



Bulletin of the Mineral Research and Exploration

<http://bulletin.mta.gov.tr>



Highly siderophile element and osmium isotope systematics of basaltic volcanics: a different approach to petrological processes

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Research Article

Keywords:

Basalt, Highly Siderophile Element, Osmium Isotope, Petrology.

ABSTRACT

The highly siderophile element (HSE) or platinum group element (PGE) and Os isotope systematics of basaltic volcanics have recently received a significant attention because of their potential to constrain the petrological processes on magma generation and evolution. The HSE and Os isotope data, which are generally observed at very low concentrations in basalts and obtained by modern enrichment and analytical techniques, are frequently used in petrological studies. The HSE contents and ratios from whole-rock analysis of basalts, and combined evaluation with the theoretical knowledge and modelling of HSE behaviour during the partial melting of mantle and the differentiation of basaltic magma would provide opportunity for geochemical modelling on mantle melting. Besides, HSE contents and Pd-PGE/Ir-PGE ratios are important indicators for the nature of mantle sulfides, the sulfur saturation conditions of the mantle source, sulfide segregation, fractional crystallization, crustal assimilation and partial melting degrees in the origin and evolution of mantle-derived magmas. Therefore, in addition to the traditional whole-rock geochemical data obtained from Cenozoic aged basalts observed widely in Turkey, HSE and Os isotope systematics of these basalts can contribute to define the geochemical features of the mantle source, and to model petrological processes which are effective in the magma evolution.

Received Date: 19.11.2020

Accepted Date: 22.03.2021

1. Introduction

The highly siderophile element (HSE) or platinum group element (PGE) contents of basaltic volcanics and their relative proportions have attracted wide attention in recent years due to their potential in the evaluation of petrological processes (partial melting, fractional crystallization, and assimilation), the effect of mantle melting-melt separation and understanding of the mantle-crust contribution (Shirey and Walker, 1998; Carlson, 2005; Day, 2013; Gannoun et al., 2016). HSE (or PGE) which is generally observed in basaltic volcanics at very low concentrations (<0.1

ppb to several ppb; Day, 2013; Gannoun et al., 2016), is frequently used in petrogenesis studies of basaltic volcanics (Chesley and Ruiz, 1998; Rehkämper et al., 1999a; McBride et al., 2001; Crochet, 2002; Crochet and Paul, 2004; Ivanov et al., 2008; Jung et al., 2011; Ma et al., 2013; Chu et al., 2013, 2017; Day, 2013; Izokh et al., 2016; Hopkins et al., 2016; Huang et al., 2017; Waters et al., 2020) with the data obtained by modern sample enrichment-preparation and analysis methods in recent years (Shirey and Walker, 1995; Qi et al., 2007, 2011; Day et al., 2016).

Citation Info: Arslan, M., Temizel, İ., Abdioğlu Yazar, E., Ar, B., Yücel, C. 2022. Highly siderophile element and osmium isotope systematics of basaltic volcanics: a different approach to petrological processes. Bulletin of the Mineral Research and Exploration 167, 83-109. <https://doi.org/10.19111/bulletinofmre.901001>

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The HSE (or PGE) contents and ratios of basaltic volcanics obtained by whole-rock analysis are used together with the available literature information on the behavior of these elements during the partial melting of mantle and melt formation-separation, and using numerical models, allowing geochemical modeling of partial melting and melt generation events in the mantle. In addition, due to the different behavior of Re and Os during partial melting, contrary to Os, the preference of Re for melt phase due to its being more incompatible leads to Re-Os fractionation and Os isotopes enables monitoring the effects of melt separation processes and obtaining chronological information about partial melting processes (Barnes et al., 1985; Chesley et al., 2004; Qi and Zhou, 2008; Wang et al., 2010; Suzuki et al., 2011; Aldanmaz, 2012; Huang et al., 2013; Aldanmaz et al., 2015; Zeng et al., 2016). Furthermore, it is claimed that post-collisional basaltic volcanics (and mantle xenoliths, if any) formed in continental settings, provide direct and reliable information about the composition and geological history of the subcontinental lithospheric mantle (SCLM) (Aldanmaz, 2012; Day, 2013; Chu et al., 2013; Aldanmaz et al., 2015; Gannoun et al., 2016; Chu et al., 2017). The main reason for this is that the mantle melts formed in post-collisional settings differentiated by ascending to the surface along deep lithospheric profiles and thus basalts (and the mantle xenoliths it contains) partially have preserved their original composition (Crocket and Paul, 2004; Aldanmaz, 2012; Aldanmaz et al., 2015; Chu. et al., 2017). Therefore, HSE contents and PPGE/IPGE ratios for the origin and evolution of mantle-derived magmas are important indicators for the nature of mantle sulfides, sulfur saturation conditions of the source mantle, sulfide segregation and fractional crystallization, melt-host rock interactions, crustal assimilation, and degree of partial melting (Barnes et al., 1985; Garuti et al., 1997; Rehkämper et al., 1999a; Crocket and Paul, 2004; Gannoun et al., 2016).

The first HSE geochemistry studies in mafic volcanic rocks around the world were carried out especially in large-volume igneous provinces (LIP; large igneous province) such as Siberia (Russia), Dekkan (India) and Emeishan (China) and Hawaiian volcanics (Crocket and Paul, 2004; Lightfoot and Keays, 2005; Qi et al., 2008; Qi and Zhou, 2008; Ireland et al., 2009; Wang et al., 2010, 2011). In these studies, most of the HSE data were obtained from

tholeiitic-picritic basalts in large volume provinces and alkaline/transitional basalts in some small volume within-plate volcanic areas, and the processes controlling the HSE content of basaltic magmas were examined and discussed.

In Western Anatolia, Central Anatolia, Eastern Pontides and Eastern Anatolian orogenic belts (Turkey), collisional and post-collisional Cenozoic basaltic volcanics are common, and traditional whole-rock and lithophile element isotope (especially Sr-Nd-Pb-Hf isotope systematics) geochemistry data have generally been used in petrological studies on these volcanics so far. However, for the first time, Aldanmaz et al. (2015) revealed highly siderophile element (HSE) and Hf-Pb-Os isotope geochemistry of Middle Miocene active continental margin lavas and Late Miocene-Quaternary oceanic island (OIB) type within-plate mafic alkaline lavas in Western Anatolia, and then evaluated the mantle source characteristics of these volcanics and petrological processes that are effective in their evolution. Hence, petrological studies using only lithophile element geochemistry data in basaltic volcanics remains sometimes limited in the modeling of petrological processes such as mantle source areas where the parent magma derived, degrees of partial melting and crustal assimilation during magma evolution. Therefore, in studies on Cenozoic basaltic volcanic rocks in Turkey, if a new and modern analytical approach used, such as HSE and Os isotope geochemistry, may provide important constraints for the petrology of volcanics and the characteristics of mantle which they derived from. In this study, definition, analytical method, and geochemical behaviors of HSE, and new approaches to reveal petrological processes by using HSE and Os isotope systematics of basaltic volcanics are evaluated in the light of the current literature.

2. Definition and Terminology of Highly Siderophile Elements

Siderophile Elements (iron (=sideron) loving (=philia)); Goldschmidt, 1954) are transition metals with paramagnetic feature, which are ferromagnetic in high density and are also soluble in iron melt or solid solution, do not form any bonds with oxygen, but often with chalcophile (Cu-loving) elements. Some of these elements are also named as chalcophile elements which tend to be separated strongly by sulfide melt and some sulfide minerals.

Siderophile elements are elements which are concentrated in the core and more sensitive to iron than sulfur. They are divided into three groups; i) slightly siderophile elements; (SSE: Mn, V, Cr), ii) moderately siderophile elements, (MSE: Ga, P, W, Co, Ag, Ni, Sb, As, Ge, Mo), iii) highly siderophile elements, (HSE: Re, Os, Ir, Ru, Pt, Rh, Au, Pd). These groups are determined according to the partition coefficients (D) calculated by the ratio of the amount of the element in the silicate melt to the amount in the metal. If this ratio is more than 10000, it is called HSE, if it is between 3 and 10000, it is called MSE, and if the ratio is above 1, it is called SSE (Walker, 2016). As with most trace elements, siderophile elements also change with parameters such as pressure and temperature, and for many siderophile elements, increasing temperature and pressure cause a decrease in D values. In addition to being a very useful element group, some moderately siderophile and highly siderophile elements also play important roles in geological studies with their radiogenic isotope systems (^{187}Re - ^{187}Os , ^{190}Pt - ^{186}Os and ^{182}Hf - ^{182}W).

Highly siderophile elements (HSEs; Re, Os, Ir, Ru, Pt, Rh, Pd and Au) can also be defined as platinum group elements (PGEs; Os, Ir, Ru, Rh, Pt and Pd) + (Re and Au). Platinum group elements are highly chalcophile elements (also defined as noble metals) and are divided into two groups as Ir-group (IPGE; Os, Ir, Ru) and Pd-group (PPGE; Pt, Pd, Rh) depending on the melting temperature and behavior of the mantle under P-T conditions (Keays, 1982; Barnes et al., 1985). PGEs are highly refractory due to their high melting temperatures and show strong affinity for iron (siderophile) and sulfur (chalcophile) (Sharpe, 1982; Barnes et al., 1985). In the definition of PGE and HSE, there is a clear distinction in economic geology, industry, or biomedical studies.

3. Analytical Methods for Highly Siderophile Element and Osmium Isotope

In whole-rock HSE and Os isotope geochemistry studies of basaltic volcanics; sample selection should be made by considering detailed field, petrographic, whole-rock lithophile element (major, trace-rare earth element, Sr-Nd-Pb-Hf isotope) geochemistry and Ar-Ar geochronology data. Samples of 400-500 g selected for this purpose are first cut into small pieces and grinded up to approximately 250 mesh in an agate ring mill. Then, 10-15 gr for each sample are

separated from the powdered samples and made ready for analysis.

Since HSE contents of basaltic volcanics are generally at very low concentrations, it requires different geochemical approaches and methods (Meisel and Horan, 2016) from traditional whole-rock analysis. In order to analyze the very low HSE concentrations in basaltic volcanics, 2-3 g of fine powdered sample is passed through some special high temperature (~220-250°C) dissolution (Carius tube technique and its development; Shirey and Walker, 1995; Qi et al., 2004, 2007; Day et al., 2016) and other modified acid dissolution (Qi et al., 2011) and enrichment processes, after that the mass spectrometry instruments (ID-TIMS and/or SF-ICP-MS, N-TIMS) is required for measuring accurately and precisely.

First of all, chemical separation and enrichment processes of HSE are performed from whole-rock powder samples. Whole-rock powder samples are dissolved using aqua regia (2:1 16 N HNO_3 and 12 N HCl , 9 ml) and stabilized with enrichments of ^{185}Re , ^{190}Os and ^{191}Ir - ^{99}Ru - ^{105}Pd - ^{194}Pt . The dissolution process is continued by separating the element Os by CHCl_3 solvent extraction (Cohen and Waters, 1996) and Os micro distillation (Birck et al., 1997). Elements Ir, Ru, Pt, Pd and Re are separated from the remaining solution using anion-exchange chromatography and then analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). Isotope fractionation is corrected using standard Ir, Ru, Pd, Pt (E-pond) and Re (NIST 3143) solutions, which are analyzed linearly and with samples.

