SERIES

Igneous Rock Associations 27. Chalcophile and Platinum Group Elements in the Columbia River Basalt Group: A Model for Flood Basalt Lavas

Stephen P. Reidel[1] **and D. Brent Barnett**[2*]

[1] *School of the Environment, Washington State University*
Tri-Cities, Richland, Washington, 99354, USA
E-mail: sreidel@wsu.edu

[2] *Pacific Northwest National Laboratory*
902 Battelle Boulevard, Richland, Washington, 99352, USA
** Deceased*

SUMMARY

The Columbia River Basalt Group is the youngest and best preserved continental Large Igneous Province on Earth. The 210,000 km^3 of basaltic lavas were erupted between 16.6 and 5 Ma in the Pacific Northwest, USA. The peak of the eruptions occurred over a 700,000-year period when nearly 99% of the basalts consisting of the Steens, Imnaha, Picture Gorge, Grande Ronde and Wanapum Basalts were emplaced. In this study we examined the Platinum Group Elements (PGEs) Pt and Pd, and the chalcophile elements Cu and Zn in the Columbia River Basalt Group. The presence of Pt, Pd and Cu in the compositionally primitive Lower Steens, Imnaha and Picture Gorge Basalts suggests that the Columbia River Basalt Group magma was a fertile source for these elements. The PGEs are contained mainly in sulphides in the earliest formations based on their correlation with immiscible sulphides, sulphide minerals and chalcophile elements. Grande Ronde, Wanapum and Saddle Mountains Basalts are depleted in PGEs and chalcophile elements compared to earlier formations. Sulphur was saturated in many flows and much of it probably came from assimilation of cratonic rock from a thinned lithosphere. We propose a model where the presence or absence of PGEs and chalcophile elements results primarily from the interaction between an advancing plume head and the crust/lithosphere that it encountered. The early lavas erupted from a plume that had little interaction with the crust/lithosphere and were fertile. However, as the plume head advanced northward, it assimilated crustal/lithospheric material and PGE and chalcophile elements were depleted from the magma. What little PGE and chalcophile elements remained in the compositionally evolved and depleted Grande Ronde Basalt flows mainly were controlled by substitution in basalt minerals and not available for inclusion in sulphides.

RÉSUMÉ

Le groupe basaltique du Columbia est une grande province ignée continentale. Il s'agit de la plus jeune et la mieux préservée au monde. Les 210 000 km^3 de laves basaltiques ont été émis entre 16,6 et 5 Ma dans le Nord-Ouest Pacifique, aux États-Unis. Le pic des éruptions s'est produit sur une période de 700 000 ans lorsque près de 99% des basaltes comprenant les basaltes de Steens, Imnaha, Picture Gorge, Grande Ronde et Wanapum ont été mis en place. Dans cette étude, nous avons examiné les éléments du groupe platine (EGP) Pt et Pd, et les éléments chalcophiles Cu et Zn dans le groupe basaltique du Columbia. La présence de Pt, Pd et Cu dans les basaltes de Lower Steens, Imnaha et Picture Gorge, de composition primitive, suggère que le magma du groupe basaltique du Columbia était une source fertile pour ces éléments. Les EGP sont principalement contenus dans les sulfures des formations les plus anciennes en fonction de leur corrélation avec les sulfures non miscibles, les minéraux sulfurés et les éléments chalcophiles. Les basaltes de Grande Ronde, de Wanapum et de Saddle Mountains sont appauvris en EGP et en éléments chalcophiles par rapport aux formations antérieures. Le soufre était saturé dans de nombreux écoulements et une grande partie provenait probablement de l'assimilation des roches cratoniques d'une lithosphère amincie. Nous proposons un modèle où la présence ou l'absence d'EGP et d'éléments chalcophiles

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résulte principalement de l'interaction entre une tête de panache en progression et la croûte / lithosphère rencontrée. Les premières laves ont été émises à partir d'un panache qui avait peu d'interaction avec la croûte / lithosphère et étaient fertiles. Cependant, à mesure que la tête du panache avançait vers le nord, elle a assimilé du matériel crustal / lithosphérique, et le magma a été appauvri en EGP et en éléments chalcophiles. Le peu d'EGP et d'éléments chalcophiles restant dans les écoulements de basalte de composition évoluée et appauvrie de Grande Ronde ont été principalement contrôlés par la substitution dans les minéraux du basalte et n'étaient pas disponibles pour l'inclusion dans les sulfures.

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INTRODUCTION

Large Igneous Provinces (LIPs) are the major source for Platinum Group Elements (PGEs) and are typically associated with sulphide deposits (Cawthorn 2005; Ernst and Jowitt 2013; among others) but they represent a difficult exploration target (Mungall 2005, and papers therein). PGE deposits in LIPs typically occur in deep seated layered intrusions that only become exposed after many millions of years of uplift and erosion. Most authors recognize that these layered intrusions fed surface lavas such as the Noril'sk-Talnakh deposits (Ryabov et al. 2014; Pavlov et al. 2019) but in many cases it is difficult to relate these intrusions to surface lavas (e.g. Naldrett et al. 1992, 2011, 2012; Pavlov et al. 2019). Typically, this is due to the lack of preservation of the lavas, but more often preserved lavas lack any economical deposit and thus there is little incentive to characterize them for PGEs and chalcophile elements.

Research on flood-basalt provinces has shown that detailed characterization is important for unraveling the history of these LIPs and to understand the petrogenetic processes that resulted in their complex compositions (e.g. Macdougall 1988; Mahoney and Coffin 1997; Hooper et al. 2007; papers in Reidel et al. 2013a; Ernst 2014). Thus, to fully understand the role of PGE and chalcophile deposits in LIPs, an understanding of the lavas is an essential requirement.

The Columbia River Flood-Basalt Province of the Pacific Northwest is one of the best characterized LIPs in the world (Fig. 1) and, thus, is an excellent target for examining the role of PGEs and chalcophile elements in LIP lava flows. The accessibility, excellent surface exposures, numerous deep boreholes, and many thousands of published ICP-MS and XRF major, minor, trace-element, and isotope analyses, have led to a good understanding of the stratigraphy, the volume and extent of the lavas, and the petrogenesis of the basalt (e.g. Reidel et al. 2013a and papers therein). Because basalt flows are the surface expression of deeper magma chamber processes and are extruded over time, the study of PGEs and chalcophile elements in well characterized flood basalts like the Columbia River Flood-Basalt Province can give new insights into how they may become distributed over time and concentrated to form deposits. One part of the story, however, is lacking in the Columbia River Basalt Group, that of the occurrence of PGEs and chalcophile elements, and their role in the petrogenesis of the basalts. Thus, the Columbia River Basalt Group provides an excellent laboratory to study the occurrence and controls on these elements and could lead to a better understanding of them in LIPs and better models for targets.

GEOLOGICAL SETTING

The Columbia River Flood-Basalt Province, Pacific Northwest, USA, is composed of the Columbia River Basalt Group (Fig. 2) which is a series of generally tholeiitic basalts to basaltic andesites and andesites with sparse alkali-olivine basalts that erupted between ~16.7–5.5 Ma (Jarboe et al. 2008; Barry et al. 2010, 2013; Kasbahm and Schoen 2018). The basalts cover more than 210,000 km^2 of Washington, Oregon, Idaho and Nevada with an estimated volume of 210,000 km^3 (Reidel et al. 2013b), and form part of a larger volcanic region that includes the Chilcotin Plateau Basalts of British Columbia, the contemporaneous silicic centres in northern Nevada, the basaltic and time-transgressive rhyolitic volcanic fields of the Snake River Plain and Yellowstone Plateau, and the High Lava Plains of central Oregon. Although the province is the smallest LIP on Earth, its location in the easily accessible Pacific Northwest, USA, has allowed the geology to be refined by over 50 years of study. Thus, the Columbia River Basalt Group has become a model for the study of similar provinces worldwide.

The Columbia River Basalt Group erupted in a back-arc setting between the Cascade volcanic arc and the Rocky Mountains along the western edge of the North American craton (Fig. 1). The flood-basalt lavas cover basement rocks that record a long and complex geological history of western North America beginning in the Proterozoic with the breakup of the supercontinent Rodina, followed by the suturing of Mesozoic accreted terranes, and deposition and deformation of Paleogene and Neogene sediments and volcanic rocks. These basement structures became the template for geological structures now superimposed on the basalt province (Reidel et al. 2013c, 2020; Reidel 2015).

Columbia River Basalt Group volcanism initially began in the Oregon Plateau and quickly spread north to the Columbia Basin through a linear fissure system (Figs. 1 and 3; Camp and Ross 2004). In the Oregon Plateau (Figs. 1 and 3), flood basalt eruptions were contemporaneous with rhyolitic volcanism at the western end of the Snake River Plain hotspot track and with a major period of crustal extension in northern Nevada that began at ca. 17–16 Ma (Camp et al. 2003). In the Columbia Basin, rapid subsidence along with folding and faulting of the basalt accompanied volcanism (Reidel et al. 1989b, 2013c). The Chilcotin Plateau Basalts of British Columbia complete the northward progression of basaltic volcanism in the Pacific Northwest from Miocene to Pliocene (Bevier 1983; Mathews 1989).

Columbia River Basalt Group

The main eruptive phase of the Columbia River Basalt Group (Fig. 2) includes the Steens, Imnaha, Picture Gorge, Grande Ronde Basalts and early part of the Wanapum Basalt when 99% of the basalt erupted in ~700,000 years (Kasbohm and Shoene 2018). The peak of the eruptions occurred during

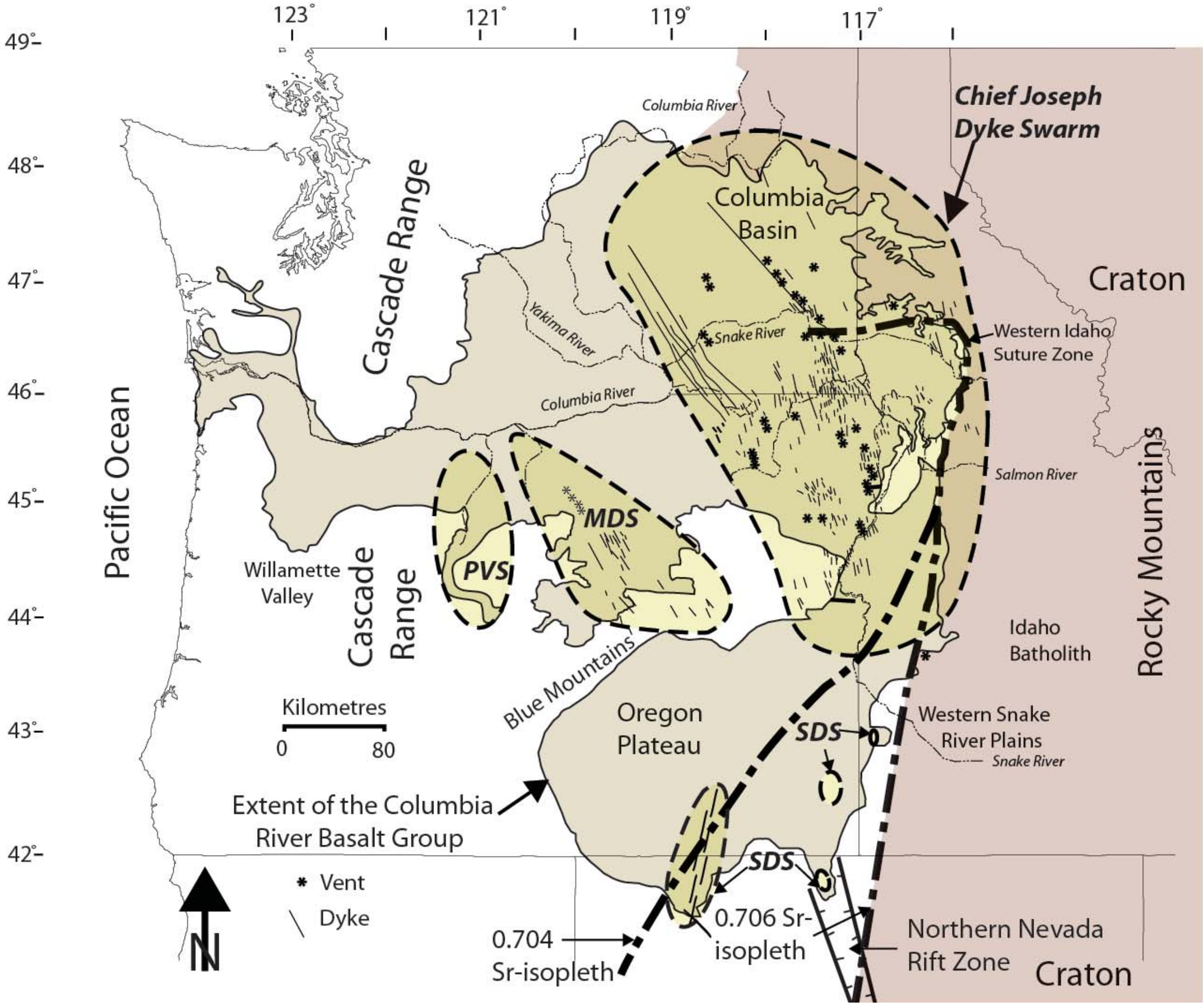

Figure 1. Location map of the Columbia River flood basalt province. This figure shows the extent of the Columbia River Basalt Group and dykes. The Columbia Basin forms the northern portion of the province and the Oregon Plateau forms the southern portion of the province south of the Blue Mountains. Geographic features include: Chief Joseph dyke swarm, Steens Basalt dyke swarms (SDS,) Monument (Picture Gorge) dyke swarm (MDS) and Prineville Basalt source area (PVS). The initial mainly granitic ^{87}Sr/^{86}Sr 0.704 and 0.706 isopleths are from Pierce and Morgan (2009) and Armstrong et al. (1977). The Precambrian craton lies east of the 0.706 isopleth, oceanic accreted terranes lie west of the 0.704 isopleth, and transitional crust with cratonic affinities lies between the two. Basement rocks include the Precambrian craton of North America east of the 0.706 line, transitional crust with cratonic affinity between the 0.706 and 0.704 lines, and Paleozoic to Mesozoic oceanic accreted terranes west of the 0.704 line.

Grande Ronde time, when ~74% of the flood-basalt volume was generated. The Picture Gorge Basalt was erupted coeval with the Grande Ronde Basalt and comingled with it (Bailey 1989; Fig. 2), although a recent study suggests that the Picture Gorge Basalt may be among the oldest of the Columbia River Basalt Group (CRBG) formations (Cahoon et al. 2020). The waning phase includes the later part of the Wanapum Basalt and Saddle Mountains Basalt that erupted over ~10-million-years but account for only a few percent of the basalt. Many of the basalt flows were of extraordinary size, commonly exceeding 1000 km^3 in volume and traveling many hundreds of kilometres from their vent systems (Tolan et al. 1989; Reidel et al. 1989b; Reidel 1998, 2005, 2015; Reidel and Tolan 2013). Although radiating dyke swarms typically are often associated with plumes, e.g. Ernst and Buchan (2001), CRBG dykes (Fig. 1) are probably more influenced by the northward progression of the plume and eruptions through pre-existing structures (Reidel et al. 2013c).

