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MASS TRANSFER AND SULFUR FIXATION IN THE CONTACT AUREOLE OF THE DULUTH COMPLEX, DUNKA ROAD Cu–Ni DEPOSIT, MINNESOTA

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ABSTRACT

Contact metamorphism of the Virginia Formation related to intrusion of the Duluth Complex near the Dunka Road Cu–Ni deposit, Minnesota, resulted in the conversion of argillaceous rock containing chlorite (Chl) + muscovite (Ms) + quartz (Qtz) + plagioclase (Plg) + ilmenite (Ilm) + pyrite (Py) + organic material (OM) to hornfels containing biotite (Bt) + cordierite (Crd) + Plg + K-feldspar (Kfs) + Qtz + Ilm + pyrrhotite (Po) + graphite (Gr) ± orthopyroxene (Opx). Distinct compositional trends are interpreted as originating from sedimentary processes and suggest that metamorphism was isochemical with respect to nonvolatile components. The similarity in the ratio of whole-rock sulfur and iron in argillites and hornfels, equilibrium compositions of fluid, and the correlation of biotite composition with the ratio of whole-rock sulfur and iron suggest that sulfur was conserved in the footwall by a reaction such as: Bt + $n\mathrm{H_2S}_{(\mathrm{Py-Po})}$ + Ilm = Ti-enriched - Fe-depleted Bt + nPo + H_2O. As dehydration reactions progressed, the mole fraction of H_2O was buffered to maximum values (0.75–0.83), with the mole fraction of H_2S not exceeding 0.01. It is unlikely that *in situ* sulfur assimilation was a factor in ore genesis.

Keywords: Duluth Complex, contact metamorphism, Dunka Road Cu–Ni deposit, devolatilization, sulfur fixation, Minnesota.

SOMMAIRE

Le métamorphisme de contact des roches argileuses de la formation de Virginia, consequence de la mise en place du complexe de Duluth (Minnesota), près du gisement Cu-Ni de Dunka Road, au Minnesota, a transformé l'assemblage chlorite + muscovite + quartz + plagioclase + ilmenite (Ilm) + pyrite (Py) + matière organique en cornéennes contenant biotite (Bt) + cordierite + plagioclase + feldspath potasssique + quartz + Ilm + pyrrhotite (Po) + graphite ± orthopyroxène. Les lignées distinctes en composition résulteraient de processus sédimentaires, et font penser que le métamorphisme a été isochimique en termes des composants non volatils. Selon les rapports semblables de soufre et de fer entre argillites et cornéennes, la composition de la phase fluide à l'équilibre, et la corrélation entre la composition de la biotite et la teneur en soufre et en fer dans les roches totales, le soufre aurait aussi été conservé dans les roches du socle, au moyen d'une réaction comme Bt + $n\mathrm{H_2S}_{(\mathrm{Py-Po})}$ + Ilm = Bt (enrichie en Ti et appauvrie en Fe) + nPo + H_2O. A mesure qu'ont progressé les réactions de déshydratation, la fraction molaire de H_2O a été tamponnée à une valeur maximale entre 0.75 et 0.83, la fraction molaire de H_2S ne surpassant pas 0.01. Il ne semble pas que l'assimilation *in situ* de soufre ait été importante dans l'épisode de minéralisation.

(Traduit par la Rédaction)

Mots-clés: complexe de Duluth, métamorphisme de contact, gisement de Cu–Ni de Dunka Road, dévolatilisation, fixation du soufre, Minnesota.

INTRODUCTION

The Duluth Complex of northeastern Minnesota has attracted attention because it hosts Cu–Ni sulfide and platinum-group-element (PGE) mineralization. Recent studies of the genesis of these metal concentrations have emphasized the importance of magma contamination, but study of the footwall rocks and their metamorphism is limited and focuses primarily on effects observed in the Biwabik Iron Formation in the Hoyt Lakes - Kawishiwi area (Fig. 1; French 1968, Perry & Bonnichsen 1966, Bonnichsen 1968, Morey *et al.* 1972, Bonnichsen 1975) and the Gunflint Iron Formation near the Ontario border (Simmons *et al.* 1974, Floran & Papike 1975, 1978). Metamorphism of the underlying, predominantly argillaceous sedimentary rocks, which are conjectured to be the source of contaminant sulfur, has received relatively little attention. Petrographic characteristics of a limited exposure of contact-metamorphosed Virginia Formation have been reported by Renner (1969), and Kirstein (1979) has studied the metamorphism of calcareous concretions. Several studies have dealt with isotopic and trace-element characteristics of the Virginia Formation and the possibility of partial melting along the contact (*e.g.*, Ripley 1981, Grant & Molling 1981, Bonnichsen 1972, Rao & Ripley 1983, Ripley & Al-Jassar 1987, Ripley & Alawi 1986). Only the studies of the Rove Formation (considered equivalent to the Virginia Formation) by Labotka *et al.* (1981, 1984) have concentrated on the metamorphism of pelitic rock and the generation of metamorphic fluids. No study has related a thorough geochemical study of footwall-rock metamorphism to the genesis of a well-characterized sulfide concentration. This paper examines a contact-metamorphosed footwall interval associated with the Dunka Road deposit (Fig. 1), a

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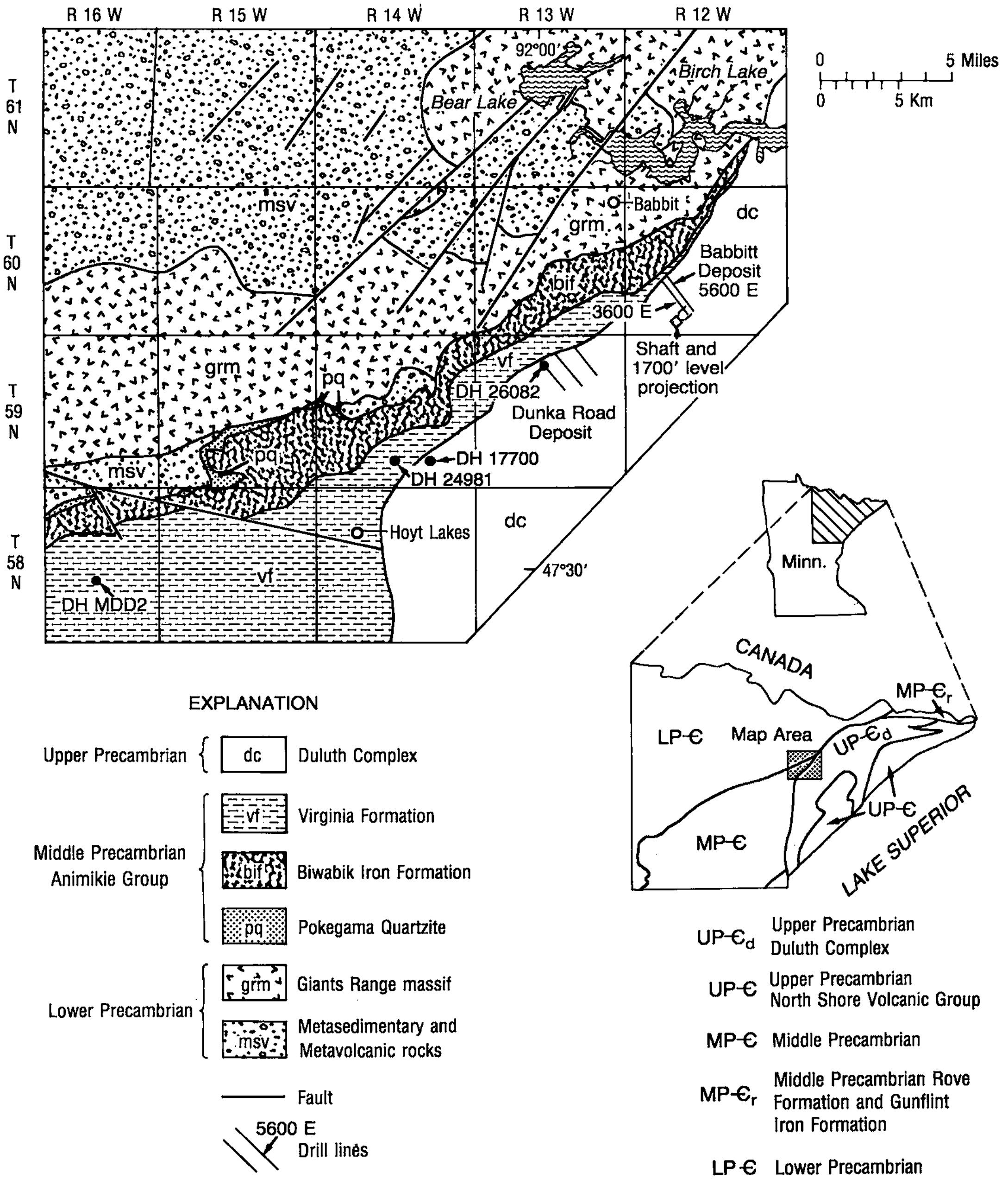

FIG. 1. Geological map of northeastern Minnesota. Solid circles mark the locations of drillholes that are referred to in the text.

relatively small but typical sulfide deposit. The purpose is to assess the importance of footwall-rock metamorphism and devolatilization in the formation of sulfide concentrations in the overlying Duluth Complex.

