



Noble Metals in Arc Basaltic Magmas Worldwide: A Case Study of Modern and Pre-Historic Lavas of the Tolbachik Volcano, Kamchatka

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Platinum-group elements (PGE) and gold are a promising tool to assess the processes of mantle melting beneath the subduction zones. However, fractionation processes in magmas inevitably overwrite the initial metal budgets of magmas, making constraints on the melting processes inconclusive. Moreover, little is still known about the geochemical behavior of a particular metal in a single arc magmatic system, from mantle melting towards magma solidification. Here we compare noble metals in lavas from several eruptions of the Tolbachik volcano (Kamchatka arc) to better understand the effects of magma differentiation, estimate primary melt compositions and make constraints on the mantle melting. We show that Ir, Ru, Rh and, to a lesser extent, Pt are compatible during magmatic differentiation. The pronounced incompatible behavior of Cu and Pd, observed in Tolbachik magmas, rules out the significant influence of sulfide melts on the early magmatic evolution in this particular case. Gold is also incompatible during magmatic differentiation; however, its systematics can be affected by the inferred gold recycling in the plumbing system of Tolbachik. Although the Tolbachik lavas show only slightly higher PGE fractionation than in MORB, a notable negative Ru anomaly (higher Pt/Ru and Ir/Ru) is observed. We attribute this to be a result of greater oxidation in the subarc mantle (by 1–4 log units), which promotes crystallization of Ru-bearing phases such as Fe³⁺-rich Cr-spinel and laurite. The estimated Pd contents for the parental melt of the Tolbachik lavas approaches 6.5 ppb. This is several times higher than reported MORB values (1.5 ± 0.5 ppb), suggesting the enrichment of Pd in the mantle wedge. Our results highlight the influence of the subduction-related processes and mantle wedge refertilization on the noble metal budgets of arc magmas.

Keywords: basalt, island arc and continental margin arc environment, subduction, platinum, PGE, gold, sulfide, immiscibility

1 INTRODUCTION

Our understanding of subduction zone structures and evolution is based on a complex array of geological, geochemical, and geophysical data. Numerous studies on the behavior of large-ion lithophile (LILE) and high-field-strength (HFSE) elements (e.g., K, Rb and Nb, REE, respectively) have significantly contributed to our comprehension of the process of mantle melting in the presence of subduction-derived fluids and/or hydrous melts (Tatsumi and Eggins, 1995; Zheng, 2019). Another potentially powerful tool in assessing the processes beneath the subduction zones is the systematics of noble metals (i.e., platinum-group elements (PGE) and gold; e.g., Kepezhinskas et al., 2002; Dale et al., 2012; Siegrist et al., 2019; Siegrist et al., 2021). However, current availability of noble metals data in arc rocks has been insufficient for using them as geochemical tracers of mantle melting and associated arc magma generation.

Noble metals have dualistic behavior and can be either chalcophile or highly siderophile depending on the conditions. In sulfide-saturated systems, PGE and Au have strong affinities to sulfide liquids and minerals (e.g., Mungall and Brenan, 2014), whereas in sulfide-undersaturated conditions they tend to form native phases (e.g., Kamenetsky et al., 2015). Under certain circumstances, some PGE (Ru, Ir and Rh) can be incorporated into the Cr-spinel lattice (Locmelis et al., 2011; Park et al., 2012; Park et al., 2017). Although they are geochemically similar, PGE can fractionate from one another, allowing their use as geochemical proxies.

Noble metal budgets in primary arc magmas are initially controlled by the bulk metal contents of the mantle wedge and subduction-related components, as well as the element host phase (e.g., sulfide or native metals), oxygen fugacity and the degree of partial melting (Fleet and Stone, 1991; Fleet et al., 1991; Kepezhinskas et al., 2002; Dale et al., 2012; Siegrist et al., 2019; Siegrist et al., 2021). Subsequent evolution of PGE and Au contents in ascending magmas is largely dependent on magma differentiation processes and parameters, such as the solubilities of metals in silicate melts (Borisov and Palme, 2000; Borisov, 2005), silicate-sulfide partitioning (e.g., Mungall and Brenan, 2014), and partitioning of noble metals into various crystallizing phases (i.e., metal nuggets, sulfides or Cr-spinel) and immiscible sulfide liquids (Dale et al., 2012; Park et al., 2012; Park et al., 2013; Zelenski et al., 2017; Hao et al., 2021). It is crucial to eliminate the effects of magma fractionation in order to use PGE and Au for assessing mantle melting processes. Subsequently, a multiplicity of factors should be considered to assess mantle wedge melting; the most important being the possible influence of the subduction influx on melting processes. This may have a direct impact on the PGE and Au budget of a primitive melt (e.g., Dale et al., 2009; Dale et al., 2012), thus affecting the geochemistry of all subsequent evolved members of a magmatic series.

In summary, our study aims to rule out the effects of magma fractionation in order to assess noble metal budgets of a primitive magma and make further constraints of mantle wedge properties and mantle melting processes. Tolbachik volcano, Kamchatka,

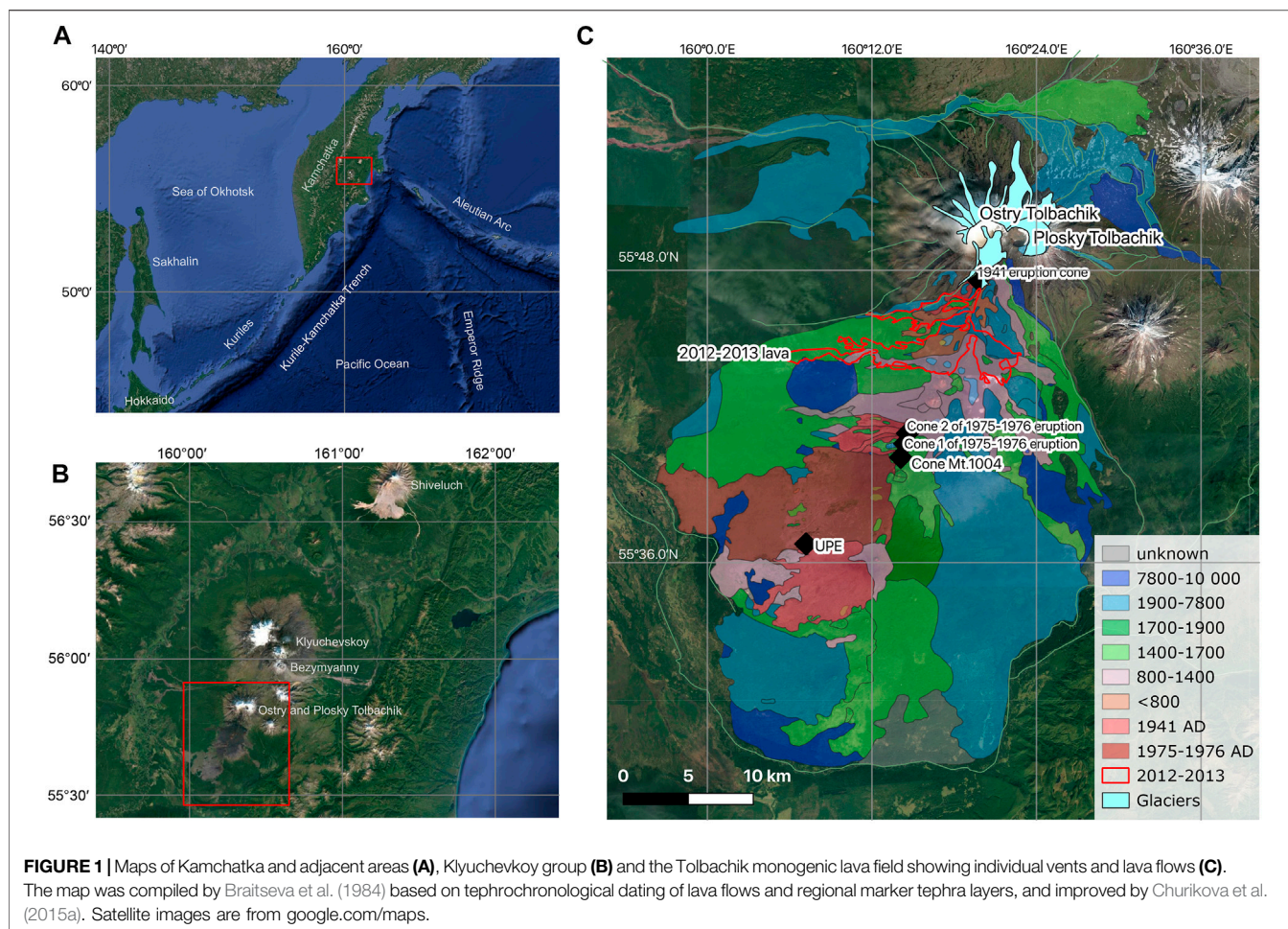
comprises the perfect example for such a study. It has been extensively studied with regards to PGE and Au contents and mineralogy (Zelenski et al., 2016; Zelenski et al., 2017), making it one of the most well-studied in terms of noble metals geochemistry arc volcanic systems in the world. Noble metals from Tolbachik have been documented both in sulfide globules, and as native Au-Ag alloys, the latter being a result of magma differentiation and assimilation of crustal components (Zelenski et al., 2016). Furthermore, the Tolbachik volcano has also been widely studied with respect to its mantle source melting (subduction influx, degree of partial melting, etc.) and differentiation processes (Flerov et al., 1984; Portnyagin et al., 2007; Churikova et al., 2015a; Churikova et al., 2015b; Portnyagin et al., 2015; Mironov and Portnyagin, 2018), providing a framework for the interpretation of new data. Therefore, it provides a great opportunity to investigate the fate of PGE and Au within a single, well-defined arc magmatic system from the mantle wedge to its volcanic vent.

