systems call for further investigation on the effect of variable CO₂ on phase equilibria of reaction between MORB-eclogite-derived basaltic andesite and peridotite. In particular, a quantitative framework needs to be developed that allows prediction of reacted melt composition (e.g., extent of alkalinity) as a function of initial andesitic melt fraction and CO₂ content.

In this study, we experimentally explore the effect of variable amounts of CO₂ (0.25–1.62 wt %) in the melt-rock system by introducing 1, 2.6, 4, and 5 wt % CO₂ in the infiltrating melt of known proportions. We demonstrate that an array of melts with degree of alkalinity directly proportional to CO₂ concentration in the bulk, as well as residues with higher orthopyroxene and garnet proportions (as compared to similar melt-rock reaction in volatile-free conditions) can be generated via such a process. In the light of our new data, we discuss how alkalic melts can be generated by reactive processes in a heterogeneous mantle below ocean islands. We also present an empirical model to characterize the source of ocean islands in terms of reacting recycled crust-derived melt mass and bulk CO₂ content.

2. Experimental and Analytical Techniques

2.1. Starting Material

The carbonated basaltic andesite melt (BAC) used in this study, on a CO₂-free basis, is similar in composition to the starting melt G2PM1 used in the study of Mallik and Dasgupta [2012], which is the composition of 8.9 wt % partial melt of a volatile-free, SiO₂-saturated MORB-eclogite [Pertermann and Hirschmann, 2003]. BAC-like CO₂-bearing basaltic andesite may be generated by (a) infiltration of deeper carbonatites into volatile-free MORB-eclogite producing carbonated silicate melt, (b) partial melt of a volatile-free MORB-eclogite scavenging CO₂ from the mantle, (c) direct redox melting of reduced C-bearing eclogite [Mallik and Dasgupta, 2013]. Basaltic andesite of the same composition as G2PM1 but with 1, 2.6, 4, and 5 wt % CO₂ were prepared by mixing reagent grade oxides and carbonates as mentioned in detail below. These starting melts are named BAC1, BAC2.6, BAC4, and BAC5, respectively (Table 1). Among these starting melt

compositions, experiments with BAC2.6 have already been reported by *Mallik and Dasgupta* [2013]. The volatile-free peridotite used in this study is the same mixture as KLB-1ox, reported by *Mallik and Dasgupta* [2013] and is similar in bulk composition to the spinel lherzolite KLB-1 as reported by *Davis et al.* [2009] and *Herzberg et al.* [1990] (Table 1). Homogeneous melt-rock mixtures were prepared with 25% and 33% of each BAC with peridotite. Absence of vesicles in any of the experimental products denotes that the bulk CO_2 concentration of the charges was below the limit of solubility in reacted melts.

The starting melts were prepared using high-grade oxides and carbonates from Alfa Aesar. SiO_2 , TiO_2 , Al_2O_3 , and MgO were fired overnight at 1000°C , Fe_2O_3 at 800°C , MnO_2 at 400°C , CaCO_3 at 250°C , Na_2CO_3 and K_2CO_3 at 110°C . All the oxides and carbonates (except one part of CaCO_3) were mixed and ground together under ethanol for 1 h in an agate mortar and fired for 24 h in a CO-CO_2 furnace at $\log f_{\text{O}_2} \sim \text{QFM-2}$ in order to reduce the Fe^{3+} in the mixture to Fe^{2+} . After reduction and decarbonation, the remainder of CaCO_3 was ground with the reduced mixture under ethanol in an agate mortar for 1 h in order to introduce CO_2 and to bring up the CaO content of the starting melt BAC1, BAC4, and BAC5 to the desired level. In case of BAC2.6, both Na_2O and CO_2 were added only as Na_2CO_3 , after the oxides and carbonates (excluding Na_2CO_3) were ground together under ethanol for 30 min and then fired in a CO-CO_2 gas mixing furnace for 24 h in order to reduce Fe^{3+} to Fe^{2+} . BACs were mixed homogeneously with KLB-1ox in proportions such that 25% and 33% of BAC-added mixtures were made. The bulk CO_2 concentration of the mixtures varied from 0.25 to 1.62 wt %.

2.2. Experimental Procedure

The experiments were performed using end-loaded piston cylinders in the experimental petrology laboratory of Rice University. Platinum-graphite double capsules were used and prior to welding, the Pt capsules with loaded graphite inner lining were stored in an oven overnight at 110°C to expel adsorbed moisture and ensure least H_2O contamination possible. Weight loss due to welding was minimal (maximum 0.3% relative). Half-inch BaCO_3 assembly described and calibrated in *Tsuno and Dasgupta* [2011] was used for all new experiments in this study and experiments were performed at 3 GPa and 1375°C — P - T conditions at the base of a mature oceanic lithosphere. The pressure was raised to 3 GPa before heating the sample to the desired temperature at $100^\circ\text{C}/\text{min}$. Duration of experiments at nominal temperature varied from 92 to 139 h. Following recovery from the cell assembly, capsules were mounted in epoxy plugs and polished using 200–600 grit silicon carbide papers and 3–0.25 μ diamond abrasive powder in the absence of water or any other liquid including ethanol. Polishing under dry conditions was done to preserve soluble and delicate carbonates in the quench aggregates.

2.3. Analysis of the Experiments

Back-scattered-electron (BSE) images were obtained and phase compositions in the experimental charges were analyzed using Cameca SX100 electron microprobe at Johnson Space Center, Houston, Texas. Energy-dispersive-spectrometry (EDS) was used to identify phases in the charges. Phase compositions were measured using wavelength-dispersive-spectrometry (WDS) and X-ray counts for each element were measured at the peak position for 20 s and half the time on each background, using accelerating voltage of 15 kV and beam current of 20 nA. The beam diameter used was 1 μ for mineral phases (olivine, orthopyroxene, clinopyroxene, and garnet) and 10–50 μ for quench aggregates (reacted melt pool). The quenched reacted melt pools were analyzed on three different sections exposed each time by polishing. Melt composition data were filtered by omitting very low frequency tails in a histogram of average major element composition and CO_2 concentration (by difference from probe totals) of reacted melts. This reduced the 1σ error in composition to a considerable extent without significantly affecting the average. For experiment B219 (25% BAC4-added run), the quenched melt aggregates were extremely coarse and heterogeneous as well as the exposed quench pool area was not large enough to obtain a statistically significant number of data points. This made reliable estimate of composition of quench aggregates very difficult. Even though three polished sections were analyzed to obtain more data for compositional analyses, we believe the melt composition estimate for this experiment is the least reliable of all, which is reflected in this melt composition being an outlier in subsequent figures. Further, unreliable melt composition for B219 propagated into unreliable phase proportion estimation for this particular experiment. Thus, we chose not to include this particular experiment in discussion of melt composition trends, phase proportion trends as well as calibration of our empirical model in future sections.

Figure 1. Modal proportions of minerals (olivine, orthopyroxene, clinopyroxene, and garnet) and reacted melt (wt %) plotted versus CO₂ concentration in reacting melt (wt %). Modal proportion estimate for 25% BAC4-added experiment may not be very reliable given the poor estimate of melt composition analysis for this experiment (see text for further details). Error bars represent $\pm 1\sigma$ standard deviation.

The standards used for phase compositions were a synthetic basaltic glass (Si, Ca, Fe, Mg), diopside (Si, Ca, Mg), fayalite (Si, Fe), almandine (Si, Al, Ca, Fe, Mg), pyrope (Mg), oligoclase (Al, Na), orthoclase (K), chromite (Cr), rutile (Ti), and rhodonite (Mn). CO₂ concentration of the reacted melt was estimated by difference of summation of concentration of all oxides from 100 wt %.

3. Results

3.1. Textures and Phase Assemblages

All BAC + KLB-1 experiments produced a quenched melt pool at the top of the capsule (where the quenched pool comprised clinopyroxene-like silicates interfingered with Ca-Fe-Na carbonates) coexisting with a four-phase residue consisting of olivine, orthopyroxene, clinopyroxene, and garnet. All 25% and 33% melt-added experiments (volatile free or carbonated) had these four phases present in their residue (Figure S1).

For 25 wt % basaltic andesite-peridotite mixture experiments, olivine modal proportions display an overall decrease from ~ 26 wt % in CO₂-free (G2PM1-bearing experiment) conditions [Mallik and Dasgupta, 2012] to ~ 22 wt % in case of BAC5-bearing experiment. Olivine modal proportions for 33 wt % basaltic andesite-peridotite mixture experiments, display an overall decrease from ~ 15 wt % in CO₂-free conditions [Mallik and Dasgupta, 2012] to ~ 9 wt % for BAC5-bearing experiment (Figure 1). Orthopyroxene modal proportions

Table 2. Summary of Melt-Rock Reaction Experiments Performed in This Study^a

Run Number	Starting Materials Used	Reacting Melt Mass (wt %)	T _{BKN} (°C)	T _{ROO} (°C)	Duration (h)	Phase Modes (wt %)					Σr ²
						Ol	Opx	Cpx	Gt	Melt	
G150 ^b	G2PM1 + MixKLB-1	25	1365	1371	45	25.7(7)	37(1)	17.6(9)	3.6(9)	16(2)	0.11
B208	BAC1 + KLB-1ox	25	1359	1424	117	23(2)	40(3)	13(1)	8(2)	16(3)	0.1(3)
B222 ^c	BAC2.6 + KLB-1ox	25	1360	1483	92	23.1(6)	43(1)	8(1)	7.8(7)	18(2)	0.2(2)
B219	BAC4 + KLB-1ox	25	1343	1387	104	17.6(5)	53(1)	9(2)	4.8(9)	16(3)	0.2(1)
B209	BAC5 + KLB-1ox	25	1338	1436	93	22(2)	44(4)	4(2)	7(1)	23(3)	0.3(2)
G132 ^b	G2PM1 + MixKLB-1	33	1359	1370	48	15.3(5)	37.0(8)	21(1)	10.9(6)	16(1)	0.63
B212	BAC1 + KLB-1ox	33	1330	1421	134	20(1)	38(2)	14.7(4)	11.0(6)	17(2)	0.14(6)
B223 ^c	BAC2.6 + KLB-1ox	33	1375	1404	139	16(1)	43(3)	12.7(7)	11.0(7)	17(2)	0.3(2)
B215	BAC4 + KLB-1ox	33	1345	1423	93	12(2)	48(4)	14(2)	11.0(1)	15(4)	1.2(4)
B211	BAC5 + KLB-1ox	33	1340	1414	130	9(2)	52(4)	9(2)	12.6(9)	17(3)	1.8(5)

^aAll experiments were performed at 3 GPa, 1375°C. The mineral phases are abbreviated as Ol (olivine), Opx (orthopyroxene), Cpx (clinopyroxene) and Gt (garnet). T_{BKN}(°C) = Temperature calculated using two-pyroxene thermometer of Brey and Kohler [1990]. T_{ROO}(°C) = Temperature calculated using garnet-clinopyroxene thermometer of Ravna [2000]. Σr² = Sum of residual squares obtained from linear regression of phase modes and phase compositions. ±1σ errors, based on replicate EPMA analyses, are mentioned in brackets and reported as least digits cited. For example, 37(1) should be read as 37 ± 1 wt %.

