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# BEHAVIOR OF THE PLATINUM-GROUP ELEMENTS DURING DIFFERENTIATION OF THE NORTH MOUNTAIN BASALT, NOVA SCOTIA

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## ABSTRACT

Differentiated rocks in thick flows of the Jurassic North Mountain Basalt, Nova Scotia, display evidence for fractionation of noble metals (Au, Pd, Pt, Rh, Ru, and Ir). Meter-thick layers of mafic pegmatite and vesicular basalt high in the flows are enriched in Au and Pd but depleted in Pt, Rh, Ru and Ir relative to undifferentiated basalt. Mineral precipitation (*e.g.*, chromite removal) cannot explain Au and Pd enrichment and Pt depletion in the mafic pegmatites. The fractionation pattern may reflect the early movement and concentration of chloride-bearing hydrothermal solutions associated with rising plumes of vesicles only months after extrusion. On average, basalts with orthopyroxene show Pd and Au depletions and Pt, Rh, Ru and Ir enrichments relative to undifferentiated basalt, but there are large differences in concentration of individual noble metals between samples. This intersample variability, resulting in Pt/Pd fractionation, could reflect noble-metal-bearing micro-inclusions in orthopyroxene. "Rhyolite" bands derived from the mafic pegmatites, possibly through silicate liquid immiscibility, contain the lowest concentrations of noble metals in the flows. Some "rhyolite" samples show Ir enrichment, potentially reflecting selective carrying capacity for magmatic fluids segregated from the "rhyolite" or, if the "rhyolites" formed through silicate liquid immiscibility, preferential partitioning of Ir into the siliceous liquid. These findings, and previous studies of other Mesozoic mafic rocks from the eastern U.S., indicate that the incompatible behavior of Pd and Au can result in substantial increases in concentration of these noble metals in the upper reaches of thick flows and intrusions.

*Keywords:* tholeiitic basalt, Jurassic, eastern North America, "rhyolite", platinum-group elements, differentiation, volatile phase, liquid immiscibility, North Mountain Basalt Formation, Nova Scotia.

## SOMMAIRE

Les roches différenciées des coulées basaltiques épaisses de la formation de North Mountain, en Nouvelle-Ecosse, d'âge jurassique, ont subi les effets d'un fractionnement en métaux nobles (Au, Pd, Pt, Rh, Ru et Ir). Les niveaux de pegmatite mafique et de basalte vésiculaire, dont l'épaisseur est à l'échelle du mètre et la position est dans la partie supérieure des coulées, sont enrichis en Au et Pd, et appauvris en Pt, Rh, Ru et Ir par rapport aux roches basaltiques primitives. Le fractionnement de minéraux, par exemple la chromite, ne pourrait expliquer l'enrichissement en Au et Pd des échantillons de pegmatite mafique, et leur appauvrissement en Pt. Par contre, ces tendances pourraient résulter du mouvement précoce et de la concentration de saumures associées avec l'ascension de bulles à peine quelques mois après l'extrusion. En moyenne, les échantillons de basalte à orthopyroxène sont appauvris en Pd et Au, et enrichis en Pt, Rh, Ru et Ir, par rapport aux échantillons de basalte primitif, mais nous documentons des différences importantes sélectives d'un échantillon à l'autre. Cette variabilité, qui est à l'origine d'une séparation de Pt et Pd, pourrait résulter de micro-inclusions contenant la suite de métaux nobles dans l'orthopyroxène. Des niveaux "rhyolitiques" dérivés de la pegmatite mafique, peut-être par immiscibilité du liquide siliceux, contiennent les plus faibles concentrations des métaux nobles. Certains échantillons "rhyolitiques" témoignent d'un enrichissement sélectif en Ir, et donc peut-être d'une capacité sélective de transfert dans une phase fluide magmatique ou, dans le cas d'une origine par immiscibilité, d'une répartition préférentielle de l'iridium dans le liquide siliceux. Ces résultats, et ceux d'études comparables de suites mafiques mésozoïques de l'est des Etats-Unis, montrent que le comportement incompatible de Pd et Au pourrait causer un enrichissement subtantiel de ces métaux nobles dans les parties supérieures de coulées épaisses et de massifs intrusifs.

(Traduit par la Rédaction)

*Mots-clés:* basalte tholéiitique, jurassique, est de l'Amérique du Nord, "rhyolite", éléments du groupe du platine, différenciation, phase volatile, immiscibilité liquide, Formation de basaltes de North Mountain, Nouvelle-Ecosse.

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## INTRODUCTION

The North Mountain Basalt sequence borders shores of the Bay of Fundy in Atlantic Canada and provides an example of continental flood-basalt volcanism associated with Jurassic rifting between northern Africa and eastern North America (Wark & Clarke 1980; Fig. 1). The basalts have attracted considerable attention as a natural laboratory for igneous processes during a major rifting event. Several authors used them to study crustal assimilation (Dostal & Dupuy 1984, Greenough *et al.* 1989). Others used this episode of volcanism to place constraints on the time of rifting as well as the absolute age of the Triassic–Jurassic boundary (Hodych & Dunning 1992).

In contrast to other flood-basalt sequences, which can be thousands of meters in thickness, the North Mountain Basalt sequence is merely a few hundred meters thick (White 1989, Papezik *et al.* 1988). However, two of the lava flows are amongst the largest known individual flows on earth, with dimensions of ~0.2 km × 100 km × 230 km (Greenough & Papezik 1987). As a result of their thickness, these two flows underwent substantial differentiation. Bowen (1917) recognized the utility of studying these rocks to help identify igneous processes that are masked where cooling is slower, as in gabbroic intrusions. These basalts preserve evidence of crystal settling, silicate liquid immiscibility and volatile movement during the differentiation of the mafic magma (Papezik *et al.* 1988, Greenough & Dostal 1992a, b).

The mechanisms controlling differentiation in the North Mountain Basalt sequence may not be well understood. However, the cooling regime for lava flows can be closely constrained; as a result, the time when various processes of differentiation occurred is reasonably well known (Greenough & Dostal 1992b). "Rhyolite" bands within the basalts demonstrate that substantial differentiation occurred (Greenough & Dostal 1992a). The basalts thus provide an opportunity to study the effects of magma differentiation on elements like the platinum-group elements (PGE), whose behavior during magma evolution is not well understood (Crocket 1981, Brügmann *et al.* 1987, Fryer & Greenough 1992). Similar outpourings of mafic magma in the U.S. demonstrate that differentiation mechanisms can enrich specific PGE more than ten-fold (Gottfried & Froelich 1988).

In this paper, we report on the PGE concentrations in various rock types from the North Mountain Basalt sequence. These data allow us to comment on the effects of differentiation on PGE concentrations.

## GEOLOGY AND SAMPLING

The Jurassic (202 ± 1 Ma: Hodych & Dunning 1992) North Mountain Basalt Formation consists of a 150- to 200-m-thick lower flow separated from an upper flow of similar thickness by a 50-m-thick middle unit of thin flows. The upper flow is locally overlain by 75 m of thin flows (Papezik *et al.* 1988, Greenough *et al.* 1989). The two thick flows are traceable and isotopically distinguishable for over 230 km

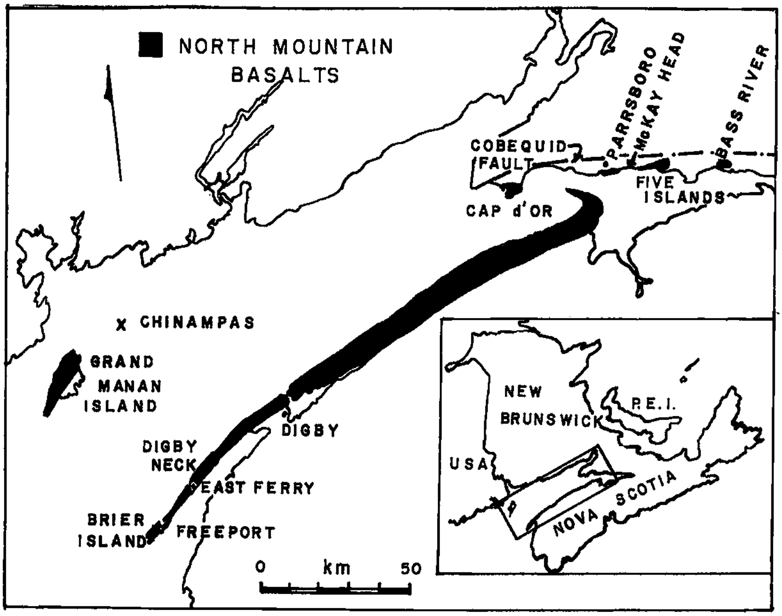

FIG. 1. Map showing the distribution of North Mountain Basalt around the Bay of Fundy. North Mountain Basalt also occurs in the Chinampas exploratory oil well (x).

along the Bay of Fundy (Fig. 1), but they cannot be distinguished on the basis of major- or trace-element geochemistry alone (Jones & Mossman 1988, Greenough *et al.* 1989). The rocks consist of high-Ti quartz-normative tholeiite (Weigand & Ragland 1970) representative of the Early Jurassic eastern North American dolerite province (Dostal & Dupuy 1984, Papezik *et al.* 1988).

