Cycling of CO₂ and N₂ Along the Hikurangi Subduction Margin, New Zealand: An Integrated Geological, Theoretical, and Isotopic Approach

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Abstract We present a quantitative assessment of the input and output of CO₂ and N₂ along the Hikurangi margin based on the chemical and stable isotope composition of sediments and basalts (from IODP 375), previously accreted metasedimentary rocks, and volcanic/hydrothermal gases (together with noble gas data for the latter). We compare these results with 3-D thermo-petrologic models for four lithologic structures, representing different plateau inputs. The model results indicate that 59%–85% of initially subducted C and 5%–12% of N is lost from the slab during metamorphism, with both volatiles being dominantly sourced from altered oceanic crust with some contribution from subducted sediment at the forearc-arc transition (75–90 km depth). The δ¹³C[sub]VPDB and CO₂/²³He values for the arc gases range from −8.3 to −1.4‰ and 2 × 10⁻² to 2.7 × 10⁻¹⁴, indicating contributions from slab carbonate, organic C, and mantle C of 67%, 30%, and 3%, respectively. The δ¹⁵N[sub]VPDB and N₂/³⁶Ar values of arc gases are −1.0 to +2.3‰ and 1.54 × 10⁻³ to 1.9 × 10⁻⁶, indicating slab and mantle contributions of 74% and 26%. The δ¹³C signature of gases requires addition of organic C by tectonic erosion and/or shallow crustal assimilation. These calculations yield whole-margin fluxes of 5.4–7.0 Tg/yr for CO₂ and 0.0022–0.0057 Tg/yr for N₂, corresponding to −2.2% and 1%–30% of the global CO₂ and N₂ flux from subaerial volcanoes worldwide (assuming no loss during transit). This unique assessment of volatile cycling could prove useful in refining regional and global estimates of volatile recycling efficiency.

1. Introduction

Volatile elements enter subduction zones as components of sediment, altered oceanic crust, and serpentined peridotite (Bebout, 1996; Hacker, 2008; Jarrard, 2003; Peacock, 1990; Poli & Schmidt, 2002). With increasing pressure and temperature during subduction, metamorphic devolatilization reactions begin to produce fluid and systematically remove volatiles, and the process continues until the subducted units reach thermochemical equilibrium with the mantle. In addition to metamorphic controls on volatile cycling, tectonic controls such as accretion and underplating may contribute significantly to crustal storage of volatiles, while processes such as tectonic erosion may lead to underestimation of subducted volatile contents (Clift, 2017; House et al., 2019). Additionally, shallow processes such as dewatering during pore compaction and associated dissolution may affect volatile budgets entering the deeper forearc (cf. Barry et al., 2019). Globally, estimations of volatile return efficiency at convergent margins cover a wide range, for example estimates for the return efficiency of subducted CO₂ to the atmosphere via arc volcanism vary between 30% and 70% (Hilton et al., 2002; Sano & Williams, 1996; also see Sadofsky & Bebout, 2003). The estimates for N cycling are even less constrained, with global N₂ outgassing estimates ranging over an order of magnitude from 0.018 to 0.55 Tg/yr (Hilton et al., 2002; Sano et al., 2001; Snyder et al., 2003).

It has been apparent for some time that volatile return efficiency at arcs is geographically variable, and single-margin studies are therefore vital to improve understanding of subduction zone processes. The central America margin, for example, undergoes little to no C loss in the deep forearc and subarc (0.15%–5% loss, Freundt et al., 2014; see also Li & Bebout, 2005), while other margins could experience more extensive loss (~100% for the Lesser Antilles proposed by Li et al., 2020). For the Central America...
margin, previous research has concluded that ~100% of sediment-bound N$_2$ is lost by subarc depths (Fischer et al., 2002; Snyder et al., 2003), a conclusion at odds with studies of exhumed metasedimentary rocks that indicate near complete forearc retention of N in white mica (Bebout et al., 2013; Busigny et al., 2003). Furthermore, along the Costa Rican segment of Central America, Zimmer et al. (2004) concluded that total N$_2$ loss was only 3%–6% of the initially subducted inventory, though this calculation also considered basalt-bound N in addition to that within sediments. In order to understand the systematics of global volatile cycling at arcs it is crucial to first understand variability among segments of individual margins (see the work by House et al., 2019, describing huge variation in C inputs along the Sunda margin, Indonesia).

In this study, we present models of fluid production and chemistry associated with progressive metamorphism for realistic subducted lithosphere and sediment inputs and compare this modeling with the chemistry of forearc and arc gases along the Hikurangi subduction zone. Toward constraining subduction inputs and possible upper-plate crustal contamination, we present whole-rock and carbonate C-O-N isotope analyses of sedimentary and metasedimentary material from offshore and within the subaerially exposed fossil forearc. This approach of synthesizing gas chemistry and rock isotope compositions with numerical model predictions allows for the assessment of slab-derived (sediment, altered oceanic crust, or serpentinized peridotite) and nonslab derived (mantle wedge, crustal assimilation) volatile sources and highlights the spatial variability of volatile production beneath the North Island. We quantify the total release of CO$_2$ and N$_2$ from the slab beneath the North Island and discuss these fluxes with respect to their initial concentrations in the incoming oceanic plate as well as global estimates for volatiles released from arc regions.

2. Geologic Background

2.1. Hikurangi Plateau

The Hikurangi plateau is a rifted fragment of the ~120 Ma greater Ongtong Java Mesozoic large igneous province (Davy et al., 2008; Taylor, 2006), and prior to subduction covered an area of roughly 0.8 million km$^2$ (Hoernle et al., 2010). Initial subduction of the plate was to the south under the Gondwana continent, beneath the present-day bathymetric high of the Chatham rise (Figure 1a). Southward subduction ceased at 105–100 Ma due to incursion of the hot and buoyant plateau into the subduction zone (Davy, 1992), and the impingement of the plateau onto the Gondwana subduction margin gave rise to the Kermadec-Hikurangi oblique subduction system during the mid-Oligocene (~28 Ma; Walcott, 1984) and ultimately the present-day Taupo Volcanic Zone (hereafter the TVZ). Two periods of volcanism are recognized within the plateau: submarine flood basalts leading to the formation of the Plateau from 118 to 96 Ma; and dispersed seamount eruptions with a distinct geochemical signature (98–87 Ma; Hoernle et al., 2010). The former event produced the largest volume of material early on, and the latter event was contemporaneous with volcanism with overlapping Sr-Nd-Pb systematics on the South Island of New Zealand indicating that the plateau was near its present location with respect to the Chatham rise by c. 95 Ma (Hoernle et al., 2010; van der Meer et al., 2017).

The thickness of the Hikurangi Plateau crust has been modeled using gravity and seismic data to be between 10 and 25 km (Davy & Wood, 1994; Davy et al., 2008; Mochizuki et al., 2019). The large range in the estimated thickness is due partly to differences in the assumed density and lithosphere structure models invoked by these authors. Sitting on top of the Plateau basement is a variably thick unit of carbonate supported volcanic breccias interspersed with pelagic chalks, muds, and limestones (unit HKB of Davy et al., 2008), all of which is overlain by Mesozoic pelagic sediments, thought to be 150–400 m thick (MES 1 & Sequence Y of Wood & Davy, 1994). Over the pelagic sediments there exists a variably thick sequence of trench-fill and turbiditic terrigenous clastic sediments that thin to the north and east from >6 to <1 km thick (Bland et al., 2015; Collot et al., 1996; Lewis, 1980). These sediments are derived from the once subaerially exposed Chatham rise and from the fossil accretionary prism of the North Island, New Zealand.
Figure 1.
2.2. North Island

The North Island crust is composed of ancient accreted units as well as overlying arc volcanics. Andesites and rhyolites within the TVZ overlie accreted Late Triassic metagraywackes of the Torlesse and Waipapa terranes (Adams & Graham, 1996; Price et al., 2015). Major and trace element analysis of these terranes was performed by Price et al. (2015). The protolith to these terranes was devoid of carbonate but had significant organic C (hereafter $C_{org}$). The crust of the North Island is actively thinning due to backarc spreading, and TVZ crustal thicknesses range from <25 km in the North beneath Whakaari to ~40 km in the south beneath Ruapehu (Harrison & White, 2006). The buoyancy of the plateau as well as associated accretion has led to large-scale uplift with the leading edge currently underneath the TVZ (red dashed line in Figure 1; after Reyers et al., 2011). The thick crust of the Hikurangi Plateau gives the downgoing plate enhanced buoyancy, and the leading edge of the plateau corresponds to a down-dip steepening of the subducting plate (Davy, 1992; Reyers et al., 2011). The buoyancy of the plateau as well as associated accretion has led to large-scale uplift within the forearc, exposing previously accreted metamorphosed sedimentary units (including Torlesse and younger units; Davy, 1992; Kelsey et al., 1995; Walcott, 1984). Subduction becomes increasingly oblique to the south giving way to strike-slip movement along the Hope fault which connects the Hikurangi margin to the Alpine fault system of the South Island (Cole & Lewis, 1981).

Along the length of the Hikurangi margin, particularly to the south, there is development of a large (>150 km wide) accretionary prism, composed dominantly of trench-fill sediments (Barnes et al., 2018; Ghisetti et al., 2016). Additionally, there is substantial evidence for sediment underplating at greater depth beneath fore-arc highs (cf. Scherwath et al., 2010). While the nature of the supra-plateau sediments are variable in time and space, seismic studies have shown that the majority of the incoming sediment is off-scraped in the shallow forearc, with only the lowermost pelagic and volcaniclastic units persisting to depths relevant for consideration in models of arc volatile sources (Barnes et al., 2010; Eberhart-Phillips & Reyers, 1999; Ghisetti et al., 2016).

2.3. Hikurangi Subduction System

The Hikurangi plateau began subducting beneath the North Island, New Zealand at ~28 Ma (Walcott, 1984), with the leading edge currently underneath the TVZ (red dashed line in Figure 1; after Reyers et al., 2011). The thick crust of the Hikurangi Plateau gives the downgoing plate enhanced buoyancy, and the leading edge of the plateau corresponds to a down-dip steepening of the subducting plate (Davy, 1992; Reyers et al., 2011). The buoyancy of the plateau as well as associated accretion has led to large-scale uplift within the forearc, exposing previously accreted metamorphosed sedimentary units (including Torlesse and younger units; Davy, 1992; Kelsey et al., 1995; Walcott, 1984). Subduction becomes increasingly oblique to the south giving way to strike-slip movement along the Hope fault which connects the Hikurangi margin to the Alpine fault system of the South Island (Cole & Lewis, 1981).

2.4. Hikurangi Margin Volatile Flux Estimates

Research has been done to determine CO\textsubscript{2} production from individual volcanoes and hydrothermally active areas throughout the North Island, but less is known about full production over the entire margin (e.g., Aiuppa et al., 2019). Assuming a CO\textsubscript{2}/SO\textsubscript{2} ratio of 5 and applying an Ar concentration correction for N\textsubscript{2} (CO\textsubscript{2}/N\textsubscript{2,CO}=102.3), Hilton et al. (2002) calculated fluxes of 3.37 Tg/yr for CO\textsubscript{2} and 0.021 Tg/yr for N\textsubscript{2} for the Hikurangi arc. These values do not factor in diffuse emissions, which are known to be significant for the hydrothermal regions in the TVZ (Bloomberg et al., 2014; Mazot et al., 2014; Rissmann et al., 2012; Werner & Cardellini, 2006). While Seward and Kerrick (1996) indirectly calculated a CO\textsubscript{2} flux of 0.38 Tg/yr for hydrothermal production throughout the North Island, Werner and Cardellini (2006) first showed that the diffuse emissions from individual hydrothermal systems in the TVZ are significant (e.g. 0.23 Tg/yr for the Rotorua system alone), and the region as a whole produces over 0.78 Tg CO\textsubscript{2}/yr (Werner et al., 2019).

Figure 1. (a) Overview map of the North Island and Hikurangi Plateau showing active and fossil subduction zones. The Plateau margin exposed on the seafloor is delineated with solid red, and the dashed red line shows the inferred subducted extent of the plateau (after Reyers et al., 2011). Arrows indicate Pacific plate motions relative to the Australian plate (mm/yr; DeMets et al., 2010). (b) Map showing sample locations, basement rock types, and model range. Simplified subduction rate varies from 47 mm/yr in the north to 43 mm/yr at the southern boundary. An idealized arc-front is shown as a black dash-dot line. The location of IODP 375 site U1520 is labeled.
3. Methods

3.1. Model Setup

We calculate the temperature field of the Hikurangi subduction zone using a 3-D steady-state thermal model that incorporates the slab geometry of Williams et al. (2013). The model is developed by using the finite-element code PGCtherm3D as described in Wada et al. (2015) and consists of a nondeforming overriding crust, a viscous mantle wedge, and a subducting slab with a prescribed velocity. The code calculates the thermal field by iteratively solving the equations of conservation of mass and momentum for the mantle flow velocity in the viscous mantle wedge and the equation of conservation of energy in the entire domain:

\[
\nabla \cdot \mathbf{v} = 0 \\
\n\nabla \cdot \sigma' - \nabla P = 0 \\
\n\nabla \cdot (k\nabla T) - \frac{1}{\rho c_p} (\mathbf{v} \cdot \nabla T) + Q_H = 0
\]

where \( \mathbf{v} \) is the flow velocity, \( \sigma' \) is the deviatoric stress tensor, \( P \) is dynamic pressure generated by mantle flow, \( k \) is thermal conductivity, \( \rho \) is density, \( c_p \) is specific heat, and \( Q_H \) is volumetric heat production, which includes radiogenic heat production \( (Q_{RH}) \) and frictional heating \( (Q_{FH}) \):

\[
Q_{FH} = \tau u = \mu' \sigma_n u
\]

where \( \tau \) is shear stress, \( \mu' \) is the effective coefficient of friction, \( \sigma_n \) is the normal stress on the subduction fault, which is approximated by the weight of the overlying rock column, and \( u \) is the subduction rate. For the viscous mantle wedge, we use rheological parameter values that are reported for dislocation creep for wet olivine (Hirth & Kohlstedt, 2003).

