THE INFLUENCE OF MAGMATIC PROCESSES AND LATE-MAGMATIC
FLUID-SEGREGATION ON THE Cu-Ni-PGE MINERALIZATION OF THE
SOUTH KAWISHIWI INTRUSION (DULUTH COMPLEX, MINNESOTA)

SUMMARY OF PHD DISSERTATION

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2013

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The Duluth Complex is comparable to many of the Earth’s mineralized igneous complexes, both in its overall size and the amount of contained mineral resources. The Complex, being part of the 1.1 Ga old Midcontinent rift system, crosscut a wide array of Archean and Proterozoic footwall rocks and some of the intrusions developed large volumes of mineralized rocks with enrichments of Cu, Ni and precious metals (mostly Pd, Pt and Au) in the form of dominantly disseminated sulfide mineralization (Eckstrand & Hulbert, 2007; Miller et al., 2002 and references therein). Discovery and exploration of ore deposits in the Complex boosted geological mapping and the reconstruction of the rift-related volcanic-intrusive system, as a whole. Despite the extensive mapping data and petrological studies, however, some parts of the system is still not understood in detail and correlation of rock units and detailed mapping of many areas are required to understand such a complex system.

There is consensus about the overall magmatic origin of sulfide mineralization including the model of assimilation of footwall rocks that resulted in sulfide-saturation and immiscibility of a sulfide liquid from the mafic magmas. Sulfide droplets accumulated in the basal units of some of the intrusions forming disseminated and patchy sulfide mineralization (e.g. Ripley, 1986; Ripley & Al-Jassar, 1987; Lee & Ripley, 1995). Additionally to the magmatic origin several authors promoted the role of magmatic fluids in the distribution of ore metals. A wide set of evidence, including spatial association of platinum-group minerals (PGMs) with hydrothermal mineral assemblages (Mogessie et al., 1991; Mogessie & Stumpfl, 1992), stable isotope data (e.g. Ripley, 1990; Mogessie & Stumpfl, 1992; Ripley et al., 1993), fluid inclusion data (Pasteris et al., 1995) have been presented that support the role of hydrothermal fluids in metal transport in the deposits. The spatial extent of hydrothermal alteration and the exact properties of the responsible fluids were however by far not completely described by these studies.

The aims of present study were therefore multifaceted. First, a complex mineralogical-petrological study is presented on the South Filson Creek area within the South Kawishiwi Intrusion. In this area a unique type of sulfide occurrence was described from the otherwise barren units of the intrusion in an unusually high stratigraphic position (‘cloud-type mineralization’), well above the basal contact, where the more significant sulfide occurrences are found. The chapter’s results are strongly based on extensive fieldwork including geological mapping and mineralogical-petrological studies carried out on the collected rock samples. The questions to be answered included:

• What is the areal extent of the unusual ‘cloud-type’ mineralization in the area?
• What is the genetic relationship to the more voluminous basal mineralizations?
• What is the predominant process that was responsible for the occurrence of the disseminated sulfide mineralization in the area? Is the mineralization really structurally controlled?
• Were there hydrothermal processes that influenced the mineralogical-geochemical properties of the mineralized rocks? What was their extent in a spatial and genetic sense? Were they causative or overprinting processes?
• What do the results on the mapped area contribute to the overall understanding of the geology and dynamics of the intrusion?

Results from the South Filson Creek area served as a basis for a more detailed suite of studies of diamond drillhole samples from the basal units of the same intrusion. The significance of magmatic fluids is investigated in more detail by studying pegmatitic rocks and other rock types that carry the most information on the late fluid-history of the magma. Detailed petrographical and mineralogical studies of mineralized rocks, platinum-group minerals and apatite and fluid and melt inclusion studies aimed to answer the following questions:

• What features of the rocks reveal information on the primary magmatic fluids?
• What were the properties of the primary magmatic fluids exsolved from the mafic magma?
• Under what conditions did the primary magmatic fluids exsolve?
• Were the segregating fluids capable of metal-remobilization and transport?
• What are the signs of remobilization of metals from the magmatic mineralization? How significant are these processes?

APPLIED METHODS

Mapping of natural outcrops was carried out in the South Filson Creek area (approximately 4 square kilometers) at the scale of 1:2500 and 1:5000 in 2007. Several hundreds of outcrops of various sizes (1 meter to 150 meters in diameter) have been mapped and digitized in a GIS database. Outcrop data from previous research and exploration campaigns was also compiled and incorporated into the GIS database.

