

The effect of organic ligands on the mobility of the PGE in soils and natural waters: Implications for exploration and the environment

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The PGE have become a potential environmental concern owing to attrition from catalytic converters and other industrial emissions. There is evidence that the PGE are both bioavailable and toxic. The degree to which the PGE are bioavailable and/or toxic depends to a large extent on their mobility in aqueous media. The degree of mobility of these elements also has implications for the use of geochemistry in the exploration for new PGE resources.

In most natural waters, the predominant inorganic PGE species are hydroxide complexes such as $\text{Pd}(\text{OH})_2^0$, yielding relatively low solubilities. Naturally occurring organic ligands such as simple carboxylate anions (e.g., acetate, oxalate, etc.) and humic and fulvic acids have been implicated in PGE mobility in the surface environment in many published field-based studies. We also suggest that siderophores (natural organic ligands secreted by microbes and plants to solubilize nutrient iron) may increase the mobility of PGE, based on published Linear Free Energy Relationships which indicate that siderophores may bind Pd as strongly as Fe. Solubility and spectroscopic investigations show that monocarboxylate anions such as acetate are not likely to increase significantly the mobility of PGE. However, dicarboxylate anions capable of bidentate chelation, such as oxalate, phthalate and salicylate, form much stronger complexes and can increase PGE solubility significantly. Amino acids have been shown to be important Pt species in seawater. Even more important in PGE mass transfer are multidentate ligands such as humic and fulvic acids. Experimental studies show that fulvic acid can increase the solubility of palladium hydroxide by orders of magnitude over a wide range of pH.

We have conducted solubility and spectroscopic studies on the interaction of two siderophores, desferrioxamine B (DFO-B) and ferrichrome, with Pd, Pt, Rh and Ir. These studies confirm strong complexation of PGE by siderophores, and show that there are significant differences in binding between different siderophores. Much more data are required to quantify fully the extent to which siderophores may increase PGE mobility in natural environments. However, they do indicate an important role for siderophores.

Effect of the trihydroxamate siderophores desferrioxamine-B and ferrichrome on the mobility of Pd, Pt, Rh and Ir

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Trihydroxamate siderophores are strong chelators for a variety of metals in near-neutral pH waters. We established that the solubility of amorphous $\text{Pd}(\text{OH})_2$ is greatly enhanced by the presence of desferrioxamine-B (DFO-B) at pH 8. Experiments involving the dissolution of metallic Pd, Pt, Rh and Ir in solutions containing DFO-B (106 to 2000 micromolal) or ferrichrome (68, 200 micromolal) at pH 8 and a ionic strength of 0.14 indicate that the dissolution rates of Pd, Pt and Rh increased with increasing DFO-B concentrations up to 300 micromolal, remained independent of DFO-B concentrations between 300 and 1000 micromolal for the first 4500 hours, and then were increased again for a DFO-B concentration of 2000 micromolal. Increased dissolution of Ir only took place in the presence of 2000 micromolal DFO-B. Equilibrium was not achieved even after 6245 hours of reaction. After this time, the Pd concentration in the 2000 micromolal DFO-B solution was 0.62 mg/kg H_2O (Pt 0.29 mg/kg H_2O , Rh 0.02 mg/kg H_2O). This value is 1.5 order of magnitude higher than that for the solubility of amorphous $\text{Pd}(\text{OH})_2$ in the absence of the siderophore. By comparison to $\text{Pd}(\text{OH})_2$, however, Pd metal dissolves between 2.5 (100 micromolal DFO-B) and 3.5 (1000 micromolal DFO-B) times more slowly. Before 4500 hours, no difference was observed in the rate of dissolution of the individual PGE between the 68 and 200 micromolal ferrichrome solutions. After this time, Pd dissolved slightly faster in the 68 micromolal than in the 200 micromolal ferrichrome solution. Pt and Rh showed similar dissolution rates between DFO-B and ferrichrome solutions, whereas the Pd concentration in the 200 micromolal ferrichrome solution attained a value 3.5 times more elevated than that in the 200 micromolal DFO-B solution after 6245 hours. Ferrichrome is much more effective in dissolving Ir than DFO-B. Whereas the Ir concentration after 3196 hours in the 200 micromolal DFO-B solution was only marginally above that in the solution without siderophore, its concentration was increased by a factor of six in the 200 micromolal ferrichrome solution. These results clearly indicate that siderophores may play an important role in the solution transport of anthropogenic or naturally occurring PGE in the environment.