The lower portions of the two thick flows tend to be massive, columnar jointed, and have accumulated orthopyroxene in the Digby area (Papezik *et al.* 1988). The percentages of orthopyroxene decrease to the

**TABLE 1. NOBLE METAL CONCENTRATIONS IN NORTH MOUNTAIN BASALT**

| Sample # | EF-1(C) | EF-1(F) | EF-2(C) | EF-3(C) | EF-3(F) | EF-6 | FP-3 | FP-4(C) | FP-4(F) | FP-7A(C) | FP-7A(F) | FP-8B(F) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Rk. type[1] | Pegmatite | Pegmatite | Pegmatite | Pegmatite | Rhyolite | Basalt | Basalt | Pegmatite | Rhyolite | Pegmatite | Rhyloite | Rhyolite |
| Unit #[2] | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Location[3] | E. Ferry | E. Ferry | E. Ferry | E. Ferry | E. Ferry | E. Ferry | Freeport | Freeport | Freeport | Freeport | Freeport | Freeport |
| Mg# | 0.33 | 0.42 | 0.37 | 0.42 | 0.18 | 0.52 | 0.53 | 0.32 | 0.35 | 0.39 | 0.28 | 0.30 |
| Noble Metals | | | | | | | | | | | | |
| Au | 3.9 | 3.3 | 5.1 | 3.9 | 0.24 | 2.7 | 4.7 | 5.6 | 1.2 | 6.6 | n.d. | 0.51 |
| Pd | 8.5 | 16 | 11 | 11 | 0.42 | 7.5 | 9.0 | 1.7 | 0.18 | 11 | 0.25 | 0.44 |
| Pt | 1.9 | 3.5 | 1.3 | 0.98 | 1.3 | 4.6 | 6.1 | 2.5 | 0.34 | 3.2 | 0.41 | 0.50 |
| Rh | 0.19 | 0.25 | 0.21 | 0.16 | 0.01 | 0.29 | 0.36 | 0.10 | 0.05 | 0.21 | 0.08 | 0.05 |
| Ru | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.17 | n.d. | n.d. | n.d. |
| Ir | 0.09 | 0.06 | 0.05 | n.d. | 0.05 | 0.06 | 0.12 | 0.10 | 1.2 | 0.11 | 0.37 | 0.10 |
| Siderophile and Chalcophile Elements | | | | | | | | | | | | |
| Cr | n.d. | n.d. | n.d. | n.d. | 19 | 56 | 258 | n.d. | n.d. | n.d. | n.d. | n.d. |
| Ni | n.d. | n.d. | n.d. | 4 | n.d. | 24 | 31 | n.d. | n.d. | 1 | n.d. | n.d. |
| Cu | 176 | 138 | 156 | 167 | 253 | 93 | 94 | 109 | 49 | 71 | 109 | 81 |

| Sample # | FP-9(C) | FP-9(F) | MCK1 | MCK2B | MCK2FG | MCK2T | MCK3B | MCK3FG | MCK3T | MH2FG | MHS2P | MCK10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Rk. type[1] | Pegmatite | Rhyolite | Basalt | Pegmatite | Rhyolite | Pegmatite | Pegmatite | Rhyolite | Pegamatite | Rhyolite | Pegmatite | Vesicular |
| Unit #[2] | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| Location[3] | Freeport | Freeport | McKay H. | McKay H. | McKay H. | McKay H. | McKay H. | McKay H. | McKay H. | McKay H. | McKay H. | McKay H. |
| Mg# | 0.42 | 0.28 | 0.57 | 0.58 | 0.43 | 0.54 | 0.46 | 0.36 | 0.47 | 0.43 | 0.44 | 0.44 |
| Noble Metals | | | | | | | | | | | | |
| Au | 3.6 | 0.74 | 1.8 | 2.1 | 0.66 | 2.2 | 2.6 | 1.1 | 2.4 | 1.6 | 3.1 | 1.2 |
| Pd | 10 | 0.21 | 8.1 | 10 | 0.41 | 7.8 | 11 | 1.6 | 9.0 | 4.6 | 7.9 | 6.0 |
| Pt | 1.2 | 0.28 | 4.6 | 0.52 | 0.29 | 0.70 | 0.73 | 0.53 | 0.93 | 0.36 | 0.58 | 3.3 |
| Rh | 0.16 | n.d. | 0.25 | 0.14 | 0.02 | 0.07 | 0.29 | 0.01 | 0.15 | 0.23 | 0.11 | 0.26 |
| Ru | n.d. | n.d. | 0.18 | 0.21 | 0.14 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Ir | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.04 | n.d. | n.d. | n.d. | 0.04 |
| Siderophile and Chalcophile Elements | | | | | | | | | | | | |
| Cr | n.d. | n.d. | 84 | 24 | 2 | 12 | 6 | 1 | 6 | 3 | 4 | 3 |
| Ni | 11 | n.d. | 34 | 36 | 1 | 27 | 10 | n.d. | 14 | 3 | 13 | 6 |
| Cu | 65 | 107 | 170 | 126 | 280 | 145 | 185 | 343 | 214 | 304 | 215 | 36 |

| Sample # | P82-23 | P82-24 | P82-25 | P82-26 | P82-33 | P82-2 | P82-27 | P82-17 | EC1 | MH14 | CD7 | CH-2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Rk. type[1] | OPX Bas. | Basalt | Pegmatite | Basalt | OPX Bas. | OPX Bas. | OPX Bas. | Basalt | Basalt | Basalt | OPX Bas. | Basalt |
| Unit #[2] | 1 | 1 | 1 | 1 | 1 | 3 | 3 | 2 | 1 | 3 | 1 | 2 |
| Location[3] | E. Ferry | E. Ferry | E. Ferry | E. Ferry | E. Ferry | Digby N. | Digby N. | Digby N. | Five Is. | McKayH. | Capd'Or | Chinampas |
| Mg# | 0.70 | 0.57 | 0.40 | 0.51 | 0.71 | 0.68 | 0.65 | 0.61 | 0.55 | 0.58 | 0.64 | 0.57 |
| Noble Metals | | | | | | | | | | | | |
| Au | 1.6 | 2.3 | 2.8 | 1.9 | 1.6 | 1.3 | 1.3 | 2.2 | 2.6 | 2.6 | 3.2 | 2.5 |
| Pd | 7.7 | 4.2 | 3.9 | 4.7 | 4.3 | 1.2 | 1.4 | 0.55 | 4.4 | 5.6 | 13 | 1.7 |
| Pt | 14 | 5.5 | 0.45 | 2.8 | 12 | 3.2 | 3.2 | 3.4 | 4.4 | 8.6 | 7.4 | 2.5 |
| Rh | 0.57 | 0.28 | 0.05 | 0.16 | 0.61 | 0.13 | 0.14 | 0.13 | 0.21 | 0.31 | 0.88 | 0.08 |
| Ru | 0.27 | n.d. | n.d. | n.d. | 0.6 | 0.15 | 0.34 | n.d. | 0.16 | n.d. | 0.92 | n.d. |
| Ir | 0.40 | 0.06 | n.d. | 0.06 | 1.02 | 0.14 | 0.15 | 0.12 | 0.02 | 0.03 | | |
| Siderophile and Chalcophile Elements | | | | | | | | | | | | |
| Cr | 368 | 85 | 10 | 41 | 528 | 396 | 324 | 243 | 80 | 142 | 380 | 107 |
| Ni | 90 | 48 | 20 | 34 | 98 | 107 | 93 | 79 | 23 | 26 | 36 | 56 |
| Cu | 97 | 147 | 192 | 158 | 81 | 131 | 50 | 14 | 161 | 101 | 171 | 58 |

