

Identifying externally-derived sulfur in conduit-type Cu-PGE deposits: the importance of multiple sulfur isotope studies

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Geology

The Proterozoic Coldwell alkaline complex (Fig. DR1) is a large, unmetamorphosed, undeformed composite intrusive body (Walker et al., 1993) emplaced at 1108 ± 1 Ma (Heaman and Machado, 1992). It is associated with the Mid-Continent Rift System and was emplaced into Archean metavolcanic, metasedimentary, and granitic plutonic rocks.

At the Marathon deposit, at least three distinct intrusive series have been recognized on the basis of cross-cutting relationships, geochemistry, and petrographic characteristics (Good et al., 2015). The three series are: 1) metabasalt, 2) Layered Series, and 3) Marathon Series, all of which comprise the Eastern Gabbro (Figs. DR1 and DR2). The Two Duck Lake gabbro (TDLG) belongs to the Marathon Series, and is the principal host to the Marathon mineralization. It intruded the Layered Series, metabasalt, and footwall rocks, which, in the vicinity of the Marathon deposit, comprise Archean intermediate pyroclastic metavolcanic rocks.

Sample selection

Nine samples from the three mineralized zones at Marathon, and 2 samples of Archean country rocks were selected for in situ secondary ion mass spectrometry (SIMS) for $\delta^{34}\text{S}$. In addition, nine samples from the three mineralized zones at Marathon were selected for sulfide mineral separation and measurements of $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ (Shahabi Far, 2016).

Secondary ion mass spectroscopy (SIMS)

One-inch diameter polished mounts from small slabs of selected sulfide-bearing rocks were prepared, and all samples were sputter-coated with Au. The sulfur isotope analyses were performed using the Cameca IMS 4f Secondary Ion Mass Spectrometer at the MAF-IIC Microanalysis Facility of Memorial University, St. John's, Newfoundland. The analyses were conducted by bombarding the sample with a Cs^+ primary-ion microbeam of 800 to 1200 pA, with an accelerating potential of 10 KeV, focused into a 5 to 15 μm diameter spot. The surface gold coating was locally penetrated by pre-sputtering for 180 s with a 25 μm square raster. To improve the homogeneity of primary-ion delivery, a smaller square raster (5 to 15 μm) was also applied to the beam during analysis. The accelerating voltage of negatively-charged secondary ions into the mass spectrometer was 4.5 KeV. Using the simple 150 μm transfer lens mode with a field aperture of 1800 μm , resulted in a 125 μm field of view in the mass spectrometer. Cyclical magnetic peak switching was used to obtain signals for $^{32}\text{S}^-$, $^{34}\text{S}^-$, and a background position at 31.67 Da, with counting times of 2 s, 6 s and 0.5 s, respectively. For magnet settling between each peak counting position, a waiting time of 0.25 s was included. An ETP 133H multiple-dynode electron multiplier and ECL-based pulse-counting electronics with an overall dead time of 12 ns were used for collecting and processing all signals. Background measurements at mass 31.67 Da were routinely less than 0.05 to 0.1 counts per second. Primary-beam currents were adjusted appropriately for each sulfide phase to maintain count rates on $^{32}\text{S}^-$ between 800,000 and 1,100,000 counts per second. The magnitude of instrumental mass fractionation (IMF) is not constant for all sulfide minerals. Therefore, measured $^{34}\text{S}/^{32}\text{S}$ ratios were corrected for IMF by comparison to replicates of mineral-specific reference materials; UL9B (pyrite; $\delta^{34}\text{S}$: +16.4‰), PoW1 (pyrrhotite; $\delta^{34}\text{S}$: +3.0‰) and Norilsk (chalcopyrite; $\delta^{34}\text{S}$:

+8.4‰). The accepted values for these reference materials listed here were determined by analysis of replicate aliquots at McGill University (using the approach described below) providing a common reference for comparison of SIMS and isotope ratio mass spectroscopy (IRMS) determinations of $\delta^{34}\text{S}$ in this study. All sulfur isotope data are reported relative to Vienna Cañon Diablo Troilite (V-CDT). Analyses produced internal precisions on $\delta^{34}\text{S}$ of typically better than ± 0.2 ‰ (1σ) and overall reproducibility was typically better than ± 0.35 to 0.40 ‰ (1σ).

