# **Spatial and temporal relationship between intrusive rocks and gold mineralisation in the Miller Dyke Complex, Abitibi greenstone belt, Ontario, Canada**

by

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A thesis submitted in partial fulfilment

of the requirements for the degree of

Master of Science (MSc) in Geology

The Faculty of Graduate Studies

Laurentian University

Sudbury, Ontario, Canada

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#### **ABSTRACT**

The Miller Dyke Complex (MDC) is located 15 km south of the Kirkland Lake gold camp. It consists of a series of narrow, structurally controlled dykes, that range from felsic to mafic in composition, and are spatially associated with Au,  $\pm$  Cu,  $\pm$  Mo mineralisation. The MDC provides an excellent locality for a careful study of the igneous petrology and the different alteration assemblages associated with the mineralisation. The study is focused on the metasomatic processes related with alkali elements. It is shown that strong sodic alteration has a strong influence on the textural, mineralogical, and geochemical features of these rocks. Previously undescribed textures and mineralisation styles are documented, as well as the existence of a Paleoproterozoic hydrothermal reactivation event with metal deposition or remobilisation. The relationship between the alkali metasomatism and gold mineralisation is discussed within the regional context of the Abitibi greenstone belt.

**Keywords:** sodic alteration, alkali metasomatism, gold mineralisation, episyenite, quartz dissolution, hydrothermal alteration, Abitibi greenstone belt.

### <span id="page-3-0"></span>**THESIS STRUCTURE AND CO-AUTHORSHIP STATEMENT**

The thesis is written as a paper that, with modification of content and length, will be submitted to the journal Ore Geology Reviews, the candidate is the first author. This paper forms Chapter 1 of the thesis and it is co-authored with my supervisors H.L. Gibson and D.J. Kontak. The candidate performed the following tasks: geological mapping; core logging of 27 drill holes (5845.3 m); selection of samples for petrography, geochemistry, and geochronology; petrographic examination of thin-sections; SEM-EDS analysis and interpretation; geochemical data treatment and interpretation; construction of all the figures, diagrams, and tables in the thesis. The co-authors read drafts of this work, made edits, suggestions, and valuable intellectual contributions according to their experience. Although the co-authors provided advice and guidance, the candidate is responsible for all the conclusions and interpretations presented in this thesis.

### <span id="page-4-0"></span>**ACKNOWLEDGEMENTS**

I would like to express my gratitude to my supervisors Dr. Harold Gibson, and Dr. Daniel Kontak; their vast experience and input to this project made me a better researcher and definitely a much better writer. They also helped me to understand many things about the Archean environment, previously unknown to me. Many thanks to Dr. Pedro Jugo, part of my thesis committee, for his valuable contributions, opinions, and edits to the final manuscript.

My infinite appreciation to Talisker Exploration Services Inc. and its directors Ruben Padilla, Terry Harbort, and Chris Lodder for many years of lessons, trust, friendship, and the opportunity to explore in amazing places of the world.

Significant recognition to George Pollock, president of NorthStar Goldcorp, for allowing me to conduct this research at the Miller Property. Osisko Mining Inc., especially its Exploration VicePresident, Mr Gernot Wober, is thanked for providing the initial funding to support this project.

All my gratitude to my family, friends, and fellow graduate students at Laurentian University.

Finally, but especially, thanks to Marie for her continuous support and motivation; for her beautiful soul and smile; for being the extraordinary woman she is; and for giving me the fortune to share with her this adventure.

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<span id="page-10-0"></span>**CHAPTER 1. Textural, mineralogical, and geochemical changes associated with strong alkali metasomatism in Archean granitoids – an example from the Abitibi Greenstone Belt, Canada**

#### <span id="page-10-1"></span>**Abstract**

Sodium and potassium are some of the most abundant and mobile elements in the Earth´s crust, consequently, they are very active participants in the formation of alteration minerals in many hydrothermal systems. However, few studies are fully devoted to examining their behaviour, characteristics, and relationship with mineralisation within systems in the Abitibi. The Miller dyke complex (MDC) located south of the Kirkland Lake camp in the Archean Abitibi greenstone belt (AGB) is a suite of felsic dykes hosted by mafic - to intermediate metavolcanic rocks, with Au ± Cu ± Mo associated mineralisation. Given the unusual character and textures of some of the altered rocks and their rarity in the AGB, the MDC is used to investigate via an integrated petrological – geochemical – geochronological study, the nature of the intense alkali metasomatic processes associated with this mineralisation. The felsic intrusive rocks show strong textural modifications that include: 1) pervasive red staining due to extensive albitehematite alteration; 2) dissolution of magmatic quartz, biotite, and hornblende; 3) development of episyenitic textures; 4) dissolution of quartz veins; and 5) different episodes of brecciation. These textural and mineralogical changes are accompanied by significant geochemical variations, such as enrichment or depletion of major and trace elements due to alteration of primary minerals and precipitation of secondary phases such as albite, chlorite, zircon, titanite, and apatite among others. In situ U-Pb zircon geochronology yielded a 2662  $\pm$ 18 Ma age, which combined with the results of Re-Os geochronology (2680  $\pm$  8 Ma) suggests that the MDC dykes are part of the Timiskaming magmatic event. These ages define a very intimate link among alkaline magmatism, alkali metasomatism, and gold mineralisation, which has been previously recognised in the AGB but which is still not fully understood. The presence of 2069  $\pm$  6 Ma titanite crystals, within dissolution cavities indicates that the earlier Archean hydrothermal system was reactivated in the Paleoproterozoic with associated mineralisation and/or remobilisation of Au, Cu, and Mo, which occurs in close association with the titanite.

#### <span id="page-11-0"></span>**1. Introduction**

Sodic and potassic alteration are an integral part of many magmatic-hydrothermal systems including Cu-Au porphyry deposits (Carten 1986; Dilles et al. 2000; Sillitoe 2010); IOCG deposits (Oliver et al. 2004; Groves et al. 2010; Richards & Mumin 2013; Kontonikas-Charos et al. 2014); rare metal pegmatites (Kontak 2006; Gysi et al. 2016); carbonatites (Wooley 1982; Garson et al. 1984; Le Bas 2008), among others. The Na, Na-K, or Na-Ca alteration assemblages developed in these hydrothermal systems can be directly associated with mineralisation or just part of accessory, and generally barren alteration zones of these systems. Albitisation is the process of replacement of a primary mineral, generally K-feldspar or plagioclase by hydrothermal albite. The process has been experimentally reproduced and the details of the replacement mechanism are carefully described by several workers (Engvik et al. 2008; Putnis 2009; Hövelmann et al. 2010; Putnis & Austrheim 2010; and Norberg et al. 2014).

The Abitibi Greenstone Belt (AGB) is one of the best-studied and most metal-endowed greenstone belts in the world. Its mineral inventory includes ore deposits such as: Au-rich and base metal volcanogenic massive sulfides (VMS), Au only deposits including orogenic lode Au, banded iron formation (BIF) hosted Au, and intrusion-related Au, as well as magmatic Ni-Cu-PGE deposits. AGB gold deposits have produced more than 120 Moz Au, which was valued at approximately \$120 billion in 2005 (Thurston et al., 2008), in addition to significant reserves and resources. The upside exploration potential for this area is reflected in continued exploration and the opening of new mines in recent years across the entire belt (e.g., West Timmins, Canadian Malartic, Goldex, Detour Lake). Although the presence of sodic metasomatic rocks is widely recognised in the gold-rich Archean Abitibi Greenstone Belt (AGB), Canada, there are no studies devoted to fully investigate their textural, mineralogical, and geochemical characteristics or their relationship with Au mineralisation.

Episyenites (Lacroix, 1920) are rocks characterised by hydrothermal leaching of quartz, generally accompanied by precipitation of alkali feldspars. The latter process produces rocks that may be albitites. Episyenites are rare and have only been reported from two locations in the AGB: the Côté Gold deposit (Katz, 2016) in the Swayze greenstone belt, where they are part

of the sodic alteration assemblage, but do not have any direct relationship with the Au mineralisation; and the Taschereau-Launay plutonic complex (Jebrak & Doucet, 2002), located north of Val d´Or where they host disseminated Au-Mo mineralisation. Albitites on the other hand, are relatively common and have been reported in several deposits in the AGB (Burrows, 1993; Morasse et al. 1995). It is our contention that episyenites in the AGB have been misinterpreted or overlooked and that they are more common than currently assumed. The present study started with the discovery of extensive zones of episyenite within a felsic dyke complex associated with gold mineralisation near Kirkland Lake, Ontario, Canada during an exploration program in 2015. Here we present a detailed description of the textural, mineralogical, and geochemical characteristics of the episyenites, and discuss their formation in context of the regional setting, their potential as host rock for mineralisation, and their ability to record multiple generations of hydrothermal events. The study is based on field mapping, and core logging with supporting lithogeochemistry, extensive petrographic work with complementary imaging and analysis using scanning electron microscopy. In addition, in situ U– Pb dating of magmatic zircon, in situ U-Pb dating of hydrothermal titanite, and Re-Os dating of molybdenite are used to constrain the timing of relevant geological events.

