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TRACE-ELEMENT GEOCHEMISTRY AND PETROGENESIS OF BARREN AND ORE-ASSOCIATED KOMATIITES

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ABSTRACT

Most komatiite-associated magmatic Ni–Cu–(PGE) sulfide deposits formed from sulfide-undersaturated magmas and are interpreted to have formed in dynamic lava channels or magma conduits by incorporation of crustal sulfur. They commonly exhibit geochemical and isotopic evidence of crustal contamination and chalcophile element depletion on the scale of individual cooling units or parts of individual cooling units that appear to be associated with the ore-forming process. It is possible, therefore, to discriminate between rocks generated during ore-forming processes and rocks generated during normal igneous processes by identifying signatures characteristic of crustal contamination (*e.g.*, Th–U–LREE enrichment, negative Nb–Ta–Ti anomalies) or sulfide segregation (*e.g.*, Co–Ni–Cu–PGE depletion) (or both) and distinguishing them from signatures characteristic of normal igneous fractionation or accumulation of crystals. The amounts of contamination and chalcophile element depletion produced during the ore-forming process depend on several factors: 1) the stratigraphic architecture of the system (*e.g.*, thickness and physical accessibility of the contaminant), 2) the fluid dynamics and thermodynamics of the lava or magma, 3) the physical, chemical, and thermal characteristics of the contaminant, 4) the amount of contaminant melted and incorporated (*e.g.*, amount of silicate partial melt), 5) the sulfur and metal content of the contaminant, 6) the initial saturation-state of sulfide in the magma, 7) the assimilation:crystallization ratio, 8) the amount of lava replenishment, and 9) the effective magma:sulfide ratio (R factor) of the system. Because these processes vary independently from deposit to deposit, from area to area within a deposit, and within a single area with time, there are many opportunities to decouple contamination from chalcophile element depletion.

Keywords: geochemical discrimination, komatiite, Ni–Cu–(PGE) deposits, contamination.

SOMMAIRE

Dans la plupart des cas, les gisements de sulfures de nickel, cuivre, et éléments du groupe du platine associés aux coulées komatiitiques se sont formés à partir de magmas sous-saturés en sulfures. Ils se seraient formés dans un milieu d'épanchement dynamique, dans des chenaux ou conduits, comme résultat de l'incorporation de soufre d'origine crustale. D'après les critères géochimiques et isotopiques, ces gisements témoignent de contamination crustale et d'un appauvrissement en éléments chalcophiles à l'échelle de venues individuelles et des parties composantes de telles venues qui semblent associées à la formation de minerai. Il est donc possible de distinguer entre les roches générées au cours de processus de minéralisation et les roches stériles générées lors d'une cristallisation normale en identifiant les signatures caractéristiques de la contamination (par exemple, enrichissement en Th, U et terres rares légères, et anomalies négatives en Nb, Ta et Ti) ou de la ségrégation de sulfures (par exemple, appauvrissement en Co, Ni, Cu et éléments du groupe du platine) (ou les deux) par rapport aux caractéristiques d'un fractionnement normal ou d'une accumulation de cristaux. Le degré de contamination et d'appauvrissement en éléments chalcophiles dépend de plusieurs facteurs: 1) l'architecture stratigraphique du système (par exemple, l'épaisseur du contaminant et l'accès à celui-ci), 2) les aspects de la dynamique des fluides et de la thermodynamique de la lave ou du magma, 3) les caractéristiques physiques, chimiques, et thermiques du contaminant, 4) la quantité de contaminant fondue et ainsi incorporée (c'est-à-dire, la proportion de fusion partielle), 5) la teneur en soufre et en métaux du contaminant, 6) l'état initial du magma par

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rapport à la saturation en phase sulfurée, 7) le rapport d'assimilation à cristallisation, 8) l'importance du réapprovisionnement de la lave, et 9) le rapport effectif de magma à sulfure (facteur R) du système. Parce que ces processus varient indépendamment d'un gisement à l'autre, d'une partie d'un seul gisement à une autre, et même dans une seule partie en fonction du temps, il y a eu plusieurs occasions de découpler le phénomène de contamination de l'appauvrissement du système en éléments chalcophiles.

(Traduit par la Rédaction)

Mots-clés: discrimination géochimique, komatiite, gisements de nickel, cuivre, et éléments du groupe du platine, contamination.

INTRODUCTION

Komatiite-associated magmatic Ni–Cu–(PGE) deposits are interpreted to have formed in lava channels or magma conduits (Leshner *et al.* 1984, Leshner 1989, Hill *et al.* 1990, 1995, Barnes *et al.* 1999) from sulfide-undersaturated magmas (Keays 1982, 1995, Leshner & Groves 1986, Naldrett & Barnes 1986). Those containing stratabound disseminated sulfides (*e.g.*, Mt. Keith, Dumont) appear to have crystallized from magmas that reached sulfide saturation at a late stage in their crystallization history, whereas those containing stratiform massive to disseminated Ni–Cu–(PGE) sulfides (*e.g.*, Kambalda, Perseverance, Raglan, Thompson) appear to have crystallized from magmas that reached sulfide saturation early in their crystallization history.

In the case of stratabound disseminated deposits, the compositions of the cumulate rocks and relict igneous olivine (Donaldson *et al.* 1986, Duke 1986, Leshner 1989) indicate that the magmas have not experienced significant degrees of fractional crystallization. A mechanism other than fractional crystallization is therefore required to bring the magmas to sulfide saturation, a process that obviously did not occur in the many cumulate komatiites that do not contain sulfides. Mass-balance calculations indicate that there may have been sufficient S in the magma to generate the amount of sulfide observed in the deposits, but even if that process involved contamination, deposits of this type appear to have formed *via* a process involving relatively large amounts of magma flow-through and the crystallization of large amounts of olivine (Donaldson *et al.* 1986, Leshner & Groves 1986, Duke 1986, Barnes *et al.* 1995, Leshner & Stone 1996). As a result of a) the large mass-fractions of magma involved, and b) the decrease in the bulk partition-coefficients for the chalcophile elements in presence of olivine (see discussion by Leshner & Burnham 2001), most deposits of this type do not exhibit geochemical evidence of contamination. In the case of stratiform massive to disseminated deposits, however, the amount of sulfides is too great to have been dissolved in the magmas (Leshner & Groves 1986, Leshner & Campbell 1993, Leshner & Stone 1996), and an external source of sulfur is required.

The compositions of the sulfides and the lavas that equilibrate with them will depend on the extent to which lava equilibrates with the sulfides (Campbell & Naldrett

1979), whether the sulfur is derived internally or externally (Naldrett 1981), the composition of the contaminant (Leshner & Burnham 1999, 2001), and whether incomplete or incongruent melting produces other components such as residues, xenoliths, xenomelts, or xenovolatiles (Leshner & Burnham 1999, 2001). However, on the scale of individual cooling units or parts of individual cooling units, most stratiform massive to disseminated deposits exhibit some geochemical and isotopic evidence of crustal contamination and chalcophile element depletion that seem to be associated with the ore-forming process (*e.g.*, Groves *et al.* 1979, Leshner & Groves 1984, Barnes & Picard 1993, Barnes *et al.* 1995, Leshner & Arndt 1995, Perring *et al.* 1996, Barnes & Maier 1999, Leshner *et al.* 1999a, b; see also Ripley 1986, Lightfoot *et al.* 1990, 1993, 1994, Naldrett *et al.* 1992, 1996, Walker *et al.* 1991, 1994a, b, 1997, Brüggmann *et al.* 1993, Lambert *et al.* 1998, Ripley *et al.* 1998). It is commonly possible, therefore, to discriminate between komatiites generated during ore-forming processes and komatiites generated during normal igneous processes by identifying characteristics of crustal contamination or chalcophile element depletion that differ from those of normal igneous fractionation or accumulation of crystals.

The purpose of this paper is to discuss the whole-rock geochemical consequences and geological interpretation of contamination and sulfide segregation in komatiitic systems. As discussed by Leshner *et al.* (1999a), many of the principles discussed here may also be applied to ferropicritic, picritic, and basaltic systems, but the focus here will be on komatiitic systems.

GEOCHEMICAL DISCRIMINATION

Komatiite geochemistry

The geochemistry of komatiites is controlled by many variables and processes, including: the composition of the source and residue, the pressure, temperature, nature, and degree of partial melting, the nature and degree of crustal contamination, the degree of fractional crystallization and accumulation, and the degree of remobilization of elements *via* alteration, metamorphism and metasomatism (*e.g.*, Nesbitt *et al.* 1979, Beswick 1982, Xie *et al.* 1993, Anderson 1994, Kerrich & Wyman 1996, Leshner & Stone 1996, Herzberg &

O'Hara 1998, Leshner *et al.* 1999, Sproule *et al.*, submitted).

The high Mg contents of aphyric and random spinifex-textured komatiites (up to 30% MgO in many areas) and the high Fo content of relict igneous olivine (up to Fo₉₄ in many areas) require derivation from a mantle source. Low abundances of incompatible trace elements indicate moderate to high degrees of partial melting (30–60%), depending on the composition of the source and the degree of prior extraction of melt (see Leshner & Stone 1996). The lower Mg contents of komatiitic basalts (up to 18% MgO) and the lower Fo contents of relict igneous olivine (up to Fo₉₁) also require derivation from a mantle source, but may be produced by lower degrees of partial melting (15–30%) depending on the composition of the source and the degree of prior melt extraction (see Leshner & Stone 1996). Sources that have experienced prior melt extraction are depleted in highly incompatible elements relative to moderately incompatible elements (*e.g.*, [Th/Sm]_{MN} < 1 and [La/Sm]_{MN} < 1), with the degree of depletion proportional to the amount of melt extracted. Conversely, sources that have been enriched (for example *via* incorporation of the sedimentary component of subducted oceanic crust) are enriched in highly incompatible elements relative to moderately incompatible elements (*i.e.*, [Th/Sm]_{MN} > 1

and [La/Sm]_{MN} > 1), with the degree of enrichment proportional to the degree of source enrichment.

The major- and trace-element geochemistry of komatiites is also strongly controlled by the retention or melting of minerals in the source (*e.g.*, Nesbitt *et al.* 1979, Herzberg & O'Hara 1998). The efficiency of this mechanism is determined by the composition of the source, the degree of melting, and also by the depth of partial melting, which influences the stability of minerals such as those of the garnet group. Komatiitic melts derived from sources in which garnet is retained will be depleted in Al, Sc, Y, and heavy rare-earth elements (*HREE*) relative to Ti, middle rare-earth elements (*MREE*), light rare-earth elements (*LREE*), and large-ion lithophile elements (*LILE*). Melts derived from sources in which clinopyroxene, orthopyroxene, and olivine are retained do not have significantly distinctive trace-element signatures.