The model domain extends from the trench to where the subducting slab surface reaches 220 km depth and from ~200 km north of North Island to the southern end of North Island. The northern and southern ends of the model domain are extended beyond the region of our interest to minimize the effects of those two model boundaries, and we present the results in the northern part of North Island only. In the model, the maximum depth of slab-mantle decoupling (MDD) is assumed to be 75 km, which is within the range of MDD reported for most subduction zones (Syracuse et al., 2010; Wada & Wang, 2009). We use the thermal conductivity of 2.5 W m\(^{-1}\) K\(^{-1}\) for the overriding crust and 3.1 W m\(^{-1}\) K\(^{-1}\) for the rest of the domain and radiogenic heat production rates of 1.3 μW m\(^{-3}\) for the overriding upper crust, 0.4 μW m\(^{-3}\) for the overriding lower crust, and 0.02 μW m\(^{-3}\) for the rest of the domain. The geotherm for the trench-side vertical boundary, representing the thermal state of the incoming oceanic plate, is calculated by using the GDH1 plate cooling model for a 130 Ma plate. The geotherm for the back-arc side vertical boundary is calculated based on a surface heat flow of 80 mW m\(^{-2}\), a mantle potential temperature of 1,350°C, a temperature gradient of 0.3°C km\(^{-1}\).

We prepared two thermal models, one with and one without frictional heating; for the former model frictional heating occurs from the trench to 15-km depth along the subduction interface. The reported value for the effective coefficient of friction is smaller than 0.05 for many subduction faults (e.g., Lamb, 2006; Wang & Suyehiro, 1999), indicating that they are generally weak, but for northern Hikurangi, it is as high as 0.13 (Gao & Wang, 2014). For the model that incorporates frictional heating a frictional coefficient \( (\mu') \) of 0.13 is used. All the figures presented in the main text are derived from the model which does not incorporate frictional heating; the effect of frictional heating is explored in the discussion section.

For the volatile flux calculation, pressure-temperature (P-T) conditions were extracted along an east-west vertical slice at 1-km horizontal spacing from North to South, creating 251 slices. For each slice, P-T conditions within the slab were extracted every 100-m along a vertical column and with an East-West horizontal spacing of 1-km from interface depths of 10–220 km (lower panel of Figure 2). The incoming modeled lithologies are subjected to the in-slab P-T conditions to determine mineralogy and devolatilization systematics. When fluid is produced in the model, it is immediately extracted without further fluid-rock interaction, thereby approximating channelized fluid flow. The total mass of fluid produced for each slice (i.e. per km of trench) is the sum of excess fluid produced at each P-T node, with each node representing a 100 × 1,000 × 1,000 m volume (0.1 km\(^3\)). The process is repeated for CO\(_2\) and includes determination of the X\(_{CO2}\) of the fluid at each node.
The model does not incorporate dewatering associated with compaction of pore space, nor does it factor in reaction kinetics. Fluid and solutes which are produced are unreactive and pass instantaneously to the plate interface. The model does not factor in updip fluid flow along the interface, and the figures produced from the model are a slab-centric view of fluid production before fluids are impacted by supraslab $P$-$T$ gradients.

### 3.2. Compositional Estimates

The four modeled lithologic sections are shown schematically in Figure 3, all of them are capped with 500m of pelagic sediment. The baseline model (“normal crust”) corresponds to subduction of a typical 12.5 km thick oceanic section consisting of (from the base up): 4 km of partially serpentinized peridotite, 6 km of gabbro, 1.4 km of altered mid ocean ridge basalt (hereafter MORB), and 600 m of heavily altered basalt. The
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Figure 3. Lithospheric compositions for the four modeled inputs, showing the concentrations of H$_2$O and CO$_2$. The full breakdown of major element compositions for each of the lithologies is shown in Table 1.

“doubled MORB” model consists of the same thickness’ of serpentinitized peridotite and gabbro but has 2.8 km of altered MORB and 1.2 km of heavily altered basalt for a total thickness of 14.5 km. The two additional models represent endmember approximations of the Hikurangi crustal structure as inferred from geophysical investigations (active seismic and gravity surveys; Davy & Wood, 1994; Davy et al., 2008; Mochizuki et al., 2019). The Davy structure is 16.5 km thick and includes 6 km of gabbro over lain by 10 km of heavily altered basalt. The Mochizuki model is 10.5 km thick and consists of 4 km of gabbro overlain by 6 km of heavily altered basalt.

For the two plateau model inputs, Davy and Mochizuki, we do not include a layer of serpentinitized peridotite at the base of the crust. These two model thicknesses were obtained from seismic and gravity surveys of the Hikurangi crust, and both assumed dry peridotite to constrain thicknesses (i.e. peridotite densities of 3,300 kg/m$^3$, as opposed to ~3,000 kg/m$^3$ for partially serpentinitized peridotite). The model based on the work of Mochizuki et al. (2019) proposes that the lithosphere beneath the plateau is plume related and did not originate at a spreading center. The choice of these authors leads to relatively thin plateau crust compared to the related Ontong Java Plateau, an observation consistent with the Hikurangi Plateau being a more distal portion of the pre-breakup Ontong Java large igneous province (Davy et al., 2008). Our plateau model inputs also include thick sections of altered basalt containing appreciable H$_2$O and CO$_2$, this is an attempt to account for the extensive seawater interactions which would occur during effusive subaqueous basalt eruptions.

Estimates for the composition of the Unit IV pelagic sequence are obtained from Barnes et al. (2019) and are based on their reported mineral abundances (~50% calcite, 30% clay, and 10% each quartz and feldspar; see Figure F5 in that article). Clay mineralogy is further separated based on powdered XRD analyses from Underwood (2020), and consists of ~52% smectite, 37% illite, and 11% chlorite + kaolinite. The mineral abundances and idealized formulas for these minerals were used to estimate composition of the Unit IV pelagic sequence (Figure 3, Table 1).

For the heavily altered plateau basalts we have used the composition of carbonate-bearing altered basalts from DSDP site 417 (Alt & Honnorez, 1984). For the less altered basalts, we use volatile-free “Normal” MORB (hereafter NMORB) from Gale et al. (2013) but modify the H$_2$O and CO$_2$ contents to 3 wt% and 0.5 wt%, respectively. For gabbro we rely on the composition from Dick et al. (2000) for site 735B from ODP leg 176 (also volatile-free) with the addition of 0.8 wt% H$_2$O and 500 ppm CO$_2$. Lastly, the partially serpentinitized peridotite has the composition determined for Losimag peridotite by Hart and Zindler (1986), with the addition of 2 wt.% H$_2$O and 500 ppm CO$_2$. Renormalized major element compositions of the model inputs are summarized in Table 1.

### Table 1

| Chemical Compositions (wt.%) Used for Perple_X Calculations |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | Unit IV         | DSDP 417        | N-MORB          | Gabbro          |
| SiO$_2$         | 30.08           | 46.48           | 49.95           | 50.88           |
| Al$_2$O$_3$     | 8.65            | 16.07           | 14.99           | 16.19           |
| FeO            | 0.67            | 8.37            | 9.72            | 7.34            |
| MgO            | 1.05            | 6.28            | 7.69            | 9.25            |
| CaO            | 29.93           | 12.94           | 11.24           | 12.57           |
| Na$_2$O        | 0.50            | 2.17            | 2.80            | 2.82            |
| K$_2$O         | 2.40            | 1.06            | 0.14            | 0.10            |
| H$_2$O         | 3.52            | 3.12            | 2.97            | 0.80            |
| CO$_2$         | 23.19           | 3.51            | 0.50            | 0.05            |

#### 3.3. Thermodynamic Calculations

Thermodynamic calculations were performed in Perple_X using the DEW thermodynamic file (v2017; Connolly, 2005; Sverjensky et al., 2014). With the exception of peridotite, all lithologies used solution models for phengite, feldspar, and carbonate from Holland and Powell (1998), and for chlorite, garnet, biotite and melt from White et al. (2014). The amphibole model is from Dale et al. (2005), omphacite from Green et al. (2007), and epidote is from Holland and Powell (2011). For peridotite, the orthopyroxene model of White et al. (2014) was added as well as olivine and spinel from Holland and Powell (2011). The melt model for peridotite is that of Jennings and Holland (2015). For all compositions the fluid is modeled by a H$_2$O-CO$_2$-CH$_2$O$_2$ solution with a generic hybrid fluid equation of state with lagged forward-calculation of aqueous electrolytes (Connelly & Galvez, 2018; Galvez et al., 2015). The calculation for the Unit IV
pelagic sequence considers both carbonate and C$_{org}$ species (the latter as partially graphitized carbonaceous material and diamond). The underlying units are modeled as containing only carbonate.

3.4. Chemical and Isotope Analyses

3.4.1. Sedimentary and Metasedimentary Rocks

Isotope analyses of carbonate-bearing samples from IODP 375 were performed at Lehigh University. Wedge and quarter round samples obtained from IODP 375 hole U1520 were dried at 50°C before being hand powdered in a mortar and pestle following crushing. 10–100 mg of dried material was reacted with 100% phosphoric acid (H$_3$PO$_4$) for 8–12 h at 27°C to produce CO$_2$ (following the procedure of McCrea, 1950). The CO$_2$ was cryogenically purified under vacuum before analysis in dual-inlet mode on a Finnigan MAT 252 mass spectrometer. Duplicates and standard analysis were performed to ensure an accuracy of ~0.2‰ for both δ$^{13}$C and δ$^{18}$O.

A 1–2 g subset of the same powders analyzed for carbonate isotopes, as well as ~1 g of powdered samples of Torlesse and Waipapa metasedimentary rocks, were reacted three times each with dilute HCl and deionized water to remove carbonate for analysis of whole-rock δ$^{15}$N and δ$^{13}$C$_{org}$. Nitrogen concentrations and isotope analyses for the metasedimentary rocks were performed at Lehigh University following the methods of Bebout et al. (2007). 10–100 mg of acid-treated sample was loaded into a 6 mm (outside diameter) borosilicate glass tube together with 1g of Cu-CO$_x$ and evacuated under vacuum for 12 h. The tubes were then sealed with a torch and heated to 1,050°C for 3 h before slowly cooling to room temperature. The sealed tubes were placed in a tube cracker attached to an extraction manifold and placed under vacuum. Analyses were carried out on a MAT 252 via a continuous He-flow GC Gas Bench II. Analysis of house standards produced a δ$^{15}$N precision of ±0.2‰. Comparison of the mass-to-signal ratio of standards and unknowns allowed for determination of N abundances with uncertainties <5%.

Reduced C analyses for all samples and δ$^{15}$N analysis of U1520 drilled samples were performed at the University of New Mexico by CF-EA-IRMS on a Thermo Delta Plus. δ$^{13}$C, δ$^{18}$O, and δ$^{15}$N analyses are referenced to PBD, VSMOW, and AIR respectively.

3.4.2. Gas Samples

3.4.2.1. Gas Chemistry

Chemical analysis of gas samples was performed at the GNS National Isotope Centre in Lower Hutt, New Zealand. Complete molecular analysis of cold gas emissions (T < 100°C) was performed on samples taken into teflon-stoppered evacuated glass flasks, and analyzed by gas chromatography, whereas high temperature emissions (T > 100 °C) were collected into the same type of evacuated flask containing 40 mls of 6N KOH. Headspace gases of these samples were likewise analyzed by gas chromatography, and acidic gases that were scrubbed into the condensate were analyzed by a combination of titrametry (CO$_2$, SO$_2$ and H$_2$S) according to methods described in Giggenbach and Goguel (1989), and ion chromatography (HCl, HBr and HF). Noting the reactivity between CO and KOH, a separate flask without KOH was also taken for headspace analysis of CO and δ$^{13}$C analysis of CO$_2$. All samples taken for noble gas isotope analysis were taken into He-resistant glass stoppered flasks.