#### <span id="page-12-0"></span>**2. Regional and Local Geological Setting**

The Archean AGB (Fig 1) is an 800 by 300 km east-west trending package of volcanic and sedimentary rocks that extends from Wawa, Ontario in its southwest extreme to the Val d´Or and Chibougamau areas of Quebec in its southeast and northeast terminations, respectively (Jackson & Fyon, 1991). The volcanic and sedimentary units of the AGB range from 2798 Ma to approximately 2670 Ma, which Ayer et al. (2005) divided into eleven assemblages based on lithological, geochemical, and geochronological features. These assemblages are separated by depositional gaps or disconformities, as defined and discussed by Thurston et al. (2008). A broad spectrum of intrusions of variable compositions, from dioritic to syenitic, crosscut the aforementioned volcano-sedimentary assemblages. Beakhouse (2011) classified these intrusions into four groups, according to their relative time of emplacement and relationship with the regional deformation events. The oldest intrusions (i.e., ca. ≈2747 Ma to ≈2680 Ma),

referred to as pre-tectonic or syn-volcanic, are characterised by their large-batholitic size and predominantly high-Al TTG geochemical signatures; examples of this group are the Round Lake, Kenogamissi, and Lake Abitibi batholiths, among others. The second group of plutons (i.e., ca. ≈2693 Ma to ≈2685 Ma), referred to early-syntectonic, is dominated by feldspar and quartzfeldspar porphyries. These are especially abundant along the major structural breaks, such as the Porcupine-Destor fault zone (PDFZ) near Timmins. The next group at (i.e., ca. ≈2686 Ma to ≈2676 Ma) include syntectonic granodioritic and lesser quartz-monzodioritic intrusions that were emplaced synchronously with the first regional deformation event, preferentially within the central part of the AGB. Finally, the late-tectonic plutons emplaced between ≈2680 and ≈2668 Ma are characterised by their alkaline affinity (i.e., syenitic), and their common spatial association with major regional faults, Timiskaming type sedimentary rocks, and Au mineralisation (e.g., syenite associated deposits; Robert, 2001).

Some of the most important gold mining camps in the AGB are located along major structural breaks, especially the PDFZ and the Cadillac-Larder Lake fault zone (CLLFZ). The area of this study is located 15 km south of the Kirkland-Lake camp (Fig 2), on the common border of the Boston, McElroy, Pacaud, and Catharine townships. The most comprehensive geological study of this area was presented by Jackson (1994), who described the stratigraphy in this area as comprising three different metavolcanic units; the nomenclature of these units was subsequently redefined by Ayer et al. (2005) for the Ontario side versus the Quebec side of the AGB. Table 1 shows the equivalence between the units proposed by Jackson (1994) and those from Ayer et al. (2005) for the study area.

**Table 1**. Comparison of stratigraphic nomenclature for the study area from Jackson (1994) and Ayer et al. (2005)





The larger study area is underlain by mafic to intermediate metavolcanic rocks that range in age from 2742  $\pm$  2 Ma in the southwest part to 2711  $\pm$  4 Ma to the north. The volcanic sequence strikes NW and dips sub-vertically to the NE with progressive younger ages in that direction. Several large granitoid bodies intrude the volcanic sequence.

The Round Lake batholith (RLB) outcrops 3 km south-west of the study area (Fig 2). The RLB is a large multiphase pluton, containing tonalitic to granodioritic phases, which is foliated along its margins. The RLB is described by LaFleur (1986) and Beakhouse (2011) and ages as old as 2743 ± 1 Ma are reported (Ketchum et al. 2008). However, the north-east margin of the RLB, which falls within the study area, has an age of  $2697 \pm 4$  Ma (Ketchum et al. 2008). Late-tectonic, alkaline plutons outcrop 4 to 6 km north-east of the study area; they are primarily syenitic, although they may include mafic and ultramafic alkaline phases. This alkaline plutons include the Otto, Lebel, and McElroy stocks (Fig 2), and ages for these plutons range from  $2680 \pm 1$  Ma for the Otto stock to 2673  $\pm$  2 Ma for the Lebel stock (Ayer et al. 2000), which agree with the age of regional alkaline magmatism and the Timiskaming sediments in the AGB (Beakhouse, 2011).

Within the detailed study area of Fig., a series of north-west striking dykes intrude the mafic and intermediate metavolcanic rocks of the Stoughton – Roquemaure and Upper Blake River assemblages. For simplicity, this group of dykes is referred to herein as the Miller Dyke Complex (MDC). The MDC is characterised by four intrusive phases, with textures and modal compositions that include equigranular quartz-monzodiorites to tonalites; porphyritic tonalites to granodiorites; fine-grained aplitic dykes, and mafic dykes. The MDC comprises three intrusive centres located approximately 500 m apart, as well as smaller isolated dykes. From south to north, the intrusive centres are referred to as the Allied zone, Planet zone, and Meilleur zone (Fig 3). Although different intrusive phases are present in each one of these zones, the contacts between them are not clear or mappable due to their small size and scarcity of outcrops.

### <span id="page-15-0"></span>**3. Methods**

### <span id="page-15-1"></span>**3.1 Fieldwork and Sampling**

Mapping conducted in 2015 by Oban Mining Corporation was reviewed by the author and modified where necessary (Fig 3). In this study, field work focused on detailed lithological and alteration re-logging of 15 drill holes drilled in 2014 by Northstar Gold Corp, and 12 drill holes drilled in 2015 by Oban Mining Corp (now Osisko Mining Inc.), for a total of 5845.3 m of core.

#### <span id="page-15-2"></span>**3.2 Petrography**

Seventy-two samples, mainly from drill core were collected for petrographic examination. Samples were selected to be representative of the spectrum of textural and compositional variations of the dykes, the different alteration assemblages, and the different mineralisation styles. Polished thin-sections were prepared and examined using an optical microscope in both reflected and transmission modes.

#### <span id="page-15-3"></span>**3.3 Scanning electron microscope (SEM) energy dispersive spectroscopy (EDS)**

The SEM analyses focused on the identification of alteration mineralogy and assessment of textural features. Of the seventy-two polished thin sections, a subset of twenty-three representative samples was examined using a JEOL6400 scanning electron microscope-energy dispersive spectrometry (SEM-EDS) in the Central Analytical Facility (CAF) at Laurentian University. The data were collected using an accelerating voltage of 20 kV, beam current of 1 nA and collection time of 5 seconds for spot analysis, although longer times were used for X-ray mapping. The data were processed using the INCA software package from Oxford Instruments.

#### <span id="page-15-4"></span>**3.4 Geochemistry**

Twenty-one samples were collected from drill core and outcrops for whole-rock geochemistry and were included as part of the petrographic study referred to above. The samples were prepared at ALS Laboratories in Sudbury, Ontario by crushing until 70% < 2 mm; splitting off 250 g; and pulverizing the split until 85% < 75 microns. Then the samples were analysed at ALS Burnaby, BC according to the procedures described in Table 2 (ALS, 2016).

**Table 2**. Summary of analytical methods used for lithogeochemical analysis of rock samples.



The lithogeochemical samples were selected to characterise the different intrusive phases, alteration types, and to evaluate element mobility during alkali metasomatic processes. Assay results from the 2014 and 2015 drilling campaigns were provided by Northstar Gold Corp and Oban Mining Corp (now Osisko Mining Inc). The assay data were used to characteristize the

different styles of mineralisation, but are not included within the thesis as the data is confidential. All the data were reviewed, processed, and analysed using ioGAS® software version 6.2.1.

### <span id="page-17-0"></span>**3.5 Geochronology**

Samples were collected to determine the age of emplacement of the dykes, to constrain the age of the main sodic alteration episodes, and to constrain the timing of Au mineralisation. A sample of a weakly altered equigranular intrusive (MI-PL-DAT-01), collected from an outcrop at the Planet zone, was submitted to the GeoAnalytical Lab at Washington State University for in situ U-Pb zircon geochronology; the complete analytical details are provided in Chang et al (2006). Additionally, a polished thin section was sent to the LA-ICP-MS facility at the University of New Brunswick for in situ U-Pb age determination of hydrothermal titanite grains with the complete analytical details described in McFarlane & Luo (2012). Lastly, three samples of molybdenite from veins and breccias, collected from the three different zones of the project (Allied, Planet, and Meilleur) were sent to the crustal geochronology laboratory at the University of Alberta for Re-Os geochronology with the detailed analytical procedures provided in Selby & Creaser (2004). Detailed results are provided in Appendix 3 and a summary for each method is presented below within the results section.

### <span id="page-17-1"></span>**4. Results**

#### <span id="page-17-2"></span>**4.1 Geology of the Miller Dyke Complex**

The MDC shown in Figure 3 (Allied, Meilleur, and Planet intrusions), as well as smaller isolated dykes, occur along fault zones associated with the Catharine Fault system (Fig 2), which extends for at least 10 km. The Allied and Planet intrusions are hosted by a mafic metavolcanic unit, consisting of y massive, aphanitic basalt with lesser pillow and variolitic flows; whereas the Meilleur intrusion is hosted by intermediate volcanic rocks that are typically porphyritic and have an andesitic composition. The alteration in both volcanic units is mainly chlorite,

carbonate, epidote, actinolite, with minor sericite zones in the andesitic unit (the latter only observed in drill core). Multiple gold occurrences occur within and around the intrusions, where they are associated with small shear or fracture zones hosting centimetre-scale quartz veins with tourmaline and pyrite. Some of these occurrences were extensively trenched or pitted and they constitute most of the surface gold anomalies shown in Figure 3. Fracturing and quartz veining associated with mineralisation typically has a NW strike, similar to the dykes and the regional orientation of the Catharine Fault zone. Despite the number of gold anomalies, no wide or well-defined veins were observed during mapping or in drill core; most of the quartz veins hosted by the MDC dykes are centimetre-scale, strike NW and dip shallowly to the NE or SW.

The dyke complex is multiphase, and displays both textural and compositional variations. Mineralisation is hosted within the dykes and their adjacent wall rocks; the different styles are described below.

