Abundances of platinum group elements in native sulfur condensates from the Niuatahi-Motutahi submarine volcano, Tonga rear arc: Implications for PGE mineralization in porphyry deposits

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Abstract

Some porphyry Cu–Au deposits, which are enriched in Pd, are potentially an economic source of Pd. Magmatic volatile phases are thought to transport the platinum group elements (PGEs) from the porphyry source magma to the point of deposition. However, the compatibilities of the PGEs in magmatic volatile phases are poorly constrained. We report PGE and Re contents in native sulfur condensates and associated altered dacites from the Niuatahi-Motutahi submarine volcano, Tonga rear arc, in order to determine the compatibility of PGEs and Re in magmatic volatile phases, and their mobility during secondary hydrothermal alteration. The native sulfur we analyzed is the condensate of a magmatic volatile phase exsolved from the Niuatahi-Motutahi magma. The PGEs are moderately enriched in the sulfur condensates in comparison to the associated fresh dacite, with enrichment factors of 11–285, whereas Au, Cu and Re are strongly enriched with enrichment factors of $\sim$20,000, $\sim$5000 and $\sim$800 respectively. Although the PGEs are moderately compatible into magmatic volatile phases, their compatibility is significantly lower than that of Au, Cu and Re. Furthermore, the compatibility of PGEs decrease in the order: Ru > Pt > Ir > Pd. This trend is also observed in condensates and sublimates from other localities.

PGE mineralization in porphyry Cu–Au deposits is characterized by substantially higher Pd/Pt ($\sim$7–60) and Pd/Ir ($\sim$100–10,500) than typical orthomagmatic sulfide deposits (e.g. Pd/Pt $\sim$0.6 and Pd/Ir $\sim$20 for the Bushveld). It has previously been suggested that the high mobility of Pd, relative to the other PGEs, may account for the preferential enrichment of Pd in porphyry Cu–Au deposits. However, the low compatibility of Pd in the volatile phase relative to the other PGEs, shown in this study, invalidates this explanation. We suggest that the PGE geochemistry of Pd-rich Cu–Au deposits is principally derived from the PGE characteristics of the magma from which the ore-forming fluid exsolved. Pd-rich porphyry Cu–Au deposits are associated with highly oxidized magmas. Prior to sulfide saturation Pd, Au and Cu behave as incompatible elements and concentrate in the melt with fractional crystallization, whereas Pt is depleted by early crystallization of a Pt-rich alloy and the other PGEs by the co-crystallization of the Pt-rich alloy and Cr spinel. As a consequence the Pd/Pt and Pd/Ir in the evolving melt and the magmatic volatile phases that exsolve from that melt, increase with increased fractionation. The high Pd content and high Pd/Pt ($\sim$7–60) of Cu–Au porphyry ores therefore require the parent magma to have undergone extensive sulfide-undersaturated fractional crystallization prior to volatile exsolution.

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Our study also showed that the altered dacites contain PGE abundances that are similar to those of fresh dacites although Pt and Rh are slightly enriched in the altered dacites, which indicates low mobility of PGEs during secondary hydrothermal alteration.

1. INTRODUCTION

Magmatic volatile phases act as metal transporting agents in magmatic-hydrothermal systems. They can scavenge ore metals from magmas during magmatic volatile exsolution and carry them to a site of deposition to form an ore deposit (Sillitoe, 1979; Richards et al., 1991; Hedenquist and Lowenstern, 1994; William-Jones and Heinrich, 2005). Numerous fluid inclusion studies of fluids associated with porphyry ore deposits show enrichment of ore metals such as Au, Cu, Ag and Mo (Heinrich et al., 1992; Audétat and Pettke, 2003; Zajacz et al., 2008). The behavior of these ore metals during volatile exsolution is also well constrained by experimental studies of the solubility of metals in magmatic volatile phases in equilibrium with silicate melts (Candela and Holland, 1984; Williams et al., 1995; Heinrich, 2005; Simon et al., 2006; Frank et al., 2011).

Over the last decade there has been a growing interest in compatibility of platinum group elements (PGEs) in magmatic volatile phases because some porphyry Cu–Au deposits contain elevated Pd and Pt with contents of up to several thousand ppb (Economou-Eliopoulos, 2005 and references therein). As a consequence PGEs may be produced as byproducts during Cu–Au mining. The estimated reserves are about 15 tons Pd and 3.5 tons Pt for the Skouries deposit, Greece and 10.5 tons Pd and 1.6 tons Pt for the Santo Tomas II deposit, Philippines (Tarkian et al., 2003; Economou-Eliopoulos, 2005). The ore samples from these deposits are characterized by enrichment in Pd relative to other PGEs. It is generally agreed that the PGEs originate from magmas and are carried by magmatic volatiles phases along with Cu and Au to the site of deposition, but two questions remain: (1) why does PGE mineralization occur only in association with highly oxidized calc-alkaline or alkaline magmas, and (2) what causes these deposits to be Pd-rich and have high Pd/Pt and Pd/Ir ratios? In order to solve these questions we need to understand the behavior of PGEs during volatile exsolution.

Thermodynamic studies (Wood, 1987; Sassani and Shock, 1990; Tagirov et al., 2013) suggested that PGEs can be soluble in highly saline solution and that their solubility increases with increasing temperature, oxygen fugacity and total chloride content although they are several orders of magnitude less soluble than Cu, Ni and Fe under the same condition. A series of experimental studies that investigated the compatibility of the PGEs in volatile phases at magmatic temperatures (600–1000 °C) showed that they can be dissolved and transported by hypersaline fluid phases under oxidizing conditions (Fleet and Wu, 1993, 1995; Hanley et al., 2005). However, their PGE contents in the experimental products vary by up to three orders of magnitude under the same run conditions due to incomplete equilibrium obtained by the quartz-trap methods used in their experiments. Simon and Pettke (2009) circumvented the problem by trapping fluid inclusions in a silicate melt and investigated Pt partitioning between a felsic melt, vapor and brine at 800 °C and ~1 kbar under sulfur-free condition. Their results showed that Pt is slightly compatible in the vapor (<10 wt.% NaCl eq.) with D values of 1–5, and more strongly compatible in a high salinity brine (40–70 wt.% NaCl eq.) with D values from 7 to 150.

