Os isotopic constraints on crustal contamination in Auckland Volcanic Field basalts, New Zealand

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Highlights

- Evidence of crustal contamination observed in Auckland Volcanic Field basalts.
- Highly radiogenic Os isotope ratios coupled with very low Os concentrations indicate a crustal metasedimentary contaminant.
- Slightly elevated Os isotope ratios with high Os concentrations indicate contamination from sulphide bearing olivines.

Abstract

The Auckland Volcanic Field (AVF) represents the youngest and northernmost of three subjacent Quaternary intraplate basaltic volcanic fields in the North Island, New Zealand. Previous studies on AVF eruptive products suggested that their major- and trace- element, and Sr-, Nd- and Pb-isotopic signatures primarily reflect their derivation from the underlying asthenospheric and lithospheric mantle. All AVF lavas however ascend through a ca. 20-30 km thick continental crust, and some do carry crustal xenoliths, posing the question whether or not crustal contamination plays a role in their formation. Here we present new Os and Pb isotopic data, and Os and Re concentrations for 15 rock samples from 7 AVF volcanic centres to investigate mantle and crustal petrogenetic processes. The samples include the most primitive lavas from the field (Mg# 59-69) and span a range of eruption sizes, ages, locations, and geochemical signatures. The data show a large range in Os concentrations (6-579 ppt) and $^{187}Os/^{188}Os$ isotope ratios from mantle-like (0.123) to highly radiogenic (0.547). Highly radiogenic Os signatures together with relatively low Os contents in most samples suggest that ascending melts experienced contamination primarily from metasedimentary crustal rocks with high $^{187}Os/^{188}Os$ ratios (e.g., greywacke). We further demonstrate that <1% metasedimentary crustal input into the ascending melt can produce the radiogenic Os isotope signatures observed in the AVF data. This low level of crustal contamination has no measurable effect on the corresponding trace element ratios and Sr-Nd-Pb isotopic compositions. In addition, high Os contents (195-578 ppt) at slightly elevated but mantle-like Os isotopic compositions ($^{187}Os/^{188}Os$ = 0.1374-0.1377) in some samples suggest accumulation of xenocrystic olivine-hosted mantle sulphides from the Permian-Triassic ultramafic Dun Mountain Ophiolite Belt, which traverses the crust beneath the Auckland Volcanic Field. We therefore infer that the AVF Os isotopic compositions and Os contents reflect contamination from varying proportions of heterogeneous crustal components, composed of Waipapa and Murihiku terrane metasediments, and ultramafic rocks of the Dun Mountain Ophiolite Belt. This demonstrates, contrary to previous models that primitive lavas from the Auckland Volcanic Field do show evidence for variable interaction with the crust.

1. Introduction

Monogenetic basaltic volcanic fields are the surface expression of small-scale magmatic systems and are found in a number of different tectonic settings, including extensional systems (e.g., Cascades, USA; Borg et al., 2000), subduction zones (e.g., Wudalianchi, China; Hwang et al., 2005), or intraplate settings relating to lithospheric rifting (e.g., Panter et al., 2006) and delamination of the lower lithosphere (e.g., Hoernle et al., 2006). The formation of individual monogenetic volcanic centres has mainly been attributed to isolated, often small-volume, batches of magma (<0.1 km^3) (e.g., Connor and Conway, 2000; Németh, 2010; Kereszturi et al., 2013), which erupt quickly (e.g., Németh, 2010), creating volcanic fields which can encompass tens to hundreds of individual centres (e.g., Condit and Connor, 1996; Conway et al., 1998; Connor and Conway, 2000; Valentine et al., 2005). The fields show a range of surface expressions, dependent on the eruption style and magma–water interaction, including tuff rings, maars, scoria cones, and lava flows (e.g., Allen and Smith, 1994; Németh, 2010; Kereszturi et al., 2014). A link between eruptive volumes of monogenetic basaltic volcanoes, and mineralogical and geochemical composition of the underlying mantle has recently been proposed (McGee et al., 2015) highlighting the importance of understanding the characteristics of different sources contributing to magmatism beneath volcanic fields.

Petrological and geochemical studies have shown that most eruptive centres in monogenetic fields are composed of silica- undersaturated basanites, nephelenites and alkaline basalts that are akin to Ocean Island Basalts (OIBs) (e.g., Huang et al., 1997; Cook et al., 2005; Valentine and Gregg, 2008). Nevertheless, eruption products can show considerable geochemical variations both within volcanic fields (e.g., Valentine and Hirano, 2010; Timm et al., 2010; McGee et al., 2013) and within individual centres, the origins of which remain controversial (e.g., Bradshaw and Smith, 1994; Valentine and Gregg, 2008; Needham et al., 2011; Brenna et al., 2010, 2011; McGee et al., 2012). Several studies have attributed these variations in geochemical and isotopic signatures, both for individual eruptions and field-wide scales, to heterogeneities in the underlying mantle (e.g., Huang et al., 1997; McBride et al., 2001; Cook et al., 2005; McGee et al., 2013), magma modification by lithospheric contamination (mantle and crust) or fractional crystallisation (e.g., Lassiter and Luhr, 2001; Alves et al., 2002; Chesley et al., 2002; Jamais et al., 2008; Timm et al., 2009). Although crustal assimilation and contamination may be facilitated by storage or ponding of magma within the crust (e.g., Bohrson et al., 1997), eruptive products in monogenetic volcanic fields are generally mafic (>8 wt.% MgO) thus arguing for limited fractional crystallization and against prolonged crustal magma storage. Therefore, the variations in major, and trace element signatures, and Sr-, Nd-, and Pb-isotopic compositions of rocks from monogenetic volcanic fields are proposed to primarily reflect the composition of the underlying mantle (e.g., Valentine and Perry, 2007; McGee et al., 2012, 2013, 2015). Nevertheless, even mafic magmas in monogenetic fields are not primary melts and therefore are likely to have undergone some interaction with the crust through which they ascend, potentially affecting the physical and chemical properties of the melts. Thus, it is a prerequisite to distinguish between the geochemical signatures of mantle heterogeneity versus crustal contamination (e.g., Blondes et al., 2008; Jung et al., 2011).

To understand the role of the crust and mantle petrogenesis beneath an archetypal continental monogenetic volcanic field we use the ^{187}Re-^{187}Os decay system. This system is highly sensitive to crustal contamination due to the large difference in incompatibility between parent (Re) and daughter (Os) elements during partial melting of mantle lithologies. During partial melting Os behaves compatibly in mantle sulphides and thus dominantly remains in the mantle, whereas Re is moderately incompatible and preferentially enters the melt. This contrast in behaviour of Re and Os therefore result in extreme fractionation (e.g., high Re/Os in melt and crust, and low Re/Os in the mantle) which, with time, leads to an overall significant contrast between the ^{187}Os/^{188}Os ratios of continental crust (up to ^{187}Os/^{188}Os = 5.0; McBride et al., 2001) versus typical mantle sources (ca. 0.12; Meisel et al., 1996). ^{187}Os/^{188}Os isotopic values in the eruptive products of volcanic systems therefore provide a unique tool to decipher the influences of crustal contamination (e.g., Central European Volcanic Province: Jung et al., 2011; Newer Volcanics Province: McBride et al., 2001) and mantle source heterogeneity.

Here we present new Os and Re concentrations, as well as Os and Pb isotope data for 15 mafic samples from the Auckland Volcanic Field, New Zealand. These new data are aimed at identifying the relative importance of mantle heterogeneity, including crustal recycling, and crustal contamination into ascending melts, in order to give new insights into dynamics of melt generation and ascent beneath the city of Auckland.

2. The Auckland Volcanic Field

The monogenetic basaltic Auckland Volcanic Field (AVF) is located 400 km west of the currently active arc, the Hikurangi Margin (e.g., Seebeck et al., 2014)(**Fig. 1.A**). The AVF is the northernmost of three intraplate monogenetic volcanic fields that become progressively younger towards the north (Ngatutura and Okete ca. 2.7-1.5 Ma; Briggs et al., 1994, and South Auckland Volcanic Field (SAVF) ca. 1.59-0.51 Ma; Cook et al., 2005) (**Fig. 1.A**).