Economic Pt and Pd in amagmatic settings?

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Experimental data on the solubility of Pt and Pd under various hydrothermal conditions suggest that transport and deposition of high levels of these elements could occur in several geological environments without the need for mafic magmatic fluids or heat.

In intracratonic rift environments, oxidized brines generated by surface evaporation and/or halite dissolution circulate to depth through a preponderance of oxidized lithologies and precipitate Pt and Pd in association with U and Au (unconformity-type U deposits) or Cu (sediment-hosted Cu deposits). Pt and Pd are likely to be transported as chloride complexes in such oxidised brines. The best known product of this process is the Coronation Hill deposit in Australia.

In deformed passive margin sequences rich in carbonaceous and pyritic metasedimentary rocks, hydrothermal fluids are most likely to be reduced and have elevated sulfur content. Under these conditions Pt and Pd would be transported as bisulfide complexes. Potentially economic levels of Pt and Pd have been reported in numerous orogenic gold deposits of the former Soviet Union (notably the Sukhoi Log deposit) and in sediment-hosted Ni and Mo deposits of southern China and north-western Canada.

Oxidized low-salinity waters in surface environments buffered by atmospheric oxygen could also lead to mobility of Pt and Pd as hydroxyl complexes. Anomalous but sub-economic levels of Pt and Pd have been reported in low-temperature hydrothermally altered rocks of the Semail ophiolite and in laterite developed on ophiolitic rocks.

These examples suggest that high grades of Pt and Pd occur in a wide range of deposit types, although there is clearly a problem in some cases with quality of analysis. A crucial question is whether there is the potential for both high grades and large tonnages of Pt and/or Pd-bearing ore in these settings. This question can be answered in part by routine analysis for Pt and Pd by exploration geologists and by further research into transport and depositional processes.

The hydrothermal Ni-Cu-PGE sulfide ore of the Fortaleza de Minas deposit, Brazil

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The hydrothermal Ni-Cu-PGE massive ore of the Fortaleza de Minas deposit

The Fortaleza de Minas Ni-Cu-PGE sulfide deposit is hosted by Archean komatiite rocks (Brenner et al., 1990) in the southwestern margin of São Francisco craton. The deposit contains 6 million tons at the average grade of 2.2%Ni, 0.4%Cu, 0.05%Co and 1.2ppm PGE+Au (Brenner et al., 1990) and comprises metamorphosed-magmatic and hydrothermal ore bodies. The former is cut by N-S and NE-trending late faults that host the hydrothermal ore. The hydrothermal ore is characterised by thin, discontinuous and irregular lenses and veins of massive sulfides hosted by serpentinite and talc schist (Almeida, 2003). It is composed mainly of pyrrhotite, pentlandite, chalcopyrite, magnetite and carbonates, with minor cobaltite-gersdorffite, sphalerite, ilmenite, serpentine and chlorite, and rare maucherite, tellurides (Pd-bearing melonite, tsumoite, tellurobismuthite and hessite) and PGM (omeiite, irarsite, testibiopalladite, Ni-bearing merenskyite and RuTeAs unknow phase). Late pyrite, chalcopyrite and carbonate fill fractures and violarite replaces sulfides. The PGM occur either included or associated with sulfides, silicates and oxides or filling fractures in pyrrhotite and chalcopyrite, indicating they started to precipitate with these minerals and continuous to precipitate after the sulfides were formed.

Geochemical Results And Interpretations

The hydrothermal ore grades are 290-2180ppb Pd, 69-1180ppb Pt, 113-282ppb Rh, 194-602ppb Ru, 156-447ppb Ir, 132-335ppb Os and 31-61ppb Au, being consistently higher than the metamorphosed, magmatic ore. In addition, the hydrothermal ore is strongly depleted in Cr when compared with the metamorphosed magmatic ore. The geological mineralogical and geochemical data suggest that the PGE were remobilized by carbonic-rich fluids and precipitated as tellurides and arsenides in the late faults.

