

Chemical and mineralogical heterogeneity in the basal zone of the Partridge River Intrusion: implications for the origin of Cu–Ni sulfide mineralization in the Duluth Complex, midcontinent rift system

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Abstract Copper–nickel sulfide mineralization in the Partridge River Intrusion of the 1.1 Ga Duluth Complex is restricted primarily to a 100 m thick zone near the base of the intrusion, which is heterogeneous at meter scales in terms of both sulfide contents and rock types, which include dunite, melatroctolite, troctolite, leucotroctolite, gabbro, olivine gabbro, gabbro-norite, and rare norite. Olivine-rich troctolites and melatroctolites appear to have required mineral accumulation on a substrate, whereas augite troctolite and gabbros are thought to have formed via in situ crystallization of magmas ranging in composition from high-Al olivine tholeiite to high-Ti tholeiite. $\delta^{18}\text{O}$ values of orthopyroxene-poor rocks in the Partridge River Intrusion range from 5.2 to 6.7‰. $\delta^{18}\text{O}$ values of 6.7‰ are consistent with less than 20% contamination by high- ^{18}O metasedimentary country rock, either via devolatilization or local partial melting. Rocks with greater than ~15% orthopyroxene, gabbro-norites, and norites, are characterized by $\delta^{18}\text{O}$ values in excess of 6.9‰, and required the assimilation of larger amounts of siliceous country rocks. Sulfur isotopic values in

leucotroctolitic rocks that contain less than ~400 ppm S and that overlie the basal zone range between –1.5 and 2‰, values that are consistent with those of mantle-derived sulfur. In contrast, $\delta^{34}\text{S}$ values in the basal zone range from –1.4 to 10.5‰, where the ^{34}S -enriched samples require an input of sulfur from metasedimentary country rocks. $\delta^{34}\text{S}$ values of the rocks in the basal zone correlate with variations in olivine Fo content but not with S abundance. The wide range in $\delta^{34}\text{S}$ values of rocks in the basal zone strongly suggests that magmas interacted with layers in the sedimentary country rocks that were themselves characterized by variable sulfide contents and $\delta^{34}\text{S}$ values. The S isotopic data suggest that the heterogeneity observed in the basal zone results from the emplacement of relatively thin sheets of compositionally distinct magma. All rock types present in the basal zone can be produced as a result of variable degrees of fractionation of a parental high-Al olivine tholeiite, followed by varying degrees of contamination of derivative liquids by country rocks. The S-contamination process was essential for the development of Cu–Ni mineralization, and was restricted to the earliest stages in the development of the Duluth Complex at a time when volatile species such as S and H_2O , and low-T partial melts of country rocks, were available to magmas.

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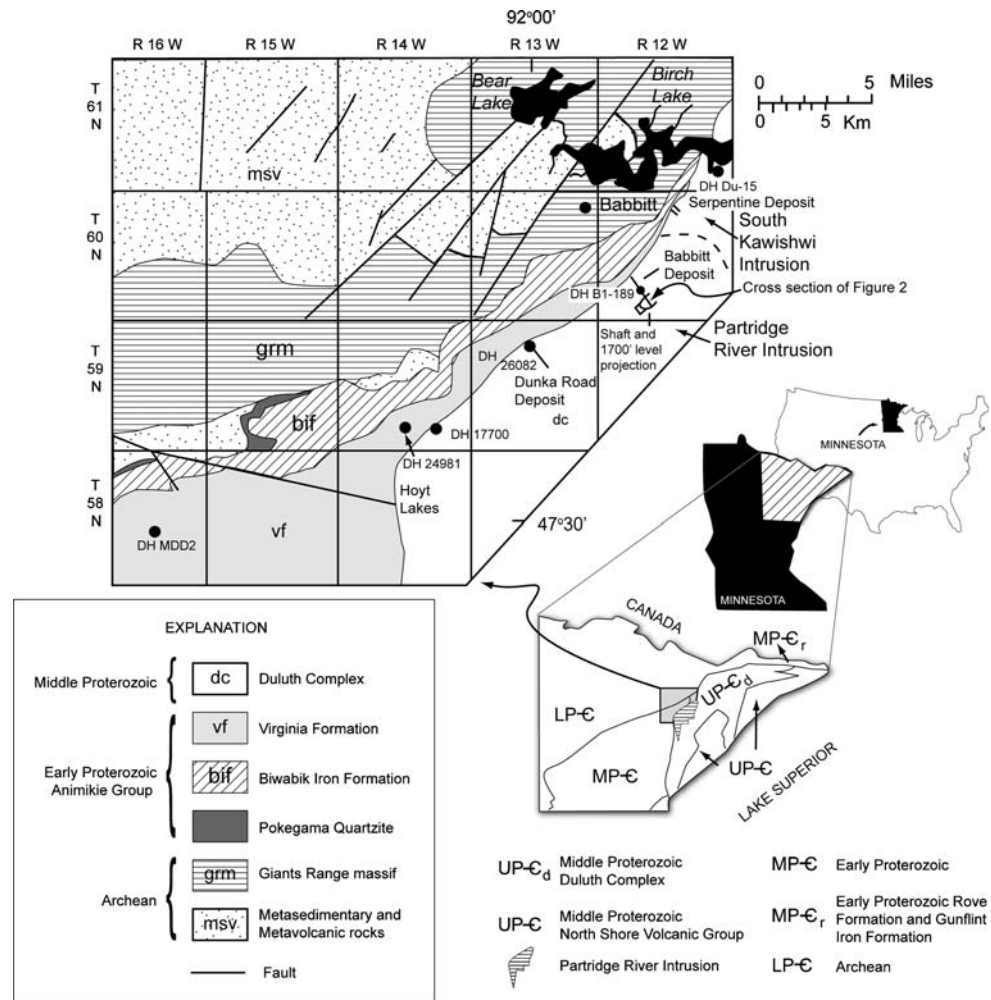
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Introduction

The ~1.1 Ga Duluth Complex is composed of a series of mafic intrusions that extend from the city of Duluth, Minnesota, northeastward to the Canadian border (Fig. 1). Copper–nickel sulfide mineralization in the

Fig. 1 Location map showing the regional geologic setting of the Partridge River Intrusion and the Babbitt Cu–Ni deposit. Drill core B1-189 is located near the area of the exploration shaft for the Babbitt deposit



Complex has been the subject of several studies conducted during the past 30 years. In these studies mineralogy, textural relationships, and geochemical characteristics of the sulfide minerals and associated silicate-rich assemblages have been stressed. It is clear that most, but not all, sulfide mineralization in the Complex is found within the basal portion of two composite intrusions, the Partridge River and South Kawishiwi, near their contacts with underlying Proterozoic metasedimentary and Archean volcano-sedimentary and intrusive rocks (e.g. Weiblen and Morey 1976; Ripley 1981; Rao and Ripley 1983; Tyson and Chang 1984; Ripley and Alawi 1986; Martineau 1989; Severson 1991; Hauck et al. 1997; Theriault et al. 2000). Sulfide mineralization occurs as massive lenses in the metasedimentary country rocks and igneous rocks, and as various types of disseminated and stringer sulfides in troctolitic to gabbroic rocks. Disseminated sulfide mineralization in the basal zone of these intrusions comprises more than 90% of the over 1 billion tons of Cu and Ni reserves, which grade in excess of 0.6 wt%

Cu and 0.2 wt% Ni. However, basal zone mineralization in both intrusions is neither continuous nor homogeneous. In the Partridge River Intrusion, intervals of unmineralized rocks are common in what Severson (1991) has termed a basal sulfide-bearing heterogeneous zone. An important aspect of the mineralization that remains unclear is whether or not potential ore-grade concentrations of sulfide minerals are associated with only one magma type in the basal zone, or with magmas of diverse origins that were emplaced during a restricted time interval. Until the Cu and Ni resources in the basal zone are exploited and visual observation is made feasible via the mining process, it may be impossible to correctly interpret both the spatial relationships between rock types and their intrusive history. However, no matter what physical mechanisms led to the heterogeneity observed today, the mineralogical and chemical variations between rock types permit an assessment of their petrogenetic relationships. In terms of understanding the generation of sulfide mineralization in the Partridge River Intru-

sion and throughout the Duluth Complex, it is critical to determine if only certain intrusive rock types are mineralized, if a particular stage in fractionation history was vital for sulfide production and accumulation, and, in either case, if contamination by country rocks was a prerequisite for sulfide genesis. In this paper, we present detailed mineralogical, chemical, and stable isotope data collected from a drill core that intersected sulfide-bearing igneous rocks of the Partridge River intrusion in the Babbitt Cu–Ni deposit. We utilize the data to evaluate possible genetic relationships between the varied rock types in the basal zone, and if such relationships played a significant role in the generation of sulfide mineralization.

Geologic setting

Over 1,000 drill holes have been drilled along a 50 km stretch of the basal contact where the Partridge River and South Kawishiwi Intrusions are in contact with Archean granitic rocks and Proterozoic iron-formation, graywacke and slate (the Virginia Formation and the Biwabik Iron Formation, Fig. 1). Our emphasis in this communication is on rocks from the Babbitt Cu–Ni deposit located within the Partridge River Intrusion (Fig. 1). The deposit contains both disseminated and massive sulfide occurrences that are representative of the styles of mineralization found within the Duluth Complex. Estimates of the size of the Babbitt deposit vary, but a conservative figure of 350 million tons of 0.84% Cu using a 0.6% Cu cut-off is reasonable (average Cu/Ni = 3).

Severson and Hauck (1990) divided the Partridge River Intrusion into eight distinct units based on mineral modes and textural features (Table 1; Fig. 2). Various types of troctolite predominate, but layers of peridotite, gabbro, and anorthosite also occur. Severson and Hauck's Unit I, sometimes referred to as the

Basal Heterogeneous Zone, hosts over 90% of the sulfide mineralization found in the Partridge River Intrusion. In this zone troctolite, anorthosite, gabbro, ferrogabbro, and gabbro-nodules are intercalated, with no easily discernible rhythmic or repetitive sequences, such as those found in overlying units, or intrusive contacts. The heterogeneity is a function of irregular changes in mineralogy, mineral modes, and textures, as described further below. Xenoliths of country rocks may be locally abundant in this zone (up to 25 vol%), but the presence or absence of country rock xenoliths does not correlate with the lithologic variability that characterizes the zone.

Sampling and analytical methods

Samples for this study were collected from drill core B1-189 at the Babbitt deposit (Fig. 2). This core is located up dip from an area of high-grade mineralization where massive sulfides are prevalent above an arch in metasedimentary rocks known as the Local Boy anticline (Fig. 2). Units I, IV, and V of Severson and Hauck (1990) can be identified in the drill core. Previous studies of the Babbitt deposit by Ripley and Al-Jassar (1987), Ripley and Alawi (1988), Ripley et al. (1993), and Arcuri et al. (1998) utilized drill cores from the Local Boy area (including B1-136, Fig. 2). Unlike these drill cores, core B1-189 is characterized by the presence of only a few small xenoliths of country rocks (orthopyroxene–cordierite–biotite hornfels) near the basal contact. A total of 220 samples were collected from core B1-189. Polished thin sections were made from 182 samples; 100 samples were chosen for chemical and isotopic analyses. Mineral modes were determined based on 1,000-point counts per section.