The AVF consists of 53 individual centres (**Fig. 1.B**; Hayward et al., 2011) that collectively cover ca. 360 km^2 (**Fig. 1**; Allen and Smith, 1994; Kermode, 1992). The centres include one or more explosion craters, tuff rings (some now occupied by lakes), scoria cones and lava flows. The individual centres are interpreted to have formed through single eruptions of small magma batches (e.g., Allen and Smith, 1994), except for Rangitoto, the youngest and largest volcano where two eruption episodes have been identified (Rangitoto 1 [553±7 cal. yrs. BP] and Rangitoto 2 [504±5 cal. yrs. BP]; Needham et al., 2011). The total volume of the AVF field is estimated at 1.7 km^3 dense rock equivalent (DRE^{tot}), ca. 41% (0.7 km^3) of which is represented by Rangitoto (Kereszturi et al., 2013). Basaltic volcanism commenced at ca. 190 ka (Lindsay et al., 2011) and shows some distinct changes in eruption frequency over time (e.g., Molloy et al., 2009; Hopkins et al., 2015), however the ages of many of the individual eruptive centres are currently poorly constrained (Lindsay et al., 2011).

The crust underlying the AVF is 20-30 km thick, and composed of Waipapa and the Murihiku terranes (**Fig. 1.C**) (e.g., Kermode 1992; Eccles et al., 2005; Horspool et al., 2006; Mortimer et al., 2014), which are overlain by up to 1-2 km of Miocene Waitemata terrane sediments. The western Waipapa and eastern Murihiku terranes mainly consist of late Triassic to late Jurassic low-grade meta-sediments, separated by the Dun Mountain terrane. This terrane represents a Permian to late Cretaceous oceanic arc ophiolite obduction event at the eastern Gondwana margin (e.g., Kimbrough et al., 1992) and mainly consists of ultramafic rocks, including dunites, lherzolites, harzburgites and werhlites (cf. McCoy-West et al., 2013). This terrane is reflected in a distinct positive magnetic anomaly known as the Junction Magnetic Anomaly (JMA), which can be traced continuously through the North and South islands of New Zealand (Hatherton and Sibson, 1970). The JMA traverses the Auckland area as a narrow (ca. 2-5 km), linear series of positive magnetic anomalies interpreted to be eastward-dipping serpentinised shear zones, extending throughout the 20-30 km thick crust beneath the AVF (Eccles et al., 2005). Direct evidence of the Dun Mountain Ophiolite Belt (DMOB) beneath the AVF occurs in the form of serpentinite xenoliths within volcanic rocks in tuff rings from Pupuke, St. Heliers and Taylors Hill volcanoes (e.g., Searle, 1959; Bryner, 1991; Jones, 2007; Spörli et al., 2015). The basement rocks that make up the region of the study area have been extensively investigated (e.g., Bryner, 1991; Kermode, 1992; Eccles et al., 2005; McCoy-West et al., 2013), allowing potential sources of crustal contamination to be well characterised.

The Auckland Volcanic Field has been the focus of previous geochemical and petrological studies (Huang et al., 1997; Smith et al., 2008; Needham et al., 2011; McGee et al., 2011, 2012, 2013, 2015). Low degrees of partial melting (≤6%), a limited proportion of fractional crystallisation, in addition to a limited range of Sr-, Nd-, and Pb-isotopic compositions of the AVF lavas were interpreted to reflect the mantle origin of the AVF lavas. Huang et al. (1997) furthermore attributed the more radiogenic $^{206}Pb/^{204}Pb$ isotopic compositions (>19.2) of the AVF rocks to the presence of 'young' HIMU signature formed in ≤ 0.2 Ga in the underlying mantle (cf. Thirlwall. 1997). Alternatively, McGee et al. (2013) suggested that AVF lavas with more radiogenic $^{206}Pb/^{204}Pb$ isotopic compositions, coupled with low SiO_2 (<48 wt.%) and Nb/U, but high CaO/Al_2O_3, Na_2O and K_2O, and elevation Ce/Pb, Nb/Ce and U/Pb represent melts derived from carbonated garnet peridotite domains hosted in a depleted mantle-like peridotitic asthenosphere. The more siliceous AVF alkali basalts (SiO_2 ≥ 48 wt.%) were in contrast attributed to interaction of ascending lithospheric melts with (or direct melting of) an EMII-type lithospheric mantle, previously metasomatised by subduction-related fluids. These interpretations of the AVF major and trace element, and Sr-, Nd-, and Pb- isotopic systematics rely on the assumption that the AVF eruption products are directly representative of their mantle sources, as proposed by McGee et al. (2013), and are not affected by contamination. However, a number of studies have noted xenolithic materials (e.g., crustal schistose and non-schistose fragments, meta-igneous rocks, and abundant large olivines) within some AVF centres, for example at St Heliers, Taylors Hill, and Mangere Mt (Spörli et al., 2015), providing direct evidence for the interaction of ascending magmas with the underlying crustal and mantle lithologies (e.g., Bryner, 1991). Therefore, traditionally used major and trace element contents and ratios, and Sr-, Nd-, and Pb-isotopes may not be sensitive enough to distinguish between crustal contamination and mantle heterogeneity. We address this problem here using the more sensitive Os isotope system.

3. Methods

3.1. Sample selection

Specific samples were chosen for this study in order to complement existing data and to cover not only a range of geochemical compositions of the field (c.f. McGee et al., 2011, 2012, 2013, 2015) but also a range in ages (Needham et al., 2011; Lindsay et al., 2011), locations, eruptive volumes and types (Kereszturi et al., 2013, 2014). Based on previous analyses, fifteen primitive samples were chosen (Mg# =59-69) from Rangitoto, Mt Wellington, Purchas Hill, Three Kings, Wiri, Puketutu, and Pupuke. New Pb isotope data are added by this study for 7 samples, and new major and trace element data are added for 5 samples (see **Table 1** for classification). For all fifteen samples new Re and Os concentrations, and Os isotope ratios are determined. Generally the selected samples contain minor olivine phenocrysts (≤3 mm across) in a plagioclase, pyroxene, and olivine-bearing groundmass, except for samples from Pupuke, which contain abundant large olivines ≥5 mm across.

3.2. Analytical techniques

Sample preparation for chemical and isotopic analyses were conducted at Victoria University of Wellington, New Zealand (VUW). Samples were chipped using a Rocklabs Boyd crusher to <15 mm, then reduced to powder in an agate ring mill. Major elements were analysed by XRF analysis at the Open University, Milton Keynes, United Kingdom (UK), on an ARL® 8420+ dual goniometer spectrometer. Powdered samples were fused with lithium metaborate and analysed following methods of Ramsey et al. (1995). Whin Sill dolerite was run as an internal standard with associated accuracy of <1% except for Na_2O (2.37%) and P_2O_5 (1.59%) and precision of <2%. For trace element concentrations 50 mg of sample powder was digested in hot concentrated HF + HNO_3 for 4 days, then dried to incipient dryness and taken up in concentrated HCl. Following this, samples were converted back into HNO_3 and left for 3 days in hot 1M HNO_3 to form the final analytical solution. Centrifuged sample dilutions were measured on an Agilent 7500CS ICP-MS at Victoria University, Wellington, using BHVO-2 as a primary standard, and BRCR-2 as a secondary internal standard. All results and standard values are reported in the supplementary material (SM) (**SM.1 and SM.2**). Precision on BCR-2 (n=15 from five digestions) was <6.5% 2sd% except for Nb, Cs, and Ba (≤8 %) and Ta, Pb, and Nb (≤20.5 %) and values were all within <6 % of the reference value, except for Cu, Cs, and Ta. All standard values are outlined in the supplementary material.

Pb isotope samples were prepared and purified in an ultra-clean chemical separation laboratory at VUW. Powdered sample was leached in ultrapure 6M HCl for 1 hour at 120°C, rinsed with MilliQ water, and digested in ultrapure conc. HNO_3 + ultrapure conc. HF, then turned into solution with 0.8M HBr. The solution was centrifuged, loaded onto 5 mm columns equipped with AG1-X8 resin, and Pb was extracted in a double-pass using 6M HCl. Pb isotopic compositions were analysed using a Neptune MC-ICP-MS at Durham University, UK, results and errors are reported in **Table 1.** International standard NBS-981 was used to monitor machine drift, with internal precisions (2SE) of $^{206}Pb/^{204}Pb$ <±0.0012, $^{207}Pb/^{204}Pb$ <±0.0013, $^{208}Pb/^{204}Pb$ <±0.0044. All data are normalised to NBS-981 standard values reported by Baker et al. (2004) ($^{206}Pb/^{204}Pb$ =16.9416, $^{207}Pb/^{204}Pb$ = 15.4998, $^{208}Pb/^{204}Pb$ = 36.7249), all standard measurements can be found in supplementary material (**SM2.3**).