To summarize, experimental studies suggest moderate solubility of Pt in saline fluids, however the results are highly variable because of differences in the melt compositions, and physical and chemical conditions used in the experiments. Some of the experiments were clearly affected by the incomplete equilibrium, as mentioned by Simon and Pettke (2009), whereas others may be compromised by the presence of micronuggets (e.g. Blaine et al., 2011). The published studies focus on the behavior of Pt, and partitioning of the other PGEs to volatile phases has been largely ignored possibly because of experimental difficulties. Furthermore, most of the experimental studies investigated PGE solubility in S-free, saline, high-density fluid whereas the volatile phase initially exsolved from the magma that underlies porphyry deposits is considered to be a S-bearing, relatively low density, low salinity fluid (Williams-Jones and Heinrich, 2005; Landtwing et al., 2010).

An alternative way to investigate the compatibility of the PGEs into magmatic volatile phases is to directly measure their abundances in volcanic gas and their sublimates or condensates, which are analogous to magmatic volatile phases. This method is particularly useful because relative compatibility of a wide range of metals can be compared under the same conditions. Zoller et al. (1983), Finnegan et al. (1990) and Crocket (2000) have measured PGE contents in airborne particles, volcanic gas, and gas condensates from Hawaiian volcanoes and showed that Ir and Os are highly enriched in those phases, suggesting a strong affinity to volatile phases. Toutain and Meyer (1989) reported elevated Ir contents in volcanic gas sublimates from Piton De La Fournaise, Indian Ocean.

The behavior of PGEs during magma degassing has been studied in only two localities in arc settings. A series of studies of the Kudryavy volcano, Kurile Arc (Korzhinsky et al., 1994; Tessalina et al., 2008; Yudovskaya et al., 2008) showed that Os is significantly enriched in gases and their sublimates compared with their associated volcanic rocks, whereas the other PGEs are only slightly enriched. Zelenski et al. (2014) studied the composition of volcanic gas from Tolbachik volcano, Kamchatka

arc. They reported that the gas condensates contain ~24 ppb Re and ~0.45 ppb Pt, but the other PGEs were below their method detection limit of 1 ppb for Pd and Rh and 0.03 ppb for Ir and Os.

The Niuatahi-Motutahi is a submarine volcano located in the northern Tonga rear arc in which metal-rich native sulfur has been found in the central cone of the caldera in association with dacites (Kim et al., 2011; Park et al., 2015). The native sulfur, which is interpreted to be produced by condensation of volcanic gas emanating from the sea floor (Kim et al., 2011), provides an opportunity to investigate the behavior of PGEs, and other metals, during volatile exsolution in an evolved arc magmatic system. Kim et al. (2011) have previously documented the partitioning of base metals and Au into the sulfur condensates. In this study we report analyses of the PGEs (Pd, Pt, Rh, Ru and Ir) and Re for the native sulfur from the Niuatahi-Motutahi volcano. The results, and previous analyses of the volcanic rocks (Park et al., 2015), are used to constrain the compatibility of PGEs and Re in the magmatic volatile phase. We also analyzed altered dacites that occur in association with the native sulfur for PGEs and Re to investigate the effect of hydrothermal alteration on the PGE and Re mobility. We use the results to discuss the formation of the Pd-rich porphyry Cu–Au deposits.

2. SAMPLE OCCURRENCE AND COMPOSITION

The Niuatahi-Motutahi is a submarine volcanic complex located in the Tonga rear arc, Southwest Pacific. The lavas from the Niuatahi-Motutahi caldera are dacite with typical island arc geochemical characteristics (Park et al., 2015). The native sulfur was collected from the cone of the Niuatahi-Motutahi volcano during the Korea Deep Ocean Study (KODOS) H-06 cruise in 2006 at water depth of ~1700 m (Kim et al., 2011). A hydrothermal plume was detected above the cone at the water depth of ~1200 m (Kim et al., 2009). The native sulfur samples were dredged as semi-solidified materials that slowly hardened during recovery (Kim et al., 2011). The samples are interpreted to have been collected from a molten sulfur lake on the floor of the crater. The occurrences of the native sulfur were generally 5–10 cm sized massive blocks or quenched flows of gray and yellow sulfur (Kim et al., 2011). Their typical Cu and Au contents are 1.9 wt.% and 2.2 ppm respectively. They are mainly composed of massive sulfur-rich matrix (>80 wt.%) with varying amounts of Fe, Cu, Mo, Ni and As, and fine inclusions of covellite, Cu–As sulfosalt (tennantite?), with secondary pyrite (Kim et al., 2011). Covellite inclusions are poorly crystallized with irregular shapes and varying sizes. Some occur as spherical inclusions, suggesting formation from a gas. Cu–As sulfosalts generally occur as intergrowths with the covellite crystals. Gold occurs as native Au or electrum. This mineral assemblage indicates that the minimum temperature of the volcanic gas was 500 °C when the condensates were formed (Williams-Jones and Heinrich, 2005 and references therein). The occurrence of numerous covellite inclusions in the sulfur matrix and the light sulfur isotopic composition (δ^{34}S = −7.5‰ to −8.2‰) indicate that the native sulfur

is a condensates of sulfur-rich magmatic volatile phases exsolved from the Niuatahi-Motutahi magma (Kim et al., 2011). Altered dacites were collected from the cone of the caldera. They are highly altered with extensive incrustation of native sulfur and pyrite mineralization. They contain Na-rich natroalunite and cristobalite, which indicate the alteration in highly acidic conditions (e.g. Herzig et al., 1998). Sulfur contents of the altered dacites range from 6.5% to 14.7% (Kim et al., 2011).