Major element analysis was carried out by fusion using lithium borate/metaborate flux, followed by sample dissolution in heated, dilute nitric acid. Minor

Table 1 Units of the Partridge River Intrusion defined by Severson and Hauck (1990)

Unit	Summary description
VIII	Known via reconnaissance mapping; resembles troctolites of Units IV through VII, with a basal serpentized peridotite–picrite
VII	Medium to coarse-grained, augite-poor troctolite; basal peridotite–picrite; sulfide-poor
VI	Homogeneous textured, medium to coarse-grained, augite-poor troctolite; grades into thick leucotroctolite zones; picrite at base
V	Coarse-grained, augite-bearing leucotroctolite; grades locally to troctolite or olivine gabbro; cross-cuts lower units
IV	Coarse-grained, augite-poor to augite-bearing troctolite; picritic unit near base is common; rare sulfides
III	Major marker bed; fine-grained leucotroctolite that grades into patches of anorthosite, troctolite, and minor picrite; olivine oikocrysts give a distinct mottled appearance
II	Abundant cyclic units of troctolite–picrite–peridotite–dunite; fine to medium-grained picrite–peridotite horizons; sporadic sulfides
I	Sulfide-bearing augite troctolite to olivine gabbro; lesser troctolite and anorthosite; extreme variations in grain size and modal mineral percentages; upper contact generally defined by a decrease in sulfide content (<1%); inclusions of Virginia Formation may be common

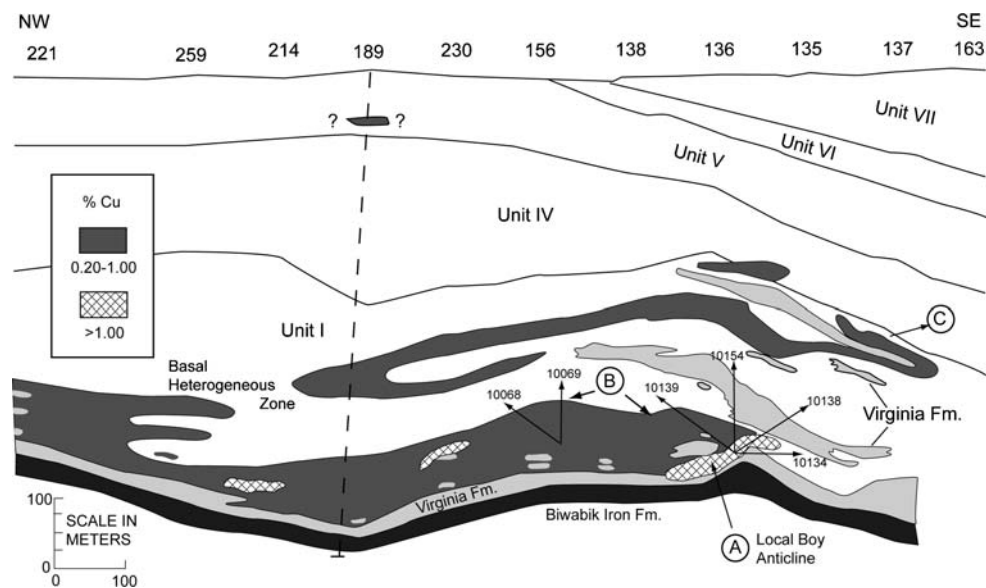


Fig. 2 Composite cross section of lines 3,600 and 4,000 E from the Babbitt deposit (Fig. 1) showing the location of drill core B1-189 and the distribution of Cu-rich sulfide mineralization. Underground workings at the 1,700 feet level (AMAX shaft) intersect the vertical projections of drill holes B1-156 and B1-136. Drill cores 10,068, 10,069, 10,139, 10,138, 10,154, and 10,134 are underground fan drill cores that project from the 1,700 feet

level. *Type A* mineralization consists of massive stringer or fracture-filling sulfides located in both metasedimentary and igneous host rocks. *Type B* is disseminated mineralization in gabbroic to troctolitic host rocks. Disseminated sulfide mineralization located well above the based contact and spatially associated with xenoliths of footwall rocks is designated *Type C*. Modified from Sevenson (1991)

and trace element analyses were undertaken by dissolving powders in concentrated nitric, hydrofluoric, and perchloric acids. Major and trace element (Cu, Ni, Ba, Sr) analyses were conducted by ICP spectrophotometry using a Jarrel Ash 975 instrument at Indiana University. Multiple replications of standards gave less than 2% relative standard deviation for SiO₂, MgO, FeO, and Al₂O₃ and less than 3% for K₂O, Na₂O, TiO₂, and MnO. P and Y analyses were conducted using a Jobin Yvon ICP2500 spectrophotometer, with a 3.8% relative standard deviation for Y and 2.6% for P₂O₅. Sulfur was analyzed using a LECO C/S 144 instrument at Indiana University. Multiple analyses of standards gave an absolute standard deviation of $\pm 0.07\%$.

Additional trace element analyses were conducted at Monash University as part of a study of radiogenic isotopic systematics in the Duluth Complex (Ripley et al. 1999). For these samples, 100–150 mg rock powders were dissolved using a series of HF-HNO₃, HNO₃, HCl digestion steps. The samples were then picked up and diluted by weight to a dilution factor of $\sim 2,000$ in 2% HNO₃, and spiked with 100 ppb indium to serve as an internal standard. Diluted rock solutions were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) using a VG Plasma Quad PO₂ + in peak jumping mode for maximum sensitivity. Total analytical blanks were typically less than 10 mg

for all elements, making blank corrections typically less than 0.1%. Precision was better than 2%, and accuracy, based on the reproducibility of standards during the run, was also better than 2%.

Analyses of olivine, plagioclase, clinopyroxene, orthopyroxene, and biotite were made using a Cameca SX-50 electron microprobe at Indiana University. Accelerating voltage was maintained at 15 KeV and sample current at 25 nA. Beam size for most analyses was 1–3 μm . Standards included native metals and synthetic, and natural minerals. Raw counts were converted to oxide concentrations using the PAP correction scheme (Pouchou and Pichoir 1984).

Oxygen isotope analyses were undertaken following the BrF₅ method of Clayton and Mayeda (1963). Whole-rock powders and mineral separates were ground to 80–100-mesh and stored in vacuum at 120°C for at least 24 h prior to analysis. Extracted oxygen was converted to CO₂ by reaction with a hot graphite disk wrapped with Pt–Rh wires. The CO₂ gas was analyzed on a Finnigan MAT 252 stable isotope ratio mass spectrometer. Results are reported in standard delta notation relative to VSMOW (Coplen 1994). NBS quartz has a value of $9.6 \pm 0.2\text{‰}$ in our laboratory. For sulfur isotope analyses, sulfide minerals were combusted with CuO in vacuum at 1,000°C. Liberated SO₂ gas was analyzed on a 6" 60°-sector Nuclide stable isotope ratio mass spectrometer. Some samples were

analyzed using elemental analyzer-continuous flow methodology, with mass spectrometric analyses made using a Finnigan MAT 252 (Studley et al. 2002). Standards utilized included IAEA S-1, S-2, and S-3, along with several laboratory standards. Results are reported in delta notation relative to VCDT (Krouse and Coplen 1997) with an analytical precision of $\pm 0.05\text{‰}$, and reproducibility, better than $\pm 0.2\text{‰}$. Whole-rock hydrogen isotopic and H_2O analyses were undertaken using elemental analyzer-continuous flow methodology. Samples were loaded into silver cups and combusted at $1,400^\circ\text{C}$ in a glassy carbon column as described by Sharp et al. (2001). Mass spectrometric analyses were made using a Finnigan Delta-Plus XP. Results are reported in delta notation relative to VSMOW. A series of six standards with δD values ranging from -65 to -110‰ were used for calibration purposes, with NBS-30 biotite having a value of -65‰ .

Results

Rock types and petrography

Rock types present in the uppermost units of core B1-189 constitute zones IV and V of Severson and Hauck (1990) and cyclic zones one through five of Taib (2001); they are dominated by troctolite and leucotroctolite (Fig. 3). Olivine occurs as granular grains with a long dimension less than 2.5 cm, and more rarely as oikocrysts. In some pegmatitic units, olivine oikocrysts may reach several centimeters in length. Olivine grains typically comprise from 20 to 30 vol% of the troctolitic rocks, and from 10 to 19 vol% of the leucotroctolites (Fig. 3; Tables of all modal and geochemical data are available as Electronic supplementary material). Plagioclase occurs as laths with aspect ratios from 1 to 7. Grains are generally fresh, with only local alteration to

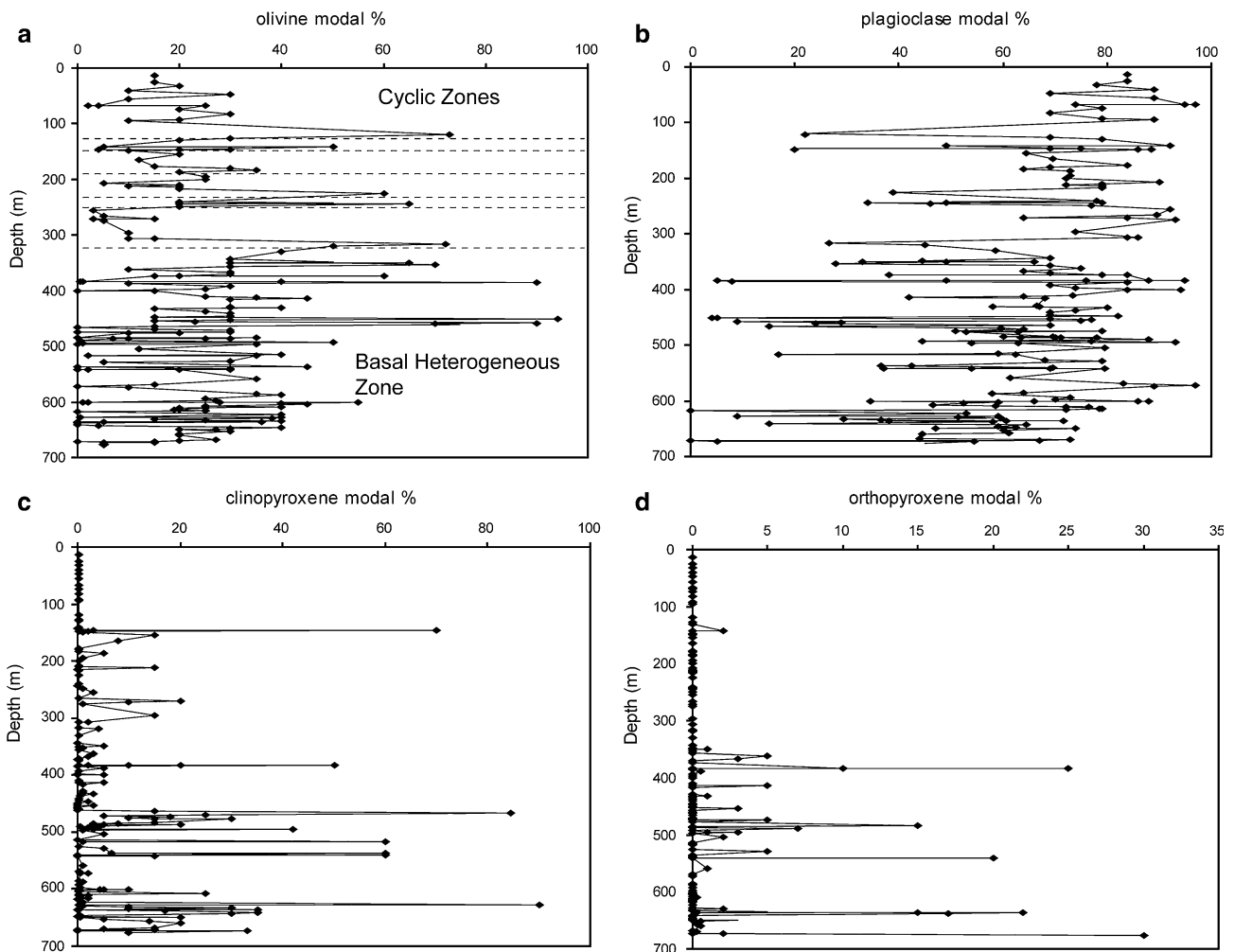


Fig. 3 Distribution of olivine (a), plagioclase (b), clinopyroxene (c), and orthopyroxene (d) in drill core B1-189. Cyclic zones above ~330 m are from Taib (2001), and are characterized by basal layers of dunite or melatroctolite