GEOLOGICAL SETTING

In the area of the Dunka Road deposit, metasedimentary rocks of the middle Precambrian Animikie Group are the immediate footwall to mafic

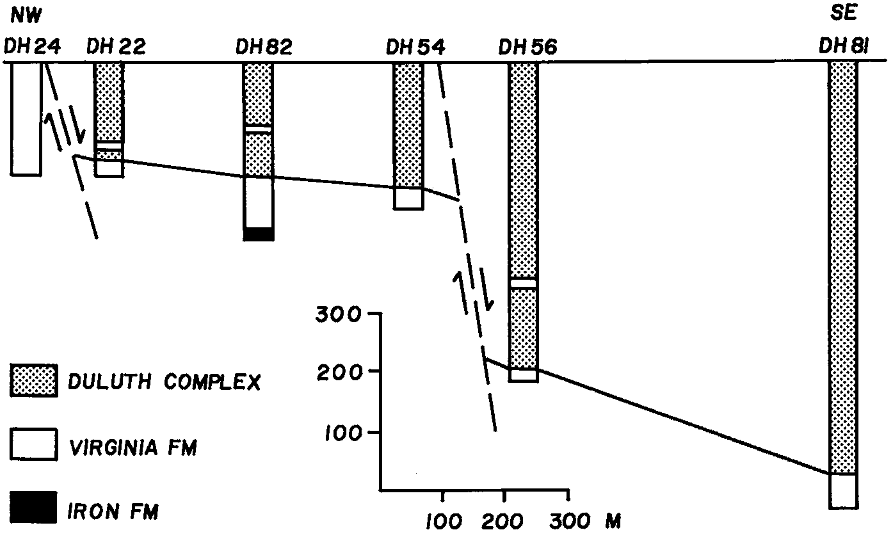

FIG. 2. Interpretive cross-section from northwest to southeast through a series of drillholes at Dunka Road. Most samples were taken from core of drillhole 82.

units of the Duluth Complex. The Animikie Group diminishes in thickness from the town of Hoyt Lakes northeastward to just south of Birch Lake (Fig. 1). The lower Precambrian Giant's Range Massif, along with metavolcanic and metasedimentary rocks, comprise the footwall to the north of this area (Fig. 1). The Rove Formation and Gunflint Iron Formation are found as contact rocks along the northernmost boundary of the Duluth Complex near the U.S. - Ontario border.

Animikie Group rocks include the Virginia Formation, Biwabik Iron Formation, and underlying Pokegama Quartzite, the last absent near the Dunka Road deposit. Sedimentary bedding generally dips from 5° to 15° to the southeast. The Biwabik Iron Formation varies in thickness from 61 to 91 meters. Contact-metamorphic zones described by French (1968) and Morey *et al.* (1972) in the East Mesabi district vary from low-grade grunerite-bearing hornfels to ferruginous pyroxene or amphibole hornfels at the immediate contact. The Virginia Formation in the Dunka Road area occurs in the form of a downward-tapering wedge, thinning to the southeast. Drillhole data indicate that the Virginia Formation varies from 30 to 180 meters in thickness. A cross section across one United States Steel Corporation drill line is shown in Figure 2. Normal faults shown are interpreted but are consistent with structural models of graben development discussed by Weiblen & Morey (1980).

Igneous rocks in the Dunka Road area include troctolite, orthopyroxene- and clinopyroxene-bearing troctolite, norite, gabbro, gabbronorite, anorthosite, and local peridotite. The mineralogy and petrogenesis of these rocks have been discussed by Rao & Ripley (1983).

ANALYTICAL METHODS

Rock samples were collected from the United States Steel Corporation's drillhole 26082 (DH 82) located in the Dunka Road area (Fig. 1). This hole penetrated an initial 183 m of pyroxene troctolite with minor metasedimentary xenoliths, 93 m of Virginia Formation, and 9 m of Biwabik Iron Formation. Also examined were several samples of argillite from drillhole MDD2 (Bonnichsen 1972, Lucente & Morey 1983), and mildly metamorphosed argillite from drill hole 24981 (Fig. 1). The samples from drillhole MDD2 have not been modified by contact metamorphism.

Bulk analyses were obtained by inductively coupled plasma atomic emission spectrometry after an initial fusion with a lithium borate flux and dissolution in HNO_3 (4% solution by vol.). Based on replicate analyses of both samples and standards, analytical accuracy for all elements is ~2.0% of the amount present. Carbon was determined using a total carbon fusion apparatus with a combustion temperature of 1000°C and a CO_2 Coulometer. Accuracy is ±0.1% of the carbon content. Total sulfur was measured with a Leco infrared absorption instrument with fusions performed at 1370°C. Analytical accuracy for S is ±1.0% of the measured concentration. Mineral compositions in 16 samples were determined using an ETEC automated electron microprobe and simple silicate standards following the procedure outlined by Klein (1974). Analyses were performed using the GEOWHIZ program of Finger (1973) with on-line data reduction using the correction factors of Bence & Albee (1968). Replicate analyses indicate a precision of better than ±2.0% for concentrations above 1.0 wt.% and ±8.0% for minor constituents. Modes were estimated by counting approximately 400 points, each identified with the microprobe energy-dispersion system using the minimum beam diameter.

All isotopic ratios were determined with a Finnigan MAT Delta E isotope ratio monitoring mass spectrometer with triple Faraday cup collectors. Oxygen was extracted from the samples using bromine pentafluoride following the procedure of Clayton & Mayeda (1963). All values are referenced to SMOW, with an accuracy of ±0.2‰ obtained by analyzing NBS #28 (9.6 ‰). Hydrogen was collected following the outline of Butler (1988). The accucacy of the δ D values is ±3 ‰, determined by the analysis of NBS 30 biotite (65 ‰). All δD values are referenced to SMOW. The determination of $\delta^{13}C$ follows the outline of DesMarais & Moore (1984), modified by Taib (1988). Carbon contained in carbonate or as surface contamination was first removed by heating the samples to 700°C under vacuum. The precision for the $\delta^{13}C$ values is ±0.05‰, with an accuracy of ±0.15 ‰ determined by analyzing NBS 21 graphite (-28.1‰).

LITHOLOGIES AND BULK COMPOSITIONS

The section of Virginia Formation examined consists predominantly of massive and laminated equigranular rocks that originated from the metamorphism of argillaceous material. These rocks have a granoblastic or hornfelsic texture and account for approximately 96% of the section of Virginia Formation in drillhole 82. They contain the assem-

TABLE 1. MODAL ANALYSES OF HORNFELS FROM DH 26082

Sample Number	388	609	618	627	670	705
Meters from contact	-212	2.7	5.4	8.2	21.3	32.0
Quartz	-	55.4	12.4	25.8	24.0	29.6
Cordierite	82.6	0.6	22.7	24.6	19.8	11.9
Biotite	1.6	1.2	24.8	14.8	9.3	14.9
K-feldspar	-	1.2	12.7	17.1	19.5	26.3
Plagioclase	-	34.5	21.7	16.7	25.8	17.3
Orthopyroxene	13.4	5.9	3.9	-	-	-
Pyrrhotite	0.8	TR	1.0	0.7	0.6	TR
Ilmenite	1.6	TR	0.8	0.5	TR	TR
Graphite	TR	TR	TR	TR	1.0	TR

Sample Number	747	803	823	852	872
Meters from contact	45.0	61.9	68.0	76.8	82.9
Quartz	17.8	33.4	18.3	22.1	27.3
Cordierite	38.2	17.4	20.9	9.2	14.6
Biotite	25.3	8.6	28.8	13.2	16.2
K-feldspar	TR	23.6	TR	32.3	18.7
Plagioclase	14.5	14.6	30.4	22.4	19.6
Pyrrhotite	2.7	0.9	0.5	0.8	2.4
Ilmenite	0.6	0.6	TR	TR	0.5
Graphite	0.8	0.9	TR	TR	0.7

TR, <0.5 vol. % -, not present
Sample 388 is from a xenolith

TABLE 2. CHEMICAL COMPOSITION OF SAMPLES FROM DRILLHOLE 26082

Sample	387	388	599	609	615	618*	627*	646
Location	-213	-212	-1.0	2.7	4.5	5.4	8.2	14.0
SiO_2	45.10	46.70	44.60	77.40	51.10	56.10	63.50	64.00
TiO_2	1.38	1.09	3.51	0.47	0.98	1.58	1.36	0.84
Al_2O_3	24.10	28.40	15.50	10.30	21.00	19.00	17.00	16.50
FeO**	15.70	11.60	18.20	4.05	13.80	9.70	7.10	5.65
MgO	9.85	9.16	5.92	1.46	4.00	5.20	3.19	2.75
CaO	0.11	0.07	9.01	3.56	0.98	1.90	1.00	0.85
MnO	0.10	-	0.15	0.05	0.05	-	-	0.05
Na_2O	0.10	0.06	2.35	2.04	1.55	2.30	2.00	2.23
K_2O	0.34	0.21	0.52	0.46	1.76	3.63	3.81	3.60
S	1.38	0.49	0.13	0.50	3.78	0.01	0.01	0.50
C	1.30	-	0.10	0.33	1.73	-	-	2.20
Total	99.46	97.78	99.99	100.62	100.73	99.42	98.97	99.17
LOI-1		.01	0	0	0	1.19	1.39	.58
LOI-2		1.30	1.44	.33	.24	2.26	2.17	1.20
Density	2.86		3.11	2.74	2.79	2.74	2.70	2.70
Assemblage	1(Xe)	1(Xe)	Db	2	3	3	4	4