^bExperiments rereported from Mallik and Dasgupta [2012].

^cExperiments rereported from Mallik and Dasgupta [2013].

display an overall increase from ~37 wt % in 25 wt %-G2PM1-bearing experiment [Mallik and Dasgupta, 2012] to ~44 wt % in 25 wt %-BAC5-bearing experiment. For experiments with 33 wt % reacting melt fraction, orthopyroxene displays an increase from ~37 to ~52 wt % from G2PM1 to BAC5-bearing experiments. Clinopyroxene modes display a steady decrease with increasing CO₂-content in the reacting melt (or CO₂ content of the bulk-melt-rock mixture) for both series of experiments, i.e., for experiments with reacting melt fraction of 25 and 33 wt %, with the modes decreasing from ~18 to ~4 wt % for the former series and ~21 to ~9 wt % for the latter series from CO₂-free condition [Mallik and Dasgupta, 2012] through BAC5-bearing experiments (Figure 1). Garnet modal proportions do not display any systematic change with increasing CO₂ content of reacting melt except that the modes from carbonated runs are higher than for CO₂-free runs. For experiments with 25 wt % reacting andesite, the garnet mass fractions vary from ~4 to ~7 wt % and for experiments with 33 wt % reacting andesite, the mass fractions vary from ~11 to ~13 wt % from CO₂-free melt through BAC5-bearing experiments. Melt modal proportions display an overall increase from ~16 to 23 wt % from CO₂-free melt-bearing through BAC5-bearing experiment in case of 25 wt % reacting melt fraction series. For the series with 33 wt % reacting melt fraction, the resulting melt fraction shows a slight increase within error from ~16 wt % for G2PM1-bearing experiment to ~17 wt % in case of BAC5-added run.

3.2. Assessment of Chemical Equilibrium

The goal of our study is to achieve equilibrium compositions of minerals and melts for wall rock domains of fertile peridotite that are impregnated with basaltic andesite. Hence it is critical to evaluate that our experiments approached equilibrium. An approach to equilibrium and maintenance of closed system during the experiments presented here can be established by the following criteria: (1) sum of residual square (Σr²) of all oxides from mass balance calculations varies from 0.1 to 1.8 (Table 2) which, considering the uncertainty in composition of reacted melt obtained from domains comprising quench crystals, is low. (2) The maximum difference between nominal temperature of experiment and temperature calculated using two-pyroxene thermometer of Brey and Kohler [1990] (T_{BKN}) across all experiments is 45°C and using garnet-clinopyroxene thermometer of Ravna [2000] (T_{ROO}) is 108°C (Table 2). Both differences in temperature are within the uncertainty of the respective thermometers; hence, they confirm that the experiments approached equilibrium. (3) $K_D^{Fe^{2+}-Mg}(ol - melt)$ varies from 0.28 ± 0.02 to 0.36 ± 0.02 (Table S1) which are within the range obtained by other experimental studies reporting olivine-carbonated silicate melt equilibria [e.g., Dasgupta et al., 2007; Dasgupta et al., 2013; Hirose, 1997; Mollo et al., 2010; Mallik and Dasgupta, 2013] and also consistent with general observations of olivine-melt equilibria in mafic-ultramafic systems [Roeder and Emslie, 1970; Kushiro and Walter, 1998; Matzen et al., 2011].

3.3. Phase Compositions

3.3.1. Reacted Melt

Reacted melt compositions derived from carbonated BACs are plotted, on a volatile-free basis, as a function of CO₂ content of the starting melts in Figure 2 and are reported in Table 3.

Figure 2. Reacted melt composition (wt %) plotted versus CO₂ concentration in reacting melt (wt %). Melt composition for 25% BAC4-added experiment may not be reliable due to poor-quality exposure of quench pool in the sample. Error bars represent $\pm 1\sigma$ standard deviation.

With increasing CO₂ dissolved in the initial basaltic andesite, the reacted melts display a slight decrease in SiO₂ concentration from 44.9 ± 0.6 to 42.8 ± 2.3 wt % and 44.4 ± 0.8 to 40.1 ± 2.3 wt % for reacting melt fraction of 25 and 33 wt %, respectively. TiO₂ concentration of the melts displays an overall decrease from 6.1 ± 0.5 to 5.2 ± 0.3 wt % and 6.7 ± 0.5 to 6.0 ± 0.4 wt % with increasing CO₂ content in the reacting melt, for 25% and 33% melt-added experiments, respectively, as the resulting melt fraction increases. Over the

Table 3. Composition of Reacted Melts^a

Run Number	G150	B208	B222	B219	B209	G132	B212	B223	B215	B211
Starting Melt	G2PM1	BAC1	BAC2.6	BAC4	BAC5	G2PM1	BAC1	BAC2.6	BAC4	BAC5
Melt Added (wt %)	25	25	25	25	25	33	33	33	33	33
n	10	44	100	19	93	23	46	158	125	46
SiO ₂	44.9(6)	44(2)	42(2)	42(1)	43(2)	44.4(8)	46.4(8)	47.3(1)	42(2)	40(2)
TiO ₂	6.1(5)	6.6(6)	6.4(4)	7.4(4)	5.2(3)	6.7(5)	6.3(1)	5.9(2)	5.7(2)	6.0(4)
Al ₂ O ₃	13.7(5)	10.6(1)	10.5(5)	10.4(2)	10.8(5)	12.6(9)	12.3(3)	11.9(4)	10.5(4)	10.1(5)
Cr ₂ O ₃	0.06(1)	0.10(3)	0.2(1)	0.1(2)	0.10(3)	0.10(3)	0.07(2)	0.2(2)	0.3(4)	0.1(1)
FeO*	10.3(8)	10(1)	10(1)	11.0(7)	9.7(7)	11(1)	9.8(2)	9.9(9)	11(1)	11(1)
MnO	0.16(2)	0.10(3)	0.12(3)	0.11(1)	0.11(3)	0.14(3)	0.09(2)	0.11(3)	0.13(4)	0.11(3)
MgO	12(1)	14(1)	15.4(7)	13.7(5)	16.2(8)	13(1)	12.3(9)	12.2(8)	14.9(8)	16.5(5)
CaO	8.4(8)	8.9(1)	10(1)	11.1(1)	11(1)	7.8(6)	7.8(2)	7.9(3)	10(1)	11(2)
Na ₂ O	3.8(4)	4.7(7)	4.0(7)	3.7(4)	4(1)	3.9(4)	4.6(4)	4.2(4)	5(1)	5(1)
K ₂ O	0.4(1)	0.4(2)	0.4(1)	0.32(8)	0.25(7)	0.4(1)	0.39(5)	0.34(5)	0.34(8)	0.3(1)
CO ₂	-	6(3)	12(6)	11(1)	9(4)	-	9(2)	4(2)	13(5)	14(4)
Mg#	68(4)	71(3)	73(3)	69(2)	75(2)	69(4)	69(1)	69(2)	70(3)	73(2)

^aAll oxide concentrations, in weight percent, are reported on a CO₂-free basis. FeO*, all Fe assumed to be FeO. Mg# = $100 \times ([\text{MgO}]/([\text{MgO}] + [\text{FeO}]))$ where [MgO] and [FeO] are molar MgO and FeO, respectively. n represents the number of electron microprobe spot analyses averaged. For description of errors in parentheses, refer to the footnote of Table 2.

same range of reacting melt CO₂ contents, Al₂O₃ content of the reacted melts decrease from 13.7 ± 0.5 to 10.8 ± 0.5 wt % and 12.6 ± 0.9 to 10.1 ± 0.5 wt % for reacting melt mass of 25 and 33 wt %, respectively. The FeO* concentration of the reacted melts do not display any trend as a function of CO₂ dissolved in the reacting melts and it ranges from 10.3 ± 0.8 to 9.7 ± 0.7 wt % for 25 wt % melt-bearing series and 11.0 ± 1.2 to 10.7 ± 1.1 wt % for 33 wt % melt-bearing series. On the other hand, the MgO concentration in the reacted melts correlate positively with increasing CO₂ dissolved in the reacting and reacted melts; MgO concentrations increase from 12.0 ± 1.4 to 16.2 ± 0.8 wt % for 25% melt-bearing and 13.0 ± 1.2 to 16.5 ± 0.5 wt % for 33% melt-bearing experiments. The trend of CaO as a function of CO₂ dissolved in the reacting melt is the same as that for MgO and the concentrations vary from 8.4 ± 0.8 to 11 ± 1 wt % and 7.8 ± 0.6 to 11 ± 2 wt % for 25 and 33 wt % melt-bearing experiments, respectively. Na₂O concentration in the reacted melts display a slight overall increase (within error) with increasing CO₂ content in the reacting melts and the concentrations range from 3.8 ± 0.4 to 4.0 ± 0.1 wt % and 3.9 ± 0.4 to 5 ± 1 wt % from 0 to 5 wt % CO₂ dissolved in the basaltic andesite, i.e., as the resulting melt becomes more CO₂ rich (see below). Mg# and CO₂ concentration in the reacted melts also increase with increasing CO₂ content in the reacting melts. While Mg# varied from 68 ± 4 to 75 ± 2 and 69 ± 4 to 73 ± 2 for 25% and 33% melt-added experiments, respectively, from CO₂-free to BAC5-bearing experiments, CO₂ concentration in the reacted melts vary from 6 ± 3 to 9 ± 4 wt % and 9 ± 2 to 14 ± 4 wt % for 25% and 33% melt-added runs.