#### <span id="page-18-0"></span>**4.2 Petrology of the Dyke Rocks**

Four intrusive phases have been recognised at the MDC (Fig 4). There are three felsic intrusive phases. The first and volumetrically most significant is equigranular, medium-grained, and mainly composed by euhedral to subhedral crystals of plagioclase ( $\approx$ 70 – 85 %), K-feldspar (15 – 20 %), quartz (5–15 %), hornblende and/or biotite (0 – 10 % combined) (Fig 4A); the feldspars are generally red in hand sample and cloudy in thin section, affected by sericite alteration and exhibiting polysynthetic, tartan and minor chessboard twinning. Biotite and hornblende are the only mafic minerals present, both always chloritised. Accessory phases include magnetite, zircon, apatite, and titanite. The second phase is medium to coarse-grained porphyritic (Fig 4B), showing euhedral to subhedral phenocrysts (60 – 70 %) of plagioclase and K-feldspar; the groundmass (30 – 40 %), contains feldspar, quartz, and accessory zircon, titanite, and apatite. Mafic minerals are uncommon but fine-grained phenocrysts of chloritised hornblende are recognised. The third felsic intrusive phase is represented by fine-grained aplitic dykes, with granular or saccharoidal texture, comprised of feldspar and quartz in similar proportions; with no mafic minerals present. A common characteristic of the three felsic phases is a red-brick to

pink colour (Fig 4A, B, C), which is variable in the equigranular and porphyritic phases and generally more intense in the aplitic phase.

The only mafic phase present is sparse, and it is fine-grained porphyritic; characterised by euhedral plagioclase and amphibole phenocrysts in a very fine-grained groundmass where only feldspars are identified. In terms of temporal relationships among the three felsic phases, the porphyritic phase crosscuts the equigranular phase and it is cut by the aplitic phase. No direct crosscutting relationship was observed between the mafic dykes and any of the felsic phases; it was only observed within the metavolcanic host rocks.

Modal compositions for the felsic dykes include quartz monzodiorite, monzodiorite, quartz diorite, and tonalite, (Fig 4). These modal classifications are based on weakly to moderately altered samples, whose texture and composition have not been completely modified by hydrothermal alteration and are assumed to reflect the original mineralogy. Textural, chemical, and mineralogical variations from this baseline are considered in further sections below. Based on twinning, plagioclase feldspar with polysynthetic twinning is more abundant than K-Feldspar with tartan twinning; hydrothermal albite characterised by chessboard twinning is also observed. SEM – EDS analyses of feldspars indicate that most of the plagioclase is end member albite  $Ab<sub>100</sub>$ . Compositions of feldspars from five least altered equigranular and porphyritic felsic dyke samples were estimated to determine the magmatic composition of the feldspar before alteration; these compositions are summarised in Figure 5. Least altered samples were selected based on the degree of textural preservation, as well as the presence of magmatic mafic minerals (hornblende, biotite), and primary K-feldspar and quartz. Point analyses for the feldspar grains indicate that remnants of calcium are present in only a few of the least altered plagioclase grains where compositions indicate oligoclase  $(An_{30-10})$ . The most calcic composition is An $_{66}$  (sample MI-PL-PET-02). A summary of the characteristics of the described intrusive phases is presented in Table 3.

**Table 3**. Summary of characteristics of the different intrusive phases observed at the MDC



### <span id="page-20-0"></span>**4.3 Mineralisation**

Three mineralisation styles were observed, and features which typify them are summarised in Table 4, including geochemical characteristics from multi-element assays. These styles are described in sequence and then their timing relationships are described.

### <span id="page-20-1"></span>*4.3.1 Quartz vein mineralisation*

The most important Au mineralisation style is represented by quartz veins, mainly hosted within the felsic dykes, although locally present in the volcanic wall-rocks. The veins are generally poor in sulfides, with <2% total pyrite, trace tellurides and bismuth minerals. Visible gold (VG) presence is sporadic and fine-grained (<500µm). Carbonate and tourmaline are locally present as accessory minerals within the veins. The veins are commonly 1-5 cm wide, flat, planar, and oriented subparallel (i.e., sheeted) rather than as stockwork zones (Fig 6A to F). Vein density ranges from 1-2 veins/m up to >20 veins/m. Zones of Au-bearing veins are intersected over 100 m wide intervals in drilling, and they represent the main exploration target for bulk mineralisation. Au assays range from a few hundred parts per billion (ppb) to several parts per million (ppm) ( $\approx$ 100 ppb Au to 1-2 ppm Au) for 1m average core samples.

### <span id="page-20-2"></span>*4.3.2 Contact hosted mineralisation*

The second style of mineralisation occurs at the contact between felsic dykes and mafic metavolcanic rocks. The contact zones are commonly intensely fractured for several meters perpendicular to the contact, and altered to a fine-grained assemblage of carbonate, albite, chlorite, pyrite and trace chalcopyrite (Fig 7A, B, C, D). Pyrite, up to 10% by volume, occurs as subhedral crystals with fine inclusions of rutile, apatite, xenotime, and chalcopyrite. Anhedral chalcopyrite was observed filling fractures and interstitial to silicate minerals. Although gold grades associated with this style are generally > 1ppm and occasionally > 10ppm Au, gold was not observed during SEM imaging. This style of mineralisation records the highest-grade intersections and represents an important exploration target.

### <span id="page-21-0"></span>*4.3.3 Disseminated and patchy mineralisation*

The third and least economically significant mineralisation style is represented by disseminated and patchy sulfides, principally pyrite, chalcopyrite, and molybdenite, that are randomly distributed within cavities in the sodic altered rocks (Fig 8D, E, F), or along the margins of some irregular, discontinuous and truncated quartz - chlorite veins (Fig 8A, B, C). Erratic gold values (e.g., from <0.1 ppm to 2.4 ppm) are associated with this style, but anomalous Cu (500 ppm – 3.5 %) and Mo (50 ppm – 5900 ppm) values are characteristic. Chalcopyrite was also observed in microfractures within titanite crystals in cavities.

The timing relationships among these three mineralisation styles are not clearly defined. The quartz vein mineralisation crosscuts all the intrusive phases, except the mafic dyke rocks. The disseminated and patchy Cu-Mo ± Au mineralisation is interpreted to postdate the quartz vein mineralisation because it occurs within the margins of, and in fractures that cut irregular quartz veins, as well as lining cavities in episyenites. The timing relationship between the contact hosted mineralisation and other styles of mineralisation styles is unknown.

**Table 4**. Summary of mineralisation styles present at the Miller Dyke Complex.





### <span id="page-22-0"></span>**4.4 Alteration**

Albite is the most abundant and important alteration mineral present at the MDC. It is the focus of this project; its characteristics and relationship with mineralisation are described and discussed in the following sections.

### <span id="page-22-1"></span>*4.4.1 Albite Alteration*

Albite alteration has been classified into three groups based on their distribution and relative timing. These three groups are explained below.

### <span id="page-22-2"></span>*4.4.1.1 Albite Alteration 1*

Albite alteration 1 is manifest as albite-pyrite envelopes mantling Au-bearing quartz veins that cross-cut felsic dyke rocks. The albite-pyrite alteration grades outward to chlorite-calcite-pyrite and then to distal calcite-chlorite (Fig 9A, B, C). However, not all Au-bearing quartz veins have this sequence of alteration uniformly developed, and in some cases, one or more of the envelope zones can be absent. The albite-pyrite envelopes range from mm to cm in width and increase with increasing vein width. Albite-pyrite alteration zones range in colour from very intense red to white, with pink being the most common colour (Fig 9D, E); pyrite is generally <1%. Two textural varieties of albite are observed: 1) large albite crystals or crystals aggregates that range between 400 µm and 1mm, often with chessboard twinning and irregular, "corroded" borders (Fig 9F); and 2) aggregates or masses of very fine-grained, anhedral albite

where singular grains are smaller than 50 µm; this type occurs in open spaces or embayments on vein margins (Fig 9F).

### <span id="page-23-0"></span>*4.4.1.2 Albite Alteration 2*

Albite alteration 2 is pervasive and affects most of the dykes at the MDC. Characteristic of this alteration is the replacement of primary plagioclase and K-Feldspar by albite (Ab<sub>100</sub>). The albitisation preserves the original euhedral to subhedral shapes of the feldspar crystals. Finegrained inclusions of sericite are abundant in albite grains, and their abundance correlates with a reddish to pink colour of the rocks (Fig 10A, B), and creates a dark-brown, rusty appearance on the crystals when observed in thin section (Fig 10E, F). Another characteristic of this alteration is the development of microporosity (Fig 10D) that ranges from  $<$ 1  $\mu$ m to  $\sim$ 50  $\mu$ m within the  $Ab_{100}$  grains. Some dykes, generally those located towards the edge of the Allied zone in the mineralised area, have a dark-grey colour rather than red (Fig 10C); however, SEM-EDS analyses indicate that in these rocks the feldspars are still predominantly albite in composition.

Albite 2 alteration is occasionally manifest by the presence of macroscopic pores or cavities in the new hydrothermal albite. The size of the pores ranges from hundreds of microns to several millimetres and their shapes can be sub-rounded to angular. The percentage of these cavities is variable, ranging from 1% up to 30%, and they impart a strong vuggy texture to the rock. (Fig 11A, B). The presence of these cavities coincides with a depletion of quartz and mafic minerals; however, the primary porphyritic or equigranular textures of these rocks are still recognised. In hand sample, the zones of Albite 2 with this texture vary in colour from very light pink to dark reddish, and the cavities are partially coated by fine pink to translucent albite (Ab<sub>100</sub>) and locally K-feldspar (Fig 11C). These pores are either completely or partially filled by different minerals including chlorite, epidote, titanite, apatite, zircon, pyrite, chalcopyrite, and molybdenite (Fig 11D, E and Fig 12A to F). After fine albite, chlorite is by far the most abundant alteration mineral within the cavities. It is fine-grained, ranging from massive to vermicular. Titanite is also very common; it is intensely fractured and generally euhedral to subhedral and up to 3 mm in size. Epidote and apatite, both as subhedral to euhedral crystals, are less common. Pyrite is the

most ubiquitous sulfide and displays variations in size (<50µm to 1 mm) and shape (subhedral to euhedral). Chalcopyrite and molybdenite are common and typically occupy the central part of the cavities (Fig 8E, F). Chalcopyrite is also present along fractures in pyrite or titanite crystals.