3. ANALYTICAL TECHNIQUE

3.1. Whole rock major and trace element analysis

Major and trace elements were analyzed by the method of Park et al. (2015). Briefly, the samples were crushed, sonicated in distilled water and dried. The fresh chips were selected under a microscope to minimize altered parts and leached in 1 M HCl for 10 min at room temperature. Major and trace elements were measured for two altered dacite (DG18–5, DG20-4) and one native sulfur (DG18-3-s) by a combination of ICP-AES and ICP-MS analysis (4LithoResearch) by Activation Laboratories, Canada. Calibration was performed using seven USGS and CANMET certified reference materials. One of the 7 standards was used during the analysis for every group of ten samples. The uncertainty on the external reproducibility of the analyses was ±5 relative%.

3.2. Whole rock PGE and Re analysis

The whole rock PGE and Re contents of the native sulfur and altered dacites were measured by the combined Ni–sulfide fire assay-isotope dilution ICP-MS method described by Park et al. (2012b). The sensitivities during analysis were 2.4–3.4 × 10^5 cps/ppb for mass 89, 140, 205 using Agilent 7700x quadrupole ICP-MS at the Australian National University (ANU).

Contents of Ir, Ru, Pt, Pd and Re were determined by isotope dilution using the ^{191}Ir/^{193}Ir, ^{99}Ru/^{101}Ru, ^{191}Ir/^{193}Ir, ^{195}Pt/^{194}Pt, ^{105}Pd/^{108}Pd, ^{185}Re/^{187}Re ratios, respectively. Palladium contents of native sulfur were determined using ^{105}Pd/^{106}Pd in order to avoid ^{92}Mo^{16}O interference on ^{108}Pd. Rhodium contents of the altered rocks were obtained using the method described in Meisel et al. (2003) and Park et al. (2012b), which used the count rate of ^{103}Rh and ^{106}Pd assuming that loss of Rh during the analytical procedure was similar to that of Pd. For some native sulfur samples, Rh and Pd contents could not be determined due to high ^{63}Cu^{40}Ar interference on ^{103}Rh and ^{65}Cu^{40}Ar interference on ^{105}Pd.

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% to 0.3%. The differences in contents before and after the correction are <0.1% for Ir, Pt and Re. The differences for Pd are <1% for altered dacites, but are 20% to 25% for native sulfur. The

differences for Ru range from 9% to 26% for most samples, but they were significantly higher for MS-1-D (51%), MS-3-D (81%), DG18-5 (>100%), and DG20-4 (42%). However, the Ru values for samples with large correction are in agreement with those with small correction, which supports the validity of the correction process.

Average procedural blanks determined from 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 Rh, 16 ± 9 for Pt, 17 ± 4 ppt for Pd, and 18 ± 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. We performed replicate analyses of the reference material TDB-1 in order to assess accuracy and precision of the analyses. The results show reproducibility of 2% and 6% for Pd and Pt respectively, and 9–14% for other PGEs and Re. The measured values are consistent with those from previous studies (Peucker-Ehrenbrink et al., 2003; Meisel and Moser, 2004) within 2σ error (Supplementary data A), although Re values of ~ 0.72 ppb in this study is slightly lower than the values ($\sim$1 ppb) reported in Ishikawa et al. (2014).

4. RESULTS

The PGE contents of the native sulfur samples are 0.379–0.710 ppb for Pd, 0.414–0.780 ppb for Pt, 0.012–0.041 ppb for Ru, <0.0003–0.0007 ppb for Ir, and 10.8–16.0 ppb for Re (Table 1). These values are consistent with the compositional range of the Niuatahi-Motutahi dacites (Park et al., 2015), whereas Au, Cu, and Re contents are $\sim$500, $\sim$150, $\sim$20 times higher respectively (Fig. 1a). Duplicate analyses of the native sulfur are nearly congruent with differences generally less than 20% except for MS-3, suggesting they are homogeneous at a sample size of 5 g.
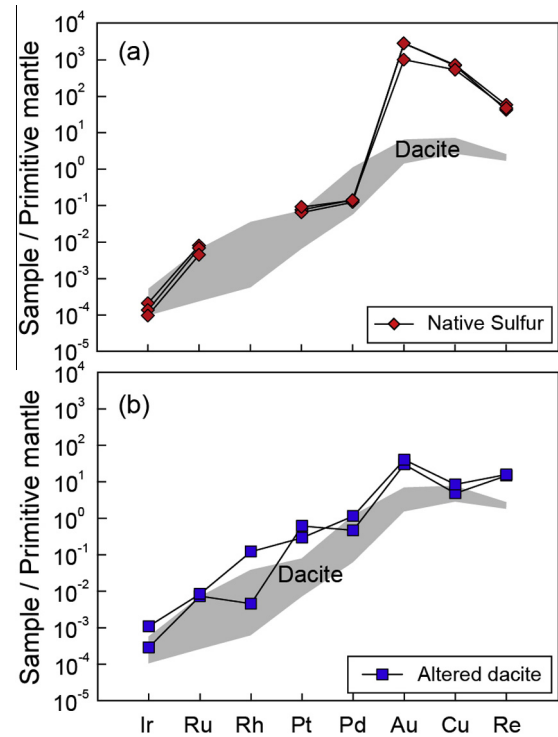

Fig. 1. Primitive mantle normalized PGE-Au-Cu-Re patterns of (a) native sulfur and (b) altered dacites from the Niuatahi-Motutahi volcano. Gray fields represent the patterns of fresh dacites from the Niuatahi-Motutahi (Park et al., 2015). Primitive mantle values are from McDonough and Sun (1995).

Furthermore, the PGE abundances in different samples, from the same native sulfur deposit, generally agree with each other (Fig. 1a and Table 1). The PGE contents in the altered dacites range from 1.82 to 4.46 ppb Pd, from 2.07 to 4.36 ppb Pt, from 0.004 to 0.110 ppb Rh, from

Table 1
Platinum group element and Re contents of native sulfur and altered dacite from the Niuatahi-Motutahi, Tonga rear arc (ppb).