epidote and chlorite. Plagioclase abundance varies from ~60% in troctolites to >90% in rare anorthosite layers (Fig. 3a). Melatroctolite, and more rarely dunite, occur as 1–5 m-thick units at the base of what Taib (2001) has termed cyclic zones overlain by troctolite and leucotroctolite. Olivine abundance may increase up to ~70 vol% in the melatroctolite layers (Fig. 3a). The degree of olivine serpentinization and epidote–chlorite alteration of plagioclase increases in these units. Biotite, clinopyroxene, orthopyroxene, ilmenite, apatite, and sulfide minerals occur as interstitial minerals in all rock types. Sulfur content exceeds 1,000 ppm in only two samples in these zones; most of the rocks in these units contain less than 400 ppm S (Fig. 4a).

Within the Basal Heterogeneous Zone (Fig. 2, below 330 m; Unit I of Severson and Hauck, 1990), troctolite is the predominant rock type, with textures similar to those found in the overlying units. However, the abundance of rocks with increased proportions of clinopyroxene, orthopyroxene, biotite, ilmenite, apatite, and sulfides is much higher in the Basal Heterogeneous Zone compared to the overlying units. Orthopyroxene may occur as rims on olivine grains, as an interstitial mineral, or locally as granular to poikilitic grains. Orthopyroxene modal abundance is normally less than 5 vol%, but some gabbronorites may contain up to 30 vol% (Figs. 3d, 5). Clinopyroxene normally occurs as an interstitial mineral, but its

abundance may locally increase to 80% in some oikocryst-rich samples (Fig. 3c). In gabbronorites, clinopyroxene may have a granular texture (Fig. 5). Biotite occurs in interstices between primocryst minerals, often in association with ilmenite and sulfides. Epitaxial biotite is locally found on olivine and clinopyroxene. Biotite modal abundance is typically between 0.25 and 1 vol%, but may locally reach values as high as 8 vol%. Ilmenite may occur as a rounded, interstitial mineral, or where its abundance exceeds ~3 vol% as angular to skeletal or blade-like grains, suggestive of a primocryst origin. In oxide-rich rocks it may form an anastomosing network around silicate grains. Apatite is also commonly associated with ilmenite, biotite, and sulfides. It is generally euhedral and forms prismatic needles. Ripley et al. (1998) have described euhedral apatite in amounts up to 10 vol% in massive sulfide accumulations in the Local Boy ore zone (Fig. 2). The increased abundance of interstitial minerals in many of the samples from the Basal Heterogeneous Zone gives rise to rock types that include gabbronorite, melagabbro, gabbro, and oxide-rich gabbro. Contacts between various rock types are often sharp (Fig. 6), and characterized by abrupt changes in mineralogy and grain size.

Sulfide minerals in the Basal Heterogeneous Zone are irregularly distributed but present in all rock types examined. Intersections of massive sulfides occur in core B1-189 (573.6–573.9 m; 595.3 m; 623.6–624.8 m),

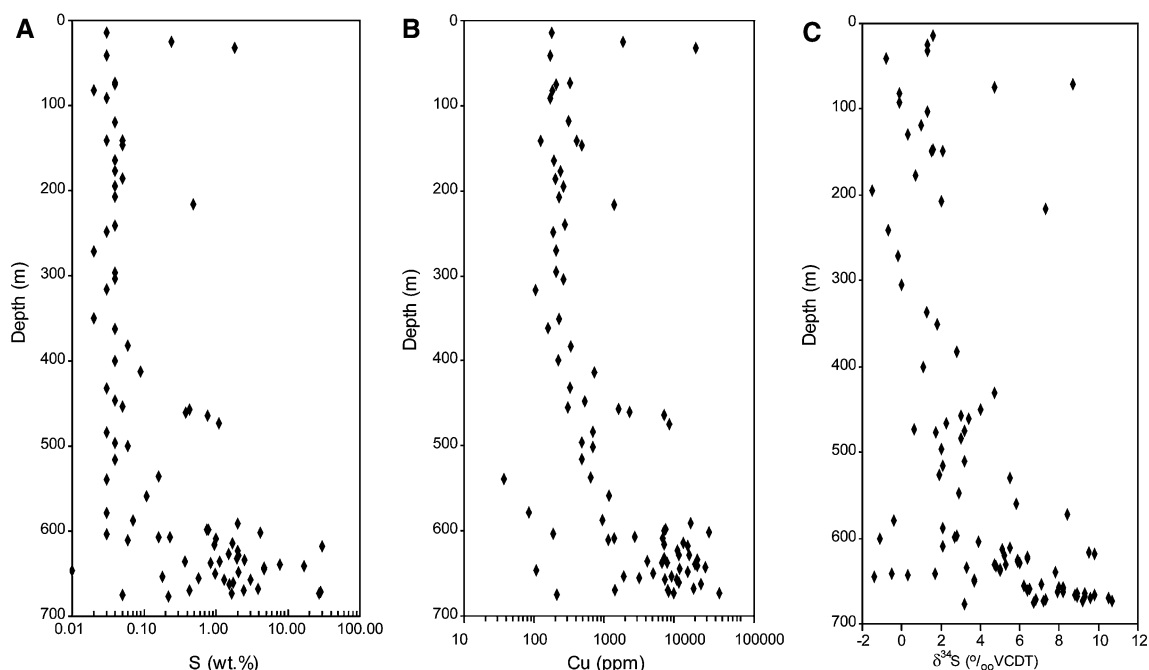


Fig. 4 Sulfur and copper contents, and $\delta^{34}\text{S}$ values of rocks from drill core B1-189

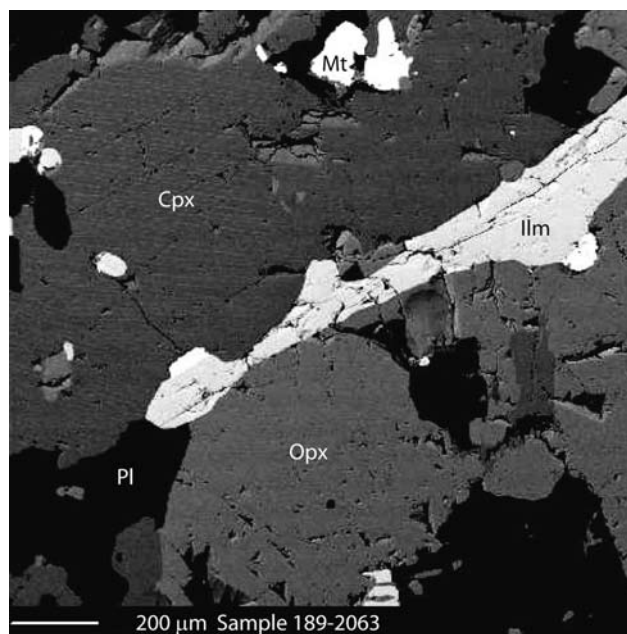


Fig. 5 Back-scattered electron image of a gabbro-norite from drill core B1-189 showing the granular form of both clinopyroxene and orthopyroxene

but are far less common than in the Local Boy ore zone to the east (Fig. 2). Sulfur content in other rocks in the Basal Heterogeneous Zone ranges from less than 100 ppm to 7 wt% (Fig. 4a). Pyrrhotite is the predominant mineral in the sulfide assemblages, along with cubanite, chalcopyrite, and minor pentlandite and bornite. Sulfide assemblages are variable, with volume percentages varying as follows: pyrrhotite 10–60%, cubanite 20–70%, chalcopyrite 1–10%, and pentlandite 0–5%. Cubanite is more abundant than chalcopyrite in

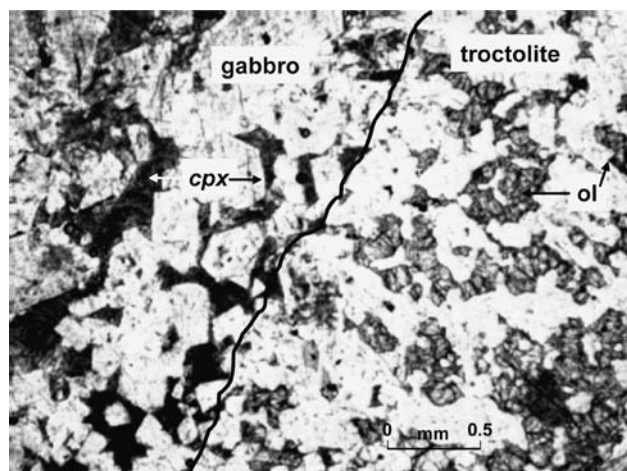


Fig. 6 Photomicrograph showing a sharp boundary between gabbro and troctolite, 583 m, drill core B1-189. *Cpx* clinopyroxene, *ol* olivine

the massive mineralization, with the reverse true where sulfide minerals are more finely disseminated. The nickel and copper content of the rocks in the basal zone are variable, ranging from 48 ppm to 2.7 wt% and 37 ppm to 4.4 wt%, respectively. Both Cu and Ni are strongly correlated with sulfur concentration (Figs. 4b, 7).