5 Drillholes have been logged in detail for the purpose of the study, with an additional 3 drillholes sampled and studied in less detail.

Whole rock chemical analysis of 71 samples from the South Filson Creek area for main and trace elements was carried out in the laboratory of ALS Minerals. Samples were analyzed for 23 base metals and trace elements using a four-acid-leach ICP-AES package, Pd, Pt, and Au were
analyzed by lead-collection fire-assay ICP-AES packages. Geochemical assays from the mineralized intercepts of the drillholes were released by Duluthmetals Ltd.

Standard, 30 μm thick, polished thin sections have been prepared from the rock samples and investigated in petrographic microscopes (86 thin sections from the South Filson Creek area and 120 thin sections from drillholes). Petrography was conducted on Olympus BX and Zeiss Axioplan series petrographic microscopes.

Microprobe analyses of minerals from the South Filson Creek samples were carried out on a JEOL Superprobe 8600 instrument by McSwiggen & Associates in Minneapolis (Minnesota, USA). Composition of minerals from drillcore samples has been determined on a Jeol JSM-6310 scanning electron microscope, equipped with an energy dispersive and one wavelength dispersive spectrometer at the Institute of Mineralogy and Petrology of the Karl-Franzens University, Graz, and on a Jeol JXA 8200 Superprobe, equipped with five wavelength dispersive spectrometers at the ‘Eugen F. Stumpfl Laboratory’ located at the University of Leoben.

Identification, petrography and qualitative compositional analyses of PGMs in all samples were carried out on an Amray-1830 IT-6 scanning electron microscope at the Institute of Geography and Earth Sciences at the Eötvös Loránd University and on the Jeol JSM-6310 scanning electron microscope at the Karl-Franzens University. PGM grains larger than ~4-5 μm in diameter were analyzed quantitatively with the Jeol JXA 8200 Superprobe in Leoben, Austria.

For fluid and melt inclusion petrography and microthermometry, doubly polished, 150 to 300 μm thick sections have been prepared. One fluid and melt inclusion-rich sample was studied by cathodoluminescent imaging in the scanning electron microscope in the Karl-Franzens University in Graz. Heating and freezing experiments on fluid inclusions have been carried out with a Linkam FTIR600 heating-cooling stage mounted on an Olympus BX51 polarization microscope at the Department of Mineralogy, Eötvös Loránd University, Budapest.

Melt inclusion microthermometry was carried out with a Linkam TS-1500 high-temperature heating stage. After determination of minimum homogenization temperatures for the melt inclusions, a furnace technique, using a Carl-Zeiss Jena high-temperature furnace, was applied to newly separated quartz grains containing melt inclusions to reproduce the original melt phase. After quenching the inclusions, the quartz grains have been polished until the quenched melt inclusions became exposed on the surface of grains. The composition of the quenched glass was analyzed with the Jeol JXA 8200 Superprobe in Leoben. Details of the method was published by Guzmics et al. (2012).

Raman-spectroscopy has been carried out on the fluid and melt inclusions on a Horiba Jobin-Yvon LabRAM HR800 instrument using a 532 nm (green) Nd:YAG frequency doubled DPSS
laser, at the Institute of Geography and Earth Sciences, Eötvös Loránd University, Budapest. 50x and 100x objectives were applied to focus the laser beam on the sample, 600 grooves/mm spectrograph grating was used with counting times between 10-120 seconds. A Linkam THMS600 heating-freezing stage was attached to the instrument in order to analyze fluid inclusions at various temperatures.

**SUMMARY AND THESES**

1. Detailed field mapping, mineralogical, petrographical and geochemical analyses have revealed the presence of two types of mineralization in the South Filson Creek area of the South Kawishiwi Intrusion. Magmatic mineralization, that have been the focus of previous work in the area (Kuhns et al. 1990), is both spatially and geochemically distinct from a hydrothermal mineralization type that has been first described as a result of present study.

2. Magmatic Cu-Ni-PGE sulfide mineralization occurs in the troctolitic rocks of the Layered Series in the South Filson Creek area. Sulfide minerals (chalcopyrite, cubanite, pyrrhotite and pentlandite) form disseminations or patches in irregular shaped zones 0.2-2 m in diameter in an area of about 0.5 km². These zones do not form layers or horizons and do not follow large-scale structural lineaments present in the area, thus the term ‘structurally controlled’ as used by previous researchers (Ripley, 1986; Kuhns et al. 1990) in the case of this type of mineralization is not confirmed. Mineralization is the product of magmatic sulfide immiscibility and the accumulation of sulfide droplets in the troctolitic melt in irregularly shaped zones.

