The Role of Late Sulfide Saturation in the Formation of a Cu- and Au-rich Magma: Insights from the Platinum Group Element Geochemistry of Niuatahi–Motutahi Lavas, Tonga Rear Arc

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ABSTRACT

Magmas enriched in Cu and Au are likely to be the most prospective for magmatic–hydrothermal deposits of these metals. However, the mechanism that leads to the formation of metal-rich magmas is not well constrained. We report major, trace and platinum group element (PGE) data for the Niuatahi–Motutahi lavas, Tonga rear arc, with the aim of studying their petrogenesis with special emphasis on the evolution of chalcophile elements during magmatic differentiation. Major and trace element contents, including S and Cl, were also measured in glasses, phenocrysts and melt inclusions to complement the whole-rock data. The Niuatahi–Motutahi lavas are associated with Cu and Au mineralization and therefore provide an opportunity to investigate the characteristics of an ore-associated magmatic system. They show a wide compositional variation from basalts to dacites with MgO contents that vary between 14 and 1 wt %. The dacites can be subdivided into high-K and low-K dacites. Geochemical modeling and their mineralogy suggest that the low-K dacites are comagmatic with the basalts and evolved by fractional crystallization. Copper, Au and Pd behave incompatibly in the basalts and andesitic glasses, whereas they become compatible in the low-K dacite. In contrast, Pt, Rh, Ru and Ir are moderately compatible in the basalts and correlate negatively with MgO, but become strongly compatible in the dacites. The Cu, Au and PGE trends can be explained by fractional crystallization of a Pt-rich alloy in the basalts and andesitic glasses, followed by sulfide saturation in the low-K dacites. The high-K dacites may have evolved from a slightly different magma source; however, their chalcophile elements fractionated in a similar manner. Chlorine and S data for melt inclusions and glasses from the basalts and dacites suggest that water-rich volatile saturation occurred during evolution of the dacites. The Niuatahi–Motutahi dacites were enriched in Cu from 80 to 200 ppm and in Au from <1 to 7 ppb by fractional crystallization as the magma evolved from basalt through andesite to dacite. We suggest that late sulfide saturation allowed Cu and Au to become enriched by a factor of two in the Niuatahi–Motutahi dacites before volatile saturation and that this played an important role in the formation of the Cu- and Au-rich mineralization. This sulfide saturation history contrasts with that of the Honshu arc volcanic rocks, Japan, where sulfide saturation occurred early. The Honshu arc volcanic rocks are not associated with porphyry Cu or Au deposits, which we suggest is due to loss of most of the Cu and Au to an early immiscible sulfide phase.
Key words: Cu-rich magma genesis; Au-rich magma genesis; magmatic–hydrothermal deposit; platinum group element; sulfide saturation; volatile exsolution

INTRODUCTION

Magmatic–hydrothermal ore deposits such as porphyry, skarn and high-sulfidation epithermal deposits are spatially and temporally related to intermediate to felsic arc magmas, which are considered to be the dominant source of ore metals (Robb, 2005). However, most arc magmas are not associated with economic ore deposits. The obvious question is: ‘Why are some arc magmatic systems ore-bearing whereas others are barren?’ Is it because some arc-related magmas are initially enriched in the ore metals such as Cu and Au and therefore more likely to form a deposit (e.g. Mungall, 2002; Sun et al., 2011), or is the magma differentiation process more critical than the initial ore metal concentration (e.g. Richards, 2003; Jenner et al., 2010; Park et al., 2013a)?

The ore metals in a magmatic–hydrothermal ore deposit are carried to the site of deposition by a volatile phase exsolved from a magma chamber (Hedenquist & Lowenstern, 1994; Candela, 1997; Williams-Jones & Heinrich, 2005; Mavrogenes et al., 2010). During this process, competition for ore metals between the volatile phase and crystallizing minerals during magma evolution is a primary factor in the formation of a metal-rich volatile phase, assuming that the magmatic vapor has an appropriate composition and that precipitation of the metals occurs in a confined area (Candela, 1997). In sulfide-saturated magmas an immiscible sulfide melt is the critical phase competing for Cu and Au with the exsolving volatile phase owing to the high partition coefficients of these elements between sulfide and silicate melts. If a magma experienced prolonged sulfide melt segregation before volatile saturation, the magma is unlikely to form a magmatic–hydrothermal Cu–Au deposit, as most of the budget of chalcophile elements would be held in sulfide phases dispersed in the solidified magma chamber and would not be available to partition into the volatile phase. The Boggy Plain zoned pluton, Australia provides an example of a barren magmatic system in which >87% of the Cu, and possibly more Au and platinum group elements (PGE: Pd, Pt, Rh, Ru and Ir), is held in dispersed Cu-rich sulfide blebs trapped in silicate minerals (Park et al., 2013b). Therefore, investigation of the sulfide saturation history in evolving magmas provides important information for evaluating the potential of the magmatic system to form a magmatic–hydrothermal Cu–Au ore deposit. Recent studies on the PGE geochemistry of intermediate–felsic rocks (Park et al., 2013a, 2013b) have shown that the variation of these elements, along with Cu and Au, can be used as a sensitive indicator of sulfide saturation in an evolving magmatic system. The abundances of all PGE, and the Pd/Cu ratio of the melt, decrease significantly when an immiscible sulfide melt starts to segregate from a magma.

The lavas from the Niuatahi–Motutahi volcano (Niuatahi and Motutahi are Tongan names for the caldera and central cone, respectively) from the Tonga rear arc are submarine volcanic rocks that erupted ~1700 m below sea level. Copper- and Au-rich native sulfur mineralization occurs in association with the Niuatahi–Motutahi lavas and the metals and sulfur are considered to have originated from the Niuatahi–Motutahi magma (Kim et al., 2011). Therefore, the Niuatahi–Motutahi lavas and native sulfur provide an example of metal transport by a volatile phase from a magmatic system below to a hydrothermal system above. We present the results of whole-rock major and trace element analyses, including PGE, Au and Re data, for the Niuatahi–Motutahi lavas. Whole-rock, mineral, glass and melt inclusion analyses are used to investigate the relative timing of sulfide and volatile saturation and the behavior of chalcophile elements during sulfide- and volatile-saturated magmatic differentiation. We use these data to show that late sulfide saturation in the Niuatahi–Motutahi lavas resulted in the magmas being enriched in Cu and Au at the time of volatile exsolution, which led to the formation of Cu–Au-rich native sulfur mineralization.

GEOLOGICAL SETTING AND SAMPLE LOCATION

The Niuatahi–Motutahi caldera, also known as Volcano O (Arculus, 2005) and MTJ-1 (Kim et al., 2009), is a rear arc volcanic complex located in the NE Lau Basin, SW Pacific Ocean (Fig. 1). The NE Lau Basin lies within a crustal extension zone between the Tonga arc and the NE Lau Basin spreading center (NELSC) (Zellmer & Taylor, 2001). Owing to its unique tectonic setting, the NE Lau Basin hosts various types of submarine volcanism produced by a combination of subduction-associated water-fluxed melting and crustal extension (Resing et al., 2011, and references therein). The geochemical features of the lavas from the NE Lau Basin vary from mid-ocean ridge basalt (MORB)-like (e.g. Mangatolu Triple Junction) to arc-like (e.g. Fonualei spreading center) (Keller et al., 2008).

Submarine lava samples used in this study were collected from the Niuatahi–Motutahi caldera and a separate volcanic region located ~5 km SE of the caldera during the Korea Deep Ocean Study (KODOS) H-06 cruise (Fig. 1c). They were dredged at water depths that range from 1300 to 1900 m. Strong hydrothermal signals detected near the cone of the caldera and sparse sediment cover (Kim et al., 2009) indicate that the volcano has been active until recently. Native sulfur...
mineralization occurs in association with dacite in the volcanic cone of the active caldera (Fig. 1c). It is a potential target for the Korea Institute of Ocean Science and Technology for submarine mineral exploration. The mineralization contains about 1.8% of Cu, 1.7 g t\(^{-1}\) of Au and 0.9 g t\(^{-1}\) of Ag (Kim et al., 2011). The occurrence of numerous poorly crystallized covellite inclusions in the sulfur matrix and the low whole-rock sulfur isotopic composition (\(\delta^{34}S = -7.5\%o\) to \(-8.2\%o\)) indicate that the metal-bearing native sulfur is a condensate produced from a sulfur-rich magmatic vapor exsolved by the Niuatahi–Motutahi magma (Kim et al., 2011).

