

## 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

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The Duluth Complex is a set of intrusive series of rocks which are the products of the 1.1 Ga old Midcontinent Rift system of North America. One of the troctolitic intrusions that host the vast majority of unexploited Cu-Ni-PGE mineralization is the South Kawishiwi Intrusion. Mantle-derived troctolitic melts intruded from a deep-seated chamber system into their current position through a magmatic plumbing system. During their ascent, they had reacted with metasedimentary rocks and this process triggered sulphide saturation producing an immiscible sulphide melt phase (Miller et al., 2001).

During formation of the South Kawishiwi Intrusion, the intruding sulphide-laden melts subsequently reacted with granitoid footwall rocks as well, resulting in contamination with a felsic partial melt component (Molnár et al., 2010). Combined analysis of primary fluid and melt inclusions provides a strong tool to understand and evaluate different components of this late magmatic – early hydrothermal stage of the ore-bearing system.

In the present study, we have investigated mostly pegmatitic, quartz-rich, sulphide-bearing samples close to the basal contact of the intrusion. Macroscopic textures of the rock samples and micropetrographic features of coeval fluid and melt inclusions in quartz show that the crystallizing melts have exsolved a magmatic fluid phase. That fluid coexisted with the late stage silicate and sulphide melt phases. Negative crystal-shaped primary fluid inclusions usually form groups in the centre of quartz grains and are dominated by relatively low density, near critical CO<sub>2</sub> (Fig. 1.). Raman-spectrometry confirmed minor amounts of methane and N<sub>2</sub> inferred from the slight decrease of the triple point of the

inclusions (~-57.2 °C) compared to pure CO<sub>2</sub>. After heating and total homogenization of inclusions well above 300 °C, small amount of H<sub>2</sub>O was also detectable by Raman-microspectrometry.

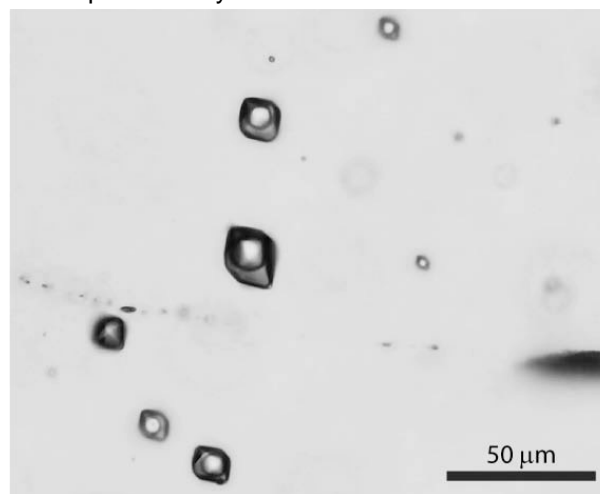


Fig. 1. Primary CO<sub>2</sub>-rich, CH<sub>4</sub>, H<sub>2</sub>O and N<sub>2</sub>-bearing fluid inclusions in quartz from a felsic rock sample close to the basal contact of the intrusion.

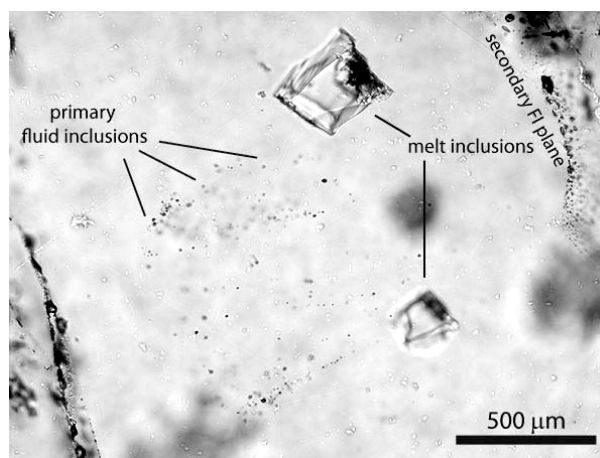


Fig. 2. Primary, coeval melt- and fluid inclusions rich in CO<sub>2</sub> in quartz from the same sample as Fig. 1.

Coeval melt inclusions in quartz appear to represent a fractionated silicate melt (Fig. 2). Daughter minerals in melt inclusions (identified by SEM and Raman investigations) are potassic feldspar, plagioclase, biotite, muscovite, apatite, calcite, and Zr- and REE-bearing phases.

Petrography of secondary fluid inclusion assemblages suggest that the primary fluids have evolved and separated to different components. One generation of later stage fluids played a role in local mobilization of metals because gas-rich, secondary fluid inclusions occur together with chalcopyrite in microcracks of pegmatitic quartz (Fig. 3). In these inclusions, gas phases identified by Raman-microspectroscopy were dominantly CH<sub>4</sub> with subordinate amounts of N<sub>2</sub> and H<sub>2</sub>O (latter was only detectable after heating the inclusions). CO<sub>2</sub> is absent from this generation of secondary inclusions.

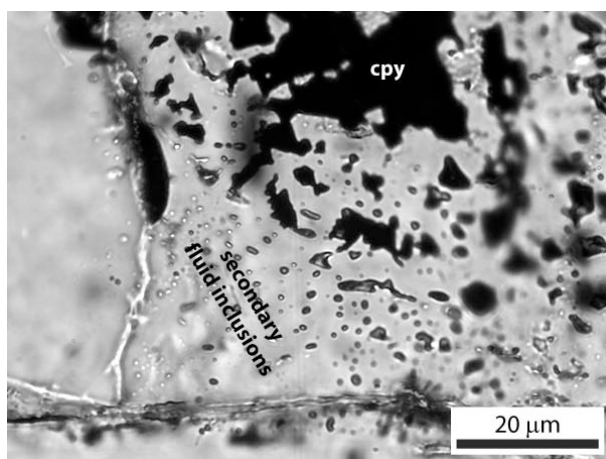


Fig. 3. Secondary vapour-rich fluid inclusions aligned along a healed microcrack partly filled by chalcopyrite in quartz

Felsic patches in the troctolitic rocks often exhibit miarolitic cavities which are filled by euhedral biotite, calcite, prehnite, chlorite and chalcopyrite. In the surroundings of these cavities occurrences of CO<sub>2</sub>-rich, methane-bearing fluid inclusions were detected in potassic feldspar. They likely represent a different stage in fluid evolution.

Inclusions type	Environment
I. Primary, CO <sub>2</sub> +CH <sub>4</sub> +N <sub>2</sub> +H <sub>2</sub> O	with melt inclusions, in qtz
II. Secondary, CH <sub>4</sub> +N <sub>2</sub> +H <sub>2</sub> O	along cpy-filled microcracks in qtz
III. Primary/secondary, CO <sub>2</sub> +CH <sub>4</sub>	associated with cpy- bearing miarolitic cavities in kspat

Table 1. Fluid inclusion generations that represent metal-mobilizing fluids from pegmatitic, quartz-rich samples.

Features listed above imply that gas-rich fluids, probably evolved from the segregated magmatic fluid component, had a potential in mobilizing metals, copper in particular (Table 1).

Presence of extremely Cl-rich apatite crystals ( $X^{Cl} > 0.8$ ) that crystallized in thin chalcopyrite and PGE-mineral bearing veinlets suggests that there was a potential of the development of a highly saline aqueous fluid as well which in turn was capable of PGE-transport in the form of chloro-complexes. Late-stage remobilization of PGEs is clearly implied by textures of platinum group minerals. The timing and the spatial variation of these processes are still under investigation.

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