Lithology

For 16-million-year-old lava flows, the Columbia River Basalt Group is remarkably fresh with little alteration. Glass in thin sections typically is used as an important discriminator to determine alteration in the flows but the Mafic Index also can

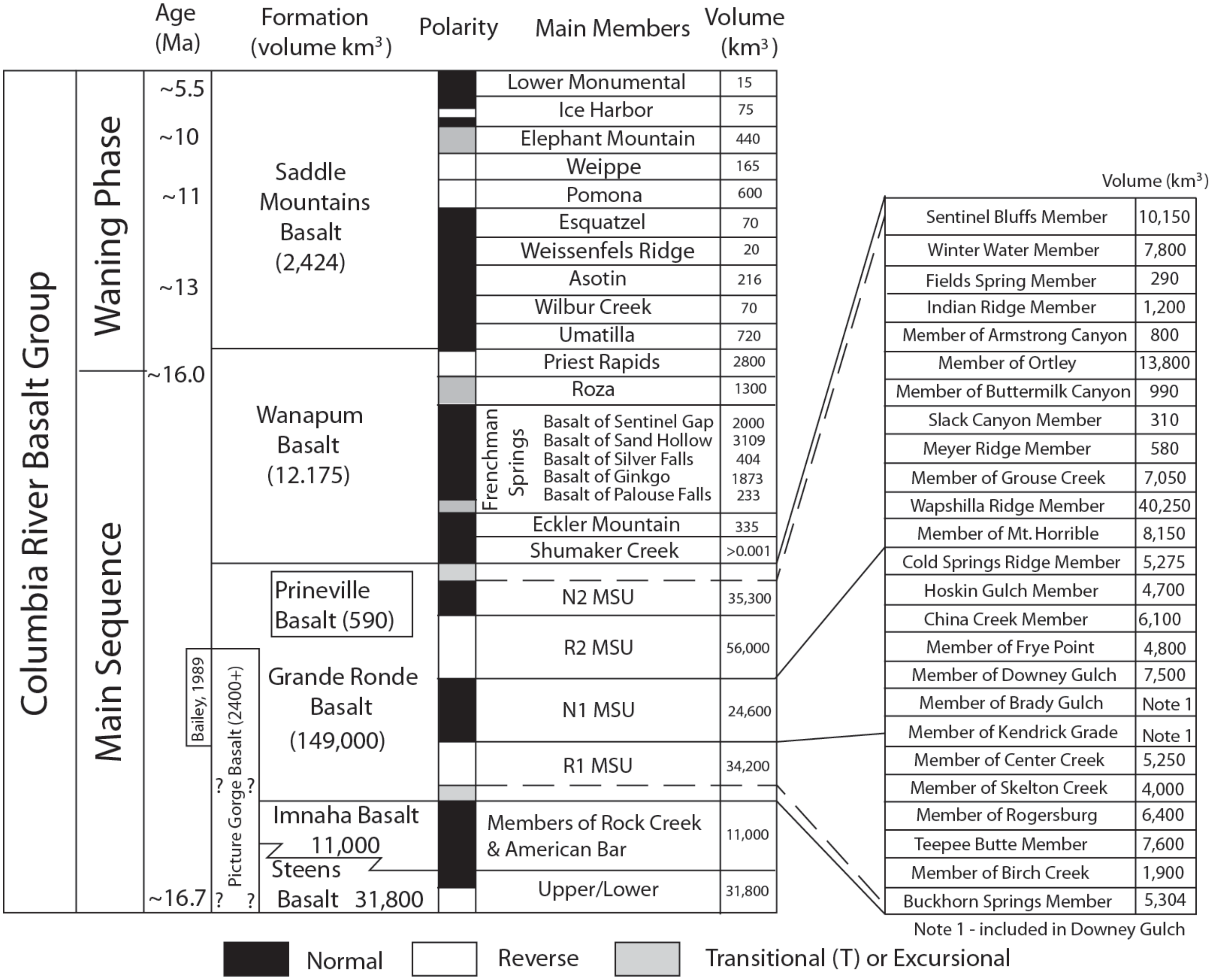

Figure 2. Generalized stratigraphy of the Columbia River Basalt Group showing the main stratigraphic units discussed in the text. Boxes around Prineville Basalt and Picture Gorge Basalt represent interfingering with the Grande Ronde Basalt. Stratigraphy, volumes, and polarities are from Reidel et al. (2013a), Reidel and Tolan (2013), Camp et al. (2013), and Reidel (2015). Picture Gorge Basalt extension is from Cahoon et al. (2020). Age dates are from Barry et al. (2010), Barry et al. (2013) and Kasbohm and Schoene (2018). N1-Normal 1; R1-Reversed 1; N2-Normal 2; R2- Reversed 2. T-Polarity transitions or excursions.

be used with the composition to evaluate the presence or absence of alteration (Baker et al. 2019). The basalt compositions used in this study are from unaltered, fresh samples. Typically, Columbia River Basalt Group flows are composed of plagioclase, clinopyroxene and glass with lesser amounts of olivine and minor amounts of orthopyroxene, ilmenite, magnetite, titanomagnetite and fluorapatite. Generally, the flows have equal amounts of clinopyroxene and plagioclase. Clinopyroxene is mainly augite-aegirine often with overgrowths of pigeonite and occasionally cores of orthopyroxene (Reidel 1983). Plagioclase typically ranges from An_{30} to An_{60}. Olivine, although minor, ranges from Fo_{20} to Fo_{65}. One of the most significant lithologic aspects of a flow is the presence or absence of plagioclase phenocrysts and olivine microphenocrysts (e.g. Swanson et al. 1979; Beeson et al. 1985; Bailey 1989; Reidel et al. 1989a; Hooper 2000). Most flows are commonly aphyric to rarely phyric, with the exception including the highly plagioclase-phyric flows of Steens, Imnaha and Picture Gorge Basalts, along with several Wanapum Basalt and Saddle Mountains Basalt flows. Although the Grande Ronde Basalt is often mischaracterized as strictly aphyric, many of these flows can be recognized by the presence of plagioclase phenocrysts and microphenocrysts (Reidel et al. 1989a; Reidel and Tolan 2013).

Composition

The Columbia River Basalt Group is a series of generally tholeiitic basalts to basaltic andesites and andesites with sparse

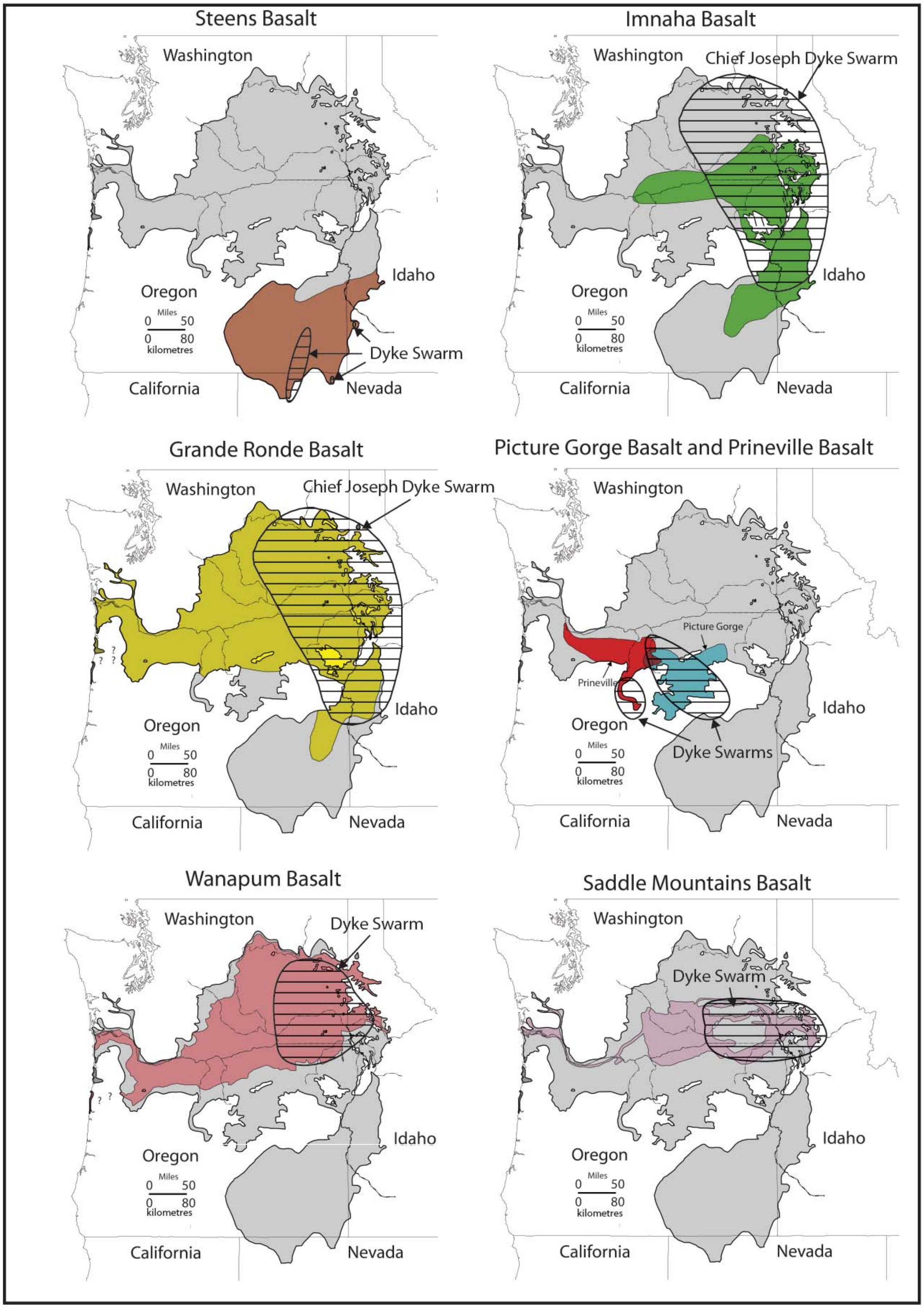

Figure 3. Extent of the seven formations of the Columbia River Basalt Group. The dyke swarms for each formation are shown as areas with horizontal lines. The Chief Joseph dyke swarm is the main swarm area for the Imnaha, Grande Ronde, Wanapum and Saddle Mountains Basalts. The Steens dyke swarm fed the Steens Basalt and the Monument dyke swarm fed the Picture Gorge Basalt. The Grande Ronde Basalt dykes cover the entire Chief Joseph dyke swarm but the Imnaha Basalt dyke swarm is confined to the southern part. The Wanapum and Saddle Mountains dyke swarms are broken out to show their limited extent. Extent of formations from Reidel et al. (2013b).

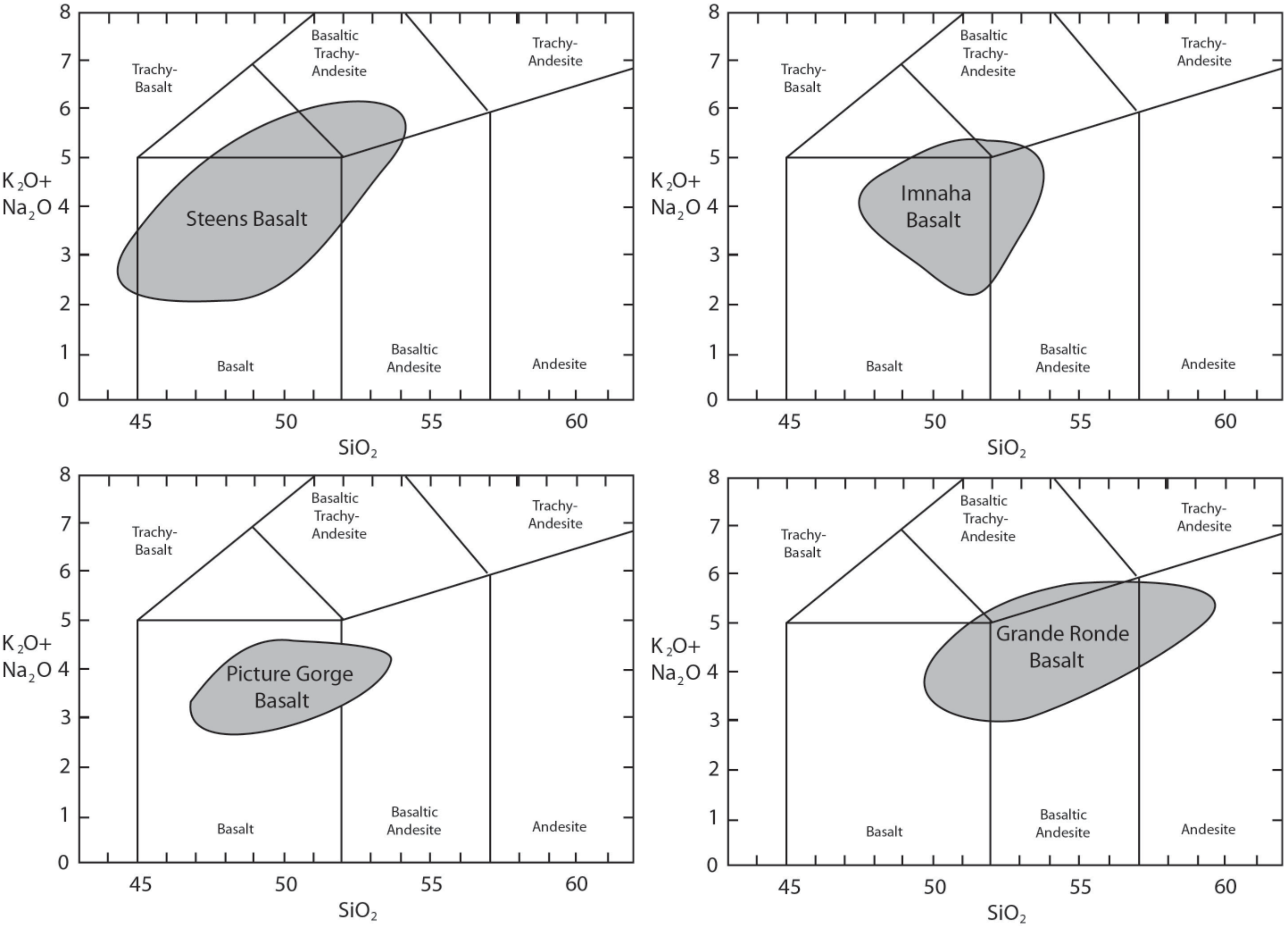

Figure 4. K_2O+Na_2O versus SiO_2 plot for the Steens, Imnaha, Grande Ronde and Picture Gorge Basalts. The diagram shows the range of established formations and is based on La Bas et al. (1986). Data from Bailey (1989), Schuster (1993), Hooper (2000), Camp et al. (2003, 2013), Wolff et al. (2008 Appendix), Reidel and Tolan (2013) and S. Reidel unpublished data.

alkali-olivine basalts (Fig. 4). By far, the composition of the lavas has proven to be one of the most important tools for recognizing and correlating flows, as well as understanding the origin of these flows (e.g. Wright et al. 1973, 1989; Hooper 1974, 1997, 2000; Swanson et al. 1979; Reidel 1983, 1998, 2005; Beeson et al. 1985; Mangan et al. 1986; Reidel et al. 1989a, b; Hooper and Hawkesworth 1993; Ramos et al. 2005, 2013; Hooper et al. 2007; Camp and Hanan 2008; Camp 2013; Rodriguez and Sen 2013). Over the last 50+ years the Columbia River Basalt Group has been extensively analyzed for major and minor oxides, trace elements and isotopes. Many lava flows have a remarkable 'bulk' compositional homogeneity despite their huge volumes and distances traveled. However, with more detailed work, the recognition of compositional heterogeneities within Columbia River Basalt Group flows now must be taken into consideration (e.g. Reidel and Fecht 1987; Reidel and Tolan 1992; Reidel 1998, 2005; Martin et al. 2013; Reidel and Tolan 2013).

Origin

The origin of the Columbia River Basalt Group has been an area of considerable debate for many years. The two main proposed sources for the basalts are: back-arc spreading and mantle plume (e.g. Hooper and Hawkesworth 1993; Camp and Hanan 2008; Camp 2013). The majority of workers now support the mantle plume hypothesis (e.g. Duncan 1982; Brandon and Goles 1988, 1995; Draper 1991; Hooper and Hawkesworth 1993; Geist and Richards 1993; Camp 1995, 2013; Dodson et al. 1997; Mege and Ernst 2001; Ernst and Buchan 2001; Hooper et al. 2002, 2007; Camp et al. 2003; Camp and Ross 2004; Caprarelli and Reidel 2004; Ramos et al. 2005; Camp and Hanan 2008; Wolff et al. 2008; Humphreys and Schmandt 2011). However, unresolved arguments on the nature and extent of the mantle plume, and the petrogenetic processes within the magma are still debated (e.g. Ivanov 2007; Smith 2007). The nearly coeval, back-arc setting of the Miocene to Pliocene Chilcotin Plateau Basalts (Bevier 1983;

Mathews 1989) that occur just north of the CRBG also have been proposed to have a mantle plume origin (Ernst and Buchan 2010) further suggesting that the CRBG mantle plume concept may be more complex than originally thought. Most petrogenetic models have concentrated on the Steens, Imnaha, and Grande Ronde Basalts. The waning phase, Wanapum Basalt and Saddle Mountains Basalt, has been attributed to increasing crustal contamination of the residual melts from a subcontinental lithospheric mantle enriched at ~2000 Ma (e.g. Hooper and Hawkesworth 1993; Hooper et al. 2007; Camp and Hanan 2008).