1. Pegmatite = mafic pegmatite, Rhyolite = rhyolite band in mafic pegmatite. Samples with the same sample number as a pegmatite (e.g. EF-1) are from that pegmatite. Basalt = massive basalt from the bottom of thick flows or basalt from the tops of flows. Vesicular = vesicular basalt from layers in the thick flows. OPX Bas. = basalt bearing an accumulation of orthopyroxene.
2. Units numbers are as follows: 1 = Lower unit thick flow, 2 = Middle unit thin flows, 3 = Upper unit thick flow.
3. E. Ferry = East Ferry, increasing sample numbers indicate increasing depths in the upper ~ 40 m of the flow. Freeport = Freeport, increasing sample numbers indicate decreasing depths in the upper ~ 40 m of the flow. McKay H. = McKay Head, see Greenough and Dostal (1992b) for depths in the flow. The precise locations of P82 samples appear in Papezik et al. (1988). Digby N. = Digby Neck. Precise locations of samples EC1, MH14, and CD7 are given in Greenough et al. (1989). The stratigraphic location of sample CH-2 is given in Greenough and Papezik (1987).
4. Copper, Ni and Cr concentrations in ppm. Noble metal concentrations in ppb. Mg# = Mg/(Mg + 0.9 Fe) atomic. N.d. = not detected.

northeast, and the mineral disappears in the Parrsboro area (Greenough *et al.* 1989). Layering in the upper 50 m or so of the thick flows was described in detail by Greenough & Dostal (1992a, b). In summary, the lowest layers consist of approximately 25-cm-thick mafic pegmatite that contains a thin (2 cm) "rhyolite" band in the middle. The layering gradually changes in character toward the top of the flows; the mafic layers become highly vesicular and nonpegmatitic, and layering disappears entirely approximately 5 m below the flow top. Both the pegmatitic and vesicular layers are horizontally traceable for tens of meters and are vertically separated from one another by approximately 130-cm-thick sections of basalt. All basalts experienced zeolite-facies metamorphism (Aumento 1966), but the Sr isotopic study of Jones & Mossman (1988) demonstrates that carefully selected samples give an accurate representation of the original geochemistry.

Similarities between the layering in the North Mountain Basalt Formation and in the Hawaiian lava lakes (Helz 1987, Helz *et al.* 1989) suggest that the layers of mafic pegmatite and vesicular basalt represent segregations of liquid siphoned into thermally induced horizontal cracks formed in the downward-growing, semirigid upper crystalline mush (Greenough & Dostal 1992b). Thus the layers form from residual interstitial liquid derived from the crystal mush.

The "rhyolite" bands consist of a brownish, vesicular aphanitic rock and is called "rhyolite" because it contains in excess of 70% $SiO_2$. The bands appeared during a second stage of formation of horizontal cracks, with interstitial liquid in the mafic pegmatites forced into the crack by effervescence and filter pressing (Greenough & Dostal 1992b). In the mafic pegmatites, interstitial, polygonal patches of microcrystalline Si-rich minerals (chemically equivalent to and traceable into the "rhyolites") and similar areas of glass-like Fe-rich stilpnomelane (enveloping skeletal Fe–Ti oxides) have bulk chemical compositions, relative proportions and total modal percentages suggesting that they once were Si-rich and Fe-rich glasses, respectively (Greenough & Dostal 1992b).

Samples used in the study come from the three lower recognized stratigraphic units (Table 1, Fig. 1). They have been divided into five rock groups: orthopyroxene-enriched (OPX) basalts, mafic pegmatites, "rhyolites", vesicular-layer basalts, and basalts. The single sample of vesicular-layer basalt reflects the difficulty in obtaining an unaltered sample. Samples categorized as basalt originate from the tops of the thick flows, from thin flows, or from the massive (noncumulate) lower portions of some thick flows.

## ANALYTICAL METHODS

Samples not used in previous studies (sample numbers prefixed with EF and FP) were powdered and analyzed for their major elements using atomic absorption spectrometry. These data can be obtained from the Depository of Unpublished Data, Canada Institute for Scientific and Technical Information, National Research Council, Ottawa, Ontario K1A 0S2, or by writing J.D.G. Concentrations of Rb, Sr, Sc, V, Cr, Ni, Cu, Zn and Ga were determined using X-ray fluorescence on pressed-powder pellets, with precision and accuracy better than ±5% for all elements except Cu (±10%). All other trace elements, except the noble metals, were determined by inductively coupled plasma – mass spectrometry (ICP–MS) following the sodium peroxide sinter procedure of Longerich *et al.* (1990). Precision and accuracy are better than 4% for these elements.

Concentrations of the noble metals (Au, Pd, Pt, Rh, Ru, and Ir, Table 1) were determined by ICP–MS on 10% aqua regia solutions after preconcentration of 10 g of rock powder by NiS fire assay. Typical reagent-blank concentrations are 0.77, 0.59, 0.57, 0.06, 0.05 and 0.04 ppb for Au, Pd, Pt, Rh, Ru and Ir, respectively. Run-specific blank concentrations were subtracted from the raw data. Average "detection limits" ($3\sigma$ above background) are equivalent to 0.20, 0.15, 0.08, 0.01, 0.10 and 0.02 ppb (in a rock sample), respectively. Jackson *et al.* (1990) should be consulted for details of the procedure. Replicate analyses of the reference material SARM–7 have given (in ppb) 245 (Au), 1452 (Pd), 227 (Rh), 3923 (Pt), 380 (Ru) and 77 (Ir), with relative standard deviations of 7% or better for all elements. All PGE values are within 10% of the certified concentrations. Replicate analyses of sample MCK1 indicate precision of 10% or better for Au, Pd and Pt, and 30% for Rh. Data on MCK 10 suggest a precision of 150% for Ir concentrations near the detection limit (0.02 ppb). All analytical work described above was done at The Memorial University of Newfoundland.

Analytical methods and major- and trace-element data (other than for the PGE and Au) for all samples that do not begin with EF or FP appear in Greenough & Papezik (1987), Papezik *et al.* (1988), and Greenough *et al.* (1989).

## RESULTS

Variation diagrams plotted in terms of Mg# [= Mg/(Mg + 0.9 Fe) atomic] illustrate the geochemical relationships among rock types (Fig. 2); average compositions for each rock type appear in Table 2. The OPX-enriched basalts tend to have the highest Mg# and Cr values, as well as the lowest concentrations of alkali elements, high field-strength elements (*HFSE*) and rare-earth elements (*REE*) of the entire suite. The basalts and mafic pegmatites, taken together with the OPX-enriched basalts, define correlation lines with concentrations of alkali elements, *HFSE* and *REE* increasing and that of "compatible"