3.3.2. Olivine

Mg# of olivines, for 0% to 5 wt % CO₂ in the reacting melts, increase from 88.2 ± 0.1 to 89.2 ± 1.8 and 87.4 ± 0.1 to 89.1 ± 1.1 for 25% and 33% melt-bearing experiments, respectively (Figure S2 and Table S1).

3.3.3. Orthopyroxene

Orthopyroxene compositions are plotted as a function of CO₂ concentration in the reacting melts in Figure S3 and tabulated in Table S2. With increasing amount of CO₂ in the reacting melt or increasing fraction of reacted melt, TiO₂, FeO*, CaO, and Na₂O in orthopyroxene display an overall decrease in concentration. On the other hand, with increasing amount of CO₂ in the reacting melt or increasing reacted melt mass, Cr₂O₃ and MgO display an overall increase in concentration. Al₂O₃ in orthopyroxene also decreases with increasing CO₂ in the reacting melt or increasing melt fraction; for 25% melt-added experiments from G2PM1 to BAC5-added runs, Al₂O₃ in orthopyroxene varies from 5.8 ± 0.5 to 4.7 ± 0.3 wt % and in 33 % melt-added runs from 4.8 ± 0.2 to 5.0 ± 0.6 wt %.

3.3.4. Clinopyroxene

Clinopyroxene compositions are plotted as a function of CO₂ concentration in the reacting melts in Figure S4 and reported in Table S3. Composition of clinopyroxene displays an overall decrease in TiO₂, Al₂O₃, FeO*, and Na₂O with increasing CO₂ concentration in the reacting melt (G2PM1 to BAC5-added experiments) as the resulting melt fraction increases. For 25% melt-added runs, TiO₂ decreases from 1.4 ± 0.1 to 1.14 ± 0.07 wt %, Al₂O₃ decreases from 8.3 ± 0.3 to 6.9 ± 0.6 wt %, FeO* from 5.0 ± 0.1 to 4.3 ± 0.2 wt %, and Na₂O

from 1.68 ± 0.03 to 1.50 ± 0.08 wt %. For 33% melt-added experiments, similar diminishing trends for TiO_2 , FeO^* , and Na_2O were noted (Figure S4). In case of Al_2O_3 , there is an initial increase from 6.9 ± 0.5 to 8.1 ± 0.2 wt % for G2PM1 to BAC1-added experiments, followed by a steady decrease to 6.6 ± 0.2 wt % in the BAC5-added experiment. Cr_2O_3 and CaO concentrations display an increase from G2PM1 to BAC5-added experiments. Cr_2O_3 concentration increases from 0.28 ± 0.03 to 0.37 ± 0.04 wt % for 25% melt-added runs and 0.19 ± 0.04 to 0.31 ± 0.03 wt % for 33% melt-added runs. CaO concentration increases from 13.1 ± 0.8 to 15.0 ± 0.7 wt % in case of 25% melt-added runs and 12.4 ± 0.6 to 14.5 ± 0.7 wt % for 33% melt-added runs. MgO concentrations do not display any systematic correlation with increasing CO_2 in reacting melt or increasing reacted melt fraction.

3.3.5. Garnet

Garnet compositions are plotted as a function of CO_2 concentration in the reacting melts in Figure S5 and given in Table S4. With increasing CO_2 concentration in the reacting melts from G2PM1 to BAC5-added experiments or increasing reacted melt fraction, FeO^* concentrations in garnet display a slight decrease in concentration from 7.9 ± 0.1 to 7.0 ± 0.2 wt % for 25% melt-added experiments and 8.0 ± 0.2 to 7.0 ± 0.2 wt % for 33% melt-added experiments. Cr_2O_3 and CaO concentrations display an increase in concentration with higher reacting melt mass. Cr_2O_3 concentrations increase from 0.48 ± 0.03 to 0.58 ± 0.04 wt % and 0.23 ± 0.04 to 0.48 ± 0.03 wt % while CaO concentrations increase from 4.9 ± 0.8 to 5.5 ± 0.7 wt % and 4.4 ± 0.6 to 5.3 ± 0.7 wt % for 25% and 33% melt-added runs, respectively. TiO_2 and MgO concentrations do not display any systematic variation with increasing CO_2 in the melt-rock system or increasing reacted melt fraction.

4. Discussion

4.1. Effect of Variable CO_2 on Evolution of Reacted Melt Composition

The effect of CO_2 on reacted melt composition is most evident in terms of SiO_2 , Al_2O_3 , MgO , and CaO contents and Mg#. Within error, SiO_2 concentration decreases with increasing CO_2 in the infiltrating melt for same melt-rock ratios and this can be attributed to the effect of increased activity coefficient of SiO_2 in the melt (where the activity of SiO_2 in the melt is buffered by olivine and orthopyroxene) [Dasgupta et al., 2007; 2013; Mallik and Dasgupta, 2013]. A similar decrease in Al_2O_3 concentrations is observed with increasing CO_2 in reacting melts which is owing to greater crystallization of garnets in the residue, increasing bulk $D_{\text{Al}_2\text{O}_3}^{\text{rock/melt}}$ from 0.10 to 0.27 (for 25% melt-added experiments) and 0.26 to 0.37 (for 33% melt-added experiments) with experiments from 0 wt % CO_2 in the reacting melt through 5 wt % CO_2 in the reacting melt. It is argued that FeO^* in silicate melts does not contribute to enhanced CO_2 solubility because Fe^{2+} may act as a network former rather than network modifier in silicate melts [e.g., Brooker et al., 2001a; Giuli et al., 2011]. This hypothesis may be supported by our data where no systematic trend in FeO^* concentration in the reacted melts is observed as a function of increasing CO_2 content in the melt-rock mixture. MgO concentration of the reacted melts for same melt-rock ratio display an increase in mean concentration with higher CO_2 in the infiltrating melt and this corroborates with CO_3^{2-} anions bonding with Mg^{2+} in the silicate melt to form MgCO_3 complexes [e.g., Guillot and Sator, 2011]. Due to the fact that Fe^{2+} does not display any effect in enhancing CO_2 content in the melt while Mg^{2+} does increase CO_2 concentrations, the net effect is that Mg# of the reacted melt does increase with increasing CO_2 in the melt-rock system and this is supported by our data in Figure 2. CO_3^{2-} anions display a strong affinity for Ca^{2+} [Dasgupta et al., 2007, 2013; Mallik and Dasgupta, 2013] and Na^+ cations [e.g., Guillot and Sator, 2011; Iacono-Marziano et al., 2012] associated with nonbridging oxygens to form CaCO_3 and Na_2CO_3 complexes, respectively. An effect of such a complexation is observed in our study where an increase in CaO and a modest increase in Na_2O concentrations are observed with higher CO_2 in the reacting melts within experiments of same melt-rock ratio. We note that because enhanced CO_2 in the bulk melt-rock mixture results in greater melt production, if complexation with CO_2 did not favor Na_2O enrichment, we should have expected to see a decrease in Na_2O with increasing melt fraction owing to incompatible nature of Na. Therefore, a modest increase in Na_2O of the reacted melt with increasing CO_2 in the reacting melt may be a product of both complexation of Na^+ with CO_3^{2-} and enhanced melting for systems with higher bulk CO_2 . Because CO_2 is perfectly incompatible in our melt-rock system, there are two factors on which the CO_2 concentration of the melt would depend on: (1) modal proportions of the reacted melt—lower is the mode, higher is the CO_2 concentration in the reacted melts and (2) CO_2 concentration of the reacting melt [Mallik and Dasgupta, 2013]—a higher concentration of CO_2 in the reacting melt would enhance the CO_2 content of the reacted melts. In this study, CO_2

concentration of the reacted melts overall increasing from BAC1 through BAC5 (Figure 2) indicates that the initial CO₂ concentration of the reacting melt dictates the CO₂ concentration of the reacted melts.

4.2. Evolution of Modal Proportions in Residue Due to Variable CO₂ Content in the Bulk Melt-Rock Mixture

It is observed from Figure 1 that proportions of olivine are lower and those of garnets are higher in carbonated melt-rock reactions than in volatile-free experiments. Further, both clinopyroxene and olivine modes show a steady decrease with increasing bulk CO₂ in melt-rock mixture, and orthopyroxene modes display a steady increase with increasing bulk CO₂ in melt-rock mixture. A chemical reaction such as the one below captures the changes in phase proportions in the carbonated melt-rock reactions:

The above end-member reaction is also supported by increase in CaCO₃ and MgCO₃ components in the melt with decreasing olivine or clinopyroxene modes and increasing orthopyroxene modes as a function of increasing CO₂ content in reacting melts (equivalent to increasing bulk CO₂ content in melt-rock mixture; Figure 1).