2 GEOLOGICAL BACKGROUND

The Kurile-Kamchatka volcanic arc is one of the most active volcanic areas on Earth (**Figure 1A**), stretching for almost 2,000 km northeast of the Japanese Islands. The Tolbachik volcanic massif belongs to the Klyuchevskoy volcanic group (**Figures 1B,C**), located at the northern end of the Kurile-Kamchatka arc. It comprises the Ostry Tolbachik volcano (extinct), Plosky Tolbachik volcano (active), and a series of monogenic cones associated with two fissure zones extending ~50 km southwards and ~14 km northwards from Plosky Tolbachik (**Figure 1C**). The volcanic field related to the monogenic cones covers an area of 875 km² (Churikova et al., 2015b). Rocks of Tolbachik are represented by low-Mg basalts, and to a lesser extent by high-Mg basalts (Churikova et al., 2015b). The most evolved varieties belong to basaltic trachyandesites (Volynets et al., 2015). The volcano is characterized by high productivity; the volume of eruptive products in dense rock equivalent estimated at 2 km³ in three eruptions over the past 80 years (e.g., Zelenski et al., 2018).

3 SAMPLES AND ANALYTICAL TECHNIQUES

Samples for this study were collected from the 1941 eruptive cone ($n = 2$), cones of the Great Tolbachik Fissure Eruption of 1975-76 (GTFE, $n = 11 + 1$ duplicate), the lava field of the 2012-13 eruption ($n = 1$), and two pre-historic sites: Cone Mt. 1004 ($n = 12 + 3$ duplicates) and the Unnamed Prehistoric Eruption (UPE, $n = 2$). Samples were ground to powder at the Geoscience Laboratories at the Ontario Geological Survey (Canada) with the usage of agate mills in order to avoid contamination, which is possible if Fe-, Ni- and Cr-alloy-based mills are used. Major and trace element contents were analyzed by XRF and ICP-MS, respectively, in the Geoscience Laboratories. Gold and PGE contents were analyzed using NiS fire assay preconcentration

**TABLE 1 |** Measurements of the TDB-1 international standard.

Source	Ir, ppb	Ru, ppb	Rh, ppb	Pt, ppb	Pd, ppb	Au, ppb
Govindaraju (1994)	0.15	0.30	0.70	5.80	22.40	6.30
Plessen and Erzinger (1998)	0.12	0.34	0.33	3.80	20.00	4.80
Peucker-Ehrenbrink et al. (2003)	0.08			4.40	24.80	
Meisel and Moser (2004)	0.08	0.18	0.47	5.01	24.30	
Savard et al. (2010)	0.06	0.16	0.27	4.79	22.35	
Savard et al. (2010)	0.08	0.25	0.47	4.64	22.82	4.00
Kutyrev et al. (2021)	0.08	0.19	0.46	4.89	23.23	
Kutyrev et al. (2021)	0.07	0.15	0.43	4.24	23.35	
Kutyrev et al. (2021)	0.08	0.17	0.43	4.52	22.08	
Kutyrev et al. (2021)	0.07	0.19	0.44	4.48	24.22	
Kutyrev et al. (2021)	0.08	0.19	0.50	4.64	23.31	
Kutyrev et al. (2021)	0.06	0.18	0.42	4.55	23.55	
This study	0.06	0.24	0.43	4.43	21.80	6.90
This study	0.06	0.25	0.45	4.64	21.50	6.00

Blanks = no data available.

followed by ICP-MS (Geoscience Laboratories, Sudbury, ON, Canada). Analysis of blanks provided values not exceeding 0.02 ppb for Pd and smaller values for other PGE and Au, thus being several orders of magnitude lower than the respective concentrations of the studied samples. Several

international standards were used, including UMT-1, OREAS 681, OREAS 682 and TDB-1. The latter is of special importance, as its PGE and Au contents are of the same order of magnitude as the studied samples. **Table 1** compares the results of TDB-1 analysis at the Geoscience Laboratories, Sudbury with the

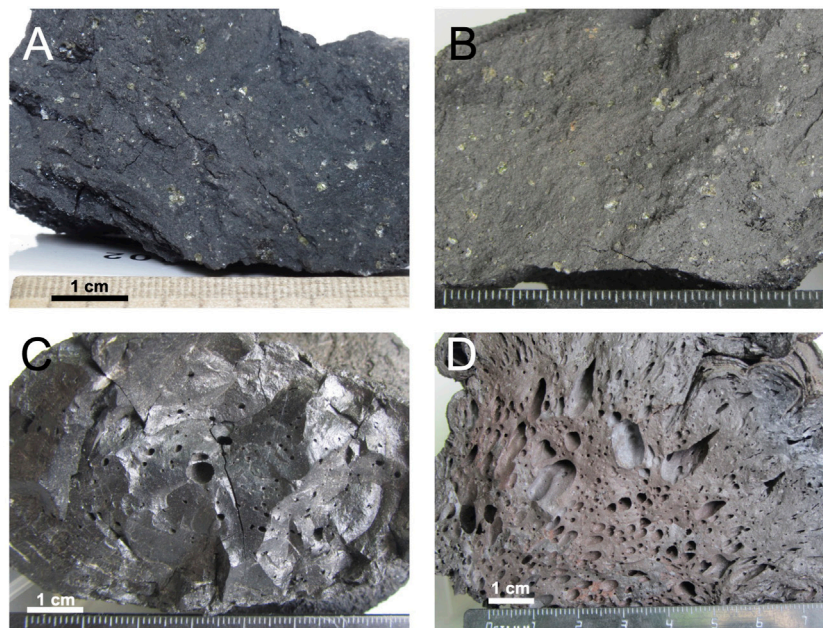


FIGURE 2 | Olivine-phyric high-Mg basalts of Cone Mt. 1004 (**A, B**) and plagioclase-phyric low-Mg basalts of the 2012–2013 eruption (**C, D**).

certified values and analysis of the same standard by isotope dilution previously published. Further details are provided in the **Supplementary Package 1** “Blanks and standards”.

4 RESULTS

4.1 Major and Trace Elements

The most Mg-rich samples are from the Cone Mt. 1004 olivine-phyric lavas (**Figures 2A,B**), which are characterized by MgO contents lying within 9.2–9.5 wt.% (**Figure 3**). Two samples from the 1941 eruption (lava and scoria) are almost identical in MgO content (8.7 wt.%), as well as in all other chemical components. One sample from the GTFE and one from the Unnamed Prehistoric Eruption (UPE) also are high-Mg. Low-Mg lavas (**Figures 2C,D**) and scoria were collected from the GTFE and 2012–2013 eruption. Their MgO contents range from 4.0 to 5.1 wt.%, however they have significantly higher Al_2O_3 , Na_2O , K_2O , and TiO_2 contents than the high-Mg basalts (**Figure 3**). One sample from each of the 1975 eruption scoria and UPE have K_2O contents significantly lower than those of equally primitive samples (**Figures 3E,F,H**). Iron contents remain almost constant across the whole compositional range, similar to the primitive melt composition calculated by Portnyagin et al. (2015). Mg# ($\text{MgO}/(\text{MgO} + \text{FeO})$, mol%) ranges from 0.58 to 0.63 for high-Mg basalts and from 0.42 to 0.55 for low-Mg lavas (**Table 2**).

4.2 Noble Metals

The concentrations of platinum-group elements (PGE) in Tolbachik lavas are summarized in **Table 2**. Iridium is enriched in high-Mg basalts (**Figure 4A**). Similar behavior is observed for Ru (**Figure 4B**); however, the difference between

high-Mg and low-Mg rocks is much less pronounced. Rhodium also defies this trend showing significantly higher concentrations in high-Mg rocks (**Figure 4C**).