Nearly all researchers agree that the CRBG cannot be the result of a simple model of decompression partial melting of a mantle plume source (e.g. Carlson et al. 1981; Hooper et al. 2007). Most agree that the Imnaha Basalt is the most primitive endmember corresponding to Carlson's (1984) C2 component. The Imnaha component is interpreted to be upwelling depleted mantle (EM) II Type Ocean-Island basalt with perhaps a small component of cratonic crust and forms the endmember for the Steens, Picture Gorge and Grande Ronde Basalt formations (e.g. Hooper and Hawkesworth 1993; Hooper et al. 2007; Camp and Hanan 2008; Wolff and Ramos 2013). Hooper and Hawkesworth (1993), Camp et al. (2003, 2013), Wolff et al. (2008) and Ramos et al. (2013) suggest that the eruption of the oldest CRBG, Steens Basalt, consists of the Imnaha component and Pacific MORB with minor subduction or assimilated accreted terrane rocks. Hooper et al. (2002) and Camp (2013) divided the Steens Basalt into a Lower and Upper series; the Lower being the more primitive and the Upper being evolved. Moore et al. (2020) propose a three-stage evolution for the Steens Basalt involving contributions from a depleted mantle and an enriched mantle. The earliest Steens, the Lower A series, is equally supplied by both. The most voluminous, the Lower Steens B, has a larger contribution from the depleted mantle and the Upper Steens has an equal contribution from both but considerable assimilation of the middle and upper crust. Fractionation is minor in the Lower Steens but may exceed recharge in the Upper Steens Basalt.

The next eruptions, Imnaha Basalt, are more primitive than the Steens Basalt (Hooper and Hawkesworth 1993; Wolff et al. 2008, 2013; Camp 2013; Ramos et al. 2013) and form an important endmember in the CRBG. This lead Camp and Hanan (2008) to propose that the plume initially impinged under the Juan de Fuca plate and mixed with it to produce the Steens Basalt. The Imnaha Basalt, however, broke through the Juan de Fuca plate encountering the oceanic crust producing the more primitive and enriched melts.

The Grande Ronde Basalt is the most voluminous of the formations and probably the most contaminated by crustal material. The Grande Ronde Basalt is distinct from the Imnaha Basalt and has led most researchers to consider them to have distinct histories or, as Camp and Hanan (2008) propose, a step-function chemical change between the two. Wolf and Ramos (2013), however, suggest the Grande Ronde Basalt is simply Imnaha Basalt with crustal contamination. The Grande Ronde Basalt has a distinct major-element pyroxene signature that has led many to argue for a peridotite-pyroxenite or ecologite partial melt (Wright et al. 1973, 1989; Reidel 1983; Takahahshi et al. 1998; Camp and Hanan 2008). The available evidence suggests that there are two equally viable alternatives to generate the Grande Ronde chemical trends: (1) through the modification of peridotite partial melts by large-scale fractional crystallization and assimilation, or (2) through direct melting of a mafic crustal source.

The role of fractional crystallization and assimilation in the Grande Ronde Basalt (GRB) is well recognized but the amount of each has been an area of debate. Most models consider fractional crystallization to be minor but crustal contamination significant. The GRB was erupted in less than 400,000 years which creates problems for strict crustal assimilation. Camp and Hanan (2008), however, solve this problem by allowing assimilation of delaminated cratonic rock, thus providing more surface area for assimilation.

The Picture Gorge Basalt is interfingered with the GRB but erupted from dykes farther west that passed through oceanic accreted terrane. Hooper and Hawkesworth (1993) suggest that the lavas were derived from a lithospheric source without significant contribution from an asthenosphere source. Wolff and Ramos (2013), however, suggest that the Picture Gorge Basalt has the Imnaha component plus depleted mantle with a subduction related fluid-fluxed arc source.

METHOD OF STUDY

We are aware of only one complete set of published PGE and chalcophile analyses from Columbia River Basalt Group flows (Table 1) and that is the USGS standard BCR-1 (Flanagan 1976) which is from the Wapshilla Ridge Member (Fig. 2) of the Grande Ronde Basalt. BCR-1 shows that at least one of the voluminous Columbia River Basalt Group flows had minor but measurable PGEs and, therefore others might also have measurable PGEs as well. The only other PGE analyses were by Chesley and Ruiz (1998), Vye et al. (2013) and Moore et al. (2020) who measured Os along with Re and Re/Os isotopic ratios for several flows. However, Oregon Sunstones that are Steens Basalt plagioclase phenocrysts that contain native copper (Wierman 2018), and immiscible sulphides in the Imnaha Basalt (Korzendorfer 1979) and Grande Ronde Basalt (Reidel 1978) demonstrate the presence of chalcophile elements in CRBG lavas. In order to get a more representative set of analyses for PGEs and chalcophile elements in the Columbia River Basalt Group, we collected a suit of 46 samples for PGEs and compiled a database of Cu and Zn from published and our unpublished analyses (e.g. Reidel 1983, 2005; Hooper and Hawkesworth 1993; Hooper et al. 1995, 2002, 2007; Hooper 2000; Camp et al. 2003; Camp and Ross 2004; Camp and Hanan 2008; Wolff et al. 2008 Appendix; Reidel and Tolan 2013). All our chalcophile element analyses were from samples analyzed at the GeoAnalytical Laboratory at Washington State University under the direction of Peter Hooper and Rick Conrey with additional analyses from Camp and Ross (2004), Bailey (1989) and the appendix in Wolff et al. (2008). We selected Pt and Pd as our representative target PGEs and had the samples analyzed at Act Labs using their Fire-Assay-ICP-MS technique. The first 21 samples (Table 2) were analyzed with a

Table 1. Published Platinum Group and Chalcophile Elements Analyses for the Columbia River Basalt Group.

Sample	Formation+	Member	Re ppb	Ru ppb	Rh ppb	Pd ppb	Os ppb	Ir ppb	Pt ppb
Standard BCR-1	GRB	Wapshilla Ridge	0.8	1	0.2	< 0.5 – 12*	0.1000	0.004	2.32
JTC-DB	IB	American Bar	0.558				0.0292		
JTC-BUK	IB	American Bar	0.659				0.0991		
JTC RC-1d	IB	Rock Creek	0.051				0.3932		
JTC RC-2-1	IB	Rock Creek	0.402				0.1700		
JTC RC-2-2	IB	Rock Creek	1.099				0.0137		
JTC RC-2-3	IB	Rock Creek	2.568				0.1623		
JTC RC-2-4	IB	Rock Creek	0.524				0.3272		
JTC RC-2-5	IB	Rock Creek	2.221				0.1981		
JTC-PHGR-1	GRB	Buckhorn Springs	1.13				0.0155		
JTC-PHGR-2	GRB	Buckhorn Springs	0.529				0.0032		
TTC-PH8-90-Tg	GRB		1.091				0.001		
JTC-LW-2	GRB		1.382				0.0021		
JTC-ROZA-14-1	WB	Roza	0.00015				ND		
JTC-ROZA-14-2	WB	Roza	2.126				0.5708		
JTC-ROZA-17-1	WB	Roza	0.835				0.0010		
JTC-ROZA-17-2	WB	Roza	2.735				0.0042		
JTC-ROZA1-1	WB	Roza	0.97				0.0020		
JTC-ROZA1-2	WB	Roza	1.365				0.0287		
JTC-ROZA3-1	WB	Roza	1.601				0.0039		
JTC-ROZA3-2	WB	Roza	3.565				0.0095		
JTC-HS1-51	SMB	Wilbur Creek	1.97				0.0077		

+GRB-Grande Ronde Basalt, IB-Imnaha Basalt, SMB-Saddle Mountains Basalt, WB- Wanapum Basalt; ND-Not Detected
JTC = Chesley and Ruiz (1998) * Two analyses for Pd in BCR-1

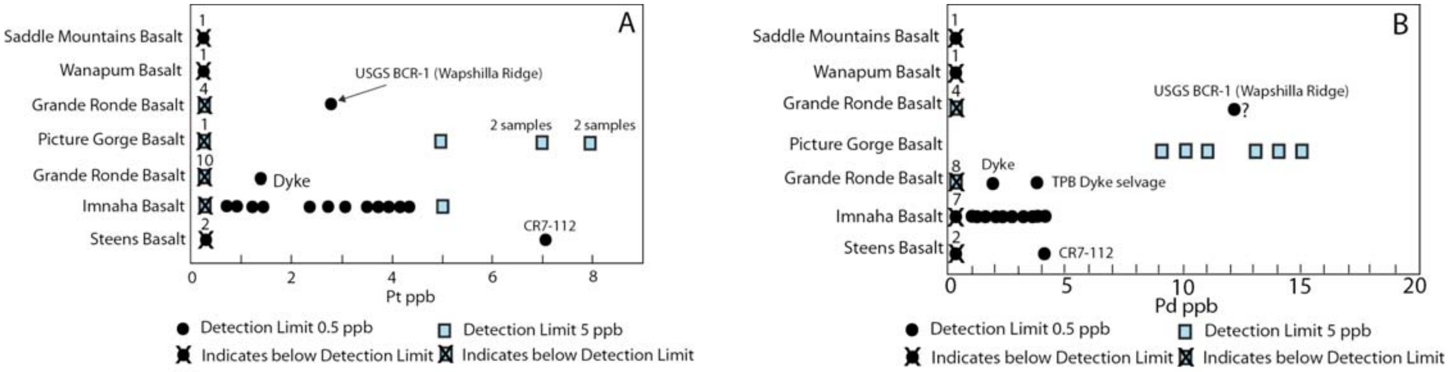

Figure 5. Pt and Pd abundances in the main formations of the Columbia River Basalt Group. A) is Pt in ppb, and B) is Pd in ppb.

detection limit of 5 ppb Pt and 4 ppb Pd as a reconnaissance for PGEs in the basalts. When this suite of samples showed that some samples contained PGEs above the detection limit, we then analyzed an additional 25 samples with a detection limit of 0.5 ppb Pt and 0.5 ppb Pd (Table 2). Our samples were from the Steens, Imnaha, Picture Gorge, and Grande Ronde Basalts. The Prineville, Wanapum and Saddle Mountains Basalts are minor by volume (Fig. 2) and represent the waning phases of the Columbia River Basalt Group. They contain low chalcophile element concentrations as shown later so we did not think a series of samples from these formations would be as useful as samples from the main phase. Our samples came from field exposures and continuous drilled core.

Results

Figure 5a and 5b summarize the Pt and Pd results for the formations we targeted and Figure 6 shows Cu and Zn from all CRBG formations. Two formations stand out for their abundance of PGEs: the Imnaha Basalt and the Picture Gorge Basalt; the few samples we have for the Steens Basalt does not allow us to say the same, but we suspect that the Lower Steens probably is rich in PGEs. The most voluminous formation, the Grande Ronde Basalt from which USGS Standard BRC-1 was obtained appears to have low PGEs concentrations as well as that of Cu and Zn. Each formation will be discussed separately from oldest to youngest.

Table 2. Columbia River Basalt Group Platinum Group Element Analyses for this Study.

Sample	Formation	Member	Pt DL	Pd DL	Pt ppb	Pd ppb
VCR7-112	Steens Basalt	Lower	0.5	0.5	7.1	4.1
VCR8-203	Steens Basalt	Lower	0.5	0.5	< 0.5	< 0.5
VCR7-122	Steens Basalt	Upper	0.5	0.5	< 0.5	< 0.5
VCR-270	Imnaha Basalt	Upper Pole Creek	0.5	0.5	2.4	1
VCR7-11	Imnaha Basalt	Upper Pole Creek	0.5	0.5	< 0.5	< 0.5
VCR-90	Imnaha Basalt	Upper Pole Creek	0.5	0.5	2.8	1.2
DBIB-9	Imnaha Basalt	American Bar	0.5	0.5	0.9	< 0.5
DBIB-11	Imnaha Basalt	American Bar	0.5	0.5	0.5	< 0.5
DBIB-12	Imnaha Basalt	American Bar	0.5	0.5	0.5	< 0.5
DBIB-14	Imnaha Basalt	American Bar	0.5	0.5	1.2	0.6
DBIB-15	Imnaha Basalt	American Bar	0.5	0.5	0.6	< 0.5
DBIB-16	Imnaha Basalt	American Bar	0.5	0.5	0.7	< 0.5
SRIBdyke-1	Imnaha Basalt	American Bar Dyke	0.5	0.5	1.4	1.9
DBIB-4	Imnaha Basalt	Rock Creek Flow	0.5	0.5	4.3	2.9
DBIB-5	Imnaha Basalt	Rock Creek Flow	0.5	0.5	3.9	3.1
DBIB-6	Imnaha Basalt	Rock Creek Flow	0.5	0.5	4.1	3
DBIB-18	Imnaha Basalt	Rock Creek Flow	0.5	0.5	2.3	1.9
DBIB-3	Imnaha Basalt	Rock Creek Flow	0.5	0.5	4.6	3.4
DBIB-10	Imnaha Basalt	Rock Creek Flow	0.5	0.5	2.1	1.6
DBIB-2	Imnaha Basalt	Rock Creek Flow	0.5	0.5	4.1	2.6
DBIB-7	Imnaha Basalt	Rock Creek Flow	0.5	0.5	3.5	2.4
DBIB-1	Imnaha Basalt	Rock Creek Flow	0.5	0.5	3.1	1.6
DBIB-13	Imnaha Basalt	Rock Creek Flow	0.5	0.5	1.4	< 0.5
SRIM02-1	Imnaha Basalt	Log Creek	5	4	5	4
SRBS-1	Grande Ronde Basalt	Buckhorn Springs Member	5	4	< 5	< 4
SRTPB-S-1	Grande Ronde Basalt	Teepee Butte selvage	5	4	< 5	4
SRTPB-D-1	Grande Ronde Basalt	Teepee Butte dyke	5	4	< 5	< 4
SRTPB-D-2	Grande Ronde Basalt	Teepee Butte dyke	5	4	< 5	< 4
SRTPB-D-3	Grande Ronde Basalt	Teepee Butte dyke	5	4	< 5	< 4
SRTPB-D-4	Grande Ronde Basalt	Teepee Butte dyke	5	4	< 5	< 4
SRTPB-D-5	Grande Ronde Basalt	Teepee Butte dyke	5	4	< 5	< 4
SRTPB-D-6	Grande Ronde Basalt	Teepee Butte dyke	5	4	< 5	< 4
SRTPB-D-7	Grande Ronde Basalt	Teepee Butte dyke	5	4	< 5	< 4
SEPG02-11	Grande Ronde Basalt	Sentinel BM at Patrick Grade	5	4	< 5	< 4
IMD-1	Grande Ronde Basalt	Dyke at JC and road	0.5	0.5	1.4	1.9
SRMH-1	Grande Ronde Basalt	Mt Horrible Member	5	4	< 5	< 4
SRMT-1r	Grande Ronde Basalt	Mt Horrible repeat	5	4	< 5	< 4
SRLGD02-1	Grande Ronde Basalt	Sentinel Bluffs Member	5	4	< 5	< 4
SRSB-1	Grande Ronde Basalt	Sentinel Bluffs-Museum	5	4	< 5	< 4
SRSB-2	Grande Ronde Basalt	Sentinel Bluffs-Museum	5	4	< 5	< 4
SRPGB-1	Picture Gorge Basalt	Franklin Mountain	5	4	< 5	13
SRPGB-2	Picture Gorge Basalt	Donney Basin	5	4	7	11
SRPGB-3	Picture Gorge Basalt	Donney Basin	5	4	5	9
SRPGB-4	Picture Gorge Basalt	Donney Basin	5	4	8	10
SRPGB-5	Picture Gorge Basalt	Camas Creek	5	4	7	15
SRPGB-6	Picture Gorge Basalt	Holmes Creek	5	4	8	14
WB-82-1	Wanapum Basalt	Roza Member	0.5	0.5	< 0.5	< 0.4
SMBHH-1	Saddle Mountains Basalt	Umatilla	0.5	0.5	< 0.5	< 0.4
BCR-1						