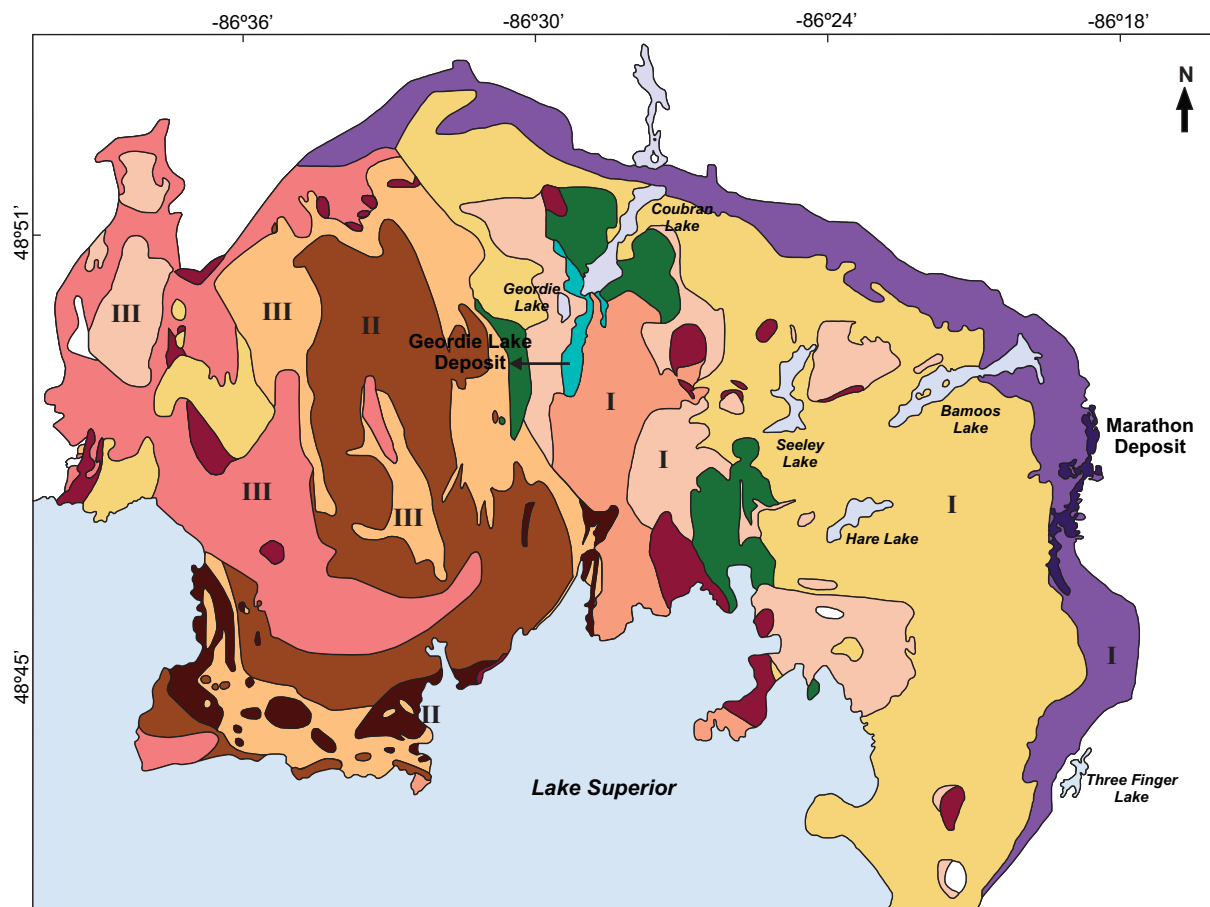
Isotope ratio mass spectroscopy (IRMS)

Selected samples for this study crushed, and sieved to liberate chalcopyrite and pyrrhotite from each other and from silicate, oxide, and other sulfide minerals. Then, chalcopyrite and pyrrhotite were separated from each sample by handpicking under a binocular microscope. The sulfur isotopic composition of these samples was measured at the Department of Earth and Planetary Sciences, McGill University. All samples were pulverized and reacted with a Cr-reducing solution at approximately 85°C to liberate sulfur from sulfide minerals as H_2S . The H_2S was then trapped using a 4% (w/w) zinc acetate solution and reacted with AgNO_3 solution (0.1 N) to produce Ag_2S , which was subsequently filtered and rinsed multiple times with NH_4OH solution (1N) and Milli-Q water and dried in an oven at 70°C (cf. Ono et al., 2006). This Ag_2S was fluorinated in a nickel reaction vessel at approximately 250°C under excess F_2 to produce SF_6 . The SF_6 was purified cryogenically and chromatographically, and analyzed using a ThermoFinnigan MAT 253 dual-inlet gas-source mass spectrometer. All sulfur isotope data are reported relative to Vienna Cañon Diablo Troilite (V-CDT). The precision of analyses (1σ) is better than 0.05 ‰ for $\delta^{34}\text{S}$ values, 0.01 ‰ for $\Delta^{33}\text{S}$ values, and 0.1 ‰ for $\Delta^{36}\text{S}$ values. Uncertainties in the measurements (1σ) based on analytical reproducibility are better than 0.1 ‰,

0.01‰, and 0.2‰ for $\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, and $\Delta^{36}\text{S}$ values, respectively.