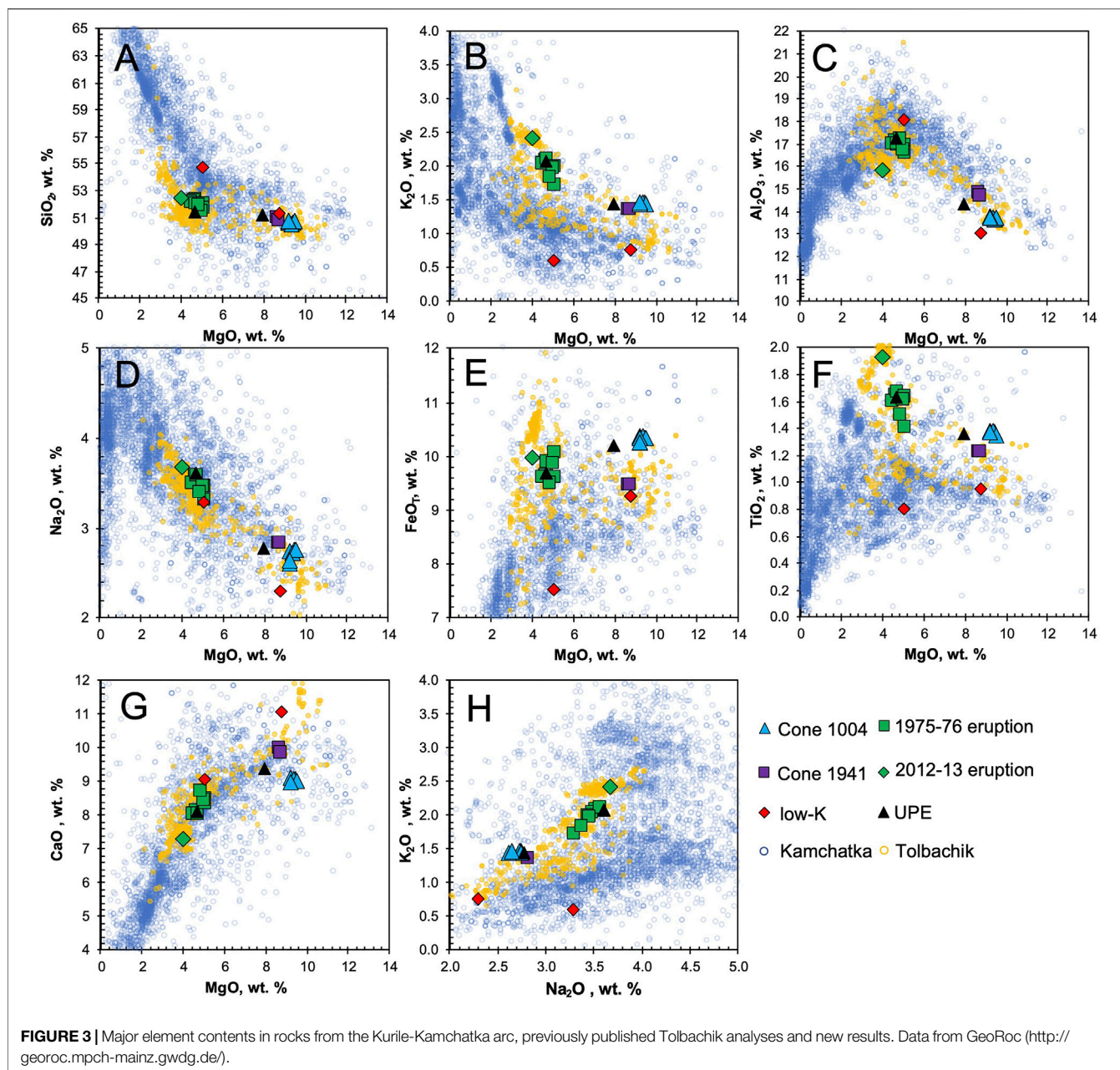
Platinum is only slightly enriched in high-Mg basalts (with the exception of three anomalous samples; **Figure 4D**). These anomalous samples are high- and low-Mg basalt from the UPE (21.5 and 15 ppb Pt, respectively), and low-Mg basalt from the GTFE 1975–76 (17.1 and 21.5 ppb Pt for sample and duplicate).

Palladium is enriched in low-Mg rocks (**Figure 4E**). High-Mg samples from the 1941 eruption and one of the samples from GTFE have high Pd contents of 8.0–8.5 ppb, whereas other high-Mg basalts have moderate Pd contents (5.7–6.5 ppb). In general, low-Mg basalts are enriched in Pd relative to high-Mg basalts. Gold distribution closely mimics that of Pd (**Figure 4F**), with significantly higher concentrations in low-Mg (2.8–3.9 ppb) relative to high-Mg samples (1.8–2.6 ppb). Several samples, two from Cone Mt. 1004 and one of the 1975–76 eruption, are anomalously Au-rich and have not been considered in the calculations.

5 DISCUSSION

5.1 Are the Platinum-Group Elements Data Representative? The Effects of Platinum-Group Elements-Bearing “Nuggets”

To determine whether PGE and Au contents are representative of the sampled lava flow, 13 samples and 3 duplicates from Cone Mt.



1004 were analyzed. The results are uniform and have relatively low standard deviations for all elements except Au (Table 3), indicating homogenous distribution of PGE-bearing phases.

Nevertheless, six samples in the full dataset ($n = 32$) showed anomalous enrichment in one noble metal. Gold-rich samples are exclusively from high-Mg basalts, either the 1941 eruption or GTFE, whereas Pt-rich samples are either from the UPE or GTFE. This can be attributed to the “nugget effect” (heterogeneous distribution of anomalously large grains of a particular metal) or occur as a result of a specific process that may have enriched the melt. The duplicate of the UPE Pt-rich sample also yielded

anomalous Pt contents. Given the established homogenous Pt distribution in samples from Cone Mt. 1004, this suggests that, for some samples, high metal contents may be an intrinsic property of the magma and cannot be ascribed to the presence of nuggets (Figure 4D).

A plausible explanation for Pt enrichment is the presence of sulfide blebs which have been reported for high-Mg basalts of the 1941 eruption and Cone Mt. 1004 (Zelenski et al., 2017). However, these blebs show a perfect Pt-Pd correlation, whereas the studied samples are enriched exclusively in Pt (Figure 5). Alternatively, such enrichment could be attributed

TABLE 2 | Composition of Tolbachik lavas.