Sample	670*	702*	705	730	747*	784	803	823
Location	21.3	31.2	32.0	39.6	45.0	56.2	61.9	68.0
SiO_2	61.80	59.60	68.60	60.60	64.00	55.90	63.70	61.70
TiO_2	0.94	0.99	0.47	0.83	1.25	1.15	0.75	0.84
Al_2O_3	16.10	16.90	15.20	17.40	16.70	20.20	16.10	17.40
FeO**	7.19	9.03	3.94	5.80	7.73	10.90	5.03	7.01
MgO	2.68	3.93	1.94	3.11	2.99	5.38	2.63	3.49
CaO	0.72	1.46	0.90	8.52	2.18	0.73	0.74	2.07
MnO	0.05	-	0.04	0.05	-	0.07	0.05	0.07
Na_2O	2.31	1.29	2.49	1.13	2.83	1.70	2.26	3.09
K_2O	3.26	3.09	4.83	0.47	1.98	4.22	4.29	1.96
S	0.68	0.53	0.12	1.14	0.04	0.22	0.52	0.45
C	2.20	0.73	0.26	1.30	1.99	0.21	2.05	0.50
Total	97.93	97.55	98.79	100.35	101.69	100.68	98.12	98.58
LOI-1	.33	.49	.65	0	0	2.24	.87	.50
LOI-2	1.12	1.49	1.09	.25	.03	3.43	1.42	1.27
Density	2.67	2.72	2.68	2.80	2.70	2.81	2.64	2.75
Assemblage	4(L)	4	4	4	4	4(L)	4(L)	4

Sample	826	840	842	843	852*	872	902	928
Location	690	73.2	73.8	74.0	76.8	82.9	92.1	100
SiO_2	52.40	61.40	58.20	64.20	60.10	63.20	62.90	49.80
TiO_2	0.18	0.90	1.23	0.79	1.19	0.74	0.80	1.34
Al_2O_3	5.43	17.60	19.80	15.60	17.50	16.30	16.00	14.50
FeO**	6.16	7.03	10.50	2.94	7.74	5.25	5.76	11.80
MgO	11.90	3.49	5.18	2.92	3.34	2.63	2.71	9.19
CaO	21.90	0.95	0.81	11.80	0.73	0.69	0.83	11.30
MnO	0.16	0.05	0.08	0.12	-	0.05	0.05	0.10
Na_2O	0.54	1.96	1.29	0.70	1.87	2.11	2.05	2.25
K_2O	0.49	3.45	3.52	0.11	4.56	4.14	4.05	0.41
S	0.00	0.70	0.00	0.00	0.40	0.60	1.04	0.01
C	0.16	2.04	0.12	0.13	-	1.70	2.51	0.08
Total	99.32	99.57	100.73	99.31	97.43	97.41	98.70	100.78
LOI-1	.33	.56	.94	.14	2.10	.87	.48	.24
LOI-2	1.01	1.34	2.10	.47	2.95	1.45	1.11	1.54
Density		2.72	2.78	2.83	2.75	2.63	2.71	3.07
Assemblage	(Dp)	4(L)	4	4	4	4(L)	4(L)	4(L)

* Analytical data from Rao & Ripley (1983). ** Total iron as FeO. Concentrations in wt.%, density in g/cm^3. Xe xenolith, Db diabase, L laminated, Dp diopsidite. Assemblages: 1. Crd + Opx + Bt + Po + Ilm; 2. Qtz + Pl + Opx + Bt + Ksp + Po + Ilm + G; 3. Crd + Bt + Qtz + Pl + Ksp + Opx + Po + Ilm + G; 4. Crd + Bt + Qtz + Pl + Ksp + Po + Ilm + G. LOI-1: "LOI"-C-S. LOI-2: "LOI"-C-S+FeO(0.111), accounts for oxidation of iron during the analyses. "Location" is the distance in meters from the intrusive contact.

blage quartz (Qtz) + plagioclase (Plg) + biotite (Bt) + cordierite (Crd) + potassium feldspar (Kfs) and local orthopyroxene (Opx). Minor constituents include ilmenite (Ilm), pyrrhotite (Po), graphite (Gr), apatite, and zircon. Near the contact, inequigranular porphyroblastic to poikiloblastic textures are present in concordance with the appearance of orthopyroxene. Table 1 lists the modal abundance of minerals in a suite of meta-argillites. Quartzofeldspathic and calc-silicate hornfels, including quite pure equigranular diopsidites, occur as thin layers 3 to 50 cm thick. Contacts between the calc-silicates and the meta-argillites are generally sharp, whereas changes are gradational between the massive and laminated varieties. The laminated rocks may show either uniform laminations dipping at an angle of 30–50 degrees or a contorted fabric. These laminations arise from variations in modal proportions of various minerals and from the subparallel orientation of biotite flakes. The average grain-size for the metasedimentary rocks is between 0.20 and 0.30 mm. In DH 82 a large xenolith occurs between 118 and 123 m and consists of the assemblage Crd + Opx + Bt + Ilm + Po.

The samples from DH MDD2 contain the assemblage chlorite (Chl) + muscovite (Ms) + Qtz + Plg + Ilm + Pyrite (Py) + organic material (OM) and appear to be unaffected by the Duluth Complex. Based on the studies of DH MDD2 by Lucente & Morey (1983) and Butler (1988), chlorite and muscovite occur in subequal amounts and together account for most of the volume of the argillites. Quartz is commonly more abundant than plagioclase, and K-feldspar is absent or a minor constituent. DH 24981 is similar but contains pyrrhotite in addition to pyrite, and the organic material tends to be well-ordered rather than amorphous. From the brief description given by Bonnichsen (1972), the section of Virginia Formation in DH 17700 contains the same assemblage as found in DH 82.

Bulk compositions (Table 2) show that the meta-argillites are characterized by CaO contents generally less than 2 wt.%. Significant negative correlations occur between SiO_2 and TiO_2, Al_2O_3, FeO, and MgO, whereas all combinations within the latter group give positive correlations. For every possible cation pair, the concentrations of the cations were plotted against one another (Andrews 1987). These plots also included compositions of argillites from DH MDD2 (Bonnichsen 1972). Though not shown here, these plots illustrate the strong similarity between the compositions of the hornfels and argillites. As shown by Figure 3, hornfels compositions are independent of the samples' proximity to the intrusive contact, except possibly within the initial 10 m. Figure 3 also shows the inverse variation of FeO with SiO_2. The observed trends in bulk compositions of the meta-argillites may be due either to original sedimentary processes, or to the redistribution of components during metamorphism. Metamorphism modified the concentrations of volatile components, but the compositional similarity of argillite and hornfels with respect to nonvolatile components, and the predominant lack of dependence of composition on contact proximity, suggest that nonvolatile components were relatively immobile during metamorphism. Analyses of element ratios,

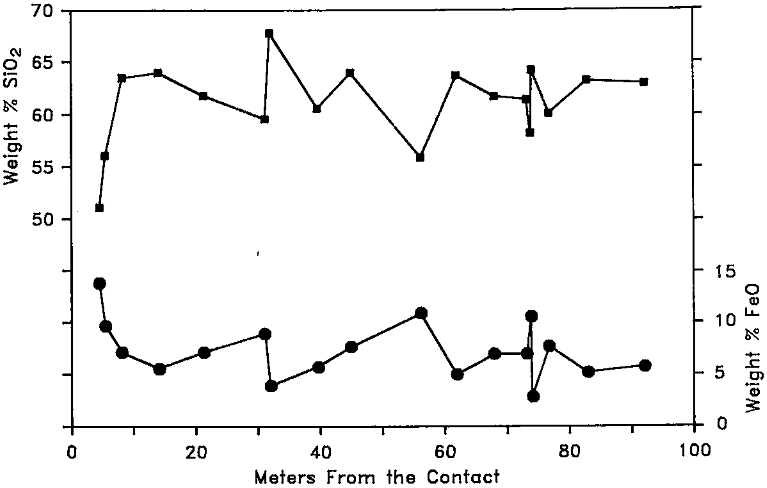

FIG. 3. Plot of whole-rock SiO_2 and FeO *versus* depth in drillhole 82. Values are in weight percent. Only values for low-Ca meta-argillites are plotted. The trends illustrate the inverse correlation between SiO_2 and FeO.

TABLE 3. ISOTOPIC DATA FOR WHOLE ROCKS FROM THE DUNKA ROAD AREA

Sample	$\delta^{18}O$(‰ SMOW)	δD(‰ SMOW)	$\delta^{13}C$(‰ PDB)
615		-82	-33.8
618	11.9		
646		-85	-32.0
670	12.9	-82	-32.2
705		-85	
803		-82	-31.8
823		-85	-32.0
842		-79	-30.9
872	12.9		
902	11.8	-91	-32.2
928		-83	-27.1
Averages for DH 82	12.4 ±.6	-84 ±3	-32.1 ±.8
Averages for[1] Virginia Fm. argillites	12.4 ±1 (11)	-63 ±4 (12)	-30.9 ±1 (14)

[1] Data from Taib (1988), Butler (1988), Ripley & Al-Jassar (1987).

covariance, and volume relationships (Andrews 1987) support the idea that major elements were generally immobile during metamorphism. Chemical compositions largely depend on primary sedimentological variations.