On a volatile-free basis, the reacting melts G2PM1, BAC1, BAC2.6, BAC4, and BAC5 are similar in composition (Table 1). All melt-rock mixtures of same melt-rock ratio thus have identical compositions on a volatile-free basis. Also, the experiments have been performed at same *P-T* conditions of 3 GPa, 1375°C. The only variable amongst the experiments of same melt-rock ratio is the CO₂ concentration of the reacting melt or the bulk CO₂ concentration of the melt-rock mixture. Thus, it can be established that the difference in phase equilibria amongst the melt-rock reaction experiments is solely due to variable concentrations of CO₂ in the system and that these experiments are well suited for understanding the effect of CO₂ on such phase equilibria. Expansion of stability field of orthopyroxene and garnet at the expense of olivine and clinopyroxene at the liquidus of basalt has been speculated by studies before [Kushiro, 1975; Brey and Green, 1975, 1977; Dasgupta *et al.*, 2007] and demonstrated by Mallik and Dasgupta [2013]. This study further confirms these prior suggestions by demonstrating a definite role of CO₂ in affecting modal proportions of minerals in the residue of melt-rock reaction. CO₂ dissolves mostly as CO₃²⁻ in alkalic basalts by forming bonds with divalent cations such as Ca²⁺, Mg²⁺, Fe²⁺, and alkalis such as Na⁺ and K⁺ [e.g., Brooker *et al.*, 2001a, 2001b; Dasgupta *et al.*, 2007; Guillot and Sator, 2011; Iacono-Marziano *et al.*, 2012; Mallik and Dasgupta, 2013] present in the melt. Although it is debated that some of them (especially Mg²⁺ and Fe²⁺) act as network formers in silicate melts by bonding with bridging oxygens [Brooker *et al.*, 2001b; Guillot and Sator, 2007], the divalent cations also act as network modifiers by bonding with nonbridging oxygens (NBOs) in the melt. Molecular dynamic simulation studies have shown that it is these divalent cations bonded to NBOs that carbonates prefer to associate themselves with [Guillot and Sator, 2011]. Thus, dissolution of CO₂ in silicate melts as carbonates decreases the activity coefficient of network modifiers, in turn increasing the activity coefficient of network formers such as SiO₂ and Al₂O₃ in the melt [Mallik and Dasgupta, 2013]. This aids in crystallization of orthopyroxene and garnet at the expense of olivine and clinopyroxene.

For volatile-free melt-rock reaction, olivine is exhausted when 50% melt is added to the peridotite [Mallik and Dasgupta, 2012]; however, when CO₂ is present in the melt-rock system, olivine is exhausted at a lower melt:rock ratio, i.e., when 40% melt is added [Mallik and Dasgupta, 2013]. Also, the residue of melt-rock reaction is shifted to progressively orthopyroxene-rich compositions with higher amount of CO₂ in the bulk melt-rock system.

4.3. Variability in Types of Primary Magma Formed Due to Melt-Rock Reaction Under the Influence of Varying CO₂

The reacted melts from 25% and 33% G2PM1 through BAC5-added experiments are plotted in Figure 3 according to the classification of basalts by Le Bas [1989]. Also plotted on the same figure are the starting composition of BAC as well as basanites, nephelinites, and melilitites from Cook Australs, St. Helena, Cape Verde, Canary Islands, Azores, Samoa, Societeies, and Hawaii, where the ocean island compositional data are corrected to be in equilibrium with olivine of Mg#88, i.e., the average Mg# of olivine in our melt-rock reaction experiments determined from Figure S2. Figure 3 demonstrates how a siliceous basaltic andesite such as BAC can evolve to greater degree of silica undersaturation from basanites to basanitic nephelinite to ultimately nephelinite as CO₂ content in the melt-rock system increases. The excellent match between

Figure 3. Reacted melt compositions and starting basaltic andesite melt from this study compared with natural ocean island basalts (GEOROC database) [França et al., 2006; Aulinas et al., 2010; Duprat et al., 2007; Dyhr and Holm, 2010; Barker et al., 2009; Martins et al., 2010; Torres et al., 2010; Mourão et al., 2010; Takamasa et al., 2009; Kawabata et al., 2011] from Cook-Australis, St. Helena, Cape Verde, Canary, Azores, Samoa, Societies and Hawaii (corrected to be in equilibrium with olivine of Fo₈₈ using Fe*-Mg $K_D = 0.3$) plotted on Le Bas [1989] classification diagram of CaO + Na₂O + K₂O (wt %) versus SiO₂ + Al₂O₃ (wt %) with fields represented by basanites, nephelinites, and melilitites. The broken (25% melt-added runs) and solid arrows (33% melt-added runs) represent direction of increasing degree of silica undersaturation or alkalinity with higher CO₂ concentration in the reacting and reacted melts. The numbers next to tick marks on arrows denote CO₂ concentration in the reacting melt that produced the respective reacted melt composition. Error bars represent $\pm 1\sigma$ standard deviation.

BAC + 75% KLB-1 ox as well as residue composition corresponding to each reacted melt are plotted on the plane of Ca-Tschermak (CaTs)—Forsterite (Fo)—Quartz (Qtz) projected from Diopside (Di) in Figure 4 according to O'Hara [1968]. Also plotted on the same figure are the starting melt BAC and peridotite KLB-1ox. Tie lines are constructed connecting each reacted melt to its residual composition through its bulk composition. In this figure, the CaTs—En join corresponds to the pyroxene—garnet thermal divide [O'Hara and Yoder, 1967] with silica-rich compositions to the right and silica-poor compositions to the left. All reacted melts from this study plot in the silica-poor side of the thermal divide implying that upon reaction with peridotite in proportions of 1:3 and 1:2 and presence of as low as 0.25 wt % bulk CO₂, a recycled oceanic crust-derived siliceous melt is capable of transforming into an alkalic melt. Also, with increasing CO₂ in the infiltrating melt/bulk source, the reacted melt shifts further away from the Qtz apex resulting in greater-degree of undersaturation. This is in keeping with Figure 3. The residue composition also evolves closer to the thermal divide with increasing CO₂ in the bulk owing to greater orthopyroxene crystallization. Thus, the melt evolving toward greater degree of Si undersaturation with the residue evolving toward the thermal divide results in tie lines crossing each other with increasing CO₂ in the infiltrating melt. This is in contrast to the nature of evolution of reacting melts for increasing infiltrating melt mass at constant CO₂ content of reacting melt [Mallik and Dasgupta, 2013, Figure S2] where the tie lines were nearly parallel to each other and the reacting melt evolved toward greater degree of Si undersaturation with lower melt-rock ratio.

We propose that reaction between andesitic melt derived from recycled MORB-eclogite and peridotite (at intermediate melt-rock ratios) containing up to 1.6 wt % bulk CO₂ (the maximum bulk CO₂ content in this study), but as low as 0.25 wt % CO₂, is a sufficient process to generate such silica-deficient lavas in certain ocean islands.

4.4. Model to Estimate Reacted Melt Composition as a Function of Basaltic Andesite-Peridotite Ratio and Bulk CO₂ in the Source

Our experimental results establish that reaction between andesitic melt derived from recycled MORB-eclogite with peridotite in the presence of variable CO₂ is a viable process to generate basanitic to nephelinitic alkalic lavas [Mallik and Dasgupta, 2012, 2013, this study]. Because our experiments were conducted

nephelinitic basanites and nephelinites produced in this study and those found in Cook-Australis, Cape Verde, Canary Islands, and Hawaii is in good agreement with numerous recent studies suggesting presence of recycled oceanic crust [e.g., Gerlach et al., 1988; Marcantonio et al., 1995; Hauri, 1996; Woodhead, 1996; Kogiso et al., 1997; Lassiter and Hauri, 1998; Christensen et al., 2001; Doucelance et al., 2003; Demény et al., 2004; Sobolev et al., 2005; Day et al., 2009; Herzberg, 2011] and CO₂ in the source of these ocean island lavas [e.g., Allegre, 1971; Hauri et al., 1993; Kogarko et al., 1995; Chauvel et al., 1997; Saal et al., 1998; Martins et al., 2010; Frezzotti et al., 2002; Hoernle et al., 2002; Jørgensen and Holm, 2002; Dixon et al., 2008; Mourão et al., 2010].

The reacted melt compositions, the bulk compositions of 25% BAC + 75% KLB-1 ox and 33%

Figure 4. Bulk compositions of 25% basaltic andesite + KLB-10x and 33% basaltic andesite + KLB-10x, their corresponding equilibrated melt, and residue compositions for initial melt compositions G2PM1, BAC1, BAC2.6, BAC4, and BAC5 plotted on the compositional space Ca-Tschemak (CaTs)—Anorthite (An)—Quartz (Qtz)—Enstatite (En)—Forsterite (Fo), projected through Diopside (Di), according to O'Hara [1968]. CaTs—En join represents garnet—pyroxene thermal divide of O'Hara and Yoder [1967]. Also plotted for comparison are reacting melt composition BAC (black star) and starting peridotite KLB-10x (green star) and modeled reacted melt composition as a function of reacting eclogite-melt fraction (solid black lines) and bulk CO₂ (blue dashed curves) isopleths. The isopleths have been constructed using equations (2) and (3) given in the text. Numbers in black next to the black isopleths represent fraction of reacting melt (wt %) each isopleth corresponds to. Similarly, numbers in blue next to the blue dashed curves represent bulk CO₂ content (wt %) each isopleth represents. The black (25% basaltic andesite-added experiments) and red (33% basaltic andesite-added experiments) dashed arrows indicate direction of increasing degree of silica-undersaturation of reacting melt with greater CO₂ concentration in the reacting and reacted melt.

with relatively high melt:rock ratio, i.e., reacting melt fraction ≥ 25 wt % and bulk CO₂ content ≥ 0.25 wt % or 2500 ppm, we need a parameterization to extrapolate our data to a wider range of conditions. We have thus developed an empirical model to predict reacted melt compositions as a function of basaltic andesite-lherzolite ratio and source CO₂ content.