Os isotope compositions and Re and Os contents were determined at Geotop, Université du Québec à Montréal, Canada, following the method of Meisel et al. (2003). For these analyses 0.8 g aliquots of whole rock powder were spiked with a known enriched tracer solution of $^{190}Os/^{185}Re$, and digested in Teflon-sealed quartz tubes with 3 ml 6M HCl and 3 ml conc. HNO_3 at 300 °C and 100 bars in a high-pressure asher unit (HPA-S, Anton-Parr). Following this, Os was extracted using the Paris Br_2 technique (Birck et al., 1997). 2 ml of chilled Br_2 was added to the digested sample and left on a hot plate at 90 °C for 2 hours. This scavenges the already oxidised Os (OsO_4) from the aqueous solution into the liquid Br_2, leaving Re (and PGEs) within the aqueous solution. 20 drops of HBr was added to the isolated liquid Br_2 (including Os) to reduce Os from volatile Os^{8+} (OsO_4) to non-volatile Os^{4+} ($OsBr_6^{2-}$), and then evaporated down. A final step of micro-distillation using Cr^{VI} containing H_2SO_4 was used to purify the Os, and make sure it was quantitatively separated from isobaric Re (after Birck et al., 1997). Samples were then measured using a Triton TIMS in negative-ion mode for Os (Creaser et al., 1991), and sector field (SF)-ICP-MS for Re. Os and Re concentrations were calculated by isotope dilution from known spike solution values. Os blanks for total procedure are 0.3 pg, and 7 pg for Re, these value are subtracted from the sample totals in data processing along with oxygen interface and sample-spike unmixing corrections. Results and errors for Os and Re analysis are reported in **Table 1.** The widely used standard Durham Romil Osmium solution (DROsS) was used with an internal precision (2SE) for $^{187}Os/^{188}Os$ of average measurements of <±0.00012 (Luguet et al., 2008; Nowell et al., 2008, see supplementary details for measurements (SM2.4)), and for Re standard NIST SRM 3143 was used, with internal precision (2SE) for $^{187}Re/^{185}Re$ of average measurements of <±0.05 (see SM.2.4). Duplicate analyses were undertaken in two ways, on aliquots of one sample solution post-digestion to test consistency of digestion techniques, and of sample powders to check the internal consistency of samples.

4. Results

4.1. Major and trace elements

Volcanic rocks from the AVF range in composition from sub-alkaline silica under-saturated basanites to alkali basalts (e.g., SiO_2 = 39.8-48.8 wt.%, **Fig. 2.**) following the rock classification of LeMaitre (2002). In general, the data for the AVF samples form a broad negative trend with MgO vs. SiO_2 and Al_2O_3 and positive trends with CaO $Fe_2O_3^t$, TiO_2, and P_2O_5 indicative of olivine and pyroxene fractionation (**Fig. 2.**). The exceptions are, two samples from Rangitoto, which have lower $Fe_2O_3^t$, TiO_2, CaO and P_2O_5 values and higher SiO_2 and Al_2O_3 values at a given content of MgO, and two samples from Pupuke, which have lower values for CaO, TiO_2 and $Fe_2O_3^t$, but higher values of MgO than the other AVF rocks.

All AVF samples used in this study show primitive mantle-normalised trace element distributions broadly similar to ocean island basalt (OIB) (normalisation values after McDonough and Sun, 1995), with typical positive Nb-Ta, and negative K anomalies (**Fig. 3.**). As previously identified by McGee et al. (2013), AVF samples with low SiO_2 contents have higher Nb and Ta relative to the large ion lithophile elements (LILE; Rb, Ba, K) (e.g., Nb/Ba ≥ 0.2), and higher Light Rare Earth Element (LREE; La, Gd, Nb) concentrations. Furthermore, these samples (those with low SiO_2 content) have high LREE relative to their heavy rare earth elements (HREE; Yb), resulting in high LREE/HREE ratios (e.g., $(La/Yb)_N$ >20), and elevated ratios of highly to moderately incompatible elements, such as Th/Yb ≥2. In comparison to the low SiO_2, two of the Rangitoto samples with high SiO_2 values have lower Nb and Ta concentrations relative to LILE (e.g., Nb/Ba ≤ 0.2) and lower LREE but similar to slightly higher HREE (e.g., $(La/Yb)_N$ <20). These high SiO_2 Rangitoto samples also have higher Th relative to HREE (e.g., Th/Yb <1), lower Ce/Pb (<20), yet higher K/Nb (>300) and Zr/Nb (>7). These Rangitoto samples also show a positive Sr-anomaly (**Fig. 3**), which is less prominent in all other samples; conversely all other samples show a prominent negative K-anomaly (**Fig. 3**), which is not observed within the Rangitoto samples.

These findings are consistent with the previous work of McGee et al. (2013, 2015), and are also comparable to samples from the South Auckland Volcanic Field (SAVF; Cook et al., 2005). Cook et al. (2005) noted higher Nb, $(La/Yb)_N$ and Th/HREE values for samples with low-SiO_2 (their Group B) and low Nb, $(La/Yb)_N$ and Th/HREE for samples with high-SiO_2 (their Group A) and contrasting incompatible trace element ratios (e.g., K/Nb, Zr/Nb and Ce/Pb). These observations are also consistent with those of Hoernle et al. (2006) and Timm et al. (2009, 2010) who divided their data from New Zealand intraplate volcanic centres and fields into 'low-SiO_2' and 'high-SiO_2' groups, showing similar major and trace element geochemical compositions to the AVF low- and high-SiO_2 samples. For the purpose of this study we have chosen not to group our data due to the limited number of samples, but highlight the similarity in geochemical signatures for the AVF samples.

4.2. Pb isotopes (combined with published Sr-, Nd-, and Pb-isotopes)

Pb isotopic data for the AVF rocks are reported in **Table 1**. Seven new Pb isotope determinations have been generated to supplement the data of McGee et al. (2013). In general the AVF Pb isotopic compositions show limited variation, with $^{206}Pb/^{204}Pb$ = 19.064-19.383, $^{207}Pb/^{204}Pb$ = 15.576-15.615, and $^{208}Pb/^{204}Pb$ = 38.485-38.931. On Pb isotope variation diagrams the AVF data plot between the mid ocean ridge basalt (MORB), HIMU (high μ = high time integrated U/Pb) and enriched mantle (EM I or II) end-members (following the classification of Zindler and Hart, 1986; **Fig. 4. A&B.**). Purchas Hill sample AU44711 shows the highest $^{206}Pb/^{204}Pb$ (19.383) and high $^{208}Pb/^{204}Pb$ (38.929), but $^{207}Pb/^{204}Pb$ similar to rocks from other AVF centres (15.613). Conversely, the two Rangitoto samples show the lowest $^{206}Pb/^{204}Pb$ (19.064), low $^{208}Pb/^{204}Pb$ (38.485), and some of the highest $^{207}Pb/^{204}Pb$ values (15.615) of all AVF volcanic rocks (**Fig. 4**.). Most other AVF samples plot between the Purchas Hill and Rangitoto samples, with the possible exception of the samples from Wiri Mt, which have the lowest $^{207}Pb/^{204}Pb$ (15.576-15.579) at intermediate $^{206}Pb/^{204}Pb$ (19.219-19.225) and $^{208}Pb/^{204}Pb$ (38.791-38.795). These Pb isotope compositions observed in AVF rocks generally overlap with those from the SAVF ($^{206}Pb/^{204}Pb$ = 18.959-19.332; $^{207}Pb/^{204}Pb$ = 15.579-15.624, and $^{208}Pb/^{204}Pb$ = 38.752-38.953: data from Cook et al. (2005), values are re-normalised to standard SRM-981 values reported in Baker et al. (2004), to maintain consistency with values from McGee et al. (2013), and this study; **Fig. 4.**).