Os concentrations and isotopic ratios are measured using negative-thermal ionization mass spectrometry (N-TIMS) (Creaser et al., 1991; Völkening et al., 1991). Samples are loaded with concentrated HBr onto Pt filaments with $\text{Ba}(\text{OH})_2$ activators and then analyzed as OsO_3^- in N-TIMS using a secondary electron multiplier in maximum jump mode. The measured Os isotope ratios are corrected using $^{192}\text{Os}/^{188}\text{Os} = 3.08271$ (Shirey and Walker, 1998) for oxygen isobaric interactions, enrichment (spike) contribution, instrumental mass fractionation.

Based on the measured $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ isotope ratios in basaltic volcanics as well as the absolute ages of the rocks and chondritic $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ isotope ratios; some calculations are

made such as initial Os isotope ratio ($^{187}\text{Os}/^{188}\text{Os}_i$), gamma (γ)-Os parameter (percent deviation relative to chondritic osmium isotope composition at time of separation from the mantle), chondritic osmium isotope composition ($^{187}\text{Os}/^{188}\text{Os}_T$) by age, and model age (T_{MA} ; Walker et al., 1989; Shirey and Walker, 1998) which represent the melt separation time from the chondritic mantle and is calculated according to Luck and Allègre (1984). In the calculations, the following formulas are used by taking the present-day chondritic values of $^{187}\text{Re}/^{188}\text{Os}=0.40186$ and $^{187}\text{Os}/^{188}\text{Os}=0.127$ and ^{87}Re decay constant ($\lambda=1.6668 \times 10^{-11} \text{ y}^{-1}$ (Selby et al., 2007).

$$^{187}\text{Os}/^{188}\text{Os}_{Initial} = ^{187}\text{Os}/^{188}\text{Os}_{Sample} - [(^{187}\text{Re}/^{188}\text{Os}_{Sample}) \times (e^{\lambda t} - 1)] \quad (1)$$

$$\gamma\text{Os} = [(^{187}\text{Os}/^{188}\text{Os}_{Sample(t)}) / ^{187}\text{Os}/^{188}\text{Os}_{Chondrite(t)}] - 1] \times 100 = [(^{187}\text{Os}/^{188}\text{Os}_{Initial}) / ^{187}\text{Os}/^{188}\text{Os}_T] - 1] \times 100 \quad (2)$$

$$^{187}\text{Os}/^{188}\text{Os}_T = ^{187}\text{Os}/^{188}\text{Os}_{Initial} + \frac{^{187}\text{Re}/^{188}\text{Os}_{Chondrite}}{(4568000000) - e^{\lambda t}} \quad (3)$$

$$T_{MA} = 1/\lambda \times \ln [((^{187}\text{Os}/^{188}\text{Os}_{Chondrite}) / ^{187}\text{Os}/^{188}\text{Os}_{Sample}) / (^{187}\text{Re}/^{188}\text{Os}_{Chondrite} - ^{187}\text{Re}/^{188}\text{Os}_{Sample})) + 1] \quad (3)$$

4. Geochemical Behavior of Highly Siderophile Elements and Their Importance in Petrology

Highly siderophile elements show different behaviors during melting. Especially palladium group elements (PPGE) (Pt, Pd; melting temperatures $<2000^\circ\text{C}$) and Re exhibit behaviors ranging from partial compatibility to partial incompatibility during melting and crystallization, while iridium group elements (IPGE) (Os, Ir and Ru; melting temperatures $>2000^\circ\text{C}$) show quite compatible behavior (Barnes et al., 1985). The different behavior of siderophile elements during partial melting is explained by the melt derived from the mantle and the differences in the absolute and relative amounts of these elements in the remnant mantle rocks (Gannoun et al., 2016). In addition, since Pt is partially compatible, Re is partially incompatible and Os is quite compatible in melt formation, the Re-Os and Pt-Os isotope systems differ significantly from the more geochemically more useful lithophile element isotope systems (Rb-Sr; Sm-Nd; Lu-Hf) which prefer melt in terms of both parent and daughter isotopes (Gannoun et al., 2016).

HSE contents and PPGE/IPGE ratios can be used as important geochemical data to determine petrological

processes (such as degree of partial melting, the nature of the mantle source, crustal assimilation) about the origin and development of mantle-derived magmas (Barnes et al., 1985; Rehkämper et al., 1999a; Crochet, 2002; Crochet and Paul, 2004; Aldanmaz et al., 2015; Zhang et al., 2015; Walker, 2016; Gannoun et al., 2016; Zeng et al., 2016; Hopkins et al., 2016; Chu et al., 2017; Huang et al., 2017). In addition, since PGE has a very high partition coefficient between sulfide liquids and silicate melt (Mungall and Brenan, 2014), the PGE contents of basaltic volcanics can also be a very sensitive indicator in determining sulfide segregation (Barnes et al., 2015). Therefore, the HSE geochemistry of basalts can reveal important limitations in petrological studies (Qi and Zhou, 2008; Ivanov et al., 2008; Wang et al., 2010; Huang et al., 2013, 2017; Aldanmaz et al., 2015; Zeng et al., 2016; Chu et al., 2017).

HSE and Os isotope geochemistry data are also used to illuminate petrological processes including metasomatic reactions associated with melt formation and transport due to different degrees of partial melting of the mantle peridotite (Allègre and Luck 1980; Brandon et al., 1996; Alard et al., 2000, 2005; Meibom et al., 2002; Luguet et al., 2003; Bockrath et al., 2004; Büchl et al., 2004; Chesley et al., 2004; Pearson et al., 2004; Lorand et al., 2008; Ireland et al., 2009; Aldanmaz, 2012; Huang et al., 2017). In this context, when HSE or PGE relative proportions and Os isotope compositions of basalts developed in different tectonic settings are evaluated together, they play an important role in understanding petrological processes that affect the development of basaltic magmas (Shirey and Walker, 1998; Carlson, 2005; Day, 2013; Walker, 2016; Gannoun et al., 2016).

Studies on the age and magmatic development of the subcontinental lithospheric mantle (SCLM) revealed that the Re-Os isotope systematics is an important radiogenic isotope system in obtaining information about the melting of the mantle and the development of the lithosphere (Allègre and Luck, 1980; Walker et al., 1989; Peucker-Ehrenbrink and Jahn, 2001; Schmidt and Snow, 2002; Rudnick and Lee, 2002; Powell and O'Reilly, 2007; Pearson et al., 2007; Ireland et al., 2009; Aldanmaz et al., 2015; Huang et al., 2017). Thus, it has been stated that there is a systematic increase in Re/Os ratios in the residual mantle with the partial melting degree and depending

on time, since the Os -which exhibits compatible behavior during the partial melting of the mantle- is kept in the residual mantle, but the more incompatible Re prefers the melt phase (Shirey and Walker, 1998; Walker et al., 1989; Schmidt and Snow, 2002; Walker, 2016). In addition, it has been emphasized in the studies that the time-dependent change of partial melting degree and the effects of metasomatic processes developing after the melt generation-separation can be geochemically modeled with Os isotopes and HSE systematics (Lorand et al., 2004; 2008; Reisberg et al., 2005; Ackerman et al., 2009; Ireland et al., 2009; Harvey et al., 2010; Aldanmaz, 2012; Huang et al., 2017).

5. Sulfide Mineral Phases Affecting Highly Siderophile Element Content in Basaltic Volcanics

It is very important to carry out analytical studies (ore microscopy, SEM, EPMA) on the petrography and mineral chemistry of primary sulfide minerals in basaltic volcanics. Because sulfide phases significantly affect the HSE content and geochemistry of basaltic volcanics. The first petrographic and mineral chemistry studies in sulfide mineral phases were carried out on magmatic sulfides associated with systems forming orthomagmatic Ni-Cu-PGE minerals (Mungall and Brenan, 2014; Barnes et al., 2017). In addition, in recent years, research has been carried out on magmatic sulfides in volcanic arc (Park et al., 2015; Keith et al., 2017; Georgatou et al., 2018; Savelyev et al., 2018) and continental post-collisional settings (Georgatou and Chiaradia, 2020). According to the formation, texture and composition of magmatic sulfides in post-collisional high-K calc-alkaline, shoshonitic and alkaline volcanic systems; it has been reported that sulfur saturation improves regardless of magma composition, geodynamic environment and whether or not it creates an economic mineral deposit (Georgatou and Chiaradia, 2020). In addition, it has been stated that the sulfide composition depends on the nature of the host mineral and the Ni/Cu ratio of sulfides decreases with magmatic evolution. In the early stage, Ni-rich and Cu-poor sulfides are hosted by early crystallized silicate minerals (olivine and pyroxene), while in the late stage, Cu-rich sulfides are hosted by Fe-Ti oxides. It has been suggested that the most common sulfides in the early saturation phase consist of Cu-poor and Ni-rich phases (pyrrhotite, pentlandite) and very little Cu-rich phases (cubanite,

chalcopyrite), while late-phase sulfides consisting of Cu-rich phases (chalcopyrite, bornite, digenite; intermediate solid solution) are hosted only by magnetite and are found only in differentiated rocks (andesite and dacite) (Georgatou and Chiaradia, 2020).

Possible sulfide types can be listed as follows in accordance with the current literature with the presence of primary sulfide phases in basaltic volcanics as inclusions in silicate and Fe-Ti oxide minerals and in the groundmass and/or their textural properties: Type 1 sulfides are rare and only hosted by olivine phenocrysts. These can mostly consist of Cu-poor phases (pyrrhotite, pentlandite). Type 2 sulfides are the most abundant and are hosted by different minerals (pyroxene, amphibole, magnetite). These may consist of Cu-poor phase (pyrrhotite \pm pentlandite) and Cu-rich phase (cubanite, chalcopyrite). Type 3 sulfides are rare and hosted by magnetite. These can mostly consist of Cu-rich phase (chalcopyrite \pm chalcocite) and pyrite. Type 4 sulfides are hosted only by magnetite and may contain only Cu-rich phases (chalcopyrite-bornite \pm digenite). Type 5 sulfides are present in groundmass as sulfide-oxide-silicate aggregates and are mostly Cu-poor phases.

6. Highly Siderophile Element and Osmium Isotope Geochemistry in Basaltic Volcanics

HSE contents in basaltic volcanics can generally be very low (<0.1 ppb to a few ppb; typically, ng/gr) (Day, 2013; Gannoun et al., 2016). Thus, sometimes Os content <0.1 ppb, Pt and Pd contents may remain at a few ppb level (Table 1; Figure 1). For example, HSE contents are Os=0.14 ppb, Ir=0.09 ppb, Ru=0.18 ppb, Pt=2.93 ppb, Pd=5.43 ppb, Re=0.16 ppb in Izu-Bonin and Grenada island arc basalts (McInnes et al., 1999; Woodland et al., 2002), Os=0.187 ppb, Ir=0.074 ppb, Ru=0.171 ppb, Pt=0.421 ppb, Pd=1.131 ppb, Re=0.106 ppb in NE China high-K basalts (Chu et al., 2013), Os=0.073 ppb, Ir=0.043 ppb, Ru=0.076 ppb, Pt=0.292 ppb, Pd=0.307 ppb, Re=0.125 ppb in Central East China continental flood basalts (Chu et al., 2017) (Table 1; Figure 1). In addition, ÓPGE contents are generally 1.08 ppb in mid-ocean ridge basalt (MORB) (Bézos et al., 2005; Day, 2013), 4.58 ppb in ocean island basalt (OIB) (Day, 2013) and 29.1 ppb in primitive mantle (Becker et al., 2006).