DL-Detection Limit in ppb < Less Than

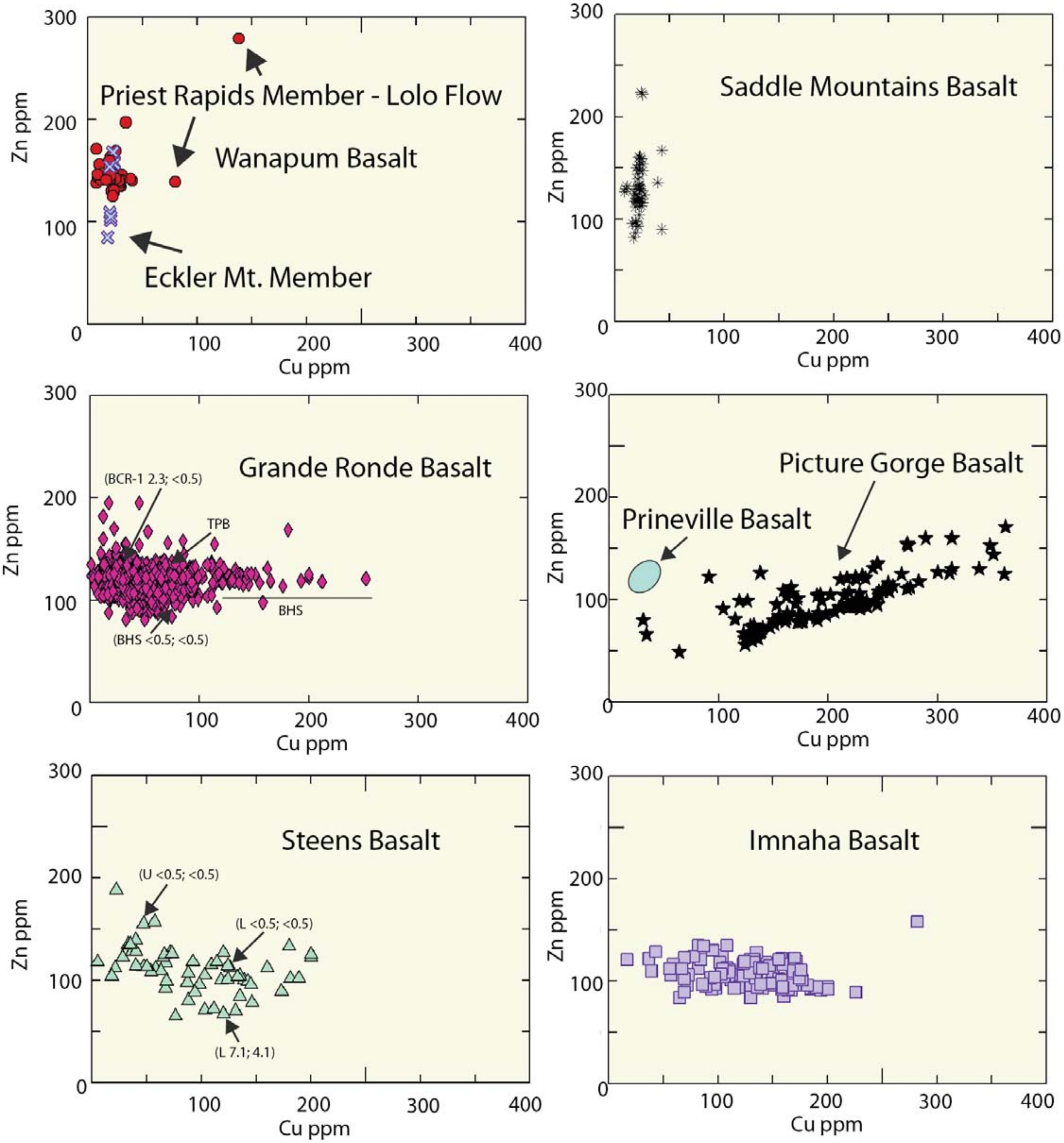

Figure 6. Variation diagram of Cu and Zn for the formations of the Columbia River Basalt Group. Data from Bailey (1989), Schuster (1993), Hooper (2000), Camp et al. (2003, 2013), Wolff et al. (2008 Appendix), Reidel and Tolan (2013) and S. Reidel unpublished data. In Steens Basalt plot, U-Upper Steens; L-Lower Steens Basalt. In Grande Ronde Basalt plot, BCR-1 is USGS standard BCR-1; BHS- Buckhorn Springs Member (see Fig. 2); TPB-Teepee Butte Member (see Fig. 2).

Steens Basalt

Three Steens Basalt samples were analyzed for PGEs; one is from the most primitive Lower B series Steens; one is from the most evolved, the Upper Steens; and one is from a flow intermediate to both although classified by Camp et al. (2013) as Lower Steens. Of those samples only the most primitive

Lower Steens Basalt has Pt and Pd above detection limits (Fig. 5). The Upper Steens and intermediate composition Lower Steens both have Pt and Pd below detection limits. The Upper Steens lavas include more evolved trachy-andesites and basaltic andesites (Fig. 4; Camp et al. 2003, 2013; Moore et al. 2020); the intermediate composition Lower Steens is transitional between the compositions of the Lower and Upper Steens Basalt. The various models for the Steens Basalt (e.g. Camp et al. 2013) conclude that the Lower Steens Basalt formed from more-primitive mantle with minor lithospheric contamination whereas the Upper Steens has undergone extensive contamination and fractionation. The intermediate composition Lower Steens may represent the initial stage of that contamination.

Immiscible sulphides and native Cu in Oregon Sunstones are present in Lower Steens Basalt but not Upper Steens Basalt (Wierman 2018). The Moore et al. (2020) model requires extensive sulphide precipitation in the Lower Steens Basalt but not in the Upper Steens Basalt to account for their high Os isotopic values.

There appears to be no correlation between Cu and Zn (Fig. 6). Zn is relatively constrained having a range of about ~100 ppm with a few outliers. Cu ranges between 5 and 200 ppm, however, Wierman (2018) reports Cu as high as 400 ppm. We plotted PGEs for our three Steens samples on Figure 6. The Lower Steens flows have more Cu than the Upper Steens, but with our limited data there appears to be no relationship between Cu, Zn and PGEs. We also plotted Cu vs. MgO and Zn vs. TiO_2 (Fig. 7), and Cu vs. Ni (Fig. 8). These plots examine the possible correlation between Cu and Zn and the basalt mineralogy. Zn is positively correlated with TiO_2 and FeO but not MgO; Cu shows no correlation with any oxide or element, a conclusion also reached by Wierman (2018). Ni, expectedly is correlated with Cr (Fig. 9).

Imnaha Basalt

The Imnaha Basalt is mainly tholeiitic basalt to basaltic andesite (Fig. 4). Hooper (1974) and Hooper et al. (1984) defined two major compositional types in the Imnaha Basalt, the Rock Creek type and the American Bar type (Fig. 2), and several minor ones. We analyzed 19 samples for PGEs with the intent to collect the major compositional types and as many minor ones as possible. Our sampling design was twofold: 1) we collected 12 samples from various field locations of the Imnaha Basalt, and 2) 7 samples through a 150-m-thick Rock Creek flow to determine how Pt and Pd were distributed within an individual flow. Segregation zones and pegmoidal patches recognized by Holden and Hooper (1976) were avoided. All Imnaha Basalt samples except one contained either some Pt or Pd or both (Fig. 5; Table 2).

Cu and Zn are plotted for the Imnaha Basalt in Figure 6. Like the Steens Basalt, Zn has a limited range but Cu ranges from nearly 0 to 250 ppm. Overall, there appears to be no correlation between Cu and Zn, and Cu and MgO. However, there is a strong correlation between Zn and TiO_2 (Fig. 7); and Zn and FeO. Zn and MgO (not shown) has a negative correlation but Zn is not correlated with CaO. Like the Steens Basalt, Ni and Cr show a positive correlation (Fig. 9).

Distributed samples

Eight samples are from outcrops of the Rock Creek chemical type and the American Bar chemical type; one sample is from the Log Creek flow (Rock Creek chemical type); three are from the upper Pole Creek (Imnaha Basalt, Oregon Plateau) of Hooper et al. (2002) and Camp et al. (2003) and one is an American Bar dyke sample. Two of the three upper Pole Creek samples contained Pt above detection limits (< 0.5 ppb) but not all contained Pd. Pt and Pd were more abundant in the Rock Creek samples than in the American Bar samples. The Rock Creek samples typically contain Pd but Pd in the American Bar samples was below detection limits. The Log Creek sample (uppermost Imnaha Basalt in Joseph Creek) is below the contact with the Grande Ronde Basalt and contains the highest Pt and Pd recorded for the Imnaha Basalt. The American Bar samples came from below the Rock Creek and Log Creek samples suggesting that the Pt and Pd contents increased with time during the eruption of the Imnaha Basalt. In general, the older American Bar samples have higher SiO_2 and lower MgO and have had significantly more plagioclase and pyroxene fractionation (Hooper et al. 1984; Hooper 1988; Hooper and Hawkesworth 1993).

Rock Creek flow

Seven samples were collected from the 150-m-thick Rock Creek flow previously studied by Holden and Hooper (1976) and Korzendorfer (1979). Korzendorfer examined three stratigraphic sections, two of which were studied previously by Holden and Hooper (1976). We sampled Korzendorfer's (1979) Section A that is 75 m east of Holden and Hooper's (1976) main western section. Korzendorfer (1979) collected 36 samples from this section to study the opaque mineralogy. Our samples were from the massive part of the Rock Creek flow at Korzendorfer's section; we avoided the zeolitized scoria flow top and segregation zones and pegmatoid like Korzendorfer had done. Holden and Hooper (1976) analyzed 6 samples from the massive part of the Rock Creek flow for major and minor elements. We reanalyzed their samples on a newer and more precise XRF machine for major, minor and trace elements. We omitted Holden and Hooper's (1976) upper most samples (16a, 16b, and 16c) as they were from the zeolitized scoria and were altered by groundwater and weathering.

Korzendorfer (1979) recognized ilmenite, titanomagnetite, disseminated sulphide minerals and immiscible sulphide droplets in the Rock Creek flow (Fig. 10) which are only visible by microscope. Chromite was not present and has not been recognized in any Columbia River Basalt Group flow. Immiscible sulphide droplets have been recognized in other Columbia River Basalt Group flows (e.g. Reidel 1978, 1983; Wierman 2018). Korzendorfer (1979) recognized two main occurrences of sulphides: 1) round, often complex, polymineralic immiscible sulphides, and 2) monomineralic sulphide grains or simple mineral combinations that he believes crystallized directly from the melt. He identified chalcopyrite and pyrrhotite as the main sulphides and lesser amounts of cubanite, pyrite, bornite, covellite and a dull, purplish gray mineral with a reflectivity of 10–15% which he was unable to identify. He did not recognize any PGE minerals.

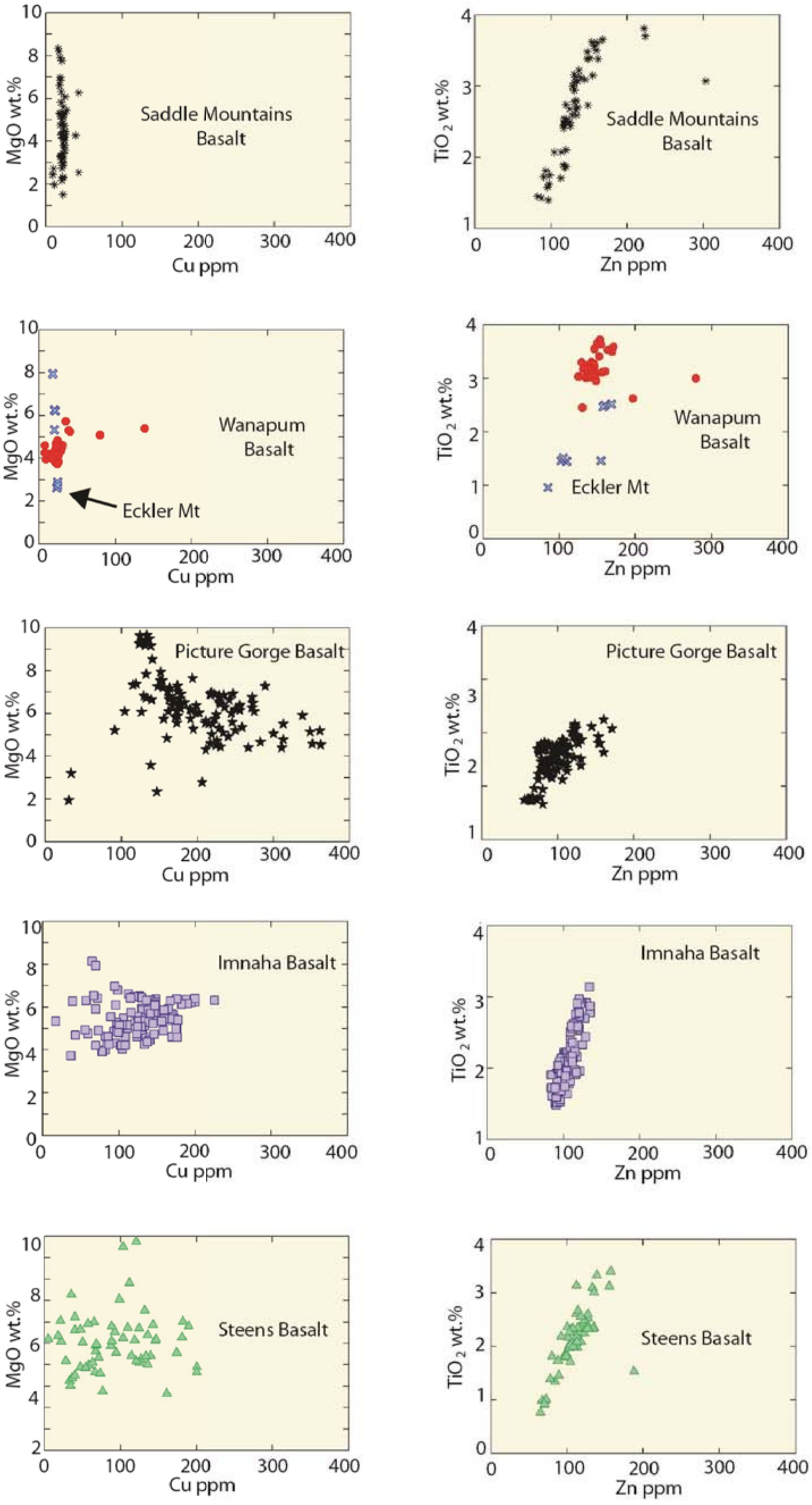

Figure 7. Variation diagrams for MgO and Cu, and TiO$_2$ and Zn for the Steens, Imnaha, Picture Gorge, Wanapum and Saddle Mountains Basalts. Data from Bailey (1989), Schuster (1993), Hooper (2000), Camp et al. (2003, 2013), Wolff et al. (2008 Appendix), Reidel and Tolan (2013), and S. Reidel unpublished data.

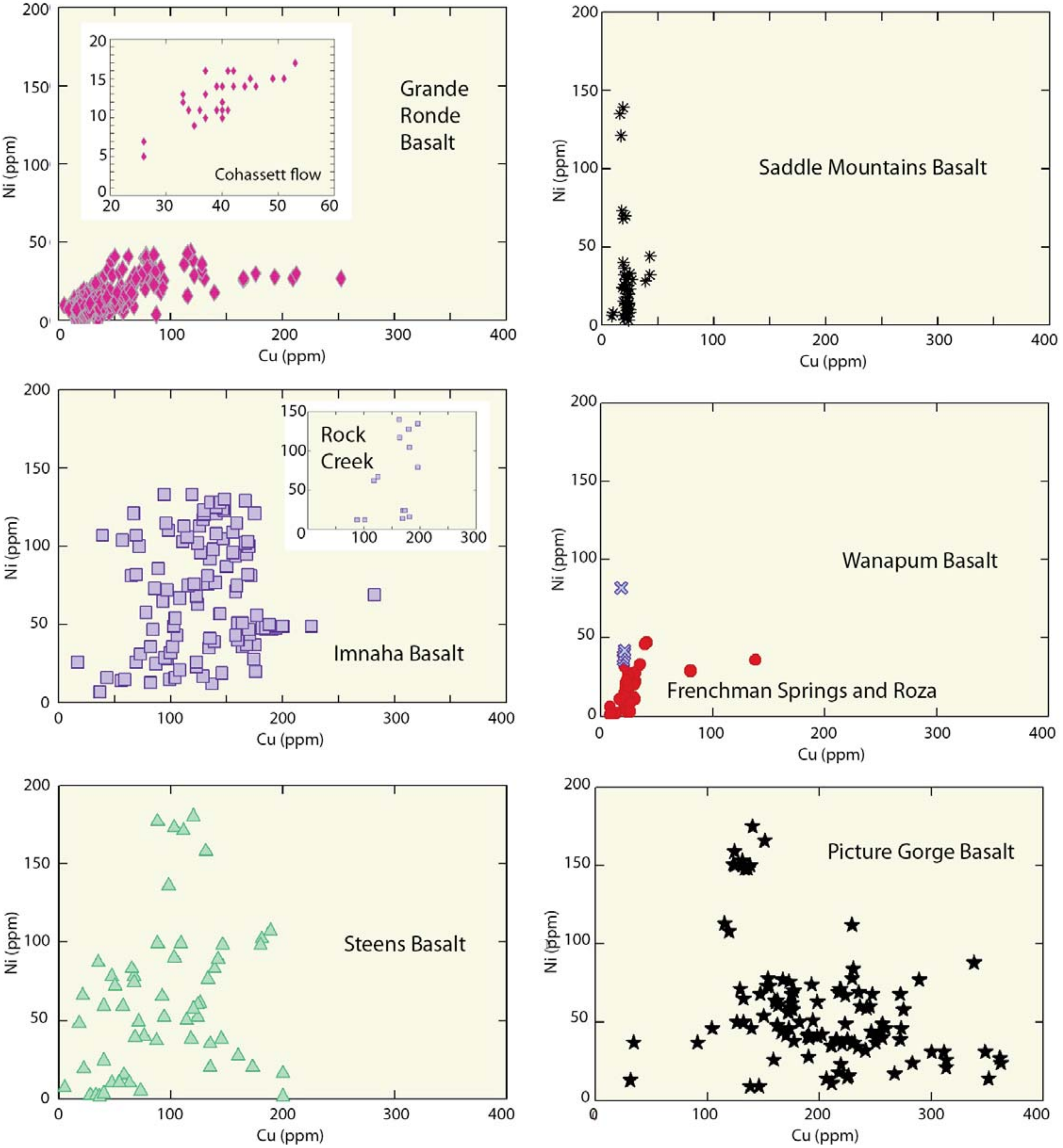

Figure 8. Variation diagram for Cu and Ni in the Columbia River Basalt Group. Data from Bailey (1989), Schuster (1993), Hooper (2000), Camp et al. (2003, 2013), Wolff et al. (2008 Appendix), Reidel and Tolan (2013), and S. Reidel unpublished data. For Wanapum Basalt, circle is Frenchman Springs Member and 'x' is Lolo flow, Priest Rapids Member (see Fig. 2).