### <span id="page-24-0"></span>*4.4.1.3 Albite Alteration 3*

Albite alteration 3 occurs in metavolcanic rocks adjacent to the felsic dykes. In hand sample (Fig 13A), this alteration has a brown-beige colour. Its consists on a fine-grained mineralogical assemblage only identifiable using the SEM-EDS (Fig 13B), which includes an assemblage of albite-calcite-chlorite-pyrite ± chalcopyrite. This alteration only occurs in highly fractured metavolcanic rocks, where the intrusions exhibit a high density of veins, or where there are numerous dykes close to the contact. This albite alteration is associated with Au grades > 1ppm, and often >10 ppm, forming drill hole intersections up to 4m with 12 ppm. Despite the high grade of these contact zones, native gold was not observed in any of the samples examined either petrographically or with the SEM. Apatite and xenotime are common accessory minerals.

#### <span id="page-24-1"></span>*4.4.2 Skarn Alteration*

The presence of "skarn-like" alteration is restricted to metavolcanic rocks near the contact with the felsic intrusive phases. It is very common, although not volumetrically significant. It consists of cm-size patches and thin (1-3cm) veins of garnet – chlorite – calcite – epidote – pyrite  $\pm$ chalcopyrite  $\pm$  magnetite (Fig 14A, B). The skarn patches may be zoned or irregular. The alteration contains up to 15% pyrite with trace chalcopyrite but is typically barren of gold.

#### <span id="page-24-2"></span>*4.4.3 Chlorite – clay and quartz-hematite alterations*

Chlorite-clay (Fig 14C, D) or quartz-hematite (Fig 14E, F), present in small veins or breccia zones, crosscut all the previously described alteration types. The chlorite-clay association is more abundant, and it forms the matrix to cm to m-size breccia zones containing fragments of felsic intrusive or metavolcanic rocks, as well as vein fragments. Chalcopyrite is often present as a

cement around some of the broken vein fragments. As this alteration is not associated with gold mineralisation it is not described or discussed further.

The silica – hematite assemblage occurs as very thin stringers, and patches of fine grained reddish quartz, which resembles jasperoid, lining fractures in altered and broken core. These veins crosscut the chlorite-clay breccias, as well as the Au-bearing quartz veins. Sulfides are not associated with this assemblage. White to locally pink carbonate is present as calcite veins, dissemination and as a breccia matrix.

#### <span id="page-25-0"></span>**4.5 Geochemistry**

The major, trace, and rare earth (REE) data for 21 analysed samples of dykes are presented in Appendix 2 and a summary of the most relevant elements used in the presented diagrams is shown in Table 5. The data are discussed in the context of rock classification, major and trace element data, and mass balance in the following sections.

#### <span id="page-25-1"></span>*4.5.1 Rock classification*

The classification of the MDC dykes is challenging due to the mobility of major elements associated with feldspars but also trace elements contained in secondary phases developed within the cavities of some of the altered dykes.

Despite the expected mobility of Na and K,  $SiO<sub>2</sub>$  seems to be relatively stable (Fig 17), and the dykes can be grouped based on their silica content. The samples fall into three main groups, which correspond to their textural and petrographic characteristics; these are mafic dykes, felsic dykes (equigranular and porphyritic) and aplitic dykes. The rocks are classified according to their position in Zr/TiO<sub>2</sub> versus Nb/Y diagram. The two mafic dyke rocks analysed have SiO<sub>2</sub> values around 50 wt. % and plot in the andesite/basalt field of the  $Zr/TiO<sub>2</sub>$  versus Nb/Y diagram (Fig 15).

**Table 5**. Geochemical data used in figures beow. Major and trace element data analyized using ALS methods ME-ICP06 and ME-MS81, respectively, as described in Table 2.



The felsic dyke samples (n=16), which include porphyritic and equigranular dykes that are commonly associated with Au-Cu mineralisation have SiO<sub>2</sub> values between 65.2 and 72.4 wt. % and save for two samples plot in the trachyandesite field (Fig 15). The two remaining samples (MI-AL-LGC-15 and MI-AL-LGC-28) plot near the limit of comendite/pantellerite with trachyandesite (Fig 15). The latter sample has extremely low TiO<sub>2</sub> compared with the rest of the felsic dykes. The remaining three samples with the highest  $SiO<sub>2</sub>$  contents (75.7 to 78 wt. %) are representative of the aplite dykes. Two of these samples fall in the trachyte field, and one

sample (MI-AL-LGC-17) falls in the comendite/pantellerite field (Fig 15) due to its lower TiO<sub>2</sub> content.

#### <span id="page-27-0"></span>*4.5.2 Major element chemistry*

In terms of alkali (Na<sub>2</sub>O + K<sub>2</sub>O) contents, the mafic dykes have an average value of 2.2 wt. %, whereas aplites and felsic dykes have values ranging from 7.35 and 11.01 wt. %, including samples with values of up to 10.2 wt. % Na<sub>2</sub>O (sample MI-AL-LGC-28). The samples retain their three separate groupings and in the subalkaline field of Figure 16, except for three samples (MI-AL-LGC-11, 13, and 28) which have elevated alkali contents (>9 wt. %).

On Harker-type plots (Fig 17), the three lithological and geochemical groups clearly plot as different populations with defined elemental trends with respect to silica. The noted exceptions relate a few samples of felsic dyke rocks which show anomalous enrichment in Na<sub>2</sub>O (7.9 to 10.2 wt. %) with complementary depletion in  $K_2O$ . Not shown in the Harker diagrams are the LOI data (see Table 5), which ranges from 0.28 to 3.03 wt. %, but does not show any particular trend.

#### <span id="page-27-1"></span>*4.5.3 Trace element chemistry*

The three lithological and geochemical groups have distinct trace elements patterns, as illustrated in a primitive mantle (PM)- normalised spidergram (Fig 18) and chondrite-normalised REE diagram (Fig 19). The mafic dyke rocks are not shown in the trace element diagrams because they have a general flat pattern and are not associated with the sodic alteration process. In contrast, the felsic dyke rocks define a distinct field with enrichment in LILE and depletion in High Field Strength Elements (HFSE), (Fig 18). The felsic dykes display positive Ba and negative Th, Ta, Nb, P, and Ti anomalies. However, three felsic dyke samples (MI-AL-LGC-12, 13, 28) depart from the general pattern as they display relative depletion of the LILE Rb, Cs and Ba, and lesser so for U and K, and variable depletion for some of the HFSE (e.g., LREE), Sr and P.

Aplitic dyke samples are characterised by negative PM-normalised anomalies of Ba, Sr, P, Ti, Ta and Nb (Fig 18); sample 17 departs from the general behaviour of the aplites for some elements such as Sr, La, Tb, Y. The REE data normalised to CI chondrite (Fig 19) reflects the patterns noted in the PM spider diagram. The felsic intrusive dyke rocks show strongly fractionated patterns. The felsic dykes are characterised by: 1) High LREE (>100 times chondrite) and steep slopes with (La/Lu)<sub>N</sub> values up to and 47; 2) Insignificant Eu anomalies (Eu\* = 0.81 to 1.18). However, two of the samples (13 and 28) depart from the pattern and show depletion of LREE and in one case also the HREE. The aplitic dykes have U-shaped REE patterns and lack Eu anomaly.

### <span id="page-28-0"></span>**4.6 Geochronology**

#### <span id="page-28-1"></span>*4.6.1 U-Pb dating of felsic dyke rocks*

A sample of least altered, medium-grained, equigranular, reddish felsic dyke rock (MI-PL-DAT-01; Fig 20) with an apparently unmodified chemical signature (Fig 18) was selected for U-Pb dating. Zircons were separated and mounted for U-Pb analysis by LA ICP-MS. The results are summarised in Table 6 and presented in detail in Appendix 3. A total of 36 spots coming from 75 separated zircons were analysed and of these 34 were used to define a concordia age of 2662 ± 18Ma (Figure 20).

### <span id="page-28-2"></span>*4.6.2 Re-Os dating of molybdenite samples*

Three samples of molybdenite (MI-PL-DAT-12, MI-AL-DAT-18, MI-ME-DAT-17) collected from drillholes from the three intrusion centres, Planet, Allied, and Mellieur, and shown in Figure 21A to C, were sent for Re-Os geochronology. The details of the method are summarised in Appendix 3 and results presented in Table 4. The pooled results provide an age of 2680  $\pm$  8 Ma, the error being reduced based on the fact that these four samples all represent the same mineralising event (R. Creaser, pers. commun., 2018). The significance of these results is

discussed in Section 5.4. In the three cases, molybdenite is accompanied by anomalous values of gold ranging between 2.1 and 6.4 ppm.