3.4.2.2. Stable Isotope Analysis of Gases (C and N)

Stable isotopes analyses of gas samples were performed at the GNS National Isotope Centre in Lower Hutt, New Zealand. Headspace CO$_2$ in the gas samples was chromatographically separated and dried via a nafion membrane prior to analysis for δ$^{13}$C$_{CO2}$ on a Geo 20–20 continuous flow IRMS. For δ$^{15}$N analysis 2-step chromatographic separation and cryogenic trapping was performed on the gas before admission of N$_2$ into the IRMS. Cryogenically trapped methane from this process was subsequently combusted and admitted to the IRMS for δ$^{13}$C$_{CH4}$ analysis. Carbon isotope analysis was done following the methods of Lyon and Hulston (1984), with standard deviations of ±0.1‰ and ±1‰ for CO$_2$ and CH$_4$, respectively.
3.4.2.3. Noble Gas Analyses

Noble gas analyses were determined at the University of Tokyo on a VG-5400 static mass spectrometer, with a modified purification and inlet system. Isotopic ratios and elemental abundances of He, Ne, and Ar were determined after purification of <~1 ml of sample gas. The purification procedure allowed for blank levels for He, Ne, and Ar of lower than $1 \times 10^{-6}$, $1 \times 10^{-8}$, $1 \times 10^{-8}$ cm$^3$ STP, respectively. Air standards were measured frequently during analysis to determine mass discrimination factors and sensitivities of the mass spectrometers for all noble gases except helium isotope ratio. The ratio of primordial $^4$He to radiogenic $^4$He is reported relative to the ratio in air (R/Ra) and was calibrated by measurements of inter-laboratory He standard HESJ, with a recommended $^3$He/$^4$He value of 20.63 ± 0.10 Ra (Matsuda et al., 2002). Errors on noble gas isotope ratios are 1σ, including statistical error during sample analysis, error in the discrimination factor, and error on the recommended $^3$He/$^4$He ratio of HESJ in the case of the helium isotope ratio. Uncertainties in the concentrations of noble gases are estimated to be about 5% for helium and argon, and 10% for neon based on the reproducibility of standard gas measurements. See Sumino et al. (2001) for further details on purification process and mass spectrometer operation.

4. Results

4.1. Perple_X Results

Bulk compositions and mineral-bound H$_2$O and CO$_2$ contents were derived from the Perple_X calculation outputs. In describing the changes in H$_2$O and CO$_2$ contents in each lithologic unit in this section, we use the P-T paths at the interface (for Unit IV), the base of the altered lithosphere section (for serpentinitized peridotite), and the center of each lithologic unit (for variably altered basalts) at northern and southern model boundaries, assuming the normal crust model shown in Figure 3. The Unit IV pelagic sequence undergoes an early (shallow) stage of fluid loss due to clay-mineral dehydration and progressive crystallization of white micas at about 0.5 GPa; a result similar to P-T conditions of dehydration determined for the Franciscan Complex by field studies (Sadofsky & Bebout, 2003; Figures 4a and S1). Further dehydration occurs at deep forearc to subarc pressures of 2.5–3.5 GPa and is more extensive to the south (magenta line in Figure 4). Following dehydration of Unit IV over this depth range, the remaining H$_2$O is retained over a pressure range extending beyond the maximum model pressures (>7.5 GPa). Unit 417 altered basalts do not undergo appreciable dehydration until deepest forearc P-T conditions of ~2.5 GPa and ~500°C, where ~60% of the mineral-bound H$_2$O is released over a narrow P-T range, associated with lawsonite breakdown (Figures 4b and S2). NMORB systematics are similar to those observed for 417 altered basalt, but dehydration is more extensive with near to complete fluid loss occurring, particularly to the south, by 3.5 GPa (Figures 4c and S3). Serpentinitized peridotite retains fluid until pressures of 5–5.5 GPa where there is complete dehydration in the backarc associated with antigorite breakdown (Figures 4d and S4). Gabbro, initially containing only 0.8 wt% H$_2$O, remains nearly unaffected during subduction, losing <5% of the initial H$_2$O (corresponding to <0.04 wt.% of the initial whole rock; Figure S5). At no point do any of the modeled P-T paths intersect the melt regime (Figure 4).

The systematics of CO$_2$ liberation are shown in Figures 4e-4h. For the Unit IV pelagic sequence, the onset of CO$_2$ loss occurs at 2.5–3 GPa (~75–95 km depth) and corresponds to ~20% loss (Figure 4e). The unit 417 altered basalt undergoes ~30% CO$_2$ loss over a range of pressures from 2.5 to 4.5 GPa (Figure 4f); this is in contrast with the removal of CO$_2$ from NMORB: ~50% loss in the North and near complete loss of CO$_2$ in the South of the modeled region (Figure 4g). Serpentinite and gabbro contain 0.05 wt% CO$_2$ initially, the serpentinite undergoes ~80% C loss gradually from 3 GPa to maximum model pressures whereas the gabbro undergoes <5% C loss, the latter similar to the case for H$_2$O (Figure S5).

4.2. Volatile Production Model Results

All four modeled lithologies indicate a shallow forearc pulse of sediment-derived H$_2$O-rich (±CH$_4$?) fluid occurring at depths to slab of ~18 km depth (0.58 GPa), following which there is a hiatus in fluid production until ~75 km depth (Figure 5). The normal crust model (Figure 5a) indicates two distinct pulses of fluid, one centered at deep forearc to subarc depths (~80 km) associated with Unit 417 and NMORB fluids, and a second concentrated pulse at ~150 km depth associated with antigorite breakdown within serpentinitized
peridotite. The doubled MORB model shows a broader extent of subarc fluid production that encompasses the area beneath all of the sample sites, this model also has a larger magnitude of fluid production at the 150 km depth due to the overlapping contributions from serpentinized peridotite and from altered basalts (Figure 5b). In both the Mochizuki and the Davy crustal models, the production of fluid from the thick stack of altered basalts is continuous from deepest forearc depths to the maximum depth of the model, with total production being greatest for the Davy model (Figures 5c and 5d). All of the models indicate increasing subarc fluid production to the south. Total fluid production estimates are shown in Table 2.

The Perple_X calculations do not constrain CO₂ liberation associated with the shallow forearc fluid pulse, and these are modeled as pure H₂O. For the case of the normal-crust and doubled-MORB models significant CO₂ production is associated with the altered basalt devolatilization, with the contributions from serpentinized peridotite being so minor as to not be apparent in Figure 5 (i.e. <0.5 kg/m² CO₂ production). Taking into account the Perple_X calculations it is apparent that some portion of the subarc CO₂ production is derived from the Unit IV pelagic sequence, but the deeper CO₂ release (>~4 GPa; ~125 km) is dominantly derived from altered basalt (Figures 4 and 5). It is interesting to note that subarc CO₂ production is greatest for the doubled MORB model, though there is more extensive CO₂ release to the backarc in both the Mochizuki and Davy models. Total CO₂ production estimates are 3.61, 4.44, 4.64, and 4.70 Tg/yr for the normal-crust, Mochizuki, Davy, and doubled-MORB models, respectively (Table 2).

4.3. Carbonate and Whole-Rock Isotope Analyses

Carbonate isotope analyses were performed on trench-fill siliciclastic sediments (n = 10), Unit IV pelagic sequence (n = 13), and Hikurangi basaltic breccias (HKB of Davy et al., 2008; n = 2). The results are summarized in Figure 6 together with C abundance data obtained during IODP 375 (downloaded from: web.iodp.tamu.edu/LORE/; see also Barnes et al., 2019; Table 3). For the trench-fill sediments, the average carbonate abundance among analyzed samples is 6.2 wt.%, with average δ¹³C = −0.3‰ and δ¹⁸O = +30.6‰ (Figures 6 and 7a). The Unit IV pelagic sequence has an average carbonate abundance of 58.8 wt.% and average δ¹³C and δ¹⁸O of +31.4‰ and +1.6‰, respectively. The two basaltic breccia samples have carbonate abundances of 5.3 and 7.3 wt.%, δ¹³C values of +31.1‰ and +32.9‰, and δ¹⁸O values of +1.8‰ and +2.4‰. These values are similar to carbonate isotope analyses from altered basalts of the Ontong Java Plateau collected on ODP Leg 192 (Figure 7a; +30 to +32‰ δ¹³C and +2.5 to +4.0‰ δ¹⁸O; Banerjee et al., 2004). The analyzed samples of Torlesse and Waipapa metasediments were devoid of carbonate, although in some areas of New Zealand correlative units contain minor carbonate veining (Pitcairn et al., 2005).

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**Table 2**

| Calculation of C Flux Over 250 km of Hikurangi Arc |
|-----------------------------------------------|
| Entire model range | Addition of non-slab C components |
|                  | MORB | Doubled | Davy | Mochizuki | MORB | Doubled | Davy | Mochizuki |
| CO₂ in (Tg/yr)⁴   | 4.54 | 5.50    | 15.40| 10.60     | 5.39 | 7.01    | 6.93 | 6.63     |
| CO₂ out (Tg/yr)⁵  | 3.61 | 4.70    | 4.64 | 4.44      | 5.00 | 5.10    | 4.70 | 4.50     |
| N₂ in (Tg/yr)     | 0.0192 | 0.0253  | 0.0896| 0.0571    | 0.0022 | 0.0042  | 0.0057| 0.0036 |
| N₂ out (Tg/yr)    | 0.0016 | 0.0031  | 0.0043| 0.0026    | 0.0022 | 0.0042  | 0.0057| 0.0036 |
| Net CO₂ recycling efficiency | 0.79 | 0.85    | 0.30 | 0.59      | 0.08 | 0.12    | 0.05 | 0.05     |
| Subarc recycling efficiency | 3.49 | 4.28    | 3.85 | 3.85      | 0.77 | 0.78    | 0.25 | 0.36     |
| % of global C flux | 1.2% | 1.6%    | 1.6% | 1.8%      | 0.3% | 0.6%    | 0.6% | 0.6%     |

¹1 Tg = 10¹² g; initial densities: 2,606 kg/m³ for UnitIV; 3,041 for 417; 3,142.5 for NMORB; 3,062 for Gabbro; 3,224.9 for Peridotite. ²assuming over depths from 70 to 120 km. ³assuming a total global flux of 300 Tg CO₂/yr; after Werner et al. (2019). ⁴assumed total global fluxes of 0.018 and 0.552 Tg/yr from Sano et al. (2001) and Hilton et al. (2002), respectively.
| Sample   | IODP sample     | Unit       | Carbonate wt.% | C\text{org} wt.% | N ppm | \(\delta^{18}O\) \text{carb} | \(\delta^{13}C\) \text{carb} | \(\delta^{13}C\) \text{org} | \(\delta^{15}N\) \text{L/}[L + O] | L/ [L + O] |
|----------|-----------------|------------|----------------|------------------|-------|----------------------------|----------------------------|----------------------------|-----------------------------|-------------|
| GSE01    | WDGE9536221     | Trench-fill| 5.95           | 0.37             | 267   | +30.2                      | −0.7                       | −24.9                      | +3.9                        | 0.66        |
| GSE02    | WDGE9543241     | Trench-fill| 1.88           | 0.24             | 170   | +28.5                      | −1.0                       | −25.5                      | +2.7                        | 0.49        |
| GSE03    | WDGE9545081     | Trench-fill| 4.24           | 0.39             | 260   | +29.7                      | −0.1                       | −25.6                      | +3.3                        | 0.57        |
| GSE04    | WDGE9547341     | Trench-fill| 5.77           | 0.61             | 498   | +31.2                      | −0.4                       | −23.9                      | +5.0                        | 0.53        |
| GSE05    | WDGE9551911     | Trench-fill| 11.84          | 0.60             | 629   | +31.7                      | −0.4                       | −23.8                      | +5.4                        | 0.70        |
| GSE06    | WDGE9570511     | Trench-fill| 8.91           | 0.56             | 480   | +32.3                      | +0.2                       | −24.7                      | +4.9                        | 0.66        |
| GSE07    | CYL9575611      | Trench-fill| 8.30           | 0.43             | 481   | +31.6                      | +0.1                       | −24.4                      | +5.1                        | 0.70        |
| GSE08    | WDGE9577741     | Trench-fill| 1.34           | 0.20             | 160   | +28.7                      | −0.8                       | −25.6                      | +2.7                        | 0.44        |
| GSE09    | WDGE9580381     | Trench-fill| 7.66           | 0.45             | 398   | +30.9                      | +0.1                       | −24.8                      | +4.6                        | 0.67        |
| GSE10    | WDGE9582031     | Trench-fill| 4.29           | 0.48             | 392   | +31.6                      | +0.0                       | −24.6                      | +4.8                        | 0.52        |
|          |                 |            | 6.02           | 0.43             | 373   | +30.6                      | −0.3                       | −24.8                      | +4.3                        | 0.59        |
| GSE11    | WDGE9585431     | Unit IV    | 63.26          | 0.22             | 244   | +32.0                      | +0.6                       | −24.9                      | +5.9                        | 0.97        |
| GSE12    | WDGE9587891     | Unit IV    | 72.57          | 0.19             | 109   | +31.9                      | +1.5                       | −27.5                      | +4.3                        | 0.98        |
| GSE13    | WDGE9589291     | Unit IV    | 55.03          | 0.16             | 149   | +32.1                      | +1.1                       | −25.6                      | +5.0                        | 0.98        |
| GSE14    | QRND9445611     | Unit IV    | 11.68          | 0.14             | 155   | +31.3                      | +0.2                       | −27.2                      | +4.1                        | 0.97        |
| GSE15    | QRND9448431     | Unit IV    | 50.85          | 0.14             | 164   | +31.6                      | +1.0                       | −25.9                      | +4.3                        | 0.98        |
| GSE16    | WDGE9450511     | Unit IV    | 32.25          | 0.23             | 118   | +31.6                      | +1.1                       | −27.8                      | +3.3                        | 0.94        |
| GSE17    | QRND9453061     | Unit IV    | 47.36          | 0.17             | 155   | +31.8                      | +1.6                       | −27.2                      | +4.1                        | 0.97        |
| GSE18    | QRND9455161     | Unit IV    | 41.88          | 0.13             | 185   | +31.3                      | +2.0                       | −26.7                      | +3.6                        | 0.98        |
| GSE19    | QRND9460391     | Unit IV    | 67.56          | 0.22             | 179   | +31.6                      | +1.7                       | −26.8                      | +5.0                        | 0.97        |
| GSE20    | QRND9462951     | Unit IV    | 85.66          | 0.17             | 126   | +30.8                      | +1.7                       | −27.5                      | +4.2                        | 0.98        |
| GSE28-1  | QRND9467201     | Unit IV    | 96.05          | 0.25             | 151   | +30.8                      | +2.3                       | −26.6                      | +5.4                        | 0.98        |
| GSE28-2  | QRND9468231     | Unit IV    | 97.39          | 0.25             | 152   | +30.7                      | +2.2                       | −26.6                      | +5.4                        | 0.98        |
|          |                 |            | 60.13          | 0.19             | 157   | +31.5                      | +1.4                       | −26.7                      | +4.6                        | 0.97        |
| GSE21    | QRND9470521     | HKB        | 7.29           |                  |      | +31.1                      | +1.8                       |                          |                            | 1.00        |
| GSE22    | QRND9472211     | HKB        | 5.33           |                  |      | +32.9                      | +2.4                       |                          |                            | 1.00        |