Our Pt and Pd analyses and our reanalyzed Holden and Hooper (1976) samples for Cu, Zn and TiO_2 are shown in Figure 10a along with Korzendorfer's (1979) sulphide, ilmenite and, titanomagnetite and our Pt, Pd, Cu, Zn and TiO_2 occurrences. Figure 10b shows Korzendorfer's (1979) ilmenite, titanomagnetite and sulphides, and our Pt and Pd analyses with

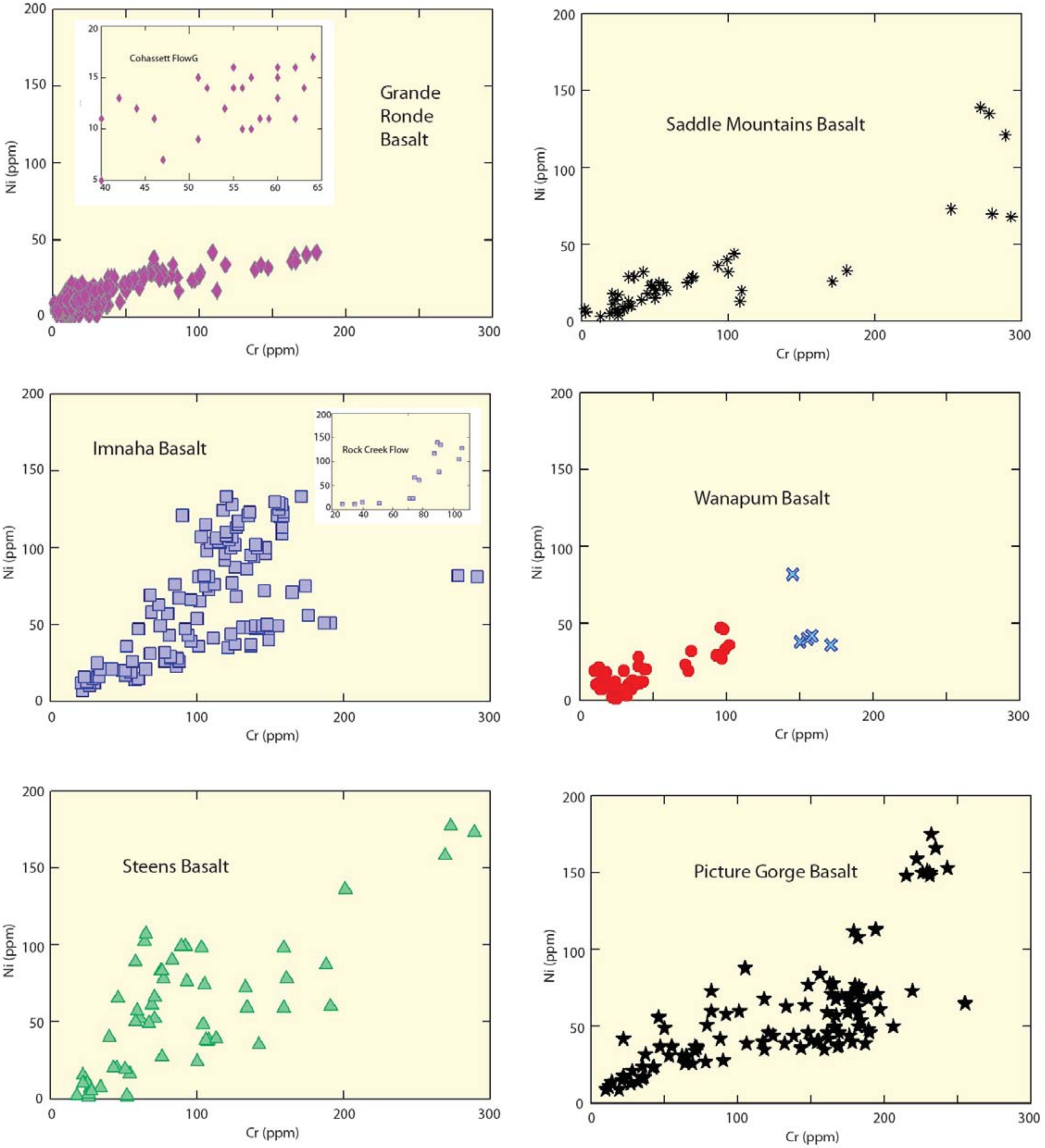

Figure 9. Variation diagram for Ni and Cr in the Columbia River Basalt Group. Data from Bailey (1989), Schuster (1993), Hooper (2000), Camp et al. (2003, 2013), Wolff et al. (2008 Appendix), Reidel and Tolan (2013), and S. Reidel unpublished data.

our reanalyzed Holden and Hooper (1976) samples for Ni, Cr, MgO, FeO$_{total}$, along with modal olivine and pyroxene from Holden and Hooper (1976). MgO, FeO$_{total}$, and Ni to a lesser degree, correlate with modal olivine and pyroxene as expected

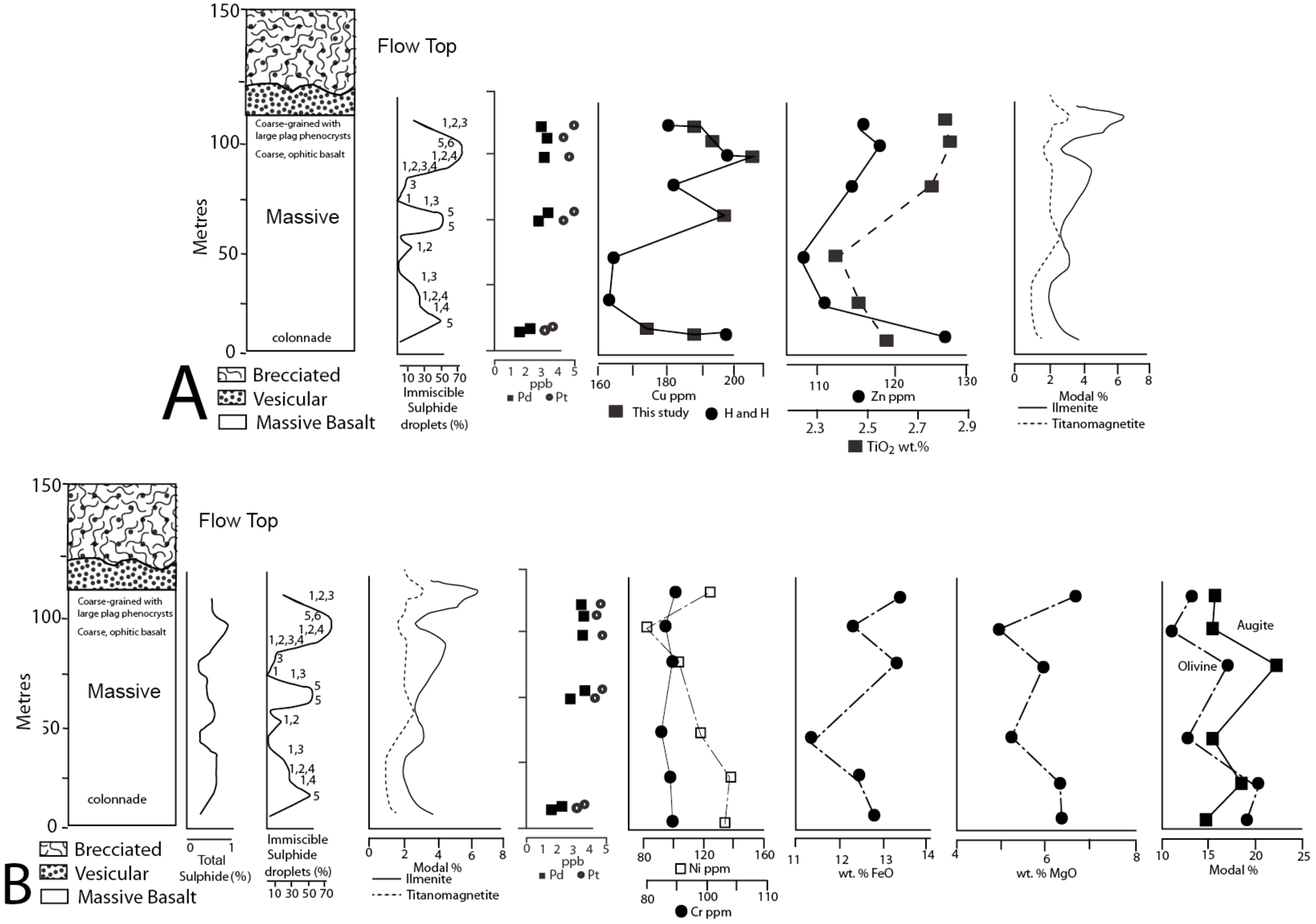

Figure 10. Compositional and mineralogical concentrations in the Rock Creek flow, Imnaha Basalt. A) Pt, Pd, Cu, Zn, Ilmenite, titanomagnetite, sulphides; B) Pt and Pd, Ni, Cr, MgO, Fe_{Total} as FeO, and modal olivine and pyroxene, ilmenite, titanomagnetite and sulphides. Pt and Pd from this study, immiscible sulphide, total sulphides, and Ilmenite and titanomagnetite abundances from Korzendorfer (1979) and Ni, Cr, MgO, Fe_{Total}, and modal olivine and pyroxene from Holden and Hooper (1976) with samples reanalyzed by this study. For Immiscible Sulphide Droplets, 1 = mainly pyrrhotite with some chalcopyrite; 2 = equal amounts of pyrrhotite and chalcopyrite; 3 = mainly chalcopyrite; 4= chalcopyrite and exsolved (?) cubanite; 5 = mainly goethite with chalcopyrite and small amount of unknown mineral; 6 = mainly bornite with chalcopyrite and minor titanomagnetite from Korzendorfer (1979).

whereas Pt and Pd appear to be independent of them but increase with height. This may reflect increasing S saturation to form PGE-scavenging sulphides or rising Cl- and S-rich volatiles that carried the PGE upward. The importance of volatiles is shown by segregation zones and pegmoidal patches in the upper part of the flow. In addition, the upper 25 m of the Rock Creek flow is a vesicular flow top atypical of the CRBG. However, in Figure 10a, Cu appears to correlate with sulphide occurrences but we did not collect samples for Pt and Pd from the low-sulphide areas so we cannot be certain that there is a perfect correlation. Nevertheless, we interpret this to suggest that Pt and Pd are probably concentrated in the sulphides with Cu whereas Ni and probably Cr are concentrated in olivine. Modal ilmenite and titanomagnetite also appear to correlate with FeO and TiO_2 but they are accessory minerals. Zn, however, correlates with TiO_2 indicating that Zn substitutes for Fe^{++} in mainly pyroxene and olivine but also for Fe^{++} in ilmenite and titanomagnetite.

Grande Ronde Basalt

We collected 14 samples for Pt and Pd from the Grande Ronde Basalt in addition to USGS Standard BCR-1. Little time had passed between the Imnaha and Grande Ronde Basalt eruptions, but the flows are different both compositionally and physically. Ten samples are from the Grande Ronde Basalt below Bailey's (1989) Picture Gorge Basalt (PGB) interval (Fig. 2) and four come from above Bailey's (1989) Picture Gorge Basalt. It is clear from Figure 5 that in most samples, Pt and Pd are below detection limits (5 ppb Pt and 4 ppb Pd). The samples using a lower detection limit (0.5 Pt; 0.5 Pd ppb) did contain PGEs but significantly less than the Imnaha Basalt and Picture Gorge Basalt (Table 2). In the samples below the PGB interval, no sample had Pt above the detection limit and only one had Pd. One sample from the oldest Grande Ronde Basalt member, the Buckhorn Springs, was collected directly above our Imnaha Basalt sample in Joseph Creek and it contained no Pt or Pd above our detection limit but did contain more Cu and Zn than later flows. Because of our higher detection limits for most Grande Ronde Basalt samples, we assume that the samples that did detect Pt at the lower detection limit are typical but Pd is surprising. Standard BCR-1 contains a recommended content of 12 ppb Pd (Flanagan 1976) and is well above the 4 ppb detection limit yet none of our samples were near that value. For BCR-1 there were only two analyses, one 12 ppb and the other < 0.5 ppb. It is probable that the lower value may be the more accurate one. We interpret this to indicate that Pd and Pt are minor.

We have a large database of chalcophile elements from the Grande Ronde Basalt. Like earlier flows, Zn has a restricted range relative to Cu (Fig. 6) with a few higher content Cu samples. In order to get a better understanding of where the higher Cu occurs, we plotted Cu content for each member (Fig. 11). This figure shows that the highest Cu content occurs in the oldest members, the Buckhorn Springs Member through the Rogersburg, (Fig. 2) and Cu content decreases up section. We then examined our GRB database and realized that the highest Cu content for the Buckhorn Springs Member occurs in down-flow samples, i.e. in the earliest part of the eruption that is distal (250 km) to the feeder dyke. Our Pt–Pd sample was from the earliest Buckhorn Springs Member flow but from the very last part of the eruption near the dyke. This suggests that the PGEs may have been in the initial eruption but were quickly depleted like Cu.

The Teepee Butte Member followed shortly after the Buckhorn Springs Member; this member has been described in detail by Reidel and Tolan (1992). Eight samples were collected from the dyke of the Joseph Creek flow of the Teepee Butte Member (Fig. 12). Platinum is below detection limits (5 ppb) for all dyke samples except one of the two selvage zones contains measurable Pd (Table 2). We did not sample the other selvage zone. The Pd in the dyke occurs in the sample with the highest Cu and Zn content (Fig. 12b) whereas Ni and Cr (Fig. 12a) follow the opposite pattern suggesting they are probably incorporated in olivine and pyroxene. In addition to the Teepee Butte dyke, we sampled another dyke that fed a stratigraphically slightly higher flow which occurs below Bailey's (1989) Picture Gorge Basalt interval. This sample (IMD-1) contained 1.4 ppb Pt and 1.9 ppb Pd which is below BCR-1 Pt and Pd content suggesting minimal Pt and Pd contents.

Of the five samples from the Grande Ronde Basalt above the Picture Gorge Basalt interval, only one sample contained detectable PGEs and that was the USGS Standard BCR-1. Our samples had a higher detection limit than BCR-1 which is more compositionally evolved than the more MgO- and CaO-rich samples of Grande Ronde Basalt like the Teepee Butte Member.

In Figure 13 we plotted 25 samples for Cu, Zn, MgO and TiO_2 through the Cohasset flow of the Sentinel Bluffs Member, the youngest member of the Grande Ronde Basalt (Fig. 2). We analyzed four samples for PGEs at the higher detection limit and found none exceeded it. Despite the relatively small range of Zn in the GRB, it is clear that Cu and Zn are inversely correlated (Fig. 13). Cu is positively correlated with MgO, CaO and Ni (Fig. 8) but negatively correlated with Rb (not shown). Zn is positively correlated with TiO_2, FeO, P_2O_5 and Zr but negatively correlated with Al_2O_3, MgO, CaO, and Y (Fig. 14). This suggests that both Cu and Zn are controlled not by sulphides in the Grande Ronde Basalt but are incorporated in the silica melt and other minerals in the basalt. This will be discussed later.