## <span id="page-29-0"></span>*4.6.3 U-Pb dating of hydrothermal titanite*

A polished thin section sample of altered felsic dyke rock (MI-AL-PET-70) containing hydrothermal titanite lining the walls of cavities in a breccia zone with quartz, calcite, chlorite, albite, and pyrite (Fig 22A, B) was selected for in situ U-Pb using LA ICP-MS methodology. Two subhedral grains (Fig 22C, D) were selected for dating and were examined using the SEM-EDS to select areas for spots analysis. The titanites are fresh, euhedral to subhedral with weak zoning due to variable Fe content, are variably fractured and contain pyrite and chalcopyrite inclusions. The points for analysis were selected in areas with few fractures so as to reduce the chance of compromising the U-Pb analysis. The low U content of the titanites, in places at or below the detection limit, compromised many of the analyses including all those from grain 2, which are therefore not reported. Of the 20 points with sufficient U to provide useful results, several were discordant (Fig 23A) and were omitted from the age calculation. The 11 remaining analyses define a concordia age of  $2069 \pm 6$  Ma (Fig 23B).







#### <span id="page-30-0"></span>**5. Discussion**

### <span id="page-30-1"></span>**5.1 Origin of secondary textures**

### <span id="page-30-2"></span>*5.1.1 Dissolution of primary quartz*

Several sodic-altered MDC intrusive rocks are characterised by low contents coinciding with the presence of cavities which are attributed to the removal of quartz. Quartz dissolution and alkali metasomatism are not necessarily related processes, but frequently occur together. This association is observed in granitic rocks globally, in localities including Africa, Australia, Brazil, and those from several Hercynian granitic massifs in western Europe. These latter settings are among the best-studied cases and documented by Cathelineau (1986), Recio et al.(1997), Rossi et al.(2005), Boulvais & Rouffet (2007), and López-Moro et al, (2013), among others.

As quartz is one of the most abundant minerals in the Earth´s crust, its behaviour in aqueous systems has been thoroughly investigated. Quartz solubility in pure water systems was first experimentally determined by Kennedy (1950), for temperatures up to 900°C and a pressure range between 200 and 1000 bars. Khitarov (1956), and Kitahara (1960) refined the model, whereas the more recent works of Manning (1994) and Akinfiev & Diamond (2009) have extended the fluid composition to include variables such of NaCl or  $CO<sub>2</sub>$  and also expanded the P-T range up to 1000°C and 2000 bars. These authors have demonstrated that quartz solubility increases with temperature and/or pressure, except for a very small window in P-T space where the solubility curves have a negative slope and is referred to as the quartz retrograde solubility region. The arrows in Figure 24 illustrate different paths to increase quartz solubility in an aqueous fluid.

Quartz dissolution at the MDC as well as that described by the aforementioned authors is a post-magmatic or sub-solidus process and therefore associated with the retrograde solubility field. Cathelineau (1986) and López-Moro (2013) estimated the temperature of this process, based on fluid inclusion studies, to have been between 250° and 400°C. The implicated fluids generally have low salinities (0-10 wt. % eq. NaCl) and were necessarily quartz undersaturated at some point. From Figure 24 it is apparent that a heating fluid or alternatively a cooling fluid within the retrograde solubility field can dissolve more silica and trigger quartz dissolution.

#### <span id="page-31-0"></span>*5.1.2 Nature of episyenites and relationship to mineralisation*

The term episyenite, as originally proposed by Lacroix (1920), refers to hydrothermally altered rocks that are depleted in quartz and whose feldspars have been modified from their original compositions. Although is found in many different geological settings, episyenitisation is one of the least studied and understood post-magmatic alteration processes. The term is rarely used outside of Europe, where it has been studied in several Hercynian granitic massifs in Italy, France, and Spain.

Episyenitisation involves the leaching of magmatic quartz from an originally granitic rock, the precipitation of new alkali (K-Na) feldspar, and the displacement of the bulk composition of the original rock towards the alkali feldspar apex of a QAP diagram (around the syenitic field) (Streckeisen, 1976). Episyenites are characterised by the presence of pores or dissolution cavities, once occupied by quartz and other minerals. Despite the presence of these cavities, the primary texture of the rock is relatively well preserved or at least still identifiable in the remaining rock. The cavities are partly or wholly filled with a wide range of secondary minerals (Fig 12A to F) that can be deposited at any time after the dissolution episode. The episyenites then have enhanced porosity and permeability. As expected, this spatial overlapping of multigeneration minerals complicates the geochronological studies and the fluid pressuretemperature (P/T) assessment of these rocks.

Another important textural feature of episyenites is their common red-brick colour. This colouring has been explained by the presence of very fine-grained hematite inclusions within

albite crystals or by the presence of  $Fe^{+3}$  within the feldspar structure. A complete discussion about the red colouring in feldspars is presented by Putnis et al. (2007).

Although there is no formal classification scheme for episyenites, they have been divided on the basis of the composition of the secondary alkali feldspar, into sodic or potassic episyenites. Classification could also reflect the secondary mineralogy present in the cavities, thus albiterich, chlorite-rich, epidote-rich, and so forth (López-Moro et al. 2013). The MDC episyenites are dominantly sodic, although some samples show a narrow rim of K-Feldspar lining the dissolution cavities (Fig 11).

Episyenites are known from many different locations and of variable ages through the geological record. Episyenites are generally barren of mineralisation, but they can contain a broad range of commodities, including U (Polito et al. 2009; Alexandre 2010; Ashton 2010; Wilde 2013; Dolníĉek et al. 2014), Sn-W (Borges et al. 2009; Charoy & Pollard 1989), and Au (Theodore et al. 1987; Jébrak & Harnois 1990; Jébrak 1992; Jébrak & Doucet 2002; Béziat et al. 2008; López-Moro et al. 2013). Many episyenites are located in shear zones or other structural features, and their enhanced porosity forms an excellent fluid pathway for metalliferous fluids. Of the many settings described for episyenites, those associated with U deposits, are the best known and studied. Episyenites associated with Au have only been described in a few localities (see summary in Fig 25) and of these, only two locations have been reported in Archean rocks from the AGB, being the examples the Mesegay gold occurrence, located north from the PDFZ on the Quebec side of the AGB, hosted by the Archean Taschereau-Launay plutonic complex (Jébrak & Harnois, 1990; Jébrak, 1992; Jébrak & Doucet, 2002); and the Côté Gold deposit, hosted by the Chester intrusive complex (Katz et al. 2016) in the Swayze greenstone belt of Ontario. Episyenites are part of the mineralisation rocks in the former place, and post-date the gold mineralisation in the latter. In both locations, magmatic intrusion-related origins are proposed by the respective authors. The MDC represents the second report of episyenites in the Ontario side of the AGB, and the first directly associated with Au, Cu, Mo mineralisation.

### <span id="page-32-0"></span>*5.1.3 Quartz vein dissolution*

A particular set of irregular quartz veins (Fig 26A to F), clearly differ from the rectilinear Aubearing veins described in previous sections, are characterised by abnormal geometry, lateral discontinuity, restriction to episyenites and strong correlation with chalcopyrite and molybdenite. These veins are interpreted here as affected by dissolution of quartz during the same event that produced the episyenites.

In other intrusion-related systems, such as porphyry systems, partial dissolution of veins is a key process in the formation of economic Cu, Mo, ± Au mineralisation. Landtwing et al. (2005), using fluid inclusions and cathodoluminescence imaging, demonstrated that the precipitation of bornite and chalcopyrite at the Bingham Canyon deposit, Utah, USA, occurred between 425° and 350°C, coinciding exactly with the quartz retrograde solubility field. The same relationship has been observed for many other porphyry deposits based on the texture of mineralised Btype veinlets in these systems (Gustafson & Hunt 1975; Sillitoe 2010). Of note is that B-type veins are characterised by granular quartz with a central or marginal suture of sulfide mineralisation (molybdenite, chalcopyrite, or pyrite) whereby the suture represents the filling of aligned dissolution cavities within the vein.

In the porphyry case, the formation and partial dissolution of B-type veins, as well as Cu-sulfide precipitation, is inferred to occur in a still hot, semi-plastic magma, near the ductile-brittle transition. In comparison, at the MDC the time lapse between vein formation and vein dissolution remains unknown. Remobilisation might explain erratic gold values around dissolved veins, but at present no textural or chemical evidence supports this scenario. Furthermore, some gold might also be genetically associated with the post-dissolution Cu-Mo mineralisation event.

#### <span id="page-33-0"></span>*5.1.4 Dissolution of mafic minerals*

Hornblende and biotite are common minerals in least altered dykes of the MDC; however, their content decrease with progressive sodic alteration and they are absent in episyenites. Previous studies on episyenites do not indicate that leaching of mafic minerals occurs with quartz dissolution, but is our interpretation that this process occurred at the MDC. As will be

illustrated, mass balance calculations indicate liberation of Fe and Mg; these elements can either be removed by fluids or incorporated into secondary phases such as pyrite, hematite, or chlorite.

### <span id="page-34-0"></span>*5.1.5 Brecciation and other textures*

The association of episyenites with fracture or fault zones as well as their enhanced permeability concentrate the flow of hydrothermal fluids and facilitates the formation of multiple breccia zones (Fig 27 A, B, F) and overprinting of alteration textures. Although in most cases the primary igneous textures are preserved, extensive dissolution accompanied by the precipitation of alkali feldspars, resulted in some unusual textures as illustrated in Figure 27C, D, E.

#### <span id="page-34-1"></span>**5.2. Mineralogical changes associated with alkali metasomatism**

Alkali metasomatism at MDC is mainly represented by different styles and episodes of albitisation, which are accompanied by a number of additional alteration minerals. Two basic mechanisms are considered for the formation of these minerals: 1) replacement of a preexisting mineral phase through coupled dissolution-precipitation (CDP), and 2) precipitation of minerals in open spaces. Both are explained below, and textural examples at the macro and micro scales are provided.