3. Geochemical features of this primary magmatic mineralization are similar to the precious metal-rich composition of the ‘confined style’ (Peterson, 2002) basal mineralization of the intrusion. The broad span of Cu/Pd ratios and some of the extremely high calculated R-factors (sensu Campbell & Naldrett, 1979) favor a dynamic magmatic model, where the rocks of the troctolitic intrusion have been crystallized from multiple magma injections. Sulfide droplets were segregated from multiple batches of silicate magma with slightly different compositions, and while seated in a dynamic intrusive environment, had the possibility to react with subsequent magma pulses. This allowed further modification and upgrading of the precious metal-content of the sulfide phase. These findings confirm some of the earlier models of e.g. Lee & Ripley (1995) and Peterson (2002) who interpreted the intrusion as a whole to be the product of multiple magma input.

4. A distinct type of precious metal poor, copper-sulfide mineralization occurs in the Anorthositic Series rocks that form the hangingwall of the intrusion in the South Filson Creek area. This type
of mineralization shows obvious signs of hydrothermal origin. Locations of the sulfide-bearing hydrothermal alteration zones are related to brittle structures and abundant secondary hydrothermal alteration consisting of fibrous green amphiboles, chlorite, albite, carbonate, prehnite and pumpellyite in disseminated patches and thin veinlets. This hydrothermal mineralization of Anorthositic Series rocks displays only elevated copper-values and some silver anomalies with neither PGE nor significant Ni enrichment. This demonstrates that fluids responsible for this alteration event were not capable to mobilize and transport PGEs or base metals other than Cu. This type of alteration overprinted the magmatic mineralization in the Layered Series troctolitic rocks, too, resulting in slightly elevated Cu/Pd ratios compared to unaltered rock samples.

5. Cl-depletion trends within apatite from pegmatitic pockets of the area suggest that there was a potential for the exsolution of a Cl-bearing magmatic fluid during the crystallization of these pegmatites that might have led to the development of saline brines with the potential to remobilize PGEs. Accordingly, some of the platinum-group minerals (PGMs) appear in secondary textures, however this alteration event was probably very subtle and acted on a local scale in the South Filson Creek area.

6. Abundant pegmatitic and various fractionated felsic rocks are often associated with patchy to semi-massive sulfides (pyrrhotite to chalcopyrite-dominated). Primary fluid and silicate melt inclusions in these quartz-bearing rock types represent the earliest magmatic fluids that coexisted with the crystallizing silicate melt. Combined application of microthermometry and Raman spectroscopy proved to be an effective tool in the complete characterization of the entrapped fluid system in primary fluid inclusions. The combination of the two methods made possible the determination of bulk fluid composition, which is difficult to estimate precisely in CO$_2$-dominated, water-poor inclusions, where the aqueous phase is only present as a thin film on the inclusion walls on laboratory temperature (Dubessy et al. 1992; Berkesi et al. 2009). The primary magmatic fluid phase, entrapped by fluid inclusions contain about 95 mol% CO$_2$, 4.5 mol% H$_2$O, ~0.4 mol% CH$_4$ and trace amount of N$_2$. Calculation of Raman peak-area ratios of the primary fluid inclusions on different temperatures allowed the determination of the total homogenization temperatures ($T_{h_{tot}}$) of the fluid inclusions. The determination of the $T_{h_{tot}}$ of the primary fluid inclusions made it possible to calculate the appropriate isochores for the fluid inclusions.

7. The original composition of the melt that coexisted with CO$_2$-rich fluids was established by homogenization and quenching the silicate melt inclusions in the same quartz that bears the primary fluid inclusions. The entrapped melt is granitoid, peraluminous, devoid of mafic components such as Mg, Ca and Ti, poor in Sr, P, F, Ba and contains variable amounts of Cl
with values up to 0.3 wt%. This melt is likely the product of partial melting of the monzonitic footwall rocks due to the excess heat of the South Kawishiwi Intrusion.

8. The presence of CO₂-bearing vapor bubbles in the quenched silicate melt inclusions and petrographic evidence suggests that primary fluid and melt inclusions were entrapped coevally. Although the fluid likely originates from the mafic magma, the two phases coexisted in equilibrium as a heterogeneous system until the entrapment as coeval inclusion assemblages. Coexistence of the two inclusion types made it possible to calculate a minimum entrapment pressure for the inclusion assemblages (Roedder, 1984). The calculated entrapment pressure is ~1.7 kbar that corresponds to about 5.8 km formation depth, which correlates with reported values from the marginal, thinner parts of the Duluth Complex (Simmons et al. 1974, Labotka et al. 1981).