Whole rock data

Whole rock assay data for the ore metals were obtained from Stillwater Canada Inc. The analyses were conducted by ALS Labs using atomic absorption spectroscopy (AAS) for copper, and fire-assay followed by ICP-atomic emission spectroscopy (ICP-AES) for Au, Pt, and Pd. The estimated accuracy and precision of the analyses are, respectively, better than 16 and 10% for Au, 16 and 13% for Pt, 8 and 6% for Pd, and 4% and 3% for Cu.



Gabbroic Rocks	Syenitic Rocks	Volcanic Rocks
Two Duck Lake Gabbro	Iron-Rich Augite Syenite	Archean Metavolcanics
Eastern Gabbro Suite	Amphibole Syenite	Mafic Volcanic, Subvolcanic, and Hypabyssal Intrusives
Geordie Lake Intrusion	Amphibole Quartz Syenite	
Western Gabbro Series	Recrystallized Amphibole Quartz Syenite	
Alkaline Gabbro Series	Nepheline Syenite	
	Amphibole Natrolite-Nepheline Syenite	

Figure DR1: Geology map of the Coldwell Complex showing the Eastern Gabbro, the syenitic rocks and the location of the Marathon deposit (modified after Good et al., 2015). The intrusive centers have been shown by Roman numerals (after Mulja and Mitchell, 1991).