References

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On the hydrothermal origin of platinum-group element deposits in layered intrusions

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There are a number of lines of evidence suggesting that volatile-rich magmatic fluids have played a dominant role in the petrogenesis of platinum-group element (PGE) deposits in layered intrusions. These include footwall sections that are unusually enriched in Cl in the higher grade deposits, potholes and other fluid-escape structures, pegmatoidal textures, relatively abundant hydrous minerals, and the ease by which sulphur can be moved in hydrothermal systems.

Models of a solidifying and degassing crystal pile illustrate how magmatic fluids can give rise to zones of PGE-enrichment in layered intrusions. Cooling through the base of a crystal + liquid column leads to solidification and eventual fluid saturation in interstitial silicate liquids. A zone of "cryptic" degassing (so named as evidence of a former fluid phases is preserved largely in compositional trends in minor element such as the halogens and S) migrates upward as volatiles degassed from underlying interstitial liquid enriches overlying, fluid-under-saturated interstitial liquids. Sulphur and sulphide is resorbed from the degassing regions and is re-precipitated in the vapor-undersaturated interstitial liquids, producing a zone of relatively high modal sulphide that also migrates upward with time. This sulphide-enriched front can mimic a conventional sulphide-in horizon and appear as the stratigraphic level at which the magma became S-saturated, but it is secondary and hydromagmatic in origin.

Owing to their strong preference for sulphide, the PGE are not significantly mobile until all sulphide is resorbed. In addition, fluid migration can result in significant chromatographic separations of ore elements. These stratigraphic "offsets" are characterized by a lower, typically S-poor, Pt- and Pd-enriched zone overlain by a zone enriched in the base metals, S and Au. The process can also produce high PGE/S ratios that mimic values conventionally interpreted as the result of high "R" values.

The fluid front and ore element transport may remain fully within the pile or it may reach the top of the pile where it can affect crystallization of the main magma body. For the former, metals may be trapped at compaction-induced porosity/composition discontinuities in the crystal pile (e.g., Great Dyke-type PGE deposits). The latter may result in significant degrees of incongruent melting of the solid assemblage due to volatile fluxing and form unconformity-type deposits (e.g., J-M Reef of the Stillwater Complex).

Tracing geochemical evolution of the Bushveld Complex with lead isotopes analyzed by LA-MC-ICP-MS

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A new investigation of Pb isotopic compositions of plagioclase and sulfide in the Bushveld Complex has been conducted to evaluate results of an earlier study, extend observations to the UG2 chromitite as well as Merensky reef, and characterize better the Pb components in the rocks. The PGE-rich UG2, like the Merensky reef, displays evidence of magmatic metasomatism and recrystallization. Analyses were obtained with the NuPlasma multicollector ICP-MS coupled with a NewWave DUV193 ArF Excimer laser. Helium was used as the carrier gas, spot sizes ranged from 80 to 150 μm and pulse rates 5 to 20 Hz, and isotopic fractionation was controlled by external normalization.

Most plagioclase and sulfide analyses fall on the $^{207}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ geochron of 2.06 Ga, which is the solidification age. This indicates that most measured ratios are equivalent to initial ones. Of the 28 samples studied, only two contain phases contaminated by young Pb. Plagioclase possesses a single composition, interpreted to represent that of the parent magma, of $^{208}\text{Pb}/^{204}\text{Pb} \approx 34.80$, $^{207}\text{Pb}/^{204}\text{Pb} \approx 15.25$, $^{206}\text{Pb}/^{204}\text{Pb} \approx 15.00$. The $^{238}\text{U}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{204}\text{Pb}$ ratios of the source were 9.2 and 38.3, respectively. Sulfide compositions are commonly different than that of plagioclase in the same thin section, confirming the original results of Mathez and Waight (2003) and their interpretation that material with a Pb isotopic composition different from that of the original magma was introduced into the rocks under conditions under which sulfide but not the plagioclase compositions could be modified. The sulfides contain Pb from two different, old sources. Some possess $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios distinctly lower than those of coexisting plagioclase. The Bushveld rocks are cut by a set of late magmatic veins, the plagioclase of which also displays anomalously low $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. Other sulfides contain Pb characterized by high $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, suggesting introduction of material from a Th-rich source substantially older than the Bushveld. The variability of Pb isotopes reflects a long and complex magmatic to subsolidus cooling history involving several episodes of melt/fluid infiltration.