Table 3

Isotope Analyses of Sediments, Altered Basalts, and Metasedimentary Rocks

Average values for GSE1-20 are listed in Table 3, which presents the isotope analyses for various samples

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Table 3

Continued

| Sample | IODP sample | Unit | C_{org} (wt.%) | N (wt.%) | δ^{13}C_{carb}‰ (VPDB) | δ^{15}N‰ (VSMOW) | L/ [L + O] ppm |
|--------|-------------|------|----------------|---------|------------------------|--------------------|----------------|
| P60553 | Waipapa     | 0.08 | 22.4           | 0.14    | 239                    | −22.4             | 3.6            |
| Average|             | 0.14 | 239            | 0.14    | 239                    | −24.9             | +3.6           |

*Samples have undergone near surface fractionation. Not included in average.*

Figure 4. (a–d) Pressure-Temperature-H_{2}O systematics of four lithologies input into the model, as well as the P-T paths within each lithologic unit at northern and southern model boundaries (A-A’ and C-C’ in Figure 2; green and magenta curves, respectively), assuming the normal-crust model shown in Figure 3. Unit IV pelagic sequence undergoes significant forearc dehydration (panel a), whereas the variably altered basalts undergo significant subarc dehydration caused by lawsonite breakdown (b and c). Dehydration in all cases is more complete to the south. Serpentinized peridotite undergoes complete dehydration due to antigorite breakdown at ~5.5 GPa (d). (e–h) Pressure-temperature-CO_{2} systematics of the same four lithologies. Unit IV and 417 altered basalts retain significant CO_{2} (e and f), whereas there is near complete loss of CO_{2} from NMORB and serpentinized peridotite (g and h). Loss of CO_{2} is greater to the south.
Whole-rock organic carbon ($C_{org}$) abundances for trench-fill sediments range from 0.2 to 0.62 wt.%, the latter value significantly higher than $C_{org}$ abundance in the Unit IV pelagic sequence (0.14–0.26 wt.%). Torlesse and Waipapa metasediments have variable $C_{org}$ contents, ranging from 0.04 to 0.46 wt.% (Figure 7b). Averages for $\delta^{13}C_{org}$ for all lithologies broadly overlap with values of −24.8, −26.7, −25.0, and −25.7‰ for trench-fill, Unit IV, Torlesse, and Waipapa, respectively (Figures 6 and 7b). In the following calculations and discussions, C in carbonate is referred to as L, and $C_{org}$ is referred to as O. The average ratio of carbonate-bound C (L) to total C (L + O) is 0.59 for trench-fill sediments and 0.97 for Unit IV; the samples from this study match well with shipboard analyses from IODP 375 (black points in Figure 6; Table 3).

Nitrogen abundance ranges from 60 to 629 ppm, again with trench-fill sediments having the highest concentration, averaging 373 ppm, followed by the Torlesse, the Waipapa, and Unit IV, with averages of 243, 233, and 158 ppm, respectively (Figure 7c). With the exception of three samples from the Torlesse terrane, all units overlap in $\delta^{15}N$ within a range from +2 to +7‰, and generally fall within the range of New Zealand metasedimentary rocks from both the North and South Islands (Pitcairn et al., 2005; Figures 6 and 7c). The Torlesse samples with $\delta^{15}N < 0$‰ are those that Price et al. (2015) found to have secondary stilpnomelane...
Figure 5. Map view distributions of H$_2$O and CO$_2$ production for the four different lithology models for the subducting material. The normal-crust and doubled-MORB models indicate large fluid pulses associated with antigorite dehydration in the backarc (a and b). The thicker sequence of altered basalt in the doubled-MORB model leads to more continuous fluid and CO$_2$ production from subarc to backarc depths (b, both panels). The Mochizuki and Davy models show continuous production of fluid and CO$_2$ initiating at subarc depths and extending to the western boundary of the model (c and d). All models show a forearc fluid pulse and increasing subarc fluid and CO$_2$ production to the south.
and/or zeolites, alteration minerals that may contribute to the negative values. Whole-rock isotope and C-N abundances are summarized in Table 3.

4.4. Gas Chemistry

We obtained gas composition and stable isotope analysis of 26 individual gas samples as well as noble gas isotope data for 29 samples (summarized in Table 4), extending from forearc to backarc. Forearc samples are CH₄-rich and display elevated radiogenic He and Ar anomalies (Figures 8 and 9; Table 4), with ³He/⁴He as low as 0.2 (R/Ra) and ⁴⁰Ar/³⁶Ar as high as 406. These samples contained concentrations of CO₂ too small for accurate isotope ratios to be obtained. Forearc samples are readily distinguished based on their high He and CH₄ concentrations (Figure 8). Notably, some of the forearc samples have ³He/⁴He ratios greater than that of atmosphere (R/Ra > 1) indicating at least some mantle He contribution (Table 4).

The hydrothermal and fumarolic samples presented here form a mixing array extending from “arc-gas” values (N₂/Ar ≈ 1,000–10,000; Giggenbach, 1992a) to atmospheric or air saturated water values (N₂/Ar of 86.7 and ~38, respectively; Figure 8). Samples with backarc affinity similarly fall along a mixing trend between N₂/Ar ratios of crustal rocks and air saturated water. The arc/backarc samples all have considerable input from primordial (mantle) He with ³He/⁴He extending from 2.17 up to 7.36 (R/Ra > 1) indicating at least some mantle He contribution (Table 4).

Ratios of major gas components to primordial noble gas isotopes vary over a few orders of magnitude. CO₂/³He ranges from 10⁹ to 10¹¹ with the gases showing a range in ¹³C of CO₂ (~−1.4 and ~+8.3‰) that is rather restricted when compared to the range of values for endmembers (Figures 9a and 9b). N₂/³⁶Ar ranges from 10⁴ to 10⁷ with a larger spread in ¹⁵N, relative to potential endmember ratios, from +4 to −1‰ (excluding the analyses of the forearc gases which extend to −5‰; Figure 9c).
Figure 7.
5. Discussion

5.1. Sources of Volatiles Within the TVZ

5.1.1. CO₂ Contributions as a Function of Bulk Composition

Subarc to backarc CO₂ production is a function of the downgoing lithologic structure as well as the in-slab P-T conditions, and therefore differs markedly between the four lithologic inputs (Figure 10). This difference is principally due to the thickness of the various units but is compounded by how the variably thick units interact with the temperature profile within the slab, i.e. altered basalt at a depth of 1 km from the interface will undergo devolatilization differently than the same unit at a depth of 5 km. These differences are represented graphically in Figure 10 for cross sections A-A’ & C-C’ from Figure 2 across all four model inputs.

For the case of normal crust (i.e. thin, 8.5 km thick crust; Figure 10a), the initial C output is derived entirely from the Unit IV pelagic sequence before simultaneous contributions from Unit 417 and NMORB begin at ~75 km depth. At interface depths of 100 km, Unit IV ceases to be a C source and all production occurs within 417 and NMORB, with minor contributions from gabbro and serpentinite. With greater depth the total CO₂ production decreases dramatically (<2 kg/m²). It should be noted that the depths over which the dominant CO₂ production occurs within the gabbro or serpentinite correspond to extremely minor cumulative productions (<1 kg/m²; see black line in Figure 10a). In the cross section at the southern model boundary (C-C’, Figure 10a bottom panel), corresponding to a warmer P-T path, the post 100 km production from gabbro and serpentinite is slightly greater.

For the case of doubled-MORB, the northern cross section (Figure 10b, upper panel) undergoes the same cumulative C-loss from Unit IV but differs markedly in the pattern of loss from the altered basalt units. The thicker Unit 417 altered basalt in this model insulates underlying NMORB from heating by the mantle wedge and creates a lag between initiation of Unit 417 and NMORB CO₂ production. The overly thick NMORB in turn insulates the deeper gabbro and serpentinite, and these units do not contribute any CO₂ to the cumulative production in the northern part of the model. In the southern section of the doubled-MORB model, at depths greater than 140 km there are minor contributions from serpentinite and gabbro to the cumulative CO₂ production (Figure 10b, lower panel). It is interesting to note that a small change in bulk composition between the altered basalts has a large influence on the extent of volatile loss, with the more altered Unit 417 basalt retaining more H₂O and CO₂ over the entire range, and contributing less to the liberated volatile budget (Figures 4b, 4c, 4f, 4g and 10b; see also Figures S2 and S3).

Both the Davy and Mochizuki models indicate C production only within Unit IV and the underlying 417 altered basalt, with the thickness of the latter unit sufficient to completely insulate the deeper gabbro (Figures 10c and 10d). Furthermore, these two models show the exact same patterns of C production to depths of 135 km in the north, and to depths of 125 km in the south (Figures 10c and 10d upper and lower panels, respectively). The Davy model is composed of a greater thickness of 417 altered basalt, but all models contain the same 500 m thickness of Unit IV pelagic material. At interface depths greater than ~125 km the basal section of Unit 417 altered basalts in the Davy model begins to undergo devolatilization.

5.1.2. Chemical Insights Into Sources of Volcanic Gas

Potential sources of CO₂ emanating from volcanoes and hydrothermal areas are derived from the mantle (either subducting lithospheric or wedge peridotite), subducted material (sediments and altered oceanic crust), and from previously accreted material (e.g. from material introduced during subduction erosion or during assimilation by magma). The Earth’s mantle has a well-constrained δ¹³C value between −5 and −8‰ (median = −6.5‰; cf. Javoy et al., 1986; Sano & Marty, 1995) and a CO₂/³He ratio of ~2 × 10⁸ (Marty

![Figure 7](image-url) Carbonate and whole rock isotope analyses for sediments and accreted metasedimentary rocks. (a) δ¹⁸O vs. δ¹³C for carbonate from IOD 375, hole U1520 showing variation among and between basalt-hosted, pelagic, and trench-fill carbonates. The red rectangle outlines the range of isotope values for basalt-hosted carbonate from the Ontong-Java Plateau (after Banerjee et al., 2004). (b) δ¹³Corg vs. organic C wt.% for all studied samples illustrating broad overlap among isotope values and a large range of C concentrations. (c) δ¹⁵N vs. N concentration for all analyzed samples. With the exception of three samples with negative δ¹⁵N all analyses occupy a narrow range. The blue field is for analyses of New Zealand (NZ) schists made by Pitcairn et al. (2005).
Table 4
Summary of Gas Analyses

| Sample                | CO₂  | CH₄  | N₂   | He    | Ar    |
|-----------------------|------|------|------|-------|-------|
|                       | ppm  | ppm  | ppm  | ppm   | ppm   |
| 2558-Waimata°         | 5,659 | 958,838 | 23,246 | 118.55 | 231.46 |
| 2559-Mangapakeha°     | 4,185 | 947,398 | 28,489 | 239.26 | 366.73 |
| 2574-Awakeri°         | 968   | 247,386 | 739,065 | 218.18 | 9,300.02 |
| 2575-Te Puia°         | 40,699 | 809,132 | 120,445 | 472.71 | 1,855.28 |
| 2576-Mahia A°         | 16,299 | 922,976 | 55,709  | 254.32 | 695.33  |
| 2577-Mahia B°         | 13,654 | 928,474 | 53,617  | 228.24 | 724.76  |
| Otopotehetehe°        | –     | –     | –     | –     | –      |
| Soda springs°         | –     | –     | –     | –     | –      |
| 2557-Tiketere fumarole| 20,595| 1,035 | 179   | 0.14  | 0.99   |
| 2536-Poly Spa         | 10,138| 6.3   | 15    | 0.0038| 0.26   |
| 2535-Rotoma soda spring| 943,700| 1,569 | 52,650 | 10.44 | 1,027.30 |
| White Island f13      | –     | –     | –     | –     | –      |
| 2556-White Island F0  | 151,077| 15    | 1,223  | 0.61  | 2.72   |
| 2551-TNP-F6           | 13,348| 237   | 170   | 0.03  | 0.32   |
| 2552-TNP-TM-F3a       | 11,030| 106   | 25,595| 0.34  | 279.64 |
| 2554-TNP-RC           | 42,838| 1,060 | 350   | 0.10  | 0.58   |
| 2555-TNP-UEL          | 40,990| 944   | 316   | 0.09  | 0.62   |
| TNP-OT°               | –     | –     | –     | –     | –      |
| 2500-Rotokawa A       | 4,719 | 142   | 75    | 0.015 | 0.46   |
| 2442-Rotokawa B       | 5,941 | 137   | 141   | 0.057 | 1.01   |
| 2394-Rotokawa fumarole| 12,284| 540   | 232   | 0.036 | 1.12   |
| 2454-Kawerau          | 49,922| 2,735 | 1,209 | 0.26  | 6.67   |
| 2484-WK-A             | 513   | 2.4   | 19    | 0.022 | 0.32   |
| 2468-Champagne Pool   | CP    | 599,101| 84,005| 313,198| 33.28 | 4,240.54 |
| 2486-Broadlands A     | 19,360| 841   | 421   | 0.065 | 1.00   |
| 2507-Broadlands B     | 10,053| 245   | 148   | 0.025 | 0.58   |
| 2499-NMA              | 6,111 | 271   | 141   | 0.085 | 1.31   |
| 2455-PKA              | 8,928 | 314   | 143   | 0.032 | 0.90   |
| PKA-duplicate         | 9,155 | 298   | 134   | 0.031 | 0.85   |
| 2497-Tokaanus A       | 1,762 | 0.84  | 137   | 0.0022| 1.58   |
| 2397-Tikitere A       | TKB   | 99,615| 5,125 | 768   | 0.64  | 6.98   |