Crustal contamination

Geochemical and mass-balance studies have shown that the depleted mantle (and magmas extracted from depleted mantle), and the continental crust (and sediments derived from the continental crust), have distinctive, yet complementary geochemical signatures (Table 1). These complementary signatures have been attributed to extraction of the continental crust at an early stage in the evolution of the Earth (Hofmann 1988). Thus, the continental crust is enriched in highly incompatible lithophile elements (Cs, U, Th, Nb, Ta, *LREE*) relative to moderately incompatible lithophile elements (*MREE*, Y, Zr, Hf) and highly compatible elements (Cr, Mg, Ni, Co). The upper crust is, however, less enriched in Ta and Nb relative to Th, and less enriched in Ti relative to *MREE*, a feature that has been attributed to retention of these elements in oxide phase(s) in eclogite during crustal recycling (*e.g.*, Weaver & Tarney 1981, Rudnick *et al.* 1998).

As a consequence, uncontaminated magmas derived by a moderate to high degree of partial melting of depleted mantle should be systematically depleted in highly incompatible lithophile elements relative to moderately incompatible lithophile elements and highly compatible elements, whereas magmas contaminated by crust should be enriched in highly incompatible lithophile elements, with pronounced negative Ta and Nb anomalies, and moderately enriched in moderately incompatible lithophile elements, with slightly negative Ti anomalies (Table 2). In detail, however, the compositions of mantle-derived magmas vary considerably owing to recycling of oceanic crust and enrichment of the subcontinental lithospheric mantle (see above), and the compositions of crustal sediments may be influenced by a wide variety of other processes related to weathering. Accordingly, the precise nature of the signature due to crustal contamination may vary from area to area.

TABLE 1. GEOCHEMICAL CHARACTERISTICS OF MAJOR GEOLOGICAL RESERVOIRS* AND KEY RATIOS USED TO DISCRIMINATE BETWEEN CRUSTAL CONTAMINATION AND CHALCOPHILE ELEMENT DEPLETION

	Continental Crust	N-MORB	Depleted Mantle	AUK	Key Ratios
HILE	strongly enriched	moderately depleted	strongly depleted	very strongly depleted	Th/La, Th/Sm, Th/Yb, La/Sm
Nb-Ta-Ti†	moderately enriched	moderately depleted	moderately depleted	strongly depleted	Nb/La, Nb/Th
MILE	slightly enriched	undepleted	undepleted to slightly enriched	slightly enriched	Zr/Y, Gd/Yb
ICE	undepleted	moderately depleted	undepleted to slightly enriched	slightly enriched	Pd/Ti, Pd/Yb
CCE	strongly depleted	strongly depleted	undepleted to slightly enriched	slightly depleted	Ni/Mg, Ni/Ni*, Ir/Mg

HILE: highly incompatible lithophile elements (Cs–Rb–Ba–Th–U–*LREE*), MILE: moderately incompatible lithophile elements (*MREE*–Y), ICE: incompatible chalcophile elements (Au, Cu, *PPGE*), CCE: compatible chalcophile elements (Co, Ni, *IPGE*). In addition, *LREE*: light rare-earth elements, *MREE*: middle rare-earth elements, *HREE*: heavy rare-earth elements, *PPGE*: Pt-group platinum-group elements, *IPGE*: Ir-group platinum-group elements, N-MORB: "normal" mid-ocean ridge basalt (10–15% partial melt of depleted mantle), AUK: Al-undepleted (Munro-type) komatiite (~50% partial melt of depleted mantle), † Nb–Ta–Ti are depleted in continental crust relative to elements of similar compatibility. Ni/Ni*: ratio of measured Ni to that expected from sulfide-free olivine fractionation or accumulation. * Compiled from Taylor & McLennan (1985), Hofmann (1988), Jochum *et al.* (1991), Rudnick & Fountain (1995).

TABLE 2. WHOLE-ROCK GEOCHEMICAL SIGNATURES OF MINERALIZED UNITS IN KOMATIITE-ASSOCIATED Ni-Cu-(PGE) DEPOSITS* RELATIVE TO UNMINERALIZED UNITS IN THE SAME SEQUENCE AND TO EXPECTED VALUES FOR UNMINERALIZED KOMATIITIC MAGMAS

	Kambalda	Perseverance	Raglan	Thompson
MgO	Higher	Higher †	Higher	Lower?
[La/Sm] _{CC1}	Lower	Higher	Higher	Higher
[Nb/Tb] _{MC} and [Nb/La] _{CC1}	Higher	Lower	Lower	Lower
[Pd/Yb] _{CC1} and [Pd/Tb] _{MC}	Higher	Lower ‡	Lower ‡	Lower ‡
[Ni/Mg] _{MC}	Higher	Lower †	Lower ‡	Lower ‡

[A/B]_{MC1} = primitive mantle-normalized ratios (McDonough & Sun 1995); † the Mineralized Units at Perseverance are less magnesian than the Main Dunitic Lens, but are more magnesian than barren flanking units (see discussion by Barnes *et al.* 1988). ‡ Whole-rock samples containing sulfides normally have higher abundances (see Figures in text), but olivine and barren whole-rock samples are commonly depleted in chalcophile elements. * As summarized from Leshner & Groves (1984), Barnes *et al.* (1988, 1995), Leshner & Arndt (1995) and Leshner *et al.* (1999a).

As a result of significant differences in their lithophile and chalcophile trace-element compositions and their modes of formation, the magma and crustal component will also exhibit significant differences in both radiogenic and stable isotopic compositions. If the crust is substantially older than the magma, it will be enriched in radiogenic Sr, Os, and Pb and unradiogenic Nd (Faure 1986, Dickin 1995). If the source of sulfur is a sedimentary rock, it may contain significant amounts of anomalously heavy or light S or C, depending on the environment of formation (Ohmoto 1986). Sulfide-bearing sedimentary rocks also usually have significantly higher S/Se values than rocks containing only magmatic sulfides (Stanton 1972).

Although crustal contamination should therefore be evident from changes in the geochemical and isotopic compositions of the magmas and associated ores, the nature of these changes will vary with the relative masses of the various components in the system (Leshner & Burnham 1999, 2001).

Depletion in chalcophile elements

Chalcophile elements, such as Co, Ni, Cu, the platinum-group elements (PGE: Pt, Pd, Rh, Ru, Ir, and Os), and Au, partition very strongly into sulfides relative to silicate magmas or silicate minerals. Experimentally and empirically determined sulfide melt – silicate melt partition-coefficients in komatiitic systems are ~30 for Co, 100–200 for Ni, 600–1000 for Cu, ~3000 for Se, and 10³–10⁵ for Au and the PGE (see reviews by Leshner & Stone 1996, Mathez 1999). Silicate magmas that equilibrate with sulfides thus will become depleted in the order PGE >> Se > Cu >> Ni > Co.

Komatiites and komatiitic basalts have PGE contents that are consistent with a high degree of partial melting of the mantle, indicating that they consumed all of the sulfide in the mantle and that they remained sulfide-undersaturated during ascent and emplacement (Keays 1982, 1995, Naldrett & Barnes 1986, Leshner & Stone 1996). An exception is the Barberton komatiites, which contain only half of the Pd levels of other komatiites (Keays 1982). Many continental flood basalts, which appear to have formed at lower degrees of partial melting, also contain normal levels of the PGE, but those that show evidence of extensive interaction with crustal rocks are strongly depleted in the PGE (Brügmann *et al.* 1993, Brooks *et al.* 1999). Mid-ocean-ridge basalts (MORB) are uniformly depleted in the chalcophile elements, a feature interpreted to indicate retention of sulfides in the source (Crocket 1979, Hamlyn *et al.* 1985, Keays 1995).

The partitioning of highly chalcophile metals between sulfides and magmas has been discussed by Campbell & Naldrett (1979), Naldrett (1981), Campbell & Barnes (1984), and Leshner & Burnham (1999, 2001). Magmas that equilibrate with sulfides at high values of the magma:sulfide ratio (R) may exhibit no significant depletion in any of the chalcophile elements, magmas that have equilibrated with sulfides at moderate R may exhibit chalcophile element depletion for elements where R < 10D, and magmas that have equilibrated with sulfides at low R may exhibit significant depletion in all of the chalcophile elements. In systems where the externally-added sulfide contains significant concentrations of chalcophile elements, the magma may appear depleted or enriched in certain chalcophile elements, depending on their relative abundances in the initial silicate and sulfide liquids, the compatibilities of the metals during olivine fractionation, and R (see discussion by Leshner & Campbell 1993, Leshner & Burnham 1999, 2001).

Enrichment in chalcophile elements

Just as magmas that have equilibrated with sulfides at various R factors may exhibit variable degrees of chalcophile element depletion, rocks containing sulfides will be variably enriched in chalcophile elements, depending on the R factors under which they formed and the abundance of sulfides. For example, rocks containing sulfides that have equilibrated with magmas at high R may be enriched in all chalcophile elements, rocks containing sulfides that have equilibrated with magmas at moderate R may be relatively enriched in Co > Ni > Cu > Se > PGE, and rocks containing sulfides that have equilibrated with magmas at low R may be only slightly enriched in chalcophile elements (see Leshner & Burnham 1999, 2001).

Alteration

Interpretations of the extent of contamination by crust and of depletion in chalcophile elements in komatiites are complicated by the effects of alteration (*e.g.*, Donaldson 1981, McGoldrick & Keays 1981, Beswick 1982, Gruau *et al.* 1992, Arndt *et al.* 1989, Leshner & Arndt 1995, Lahaye *et al.* 1995, Lahaye & Arndt 1996, Leshner & Stone 1996). Alkali elements (Cs, Rb, K, Na) and alkaline earth elements (Ba, Sr, Ca, Eu^{2+}) have low charges and large ionic radii, are easily complexed in hydrothermal and metamorphic fluids, and are hosted by readily altered igneous phases (*e.g.*, glass, feldspar) or common metamorphic phases (micas), so they are commonly mobile in komatiites during seafloor alteration, hydrothermal alteration, and regional metamorphism. Some chalcophile elements (*e.g.*, S, Au, Cu, Zn, Pb) also are easily complexed in many hydrothermal and metamorphic fluids and are hosted by readily altered sulfides, so they are also commonly mobile. U^{6+} may be mobile in oxidizing fluids and the *LREE* may be mobile in CO_2 -rich fluids. Other high-field-strength elements (U^{4+} , Th, Ta, Nb, Zr, Y, *HREE*³⁺), Al, many first-period transition elements (Sc, Ti, V, Cr; Mn, Co, Ni), and highly siderophile elements (Fe, PGE) are not as easily complexed in hydrothermal or metamorphic fluids and are stable in relict igneous phases or metamorphic products. Thus, they typically appear to have been relatively immobile during alteration at low fluid:rock ratios.

EXAMPLES

Geochemical data relevant to crustal contamination and chalcophile element depletion are available for four komatiite-associated Ni–Cu–(PGE) deposits: Kambalda, Western Australia (Leshner *et al.* 1981, Leshner & Groves 1984, Arndt & Jenner 1986, Leshner & Arndt 1995, Leshner & Keays, unpubl. data); Perseverance, Western Australia (Barnes *et al.* 1988, 1995); Raglan, New Quebec (Burnham *et al.* 1999a, Leshner *et al.* 1999a), and the Thompson Nickel Belt, Manitoba (Leshner *et al.* 1999a, Burnham *et al.* 1999b, in prep.). We have utilized data from those studies and have analyzed additional samples for this study using methods described below.