Previously published Sr and Nd isotope data for the same samples analysed in this study show a restricted range from $^{87}Sr/^{86}Sr$ = 0.702710 to 0.703125 and from $^{143}Nd/^{144}Nd$ = 0.512939 to 0.512956 (McGee et al., 2013; **Fig 4. C&D.**, reported in supplementary material SM.1.). Although no obvious trend has been identified between Sr and Nd isotopic compositions, some of the AVF data (McGee et al., 2013) show similar trends to those observed by Cook et al. (2005) in the SAVF samples. Some samples have distinctly higher $^{87}Sr/^{86}Sr$ (ca. 0.7032) than the samples from the other centres at similar $^{143}Nd/^{144}Nd$ values (ca. 0.5129) (**Fig. 4.C&D.**). Similarly there is no clear correlation observed between $^{206}Pb/^{204}Pb$ and $^{143}Nd/^{144}Nd$, although $^{206}Pb/^{204}Pb$ and $^{87}Sr/^{86}Sr$ show a poorly defined negative trend (Cook et al., 2005; McGee et al., 2013; **Fig. 4.C.**). Similar to most AVF samples, the SAVF 'Group B' type (Cook et al., 2005) are characterised by lower $^{87}Sr/^{86}Sr$ values (≤0.7028) at similar $^{143}Nd/^{144}Nd$ values (0.51296-0.51298), coupled with higher $^{206}Pb/^{204}Pb$ (19.210-19.332), higher $^{208}Pb/^{204}Pb$ (38.862-38.935) and lower $^{207}Pb/^{204}Pb$ values (15.579-15.600). In comparison, SAVF 'Group A' type (Cook et al., 2005), has higher $^{87}Sr/^{86}Sr$ values (≥0.7029) and similar $^{143}Nd/^{144}Nd$ values (0.51294-0.51298), coupled with lower $^{206}Pb/^{204}Pb$ (18.959-19.286), lower $^{208}Pb/^{204}Pb$ (38.752-38.905), and higher $^{207}Pb/^{204}Pb$ values (15.597-15.624) similar to samples from Rangitoto (See **Fig. 4.**).

4.3. Re, Os, and $^{187}Os/^{188}Os$

$^{187}Os/^{188}Os$ values and Re and Os concentrations are given in **Table 1**. The AVF samples show a wide range in Os and Re concentrations (Os = 5.8-578 ppt, Re = 25.9-411.9 ppt; **Fig. 5.**), but concentrations fall in the range of contents reported from other OIB-type lavas (Os = 1-600 ppt: Schiano et al., 2001; Re = 100-642 ppt: Hauri and Hart, 1997). Similarly, the AVF volcanic rocks have a significant range in Os isotope compositions from mantle-like $^{187}Os/^{188}Os$ of 0.1230 (cf. Meisel et al., 2000) to radiogenic values up to $^{187}Os/^{188}Os$ = 0.5470 (**Fig. 6**.). The majority of samples (n = 19; including duplicates) have $^{187}Os/^{188}Os$ ≥0.15, higher than the range inferred for mantle-derived magmas (Lassiter and Hauri, 1998; Widom et al., 1999; Rasoazanamparany et al., 2015). In general no obvious correlations between Os and Re concentrations, $^{187}Os/^{188}Os$ values and MgO, Ni, Cu or Zr concentrations or trace element ratios are observed. The exceptions are samples from Pupuke, which have high MgO, Ni, and Os concentrations (**Fig. 5**.), but relatively unradiogenic $^{187}Os/^{188}Os$ values (**Table 1.**).

The overall range in $^{187}Os/^{188}Os$ values in the AVF rocks (0.1230 to 0.5470) is larger than those observed in most OIB-like basalts (ca. 0.11 to 0.14; Reisberg et al., 1993; Hauri and Hart, 1993; Roy-Barman and Allègre, 1995; Marcantonio et al., 1995; Widom and Shirey, 1996; Lassiter and Hauri, 1998; Schiano et al., 2001; Day et al., 2010), and overlap with those in alkali basaltic and tholeiitic lavas from other continental intraplate volcanic fields. These include Newer Volcanic Province, SE Australia ($^{187}Os/^{188}Os$ = 0.1342-0.4456; McBride et al., 2001); Central European Volcanic Province, Germany ($^{187}Os/^{188}Os$ = 0.1487-0.7526; Jung et al., 2011) and the East African Rift System ($^{187}Os/^{188}Os$ = 0.1239-0.4366; Nelson et al., 2012) (**Fig 6.**). Samples with more radiogenic Os isotopic composition generally contain less Os (e.g., Rangitoto sample AU59309: $^{187}Os/^{188}Os$ = 0.5470, Os = 5.8 ppt), and those with lower $^{187}Os/^{188}Os$ contain more Os (e.g., Wiri Mt. sample AU43931: $^{187}Os/^{188}Os$ = 0.1283, Os = 194 ppt). In addition, low Os concentration samples (<40 ppt) generally have more variable Os isotope signatures (0.1623-0.5470), becoming less variable (0.1230-0.1374) with increasing Os contents (>100 ppt). On an $^{187}Os/^{188}Os$ versus Os diagram (**Fig. 6.**) the AVF data generally plot between crustal and mantle end-member fields, similar to other Pacific OIB fields (**Fig. 6.**)

Duplicate analyses of the same sample using the same digestion, and same sample quantities, show highly reproducible results (e.g., Purchas Hill and Wiri samples; Table 1), however, duplicate analyses of the same sample using different digestions show results which plot along a positive trend between high Os with low $^{187}Os/^{188}Os$, and low Os with high $^{187}Os/^{188}Os$)(**Fig. 6.**). These include samples from AVF centres Rangitoto, Three Kings, Purchas Hill, Mt Wellington, and Puketutu. This effect has previously been observed (e.g., Allègre and Luck, 1980; Potts, 1987; Alves et al., 2002) and termed the ‘nugget effect’. This suggests that the variable $^{187}Os/^{188}Os$ in an individual digestion is caused by sampling differing amounts of mineral-hosted sulphides, or oxide micro-inclusions, with either inherited crustal, or mantle $^{187}Os/^{188}Os$ signatures in a single powdered sample. The high reproducibility of Os contents and $^{187}Os/^{188}Os$ for a split of the same digestion (c.f. **Table 1**) demonstrates effective digestion of the sample, and argues against the variability in the results from different digestions of the same sample being due to incomplete sample dissolution. Single samples are likely to contain sulphide populations that have different Os contents and $^{187}Os/^{188}Os$ values, which are variably sampled by duplicate sample splits.

5. Discussion

5.1. The effects of mantle source heterogeneity and fractional crystallisation on Os signatures

The petrogenesis of the AVF basalts has been the subject of a number of geochemical and isotopic studies detailed in **section 2** (Huang et al., 1997; Needham et al., 2011; McGee et al., 2011, 2012, 2013, 2015). The isotopic data, with specific emphasis on Pb isotope ratios, have been used previously (Huang et al., 1997; McGee et al., 2013, 2015) to identify and fingerprint three heterogeneous mantle sources, which are variably mixed to produce the isotopic and geochemical variability observed within the AVF eruptive products. New Pb isotope data added by this study (**Fig. 4 A&B.**) are consistent with those published for the AVF (McGee et al., 2013) and the SAVF (Cook et al., 2005), however, new Os isotope data obtained by this study show no correlation to the Pb-Sr-Nd isotope systems (**Fig. 7**), suggesting that different processes control these isotopic signatures within the AVF melts. This hypothesis is further supported by the lack of correlation between Os and Re contents and the major and trace element concentrations of the AVF rocks (**Fig. 5.**). In addition, no correlation is observed between the key trace element ratios, and trace element anomalies (K and Sr) that have previously been used to determine the mantle source signatures of the AVF rocks (e.g., La/Yb ratios; McGee et al., 2013, 2015). The different behaviours of the major and trace element concentrations and isotope systems therefore question whether or not a heterogeneous mantle source alone is responsible for the AVF Os signatures.