Sample	Ir	Ru	Rh	Pt	Pd	Re
Native sulfur						
MS-1	0.0006	0.040	n.d.	0.55	n.d.	12.7
MS-1-duplicate	0.0007	*0.041*	n.d.	0.54	0.55	10.8
MS-2	<0.0003	n.d.	n.d.	0.51	n.d.	n.d.
MS-2-duplicate	0.0006	0.034	n.d.	0.41	0.48	16.0
MS-3	<0.0003	0.033	n.d.	0.52	0.38	13.5
MS-3-duplicate	0.0003	*0.012*	n.d.	0.78	0.71	12.9
Weighted mean	0.0005	0.032	n.d.	0.55	0.53	13.2
Enrichment factor[*]	25	280		75	11	820
Altered dacite						
DG18-5	0.0009	*0.036*	0.004	4.36	1.82	4.1
DG20-4	0.0035	*0.042*	0.11	2.07	4.46	4.4
Fresh dacite[**]						
Average (n = 10)	0.0007	0.004	0.007	0.27	1.72	0.60
1σ	0.0007	0.009	0.012	0.17	1.17	0.07
Range	<0.0003–0.002	<0.0012–0.032	<0.0005–0.033	0.05–0.52	0.22–4.01	0.51–0.70

n.d., not determined; numbers in italics are data with large interference correction (>50%).
[*] See the text for calculation method.
[**] Data from Park et al. (2015), detection limit values were used for the samples with PGE concentrations below detection limits.

0.036 to 0.042 ppb Ru, from 0.0009 to 0.0035 ppb Ir, and from 4.1 to 4.4 ppb Re (Table 1). These contents are similar to or slightly higher than the values for fresh dacites, except for Pt and Re, which are about 10 times higher in the altered dacites than in the average fresh dacite values (Fig 1b). Primitive mantle normalized patterns of both native sulfur and altered dacites resemble those for fresh dacites with the exception of Au, Re and Cu, which show substantial enrichment in the native sulfur (Fig. 1).

5. DISCUSSION

5.1. Behavior of PGE, Au, Cu and Re during magma degassing

The partitioning of an element between volcanic gas and magma during degassing can be quantified by the enrichment factor (Zoller et al., 1983), which is defined as

$$\frac{(X/R)_{\text{gas}}}{(X/R)_{\text{magma}}}$$

where X and R are the content of the element of interest and reference element in the gas and magma respectively. Volcanic gas emitting from magma consists of two fractions: a volatile gaseous phase and a silica-rich aerosol (Symonds and Reed, 1993). An element can be carried by both the volatile gaseous species and as silicate aerosols in the volcanic gas. Therefore the total amount of the element in volcanic gas represents the sum of these two fractions. Our sulfur condensates sample both components. A particular element that has extremely low affinity to the volatile gaseous phases should be selected as a reference element with assumption that the element is only transported by silicate aerosols. In previous studies, Al, Mg, Ti and Th have been used as reference elements (Zoller et al., 1983; Symonds et al., 1987; Moune et al., 2006; Calabrese et al., 2011). We selected Al in this study because it is rarely carried by volatile phases and is a commonly measured element for gas condensates and sublimates from other localities, which allowed us to compare data from other sources with the Niuatahi-Motutahi condensates. The average compositions of the Niuatahi-Motutahi dacites ($n = 10$; Park et al., 2015) and native sulfur condensates ($n = 3$) were used as magma and gas composition respectively (Tables 1 and 2). If enrichment factor is 1, the element is only transported by silica-rich aerosol. The enrichment factor becomes greater than one if more of the element is carried by volatile gaseous phases.

The enrichment factors of the PGEs, Re, Au, Cu, and other trace elements for the native sulfur are reported in Tables 1 and 2. The result shows that Au, Cu and Re are efficiently transported by volatile phases with enrichment factors of ~20,000, ~5,000 and ~800 respectively. The enrichment factors of the PGEs range from 280 for Ru to 11 for Pd, which are more than two orders of magnitudes lower than those of Au and Cu. These results suggest that PGEs have appreciably weaker affinities to magmatic volatile phases in the Niuatahi-Motutahi magma system than Au and Cu. The higher compatibility of Au and Cu relative to PGEs are consistent with similar conclusions based on

thermodynamic and experimental studies (Wood, 1987; Simon et al., 2006; Simon and Pettke, 2009). The affinity of the PGEs for volatile phases decreases in the order Ru > Pt > Ir > Pd. Zinc show moderate compatibility to the volatile phases with the enrichment factor of 18. The enrichment factor of rare earth elements (REE) were ~1, suggesting that they are dominantly carried by silicate aerosols. Barium, Nb, Hf, and Ta show slightly higher affinity for volatile phases with enrichment factors of >2 (Table 2).

It might be argued that precipitation of PGEs could have occurred during ascent of the volcanic gasses as a consequence of cooling and interaction with the wall rocks. A study of gas sublimation in silica tubes (Zelenski et al., 2013) provides an insight as to what to expect. Zelenski et al. (2013) reported that Au deposits at the high temperature (800–1000 °C), close to fumarole vents, and tends to precipitate together with, or prior to, PGEs forming Au-PGE alloys. The high Au contents in the Niuatahi-Motutahi condensates imply that the loss of PGE during ascent of volcanic gas is unlikely. If it had occurred, the Au content of the Niuatahi-Motutahi native sulfur would have been substantially depleted.

Fig. 2 shows the enrichment factors of PGEs, Re, Au, Cu, Ba and Th for the Niuatahi-Motutahi native sulfur condensates compared with gas sublimates and condensates from other localities (Supplementary data A). The absolute enrichment factors for these metals vary significantly with location, which is partially due to the differences in the content of the reference element Al. The Al contents are about two orders of magnitude lower in gas sublimates from the Erta Ale and the Tolbachik volcanoes, which result in high enrichment factor values, relative to those of gas condensates from Niuatahi-Motutahi and Kudryavy volcanoes (Supplementary data A).