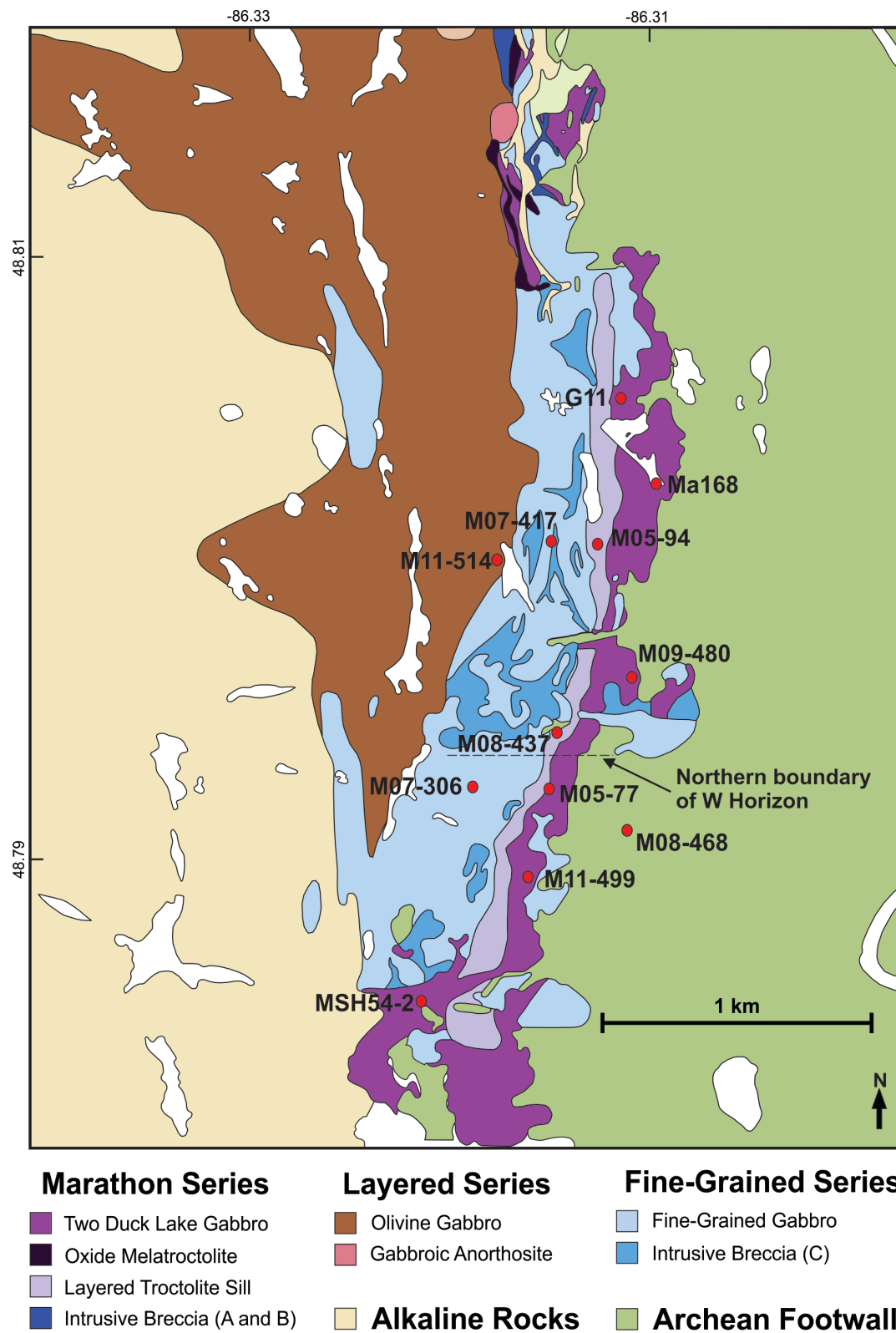


Figure DR2: Geology map of the Marathon deposit showing the relationship of the TDLG with other gabbros and Archean country rocks (modified after Good et al., 2015). Red circles show the location of the samples.