The generally low and variable Os concentrations, and lack of correlation between Os and Re and the other major and trace element concentrations could be explained through partial melting and fractional crystallisation. However, the concentrations of Os and Re in most AVF samples show no obvious correlation between $^{187}Os/^{188}Os$ and MgO or, Ni, Cu or Zr (**Fig 5**.), suggesting that fractional crystallisation of the major phases found within the AVF rocks (olivine and pyroxene ±plagioclase) has an insignificant influence on the Os and Re budgets. However, Platinum Group Elements (PGE), including Os, in addition to being siderophile are also chalcophile, and thus are relatively concentrated in sulphide minerals or PGE-rich metal alloys (e.g., $D_{Os} \sim 10^4$ between sulphides and silicate melt; Roy-Barman et al., 1998; Jamais et al., 2008; Park et al., 2013; McCoy-West et al., 2015). Very minimal amounts of sulphide fractionation will therefore preferentially remove Os from a melt, without a strong co-variance with other elements. This is likely to contribute to the low Os concentrations that are seen in the majority of AVF samples. Conversely, Re is less compatible to moderately incompatible in sulphides and thus is not preferentially incorporated into them. Sulphides formed through fractional crystallisation are either retained in residual minerals in the mantle (e.g., olivine; Lorand et al., 2010) or segregate during magma transport and emplacement (e.g., Bézos et al., 2005). The PGE concentrations in the melt therefore depend on the degree of partial melting, as only high degrees of partial melting (ca. ≥20%) will completely exhaust Base Metal Sulphides (BMSs) from the mantle source, resulting in a PGE-enriched melt (e.g., Rehkämper et al., 1999; Lorand et al., 2010; Dale et al., 2012). Accordingly, lower-degree partial melts will result in lower and more variable HSE contents due to incomplete breakdown of sulphide in the mantle source (e.g., Day et al., 2010). As low degrees of partial melting have been suggested to occur beneath the AVF (≤6 %; McGee et al., 2013) variable and generally low Os contents are therefore expected in the AVF melts. However, the absence of co-variance between the above-mentioned elements and Os suggest that partial melting and silicate + sulphide phase fractionation cannot alone cause the variability in Os contents observed in the AVF rocks. Some of the AVF samples have high Os contents together with high MgO and Ni contents (**Fig. 5.)**, suggestive of the accumulation of xenocrystic olivine (±pyroxene)-hosted sulphides into the AVF melts during ascent (e.g., Alard et al., 2002). However, PGEs reveal an even more complex behaviour depending on fO_2, fS_2, temperature and pressure prevailing during mantle melting, crystal fractionation and during melt ascent and eruption. Regardless of the behavioural complexity of BMSs, due to their low melting temperatures and low viscosities, they are soluble in basaltic melts and will therefore be partially incorporated into the ascending magmas (Alard et al., 2002). It is therefore likely that ascending melt will become contaminated with mantle or crustal sulphides if the magma passes through an appropriate sulphide-bearing source. We therefore propose that the Os systematics of the AVF are not controlled by mantle source heterogeneity or fractional crystallisation, and instead are most likely controlled by contamination and assimilation processes. This possibility is further investigated below in regards to the Os isotopes and Os concentrations of the AVF basalts.

5.2. Contamination and assimilation

On an $^{187}Os/^{188}Os$ versus Os diagram (**Fig. 6**) most data from the AVF samples plot on a curved array between mantle-like unradiogenic $^{187}Os/^{188}Os$ with elevated Os concentrations, and radiogenic $^{187}Os/^{188}Os$ with low Os concentrations. This array is indicative of a mixing end member (into a mantle-like source) with an elevated Os isotope ratio but a low Os content (**Fig. 6**.). However, $^{187}Os/^{188}Os$ vs. Sr-, Nd-, or Pb- isotopic systems (**Fig. 4.**) show no indication of a source for this signature, with no obvious trends towards either a combined mantle (e.g., young HIMU, EMII-type pelagic sediments, or carbonatite) or continental crustal signature (**Fig. 7**.). The source of this mixing end member therefore remains unclear, and so potential contributors to contamination or assimilation in the mantle and crust are discussed below.

5.2.1. Mantle Source

Typical primitive mantle values for $^{187}Os/^{188}Os$ are ≤ 0.1290 (Meisel et al., 1996), with variable Os concentrations between 1-600 ppt (Schiano et al., 2001). However, in subduction zones the Os isotopic signatures of lithospheric mantle can be increased through the incorporation of highly radiogenic oceanic crust (e.g., Alves et al., 1999; Borg et al., 2000; Dale et al., 2007; Suzuki et al., 2011). In addition, fluids derived from the subducting plate will cause metasomatism of the subcontinental lithosphere, leading to more oxidising conditions in the mantle by increasing the fO_2 and fS_2. Mantle hosted sulphides, which are more stable under reducing conditions, will destabilise and oxidise to sulphates (e.g., Carroll and Rutherford, 1985), releasing sulphide-bonded metals, which include high concentrations of Os, and PGEs (e.g., Jugo, 2009; Suzuki et al., 2011). Subduction-metasomatised lithosphere can therefore host a more radiogenic Os isotope signature than the ambient mantle, and has the potential to contain higher concentrations of Os in partial melts. However, because Os is compatible with residual mantle sulphides during low degree partial melting, any erupted lavas will likely have elevated radiogenic isotope signature and a low Os concentration (e.g., Widom et al., 1999).

The lithosphere beneath the AVF was exposed to multiple episodes of subduction at least from the Cretaceous (e.g., Mortimer et al., 2006) and from Oligocene to Miocene (30 to ca. 20 Ma: Seebeck et al., 2014). In addition, studies on peridotitic xenoliths from the South Island volcanic groups (e.g., Scott et al., 2014; McCoy-West et al., 2015) present evidence for subduction-related carbonatitic metasomatism. Carbonatites typically have low Os concentrations and elevated Os isotope ratios (Widom et al., 1999; Escrig et al., 2005), and therefore could represent a mantle end-member causing the radiogenic signature seen for the AVF samples. However, with the exception of the high La/Yb ratio for the Purchas Hill samples, the AVF samples do not show the geochemical signatures (e.g., low Ti/Eu or low wt.% Al_2O_3) that have been attributed to carbonatite metasomatism (e.g., Scott et al., 2014). In addition, the $^{206}Pb/^{204}Pb$ and $^{87}Sr/^{86}Sr$ isotope values in the AVF rocks are lower than the HIMU-type South Island xenoliths ($^{206}Pb/^{204}Pb$ >20). Using $^{187}Os/^{188}Os$ values from Widom et al. (1999) (e.g., $^{187}Os/^{188}Os$ = 0.6), and Os concentration from Escrig et al. (2005) (e.g., Os = 15 ppt) modelling input of carbonatite into the system cannot readily explain the complete spread in Os (ppt) versus $^{187}Os/^{188}Os$ data spread of the AVF samples used in this study (**Fig. 8.**).

Alternative models to explain the radiogenic $^{187}Os/^{188}Os$ geochemical composition involve the presence of eclogitic or pyroxenitic or carbonated peridotite domains in the asthenospheric or lithospheric mantle (e.g., Hoernle et al., 2006; Sprung et al., 2007; Timm et al., 2009; McCoy-West et al., 2010; McGee et al., 2013, 2015). This poses the question whether or not partial melting of different mantle domains (peridotite vs. pyroxenite ± CO_2 beneath the AVF, as originally proposed by McGee et al. (2013), may lead to the radiogenic Os isotope signature of the AVF samples. In general neither the AVF Os isotope ratios, nor the Os concentrations correlate with the typical geochemical tracers for carbonated peridotite, carbonatite metasomatism (e.g., low wt.% SiO_2 and low MgO#, or elevated CaO/Al_2O_3, Ce/Pb, Nb/Ce; Scott et al., 2014; McGee et al., 2015) or pyroxenite (e.g., elevated Al_2O_3 coupled with radiogenic $^{187}Os/^{188}Os$; Marchesi et al., 2014). This is in agreement with a recent study by McCoy-West et al. (2015) concluding that because the PGE budget is primarily controlled by residual sulphides, carbonatitic metasomatism beneath Zealandia (the wider micro-continent on which New Zealand sits) does not affect the PGE budget of the subcontinental peridotites. These results also support previous conclusions by Handler et al. (1997) who also showed that for wherlite and apatite-bearing peridotites, interaction with carbonatitic melt has no effect on the Os isotope composition or concentrations of Os or Re.