Some evidence for metasomatism does exist and is to be expected. Figure 3 shows a progressive loss od SiO_2 and enrichment in FeO within 10 m of the contact. Though this trend may also be the result of sedimentation, other evidence suggests that partial melting or diffusive mass-transfer could be responsible. These samples are texturally distinct, containing quartz and K-feldspar poikiloblasts along with orthopyroxene. In addition, metasomatism must be cited in explaining thin layers of diopsidite, though in terms of volume this lithology is insignificant.

Isotope data obtained for DH 82 are compiled in Table 3, along with average values for the Virginia Formation argillites. The contact-metamorphosed rocks and argillites have very similar oxygen and carbon isotopic compositions, but quite different δD values. The isotopic values for all three elements are extremely consistent throughout DH 82.

INTENSIVE PARAMETERS

Pressure

The pressure attending contact metamorphism of the sedimentary sequence is difficult to determine, both because of the absence of accurate mineral geobarometers and the structural nature of the Duluth Complex itself. According to the model of Weiblen & Morey (1980), sedimentary rocks of the Animikie Group were initially overlain by the North Shore volcanic suite, with later intrusion of the Duluth Complex along the volcanic–sedimentary contact. The Complex thins eastward and northward from Lake Superior, where the thickness is approximately 15 km (Weiblen & Morey 1980, Labotka *et al.* 1981). In his investigations of the Biwabik Iron Formation approximately 1 km west of DH 82, French (1968) estimated an overburden of 8–12 km (2.2–3.4 kbars, using a gradient of 3.5 km/kbar). From the metamorphic effects on the Giant's Range Batholith in an area just to the north of Birch Lake, Green (1970) suggested a pressure of 1.5 to 2.5 kbar (5.3 to 8.7 km). Sphalerite geobarometry of samples from a location several kilometers to the north of DH 82 indicates a pressure of 1 to 2 kbar (Alawi 1985). A pressure of 2 kbar is generally consistent with other data (Bonnichsen 1975, Labotka *et al.* 1981, 1984) and will be used herein.

Temperature

The only calibrated geothermometer found applicable to DH 82 is the two-feldspar method of Stormer (1975). Calculated temperatures have an assumed error of ±25°C. Except within 10 m of the contact (630 to 660°C), feldspar compositions (An_{21-41}) give fairly constant temperatures of 500 to 550°C. These must be taken as minima, reflecting the conditions under which feldspars become closed to alkali exchange and diffusion.

Much recent work has focused on prograde reactions in pelitic bulk compositions in the system $K_2O–FeO–MgO–Al_2O_3–SiO_2–H_2O$, a set of components that can account for as much as 95 wt.% of meta-argillites from the drillholes studied. In experimental studies of this system, Hoffer & Grant (1980) indicated that the assemblage Bt $X_{Mg} = 0.5$) + Ab + Crd (X_{Mg} = 0.5) + Qtz + Opx + Kfs + V is stable between 675 and 700°C at 2 kbar [$P(H_2O) = P_f$]. Both the bulk composition and mineral compositions closely approximate those of the immediate footwall at Dunka Road. The experiments also indicate that melting is initiated at 700°C. Lower activities of H_2O would result in lower thermal stability of the hydrous phases and higher melting temperatures. The influence of $P(H_2O)$ is particularly important because of the presence of graphite, which limits $P(H_2O)$ to $0.75P_f$ at 600°C and equilibrium conditions (discussed below).

The contrasting mineral assemblages of DH 24981 and DH 82 (Fig. 4) suggest a reaction involving the appearance of biotite, cordierite, and K-feldspar at the expense of chlorite and muscovite. This transition is important because of the modal abundances of the minerals involved, and the quantity of H_2O that is released as a product. It is unfortunate that samples examined in this study do not contain the critical assemblage Chl + Ms + Qtz + Bt + Crd necessary for any attempt at understanding the nature of dehydration reactions. Reactions most

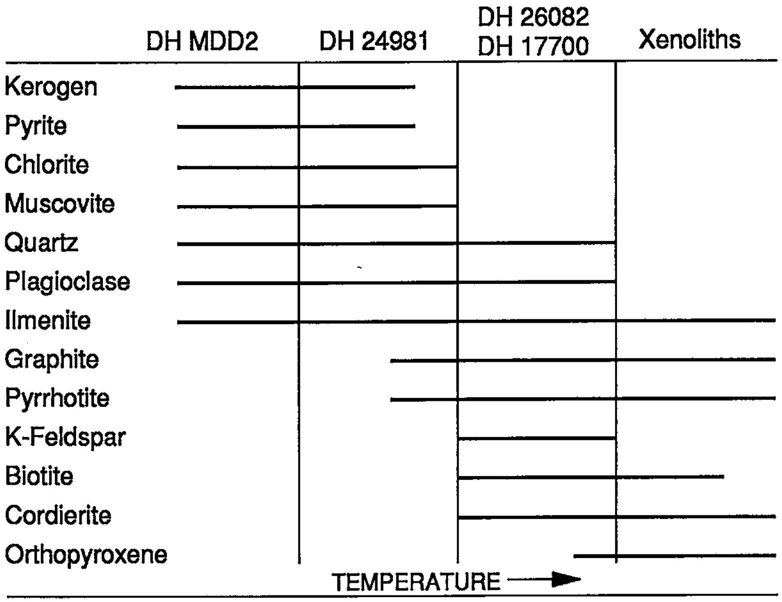

FIG. 4. Schematic plot of mineral assemblages observed in DH MDD2, DH 24981, DH 17,700 and DH 82.

commonly cited to account for this transition include:

$$Chl + Ms + Qtz = Bt + Crd + H_2O \qquad (1)$$
$$Bt + Ms + Qtz = Crd + Kfs + H_2O \qquad (2)$$

(Labotka *et al.* 1981, 1984, Seifert 1970, Burnell & Rutherford 1984, Pattison & Harte 1985). The fine grain-size of the argillites prevented analysis of chlorite and muscovite; however, if ideal formulae are used for mineral compositions, the bulk compositions of hornfels can be recast into argillaceous modes. Table 4 gives the results of modal calculations that are in good agreement with the mineralogical assessment of DH MDD2 by Lucente & Morey (1983).

Obviously, many variables exist which would have influenced the progress and timing of the disappearance of chlorite and muscovite, including $P(H_2O)$, the initial composition of the reactants, associated reactions affecting iron availability, *etc.* The influence of FeO is to enhance the stability of the assemblage Chl + Ms + Qtz, and the exchange of Fe and Mg between products and reactants allows reaction 1 to be continuous over a range of 30°C or more (570 to 600°C at 2 kbars; Burnell & Rutherford 1984). As shown by the thermochemical calculations of Andrews (1987), lowering $X(H_2O)$ to 0.4 results in a 60°C decrease in the reaction temperature.

TABLE 4. AVERAGE MODE OF ARGILLITE, AS RECALCULATED FROM CHEMICAL DATA ON HORNFELS

	For 100g of rock		Approximate
	grams	moles	Volume %
Pyrite	1.31	.011	.69
Ilmenite	1.93	.013	1.07
Anorthite	5.44	.020	5.25
Albite	18.28	.070	18.32
K-feldspar	5.42	.019	5.38
Chlorite*	15.28	.035	19.29
Muscovite	21.24	.053	19.43
Quartz	31.09	.517	30.56

*Average Fe/(Fe+Mg)=.49

The Fe and Mg exchange between cordierite and biotite (Tables 5, 6) was also investigated for its usefulness as an indication of temperatures. The values for this K_d, given by

$$K_d^{Crd\text{-}Bt} = (Mg/Fe)^{Crd}/(Mg/Fe)^{Bt}$$

vary between 1.7 and 1.9 through most of DH 82. Anomalously high values occur at the contact for samples containing orthopyroxene, and biotite with significantly lower octahedrally coordinated aluminum. Though this small range of values for K_d could reflect a uniform maximum temperature throughout DH 82, it is interesting to note that the exchange reaction has an unusually low enthalpy change, so that K_d is not expected to be a function of temperature (Holdaway & Lee 1977, Perchuk & Lavrent'eva 1983).