#### <span id="page-34-2"></span>*5.2.1 Coupled dissolution-precipitation (CDP)*

The CDP concept was originally proposed by Goldsmith & Laves (1954), as discussed in Ruiz-Agudo et al. (2014), to account for the transformation of feldspars under hydrothermal conditions. CDP is an important geological process that explains how a mineral is transformed into another in the presence of a fluid, in contrast to replacement by solid state diffusion. The CDP process can be applied to many types of hydrothermal alteration or metasomatism present and associated with multiple ore deposit types (Putnis & Austhreim, 2010). Despite this, the CDP process is rarely referred to in the ore deposit literature, reflecting the need for detailed

work at the microscopic scale and integration of the SEM or similar equipment. CDP is triggered by disequilibrium between a solid phase and a surrounding fluid, resulting in the dissolution of the solid at the mineral-fluid interface. Simultaneously, the fluid becomes saturated in one or more new minerals and starts precipitating them in the newly generated space around the partially dissolved parental crystal (Fig 28). Porosity and permeability are both necessary for maintaining fluid flow towards the centre of the original crystal and replacing it with the new mineral. This porosity may be generated by different mechanisms, such as differences in the molar volume between primary and secondary minerals, differences in the dissolution and precipitation rates, or fracturing. If the permeability is maintained, the process advances until eventually the parental crystal is entirely replaced by the new mineral with preservation of the external shape (i.e., pseudomorphic replacement). If ideal conditions are not maintained, the replacement can take place without preservation of crystal shape, creating abnormal crystals, crystals aggregates, or mineral zoning with the parental mineral preserved in the core surrounded by the newly formed mineral. Experimental reproductions of the CDP process, especially for different feldspar minerals, have been conducted extensively in recent years (Putnis 2002; Engvik et al. 2008; Putnis 2009; Hövelmann et al. 2010; Putnis & John 2010; Putnis & Austrheim 2010; Norberg et al. 2011; Ruiz-Agudo 2014; Norberg et al. 2014; and Putnis 2015). Such work has shown that the replacement of any feldspar by albite is an extremely fast process, with crystal growth rates of 50 to 100 µm attained in only a few weeks, at temperatures of 600°C. Such reaction rates are instantaneous with respect to geological time (e.g., 1 cm crystal only requiring a few years). Depending how much fluid can circulate through a magmatic-hydrothermal system and how long it can remain active, which is an average of 2.5 to 4 Ma in the case of porphyry deposits (e.g., Sillitoe & Mortensen 2010), the albitisation process could occur continuously and repeatedly over long periods of time. The process can also occur in different directions, for example: an original orthoclase crystal might be dissolved by a sodium-rich fluid and then albitised, but the character of the fluid can change, and the newly formed albite might be in disequilibrium with the surrounding fluid; resulting in potassic alteration, and formation of secondary orthoclase. The result of such a scenario is that two secondary feldspars spatially overlap in the same crystal leaving no evidence of the primary
magmatic mineralogy. Sodic alteration at the MDC is an example of this process, where the final observed product of extensive alteration is mostly albite, but in a few cases, remnants of K-feldspar are observed as either cores or rims in the aforementioned albite crystals (Fig 29). It is suggested here that the CDP process is responsible for the formation of most of the secondary albite present in the MDC, except for albite hosted within dissolution cavities or around dissolved veins. The process also accounts for other observed alteration reactions, such as sericite replacing feldspars through dissolution along twinning planes, and chlorite replacing biotite and hornblende with pseudomorphic textures.

### *5.2.2 Precipitation in open spaces*

In addition to the CDP process, which is responsible for mineral modifications at the crystal scale, occluding an open space is another way of forming a new alteration mineral in a host rock. For example, this is the mechanism by which veins are generated. A dilating fracture facilitates the circulation of hydrothermal fluids which can subsequently precipitate different minerals. Although several types of veins are common in the MDC, this section will focus on open spaces generated by dissolution of minerals, especially quartz, associated with the alkali metasomatism processes. Three specific types of open spaces were generated and subsequently used by fluids for mineral precipitation: 1) dissolution cavities associated with episyenitic textures, 2) dissolved margins of pre-existent quartz veins, and 3) micro-porosity generated in newly formed crystals due to negative molar volumes changes during the CDP process.

As previously discussed, dissolution cavities are generated by the dissolution of quartz, biotite and hornblende. These cavities were partially or totally filled with a variety of alteration minerals (Fig 12A to F), including albite, K-feldspar, chlorite, epidote, titanite, apatite, zircon, pyrite, chalcopyrite, and molybdenite. Dissolved veins margins are filled essentially by finegrained chlorite and sulfides and provide an excellent time marker for the dissolution process. Micro-porosity in secondary albite crystals can be abundant, and it provides a host for

precipitation of minerals at a very small scale ranging from ~50 µm to nanometre size. Common minerals found in these pores include zircon and apatite.

## **5.3. Geochemical changes associated with alkali metasomatism**

### *5.3.1. Major element chemistry*

Alteration of the felsic dyke rocks resulted in modification of some major elements, such as Na, K, Al, Ca, and Fe, which reflects mineralogical changes in the altered rocks, such as the loss of quartz and mafic minerals. Despite the leaching of quartz,  $SiO<sub>2</sub>$  remained relatively stable due to the extensive crystallisation of albite, which contains  $67\%$  SiO<sub>2</sub>. As an example, the least altered felsic dykes contain between 60 and 75 % total modal feldspar, whereas episyenites contain 90 – 95 % albite; the formation of this new albite requires a significant amount of  $SiO<sub>2</sub>$ , that we interpret as coming from the leached quartz. The primary igneous composition of the dykes can not be accurately determined but only be approximated from the composition of the least altered sample, which petrographically equates to a quartz-monzodiorite and compositionally, based on the  $Zr/TiO<sub>2</sub>$  versus Nb/Y plots, falls in the trachy-andesite field (Fig 15). In that sense, we believe that the MDC comprises a group of dykes with different compositions, some of them towards the tonalitic side of the QAP diagram and others towards the granite or monzogranite side that have been homogeneized via albitisation.

Although Al is traditionally considered an immobile element, alkali metasomatic environments are one of the few situations where it can behave strongly mobile (Hövelmann et al, 2010; Norberg et al, 2014). Al<sub>2</sub>O<sub>3</sub> was mobile during the destruction of original Ca-bearing plagioclase which for our least altered dyke may contain up to  $\approx$  25% Al<sub>2</sub>O<sub>3</sub> (An<sub>30</sub>) and precipitation of albite which only contains 20% Al<sub>2</sub>O<sub>3</sub>; biotite was also removed and contains up to 12% Al<sub>2</sub>O<sub>3</sub>. The dissolution of calcic plagioclase indicates the mobility of Ca, although the Ca content might be reflecting the presence of calcite as an alteration product. The femic elements,  $Fe<sub>2</sub>O<sub>3</sub>$  and MgO, were mobile during the dissolution of biotite and hornblende, but a certain amount of Fe is retained in pyrite and chlorite. As illustrated in Figure 30, all the felsic dyke samples have

sodium values higher than those typical of comparable igneous compositions. As most of the feldspars are sodic end-member  $(Ab_{100})$ , the addition of Na to the system is strictly necessary. For example, some of the most altered samples with well developed episyenitic texture, especially sample MI-AL-LGC-28 show ( $\approx$ 10.2% Na<sub>2</sub>O – 70.7% SiO<sub>2</sub> – 18.2% Al<sub>2</sub>O<sub>3</sub>), values that almost perfectly match the composition of ideal albite (≈11% Na<sub>2</sub>O – 67% SiO<sub>2</sub> – 20% Al<sub>2</sub>O<sub>3</sub>), suggesting the total replacement of all the primary feldspars by albite, the destruction of all other magmatic minerals and the precipitation of a significant amount of albite within the dissolution cavities. Potassium values (Fig 30) for some samples, lie along a typical trend; however, some of the samples have low K, consistent with destruction of biotite and albitisation of orthoclase.

#### *5.3.2. Trace and REE chemistry*

Aplitic dykes display U-shaped HREE pattern, which is commonly observed in several aplites (Glazner et al. 2008). According to this author, the U-shape is caused by fractionation of hornblende and titanite in the parental magma and indicates a genetic relationship between the aplite and the pluton that is hosting it. Variations in the REE patterns for felsic dykes can be explained in terms of two processes: 1) alteration or dissolution primary REE-bearing minerals such as zircon, apatite, and titanite, which needs to be addressed with additional SEM work and 2) precipitation of similar REE-bearing phases within dissolution cavities; titanite, apatite and zircon were observed. Additionally, xenotime was observed in contact alteration zones. Although minerals such as zircon, titanite and apatite are generally resistant to weathering and other physical processes, it has been shown that they can be also be affected by CDP processes, especially in strongly alkaline environments (Rubatto, 2008, Seydoux-Guillaume, 2012; Putnis 2002; Harlov et al. 2005). These workers have shown textural variations between pristine cores and generally porous reprecipitated rims, with significant differences in REE contents between the two zones. Also noted in these studies is the occurrence of new REE and HFSE-rich mineral phases (e.g., zircon, apatite, titanite) which precipitate in micro-pores and fractures of other alteration minerals. The CDP process affecting these phases may be triggered by either one or all of the following: 1) intense fluid mediated alteration; 2) deformation; or 3) radiation damage

where enrichment in U or Th is a factor. In the case of the latter, detailed geochronological studies of dissolved – reprecipitated zircons reveal substantial age differences between the time of formation of the original magmatic phase and the alteration event (Tomaschek et al, 2003).