| Sample          | O₂   | H₂O  | δ¹³C⁻CO₂ | δ¹³C⁻methane | δ¹⁵N  | ³He/⁴He |
|-----------------|------|------|----------|--------------|-------|---------|
|                 | ppm  | ppm  | % (VPDB) | % (VPDB)     | % (AIR) | (R/Ra)  |
| 2558-Waimata°   | 1,983| –    | –        | –45.8        | –3.5   | 1.62    |
| 2559-Mangapakeha°| 2,919| –    | –        | –35.6        | –5.1   | 0.86    |
| 2574-Awakeri°   | 2,414| –    | –        | –39.1        | –0.1   | 0.20    |
| 2575-Te Puia°   | 6,317| –    | –        | –41.1        | –3.3   | 1.67    |
| 2576-Mahia A°   | 3,371| –    | –        | –60.8        | –3.2   | 1.42    |
| 2577-Mahia B°   | 2,037| –    | –        | –60.7        | –3.2   | –       |
| Otopotehetehe°  | –    | –    | –        | –            | –      | 1.12    |
| Soda springs°   | –    | –    | –        | –            | –      | 0.20    |
Table 4

% Continued

| Sample                        | O₂          | H₂O         | δ¹³C CO₂   | δ¹³C methane | δ¹⁵N | ³He/⁴He (R/Ra) |
|-------------------------------|-------------|-------------|------------|--------------|------|----------------|
|                               | ppm         | ppm         | % (VPDB)   | % (VPDB)     | % (AIR) |                |
| 2557-Tiketere fumarole        | –           | 9.77 × 10⁵  | –6.5       | –27.6        | –0.4 | 6.02           |
| 2536-Poly Spa                 | 0.03        | 9.87 × 10⁵  | –          | –32.2        | –     | 7.05           |
| 2535-Rotoma soda spring       | 701.80      | –           | –3.8       | 11.7         | +0.3 | 6.38           |
| White Island f13              | –           | –           | –          | –            | –     | 5.93           |
| 2556-White Island F0          | 0.15        | 8.36 × 10⁵  | –6.5       | –25.9        | +3.2 | 6.39           |
| 2551-TNP-F6                   | 1.032       | 9.85 × 10⁵  | –7.3       | –24.7        | +1.4 | 5.79           |
| 2552-TNP-TM-F3a               | –           | 9.61 × 10⁵  | –7.4       | –25.5        | –0.3 | 2.53           |
| 2554-TNP-RC                   | 0.04        | 9.55 × 10⁵  | –6.6       | –24.0        | +1.0 | 5.07           |
| 2555-TNP-UEL                  | –           | 9.56 × 10⁵  | –6.7       | –23.3        | +0.9 | 5.30           |
| TNP-OT                        | –           | –           | –          | –            | –     | 5.70           |
| 2500-Rotokawa A               | –           | 9.95 × 10⁵  | –6.9       | –23.9        | +1.3 | 6.00           |
| 2442-Rotokawa B               | 0.24        | 9.93 × 10⁵  | –7.4       | –           | +2.3 | 6.32           |
| 2394-Rotokawa fumarole        | 0.32        | 9.87 × 10⁵  | –8.3       | –26.1        | +0.5 | 5.08           |
| 2454-Kawerau                  | 0.25        | 9.45 × 10⁵  | –6.3       | –29.1        | +1.8 | 3.83           |
| 2484-WK-A                     | 0.02        | 9.99 × 10⁵  | –          | –27.4        | +0.8 | 5.71           |
| 2468-Champagne Pool           | 8,151       | 2.82 × 10⁴  | –6.0       | –27.2        | –1.1 | 6.39           |
| 2486-Broadlands A             | –           | 9.79 × 10⁵  | –7.4       | –26.7        | +1.8 | 4.23           |
| 2507-Broadlands B             | –           | 9.89 × 10⁵  | –7.2       | –26.5        | +1.9 | 2.73           |
| 2499-NMA                      | –           | 9.93 × 10⁵  | –6.3       | –25.0        | +2.2 | 6.86           |
| 2455-PKA                      | 0.04        | 9.90 × 10⁵  | –6.5       | –28.7        | +1.3 | 2.77           |
| PKA-duplicate                 | 0.06        | 9.90 × 10⁵  | –6.5       | –28.7        | +1.2 | 3.91           |
| 2497-Toaano A                 | 31.96       | 9.98 × 10⁵  | –5.5       | –28.9        | +1.6 | 2.17           |
| 2397-Tiketere A               | 5.25        | 8.81 × 10⁵  | –          | –30.3        | +1.8 | 7.36           |

Endmembers

| Sample       | O₂          | H₂O         | δ¹³C CO₂   | δ¹³C methane | δ¹⁵N | ³He/⁴He (R/Ra) |
|--------------|-------------|-------------|------------|--------------|------|----------------|
|              | ppm         | ppm         | % (VPDB)   | % (VPDB)     | % (AIR) |                |
| M (mantle)   | –           | –           | –6.5       | –            | –     | –5.0           |
| O (organic C)| –           | –           | –25.5      | –            | –     | +4.0           |
| L (carbonate)| –           | –           | +1.6       | –            | –     | +4.6           |
| S (bulk sediment) | –     | –           | –          | –            | –     | +4.2           |
| W (air saturated water) | – | –           | –          | –            | –     | 0.0            |

Sample | ⁴He/³²Ne | ³⁸Ar/³⁶Ar | ⁴⁰Ar/³⁶Ar | CO₂/³⁸He | N₂/³²Ar |
|--------|---------|---------|---------|---------|---------|
| 2558-Waimata a | 18,458 | 0.1879 | 405.62 | 2.13 × 10⁷ | 4.09 × 10⁴ |
| 2559-Mangapakeha a | 14,355 | 0.1871 | 345.92 | 1.48 × 10⁷ | 2.70 × 10⁴ |
| 2574-Awakeri a | 28 | 0.1844 | 293.36 | 1.58 × 10⁷ | 2.34 × 10⁴ |
| 2575-Te Puia a | 303 | 0.1877 | 306.72 | 3.74 × 10⁷ | 2.00 × 10⁴ |
| 2576-Mahia A a | 11,595 | 0.1878 | 329.37 | 3.27 × 10⁷ | 2.65 × 10⁴ |
| 2577-Mahia B a | – | – | – | – | – |
| Otopotetetehehe a | – | 0.1883 | 320.14 | – | – |
| Soda springs a | – | 0.1898 | 305.34 | – | – |
| 2557-Tiketere fumarole | 18 | 0.1876 | 300.15 | 1.74 × 10¹⁰ | 5.43 × 10⁴ |
| 2536-Poly Spa | 7 | 0.1881 | 300.12 | 2.75 × 10¹¹ | 1.66 × 10⁴ |
| 2535-Rotoma soda spring | 16 | 0.1877 | 299.76 | 1.01 × 10¹⁰ | 1.54 × 10⁴ |
Table 4
Continued

| Sample           | $^4\text{He}/^{20}\text{Ne}$ | $^{38}\text{Ar}/^{40}\text{Ar}$ | $^{40}\text{Ar}/^{36}\text{Ar}$ | $\text{CO}_2/\text{He}$ | $\text{N}_2/^{36}\text{Ar}$ |
|------------------|-------------------------------|---------------------------------|-----------------------------|--------------------------|-----------------------------|
| White Island f13 | 16                            | 0.1876                          | 300.11                      | –                        | –                           |
| 2556-White Island F0 | 340                      | 0.1863                          | 298.29                      | $2.81 \times 10^{10}$ | $1.35 \times 10^4$          |
| 2551-TNP-F6      | 114                           | 0.1862                          | 309.69                      | $5.84 \times 10^{10}$ | $1.67 \times 10^4$          |
| 2552-TNP-TM-F3a  | 1                             | 0.1889                          | 302.03                      | $9.26 \times 10^9$    | $2.78 \times 10^4$          |
| 2554-TNP-RC      | 77                            | 0.1871                          | 313.42                      | $6.00 \times 10^{10}$ | $1.90 \times 10^4$          |
| 2555-TNP-UEL     | 11                            | 0.1888                          | 304.21                      | $6.54 \times 10^{10}$ | $1.56 \times 10^4$          |
| TNP-OT           | –                             | 0.1873                          | 309.56                      | –                        | –                           |
| 2500-Rotokawa A  | 223                           | 0.1877                          | 300.64                      | $3.88 \times 10^{10}$ | $4.96 \times 10^4$          |
| 2442-Rotokawa B  | 16                            | 0.1888                          | 299.78                      | $1.19 \times 10^{10}$ | $4.19 \times 10^4$          |
| 2394-Rotokawa fumarole | 6                        | 0.1849                          | 293.26                      | $4.86 \times 10^{10}$ | $6.11 \times 10^4$          |
| 2454-Kawerau     | 29                            | 0.1875                          | 301.75                      | $3.69 \times 10^{10}$ | $5.49 \times 10^4$          |
| 2484-WK-A        | 13                            | 0.1871                          | 298.98                      | $2.95 \times 10^9$    | $1.75 \times 10^4$          |
| 2468-Champagne Pool | 29                     | 0.1882                          | 300.49                      | $2.04 \times 10^9$    | $2.23 \times 10^4$          |
| 2486-Broadlands A | 7                             | 0.1887                          | 301.50                      | $5.09 \times 10^{10}$ | $1.28 \times 10^4$          |
| 2507-Broadlands B | 13                            | 0.1882                          | 301.72                      | $1.07 \times 10^{11}$ | $7.68 \times 10^4$          |
| 2499-NMA         | 68                            | 0.1878                          | 303.04                      | $7.69 \times 10^9$    | $3.27 \times 10^4$          |
| 2453-PKA         | 6                             | 0.1884                          | 304.21                      | $7.25 \times 10^{10}$ | $4.79 \times 10^4$          |
| PKA-duplicate    | 22                            | 0.1885                          | 300.62                      | $5.51 \times 10^{10}$ | $4.77 \times 10^4$          |
| 2497-Tokaanu A   | 2                             | 0.1877                          | 297.13                      | $2.67 \times 10^{11}$ | $2.59 \times 10^4$          |
| 2397-Tikitere A  | 84                            | 0.1859                          | 293.90                      | $1.53 \times 10^{10}$ | $3.25 \times 10^4$          |

Endmembers

- M (mantle) $2.0 \times 10^9$ $3.5 \times 10^6$
- O (organic C) $1.0 \times 10^{13}$
- L (carbonate) $1.0 \times 10^{13}$
- S (bulk sediment) $3.5 \times 10^4$
- W (air saturated water) $1.3 \times 10^4$

| Sample          | Endmember C contributions | Endmember N contributions |
|-----------------|---------------------------|---------------------------|
|                 | M    | O     | L     | L/[L + O] | M    | S     | W     | S/(S + M) |
| 2558-Waimataa   | 0.69 | (−0.01) | 0.32 | −0.01 |
| 2559-Mangapakehaa | 0.79 | (−0.27) | 0.48 | −0.52 |
| 2574-Awakeria   | 0.21 | 0.23 | 0.55 | 0.52 |
| 2575-Te Puiaa   | 0.52 | (−0.17) | 0.65 | −0.49 |
| 2576-Mahia Aa   | 0.58 | (−0.07) | 0.49 | −0.14 |
| 2577-Mahia Bb   | 0.09 | 0.27 | 0.64 | 0.70 |
| Otopoteteteheba | 0.39 | 0.37 | 0.24 | 0.49 |
| Soda springsa   | 0.15 | 0.15 | 0.70 | 0.82 |
| 2575-Tiketere fumarole | 0.05 | 0.10 | 0.85 | 0.89 |
| 2536-Poly Spa   | 0.04 | 0.12 | 0.84 | 0.75 |
| 2556-White Island F0 | 0.03 | 0.32 | 0.65 | 0.67 |
| 2551-TNP-F6     | 0.07 | 0.84 | 0.09 | 0.92 |
Table 4