In this model, we have defined an “enrichment factor” for each of the relevant oxides in the melt as follows:

$$\text{Enrichment factor} = \frac{\text{Conc. Reacted melt} - \text{Conc. BAC}}{\text{Conc. BAC}} \quad (2)$$

where, Conc._{Reacted melt} and Conc._{BAC} are oxide concentrations in the resulting melt and starting CO₂-bearing andesitic melt in weight percentage.

We have fitted the following empirical function by least squares method.

$$\text{Enrichment factor}_{\text{calculated}} = a + b \times F + c \times \text{CO}_{2\text{Bulk}} + d \times F \times \text{CO}_{2\text{Bulk}} + e \times F^2 \quad (3)$$

where a , b , c , d , e are fitting parameters, F is the reacting melt fraction by weight, and CO_{2Bulk} is the CO₂ concentration in the bulk melt-rock mixture in weight percentage.

The modeled concentration of reacted melt can be calculated from equations (2) and (3). Based on the reacted versus reacting melt fraction trend for CO₂-free andesite-peridotite system [Mallik and Dasgupta, 2012], we argue that our model can be used for reacting eclogite melt as low as 3–5% and up to intermediate reacting melt fraction of 33% (where the melt is in equilibrium with an olivine-orthopyroxene-bearing residue) and a source CO₂ range from 0 to 2 wt %. Also, both 2.5 and 3 GPa reacted melt compositions from Mallik and Dasgupta [2012] were taken into consideration during fitting the function as no discernible effect of pressure on melt composition was found within this narrow range of pressure. Table 4 displays the values

Table 4. Fitting Parameters for Modeling Reacted Melt Composition as a Function of Reacting Eclogite Melt Fraction Relative to Peridotite and Source CO₂ Concentration^a

	a	b	c	d	e	Σr^2
SiO ₂	−0.198	−0.059	−0.055	0.041	0.257	0.008
TiO ₂	−0.567	3.199	0.020	−0.408	−2.632	0.057
Al ₂ O ₃	−0.092	−0.501	−0.302	0.643	0.593	0.022
FeO*	0.055	0.908	0.033	0.034	−0.963	0.041
MgO	4.998	−2.150	2.114	−4.225	−2.848	1.466
CaO	0.657	−2.642	0.347	−0.301	1.985	0.051
Na ₂ O	−0.564	2.516	0.149	−0.149	−1.952	0.066
K ₂ O	−0.161	5.184	−0.575	0.783	−5.023	0.290

^aAll oxide compositions are in weight percent. a,b,c,d,e = Fitting parameters for empirical model (equations (3) and (4) in text). Σr^2 = Sum of residual squares; it is the square of the difference between measured composition of the experimental melts and composition calculated using the empirical model given by equations (3) and (4) in the text.

of fitting parameters and Σr^2 obtained from the regression. Figure 5 compares the measured versus modeled concentrations of oxides in reacted melts. We also compared our calculated concentrations with concentrations of volatile-free peridotite partial melt (generated at 3 GPa, 1445°C), partial melt of 1 wt % CO₂-bearing peridotite (generated at 3 GPa, 1350–1400°C) and reacted melt generated from 8% and 33% eclogite-melt infiltrating peridotite at 3 GPa, 1440°C [Mallik and Dasgupta, 2012] to evaluate the temperature range across which our model can be used. Given the uncertainties in measured melt composition because of quench heterogeneities, we argue that our modeled compositions match reasonably well with measured compositions across a temperature range of 1350–1445°C for all oxides. The only caution that should be exercised is that in case of TiO₂ and Na₂O, the model overestimates the concentration of these oxides for melts generated at 1440°C and $F > 0$ with the degree of overestimation increasing with F . This is because the model does not take into account the counteracting effect of dilution of TiO₂ and Na₂O due to significant increase in the resulting melt-fraction at higher temperatures over increase in infiltrating eclogite-melt fraction (which enriches the system in TiO₂ and Na₂O).

In Figure 4, the isopleths of F and bulk CO₂ were constructed using our empirical model. These isopleths, on the projection plane of CaTs-Fo-Qtz from Di, lie on the silica-undersaturated side of the thermal divide (CaTs-En join), which indicates that irrespective of bulk CO₂ concentration, reacted melts, corresponding to reacting melt fraction (F) of up to 35 wt % in the melt-rock system, are alkalic. The isopleths indicate that both lower fraction of reacting melt and higher bulk CO₂ drive the reacted melt toward greater degrees of alkalinity, in agreement with the previous studies [Mallik and Dasgupta, 2012; 2013].

4.5. Distinguishing Peridotite Versus Hybrid Pyroxenite as Source of Primary Magmas Using CaO Versus MgO Characteristic of Melts

One of the key questions is how to identify the presence and determine the quantity of eclogitic heterogeneity in the source regions of basalts. Herzberg and Asimow [2008] proposed that peridotite-derived and pyroxenite-derived melts can be distinguished by the equation: $\text{CaO} = 13.81 - 0.274 \text{ MgO}$, where, CaO and MgO are oxide concentrations in primary melt (wt %). Melt compositions plotting above the line defined by this equation in Figure 6 are primary peridotite-derived melts and those below are primary pyroxenite-derived melts. However, our model isopleths are observed to transgress the green line from the field of pyroxenite-derived partial melts into peridotite-derived melts irrespective of bulk CO₂ or melt fraction in the source. This implies that the above equation is not adequate to distinguish between peridotite and pyroxenite-derived melts, especially for a pyroxenite-peridotite hybrid source, such as the one used in this study. The presence of MORB-eclogite component in the distal mantle source regions of ocean islands cannot be excluded simply because the near-primary magma has relatively high CaO at a given MgO content. Similarly, the mantle source may be olivine bearing, although with lower modal abundance than expected for fertile peridotite, even though the primary magma has low CaO at a given MgO content. Herzberg and Asimow [2008] and Herzberg [2011] do discuss that certain high CaO pyroxenite-derived melts [e.g., Hirschmann et al., 2003; Kogiso et al., 2003; Keshav et al., 2004] may plot above the green line in Figure 6, although, these authors express dubiousness about these high MgO-garnet pyroxenites being sources of oceanic island basalts (OIBs) as opposed to those formed by reaction of siliceous recycled-oceanic-crust-derived melt with peridotite [Sobolev et al., 2005, 2007; Herzberg, 2006; Mallik and Dasgupta, 2012, 2013]. We agree with the notion that hybrid “pyroxenite” produced by siliceous melt-peridotite reaction is likely to be much

Figure 5. Modeled versus analyzed oxide concentrations of reacted melts, showing the reliability of our parameterization in predicting reacted melt compositions in eclogite-peridotite systems at ~ 3 GPa. The experimental data are from Mallik and Dasgupta [2012, 2013] and this study. Error bars in measured concentration represent $\pm 1\sigma$ standard deviation. The dashed lines represent 10% error envelope with respect to the 1:1 line.

more prevalent in the OIB source as compared to the silica-deficient garnet pyroxenites; however, we show that primary melts generated from such hybrid sources (without a high Ca-lithology) can also lie on either “peridotite” or “pyroxenite” field. This is particularly so if the mantle source region is CO_2 rich and infiltrated with relatively lower eclogite melt fraction. Therefore, caution must be exercised upon using such discrimination schemes to comment on source characteristics of natural lavas.

4.6. Quantifying the Source Characteristics of Individual Islands in Ocean Island Groups

Our model can be used to estimate the contributions from eclogitic crust and CO_2 required in the broadly peridotitic source of alkalic ocean island basalts. To illustrate, we have chosen four ocean island groups such that the lava compositions span the entire range of degree of silica undersaturation according to Le

Figure 6. CaO (wt %) versus MgO (wt %) space with green line, given by equation $\text{CaO} = 13.81 - 0.274 \text{ MgO}$, dividing the fields of peridotite-derived from pyroxenite-derived primary melts as defined by Herzberg and Asimow [2008], compared with the reacted melt compositions of andesite-peridotite hybrids and modeled reacted melt compositions as a function of eclogite-derived reacting melt fraction and bulk CO_2 content. The numbers against isopleths denote reacting melt fraction and source CO_2 concentration in wt %. Melt-rock reaction in eclogite-peridotite systems produces equilibrated melt compositions that transgress the field of pyroxenite-derived and peridotite-derived primary melts.

using $K_D^{\text{Fe}^*-\text{Mg}}(\text{ol}-\text{melt}) = 0.3$ [Roeder and Emslie, 1970]. Although Matzen *et al.* [2011] have used $K_D^{\text{Fe}^*-\text{Mg}}(\text{ol}-\text{melt}) = 0.34$ for calculating parental magma composition for Hawaii, they note in their study that a value of 0.34 is applicable for olivine fractionation corrected lava compositions that have SiO_2 concentrations between 46–52 wt % and $(\text{Na}_2\text{O} + \text{K}_2\text{O}) < 3$ wt %. Appropriate $K_D^{\text{Fe}^*-\text{Mg}}(\text{ol}-\text{melt})$ values for lava compositions that have less than 46 wt % SiO_2 and greater than 3 wt % $(\text{Na}_2\text{O} + \text{K}_2\text{O})$ are less than 0.34 [Gee and Sack, 1988; Toplis, 2005]. While Hawaiian shield lavas may fall in this compositional range, the lavas chosen here from Canary Islands, Cape Verde, Cook-Australis and Hawaii have $\text{SiO}_2 < 46$ wt % and $(\text{Na}_2\text{O} + \text{K}_2\text{O}) > 3$ wt %. Hence, in order to avoid any bias in terms of choice of $K_D^{\text{Fe}^*-\text{Mg}}(\text{ol}-\text{melt})$ varying with lava composition, we have used a value of 0.3 for all lavas. We chose to correct the natural basalt compositions to Fo_{88} because that is the average residual olivine composition from our study. Also, within each island group, only individual islands with at least 15–20 data points that passed the above filter have been considered so that a representative sample population is included in the discussion. CaO versus SiO_2 concentrations of islands from these four island groups have been plotted in Figures 7–10. Also plotted on each figure is the line proposed by Herzberg and Asimow [2008] as an approximate filter to distinguish CO_2 -bearing primary melts to the left of the line from CO_2 -free melts, given by the equation $\text{CaO} = 2.318\text{SiO}_2 - 93.626$. As observed in Figures 7–10, most of our modeled CO_2 -free isopleth lies to the right of the filter along with some part of the low CO_2 -isopleth, especially toward high F . This reaffirms the statement by Herzberg and Asimow [2008] that their filter to track the presence or absence of CO_2 in the mantle source is “approximate” and should not be taken as a rigid boundary.