Reference

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The roles of fluid in the genesis and modification of reef-type PGE deposits in large layered intrusions

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Several hypotheses have been proposed for the origin of reef-type PGE deposits in large layered intrusions. These include: (1) alloy or immiscible sulfide liquid segregation from magma and (2) concentration by magmatic fluid. Our results of textural, mineralogic and isotopic studies indicate that fluids played important roles in the genesis and modification of the reef-type PGE deposits.

The Merensky Reef of the Bushveld Complex is a good example where magmatic fluid played a major role in the development of the reef. Abundant composite mineral inclusions are found in many chromite crystals in the basal chromite seam of the reef. Phlogopite and orthopyroxene are most abundant in the inclusions. The average compositions of the inclusions are characterized by higher MgO, Na₂O and H₂O, and lower CaO and FeO than the parental magma of the Merensky Reef. The chemical compositions of the inclusions are consistent with melts formed by hydration melting of orthopyroxene cumulate on the floor of the chamber in response to addition of fluid. Sulfide saturation in the Merensky Reef may have been induced by addition of S from the fluid.

In the J-M reef of the Stillwater Complex, replacement of braggite by the mixture of Pt alloy and base metal sulfides is found in unaltered ore samples from the Stillwater Mine. This is direct evidence for desulfurization of Pt-Pd sulfides by S-undersaturated magmatic fluid.

In the PGE-rich Main Sulfide Zone of the Great Dyke the base metal sulfides are variably replaced by actinolite, epidote and carbonates. PGM mostly occur within base metal sulfides, and to a much less extent in their replacement aureoles.

Our observations suggest that primary concentration of PGE in the reefs resulted from fluid-induced sulfide saturation and segregation whereas decoupling of PGE at sample scale was due to subsequent hydrothermal modification.

Re/Os isotopic and fluid inclusion studies of fluid-rock interaction in the contact aureole of the Duluth Complex, Minnesota

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Re/Os isotopic data from igneous rocks and massive sulfides from the Duluth Complex of Minnesota, along with sulfide-bearing Proterozoic (~1.85 Ga) country rocks of the Virginia Formation, indicate a complex history of assimilation and fluid-rock interaction. Sulfide-free troctolites plot along a chondritic 1.1 Ga reference isochron, and show little or no geochemical evidence for contamination by country rocks. Troctolites with disseminated sulfides and massive sulfides are variably anomalous with γ_{Os} (1.1 Ga) values from 3 to 1200.

Sulfide separates from metasedimentary country rocks located outside of the contact aureole have Os isotopic values that are distinct from whole rock and kerogen values. The shale/siltstone is only slightly recrystallized, yet Re/Os isotopic values of sedimentary sulfide minerals indicate mixing at the time of emplacement of the Duluth Complex, and plot along a 1.1 Ga chondritic reference isochron. Quartz veins and stringers occur along pyrite beds in the sedimentary country rocks, and contain up to 15% of pyrrhotite, and lesser amounts of chalcopyrite, cubanite, bornite, pentlandite, and sphalerite. This assemblage is very similar to that found in the magmatic sulfide mineralization of the Duluth Complex. Fluid inclusions found in the quartz veins homogenize at ~300° to 380°C, and with a minimum P correction suggest that a fluid of ~500°C reached the outer margins of the contact aureole along microfractures. Although the initial water content of the Duluth Complex magma is not considered to have been anomalous, water saturation would have been achieved in the melt interstitial to primocrystic olivine and plagioclase. The Re/Os isotopic characteristics of sedimentary sulfides in the country rocks are consistent with exchange and mixing between minerals and a Re-rich magmatic fluid characterized by a chondritic ¹⁸⁷Os/¹⁸⁸Os ratio. This fluid appears to have been derived from uncontaminated mafic magma, rather than the contaminated magma that produced sulfide-bearing troctolites.