Whole rock major and trace element variations

Whole rock variations in Al_2O_3 , FeO, Na_2O , and MgO are shown relative to SiO_2 in Fig. 8, and trace element variations in different rock types are compared in Fig. 9 (representative values in Table 2). The variations exhibited with respect to SiO_2 concentration in part reflect the enrichment of Fe-rich sulfides $\pm$ oxide minerals at the expense of aluminous minerals, primarily plagioclase. Samples with less than ~ 45 wt% SiO_2 are enriched in olivine, plus sulfides and/or ilmenite. MgO content of sulfide- and ilmenite-bearing samples tends to show relatively little variation with SiO_2 content; MgO is distributed between olivine with

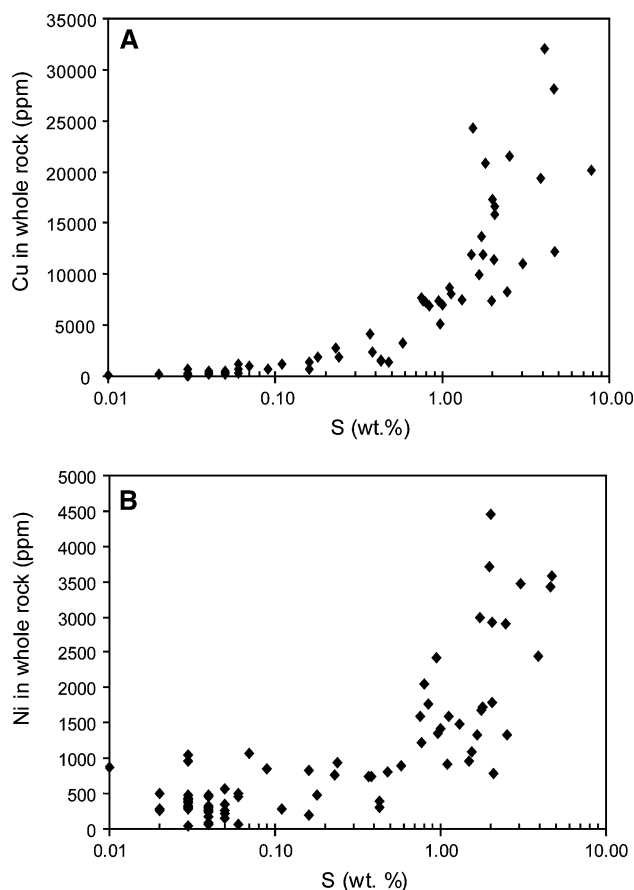


Fig. 7 Concentrations of Cu (a) and Ni (b) versus S in drill core B1-189

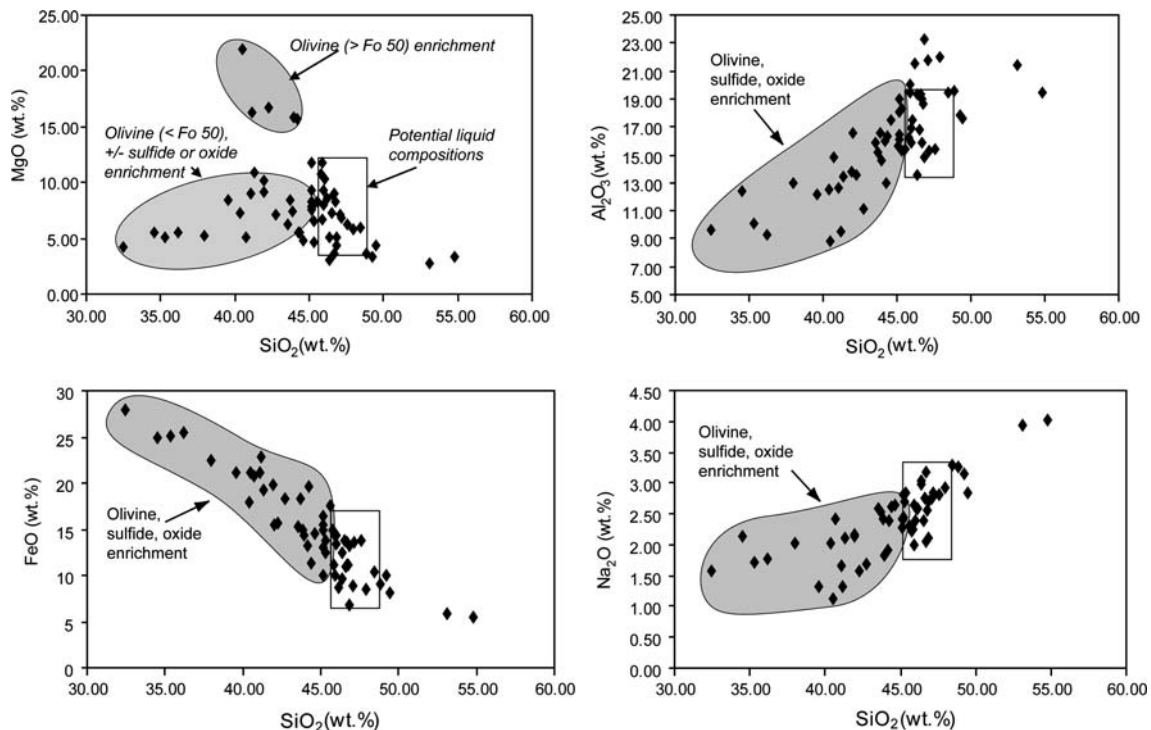


Fig. 8 Major element compositional variations among rock types in drill core B1-189. Potential liquid compositions produced as a result of up to 75% crystal fractionation from high-Al tholeiites contain from ~46 to 49% SiO₂. Samples with SiO₂ concentrations

Fo content less than 50 mol%, clinopyroxene, orthopyroxene, and biotite. Samples with low SiO₂ but relatively high MgO illustrate the effect of olivine (Fo > 50) enrichment.

Figure 9 illustrates that gabbros and gabbro-norites from the Basal Heterogeneous Zone are enriched in trace elements compared with troctolites. Incompatible elements such as Y and P show strong positive correlations (Fig. 10). They also tend to be linearly correlated with olivine Fo content (Fig. 11a). Although ilmenite is normally an interstitial mineral, the inclusion of Ti as an incompatible element may be misleading for some oxide-rich gabbros or gabbro-norites. However, TiO₂ does correlate positively with Y and P₂O₅, and negatively with olivine Fo content (Fig. 11b). The trace element trends of the gabbros and gabbro-norites overlap those shown by various basaltic rock types from the overlying North Shore Volcanic Group (Fig. 9).

Mineral chemistry

Olivine In the Basal Heterogeneous Zone, olivine compositions range from Fo 68 to Fo 18 (Fig. 12). The more Mg-rich compositions are found in dunites and melatroctolites where olivine abundance exceeds

less than ~46 wt% are enriched in either sulfide minerals (> ~3 wt% S), Fe-Ti oxides, or olivine. High Al₂O₃ samples are enriched in plagioclase; high SiO₂ samples are enriched in either plagioclase or pyroxene, but depleted in olivine

~40 vol%. Nickel contents of olivines vary from 500 to 1,600 ppm; a correlation between Ni abundance and Fo content is observed, but Ni concentrations for a particular Fo value are variable (Fig. 13).

Plagioclase Plagioclase in all rock types in the Basal Heterogeneous Zone shows normal, reverse, and oscillatory zoning; locally all three types of zoning are found on the scale of a thin section, although normal zoning is prevalent in all samples. Cores of plagioclase grains range in composition from An 73 to An 50, and vary with olivine Fo contents (Fig. 14a).

Pyroxene Interstitial clinopyroxene ranges from Wo₁₆ En₅₃ Fs₃₀ to Wo₄₅ En₄₃ Fs₁₂. Mg numbers vary from 85 to 60 and correlate with olivine Fo and plagioclase An content (Fig. 14b). Orthopyroxene compositions also show a strong relationship with olivine Fo (Fig. 14c); Mg numbers vary from 73 to 47.

Biotite Biotite Mg numbers range from 76 to 47, and also show a positive relationship with olivine Fo values (Fig. 14d).

δ¹⁸O values

Whole rock δ¹⁸O values range from 5.2 to 7.4‰ (Fig. 15), with 85% of the values between 5.4 and 6.5‰. A limited number of mineral separates were

Fig. 9 Average trace element variations in representative basaltic (primitive olivine tholeiite, intermediate olivine tholeiite, transitional basalt, and Fe-rich olivine tholeiite) rocks from the North Shore Volcanic Group (Brannon 1984), and Duluth Complex. *Open symbols* (189–609, 1062, 1197, and 1736) are troctolites and *solid symbols* are gabbros and gabbro-norites

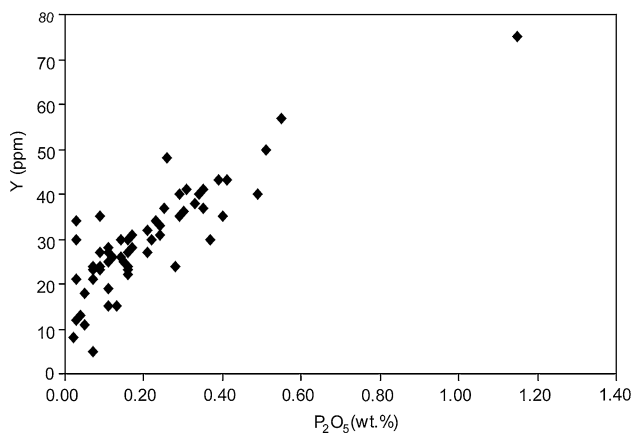
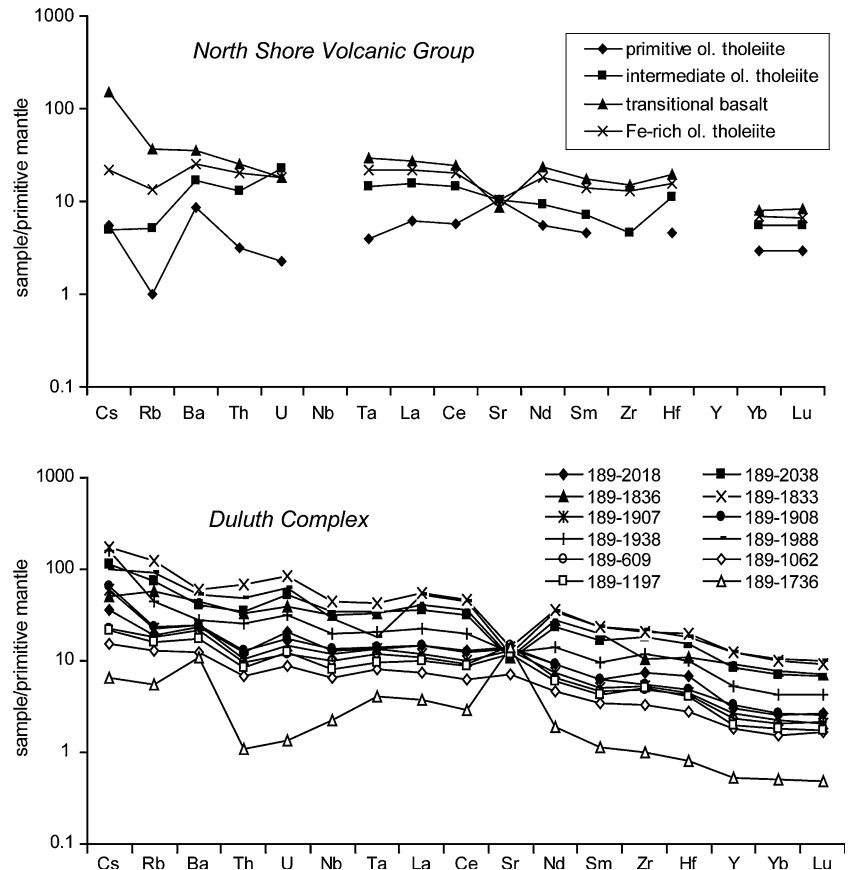


Fig. 10 Y versus P_2O_5 for rocks in drill core B1-189

analyzed with ranges as follows: olivine 5.2–6.1‰; plagioclase 6.4–7.0‰; biotite 4.8–5.2‰; ilmenite 5.5–6.1‰. Values of $\delta^{18}O$ of N-MORB reported by Eiler (2001) range from ~5.3 to 5.8‰, with plagioclase values expected to be near 6.1‰. Many values from the Partridge River Intrusion are slightly enriched compared to values expected for uncontaminated mantle; strongly anomalous $\delta^{18}O$ values in excess of 6.9‰ are restricted to orthopyroxene-rich rocks (Figs. 3d, 15).