#	Sample id	Location/eruption	MgO	SiO ₂	Mg#	Cr	Cu	Ir	Ru	Rh	Pt	Pd	Au		
			wt. %	wt. %		ppm	ppm	ppb	ppb	ppb	ppb	ppb	ppb		
Detection limits															
			0.01	0.04				2.90	0.04	0.01	0.08	0.04	0.17	0.12	4.0
1	Tol-1-18	1941 eruption	8.7	51.0	0.62	563	165	0.19	0.14	0.28	5.99	8.49	2.5		
2	Tol-2-18	1941 eruption	8.7	50.7	0.62	587	174	0.21	0.17	0.28	6.13	8.65	2.6		
3	Tol-3-18	2013 eruption	4.0	52.4	0.42	139	304	0.06	0.11	0.05	3.06	5.82	3.9		
4	Tol-9-18	1975-76 eruption	5.1	54.7	0.55	140	77	0.03	<0.08	0.04	1.37	1.73	1.2		
5	Tol 2106-2	1975-76 eruption	8.7	51.3	0.63	556	90	0.18	0.09	0.34	7.19	7.95	11.9		
6	Tol-10-18	1975-76 eruption	4.8	52.3	0.47	131	228	0.07	<0.08	0.13	3.90	8.14	2.7		
7	Tol-12-18	1975-76 eruption				228	254	0.08	0.11	0.12	3.85	7.34	2.5		
8	Tol-13-18	1975-76 eruption	4.7	52.2	0.47	119	255	0.04	<0.08	0.13	17.10	6.98	2.4		
9	Tol-13-18 dup	1975-76 eruption						0.06	0.08	0.13	18.00	7.49	2.6		
10	Tol 2206-11	1975-76 eruption	4.5	52.1	0.46	176	259	0.07	0.12	0.15	4.10	7.72	3.5		
11	Tol 2206-13a	1975-76 eruption	4.8	52.0	0.46	161	257	0.07	0.09	0.16	4.25	8.40	3.0		
12	Tol 2206-15	1975-76 eruption	5.1	52.0	0.49	154	204	0.09	0.10	0.23	5.01	8.82	2.9		
13	Tol 2206-16	1975-76 eruption	5.1	51.6	0.48	226	248	0.08	0.14	0.16	4.40	7.64	2.8		
14	Tol 2206-17	1975-76 eruption	5.0	51.5	0.48	201	240	0.07	0.08	0.17	4.16	8.24	2.9		
15	Tol 2206-18	1975-76 eruption	4.9	51.9	0.48	161	228	0.06	<0.08	0.19	5.34	8.06	2.8		
16	Tol 2306-1	UPE	4.7	51.4	0.46	150	245	0.06	0.08	0.15	21.50	8.39	3.0		
17	Tol 2306-2	UPE	7.9	51.2	0.58	429	174	0.13	0.10	0.23	15.00	6.05	2.8		
18	Tol 1004-1	Cone Mt. 1004	9.4	50.6	0.62	568	158	0.18	0.13	0.26	5.40	5.72	2.0		
19	Tol 1004-1 dup	Cone Mt. 1004				571	176	0.16	0.09	0.25	5.47	5.90	2.0		
20	Tol 1004-3	Cone Mt. 1004	9.4	50.5	0.62	576	176	0.14	0.08	0.24	5.04	6.01	2.2		
21	Tol 1004-4	Cone Mt. 1004	9.5	50.8	0.62	569	166	0.20	0.13	0.26	5.25	6.50	1.8		
22	Tol 1004-5	Cone Mt. 1004	9.2	50.7	0.62	546	223	0.24	0.12	0.37	7.19	6.39	7.2		
23	Tol-6-18	Cone Mt. 1004	9.2	50.7	0.62	539	207	0.21	0.19	0.22	4.87	5.91	12.6		
24	Tol-6-18 dup	Cone Mt. 1004						0.18	0.08	0.24	5.01	6.20	13.3		
25	D1820-1	Cone Mt. 1004						0.16	0.10	0.23	4.93	5.22	2.1		
26	D1820-2	Cone Mt. 1004						0.23	0.17	0.29	5.46	6.12	1.9		
27	D1820-2-1	Cone Mt. 1004						0.21	0.14	0.31	5.79	6.48	1.9		
28	D1820-3	Cone Mt. 1004						0.19	0.12	0.27	5.52	5.92	2.2		
29	D1820-6	Cone Mt. 1004						0.17	0.11	0.23	5.17	5.84	2.3		
30	D1820-6 dup	Cone Mt. 1004						0.16	0.15	0.24	5.27	5.88	2.3		
31	D1820t	Cone Mt. 1004						0.18	0.18	0.27	5.41	6.42	2.9		
32	D1820t1	Cone Mt. 1004						0.18	0.10	0.38	5.26	6.72	2.2		

Mg# = (MgO/(MgO + FeO)), mol%. Blanks = element was not analyzed. Please, find the complete dataset in the **Supplementary Table S1**.

to the ability of Pt to form inclusions within Cr-spinel (Finnigan et al., 2008; Kamenetsky et al., 2015) or as separate nuggets (Park et al., 2013). Selective enrichment of Pt over Pd may be explained in terms of their relative solubilities in silicate melts, e.g. at a given oxygen fugacity, Pd solubility is more than two orders of magnitude higher than Pt (Borisov and Palme, 2000). Therefore, Pd is retained in the melt, whereas Pt precipitates as Pd-free alloys.

Despite working well for Pt, this phenomenon cannot explain the presence of gold nuggets. Gold solubility in basaltic melts is far too high, restricting its direct precipitation at a wide range of temperatures and fO_2 . For example, the Au solubility estimated by Borisov and Palme (2000) ranges from 40 ppb for QFM-2 at 1,200°C to 5,000 ppb for QFM+2 at 1,350°C, or even higher if sulfide complexation is considered (Botcharnikov et al., 2010). The estimated fO_2 for Tolbachik lavas is QFM+1 to +2, based on chromian spinel compositions (Kamenetsky et al., 2017; Nekrylov et al., 2018) and olivine-sulfide pairs (Zelenski et al., 2018). At this fO_2 , Au solubility might have approached 400 ppb. However, this is two orders of magnitude higher than the most enriched samples (13.3 ppb), making direct gold precipitation from

Tolbachik magmas unrealistic. Therefore, the idea of Au enrichment as a result of crustal assimilation, discussed in Zelenski et al. (2016), appears to be the most plausible explanation.

5.2 Behavior of Platinum-Group Elements During Arc Magma Evolution

Iridium, Ru and Rh show compatible behavior, reflected in their lower contents within more evolved Al-rich basalts. Similar trends have been observed in various volcanic arcs (Figures 6A,B), and can be explained by the capturing of these elements either as admixtures in Cr-spinel (Park et al., 2012; Park et al., 2017), or as nuggets (Kamenetsky et al., 2015). Their accumulation in Cr-spinel is attributed to a redox related response to mineral growth or re-equilibration with the melt surrounding Cr-spinel crystals (Finnigan et al., 2008). Local reduction within the mineral-melt interfacial region occurs as a consequence of the selective uptake of trivalent over divalent Cr and Fe from the melt by spinel (Finnigan et al., 2008).

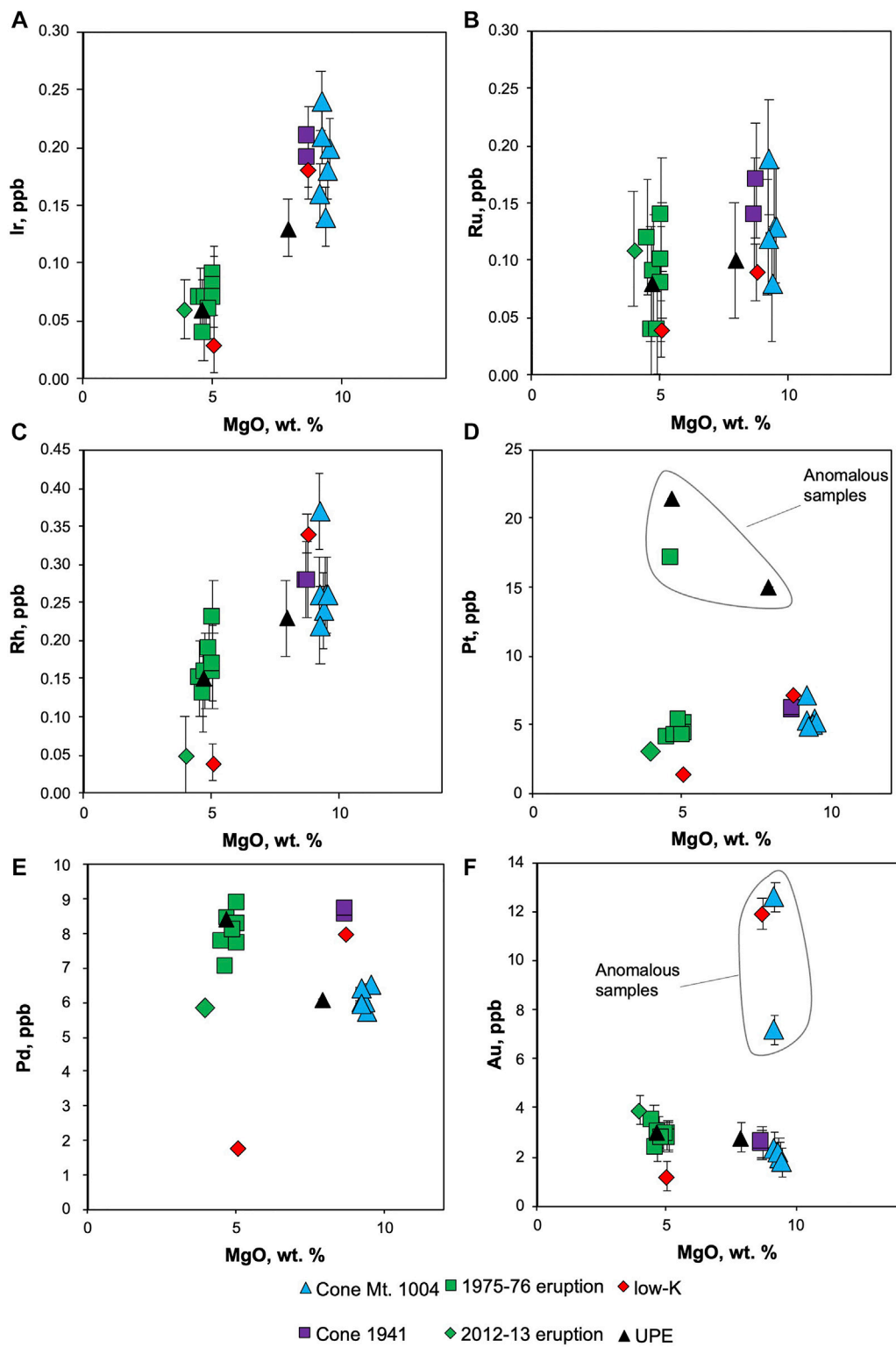


FIGURE 4 | Platinum-group element variation across different MgO contents for Tolbachik lavas. Error bars are provided for Ir, Ru, Rh and Au; for Pt and Pd they are smaller than the size of a symbol.