| Sample                  | Endmember C contributions | Endmember N contributions |
|-------------------------|---------------------------|---------------------------|
|                         | M  | O  | L  | L/[L + O] | M  | S  | W  | S/(S + M) |
| 2552-TNP-TM-F3a         | 0.16 | 0.28 | 0.56 | 0.66 | 0.28 | 0.26 | 0.47 | 0.48 |
| 2554-TNP-RC             | 0.02 | 0.30 | 0.68 | 0.70 | 0.32 | 0.62 | 0.06 | 0.66 |
| 2555-TNP-UEL            | 0.02 | 0.30 | 0.68 | 0.69 | 0.32 | 0.60 | 0.08 | 0.65 |
| TNP-OT                  | 0.04 | 0.30 | 0.66 | 0.69 | 0.20 | 0.54 | 0.26 | 0.73 |
| 2500-Rotokawa A         | 0.13 | 0.29 | 0.58 | 0.66 | 0.07 | 0.63 | 0.31 | 0.90 |
| 2442-Rotokawa B         | 0.03 | 0.36 | 0.61 | 0.63 | 0.31 | 0.48 | 0.21 | 0.61 |
| 2394-Rotokawa fumarole  | 0.03 | 0.28 | 0.69 | 0.71 | 0.26 | 0.61 | 0.23 | 0.74 |
| 2454-Kawerau            | 0.04 | 0.30 | 0.66 | 0.69 | 0.20 | 0.54 | 0.26 | 0.73 |
| 2484-WK-A               | 0.04 | 0.32 | 0.65 | 0.67 | 0.22 | 0.69 | 0.10 | 0.76 |
| 2468-Champagne Pool     | 0.20 | 0.23 | 0.57 | 0.71 | 0.04 | 0.57 | 0.40 | 0.93 |
| 2486-Broadlands A       | 0.02 | 0.29 | 0.69 | 0.70 | 0.19 | 0.54 | 0.27 | 0.74 |
| 2507-Broadlands B       | 0.03 | 0.29 | 0.68 | 0.70 | 0.20 | 0.53 | 0.27 | 0.73 |
| 2499-NMA                | 0.01 | 0.26 | 0.73 | 0.74 | 0.05 | 0.45 | 0.50 | 0.90 |
| 2455-PKA                | 0.03 | 0.29 | 0.67 | 0.70 | 0.20 | 0.54 | 0.26 | 0.74 |
| PKA-duplicate           | 0.03 | 0.29 | 0.68 | 0.70 | 0.20 | 0.53 | 0.27 | 0.73 |
| 2497-Tokaanu A          | 0.01 | 0.26 | 0.73 | 0.74 | 0.05 | 0.45 | 0.50 | 0.90 |
| 2397-Tikitere A         | 0.01 | 0.29 | 0.67 | 0.70 | 0.20 | 0.54 | 0.26 | 0.74 |
| Medianb                 | 0.03 | 0.29 | 0.67 | 0.70 | 0.20 | 0.54 | 0.27 | 0.74 |

*Forearc sample. Samples with negative endmember contributions omitted from median calculation.

& Jambon, 1987). The results of this study indicate that C$_{org}$ within both the subducting sediments and the previously accreted metasedimentary rocks has an average $\delta^{13}$C value of $-25.5 \pm 1.5\%$o, and that carbonate within the subducting material has an average $\delta^{13}$C of 1.6 $\pm 0.7\%$o. Taking the canonical CO$_2$/He ratio for crustal rocks of 1 $\times$ 10$^{13}$ (Sano & Marty, 1995) we are able to calculate the contributions to sampled gases from these three endmembers (Figures 9a and 9b; Table 4). The mantle C contributions calculated using this method are highly dependent on the CO$_2$/He ratio inferred for the mantle, which shows considerable variation in reality (see discussion in supplementary data of House et al., 2019). The effect is more muted for contributions from crustal C sources (carbonate and C$_{org}$).

In this study, we have slightly changed the nomenclature of Sano and Marty (1995), with carbonate-derived C labeled as L, C$_{org}$ being labeled as O, and mantle C labeled as M (as opposed to L, S, and M, respectively). The vast majority of the L component (carbonate) is derived from the subducted slab, either from pelagic carbonate within Unit IV or from carbonate within the underlying basalts (±contributions from gabbro and serpentinized peridotite). While there may be minor carbonate within crustal metasedimentary rocks, it is not primary and was not identified in any of the graywacke samples analyzed in the present study (see Price et al., 2015 for whole-rock analyses of these samples). The O component (C$_{org}$) is derived only in part from the subducted slab, being present as a minor constituent of Unit IV, with the remainder coming from crustal sources (likely accreted sediments or metasedimentary rocks in the hanging wall). Due to the overlap in $\delta^{13}$C$_{carb}$ (L component) between Unit IV and Unit 417, and in $\delta^{13}$C$_{org}$ (O component) between trench-fill, Unit IV, and Torlesse/Waipapa the gas isotopes/chemistry cannot differentiate between the various contributions to the L and O components. Lastly, the M (mantle) component is likely acquired during interaction of slab-derived fluids with primitive melts and/or mantle wedge peridotite.

With the exception of a single sample (Champagne Pool), the mantle CO$_2$ contribution to volcanic gases is very low, with a median value of 3%, though there are four samples with mantle endmembers >10% (Figures 9a and 9b; TNP-TM-F3a, Champagne Pool, NMA, and RKB in Table 4). The C$_{org}$ (O) and slab carbonate...
(L) contributions are relatively uniform with median values of 30% and 67%, respectively, and only three samples differ markedly from these values (e.g. White Island, \( L = 85\% \); Figure 9b). Such similar O/L ratios indicate that either the subducted C component is nearly identical along strike or that some process other than introduction of C\(_{\text{org}}\) by subducted sediment is occurring.

The CO\(_2\) which cycles through volcanic arcs is generally regarded as magmatic in origin but is ultimately derived, at least in part, from intra-slab sources. Following metamorphic devolatilization, CO\(_2\) from the downgoing slab must transit the mantle wedge where it interacts with C-bearing wedge peridotites and any melt which has been produced, thereby obtaining its small but important mantle C component. This CO\(_2\) exsolves as magmas rise toward the surface (analogous to the process for H\(_2\)O cycling within the TVZ put forth by Giggenbach, 1992a; i.e. slab-derived volatiles equilibrated with andesitic magma). Furthermore, crustal assimilation may contribute to the CO\(_2\) budget emanating from the arcs. Lastly, when in the shallow crust there is additional opportunity for the exsolved CO\(_2\) to undergo isotopic reequilibration/fractionation such as has been hypothesized for White Island volcano and the Ohaaki hydrothermal field (Rissmann et al., 2012; Werner et al., 2008, respectively).

5.2. Model Outgassing Estimates and Sensitivity

With the exception of minor CO\(_2\) production due to devolatilization of subducting serpentinized peridotite and gabbro, all CO\(_2\) in the model is sourced from the pelagic Unit IV and the altered basalt units (both Unit 417 and NMORB). The modeled volatile production, therefore, only accounts for CO\(_2\) liberated from the subducted assemblage and does not account for the contributions from the overriding mantle, crust, or previously accreted material. Our isotope analysis as well as that of Banerjee et al. (2004), however, show general overlap of \( \delta^{13}\)C among the pelagic and basalt-hosted carbonates (Figures 6 and 7a), indicating that the signature from these two reservoirs is indistinguishable during isotope analysis of gases (i.e. the calculated L endmember is derived from pelagic and altered basalt carbonates).
Active source seismic imaging of the shallow Hikurangi forearc indicates that the majority of the sediment section, including all units above the pelagic sequence Y (Davy et al., 2008), are accreted and do not directly contribute to the subducted C component (see Figure 6b in Barnes et al., 2010). This material may be later dragged to depth during subduction erosion, but it is not included in our modeled inputs. All of the modeled inputs are topped by 500 m of Unit IV pelagic sediments with a L/[L + O] (i.e. ratio of carbonate C to C_{tot}) of 0.97 (blue dashed line in Figure 9b). The calculated endmember CO$_2$ contributions (O, L, and M in Figures 9a and 9b; Table 4) obtained from gas analysis can be used to determine the amount of CO$_2$ derived from mantle and C$_{org}$ sources in excess of that from Unit IV alone (i.e., samples with L/[L + O] < 0.97).

5.2.1. Cumulative Volatile Release

Estimates for total CO$_2$ production are summarized in Table 2; total fluxes off the slab range between 3.6–4.7 Tg CO$_2$/yr representing between 30% and 85% cumulative loss of subducted CO$_2$ to the depths modeled. Using the median endmember gas contributions of 67:30:3 (carbonate [L]: C$_{org}$ [O]: Mantle [M]) these values can be updated to 5.4–7.0 Tg CO$_2$/yr to account for C from non-slab sources (the range of 3.6–4.7 Tg/yr represents slab-derived CO$_2$ only, which is ~67% of the total CO$_2$ inferred from $\delta^{34}$C of gases). These values represent 1.8%–2.3% of the global CO$_2$ flux from subaerial volcanic regions (global flux ≈ 300 Tg/yr; Werner et al., 2019).
Figure 10. \( \text{CO}_2 \) sources and masses produced for two cross sections across all models. The units correspond to kg of \( \text{CO}_2 \) per unit area (m\(^2\)) in map view. Gray fields indicate depths over which there is no fluid production. See Figure 2 for location of cross sections A-A’ and C-C’. (a) The normal-crust model has an initial pulse (black line) at \( \sim 80 \) km depth with \( \text{CO}_2 \) derived from the Unit IV pelagic sequence (normalized area chart), with deeper contributions from altered basalts. At greater depths \( \text{CO}_2 \) is also sourced from gabbro and serpentinized peridotite, but the total mass produced is minor. The southern cross section (C-C’) has greater total production and greater contribution from peridotite and gabbro. (b) For the doubled MORB model, the northern cross section (A-A’) undergoes \( \text{CO}_2 \) production only within Unit IV and the altered basalts, whereas the southern cross section has minor inputs from deeper units. This model also has an offset between depths of \( \text{CO}_2 \) production initiation from unit 417 and NMORB altered basalts (75 and 78 km respectively). (c) The Mochizuki and (d) Davy models indicate \( \text{CO}_2 \) production from Unit IV and 417 altered basalts only, and have identical production patterns until depths of >125 km.
The four model inputs show substantial differences in total CO$_2$ production, and can be thought of as end-member scenarios. The normal-crust model (Figures 3 and 5a; total flux of 5.4 Tg CO$_2$/yr), represents the possible volatile distribution prior to incursion of the Hikurangi Plateau, and is not applicable to modern day volatile cycling. The Davy et al. (2008) crustal structure, with a total calculated flux of 6.9 Tg CO$_2$/yr is at the other extreme and represents a plateau composed almost entirely of altered basalts, and therefore corresponds to a large volume of subducted C. The two other models, that with the doubled-MORB and the Mochizuki models, are intermediate to the endmembers and are the most likely scenarios for the actual composition of the Plateau (with total fluxes of 7.0 and 6.6 Tg CO$_2$/yr, respectively).

### 5.2.2. North-South Variability of Modeled Volatile Flux

All of the models show variability in CO$_2$ production from north to south (Figure 5). Taking into account the decreasing subduction rate to the south the total CO$_2$ production per km from north to south can be assessed for each model (Figure 11). The normal-crust and doubled-MORB models have relatively constant cumulative production extending for ~150 km from the northern boundary, coinciding with White Island. Red circles indicate δ$_{13}$C value of gas samples, M is the mantle δ$_{13}$C value (~6.5‰). (b) Fraction of C removed from subducted plate over the model range. The normal-crust and doubled-MORB models undergo complete C-loss in the southern-most part of the model range whereas Mochizuki and Davy models undergo only moderate C removal.

The four model inputs show substantial differences in total CO$_2$ production, and can be thought of as end-member scenarios. The normal-crust model (Figures 3 and 5a; total flux of 5.4 Tg CO$_2$/yr), represents the possible volatile distribution prior to incursion of the Hikurangi Plateau, and is not applicable to modern day volatile cycling. The Davy et al. (2008) crustal structure, with a total calculated flux of 6.9 Tg CO$_2$/yr is at the other extreme and represents a plateau composed almost entirely of altered basalts, and therefore corresponds to a large volume of subducted C. The two other models, that with the doubled-MORB and the Mochizuki models, are intermediate to the endmembers and are the most likely scenarios for the actual composition of the Plateau (with total fluxes of 7.0 and 6.6 Tg CO$_2$/yr, respectively).
The increase in CO₂ production to the south does not match observations of volatile release from volcanoes and geothermal areas throughout the North Island, where CO₂-rich fluids tend to be restricted between the edges of the southward-verging central volcanic region (cf. Giggenbach et al., 1993). This disagreement could be caused by inaccuracies in the model parameters, by supra-slab processes (e.g., fluid migration in the mantle wedge or overlying crust), or by some combination of these two.

Toward the south, along the Hikurangi margin, there is increasing obliquity of the convergence between the Plateau and the North Island, eventually giving way to transform motion and linking with the alpine fault on the South Island. This change in the margin kinematics is likely to affect the pattern of mantle wedge flow and thus the thermal structure (e.g., Bengston & van Keken, 2012). In particular, with the southward increase in the obliquity, the sinking rate of the subducting slab (i.e., the margin-normal component of the subduction velocity x sine(slab dip)) decreases. This likely results in a cooler mantle wedge as slower sinking results in less addition of hot asthenospheric mantle brought into the mantle wedge from the back-arc region. The cooler temperature leads to stronger mantle, which further reduces the vigor of the mantle flow and temperature by causing deeper slab-mantle decoupling (Wada et al., 2008). In our model, the maximum depth of slab-mantle decoupling is prescribed to be 75 km, which is within a range that is reported by global studies on subduction zone thermal structures (Syracuse et al., 2010; Wada & Wang, 2009) However, the increasing obliquity and the transition to a transform fault in the south make southern Hikurangi anomalous in that the maximum decoupling depth is likely to be deeper due to the feedback between mantle wedge flow and temperature, resulting in potentially much cooler conditions. This is consistent with the low seismic attenuation in the mantle wedge in southern Hikurangi (Eberhart-Phillips et al., 2008). Along similar lines, Reyners et al. (2006), using Vp/Vs ratios, found a N-S change in mantle flow patterns and distribution of partial melt in the mantle wedge. This study also concluded that there is less heating of the slab to the south, attributing it to reduced vigor of 3-D corner flow due to the presence of a thicker overriding crust. Therefore, the temperatures in the southern portion may be overestimated in our model.