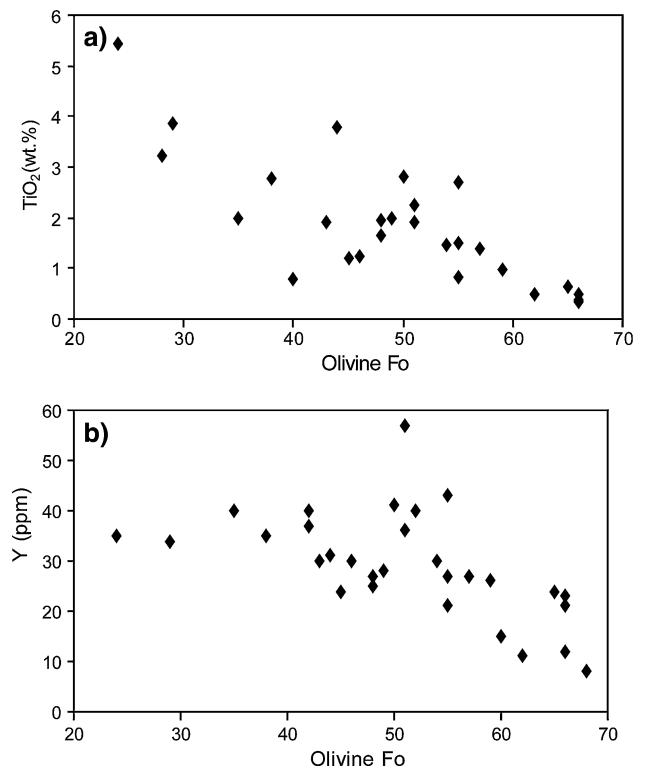


Fig. 11 TiO_2 and Y versus olivine Fo for samples from drill core B1-189

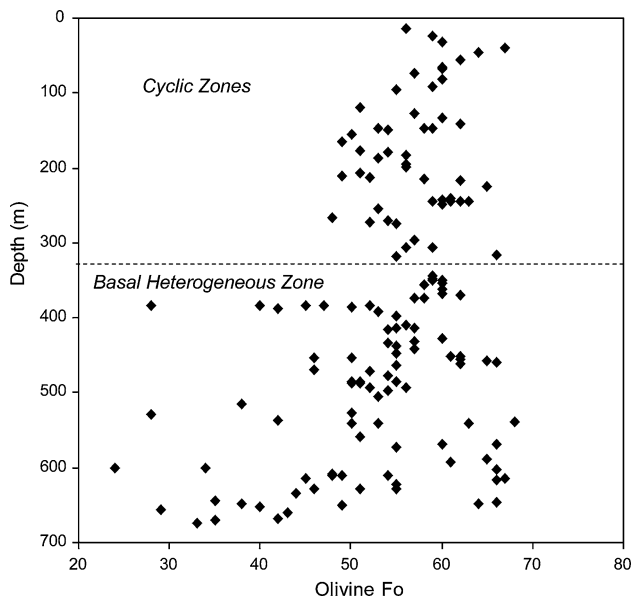


Fig. 12 Olivine Fo versus depth in drill core B1-189

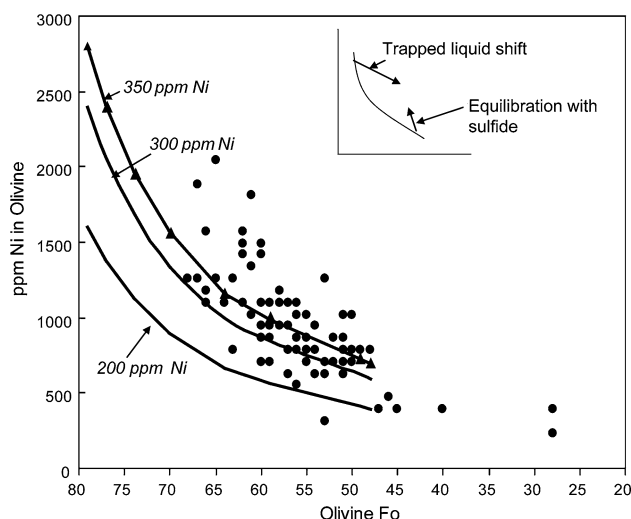


Fig. 13 Olivine Fo versus ppm Ni in olivine. Solid lines represent fractional crystallization of high-Al olivine tholeiite parental magma (Table 3, number 1) with 350, 300, and 200 ppm Ni. Modeling was done using MELTS (Ghiorso and Sack 1995) at 2 kb, OFM-2, and 0% H₂O; mineral/magma D (Ni) values were 7 and 0 for olivine and plagioclase, respectively, (Lee and Ripley 2003). For this starting composition plagioclase undergoes ~7% crystallization before the onset of olivine crystallization. The extreme range of olivine Ni content for a given Fo value strongly suggests that distinct magmas with different Ni concentrations were involved in the genesis of the rocks. For olivine-rich rocks that were produced via crystal accumulation, reaction with trapped silicate and sulfide liquid could have also contributed to the variability

Troctolites and leucotroctolites are characterized by $\delta^{18}\text{O}$ values less than 6.7‰. Three samples of Virginia Formation located below the contact with igneous

rocks gave $\delta^{18}\text{O}$ values of 8.2–13.3‰, in line with the range of 8 to 14‰ for the Virginia Formation recorded by Ripley and Al-Jassar (1987) and Arcuri et al. (1998).

$\delta^{34}\text{S}$ Values

$\delta^{34}\text{S}$ values of sulfide minerals fall within a broad range of –1.4 to 10.5‰ (Fig. 4c). All samples with $\delta^{34}\text{S}$ values greater than 3‰ occur in the Basal Heterogeneous Zone, and samples with $\delta^{34}\text{S}$ values in excess of 5‰ occur only in the lowermost 80 m of the core. In the uppermost units of the core (Units IV and V of Severson and Hauck 1990) $\delta^{34}\text{S}$ values range between –1.5 and 2‰, values considered normal for sulfur of mantle derivation. Although elevated $\delta^{34}\text{S}$ values occur in the lower 80 m of the core, it is important to note that they are interspersed with values as low as –1.4‰ (Fig. 4c).

δD values

δD values of whole rocks in the Basal Heterogeneous Zone range from –70 to –114‰, with over 95% of the values ranging between –80 and –100‰ (Fig. 16a). Water contents range from 0.25 to 4.61 wt% (Fig. 16b). Samples with greater than 4 wt% H₂O show the lowest δD values.

Discussion

Previous hypotheses to explain lithologic and chemical variability in the Partridge River and South Kawishiwi Intrusions

Sassani (1992) proposed that many intrusive units in the Duluth Complex represent inputs of thin sheets of magma, a process similar to that proposed for the generation of gabbroic rocks in the oceanic crust (e.g. Dick et al. 1991; Hébert et al. 1991). Lee and Ripley (1996) also proposed such a mechanism for units of the South Kawishiwi Intrusion, and suggested that the thickness of individual sheets of magma ranged from only 3 to 20 m. Natland and Dick (2001) have also discussed similarities between intrusive units in the Duluth Complex and gabbros of the oceanic crust. The variability in some areas of the basal zone of the Partridge River Intrusion suggests that if this scenario is correct, some intrusive pulses might have been even thinner than those proposed by Lee and Ripley (1996).

Another scenario related to the intrusion of multiple magmas is that the heterogeneity in the basal zone reflects a complex contact zone between several larger intrusions. In this regard it is important to note that

Fig. 14 Olivine Fo versus **a** plagioclase An core compositions, **b** Mg number of clinopyroxene, **c** Mg number of orthopyroxene, and **d** Mg number of biotite

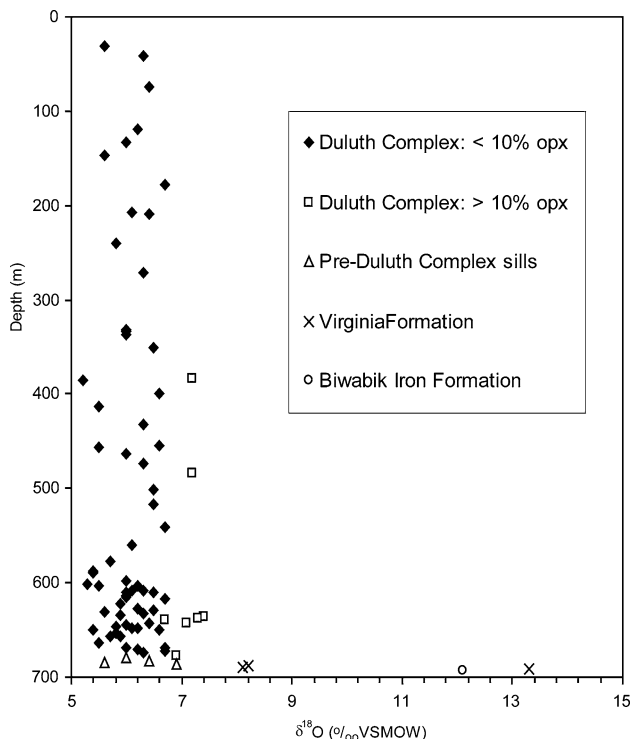
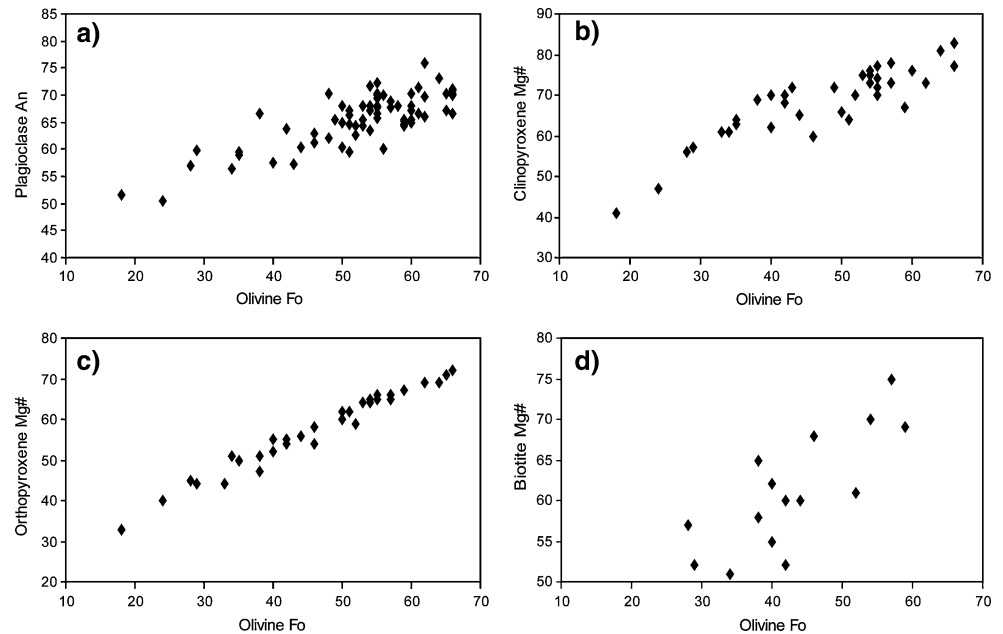


Fig. 15 Whole rock $\delta^{18}\text{O}$ values for samples in core B1-189. Only orthopyroxene-rich samples in the Partridge River Intrusion have $\delta^{18}\text{O}$ values in excess of 6.9‰