TABLE 3 | Summary statistics for 12 samples and 3 duplicates of Cone Mt. 1004.

	Ir	Ru	Rh	Pt	Pd	Au
Min	0.14	0.08	0.22	4.87	5.22	1.80
Max	0.24	0.19	0.38	7.19	6.72	13.30
Mean	0.19	0.13	0.27	5.44	6.08	3.26
Standard deviation	0.03	0.03	0.05	0.56	0.39	3.02
Analytical uncertainty	0.03	0.08	0.05	0.19	0.20	0.60
Relative standard deviation, %	15.4	26.1	17.8	10.3	6.4	92.4

Both Pt and Pd show no correlation with MgO from primitive compositions, studied here and from other magmatic arcs, down to ~9 wt.% MgO (Figures 6C–F). Their behavior, however, becomes variable for evolved compositions from global arcs, where Pt and Pd contents often drop drastically, whereas, in Tolbachik, their concentrations remain stable as MgO decreases progressively, indicating a lack of sulfide saturation for the latter, at least up to 4 wt.% MgO. In contrast, Pd contents of MORB lavas with less than ~9.5 wt.% MgO vary drastically (Dale et al.,

2012; Hao et al., 2021). This suggests that MORB and some arc melts achieved sulfide saturation at ~9–9.5 wt.% MgO, producing Pd and Pt depletion, and that other arc melts either did not reach sulfide saturation, or that sulfide saturation did not affect the metal budget.

However, the Tolbachik samples reveal that low-Mg lavas bear slightly higher amounts of Pd than high-Mg lavas (Figure 4E). This indicates incompatible Pd behavior and may be evidence against sulfide saturation during the Tolbachik magmas evolution. Although previous studies reported sulfide-silicate immiscibility in Tolbachik lavas (Zelenski et al., 2018), this process was limited to a small amount of melt and did not significantly affect the overall PGE budget. Moreover, sulfide precipitation itself is not sufficient to affect the PGE budget; rather, the extraction/removal of newly formed sulfide (liquid or crystalline) from a melt is more crucial.

Slight Pt enrichment in high-Mg lavas suggests it behaves compatibly during magma evolution from 10 down to 4 wt.% MgO (Figures 4D, 6C,D). This does not support sulfide saturation as the cause for Pt fractionation, because Pd

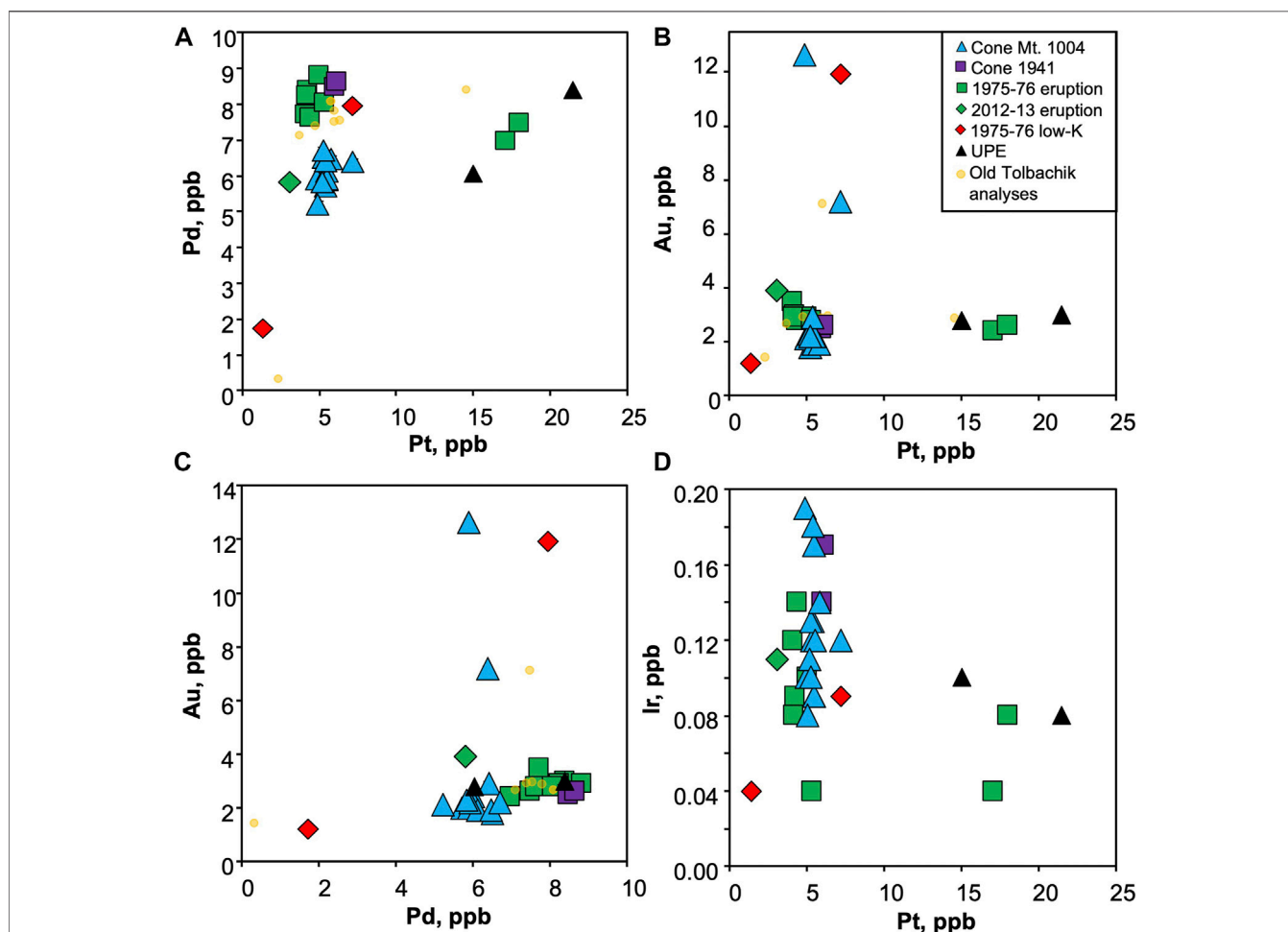
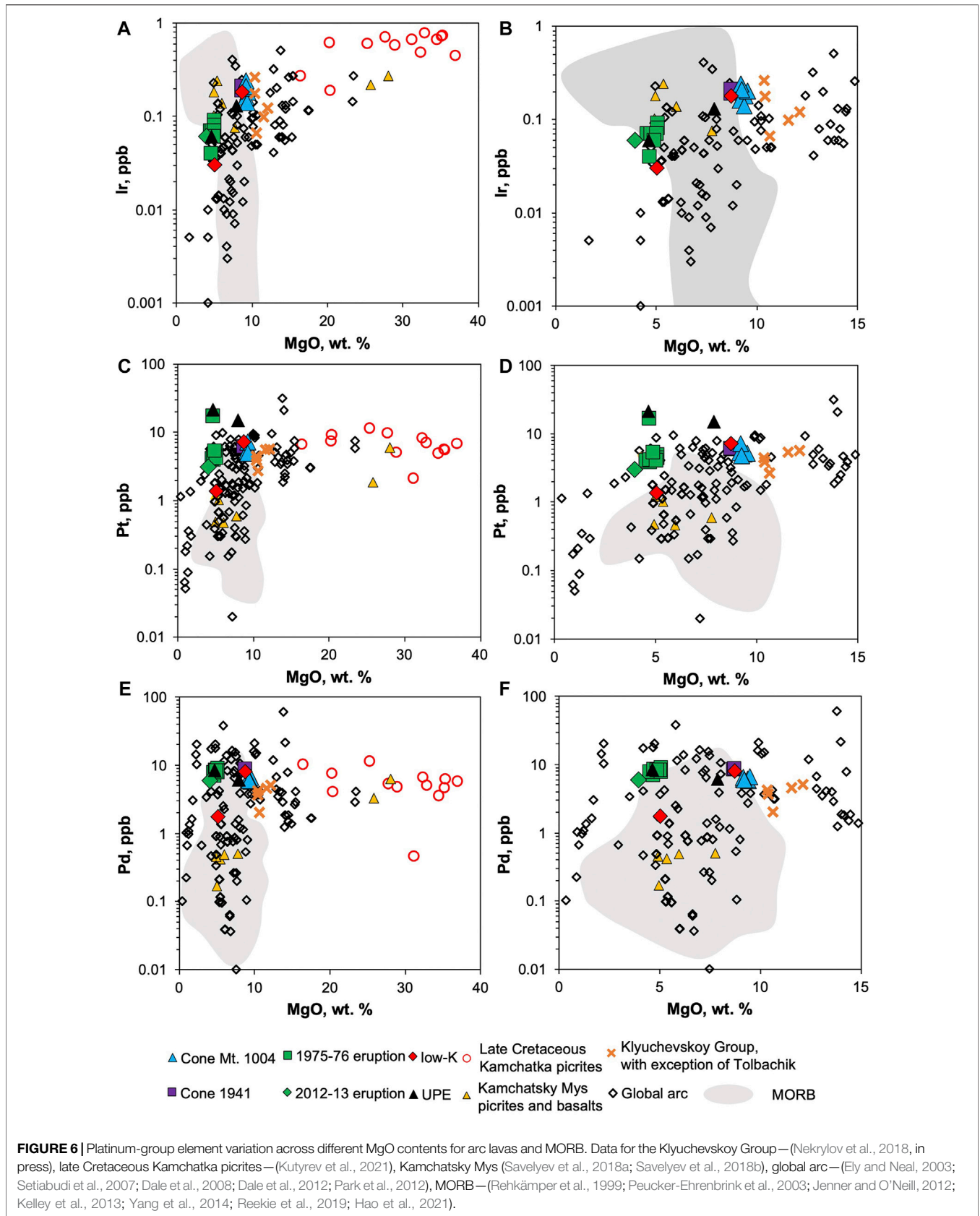