Canary Islands—Alkalic basalt compositions from six islands (La Palma, Gran Canaria, Tenerife, Lanzarote, Fuerteventura, and El Hierro) are plotted in Figure 7. In case of La Palma, Tenerife, and El Hierro, low CaO, low SiO_2 compositions (to the left of the filter) have high TKP ($0.5\text{TiO}_2 + \text{K}_2\text{O} + \text{P}_2\text{O}_5$ in wt %) content. This is not what would be expected if the high TKP lavas represented low-degree partial melts of a fixed carbonated source where low-degree melts would have higher CaO content with lower SiO_2 [Hirose, 1997; Dasgupta *et al.*, 2007, 2013]. The enrichment in incompatible elements in these four islands is observed toward higher F isopleths, which implies that this enrichment is due to higher TKP concentrations in the source lithologies that underwent partial melting (due to higher fraction of infiltrating eclogite-derived melt in the source). Based on the comparison between the F - CO_2 grids and the natural basalts from these three islands in the CaO- SiO_2 space, as much as 15–35 wt % eclogite melt in the peridotite source region can be argued. Moreover, variable extent of eclogite-melt fluxing seems necessary even within one island perhaps suggesting heterogeneous distribution of eclogite component in the mantle source. In case of Fuerteventura and Gran

Bas [1989]. Accordingly, the ocean island groups chosen here are Canary Islands, Cape Verde, Cook Australis and Hawaii. The data of alkalic basalts from these islands along with the references from which they have been taken are reported in supporting information. Whole rock and glass with MgO between 8 and 16 wt % have been considered as representative samples from the ocean island groups to minimize effects of fractional crystallization of plagioclase and clinopyroxene. Intrusives and cumulate compositions have been excluded. Hence, we have corrected each average composition by adding back only olivine to the melt composition till the melt is in equilibrium with olivine of forsterite content 88% (Fo_{88}) by

Figure 7. Natural lava compositions from Canary Islands (La Palma, Gran Canaria, Tenerife, Lanzarote, Fuerteventura, and El Hierro) corrected to be in equilibrium with $F_{0.88}$ by adding back olivine, using $K_D^{Fe^{2+}-Mg}(ol-melt) = 0.3$ [Roeder and Emslie, 1970], plotted on CaO versus SiO_2 space along with model isopleths for bulk CO_2 and F (infiltrating MORB-eclogite melt fraction relative to peridotite) in the source. The references from which the lava compositions are taken have been provided in supporting information. The model isopleths are plotted using equations (2) and (3) (see text for further details). The numbers against isopleths denote reacting eclogite melt mass in wt % (black) and source CO_2 concentration in wt % (blue). The red line is given by the equation $CaO = 2.318SiO_2 - 93.626$, represents an approximate filter for separating CO_2 -bearing primary mantle melts to the left from CO_2 -free melts to the right [Herzberg and Asimow, 2008]. The lava compositions are shaded according to their concentration of TKP ($0.5TiO_2 + K_2O + P_2O_5$) as per the gray scale bar in the figure. TiO_2 , K_2O , and P_2O_5 are incompatible components in the system. TiO_2 concentrations are roughly a factor of 2 higher than $K_2O + P_2O_5$ concentrations; hence, they have been halved to ensure that TiO_2 concentration does not dominate the incompatible element budget.

Canaria, basalts with $SiO_2 < 42$ wt % show enrichment in TKP at a near-constant CaO concentration of ~ 10 – 12 wt %. This trend follows a trajectory of simultaneous increase in bulk CO_2 and F in the source lithology, suggesting that both eclogite component and source CO_2 may be variable and their enrichment or depletion is likely coupled. F and bulk CO_2 may vary from >35 and 2 wt % CO_2 to <5 and 0 wt %, respectively. Lanzarote basalts display two trends: the first trend shows decreasing SiO_2 with near-constant CaO at ~ 10 wt % commensurate with enriched TKP (similar to the trend shown by Gran Canaria); the second trend displays increasing CaO with decreasing SiO_2 along with maximum enrichment in TKP at highest CaO concentrations. This latter trend can be generated by differential degrees of melting of carbonated peridotite [e.g., Hirose, 1997; Dasgupta et al., 2007, 2013; Herzberg and Asimow, 2008], i.e., SiO_2 increases and CO_2 in the melt

Figure 8. Natural lava compositions from islands in Cape Verde (São Nicolau, Santo Antão, Santiago, São Vicente) corrected to be in equilibrium with Fo₈₈ using $K_D^{Fe^{2+}-Mg}(ol-melt) = 0.3$ [Roeder and Emslie, 1970], plotted on CaO versus SiO₂ space along with model isopleths for bulk CO₂ and F (infiltrating melt mass) in source. The numbers against isopleths denote reacting melt mass in wt % (black) and source CO₂ concentration in wt % (blue). The references from which the natural lava compositions are taken have been provided in supporting information. The red line and shading of the symbols mean the same as in Figure 7.

decreases with increasing degree of partial melting of carbonated peridotite. However, TiO₂ content in these OIB lavas is higher to be explained by melting of carbonated peridotite alone (Figure S6), which implies the involvement of a mafic lithology in the source. Presence of recycled oceanic crust in the source for Canary Islands has been evaluated by studies before [Herzberg, 2011]. Thus, the trend represents partial melting for a fixed hybrid lithology (peridotite infused with partial melt derived from MORB-eclogite).

Cape Verde—Alkalic lava compositions from São Nicolau, Santo Antão, Santiago, São Vicente and Sal are plotted in Figure 8. The islands of Santo Antão and Santiago display a weak positive correlation of CaO

Figure 9. Natural lava compositions from two islands in Cook Australs (Tubuai, Aitutaki) corrected to be in equilibrium with Fo_{88} using $K_D^{\text{Fe}^{2+}-\text{Mg}}(\text{ol}-\text{melt}) = 0.3$ [Roeder and Emslie, 1970], plotted on CaO versus SiO_2 space along with model isopleths for bulk CO_2 and F (infiltrating eclogite melt mass) in source. The numbers against isopleths denote reacting melt mass in wt % (black) and source CO_2 concentration in wt % (blue). The references from which the natural lava compositions are taken have been provided in supporting information. The red line and shading of the symbols mean the same as in Figure 7.

versus SiO_2 in terms of lava composition and in these islands along with São Nicolau, enrichment in TKP is observed to increase toward low CaO, low SiO_2 . This trend corresponds well with that of Tenerife, Canary Islands, i.e., the incompatible element enriched lavas correspond to a higher eclogite- F and higher CO_2 -bearing source. Lower SiO_2 content in enriched lavas is an effect of higher CO_2 in the source. São Vicente and Sal basalts display a negative correlation between CaO and SiO_2 with higher CaO content lavas being more enriched in TKP across a narrow range of eclogite- F isopleths. This trend can be explained by differential degrees of partial melting of a CO_2 -bearing hybrid source lithology with lower-degree partial melts corresponding to high CaO, low SiO_2 , enriched lavas.

Cook Australs—Alkalic basalt compositions from the islands of Tubuai and Aitutaki are plotted in Figure 9. The island of Tubuai shows a similar trend as Santo Antão, Cape Verde while Aitutaki shows a trend similar as São Vicente, Cape Verde. Therefore, Tubuai lavas may be generated from a source that has both an eclogite-melt poor, CO_2 -poor component (relatively high CaO, high SiO_2) and an eclogite-melt-rich, CO_2 -rich component (relatively low CaO, SiO_2). Similarly, fractionation-corrected Aitutaki lavas can be generated by variable extent of melting of a hybrid ($\pm$ olivine)-websterite lithology fluxed with CO_2 .

Hawaii—Postshield lava compositions from Hawaii, postshield and rejuvenated compositions from Maui as well as rejuvenated compositions from Oahu and Kauai are plotted in CaO- SiO_2 space (Figure 10). The alkalic basalts from the island of Hawaii display a general enrichment in TKP with lower CaO content across a range of SiO_2 concentrations and TKP decreases with increasing CaO for a given SiO_2 content. This trend can be considered to be similar to São Nicolau, Cape Verde. Maui, Oahu and Kauai, on the other hand, display an overall enrichment in TKP with increasing CaO and decreasing SiO_2 content of lavas similar to São Vicente, Cape Verde. In other words, the CaO- SiO_2 trends for Maui, Oahu, and Kauai all suggest variable degree of melting of a carbonated source where the width of the arrays may derive from variable extent of eclogite-melt fluxing.