The lack of Eu anomalies for the felsic dyke rocks is noted. This feature is known to characterize other felsic suites in the AGB (Beakhouse, 2011) and has been interpreted to reflect an oxidised melt which stabilizes Eu<sup>3+</sup> over Eu<sup>2+</sup>, a feature also known in some oxidised Phanerozoic porphyry deposit settings (Trail et al, 2012). In fact, Eu and Ce anomalies are often used as a proxy to determine the oxygen fugacity of the magmatic system. Europium speciation as  $Eu^{3+}$ inhibits partitioning of Eu into plagioclase and precludes, therefore, the formation of Eu anomalies.

In terms of the other trace elements, three strongly altered samples (MI-AL-LGC 12, MI-AL-LGC 13 and MI-AL-LGC-28) are depleted in some of the LILE, specifically Cs, Rb, Ba. These three elements are commonly associated with K in minerals such as feldspars and biotite, and their depletion coincides with the dissolution of these minerals in the felsic dyke rocks at MDC. Uranium and Th depletion coincides with negative anomalies in P, and Zr, suggesting again the alteration of phases such as apatite, zircon or titanite. Strontium displays both positive and negative anomalies in a chondrite-normalised plot (Fig 18). Strontium is preferentially accommodated in calcium-bearing plagioclase which was extensively replaced by albite.

## *5.3.3. Mass Balance*

Mass balance is used to quantitatively assess the mobility of elements during hydrothermal alteration, metamorphism, and other geological processes. The isocon method (Grant, 1986) is a simple technique which provides a graphical estimate of mass or volume variations and mobility of chemical elements without significant data manipulation. The method is based on the graphical comparison of an altered sample with a least altered sample interpreted to be representative of its probable original composition. The immobile elements define the isocon

line, whereas elements showing relative gains and losses depart from this line and plot above or below the isocon, respectively.

Mass balance assessment of alteration for the MDC dykes is a challenge because superimposed alteration events has preculded recognition of precursors to monitor the successive stages (yypes) of altetraion. Thus, a least altered samples was used as a precursor from which to measure element mobility associated with multiple alteration events that reflect the entire alteration history of each sample. Additionally, geochemistry and petrography clearly indicate the mobility of major and trace elements that are traditionally considered immobile (Al, Zr, Ti, REE), complicating the construction of the isocon line.

Four samples with various degrees of alkali metasomatism were selected and individually compared with a representative least altered sample, basically to illustrate the issues with the mass balance at the MDC. The least altered sample was chosen based on preservation of magmatic K-feldspar and quartz, biotite and hornblende, preservation of the original magmatic texture,. The alteration intensity of the altered samples was assessed using compositional parameters, such as Na<sub>2</sub>O, K<sub>2</sub>O and Sr contents, the presence of Au mineralisation, and modification of primary textures. Of the aforementioned criteria, the Na<sub>2</sub>O content seems to be the most appropriate parameter and samples are ranked in Table 7 in terms of their relative degree of alteration.



**Table 7**. Summary of samples used for the mass balance calculation

Figure 31 is a summary of the mass balance analysis for the samples listed in Table 4. Despite the problems described before, some patterns can be observed and are worth to mention here. Na<sub>2</sub>O is enriched in all samples, up to 105% in the most altered sample. When mineralisation is present, as in samples LGC-15 and LGC-13, Au is strongly enriched along with elements

contained in sulfides such as Ag, Te, Bi, and S. Cu and Mo are generally lost indicating an initial enrichment in the least altered sample, but also indicating a poor correlation of these two elements with Au.  $K<sub>2</sub>O$  is lost in all samples from 50% to 85%, as well as the large ion lithophile elements (LILE) associated with feldspars. CaO is generally lost up to nearly 100% as a consequence of the albitisation, except in the sample LGC-15 which seems to have an overprinting of carbonate alteration, indicated by a 500% gain in C. Mass changes are difficult to determine graphically because the isocon is not reliable; development of cavities suggests a loss of mass, but the general preservation of the texture indicates the volume could be preserved suggesting changes in the density of the rock.

# **5.4. Implications of the geochronological data**

A goal of this study was to constrain the ages of: (a) the magmatism generating the MDC, (b) the alkali metasomatic processes affecting it, and (c) the mineralising events. The MDC is located between two clearly different magmatic domains: 1) the 2697  $\pm$  4 Ma Round Lake batholith (Ketchum et al., 2008) which outcrops ~3 km SE from the study area (Fig 2) and is a pre-tectonic intrusion (Beakhouse, 2011); and 2) a group of late-tectonic plutons located near Kirkland Lake and which includes the Lebel and Otto stocks (Fig 2) with ages of 2673  $\pm$  2 Ma and 2680 ± 1 Ma, respectively (Ayer & Trowell, 2000). Despite the significant error, the U-Pb zircon age of 2662  $\pm$  18 Ma obtained for a least altered sample of the MDC overlaps with the Timiskaming magmatic event (2680 – 2668 Ma) (Beakhouse, 2011). The Timiskaming magmatic event represents widespread clastic sedimentation, alkaline magmatism and spatially related Au mineralisation.

Two mineralisation events are well defined at MDC: 1) the gold-bearing quartz veins that predate the episyenitisation process, and 2) the Cu - Mo  $\pm$  Au mineralisation hosted by dissolution cavities, which post-dates episyenitisation and quartz veining. The pooled results from Re-Os geochronology (2680  $\pm$  8 Ma), combined with the magmatic age suggests that the emplacement of the dykes, early albitisation, quartz veining, first Au mineralisation event, episyenitisation, and second Au – Cu - Mo mineralisation event occurred in a relatively short

period of time (2680 – 2674 Ma). This window of time implies that both mineralisation events are associated with the Timiskaming event.

The titanite hosted by dissolution cavities in the episyenites yielded an age of 2069  $\pm$  6 Ma, which is significantly younger than the dykes and the Au mineralisation. The MDC titanite is hosted by a dissolution-brecciated zone very rich in Na, but also in metals with Au values as high as 3 ppm, Ag up to 4 ppm, Cu 1%, and Mo up to 6 ppm. In particular, the titanite analysed is cut by fractures with chalcopyrite (Fig 22C inset) which most likely indicates Paleoproterozoic remobilisation of metals at the local scale. This age is anomalous for the AGB, as noted by the fact that it is only the second Paleoproterozoic age reported from a gold deposit in the southern AGB. It follows on the recently reported  $1730 \pm 5$  Ma U-Pb monazite age from carbonate-quartz-epidote-hematite veins at the Young-Davidson deposit ~50 km SW of Kirkland Lake (Zhang et al., 2014). These veins crosscut the Au-bearing syenite and post-mineral diabase dykes but are not directly associated with any mineralisation. In that case, the growth of monazite and vein formation is attributed to the far field 1750 – 1700 Ma Killarnean or Yavapai magmatic/metamorphic event, which may have reactivated Archean structures.

A number of dyke swarms have been dated through the Superior Province with ages between 2.2 and 2.0 Ga, from which the closest ones are the Marathon, Fort Frances, Senneterre, and Biscotasing (Hall & Davis, 2004), and they may be associated with the Paleoproterozoic hydrothermal activity at the MDC. Regardless of the source of the Paleoproterozoic fluids, reactivation of the Catharine fault system with related fluid circulation is considered a probable mechanism for the metal mobilisation through the already emplaced dykes. Thus the geochronological data and all the crosscutting relationships are used as the evidence for the paragenesis proposed for the MDC (Fig 33).

# **5.5. Considerations about the alkaline fluids**

Results of the research provide the foundation for interpreting a hierarchy of fluid flow pathways and related alteration in the hydrothermal system at the MDC. Assuming that the source of the fluids resulting in the intense metasomatism of the MDC is the group of plutons

that comprise the Otto and Lebel stocks, and that the MDC is temporally related to this magmatic event around ~2680 Ma, it is suggested that the Catharine fault system acted as a first-order structure that permitted the emplacement of the dykes and later was a long-lived and reactivated conduit for fluid flow during the various stages of alteration. The Catharine fault system (Fig 2) is an NW striking structural zone running close to the contact between the mafic rocks of the Stoughton-Roquemare assemblage and the intermediate to felsic rocks of the Upper Blake River assemblage. The fault is not considered to be a single structure but a composite one (Fig 32A), because some of the dykes of the MDC are located on its north side (Meilleur zone) whereas the rest is on its southern side (Allied and Planet zones). The Catharine fault has been interpreted as formed synchronously or slightly after the emplacement of the Round Lake batholith (2697  $\pm$  4 Ma), and to dip at a high angle to the NE (Jackson, 1994). The fault zone is characterised by abundant carbonate alteration and associated sulfides, fracturing, and quartz veining which comprise a number of small mineral occurrences.

Second order pathways are represented by small fracture or fault zones crosscutting the dyke rocks, which host intense alteration zones such as breccia and episyenite bodies. The size of these metasomatic alteration zones ranges from  $\sim$ 5 m up to  $\sim$ 60 m (Fig 32B) in apparent thickness in drill core. Within these alteration zones, the fluids moved through micro-fractures but also through the dissolution cavities generated by the episyenitisation process (Fig 32C), which seem to be interconnected. For an individual crystal, the CDP process can proceed in two different ways (Fig 32D, E): 1) inwards from the external fluid-grain interface towards the center of the crystal using micro-porosity, or 2) if the crystal is previously fractured, the fluid can go directly to the center of the crystal and then replace it outwards from the core to the margins of the grain. Figure 32 shows a summary of these different scales of fluid movement. We have demonstrated that sodic alteration is spatially associated with the various styles Au mineralisation at the MDC. However, clear evidence of a genetic relationship between alteration and mineralisation is lacking. The same situation is observed in many different Au settings through the AGB where sodic metasomatism, such as in albitite dykes, has been recognised regionally and shown to be spatially and temporally associated with gold in several

orogenic and intrusion-related deposits, (Burrows et al, 1993; Ayer et al., 2005), but its role or relationship with the mineralisation is not clear.