The compositions of the volcanic gas may have also played an important role. Experimental studies on PGE solubility in saline fluid (Fleet and Wu, 1993, 1995; Ballhaus et al., 1994; Hanley et al., 2005) show that the PGEs, particularly Pt, can be transported as a chloride species under oxidizing conditions and at magmatic temperatures. Peregoedova et al. (2006) demonstrated that PGEs and Ni could also be carried by a S-dominated vapor at magmatic temperature. Zoller et al. (1983) suggested that Ir enrichment in airborne particulates from the eruption of Kilauea volcano is probably due to the high fluorine contents of the volcanic gas and Ir may have been carried as IrF_6. These results may account for the variation in the PGE contents of gas sublimates and condensates from the volcanoes. The enrichment factors of Os, Re, Pt, and Ir for the condensates from the Erta Ale, Ethiopia and Tolbachik volcanos, Kamchatka are significantly higher than those of the Niuatahi-Motutahi and Kudryavy volcanos (Fig. 2). The gas composition of the Erta Ale is typical of volcanos associated with mantle plumes (Zelenski et al., 2013). The Erta Ale gas has SO_2 and HF contents of 10.9 mol% and 0.34 mol% respectively, which are about a factor of five times higher than those from typical arc volcanoes ($SO_2 = 1.44$ mol% and HF = 0.06 mol%; Gerlach, 2004). The Tolbachik gas is also characterized by relatively high HF and HCl contents (0.34 mol% and 1.37 mol%;

Table 2
Major and trace element contents of altered dacites and native sulfur.

	Average fresh dacite[#]		Altered dacite		Native sulfur	Enrichment factor
	n = 13	1σ	DG18-5	DG20-4	DG18-3-S	
Major elements (wt.%)						
SiO$_2$	66.0	2.37	65.4	35.7	2.63	
Al$_2$O$_3$	13.0	0.49	12.9	15.4	0.36	
FeO(T)	6.92	0.71	6.04	14.2	0.62	
MnO	0.14	0.01	0.01	0.01	0.004	
MgO	1.50	0.47	0.97	1.41	0.04	
CaO	5.34	0.67	3.59	0.79	0.13	
Na$_2$O	2.88	0.21	3.08	2.54	0.34	
K$_2$O	1.31	0.17	0.60	0.92	0.01	
TiO$_2$	0.56	0.04	0.56	0.67	0.04	
P$_2$O$_5$	0.22	0.02	0.18	0.16	<0.01	
LOI	1.26	0.65	5.03	25.2	91.8	
Total	99.1	0.56	98.4	96.9	96.0	
SO$_2$			12.9	29.4	35.8	
Trace elements (ppm)						
Au	0.004	0.002	0.030	0.041	2.2[*]	20,300
Sb	n.d.		0.9	1.6	26.1[*]	
Se	n.d.		23	36	5.1[*]	
Cu	131	37	145	253	19,400[*]	5,340
Zn	90	8	76	73	45[*]	18
Sr	257	11	252	319	10	1.4
Nb	6.5	0.7	5	6	0.4	2.2
Ba	287	22	251	170	18	2.3
La	10.7	0.6	8.6	10.6	0.34	1.1
Ce	21.8	1.2	17.7	20.2	0.67	1.1
Pr	2.75	0.13	2.16	2.32	0.08	1.1
Nd	12.1	0.6	9.10	8.70	0.32	1.0
Sm	2.88	0.10	2.10	1.60	0.08	1.0
Eu	0.87	0.05	0.83	0.43	0.02	1.0
Gd	3.08	0.13	2.10	1.10	0.08	0.9
Tb	0.49	0.03	0.40	0.20	0.02	1.5
Dy	3.21	0.18	2.50	0.90	0.1	1.1
Ho	0.68	0.04	0.50	0.20	0.02	1.1
Er	2.13	0.13	1.60	0.50	0.06	1.0
Tm	0.31	0.02	0.27	0.08	0.01	1.2
Yb	2.17	0.12	1.90	0.50	0.07	1.2
Lu	0.34	0.02	0.30	0.07	0.01	1.2
Hf	1.62	0.10	1.60	1.70	0.10	2.2
Ta	0.36	0.04	0.30	0.40	0.02	2.0
Th	1.57	0.09	1.50	1.50	0.08	1.8
U	0.58	0.05	0.70	5.70	0.02	1.3

n.d., not determined.
[#] Data from Park et al. (2015).
[*] Average of sulfur 1 (MS-1), 2 (MS-2) and 3 (MS-3) in Kim et al. (2011).

Zelenski et al., 2014) compared with typical arc values (Gerlach, 2004). We suggest that the high abundances of HF, SO$_2$ and HCl in the magmatic volatile phases may have enhanced the transport capability of Os, Re, Pt, and Ir and resulted in enrichment of these elements in the Erta Ale and Tolbachik condensates relative to the Niuatahi-Motutahi and Kudryavy condensates, which originated from arc volcanic gas (Taran et al., 1995).

Despite the discrepancy in the enrichment factor of metals between localities, there are some common features in the relative compatibility of the metals in volatile gaseous phases (Fig. 2). First, Au, Cu and Re are more efficiently transported by the gaseous volatile phases than most PGEs,