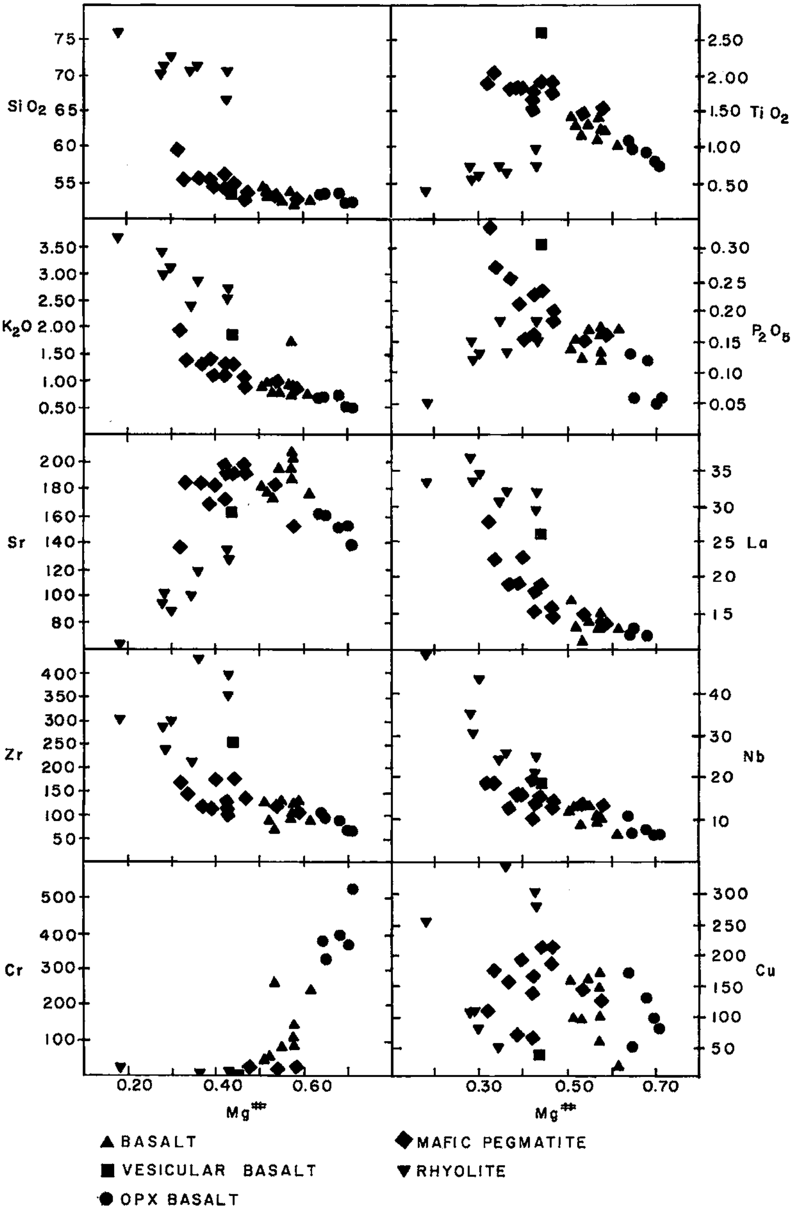

FIG. 2. Variation diagrams showing selected major element (wt. % oxides, volatile free) and trace elements (ppm) plotted against Mg# [Mg# = Mg/(Mg + 0.9 Fe) atomic]. OPX basalt: orthopyroxene-enriched basalt; see text for usage of "rhyolite".

elements decreasing as Mg# decreases. The single vesicular-layer basalt is distinctive in having the highest $TiO_2$ and $P_2O_5$ concentrations observed, and *REE* concentrations approaching those of the "rhyolites". The "rhyolite" samples are characterized by their high $SiO_2$, $K_2O$, Zr and La concentrations, and low $TiO_2$ and Sr. Copper concentrations tend to increase as Mg# decreases in the mafic rocks, but there is considerable scatter; individual samples of "rhyolite" contain the highest and amongst the lowest Cu values.

The distinction among rock types is not as apparent in the noble metal data (*cf.* Figs. 2, 3), partly reflecting the lower precision at low concentrations (Table 1). Nevertheless, means for many elements (23 of 30 pairs tested) between rock types are statistically different at the 0.10 level of significance or better

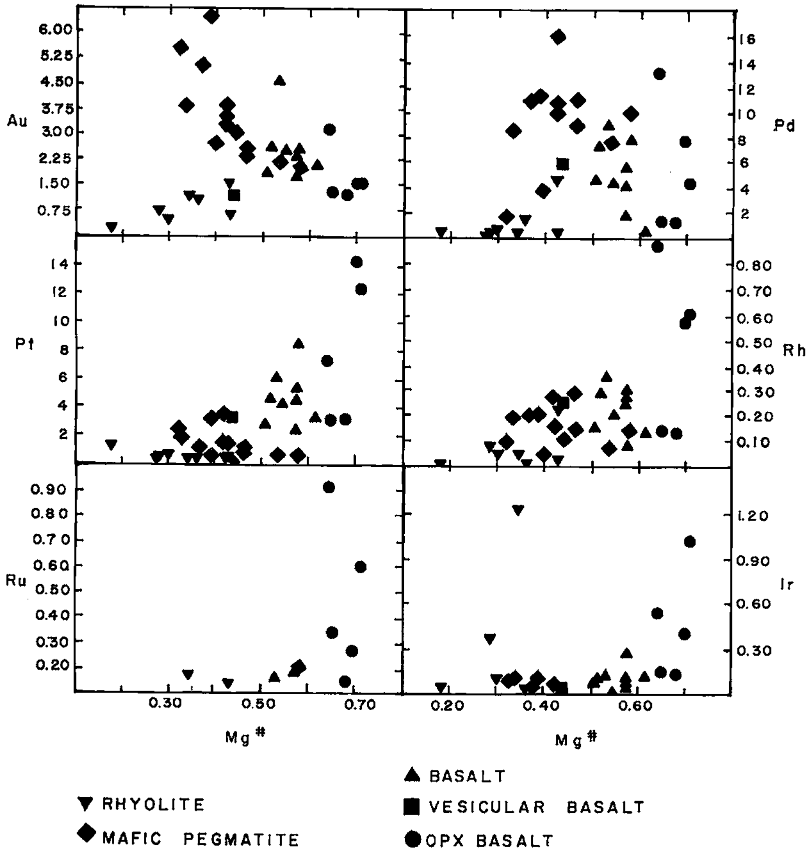

FIG. 3. Variation diagrams showing the noble metals (ppb) plotted against Mg#. OPX basalt: orthopyroxene-enriched basalt; see text for usage of "rhyolite".

(Table 2, footnote). Gold (correlation coefficient, $r = -0.69$) and, to a much lesser extent, Pd ($r = -0.34$, level of significance of correlation = 0.10) seem to increase with decreasing Mg# in the mafic rocks; the "rhyolite" samples contain the lowest concentrations of these elements (Fig. 3, Tables 1, 2). In contrast, levels of Pt, Rh, Ru and Ir tend to decrease with decreasing Mg#. The concentrations of Ru and Ir commonly fall below detection limits except in the OPX-enriched basalts.

Average mantle-normalized patterns indicate substantial fractionation of the noble metals after extrusion (Fig. 4, averaged values given in Table 2). The pattern representative of basalt is straight, with a slight negative Ir anomaly. On average, the OPX-enriched basalts show higher concentrations of Ni, Ir, Rh and Pt than the basalts, but the pattern flattens out between Pt and Au. The pattern for mafic pegmatite displays the opposite relationships, with average concentrations of Ni to Pt below, and Pd and Au above, those in the basalt. The vesicular-layer basalt sample displays similarities to both the basalts and mafic pegmatites. The pattern representing the average "rhyolite" shows a positive Ir anomaly; concentrations of the other noble metals fall below those in the other rock types.

## DISCUSSION

### *Interpretation of major-element and trace-element data*

Although the samples come from several flows and outcrops up to 200 km apart, the coherency of major- and trace-element data (Fig. 2) point to 1) similar initial composition of the mafic magma, 2) similar igneous geochemical processes at all localities, and 3) minimal effects of alteration. The first point is emphasized by the incompatible trace elements because small initial variations in concentration tend to be enhanced during differentiation. The wide range of values of Mg# (0.70 – 0.20) and $SiO_2$ contents (53 – 75 wt.%, volatile-free basis) emphasize the extent of differentiation. The processes responsible for differentiation are equivocal, as reviewed below.