A number of studies (e.g., Kumar et al., 1996; Saal et al., 2001; Pearson and Nowell, 2004; Luguet et al., 2008) present evidence that mantle pyroxenites and eclogites can contain secondary metasomatised sulphides with highly radiogenic $^{187}Os/^{188}Os$ of >2, coupled with high concentrations of Os. If the AVF melts accumulated or interacted with such secondary sulphide of metasomatic origin, one would expect a correlation between high Os concentration and high $^{187}Os/^{188}Os$, the contrary to what is generally observed. Only three of the AVF samples analysed (from Pupuke, and Wiri centres) do show slightly elevated $^{187}Os/^{188}Os$ of 0.1374-0.1377 coupled with high Os concentrations (>200 ppt; **Fig. 6.**), potentially indicative of a mantle-derived origin. Given that the latest lithospheric metasomatism event occurred 20-30 Ma ago, and based on the decay of ^{187}Re to ^{187}Os, the Os isotopic ratio of the present peridotitic lithospheric mantle would be ca. $^{187}Os/^{188}Os$ = 0.1473-0.1524 (assuming $^{187}Re/^{188}Os$ = 50 in recycled crust: Widom et al., 1999; and an original ambient mantle value of $^{187}Os/^{188}Os$ = 0.1231-0.1283, from this study). This $^{187}Os/^{188}Os$ ratio is however significantly higher than the values recorded in lithospheric mantle xenoliths from Zealandia (including dunite and wherlite samples from Ngatutura Point: $^{187}Os/^{188}Os$ = 0.1282±0.0012 ca. 80 km south of Auckland; McCoy-West et al., 2013). Although the $^{187}Os/^{188}Os$ and Os content is likely to be variable beneath North Island, New Zealand, the generally lower peridotite mantle-like $^{187}Os/^{188}Os$ values in Zealandia xenoliths suggests that the slightly elevated $^{187}Os/^{188}Os$ at high Os contents observed in the Pupuke and Wiri Mt samples are derived from a different source, which is discussed below.

5.2.2. Crustal source

The trace element signature for the Waipapa terrane crustal rock is plotted on **Figure 3** (data from Price et al., 2015), highlighting the difference in concentrations between trace elements such as Nb and Ta. Due to the different geochemical signatures of crustal and mantle rocks, previous studies have suggested that certain trace element ratios can be indicative of crustal contamination, typically showing high La/Ta (>22) and La/Nb (>1.5) ratios (e.g., Abdel-Fattah et al., 2004) and low Nb/U (<37) ratios (e.g., Hofmann et al., 1986). All AVF samples fall outside of these ranges; exhibiting low La/Ta ratios (8.56 to 13.4) and low La/Nb ratios (0.58 to 0.75), coupled with high Nb/U signatures (42.61 to 53.36), with the exception of Rangitoto sample AU59309, which shows a slightly lower Nb/U value (35.75) at low La/Ta and La/Nb values. This, coupled with the lack of correlation between the major and trace element signatures and the Os, Re concentrations and Os isotope signatures, indicates that the major and trace element geochemistry of the AVF samples are not affected by crustal contamination.

Radiogenic isotope systems can however be more sensitive to crustal input in comparison to the major and trace element compositions (e.g., Wilson, 1989). Sr-, Nd-, and Pb-isotope values for the Waipapa terrane (Price et al., 2015) are plotted on **Fig 4** in relation to the AVF samples. Binary mixing of the two signatures (Waipapa and EMII) into an AVF mantle-like source suggest that a ≤10% input from Waipapa terrane rocks and ≤ 5% input from an EMII-like source could be used to explain the spread in the Pb-isotope values (**Fig. 4 A&B**). However, this input would produce a much larger range in Sr- and Nd- isotope signatures, which is not observed within the AVF samples (**Fig. 4C&D**). This suggests that these isotope systems are also not controlled by crustal contamination and show decoupled signatures to the Os isotopic system (**Fig. 7.**). Therefore the contamination highlighted by the Os signatures must be minimal in order to not show any impacts on the trace elements or Sr-, Nd- or Pb-isotopes.

For the Pupuke samples (as discussed previously) that show slightly elevated $^{187}Os/^{188}Os$ at high Os contents, an alternative source potentially causing the contamination with sulphide-bearing olivine is ultramafic rocks of the Dun Mountain Ophiolite Belt (DMOB) (primarily serpentinised dunite and harzburgite) (e.g., Coombs et al., 1976; Sivell and McCulloch, 2000; Eccles et al., 2005). Parts of the DMOB cross directly beneath Pupuke at shallow levels (≥ 1.5 km depth, **Fig 1.C.**) making these rocks a likely melt contaminant. Although no DMOB rocks were analysed for Os isotopes or Os concentrations, O'Driscoll et al. (2012) report Os contents and isotope ratios from the Shetland ophiolite complex. The latter, although older (429 Ma), has similarities to the DMOB in formation (obduction at an arc collision zone), and lithology (serpentinised dunite and harzburgite). $^{187}Os/^{188}Os$ isotope values reported for rocks from the Shetland ophiolite complex range from 0.1204 to 0.1502 with Os concentrations of 300-8000 ppt (O'Driscoll et al., 2012). Assuming a mean value of $^{187}Os/^{188}Os$ = 0.1353 and Os = 4150 ppt, (within range of the Shetland rocks) simple binary mixing modelling (**Fig. 8**.) requires <10% input from the ultramafic rocks into our proposed ambient mantle values (of $^{187}Os/^{188}Os$ = 0.1231-0.1283 and Os = 50-200 ppt) to explain the $^{187}Os/^{188}Os$ value and Os content observed in the Pupuke samples. However only ca. 5% olivine accumulation is required to explain the higher MgO, Ni and Cr contents of these samples (**Fig. 2.**), suggesting that either the Os concentration in the contaminant needs to be ≥6000 ppt (still within the range reported by O'Driscoll et al., 2012) or Os-bearing sulphides or metal alloys will dissolve more efficiently than silicates and therefore more readily contaminate the ascending melts. Regardless, we therefore attribute samples with elevated $^{187}Os/^{188}Os$ and high Os contents to the accumulation of, or interaction with, the DMOB ultramafic rocks containing ancient subduction metasomatised domains.

The interaction between the DMOB and ascending melts cannot however explain the highly radiogenic Os isotope signatures ($^{187}Os/^{188}Os$ = 0.1623-0.5470) and low Os concentrations (<50 ppt) in most other AVF samples. These highly radiogenic $^{187}Os/^{188}Os$ isotope ratios exceed all values reported from the lithospheric mantle beneath New Zealand (<0.133: cf. McCoy-West et al., 2015; Liu et al., 2015) and carbonatitic sources (<0.6: Widom et al., 1999) as previously discussed. Continental metasediments typically show highly radiogenic $^{187}Os/^{188}Os$ values (0.165-2.323: Saal et al., 1998) and low Os contents (20 to 100 ppt: Saal et al., 1998; Widom et al., 1999), suggesting that crustal derived rocks are most likely acting as a contaminating agent to explain the high $^{187}Os/^{188}Os$ and low Os concentration in most AVF lavas.

5.3. AFC modelling

In order to quantify the amount of fractional crystallisation and crustal contamination acquired by the AVF samples, we used the combined assimilation fractional crystallisation model of DePaolo (1981) (**Fig. 8**.). Potential crustal contaminants have to be a known basement lithology, with a highly radiogenic Os isotope signature and low Os concentration. In addition, the eruptive products must have undergone low levels of fractional crystallisation (<6%; McGee et al., 2013), and the mixing proportions between contaminant and melt have to be low enough in order to have little effect on trace element values or the Sr-Nd-Pb isotope systems (e.g., **Fig.4,** discussed in section 5.2.2.). Field studies mapping the basement terranes and crustal xenoliths in lavas indicate that, in addition to DMOB rocks, both Waipapa and Murihiku terrane greywacke metasediments are found beneath the AVF (**Fig. 1.B**: e.g., Kermode, 1992). Although no Os isotopic analyses exist for these terranes specifically, similar greywacke metasediments have been studied in Australia (Saal et al., 1998) and India (Wimpenny et al., 2007), and generally have highly radiogenic $^{187}Os/^{188}Os$ of 1.2832 to 5.1968 and low Os concentrations of 40-100 ppt (Wimpenny et al., 2007). Os values similar to those exhibited by Wiri Mt AU43931 is chosen as representative of the mantle melt as it plots (along with Rangitoto sample AU59309) within the OIB field for Os concentrations, Os isotopic and Pb isotopic values (**Fig. 6. and 7.**), but does not have the analytical error that is associated with the Rangitoto sample (**Table 1**).