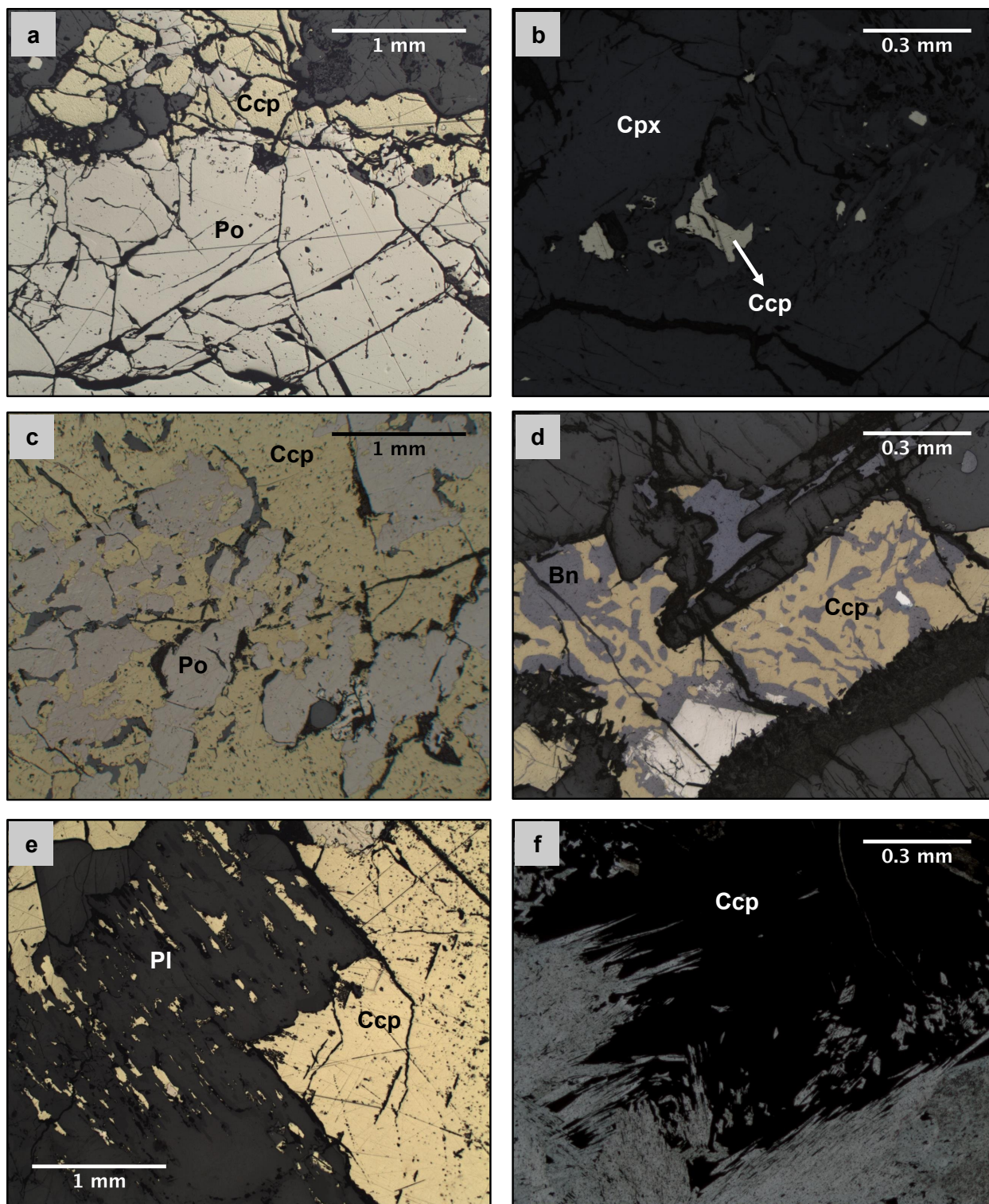


Figure DR3: Photomicrographs representing different sulfide occurrence and assemblages in the Marathon deposit. a) massive sulfide from the Footwall Zone, b) disseminated chalcopyrite, c) chalcopyrite replacing primary magmatic pyrrhotite, d) Bornite blebs and lamellae within chalcopyrite, e) Chalcopyrite blebs within resorption rim of plagioclase crystal, and f) Chalcopyrite intergrown with hydrous minerals.

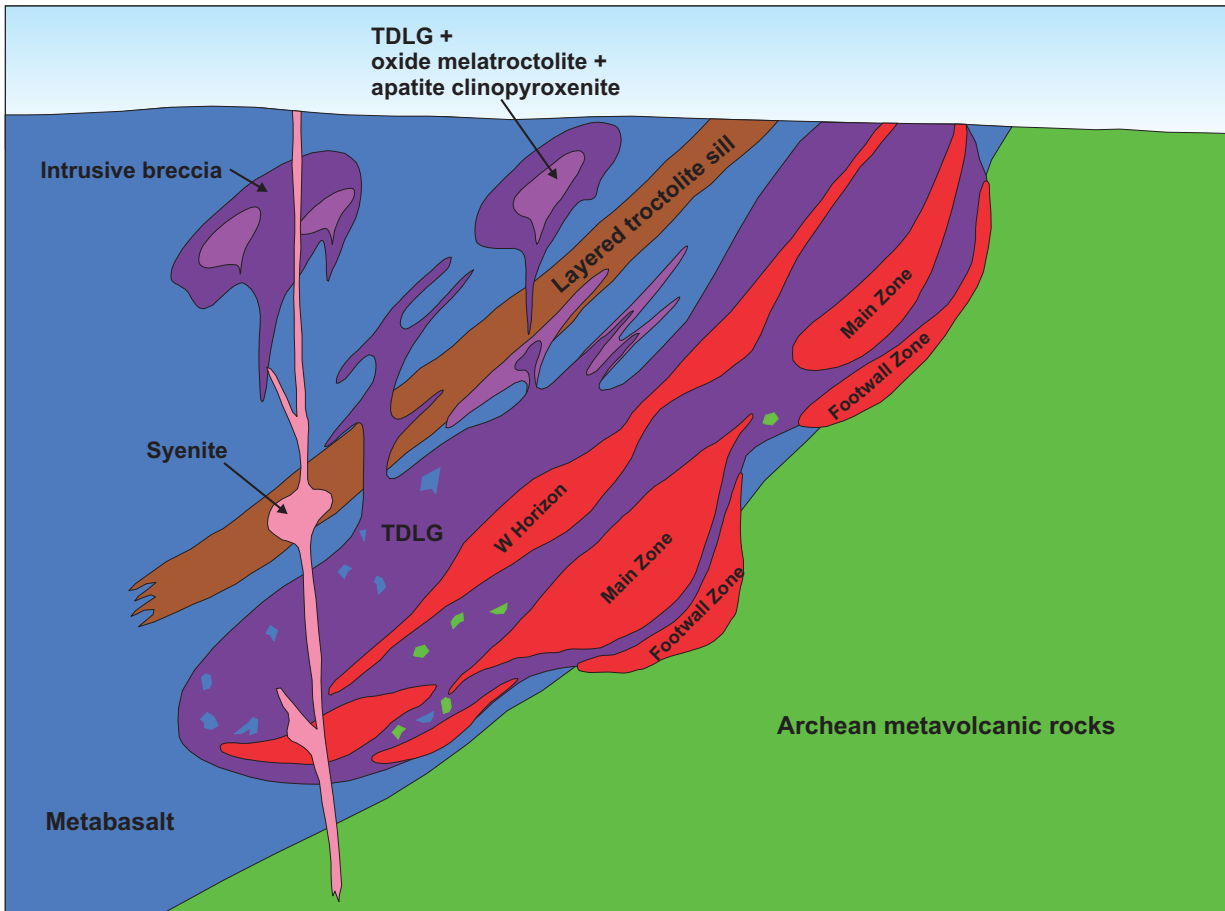


Figure DR4: A schematic cross section of the Marathon deposit showing the stratigraphic distribution of three different mineralized zones and their relationship.