Possible Ir, Ru, Pt and Pd depletion or enrichment in chondrite-normalized HSE element distribution

Table 1- Abundances of highly siderophile element (HSE) or platinum group element (PGE) in chondrite, mantle, crust, and basaltic volcanics from different tectonic setting.

	Os (ppb)	Ir (ppb)	Ru (ppb)	Rh (ppb)	Pt (ppb)	Pd (ppb)	Re (ppb)	ÓPGE	Pd/Ir	Pt/Pd	Reference
Chondrite (C1)	450	424	631	130	864	563	37.3	3062	1.33	1.53	Fischer-Gödde et al. (2010)
Bulk silicate earth	3.9	3.5	7	1.2	7.6	7.1	0.35	30.30	2.03	1.07	Fischer-Gödde et al. (2010)
Primitive mantle	3.9	2.9	6.3	1.03	6.2	5.38	0.35	25.71	1.86	1.15	Barnes et al. (2015) (Re: Becker et al. (2006))
Lower continental crust	0.05	0.05	0.75	-	2.7	2.8	0.18	6.35	56	0.96	Rudnick and Gao, (2004)
Upper continental crust	0.031	0.022	0.34	-	0.5	0.52	0.198	1.41	23.64	0.96	Rudnick and Gao (2004)
Bulk continental crust	0.041	0.037	0.57	-	1.5	1.5	0.188	3.65	40.54	1	Rudnick and Gao (2004)
Mid-ocean ridge basalt	0.03	0.055	0.061	-	0.053	1.19	0.86	1.39	21.64	0.04	Bézoz et al. (2005); Gannoun et al. (2007)
Ocean island alkaline basalt	0.07	0.17	0.34	-	2.6	1.4	0.39	4.58	8.24	1.86	Day (2013)
Ocean island tholeiitic basalt	0.64	0.45	1.11	-	2.27	2.2	0.38	6.67	4.89	1.03	Day (2013)
Ocean island basalt (Azore Islands) (<i>n</i> =30)	0.071	0.154	0.141	-	1.233	1.531	0.232	3.13	9.94	0.81	Waters et al. (2020)
Island arc basalt (Izu-Bonin and Grenada) (<i>n</i> =23)	0.14	0.09	0.18	-	2.93	5.43	0.16	8.77	60.33	0.54	McInnes et al. (1999); Woodland et al. (2002)
Island arc basalt (Kamchatka) (<i>n</i> =6)	0.28	0.078	0.32	-	2.74	11.71	0.31	15.13	150.13	0.23	Ivanov et al. (2008)
Continental flood basalt (N Vietnam) (<i>n</i> =11)	-	0.112	0.302	0.216	3.803	4.609	-	9.04	41.15	0.83	Li et al. (2016)
Continental flood basalt (Tarim, China) (<i>n</i> =11)	-	0.016	0.012	0.004	0.029	0.109	-	0.17	6.81	0.27	Yuan et al. (2012)
Continental flood basalt (Siberia, Russia) (<i>n</i> =21)	0.047	0.087	0.395	0.209	45.339	8.911	-	54.99	102.43	5.09	Izokh et al. (2016)
Continental within-plate basalt (Syria) (<i>n</i> =21)	0.044	0.036	0.085	0.022	0.384	0.306	0.094	0.88	8.50	1.25	Ma et al. (2013)
Continental within-plate basalt (N China Craton) (<i>n</i> =42)	0.041	0.029	0.072	0.017	0.170	0.126	-	0.46	4.34	1.35	Zhang et al. (2015)
Continental alkaline basalt (E China) (<i>n</i> =24)	-	0.086	0.195	0.057	0.365	0.355	-	1.06	4.13	1.03	Zeng et al. (2016)
High-K basalt (NE China) (<i>n</i> =18)	0.187	0.074	0.171	-	0.421	0.131	0.106	0.98	1.77	3.21	Chu et al. (2013)
Continental alkaline basalt (Central East China) (<i>n</i> =15)	0.214	0.194	0.377	-	0.633	0.472	0.106	1.89	2.43	1.34	Chu et al. (2017)
Continental tholeiitic basalt (Central East China) (<i>n</i> =6)	0.073	0.043	0.076	-	0.292	0.307	0.125	0.79	7.14	0.95	Chu et al. (2017)
Continental alkaline basalt (SE China) (<i>n</i> =14)	-	0.287	0.428	0.170	0.755	0.554	-	2.19	1.93	1.36	Huang et al. (2017)
Continental tholeiitic basalt (SE China) (<i>n</i> =26)	-	0.084	0.215	0.037	0.252	0.184	-	0.77	2.19	1.37	Huang et al. (2017)
Kula basalt (Western Anatolia) (<i>n</i> =4)	0.02	0.20	0.13	-	1.57	0.26	0.17	2.18	1.30	6.04	Aldanmaz et al. (2015)
Çanakkale and Thrace basalts (Western Anatolia) (<i>n</i> =22)	0.10	0.09	0.18	-	2.66	0.25	0.13	3.28	2.78	10.64	Aldanmaz et al. (2015)

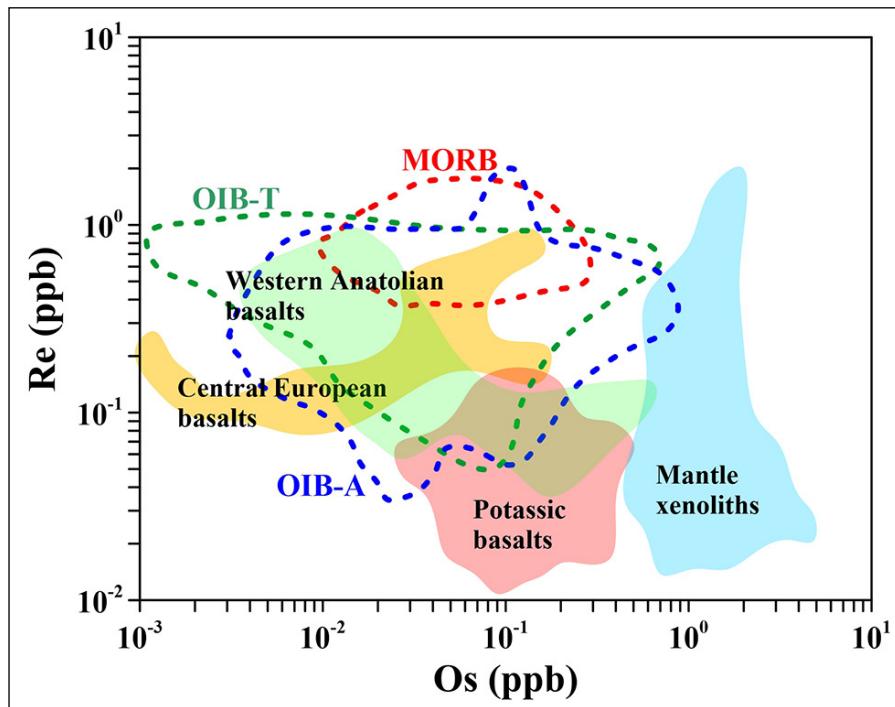


Figure 1- Os (ppb) versus Re (ppb) variation diagram of basaltic volcanics. Fields are mid-ocean ridge basalts (MORB), ocean island tholeiitic basalts (OIB-T) and ocean island alkaline basalts (OIB-A) from Shirey and Walker (1998); Miocene-Quaternary Western Anatolian basalts from Aldamaz et al. (2015); Miocene Central European basalts (Vogelsberg, Germany) from Jung et al. (2011); Quaternary potassic basalts (NE China) from Chu et al. (2013); mantle xenoliths within potassic basalts (Kelu, NE China) from Zhang et al. (2011).

diagrams of basaltic volcanics may reflect the segregation or addition of PGE-rich nano-nuggets such as native metals, alloys or platinum group minerals normally associated with sulfides (Figure 2). In the basaltic volcanics positive correlation in Ir against other HSE diagrams and negative correlation in Ir versus Pd/Ir ratio diagram indicate that the IPGEs behave compatible in the basaltic magma origin, while the IPGE and PPGE are fractionated during the magma formation and/or evolutionary process.

Although the $^{187}\text{Os}/^{188}\text{Os}$ isotope ratio of the primitive mantle is reported as 0.1296 (Meisel et al., 2001), $^{187}\text{Os}/^{188}\text{Os}$ isotope ratio of ocean island basalts (OIB) is between 0.1082 and 0.22227 (Day, 2013), the $^{187}\text{Os}/^{188}\text{Os}$ isotope ratio of mid-ocean ridge basalts (MORB) is between 0.126 and 0.148 (avg.= 0.133) (Gannoun et al., 2016) and the $^{187}\text{Os}/^{188}\text{Os}$ isotope ratio of subduction-related basalts varies in a very wide range between 0.1268 and 1.524 (Gannoun et al., 2016) (Table 2).

Os versus $^{187}\text{Os}/^{188}\text{Os}$ isotope composition variation in basaltic volcanics may indicate lithospheric mantle

assimilation, fractional crystallization, and crustal assimilation. On the other hand, trends in $^{187}\text{Os}/^{188}\text{Os}$ isotope versus $1/\text{Os}$ and $\text{Pd}_{\text{N}}/\text{Ir}_{\text{N}}$ diagrams can indicate whether primary sulfide and/or secondary sulfide addition exists (Figure 3).

Positive (+) γ_{Os} values calculated in basaltic volcanics are defined as enriched or radiogenic and show a long-term increasing isotope ratio of $^{187}\text{Re}/^{188}\text{Os}$ compared to chondrite. On the other hand, negative (-) γ_{Os} values are defined as depleted or non-radiogenic and show the isotope ratio $^{187}\text{Re}/^{188}\text{Os}$ decreasing for a long time compared to chondrite (Figure 4). The range of γ_{Os} values in basaltic volcanics varies considerably between (-10) and (+300). There are two possibilities regarding the negative (-) $^{187}\text{Os}/^{188}\text{Os}_i$ and especially negative (-) γ_{Os} values observed in some samples: (1) Since the depleted mantle has negative (-) γ_{Os} values, small negative (-) values (such as $\gamma_{\text{Os}}= -1$ and -5) are due to olivine and/or clinopyroxene xenocrystals found as possible mantle residues in basaltic volcanics. (2) Negative (-) values (such as $\gamma_{\text{Os}}= -200$ and -500) are related to the modification of the

Table 2- Abundances of osmium isotope in chondrite, mantle reservoirs, and basaltic volcanics from different tectonic setting.