except for the gas condensates from the Kudryavy volcano (Yudovskaya et al., 2008). The enrichment factor of Au and Cu are 4 and 74 respectively for the Kudryavy samples which are lower than those of Os (~500) and Ir (~246). Temperature of the Kudryavy volcanic gas ranges from ~300 to 800 °C (Yudovskaya et al., 2008), which is lower than for Tolbachik and the Erta Ale (>1000 °C; Zelenski et al., 2013, 2014). We suggest some Au was lost from the Kudryavy volcanic gas during ascent to the surface. Second, although Os, Ru, Ir and Pt show high compatibility to volatile phases in some localities, Pd consistently show weak affinity for the volatile phases with the lowest enrichment factor values among the PGEs.
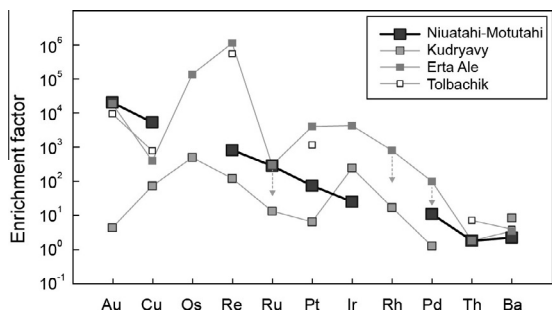
Fig. 2. Enrichment factors for PGE, Au, Cu, Th, and Ba in native sulfur from the Niuatahi-Motutahi, gas condensates from the Kudryavy, Kamchatka (Taran et al., 1995; Yudovskaya et al., 2008), and gas sublimates from the Erta Ale, Ethiopia (Zelenski et al., 2013) and the Tolbachik, Kamchatka (Zelenski et al., 2014). The Os, Rh and Pd contents of the Erta Ale gas sublimates were below the detection limits of 0.3, 0.6 and 12 ppb respectively. The maximum enrichment factors were calculated using analytical detection limit values for Os, Rh and Pd for the Erta Ale gas sublimates (gray square with arrow headed dotted lines).

5.2. Behavior of PGE, Au, Cu and Re during hydrothermal alteration

Whole rock major and trace element composition of the altered and fresh dacites ($n = 10$; Park et al., 2015) are reported in Table 2. The two altered dacites are characterized by high LOI (5–25 wt.%) and SO_2 contents (13–30 wt.%), and relatively low MgO, CaO, MnO, K_2O, and Ba compared to the fresh dacites (Table 2). The marked increase in the water content accompanied by loss of alkali and alkaline earth metals indicates breakdown of primary igneous minerals by fluid-rock interactions. The high sulfur abundances of the altered dacites suggest introduction of a substantial amount of sulfur by the hydrothermal fluid. The high total FeO content of DG20-4 can be attributed to the abundant secondary pyrite crystallization.

The PGE contents of the altered dacites are comparable to those of the fresh dacites except for Pt and Rh (Table 1; Fig. 1b). The Pt contents of the altered rocks are typically about ~15 times higher than those of average fresh dacites and Rh is ~10 times enriched in one sample, DG20-4 (Table 1). The altered dacites also contain 10 times more Au and Re than the fresh dacites together with slight enrichment in Cu. Given the high degree of alteration, it is remarkable that both fresh and altered dacites have such similar PGE contents and similar mantle-normalized patterns (Table 1; Fig. 1b). These results suggest that PGEs are little affected by strong hydrothermal alteration process although Pt and Rh can be moderately mobile. This conclusion is consistent with the study of Crocket (2000) in which they investigated the effect of alteration on Ir, Pd and Au by comparing the composition of altered basalts with fresh basalts from the Kilauea volcano, Hawaii. They showed that there were small differences in Pd and Ir contents between altered and fresh basalts whereas Au values are systematically enriched in the altered rocks, suggesting limited mobility of the PGEs compared to Au. At the Niuatahi-Motutahi, Pt and Rh have been introduced into the altered dacites, along with Au, Cu, and Re, by low temperature hydrothermal fluid.

There has been growing interest in the application of PGE geochemistry in felsic and intermediate volcanic rocks to determine the timing of sulfide saturation in igneous suites associated with porphyry deposits (e.g. Park et al., 2013, 2015). These studies assumed that PGE contents of slightly altered volcanic and intrusive rocks from porphyry deposits are of dominantly magmatic origin. This study confirms the low mobility of PGEs during secondary hydrothermal alteration compared with Cu and Au.

5.3. Implications for the formation of Pd and Pt bearing porphyry Cu–Au deposits

It has been suggested that some porphyry Cu–Au deposits can be a potential source of PGE. The examples include the Skouries deposit, Greece (Economou-Eliopoulos and Eliopoulos, 2000), the Elatsite deposit, Bulgaria (Augé et al., 2005), the Mount Milligan deposit, Canada (LeFort et al., 2011), the Kalmakyr deposit, Uzbekistan (Pašava et al., 2010), the Sora, Aksug and Zhirenken deposits, Russia and the Erdenetiun-Obo deposit, Mongolia (Sotnikov et al., 2001), the Santo Tomas II deposit, Philippines (Tarkian and Koopmann, 1995), and the Grasberg deposit, Indonesia (Tarkian and Stribrny, 1999). PGE-rich porphyry deposits are commonly associated with oxidized calc-alkaline or alkaline porphyry intrusions in subduction or collision related tectonic environments (Tarkian and Stribrny, 1999; Economou-Eliopoulos, 2005). The porphyry intrusions are typically monzonite, granodiorite and/or syenite.

The PGE mineralization in porphyry Cu–Au deposits is characterized by Pd and Pt-rich ore samples without significant IPGE enrichment. The Ir contents of ore samples are <1 ppb in many deposits and Pd/Ir ratios range from ~100 to 10,500 (Augé et al., 2005; Economou-Eliopoulos, 2005). The Pd and Pt-bearing phases, such as merenskyite, are closely associated with bornite, chalcopyrite, pyrite and magnetite from early vein-type ores in potassic alteration zones as indicated by their association with hydrothermal K-feldspar and biotite (Economou-Eliopoulos, 2005 and reference therein). This textural evidence indicates that the PGEs and Cu have been transported by magmatic volatile phases and were precipitated simultaneously during the main stage of mineralization (Economou-Eliopoulos, 2005 and reference therein). It should also be noted that Pd is more enriched than Pt in most of these deposits. For example, the average Pd/Pt values of ore samples from the Elatsite ($n = 37$), Skouries ($n = 9$), Kalmakyr ($n = 4$), and the Santo Tomas II porphyry Cu deposits ($n = 4$) are 16, 60, 22 and 7, respectively (Tarkian and Koopmann, 1995; Augé et al., 2005; Tarkian et al., 2003; Economou-Eliopoulos and Eliopoulos, 2000; Pašava et al., 2010).