**ANALYTICAL TECHNIQUES**

**Electron microprobe analyses**

The major element compositions of silicate, oxide and sulfide minerals, melt inclusions and glasses were...
measured by a CAMECA EX100 electron microprobe at the Australian National University (ANU), operated at 15 kV with a 20 nA beam current. A beam size of 1 µm was used for mineral analyses but the beam was defocused to 5 µm and 10 µm for analyses of melt inclusions and glasses. The CAMECA set of synthetic and natural minerals and USGS VG-2 glass were used as standards. The 2σ analytical error, obtained from replicate measurements \((n = 13)\) of the USGS VG-2 glass standard, was 0.7% for SiO₂, 1.1% for MgO and CaO, 1.5% for TiO₂, 0.8% for Al₂O₃ and FeO, 6.6% for Na₂O, and 19% for P₂O₅ and MnO, with all errors expressed as a percentage of the element concentration (Supplementary Data A; supplementary data are available for downloading at http://www.petrology.oxfordjournals.org). Detection limits for Cl and S were \(~200\) ppm and the analytical 2σ errors were 11% and 14% respectively.

**LA-ICP-MS analyses**

Trace element concentrations in glasses and a sulfide were measured by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the ANU. The system is composed of a Lambda Physik COMPex 110 excimer laser \((\lambda = 193\) nm), ANU-designed HeEx ablation cell, and an Agilent 7700 ICP-MS system. The analyses were carried out using spot sizes that varied between 81 and 105 µm and a laser pulse rate of 5 Hz. Each analysis consists of 25 s of background measurement and 40 s of sample ablation. NIST 610 glass (Jochum et al., 2011) was used as the primary standard for trace elements and CANMET po727 FeS (Fonseca, 2007) was used for the PGE. To correct for yield differences between standards and unknown samples, 43Ca and 57Fe, measured by electron microprobe, were used for the trace element and PGE data reduction, respectively. Gold contents of the microcrystalline groundmass of the rocks and glasses were measured using NIST 610 glass with 48Si as the internal standard.

Data reduction was performed using the Iolite software package (Paton et al., 2011) for trace elements, and an in-house Excel spreadsheet for the PGE using the relationship described by Longerich et al. (1996) and Sylvester & Eggins (1997). The isotopes used to determine the concentrations are as follows: 28Si, 31P, 43Ca, 46Sc, 49Ti, 51V, 53Cr, 56Mn, 57Fe, 59Co, 60Ni, 61Ni, 65Cu, 66Zn, 85Rb, 89Y, 90Zr, 92Nb, 108Pd, 111Cd, 133Cs, 137Ba, 139La, 140Ce, 141Pr, 146Nd, 147Sm, 153Eu, 157Gd, 159 Tb, 163Dy, 165Ho, 166Er, 169Tm, 172Yb, 175Lu, 178Hf, 181Ta, 195Pt, 197Au, 208Pb, 232Th, 238U. For the PGE analysis isobaric interferences by metal oxides and metal argides were corrected according to the method described by Park et al. (2012a) using sphalerite and R33 zinc. The correction assumes that blank-corrected signals of 106Pd in sphalerite and R33 zinc result from argide or oxide interferences. The isobaric interferences by 68Zn, 40Ar⁺, and 92Zr⁶⁺ at 108Pd were corrected and the corrections were 30–50% for glasses and ~20% for sulfides. The detection limits for Pd, Pt and Au were 3 ppb, 6 ppb and 1–2 ppb respectively. Multiple analyses of BCR-2 g were carried out to check the accuracy and precision of the analyses, and the results agree with reported values (Supplementary Data A).

**Whole-rock major and trace element analyses**

Prior to whole-rock analysis samples were crushed, sonicated in distilled water and dried. Crushed fragments were hand-picked under a microscope to exclude altered particles. Before final grinding, samples were leached in 1 M HCl for 10 min at room temperature. Major and trace elements for 12 samples were determined by a combination of inductively coupled plasma atomic emission spectrometry (ICP-AES) and ICP-MS analysis (4LithoResearch) by Activation Laboratories, Canada. Samples were prepared and analyzed in a batch system. Each batch contains a method reagent blank, certified reference material and 17% replicates \((n = 4)\). Samples were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The melt was immediately poured into a solution of 5% nitric acid containing an internal standard, and mixed continuously until completely dissolved \((~30\) min). The samples were analyzed for major oxides and selected trace elements on a combination simultaneous–sequential ICP-AES (Thermo Jarrell–Ash ENVIRO II) and ICP-MS (Perkin–Elmer ELAN 6000) system. Calibration was performed using seven prepared USGS and CANMET certified reference materials. One of the seven standards was used during the analysis for every group of 10 samples. The uncertainty on the external reproducibility of the analyses was within ±5 relative %. Major and trace element data for an additional three samples were measured by X-ray fluorescence (XRF) (Bruker S8 Tiger) and ferrous iron concentrations for five samples were measured by the titration method at Geoscience Australia.

**Whole-rock PGE and RE analyses**

Whole-rock PGE and Re concentrations in the Niutahiti–Motutahi lavas were measured using the Ni-sulfide fire assay-isotope dilution method described by Park et al. (2012b). Briefly, ~300 g of fresh rock fragments collected from each sample were ground to a fine powder in an agate mill. A 5 g split of this powder was thoroughly mixed with 0.5 g of Ni, 0.25 g of S and 5 g of sodium borax, and an enriched PGE spike solution \((99Ru, 105Pd, 186Re, 191Ir\) and 199Pt) was added to the mixture. The spiked powder was dried at 100°C for 60 min and fused in a preheated open furnace at 1100°C for 30 min. Nitrogen gas was introduced into the furnace at a flow rate of ~0.03 m³ min⁻¹ and a second outside crucible, containing ~0.1 g of flour, was used to provide reducing conditions during fusion. After quenching, Ni-sulfide beads were collected and dissolved in 6 M HCl. The solution was then filtered through a Millipore filter paper (0.45 µm cellulose membrane) to collect the PGE-bearing minerals. The
filter paper containing the PGE minerals was then digested in aqua regia. After complete digestion, the solutions were dried down to ~100 µl and diluted with 2% HNO₃.

An Agilent 7700 x quadrupole ICP-MS system at the ANU was used to measure the PGE and Re isotopes. The sensitivities in each analysis were 2.4 to 3.4 x 10⁷ c.p.s. ppb⁻¹ for masses 89, 140 and 205. Potential molecular interferences on the analyzed isotopes by Ni, Cu, Zn, Co, Hf, Mo, Zr and Ta argides or oxides were monitored and the effects of the interferences were subtracted using measured oxide and argide production rates. Argide production rates were 0.003–0.006% and oxide production rates 0.2–0.3%. The interference correction is <0.2% for all PGE and Re, except for Ru for which the correction is 2–13%. Concentrations of Ir, Ru, Pt, Pd and Re were determined by isotope dilution using the ¹⁹¹Ir/¹⁹³Ir, ¹⁹⁵Pt/¹⁹⁴Pt, ¹⁰⁵Pd/¹⁰⁶Pd and ¹⁸⁵Re/¹⁸⁷Re ratios, respectively. Concentrations of Rh were obtained using the method described by Meisel et al. (2003) and Park et al. (2012b), which uses the count rates of ¹⁰³Rh and ¹⁰⁶Pd, assuming that the loss of Rh during the analytical procedure was similar to the loss of Pd.