Mass-balance calculations based on major elements indicate that the mafic pegmatites can, to a first approximation, be derived by crystal–liquid differentiation from the basaltic melt (Papezik *et al.* 1988). However, similar calculations show that the most chemically evolved mafic rocks, the vesicular layers, show a poor fit; problems arise owing to their elevated concentrations of alkalis (Greenough & Dostal 1992b). The calculated rate of upper-crust growth on the flow indicates that the first of these vesicular layers (depth ~5 m) formed after only about 6 months of cooling (Greenough & Dostal 1992a). The vesicular nature of these layers and the fact that they formed early led Greenough & Dostal (1992b) to propose that their chemical characteristics are in part a result of the early upward transport of elements in vesicle plumes either as volatile complexes dissolved in the magma or in a separate fluid phase. Vesicle plumes are commonly preserved near the base of mafic lava flows, including the North Mountain basalt flows.

Mass-balance calculations involving primary phases suggest that crystal fractionation is incapable of producing the "rhyolite" (Greenough & Dostal 1992a), which may thus result from a Si-rich immiscible liquid derived from the mafic pegmatites. Along with petrographic data already discussed, the mafic pegmatites have bulk compositions similar to rocks known to produce immiscible liquids, and the "rhyolite" resembles known Si-rich glass produced by immiscibility (Philpotts 1982, Greenough & Dostal 1992b). Nevertheless, Th, Zr, Hf and Ba behaved antithetically to what synthetic-system experiments pre-

TABLE 2. AVERAGE COMPOSITION OF ROCK TYPES IN THE NORTH MOUNTAIN BASALT

| | Basalt | OPX Basalt | Mafic Pegmatite | Vesicular Basalt | Rhyolite |
|---|---|---|---|---|---|
| No. of Samples[1] | ≤9 | ≤5 | ≤13 | 1 | ≤8 |
| **Major Elements Oxides** | | | | | |
| $SiO_2$ | 53.13 (0.55) | 53.15 (0.54) | 54.86 (1.68) | 53.66 | 71.32 (2.47) |
| $TiO_2$ | 1.27 (0.13) | 0.92 0.12) | 1.78 (0.16) | 2.64 | 0.68 (0.15) |
| $Al_2O_3$ | 14.31 (0.38) | 12.75 (0.45) | 12.58 (0.80) | 12.26 | 10.55 (0.53) |
| $Fe_2O_3$ | 11.27 (0.50) | 9.96 (0.27) | 13.78 (0.63) | 14.53 | 7.37 (1.42) |
| MnO | 0.17 (0.02) | 0.16 (0.02) | 0.21 (0.05) | 0.29 | 0.11 (0.05) |
| MgO | 6.47 (0.66) | 9.52 (1.02) | 4.82 (1.40) | 5.14 | 1.73 (0.68) |
| CaO | 9.66 (0.54) | 10.91 (0.54) | 7.91 (1.15) | 6.06 | 2.20 (0.77) |
| $Na_2O$ | 2.64 (0.58) | 1.92 (0.13) | 2.63 (0.17) | 3.27 | 2.92 (0.20) |
| $K_2O$ | 0.93 (0.29) | 0.63 (0.08) | 1.20 (0.28) | 1.84 | 2.98 (0.40) |
| $P_2O_5$ | 0.15 (0.02) | 0.09 (0.03) | 0.22 (0.05) | 0.31 | 0.14 (0.04) |
| Mg# | 0.56 | 0.68 | 0.43 | 0.44 | 0.34 |
| **Alkali and alkaline earth metals** | | | | | |
| Rb | 27 (3) | 19 (4) | 39 (11) | 49 | 101 (14) |
| Cs | 1.2 (0.3) | 0.58 (0.20) | 1.20 | | |
| Sr | 190 (11) | 153 (8) | 181 (18) | 163 | 103 (22) |
| Ba | 213 (38) | 174 (19) | 252 (67) | 298 | 602 (65) |
| **High Field Strength Elements** | | | | | |
| Th | 3.12 (0.39) | 2.32 (0.23) | 3.99 (1.01) | 5.96 | 11.3 (1.4) |
| U | 0.88 (0.34) | 0.48 (0.07) | 1.10 | | |
| Zr | 107 (18) | 83 (13) | 134 (25) | 255 | 317 (69) |
| Hf | 3.05 (0.57) | 2.64 (0.37) | 3.66 (0.82) | 6.32 | 8.25 (1.94) |
| Nb | 11 (2) | 8 (2) | 15 (3) | 19 | 32 (9) |
| Ta | 2.1 (1.8) | 1.0 (0.2) | 3.1 (3) | 1.6 | 11.5 (10.9) |
| Y | 26.3 (4.5) | 23.4 (3.4) | 30.7 (6.8) | 41.0 | 43.0 (4.5) |
| **Rare Earth Elements** | | | | | |
| La | 13.9 (1.5) | 11.4 (1.2) | 18.6 (3.9) | 26.1 | 32.9 (2.1) |
| Ce | 29.7 (3.2) | 23.2 (3.2) | 40.0 (7.7) | 61.0 | 69.9 (4.7) |
| Pr | 3.38 | | 5.47 (1.04) | | 8.62 (0.40) |
| Nd | 15.3 (2.1) | 11.2 (1.2) | 22.6 (4.2) | | 33.0 (1.9) |
| Sm | 3.75 (0.36) | 2.88 (0.32) | 5.42 (0.88) | 7.78 | 8.22 (0.65) |
| Eu | 1.20 (0.12) | 0.90 (0.09) | 1.49 (0.17) | 2.03 | 1.91 (0.50) |
| Gd | 3.35 | | 5.39 (1.00) | | 7.04 (0.69) |
| Tb | 0.71 (0.08) | 0.58 (0.07) | 0.93 (0.16) | 1.22 | 1.42 (0.10) |
| Dy | 3.86 | | 6.21 (1.14) | | 8.67 (0.72) |
| Ho | 0.77 | | 1.26 (0.23) | | 1.76 (0.15) |
| Er | 2.28 | | 3.59 (0.68) | | 5.25 (0.43) |
| Tm | 0.31 | | 0.51 (0.10) | | 0.76 (0.06) |
| Yb | 2.32 (0.27) | 1.96 (0.23) | 3.18 (0.54) | 3.79 | 4.59 (0.56) |
| Lu | 0.36 (0.04) | 0.31 (0.04) | 0.75 (0.97) | 0.61 | 0.67 (0.10) |
| **Siderophile and Chalcophile Elements** | | | | | |
| Sc | 41.0 (4.3) | 46.6 (4.8) | 38.5 (6.4) | 33.0 | 8.97 (3.78) |
| V | 284 (18) | 246 (19) | 355 (53) | 345 | 28 (24) |
| Cr | 122 (74) | 399 (69) | 10 (7) | 3 | 6 (7) |
| Co | 54 (3) | 63 (9) | 67 (11) | 52 | 70 (17) |
| Ni | 39 (17) | 85 (25) | 15 (10) | 6 | 2 |
| Mo | 6 (3) | 3 (2) | 3 | | |
| Cu | 111 (50) | 106 (42) | 151 (47) | 36 | 191 (108) |
| Zn | 73 (8) | 66 (10) | 74 (9) | 73 | 50 (13) |
| Ga | 18 (3) | 15 (2) | 19 (2) | 20 | 18 (3) |
| **Noble Metals** | | | | | |
| Au | 2.6 (0.8) | 1.8 (0.7) | 3.6 (1.3) | 1.2 | 0.85 (0.42) |
| Pd | 5.1 (2.7) | 5.6 (4.5) | 9.1 (3.4) | 6.0 | 1.0 (1.4) |
| Pt | 4.7 (1.8) | 8.1 (4.7) | 1.4 (1.0) | 3.3 | 0.50 (0.30) |
| Rh | 0.23 (0.09) | 0.47 (0.29) | 0.16 (0.07) | 0.26 | 0.06 (0.07) |
| Ru | 0.17 - | 0.46 (0.27) | 0.21 | | 0.16 |
| Ir | 0.09 (0.08) | 0.45 (0.32) | 0.08 (0.02) | 0.04 | 0.36 (0.45) |

1. Major element oxides in wt. % recalculated to 100% volatile free with total Fe as $Fe_2O_3$. Trace elements in ppm except noble metals in ppm except noble metals in ppb. The standard deviation is given in brackets. N.d. = not detected. A blank = not determined or in the case of the standard deviation there were ≤2 samples. Mg# = Mg/(Mg + 0.9 Fe) atomic).
2. No. of samples is the number analyzed for the major elements, most of the trace elements and all the noble metals. Because a few trace elements were not determined in all samples n will be less for these elements. A few trace elements (e.g. Cr and Ni) and the noble metals (Table 1) were not detected in some samples thus the mean is based on fewer data points.
3. See Table 1 for rock type definitions.
4. Using the student t-test, means for Au, Pd, Pt, Rh and Ir in each rock group (except the vesicular-layer basalt) are different from one another at the 0.10 level of significance with the following 7 exceptions out of 30 tested: the means for Ir between basalt and mafic pegmatite, basalt and "rhyolite", and mafic pegmatite and "rhyolite"; the means for Pd between basalt and OPX-enriched basalt, and mafic pegmatite and OPX-enriched basalt; the means for Au between basalt and OPX-enriched basalt.