	Re (ppb)	Os (ppb)	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}$	γOs	Reference
Chondrite (C1)	38.1	460.5	0.3924	0.1262	-	Horan et al. (2003); Fischer-Gödde et al. (2010)
Primitive mantle	0.35	3.9	0.4358	0.1296	-	Meisel et al. (2001) (Re and Os: Becker et al. (2006))
Enriched mantle-I (EM-I)	-	-	-	0.148	16.5	van Keken et al. (2002)
Enriched mantle -II (EMII)	-	-	-	0.150	18	van Keken et al. (2002)
High- μ mantle (HIMU)	-	-		0.150	18	van Keken et al. (2002)
Depleted MORB mantle (DMM)	-	-	-	0.123	-3	van Keken et al. (2002)
Oceanic crust	0.7	0.05	-	0.15		Peucker-Ehrenbrink et al. (2012)
Continental crust	0.20	0.03	-	1.1	-	Peucker-Ehrenbrink and Jahn (2001)
Mid-ocean ridge basalt ($n=7$)	1.168	0.027	-	0.1376	-	Day (2013)
Mid-ocean ridge basalt (Pacific Ocean) ($n=14$)	1.40	0.01	2565.14	0.1320	-	Gannoun et al. (2007)
Mid-ocean ridge basalt (Atlantic Ocean) ($n=14$)	1.14	0.02	981.86	0.1345	-	Gannoun et al. (2007)
N-type mid-ocean ridge basalt (SW Indian Ocean Ridge) ($n=14$)	0.60	0.025	575.29	0.17282	-	Yang et al. (2013)
Iceland basalts ($n=15$)	0.287	0.114	-	0.13307	-	Debaille et al. (2009)
Ocean island basalt ($n=24$)	0.254	0.197	-	0.1318	-	Day (2013)
HIMU-type ocean island basalt (Cook-Austral islands) ($n=21$)	0.210	0.132	-	0.1446		Hanyu et al. (2011)
Ocean island basalt (Great Comoro island, Indian Ocean) ($n=13$)	0.23	0.058	42.78	0.1499		Class et al. (2009)
Ocean island basalt (Samoan islands, S Pacific Ocean) ($n=19$)	0.396	0.547	16.17	0.13255		Jackson and Shirey (2011)
Ocean island basalt (Galapagos islands) ($n=23$)	0.343	0.094	-	0.14959	15.42	Gibson et al. (2016)
Ocean island basalt (Azores islands) ($n=30$)	0.232	0.071	-	0.13526	-	Waters et al. (2020)
Oceanic alkaline basalt (Cameroon) ($n=13$)	0.348	0.031	147.8	0.1545	-	Gannoun et al. (2015)
Ocean island basalt (Tristan da Cunha) ($n=3$)	-	-	506	0.1847	40	Rocha-Júnior et al. (2012)
Continental alkaline basalt (Cameroon) ($n=8$)	0.497	0.021	322.9	0.3157	-	Gannoun et al. (2015)
Continental within-plate basalt (S Australia) ($n=9$)	0.151	0.068	25.26	0.24779	95.08	McBride et al. (2001)
High-K basalt (NE China) ($n=18$)	0.106	0.187	3.67	0.14036	11.52	Chu et al. (2013)
Continental flood basalt (Parana, Brazil) ($n=11$)	-	-	47.3	0.23382	3.05	Rocha-Júnior et al. (2012)
Within-plate basalt (Auckland, New Zealand) ($n=26$)	0.183	0.0521	-	0.27205	-	Hopkins et al. (2016)
Continental alkaline basalt (Central East China) ($n=15$)	0.106	0.214	14.44	0.17466	34.67	Chu et al. (2017)
Continental tholeiitic basalt (Central East China) ($n=6$)	0.125	0.073	14.10	0.29061	126.07	Chu et al. (2017)
Kula basalt (Western Anatolia) ($n=4$)	0.17	0.020	40.97	0.39346	209.5	Aldanmaz et al. (2015)
Çanakkale and Thrace basalts (Western Anatolia) ($n=22$)	0.13	0.10	29.70	0.22067	77.7	Aldanmaz et al. (2015)

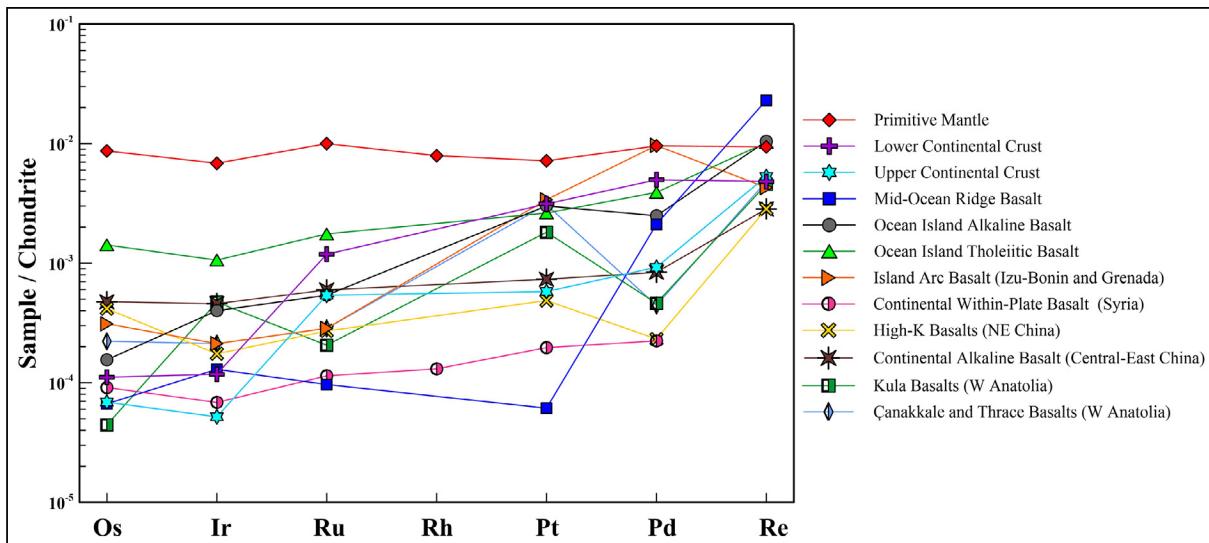


Figure 2- Chondrite-normalized HSE distributions of basalts formed in different tectonic settings. Chondrite (C1) normalization values are from Fischer-Gödde et al. (2010). Primitive mantle from Barnes et al. (2015) (Re; Becker et al., 2006); Lower continental crust and Upper continental crust from Rudnick and Gao (2004); Mid-ocean ridge basalt from Bézos et al. (2005) and Gannoun et al. (2007); Ocean island alkaline basalt and tholeiitic basalt from Day (2013); Island arc basalts (Izu-Bonin and Grenada) from McInnes et al. (1999) and Woodland et al. (2002); Continental within-plate basalts (Syria) from Ma et al. (2013); High-K basalts (NE China) from Chu et al. (2013); Continental alkaline basalts (Central-East China) from Chu et al. (2017); Kula, Çanakkale and Thrace basalts (W Anatolia) from Aldanmaz et al. (2015).

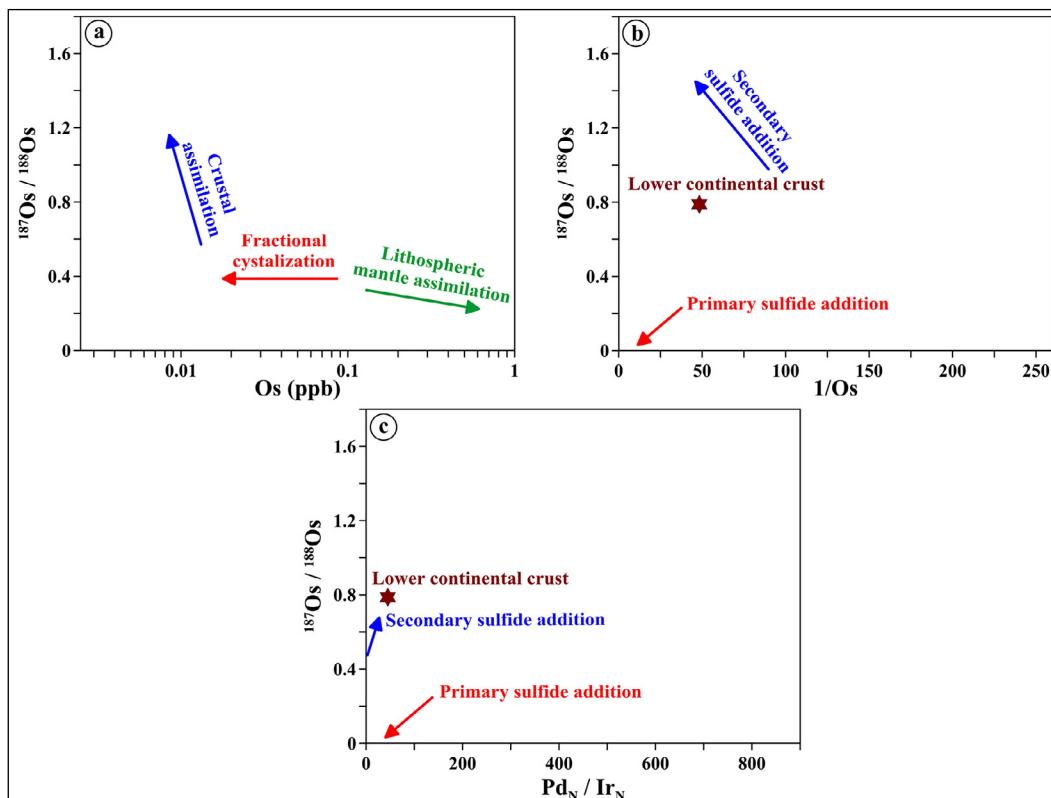


Figure 3- a) Os versus $^{187}\text{Os} / ^{188}\text{Os}$, b) $1/\text{Os}$ versus $^{187}\text{Os} / ^{188}\text{Os}$, and c) $\text{Pd}_N / \text{Ir}_N$ versus $^{187}\text{Os} / ^{188}\text{Os}$ variation diagrams. Lithospheric mantle assimilation, fractional crystallization, crustal assimilation, primary sulfide addition and secondary sulfide addition trends from Chu et al. (2013), $^{187}\text{Os} / ^{188}\text{Os} = 0.8$ and Os = 0.049 ppb) from Saal et al. (1998), Pd and Ir contents of lower continental crust from Rudnick and Gao (2004) and chondrite composition for the normalized ratio ($\text{Pd}_N / \text{Ir}_N = \sim 42$) from Fischer-Gödde et al. (2010).