Two key questions regarding the formation of PGE mineralization in porphyritic systems are: (1) why are they only found in association with highly oxidized alkaline and calc-alkaline magmas and (2) why is porphyry mineralization enrichment in Pd relative to other PGEs. Thompson et al. (2001) and Augé et al. (2005) studied the PGE mineralization in five alkaline porphyries from British Columbia, and the Elatsite porphyry in Bulgaria, respectively and

suggested the PGEs in the ore samples may have been derived from PGE-rich magmatic sulfides in comagmatic mafic intrusive rocks or the mafic country rocks adjacent to the porphyry system. They argue that secondary hydrothermal fluids preferentially remobilize Pd relative to other PGEs and deposit them at the site of porphyry mineralization, which resulted in the high Pd/Ir and Pd/Pt characteristics of ore samples. In contrast, Tarkian et al. (2003) concluded that Pd and Pt were transported as chloride complexes in high temperature (400–>700 °C) magmatic volatile phases derived from the evolved magma of the porphyry systems. They attributed the high Pd/Pt of the mineralized samples to Pd being more compatible that Pt in magmatic volatile phases.

This study shows that Pd is appreciably less compatible than other PGEs in magmatic volatile phases and has low mobility during low temperature hydrothermal alteration, which contradicts the previously suggested genetic models (Thompson et al., 2001; Tarkian et al., 2003; Augé et al., 2005). In addition, the association of PGMs with high-temperature bornite-chalcopyrite-magnetite assemblage in potassic alteration zone, and the rare occurrence of PGMs in low-temperature alteration zone (Economou-Eliopoulos, 2005) suggest that secondary redistribution of PGEs is negligible. Fig. 3 shows primitive mantle normalized patterns of mineralized samples from the Elatsite porphyry deposit and three of the deposits from central British Columbia (Augé et al., 2005 and references therein). Their patterns are generally sub-parallel to each other, which suggests that secondary remobilization of PGE is unlikely. Although there is some evidence for Cu and Au mobility, as witnessed from variation in Au/Pd and Cu/Pd ratios, low variations in Pt/Pd indicate limited mobility of these elements. The small variations of Pt/Pd are attributed to Pt rather than Pd loss or gain because of its higher solubility in hydrothermal fluids.

We suggest that the observed Pd-enriched mineralization originates from the melt composition and does not require the remobilization of PGEs or anomalously high affinity of Pd for magmatic volatile phases as suggested in previous studies. Recent PGE studies of arc-related oxidized magmas show that they become depleted in Pt, Rh, Ru, Ir and Os by the early crystallization of IPGE-enriched Cr-spinel and Pt-rich alloys, whereas Pd, Au and Cu behave as incompatible elements prior to sulfide saturation and are enriched by fractional crystallization (Pagé et al., 2012; Park et al., 2013, 2015). As a consequence, the Pd/Pt and Pd/Ir are increased by fractional crystallization from 1.4 and 71 to 18 and 4900 respectively in the Pual Ridge magma, Eastern Manus Basin (Fig. 4; Park et al., 2013). Therefore, magmatic volatile phases exsolved from highly fractionated magmas will have high Pd/Pt and very high Pd/Ir and form Pd-rich ores because the increase in these ratios overwhelm the slightly higher compatibility for Pt and Ir compared with Pd in the magmatic volatile phases. This conclusion is consistent with the primitive mantle normalized patterns of ore samples from porphyry deposits, which mimic those of evolved arc magmas following prolonged sulfide-undersaturated differentiation (Fig. 3). Fig. 4 shows Pd/Pt variations of the Pual Ridge
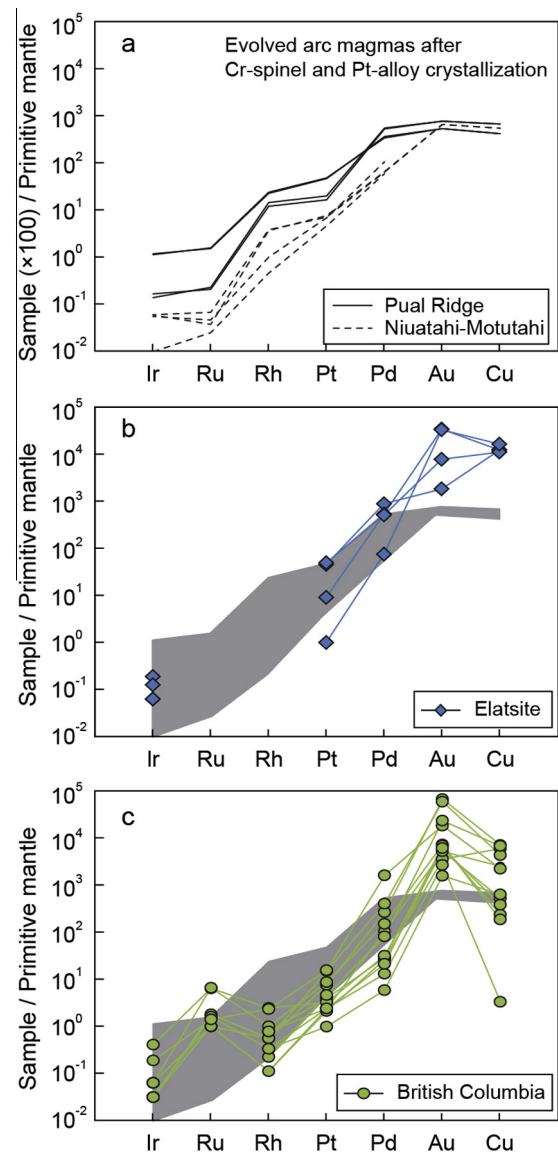

Fig. 3. (a) Primitive mantle normalized PGE-Au-Cu patterns of evolved lavas from the Pual Ridge (MD101b and 86 DR; Park et al., 2013) and Niuatahi-Motutahi (DG17-1, DG17-4, DG20-1; Park et al., 2015), which underwent prolonged sulfide-undersaturated magma differentiation that involved the co-crystallization of Pt-rich alloy and Cr spinel. (b) and (c) Primitive mantle normalized PGE-Au–Cu patterns of the ore samples from the Elatsite deposit, Bulgaria and three deposits from British Columbia (Augé et al., 2005). The gray area is the field covered by the evolved lavas from Pual Ridge and Niuatahi-Motutahi taken from (a).