Average procedural blanks determined by sample-free analyses (n = 5) were 0.8 ± 0.1 ppt for Ir, 2.1 ± 0.4 ppt for Ru, 0.8 ± 0.2 ppt for Pt, 16 ± 9 ppt for Pd, 17 ± 4 ppt for Pd, and 10 ± 2 ppt for Re. The method detection limits (MDL), taken to be three standard deviations of the procedural blanks after subtraction of average procedural blank values, were 0.3 ppt for Ir, 1.2 ppt for Ru, 0.5 ppt for Rh, 26 ppt for Pt, 11 ppt for Pd, and 5 ppt for Re. To assess the accuracy and precision of the analyses we performed replicate analyses of the reference material TDB-1. The reproducibilities for Pd and Pt were 2% and 6% respectively, and 9–14% for the other PGE and Re. The reported values are consistent with those of Peucker-Ehrenbrink et al. (2003) and Meisel & Moser (2004) to within 2σ error (Supplementary Data A) although our Re value of ~0.72 ppb is slightly lower than the ~1 ppb reported by Ishikawa et al. (2014).

RESULTS

Petrography and mineralogy of the Niuatahi–Motutahi lavas

The lavas from the volcanic complex SE of the Niuatahi–Motutahi caldera are olivine- and clinopyroxene-bearing basalts. They are composed of a microcrystalline groundmass with varying amounts of olivine and clinopyroxene phenocrysts (~20–40 modal %), and minor plagioclase and Cr spinel (Fig. 2b; see Supplementary Data A for mineral compositions). Andesitic vesicle-filling glasses occur in one sample (Fig. 2f); these are interpreted to form when residual melt flows into early formed vesicles (Smith, 1967; Upton & Wadsworth, 1971). Upton & Wadsworth (1971) suggested that residual melt is ‘segregated into the partly vacated vesicle cavities by a process of suction towards low-pressure sites, and there congealed as a glass’. The olivine and clinopyroxene crystals are euhedral to subhedral and range in size from 300 µm to 2 mm. The Fo contents of the cores of olivine phenocrysts vary between Fo₉₀ and Fo₉₉ with variations within a single sample typically <5 mol %. Olivine crystals are rarely zoned, but some large crystals (>800 µm) show normal zoning with their cores having Fo contents that are two or three units higher than their rims. The high-Fo olivines (Fo₈₆–₉₉) would have been in equilibrium with parental magmas containing about 8–11 wt % MgO, assuming an Mg–Fe partition coefficient (k₃) of 0.3 ± 0.04. This suggests that some basalt samples with high MgO contents (~12 wt %) resulted from
accumulation of olivine phenocrysts. Clinopyroxene phenocrysts have Mg# of 80–88. Like olivine, the Mg# variation in clinopyroxene within single samples is <5 mol %. Cr spinels mostly occur as 5–50 μm sized inclusions within olivine or clinopyroxene and have Cr# [Cr# = 100X_{Cr}/(X_{Cr} + X_{Al})] ranging from 72 to 84, except for one sample, DG26-3, which has relatively low Cr# ranging from 55 to 62.

Whole-rock major and trace element geochemistry
Whole-rock analyses of the Niuatahi–Motutahi lavas plot in the fields of basalt, basaltic andesite and dacite in a total alkalis–silica diagram (Fig. 4; Table 1). The vesicle-filling glass from the basalt is andesitic and the dacite glasses are identical in composition to their host rocks (Fig. 4). Most samples plot on the boundary between medium- and low-K series (island arc tholeiite series) on a K2O vs silica diagram, and follow a trend similar to that of the other Tonga arc lavas (Fig. 4). The tholeiitic index (THI; Zimmer et al., 2010), calculated using the Fe contents of Niuatahi–Motutahi basalts (7 wt % < MgO < 9 wt %) and the vesicle-filling glasses (3 wt % < MgO < 5 wt %), is 0.94, which indicates a moderate Fe depletion trend. This suggests that the lavas are slightly more calc-alkaline than tholeiitic. This value is
similar to that of arc lavas (THI < 1; Zimmer et al., 2010) and is distinct from those of typical back-arc basin lavas (1.2 < THI < 1.8; Zimmer et al., 2010).

Major element variations plotted against the MgO content of the lavas are consistent with fractional crystallization trends of transitional calc-alkaline magmas (Fig. 5; Table 1). The high MgO contents (>12 wt % MgO) of two basalt samples can be attributed to olivine accumulation (Fig. 5a). The decrease in Al₂O₃ and CaO below ~5 wt % MgO reflects plagioclase becoming the dominant crystallizing mineral. FeO and TiO₂ decrease significantly below 3 wt % MgO, suggesting the onset of Ti-bearing magnetite crystallization (Fig. 5d and f). Variations in trace elements correspond to those of the major elements (Fig. 6; Table 1). The continuous decrease of Sc reflects fractional crystallization of clinopyroxene from the basalts and dacites. Vanadium and Sr reach their maximum abundances at ~5 wt % MgO and progressively decrease in dacite, corresponding to the onset of magnetite and plagioclase crystallization, respectively. The major and trace element variations are consistent with the occurrence and abundance of the phenocryst mineral assemblages. However, it should be noted that three samples (DG17-4, DG17-1, DG20-1; shown as light-coloured diamonds in Fig. 4) have higher K₂O than the majority of the dacites (Fig. 4b). They are also enriched in large ion lithophile elements [LILE; Ba, Rb, Cs, light rare earth elements (LREE)] and some refractory elements such as Hf, Zr and Ta (Fig. 6 and Table 1) compared with the other dacites. Therefore, the Niuatahi–Motutahi dacites can be subdivided into two

Fig. 3. Phase relations in the Cu–Fe–S system at 1000 °C, modified from Kullerud et al. (1966), for a sulfide bleb from the Niuatahi–Motutahi dacite. The composition of quenched sulfide melt and MSS, ISS and bornite exsolved from the melt from the experimental study of Ebel & Naldrett (1997) are shown for comparison. L, liquid; bns, bornite solid solution; poss, pyrrhotite solid solution; mss, monosulfide solid solution; iss, intermediate solid solution.

Fig. 4. (a, b) Total alkalis vs silica (TAS) diagram and K₂O vs silica diagram (after Le Maitre et al., 1984). Open and filled diamonds represent dacite glasses and whole-rock dacite, respectively. The grey field represents the compositions of Tonga arc volcanic rocks (GEOROC database http://www.georoc.mpch-mainz.gwdg.de).
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<th>Rock type: Basalt</th>
<th>Vesicle-filling glass</th>
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**Table 1: Major and trace element compositions of the Niutah–Motutahi lavas**

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<th>Major element</th>
<th>S</th>
<th>TiO₂</th>
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<th>Fe₂O₃</th>
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**Notes:**

- n.d. = not determined
- Values are given in weight percent (wt%) for major elements and in parts per million (ppm) for trace elements.


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<tr>
<th>Rock type</th>
<th>Basalt Vesicle-filling glass</th>
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Copper, gold and platinum group element geochemistry

The Niuatahi–Motutahi basalts contain 80–120 ppm Cu, 5.4–6.1 Au ppb, 6.72–8.25 ppb Pd, 1.18–4.73 ppb Pt, 0.03–0.32 ppb Rh, 0.027–0.089 ppb Ru, 0.016–0.055 ppb Ir and 0.28–0.32 ppb Re (Fig. 8; Table 2). The andesitic vesicle-filling glasses are more enriched in Cu, Au and Pd than the basalts, with 185–234 ppm of Cu, 4.7–6.9 ppb Au and 10–20 ppb of Pd. The uncertainty introduced by the correction was taken into account when propagating the uncertainty in the LA-ICP-MS Pd and Au values. Platinum and Ir-group platinum group element (IPGE) concentrations are positively correlated with MgO in the basalt, indicating that a Pt- and IPGE-rich phase crystallized along with the early formed olivine and clinopyroxene. On the other hand, Cu, Au and Pd increase with decreasing MgO and this trend continues into the andesitic vesicle-filling glasses (Fig. 8), indicating that these elements are behaving as incompatible elements during the early to middle stages of fractionation.