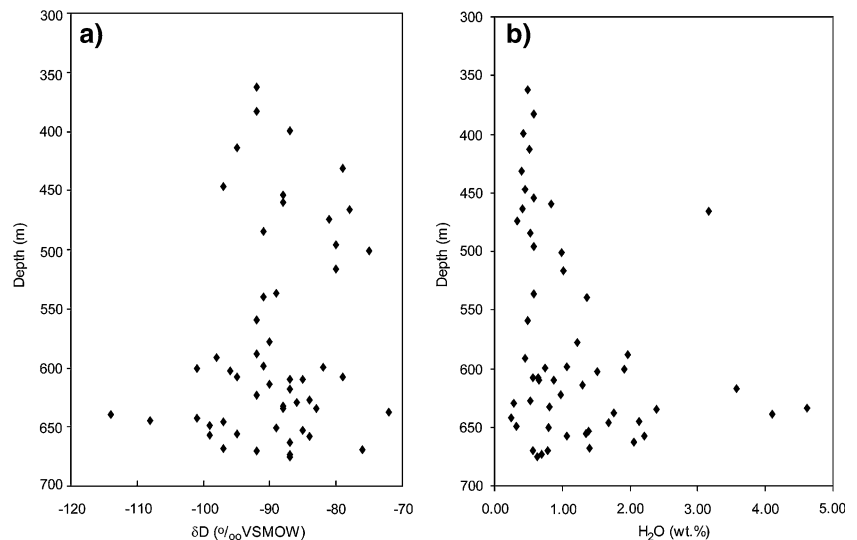
Martineau (1989) has divided troctolitic and gabbroic rocks in the Babbitt area into a sequence that radically differs from that proposed by Severson and Hauck (1990). Martineau (1989) proposed that ferrogabbroic intrusions were sulfide-bearing and that troctolitic

intrusions were typically sulfide-barren, and that both the Partridge River and South Kawishiwi Intrusions were actually composed of several different intrusions of both ferrogabbroic and troctolitic affinity. Contact zones between the two types of intrusions were thought to be characterized by interlayering, producing the type of heterogeneity found in the basal zone.

A third possibility, which could result from either of the mechanisms mentioned above, is that the Basel Heterogeneous Zone represents a breccia horizon. In the South Kawishiwi Intrusion to the north (Fig. 1), geologists from International Nickel Company, influenced by studies on the fragmental rocks near the base of the Sudbury impact site, coined the term “Spruce” or “Spruce Road” breccia for heterogeneous rocks in the basal zone of that intrusion. Miller and Ripley (1996) also discuss the possibility that the sequence represents a breccia zone due to the restricted thickness and lateral extent of individual rock types. What rock type would represent the matrix of the breccia is not clear. In addition, the variety of rock types present strongly suggests that a local source was unlikely, and that the xenoliths would have to have been transported from depth. The mechanism by which multiple xenolith types could be transported to shallower depths is uncertain.

A fourth interpretation of the variability found in the Partridge River Intrusion was put forth by Chalokwu et al. (1993, 1996). Mineralogical and chemical variability was attributed to the interaction between olivine and plagioclase and a trapped liquid that was not in equilibrium with the primocryst minerals. Vari-

Fig. 16 Variations of δD (a) and H_2O (b) content in the Basal Heterogeneous Zone of the Partridge River Intrusion



ations in mineral modes and textures were attributed to local scale crystal settling or floating. This model involves the emplacement and in situ crystallization of a crystal mush rather than a history involving multiple intrusive pulses. They concluded that the magma chamber was closed with respect to other magma reservoirs, and that multiple inputs of compositionally distinct magmas were not necessary to explain the geochemical features of the intrusion. Chalokwu and Grant (1990) proposed that the wide range in olivine Fo contents observed in the lower portion of the intrusion resulted from exchange between variable proportions of an evolved, Fe-rich interstitial liquid and primocryst olivine. This interpretation represents an end-member scenario for closed system, in situ crystallization of a single magma pulse. Chalokwu et al. (1993) emphasized that the fine-grained material at the basal contact with the Virginia Formation, which they interpreted as a chilled margin, was more evolved than the parental magma for the bulk of the intrusion. They suggested that the contact rock represented a “leading-edge” ferrodioritic liquid that may have segregated from a compositionally stratified chamber at depth.

Lee and Ripley (1996) also proposed that in situ crystallization was important for the development of the South Kawishiwi Intrusion. However, they suggested that cyclic zones developed in response to periodic recharge of primitive, high-Al olivine tholeiitic magma. In their model, early formed, relatively Mg-rich olivine collected in a lower layer to generate melatroctolite. Crystallization advanced in boundary layers (e.g. Langmuir 1989; Nielsen and DeLong 1992) or crystallization fronts (Marsh 1996) with evolved, buoyant liquid added to overlying magma. Equilibrium crystallization of the boundary layers led to the

generation of more Fe-rich olivine. This process would have produced a relatively restricted range of olivine compositions, from ~Fo 70 in melatroctolites to Fo 50 in overlying troctolites. Recharge of fresh magma would have initiated a new cycle. For core B1-189, Taib (2001) divided Severson and Hauck’s (1990) Zones IV and V into five cyclic zones (Fig. 3) similar to those described by Lee and Ripley (1996) in the South Kawishiwi Intrusion. Taib (2001) also modelled the cyclic zones in terms of in situ, boundary layer equilibrium crystallization.

A fifth model to explain lithologic and chemical variations in the basal zone of the Partridge River Intrusion centers on local magma contamination by country rocks. Ripley et al. (1999) showed using both radiogenic (Pb, Sm/Nd, Re/Os) and stable isotopes that all of the troctolitic and gabbroic rocks of the Partridge River Intrusion have experienced relatively low (3–5%) degrees of contamination by metasedimentary country rocks. Localized assimilation of country rocks was described by Ripley and Alawi (1988) and Ripley and Taib (1989) who highlighted the history of partial melting experienced by xenoliths of Virginia Formation that are now found in the Partridge River Intrusion. Thériault and Barnes (1998) and Thériault et al. (2000) have also stressed the importance of localized contamination by country rocks in the formation of noritic rocks in the basal zone. However, Ripley and Al-Jassar (1987) noted that oxygen isotopic anomalies are restricted to within ~5 m of xenolith contacts in drill cores located to the east of core B1-189 (Fig. 2), and that not all of the rocks in the anomalous isotopic halo are norite. In fact, the isotopic data strongly suggest that the preserved oxygen isotopic values were produced via subsolidus exchange, and that contami-

nated melt may have been largely removed from the system. Arcuri et al. (1998) showed that troctolite, norite, and gabbro-norite may be in direct contact with xenoliths, and that oxygen isotopic anomalies are not present in any of the surrounding rock types. Similar conclusions with respect to contamination of the Partridge River Intrusion were reached by Grant and Molling (1981) and Grant and Chalokwu (1992) using Sr isotopic compositions of whole rocks and feldspars. All samples of the Partridge River Intrusion are characterized by elevated initial Sr isotopic ratios in the range of 0.7048–0.7063, consistent with the overall contamination discussed by Ripley et al. (1999). Higher $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios were found only in the vicinity of xenoliths or near the footwall, but Grant and Chalokwu (1992) stressed that anomalous Sr isotopic ratios are not ubiquitously found at contacts with country rocks.

Chemical heterogeneity in the basal zone of the Partridge River Intrusion

There are two fundamental tenets, which encompass the models to explain the chemical variations in the Partridge River and South Kawishi Intrusions discussed above. One is that the processes in a magma chamber produced different lithologies (e.g., fractional crystallization, crystal sorting, possible extrusion and replenishment) and the other is that the basal zone represents the emplacement and crystallization of a variety of compositionally distinct parental magmas. In the Basal Heterogeneous Zone, regular trends in mineralogy and chemistry are difficult to define. However, the similarity in rock types and mineral chemistry found in the Basal Heterogeneous Zone to those found in the overlying cyclic zones suggest that similar processes were involved in their genesis. The interpretation of observed chemical and mineralogical heterogeneity found in the Basal Heterogeneous Zone must be linked to an evaluation of the covariations shown in Figs. 8, 10, 11, 13, and 14, the trace element distribution shown in Fig. 9, and isotopic variations shown in Figs. 4, 15, and 16. Covariations between olivine Fo values, olivine Ni content, plagioclase An, and incompatible elements such as Y and P are predicted as a result of fractional crystallization of a basaltic magma. However, features such as the absence of zoning in olivine and the presence of strong zoning in plagioclase make all crystallization models difficult to apply to the Partridge River Intrusion. Relatively rapid diffusion of Fe and Mg in olivine and slower diffusion of Ca, Na, and Al in plagioclase can account for compositional variations in olivine and plagioclase

formed during in situ crystallization that are similar to those observed in the Partridge River Intrusion. Changes in olivine composition related to a “trapped liquid shift” (e.g. Chalokwu and Grant 1990; Barnes 1986) result from the interaction between olivine crystals and surrounding liquid with which the olivine is not in equilibrium. In closed systems where olivine has crystallized from the source magma, compositions of olivine produced from equilibrium crystallization will record the most Fe-rich end-member in terms of a “trapped liquid shift.” In other words, olivine that may accumulate via settling or flow differentiation will not become as fayalitic as olivine that forms via perfect equilibrium crystallization because the olivine accumulation process reduces the mass of interstitial residual melt with which the olivine may react. This is important in the assessment of the most forsteritic olivine compositions found in the basal zone. The scatter observed in the olivine Fo versus Ni plot (Fig. 13) is in part attributed to exchange between Ni in olivine and Fe in coexisting silicate and sulfide liquid, and in part to differences in the Ni content of parental magmas.

Enrichments in incompatible elements such as those illustrated in Fig. 9 must be related either to the abundance and/or the composition of liquid interstitial to olivine and plagioclase. Although these chemical relationships could be produced via fractional crystallization of a single pulse of magma, vertical variations in mineral modes and chemical compositions that would be consistent with in situ fractional crystallization are rarely observed in the Basal Heterogeneous Zone. Sulfur isotopic values provide a key indication of the nature of heterogeneity in the basal zone. Throughout much of the overlying cyclic zones, $\delta^{34}\text{S}$ values are in the range of $0 \pm 2\text{‰}$, considered to be normal for sulfur of mantle origin. In the Basal Heterogeneous Zone, $\delta^{34}\text{S}$ values show a range in excess of 10‰ , with stratigraphic variations of $\pm 2\text{‰}$, restricted to zones that vary from 1 to 30 m in thickness. We discuss sulfur isotope data further below, but stress that the observed variability strongly argues for the involvement of distinct sheets of magma whose thicknesses were less than ~30 m.