One conclusion that can be reached from the comparison of the natural OIB data CaO- SiO_2 arrays with our reacted melt composition data and model is that relatively large amount of eclogite melt fluxing (as high 30–40% by weight with respect to the peridotite source) with variable CO_2 content may be reasonable to invoke for the source regions of many ocean islands with strongly alkalic, silica-poor basalts. In case of the Hawaiian Islands Maui, Oahu and Kauai, several lava compositions that plot on the isopleth grid span nearly the entire range of eclogite-melt fraction and bulk CO_2 on the grid. However, one may ask whether such conclusion is in accordance with other major and minor elements. Perhaps more importantly, can one

Figure 10. Natural lava compositions from four islands in Hawaiian Islands (Hawaii, Maui, Oahu, and Kauai) corrected to be in equilibrium with Fo₈₈ using $K_D^{Fe^{2+}-Mg}(ol-melt) = 0.3$ [Roeder and Emslie, 1970] plotted on CaO versus SiO₂ space along with model isopleths for bulk CO₂ and F (infiltrating melt mass) in source. The numbers against isopleths denote reacting melt mass in wt % (black) and source CO₂ concentration in wt % (blue). The references from which the natural lava compositions are taken have been provided in supporting information. The red line and shading of the symbols mean the same as in Figure 7.

unambiguously argue for silica-poor, alkalic OIBs being exclusively generated by eclogite-melt-peridotite $\pm$ CO₂ reaction as modeled in CaO-SiO₂ plots, i.e., without any contribution from direct partial melting of peridotite above the volatile-free peridotite solidus? This distinction between eclogite-peridotite reacted melt being the sole entity in primary OIB versus eclogite-peridotite reacted melt being just one of the two components in primary OIB (the other component being peridotite partial melt) is critical as this has direct bearing on the geodynamic and thermal conditions at which primary OIBs are generated. Therefore, in the following section we evaluate other major and minor element spaces that may also provide constraints on how much eclogite melt and source CO₂ are necessary and permissible by the fractionation corrected OIB data.

In Figure S7, we plot our model results showing how reacted melt compositions in MgO-oxide spaces evolve as a function of reacting eclogite melt F and bulk CO₂ isopleths. The average of the ocean island basalt compositions from six islands in the Canaries, five islands from Cape Verde, two from Cook-Australis and four from Hawaiian islands as well as high μ (HIMU) average composition from Jackson and Dasgupta [2008] (Table S6) have also been plotted in the same figure for comparison. Jackson and Dasgupta [2008] only used shield-stage silicate lavas with MgO contents between 8 and 16 wt % to determine average ocean island compositions. This was done to avoid cumulates and minimize effects of crystal fractionation.

Figure 11. Isopleths of reacting melt fraction (solid lines) and source CO₂ (broken lines), after mixing with 40% by weight of volatile-free peridotite partial melt (composition reported in Table S5), constructed using the empirical model from this study plotted on MgO versus oxide (SiO₂, TiO₂, Al₂O₃, FeO*, and CaO) compositional space. The numbers against isopleths denote reacting melt fraction in wt % (5–35) and source CO₂ concentration in wt % (0–2). Also plotted for comparison are average alkalic basalt compositions from the islands of Canary, Cape Verde, Cook-Australs, and Hawaiian Islands (composition reported in Table S6) as well as HIMU average composition [Jackson and Dasgupta, 2008], partial melts of carbonated peridotite generated at temperatures from 1350 to 1400 °C, pressures from 2 to 4 GPa [Dasgupta et al., 2007, 2013] and partial melts of volatile-free peridotite up to 20% melting degree and pressure of equilibration of 2.5–4 GPa from previous experimental studies [Walter, 1998; Hirose and Kushiro, 1993; Takahashi, 1986; Davis et al., 2011]. The average basalt compositions are corrected to be in equilibrium with Fo₈₈ by adding back equilibrium olivine (see text for details). The average compositions from Cape Verde plot off the isopleth grids in the oxide spaces (toward lower SiO₂ and Al₂O₃ and higher CaO). This is because Cape Verde requires contribution from carbonated peridotite partial melt (as shown in Table 5), not volatile-free peridotite partial melt (which has been used in the example mixing calculation in this figure). The average compositions from Maui and Hawaii (before olivine fractionation correction) have MgO concentrations lower than 11 wt %, hence, plot outside the area of the figure. Maui and Oahu (after olivine fractionation correction) have FeO* concentration higher than 13 wt %, hence plot outside the MgO versus FeO* space.

We also plotted partial melts of volatile-free and carbonated peridotite in Figure S7 to evaluate how volatile-free and carbonated peridotite partial melts compare to ocean island averages.

The most likely constraints to be used for estimating source characteristics of ocean islands are SiO₂, Al₂O₃, MgO, and CaO concentrations because these four oxides are profoundly influenced by presence of CO₂ in the source, hence, can be effective tracers of varying bulk CO₂ content in the source. However, in the plots of Al₂O₃ versus MgO and CaO versus MgO in Figure 11, several volatile-free peridotite partial melts plot

Table 5. Source Characteristics for Ocean Islands and HIMU Average Estimated From Empirical Model^a

Ocean Island Group	Island	Reacting Eclogite Melt Percent ^b	Source CO ₂ Concentration (wt %) ^b	Weight Percent of Peridotite Partial Melt ^c	Σr ²
Canary Islands	La Palma	27	1.9	39 ^d	0.4
	Tenerife	26	2.0	45 ^d	0.7
	Gran Canaria	25	1.3	31 ^d	4.4
	Fuerteventura	31	2.0	49 ^d	0.6
	Lanzarote	45	2.0	44 ^d	3.0
	El Hierro	25	1.8	25 ^d	3.3
Cape Verde	Santo Antão	31	1.5	26 ^e	0.6
	São Vicente	39	1.6	45 ^e	0.9
	São Nicolau	15	0.2	33 ^e	1.1
	Santiago	15	0.3	31 ^e	0.7
	Sal	39	2.0	55 ^e	3.7
Cook-Austral	Tubuai	23	2.0	51 ^d	1.0
	Aitutaki	28	2.0	42 ^d	2.5
Average HIMU		24	2.0	45 ^d	1.1

^aΣr²—sum of residual squares obtained from least square minimization.

^bIn a two stage hybridization process, this represents the first step where reacting melt or eclogite partial melt reacts with subsolidus peridotite + CO₂. Thus, reacting melt fraction and source CO₂ concentration refer to the amount of eclogite melt and CO₂ content required to form reacted melt in the first step of the hybridization process, prior to peridotite-melt mixing (see text for details).

^cIn a two stage hybridization process, this represents the second step where reacted melt from the first step (see above) undergoes mixing with peridotite-derived melt (CO₂-bearing or not). The composition of peridotite partial melts used in this step are reported in Table S5. Thus, the weight percent here is the percentage of peridotite-derived melt required in the total contribution comprising peridotite partial melt and reacted melt from hybridization process in the first step.

^dVolatile-free peridotite partial melt has been used in the mixing calculation (composition in Table S5).

^eCarbonated peridotite partial melt has been used in the mixing calculation (composition in Table S5).

within the space of our modeled isopleths rendering it difficult to distinguish source characteristics just based on the location of melt composition in these plots. In fact, as discussed earlier, the inability of a filter suggested by *Herzberg and Asimow* [2008] (green line in Figure 6) to distinguish between peridotite-derived versus pyroxenite-derived melts underscores this problem even further. However, in the space of TiO₂ versus MgO, peridotite-derived melts and our modeled isopleths do plot in distinct fields highlighting TiO₂ as a key proxy for pyroxenite assimilation in ocean island sources [e.g., *Prytulak and Elliott*, 2007]. Thus, we consider TiO₂ as another reliable compositional constraint for determining source characteristics.

Figure S7 shows that covariation of SiO₂, Al₂O₃, MgO, and CaO of average OIBs from Hawaii, Cape Verde, Canary, and Cook Austral islands can be matched by reacted melt compositions of eclogite-lherzolite system in the presence of CO₂. For majority of the individual islands among these groups, 10–35 wt % reacting eclogite melt fraction and 0–1.2 wt % bulk CO₂ content seem appropriate to drive the reacted melt compositions toward natural OIBs. However, our reacted melt compositions and modeled isopleths, especially for relatively high (10–35 wt %) reacting melt fraction, yield much higher TiO₂ concentration compared to those in average primitive ocean island and HIMU basalts (except for Santo Antão, Cape Verde). In order to satisfy the TiO₂ contents of average alkalic OIBs, reacting eclogite melt fraction needs to be ≤5 wt % relative to lherzolite. Therefore, concentrations of major (SiO₂, Al₂O₃, MgO, CaO) and minor (TiO₂) elements of modeled reacted melts suggest divergent estimates of eclogite contributions to OIB source regions. Therefore, it appears unlikely that silica-poor basanites to melilititic nephelinites from ocean islands can be produced by eclogite melt (±CO₂)-subsidiolus peridotite reaction alone. This problem can be overcome; however, if we consider that at conditions similar to those of our experiments, carbonated silicate melt is generated from peridotite as well [*Wendlandt and Mysen*, 1980; *Hirose*, 1997; *Dasgupta et al.*, 2007, 2013], or at similar pressure (~2.5 GPa) but temperature slightly hotter than our experiments, volatile-free peridotite partial melt is also generated.

Therefore, we propose that for alkalic OIB generation, a two-step process of melt-rock reaction and melt-melt mixing may be necessary. In a mantle domain with heterogeneous distribution of recycled oceanic crust (comprising an eclogite-rich mantle zone and an eclogite-free or an eclogite-poor mantle zone), the first stage consists of eclogite-melt-peridotite + CO₂ reaction in an eclogite-bearing mantle domain and the second stage involves mixing of reacted melt from the first stage with peridotite ± CO₂-partial melt. The most likely scenario of eclogite-peridotite hybrid melt and peridotite partial melt interaction is where the

generation of the former takes place in the deeper portion of the upwelling mantle, i.e., below the peridotite solidus, and the reacted melt upon ascent mixes with peridotite partial melts generated from eclogite-poor mantle domains.