The Niuatahi–Motutahi dacites contain 80–201 ppm of Cu, <1–6.9 ppb of Au, 0.22–3.03 ppb of Pd, 0.05–0.52 ppb of Pt and <0.0006–0.0033 ppb of Rh. Ruthenium and Ir concentrations of most samples are below the method detection limit of 1.2 ppt for Ru and 0.3 ppt for Ir, although some samples contain Ru and Ir concentrations of up to 0.032 ppb and 0.002 ppb, respectively (Tables 1 and 2). The Re contents of 0.51–0.70 ppb are significantly higher than those of the basalts. The abundances of Cu, Au, Pd, Pt and Rh decrease with decreasing MgO (Fig. 8), which shows that they behave compatibly during dacite differentiation. Rhenium abundance in the dacites ranges from 0.51 to 0.70 ppb and shows no clear correlation with increasing fractional crystallization. The Cu, Au and PGE data of the high-K and low-K dacites form a continuous trend, although the high-K dacites contain higher Cu, Au and...
PGE contents than the low-K dacites because they have higher MgO.

The Niuatahi–Motutahi lavas show highly fractionated PGE patterns on a primitive mantle normalized diagram (Fig. 9) with Pd/Ir ratios of 140–516 for the basalts and >700 for the dacites. Dale et al. (2012), who analyzed the PGE concentrations of several Tonga arc lavas, including the Niuatahi–Motutahi lavas, also described similarly fractionated patterns (Fig. 9a). Patterns in the basalts rotate anticlockwise as MgO decreases, caused by the combined effects of the incompatible behavior of Pd, Au and Cu and compatible behavior of Pt, Rh, Ru and Ir during fractionation. In contrast, the patterns of the dacites are subparallel to each other and do not show any fractionation, although their abundances vary by more than an order of magnitude.

**Description and composition of melt inclusions**

Silicate melt inclusions occur in olivine and clinopyroxene phenocrysts in basalts and augite, pigeonite and plagioclase phenocrysts in dacites. The inclusions are mostly glassy, but some contain quench crystals. Fluid bubbles commonly occur within the glass inclusions. The size of the inclusions ranges from 10 to 100 μm. Some inclusions show evidence of post-entrapment crystallization along the inclusion walls and some olivine-hosted inclusions have Al-rich augite and magnetite as daughter minerals (Fig. 2d).

Melt inclusions without visible quench crystals were selected to correct for post-entrapment modification of the inclusions by crystallization of minerals along the inclusion walls. The correction was performed using the host mineral compositions, assuming equilibrium Mg–Fe partitioning between the host mineral and silicate melt (Putirka, 2008). Equilibrium olivine or pyroxene was incrementally added (0–1%) to the melt until its composition is in equilibrium with the host mineral. Before each addition Fe$^{3+}$/Fe$^{2+}$ in the melt was calculated using the expression of Kress & Carmichael (1991) at 1200°C, 4 kbar, FMQ + 1 log units (where FMQ is fayalite–magnetite–quartz buffer) for inclusions from the basalts and 1000°C, 2 kbar, FMQ + 0.5 for inclusions from the dacites. The degree of post-entrapment crystallization obtained from the calculation was applied to correct the Cl and S concentrations, assuming both

![Fig. 5. (a–f) Major element variation diagrams for the Niuatahi–Motutahi lavas, melt inclusions and the glasses within them. MI, melt inclusion.](http://petrology.oxfordjournals.org/)

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elements are highly incompatible with a crystal–melt partition coefficient of 0.001.

The corrected melt inclusion compositions are illustrated in Fig. 5 (see Supplementary Data A for the melt inclusion compositions). The major element compositions of melt inclusions are generally consistent with the whole-rock or glass compositions, although Al₂O₃ concentrations of some melt inclusions extend to lower concentrations than those of the whole-rocks. It is also noteworthy that melt inclusions from the same sample are generally similar in composition (Fig. 5). This suggests that the phenocryst minerals that host the melt inclusions in a given rock are not xenocrysts. The melt inclusions from xenocrysts often have significantly different compositions compared with bulk-rocks and show wide compositional variations within a sample (e.g. Kamenetsky et al., 2006). Danyushevsky et al. (2000) suggested that Fe loss can be caused by re-equilibration during cooling in olivine-hosted melt inclusions. Some olivine-hosted melt inclusions have lower FeO contents than their associated whole-rock, which is probably due to Fe loss during cooling. The low Al₂O₃ contents, relative to the bulk-rock compositions, may result from neglected Al-rich augite daughter crystals that could not be corrected for (Fig. 2d). The Na₂O contents of the melt inclusions are not

![Fig. 6. (a–h) Selected trace element variation diagrams for the Niutahi–Motutahi lavas.](http://petrology.oxfordjournals.org/)

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focused inclusions from the dacites were analyzed using a de-
teter (960–1040°C from the clinopyroxene thermometer (1150–1200°C for N-MORB values of Sun & McDonough (1989)). The compositions of the Tafahi and Niutapu Tonga arc volcanic rocks are taken from the GEOROC database (http://www.georoc.mpch-mainz.gwdg.de).

Because of their small size (<20 μm), most of the melt inclusions from the dacites were analyzed using a de-focused 5 μm beam at 20 nA, which resulted in high current density leading to Na loss.

**Temperature, pressure and oxygen fugacity**

The liquidus temperatures and pressures of the Niuatahi–Motutahi melts were constrained by various thermobarometers (Supplementary Data A). Clinopyroxene and augite crystals and melt compositions were selected after applying the equilibrium test described by Putirka (2008). The clinopyroxene–melt thermometer (Putirka et al., 2003) yielded temperatures of 1180–1220 °C for the basalts and 880–1070 °C for the dacites. These are similar to the temperature estimates from the clinopyroxene thermometer (1150–1200 °C for the basalt; Nimis & Taylor, 2000) and liquid thermometer (960–1040 °C for the dacite; Putirka, 2008). The high-K dacites have slightly higher temperatures than the low-K dacites, which is consistent with their higher MgO content. The pressure estimates, constrained by a clinopyroxene–melt barometer (Putirka, 2008), are in the range of 3.7–7.0 kbar (average = 5.5 ± 0.9, n = 11) for the basalt, 0.9–2.9 kbar (average = 1.9 ± 0.7, n = 11) for the low-K dacite, and 2.5–3.5 kbar for the high-K dacite (average = 2.8 ± 0.4, n = 8). Given that the Niuatahi–Motutahi lavas erupted at ~1700 m below sea level, ~0.2 kbar of the pressure can be attributed to seawater.

The olivine–spinel thermo-oxybarometer (Ballhaus et al., 1991) was applied to olivine–Cr spinel pairs from the basalt. The temperature range obtained is 990–1110 °C at 5.5 kbar, which is systematically ~100 °C lower than the values estimated from the other thermometers. This may result from subsolidus re-equilibration between olivine and Cr spinel during cooling, or from a systematic bias in this method compared with other thermometers. The oxygen fugacity (fO2), relative to the FMQ oxygen buffer, ranges from FMQ + 0.5 to FMQ + 2.9. The more mafic samples, DG26-1 and DG26-2, show lower fO2 (average = FMQ + 1.0 ± 0.3, n = 16) compared with the less mafic sample, DG26-3 (average = FMQ + 2.5 ± 0.2, n = 6). The Cr spinels from DG26-3 are characterized by low Cr# (55–62) and their host olivines have low Mg# (80–83), showing that they have crystallized from a more evolved magma.

Bulk-rock Fe3+/Fe2+, measured by titration, was used to constrain the fO2 of the dacites using the equation of Kress & Carmichael (1991). The estimated fO2 at 1000 °C and 2 kbar ranges from FMQ + 0.1 to 1.6. However, Sossi & O’Neill (2011) pointed out that the presence of reduced species such as S2– in a silicate melt would lead to an underestimation of the bulk-rock Fe3+/Fe2+ ratio because of the oxidation of S2– to S6– during titration. The sulfur contents in melt inclusions from the high-K dacite and low-K dacite are in the range of <190–207 ppm and 200–544 ppm, respectively. Assuming that 50% of S is dissolved as S2– in a melt at an fO2 of FMQ + 0.1 to +1.6 (Carroll & Rutherford, 1988), the corrected fO2 values relative to the FMQ buffer are FMQ + 0.6 to +1.9 for the high-K dacites and FMQ + 0.4 to +0.5 for the low-K dacites (Table 1).