FIGURE 5 | Interelement PGE and Au variation for the Tolbachik volcano. Note Au and Pt anomalies, uncorrelated with concentrations of any other element analyzed.



contents would also be expected to decrease. Nevertheless, the lack of significant Pt–MgO correlations is evident across a range of compositions (9–37 wt.% MgO), i.e., rocks which are likely cumulates of olivine and chromian spinel. This implies that in spite of evidence for Pt–Fe alloy coprecipitation with chromian spinel (Finnigan et al., 2008; Kamenetsky et al., 2015; Arguin et al., 2016), their fractionation does not contribute significantly to the Pt budget of arc magmas in general.

5.3 Platinum Group Element Contents in Parental Melts

The understanding of the PGE budget in parental melts is hindered by fractionation processes. The plurality of factors involved in the formation of particular lava makes precise evaluation of the primitive melt composition almost impossible. Nevertheless, a rough estimation is possible for at least some elements. Due to the lack of significant sulfide saturation, Pd contents show the following: 1) moderate enrichment from ~9 to ~5 wt.% MgO in Tolbachik lavas, and 2) no correlation across the range between 37 and 9 wt.% MgO (Figures 6E,F). This long flat trend suggests that during evolution from the assumed parental melt (~14 wt.% MgO Portnyagin et al., 2015) to the high-Mg basalt, Pd contents did not change significantly, and thus the mean concentration of 6.5 ppb is close to that of primitive mantle-derived melts. For Pt, such an estimate is more complex as it behaves slightly incompatibly. However, other arc rocks show minimal effects Pt contents decrease towards Mg-poor compositions (Figure 4D). Therefore, mean Pt contents in high-Mg basalts (5.8 ppb, ignoring three anomalous samples) may be used as a lower estimate of initial Pt abundances in the Tolbachik primitive melt.

Iridium, unlike Pt and Pd, shows a broad correlation with MgO due to strong compatibility with chromian spinel (Figure 4A). The parental melt of the studied lavas should thus be significantly enriched in Ir. Statistical analysis of previously published data of arc rocks provides an adequate MgO–Ir linear correlation with $R^2 = 0.82$. This allows for the extrapolation of mean Ir contents in low- and high-Mg lavas to 14 wt.% MgO, which results in 0.29 ppb Ir. Normalization of estimated Ir, Pt and Pd contents in the parental melt to primitive mantle values (Lyubetskaya and Korenaga, 2007) yields 0.1, 1.3 and 1.8 ppb, respectively, and a Pd_N/Ir_N (“N” stands for primitive mantle normalization) ratio of 20. This indicates that the fractionated pattern of the Tolbachik lavas is not only the result of fractional crystallization, but also inherited from the mantle-derived melt.

5.4 Comparison Between Arc and MORB Primitive Magmas

Mechanisms of metal transfer from mantle to melt are variable in subduction and oceanic rift environments (e.g., Dale et al., 2012; Mungall and Brenan, 2014; Park et al., 2017). The main PGE hosts in the mantle are sulfides (Keays et al., 1981; Kepezhinskias et al., 2002; Barnes et al., 2015) and alloys (e.g., Rehkämper et al., 1999). Oxidizing conditions in the sub-arc mantle during magma

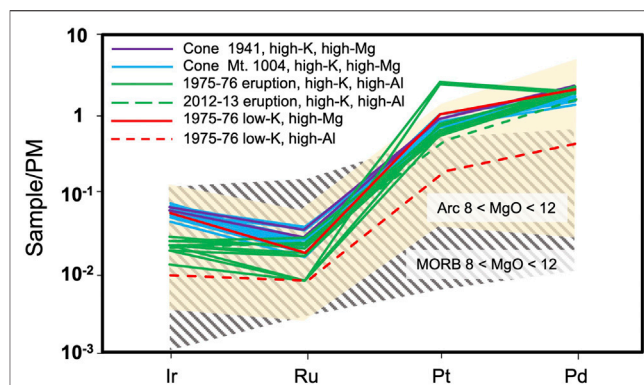


FIGURE 7 | Primitive mantle-normalized PGE patterns of the Tolbachik lavas compared to arc and MORB rocks. Only samples with MgO contents between 8 and 12 wt.% are displayed. Same references as **Figure 8**. Values normalized following Lyubetskaya and Korenaga (2007).

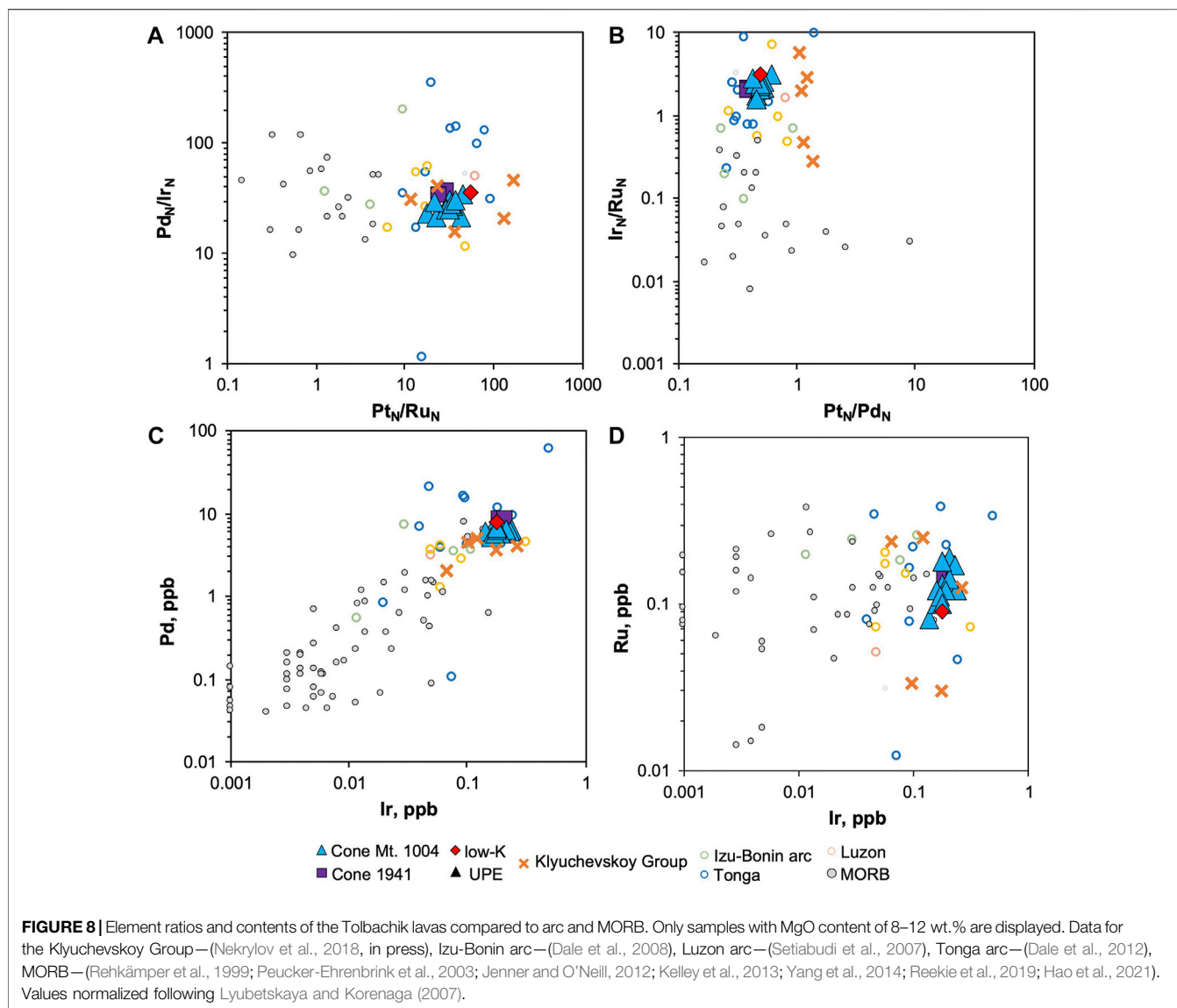
generation should result in complete sulfide consumption. Therefore, Pd, and to a lesser extent Pt, partition into the melt, whereas Ir, Os and Ru are retained in the source residue (Dale et al., 2012). Thus, a comparison between PGE contents in primitive arc and MORB melts may provide insights into the role of the subduction flux on the PGE budget.