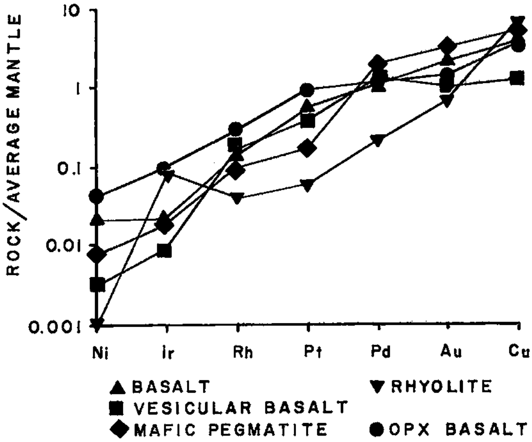

FIG. 4. Average mantle-normalized concentrations of the noble metals in each of the major rock types in the North Mountain Basalt sequence. Note that the pattern for the vesicular-layer basalt is represented by a single sample. The significance of differences between data points can be evaluated with the standard deviation and T-test data in Table 2. The values used for normalization are from Barnes *et al.* (1988). OPX basalt: orthopyroxene-enriched basalt; see text for usage of "rhyolite".

dict for silicate–silicate liquid immiscibility (Watson 1976, Ryerson & Hess 1978); although much of the evidence supports immiscibility, it is not conclusive (Greenough & Dostal 1992a).

Papezik *et al.* (1988) concluded on the basis of major-element mass-balance calculations and trace-element modeling that the evolved mafic rocks in the Digby area can be formed from normal basalts by the fractionation of minerals present in the orthopyroxene-enriched basalts.

### *The distribution of noble metals in mafic rocks*

Average chondrite-normalized patterns for the noble metals in basalts, mafic pegmatites and OPX-enriched basalts (Fig. 4, Table 2) show that the high-melting-point noble metals (Ir, Ru and Rh), as well as Pt, occur at higher concentrations in the OPX-enriched basalts than in the basalts. Pd and Au concentrations are similar or lower in the OPX-enriched basalts than in the basalts. Relationships between the mafic pegmatites and basalts are the reverse of those between the OPX-enriched basalts and basalts. Although the mafic pegmatite and OPX-enriched basalt patterns are complementary, crystallization of OPX-enriched basalt is probably not directly related to mafic pegmatite formation because OPX-enriched basalts do not occur in the northeast (*e.g.*, McKay Head). Mechanisms proposed to explain changes in the concentration of the noble metals in evolving magmas were reviewed by Crocket (1981), Naldrett (1981), Barnes *et al.* (1985, 1988), Brügmann *et al.* (1987), Greenough & Fryer (1990) and Naldrett *et al.* (1990).

Nucleation and segregation of an immiscible sulfide liquid (Hertogen *et al.* 1980, Hamlyn *et al.* 1985) should effectively remove all the noble metals during magma evolution; measured sulfide liquid – mafic magma partition coefficients ($K_d$) are on the order of $10^4$ to $10^5$ (Peach *et al.* 1990, Stone *et al.* 1990). Pd and Au concentrations tend to increase between the basalts and mafic pegmatites (bulk $K_d < 1$), arguing against removal of sulfide liquid as a significant process. Similarly, Cu is higher in the mafic pegmatites and slightly lower in the OPX-enriched basalts than in the basalts (Table 2, Fig. 4). Thus the behavior of Cu indicates that not more than 0.4% of fractionating phases (for a bulk $D \leq 1$) could be sulfide because the Cu sulfide liquid – silicate liquid partition coefficient is high (~250, Rajamani and Naldrett 1978).

The fractionation of oxide phases (Crocket & Chyi 1972, Agiorgitis & Wolf 1978), PGE-bearing alloys (Bird & Basset 1980, Keays 1982) or olivine (Brügmann *et al.* 1987) has been proposed as a means of removing the high-melting-point PGE (*i.e.*, Ru, Ir and Os) from evolving mafic magmas. The formation of PGE alloys appears associated with chromite precipitation (*e.g.*, Brügmann *et al.* 1987) and may not be an important process by itself. Olivine does not occur in the North Mountain Basalt. Chromite fractionation can help explain the high Cr values in the OPX-enriched basalts (Fig. 2), but chromite is not an important phase in this suite. Furthermore, major-element mass balance coupled with trace-element modeling show that augite removal alone can explain the variation in Cr (Papezik *et al.* 1988). Another problem with calling on chromite fractionation is that the level of Pt also is higher, on average, in the OPX-enriched basalts and lower in the mafic pegmatites than in the basalts (Table 2). Normally, Pt follows the low-melting-point PGE along with Au in evolving magmas (Barnes *et al.* 1988, Greenough & Owen 1992).

The results obtained for the North Mountain Basalt sequence are similar to the results of studies of Pt and Pd in sheets of Mesozoic high-Ti quartz-normative tholeiitic diabase in the eastern United States (Gottfried & Froelich 1988, Talkington *et al.* 1988, Gottfried *et al.* 1990). Chemical similarities between the North Mountain Basalt and these rocks have been emphasized by Puffer & Hurtubise (1982) and Dostal & Greenough (1992). The PGE studies indicate that orthopyroxene cumulates in the Mesozoic diabase sheets show Pt enrichment and Pd depletion relative to undifferentiated diabase. In contrast, ferrogabbro higher in the sheets and locally "pegmatitic" in texture can have Pd enriched up to 10 times (165 ppb) that in the undifferentiated basalt. Platinum concentrations can be higher (up to 2.5 times) or even lower than in the contact basalt. The Pd enrichments are accompanied by elevated Au and Cl concentrations. These enrichments do not appear related to thickness of the diabase sheets. Similar enrichments (150–200 ppb Pd) are observed in the York Haven diabase sheet (~550 m: Gottfried *et al.* 1990) and Palisades sill (~300 m: Talkington *et al.* 1988), whereas the marginally thinner North Mountain Basalt flows (~200 m) show maximum Pd concentrations of <16 ppb. Maximum Pd enrichment occurs in narrow zones; thus there is the possibility that our sampling of the North Mountain Basalt missed the most strongly enriched layers.

Authors of the papers on the eastern U.S. rocks provided no mechanism for the Pt enrichment other than to associate it with orthopyroxene accumulation. The enrichment in Pd and Au in the ferrogabbro was attributed to movement by "late- to post-magmatic fluids and volatiles enriched in Cl and S" (Gottfried *et al.* 1990, Gottfried & Froelich 1988).

The degree of Pd enrichment and Pd/Pt fractionation is not as extreme in the North Mountain Basalt as in some of the eastern U.S. diabase sheets. Nevertheless, the above model for Pd and Au enrichment fits well with data available for the North Mountain Basalt, except that using the basalts, it is possible to show that the "late-stage" enrichment probably occurred early after emplacement

(Greenough & Dostal 1992b). As noted above, rising plumes of volatiles probably altered the major-element and trace-element geochemistry of vesicle-rich layers and may have had a similar though less extensive effect on the layers of mafic pegmatite (Greenough & Dostal 1992a, b). Through comparison with Hawaiian lava lakes, we know that these layers formed very early in the cooling history of the lava flow.