References

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TABLE DR1. CHARACTERISTICS OF MINERALIZED ZONES COMPRISING THE MARATHON PGE-CU DEPOSIT

(GOOD ET AL., 2015)

Mineralized zone	Sulfide occurrence	PGE grade (ppm)	S content (ppm)	Cu/Pd
<i>Footwall Zone</i>	Semi-massive to net-textured magmatic	<~1	Up to 20000 to 30000	> 6000 to 35000
<i>Main Zone</i>	Disseminated magmatic and replacing primary magmatic sulfides	<1 to 3	500 to 10000	1000 to 20000
<i>W Horizon</i>	Disseminated	~1 to 70	500 to 4000	~ 10 to 1000

**TABLE DR2. LIST OF SELECTED SAMPLES FOR SULFUR ISOTOPE ANALYSES
USING SIMS AND IRMS FROM THE MARATHON DEPOSIT**

Sample No.	Drill hole No.	Depth (m)	GPS coordinate [#]		Zones
			Northing	Easting	
59375	M-07-306	153.92	5404392.8	550045.8	W Horizon
59385	M-07-306	203.85	5404392.8	550045.8	Main Zone
59415C	M-07-306	155.60	5404392.8	550045.8	W Horizon
59395b	M-05-077	138.20	5404398.7	550264.4	Footwall Zone
G11-1I	G-11	119.00	5405790.0	550550.8	Footwall Zone
G11-2	G-11	50.00	5405790.0	550550.8	Above the Main Zone
G11-3	G-11	80.00	5405790.0	550550.8	Main Zone
G11-7I	G-11	84.00	5405790.0	550550.8	Main Zone
G11-8I	G-11	80.00	5405790.0	550550.8	Main Zone
M05-94-195.6-1	M-05-94	195.60	5405276.0	550448.3	Footwall Zone
M07-417-318.55	M-07-417	318.55	5405275.0	550300.0	Footwall Zone
M08-468-129.35	M-08-468	129.35	5404200.0	550550.0	
M11-514-449.65	M-11-514	449.65	5405197.0	550096.9	Footwall and Main Zone transition
M11-514-450.43	M-11-514	450.43	5405197.0	550096.9	Footwall and Main Zone transition
M11-514-483.64	M-11-514	483.64	5405197.0	550096.9	Footwall and Main Zone transition
M08-437-171.71	M-08-437	171.71	5404575.0	550325.0	Archean rocks
M09-480-59.22	M-09-480	59.22	5404794.0	550585.3	Footwall Zone
M11-499-22.86	M-11-499	22.86	5404029.0	550193.5	W Horizon
Ma168	N.A.*	N.A.*	5405470.0	550683.0	Main Zone
MSH54-2	N.A.*	N.A.*	5403591.0	549810.0	W Horizon