Palladium can fractionate from Ir during common magma differentiation processes, including the formation of immiscible sulfide melts and the partitioning of Ir in Cr-spinel (Barnes et al., 1985; Park et al., 2012; Barnes et al., 2015). It has been shown, however, that the fractionated patterns of arc rocks are partly inherited from their mantle source or produced during partial melting (Park et al., 2017). This is also supported by the estimated Pd_N/Ir_N value for the Tolbachik primitive magmas (20). The difference in Pd_N/Ir_N between MORB and arc rocks across the range of 8.5–12.0 wt.% MgO is not significant, yielding 35.8 and 53.4, respectively (Figures 7, 8A). This similarity is also observed for Pt_N/Pd_N (Figure 8B). The principal difference between arc and MORB is related to Ru. For example, ratios of Pt_N/Ru_N (Figure 8A) or Ir_N/Ru_N (Figure 8B) are much greater in arc rocks.

The differences in individual element contents are more prominent than their ratios (Figures 8C,D). For instance, the average Pd content in MORB samples containing MgO from 8.5 to 14 wt.% is 0.4 ppb, which is ~15 times less than the corresponding arc values (6.4 ppb). Such a drastic difference evokes the idea that fractionation processes may in fact produce low Pd concentrations in MORB. However, Hao et al. (2021) calculated primitive MORB Pd content to be 1.5 ± 0.5 ppb, which is significantly lower than our estimates of Pd content in the primitive Tolbachik melt (~6.5 ppb). This implies that unfractionated primitive arc melts are enriched in Pd relative to MORB.

The differences between the primitive or near-primitive arc and MORB melts are summarized as the following:

1. Palladium contents are significantly higher in primitive arc magmas than those reported for parental MORB melts.



- Iridium, Rh and Pt contents have not been evaluated for the parental MORB melt; however, comparing high-Mg arc and MORB analyses reveals that the former are systematically enriched in these elements.
- Ruthenium contents of near-primitive arc and MORB melts are similar.

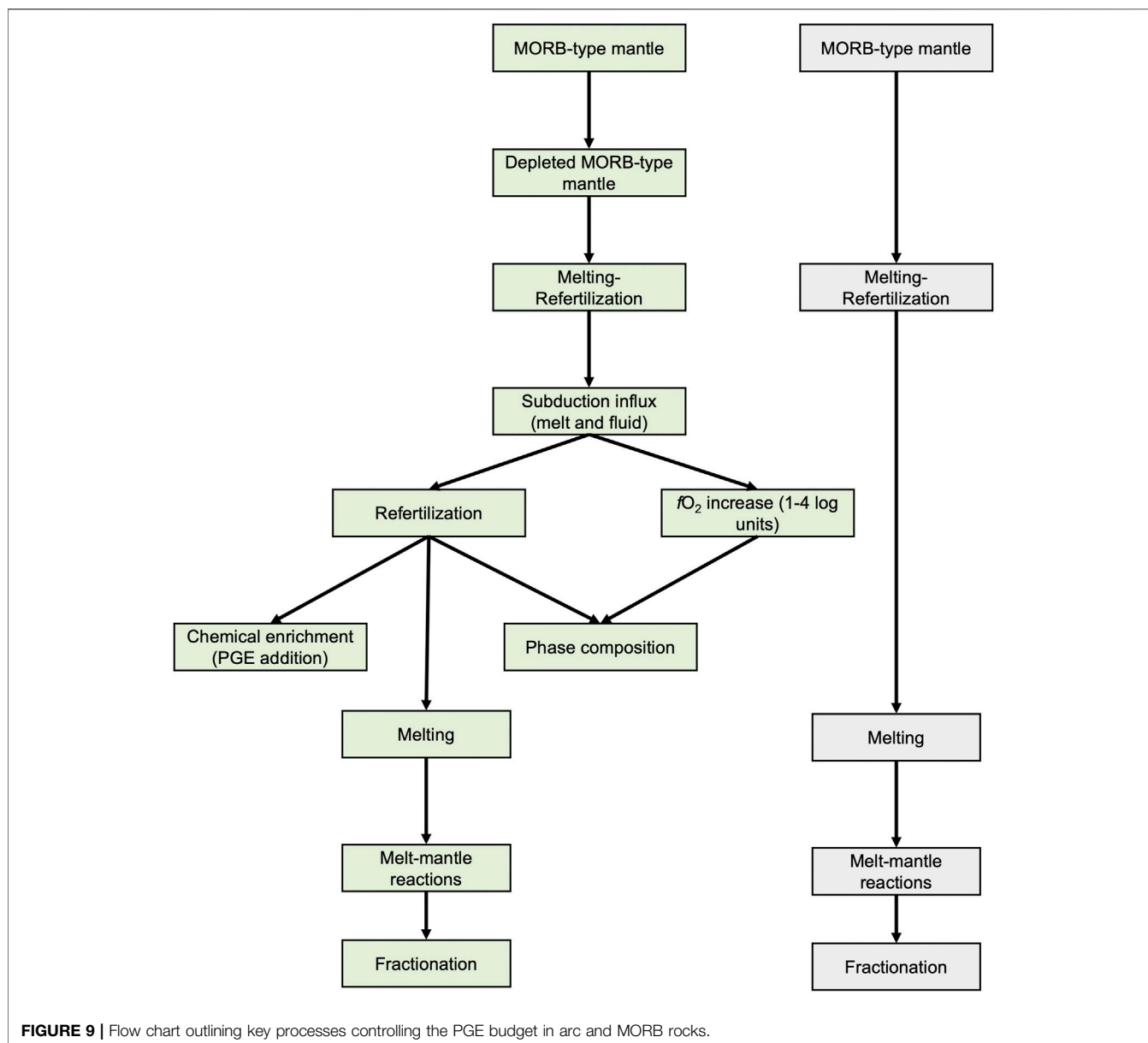
5.5 Mantle Source Controls on the Behavior of Platinum-Group Elements in Primitive Arc Melts

Factors influencing PGE contents in primitive arc and MORB melts are summarized in **Figure 9**. Each process, from partial melting of a MORB-type mantle (depletion) to subsequent alteration in subduction zones (accompanied by potential refertilization), and melt-mantle reactions, precede

fractionation processes *en-route* to, and following emplacement at, the Earth's surface or crust.

5.5.1 Mantle Depletion

It is supposed that prior to melting in supra-subduction environments, peridotites of the mantle wedge may have experienced repeated melting beneath spreading ridges. The degree of depletion may vary depending on the number of melting cycles. For example, the mantle wedge beneath some parts of the modern Kamchatka arc is considered to be moderately depleted relative to depleted MORB mantle (DMM) (e.g., Portnyagin et al., 2007). Accounting for the preceding DMM depletion is especially important in the case of an intra-oceanic arc with active back-arc basins (e.g., Pearce and Parkinson, 1993). As near-primitive MORB rocks show fractionated PGE patterns (**Figure 7**), it is reasonable to expect that the mantle source must



be depleted in Pd and Pt relative to other PGEs. Moreover, due to extremely high sulfide-silicate partition coefficients for PGE, the presence of even minute quantities of residual sulfide in the source region produces melts strongly depleted in PGE (“all or nothing” behavior, Barnes et al., 2015; Waterton et al., 2021). Indeed, most studied abyssal peridotites show depletion in Pt and Pd, whereas there is only a limited record of fertile oceanic mantle rocks (Prichard H. M. et al., 1996). However, this contradicts the Pt and Pd enrichment observed for near-primitive arc rocks, implying that there must be a process that suppresses the effects of mantle depletion.