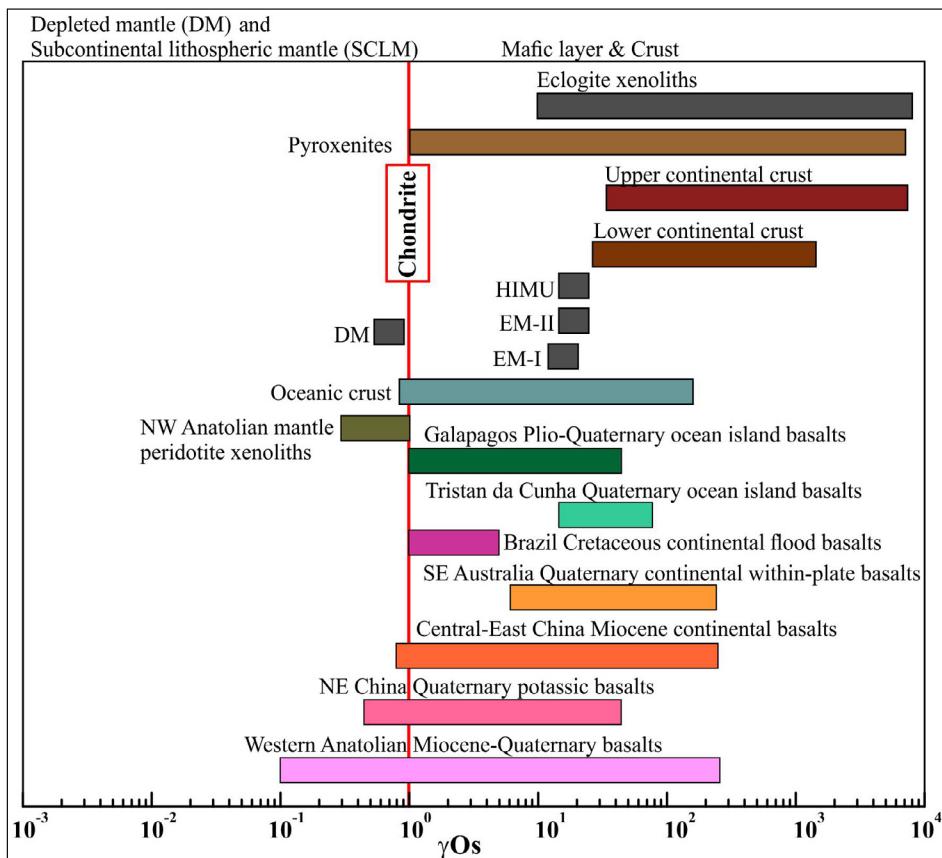


Figure 4- Osmium isotope compositional range as γ_{Os} in basaltic volcanics and mantle reservoirs. Galapagos Plio-Quaternary ocean island basalts (Gibson et al., 2016); Tristan da Cunha Quaternary ocean island basalts (Rocha-Júnior et al., 2012); Brazil (Parana) Cretaceous continental flood basalts (Rocha-Júnior et al., 2012); SE Australia Quaternary continental within-plate basalts (McBride et al., 2001); Central-East China Miocene continental basalts (Chu et al., 2017); NE China potassic basalts (Chu et al., 2013); Western Anatolian Miocene-Quaternary basalts (Aldanmaz et al., 2015); NW Anatolian mantle peridotite xenoliths (Aldanmaz, 2012), pyroxenites (Reisberg et al., 1991; Pearson and Nowell, 2004; Wang and Becker, 2015); eclogite xenoliths (Pearson et al., 1995); oceanic crust (Blusztajn et al., 2000; Peucker-Ehrenbrink et al., 2003; Dale et al., 2007; Day, 2013); lower continental crust (Saal et al., 1998); upper continental crust (Egger and Turekian, 1993; Peucker-Ehrenbrink and Jahn, 2001; Chen et al., 2016); enriched mantle-1 (EM-I; $\gamma_{\text{Os}} = 16.5$), enriched mantle-2 (EM-II; $\gamma_{\text{Os}} = 18$), HIMU (high μ ; $\mu = ^{238}\text{U} / ^{204}\text{Pb}$; $\gamma_{\text{Os}} = 18$) and depleted mantle (DM; $\gamma_{\text{Os}} = -3$) (van Keeken et al., 2002).

Re-Os systematic after eruption of basaltic volcanics, and generally reflect the trace of hydrothermal alteration associated with secondary sulfide formation (mostly pyrite) commonly developed in basaltic rocks.

The Re-Os model ages (T_{MA}) calculated in basaltic volcanics can reach very low or very high values, sometimes not meaningful for the actual age of the melt separation. Because model age (T_{MA}) gives the real age when Re is not modified by later geological events, while it corresponds to older or younger ages when Re is added and depleted (Rudnick and Walker, 2009).

The geochemical behavior of the Re and Os elements checks the reliability of the Re-Os isotope geochemistry and thus the geochronology. Since both Re and Os elements are not hosted by silicate minerals, and are also insoluble in reducing aqueous fluids, there are only two ways of separating the phases containing the Re or Os elements from each other; 1) remaining adjacent to another phase with a comparable affinity for the element Re or Os under conditions that allow diffusion or 2) interacting with an oxidizing fluid (Stein and Hannah, 2015). An isolated sulfide mineral surrounded by silicates does not lose the Re or Os element, but surface alteration or any oxidizing

fluid interaction causes the Re-Os isotopic system to breakdown (Georgiev et al., 2012). However, it is known that it is possible to obtain the eruption age of basaltic magma by using Re-Os geochronology in whole-rock and/or mineral separations in Cenozoic basaltic volcanics.

7. Evaluation of Petrological Processes

7.1. HSE Characteristics of Parent Magmas and the Nature of the Mantle Source

HSE abundances in mantle-derived basaltic melts (magmas) are generally controlled by parameters such as the degree of partial melting, the mineralogy of the mantle source and sulfide segregation in the mantle source. PGE has a very high partition coefficient between sulfide liquids and silicate melt (Mungall and Brenan, 2014). Since Os and Ir (IPGE) are more compatible with olivine, HSE contents of basalts are important in determining sulfide segregation (Barnes et al., 2015). In general, it has been suggested that when the partial melting degree is low, S-saturated melts are produced causing the sulfides in the source mantle to not dissolve completely, and therefore PPGE bearing interstitial sulfide effectively fractionates from the silicates surrounded by IPGE bearing a mono-sulfide solid solution (Ballhaus et al., 2006; Ireland et al., 2009; Day et al., 2010; Day, 2013; Aldanmaz et al., 2015).

Basaltic volcanics generally have low ÓPGE contents and relatively differentiated HSE distributions with much higher and variable Pd/Ir ratios than chondrite ($\text{Pd/Ir} = 1.33$; Fischer-Gödde et al., 2010), which can be interpreted as source characteristics, indicating that they may contain IPGE-depleted mantle source component (MORB). However, this case will still require effective consumption of PGE from the mantle source (possibly with PGE containing sulfides entering the melt), although this is S-saturated during melting in the mantle, the melts (magmas) will be S-undersaturated because of sulfide segregation by decompression during melt (magma) ascent (Ballhaus et al., 2006; Aldanmaz et al., 2015). Alternatively, differentiated IPGE/PPGE ratios may occur as a result of low to medium partial melting at moderately high oxygen fugacity, which will reduce the amount of sulfides to produce S-undersaturated melts (Mungall et al., 2006; Mungall and Brenan, 2014; Aldanmaz et al., 2015).

Some HSE ratios (e.g., Pt/Pd and Pd/Ir) in mantle-derived basaltic rocks are interpreted as indicators of mantle metasomatism (Maier and Barnes, 2004). While basalts formed by fluid-rich melting events in the metasomatized lithospheric mantle have $\text{Pt/Pd} = \sim 1-1.8$ and $\text{Pd/Ir} = \sim 2-40$ ratios close to chondritic ratios, basalts derived from a mantle source without strong fluid/melt metasomatism are generally sub-chondritic Pt/Pd and super-chondritic Pd/Ir ratios (Maier and Barnes, 2004).

The non-chondritic HSE distributions generally observed in basaltic volcanics are mostly due to partial melting and metasomatism processes in the lithospheric mantle (Rehkämper et al., 1999b; Alard et al., 2000; Lorand et al., 2009). HSE fractionation in subduction-related basaltic volcanics may be due to the mobility of HSEs in fluids/melts derived from the subducted plate (Brandon et al., 1996), and/or may result from the formation of PGE alloys during hydrous melting (McInnes et al., 1999; Kepezhinskas and Defant, 2001). On the other hand, collisional-post-collisional magmatism usually includes partial melting of subcontinental lithospheric mantle (SCLM) which has undergone subduction-related metasomatism, and/or lower crust melts (Hou et al., 2013; Locmelis et al., 2016; Fiorentini et al., 2018; Holwell et al., 2019). This process can produce hydrous/anhydrous, alkaline-rich melts that emplace and differentiate at various depths of the crust (Richards, 2009). The heat source for melting is provided by asthenospheric upwelling due to lithospheric extension and/or slab break-off and delamination, and/or post-collisional thermal rebound (Richards, 2011).

When $(^{187}\text{Os}/^{188}\text{Os})_i$ composition is correlated with $(^{87}\text{Sr}/^{86}\text{Sr})_i$ and $(^{143}\text{Nd}/^{144}\text{Nd})_i$ compositions in basaltic volcanics, they can be distributed over a wide range from sublithospheric mantle, continental lithospheric mantle to EM-I and HIMU mantle source areas (Figure 5). In addition, initial Sr and Nd isotope changes against the initial Os isotope composition can reveal the importance of continental crust components in the petrological evolution of basaltic volcanics. However, the mismatches in the initial Os-Sr and Os-Nd isotope correlation distributions may result from early melt differentiation of the Re-Os isotope system (sensitive to sulfide fractionation) due to the fact that the Os element is siderophile, whereas the Rb-Sr and Sm-Nd isotope systems (sensitive to silicate fractionation)

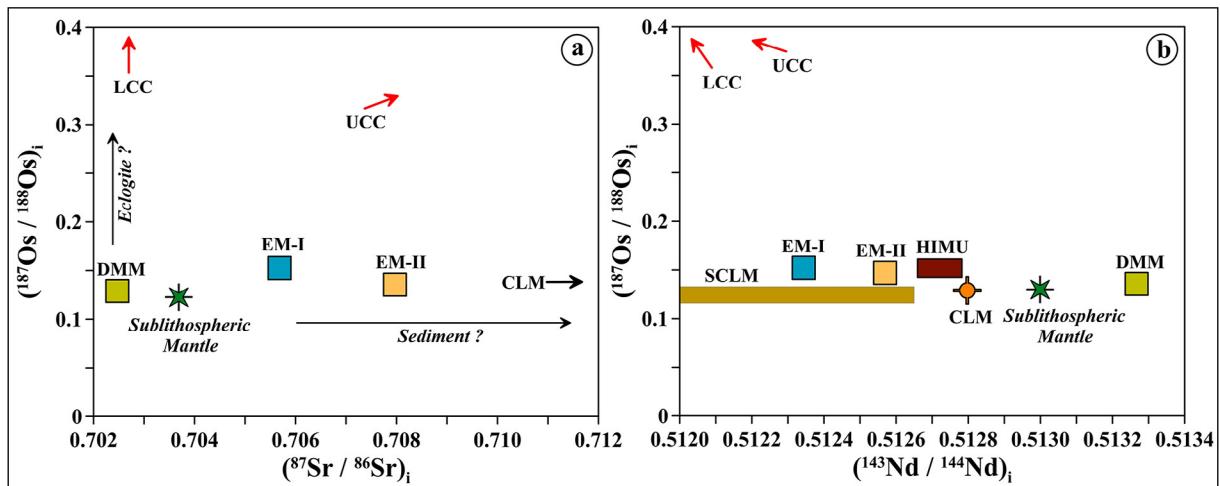


Figure 5- a) Initial $(^{87}\text{Sr} / ^{86}\text{Sr})_i$ versus initial $(^{187}\text{Os} / ^{188}\text{Os})_i$, and b) initial $(^{143}\text{Nd} / ^{144}\text{Nd})_i$ versus initial $(^{187}\text{Os} / ^{188}\text{Os})_i$ diagrams showing Os-isotope composition of the mantle source areas of basaltic volcanics. Depleted MORB mantle (DMM) composition from Hart et al. (1992) and van Keken et al. (2002), EM-I, EM-II and HIMU compositions from Zindler and Hart (1986), Shirey and Walker (1998), Walker et al. (2002) and Jackson and Shirey (2011), continental lithospheric mantle (CLM) composition from McBride et al. (1996) and Aulbach et al. (2016), sublithospheric mantle composition (arc-mantle peridotite representing depleted mantle-derived melts) from Tatsumoto et al. (1992), Hart et al. (1997), Handler et al. (2005) and Rocha-Júnior et al. (2012).

are more sensitive in late-stage differentiation events since the Sr-Nd elements are lithophile.