**DISCUSSION**

**Magmatic differentiation of the Niuatahi–Motutahi magma**

The Niuatahi–Motutahi lavas are temporally and spatially related to each other and occur within a limited area of ~15 km² around the Niuatahi–Motutahi volcano, which has been active until recently. Phenocrysts in the Niuatahi–Motutahi lavas are euhedral to subhedral and their compositions are in equilibrium with the bulk-rock compositions, although some mafic basalt (>10 wt % MgO) samples contain accumulated early formed olivine. The phenocrysts are normally zoned with limited compositional variation and there is no mineralogical or petrological evidence for mixing or mingling between magma batches. Melt inclusions in phenocrysts have compositions consistent with those of the bulk-rocks. The major and trace element contents of the basalts, andesitic vesicle-filling glasses and dacites vary continuously, which can be explained by fractional crystallization of the observed phenocryst assemblages. MORB-normalized trace element patterns are subparallel to each other. Therefore, all the petrological and geochemical data suggest that the basalts and dacites are likely to be comagmatic and their compositional variations are dominated by fractional crystallization.

However, some dacites contain higher K2O, LILE and Zr, Nb, Ta and Hf than the majority of the other dacites at the same MgO content (Figs 4–6). These high-K dacites (DG17-4, DG17-1, DG20-1) are characterized by higher Nb/Yb (2.7–3.7) and Ba/Yb (132–161) than the remainder of the Niuatahi–Motutahi dacites (Nb/Yb = 2.6–3.0; Ba/Yb = 110–143) (Fig. 6; Table 1). Nb/Yb...
represents mantle fertility, and to some extent, degree of partial melting, whereas Ba/Yb is principally a measure of subduction input because Nb and Yb are immobile in subduction zones whereas Ba is subduction-mobile (Pearce & Stern, 2006). This suggests the high-K dacite primary magma may have been derived from a slightly more fertile source, or was produced by lower degree of partial melting with a larger subduction component than that of the low-K dacite. However, it should be noted that the Cu, Au and PGE contents of the high-K dacites are consistent with those of other dacites at the same degree of fractionation (Fig. 8), suggesting that chalcophile element contents in the parental magmas of both dacites were similar.

To investigate the genetic relationship between the basalts and two types of dacite we assessed the degree of fractional crystallization required to generate the dacites from the basalts using the least-squares mass-balance model of Cabero et al. (2012) and the observed crystal compositions (Table 3). About 50%
Table 2: Platinum group element and Re concentrations (ppb) of the Niuatahi–Motutahi lavas

<table>
<thead>
<tr>
<th>Sample</th>
<th>Re</th>
<th>Pd</th>
<th>Pt</th>
<th>Rh</th>
<th>Ru</th>
<th>Ir</th>
<th>Pd/Cu × 1000</th>
<th>Pd/Au</th>
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<td>Basalt</td>
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<td>DG26-1</td>
<td>0.282</td>
<td>7.76</td>
<td>4.733</td>
<td>0.167</td>
<td>0.089</td>
<td>0.055</td>
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<td>DG26-2</td>
<td>0.324</td>
<td>6.72</td>
<td>3.678</td>
<td>0.318</td>
<td>0.078</td>
<td>0.041</td>
<td>84</td>
<td>1.2</td>
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<tr>
<td>DG26-3</td>
<td>0.325</td>
<td>8.25</td>
<td>1.183</td>
<td>0.030</td>
<td>0.027</td>
<td>0.016</td>
<td>69</td>
<td>1.4</td>
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<td>Andesitic vesicle-filling glass from basalt*</td>
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<tr>
<td>DG26-2-VFG-2</td>
<td>n.d.</td>
<td>17.0 ± 3.5</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
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<td>DG26-2-VFG-3</td>
<td>n.d.</td>
<td>17.6 ± 3.8</td>
<td>n.d.</td>
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<td>DG26-2-VFG-4</td>
<td>n.d.</td>
<td>10.3 ± 4.5</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
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<td>DG26-2-VFG-6</td>
<td>n.d.</td>
<td>20.4 ± 3.1</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>80</td>
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<td>High-K dacite</td>
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<td>DG17-4</td>
<td>0.636</td>
<td>3.03</td>
<td>0.300</td>
<td>0.002</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>15.1</td>
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<td>DG17-1 (#1)</td>
<td>0.526</td>
<td>2.47</td>
<td>0.520</td>
<td>0.032</td>
<td>0.002</td>
<td>0.002</td>
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<td>DG17-1 (#2)</td>
<td>0.536</td>
<td>2.41</td>
<td>0.486</td>
<td>0.033</td>
<td>0.003</td>
<td>0.002</td>
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<td>DG20-1 (#1)</td>
<td>0.608</td>
<td>2.26</td>
<td>0.315</td>
<td>0.004</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
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<td>DG20-1 (#2)</td>
<td>0.515</td>
<td>4.01</td>
<td>0.469</td>
<td>0.009</td>
<td>0.002</td>
<td>0.002</td>
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<td>DG20-1 (#3)</td>
<td>0.513</td>
<td>1.92</td>
<td>0.270</td>
<td>0.004</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
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<td>Low-K dacite</td>
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<td>DG18-1</td>
<td>0.701</td>
<td>1.33</td>
<td>0.354</td>
<td>0.001</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>10.2</td>
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<td>DG24-1</td>
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<td>1.07</td>
<td>0.090</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>8.9</td>
<td>0.2</td>
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<tr>
<td>DG24-3</td>
<td>0.701</td>
<td>0.96</td>
<td>0.216</td>
<td>0.002</td>
<td>0.032</td>
<td>b.d.l.</td>
<td>7.4</td>
<td>0.3</td>
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<tr>
<td>DG23-1</td>
<td>0.653</td>
<td>0.22</td>
<td>0.064</td>
<td>0.001</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>2.2</td>
<td>0.1</td>
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<tr>
<td>DG16-4</td>
<td>0.622</td>
<td>0.66</td>
<td>0.051</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>6.0</td>
<td>0.5</td>
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<tr>
<td>DG16-1</td>
<td>0.609</td>
<td>0.28</td>
<td>0.062</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>b.d.l.</td>
<td>3.4</td>
<td>0.1</td>
</tr>
</tbody>
</table>

n.d., not determined. b.d.l., below detection limit.

*Pd concentrations of the vesicle-filling glass are average of replicate analyses by LA-ICP-MS. The raw data are presented in Supplementary Data A. Large uncertainties (1σ) were derived from isobaric interference correction.

crystallization of the vesicle-filling glasses from basalts generated a good match for the composition of the least evolved low-K dacite, DG18-1; however, the model failed to produce the high-K dacite (DG 17-4). The sum of squared errors (SSE) of 0.21 is largely derived from Na₂O, which may be due to the Na loss during microprobe analysis of the vesicle-filling glass, as suggested above. If Na₂O is excluded from the model, the SSE decreases to <0.01. The REE contents of the low-K dacites were modeled using the mineral proportions from the least-squares model (Fig. 10). The REE abundances and patterns of the low-K dacites are also consistent with ~50% perfect fractional crystallization from the vesicle-filling glass from the basalt. The REE patterns of high-K dacites are characterized by enrichment of LREE and depletion of HREE relative to the low-K dacites and model estimates.

The Niuatahi–Motutahi basalt is considered to be representative of the parental magma of the low-K dacite, based on modeling constraints, and this conclusion is supported by their close temporal and spatial relationship, together with their mineralogy and geochemistry. A crystallization pressure of ~5 kbar obtained from clinopyroxene geobarometry indicates that the basaltic magma initially evolved in a magma chamber at a depth of ~15 km, the approximate depth of the crust–mantle boundary in this area (Contreras-Reyes et al., 2011), and erupted directly through a NE–SW-trending fracture zone to form the volcanic complex SE of the caldera (Fig. 1). The augite from the low-K dacite crystallized at a pressure of 1.9 ± 0.7 kbar, suggesting that some of the evolved basaltic magma ascended to a high-level magma chamber at ~3–7 km depth and

Fig. 9. (a, b) Primitive mantle-normalized PGE patterns for the Niuatahi–Motutahi lavas. The PGE data for Tonga arc lavas (Dalis et al., 2012) are shown for comparison. Dashed line represents method detection limits for Ir, Ru and Rh.
produced the low-K dacite by fractional crystallization. The high-K dacite may have been derived from a slightly different parental magma, which was produced by a lower degree of melting or melting of an enriched source with a larger subduction component. 