*N.A.= not applicable
[#] GPS coordinates are NAD27 zone 16

TABLE DR3. SULFUR ISOTOPE COMPOSITION ($\delta^{34}\text{S}$) OF THE MARATHON DEPOSIT BY SIMS

Sample No	Distance from basal contact	Zone	Texture	Mineral	$\delta^{34}\text{S}$ (‰)	SEM (‰)	$^{34}\text{S}/^{32}\text{S}$ (meas)	2SD
G11-1I	0.00	Footwall	Massive- sulfide	Po	0.4	0.15	0.043416	0.000115
G11-1I	0.00	Footwall	Massive- sulfide	Po	0.6	0.14	0.043427	0.000108
G11-1I	0.00	Footwall	Massive- sulfide	Po	0.9	0.18	0.043437	0.000129
G11-1I	0.00	Footwall	Massive- sulfide	Ccp	1.6	0.21	0.043578	0.000155
G11-1I	0.00	Footwall	Massive- sulfide	Ccp	0.2	0.19	0.043514	0.000140
M05-94-195.6-1	0.00	Footwall	Massive- sulfide	Po	1.2	0.19	0.043451	0.000146
M05-94-195.6-1	0.00	Footwall	Massive- sulfide	Ccp	-0.4	0.21	0.043491	0.000154
M05-94-195.6-1	0.00	Footwall	Massive- sulfide	Ccp	0.2	0.20	0.043517	0.000148
G11-2	67.81	Above Main Zone	Magmatic equilibrium	Po	0.8	0.19	0.043436	0.000142
G11-2	67.81	Above Main Zone	Magmatic equilibrium	Po	0.8	0.24	0.043432	0.000183
G11-2	67.81	Above Main Zone	Magmatic equilibrium	Ccp	-0.1	0.16	0.043501	0.000121
G11-2	67.81	Above Main Zone	Magmatic equilibrium	Ccp	0.2	0.19	0.043514	0.000140
G11-3	37.81	Main Zone	Magmatic equilibrium	Po	-0.2	0.17	0.043389	0.000131
G11-3	37.81	Main Zone	Magmatic equilibrium	Ccp	0.7	0.13	0.043538	0.000098
G11-3	37.81	Main Zone	Magmatic equilibrium	Ccp	-0.2	0.16	0.043500	0.000121
G11-3	37.81	Main Zone	Magmatic equilibrium	Ccp	1.1	0.20	0.043556	0.000147
G11-3	37.81	Main Zone	Magmatic equilibrium	Ccp	0.5	0.14	0.043530	0.000105
G11-3	37.81	Main Zone	Intergrown with hydrous minerals	Ccp	0.5	0.15	0.043528	0.000115
G11-3	37.81	Main Zone	Magmatic equilibrium	Ccp	0.0	0.25	0.043506	0.000184
G11-7I	33.81	Main Zone	Ccp* replacing Po [#]	Po	-0.2	0.14	0.043392	0.000106
G11-7I	33.81	Main Zone	Ccp replacing Po	Po	0.5	0.15	0.043419	0.000105
G11-7I	33.81	Main Zone	Ccp replacing Po	Po	0.2	0.15	0.043405	0.000109
G11-7I	33.81	Main Zone	Ccp replacing Po	Ccp	1.2	0.16	0.043561	0.000123

G11-7I	33.81	Main Zone	Intergrown with hydrous minerals	Ccp	0.5	0.20	0.043527	0.000151
G11-7I	33.81	Main Zone	Ccp replacing Po	Ccp	0.4	0.18	0.043527	0.000133
G11-7I	33.81	Main Zone	Along plagioclase twinning	Ccp	-0.3	0.18	0.043493	0.000133
G11-8I	37.81	Main Zone	Ccp replacing Po	Po	-0.3	0.14	0.043388	0.000103
G11-8I	37.81	Main Zone	Ccp replacing Po	Po	-0.2	0.17	0.043392	0.000128
G11-8I	37.81	Main Zone	Along plagioclase twinning	Ccp	-0.3	0.13	0.043496	0.000097
G11-8I	37.81	Main Zone	Ccp replacing Po	Ccp	-0.2	0.21	0.043501	0.000154
G11-8I	37.81	Main Zone	Intergrown with hydrous minerals	Ccp	-0.4	0.18	0.043489	0.000138
G11-8I	37.81	Main Zone	Intergrown with hydrous minerals	Ccp	-0.4	0.19	0.043490	0.000142
G11-8I	37.81	Main Zone	Magmatic equilibrium	Ccp	0.1	0.16	0.043510	0.000120
M11-514-449.65	6.85	Footwall and Main Zone transition	Intergrown with hydrous minerals	Po	0.2	0.14	0.043405	0.000107
M11-514-449.65	6.85	Footwall and Main Zone transition	Ccp replacing Po	Po	0.6	0.28	0.043425	0.000201
M11-514-449.65	6.85	Footwall and Main Zone transition	Intergrown with hydrous minerals	Po	-0.3	0.16	0.043387	0.000119
M11-514-449.65	6.85	Footwall and Main Zone transition	Intergrown with hydrous minerals	Po	-0.1	0.20	0.043395	0.000144
M11-514-449.65	6.85	Footwall and Main Zone transition	Intergrown with hydrous minerals	Po	0.3	0.19	0.043413	0.000139
M11-514-449.65	6.85	Footwall and Main Zone transition	Intergrown with hydrous minerals	Ccp	0.1	0.23	0.043511	0.000170
M11-514-449.65	6.85	Footwall and Main Zone transition	Ccp replacing Po	Ccp	-0.3	0.21	0.043494	0.000153