Analytical methods

Rocks were analyzed for the major elements (Si, Ti, Al, Fe, Mg, Mn, Ca, Na, K, P) on fused glass disks by wavelength-dispersion X-ray-fluorescence spectrometry (WD–XRF) at the Laurentian University Central Analytical Facility (LU–CAF: Dr. J. Huang, analyst), the Ontario Geoscience Laboratories (OGL), or the University of Western Ontario (Dr. C. Wu, analyst). These rocks were analyzed for selected trace elements (Ba, Rb, Sr, Sc, Cr, V, Co, Ni, Cu, Y, and Zr) on pressed powder

pellets at the same laboratories. Routine analytical precision, as determined on replicate analyses of international reference materials and in-house standards, is $\pm 2\%$ or better for most major elements, $\pm 5\%$ or better for most minor elements, and $\pm 10\%$ or better for most trace elements. Some samples were analyzed for base metals by inductively coupled plasma – optical emission spectrometry (ICP–OES) at the OGL. Routine analytical precision is $\pm 5\%$ or better. No systematic differences have been detected in duplicate samples analyzed at different laboratories.

Samples were analyzed for the rare-earth elements (*REE*: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), Y, Zr, and highly incompatible lithophile elements (*HILE*: Cs, U, Th, Ta, Nb) by inductively coupled plasma – mass spectrometry (ICP–MS; Jenner *et al.* 1990, Longerich *et al.* 1990) at the OGL using a Perkin Elmer SCIEX Elan 5000 ICP–MS and 10-day, closed-beaker, ultra-pure mixed-acid dissolution technique (Tomlinson *et al.* 1998). Routine analytical precision is $\pm 10\%$ or better. No systematic differences have been detected in duplicate samples analyzed by different methods.

Samples were analyzed for the platinum-group elements (PGE: Pt, Pd, Rh, Ru, Ir) and Au by ICP–MS at the OGL–LU Low-Level PGE Facility (T. Richardson, analyst) using a Ni-sulfide fire-assay preconcentration and Te coprecipitation technique (Jackson *et al.* 1990, Sun *et al.* 1993). Routine analytical precision is $\pm 10\%$, or better.

Data presentation

In order to facilitate comparison, the data will be summarized on Ni *versus* MgO, Pd *versus* MgO, $[\text{La}/\text{Sm}]_{\text{MN}}$ *versus* MgO, and $[\text{Nb}/\text{Th}]_{\text{MN}}$ *versus* $[\text{Th}/\text{Yb}]_{\text{MN}}$ diagrams. Ni and Mg are both compatible in olivine, but Ni partitions much more strongly into sulfide ($D_{\text{Ni}}^{\text{Sul/Liq}} \approx 100\text{--}200$ *versus* $D_{\text{Ni}}^{\text{Ol/Liq}} \approx 1\text{--}2$: see review by Leshner & Stone 1996); Ni thus is a moderately good indicator of interaction of the magmas with large masses of sulfides (Campbell & Naldrett 1979, Naldrett 1981, Campbell & Barnes 1984, Leshner & Burnham 1999, 2001). Pd is incompatible in olivine, but partitions very strongly into sulfide ($D_{\text{Pd}}^{\text{Sul/Liq}} \approx 10^4$: see review by Leshner & Stone 1996); Pd thus is an excellent indicator of interaction of the magmas with large masses of sulfides (Keays 1982, and references above). The ratios La/Sm and Nb/La are commonly used as indicators of crustal contamination, but *LREE*, in general, and La, in particular, may be mobile during metamorphism (see above). We prefer to use Th/Yb and Nb/Th as indicators of crustal contamination, but more data are available for *LREE*, so these data are plotted as well. Most uncontaminated komatiitic magmas have $[\text{Nb}/\text{Th}]_{\text{MN}}$ and $[\text{La}/\text{Nb}]_{\text{MN}}$ values slightly greater than unity, whereas most crustal rocks have $[\text{Nb}/\text{Th}]_{\text{MN}}$ and $[\text{Nb}/\text{La}]_{\text{MN}}$ values much less than unity. The $[\text{Pd}/\text{Ti}]_{\text{MN}}$ ratio

is an excellent indicator of chalcophile-element depletion (see Sun *et al.* 1991, Barnes & Picard 1993). However, Ti is commonly measured by WD-XRF of fused glass disks and reported with a precision less than 0.01wt% (which may represent $\pm 20\%$ relative precision for cumulate komatiitic rocks with very low TiO_2 contents) and this ratio may also be modified by contamination (see above). As a consequence, we prefer to use the $[\text{Pd}/\text{Yb}]_{\text{MN}}$ ratio as a measure of PGE depletion when REE data are available. Like $[\text{Pd}/\text{Ti}]_{\text{MN}}$, most barren, sulfide-undersaturated komatiitic magmas have $[\text{Pd}/\text{Yb}]_{\text{MN}}$ near 1, magmas that have equilibrated with sulfides have $[\text{Pd}/\text{Yb}]_{\text{MN}}$ values much less than 1, and rocks that have accumulated sulfides have $[\text{Pd}/\text{Yb}]_{\text{MN}}$ values much greater than 1. Available data for Kambalda, Perseverance, Raglan, and Thompson are summarized in Figures 1–4 and Table 2.

We have shown the general trajectories for olivine fractionation, olivine accumulation, sulfide fractionation, sulfide accumulation, and crustal contamination on Figures 1–4. It is possible to calculate specific trajectories (see Barnes *et al.* 1995, Leshner & Arndt 1995, Leshner & Stone 1995, Leshner *et al.* 1999a), but because the relative proportions of olivine, sulfide, and contaminant vary with location in the system, there is no unique trajectory. The emphasis in this paper will be on the general trends in the data and the implications that these have for the processes involved in producing the variations.

Kambalda, Western Australia

The Kambalda Komatiite Formation (KKF) comprises two members (Gresham & Loftus-Hills 1981, Cowden & Roberts 1990, Stone & Masterman 1998): the lower Silver Lake Peridotite (SLP) member of channelized komatiitic peridotite sheet-flows, separated by thin, sulfidic interflow metasediments, and the upper Tripod Hill Komatiite (THK) member of thin spinifex-textured metakomatiite lava lobes. It is underlain by the Lunnon Basalt, which is part of the low-magnesium-series basalts (LMSB) of Redman & Keays (1985), and is overlain by the Devon Consults Basalt (DCB) and the Paringa Basalt (PB), which are part of the high-magnesium-series basalts (HMSB) and siliceous high-magnesium-series basalts (SHMSB) of Redman & Keays (1985). On the basis of their major-element, trace-element, and Nd isotope geochemistry, the rocks in the DCB and PB have been interpreted to be komatiites contaminated by upper crust (Chauvel *et al.* 1985, Arndt & Jenner 1986, Leshner & Arndt 1995). The stratiform massive – net-textured – disseminated Ni–Cu–(PGE) mineralization at Kambalda is restricted almost exclusively to lava-channel facies of the Silver Lake Peridotite (SLP) member (Leshner *et al.* 1984, Cowden & Roberts 1990) and has been interpreted on the basis of a wide range of geological, stratigraphic, geochemical, isotopic, and theoretical evidence to have

been generated by thermomechanical erosion of interflow sulfidic sediments (Groves *et al.* 1979, 1986, Huppert *et al.* 1984, Leshner *et al.* 1984, Huppert & Sparks 1985, Frost & Groves 1989, Leshner 1989, Williams *et al.* 1998, 1999, Leshner & Burnham 2001).

The majority of the analyzed metakomatiites and metaperidotites at Kambalda define geochemical trends that are consistent with fractional crystallization from or accumulation of olivine (up to Fo_{94}) into a parental magma containing $\sim 31\%$ MgO (Leshner *et al.* 1981, Leshner & Groves 1984, Redman & Keays 1985, Arndt & Jenner 1986, Leshner 1989, Leshner & Arndt 1995). Most of the cumulate and non-cumulate rocks in the lava-channel facies of the SLP and most of the cumulate rocks in the sheet-flow facies of the SLP have normal Ni and PGE contents (Figs. 1a, b) and are depleted in HILE relative to MILE (Figs. 1c, d), consistent with derivation from a sulfide-undersaturated magma formed *via* a high degree of partial melting of (normal) depleted mantle. In contrast, many of the non-cumulate rocks in the sheet-flow facies of the SLP are moderately to strongly depleted in Ni (Fig. 1a) and PGE (Fig. 1b), and are variably enriched in HILE relative to MILE (Figs. 1c, d), consistent with contamination and sulfide segregation during emplacement (Leshner & Arndt 1995). The channel-flow facies samples that are depleted in Ni and Pd (Figs. 1a, b) all come from one locality and may be misclassified or may represent a volcanologically complex system. Samples of the THK member are uniformly slightly enriched in HILE relative to MILE (Figs. 1c, d), consistent with up to 5% crustal contamination during ascent (Leshner & Arndt 1995), but have normal Ni and PGE contents (Figs. 1a, b), indicating that they were not saturated in sulfide (Keays 1982). Samples of the DCB and PB units are moderately to strongly enriched in HILE relative to MILE, and have anomalously low Nb/Th values (Figs. 1c, d), consistent with up to 30% crustal contamination during ascent (Arndt & Jenner 1986, Leshner & Arndt 1995), but they have normal Ni and PGE contents (Figs. 1a, b), indicating that they were not saturated in sulfide (Redman & Keays 1985).

The geochemical variations at Kambalda are consistent with increasing degrees of contamination by rocks of the upper crust upward through the stratigraphic sequence (SLP < THK < DCB < PB), as the magmas gradually heated up their conduits, with only local contamination by interflow sulfidic sediments in the SLP member (Leshner & Arndt 1995).

Perseverance, Western Australia

The Perseverance Ultramafic Complex (PUC) occurs in the northern part of the 2.7 Ga Norseman–Wiluna Greenstone Belt in Western Australia (Barnes *et al.* 1988, 1995, 1999, Libby *et al.* 1998). It comprises a 2- to 3-km-wide \times 0.5-km-thick lens of adcumulate metadunite and mesocumulate metaperidotite (Dunite Lens: DL) that is underlain by a relatively thin Main

Mineralized Flow (MMF). These units occupy a broad embayment in the underlying and adjacent sequence of felsic fragmental metavolcanic rocks that is interpreted as a deformed thermomechanical erosion channel (Barnes *et al.* 1988, Williams *et al.* 1999, in press). The DL is flanked to the north and south by barren orthocumulate and spinifex-textured metakomatiites (PUN and PUS units). The Rocky's Reward ultramafic unit (RR) to the north is interpreted as an attenuated tectonic slice off the bottom of the PUC (Libby *et al.* 1998). The Ni–Cu–(PGE) mineralization at Perseverance occurs as variably tectonized stratiform massive – net-textured – disseminated sulfides within the MMF and adjacent country rocks, and as stratabound disseminated mineralization within the DL (Barnes *et al.* 1988, 1995, 1999, Libby *et al.* 1998), and has been interpreted on the basis of geological, stratigraphic, geochemical, and theoretical evidence to have been generated by incorporation of sulfur from the footwall rocks (Barnes *et al.* 1988, 1995, 1999, Williams *et al.* 1999, in press). All of the rocks and ores have been metamorphosed to middle amphibolite facies.