Modelling suggests that ≤1% bulk assimilation of greywacke metasediments with Os = 44.5 ppt and $^{187}Os/^{188}Os$ = 1.2832 (Saal et al., 1998) into a mantle melt ($^{187}Os/^{188}Os$ = 0.1283; Os = 194 ppt; Wiri Mt value from this study), coupled with ≤ 5% fractional crystallisation, can reproduce the range of observed radiogenic Os isotope signatures (and low Os contents) in the AVF samples (**Fig 8.**). Variations in mantle source signature between $^{187}Os/^{188}Os$ = 0.1 and 0.15, and Os content 50 to 200 ppt (to simulate heterogeneity in the mantle) have little impact on the percentage contribution from the contaminant, which remains at ≤ 1% for these ranges (details can be found in the supplementary material). Such low percentages of crustal contamination have little to no effect on the Sr-, Nd-, or Pb-isotope signatures as modelled in Figure 4.

5.4. Implications for magma origin, generation and ascent

The AVF $^{187}Os/^{188}Os$ and Os contents fall into the range of $^{187}Os/^{188}Os$ and Os contents from other intraplate volcanic fields (e.g., Newer Volcanic Province; Central European Volcanic Province) and oceanic islands (e.g., Canary Islands; Cook Austral Islands, Comores; Hawaiian Islands, **Fig. 6.**). Although the formation of large oceanic island volcanoes, such as the Canary or Hawaiian Islands has mainly been attributed to the presence of relatively stationary thermal anomalies in the mantle (e.g., Morgan, 1971; Bennett et al., 1996; Montelli et al., 2006), the origin of small-scale intraplate volcanism is much less clear. Models to explain the origin of small continental intraplate volcanoes or volcanic fields include local lithospheric extension (e.g., Weaver and Smith, 1989; McCoy-West et al., 2013), lithospheric delamination (e.g., Jull and Kelemen, 2001; Elkins-Tanton, 2007), or edge driven convection (e.g., King, 2006). The processes driving melt generation beneath the Auckland and other Quaternary Volcanic Fields on North Island, New Zealand is a matter of current debate, but there is a general consensus that extension-related magmatism is involved (Weaver and Smith, 1989; Smith et al., 1993; Huang et al., 1997; Cook et al., 2005; Needham et al., 2011).

As a consequence of long-lasting exposure of the lithospheric mantle to subduction metasomatism (through the influx of fluids during the Mesozoic), and plume-related magmatism during the Cretaceous, Huang et al. (1997) and Cook et al. (2005) argue that both the 'young' HIMU and EMII-type signatures observed in the volcanic field geochemistry originate in a partially melted zone in the lithospheric mantle. Conversely, McGee et al. (2013, 2015) suggest that the 'young' HIMU-type signature is linked to carbonated domains within the upper asthenosphere. Between 70-90 km depth beneath the Auckland region seismic experiments revealed a low velocity zone, which is interpreted to represent regions of partial melt within the mantle caused by crustal extension following rollback of Pacific Plate subducting beneath the North Island of New Zealand (Horspool et al., 2006). Beneath South Island New Zealand, the base of the lithosphere has been estimated to lie at ca. 100 km (e.g., Molnar et al., 1999), which would place this proposed partially melted zone within the lithospheric mantle. However, because this lithospheric thickness of ca. 100 km has been determined on the Pacific Plate (Molnar et al., 1999), there is some uncertainty as to how representative this thickness is of the Auckland area, which sits on the Indo-Australian Plate (e.g., Stratford and Stern, 2004). Regardless, regional lithospheric extension events may sufficiently thin the lower lithosphere to facilitate regional influx of hot MORB-like asthenospheric mantle and subsequent partial melting of the uppermost asthenospheric and lithospheric mantle via decompression and heating.

As previously outlined, the geochemical composition of lavas from Rangitoto is consistent with their derivation from the metasomatised lithosphere (e.g., Needham et al., 2011; McGee et al., 2015). Accordingly the lowest $^{187}Os/^{188}Os$ of 0.123 in lavas from Rangitoto could be representative of the $^{187}Os/^{188}Os$ of the lithospheric mantle beneath the Auckland Volcanic Field. This would be consistent with the unradiogenic $^{187}Os/^{188}Os$ values of peridotite xenoliths from Zealandia (ca. 0.12-0.13; McCoy-West et al., 2013; Liu et al., 2015), however the error associated with this measurement mean constraining an accurate value is problematic. Alternatively, the low-silica lavas from Wiri Mt. show $^{187}Os/^{188}Os$ of 0.128 similar to the Os isotopic composition of peridotite xenoliths in the 1.68±0.15 Ma intraplate Ngatutura Volcanics (e.g., Briggs et al., 1994). Based on the major and trace element and Sr-, Nd-, and Pb-isotopic composition in lavas from Wiri, McGee et al. (2013) proposed a predominately garnet-bearing peridotitic source for these lavas (± carbonate; McGee et al., 2015). However, because Wiri is located above the DMOB, we cannot be sure that the $^{187}Os/^{188}Os$ in these lavas are representative of the present day mantle beneath the AVF, or reflect minor contamination from the DMOB.

Regardless of mantle melt generation complexities beneath the AVF most of our new Os isotope data are more radiogenic than typical mantle values, suggesting that the ascending melts assimilated radiogenic $^{187}Os/^{188}Os$ isotope signatures from the metasedimentary Murihiku or Waipapa terranes beneath Auckland. The exceptions to this are the olivine-bearing samples from Pupuke (and potentially Wiri Mt.), indicating the significant assimilation of sulphide-bearing olivine from the subsurface DMOB (Eccles et al., 2005). Of note is that both Pupuke and Wiri Mt. are located near or on faults separating the DMOB from adjacent rocks of the Murihiku Terrane (c.f. **Fig. 1.C**; Eccles et al., 2005), which suggests olivine accumulation beneath the AVF could occur while magma ascends along faults cutting or bounding the ultramafic rocks of the DMOB (Eccles et al., 2005). Generally terrane boundaries represent crustal (and potentially lithospheric) weak-zones, which are commonly associated with shear zones and intense faulting (e.g., Smith and Mosley, 1993). Because all three main Quaternary intraplate volcanic field in the North Island of New Zealand are roughly spatially correlated to the position of the DMOB, and the crustal-scale Taranaki fault (e.g., Giba et al., 2010; **Fig. 1.C.**), we suggest that feeder melts may exploit the faults and shear-zone along this major terrane boundary to ascend to the surface (**Fig. 9**.) rapidly rather than forming large crustal magma-reservoirs. Even though ascent may be rapid the high solubility of sulphides in basaltic silicate melt provides an effective way of contaminating rising melts with crustal sulphides.

6. Conclusions

In summary, we show that most of the AVF samples studied show Os isotopic compositions higher than typical mantle values (≥0.13) and Os contents lower than 50 ppt. Conversely, a minority of samples (from Pupuke, Wiri and Rangitoto) show unradiogenic Os isotopic ratios coupled with high (>150 ppt) Os concentrations. Neither of these signatures shows any obvious correlation to the tracers of mantle sources, implying that they are not primarily caused by source heterogeneity, nor do they show co-variance with elements dominant in olivine or pyroxene minerals, suggesting that they are not primarily caused by fractional crystallisation. Contrary to previous interpretations our results suggest that AVF melts do interact with continental crust during ascent leading to contamination signatures. From these two signatures two differing sources of crustal contamination are identified; 1) metasediments (e.g., Waipapa and Murihiku Terranes) which contain highly radiogenic Os coupled with minimal Os concentrations and 2) xenocrystic olivine hosted sulphides (from the

DMOB) with unradiogenic mantle-like $^{187}Os/^{188}Os$ and high Os contents. Less than 1% contamination from the crust coupled with ≤5% fractional crystallisation, and ≤10% contamination from xenocrystic olivine-bearing sulphide is sufficient to reproduce the Os contents and isotopic compositions observed in the AVF rocks.

The presence of mantle-derived sulphide hosted in olivines in eruptive products from centres located above the DMOB strongly argues for their derivation from crustal levels. We therefore propose that, although there is no evidence for long residence time of melts within the crust, crustal contamination does occur beneath most of the AVF. However, the low amount of crustal contamination is insufficient to affect the primitive geochemical and Sr-, Nd- and Pb-isotopic signatures of the AVF products.