M11-514-449.65	6.85	Footwall and Main Zone transition	Intergrown with hydrous minerals	Ccp	1.6	0.20	0.043575	0.000128
MSH54-2	N.D.**	W Horizon	Intergrown with hydrous minerals	Ccp	-0.7	0.20	0.043475	0.000149
MSH54-2	N.D.**	W Horizon	Ccp replacing Po	Ccp	0.7	0.18	0.043536	0.000136
MSH54-2	N.D.**	W Horizon	Magmatic equilibrium	Ccp	-1.1	0.17	0.043458	0.000127
MSH54-2	N.D.**	W Horizon	Magmatic equilibrium	Ccp	-1.5	0.19	0.043442	0.000143
MSH54-2	N.D.**	W Horizon	Intergrown with hydrous minerals	Ccp	-1.0	0.18	0.043462	0.000134
59375	90.93	W Horizon	Magmatic equilibrium	Ccp	-0.4	0.23	0.043489	0.000174
59375	90.93	W Horizon	Magmatic equilibrium	Ccp	-0.5	0.14	0.043485	0.000107
59375	90.93	W Horizon	Magmatic equilibrium	Ccp	0.2	0.19	0.043515	0.000139
59375	90.93	W Horizon	Magmatic equilibrium	Ccp	0.8	0.18	0.043540	0.000133
M08-468-129.35	0.00	Footwall Archean metavolcanic-1	Magmatic equilibrium	Py ^{##}	-2.6	0.18	0.043365	0.000132
M08-468-129.35	0.00	Footwall Archean metavolcanic-1	Magmatic equilibrium	Py	-2.0	0.21	0.043388	0.000155
M08-468-129.35	0.00	Footwall Archean metavolcanic-1	Magmatic equilibrium	Py	-2.6	0.18	0.043362	0.000132
M08-437-171.71	0.00	Footwall Archean metavolcanic-2	Magmatic equilibrium	Py	4.7	0.18	0.043681	0.000134
M08-437-171.71	0.00	Footwall Archean metavolcanic-2	Magmatic equilibrium	Py	3.4	0.19	0.043623	0.000146
G11-3	37.81	Main Zone	Magmatic equilibrium	Py	1.4	0.19	0.043535	0.000137
G11-3	37.81	Main Zone	Magmatic equilibrium	Py	-0.5	0.16	0.043454	0.000115

*Ccp= chalcopyrite

#Po= pyrrhotite

**N.D.= not determined

##Py= pyrite

TABLE DR4. MULTIPLE SULFUR ISOTOPE DATA FROM THE MARATHON DEPOSIT BY IRMS

Samples	Zone	Mineral	Textures	Minimum distance from basal contact	$\delta^{33}\text{S}$ (‰)	$\delta^{34}\text{S}$ (‰)	$\delta^{36}\text{S}$ (‰)	$\Delta^{33}\text{S}$ (‰)	$\Delta^{36}\text{S}$ (‰)	Cu/Pd
M07-417-318.55	Footwall Zone	Po	Massive to semi-massive	0.00	0.06	1.9	4.45	-0.91	0.88	13351
M07-417-318.55	Footwall Zone	Ccp	Massive to semi-massive	0.00	0.16	2.0	4.64	-0.88	0.80	13351
59395b	Footwall Zone	Po [*]	Massive to semi-massive	0.17	0.27	2.2	5.15	-0.88	0.90	7474
59395b	Footwall Zone	Ccp [#]	Massive to semi-massive	0.17	-1.04	-0.5	-0.10	-0.76	0.92	7474
M11-514-450.43	Footwall and Main Zone transition	Po	Magmatic equilibrium	6.07	0.25	1.9	4.21	-0.71	0.66	10172
M11-514-483.64	Footwall and Main Zone transition	Po	Magmatic equilibrium	12.44	-0.13	1.4	3.44	-0.84	0.80	8301
M11-514-483.64	Footwall and Main Zone transition	Ccp	Magmatic equilibrium	12.44	0.00	1.6	3.89	-0.84	0.81	8301
G11-7I	Main Zone	Po	Ccp replacing Po	25.00	0.50	1.3	2.94	-0.19	0.39	1740
G11-7I	Main Zone	Ccp	Ccp replacing Po	25.00	0.52	1.4	2.87	-0.18	0.28	1740
59385	Main Zone	Ccp	Intergrown with hydrous minerals	40.98	0.37	1.2	2.51	-0.22	0.32	3984
Ma168	Main Zone	Po	Intergrown with hydrous minerals	68.00	0.74	1.5	2.98	-0.04	0.08	N.D.**
Ma168	Main Zone	Ccp	Intergrown with hydrous minerals	68.00	0.78	1.7	3.19	-0.07	0.06	N.D.**
M11-499-22.86	W Horizon	Ccp	Disseminated	60.00	0.51	1.0	1.72	0.00	-0.16	847
59415C	W Horizon	Ccp	Disseminated	70.00	0.23	0.6	1.11	-0.06	0.04	166

^{*}Po= pyrrhotite
[#]Ccp= chalcopyrite
^{**}N.D.= not determined