The majority of the analyzed metakomatiites at Perseverance define geochemical trends that are consistent with fractional crystallization from or accumulation of olivine into a parental magma containing ~32% MgO (Barnes *et al.* 1988, 1995). With a few isolated exceptions, the cumulate and non-cumulate rocks on the southern flank of the dunite lens (PUS) have normal Ni and PGE contents (Figs. 2a, b) and are depleted to enriched in HILE relative to MILE (Figs. 2c, d). Cumulate and non-cumulate rocks on the northern flank of the dunite lens (PUN) also have normal Ni and PGE contents (Figs. 2a, b), but are enriched in HILE relative to MILE (Figs. 2c, d). Cumulate rocks in the MMF and DL units are enriched in Ni and PGE (Figs. 2a, b) and are variably enriched in HILE relative to MILE (Figs. 2c, d). The abundances of HILE in the most magnesian adcumulate rocks in the DL are near or below detection limits, and are consequently more susceptible to metamorphic modification than those in less magnesian rocks.

The variations in incompatible elements at Perseverance are consistent with variable degrees of contamination by a component with a Th:Yb ratio similar to that in Archean or modern upper crust, but with a higher La:Sm ratio and lower Nb:Th ratio. Although the composition of the footwall felsic metavolcanic rocks has not been sufficiently characterized in terms of Nb and Th contents, their La:Sm ratio appears to be lower than in some of the ultramafic rocks. Unless the *LREE* enrichment can be attributed to metasomatic alteration or unless the two analyzed samples are not representative of the entire footwall sequence (which seems likely in any case), therefore, they are not sufficiently enriched to represent the contaminant. Additional geochemical work is planned to address this question.

Raglan, New Quebec

The Ni–Cu–(PGE) mineralization in the Raglan Formation of the Proterozoic Cape Smith Belt is hosted by a series of mesocumulate peridotite complexes that occur at or near the base of the Chukotat Group. It is overlain by (from base to top) olivine-, pyroxene-, and plagioclase-phyric basalts of the Chukotat Group, and underlain by pelitic metasediments and plagioclase-phyric basalts of the Povungnituk Group (Francis *et al.* 1983, St. Onge & Lucas 1994). Some of the mineralized complexes appear to represent channelized sheet-flows (*e.g.*, Cross Lake), whereas others appear to represent lava channels or very shallow sills with lateral “levee” facies breccias and peperites (Leshner 1999). Differentiated gabbro–peridotite sills that occur along the same contact (*e.g.*, Katinniq Gabbro) and within the upper part of the Povungnituk Group (identified here as North and South Claim sills) are less commonly mineralized and normally contain only subeconomic reef-style PGE mineralization (Giovenazzo *et al.* 1989; Thibert 1993). All of the rocks and ores have been metamorphosed to lower greenschist facies, but original textures and structures are extremely well preserved.

The komatiitic metabasalts, metapyroxenites, and metaperidotites in the east-central Cape Smith Belt define geochemical trends that are broadly consistent with fractional crystallization from or accumulation of olivine and minor magnesiochromite into a parental magma containing ~18% MgO (Francis *et al.* 1983, Burnham *et al.* 1999a, Leshner *et al.* 1999a). The most primitive komatiitic basalts have normal Ni and PGE contents (Figs. 3a, b) and are depleted in HILE relative to MILE (Figs. 3c, d). Most of the metaperidotites in mineralized units are enriched in Ni and PGE (Figs. 3a, b), consistent with the ubiquitous presence of finely disseminated sulfides, and enriched in HILE relative to MILE (Figs. 3c, d), consistent with contamination by rocks of the upper crust (or sediments derived from these, like those in the upper Povungnituk Group). Only a few samples from the Expo Ungava area south of the Raglan area and a “North Claim” sill in the upper part of the Povungnituk Group (in a repeated thrust slice) appear to be depleted in Ni (Figs. 3a). Most of the metaperidotites in unmineralized units have normal Ni and PGE contents (Figs. 3a, b) and are less enriched in HILE relative to MILE (Figs. 3c, d).

Thompson, Manitoba

The Thompson Nickel Belt (TNB) lies within the Manitoba section of the external zone of the Proterozoic Trans-Hudson Orogen (Bleeker 1990a, b) and comprises a cover sequence of multiply deformed and metamorphosed fine-grained clastic sedimentary rocks and silicate–sulfide facies iron-formations (Ospwagan Group) and komatiitic basaltic volcanic rocks (Bah Lake

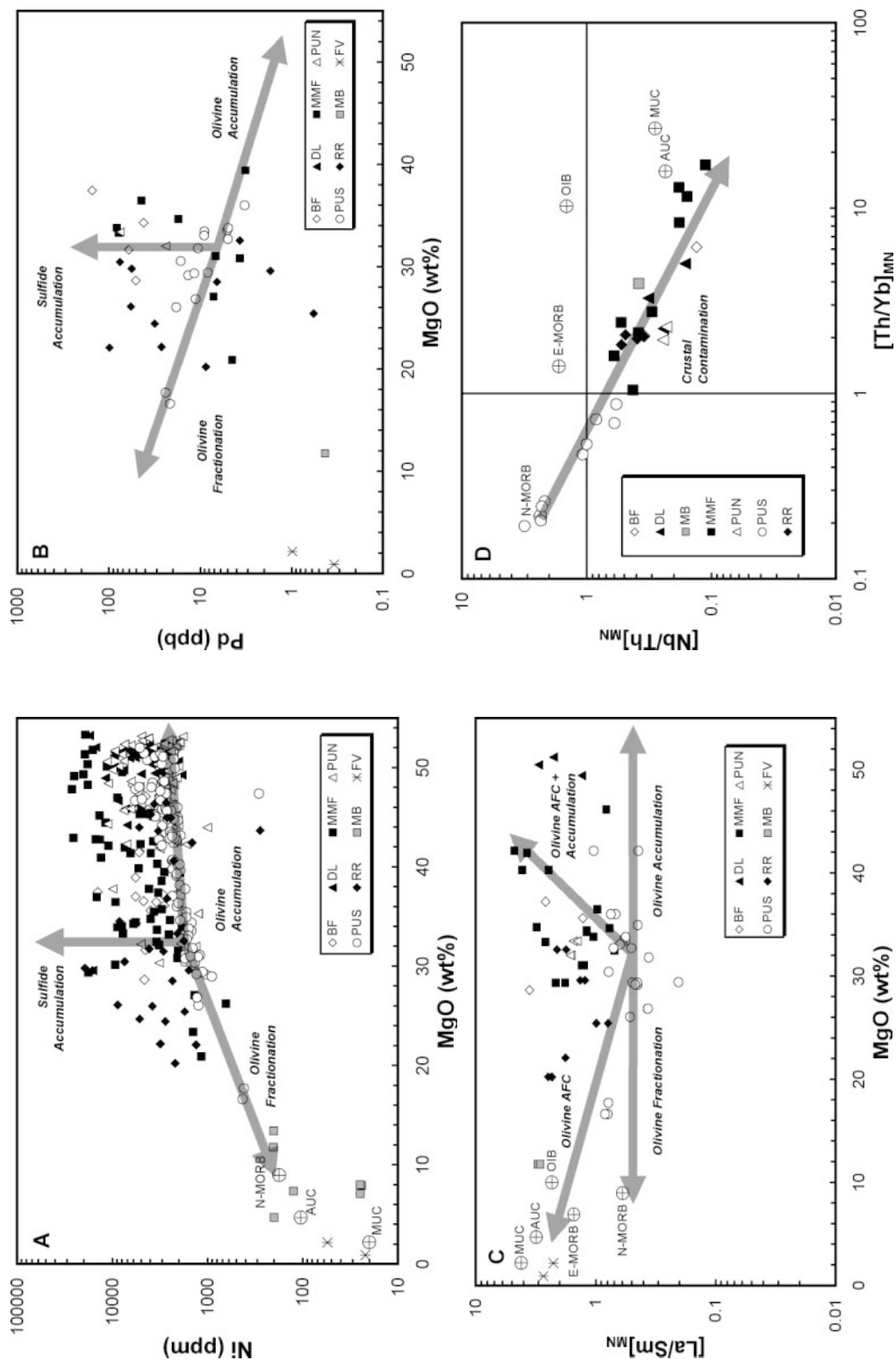


FIG. 2. Selected geochemical data for Perseverance (data from Barnes *et al.*, 1988, 1995, this study). A: Ni versus MgO; B: Pd versus MgO; C: [La/Sm]_{MN} versus MgO; D: [Nb/Th]_{MN} versus [Th/Yb]_{MN}. 60A: barren ultramafic body in footwall; BF: komatiite units underlying Dunitite Lens; MMF: Main Mineralized Flow underlying Dunitite Lens; PUS: Perseverance Ultramafic South; PUN: Perseverance Ultramafic North; RR: Rocky's Reward; FV: felsic metavolcanic rocks; MB: magnesian basalts. Other abbreviations and normalizing values are as in Figure 1.