7.2. Sulfur Saturation Conditions of Parent Magmas

The HSE geochemistry of basaltic volcanics is mainly closely related to the sulfur saturation condition in the source area during partial melting and in the ascending magmas. Most of HSE is hosted in sulfide phases with high sulfide/silicate partition coefficients up to 10^5 (Stone et al., 1990; Bezmen et al., 1994; Keays, 1995; Fleet et al., 1996; Crocket et al., 1997). Since Cu/Zr, Pd/Zr and Pd/Cu ratios (McDonough and Sun, 1995) use strongly incompatible elements in S-undersaturated magmas and thus concentrate in the residual silicate melt rather than silicate or oxide minerals formed in differentiating magmas, these ratios can be used to determine the S-saturation condition of the magmas that have undergone differentiation (Yuan et al., 2012). However, when magma reaches S-saturation, Cu/Zr, Pd/Zr and Pd/Cu decrease due to the very high chalcophile nature of Cu and Pd; however, since Pd has a much greater sulfide/silicate partition coefficient than Cu, the Pd/Cu ratio is particularly sensitive to sulfur saturation (Keays and Lightfoot, 2007). Low Cu, Ni and HSE contents and low Cu/Zr, Pd/Zr and Pd/Cu ratios reflect the characteristics of S-saturated magmas whose chalcophile elements have been segregated during

the formation of immiscible sulfide melt (Keays, 1995; Lightfoot et al., 1997; Vogel and Keays, 1997; Lightfoot and Keays, 2005).

The generally low ÓHSE (or ÓPGE) contents of basaltic volcanics indicate that the mantle sources are probably S-saturated during partial melting (Keays, 1995). This situation means that the sulfides in the source mantle peridotite will be stable during partial melting, and the basaltic melts formed as a result will be poor in sulfur and low in HSE content. Therefore, low Ni, Cu and HSE contents and low Cu/Zr, Pd/Zr and Pd/Cu ratios in basaltic volcanics show that they have been consumed in terms of chalcophile elements. In addition, most basaltic volcanics are like mid-ocean ridge basalts (MORB), which have been depleted in terms of Cu and HSE by the segregation of immiscible sulfides due to very low Pd and Cu contents and S-saturation (Hertogen et al., 1980; Keays, 1995; Bézot et al., 2005).

In basaltic melts, changes in pressure, temperature, oxygen and sulfur fugacity and sulfur content in the surrounding mantle wall can cause changes in sulfur solubility and thus sulfur saturation conditions in basaltic magmas. The interactions between the primary basaltic magmas and the subcontinental lithospheric mantle (SCLM) increase the sulfur content in the melts, while the decrease in pressure and the increase

in the oxygen fugacity of the ascending melts decrease the sulfur solubility (Haughton et al., 1974).

The behavior of Pd and Cu elements in basaltic volcanics is largely controlled by the S-saturation condition of the magma (Figure 6). Because although both are siderophile elements associated with sulfides, element Pd (~ 35000) has a much higher sulfide/silicate partition coefficient than element Cu (245 - 1383) (Peach et al., 1990; Keays, 1995; Maier et al., 1998). $Cu/Pd > 6500$ (primitive mantle) indicates source S-saturation and/or melt development containing the sulfide fraction (Maier et al., 1998). High Cu/Pd ratios (>100000) and low HSE contents were observed in S-saturated Paleogene flood basalts having relatively low degree of partial melting in East Greenland (Momme et al., 2006). In addition, Cenozoic basalts in the North China craton have very high Cu/Pd ratios (193000-1400000) and low HSE contents, it has been suggested that these basaltic melts may have formed under S-saturated conditions with low-degree partial melting (Zhang et al., 2015). Since Cu has affinity for sulfur and Zr is absent, it has been suggested that the ascending magma may be in S-saturated state if $Cu/Zr < 1$ in basaltic volcanics (Lightfoot et al., 1994; Lightfoot and Keays, 2005). While the Cu/Zr ratio does not change during fractional crystallization in S-undersaturated magma, it decreases substantially when sulfide fractionation occurs in S-saturated magma (Figure 6).

7.3. Partial Melting

HSE changes in basaltic volcanics may also result from partial melting (Keays, 1995). Due to the different compatibility of PGEs, changes in the partial melting degree will produce different ratios of PGE. If the La/Sm ratio is taken as an indicator of the degree of partial melting, the Pd/Ir ratio will increase with increasing melt fraction (Greenough and Fryer, 1990; Greenough and Owen, 1992). It is suggested that most alkaline basalts are formed as plumes rising from the deep mantle source by relatively low-degree partial melting of enriched mantle sources at high pressure, while tholeiites are formed with high-degree partial melting at lower pressures (Jaques and Green, 1980). Melts of high partial melting degree (e.g., tholeiites) are expected to have lower Pd/Ir and higher Pt/Pd ratios than those of low partial melting degree (e.g., alkaline basalts).

Whether the magmatic sulfides are retained during the partial melting of the mantle has a critical effect on the PGE content of the melts (Barnes et al., 2015). Even a small amount of residual sulfide is sufficient to generate a strong PGE depletion in sulfide-saturated mantle melts in the source region (Hamlyn and Keays, 1986; Mungall and Brenan, 2014). Since the PGE content of the primary magma depends on the partial melting degree and the sulfur concentration in the mantle source, PGEs will be retained in the mantle source during low-degree partial melting under

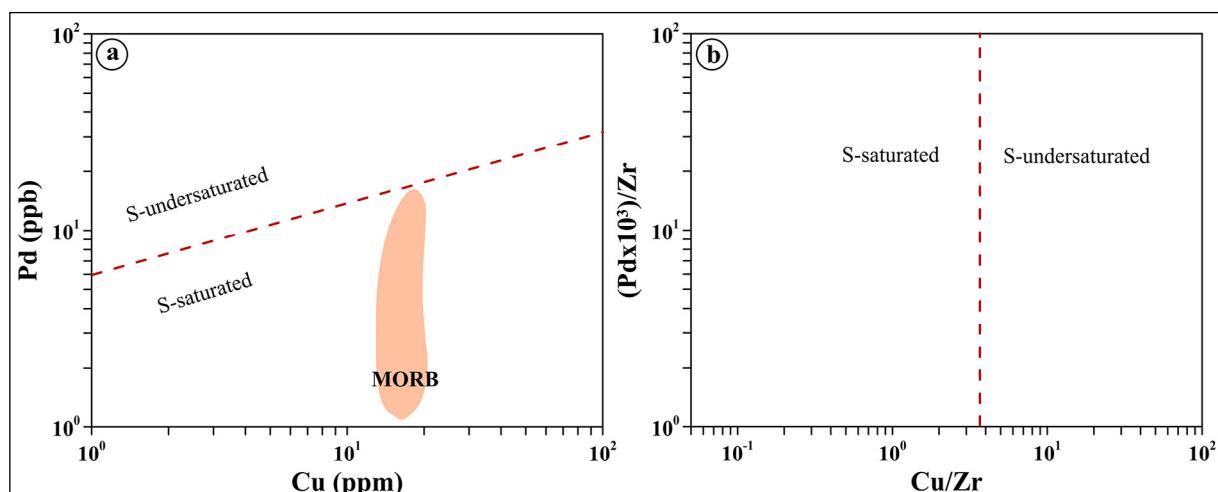


Figure 6- a) Cu versus Pd, and b) Cu/Zr versus $(Pdx10^3)/Zr$ diagrams discriminating S-saturation in basaltic volcanics. Dashed lines dividing S-saturated and S-undersaturated magmas in Cu versus Pd diagram from Vogel and Keays (1997) and in Cu/Zr versus $(Pdx10^3)/Zr$ diagram from Lightfoot et al. (1994) and Lightfoot and Keays (2005), Mid-ocean ridge basalts (MORB) field from McDonough and Sun (1995).

S-unsaturated conditions, in which case the sulfides remain in the mantle due to the high sulfide/silicate melt partition coefficients (Fleet et al., 1991; Keays, 1995). When there is at least $\sim 25\%$ partial melting in the mantle, S-undersaturated and non-PGE-depleted primary magmas can be formed by the complete depletion of sulfide in the mantle (Keays, 1995; Rehkämper et al., 1999a).

Due to the inverse relationship between sulfur solubility and pressure, most magmas in the lower crust will be sulfide saturated (Mavrogenes and O'Neill, 1999). During the ascent of the magma, sulfide liquid droplets containing a large part of the chalcophile element content will begin to redissolve in the silicate melt due to the increase in sulfur solubility in the magma because of the decrease in pressure (Kerr and Leitch, 2005). Magmas differentiating in the middle-upper crust and not saturated with sulfides (Mavrogenes and O'Neill, 1999) have the potential to carry highly fractionated chalcophile and siderophile elements that are depleted in Os, Ir, Ru and Rh but enriched in Cu and Au (and possibly Pt and Pd) (Holwell et al., 2019).

Since anhydrous mafic magmas are associated with variable partial melting degrees that make up $>15\%$ of mantle melting, almost all sulfides in the mantle source are consumed and the chalcophile elements are effectively transferred to the melt (Naldrett, 2011). Low-degree partial melting ($<10\%$) of metasomatized SCLM in post-collisional magmatism is suggested to be a trigger for the transfer and concentration of metals and volatiles (Holwell et al., 2019). In addition, the relatively low-degree partial melting of the metasomatized mantle source increases the concentration of preferably sulfur and incompatible trace metals with incongruent sulfide melting (Ballhaus et al., 2006). During the low-degree partial melting of the mantle, some Ni-Os-Ir-Ru rich monosulfide solid solution (mss) is left behind with the incongruent melting of sulfides, while Cu-sulfide and Au-Pt-Pd phases with low melting temperatures will be released, so mantle melts enriched with incompatible elements will occur (Ballhaus et al., 2006).

In order to estimate the amount of immiscible sulfide removal, the sulfur saturation condition can be modeled in the Pd against Cu/Pd diagram by using

the primary PGE composition of the depleted MORB mantle (DMM) and selected different amounts of residual sulfides (Huang et al., 2017). In other words, it can be said whether there is residual sulfide in the mantle source area of basaltic volcanics and sulfide removal takes place during magma ascent or not (Figure 7).

7.4. Fractionation

Sulfides are the most important source for HSEs with their partition coefficients between sulfide and silicate (melt) at 10^4 levels (Peach et al., 1994). Thus, fractionation of small amounts of sulfides (at the ppm level) will significantly reduce the HSE content of the remaining magma. Sulfide fractionation is generally suggested for HSE separation from basaltic magma, resulting in the remaining melt being consumed for HSE.