TABLE 5. REPRESENTATIVE ELECTRON-MICROPROBE DATA ON CORDIERITE

Sample	388	618	627	670	702	747	803	872	902
SiO2, wt.%	49.00	49.20	48.60	48.60	47.90	48.30	48.20	49.70	49.70
TiO2	-	-	-	0.04	-	-	-	-	-
Al2O3	33.00	33.70	33.80	34.20	33.50	34.70	34.60	32.70	33.20
FeO	7.34	6.95	9.02	8.29	9.80	8.88	8.29	8.56	7.78
MgO	9.39	10.10	8.85	8.49	8.01	8.48	8.56	8.45	8.97
MnO	0.04	0.17	0.22	0.21	0.21	0.16	0.18	0.20	0.24
Na2O	0.08	0.16	0.12	0.20	0.12	0.13	0.15	0.16	0.15
Total	98.85	100.28	100.61	100.03	99.54	100.65	99.98	99.77	100.04
Formula proportions based on a total positive charge of 36									
Si	4.99	4.94	4.92	4.92	4.91	4.88	4.88	5.04	5.01
Ti	-	-	-	0.00	-	-	-	-	-
Al	3.96	3.99	4.02	4.08	4.05	4.13	4.13	3.91	3.94
Fe	0.62	0.58	0.76	0.70	0.84	0.75	0.70	0.73	0.65
Mg	1.42	1.50	1.33	1.28	1.22	1.27	1.29	1.28	1.34
Mn	0.00	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.02
Na	0.01	0.03	0.02	0.04	0.02	0.02	0.03	0.03	0.03
Total	11.00	11.05	11.07	11.04	11.06	11.06	11.04	11.00	10.99

TABLE 6. REPRESENTATIVE ELECTRON-MICROPROBE DATA ON BIOTITE

Sample	388	618	627	670	702	747	803	872	902
SiO2 wt.%	38.90	36.90	36.90	37.40	36.20	37.10	37.80	37.20	37.40
TiO2	1.45	3.19	5.30	4.44	3.47	3.47	3.89	4.52	5.00
Al2O3	16.50	15.00	14.80	16.00	16.00	16.00	17.10	16.70	16.00
FeO	15.70	18.80	20.00	18.00	21.30	20.40	17.60	18.60	17.20
MgO	14.00	12.30	9.82	10.60	9.42	10.60	10.50	10.10	12.00
MnO	0.04	0.18	0.09	0.04	0.06	0.12	0.07	0.03	0.07
Na2O	-	-	0.08	0.16	0.09	0.09	0.10	0.24	0.11
K2O	12.00	10.40	10.40	10.90	10.60	10.00	10.50	10.60	10.70
Total	98.59	96.77	97.39	98.17	98.44	97.78	97.56	97.99	98.48
Normalized formula proportions based on a total positive charge of 22									
Si	2.88	2.67	2.76	2.77	2.70	2.76	2.81	2.76	2.73
Ti	0.08	0.29	0.30	0.25	0.27	0.19	0.21	0.25	0.27
Al IV	1.12	1.33	1.24	1.23	1.30	1.24	1.19	1.24	1.27
Al VI	0.32	0.00	0.06	0.23	0.10	0.16	0.31	0.23	0.10
Fe	0.97	1.13	1.25	1.11	1.33	1.27	1.10	1.15	1.04
Mg	1.55	1.33	1.09	1.16	1.04	1.17	1.16	1.12	1.30
Na	0.00	0.00	0.01	0.02	0.01	0.01	0.01	0.01	0.01
K	1.13	0.96	0.99	1.03	1.00	0.95	1.00	1.00	0.99
Total	8.05	7.66	7.70	7.80	7.75	7.75	7.79	7.76	7.71

The results in Figure 4 suggest that the initial mineralogical transitions during prograde metamorphism were the graphitization of organic material and desulfidation of pyrite. Data from Durand & Monin (1980) and Oberlin *et al.* (1980), in supporting experiments, indicate a major period of methane loss from kerogen between 400 and 500°C. The hydrogen-carbon ratio is reduced from approximately 1.5 to 0.5 during this phase of graphitization. French's (1968) study of argillaceous zones within the Biwabik Iron Formation near Dunka Road showed that the transition from amorphous organic material to graphite occurs over a small range of temperatures near 400°C. It is generally agreed that by 500°C, partly crystalline graphite is stable (Durand & Monin 1980, Oberlin *et al.* 1980, Landis 1971).

A contact temperature of 650°C is considered tenable and is in agreement with estimates by Bonnichsen (1975: 650 to 700°C), Green (1970: 600 to 675°C), and Kirstein (1979: >600°C). The main phase of dehydration, signalled by the appearance of biotite and cordierite, most likely occurred over a maximun range of 100°C, between 500 and 600°C. Labotka *et al.* (1981, 1984) have investigated the progressive metamorphism of argillites of the Rove Formation along the northeastern Minnesota-Ontario border and concluded that reactions limiting the stability of chlorite and muscovite occur between 500°C [$X(H_2O)$, = 0.2] and 600°C [$X(H_2O)$ = 1.0] at an average $P(H_2O)$ of $0.5P_f$.

Finally, graphitization of kerogen reflects temperatures between 350 and 450°C. This last estimate is supported by homogenization temperatures of 375°C for fluid inclusions in quartz from DH 24981 (Butler 1988).

FLUID MIGRATION

There is no doubt that fluids migrated out of the Virginia Formation as it underwent metamorphism. A 3% loss of H_2O is considered a maximum relative to a comparison of argillite and hornfels compositions. Using molar volume data from Burnham *et al.* (1969) and Helgeson *et al.* (1978), every 1000 cm^3 of argillite would lose 130 cm^3 of fluid. Walther & Orville (1982) suggested that at low rates of dehydration (regional metamorphism), volatiles may escape by diffusion through an adsorbed grain-boundary film. At higher rates of reaction, the fluid phase will have a fluid pressure (P_f) approaching or even slightly exceeding lithostatic pressure (P_r). This latter process is envisioned for most of the contact aureole at Dunka Road. Local movement of fluid must have been directed downward, away from advancing isotherms, or laterally along bedding planes. Since metamorphism was accompanied by substantial tectonism, it seems reasonable that larger, subvertical and continuous fracture-zones existed in the footwall. Normal faulting is almost a necessity for correlations to be made across drillhole lines (Fig. 2). Within these continuous vertical fractures, fluid pressures were likely less than the lithostatic pressure. Fluid movement would result from the pressure gradient between fracture zones ($P_f < P_r$) and adjacent cohesive rock ($P_f = P_r$). The fracture zones would channel fluids upward, toward the intrusive contact.

Several other points should be noted. Firstly, the bulk of the fluid produced in the Virginia Formation simply cannot be accounted for. Secondly, the predominant absence of retrogradation suggests that most of this fluid was able to leave the footwall rock by the peak of metamorphism. Thirdly, this speculative process, in which evolving fluids are quickly isolated in major conduits, is consistent with the hydrogen isotope modeling of Butler (1988). Finally, dehydration reactions were driven by the addition of substantial amounts of heat into the footwall from the cooling magma(s) of the Duluth Complex. The Complex probably evolved through multiple intrusive episodes over a period as long as 10 to 20 Ma (Silver & Green 1963, Weiblen & Green, pers. comm.). Systematic trends observed through the complex at Dunka Road and several kilometers to the north do suggest separate intrusions (Grant & Molling 1981, Rao & Ripley 1983). Therefore, dehydration in the footwall must have also been episodic.

Equilibrium calculations

Procedures for calculating compositions of the volatile phase in the C–O–H–S system were reviewed by Ohmoto & Kerrick (1977), Ferry & Burt (1982), and Nesbitt & Essene (1983), among many others. In this paper, ideal mixing in a real fluid is assumed, so that the fugacity of each species (f_i) is given by $f_i = \gamma_i P_i$, where P_i and γ_i are the partial pressure of species *i*, and the fugacity coefficient, respectively. The activity coefficients of each species in solution are equal to one. The species considered are H_2O, CO_2, CO, COS, H_2S, CH_4, SO_2, H_2, S_2, and O_2. The result is a system of equations with four degrees of freedom, as formulated by Ohmoto & Kerrick (1977). If values are selected for P_f, T, and the various fugacity coefficients, an $f(O_2)$-$f(S_2)$ diagram can be used to illustrate volatile equilibria. In these calculations it is assumed that fluid pressures approached lithostatic pressures as dehydration reactions progressed. Fugacity coefficients are taken from the following sources: H_2O from Burnham *et al.* (1969), CO_2 from Shmonov & Shmulovich (1975), H_2, CO, O_2, CH_4 and H_2S from Ryzhenko & Volkov (1971). As suggested by Ohmoto & Kerrick (1977), fugacity coefficients for SO_2 and COS are calculated with equations from Ryzhenko & Volkov (1971) and critical data. The fugacity coefficient for S_2 is assumed to be one.

The stability of various oxide and sulfide minerals can be shown on $f(O_2)$-$f(S_2)$ diagrams if equilibrium constants for appropriate mineral–volatile reactions are available. Froese (1977), Tso *et al.* (1979), Nesbitt & Essene (1983), and Nesbitt & Kelly (1980) have applied information from mineral assemblages in obtaining limits of $f(O_2)$ and $f(S_2)$ conditions during metamorphism. Results of these calculations are shown in Figures 5a and 5b, which are drawn at the estimated boundary temperatures of dehydration, 500 and 600°C. Equilibrium constants and equations are listed in Table 7. For DH 82 and DH 24981, the assemblage Po + Gr + Ilm is ubiquitous, and though this association places only broad limits on $f(O_2)$ and $f(S_2)$, it does suggest that the mole fraction of H_2S was restricted to values less than 0.01.