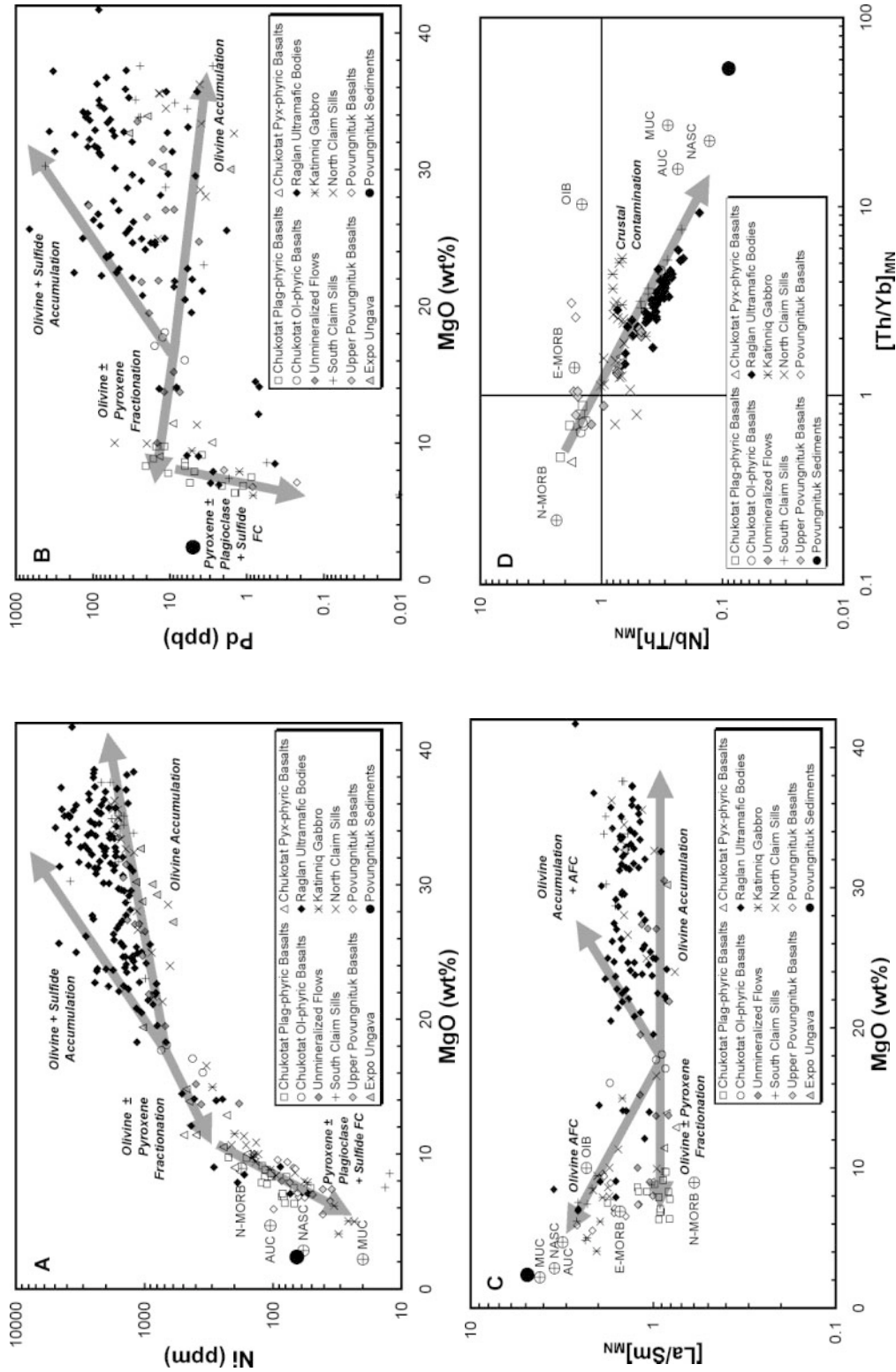


FIG. 3. Selected geochemical data for the Raglan area of the east-central Cape Smith Belt (data from Francis *et al.* 1983, Burnham *et al.* 1999a, in prep., Leshner *et al.* 1999a, this study). A: Ni versus MgO. B: Pd versus MgO. C: [La/Sm]_{MN} versus [Th/Yb]_{MN}. Chukotat Ol-, Px-, and Pl-phyric basalts; olivine-, pyroxene-, and plagioclase-phyric basalts overlying mineralized lava-channels; Raglan ultramafic bodies; mineralized komatiitic peridotite units; Unmineralized Flows: levee facies and thick layered flows overlying mineralized units; Katimniq Gabbro; thick gabbro unit underlying mineralized unit at Katimniq; North and South Claim Sills: structurally equivalent gabbro-peridotite sills intruded into slates in the upper part of the Povungnituk Group; Expo Ungava: small deposit in the central part of the Povungnituk Group, ~11 km south-southeast of the Donaldson deposit; Povungnituk basalts: high-Ti tholeiitic basalts underlying the Raglan Horizon. Other abbreviations and normalizing values are as in Figure 1.

Formation) that unconformably overlie Archean gneisses of the Superior Province (Bleeker & Macek 1996). The sedimentary rocks have been interpreted to have been deposited onto a subsiding rifted continental margin, and the overlying volcanic rocks have been interpreted to have erupted into relatively deep water. Komatiitic peridotite–dunite sills and granitic pegmatites have intruded throughout the basement and Proterozoic cover sequence, but the economic Ni–Cu–(PGE) sulfide mineralization in the TNB is associated with sills that have intruded at discrete stratigraphic levels, typically associated with sulfide-facies iron-formations of the Pipe Formation (Bleeker & Macek 1996). All of the rocks and ores have been metamorphosed to the middle to upper amphibolite facies, the sills are bouinaged, and the ores are strongly tectonized.

The komatiitic metabasalts, metaperidotites, and metadunites in the TNB define geochemical trends that are broadly consistent with fractional crystallization

from or accumulation of olivine (up to Fo₉₂) and minor magnesiochromite into a parental magma containing ~22% MgO. Pyroxenites from the Thompson mine and Ospwagan Lake ultramafic body define a separate trend reflecting accumulation of pyroxene. This is particularly evident on the Ni *versus* MgO diagram (Fig. 4a) in which pyroxene-rich cumulates exhibit low Ni concentrations that reflect at least in part their lower olivine contents, rather than Ni depletion owing to equilibration with sulfide. The cumulate rocks are variably enriched in Ni and PGE (Figs. 4a, b) and variably enriched in HILE relative to MILE (Figs. 4c, d), but are less enriched in Nb–Ta–Ti relative to elements of similar incompatibility, consistent with contamination by rocks of the upper crust or, more likely given the variability, local rocks derived from upper crust (*i.e.*, pelites and iron-formations of the Pipe Formation). Although the ultramafic sills have previously been interpreted to represent feeders for the overlying komatiitic basaltic vol-

TABLE 3. AMOUNT OF SULFIDES PRODUCED, ORE TENOR, ORE GEOCHEMICAL CHARACTERISTICS ($\delta^{34}\text{S}$, $^{206}\text{Pb}/^{204}\text{Pb}^\ddagger$, γ_{Os}), APPARENT DEGREE OF LAVA CONTAMINATION, LAVA GEOCHEMICAL CHARACTERISTICS (ϵ_{Nd} and ϵ_{Sr}), AND DEGREE OF CHALCOPHILE ELEMENT DEPLETION IN TERMS OF FLOW DURATION AND FLOW RATE FOR A HIGH-MG KOMATIITE SYSTEM[‡].

	Higher Flow Rate	Intermediate Flow Rate	Lower Flow Rate
Longer Flow Duration	Larger amount of sulfides Higher ore tenor Mantle $\delta^{34}\text{S}$, $^{206}\text{Pb}/^{204}\text{Pb}$, γ_{Os}	Larger amount of sulfides Intermediate ore tenor Mantle $\delta^{34}\text{S}$, crustal $^{206}\text{Pb}/^{204}\text{Pb}$, γ_{Os}	Larger amount of sulfides Lower ore tenor Crustal $\delta^{34}\text{S}$, $^{206}\text{Pb}/^{204}\text{Pb}$, γ_{Os}
	Minor contamination Mantle ϵ_{Nd} and ϵ_{Sr}	Intermediate contamination Crustal ϵ_{Nd} and ϵ_{Sr}	Strong contamination Crustal ϵ_{Nd} and ϵ_{Sr}
	Minor PGE depletion	Intermediate PGE depletion	Strong PGE depletion
Intermediate Flow Duration	Intermediate amt. sulfides Higher ore tenor Mantle $\delta^{34}\text{S}$, $^{206}\text{Pb}/^{204}\text{Pb}$, γ_{Os}	Intermediate amt. sulfides Intermediate ore tenor Mantle $\delta^{34}\text{S}$, crustal $^{206}\text{Pb}/^{204}\text{Pb}$, γ_{Os}	Intermediate amt. sulfides Lower ore tenor Crustal $\delta^{34}\text{S}$, $^{206}\text{Pb}/^{204}\text{Pb}$, γ_{Os}
	Minor contamination Mantle ϵ_{Nd} and ϵ_{Sr}	Intermediate contamination Crustal ϵ_{Nd} and ϵ_{Sr}	Strong contamination Crustal ϵ_{Nd} and ϵ_{Sr}
	Minor PGE depletion	Intermediate PGE depletion	Strong PGE depletion
Shorter Flow Duration	Smaller amount of sulfides Higher ore tenor Mantle $\delta^{34}\text{S}$, $^{206}\text{Pb}/^{204}\text{Pb}$, γ_{Os}	Smaller amount of sulfides Intermediate ore tenor Mantle $\delta^{34}\text{S}$, crustal $^{206}\text{Pb}/^{204}\text{Pb}$, γ_{Os}	Smaller amount of sulfides Lower ore tenor Crustal $\delta^{34}\text{S}$, $^{206}\text{Pb}/^{204}\text{Pb}$, γ_{Os}
	Minor contamination Mantle ϵ_{Nd} and ϵ_{Sr}	Intermediate contamination Crustal ϵ_{Nd} and ϵ_{Sr}	Strong contamination Crustal ϵ_{Nd} and ϵ_{Sr}
	Minor PGE depletion	Intermediate PGE depletion	Strong PGE depletion

[†] $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ should behave similarly.

[‡] Geochemical and isotopic characteristics will differ in other areas depending on elemental abundances and isotopic ratios, and may be modified by alteration.