Previous studies of fluid chemistry from New Zealand’s hydrothermally active areas have also demonstrated that CO₂ concentrations decrease to the south (Giggenbach et al., 1993; Reyes et al., 2010). This is potentially caused by the cessation of crustal thinning in the southern reaches of the TVZ (Harrison & White, 2004, 2006). The disagreement between modeled results and observed field relations may in part also be due to the released volatiles not being transported through the (stagnant?) mantle wedge and/or thicker crust of the southern North Island.

5.2.3. Geographic Variability of Analyzed Gases

The geographic distribution of δ¹³C₀₂ shows a subtle trend of decreasing values to the south (Figure 11a; red circles) but is only substantiated by two data points; future sampling may further elucidate this trend. A more robust trend exists when the gas data is plotted with distance from the eastern-most limit of the active arc and compared with results from previous investigations (black dash-dot line in Figure 1b; Figure 12a). Extending west from the arc front for ~15 km there is a trend of increasing δ¹³C, after which there is no discernable trend in the sparse data. The observed variation in δ¹³C ranges from ~−12‰ to +2‰ and crosses the mantle value of ~6.5‰ (Figure 12b). Within ~5 km of the arc-front, the gases have δ¹³C values lower than that of mantle C (e.g. consistent with a contribution from C₀₂), whereas at greater distance there is an increased proportion of carbonate component (δ¹³C > ~6.5‰). Furthermore, a comparison of the C₀₂/O/ (L + O) contribution to the gas flux (taking into account both δ¹³C and CO₂/³He) shows a decrease from ~35% at the arc front to ~15% at 15 km (Figure 12c; using the nomenclature of Figure 9). The observed trend with distance from the arc is strikingly similar to the rapid decrease in B/Cl ratios observed by Giggenbach (1989) who ascribed the spatial variation to recent magma injection in the east, where heating of Torlesse metasediments within the crust has led to B mobilization. This effect was not seen to the west because the Torlesse in these regions had already reached thermal equilibrium with injected magma.

5.3. Source of Organic Carbon Signature: Slab Derived or Assimilation?

The analyzed gases have a median value of 67% CO₂ sourced from subducted seafloor carbonate (L component), with the remainder of the CO₂ coming from (meta)sedimentary material containing significant biogenic C₀₂ (O) or from primitive mantle (M) sources (median values of 30% and 3%, respectively; Figure 7a).
Figure 12. Variation in the organic C contribution to analyzed gases with distance from the arc front toward the back-arc. (a) Gas sample $\delta^{13}C$ vs. distance from eastern edge of active arc for data from this study and from Giggenbach, 1995. The arc-front delineation is shown as a black dash-dot line in Figure 1b. Within ∼15 km of this line there is an increase in $\delta^{13}C$ values from $<-6\%$ to $-2\%$o. There is no apparent trend within gases sampled >20 km from the arc front. Dashed box is range of (b). (b) Annotated plot of $\delta^{13}C$ from gases within 15 km of the arc front. Samples furthest East have $\delta^{13}C < -6.5\%$ (i.e. contributions from $C_{org}$), whereas western samples show progressive addition of $\delta^{13}C$ with a carbonate-derived signature. (c) Calculated contribution of $C_{org}$ to the total C content of gases (as $O/[O+L]$), indicating a decrease from East to West from ∼35% to 15% $C_{org}$. 

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Given that $L/[L + O] = 0.97$ within the Unit IV pelagic sequence, the O component must be added to the gas by some other process, likely either tectonic erosion of previously accreted material and/or assimilation during magmatic processes in the shallow crust.

For the case of the normal crust model input (i.e. the lowest CO$_2$ production), and a hypothetical sediment with a high C$_{org}$ content of 0.5 wt.%, subduction of a 2.3–2.6 km thick sediment package would be required to match the observed gas chemistry. Previous active source seismic studies have shown that the Hikurangi margin, particularly to the south, is an accretionary margin and only minor amounts of sediment are inferred to be subducted (Barnes et al., 2010; Ghisetti et al., 2016). These studies imaged laminar features beneath the main decollement in the shallow Hikurangi forearc, which were identified as subducted pelagic sediment, but due to uncertainties in seismic velocities thicknesses were not calculated (see Figure 4 in Barnes et al., 2010). Further evidence to support accretion of trench-fill sediments, and subduction of pelagic material is the composition of previously accreted material, now preserved as metasedimentary graywackes throughout the North Island. These rocks are seemingly devoid of primary carbonate, and indicate that accretion of terrigenous sediments during subduction along the margin has been the status quo since at least the Late Jurassic (Price et al., 2015).

Two other processes can deliver gases with isotopically light C (e.g. C$_{org}$) to the subarc region: subduction erosion of previously accreted material, and shallow crustal assimilation of metasedimentary country rocks. These two processes involve (meta)sediments with overlapping δ$^{13}$C signatures and cannot be distinguished based on isotope analysis alone. The analyzed gases require addition of, and/or equilibration with ~30% C$_{org}$ to obtain their δ$^{13}$C signature (Figure 9b). This value is in excess of previously determined estimates of assimilation required to account for stable and radiogenic variability of volcanic rocks from the North Island. Previous estimations for assimilation have relied on analysis of volcanic rocks using a variety of isotope systems and have concluded that crustal assimilation is ubiquitous (e.g. 4%–7% assimilation of Torlesse proposed by Macpherson et al., 1998, using variations in whole-rock δ$^{18}$O, δ$^{57}$Sr/δ$^{86}$Sr, and 143Nd/144Nd; ~10% assimilation inferred from Pb isotopes by Burt et al., 1995 at Whale Island; cf. Gamble et al., 1993). Using Hf-Nd isotopes Waight et al. (2017) similarly found that addition of a Torlesse-equivalent material was required in both the source region and as a crustal contaminant.

The trend of decreasing C$_{org}$ contributions with distance west of the arc front indicates that at least some of the CO$_2$ is derived from crustal assimilation, but that there may be additional sources. We propose that some of the C$_{org}$ signature is introduced by tectonic erosion of terrigenous material from accretionary and/or underplated units in the forearc and equilibrated with carbonate and/or devolatilized at subarc depths. Additional C$_{org}$ is sourced from assimilated Torlesse material, particularly on the eastern edge of the active andesitic arc. In this model, recently injected andesitic magma (~50 ka; Cole & Lewis, 1981) leads to a propagation of heat into the relatively cool Torlesse metasediments to the East of the arc releasing volatiles, and thereby leading to the observed trend in increasing C$_{org}$ content (as proposed for B/Cl ratios by Giggenbach, 1989). The metasediments west of this front, within the western arc and backarc, have already reached thermal equilibrium and therefore do not contribute significant C$_{org}$ to the system.

While it is possible that some of the C$_{org}$ signature may have been obtained in the shallow subsurface during phase separation, contamination, and/or fluid mixing, we see no evidence to support this as a major control on the natural data, with the exception of N in the forearc (see Section 5.4). Substantial fractionation and contamination in the near surface tends to produce δ$^{13}$C CO$_2$ values below the mantle value of −6.5, while noble gas ratios remain at, or approach, atmospheric value ($^{3}$He/$^{4}$He: Inguaggiato et al., 2005; CO$_2$/$^{4}$He: Ray et al., 2009; $^{3}$He/$^{4}$He: Ruzié et al., 2013), which has not been observed in the present data set. Perhaps the strongest support for C$_{org}$ contamination occurring at substantial depths is the decreasing C$_{org}$ contribution with distance west of the arc front (Figure 12). This trend indicates that the addition of isotopically light C is a regional trend and is not greatly affected by local conditions at each sampled locality.

### 5.4. Estimates of N$_2$ Production

Nitrogen, as NH$_4^+$, is found dominantly replacing K$^+$ within mica in metamorphic rocks (Honma & Ithiara, 1981), and the release of N is principally caused by fluid-rock interaction and/or breakdown of mica...
during metamorphism (Bebout & Fogel, 1992; Halama et al., 2016). We have not directly modeled N production but given data on the N/K ratios of the various lithologies, the devolatilized fluids K-content, and assuming a N-K mineral-fluid exchange coefficient equal to unity, we can make approximate estimations of the N flux (Figures 13 and S6). A N/K ratio of 0.017 (Bebout et al., 2013; Busigny et al., 2003) is used for all lithologies, as well as the resulting fluid (due to the assumption of a 1:1 mineral/fluid exchange), and fluid K contents are extracted from Perple_X. Nitrogen loss estimates from the downgoing slab are 0.0016, 0.0026, 0.0031, and 0.0043 Tg/yr for normal-crust, Mochizuki, doubled-MORB, and Davy models, respectively (Table 2). The global N flux from volcanoes is poorly resolved, ranging from 0.018 to 0.55 Tg/yr (Hilton et al., 2002; Sano et al., 2001, respectively). Snyder et al. (2003) separately determined a total arc volcanic flux of N of 0.08–0.15 Tg/yr. The calculated fluxes from the slab beneath the TVZ represent minimum estimates since the N-K fluid-mica distribution coefficient is in reality higher than unity (~1.6–1.8 at subarc conditions; Melzer & Wunder, 2000), and because our analysis does not include recrystallization induced N-loss (see discussions in Bebout et al., 2013; Epstein et al., 2021).

Analysis of endmember contributions can be performed for sources of N using $^{35}$N and N$_{36}/$Ar ratios of gases (Sano et al., 1998, 2001), with endmembers being mantle (M), bulk sediment (S), and contamination by air saturated water (W). We use mantle values of $-5.0$‰ and $3.5 \times 10^{-8}$ for $^{35}$N and N$_{36}/$Ar, respectively (Labidi et al., 2020; Marty, 1995; Sano et al., 1998), and values of 0.0‰ and 1.3 $\times 10^{-8}$ for air saturated water. The average $^{35}$N for the analyzed samples (excluding those thought to have undergone hydrothermal reequilibration) is $+4.2$‰, and we use a value for N$_{36}/$Ar of $3.5 \times 10^{-8}$ (after Labidi et al., 2020). Endmember contributions for N$_3$ indicate significant contamination/sequilibration with air saturated water as well as a broad range of mantle (M) to bulk sediment (S) contributions (26%–93% S/[S + M], average 74%; Figure 9c & Table 4). This endmember analysis does not account for the trend seen in the forearc samples, where $^{35}$N values extend to $-5$‰ while retaining low N$_{36}/$Ar ratios on the order of $10^{-8}$ (indicative of little to no mantle contribution). Labidi et al. (2020) recently demonstrated that negative $^{35}$N values can occur due to mass dependent fractionation of atmospheric nitrogen in near surface environments. A similar fractionation was identified in $^{13}$C isotopes in the southern volcanic zone of Chile by Ray et al. (2009). While this phenomenon may account for some of the scatter in the arc data, it is not the dominant mechanism controlling $^{35}$N systematics within the arc.

Compared to C, N is retained within slab lithologies much better, with losses of only 5%–12%. When compared to global arc fluxes, the thermodynamic models N production beneath the North Island corresponds to 0.4%–34% of the global N flux. The lower limit of the global flux (as determined by Sano et al., 2001) is likely too low, and the contribution to the global N flux is likely similar or less than that for CO$_2$ (i.e., $\leq 2$%). This result indicates that the global N$_3$ flux proposed by Sano et al. (2001) is potentially ~1 order of magnitude too small.

5.5. Comparison With Existing Thermo-Petrologic and Geochemical Models

The current investigation indicates a shallow (~18 km depth; 0.58 GPa) release of fluid during forearc metamorphism associated with pelagic sediment dehydration (Figures 4a and 5). The thermodynamic calculation further indicates that this fluid pulse is H$_2$O-rich and does not lead to appreciable loss of C from pelagic unit IV (Figure 4e). A recent geochemical model for the Central America subduction zone proposes significant loss of C within the shallow forearc (Barry et al., 2019). This study, assuming Rayleigh fractionation of $^{13}$C, concluded that the total abundance of C (as DIC) in forearc cold spring waters corresponds to only ~10% of the actual liberated C, with the rest being deposited as calcite within crustal vein networks. We note that a combination of thermodynamic modeling and field observations in general indicates minimal loss of C via decarbonation to depths of 70–80 km (except in relatively warm margins such as Cascadia; see Collins et al., 2015; Gorman et al., 2006; this study), where the slab/sediment section experiences heating due to exposure to the convecting mantle asthenosphere.

Solubility relations for calcite in H$_2$O-rich fluid are such that much of the forearc slab interface would experience calcite precipitation from fluids flowing upward along the interface, rather than dissolution (see Caciagli & Manning, 2003), and that there is abundant evidence from HP/UHP metamorphic studies for the carbonation of interface lithologies at these depths (e.g., abundant carbonate-bearing veins; more
pervasive carbonation; Epstein et al., 2020, 2021; Jaeckel et al., 2018; Piccoli et al., 2016, 2018; Sadofsky & Bebout, 2003; Scambelluri et al., 2016). It is thus possible that any fractionation in the C isotope compositions of fluids emanating from the Central America forearc (or forearcs in general) reflects carbonate precipitation along the interface, perhaps with some additional precipitation in the hanging wall. Interestingly, the carbonate precipitated along the interface can then contribute to the C cycling in the downgoing slab section to depths approaching those beneath volcanic fronts (and beyond), where it could again decarbonate or dissolve and contribute to C enrichment in fluids (see the discussion of carbonate subduction zone residence time by Piccoli et al., 2016).