Pd and Ir have similar silicate-melt and sulfide-melt partition coefficients (Fleet et al., 1991; Peach et al., 1994) and thus show similar compatible behavior during S-saturated differentiation. Since the Cu/Zr ratios of the basaltic magmas that are not depleted in terms of chalcophile metals are around 1, the Cu/Zr ratios are lower in magmas that have undergone sulfide segregation (Lightfoot and Keays, 2005). Since Cu is much less chalcophile than Pd, in case of sulfide fractionation in a magma, the Cu/Pd ratio increases, and this ratio is an important indicator of sulfide fractionation (Barnes and Maier, 1999). On the other hand, if silicate, spinel, and possibly platinum group minerals (PGM) instead of sulfide are fractionated in a magma, the Cu/Pd ratio remains constant (Barnes and Maier, 1999). Therefore, the fact that the variable Cu/Pd ratio in basaltic volcanics generally indicates that the melt (magmas) is S-saturated during magmatic differentiation, whereas the constant Cu/Pd ratios shows that the melt (magma) is S-undersaturated during magmatic differentiation (Figure 8).

Fractionation of olivine (Hart and Ravizza, 1996), chromite (Philipp et al., 2001) and sulfide (Burton et al., 2002) has been proposed for the changes in HSE content and PPGE/IPGE ratios in basaltic volcanics. Fractional crystallization of olivine and clinopyroxene will decrease Ni or Cr but increase the PGE content as the PGE partition coefficients for olivine and clinopyroxenes are <1 (Roy-Barman et al., 1998;

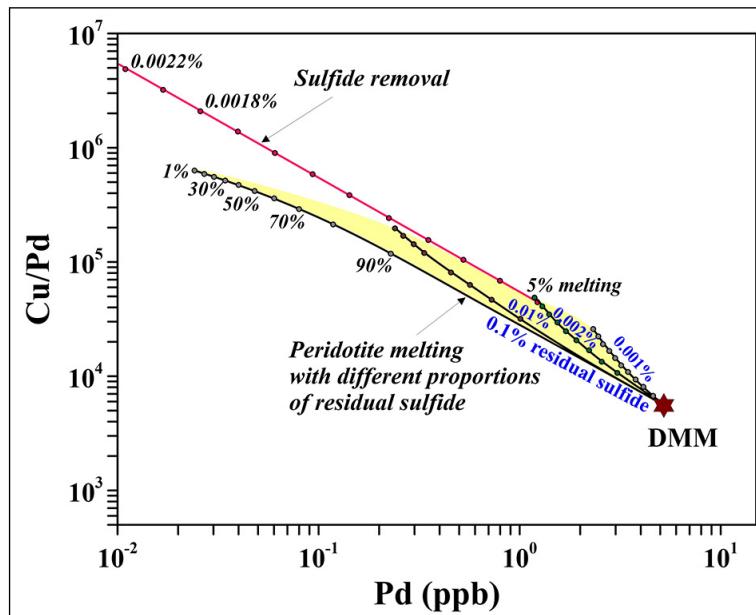


Figure 7- Pd versus Cu/Pd diagram showing the degree of partial melting in the mantle and sulfide removal. Black curves represent simple batch-melting curves for peridotite with residual sulfide (the modal proportions of residual phases during the melting were accepted as 62% olivine, 14.9% clinopyroxene, 15% orthopyroxene, 8% garnet, 0.1-0.001% sulfide) (Huang et al., 2017). The depleted MORB mantle (DMM) composition is from Salters and Andreas (2004).

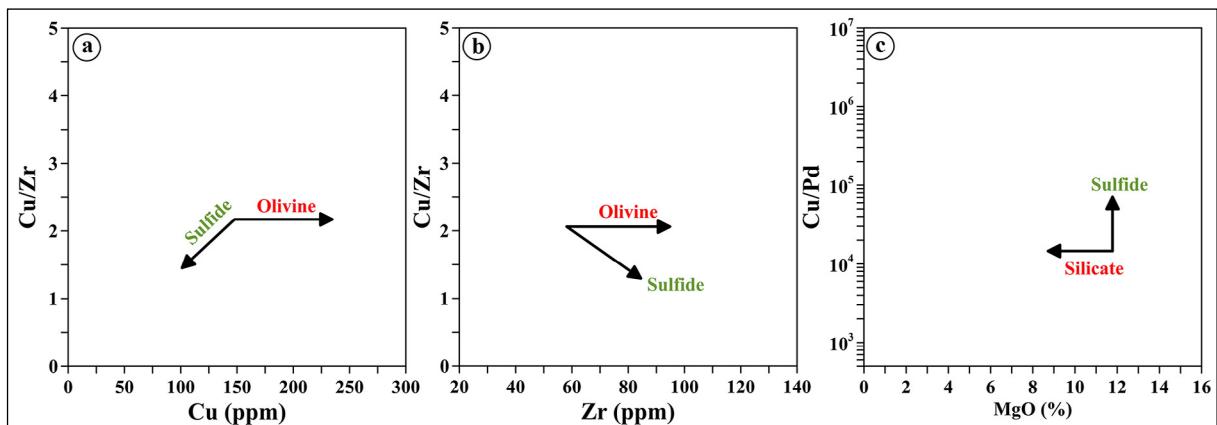


Figure 8- a) Cu versus Cu/Zr, b) Zr versus Cu/Zr, and c) MgO versus Cu/Pd diagrams showing sulfide and silicate fractionation trends. Silicate, olivine, and sulfide fractionation vectors are from Huang et al. (2017).

Burton et al., 2002; Ely and Neal, 2003; Brenan et al., 2003, 2005), although the increase is slow.

HSE compatibility during fractional crystallization in basaltic magmas can be compared with that during melt separation from the mantle (Os>Ir>Ru>Pt>Pd>Re; Barnes et al., 1985); thus, the separation of mineral phases (olivine, clinopyroxene and less oxides and sulfides) in basaltic volcanics can be interpreted as

increasing PPGE/IPGE ratios of melts (Aldanmaz et al., 2015). HSE provides information on fractionating mineral phases for mafic melts due to their relatively high crystal/liquid partition coefficients. The consumption of IPGE most likely reflects the early crystallization of olivine±chromite and associated phases with high crystal/liquid partition coefficient for IPGE (Pitcher et al., 2009; Aldanmaz et al., 2015).

Relationships between Ir versus Pd_N/Ir_N and MgO versus $(Pd/Cu) \times 10^3$ in basaltic volcanics may indicate sulfide and/or silicate fractionation in magma evolution (Figure 9; Aldanmaz et al., 2015). Correlation between Pd content and MgO in basaltic volcanics may be attributed to the fact that this element is outside of the early crystallizing phases (Aldanmaz et al., 2015), so this situation is consistent with experimental studies showing that Pd is moderately incompatible during fractionation of silicate minerals in basaltic magma (Pitcher et al., 2009). Re content does not show a significant correlation with MgO, which is interpreted as a result of the relatively incompatible behavior of Re with fractionated phases or Re fluctuation associated with the degassing of the basaltic magma before eruption (Jamais et al., 2008; Aldanmaz et al., 2015). Pt content does not show a systematic correlation with MgO, changes in Pt content are explained by events other than fractionating phases and are generally described as the nugget effect (Pitcher et al., 2009; Aldanmaz et al., 2015) and are associated with the presence of Pt-rich alloy consistent with the low solubility of Pt in the basaltic melt (Norman et al., 2004; Ireland et al., 2009).

Although the role of spinel fractionation is not well constraint, some experimental results (Righter et al., 2004) show that Pd may be incompatible while Ir may be compatible in chromites under high temperature and pressure conditions. However, the studies on chromites of ophiolitic rocks using in-situ analytical techniques shows that the previously

reported high PGE content in chromites can simply reflect the presence of platinum group minerals and alloys as nano-sized inclusions, and high Al chromite (geochemically closer to spinel observed in basalts) is systematically poor in both PGE ($\leq 0.1 \times$ chondrite) and platinum group minerals (González-Jiménez et al., 2011).

7.5. Crustal Assimilation

Since it has been suggested that HSE behaves compatible in general during mantle melting and also in the fractional crystallization process, it has been emphasized that these elements are very sensitive to petrological processes associated with crustal contamination or assimilation (Turner et al., 2009; Bezard et al., 2015). Besides, because Re and Os behave differently, Os isotopes are used as an indicator of crustal assimilation in basaltic volcanics since there is excessive fractionation between the continental crust (up to $^{187}\text{Os}/^{188}\text{Os} = 5$; McBride et al., 2001) and mantle ($^{187}\text{Os}/^{188}\text{Os} = 0.12$; Meisel et al., 1996) in terms of Os isotopic compositions (Gannoun et al., 2016).

It is suggested that the high $^{187}\text{Os}/^{188}\text{Os}$ ratios in subduction-related lavas are due to radiogenic Os enrichment due to crustal assimilation during magma ascent (Lassiter and Luhr, 2001; Suzuki et al., 2011) and/or contamination of the mantle wedge by subduction-fluids/melts (Borg et al., 2000; Alves et al., 2002; Suzuki et al., 2011; Hopkins et al., 2016). In addition, considering the mantle melting and crustal

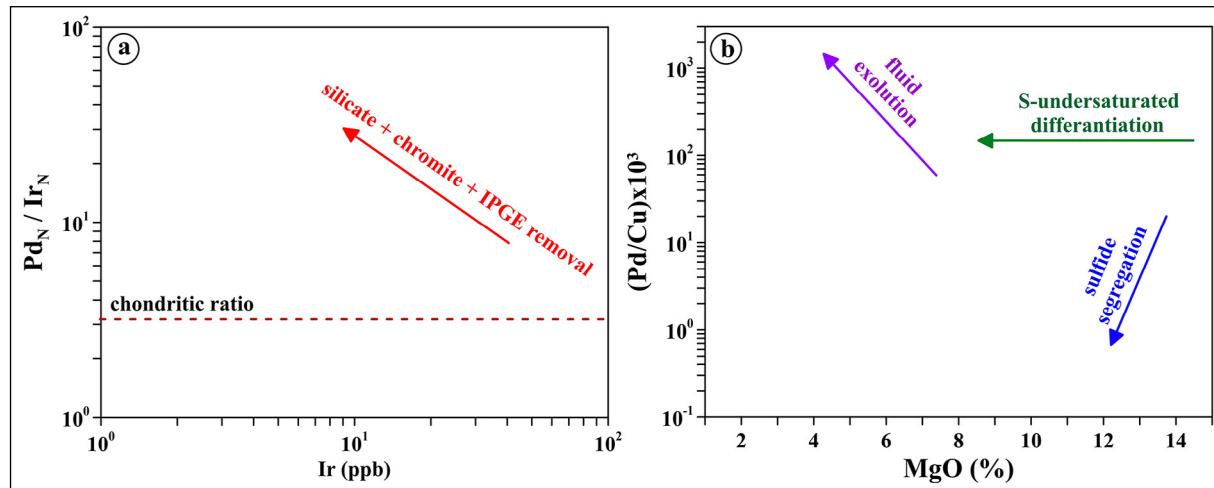


Figure 9- a) Ir versus Pd_N/Ir_N and b) MgO versus $(Pd/Cu) \times 10^3$ diagrams showing sulfide and silicate fractionation trends (Aldanmaz et al., 2015). Chondrite composition for normalized (N) values and dashed line chondrite ratio is from Fischer-Gödde et al. (2010).

contribution in magma formation in different tectonic settings, since the oceanic and continental crust has a high Re/Os ratio and radiogenic Os isotopes will increase over time, the decay of ^{187}Re to ^{187}Os plays a distinctive role in revealing the crustal material cycle (Figure 10; Walker, 2016; Gannoun et al., 2016).