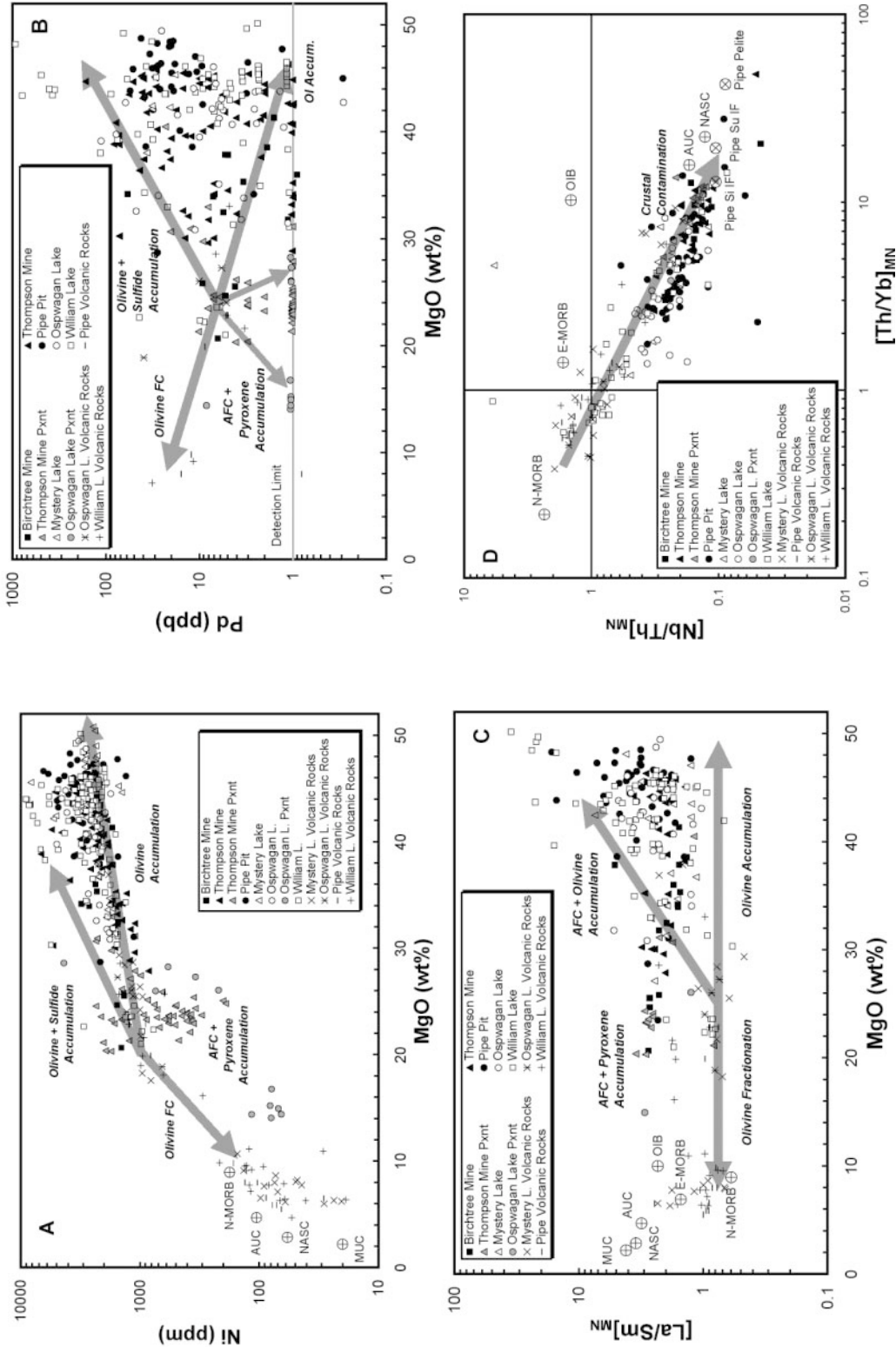


FIG. 4. Selected geochemical data for the Thompson Nickel Belt (data from Burnham *et al.* 1999b, in prep., Leshar *et al.* 1999a, this study; L. Hulbert, unpubl.). A: Ni versus MgO. B: Pd versus MgO. C: [La/Sm]_{MN} versus MgO. D: [Nb/Th]_{MN} versus [Th/Yb]_{MN}. Solid symbols: mineralized ultramafic bodies; open symbols: unmineralized basalts and picrites; grey symbols: pyroxenites in ultramafic bodies; crosses and dashes: basalts and picrites of the Bah Lake Formation. Other abbreviations and normalizing values are as in Figure 1.

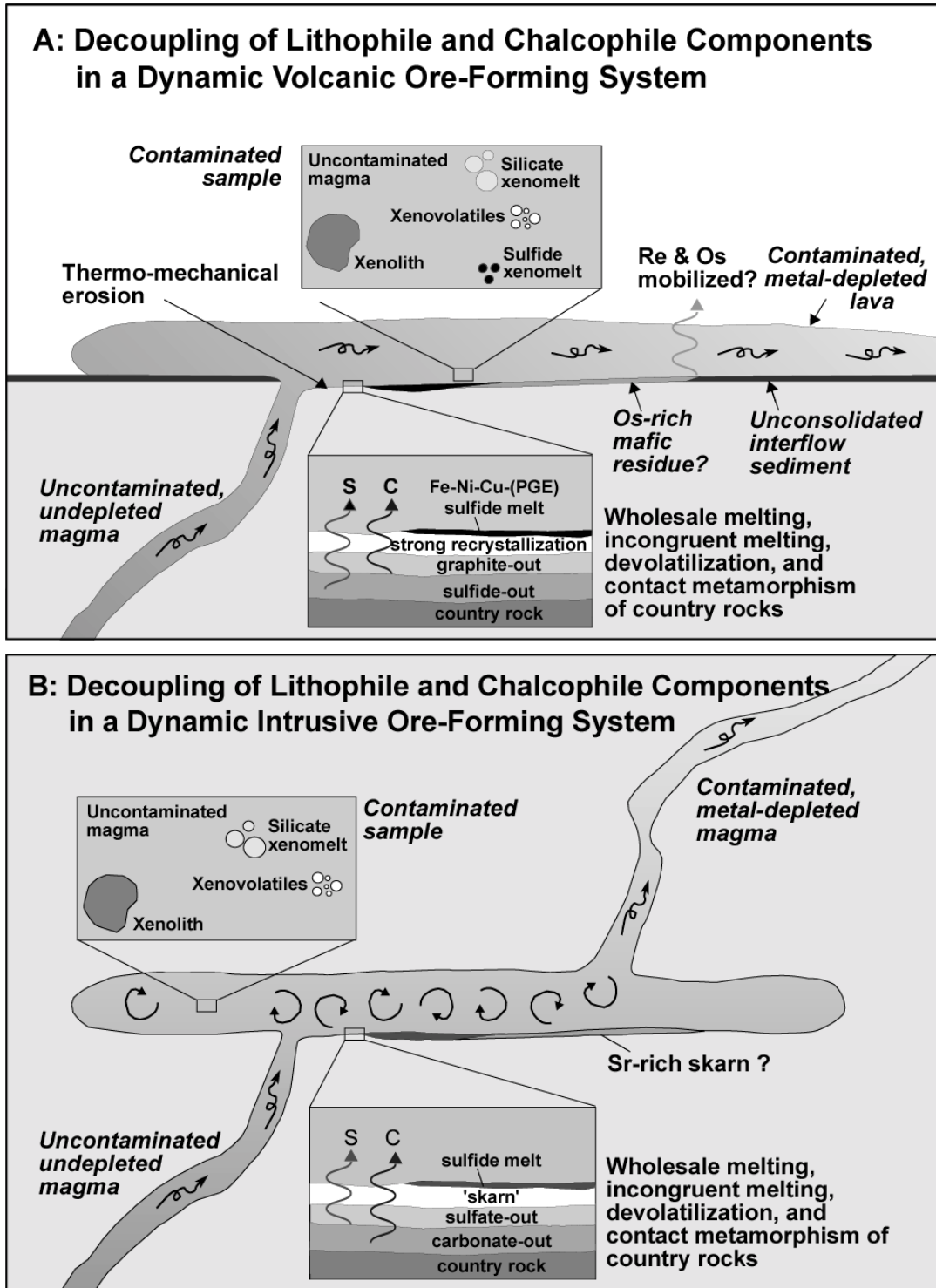


FIG. 5. A. Volcanic thermal-mechanical erosion model for komatiite-associated Ni-Cu-(PGE) deposits. B. Subvolcanic thermal-mechanical erosion model for komatiite-associated Ni-Cu-(PGE) deposits (both adapted from Lesher *et al.* 1999a).

canic rocks, the basalts appear to be derived from less magnesian magmas (up to 15% MgO), are neither enriched in HILE nor depleted in chalcophile elements, as would be expected if they were cogenetic with the mineralized sills (Burnham *et al.* 1999b).

DISCUSSION

Prevailing models for the genesis of extrusive komatiite-associated Ni–Cu–(PGE) deposits (see re-

views by Lesher 1989, Lesher & Stone 1996, Barnes *et al.* 1999, Lesher *et al.* 1999a, b, Lesher & Burnham 1999, 2001) involve melting of sulfidic footwall rocks to form 1) a silicate melt that is normally, but not invariably (Frost & Groves 1989), miscible and mixed into the komatiite lava, 2) local mafic residues (preserved as mafic “metasediments” and massive chloritites adjacent to the lava channels at Kambalda, as xenoliths or skarns in other types of deposit: see Lesher & Burnham 1999, 2001), and 3) sulfide ores (localized in footwall

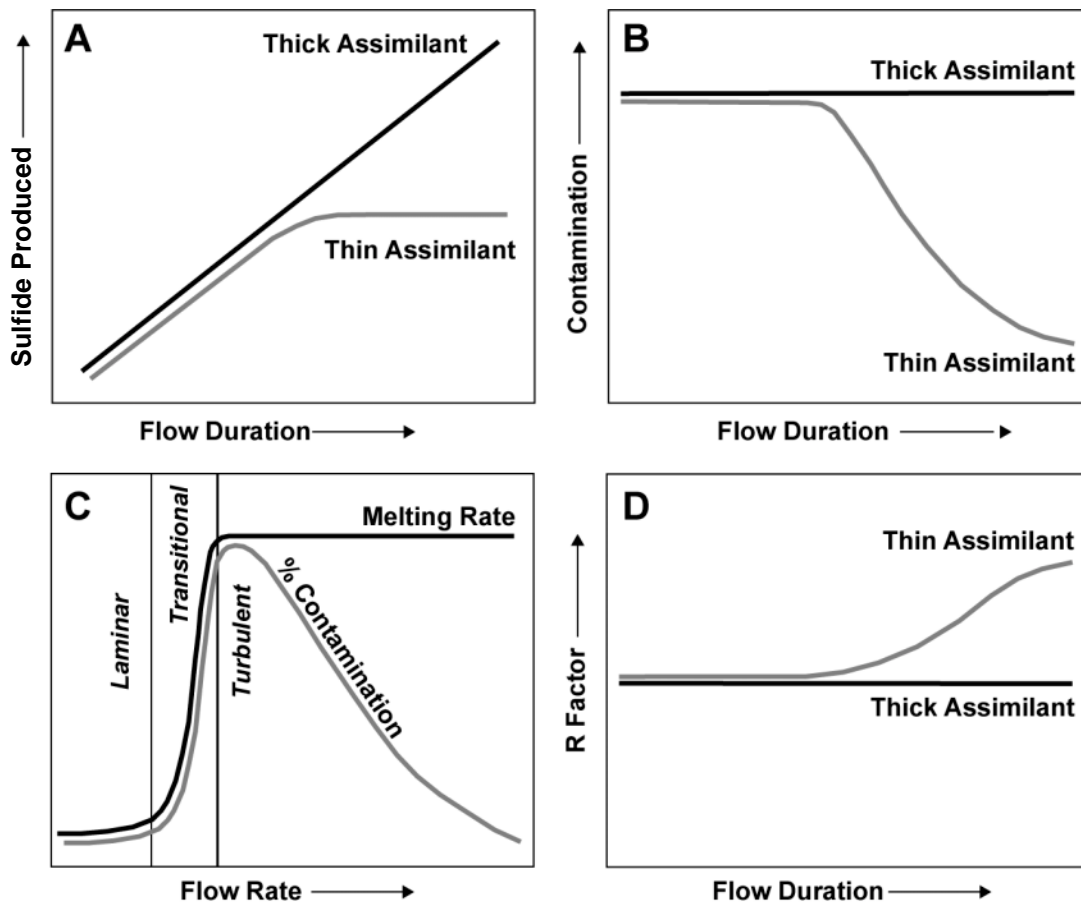


FIG. 6. A. Schematic diagram illustrating amount of sulfide produced as a function of duration of lava flow for a thin S-bearing assimilant overlying a refractory substrate (*e.g.*, interflow sediment) and a thick S-bearing assimilant (*e.g.*, thick sediment or felsic volcanic rock), assuming all else equal. B. Schematic diagram illustrating degree of contamination as a function of duration of lava flow for a thin assimilant overlying a refractory substrate (*e.g.*, interflow sediment) and a thick assimilant (*e.g.*, thick sediment or felsic volcanic rock), assuming all else equal. C. Schematic diagram illustrating the degree of substrate melting and percent contamination of the lava as a function of rate of flow of lava. The melting rate and degree of contamination are low at low rates of flow, owing to the presence of a lower laminar boundary-layer. Both increase during the transition to turbulent flow and peak as fully turbulent flow is reached. However, at higher flow rates the melting rate remains relatively constant and the degree of contamination declines at higher flow-rates. D. Schematic diagram illustrating change in magma:sulfide mass ratio (R factor) as a function of duration of lava flow for a thin assimilant overlying a refractory substrate (*e.g.*, interflow sediment) and a thick assimilant (*e.g.*, thick sediment or felsic volcanic rock), assuming all else equal.

embayments) (Fig. 5a). Similar models can be developed for intrusive komatiite-associated Ni–Cu–(PGE) deposits such as Thompson and possibly Namew Lake, Manitoba (Fig. 5b), as well as intrusive Ni–Cu(PGE) deposits associated with basaltic magmas such as Duluth and Noril'sk (Thériault & Barnes 1998, Lightfoot & Naldrett 1999, Naldrett & Lightfoot 1999).