and Niuatahi-Motutahi lavas against MgO as a measure of fractional crystallization. Given the Pd/Pt of arc primitive magmas (>12% MgO) is ~1, the magmas associated with Pd-rich porphyry Cu–Au deposits must have undergone extensive sulfide-undersaturated magma fractionation, which included precipitation of a Pt-rich alloy (e.g. Park et al., 2012a; Kamenetsky et al., 2015), to explain the high Pd/Pt in porphyry Cu–Au deposits. This conclusion is consistent with the close genetic relationship between
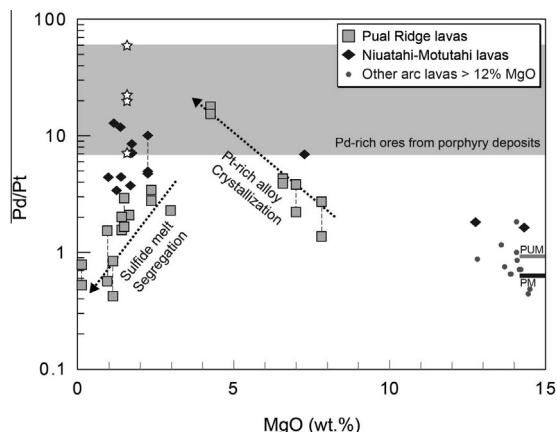
Fig. 4. A plot of Pd/Pt against MgO of the Pual Ridge lavas, Eastern Manus Basin (Park et al., 2013) and the Niuatahi-Motutahi lavas, Tonga rear arc (Park et al., 2015). Arrow headed dotted lines show Pd/Pt variations of the Pual Ridge magma produced by sulfide undersaturated magma differentiation, which initially increases due to precipitation of a Pt-rich alloy, then decreases once the magma becomes saturated with an immiscible sulfide at ca. MgO >3.5 wt.%. Solid circles are compiled PGE data from primitive arc lavas (>12 wt.% MgO) from the Tonga arc (Dale et al., 2012) and the Lesser Antilles arc (Woodland et al., 2002). Pd/Pt values of primitive upper mantle (PUM) and primitive mantle (PM) are from Becker et al. (2006) and McDonough and Sun (1995) respectively. The gray field represents the range of Pd/Pt for ore samples from the Pd-rich porphyry deposits (Tarkian and Koopmann, 1995; Economou-Eliopoulos and Eliopoulos, 2000; Augé et al., 2005; Pašava et al., 2010). Stars represent Pd/Pt of porphyry ore samples at the MgO contents of the associated magma (~1.5 wt.% MgO; Tarkian et al., 2003; Economou-Eliopoulos and Eliopoulos, 2000).

the Pd-bearing porphyry Cu–Au deposits and highly oxidized arc calcalkaline and alkaline magmas because sulfide saturation is less likely to occur under highly oxidized conditions. A recent study of Pd-rich porphyry deposits in the Balkan area (Eliopoulos et al., 2014) showed that the Pd + Pt content and Pd/Pt ratio of ore samples increase with decreasing Cr, confirming the importance of extensive fractional crystallization in the formation of Pd-rich porphyry Cu–Au deposits.

Our hypothesis does not underestimate the importance of the initial composition of magmas. PGE-rich alkaline magmas can be produced at post-collisional tectonic settings as suggested by McInnes et al. (1999) and Richards (2009), which will increase the potentiality for the formation of Pd-rich porphyry Cu–Au deposits. However, it cannot explain the high Pd/Pt and Pd/Ir of the porphyry ores unless there is significant fractionation of Pd from the other PGEs during partial melting. The mantle-derived primitive magmas have Pd/Pt close to mantle values of ~1 (Fig 4).

6. CONCLUSION

We report PGE and Re contents of native sulfur condensates and altered dacite samples from the Niuatahi-Motutahi submarine volcano, Tonga rear arc, to investigate the compatibility of the PGE and Re a magmatic volatile phase and their behavior during hydrothermal alteration. PGEs in altered dacites, with the exception of Pt and Rh, are not enriched when compared to the fresh dacites, indicating low mobility of PGE during secondary hydrothermal alteration. As a consequence, PGE contents in igneous rocks from porphyry deposit, especially those that show low to moderate alteration, retain PGE contents that are close to primary igneous values.

Enrichment factors for PGEs partitioning between magma and magmatic volatile phase are two to three orders of magnitude lower than those for Cu or Au, and Pd is generally less soluble in magmatic volatile phases than other PGEs. PGE mineralization in porphyry Cu–Au deposits is characterized by high Pd contents, high Pd/Pt and very high Pd/Ir in ore samples. These characteristics have been attributed either to preferential enrichment of Pd relative to the other PGEs by secondary remobilization of these elements from magmatic sulfides in mafic rocks, or to the higher partition coefficient of Pd, relative to Pt and Ir, into magmatic-hydrothermal fluids. However, this study shows that the enrichment factor for Pd is less than that of the other PGEs, Au and Cu, which is inconsistent with these hypotheses. We suggest the Pd-rich characteristic of Cu–Au porphyry ores, and their high Pd/Pt and Pd/Ir, are derived from the magma from which magmatic volatile phases exsolved. This requires the magma to have undergone extensive fractional crystallization, without becoming sulfide saturated, prior to volatile saturation. During this period Cu, Au and Pd behave as incompatible elements whereas Pt is sequestered into an early crystallizing Pt-rich alloy and Rh, Ru, Ir and Os into both the metal alloy and Cr-spinel. The resulting magma is enriched in Pd, Cu and Au, with high Pd/Pt and very high Pd/Ir, as required for the source magma of Pt-rich Cu–Au porphyry systems.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2015.11.026.

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