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Figure Captions

Figure 1. *Schematic map of the Auckland Volcanic Field (AVF). (A) Location of the AVF within the North Island, New Zealand, inset shows the location of New Zealand in relation to the east coast of Australia. (B) DEM map and location of the volcanic centres in the AVF, highlighted are those sampled for this study, shaded zones show the proposed terranes at 1.5 km depth (from Eccles et al., 2005). The green dashed line (A&B) indicates the Dun Mountain Ophiolite Belt identified by the Junction Magnetic Anomaly (JMA) (Eccles et al., 2005). (C) Schematic diagram adapted from Kermode (1992) and Eccles et al. (2005) outlining the basement geology beneath the AVF: cross section A-A' is shown in diagram A.*

Figure 2. *Diagram panels showing major elements vs. MgO (wt.%) for studied samples. Grey symbols represent previously published data from the SAVF, with squares denoting Group A and crosses denoting Group B samples, as assigned by Cook et al. (2005); and circles showing data from Briggs et al. (1994), which were ungrouped. Also shown in the SiO_2 vs. MgO panel is the impact of mixing olivine into the samples, showing that the addition of 5% Dun Mountain derived olivine (values from Sano and Kimura, 2007) could produce the Pupuke sample signatures.*

Figure 3. *Diagram showing representative primitive mantle-normalised multi-element compositions to present the AVF trace element data range (McGee et al., 2013). The end members are exemplified by Purchas Hill and Rangitoto 2. Wiri Mt. samples show intermediate trace element ratios. The grey field marks the range from the AVF, black line shows a typical OIB-type signature (OIB values from Sun and McDonough, 1989, and normalisation values from McDonough and Sun, 1995), and blue dashed line show the composition of the Waipapa terrane metasediments (from Price et al., 2015).*

Figure 4. *$^{206}Pb/^{204}Pb$ vs. (A) $^{207}Pb/^{204}Pb$, (B) $^{208}Pb/^{204}Pb$, (C) $^{87}Sr/^{86}Sr$, and D) $^{143}Nd/^{144}Nd$ for all samples from the Auckland Volcanic Field (this study and McGee et al., 2013), and South Auckland Volcanic Field (Cook et al., 2005).The inset shows the mantle reservoir end members from Zindler and Hart (1986): Enriched Mantle (EMI and EMII), Pacific MORB Mantle, and HIMU. Values for Northland from Huang et al. (2000), for Otago from Timm et al. (2010), for Banks Peninsular from Timm et al. (2009), and for Lookout Volcanics from McCoy-West et al. (2010), for Waipapa metasediments from Price et al. (2015). Modelling lines show binary mixing of Waipapa metasediments (blue) and lithospheric mantle (EMII; green) into AVF mantle-like source, with the shaded area showing the potential signatures caused by these inputs.*

Figure 5. *Os and Re concentrations versus MgO (in wt.%), Ni, Cu and Zr (all in ppm) contents for samples analysed in this study. Symbols are as in **Figure 2**. Note that only 5 samples were analysed by this study for major and trace elements. Previous studies (McGee et al., 2013) did not present Cu data for these samples, therefore a reduced number of samples are plotted in Cu vs. Os and Re plots.*

Figure 6. *$^{187}Os/^{188}Os$ vs Os (ppt) for all samples from the AVF. Also shown in grey symbols are global OIB values for Pacific regions: Austral-Cook (Hauri and Hart, 1993; Reisberg et al., 1993; Hanyu et al., 2011); Samoa (Jackson and Shirey, 2011); Newer Volcanic Province, Australia (NVP; McBride et al., 2001); Louisville Seamount Chain (Tejada et al., 2015), and for the Atlantic regions: the Canary Islands (Marcantonio et al., 1995; Widom et al., 1999; Day et al., 2009); St Helena and Comores (both from Reisberg et al., 1993); Cape Verde Islands (Escrig et al., 2005); Azores (Widom and Shirey, 1996; Larrea et al., 2014); Central European Volcanic Province (CEVP; Jung et al., 2011). Error bars are shown for one Rangitoto sample, for all other analyses the errors are smaller than the symbol size.*

Figure 7. *Diagram after Day (2013), to show mixing relationships for various potential contaminants in (A)$^{206}Pb/^{204}Pb$, (B) $^{143}Nd/^{144}Nd$, and (C) $^{87}Sr/^{86}Sr$ vs. $^{187}Os/^{188}Os$ isotope space. Data values for MORB and OIB from Widom et al. (1999), Hofmann (1997), and Day et al. (2010); pelagic sediments from Roy-Barman*

and Allègre (1995) and Eisele et al. (2002); carbonatite from Widom et al. (1999) and Escrig et al. (2005); young HIMU from Day et al. (2009); and continental crust from Saal et al. (1998) and Widom et al. (1999).

Figure 8. *Whole-rock $^{187}Os/^{188}Os$ vs Os concentration (ppt) for AVF samples with proposed methods of signature formation. Sulphide assimilation is modelled (green) using binary mixing from AVF mantle values with values measured for sulphides found in dunite within Shetland Ophiolite complex ($^{187}Os/^{188}Os$ = 0.1353, Os = 4150 ppt: O'Driscoll et al., 2012). Fractional crystallisation is modelled (blue) using the Rayleigh equation for samples from 50 to 7 ppt, showing that it requires ≤10% fractional crystallisation to reduce the Os concentrations. Crustal assimilation is modelled (orange) through binary mixing of post 10% fractional crystallisation of the mantle-derived melt ($^{187}Os/^{188}Os$ = 0.1283, Os = 7 ppt) with <10 % crust, with values reflective of greywacke ($^{187}Os/^{188}Os$ = 1.283, Os = 44.5 ppt: Saal et al., 1998). Assimilation fractional crystallisation (AFC) is modelled (after DePaolo, 1981) with D_{Os}= 20 (Widom et al., 1999), r (rate of fractional crystallisation) = 0.95, for mantle values ($^{187}Os/^{188}Os$ = 0.1283, Os = 194 ppt (Wiri sample) with crustal values of greywacke (black line, $^{187}Os/^{188}Os$ = 1.283, Os = 44.5 ppt; Saal et al., 1998), and carbonatite (grey line, $^{187}Os/^{188}Os$ = 0.6, Os = 15 ppt; from Widom et al., 1999 and Escrig et al., 2005).*

Figure 9. *Schematic model to illustrate the proposed magma ascent pathways for the AVF eruptions. Melts are derived from a heterogeneous source, including ambient peridotite mantle containing HIMU-like carbonated peridotite veins (McGee et al., 2015) at a depth of >80 km, and a subduction metasomatised lithosphere at <80 km depth, all of which give the ascending magma its Sr-, Nd-, Pb-isotopic and major and trace element signatures (McGee et al., 2013). Minimal fractionation occurs on ascent, efficiently reducing the Os concentration from mantle values, followed by preferential assimilation of olivines from the Dun Mountain Ophiolite Belt (DMOB) as xenocrystic material causing increase in Os concentration, and finally minor crustal contamination of magmas causing the radiogenic isotope signatures. A crustal depth of 20-30 km and the positions of the low velocity melt zone region are from tomography by Horspool et al. (2006), and upper cross section is adapted from Seebeck et al. (2014).*

Table Caption

Table 1. *Selected geochemical data for AVF centres, * denotes data from lavas previously analysed by McGee et al. (2013). Suffixes 'i, ii, iii' etc denote duplicate analyses from the same sample but with a different digestion, (2) denotes duplicate analysis of the same sample and same digestion.*

Supplementary Material

SM1 – All major and trace element, and isotopic values for samples analysed used in this study.

SM2 – All standard data for analysis of major, trace and isotopes.

- **SM2.1**. Major elements by XRF.
- **SM2.2**. Trace elements by solution ICP-MS.
- **SM2.3.** Pb isotope analysis by multi-collector ICP-MS.
- **SM2.4.** Os isotope analysis by TIMS.
- **SM2.5.** Re isotope analysis by sector field ICP-MS.

SM3 – Modelling parameters for the contamination effects on other isotope systems

- **SM3.1.** Values used for modelling
- **SM3.2.** Calculations for $^{206}Pb/^{204}Pb$ vs $^{87}Sr/^{86}Sr$
- **SM3.3.** Calculations for $^{206}Pb/^{204}Pb$ vs $^{143}Nd/^{144}Nd$
- **SM3.4.** Calculations for $^{206}Pb/^{204}Pb$ vs $^{208}Pb/^{204}Pb$
- **SM3.5.** Calculations for $^{206}Pb/^{204}Pb$ vs $^{207}Pb/^{204}Pb$

SM4 – Modelling parameters for AFC calculations

- **SM4.1.** Optimum values used for plotting figure 8.
- **SM4.2.** Variations in mantle source signature.
- **SM4.3.** Variations in r value.