There is no systematic correlation between the degrees of contamination (*e.g.*, *LREE* enrichment, Nb depletion) and depletion in chalcophile elements in studies of this type (*e.g.*, Barnes *et al.* 1995, Lesher & Arndt 1995, Perring *et al.* 1996, this study). For example, the Paringa Basalt at Kambalda is interpreted to be contaminated by up to 30% upper crust (Lesher & Arndt 1995), but is undepleted in PGE (Redman & Keays 1985), indicating that contamination by itself is not sufficient to induce sulfide saturation in komatiitic magmas. Importantly, the non-cumulate portions of the sheet-flow facies at Kambalda are weakly contaminated (Lesher & Arndt 1995), but significantly depleted in Ni and PGE (Fig. 1), indicating that these rocks (and only these rocks) equilibrated with sulfides. The amounts of contamination and PGE depletion produced during this process depend on several factors: 1) the stratigraphic architecture of the system (*e.g.*, thickness and physical accessibility of the contaminant), 2) the fluid dynamics and thermodynamics of the lava or magma, 3) the physical, chemical, and thermal characteristics of the contaminant, 4) the amount of contaminant melted and incorporated (*e.g.*, the amount of silicate partial melt: see Lesher & Burnham 1999, 2001), 5) the sulfur and metal content of the contaminant, 6) the initial sulfide-saturation state of the magma, 7) the assimilation: crystallization ratio, 8) the amount of lava replenishment, and 9) the effective magma:sulfide ratio (*R* factor) of the system. Because these processes vary independently from deposit to deposit, from area to area within a deposit, and within a single area with time, there are many opportunities to decouple contamination from depletion in chalcophile elements.

For example, with all else equal (*e.g.*, S content of assimilant), the amount of sulfide produced (Fig. 6a) increases relatively linearly if the assimilant is thick or continuously accessible (*e.g.*, Perseverance, Raglan, Thompson), but increases to a fixed plateau if it is thin (*e.g.*, Kambalda) or inaccessible. Similarly, with all else equal, the amount of contamination (Fig. 6b) remains relatively constant if the substrate is thick and continuously accessible (*e.g.*, Perseverance, Raglan, Thompson), but decreases if it is thin (*e.g.*, Kambalda) or inaccessible. The rate of melting and amount of contamination vary with flow rate (Fig. 6c); because the rate of thermal erosion is dependent primarily on the rate of heat conduction into the substrate or wall rock (Huppert & Sparks 1985, Williams *et al.* 1998, 1999, *in press*), which reaches a maximum as fully turbulent flow is reached, the melting rate is relatively constant at moderate to high flow-rates, but the amount of contamina-

tion is higher at moderate flow-rates than it is at high flow-rates. This is simply a function of dilution. Finally, because the amount of sulfides produced will vary with flow duration and accessibility of the assimilant (Fig. 6a), the magma:sulfide ratio may also vary with flow duration (Fig. 6d), resulting in some cases in dissolution of sulfide (Lesher & Campbell 1993, Lesher & Stone 1996, Lesher & Burnham 1999, 2001).

There are many other factors that may also result in decoupling of contamination and depletion in chalcophile elements. For example, because komatiites are so strongly undersaturated in sulfide (Keays 1982, 1995), a considerable amount of contamination may occur in komatiites before they reach sulfide saturation (Lesher & Groves 1986, Lesher & Stone 1996), which means that an increase in the proportion of felsic components (Irvine 1977, Naldrett 1989) is not as viable a process for inducing sulfide saturation in komatiitic systems as it is in mafic systems. Another factor is that sulfide liquids (produced by either melting of the sulfide component of the substrate or exsolution from the magma) are normally immiscible and rapidly deplete the lava in chalcophile elements owing to their very high $D^{\text{sil/liq}}$, whereas silicate xenomelts (produced by melting of the silicate component of the substrate) are normally miscible, but in some cases immiscible, and have less effect on the composition of the lava owing to their lower $D^{\text{sil/liq}}$. The net result is that the amount of sulfides produced (the potential size of the ore deposit), the tenor of the sulfide ores (as a consequence of different *R* factors), and the geochemical characteristics of the lava (amount of apparent contamination) do not necessarily correlate with each other (Table 3).

The best ore deposits, *i.e.*, those with the highest grades, highest tenors, and largest masses, are probably produced at relatively high flow-rates during long eruptions. Ironically, this is also the situation where geochemical evidence indicative of the ore-forming process (contamination, depletion in the PGE) is most likely to be obscured.

These factors may explain the different locations of contaminated, chalcophile-element-depleted lavas in the areas considered (Table 2): the thin (originally ~3 m) interflow sediments at Kambalda would normally have been completely eroded upstream, exposing refractory basaltic or komatiitic substrates (depending on stratigraphic position), whereas the very thick (~1 km) felsic fragmental substrate at Perseverance, the very thick (~1 km) semipelitic sediments at Katinniq, and the thick (up to tens of m) semipelitic sediments and thin (up to 10 m), albeit very sulfide-rich (up to 100%), iron-formations at Thompson would have been continuously available for erosion (Figs. 7, 8).

The application of chalcophile-element depletion in mineral exploration depends on the scale and location of the depletion (adapted from Lesher & Stone 1996):

- 1) The identification of an entire volcanic *sequence* that is contaminated or depleted in chalcophile elements

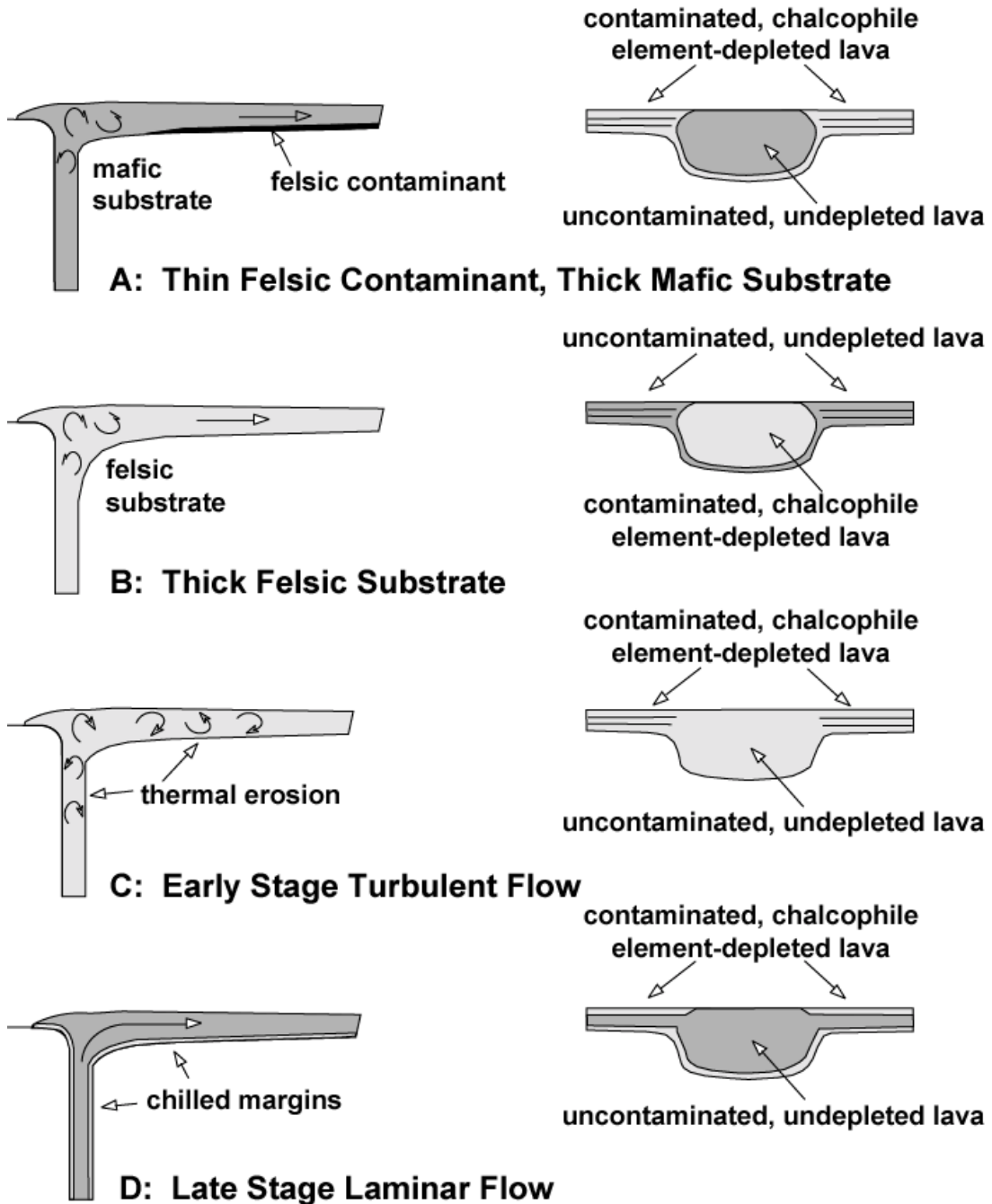


FIG. 7. Influence of nature and thickness of substrate and lava-replenishment processes on the distribution of contaminated lavas (adapted from Leshner & Arndt 1995, Leshner & Stone 1996, Leshner *et al.* 1999a). A. Thin felsic assilant, refractory mafic substrate (*e.g.*, Kambalda). B. Thick assilant (*e.g.*, Perseverance, Raglan, Thompson). C. Early-stage turbulent flow. D. Late-stage laminar flow (*cf.* Figure 6).