9. In the studied CO₂-rich fluid – silicate melt system, Cl behaved compatible to the melt phase rather than partitioning into the CO₂-predominated fluid, indicated by the high Cl-content of the silicate melt inclusions. CO₂-rich fluids that coexisted in equilibrium with the crystallizing magma increased the affinity of Cl to the silicate melt and may inhibited its exsolution until the latest stages of crystallization, thus increasing the potential to produce late-stage saline brines. The primary CO₂-rich fluid was probably only capable of the transport of Cu and not the PGEs, as exemplified by the intimate association of miarolitic cavities, chalcopyrite and CO₂-rich fluid inclusions in the gangue minerals around these cavities. These miarolitic cavities may represent the same primary magmatic fluids under a ductile environment that were later responsible for the Cu-rich hydrothermal mineralization of the Anorthositic Series rocks in the South Filson Creek Area along brittle structures.

10. Variations in the halogen-content of apatite from various rock types in drillcore made it possible to further trace the behavior of Cl in the crystallizing magmatic pile. Apatite becomes enriched in Cl in the pegmatitic pockets of the intrusion, compared to ‘regular’ troctolitic rocks. This trend implies that the Cl-contents of the silicate melt increases with progressive crystallization and thus apatite that crystallized in a closed system environment in equilibrium with the melt will have elevated Cl-contents. On the other hand, apatite is becoming gradually Cl-depleted in some fractionated melt pockets that intruded into and solidified in possibly structural zones. This indicates that, if suitable channels are available, Cl can be exsolved from the silicate melt, probably into an aqueous fluid phase that will migrate away from its source under open system conditions. This is, however, only possible after the primary CO₂-rich fluid is cleared from the system and is no longer in equilibrium with the silicate magma.
Petrography of PGMs has shown that, besides magmatic textures, apparently secondary generations of PGMs are present: these grains are in close association with chlorapatite in late-stage Cu-rich sulfide veinlets or fill microcracks that crosscut silicate minerals and are present in felsic pegmatites and granophyric patches, too. These observations coincide with the reconstructed fluid history and imply that exsolution of the later, Cl-bearing saline brines caused remobilization of PGEs from the magmatic mineralization in the South Kawishiwi Intrusion.

REFERENCES


Lee I, Ripley EM. Genesis of Cu-Ni sulfide mineralization in the South Kawishiwi intrusion, Spruce Road area, Duluth Complex, Minnesota. Canadian Mineralogist 1995; 33:723–43.

Mogessie A, Stumpfl EF, Weiblen PW. The role of fluids in the formation of platinum-group-minerals, Duluth Complex, Minnesota; Mineralogic, textural and chemical evidence. Economic Geology 1991; 86:1506-18.


Peterson DM. Variation in the Cu-Ni-PGE Mineralization in the South Kawishiwi Intrusion, Duluth Complex, Northeastern Minnesota. 9th International Platinum Symposium, Billings, Montana, USA, July 21-25. 2002.

Ripley EM. Origin and concentration mechanisms of copper and nickel in Duluth Complex sulfide zones—a dilemma. Economic Geology 1986; 81/4:974-78.


Roedder E. Fluid inclusions. Reviews in Mineralogy 12, Mineralogical Society of America, 1984; 644 p.


**PUBLICATIONS BY THE AUTHOR**

**Scientific papers**


Selected conference abstracts


Gál B, Molnár F, Mogessie A, Peterson DM. Segregation of magmatic fluids during the crystallization of the Cu-Ni-PGE-mineralized South Kawishiwi Intrusion of the Duluth Complex, Minnesota, USA – GSA Annual Meeting in Minneapolis, 2011

Gál B, Molnár F, Mogessie A, Peterson DM. Raman-spectroscopic investigations of fluid and melt inclusions from the South Kawishiwi Intrusion, Duluth Complex, Minnesota, U.S.A. – the role of gas rich late-magmatic hydrothermal fluids in the formation of Cu-Ni-PGE mineralization – European Current Research on Fluid Inclusions XXI., Leoben, Austria, 2011


Gál B, Molnár F, Peterson DM. Magmatic vs. hydrothermal processes in the South Filson Creek mineralization, South Kawishiwi Intrusion, Duluth Complex – Institute on Lake Superior Geology 55th Annual Meeting Proceedings, Vol. 55, 2009