Platinum-rich alloy saturation in the Niuatahi–Motutahi magma

The occurrence of Pt-rich alloys in arc-related settings suggests that Pt-rich alloy saturation may be a common feature of oxidized, subduction-related magmas. Park

Table 3: Least-squares fractional crystallization modeling of the Niuatahi–Motutahi lavas

<table>
<thead>
<tr>
<th>Melt composition</th>
<th>Parent (DG26-2-vesicle-filling glass)</th>
<th>Daughter (DG18-1)</th>
<th>Calculation</th>
<th>Difference</th>
<th>SSE</th>
<th>$R^2$</th>
<th>F/C%</th>
</tr>
</thead>
<tbody>
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*Average composition of the vesicle-filling glasses (>5 wt % MgO), normalized to 100%.
†Average compositions of augite, magnetite and pigeonite from the low-K dacites.
‡Average compositions of clinopyroxene and plagioclase from DG26-3.
SSE, sum of squared errors; F/C%, amount of crystallization from the parent melt.

Fig. 10. Calculated REE patterns for the Niuatahi–Motutahi lavas with varying degrees of fractional crystallization from a basaltic andesitic parent, taken from the average composition of the vesicle-filling glasses. The chondrite normalizing values are from McDonough & Sun (1995). Mineral proportions used in the calculations are from Table 3. Mineral–melt partition coefficients are from McKenzie & O’Nions (1991), except for magnetite (Lemarchand et al., 1987).
et al. (2013a) investigated variations in PGE contents of andesitic-basaltic lavas of the Pual Ridge, Eastern Manus Basin, and showed that Pt behaved compatibly whereas Pd behaved incompatibly prior to sulfide saturation. They also compared PGE concentrations between phenocryst-bearing and glassy samples, finding that the former are enriched in Pt and IPGE, but not Pd. They attributed these trends to the crystallization of a Pt-rich alloy along with the other silicate minerals during magma differentiation. Magmatic Pt-rich alloy inclusions were also observed in Cr spinels from the Ambae lavas, Vanuatu (Park et al., 2012a) and volcanic ankaraites, Urals, Russia (Pushkarev et al., 2014), indicating co-crystallization of Pt-rich alloy and Cr spinel. This is consistent with the presence of abundant Pt-rich alloys in arc cumulate rocks from the Greenhills complex, New Zealand (Spandler et al., 2000, 2003), and the Uralian–Alaskan type Kytlym and Uktus complex, Russia (Garuti et al., 2002).

The Pt contents of the Niutahi–Motutahi basalts correlate positively with MgO (Fig. 8), and Pt and other PGE show positive correlations with each other except for Pd (Fig. 11 and Table 2). These trends are similar to those of the Pual Ridge lavas (Park et al., 2013a), which were affected by Pt-alloy saturation. As mentioned above, the high-MgO basalts (>12 wt % MgO) resulted from the accumulation of early formed phenocrysts. Therefore, the high PGE contents of the high MgO samples, with the exception of Pd, are likely to be caused by the presence of Pt- and IPGE-rich phases trapped in phenocrysts. Cr-spinel fractionation may account for some of the Rh, Ru and Ir decrease as the Niutahi–Motutahi lavas are oxidized (e.g. Park et al., 2012a); however, Pt is not compatible in Cr spinel. Therefore, we suggest that Pt variation in the basalt can be explained only if the magma is saturated with a Pt-rich alloy.

The Pt-rich alloy saturation in subduction-related magmas is probably due to their low temperature, high Pt contents and delayed sulfide saturation. The liquidus temperature of arc basalts ranges from ~1100 to ~1200°C, which is ~100 to ~200°C lower than those of primitive ocean island basalts and komatiites. The Pt solubility is highly dependent on temperature and decreases with decreasing temperature (Fortenfant et al., 2003). Under the conditions of formation of arc basalts, it falls to ~2 to ~10 ppb (e.g. Park et al., 2013a) and this range overlaps with the reported Pt contents of basalts and picrites (Woodland et al., 2002; Da et al., 2012; Park et al., 2012a, 2013a; this study). Mungall & Brenan (2014) suggested that the S content of a melt might increase its Pt solubility. However, this is unlikely to be an important consideration for the oxidized melts from which the Niutahi–Motutahi Pt-rich alloys precipitated, because sulfate is expected to have been the dominant S species in the melt, and the presence of sulfate should not affect Pt solubility.

Dale et al. (2012) reported mildly compatible behavior for Pt in Volcano A, Tonga arc, but in this case it is unlikely to be due to Pt-rich alloy crystallization because the other PGE, including Pd, also behave compatibly in the suite. Given the mildly compatible behavior of all the PGE but the incompatible behavior of Cu in volcanic rocks from Volcano A, the magma may have undergone limited or localized sulfide segregation, resulting in a bulk D of >1 for the PGE, but bulk D < 1 for Cu.

### Sulfide saturation history of the Niutahi–Motutahi magma

Recent studies on the PGE geochemistry of intermediate to felsic rocks (Park et al., 2013a, 2013b) show that sulfide saturation can be identified from variations in PGE, along with Cu and Au, in evolving magmatic systems. The Cu, Au and Pd contents progressively increase in the basalts and andesitic vesicle-filling glasses but abruptly decrease in the dacites (Fig. 8). The order of the rate of depletion is Pd > Au > Cu which is in order of decreasing partition coefficient and leads to a decrease in Pd/Cu and Pd/Au with decreasing MgO following sulfide saturation in the dacites (Fig. 8g and h). This suggests that the Niutahi–Motutahi magma became sulfide saturated when it entered the dacitic phase of its evolution. This hypothesis is consistent with the presence of a Cu-rich sulfide bleb in the glass matrix of dacite sample DG24-3, which contains ~460 ppb of Pd and 1.2 ppm of Au (Fig. 2c; Supplementary Data B). We suggest that sulfide saturation occurred just before the magma evolved to a dacitic composition because the dacites still contain high abundances of chalcophile elements. Pd/Au ratios in the andesitic vesicle-filling glasses are slightly higher than those of basalts. This may be attributed to preferential Au loss by degassing during the formation of the vesicle-filling glasses, which are characterized by abundant bubbles (Fig. 2f). In contrast to other chalcophile elements, Re contents are higher in the dacites than in the basalts, showing that Re continues to behave as an incompatible element following sulfide saturation. This is because \( D_{\text{Fluid-melt}} \) is negatively correlated with oxygen fugacity and becomes <1 at QFM + 0.5 (Fonseca et al., 2007). Magnetite
crystallized from the dacites and can host some Re ($D_{\text{magnetite-melt}}^{\text{Re}} \sim 20$; Righter et al., 1998); however, the bulk $D$ value for the dacites is $<1$ because the modal abundance of magnetite $<5\%$. This conclusion is supported by the least-squares model (Table 3).

The MgO content at sulfide saturation can be estimated from the intersection of extrapolations of Pd trends in the low-K dacites, vesicle-filling glasses and basalts. The two trend lines intersect at $\sim 2.7$ wt % MgO, shortly after magnetite saturation (Fig. 8), at an estimated Pd concentration of $\sim 17$ ppb (Fig. 8). The extrapolation of the Cu and Pd/Cu variation trends also provides consistent results, with intercepts at 2.6 wt % MgO (250 ppm Cu), and at 2.7 wt % MgO, where Pd/Cu is $6.6 \times 10^{-6}$. This timing of sulfide saturation for the Niuatahi–Motutahi lava is relatively late compared with other arc lavas, most of which show earlier sulfide saturation (e.g. Lee et al., 2012). Late sulfide saturation resulted in the Cu and Au content of the Niuatahi–Motutahi magmas increasing from 80 to 200 ppm Cu and from 5 to 7 ppb Au prior to sulfide saturation and the formation of the first dacites. These values are significantly higher than those of the average arc dacite ($\sim 30$ ppm Cu and $\sim 1$ ppb Au; Robb, 2005).