Isotopic data can be used to further restrict fluid composition. Recent work on the effect of devolatilization on the hydrogen isotopic signature of Virginia Formation argillites (Butler 1988) shows that variations in δD can be successfully reproduced by a modified Rayleigh distillation model. In essence this model suggests that "batches" of fluid were continually produced, reached equilibrium with Chl + Bt + Ms, and migrated out of the system. The constancy of δD values throughout DH 82 suggests that dehydration progressed in the same manner throughout the contact aureole. If graphite also reached equilibrium with each "batch" of fluid, the strong similarity in

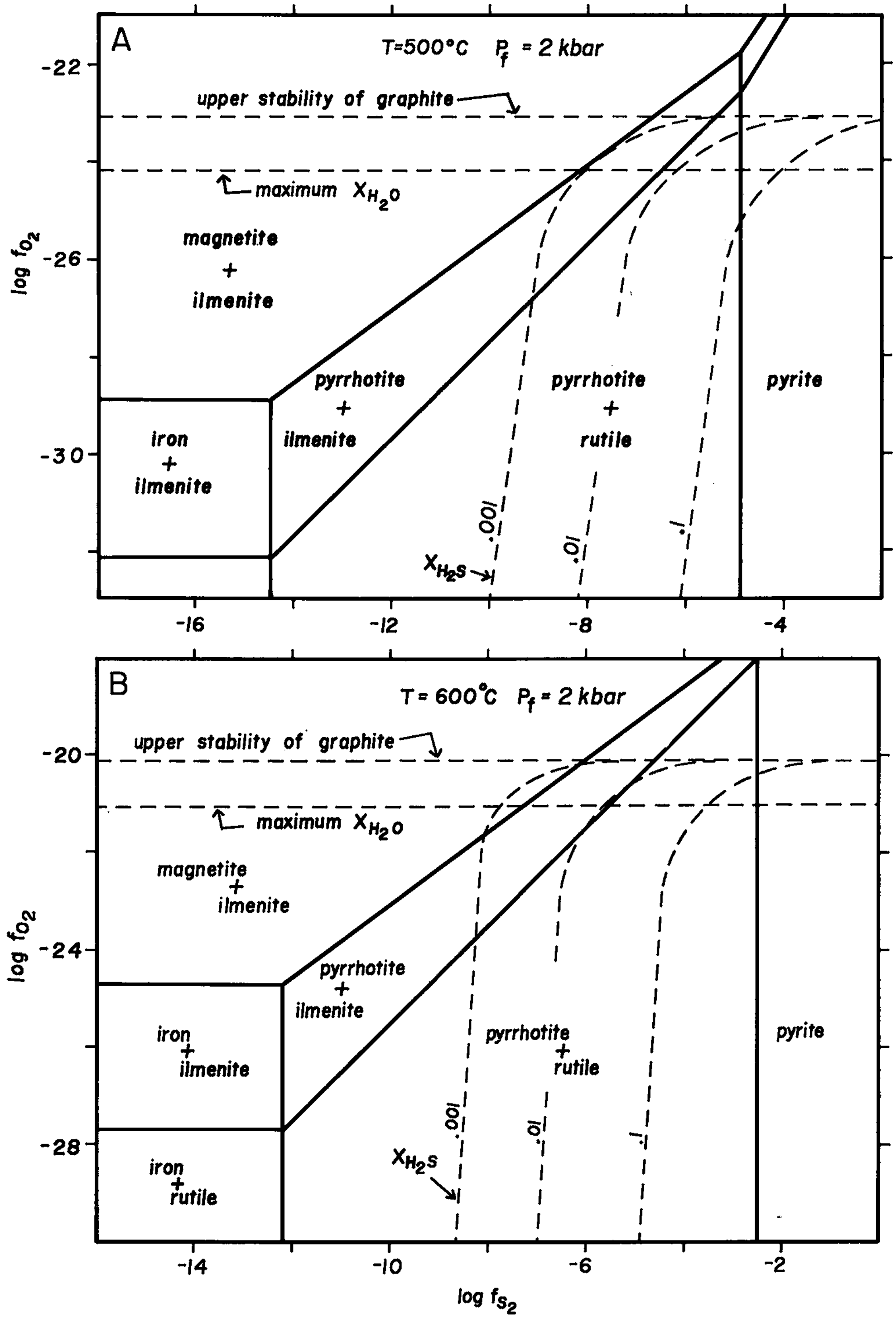

FIG. 5A–B. Stability fields of iron sulfides and oxides at 2 kbars and 500°C (A), and 600°C (B). Vertical dashed lines are contours of the mole fraction of H_2S in associated fluids. The upper dashed horizontal line is the stability limit of graphite, and the lower dashed line is a contour for the maximum mole fraction of H_2O that can exist in the presence of graphite. $a_{FeS} = 1$.

TABLE 7. EQUILIBRIUM CONSTANTS USED IN CONSTRUCTING FIGURES

Reaction	Equation for log K
a) $C_s + O_2 = CO_2$	$0586/T + .0421 + 0.028[(P-1)/T]$
b) $CO + 1/2O_2 = CO_2$	$14751/T + 4.535$
c) $H_2 + 1/2O_2 = H_2O$	$12510/T + 0.483 - 0.979(\log T)$
d) $CH_4 + 2O_2 = CO_2 + 2H_2O$	$41997/T - 2.404 + 0.719(\log T)$
e) $1/2S_2 + O_2 = SO_2$	$18929/T - 3.783$
f) $CO + 1/2S_2 = COS$	$4731/T - 4.338$
g) $1/2S_2 + H_2O = H_2S + 1/2O_2$	$-8117/T - 0.352 + 0.188(\log T)$
h) $FeS + 1/2S_2 = FeS_2$	$8035/T - 7.8676 - .02998[(P-1)/T]$
i) $Fe + 1/2S_2 = FeS$	$7847/T - 2.7445 - 0.0580[(P-1)/T]$
j) $3Fe + 2O_2 = Fe_3O_4$	$56819/T - 15.38 - 0.1214[(P-1)/T]$
k) $FeTiO_3 = Fe + TiO_2 + 1/2O_2$	$-15080/T + 3.3346 + 0.0301[(P-1)/T]$
l) $FeTiO_3 + 1/2S_2 = FeS + TiO_2 + 1/2O_2$	$-7234/T + 0.5796 - 0.02784[(P-1)/T]$

Sources of data: a Huebner (1971), b, c, d, e and g Holland (1965), f Ohmoto & Kerrick (1977), h Froese & Gunter (1976), i Richardson & Jeffes (1952); j, k and l were calculated from the data of Robie et al. (1978). Temperature is expressed in kelvins, and pressure, in bars.

$\delta^{13}C$ values for argillites and hornfels (Table 3; see also Taib 1988) suggests that CH_4 and CO_2 existed in subequal amounts. Fractionation factors for these two species for temperatures between 350 and 550°C (Bottinga 1969) suggest that a CH_4 to CO_2 ratio between 0.5 and 2 would explain this lack of fractionation. Within ±0.3 log $f(O_2)$ units of H_2O_{max} (Fig. 6), the ratio of CH_4 to CO_2 varies between approximately 5 and 0.2. H_2O_{max} is the maximum mole fraction of H_2O that can exist in a fluid in equilibrium with graphite at a given $f(S_2)$.

Given the restrictions discussed above, the composition of the evolving fluid is bracketed by the values in Table 8. Mole fractions of species not listed in this table do not exceed 0.001. It seems that dehydration reactions efficiently maintained the mole fraction of H_2O near its maximum value. The predominant S-bearing species is H_2S, and its mole fraction is limited to values less than 0.01.

Evolution of sulfur in the contact aureole

The sulfide concentrations along the base of the Duluth Complex at Dunka Road have been characterized by Ripley (1981) and Rao & Ripley (1983). Sulfur isotopic data presented in these studies strongly suggest that sulfur derived from a nonmagmatic source has been involved in ore genesis. The $\delta^{34}S$ values for sulfides at the Dunka Road deposit range from 0.2 to 15.3 ‰, with a similar range for Virginia Formation hornfels and argillites. Based on these values, Ripley (1981) cited a maximum magmatic sulfur content of 25%. The petrographic and compositional data of Rao & Ripley (1983) suggest that most sulfide enrichment exists within 150 m of the contact, and that an appropriate average for the volume of sulfides is 1.5% (0.9% pyrrhotite, 0.6% chalcopyrite).

Using these data, and molar volume data from Burnham *et al.* (1969) and Helgeson *et al.* (1978), a reference volume of magma 150 m high and 1 cm^2 in cross section contains 373 g of sulfur. At the very minimum, 280 g of this sulfur is nonmagmatic and must be accounted for either by *in situ* or preintrusive assimilation.