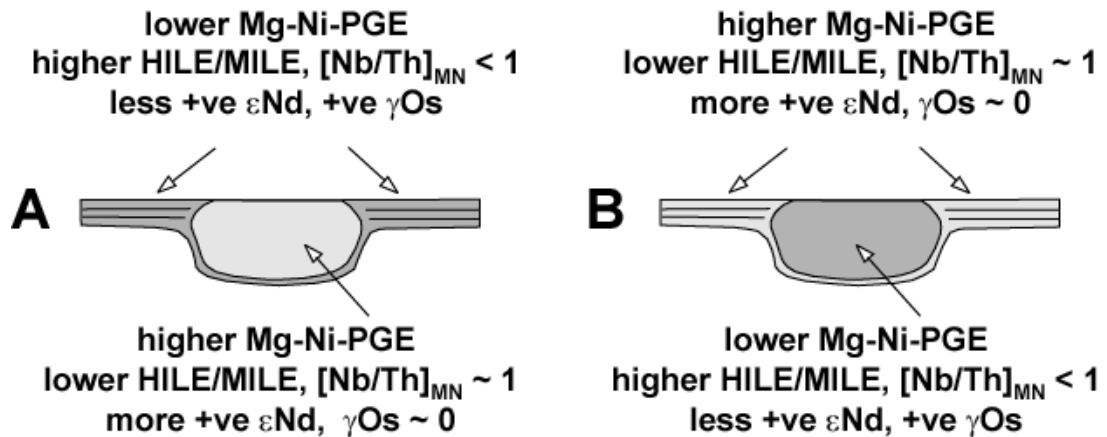


FIG. 8. Geochemical facies resulting from differences in the nature and thickness of the substrate (adapted from Leshner & Stone 1996, Leshner *et al.* 1999a; *cf.* Figure 7). A. Uncontaminated lava channel (*e.g.*, Kambalda), B. Contaminated lava channel (*e.g.*, Perseverance, Raglan, Thompson).

(or both) indicates that contamination or sulfide segregation (or both) occurred prior to eruption, probably during ascent through the crust or during processing in a magma chamber in the deep crust. It is unlikely that an entire sequence of lavas would have been erupted through a high-level magma chamber. The sulfides that segregated at this stage would have been most likely lost, owing to their very high density, very low viscosity, and very high surface-tension and the low viscosity of the komatiitic magmas, which would facilitate coalescence and settling of sulfides (Leshner & Groves 1986). Furthermore, any sulfides that formed during later stages would be depleted in chalcophile elements (Campbell & Naldrett 1979). Thus, this geological environment is probably less favorable than those below.

2) The identification of a specific volcanic stratigraphic unit (cooling unit) that is contaminated and depleted in chalcophile elements within a sequence of otherwise uncontaminated, chalcophile-element-undepleted lavas indicates that contamination and sulfide segregation occurred at a specific stage of the eruptive event or within a specific part of the plumbing system. It is more likely that this process occurred at higher levels in the system, perhaps even within the volcanic system. However, sulfide segregation could have occurred in a low-level magma chamber or kilometers upstream from the analyzed location. This situation is more favorable than the one above, but less favorable than the one below.

3) The identification of a zone or facies of a cooling unit that is contaminated and depleted in chalcophile elements within a unit of otherwise uncontaminated, chalcophile-element-undepleted lavas indicates that contamination and sulfide segregation occurred within

that specific unit. This geological environment is more favorable than those above.

Most studies of this type indicate that the majority of the lavas, especially those interpreted to represent parental magmas, are *not* depleted in chalcophile elements. In other words, they did not equilibrate with a sulfide (or metal) phase in the mantle source-region and did not exsolve a sulfide (or metal) phase during ascent or eruption (Keays 1982, Leshner & Groves 1986, Naldrett & Barnes 1986, Keays 1995, Leshner & Stone 1996). The observation that depletion in chalcophile elements is observed only in parts of the host units, stratigraphically correlated with Ni–Cu–(PGE) mineralization, indicates unequivocally that sulfide saturation occurred “locally”, upstream from the present ore zones, not in a subsurface magma chamber.

In the case of Kambalda, where the most likely contaminant is a thin (originally ~3 m) sulfidic interflow sediment overlying a refractory basaltic or komatiitic substrate, the identification of a zone of contaminated, chalcophile-element-depleted lavas within a unit of otherwise uncontaminated, chalcophile-element-undepleted lavas indicates that contamination and sulfide segregation must have occurred locally. In the case of Perseverance, Raglan, and Thompson (and probably also Noril’sk, Russia and Voisey’s Bay, Labrador), where the most likely contaminants are thick sequences of sediments or felsic volcanoclastic rocks, the identification of large units of contaminated, chalcophile-element-enriched lavas associated with zones of uncontaminated, chalcophile-element-undepleted lavas indicates that contamination and sulfide segregation occurred locally, although there is less certainty that the units are related. In all cases, the contamination and ore-forming pro-

cesses may have occurred a significant distance “upstream” from the present ore zones.

The physical volcanological environment is the major control on whether or not contaminated or chalcophile-element-depleted lavas are preserved. Contaminants drawn into rapidly and turbulently flowing channel-flow facies, regardless of whether extrusive or intrusive, are more likely to be assimilated, dispersed, and diluted. Furthermore, because the host units in stratiform deposits crystallize from lavas that were emplaced after the mineralizing event, they may be chemically and genetically unrelated to earlier lavas, which is clearly the case at Kambalda (Leshner *et al.* 1984, Leshner & Arndt 1995), Perseverance (Barnes *et al.* 1988, 1995), and Katinniq (Burnham *et al.* 1999a). Contaminants drawn into less rapidly and less turbulently flowing sheet-flow facies, regardless of whether intrusive or extrusive, are more likely to be preserved, but they do not necessarily have to be preserved. The point is that the presence of contaminated or chalcophile-element-depleted rocks may be regarded as a positive indicator of favorable ore-forming processes. However, the absence of such rocks should not be regarded as a negative indicator.

Other methods of discrimination

Several other geochemical and mineralogical methods of discrimination have been used to distinguish between mineralized and unmineralized komatiites (see reviews by Leshner 1989, Naldrett 1989, Leshner & Stone 1996), including Zn in chromian spinel, Ni in olivine, Al–Fe–Mg–Ni in whole rocks, and Ni–Cr in whole rocks. These methods seem to be less reliable than those described in this paper, but some may be useful in certain situations.

Zn enrichment in chromian spinel (*e.g.*, Groves *et al.* 1977) may be a useful tool for exploration in areas where the contaminant is enriched in Zn relative to the magma and where metamorphic grades are low. However, not all contaminants are enriched in Zn, chromian spinel commonly re-equilibrates with the intercumulus liquid during cooling, and Zn has been mobile in many cases during metamorphism. For example, H. Papunen (pers. commun., 1996), Baird (1999), and Barnes (2000) have shown that Zn is commonly added to chromian spinel during low-temperature alteration and further concentrated in the core of grains during prograde metamorphism. Thus, highly Zn-enriched chromian spinel, as at Widgiemooltha and Kambalda (see discussion by Barnes 2000), may result from proximity to sedimentary Zn sources during metamorphism and may not necessarily result from igneous processes.

Ni depletion in olivine occurs as part of the chalcophile-element-depletion process affecting the whole rock (Duke & Naldrett 1978, Leshner & Burnham 1999, 2001) and may be a useful tool for exploration in areas where it is preserved. Although olivine is suscep-

tible to post-cumulus or metamorphic modification and is commonly pervasively serpentinized, Ni is relatively immobile on the hand-sample scale in olivine cumulate rocks (Donaldson 1981). The level of Ni in olivine thus can be estimated from whole-rock analytical data. For example, an extensive Ni depletion halo was identified in the lower part of the Perseverance dunite body, both in modified igneous olivine compositions and in whole-rock elemental data (Barnes *et al.* 1988). Such haloes are a feature of large mineralized flow systems at low R factors.

Whole-rock Al–Fe–Mg–Ni (Leshner & Groves 1984, Leshner 1989) and Cr–Ni–Mg variations (Woolrich & Giorgetta 1978, Leshner & Stone 1996, Barnes & Brand 1999) may aid in the identification of channel-flow facies that are more likely to host Ni–Cu–(PGE) mineralization than sheet-flow, lava-pond, or lava-lobe facies. This is because channel-flow facies rocks normally crystallize from more magnesian lavas or from magmas that, if komatiitic, are more likely to a) be undersaturated in magnesiochromite, b) crystallize more magnesian olivine, and c) accumulate larger amounts of olivine, than those in sheet-flow, lava-pond, or lava-lobe facies. However, these processes are not directly related to ore genesis; not all high-Mg, low-Cr cumulate rocks are mineralized, and any mafic magma more evolved than ~20% MgO will be saturated in chromian spinel (Murck & Campbell 1986) and will produce Cr-rich cumulate rocks (see discussion by Leshner & Stone 1996). A further complication is that high-Mg channel-flow facies as a group exhibit a wide range of Cr contents that reflect a) the kinetics of crystallization of the chromian spinel (Barnes 1998) or b) accumulation of olivine then olivine + chromian spinel from lavas that fractionated and became saturated in chromian spinel *during* crystallization (Leshner & Stone 1986), or c) both. These complications have been discussed by Barnes & Brand (1999), who showed that mineralized komatiite sequences on average have substantially lower Cr contents and Cr:Ni ratios than unmineralized sequences, but that there is no systematic difference between barren and mineralized units from the same flow environment.

The presence of sulfides is a very reliable indicator of sulfide saturation, but many sulfide-saturated cumulate rocks are non-economic, and the absence of sulfides does not necessarily indicate that the unit did not form an ore deposit. Although lavas or magmas that have achieved sulfide saturation will normally continue to exsolve a sulfide liquid as they cool, crystallize, and oxidize (see review by Naldrett 1989), continued flowage through the lava channels may drive the lava or magma away from sulfide saturation, leaving essentially barren cumulate rocks over the ore zones. For example, at many of the Kambalda shoots (Leshner *et al.* 1984, Leshner 1989), at Perseverance (Barnes *et al.* 1988, 1995), and at Digger Rocks (Perring *et al.* 1995), sulfide-bearing cumulates are overlain by sulfide-free cumulates in the same lava channel, indicating that the lava

evolved from sulfide-saturated to sulfide-undersaturated during the eruption. The later lavas flowed over a bed of early-formed cumulates and flushed out the earlier sulfide-saturated, contaminated lavas. The resulting cumulates retain no trace of the mineralizing processes. Thus in some areas, contaminated lavas may be preserved in close proximity to the ores (Perseverance: Barnes *et al.* 1995; Digger Rocks, Perring *et al.* 1995; Raglan: this study), in some areas they may only be preserved in lateral flanking facies (*e.g.*, Kambalda: Leshner & Arndt 1995), and in some areas they may not be preserved at all (*e.g.*, parts of the Thompson Nickel Belt: this study). These complexities must be considered when interpreting komatiite geochemistry, which must always be viewed from the standpoint of physical volcanology.

CONCLUSIONS

The signatures indicative of crustal contamination and chalcophile-element-depletion reviewed in this paper and discussed in several chapters of Keays *et al.* (1999) vary in nature and degree from environment to environment, but they support current models for the generation of Ni–Cu–(PGE) sulfide deposits in lava channels and magma conduits (Leshner 1989, Naldrett 1989, Leshner & Stone 1996, Naldrett 1999). The restriction of contamination to specific facies of the lava channels and magma conduits, or to specific lavas derived from those units, indicates that crustal contamination or sulfide segregation (or both) occurred locally, and that the processes of devolatilization, melting, and incorporation of crustal rocks were an integral part of the ore-forming process. Provided that these geochemical signatures are interpreted and applied within the context of the geological controls reviewed in this paper, they provide important information relevant to mineral exploration for magmatic Ni–Cu–(PGE) sulfide deposits.

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