Although there is disagreement on whether hydrothermal movement of the PGE directly results in ore deposits, most authors would agree that such solutions are capable of at least local movement of the metals (Barnes & Campbell 1988, Wood *et al.* 1992). As in the eastern U.S. diabase sheets (Belkin 1989), studies of fluid inclusions and halogen-bearing minerals in intrusions such as the Bushveld and Stillwater complexes suggest that the PGE can be moved by Cl-rich fluids (Boudreau *et al.* 1986, Ballhaus & Stumpfl 1986, Boudreau 1988, Harney & Merkle 1990). Thermodynamic calculations predict significant solubility of Pd in Cl-rich magmatic–hydrothermal solutions (Sassani & Shock 1990). Preliminary experimental results suggest even higher solubilities of Pd than predicted from calculations (Hsu *et al.* 1991). Although the theoretical and experimental work supports the possibility of moving the PGE with Cl-rich fluids, it cannot as yet quantitatively explain fractionation of the PGE or assess the importance and effect of other species (*e.g.*, S, $NH_3$ and other cations) on PGE solubility.

Volatile complexing provides a tentative explanation for Pd and Au enrichment in the mafic pegmatites, but it does little to explain Pt enrichment (relative to basalt) in the average OPX-enriched basalt (Table 2, Fig. 4). One possible explanation is that orthopyroxene has an affinity for Pt and the high-melting-point PGE, much as olivine seems to have an affinity for the high-melting-point PGE alone (Brügmann *et al.* 1987). Unfortunately, it has not been demonstrated that any silicates have an affinity for the PGE that cannot be explained by microinclusions of sulfides, chromite or PGE alloys. Studies of ultramafic rocks show that olivine has relatively low concentrations of the PGE (Mitchell & Keays 1981). Incorporation of the PGE in microinclusions in early-formed phases such as olivine or orthopyroxene could explain why PGE concentrations are somewhat erratic in the OPX-enriched basalts. The number and size of inclusions and hence the concentrations of the PGE would be dependent on nucleation kinetics and growth rates of both the inclusions and host phase. If the inclusions were globules of immiscible sulfide, then fractionation of Pd and Au might be attributed to scavenging of these elements by volatile constituents, which prevented their incorporation in the sulfides. We know of no data indicating the effect of volatiles on sulfide liquid – silicate liquid partition coefficients for the PGE.

### *The distribution of the noble metals in the "rhyolite" bands*

Regardless of whether the "rhyolite" bands formed by crystal fractionation or silicate liquid immiscibility, Figure 4 shows that the average "rhyolitic" liquid was strongly depleted in most of the PGE and Au, but enriched in Ir. Figure 3 illustrates that the Ir anomaly only occurs in a few "rhyolite" samples, where it is pronounced. The high variability could be related to a sampling problem caused by a "nugget effect". Concentrations of Cu are similarly variable in these rocks, but there is no correlation between Cu and Ir, and thus no indication that the Ir resides in a sulfide phase. Analogous rocks termed "granophyres" from eastern U.S. diabase sheets also contain extremely low levels of Pd and Pt (Gottfried & Froelich 1988).

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## REFERENCES

AGIORGITIS, G. & WOLF, R. (1978): Aspects of osmium, ruthenium and iridium contents in some Greek chromites. *Chem. Geol.* **23**, 267-272.

AUMENTO, F. (1966): Zeolite minerals, Nova Scotia. *In* Geology of Parts of the Atlantic Provinces. *Geol. Assoc. Can. – Mineral. Assoc. Can., Guidebook*, 71-78.

BALLHAUS, C.G. & STUMPFL, E.F. (1986): Sulfide and platinum mineralization in the Merensky reef: evidence from hydrous silicates and fluid inclusions. *Contrib. Mineral. Petrol.* **94**, 193-204.

BARNES, S.-J., BOYD, R., KORNELIUSSEN, A., NILSSON, L.-P., OFTEN, M., PEDERSEN, R.B. & ROBINS, B. (1988): The use of mantle normalization and metal ratios in discriminating between the effects of partial melting, crystal fractionation and sulphide segregation on platinum group elements, gold, nickel and copper: examples from Norway. *In* Geo-Platinum 87 (H.M. Prichard, P.J. Potts, J.F.W. Bowles & S.J. Cribb, eds.). Elsevier, New York, N.Y. (113-141).

________, NALDRETT, A.J. & GORTON, M.P. (1985): The origin of the fractionation of platinum group elements in terrestrial magmas. *Chem. Geol.* **53**, 303-323.

Barnes, S.J. & Campbell, I.H. (1988): Role of late magmatic fluids in Merensky-type platinum deposits: a discussion. *Geology* **16**, 488-491.

Belkin, H.E. (1989): Fluid inclusion and mineralogic studies of a palladium–platinum anomaly zone in the Reeser's Summit diabase, Pennsylvania: evidence for hydrothermal transport. *In* U.S.G.S. Research on Mineral Resources – 1989 (K.S. Schindler, ed). *U.S. Geol. Surv., Circ.* **1035**, 4-6 (abstr.).

Bird, J.M. & Bassett, W.A. (1980): Evidence of a deep mantle history in terrestrial osmium – iridium – ruthenium alloys. *J. Geophys. Res.* **85**, 5461-5470.

Boudreau, A.E. (1988): Investigations of the Stillwater Complex. IV. The role of volatiles in the petrogenesis of the J–M reef, Minneapolis adit section. *Can. Mineral.* **26**, 193-208.

———, Mathez, E.A. & McCallum, I.S. (1986): Halogen geochemistry of the Stillwater and Bushveld Complexes: evidence for transport of the platinum-group elements by Cl-rich fluids. *J. Petrol.* **27**, 967-986.

Bowen, N.L. (1917): Discussion of "Magmatic differentiation in effusive rocks". *Trans. Am. Inst. Mining Engineers* **54**, 455-457.

Brügmann, G.E., Arndt, N.T., Hofmann, A.W. & Tobschall, H.J. (1987): Noble metal abundances in komatiite suites from Alexo, Ontario, and Gorgona Island, Columbia. *Geochim. Cosmochim. Acta* **51**, 2159-2169.

Crocket, J.H. (1981): Geochemistry of the platinum group elements. *In* Platinum Group Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). *Can. Inst. Mining Metall., Spec. Vol.* **23**, 47-64.

——— & Chyi, L.L. (1972): Abundances of Pd, Ir, Os and Au in an alpine ultramafic pluton. *24th Int. Geol. Congress* **10**, 202-209.

Dostal, J. & Dupuy, C. (1984): Geochemistry of the North Mountain basalts (Nova Scotia, Canada). *Chem. Geol.* **45**, 245-261.

——— & Greenough, J.D. (1992): Petrogenesis of the Early Mesozoic North Mountain Basalts of Nova Scotia, Canada. *In* Eastern North American Mesozoic Magmatism (J.H. Puffer & P.C. Ragland, eds.). *Geol. Soc. Am., Spec. Pap.* **268**, 149-159.

Fryer, B.J. & Greenough, J.D. (1992): Evidence for mantle heterogeneity from platinum-group-element abundances in Indian Ocean basalts. *Can. J. Earth Sci.* **29**, 2329-2340.

Gottfried, D. & Froelich, A.J. (1988): Variations of palladium and platinum contents and ratios in selected Early Mesozoic tholeiitic rock associations in the Eastern United States. *In* Studies of the Early Mesozoic Basins of the eastern United States (A.J. Froelich & G.R. Robinson, eds.). *U.S. Geol. Surv., Bull.* **1776**, 332-341.

———, ———, Rait, N. & Aruscavage, P.J. (1990): Fractionation of palladium and platinum in a Mesozoic diabase sheet, Gettysburg basin, Pennsylvania: implications for mineral exploration. *J. Geochem. Explor.* **37**, 75-89.

Greenough, J.D. & Dostal, J. (1992a): Layered rhyolite bands in a thick North Mountain Basalt flow: the products of silicate liquid immiscibility? *Mineral. Mag.* **56**, 309-318.