In considering the quantity of volatiles derivable from Virginia Formation argillites, a reference volume 100 m by 1 cm^2 is used. The estimation incorporates the sulfur contents of eighteen meta-argillite samples from DH 82, each representing an

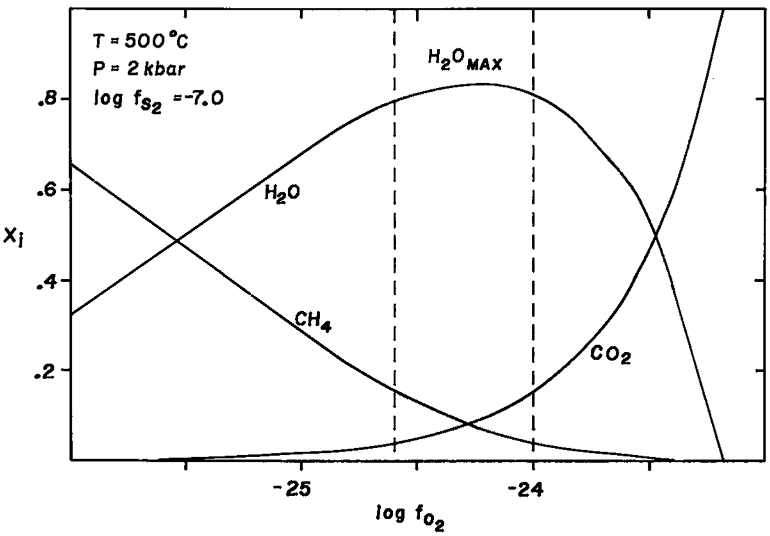

FIG. 6. Plot of the mole fractions of H_2O, $f(S_2)$, CH_4, and CO_2 *versus* log $f(O_2)$ for the conditions T = 500°C, P_f = 2 kbars, and log $f(S_2)$ = -7.0. The dashed vertical lines bracket the most likely composition of evolving metamorphic fluids in the Virginia Formation at Dunka Road.

TABLE 8. ESTIMATED COMPOSITION OF VOLATILE PHASE

Species	500 °C	600 °C
X_{H_2O}	0.79 - 0.83	0.70 - 0.75
X_{CO_2}	0.04 - 0.15	0.05 - 0.21
X_{H_2}	0 - 0.01	0 - 0.01
X_{CH_4}	0.04 - 0.16	0.06 - 0.22
X_{H_2S}	0 - 0.01	0 - 0.01

interval determined by the proximity of other samples. The integration gives an average of 0.60 wt.% S, or 162 g in the reference volume. In addition, an average loss of 3.0 wt.% H_2O equates with 835 g or 46.3 moles of H_2O derived from the reference volume.

As pyrite and pyrrhotite are the predominant sulfide minerals in Virginia Formation argillites and hornfels, respectively, the question as to whether *in situ* sulfur derivation was important must hinge on the nature of the pyrite–pyrrhotite transition. Ferry (1981) discussed this transition in the context of regional metamorphism and suggested several possible mechanisms of reaction. One alternative is whole-rock desulfidation, which could have resulted in magma contamination. Desulfidation can be represented by a reaction (Ripley 1981) such as:

$$3H_2O + 5/2C + FeS_2 = FeS + H_2S + 3/2CO_2 + CH_4 \qquad (3)$$

in which every mole of pyrite produces one mole of pyrrhotite and H_2S. If a mechanism such as that represented by reaction 3 operated during metamorphism, the sulfur concentration in the hornfels records the amount of H_2S liberated. This amount was calculated above. To account for a minimum of 280 g of nonmagmatic sulfur in the ore zone, every cm^3 of magma must have acquired sulfur from 1.15 cm^3 of argillite. This also requires that each cm^3 of magma interacted with 0.25 cm^3 of fluid, based on molar volumes at 900°C and 2 kbar. Using reaction 3, observed concentrations of sulfur, and the amount of evolved H_2O, the resulting fluid would have a composition similar to the following: $X(H_2O)$ = 0.64, $X(CO_2)$ = 0.16, $X(CH_4)$ = 0.10, $X(H_2S)$ = 0.10.

The value for H_2S is, at the least, one order of magnitude greater than suggested by equilibrium calculations (Table 8), though the above calculation assumes that all of the fluids are evolved from the immediate rocks. Ferry (1981) and Peacock & Spear (1981) arrived at a similar conclusion regarding sulfide-rich pelitic rocks in Maine and New Hampshire. They suggested that the desulfidation reaction is driven by influx of large volumes of externally derived fluids. For the contact-metamorphic environment at Dunka Road, neither mineralogical nor isotopic data ($\delta^{18}O$: Ripley & Al-Jassar 1987, Andrews 1987; $\delta^{13}C$: Taib 1988; δD: Butler 1988) suggest that large volumes of fluid permeated the metasedimentary sequence.

Diffusion of a sulfur species through the footwall also must be considered as a desulfidation mechanism. Diffusion of sulfur away from reaction sites would allow the pyrite–pyrrhotite transition to proceed. In DH 24981, pyrrhotite has formed from pyrite before the initiation of dehydration. The assemblage in DH 24981 is Chl + Ms + Ilm + Po + Py + OM. Desulfidation may have been coupled with the catagenesis of organic material, with released methane reacting with pore fluids to provide the H_2 necessary for the breakdown of pyrite. Possible reactions include:

$$2FeS_2 + CH_4 = 2H_2S + 2FeS + C \quad \text{(see Ferry 1981)} \qquad (4)$$

or

$$4FeS_2 + CH_{4(OM)} + 2H_2O = 4FeS + 4H_2S + CO_2 \qquad (5)$$

These processes would result in high concentrations of $H_2S + CO_2$, and lower fugacities of H_2O at reaction sites, and are limited by available CH_4, pore water, and the amount of energy required to drive catagenesis. This "energy" must be the addition of heat to the footwall. As rates of diffusion are significantly lower than rates of heat conduction, and as diffusion is unlikely to be a viable process once dehydration reactions induce fluid flow, it is hard to imagine that diffusion of H_2S through the footwall is significant in providing sulfur to the magma. For example, consider the initial 10 m of argillite adjacent to the intrusive contact. Based on the heat-conduction calculations of Andrews (1987), the dehydration front would have passed through this section after approximately 40 years. Using a chemical diffusivity (D) of 10^{-6} cm^2 s^{-1} (a reasonable value for diffusion through a grain-boundary film; see Farooque & Fahidy 1978, Lasaga 1981), and the approximation that $x = (Dt)^{1/2}$ for the total distance of advance of a diffusion front, diffusion of H_2S across this 10-m section would require approximately 31,700 years. However, the coupling of catagenesis and desulfidation is still plausible, with high concentrations of CO_2 and H_2S existing in pore fluids just prior to the initiation of dehydration reactions. Labotka *et al.* (1984) calculated fluid compositions accompanying contact metamorphism of the Rove Formation and suggested that low fugacities of H_2O existed in the rock during the early stages of dehydration.

The final alternative is that sulfur was conserved in footwall rocks. The process would be one in which sulfur released by the decomposition of pyrite scavenges iron from associated oxides and silicates. Similar processes for regional metamorphism have been described by Thompson (1972), Bachinski (1976), Robinson & Tracy (1977), and Mohr & Newton (1983). Ferry (1981) suggested the reaction:

$$2FeS_2 + 2FeO(\text{silicates}) + C = 4FeS + CO_2 \qquad (6)$$

The component FeO in the Dunka Road rocks could

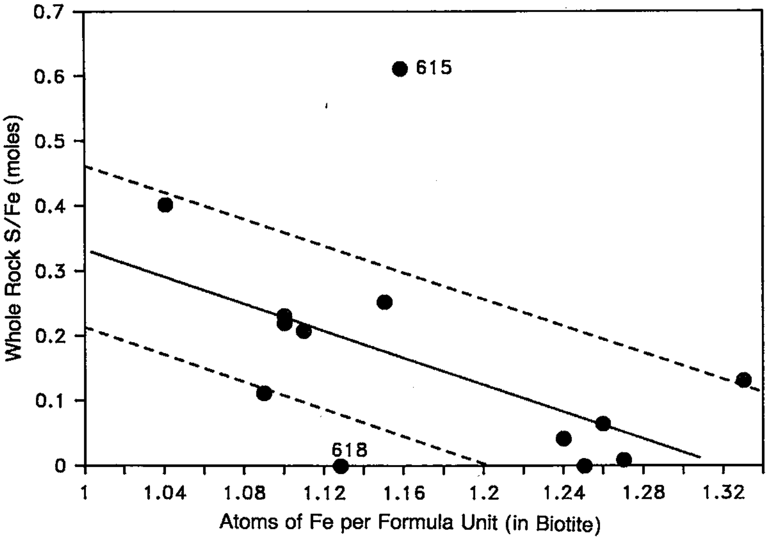

FIG. 7. Plot of the ratio of whole-rock iron and sulfur (in mole %) *versus* the proportion of iron in biotite (atoms per formula unit). The line represents a linear regression of data with a correlation coefficient of –0.77. Samples 615 and 618 are not included in the regression because of their proximity to the intrusive contact.