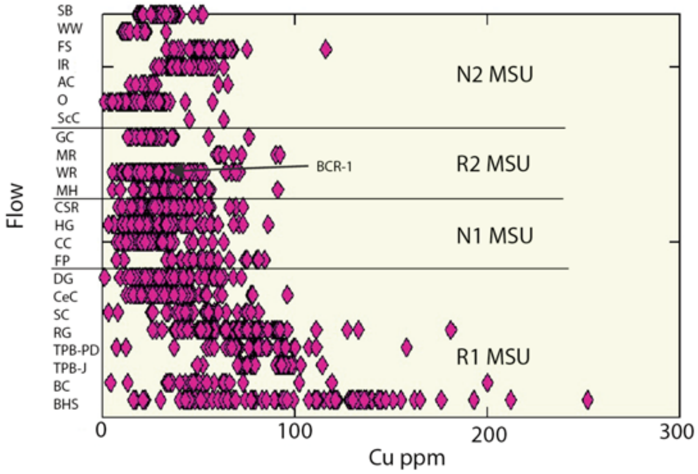

Figure. 11. Concentration of Cu in members of the Grande Ronde Basalt. Oldest is on the bottom and youngest on top. Smaller volume flows have been omitted. From oldest to youngest: BHS – Buckhorn Springs; BC – Birch Creek; TPB-J – Teepee Butte, Joseph Creek flow; TPB-PD – Teepee Butte, Pruitt Draw flow; RG – Rodgersburg; SC – Skelton Creek; CeC – Center Creek; DG – Downey Gulch; FP – Frye Point; CC – China Creek; HG – Hoskin Gulch; CSR – Cold Springs Ridge; MH – Mt. Horrible; WR – Wapshilla Ridge; MR – Meyer Ridge; GC – Grouce Creek; ScC – Slack Canyon; O – Ortley; AC – Armstrong Canyon; IR – Indian Ridge; FS – Fields Spring; WW – Winter Water; SB – Sentinel Bluffs. Data from Schuster (1993), Hooper and Hawkesworth (1993), Hooper (2000), Wolff et al. (2008 Appendix), Reidel et al. (2013b), Reidel and Tolan (2013), and S. Reidel unpublished data.

Picture Gorge Basalt

The Picture Gorge Basalt (PGB) was erupted during Grande Ronde Basalt time but from the Monument dyke swarm west of the Chief Joseph dyke swarm (Fig. 3). The PGB is mainly basalt with some basaltic andesites (Bailey 1989; Fig. 4). The Mt. Horrible Member of the Grande Ronde Basalt (Fig. 2) directly overlies the PGB indicating that the PGB eruptions ended before the voluminous Wapshilla Ridge Member of BCR-1.

We collected six Picture Gorge Basalt samples mainly from the lower part of Bailey's (1989) section, the Twickenham and Monument Mountain Members (Fig. 15). The Twickenham Member is the oldest member and plagioclase- and olivine-phyric. Later members are more aphyric. We collected three samples from the Basalt of Donnely Basin, a plagioclase-phyric flow like the Imnaha Basalt and the oldest flow recognized by Bailey (1989). Except for Pt in the Basalt of Franklin Mountain, the PGB suggests an increase in Pt and Pd with decreasing age (Fig. 15). We sampled the Mt. Horrible Member of the Grande Ronde Basalt directly above the PGB and found no Pt or Pd above the limit of detection. The Mt. Horrible Member was erupted from a dyke 100 km east of the Picture Gorge area.

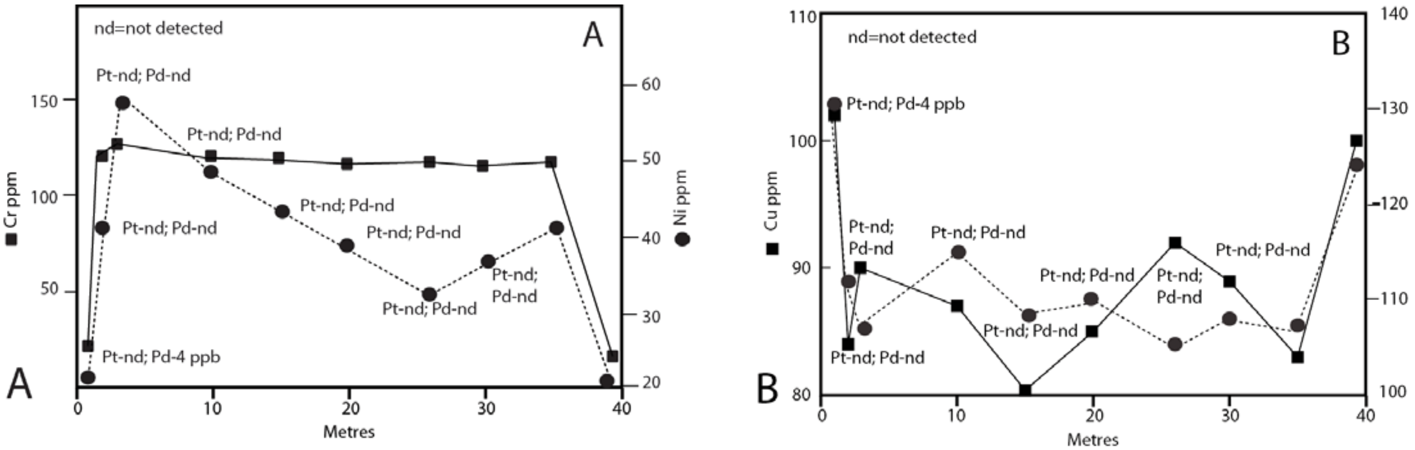

Figure 12. Selected trace element concentrations in the Joseph Creek dyke, Teepee Butte Member, Grande Ronde Basalt. Pt and Pd from this study, Cu, Zn, Ni and Cr from Reidel and Tolan (1992). A) Pt, Pd, Ni and Cr. B) Pt, Pd, Cu and Zn.

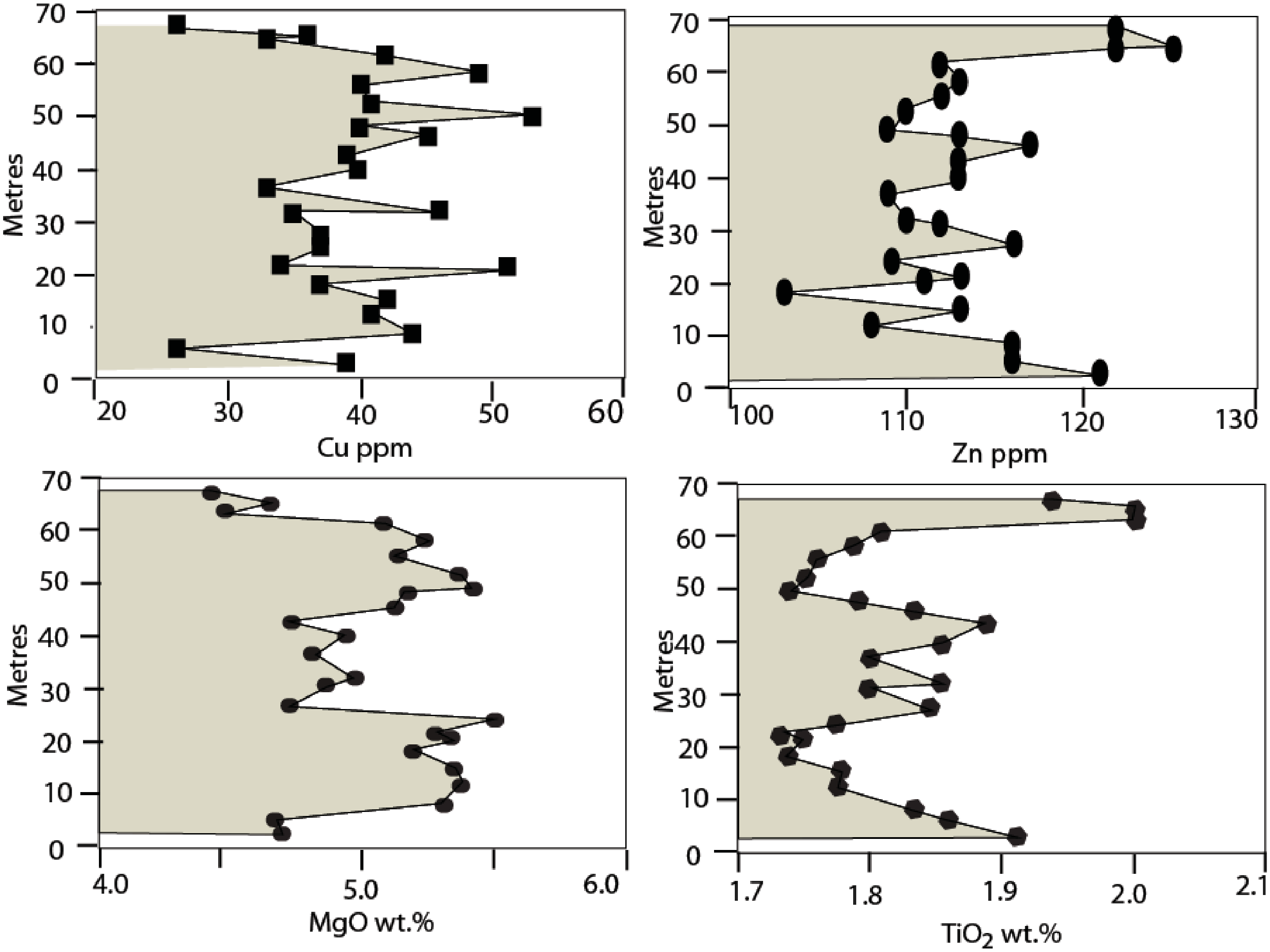

Figure 13. Concentration of Cu, Zn, MgO and TiO_2 with height from base of the Cohasset flow, Sentinel Bluffs Member, Grande Ronde Basalt. Data from Reidel (2005).

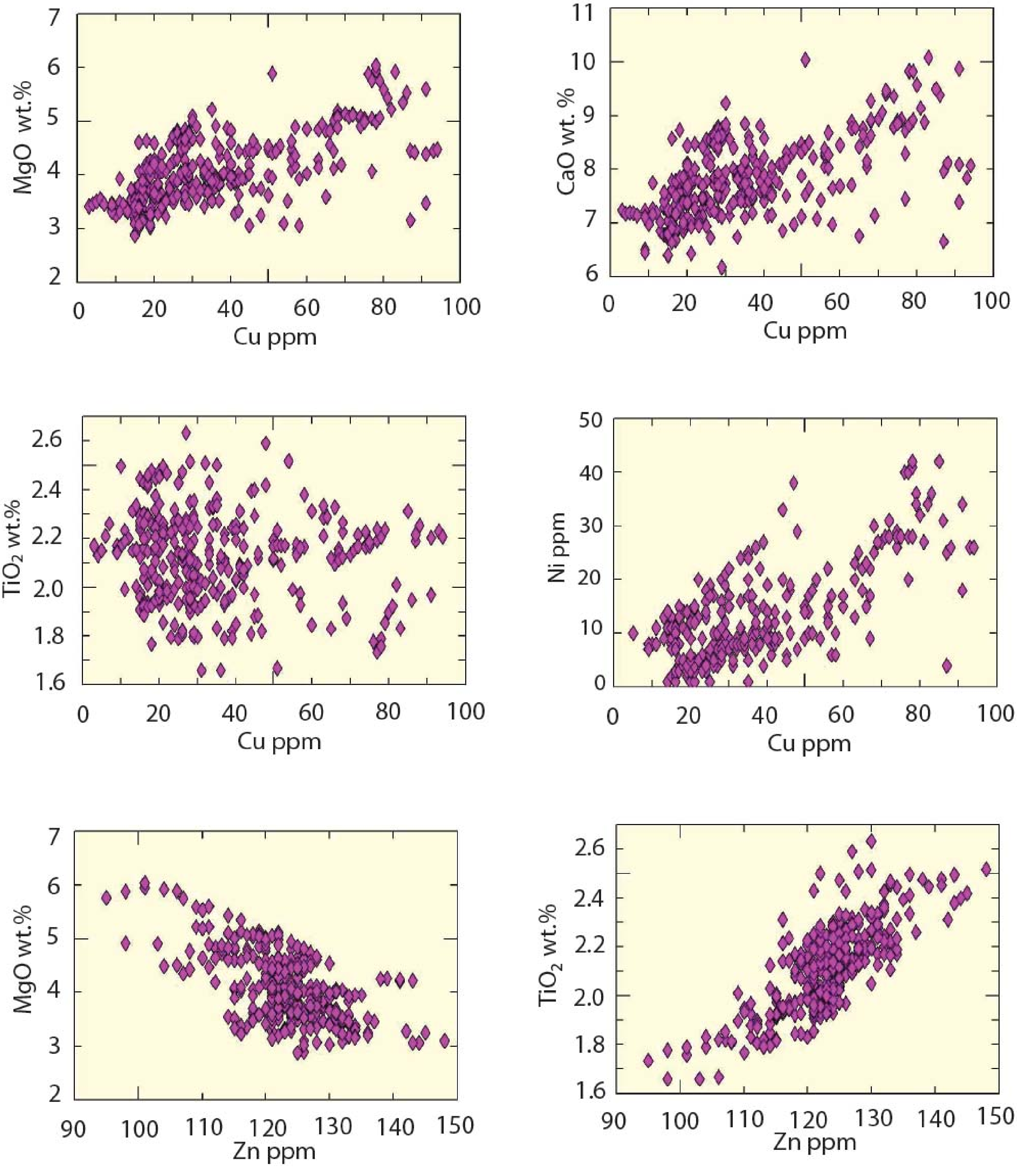

Figure 14. Variation diagrams for Cu vs. MgO, TiO_2, CaO and Ni, and Zn vs. MgO and TiO_2 for the Grande Ronde Basalt. Data from Reidel and Tolan (1992, 2013), Schuster (1993), Hooper and Hawkesworth (1993), Hooper (2000), Reidel (2005) and S. Reidel unpublished data.

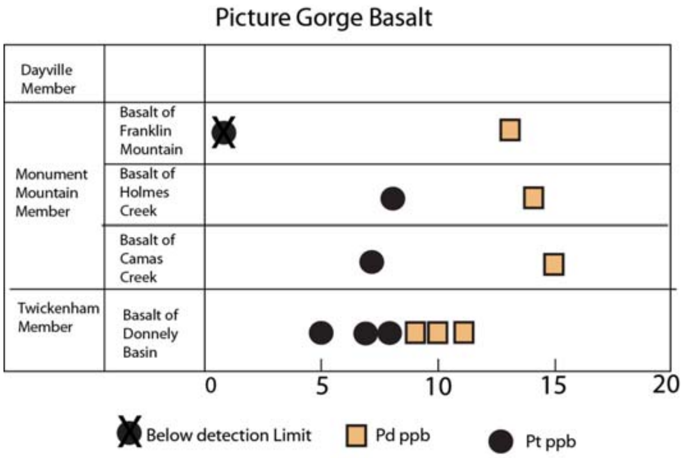

Figure 15. Pt and Pd abundance in Picture Gorge Basalt. Stratigraphic nomenclature based on Bailey (1989). Data from this study (Table 2).

Although Zn has a restricted range compared to Cu, there is a positive correlation between the two (Fig. 6). Furthermore, Zn content, although somewhat scattered, and Cu show no trend with younger flows (Fig. 16). Cu and Zn have a poor inverse correlation with MgO and CaO (not shown) while Zn also is positively correlated with TiO_2 (Fig. 7) and FeO. In the Picture Gorge Basalt Cu and Ni (Fig. 8) are not correlated whereas Ni and Cr are positively correlated (Fig. 9).

Wanapum Basalt and Saddle Mountains Basalt

We collected one sample each from the upper two formations but Pt and Pd were below detection limits. These formations contain low chalcophile element concentrations compared to the other formations (Fig. 6). We did not concentrate on these two formations because they are not part of the main phase and represent the declining magma. The Wanapum Basalt represents only 5.8% of the Columbia River Basalt Group and the Saddle Mountains Basalt only ~1%.

For both the Wanapum and Saddle Mountains Basalts, Cu and Zn have very restricted ranges (Fig. 6) except for the youngest flow of the Wanapum Basalt, the Basalt of Lolo. Cu shows no correlation with any other oxide or element but when considering only the Frenchman Springs and Roza Members, Cu and Ni (Figs. 8 and 17) are positively correlated.

For the Wanapum Basalt, Zn is correlated with TiO_2 FeO (Fig. 7) P_2O_5, Zr and Y and negatively correlated with Al_2O_5, MgO, CaO and Cr. The Saddle Mountains Basalt Cu is not correlated with any oxide or element except for the Umatilla Member which has a negative correlation with Ba and a positive correlation with both V and Zr. The Umatilla Member is the most contaminated basalt of all the CRBG (Reidel 1998). Ni and Cr are positively correlated (Fig. 9) in both the Wanapum Basalt and Saddle Mountains Basalt whereas in the Wanapum Basalt Cu and Ni (Fig. 8) are positively correlated yet not in the Saddle Mountains Basalt.

DISCUSSION

Naldrett (2011, 2012) described seven steps deemed necessary to form a magmatic sulphide deposit. These included: 1) Birth of the source, i.e. the generation of a mafic magma due to mantle melting; 2) Development of the source by assent of the magma through the mantle and into the crust; 3) Fertilization of the source by contamination of the magma with the crust and development of immiscible sulphides; 4) Delivery by farther ascent into crust; 5) Growth or concentration of the sulphides; 6) Nourishment or enrichment due to additional interaction with a continuing supply of magma; and 7) Full maturity. Furthermore, understanding the effect of composition, temperature, and pressure on sulphide solubility in a silicate melt, partial melting and partitioning of the chalcophile and PGEs between magma, silicates and liquid sulphides and the phase equilibria are equally important.