Re/Os isotopic studies of oxide minerals in the Birch Lake PGE prospect, Duluth Complex, MN

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The Birch Lake platinum group element (PGE) prospect is located along the western edge of the South Kawishiwi Intrusion (SKI) of the 1.1 Ga Duluth Complex in northeastern Minnesota. Country rocks include the Proterozoic Biwabik Iron Formation (BIF) and Archean-aged, greenstone belt-related plutonic and volcanic rocks. In the Birch Lake area the SKI consists of a layered troctolitic series that contains layers of semi-massive to massive oxides, as well as distinct inclusions of the BIF. Strong serpentinization of the oxide-melatroctolite rocks in the area is also distinctive. Zones of enriched PGE concentrations that are associated with Cr-rich oxides were detected during early mineralogical evaluations. Based on these associations, a hypothesis emerged which related PGE enrichment to areas of BIF assimilation. Further mineralogical and isotopic studies of the oxide minerals from the SKI and the BIF have aided in evaluating this potential relationship.

Three samples of unmetamorphosed BIF have Re/Os isotopic values that fall along a chondritic 2.23 Ga reference isochron. The values suggest that seawater Os isotopic composition was controlled by either leaching of young oceanic crust, potentially in a back arc environment, or by input of hydrothermal fluids with a near chondritic isotopic ratio. One sample of BIF from the contact aureole falls near the 1.1 Ga reference isochron, suggesting exchange between magnetite and a Re-rich magmatic fluid at the time of emplacement of the Duluth Complex. Most samples of both BIF xenoliths and layered massive to semi-massive oxides in the troctolites plot above the isochron formed by the unmetamorphosed BIF samples at $^{187}\text{Re}/^{188}\text{Os}$ ratios less than 10. These values are suggestive of Re loss after a magma contamination event at 1.1 Ga. Oxygen and hydrogen isotopic values of serpentine suggest that the fluid involved in the serpentinization process was primarily of meteoric origin. Interaction with this fluid is thought to be responsible for the anomalously low Re/Os ratios of oxides in the metamorphosed BIF and melatroctolitic rocks in the Birch Lake area.

Reference

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PGE mobility and PGM crystallization under hydrothermal conditions

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PGE-bearing associations from non-conventional geological occurrences (Kupferschiefer type shales; black shales; porphyry copper ores; hydrothermal ores; metamorphosed sediment and sediment-volcanic depots, Cu-rich metamorphosed ores; metalliferous coals; U-ores and oth.) are discussed. The list of PGM from these associations includes about 20 species with Pd, Pt, Te, S, Se, As, Sb, Au as characteristic elements of composition: Pd-Pt sulfides, selenides, tellurides, (Pt,Fe), (Pd,Pt,Au), Pd- (Sb,As,Te,Sn) minerals etc. (Pashava J., Tarkian M., Jedwab J., Moralev G., Seredin V. and oth.).

These PGM are associated often with minerals characterized by layered structure, i.e. Fe-Mn oxides, hydroxides (goetite), "hybride" minerals (valleriite), clay minerals (halloisite, smectite), silicates (chlorite) etc. Tiny grains of PGM and "layered" mineral are closely intergrown forming specific aggregates. This is the reason of "strange" PGM compositions reported by some researchers.

According to the detail study PGM associated with clay minerals are presented by submicro- and nanoparticles often located on the surface or edges of layers. PGE are transported in nature by. PGM precipitation could be reasoned by the non-equilibrated charge of structure layer surface, and by the composition of solution determining the decomposition of PGM-bearing complexes. The information on the composition of mineral-forming solution/fluids could be obtained due to the analysis of mineral composition and mineral associations as shown on some examples.