——— & ——— (1992b): Cooling history and differentiation of a thick North Mountain Basalt flow (Nova Scotia, Canada). *Bull. Volcanol.* **55**, 63-73.

——— & Fryer, B.J. (1990): Distribution of Au, Pd, Pt, Rh, Ru and Ir in ODP Leg 115 (Indian Ocean) hot-spot basalts: implications for magmatic processes. *In* Proc. Ocean Drilling Program, Scientific Results, vol. **115** (R.A. Duncan, J. Backman, L.C. Peterson *et al.*, eds.). Ocean Drilling Program, College Station, Texas (71-84).

———, Jones, L.M. & Mossman, D.J. (1989): Petrochemical and stratigraphic aspects of North Mountain basalts from the north shore of the Bay of Fundy, Nova Scotia, Canada. *Can. J. Earth Sci.* **26**, 2710-2717.

——— & Owen, J.V. (1992): Platinum group element geochemistry of continental tholeiites: analysis of the Long Range Dyke swarm, Newfoundland, Canada. *Chem. Geol.* **98**, 203-219.

——— & Papezik, V. S. (1987): The Petrology of North Mountain basalts from the wildcat oil well Mobil Gulf Chinampas N-37, Bay of Fundy, Canada. *Can. J. Earth Sci.* **24**, 1255-1260.

Hamlyn, P.R., Keays, R.R., Cameron, W.E., Crawford, A.J. & Waldron, H.M. (1985): Precious metals in magnesian low-Ti lavas: implications for metallogenesis and sulfur saturation in primary magmas. *Geochim. Cosmochim. Acta* **49**, 1797-1811.

Harney, D.M.W. & Merkle, R.K.W. (1990): Pt–Pd minerals from the upper zone of the eastern Bushveld Complex, South Africa. *Can. Mineral.* **28**, 619-628.

Helz, R.T. (1987): Differentiation behavior of Kilauea Iki lava lake, Kilauea Volcano, Hawaii: an overview of past and current work. *In* Magmatic Processes, Physicochemical Principles (B.O. Mysen, ed.). *Geochemical Soc., Spec. Publ.* **1**, 241-258.

———, Kirschenbaum, H. & Mainenko, J.W. (1989): Diapiric transfer of melt in Kilauea Iki lava lake, Hawaii: a quick, efficient process of igneous differentiation. *Geol. Soc. Am., Bull.* **101**, 578-594.

Hertogen, J., Janssens, M.-J. & Palme, H. (1980): Trace elements in ocean ridge basalt glasses: implications for fractionations during mantle evolution and petrogenesis. *Geochim. Cosmochim. Acta* **44**, 2125-2143.

HODYCH, J.P. & DUNNING, G.R. (1992): Did the Manicouagan impact trigger end-of-Triassic mass extinction? *Geology* **20**, 51-54.

HSU, L.C., LECHLER, P.J. & NELSON, J.H. (1991): Hydrothermal solubility of palladium in chloride solutions from 300° to 700°C: preliminary experimental results. *Econ. Geol.* **86**, 422-427.

JACKSON, S.E., FRYER, B.J., GOSSE, W., HEALEY, D.C., LONGERICH, H.P. & STRONG, D.F. (1990): Determination of the precious metals in geological materials by inductively coupled plasma – mass spectrometry (ICP–MS) with nickel sulphide fire-assay collection and tellurium coprecipitation. *Chem. Geol.* **83**, 119-132.

JONES, L.M. & MOSSMAN, D.J. (1988): The isotopic composition of strontium of the Early Jurassic North Mountain basalts, Nova Scotia. *Can. J. Earth Sci.* **25**, 942-944.

KEAYS, R.R. (1982): Palladium and iridium in komatiites and associated rocks: application to petrogenetic problems. *In* Komatiites (N.T. Arndt & E.G. Nisbet, eds.). Allen & Unwin, London, U.K. (435-457).

LONGERICH, H.P., JENNER, G.A., FRYER, B.J. & JACKSON, S.E. (1990): Inductively coupled plasma – mass spectrometric analysis of geologic samples: a critical evaluation based on case studies. *Chem. Geol.* **83**, 105-118.

MITCHELL, R.H. & KEAYS, R.R. (1981): Abundance and distribution of gold, palladium and iridium in some spinel and garnet lherzolites: implications for the nature and origin of precious metal-rich intergranular components in the upper mantle. *Geochim. Cosmochim. Acta* **45**, 2425-2442.

NALDRETT, A.J. (1981): Platinum-group element deposits. *In* Platinum- Group Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). *Can. Inst. Mining Metall., Spec. Vol.* **23**, 197-231.

________, BRÜGMANN, G.E. & WILSON, A.H. (1990): Models for the concentration of PGE in layered intrusions. *Can. Mineral.* **28**, 389-408.

PAPEZIK, V. S., GREENOUGH, J. D., COLWELL, J.A. & MALLINSON, T.J. (1988): North Mountain basalt from Digby, Nova Scotia: models for a fissure eruption from stratigraphy and petrochemistry. *Can. J. Earth Sci.* **25**, 74-83.

PEACH, C.L., MATHEZ, E.A. & KEAYS, R.R. (1990): Sulfide melt – silicate melt distribution coefficients for noble metals and other chalcophile elements as deduced from MORB: implications for partial melting. *Geochim. Cosmochim. Acta* **54**, 3379-3389.

PHILPOTTS, A.R. (1982): Compositions of immiscible liquids in volcanic rocks. *Contrib. Mineral. Petrol.* **80**, 201-218.

PUFFER, J.H. & HURTUBISE, D.O. (1982): Early Jurassic basalt of Fundy Basin, Nova Scotia. *Geol. Soc. Am., Abstr. Programs* **14**, 74.

RAJAMANI, V. & NALDRETT, A.J. (1978): Partitioning of Fe, Co, Ni and Cu between sulfide liquid and basaltic melts and the composition of Ni–Cu sulfide deposits. *Econ. Geol.* **73**, 82-93.

RYERSON, F.J. & HESS, P.C. (1978): Implications of liquid–liquid distribution coefficients to mineral–liquid partitioning. *Geochim. Cosmochim. Acta* **42**, 921-932.

SASSANI, D.C. & SHOCK, E.L. (1990): Speciation and solubility of palladium in aqueous magmatic–hydrothermal solutions. *Geology* **18**, 925-928.

STONE, W.E., CROCKET, J.H. & FLEET, M.E. (1990): Partitioning of palladium, iridium, platinum, and gold between sulphide liquid and basalt melt at 1200°C. *Geochim. Cosmochim. Acta* **54**, 2341-2344.

TALKINGTON, R., GOTTFRIED, D., LIPIN, B., RAIT, N., PUFFER, J. & SHIRLEY, D. (1988): The distribution of the platinum-group elements in the Palisades sill, New Jersey and New York. *In* Geo-Platinum'87 (H.M. Prichard, P.J. Potts, J.F.W. Bowles & S.J. Cribb, eds.). Elsevier, New York, N.Y. (255-256).

WARK, J.M. & CLARKE, D.B. (1980): Geochemical discriminators and the palaeotectonic environment of the North Mountain basalts, Nova Scotia. *Can. J. Earth Sci.* **17**, 1740-1745.

WATSON, E.B. (1976): Two-liquid partition coefficients: experimental data and geochemical implications. *Contrib. Mineral. Petrol.* **56**, 119-134.

WEIGAND, P.W. & RAGLAND, P.C. (1970): Geochemistry of Mesozoic dolerite dikes from eastern North America. *Contrib. Mineral. Petrol.* **29**, 195-214.

WHITE, R.S. (1989): Igneous outbursts and mass extinctions. *Trans. Am. Geophys. Union* **70**(46), 1480, 1490.

WOOD, S.A., MOUNTAIN, B.W. & PAN, PUJING (1992): The aqueous geochemistry of platinum, palladium and gold: recent experimental constraints and a re-evaluation of theoretical predictions. *Can. Mineral.* **30**, 955-982.

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