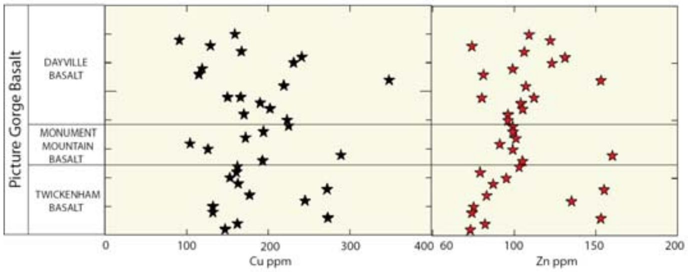

Figure 16. Cu and Zn in the Picture Gorge Basalt. Stratigraphic nomenclature and data based on Bailey (1989), Hooper and Hawkesworth (1993) and Wolff et al. (2008 Appendix).

The Columbia River Basalt Group qualifies in the first four stages. It is a LIP that produced large volume lava flows in a short period of time. A general agreement is that the main phase of magmatism (Steens, Imnaha, Grande Ronde, and Picture Gorge Basalts) is derived from a mantle plume that underwent some degree of fractionation and crustal contamination (e.g. Reidel 1983; Hooper and Hawkesworth 1993; Camp and Hanan 2008; Hooper et al. 2007; Camp 2013). Crustal contamination has been suggested to be minor in the Lower Steens, Imnaha and Picture Gorge Basalts but could reach 20% or greater in the Upper Steens Basalt and Grande Ronde Basalt (e.g. Hooper and Hawkesworth 1993; Camp and Hanan 2008). Thus, the Columbia River Basalt Group should be an excellent candidate to contain PGEs.

Our study shows that the Columbia River Basalt Group contains measurable PGEs. The oldest members, the Lower Steens, Imnaha and Picture Gorge Basalts, all contain Pt and Pd in abundances similar to that of the mantle (6.6 Pt, 3.27 Pd, Palme and O'Neill 2005; 7.1 Pt, 3.9 Pd, McDonough and Sun 1995). The two principal collectors of PGEs in a basaltic magma are sulphides and chromite (Mungall 2005). Chromite has not been recognized in any Columbia River Basalt Group flow but Cr, Ni and MgO (Fig. 9) are positively correlated in all the CRBG formations suggesting that Cr and Ni are compatible with olivine and pyroxene. However, immiscible sulphides and sulphide minerals have been recognized in the Steens Basalt, Imnaha Basalt and the oldest Grande Ronde Basalt flows (e.g. Reidel 1978; Korzendorfer 1979; Wierman 2018).

The Cu abundance decreases with younger CRBG flows. Cu is most abundant in the earliest part of the main phase (Steens, Imnaha, Picture Gorge and oldest Grande Ronde

Basalts) thus correlating with PGE abundance in the flows. Except for the small volume Eckler Mountain Member, Wanapum Basalt (Fig. 6), Cu decreases through the Wanapum Basalt and Saddle Mountains Basalt. Thus, higher Cu concentrations also suggest that some PGEs are controlled by sulphides and Cu contents maybe an excellent prospecting tool in the Columbia River Basalt Group.

Fertility, Crustal Contamination and Sulphur Saturation

The two major factors to consider in determining the Cu–PGE prospectively of a set of igneous rocks are: fertility and S saturation of the host (Jowitt and Ernst 2013; Jowitt et al. 2014). Fertility is depletion or enrichment of PGEs and chalcophile elements. Because Cu will act as an incompatible element in S-undersaturated silicate melts, a ratio of Cu and a similar incompatible element as is Zr, can reflect the effects of silicate fractionation or accumulation in the magma. Thus, following Jowitt and Ernst (2013), we plot the abundance of chalcophile elements in the CRBG relative to MgO (Fig. 17). The Cu/Zr ratio, relative to the primitive mantle (PM), reflects the sulphide budget of the magma; that is, sulphide accumulation or segregation. In general, all formations are greatly depleted in Cu except for the Lower Steens Basalt and Picture Gorge Basalt. The most depleted are the Grande Ronde, Wanapum and Saddle Mountains Basalts, the last formations to be emplaced. This suggests that chalcophile elements and PGEs have been depleted from the magma prior to their eruptions.

A thinned and metasomatized craton edge has been suggested as a necessary requirement for PGE deposits because magmas cannot melt a thick lithosphere (Kerrich et al. 2005; Begg et al. 2010; Ernst 2014). Melting of the craton and transport of magma through it can be an important source of sulphur, sulphide concentration and segregation of PGEs (Naldrett 1997; Ernst 2014). Geophysical studies indicate the lithosphere is only about 40–50 km thick under the Columbia River flood basalt province (e.g. Catchings and Mooney 1988). The Columbia River Basalt Group magma ponded along the craton-accreted terrane boundary (Fig. 1; 0.704 and 0.706 Sr-isopleth lines; Armstrong et al. 1977; Camp et al. 2003; Camp and Ross 2004; Pierce and Morgan 2009; Camp 2013) and thus, many of the dykes for Columbia River Basalt Group flows passed through craton and oceanic accreted terrane rocks. The Picture Gorge Basalt and Prineville Basalt, however, erupted only in oceanic accreted terrane rocks west of the craton-accreted terrane boundary.

Tectonic studies support an interaction between the plume and crust; studies have shown that the Columbia Basin was subsiding at the same rate that the basalts were erupting (Reidel et al. 1989b, 2013c). The greatest rate of subsidence occurred during the main phase of the CRBG and declined as the rate and volume of eruptions declined. Furthermore, a series of grabens (e.g. Lewiston Basin) developed along the craton-accreted terrane boundary and their rate of development also matched the rate of basalt eruptions suggesting crustal magma storage. Delamination and subsiding of the crust into the plume, as suggested by Camp and Hanan (2008), provides a viable mechanism for the magma to assimilate crust and acquire sulphur.

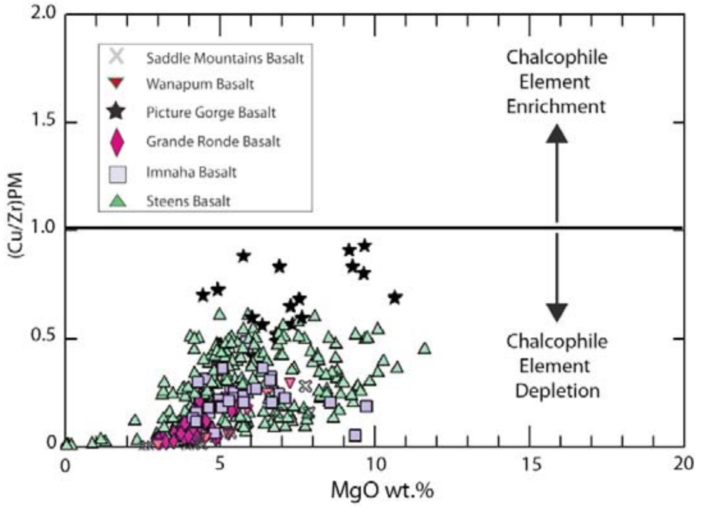

Figure 17. Diagram showing (Cu/Zr)PM and MgO. The ratios are normalized to primitive mantle values (PM) of McDonough and Sun (1995) and Jowitt et al. (2014). This figure shows the abundance of chalcophile elements in the CRBG. The Cu/Zr(PM) reflects the sulphide budget of the magma and suggests that all formations are greatly depleted in Cu with the Steens Basalt and Picture Gorge Basalt being the least depleted. The most depleted are the Grande Ronde Basalt, Wanapum Basalt and Saddle Mountains Basalt, the last formations to be emplaced.

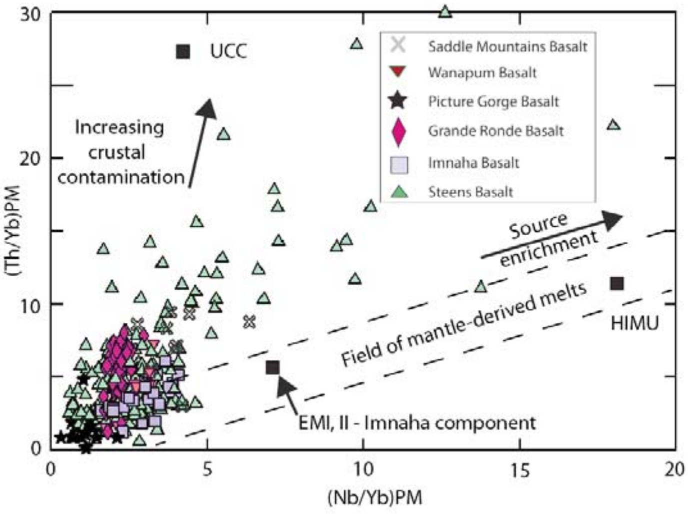

Figure 18. Diagram showing variation in (Nb/Yb)PM and (Th/Yb)PM. The ratios are normalized to primitive mantle values (PM) of McDonough and Sun (1995) following Jowitt and Ernst (2013) and Jowitt et al. (2014). N-MORB is from Hofmann (1988); Upper Continental Crust (UCC) composition is from Taylor and McLennan (1985) and Enriched Mantle (EMI, EMII –the Imnaha component of Hooper and Hawkesworth 1993) and HIMU values concentrations from Condie (2001). This diagram assesses the probability of the Columbia River Basalt Group magmas assimilating significant amounts of crustal material prior to emplacement. Note that the Grande Ronde, Upper Steens, Wanapum and Saddle Mountains Basalts show evidence of crustal contamination. Picture Gorge, Imnaha, and Lower Steens Basalts indicate little crustal contamination as has been shown by Hooper and Hawkesworth (1993), and Camp and Hanan (2008).

Lithospheric contamination can account for as much as ~20% of the Grande Ronde Basalt (e.g. Hooper and Hawkesworth 1993; Camp and Hanan 2008). Figure 18 shows variations in (Nb/Yb)PM and (Th/Yb)PM for the CRBG following Pearce (2008), Jowitt and Ernst (2013) and Jowitt et al. (2014). The effects of crustal contamination and variations in mantle source regions on the basalts are shown. The Lower Steens, Imnaha and Picture Gorge Basalts plot close to, or within the field of mantle derived melts (EMII, Imnaha component) supporting previous work (e.g. Hooper and Hawkesworth 1993; Camp and Hanan 2008). The Upper Steens, Wanapum, Saddle Mountains and most of the Grande Ronde Basalt show evidence of increasing contamination, again supporting previous work.

The difference in abundance between PGEs and chalcophile elements in the Lower Steens to Upper Steens, and from Imnaha Basalt to near absence in the Grande Ronde Basalt may be due to sulphur availability. The Upper Steens Basalt and Grande Ronde Basalt assimilated a substantial amount of cratonic material while the Lower Steens Basalt and Imnaha Basalt did not. This may have allowed the depletion of PGEs and chalcophile elements as they encountered sulphur from the cratonic crust. The inclusion of PGEs in the coerupting Picture Gorge Basalt may be due to the lack of sulphur in the oceanic accreted-terrane rocks that basalt passed through. Thus, assimilation of cratonic material may have been an important factor in depleting PGEs and chalcophile elements from the basalt.

In order to evaluate whether the CRBG magma assimilated significant amounts of crustal material prior to eruption, we employed the Jowitt and Ernst (2013) and Jowitt et al. (2014) (Nb/Th)PM ratio vs. (Th/Tb)PM diagram (Fig. 19). These ratios correlate with the amount of crustal material assimilated. Low (Nb/Th)PM values and high (Th/Yb)PM values are consistent with assimilation of crustal material (Jowitt and Ernst 2013). High (Nb/Th)PM and low (Th/Yb)PM are more consistent with mantle compositions (Lightfoot and Hawkesworth 1988; Lightfoot et al. 1990; Jowitt and Ernst 2013; Jowitt et al. 2014). CRBG samples trend between an average mantle composition (N-MORB, Hofmann 1988) with high (Nb/Th)PM and low (Th/Yb)PM ratios and typical crustal contamination with low (Nb/Th)PM and high (Th/Yb)PM (Jowitt et al. 2014; Jowitt and Ernst 2013 and references therein). The Steens Basalt shows a consistent mixing line. The Lower Steens samples lie closer to primitive mantle and the Upper Steens show crustal contamination suggesting that the Steens Basalt became progressively contaminated with time as suggested by Camp and Hanan (2008) and Moore et al. (2020). The Imnaha Basalt corresponds more closely with N-MORB or OIB as Hooper and Hawkesworth (1993) have concluded. The Grande Ronde Basalt, Wanapum Basalt and Saddle Mountains Basalt all show varying degrees of crustal contamination.

Mavrogenes and O'Neill (1999) suggest that most basaltic magmas will never achieve S-saturation under near-surface conditions unless they have undergone at least 60% fractional crystallization. However, Jowitt and Ernst (2013) have suggested that for mantle partial melting, if, for example, the mantle originally contained 250 ppm sulphur, partial melting of 25% of the mantle will result in immiscible sulphide melts being assimilated by the basaltic magmas, and the basaltic magmas can assimilate up to 1000 ppm of sulphides (Mavrogenes and O'Neill 1999; Jowitt and Ernst 2013). Once the sulphides have been assimilated, where the chalcophile elements ends up depends only on their partitioning. As these elements, especially PGEs, are either incompatible or highly incompatible in S-undersaturated magmas (Keays 1995), rather than remaining in the depleted mantle, the chalcophile elements would preferentially partition into a S-undersaturated partial melt, thus producing fertile magmas. Magmas produced by less than 25% partial melting may, depending on the conditions of melting, leave residual sulphide and therefore chalcophile elements in the mantle.

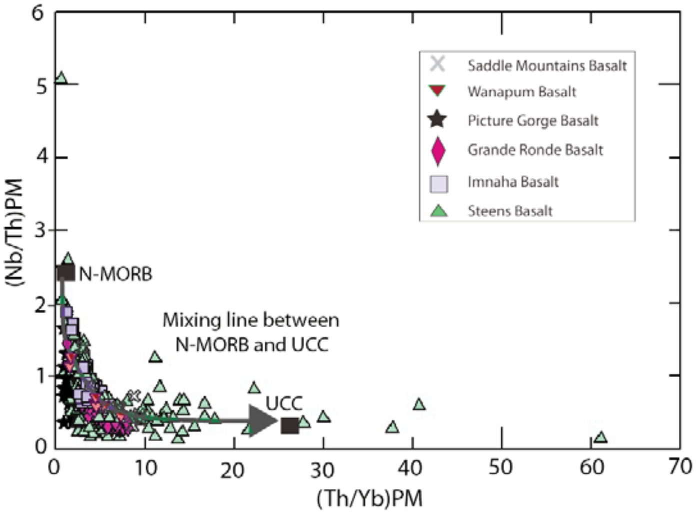

Figure 19. Diagram showing variations in (Nb/Th)PM and (Th/YB)PM ratios after Jowitt and Ernst (2013) and Jowitt et al. (2014). The ratios are normalized to primitive mantle values of McDonough and Sun (1995). This trend corresponds with mixing between primitive mantle (PM) compositions (N-MORB, Hofmann 1988) with high (Nb/Th)PM and low (Th/Yb)PM ratios and typical crustal contamination (UCC; Taylor and McLennan 1985) with low (Nb/Th)PM and high (Th/Yb)PM. The Steens Basalt shows a consistent mixing line. The Lower Steens samples lie close to primitive mantle and the Upper Steens show crustal contamination suggesting that the Steens Basalt became progressively contaminated with time as suggested by Camp and Hanan (2008). The Imnaha Basalt corresponds more closely with N-MORB or OIB as Hooper and Hawkesworth (1993) have concluded.