5.5.2 Refertilization Prior to Subduction

There is evidence for abyssal peridotite refertilization caused by incremental melts *en-route* to the surface. Harzburgites enriched

in sulfides were reported in the Kane Fracture Zone in the Middle-Atlantic Ridge (Luguet et al., 2003). These rocks display elevated $(\text{Pd}/\text{Ir})_N$ ratios, which positively correlate with sulfide modal abundances. In addition, Pt contents were not significantly affected by refertilization.

5.5.3 Subduction Influx: Refertilization

Mantle peridotites may be refertilized in the supra-subduction environment by slab-derived melts and fluids. For instance, Prichard et al. (1996) concluded that the supra-subduction Shetland peridotites, which are enriched in Pt and Pd, were refertilized by boninitic melts, based on comparisons with Pt- and Pd-poor Oman and Troodos peridotites. Mantle wedge xenoliths in subduction zones can be variably enriched in Pt and Pd (McInnes et al., 1999; Kepezhinskis et al., 2002).

However, Pt and Pd may be depleted in mafic oceanic crust that has been metamorphosed under conditions similar to those of subduction zones, inferring that these elements may be transferred to the mantle wedge *via* slab-derived fluids (Dale et al., 2009).

5.5.4 Subduction Influx: Increase of fO_2

It is problematic to explain the elevated PGE budget in arc magmas simply as a consequence of more oxidized conditions during mantle wedge melting, as the arc magma source is 1–4 log units more oxidized than MORB (e.g., Evans et al., 2012), which leads to sulfide destruction. However, prior to sulfide exhaustion, a hypothetical melt would be PGE-depleted due to extreme partitioning of PGE into residual sulfide. After sulfide breakdown, Pd is removed by the melt (as a result of extremely high Pd solubility in silicate melts, Borisov and Palme, 2000; Borisov, 2005), whereas all other PGE may remain in the residue as alloy phases. This may adequately explain Pd abundances in MORB (Mungall and Brenan, 2014), but does not account for the difference between Pd contents in arc and MORB melts, nor for the fractionation of Pt from IPGE and Rh. Several factors have been suggested to resolve the latter problem.

Base-metal sulfides (BMS) in the mantle are composed of monosulfide solid solution (MSS) and/or intermediate solid solution (ISS) (Luguet et al., 2003; Bockrath et al., 2004a; Luguet et al., 2004). BMS melt incongruently producing Cu-Ni-rich sulfide liquid, whereas residual MSS becomes more Fe-rich. Partitioning of PGE between MSS and sulfide liquid varies considerably; from compatible to highly incompatible, in the following sequence $Ir \approx Ru \gg Pt > Pd$ (Li et al., 1996; Mungall et al., 2005). Hence, Pt and Pd fractionate from other PGE via the exhaustion of sulfide liquid in the mantle and leaving residual MSS (Dale et al., 2012). Though this mechanism can explain fractionation in general, it still cannot account for the elevated Pd and Pt concentrations in primitive arc melts relative to primitive MORB (Figures 6, 7C), as well as for their approximately similar Pd/Ir ratios (Figure 8A).

Some PGE may be retained in phases other than sulfides and alloys, such as Ru which has been measured up to 500 ppb in Cr-spinel (Locmelis et al., 2011). Moreover, Ir, Ru and Rh content in Cr-spinel can reach 101, 185 and 95 ppb, respectively, showing a positive association only in Fe^{3+} -rich arc spinels (Park et al., 2017). As the arc mantle is significantly more oxidized than MORB (e.g., Evans et al., 2012), its spinel is expected to be Fe^{3+} -rich and host significant amounts of Ir, Ru and Rh. O'Driscoll and González Jiménez, 2016 argued that since Cr-spinel is an accessory mineral comprising 1–2% of mantle peridotite, its contribution to the PGE budget should be negligible. However, given the presence of ~200 ppb Ru in arc Cr-spinel (Park et al., 2017), the mantle may contain up to 3.7 ppb Ru, which approaches primitive mantle estimates (5 ppb, Lyubetskaya and Korenaga, 2007). As the partition coefficient between Cr-spinel and melt is higher for Ru than for Ir and Rh (Park et al., 2017), this process can adequately account for the positive Ru-anomalies typical for arc magmas (Figure 7).

Another mineral that can be responsible for the Ru anomaly is laurite RuS_2 (Dale et al., 2012; Nekrylov et al., 2018, in press). This

sulfide can precipitate from sulfide-undersaturated basaltic melts (Bockrath et al., 2004b), which suggests that it can possibly act as a residual phase in the mantle. This is also supported by the mineral assemblage of ophiolitic ultramafics, in which laurite is one of the most abundant minerals (Lorand and Ceuleneer, 1989; Garuti et al., 1999; Tolstykh et al., 2009; Prichard et al., 2017; Zaccarini et al., 2018). However, the question of why laurite retains Ru in subduction environments, and not in spreading centers, remains. A possible explanation is that laurite can only form in sulfide-undersaturated conditions, hence high fO_2 (otherwise, MSS will retain Ru, Bockrath et al., 2004b). This scenario corresponds to subduction settings, implying that mantle residue following arc melting must be enriched in laurite and have a positive Ru anomaly, thus mirroring PGE distribution in arc rocks. Indeed, such anomalies have been reported, including within xenoliths of the Kharchinsky volcano (75 km north of Tolbachik, Siegrist et al., 2021). Evidently, the formation of laurite at the expense of MSS contradicts previously suggested explanations of IPGE/PPGE fractionation.

PGE contents are also invariably affected by the stability of alloy phases during mantle melting following sulfide exhaustion. Solubilities of PGE have been established in artificial silicate melts (Borisov and Palme, 2000), however these may be significantly different in natural magmas. Nonetheless, the general rule is clear: PGE solubility increases gradually with temperature and drastically with fO_2 . The temperature of relatively dry mantle melting in spreading ridges is higher than those of fluid-assisted subduction conditions, which should lead to more efficient alloy dissolution in the former. However, this difference appears to be negligible compared to the effects of higher fO_2 of arc settings. Consequently, this indicates that PGE-bearing alloys should more easily transfer into the melt during subduction-related melting.

In summary, fractionation of PPGE from IPGE can be satisfactorily explained by a combination of processes and factors, including IPGE-rich MSS retention, variable PGE solubility after sulfide exhaustion, and/or IPGE partitioning within the lattice of Cr-spinel in the arc mantle. Furthermore, elevated Pd contents in arc rocks should be directly inherited from the mantle source, which, in turn, must be enriched by preceding refertilization processes.

6 CONCLUSION

1. The incompatible behavior of both Cu and Pd in magmas within the compositional range of 4–10 wt.% MgO implies a limited influence of sulfide-silicate immiscibility on the PGE budget. As the Tolbachik magmas are oxidized (QFM + 1–2), typical for arc magmas, sulfide saturation was limited to restricted portions of melt and periods of time, and thus did not allow sulfide accumulation and extraction of noble metals from the melt. Previously reported sulfide globules, preserved in olivine phenocrysts, are the products of such limited sulfide saturation.
2. Gold enrichment, observed for several samples, is not accompanied by correspondingly elevated PGE concentrations, and thus cannot be a result of sulfide accumulation. Instead, gold anomalies are interpreted in

terms of previously supposed gold recycling in the plumbing system of Tolbachik.

- The Tolbachik lavas and arc rocks show higher degrees of fractionation than MORB; however, the difference is moderate (Pd_N/Ir_N is 53.4 and 35.8, respectively). The only prominent dissimilarity is the negative Ru anomaly in arc rocks. This is due to the subarc mantle being 1 to 4 log units more oxidized than MORB, leading to the crystallization of Fe^{3+} -rich Cr-spinel and laurite, which are both known for hosting Ru.
- Palladium contents in the parental melt of Tolbachik are close to 6.5 ppb, which is four times higher than reported MORB values (1.5 ± 0.5 ppb). An influx of Pd during refertilization processes of the subarc mantle may be responsible for Pd enrichment of arc melts.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

AK, MZ, and VK conceived the idea of the study and organized fieldwork on the Tolbachik volcano with a help of DS and NN.

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Samples were processed by AK, MZ, and DS. All co-authors contributed to the discussion, conclusions, and a final draft for review.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/feart.2021.791465/full#supplementary-material>

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