Mixing between equilibrated melts from eclogite melt-peridotite + CO₂ systems and peridotite ± CO₂ systems generated at similar or somewhat shallower depths (equivalent to ~2–4 GPa, 1350–1400°C) provide the relative contributions of peridotite-eclogite ± CO₂ hybrid partial melt (melt 1) and peridotite ± CO₂-bearing partial melt (melt 2; Table 5). We have modeled mixing between melt 1 and 2 where melt 2 is either a carbonated peridotite partial melt or a volatile-free peridotite partial melt (compositions reported in Table S5) in order to determine the relative proportions of melts 1 and 2 required to produce major element composition of OIB averages (Figure 11). We have estimated the values of eclogite-melt fraction, bulk CO₂ and fraction of peridotite partial melt that would best match the ocean island average composition in terms of SiO₂, TiO₂, Al₂O₃, MgO, and CaO. For the purpose of modeling, we have chosen two peridotite partial melt compositions (Table S5)—a volatile-free lherzolite partial melt generated at 2.5 GPa, 1425°C [Hirose and Kushiro, 1993] and a partial melt of 1 wt % CO₂-bearing peridotite generated at 3 GPa, 1350°C [Dasgupta et al., 2007]. Whether a volatile-free peridotite partial melt or a carbonated peridotite partial melt contributes to the ocean island lava was decided on the basis of which peridotite-melt yielded better convergence in optimization. In case of Canary Islands, Cook-Austral Islands, Hawaiian Islands and average HIMU, mixing melt 1 with volatile-free peridotite partial melt produced a better convergence in terms of SiO₂, TiO₂, Al₂O₃, CaO, and MgO. On the other hand, for Cape Verde islands, a tighter constraint of amount of eclogite-melt and CO₂ in the source prior to mixing with melt 2 is obtained by mixing melt 1 with carbonated peridotite partial melt.

Our two-stage melt-rock reaction and melt-melt mixing calculation suggests that the deeper portion of alkalic OIB source regions, i.e., below the peridotite solidus, can be significantly CO₂ rich (0.3–2.0 wt % in the mixed source) and may observe a significant fraction of eclogite melt infiltration.

While the match between modeled melt composition (result of melt-rock reaction and subsequent melt-melt mixing) and target melt composition (ocean island average composition) is overall good for Canary Islands, Cape Verde, Cook Australs and average HIMU (based on the sum of residual squares as reported in Table 5), the match is not as good for Hawaiian Islands. Our model overestimates TiO₂ and CaO concentrations for the Hawaiian Islands significantly. Lassiter et al. [2000] have invoked the presence of pyroxenite in the source of alkalic posterosional Hawaiian lavas. However, we find that involving siliceous partial melts of hybrid pyroxenite (formed by reaction of siliceous eclogite-melt with peridotite, akin to the residues of melt-rock reaction from this study) formed at 3.5 GPa [Sobolev et al., 2007] in our model does not resolve the problem with overestimation of TiO₂ and CaO. Thus, the alkalic basalts in Hawaiian Islands require a lithology in their source that will produce SiO₂ and CaO-poor melts in the upper mantle. CO₂-present partial melting of a lithology will not be applicable in this case because CO₂ can decrease the SiO₂ content but will simultaneously enhance the CaO concentration of the melt [Hirose, 1997; Dasgupta et al., 2007, 2013]. Partial melting of garnet pyroxenite [Hirschmann et al., 2003] or mixed peridotite-pyroxenite sources [Kogiso et al., 1998; Yaxley and Green, 1998] can produce appropriate low SiO₂, low CaO melts. However, these partial melts being more aluminous for a given MgO content than the Hawaiian alkalic basalts, calls for a pressure of melting greater than 3 GPa.

One aspect of experimentally equilibrated melt from eclogite-peridotite-CO₂ systems and their derivatives produced via mixing with experimental partial melts of peridotite is that FeO* concentration is lower by a few weight percent as compared to the plotted alkalic OIBs and HIMU averages. One possible explanation for this could be that our experimental conditions (having been performed in graphite inner capsules) are more reduced (~QFM – 2) compared to those in the source of these OIBs, which may contain Fe₂O₃ even up to the concentration of TiO₂ [Herzberg and Asimow, 2008]. Presence of higher Fe³⁺/Fe_{total} in the system would elevate total FeO* content in the reacted melts owing to greater incompatibility of Fe₂O₃ during melting and melt-mantle equilibration. To test this, we have estimated the Fe³⁺/Fe_{total} of the carbonated reacted melts from this study using Kress and Carmichael [1991] and the values are in the range of 0.02–0.03. We have also estimated the Fe³⁺/Fe_{total} of the olivine fractionation corrected ocean island averages in Table S6 assuming that Fe₂O₃ content of the ocean island averages are equal to their TiO₂ content [Herzberg and Asimow, 2008] and the values are in the range of 0.2–0.3. Therefore, there is an increase in Fe³⁺/Fe_{total} by a factor of 10 between our experimental melts and natural ocean island lavas. In order to demonstrate

that such an increase in $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ can increase $\text{FeO}_{\text{total}}$, we have estimated the change in $\text{FeO}_{\text{total}}$ as a function of $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ in rhyo-dacitic melts generated at 3 GPa, 1050°C from *Jégo and Dasgupta* [2014, in press]. An increase in $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ by a factor of 10 is observed to increase FeO^* by ~ 2.5 wt %. Thus, higher oxygen fugacity at the source of ocean island basalts can be a plausible reason to explain the FeO^* mismatch between our experimental melts and alkalic ocean island basalts.

4.7. Temperatures of Generation of Primitive Silica-Poor Basanites to Melilititic Nephelinites

Our reacted melt compositions and those that could be produced by mixing such hybrid melts [*Mallik and Dasgupta*, 2012, 2013, this study] and carbonated peridotite partial melts have implications for temperature estimates of primary basalts. For intermediate melt-rock ratio (applicable to sources of several ocean islands according to Table 5), the MgO concentration of the reacted melts, on a volatile-free basis, vary from 12 to 16 wt % with increasing melt CO_2 concentration from 0 to 9 wt %. The MgO contents of the reacted melt after mixing with 30% of carbonated peridotite partial melt (30% being the average proportion of peridotite partial melt applicable to several islands of Cape Verde according to Table 5) is 14 to 19 wt % with corresponding CO_2 concentration in the melt increasing from 0 to ~ 11 wt %. As an example, using the MgO-in melt thermometer of *Herzberg and Gazel* [2009], such MgO concentrations correspond to a range of mantle potential temperatures (T_p) from 1438°C to 1543°C which is, 88 to 193°C, respectively, higher than the T_p of 1350°C that would be applicable for our experiments. Thus, a melt-rock reaction between recycled oceanic crust-derived melt and peridotite without or with up to 11 wt % CO_2 in the melt can produce a biased signature of high T_p . Hence, caution must be exercised when using such thermometers and the possibility of introducing a correction factor for melt-rock reaction and presence of CO_2 (as pointed out by *Herzberg and Asimow* [2008]) must be introduced. In this case, we observe that reaction between MORB-eclogite-derived partial melt and peridotite causes an overestimation of mantle potential temperature (ΔT_p) by 88°C with no CO_2 present in the reacted melt followed by ΔT_p of $\sim 18^\circ\text{C}/\text{wt } \%$ CO_2 in the reacted melt. In other words, for 1000 ppm CO_2 in the mantle source, a silicate melt with up to 6 wt % CO_2 (corresponding to a melt fraction of 1.7 wt %) can give an apparent T_p overestimation by 100°C.

The fact that Canary Islands and Cook-Australis require contribution from volatile-free peridotite partial melt as opposed to carbonated peridotite partial melt in case of Cape Verde has geodynamic implications. In order to partially melt volatile-free peridotite at $P \sim 3$ GPa, $T \geq 1445^\circ\text{C}$ [*Davis et al.*, 2011], i.e., temperature higher than that at which the experiments from this study are performed, is required. This implies that a thermal perturbation from a nearby plume or the core of a thermally zoned plume is needed to facilitate volatile-free partial melting, hence, Canary Islands and Cook-Australis likely have $T_p > 1350^\circ\text{C}$ (T_p applicable to mid-ocean ridge mantle and corresponding to P - T conditions of experiments in this study). On the other hand, carbonated peridotite can undergo partial melting at the P - T condition of experiments from this study [*Hirose*, 1997; *Dasgupta et al.*, 2007] which implies that the necessity of a thermal plume to generate alkalic basalts is precluded in case of Cape Verde. We cannot specifically comment on the thermal condition of the mantle required for postshield and rejuvenated stage magmatism in Hawaiian Islands, given the poor match between the Hawaiian alkalic melts and our modeled melt compositions.

5. Conclusions

We demonstrate that, at intermediate melt-rock ratios, recycled oceanic crust-derived andesite upon reaction with peridotite can evolve to alkalic basalts in the presence of 0–1.67 wt % CO_2 in the melt-rock mixture. The degree of silica undersaturation or alkalinity of the reacted melts increase with greater CO_2 content in the system where the reacted melts evolve from a basanite to a nephelinite. The increasing degree of silica undersaturation in the reacted melt with greater CO_2 is accompanied by crystallization of orthopyroxene and garnet in the residue. We have developed an empirical model to estimate source characteristics (infiltrating MORB-eclogite-derived melt mass and CO_2 content in the source) as well as subsequent contribution from peridotite ($\pm \text{CO}_2$)-derived melt for ocean islands from our experimentally produced primary reacted melt compositions. Our model underscores the importance of such melt-rock reactions and presence of minor CO_2 in the mantle source in elevating MgO contents of reacted melts which raises the possibility of estimating erroneously high T_p under some ocean islands. We also predict, from our model, that Canary Islands and Cook Australis require contribution from volatile-free peridotite partial melt in addition to hybridization of MORB-eclogite-derived melt with peridotite in presence of CO_2 ,

whereas, Cape Verde requires contribution from carbonated peridotite partial melt along with hybridization of MORB-eclogite-derived melt and peridotite. This implies that Canary Islands and Cook-Australis require a thermal perturbation and T_p of at least 1425–1450°C while Cape Verde does not require any such thermal anomaly and T_p of ~1350°C is sufficient for genesis of alkalic basalts.

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