The role of sulphur saturation in the CRBG is difficult to access but several studies have measured sulphur in the CRBG lavas. Knowing the extent of partial melting is an important consideration. The CRBG has undergone various degrees of partial melting (e.g. Hooper and Hawkesworth 1993) but because of the highly evolved nature of the lavas, the amount of partial melting is difficult to determine. Blake et al. (2010) developed a numerical model for determining S-saturation in basalts and S release based on only total iron (FeO_{total}), assuming initial sulphide saturation of basaltic magmas. Davis et al. (2017) determined that some Wapshilla Ridge Member phenocrysts contained Fe-saturated-sulphide melt (pyrrhotite) on quenching. Figure 20 shows the S wt.% that could be contained in the main CRBG based on the model of Blake et al. (2010) and, again assuming that all magmas were S-saturated. On this we have plotted the measured S content for the Wapshilla Ridge and Meyer Ridge Members of the Grande Ronde Basalt from Davis et al. (2017) and for the Roza Member (Thordarson and Self 1996), the Ginkgo (Ho and Cashman

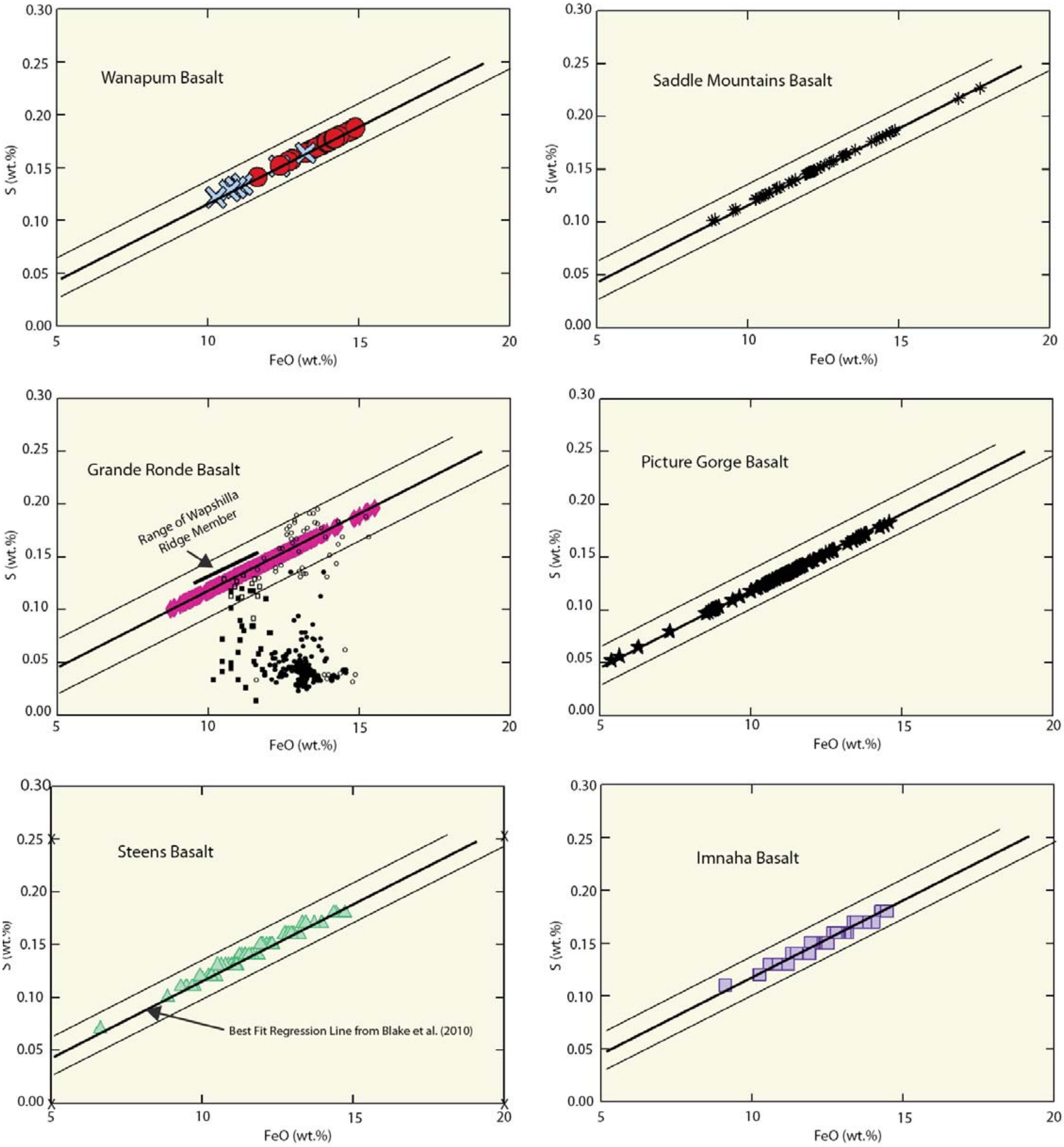

Figure 20. Diagram showing the potential sulphur saturation of the Columbia River Basalt Group (CRBG). Diagram is based on the Blake et al. (2010) numerical model for determining S-saturation in basalts and S release based on only total iron (FeO_{total}), assuming initial sulphide saturation of basaltic magmas. This diagram shows the Sulphur wt.% that could be contained in the main CRBG based on that model assuming that all magmas were S-saturated. Also plotted are the measured S content for the Wapshilla Ridge and Meyer Ridge Members of the Grande Ronde Basalt (Davis et al. 2017), the Roza Member (Thordarson and Self 1996), the Ginkgo (Ho and Kashman 1997), Sand Hollow and Sentinel Gap flows, Frenchman Springs Member, Wanapum Basalt (Blake et al. 2010; Martin et al. 2013). The lines are the best-fit regression line and error lines of +1 sigma.

1997), Sand Hollow and Sentinel Gap flows (Blake et al. 2010) of the Wanapum Basalt. These data suggest that at least some of the Grande Ronde Basalt and the Wanapum Basalt were S-saturated. The presence of immiscible sulphides in the Lower Steens suggest that they were S-saturated. Unfortunately, we do not have data for the other formations so we cannot assess their S-saturation.

PGEs partition more readily into sulphides than do Cu and Ni (Peach et al. 1990); this suggests that any PGEs present in the S-saturated Grande Ronde Basalt and Wanapum Basalt flows should be in sulphides. The main sulphide in the Wapshilla Ridge and Meyer Ridge flows is pyrrhotite (Davis et al. 2017) although chalcopyrite is present in the oldest GRB flows. Pt in standard BCR-1 probably resides in sulphur melt inclusions that were identified by Davis et al. (2017).

A Model for PGEs and Chalcophile Elements in the CRBG

Nearly all world-wide PGE-chalcophile deposits occur in intrusives and not in surface lavas (e.g. Mungall 2005). Most North America PGE localities occur in basaltic dykes and intrusives of Precambrian age (Ernst and Hubbart 2003) but there are localities where PGE and chalcophile elements occur in lava flows. For example, the East Greenland Igneous Province (Momme et al. 2002), the Kerguelen Plateau (Chazey and Neal 2005) and the Deccan (Andreasen et al. 2002). Unfortunately, these studies do not provide good models for PGEs in lava flows. They do, however, share similarities with the CRBG lavas. For example, the PGEs occur mainly in more primitive high-MgO lavas and, like the CRBG, are sparce to absent in low-MgO flows like those observed in the CRBG.

The Keweenaw basalts near Lake Superior are famous for native Cu deposits in the flow-top breccias of lavas, but they also contain Cu sulphide deposits. Steens Basalt plagioclase phenocrysts also contains native Cu (Oregon Sunstones) whereas the Keweenaw deposits are not derived from a magmatic plume but are probably either due to metamorphism or meteoric waters (Brown 2006). Pavlov et al. (2019) concluded that, like the CRBG, the Siberian Traps were emplaced rapidly and Latyshev et al. (2020) showed that all main ore-bearing intrusions of the Noril'sk Complex, as well as weakly mineralized and barren intrusions, are coeval with the Morongovsky–Mokulaevsky level of the volcanic sequence. However, models for the Noril'sk deposits range from magmas that fed the deposits also feeding lava flows (e.g. Naldrett 1997; Naldrett et al. 1992) to those not being related to the lava flows (Czamanske et al. 1994, 1995; Latypov 2002). Our study conclusively shows that the PGEs in the CRBG are magmatic and their abundance in the lavas are directly controlled by petrogenetic processes.

The volcanic, tectonic, and petrologic history of the CRBG form the basis for understanding the occurrence of PGEs and chalcophile elements in the flows. We use that knowledge here to provide a model of how the PGEs and chalcophile elements fit into the evolution of the CRBG LIP.

The Lower Steens Basalt marks the beginning of the Columbia River Basalt volcanic episode with the initial eruptions occurring as the plume encountered the lithosphere. The Lower Steens Basalt contains PGEs and Cu and Zn but the younger Upper Steens Basalt does not. Sulphides have been recognized in the Steens Basalt (Wierman 2018) suggesting S-saturation. There is no correlation between Cu and/or any other oxide or trace element suggesting that Cu, like the PGEs, probably occurs in microscopic sulphides or as immiscible sulphides. Wierman (2018) found that magnetite followed by pyroxene and olivine contain the most Cu other than that in sulphides and Oregon Sunstones. Zn is positively correlated with TiO_2 and FeO but not with MgO or CaO suggesting that Zn appears to occur predominantly in ilmenite and titanomagnetite. Ni and Cr are positively correlated with MgO but not Cu or Zn suggesting only minor amounts of Cu and Zn are in pyroxenes and olivine as Wierman (2018) found. The contaminated Upper Steens Basalt appears depleted in PGEs and Cu. This suggests that the first Steens Basalt eruptions were fertile with PGEs and chalcophile elements but as the eruptions continued the plume began to assimilate crustal material containing sulphur depleting PGEs and chalcophile elements from the magma prior to eruption.

The Imnaha Basalt episode marks the beginning of the northward spread of the plume head. Camp (2013) argued that previously the plume had encountered the subducting Juan de Fuca Plate but by Imnaha Basalt time, the plume broke through the subducting plate and had little interaction with the crust. As the plume head progressed northward, the magma was recharged and replenished with PGEs and chalcophile elements. The presence of sulphides in the Imnaha Basalt suggests that at least some of the Imnaha Basalt flows were S-saturated upon eruption and its magma was fertile with PGEs and chalcophile elements. Sulphides are distributed throughout the Rock Creek flow suggesting that S-saturation had been achieved. Because PGEs are more readily partitioned into sulphides than Cu and Zn (Peach et al. 1990), these sulphides probably contain the PGEs we detected. Zn, however, correlates with FeO and TiO_2 and, thus, Zn^{+2} is probably substituting for Fe^{+2} mainly in titanomagnetite and ilmenite. Ni, while a common element in many Ni–Cu-sulphide deposits in layered igneous intrusions, is a minor component in Columbia River Basalt Group sulphides. Korzendorfer (1979) measured only 0–1.3% Ni in chalcopyrite in the Imnaha Basalt. Ni and Cr are correlated with MgO suggesting they were incorporated in olivine and pyroxene.

Following the Imnaha Basalt eruptions, the plume continued to be recharged and replenished with PGEs and chalcophile elements as the plume head advanced northward and the most voluminous Grande Ronde Basalt began erupting. The lavas were largely depleted in PGEs and chalcophile elements relative to the earliest formations, yet the many flows reached S-saturation precipitating pyrrhotite rather than Cu sulphides. Depletion probably occurred as the magma assimilated crustal and lithospheric material progressively contaminating it. Camp and Hanan (2008) propose delamination and assimilation as a viable scenario for this process.

Chalcophile elements are more abundant at the distal end of the earliest GRB flows but became depleted in the proximal near dyke/vent end. In addition, some of the youngest flows contain the highest concentration of Cr and Ni but they occur in olivine and pyroxene. The early GRB Teepee Butte Member dyke contains Pd but only in the evolved selvage zone which is the first erupted basalt. However, in the main part of the dyke, PGEs are below our detection limits and Cu and Zn are depleted compared to the selvage zones. USGS Standard BCR-1 did contain some PGEs but was generally depleted in chalcophile elements as is the majority of the Grande Ronde Basalt. This suggests that the magma chamber became a repository for PGEs and chalcophile elements.

The low Cu and Zn concentrations in the voluminous Grande Ronde Basalt appear to be controlled mainly by silicate and oxide mineral phases (e.g. pyroxene, ilmenite) or mesostasis. The correlation of Cu and Ni with MgO and CaO (Fig. 12) suggests what little Cu present may be incorporated in pyroxene and olivine. Wager and Brown (1967, p. 180, fig. 122) recognized Cu in pyroxene and olivine from the Skaergaard intrusion as did Wierman (2018) in the Lower Steens Basalt. Zn correlates with FeO and TiO_2 in Grande Ronde Basalt (Fig. 7) which is probably due to Zn^{+2} substituting for Fe^{+2} mainly in titanomagnetite and ilmenite. In the Grande Ronde Basalt, Zn inversely correlates with MgO and CaO suggesting that there may be some substitution for Fe in pyroxenes or olivine but is mainly in ilmenite and titanomagnetite.

The Picture Gorge Basalt erupted through Mesozoic accreted terranes west of the Chief Joseph dyke swarm and Cahoon et al. (2020) suggested it may encompass the entire CRBG episode up to nearly the end of the Grande Ronde Basalt (Fig. 2). Camp and Ross (2004) suggested that the Picture Gorge Basalt is a separate lobe of the main plume head. The Picture Gorge Basalt has PGEs like that of the Imnaha Basalt and significantly greater than the coeval Grande Ronde Basalt. However, some flows are more enriched in chalcophile elements (Fig. 17) than either the Steens Basalt or Imnaha Basalt. In the Picture Gorge Basalt, Cu correlates with Zn (Fig. 6) but with no other oxide or element. This could imply that Cu and PGEs may be in sulphides; however, the most detailed study of the Picture Gorge Basalt by Bailey (1989) did not report any sulphides. Zn correlates with the high-field strength elements TiO_2, FeO, P_2O_5, V and Y but has no correlation with any other oxide or element. We suggest that Zn, like in other CRBG formations is mainly incorporated in ilmenite and titanomagnetite and possibly pyroxene. We suspect that the Picture Gorge Basalt may not have been S-saturated because the Picture Gorge Basalt, unlike the Imnaha Basalt and Steens Basalt did not get emplaced in the a cratonic crust but in accreted oceanic crust and has not undergone significant crustal contamination (Fig. 18). It probably lacked sufficient S to allow saturation and thus, the PGEs and chalcophile elements were partitioned to the silicate melt.

The eruption of the PGB in the Monument dyke swarm west of the Chief Joseph dyke swarm probably represents a separate lobe of the advancing plume as Camp and Ross (2004) have suggested. While the Chief Joseph dyke swarm was erupting Grande Ronde Basalt lavas depleted in PGEs and chalcophile elements, the Picture Gorge Basalt was erupting undepleted flows at the same time. As Camp and Ross (2004) have suggested, the two magma chambers were separate lobes. This allows us to reject the model of Wolff et al. (2008) where they proposed that a centralized magma chamber located under the Oregon Plateau fed all the CRBG. It is clearly difficult for a centralized magma chamber to have fed depleted Grande Ronde Basalt while simultaneously feeding the undepleted Picture Gorge Basalt.

Wanapum Basalt and Saddle Mountains Basalt represent the waning stages of the CRBG magmatism. By this point the Yellowstone plume had been sheared off by the southwestward movement of the North American Plate and only residual magma from the plume head remained (Camp and Ross 2004). PGEs have been depleted and Cu is minor in the residual magma, but Zn has concentrations similar to other CRBG formations. Cu, Zn and Ni behave independently in the Frenchman Springs and Roza Members and the Wanapum Basalt, and show no correlation with other elements. Copper is independent in the Saddle Mountains Basalt and is not correlated with any oxide or element; Zn, however, is correlated with FeO, TiO_2, P_2O_5, Zr, Y and Nb suggesting that it probably is incorporated in ilmenite and titanomagnetite as well.

CONCLUSIONS

The plume that produced the Columbia River Basalt Group was fertile with PGEs and chalcophile elements. The magma was erupted along the thinned edge of the craton where it was juxtaposed to both cratonic rocks and oceanic accreted terranes. The earliest formations, Lower Steens, Imnaha and Picture Gorge, contain the greatest amounts of PGEs and chalcophile elements. The correlation of PGEs with chalcophile elements in the Imnaha Basalt indicates PGEs are contained within sulphides. Sulphur was readily available from both the initial magma and assimilation of cratonic rock. The eruption of the Picture Gorge Basalt through accreted oceanic crust indicates that PGEs may not occur in sulphides because of the lack of abundant sulphur in the accreted oceanic crust. This is further supported by the absence of sulphide minerals or immiscible sulphides in the study by Bailey (1989).

The general absence of PGEs and depleted chalcophile elements in the voluminous, contaminated and evolved Grande Ronde Basalt flows and evolved Upper Steens Basalt indicate that the magma assimilated sufficient crustal material containing sulphur and the PGEs were depleted from the magma before eruption. The chalcophile elements Cu and Zn were present in the earliest erupted GRB lava probably as immiscible sulphides. Much lower concentrations of Cu and Zn in the GRB flows probably were incorporated into basaltic minerals – Cu in pyroxene and Zn in ilmenite and titanomagnetite with some minor substitution for Fe^{+2} in pyroxenes. The final eruptions of the CRBG, the Wanapum Basalt and Saddle Mountains Basalt were erupted from a magma that already had been depleted of PGEs and chalcophile elements.

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