Given that Cu is incompatible in the major crystallizing minerals in the dacites (e.g. Park et al., 2013a, 2013b), removal of a sulfide melt has a major influence on the Cu content of the silicate melt. The fraction of sulfide melt precipitating from the silicate melt required to explain the observed variation in Cu in the Niuatahi–Motutahi dacites is $0.2$ wt %, assuming $D_{\text{Cu}}^{\text{sulfide-melt}} = 1300$ (Ripley et al., 2002). This is consistent with the sulfide fraction of $0.2–3$ wt % determined for other sulfide-saturated magmas (e.g. Jamais et al., 2008; Park et al., 2013a).

There is a limited number of experimental studies on sulfur solubility in silicate melts at temperatures below $1100^\circ$C. Carroll & Rutherford (1985, 1988) and Luhr (1990) investigated the sulfur solubility in a hydrous trachyandesite at $\sim 950–1000^\circ$C and 2 kbar with $O_2$ varying between FMQ and FMQ $+1$, conditions similar to those of the Niuatahi–Motutahi magma. They showed $\sim 300–550$ ppm of S dissolved in a melt in equilibrium with FeS. The sulfur contents of melt inclusions in the low-K dacites range from $<200$ to $544$ ppm, which is consistent with the experimental constraints. However, the sulfur concentrations of the melt inclusions in the high-K dacites only rarely exceed 200 ppm, suggesting that the melt inclusions may have been trapped after magma degassing.

The sulfur solubility in a silicate melt is a function of several parameters, including $O_2$, temperature and the FeO content of the melt (Carroll & Rutherford, 1985; Luhr, 1990; O’Neill & Mavrogenes, 2001). The onset of magnetite crystallization decreases not only the Fe content of the melt but also $Fe^{2+}/Fe^{3+}$, which lowers $O_2$ and sulfur solubility in the melt (e.g. Jenner et al., 2010), converting highly soluble sulfate in the melt to less soluble sulfide. The total FeO, Ti and V contents decrease below 3 wt % MgO in the Niuatahi–Motutahi dacites, which suggests that the onset of magnetite crystallization at $\sim 3$ wt % MgO (Fig. 5) was the trigger for sulfide saturation. Furthermore, magnetite is a common phenocryst mineral in these rocks. This is also consistent with the difference in the estimated $O_2$ between the basalts and the dacites. The $O_2$ increased in the basalt from FMQ $+1$ to FMQ $+2.5$ during the early stages of magma differentiation, which are dominated by olivine fractionation. However, following magnetite saturation this falls to $\sim$ FMQ $+0.5$ in the dacite (Table 1 and Supplementary Data A).

Volatile saturation history of the Niuatahi–Motutahi lava

The Niuatahi–Motutahi basalts and dacites have varying amounts of vesicles. This indicates magma degassing during ascent prior to eruption. A CO$_2$-rich vapour phase predominates in basaltic magmas at high pressure, but H$_2$O becomes the dominant component in more evolved magmas at low pressure (Dixon & Stolper, 1995; Newman & Lowenstern, 2002; Lesne et al., 2011; Baker & Alletti, 2012). Sulfur and Cl behave incompatibly during magma evolution at high pressure, but start to degas at shallow depths of $< \sim 2$ kbar (Lesne et al., 2011).

Native sulfur mineralization occurs in association with the dacites, which suggests that a S-rich magmatic gas exsolved from the dacitic magma. Volatile element analyses provide information on the composition of the magmatic gas and the timing of volatile saturation. Chlorine contents in melt inclusions and vesicle-filling glass from the basalts range from 987 to 1596 ppm, which is about half of the Cl contents in melt inclusions and glasses (2210–3850 ppm) in the dacites (Supplementary Data A). The Cl concentrations broadly increase with decreasing MgO in the basalts, andesitic vesicle-filling glasses and dacites (Fig. 12). Sulfur concentrations in the melt inclusions from the basalts range from $<150$ to 513 ppm. The melt inclusions from the dacites contain a similar range of S contents from $<190$ to 544 ppm, although most of the melt inclusions from the high-K dacites contain less than 190 ppm S. It should also be noted that the S contents of the vesicle-filling glasses in the dacites and the dacitic glasses themselves are below the detection limit of $\sim 200$ ppm, which is consistently lower than those of melt inclusions owing to S loss during eruption.

Fractional crystallization modeling of Cl and S contents in a melt was carried out using the average composition of the melt inclusion, and assumed mineral–melt partition coefficients for Cl and S of 0–0.01. The bulk partition coefficient for Mg of 3.24 was calculated from the mineral proportions and its composition from the least-squares model of Cabero et al. (2012) (Table 3). As suggested by the Pd and Cu data, 0.2% of sulfide melt removal was added to the model for MgO.
values below 2.7 wt % (Model 1 in Fig. 12). Model 1 explains the variation of Cl, but the S contents of the dacites are substantially lower than the estimated values. This requires additional S loss by degassing of the S-rich magma. During magmatic gas exsolution both Cl and S partition into the gas phase; however, S generally starts to degas earlier than Cl during magma ascent and evolution (Lesne et al., 2011) and the partition coefficient between the magmatic vapor and melt is much higher for S than Cl (Botcharnikov et al., 2004). Model 2 added 5% of gas exsolution to Model 1 using $D_{\text{Cl}}^{\text{vapor-melt}} = 10$ (Webster et al., 2009) and $D_{\text{S}}^{\text{vapor-melt}} = 50$ (Webster & Botcharnikov, 2011), with exsolution starting at 2 wt % MgO. Model 2 is generally consistent with the trends for S and Cl contents in the melt inclusions from the dacites. This suggests that S- and Cl-bearing gas exsolution may have occurred during dacitic magma evolution. Copper and Au partition into the volatile phase together with S and Cl (Hedenquist & Lowenstern, 1994; Williams-Jones & Heinrich, 2005; Mavrogenes et al., 2010) so that when the magmatic vapor ascended to the ocean floor it condensed to form the observed Cu- and Au-rich native sulfur mineralization (Kim et al., 2011).

The role of sulfide saturation in the formation of Cu- and Au-rich magmas

Most magmatic–hydrothermal Cu and/or Au deposits, such as porphyry deposits, are genetically linked to arc magmas (Seedorff et al., 2005; Sillitoe, 2010). However, the majority of arc magmas are barren and not associated with economic mineralization. This has led to studies aimed at identifying the distinctive characteristics of ore-bearing arc magmas compared with barren systems. It has been suggested that certain types of arc-associated magmas have a close relationship with large Cu and/or Au deposits. Among these are adakitic magmas, as described by Mungall (2002) and Sun et al. (2011), and alkali magmas, as described by McInnes et al. (1999). These workers emphasized the importance of magma sources and melting conditions in the formation of Cu and/or Au deposits. They suggested that these types of arc magmas contain higher initial abundances of chalcophile elements than normal arc magmas, which makes them fertile sources for mineralization.

However, the chalcophile element geochemistry of the Niuatâhí–Motutahi lavas shows that the timing of sulfide saturation may also play an important role in the formation of fertile (i.e. Cu- and Au-rich) magmas as was previously suggested by several researchers (Candela & Holland, 1986; Keith et al., 1997; Jenner et al., 2010; Richards, 2011; Wilkinson, 2013). Figure 13 shows the Cu data for the Niuatâhí–Motutahi lavas and compares these with those for volcanic rocks from the Honshu arc. The Cu concentrations of the majority of

Fig. 12. (a, b) Chlorine and S variation diagrams for melt inclusions (MI), glass and vesicle-filling glass from the Niuatâhí–Motutahi lavas. Model 1 represents the fractional crystallization trend for silicate and oxide minerals with removal of sulfide melt at 2.7 wt % MgO, assuming a sulfide fraction of 0.2 wt %. Model 2 includes 5 wt % gas exsolution at 2 wt % MgO. The average composition of melt inclusions from the basalts was used as the parent magma. For plotting purposes, S values below the detection limit are plotted as zero.