Possible parental magmas to the intrusions of the Duluth Complex have been reviewed by Chalokwu et al. (1993), Klewin (1989), Miller and Weiblen (1990), Lee and Ripley (1996), and Miller and Ripley (1996). In Table 3 potential parental magmas are compared, along with the average transitional basalt from Brannon's (1984) study of the overlying North Shore Volcanic Group and compositions linked to the troctolite-rich Hettasch and Kiglapait Intrusions in Labrador

(Berg 1980; Morse 1981). As an example of the types of processes that could generate the diversity of rock types found in the Basal Heterogeneous Zone we have used the MELTS program of Ghiorso and Sack (1995) to compare models of fractional and equilibrium crystallization for a high-Al olivine tholeiite (Lee and Ripley 1996) and the average transitional basalt liquid of Brannon (1984). The average transitional basalt represents a low-Al, high-Ti liquid that itself may be derived from a high-Al olivine tholeiite via fractional crystallization of olivine, plagioclase, and clinopyroxene (e.g. Klewin 1989; Table 4). Fractionation of 20–50% of cotectic proportions of olivine and plagioclase from a high-Al olivine tholeiite liquid results in only small changes in SiO₂ concentration of residual liquids (Table 4). Magmas containing from ~46 to 49 wt% SiO₂ could be generated as a result of fractionation in deeper staging chambers. Emplacement of the variably fractionated magmas into shallower environments could be followed by either equilibrium or additional in situ fractional crystallization. Table 5 illustrates mineral assemblages that are produced due to equilibrium crystallization of high-Al olivine tholeiite or average transitional basalt liquids. Equilibrium crystallization of the dry, high-Al olivine tholeiite of Lee and Ripley (1996) produces 17% olivine (Fo 56), 14% clinopyroxene (Mg # 57), and 63% plagioclase (An 60). These compositions are similar to those found in olivine gabbros and augite troctolites in the Basal Heterogeneous Zone. The addition of from 1 to 2 wt% water

to the high-Al olivine tholeiite composition results in the suppression of feldspar crystallization, additional clinopyroxene, and the formation of more Fe-rich olivine (e.g., Fo 44, Table 5). Crystallization of a high-Al olivine tholeiite with 1 wt% H₂O produces mineral assemblages that include olivine (14%), plagioclase (58%), clinopyroxene (24%), biotite (3.5%), Fe–Ti oxide (0.5%) and apatite (0.8%). This assemblage is similar to that found in the gabbroic rocks. Equilibrium crystallization of the average transitional basalt composition produces a similar mineral assemblage, but with more evolved compositions (Tables 5 and 6). The addition of H₂O results in even more Fe-rich olivine compositions (Fo 30) and low-An plagioclase (An 36). In Fig. 8 we show that the trace element contents of the gabbros and gabbroic rocks cover a range that is similar to that of basaltic rocks from the North Shore Volcanic Group, suggesting that the gabbroic rocks may represent liquid compositions. Although the zoning found in plagioclase throughout the basal zone indicates that equilibrium crystallization has not occurred, we propose that the gabbroic rocks of the Basal Heterogeneous Zone can be the products of in situ crystallization of liquid compositions that varied from high-Al olivine tholeiite to low-Al, high-Ti tholeiite.

Melatroctolites and troctolites with greater than ~20% olivine require the accumulation of olivine; oxide-rich gabbros and troctolites with greater than ~5% ilmenite are also not likely to represent liquid compositions and require the accumulation of ilmenite

Table 2 Representative major and trace element analyses of samples from the Basal Heterogeneous Zone of the Partridge River Intrusion

		189-1402 ^a	189-1414 ^b	189-1574 ^c	189-1823 ^d	189-1852 ^e	189-1998 ^f	189-2059 ^g
Values in wt%								
SiO ₂	40.51	49.24	46.36	44.27	45.16	47.18	46.53	
Al ₂ O ₃	8.82	17.88	13.57	13.01	16.47	15.29	15.23	
FeO	21.18	9.92	12.48	19.71	15.45	13.60	13.71	
MgO	21.94	3.32	5.09	5.58	8.34	6.80	7.26	
CaO	4.23	11.68	9.85	7.51	8.84	9.10	8.92	
Na ₂ O	1.12	3.15	3.05	2.38	2.41	2.84	2.39	
K ₂ O	0.32	0.69	1.24	0.92	0.56	0.67	1.09	
MnO	0.25	0.13	0.17	0.20	0.20	0.14	0.18	
TiO ₂	0.33	2.69	6.66	3.85	1.96	1.33	2.77	
P ₂ O ₅	0.03	0.39	0.51	0.09	0.11	0.14	0.28	
H ₂ O	0.83	0.41	1.02	1.07	0.64	1.35	0.63	
S	0.38	0.77	0.04	0.75	0.23	0.58	0.05	
Total	99.94	100.20	100.04	99.34	100.37	99.02	100.55	
Values in ppm								
^a Melatroctolite	Cu	2,327	7,331	481	7,650	2,790	3,238	210
^b Augite troctolite	Ni	747	1,223	88	1,589	757	905	145
^c Oxide-gabbro	Pb	nd	159	88	255	326	187	14
^d Oxide leucotroctolite	Ba	50	671	459	668	474	658	1,331
^e Melagabbro	Sr	116	97	23	176	65	135	258
^f Troctolite	V	119	235	608	297	979	224	231
^g Gabbroic rock	Y	12	43	50	35	25	26	24

Table 3 Magma compositions related to the development of troctolitic rocks in the Duluth Complex and other intrusions

	1 ^a	2 ^b	3 ^c	4 ^d	5 ^e	6 ^f
SiO ₂	47.58	48.50	47.74	47.35	47.94	47.46
TiO ₂	1.28	0.68	2.94	2.96	1.24	0.81
Al ₂ O ₃	19.82	17.80	14.29	14.73	18.95	19.46
FeO	10.97	8.50	15.37	15.67	11.67	11.08
MnO	0.13	0.13	0.22	0.22	0.14	0.15
MgO	7.07	10.00	5.81	5.65	7.67	8.04
CaO	9.65	10.80	9.75	9.52	8.60	9.27
Na ₂ O	2.66	2.20	2.45	2.15	3.21	3.13
K ₂ O	0.50	0.20	1.16	0.81	0.40	0.22
P ₂ O ₅	0.18	0.05	0.28	0.32	0.13	0.09
Total	99.84	98.86	100.01	99.38	100.06	99.96

^a High-Al olivine tholeiite, summation of units in the South Kawashiwi Intrusion, Lee and Ripley (1996)

^b P-magma of Miller and Weiblen (1990)

^c Potential parental Magma to the Partridge River Intrusion determined by Chalokwu et al. (1996)

^d Average transitional basalt from the North Shore Volcanic Group, Brannon (1984)

^e Average of 5 marginal samples to the Hettasch Intrusion (Berg 1980)

^f Summation of units in the Kiglapait Intrusion, Morse (1981)

Table 4 Liquid compositions produced as a result of fractional crystallization of a high-aluminum olivine tholeiite at 2Kb, QFM-2, and 0% H₂O

	31%	42%	55% ^a	68% ^b	71%
SiO ₂	47.85	47.95	47.97	48.00	47.69
TiO ₂	1.85	2.19	2.86	3.89	3.86
Al ₂ O ₃	17.32	16.27	14.53	12.42	12.15
Fe ₂ O ₃	0.85	0.95	1.05	1.21	1.25
FeO	13.09	14.36	16.39	18.44	18.99
MgO	6.47	5.81	4.76	3.19	3.06
CaO	8.58	8.25	7.88	7.85	7.83
Na ₂ O	2.86	2.92	2.93	2.84	2.87
K ₂ O	0.69	0.81	1.01	1.35	1.43
P ₂ O ₅	0.26	0.31	0.40	0.58	0.62

Values in wt%

^a This composition is similar to that of the average transitional basalt from the North Shore Volcanic Group, Table 3, number 4, and the estimate by Chalokwu et al. (1996) of the parental magma to the Partridge River Intrusion, Table 3, number 3

^b First appearance of clinopyroxene

(Fig. 8). For olivine-rich rocks, an accumulation process similar to that outlined by Lee and Ripley (1996) is feasible, originating from either crystal settling prior to in situ crystallization, collection from an olivine-plagioclase crystal mush, possibly from flow differentiation as described by DeWaal et al. (2004), or due to compaction and buoyant rise of interstitial liquid (e.g., Shirley 1986). Although the gabbroic rock types that are found in the Basal Heterogeneous Zone could

represent liquids that crystallized in situ, the olivine-rich troctolites and melatroctolites must either represent the remnant basal layers of intrusive pulses whose overlying members have been dissected by later magma pulses, or fragments derived from deeper bodies that had experienced crystal fractionation. Olivine in the melatroctolite layers has a maximum Fo value of 66. Fractional crystallization of up to 25 wt% of a high-Al olivine tholeiite with 1 wt% H₂O produces olivine between Fo79 and Fo72. Mass balance computations indicate that crystallization of interstitial liquid and re-equilibration of olivine and Fe-enriched residual liquid could account for the observed olivine Fo values of ~66.

Oxygen and hydrogen isotopic evidence for magma contamination by country rocks

$\delta^{18}\text{O}$ values of the Virginia Formation below the Partridge River Intrusion in core B1-189 (8.2–13.3‰) are in the same range (8–14‰) as Virginia Formation samples measured by Ripley and Al-Jassar (1987) and Arcuri et al. (1998). Most of the igneous rock samples from drill core B1-189 are in a range that is considered to be normal to slightly elevated for igneous rocks of mantle derivation. Assuming a $\delta^{18}\text{O}$ value of 5.8‰ for magma of mantle derivation, approximately 10–15% contamination by a 10–12‰ partial melt derived from the Virginia Formation would have been required to elevate $\delta^{18}\text{O}$ values in the igneous rocks to ~6.5‰. This is in excess of the 3–5% suggested by Ripley et al. (1999) using Pb, Nd, and Os isotopes, but not out of line with the Sr isotope data of Grant and Chalokwu (1992). More than 20% of bulk contamination by country rocks would have been required to account for the $\delta^{18}\text{O}$ values in excess of 6.9‰ that characterize orthopyroxene-rich rocks. Ripley and Alawi (1988) have shown that a high- ^{18}O siliceous partial melt has been removed from Virginia Formation that is now preserved as xenoliths in many areas of the Partridge River Intrusion. However, only norites with orthopyroxene in excess of ~10% show mineralogical evidence of interaction with a siliceous high- ^{18}O contaminant. The contamination must have been local in nature as norite/gabbro-norite is found only in a very thin zone at the basal contact, and sporadically in other areas of core B1-189, and throughout the Partridge River Intrusion (Fig. 3).