The morphology of PGM particles obtained during the hydrothermal experiments is analysed. Generally they are presented by dendrites or rounded grains. Using this fact and taking into account the composition of various complexes the mechanism of PGM crystal growth is proposed and discussed using data on PGM from other geological occurrences.

A magmatic end-member fluid at Sudbury, Canada?

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Veins and patches of granophyre are common in the brecciated/partially-melted footwall, and igneous sublayer of the Sudbury Igneous Complex. Cross-cutting relationships demonstrate that the granophyre veins in the footwall post-date the impact event and formation of massive sulfide ore along the footwall contact of the Sudbury Igneous Complex (SIC), but crystallized *prior* to the emplacement of Cu-PGE-enriched sulfide veins in the footwall. The granophyre veins are comprised of a symplectic intergrowth of quartz + orthoclase ± hornblende and preserve a primary, high temperature fluid inclusion assemblage derived from entrapment of an exsolved fluid phase. Trace element composition and structural considerations do not support the granophyre veins as forming in-situ (e.g., by host-rock melting). Rather, the granophyre may represent a K-enriched residua which was mobilized during the late stages of crystallization of the SIC. Brine inclusions within the granophyre phase homogenize at $543 \pm 55^\circ\text{C}$ ($n=82$, 1σ), corresponding to a salinity of 66 ± 8 wt% NaCl eq.

Microanalytical data (by LA-ICP-MS) show that the highest temperature, highest salinity brine inclusions contain a Na-Fe-K-Ca-Cl-rich fluid (up to 28 wt% K). All other brine compositions identified in the footwall environment fall on a mixing line between the high-temperature, Na-Fe-K-rich end-member and regional saline groundwaters. The range in brine inclusion compositions observed at Sudbury requires up to 90% (by mass) groundwater in the mixture. Base and precious metals (Cu – up to 1 wt%, Pt, Bi, Ag all in the 1-10 ppm range) were only detected in brine inclusions from granophyres occurring in close proximity to, or overprinted (replaced) by massive sulfide veins; this, along with cross-cutting relationships suggest that brines were in contact with sulfide liquids prior to the final crystallization of the sulfides in the footwall ore zones. Late secondary inclusions contain a saline fluid that is comparable in composition to the primary brine but contains much lower overall concentrations of major and trace elements. The late fluid may represent a cooled, diluted form of the primary, high-temperature brine. Ore metals were lost from the brine prior to entrapment of the secondary inclusions as the metal contents of the secondary inclusions are unremarkable.

High resolution LA-ICP-MS analyses of PGMs and sulphides, Marathon Pd-Cu deposit, Ontario

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The Marathon platinum group element (PGE)-Cu deposit is hosted by the 1108 Ma Coldwell intrusive complex. Three styles of mineralization occur in the deposit: (1) massive to net-textured Fe-rich sulphides in a massive, fine-grained gabbro (the Basal Zone); (2) disseminated, Cu-rich sulphides within variably-textured (medium-grained to pegmatitic) gabbroic rocks (the Lower Zone); and (3) magnetite layers in layered olivine gabbro (the Upper Zone). PGE mineralization is Pd-rich and is principally associated with Cu-rich intervals in the Lower Zone, which generally occur several tens of metres stratigraphically above the sulphide-bearing, Basal Zone rocks. The magnetites of the Upper Zone also host Cu-PGE mineralization.

Magmatic and hydrothermal sulphide textures exist within the different mineralized zones. LA-ICP-MS analyses of sulphides and platinum group minerals (PGMs) demonstrate stratigraphic chemical and mineralogical zonation. Basal Zone sulphides are As-rich and PGMs are Pb-poor, varying from arsenides to bismuth-tellurides to antimonides. The Lower Zone has As-poor and Te-rich sulphides and PGMs of extreme chemical variability. Upper Zone sulphides are Pb-rich as are the PGMs which are As-poor bismuth-tellurides and more Au-rich than PGMs in the other zones.

Strong zonation and a wide variety of PGMs is not unusual for PGE-rich mineral districts but this usually relates to lateral changes in footwall compositions while at Marathon it occurs within a single stratigraphic section of a few hundred meters.