Os isotope systematics, unlike other isotope systems (Sr, Nd, Hf and Pb) where both parent and daughter elements preferentially pass into the melt, is used to distinguish petrological processes associated with the assimilation of crust having a high $^{187}\text{Os}/^{188}\text{Os}$ ratio (Chesley and Ruiz, 1998; Widom et al., 1999; Shirey and Walker, 1998; McBride et al., 2001; Chesley et al., 2004; Jung et al., 2011; Hopkins et al., 2016). In fact, the radiogenic Os isotope composition increases due to crustal contamination during the upward ascent of the basaltic magma in the old continental crust (McBride et al., 2001; Chesley et al., 2004; Rudnick and Walker, 2009). Therefore, Os isotope systematics together with HSE content can provide important constraints in determining the possible continental crust contribution (assimilation) in the evolution of basaltic magma (Chu et al., 2013; Aldanmaz et al., 2015; Hopkins et al., 2016).

It has been stated that basalts having Os content >0.004 ppb are less sensitive to crustal assimilation (Widom et al., 1999; Class et al., 2009). In addition,

it has been suggested that when the Os isotope composition is low (mostly $^{187}\text{Os}/^{188}\text{Os} < 0.15$) in basalts, there is no significant crust assimilation (Chu et al., 2013; Sun et al., 2014), whereas continental crust (especially mafic lower crust) assimilation plays an important role in cases where the Os isotope composition is very high ($^{187}\text{Os}/^{188}\text{Os} = 1-3$) (Chesley and Ruiz, 1998). However, basaltic magmas will probably take up some primary sulfides or PGE micro-alloys of mantle origin during the mantle melting and/or the ascent of magmas along the SCLM (Widom et al., 1999; Jackson and Shirey, 2011; Chu et al., 2013; Day, 2013; Hopkins et al., 2016), so they reach the crust with a certain Os content and magmas having high Os are formed (Chu et al., 2017). Therefore, it is not easy to limit the degree of crustal assimilation by AFC modeling (McBride et al., 2001; Xu et al., 2007). In addition, interstitial sulfides (formed along the border of silicate mineral grains, rich in Re, poor in Os, developed in high Re environment, having variable and radiogenic Os isotope and high Pd/Ir ratios) in the mantle source may preferentially be melted during mantle melting (Alard et al., 2005; Dale et al., 2007; Harvey et al., 2011; Day, 2013). In addition, basaltic magmas can selectively assimilate sulfide phases at the grain boundary with lower melting temperature while passing through the lithosphere, and thus increase their Pt and Pd concentrations and $^{187}\text{Os}/^{188}\text{Os}$ ratios (Sen et al., 2011; Wang and Becker, 2015). These factors make more complicated to constraint crustal assimilation by using Os isotopes (and PGE) (Chu et al., 2017).

The degree of crustal assimilation in basaltic volcanics can be evaluated by a simple binary mixture model using Os and $^{187}\text{Os}/^{188}\text{Os}$ isotope compositions (Figure 11; Chu et al., 2013). However, Ni-Os correlations in basaltic volcanics, instead of simple binary mixing, it can also be explained by the variable assimilation of the continental crust through assimilation-fractional crystallization (AFC) (Figure 12; Aldanmaz et al., 2015). In addition, even if the amount of assimilated crust is quite small, large differences may occur in Os isotope changes of basaltic volcanics due to the large compositional difference between mantle-derived magma (melt) and assimilated crust (Aldanmaz et al., 2015). Therefore, a small amount of crustal contamination that is not so apparent in lithophile element (Sr, Nd) isotope systematics will be represented by high $^{187}\text{Os}/^{188}\text{Os}$

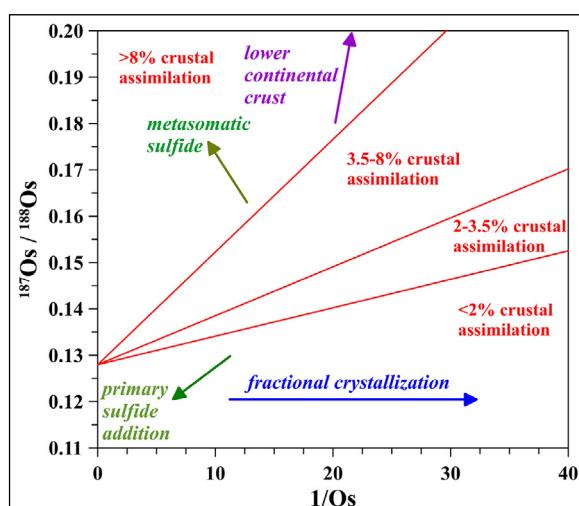


Figure 10- $1/\text{Os}$ versus $^{187}\text{Os}/^{188}\text{Os}$ diagram showing different degrees of crustal assimilation. Lines show binary mixing lines, and fields exhibit 2%, 3.5% and 8% lower continental crust assimilation of basaltic magma (Gannoun et al., 2016).

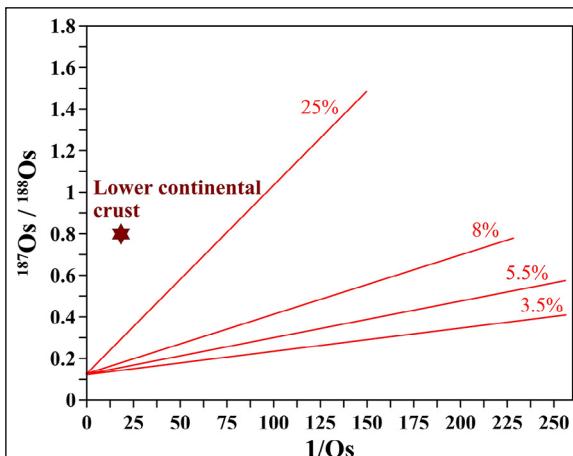


Figure 11- Binary mixing model showing the assimilation between basaltic magma and the lower crust (Chu et al., 2017). $^{187}\text{Os}/^{188}\text{Os} = 0.128$ for parent magma (Chu et al., 2017), and $^{187}\text{Os}/^{188}\text{Os} = 0.8$ and Os= 0.049 ppb for lower continental crust (Saal et al., 1998).

ratio and low Os content in basaltic volcanics. Furthermore, wide variation ranges in Th/La and 1/Pb ratios against the limited change in $^{187}\text{Os}/^{188}\text{Os}$ composition of basaltic volcanics may indicate a small amount of sediment contribution in addition to crustal contamination (Figure 12; Aldanmaz et al., 2015).

8. Results

Petrological studies to be carried out using whole-rock HSE and Os isotope systematics of basaltic volcanics can reveal data; 1) to determine the geochemical characteristics of the subcontinental lithospheric mantle (SCLM) from which the magmas are derived, 2) data that will contribute to the modeling of magmatic processes (partial melting, fractionation, crustal assimilation, etc.) that are effective during magma generation from the lithospheric mantle and magma-crust interaction.

It is suggested to use new and modern analytical approaches such as whole-rock HSE contents and Os isotope data as well as the traditional lithophile element geochemistry data (whole-rock major-trace element geochemistry and Sr-Nd-Pb-Hf isotope systematics) in order to determine mantle source areas of partial melts that form the parent magmas, and to evaluate petrological processes such as fractional crystallization and crustal assimilation during magma evolution in widely observed Cenozoic basaltic volcanics in Turkey.

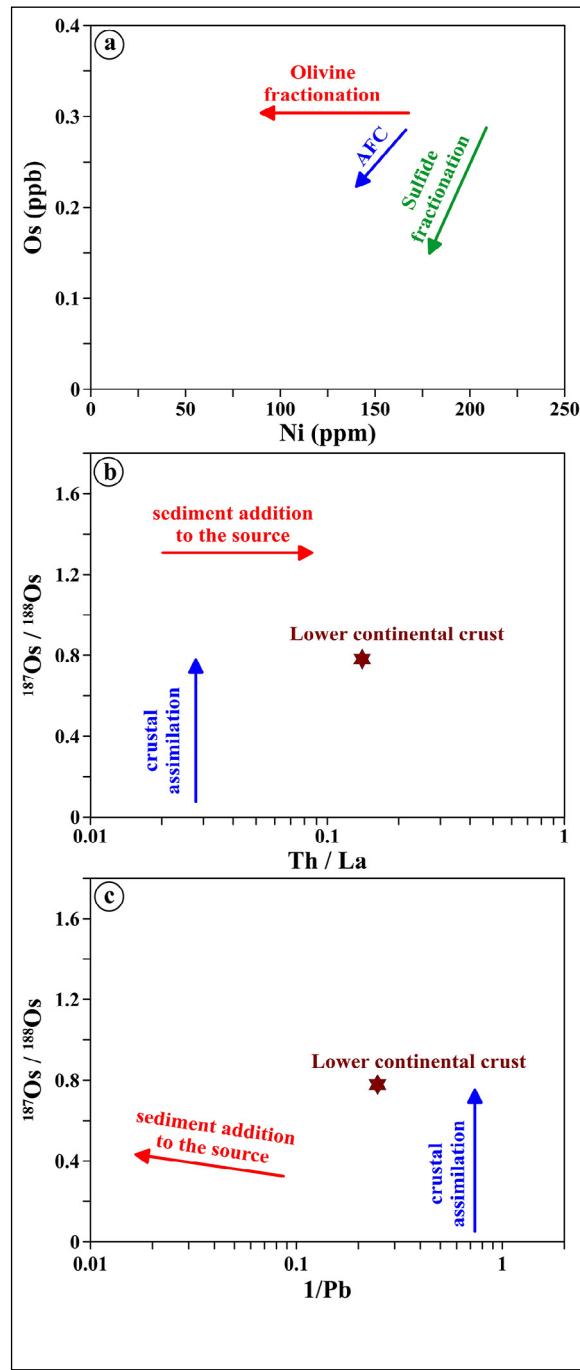


Figure 12- a) Ni versus Os, b) Th/La versus $^{187}\text{Os}/^{188}\text{Os}$ and c) $1/\text{Pb}$ versus $^{187}\text{Os}/^{188}\text{Os}$ diagrams showing trends of fractionation, crustal assimilation and sediment addition to the source. Trends of olivine and sulfide fractionation, fractional crystallization accompanied with assimilation (AFC), crustal assimilation and sediment addition to the source from Aldanmaz et al. (2015), Os-isotope composition of lower continental crust ($^{187}\text{Os}/^{188}\text{Os} = 0.8$) from Saal et al. (1998), Th (1.2 ppm), La (8 ppm) and Pb (4 ppm) contents of lower continental crust from Rudnick and Gao (2004).

Since the primary as inclusions and secondary sulfide minerals in groundmass that can be found in rocks will affect the whole-rock HSE and Os isotope abundances of basaltic volcanics, petrographic (ore microscopy) and mineral chemistry (SEM and/or EPMA) studies for these minerals will be of great benefit.

Acknowledgements

This study was supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK-ÇAYDAG, Project no: 117Y075). The authors would like to thank editor-in-chief Halim MUTLU, technical editor Oğuz ALTUN, assistant editor Pınar ŞEN and referees for their contributions.

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