Although partial melting of Virginia Formation appears to be restricted to xenoliths or localities very near the basal contact, devolatilization was a more widespread process (e.g., Andrews and Ripley (1989); Ripley and Alawi 1988). As noted above, hydrous

magmas are important for the production of gabbros that contain Fe-rich olivine. The fractionation of olivine and plagioclase will lead to H₂O enrichment in derivative liquids, but the assimilation of H₂O from country rocks may have been necessary to elevate H₂O contents to the levels required to promote the crystallization of Fe-rich olivine. The crystallization of interstitial minerals may lead to fluid saturation and the liberation of an H₂O-bearing fluid during late stages of solidification (see Tables 5, 6). Although biotite and apatite are the primary OH-bearing minerals in the gabbroic and troctolitic rocks, Ripley et al. (1993) have shown that alteration minerals, primarily serpentine, chlorite, and amphibole may compose a significant fraction of the hydrous mineral assemblage. Hydrogen isotopic composition of the Virginia Formation varies as a function of the degree of dehydration, ranging from ~40‰ in unmetamorphosed samples with 4–5 wt% H₂O to <–90‰ in orthopyroxene–corderite hornfels with ~1 wt% H₂O (Ripley et al. 1992). The δ D value of the bulk fluid liberated in the dehydration process was near –50‰. Gabbroic and troctolitic rocks in the Basal Heterogeneous Zone are characterized by much lower δ D values than this, implying that either H₂O from the Virginia Formation contributed little to the magma value, or that a D-enriched fluid was liberated from the system. The hydrogen isotopic fractionation between a fluid and residual melt is unknown for mafic systems, but experimental studies of more felsic systems by Kuroda et al. (1982), Taylor and Westrich (1985), and Dobson et al. (1989) have shown that water exsolved from a melt may be characterized by δ D values from 20 to 50‰ greater than those of the

Table 5 Mineral assemblages produced as a result of equilibrium crystallization at 2 Kb and log fO₂ of QFM-2

	0% H ₂ O ^a	1% H ₂ O ^a	1% H ₂ O ^b
Olivine	16.8 (Fo56)	13.8 (Fo44)	19.9 (Fo30)
Clinopyroxene	14.0 (Mg # 57)	24.3 (Mg # 55)	19.5 (Mg # 58)
Plagioclase	63.1 (An60)	58.0 (An59)	33.7 (An36)
Spinel/ rhombic oxide	3.5	0.04	4.0
Apatite/ whitlockite	0.3	0.4	0.7
Biotite	0	3.4	0
Water	0	0.8	0.1
K-spar			4.5

Values in wt%

^a High-aluminum olivine tholeiite, Table 2, number 1

^b Average transitional basalt from the North Shore Volcanic Group, Table 2, number 4. Values are for 85% crystallization

Table 6 Fractional crystallization of a high-aluminum olivine tholeiite, followed by equilibrium crystallization of the residual liquid, 2 Kb QFM-2, 1% H₂O

Liquid composition after 25% fractional crystallization		Mineral assemblage as a result of equilibrium crystallization		
SiO ₂	47.97	Olivine	13.94	Fo36
TiO ₂	1.69	Clinopyroxene	25.59	
Al ₂ O ₃	18.60	Plagioclase	54.77	An49
Fe ₂ O ₃	0.79	Biotite	0.08	
FeO	11.45	Spinel	0.08	
MgO	5.10	Apatite	0.48	
CaO	8.96	Water	1.10	
Na ₂ O	3.06			
K ₂ O	0.65			
P ₂ O ₅	0.24			
H ₂ O	1.32			

Values in wt%

melt. Assuming that a primitive mantle melt may be characterized by a δ D value near –70‰, δ D values of gabbroic rocks in the Basal Heterogeneous Zone of –75 to –90‰ are consistent with the loss of a vapor phase and with the development of alteration assemblages involving a magmatic fluid. δ D values less than –100‰ are locally found in association with samples of high H₂O content and anomalous amounts of serpentine. These samples confirm earlier studies (Ripley et al. 1992), which suggested that isotopically depleted meteoric water was locally involved in hydrothermal alteration.

Sulfide distribution and heterogeneity of δ^{34} S values

It is of paramount importance in understanding the genesis of sulfide mineralization in the Partridge River Intrusion to emphasize that all of the rock types found in the Basal Heterogeneous Zone may be characterized by the presence of anomalous percentages of sulfide minerals. It is of equal importance to note that not all intervals in the Basal Heterogeneous Zone are mineralized (some rocks have S contents as low as 100 ppm; Fig. 4a), and that δ^{34} S values vary from ~–1 to 10‰ but are not correlated with S abundance (Fig. 17a). Massive sulfide mineralization in the Basal Heterogeneous Zone is characterized by a relatively narrow range of δ^{34} S values (6.7–7.8‰). In the lower 100 m of the core, gabbroic rocks show two populations of δ^{34} S values, one ranging from –1.4 to 0.3‰ and the other from 8.2 to 10.5‰. The latter population correlates with rocks that contain olivine with Fo values less than ~45 (Fig. 17). Sulfides in troctolites or melatroctolites have δ^{34} S values from 2.1 to 6.5‰. Sulfur isotopic variability of this magnitude in such a

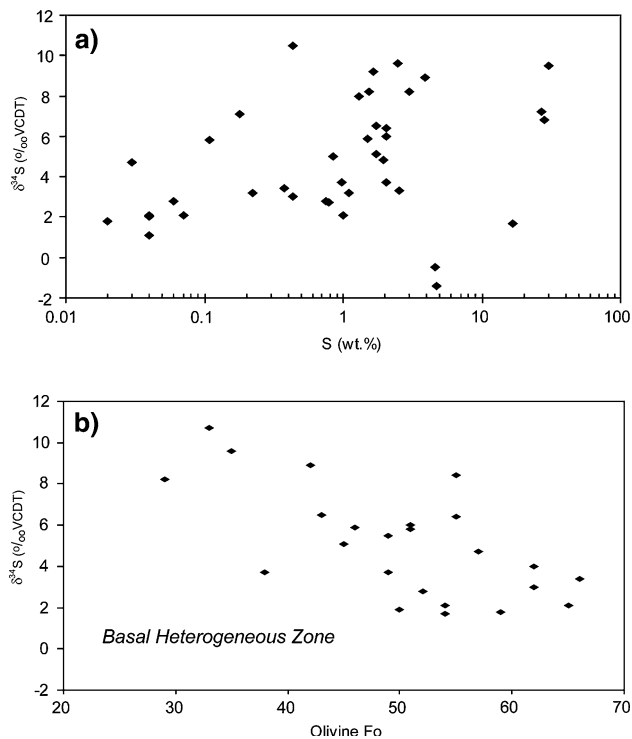


Fig. 17 **a** Sulfur content versus $\delta^{34}\text{S}$ for samples from the Basal Heterogeneous Zone. **b** Olivine Fo versus $\delta^{34}\text{S}$ for samples from the Basal Heterogeneous Zone

restricted spatial area is extreme, but consistent with the overall heterogeneity of the basal zone. Ripley and Al-Jassar (1987) and Arcuri et al. (1998) have illustrated the extreme variability in $\delta^{34}\text{S}$ values of sulfide minerals in the Virginia Formation ($\sim 0\text{--}30\text{‰}$), and hence the range in $\delta^{34}\text{S}$ values observed in rock types from the Basal Heterogeneous Zone in drill core B1-189 is in line with major sulfur derivation from Animikie Group country rocks. However, the heterogeneity in the $\delta^{34}\text{S}$ values argues strongly for contamination processes that may have involved several different sulfidic layers of the Virginia Formation that were characterized by different $\delta^{34}\text{S}$ values. Magmas representing various stages of fractionation may either have been derived from distinct crustal chambers, or from expanding crustal chambers that derived sulfur from isotopically distinct country rock layers. In addition, individual magma pulses may have followed different paths through the Animikie Group rocks, and hence interacted with potential contaminants characterized by a wide range of $\delta^{34}\text{S}$ values.

The distribution of sulfide minerals in the Basal Heterogeneous Zone suggests that the process of sulfide liquid accumulation was operative throughout the formation of high-olivine troctolites as well as more evolved gabbroic rocks. Because of the incompatible

nature of Cu with respect to early crystallizing silicate minerals, there is no reason to expect changes in the Cu content of the sulfide liquid as a function of the degree of silicate fractionation. However, because Ni is accommodated in the olivine structure, the Ni content of the sulfide liquid may be affected by the timing of contamination. Because of the number of factors that may contribute to Ni distribution between sulfide and silicate, evaluating this possibility is difficult. Part of the variability in the Ni content of accumulated olivine as a function of the extent of fractionation (Fig. 13) is thought to be due to exchange with variable amounts of trapped silicate liquid, as well as sulfide liquid. Figure 18 illustrates the extreme variability in the Ni content of olivine with respect to whole rock sulfur abundance. This variability is consistent with that illustrated in Fig. 13. The wide range in Ni contents of olivine with similar Fo contents virtually demands an origin involving multiple pulses of magma characterized by different Ni concentrations.

It is also clear that contamination processes (in the case of rocks in the Basal Heterogeneous Zone found in core B1-189, primarily the addition of volatile phases such as sulfur and water) affected intrusive rocks that now occur in contact with the Virginia Formation, and that contaminated units were emplaced early in the development of the Partridge River Intrusion. Later-emplaced units (e.g., Units IV and V in core B1-189) show only sparse evidence for country rock contamination and are poor prospects for Cu–Ni–PGE mineralization. However, not all of the magmas that produced rocks now represented in the Basal Heterogeneous Zone were contaminated to similar degrees. For example, the lack of sulfide enrichment in the fine-grained gabbro-norite located at the immediate contact

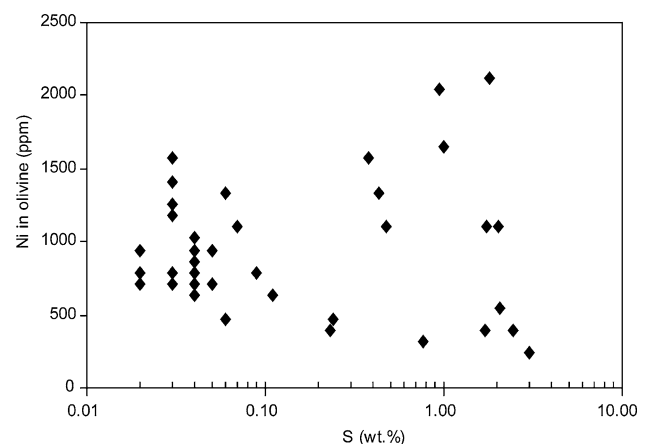


Fig. 18 Olivine Fo versus whole rock S content for samples from drill core B1-189

with the Virginia Formation (Figs. 3, 5) is indicative of two important points. One is that in situ S derivation from immediate country rocks did not occur uniformly. The second is that although Si-contamination may have been the primary cause of orthopyroxene crystallization, concomitant S-contamination of the source magma frequently did not occur. We propose that because of the uneven distribution of sulfur in the Animikie Group sedimentary rocks, Si-contamination of mafic magmas may have occurred in the absence of S-contamination.

Conclusions

We propose that the Basal Heterogeneous Zone of the Partridge River Intrusion represents a zone characterized by multiple intrusive pulses. Covariations in mineral compositions and trace element characteristics indicate that troctolites and gabbros may have been derived from similar source magmas (primarily high-Al olivine tholeiites), but have been modified, to differing degrees, by processes such as fractional crystallization in staging chambers, variable degrees of contamination by country rocks, and in situ crystallization in shallow environments. Elevated water contents of some magmas resulted in the suppression of plagioclase crystallization and the formation of Fe-enriched olivine. Sulfide mineralization is present in all rock types present in the basal zone, but is not ubiquitous. Source magmas experienced limited major element contamination by country rocks, but the addition of S derived from country rocks was essential for the genesis of sulfide mineralization. The variability in $\delta^{34}\text{S}$ values of the mineralized rock types and in sulfide distribution indicate that magmas at depth interacted with country rocks that were themselves characterized by widely variable $\delta^{34}\text{S}$ values and sulfide mineral distribution. The process of S contamination and resultant sulfide accumulation affected magmas that are preserved in the basal portion of the Partridge River Intrusion. Overlying troctolites and leucotroctolites are characterized by low S contents and $\delta^{34}\text{S}$ values of $0 \pm 2\%$ that are indicative of essentially uncontaminated mantle-derived magma. If the sulfide-bearing intrusive rocks represent early pulses of magma in the evolution of the Duluth Complex, then once crustal country rocks were heated and devolatilized by the passage of initial magmas, further enrichment in S and H_2O was impossible. Alternatively, magmas now represented by the overlying, low-sulfide, intrusive rocks may have been emplaced at a rate that inhibited extensive interaction with country rocks.

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