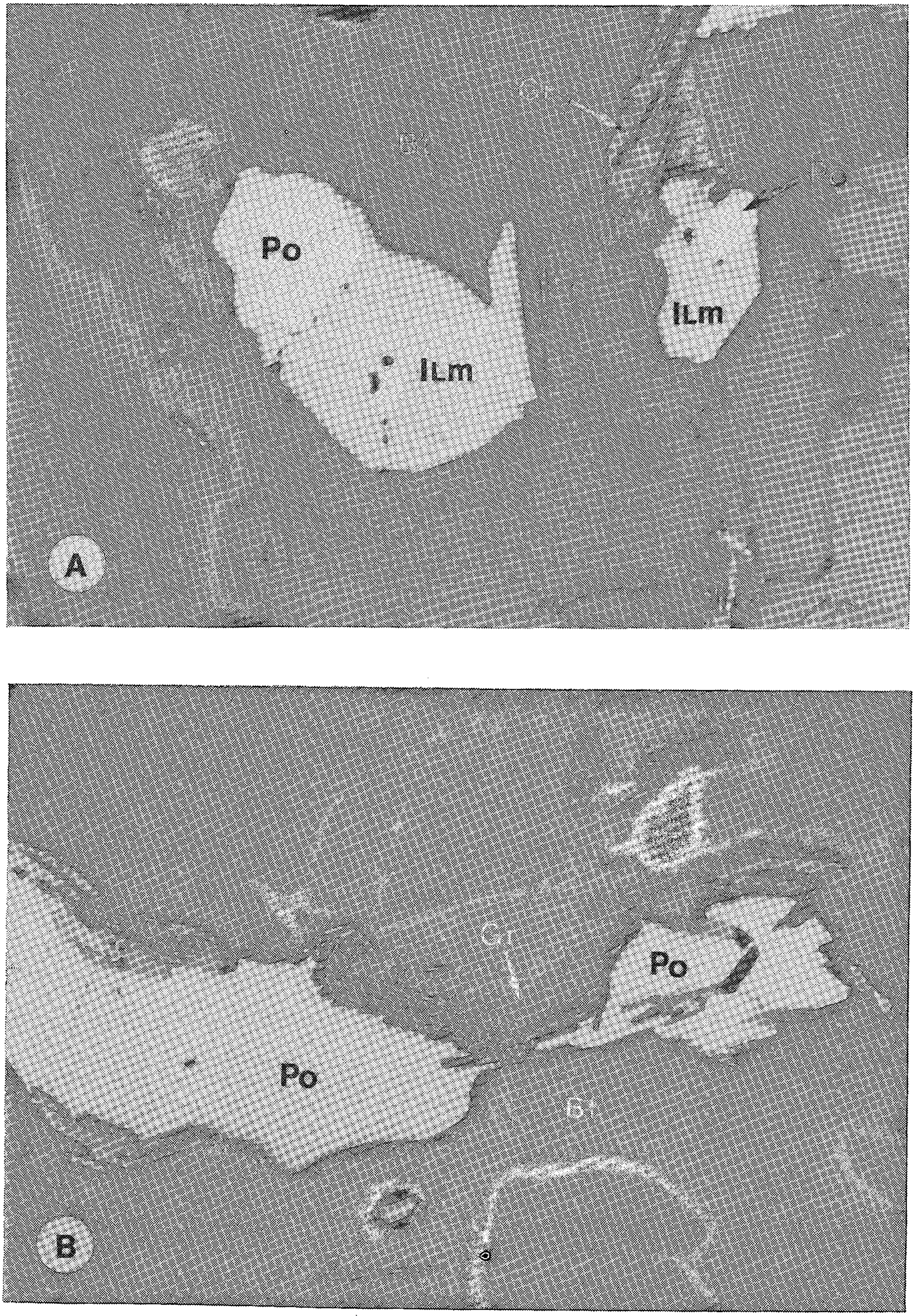

FIG. 8A–B. Photomicrographs illustrating the intergrowth of biotite (Bt) with ilmenite (Ilm), pyrrhotite (Po), and graphite (G). Both photomicrographs are from sample 747 of drillhole 82, and the width of each represents 0.45 mm.

be obtained from ilmenite, biotite, cordierite, or chlorite. According to reaction 6, each mole of pyrite in the initial argillaceous protolith reacted to give two moles of pyrrhotite in the contact-metamorphic zone.

If sulfur was conserved in the footwall, the ratio of whole-rock sulfur and iron should be similar in the argillites of DH MDD2 and the meta-argillites from DH 82. The sixteen low-Ca meta-argillites in Table 2 have S/Fe (molar) values ranging between 0.61 and 0, and averaging 0.16. Using analyses presented by Rao & Ripley (1983) and Bonnichsen (1972), low-Ca argillites form DH MDD2 have S/Fe values ranging between 0.42 and 0.06, with an average of 0.21. The significant overlap of two sets of data is more consistent with sulfur conservation within the footwall than with sulfur loss.

In addition, consider a situation where two samples of argillite with identical modes and compositions, except for pyrite abundance, are metamorphosed and sulfur is conserved. In the sample with an initially higher S/Fe value, one would expect either a lower modal content of ferruginous silicates or ilmenite (or both), or a lower value for Fe/Mg in the silicates. Molar whole-rock S/Fe *versus* the moles of iron in biotite from DH 82 is plotted in Figure 7. If samples 615 and 618 are ignored, a negative correlation is apparent between these two variables. Samples 615 and 618 are from the zone immediately adjacent to the intrusive contact, where bulk compositions may have been modified by incipient partial melting. In addition, sample 615 has an anomalous modal mineralogy, containing 24% opaque minerals (Gr + Ilm + Po) but only 3% biotite (1,400 points counted). The solid line in Figure 7 represents a linear regression of the data and has a correlation coefficient of -0.77. The observed S–Fe variations could be the result of the formation of sedimentary pyrite in an environment where diagenetic H_2S production is a function of carbon availability, and sufficient iron is present to cause precipitation of iron sulfide (*e.g.*, Raiswell & Berner 1985). However, the necessary range in the iron content of chlorite as a function of sulfur content is not found in unmetamorphosed parts of the Virginia Formation. Although an analysis of this type does not preclude a loss of some sulfur, it strongly suggests that a metamorphic equilibration between pyrrhotite and silicates was approached, and that iron from silicates was utilized in the production of additional pyrrhotite.

In summary, the premise that sulfur was largely conserved within the footwall at Dunka Road is supported by the similarity in whole-rock S/Fe in argillites and hornfels, and the negative correlation between biotite compositions and whole-rock S/Fe. Sulfur immobility also is consistent with the calculations of fluid equilibrium presented above, with $X(H_2S)$ in evolving fluids less than 0.01. Finally, the nearly ubiquitous presence of intimate intergrowths of pyrrhotite, biotite, and ilmenite in the samples from DH 82 (Fig. 8) are consistent with the occurrence of a process similar to:

$$\begin{aligned}&\text{Bt} + n\text{H}_2\text{S} + \text{Ilm} = \\ &\text{Ti-enriched, Fe-depleted Bt} + n\text{Po} + \text{H}_2\text{O} \qquad (7)\end{aligned}$$

The only other *in situ* process that could provide sulfur to the magma is the partial assimilation of xenolithic blocks of country rock. Samples 387 and 388 are taken from an inclusion intersected in DH 82. The refractory mineralogy and composition of these samples are suggestive of partial melting. Rao & Ripley (1983) examined the igneous rocks inmediately adjacent to this xenolith and cited the following evidence for contamination: anomalous $\delta^{18}O$ values, greater modal biotite, ilmenite, sulfide, and orthopyroxene, less modal olivine (or none at all), and a slight enrichment in SiO_2 content. This contamination is restricted to distances of less than 10 m from xenolith borders.

From the data, significant migration of sulfur out of the immediate country rock occurred only in association with major-element mobility, *i.e.*, partial melting and diffusive mass-transport. Mass-balance calculations presented above suggest that a certain volume of magma would have to acquire sulfur from an equal or greater volume of argillite. Accomplishing this through the partial assimilation of xenoliths is extremely unlikely. We conclude that the derivation of sulfur from immediately adjacent country-rocks could not have been an important factor in the localization of Cu-Ni sulfide mineralization.

The principal alternative is that the magmas acquired sulfur prior to their final emplacement, either during ascent or while residing in a larger chamber that existed below the rift zone. Partial melting of xenoliths and magma mixing may proceed more readily in an environment where heat loss is less rapid. In addition, higher temperatures and slower cooling rates will be more conducive to diffusive mass-transfer at the margin of a magma body. In addition, it is reasonable to speculate that a more sulfur-rich source rock exists at depth. Based on mineralogical and sulfur isotopic distributions and the copper-rich nature of sulfide assemblages, Ripley & Alawi (1986) and Chalokwu (1985) also have suggested that the igneous rocks that host mineralization in the Babbitt – Dunka Road area contained the bulk of their sulfur prior to final emplacement.

CONCLUSIONS

1) Metamorphism of the Virginia Formation in the area of the Dunka Road Cu–Ni deposit resulted in the conversion of argillaceous rocks containing the

assemblage Chl + Ms + Qtz + Plg + Ilm + Py + OM to hornfels containing Bt + Crd + Plg + Kfs + Qtz + Ilm + Po + Gr + Opx. This conversion was isochemical except for the loss of approximately 3.0 wt.% H_2O and minor amounts of carbon and sulfur. Whole-rock chemical trends are interpreted as resulting from sedimentary processes.

2) Evolving "batches" of fluid reached equilibrium with associated minerals and were then isolated in major conduits within the footwall. The bulk of this fluid simply cannot be accounted for. The mole fraction of H_2O was buffered to maximum values (0.75 to 0.83), and the mole fraction of H_2S never exceeded 0.01 as dehydration reactions progressed.

3) It is unlikely that *in situ* sulfur assimilation was important in ore genesis. The data support the idea that sulfur was conserved within the footwall section through some mechanism involving associated iron oxides and ferrruginous silicates. Minor quantities of sulfur certainly entered the melt during partial assimilation of xenoliths along the footwall, but preintrusive sulfur saturation is more consistent with the data contained herein and with the characteristic enrichment of copper in the ore. It now seems more likely that significant contamination occurred prior to the final emplacement of the magmas.

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