Fig. 13. Comparison of Cu variations in the Niuatâhí–Motutahi lavas, Pual Ridge lavas from the eastern Manus Basin and Honshu arc volcanic rocks. Continuous-line and dashed-line arrows represent the inferred magma differentiation paths of the Niuatâhí–Motutahi lavas and Honshu arc volcanic rocks, respectively. The MgO and Cu data for the Pual Ridge lavas are from Sun et al. (2007) and those for the Honshu volcanic rocks are from the GEOROC database (http://www.georoc.mpch-mainz.gwdg.de).
the Honshu volcanic rocks decrease with decreasing MgO, highlighting the influence of sulfide saturation on the magma differentiation trend, which is distinct from that defined by the Niutahi–Motutahi lavas. Early sulfide saturation results in very low Cu contents (average 19 ppm) in the dacites of the Honshu arc. This suggests that the absence of porphyry Cu deposit in Japan is probably due to the low Cu contents of the evolved volcanic rocks, especially the dacitic porphyries, as suggested by Sato (2012) and Richards & Mumin (2013), because the potentially Cu deposit-forming volatiles originate from these Cu-poor magmas (Seedorff et al., 2005).

It should be noted that the Cu contents of both the Niutahi–Motutahi lavas and Honshu volcanic rocks with MgO contents higher than 10 wt % are comparable, which suggests that the initial Cu contents of the primary magmas were similar. What produced the two different Cu trends in the magma differentiation processes? The basement of the Japanese islands, which was intruded by Cretaceous to Paleogene Honshu arc magmas, consists mainly of a Paleozoic accretionary complex containing carbonaceous sedimentary rocks (Sato, 2012, and references therein). Therefore, the Honshu magmas were likely to assimilate lower crustal, carbon-rich, sedimentary materials, which may have lowered the \( f_O^2 \) of the melt, leading to early sulfide saturation (Sato, 2012; Richards & Mumin, 2013). This suggestion is consistent with the result of a recent study by Tomkins et al. (2012) on the petrogenesis of the Opirarukaomappu Gabbric Complex (OGC), Japan, which is associated with massive-disseminated sulfide Ni–Cu mineralization. They suggested that mixing between a S- and Cu-rich mantle-derived basaltic magma and a C-rich crust-derived tonalitic magma caused the sulfide mineralization. The intrusion of basalt into the carbonaceous lower crust induced crustal melting and produced carbon-rich, reduced felsic magmas. This process might be a common feature of arc magmas because the exposed island arc sequences often contain carbon-rich accretionary complexes (Tomkins et al., 2012).

In contrast, the early stage of evolution of the Niutahi–Motutahi magmas was dominated by fractional crystallization of Cu-poor minerals, which concentrated Cu in the melt. Sulfide saturation was delayed until a late stage in magma evolution. This allowed the Niutahi–Motutahi magmas to become enriched in chalcophile elements until S-rich volatile exsolution occurred at ~2 wt % MgO. It should be noted that the Cu and Au contents of the Niutahi–Motutahi dacites were about an order of magnitude higher than those of the Honshu dacites (19 ppm Cu and 0.2 ppb Au; Togashi & Terashima, 1997) at the time of volatile exsolution. We suggest that this magmatic vapor produced the Niutahi–Motutahi Cu–Au-rich native sulfur mineralization. The highly oxidized nature of the Niutahi–Motutahi basalt (QFM +1 to +2.5) may have been a critical factor in delaying sulfide saturation because within this \( f_O^2 \) range sulfur solubility in the melt is strongly \( f_O^2 \) dependent (Carroll & Rutherford, 1988; Jugo, 2009). In addition, the Niutahi–Motutahi magma ascended through the Tonga arc crust, which is thin (~15–20 km) and composed of basaltic rocks (Contreras-Reyes et al., 2011). Therefore, crustal assimilation would have been minimal and any crust that was assimilated would have been C-poor. The Pual Ridge lavas of the Eastern Manus Basin, which are associated with seafloor Cu–Au mineralization, are also characterized by incompatible behavior of Cu and Au during early magma differentiation (Park et al., 2013a), which suggests that late sulfide saturation resulted in the Pual Ridge magma being enriched in Cu and Au by the time of water-rich volatile exsolution.

It has been suggested that sulfide blebs can act as a reservoir of ore metals and S (e.g. Keith et al., 1997; Halter et al., 2002; Nadeau et al., 2010). Halter et al. (2002) investigated Cu, Au and Fe contents in silicate and sulfide melt inclusions in amphibole phenocrysts from volcanic and intrusive rocks from the Farallon Negro Volcanic Complex in northwestern Argentina that hosts the large Bajo de la Alumbrera porphyry Cu–Au deposit. Based on Cu and Au concentrations, and the similar Au/Cu ratio of sulfide melt inclusions and fluid inclusions of an early hydrothermal brine, they suggested that the magma associated with the deposit was sulfide saturated but that the early formed sulfide blebs were destabilized during volatile exsolution and the Cu, Au and S in the sulfide blebs migrated into the ore-forming fluid. Nadeau et al. (2010) studied sulfide and silicate melt inclusions that occur in the volcanic rocks from the Merapi Volcano, Indonesia. They reported numerous partially or almost completely dissolved sulfide inclusions associated with silicate melt inclusions and fluid inclusions, and argued that these textures suggest interaction between the sulfide blebs and a hydrothermal fluid. Based on this evidence, and similar metal ratios in sulfide melt inclusions and volcanic gas collected from the volcano, they proposed that sulfide blebs in a mafic magma were injected into a more evolved felsic magma where they dissolved and that the metals in the sulfide blebs were transferred to a volcanic gas phase during decompression of the mafic magma.

Volatil e exsolution and sulfide segregation occur at the same time in the Niutahi–Motutahi dacites so it is likely that there was some interaction between sulfide blebs and the exsolved magmatic vapor in the magma chamber; however, the decrease of PGE in the dacites rules out complete dissolution of the sulfide blebs. Furthermore, dissolution of the sulfide blebs would have been limited to those held in suspension in the convecting magma and blebs near the crystal–liquid interface of the solidifying magma chamber. We therefore suggest that localized or limited dissolution of sulfide blebs may have additionally enriched the magmatic gas in Cu and Au at Niutahi–Motutahi.
This study shows that the timing of sulfide saturation is a critical factor to form a magma enriched in chalcophile elements. Once a mantle-derived basaltic magma rises into the crust, the $f_{O_2}$, temperature and FeO content of the magma control sulfur solubility in the silicate melt. Assimilation of reducing crustal materials and mixing with a crust-derived silicic magma are the processes most likely to result in sulfide saturation during open-system magma differentiation, whereas reduction produced by magnetite crystallization is likely to be the dominant process in closed systems. A magma that reaches sulfide saturation early and precipitates a significant amount of sulfide melt before it becomes volatile saturated is unlikely to produce a magmatic—hydrothermal ore deposit because ore metals, such as Cu and Au, will be held in the crystallizing magma chamber, leading to a residual magma that is depleted in these elements.

**CONCLUSIONS**

The Niutahai–Motutahi lavas are temporally and spatially associated basaltic and dacitic submarine volcanic rocks. They show geochemical features that are typical of island arc magmas, with enrichment of LILE relative to MORB and pronounced negative Nb and Ta anomalies. Two types of dacites occur within the Niutahai–Motutahi region: the high-K dacite and low-K dacite. Modeling shows that the low-K dacites can be produced by 50% fractional crystallization of the magma, as represented by andesitic glass found as a vesicle filling in the basalts, indicating a comagmatic origin for the low-K dacites and basalts. The high-K dacites may have originated from a slightly different parental magma that is more fertile and more enriched in subduction components relative to that of the low-K dacites. The PGE geochemistry of the Niutahai–Motutahi lavas suggests Pt-rich alloy crystallization during fractionation of the basalts and andesites and sulfide saturation in the dacite. The timing of sulfide saturation was late, which allowed the Niutahai–Motutahi dacite to concentrate Cu and Au prior to volatile saturation, and form the Cu- and Au-rich native sulfur mineralization in this region, despite unremarkable chalcophile element concentrations in the parental magma. In contrast, the Honshu arc magmas are characterized by early sulfide saturation and the Honshu dacites are impoverished in Cu, and probably Au and Pd, which accounts for the absence of Cu porphyries in Japan. This study shows that the timing of sulfide saturation and the amount of sulfide precipitation during magma differentiation play important roles in the formation of fertile (Cu- and Au-rich) magmas.

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**SUPPLEMENTARY DATA**

Supplementary data for this paper are available at Journal of Petrology online.

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