In the present study, we model fluid as unreactive after devolatilization; upon being produced it instantaneously passes through the slab to the interface. The shallow forearc fluid production is associated with clay mineral breakdown, which occurs in a region where carbonate is stable and the solubility of C-species is exceedingly low, leading to the observed H₂O-rich nature of the fluid (Figure S1). If after production this fluid reacts with carbonate/sediment within the slab, it may acquire additional carbonate, however the mobilization of carbonate into the overlying crust is less certain. Again, at these shallow levels, if vertical and/or up dip flow of fluid occurs, the fluid is flowing down the solubility gradient. A fluid saturated with CO₂ and traveling down a solubility gradient would lead to deposition of carbonate within the slab or along the interface. This highlights the potential for minor scale C-mobilization within the forearc, but not for wholesale loss from the slab. Instead, primary carbonate taken up into solution may be resequestered as veins within the downgoing slab (similar to what has been proposed for the deeper forearc; cf. Epstein et al., 2021).

The potential for C mobilization within the forearc brings into question the mechanism of fluid flow during subduction related devolatilization. A reactive fluid pervasively flowing through the subducting slab will potentially lead to more extensive volatile release than a channelized fluid. Gorman et al. (2006) performed thermodynamic calculations to compare these two endmember scenarios and came to the conclusion that pervasive flow leads to significantly greater mobilization, with the primary control being the thickness and extent of the serpentinized peridotite layer. A more recent model for fluid liberation from subducted serpentinites indicates that both modes of fluid flow occur, but that pervasive flow is subordinate to channelization, particularly away from the zones of fluid production (Plümper et al., 2017). In this model there is self-organization of channel networks due to initial reactive flow. Therefore, while it is clear to see how pervasive flow leads to higher degrees of volatile production, its role is likely minor compared to channelized flow. A further complexity occurs when pervasive flow is modeled within the crustal structures used in the present study, namely rehydration and carbonation of mafic units. Upon serpentinite breakdown the fluid interacts with the low-H₂O gabбро, leading to hydration and carbonation of this assemblage. The net effect is that pervasive flow does not appreciably alter the conclusions of this study (Figure S7), particularly due to the minor role that it plays in subduction zone fluid flow.

Lastly, the effect of shear heating in controlling the thermal structure of global subduction zones has long been debated (Peacock, 1992), and is thought to play a role at shallow depths along the Hikurangi margin (Gao & Wang, 2014). For the Hikurangi margin, a high frictional coefficient of 0.13 leads to a substantial increase in shallow forearc slabtop temperatures (∼60°C at 18 km depth), and a smaller increase at deeper levels (∼13°C at 80 km depth). Shear heating therefore leads to a larger loss of H₂O-rich fluid in the shallowest forearc and a 15%–20% increase in volatile loss at deep forearc and subarc depths (Figure S8). The increase in volatile loss due to inclusion of shear heating is still insufficient for complete C-loss from the subducted lithosphere.

5.6. Comparison With the Exhumed Rock Record

In the shallow forearc, fluid is dominantly liberated during compaction and collapse of pore space (Saffer & Tobin, 2011, and references therein). At the Hikurangi margin, modeling of shallow forearc fluid production performed by Ellis et al. (2015) indicates that clay dehydration only accounts for ~10% of fluid production at 12 km depths. Our thermodynamic models do not account for compaction-related fluid production and likewise do not incorporate sub-greenschist fluid loss associated with progressive ordering of clays (e.g. the smectite-illite transition) or opal dehydration (Spinelli & Underwood, 2004). Initial dehydration in our model coincides with the transition of ordered clays to white micas and occurs within Unit IV at 15–18 km depths (0.5 GPa and >100°C; Figures 2, 4a and 5, S1). This P-T range is similar to the conditions inferred for
initial dehydration of metasedimentary rocks from the Franciscan Complex associated with the stabilization of white mica and loss of clay and chlorite (0.3 GPa and ∼150°C; Sadofsky & Bebout, 2003). Following these depths, there is a hiatus in fluid production until deep forearc depths.

Previous investigation of exhumed rocks in the European Western Alps indicates that C mobilization may occur in the deep forearc, particularly along structures acting as fluid conduits (e.g., mélangé and other zones of enhanced deformation; Epstein et al., 2021; Jaeckel et al., 2018; Piccoli et al., 2016; Scambelluri et al., 2016; Vitale Brovarone et al., 2020), but that away from such structures there is relatively modest C removal (mostly in the deep forearc; Collins et al., 2015; Cook-Kollars et al., 2014; Epstein et al., 2020; Stewart & Ague, 2020) but considerable redistribution (Lefeuvre et al., 2020). These observations are consistent with the modeling results presented: shallow forearc fluid pulses liberate minor amounts of C (<<1%), and most of the subducted C is retained to depths greater than 75 km (Figures 5 and 10, Table 2). They also lend support to the type of fluid flow modeled in the present study, i.e. channelized fluid flow (cf. Angiboust et al., 2014).

In the Western Alps, rocks that were exhumed from the deep subarc and are now exposed along the Cottian Alps (Finestre) and at Lago di Cignana display chemical and isotopic characteristics consistent with the onset of C mobilization (Frezzotti et al., 2011; Cook-Kollars et al., 2014). These rocks record pressures of 2.5–3.0 GPa, corresponding to depths of 80–95 km, and match well with the inferred depths of devolatilization derived from our models (>75 km; Figure 10). The slight discrepancy is due to the P-T pathways for the Hikurangi Margin being slightly hotter than those proposed for the Western Alps (Agard et al., 2001).

Other studies of exhumed rocks from the Alps have additionally shown that there is partial equilibration of δ13C between coexisting carbonate and Corg at deep forearc P-T conditions (Cook-Kollars et al., 2014), or at moderate depths where rocks are highly deformed (Epstein et al., 2021). These studies further showed that such equilibration is only evident in the less abundant Corg phase, with little change in the δ13C of carbonate. As an example, if the Unit IV pelagic sequence (L/[L + O] = 0.97) was fully equilibrated at 700°C, the L endmember would decrease from +1.6‰ to a value of + 0.8‰. Full equilibration is contingent upon the proximity of the two phases as well as the extent of transposition and mixing, both of which likely limit the approach to full equilibration in subduction zones (see Epstein et al., 2020 for a discussion of isotope equilibration in subducted sedimentary rocks). The isotope value of the L endmember may be decreased further due to addition of tectonically eroded material with abundant Corg, but this would only affect the relatively thin sedimentary veneer, as the underlying altered basalts are devoid of Corg. While isotope equilibration may lead to slight changes of the endmember compositions, it likely does not have a primary control over the systematics.

Within metamorphosed marine sediments of the Western Alps Busigny et al. (2003) and Bebout et al. (2013) found a strong correlation between K and N regardless of metamorphic grade, supporting the hypothesis that these elements (for N, as NH4+) behaved similarly to depths approaching those beneath volcanic fronts (70–80 km). In zones of channelized fluid flow, Epstein et al. (2021) found a trend of decreasing N/K with increasing fluid to rock ratios but concluded that this behavior was volumetrically minor. Our treatment of N production in the current study assumes that N and K are equivalently liberated during metamorphic reactions and disregards the volumetrically minor effect of preferential N mobilization during fluid-rock interaction (i.e., nonchannelized, pervasive fluid flow). The results from the modeling are consistent with N production due to breakdown of hydrous phases and a corresponding loss of mineral-bound cations to the electrolyte fluid. Oddly, within the Unit IV sediments this does not manifest as a decrease in the modal abundance of phengitic white mica, but as a decrease in the modal abundance of lawsonite. The lawsonite breakdown, when modeled as occurring in equilibrium with a K-bearing phase and a simple H2O-CO2 binary fluid, leads to an increase in the modal abundance of white mica (with K sourced from other equilibrium solid-solution phases). When this breakdown is instead modeled in equilibrium with a fluid capable of dissolving cation species (e.g. the electrolyte fluid model used herein) the excess K is added to the fluid and the white mica content remains relatively constant (Figure S1). The observed trends in K loss, and the associated minor N liberation to the fluid matches the conclusions of Busigny et al. (2003). Loss of N would be more extensive along margins with warm P-T paths where phengite would be fully destabilized by partial melting (e.g. Cascadia).
5.7. Fate of Volatiles Subducted Along the Hikurangi Margin

All of the models presented in this paper indicate partial retention of C and N to depths of 220 km within the Hikurangi subduction zone (Table 2). The normal-crust model helps constrain cycling estimates for typical subducted oceanic crust but is not particularly applicable to subduction of the Hikurangi Plateau. At the other extreme is the Davy et al. (2008) crustal model which consists of a very large thickness of altered basalts and is likely an overestimation of the masses of subducted volatiles. In between these two are the doubled MORB and Mochizuki et al. (2019) lithologic models, which are likely better representations of the subducting lithologies beneath North Island. These two intermediate models indicate that beneath the North Island there is 4.4–4.7 Tg/yr of CO$_2$ liberated, and that this represents 59%–85% CO$_2$ loss from the subducting slab. Calculated loss of N is much less, ranging from 5% to 12% between the two models. These models suggest that a significant portion of subducted C is retained to depths past the arc and backarc and is therefore likely added to the mantle C budget. Additionally, the vast majority of subducted N is also retained within the subducted material as inferred from studies of exhumed rocks (Busigny et al., 2003). These values for CO$_2$ flux are likely to be maximum estimates, as the model indicates significant increase in CO$_2$ production to the south, which is not corroborated by field evidence. The southern increase in production is not as large for N (Figure 13). If all of the CO$_2$ produced is vented at the surface these values indicate that

![Figure 13](image-url)

**Figure 13.** Estimates of N$_2$ production inferred from K content of fluids liberated from the subducting slab. All models show minor/negligible increases in N$_2$ production to the south, in contrast with the results for CO$_2$ production. (a) The normal-crust model shows initial subarc production from sediment and altered basalt, with a concentrated pulse associated with loss of antigorite in serpentinite. (b) In the doubled-MORB model there is similarly a large pulse of N$_2$ associated with serpentinite dehydration, but this model also shows significant production from altered basalt extending to the western edge of the model. (c) For the Mochizuki model there is continuous production of N$_2$, with slight increases toward the backarc. (d) The Davy crustal model has a substantial increase in post-arc N$_2$ production in the north of the model, derived from the very thick altered basalt.
the TVZ is responsible for 2.2%–2.3% of the global subaerial volcanic flux. The global flux of N is less certain, and the modeled values indicate that the TVZ accounts for 0.8%–25% of the global arc N flux.

6. Conclusions

Of the four models presented here, those based on the lithologic structures of Mochizuki et al. (2019) and the doubled-MORB model best fit the observations of volatile cycling. The broad conclusions from these models are:

1. The majority of CO₂ is derived from altered basalts, with sediments having a significant contribution over a restricted depth range from 75 to 100 km (deepest forearc to shallow subarc; Figure 10). This is in line with recent studies highlighting the significance of this often-overlooked basaltic reservoir. Gabbronor and serpentinized peridotite do not contribute appreciably to the total CO₂ production.

2. The model-predicted thermal structure leads to increased CO₂ production in the southern TVZ, a result which does not match field observations (Figure 5). This discrepancy could be caused by: (a) cooler thermal structure to the south due to, for example, reduced corner flow, that is not accounted for by our model, or (b) thickened crust impeding upward volatile transfer.

3. The analysis of δ¹³C from arc gases indicates a median 30% contribution from C_{org} to the total CO₂ budget. This amount is at odds with the observation that the Hikurangi margin is largely accretionary, with most of the more C_{org}-rich terrigenous sediment removed by that process. The material that is subducted to beyond the accretionary prism has a L/[Sr + O] (carbonate C to total C) value of ~0.97 (Table 3).

4. There are two processes that can account for the observed C_{org} component of the arc gases: (a) tectonic erosion of previously accreted material, and (b) assimilation of Torlesse metasediments at shallow crustal levels. It is proposed that both processes are occurring beneath the North Island, but due to overlapping δ¹³C signatures these reservoirs cannot be disentangled.

5. The δ¹³C_CO₂ analyses suggests that the C_{org} component of the arc gases decreases toward the west, or away from the active arc front (Figure 12). This is evidence of assimilation of crustal metasedimentary rocks, perhaps due to heating by recent andesitic intrusions (<50 ka; Christenson et al., 2002; Cole & Lewis, 1981; Giggenbach, 1989).

6. Taking into account the contributions from mantle and organic C we estimate that there is 5.4–7.0 Tg CO₂/yr liberated beneath the North Island. Excluding the Davy model input which is likely an overestimation of in-slab C content, these values represent removal of 59%–85% of initially subducted CO₂. If we assume 100% transfer of this CO₂ to the surface this equates to 2.2%–2.3% of the global flux from arc regions.

7. Slab-derived N is dominantly sourced from altered basalts, with potential additions from tectonically eroded/assimilated components. Nitrogen within the pelagic sediments is mostly retained due to reten-

Data Availability Statement

Data presented in this article has been archived in the EarthChem database available at https://doi.org/10.26022/IEDA/112055

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