In addition, the presence of primary alkaline intrusive rocks as small plutons proximal to the two most important structural breaks, the PDFZ and CLLFZ, is well established (e.g., Ayer et al., 2005; Beakhouse, 2011). These intrusions have a strong temporal and spatial relationship with Au mineralisation and have been recognised as forming a distinctive type of gold deposit which is informally referred to as syenite-associated (Robert, 2001; Robert et al., 2007; Kontak et al., 2008). The type of dykes, mineralisation styles, geochronological data, and alteration characteristics allow to classify the Au mineralisation present at the MDC as belonging to that group.

Nevertheless, the nature of the mineralising fluid is not understood and furthermore, the fluid and alteration are not necessarily related to alkaline magmatism. In contrast, the spatial proximity of the MDC to alkaline plutons, the strong alkaline metasomatism caused by fluids which probably originated from these intrusions, and their emplacement as part of the same magmatic event at ca. 2680 Ma, indicate that there is an intimate association of magmatism, alteration, and mineralisation. Although further study is warranted, the observations presented are considered to be sufficient to argue for a causative association between magmatism and fluids.

Sodic alteration can be present in many magmatic-hydrothermal systems, such as IOCG, porphyry, VMS, and albitite-hosted uranium deposits. The causative fluids in each case can have different origins, including magmatic, basinal brines, metamorphic, seawater or mixed (Lang et al. 1995). In some of these deposits, the sodic alteration can be directly associated with the ore, whereas in others it is simply an accessory alteration. Sodic alteration in some Archean provinces, such as the AGB, appear to be more common and widespread than in some Phanerozoic magmatic provinces. The same empirical observation has been noted for the western United States, where Battles & Barton (1996) pointed out that Na and Na-Ca alteration assemblages are very common in Permian and Jurassic rocks, but uncommon in Cretaceous and younger rocks. These authors suggested this difference was attributable to the transition from a marine environment to a fully emergent continental arc wherein the latter setting seawater

was not available. We suggest that a similar argument might be applied when comparing the AGB to modern arc environments where Na alteration is generally restricted to specific parts of magmatic hydrothermal settings.

Episyenitic textures have previously been reported in only two localities in the AGB: 1) the Taschereau – Launay plutonic complex in Quebec, where Jebrak and Doucet (2001) proposed a porphyry model for the Au-Mo mineralisation present; and 2) the Côte Gold deposit in the Swayze greenstone belt, where Katz (2016) reported the existence of the texture after tonalite, but its formation post-dated the Au mineralising event. Recognition of the episyenitisation process at the MDC and its association with Au-Cu-Mo mineralisation is one of the main contributions of this work. Furthermore, the results of the study demonstrate that episyenites may represent a previously unrecognised target for mineralisation in the AGB. That episyenites had not previously been recognised or overlooked may reflect a lack of awareness of their nature, origin, and potential to host mineralisation, although they are recognised globally (Fig 25) to be important as an ore host. Additional studies and further understanding of these rocks and the alteration/mineralisation process might open exploration opportunities for disseminated Au-Cu-Mo deposits in the AGB.

### **6. Conclusions**

A combined petrographical, geochemical, and geochronological study of the MDC felsic dykes illustrates how strong alkali metasomatism can modify the mineralogy, texture, and chemistry of a rock. Major and trace elements are gained or lost by the transformation of feldspars, the liberation of LILE and dissolution-reprecipitation of REE-bearing minerals. Textural modifications go from pseudomorphic replacement which generally preserves magmatic textures, to development of episyenitic textures and different styles of brecciation associated with dissolution processes. Future work should include isotopic studies to understand how Sr and other LILEs behave as they are released from a dissolved feldspar crystal.

It is empirically suggested that the dykes from the MDC were emplaced at a shallow level in the crust and based on the conditions necessary to develop episyenites, the main sodic alteration

and dissolution stages occurred at temperatures from ~370°C to ~520°C with pressures between 150 and 600 bars. However, a detailed fluid inclusion study of the veins combined with oxygen isotopes in different generations of feldspars would help to determine those conditions more accurately.

The textural characteristics of episyenites make them good recorders of hydrothermal events, as evidenced by the age obtained for hydrothermal titanite hosted within dissolution cavities (2069  $\pm$  6 Ma). This Paleoproterozoic hydrothermal event was accompanied by precipitation or remobilisation of Cu, Mo, Au, Ag, and has not been previously reported in the AGB. Generation of open spaces via dissolution is an excellent mechanism to provide the permeability required to host mineralisation, as proven by global examples of deposits such as U, Sn, REE in episyenites, and/or Au-Ag in advanced argillic vuggy silica textured rocks. Alkali metasomatism is widely present in Archean magmatic-hydrothermal systems and its close relationship with alkalic magmatism and gold mineralisation is undeniable, although poorly understood. Archean intrusion-related systems appear to have better developed and more extensive sodic alteration zones than some Phanerozoic counterparts such as porphyry deposits.

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**Figure 1.** Regional geological map of the Abitibi Greenstone Belt showing main lithological assemblages, structures, and some of the main deposits. Modified from Thurston et al. (2008).



**Figure 2.** Sub-regional geological map of the south part of the Kirkland Lake camp. The black box shows the area of this study at the NE margin of the Round Lake Batholith. Relevant U-Pb ages of the metavolcanic units and near granitoid bodies have been highlighted. Purple and yellow diamonds in the work area represent Cu and Au prospects or occurrences, respectively. Modified from Ayer et al. (2000)



Figure 3. Geological map of the study area showing the stratigraphic units according to Jackson (1994) as well as the three intrusive centers recognized at the MDC and surface rock sampling with Au whole rock content from Oban Mining.



**Figure 4.** Textural characteristics at macro and microscopic scale of the four different types of dykes observed at the MDC. The IUGS classification diagrams used for each rock are shown in the lower part indicating the modal compositional range of different samples examined. A) Equigranular intrusion mainly composed by plagioclase feldspar with minor K-Feldspar, quartz, biotite, and hornblende; the modal classification from petrographic examination include quartz monzodiorite, monzodiorite, quartz diorite, and tonalite (n=16). B) Porphyritic to crowded porphyritic intrusion with plagioclase and locally K-Feldspar phenocrysts in a fine-grained groundmass with the same minerals plus quartz; modal classification include granodiorite, tonalite and quartzdiorite (n = 11). C) Fine grained aplitic intrusion with granular-saccharoidal texture where only plagioclase feldspar and quartz can be identified; this rock is tonalitic based on petrographic examination (n=6). D) Fine grained porphyritic mafic dykes with plagioclase and amphibole phenocrysts in a fine-grained groundmass where only plagioclase can be identified in thin section; (n=2). The red dashed area in the classification diagrams represent the zone where examined samples plotted after counting an average of 100 points for each thin section  $(Q =$  quartz, A = alkali feldspar, P = plagioclase). For the mafic dykes, an approximate composition is plotted based on composition of phenocrysts since the groundmass is too fine to count points ( $P =$  plagioclase,  $H =$  hornblende,  $Px = Pyroxene$ ).



**Figure 5.** Summary of the compositions of feldspars (n=66) as determined from SEM-EDS analysis from five "weakly" altered samples of felsic dykes. The feldspars analyzed are euhedral to subhedral crystals from equigranular and porphyritic dykes from the Allied and Planet zones.



**Figure 6.** Examples of vein associated mineralisation. A) Two parallel quartz veins with pyrite and visible gold hosted by a light pink coloured albitized equigranular dyke. B) Quartz vein with small pyrite crystals crosscutting a contact between an equigranular (I) and a porphyritic (II) dyke showing a slight dextral movement along the vein plane. C) Quartz vein with fine grain tourmaline bands parallel to its margin, the proximal halo of the vein is strongly albitized. D) Quartz vein with pyrite showing a proximal halo of albite and hematite and a more distal chlorite alteration zone. E) Photomicrograph of a millimetric quartz vein with associated pyrite and a narrow albite alteration halo. F) Normal density of quartz veins in the mineralized zones showing alteration haloes around some of them and preferential parallel "sheeted" geometry. Ab=Albite, Py=Pyrite, Hem=Hematite, VG=Visible Gold, Tur=Tourmaline, Chl=Chlorite, Qz=Quartz.



**Figure 7.** Examples of contact hosted mineralisation. A) Contact zone between felsic dyke (FD) and mafic volcanic rock (MV) showing intense alteration in the volcanic rock characterised by beige-greenish colour with abundant fine sulfide, mostly pyrite. Some quartz veinlets in the felsic dyke seem to continue along the contact and then become sinuous in the volcanic rock. B) Contact between felsic dyke (FD) and mafic volcanic rock (MV) with strong alteration in the latter accompanied by abundant pyrite dissemination; dark pink, beige, and green colours suggest the presence of albite, sericite, and chlorite, respectively. C) Beige and green bands in pervasively altered volcanic rock in a mineralized contact zone. Late calcite stringers are also observed crosscutting the described alteration. D) Photomicrograph of the fine-grained alteration in the volcanic rock where very fine anhedral crystals and aggregates of albite, carbonate, and coarser disseminated pyrite. MV= Mafic Volcanics, FD= Felsic dyke, Py= Pyrite, Ab=Albite, Cal=Calcite.



Figure 8. Examples of Cu-Mo ± Au mineralization hosted in cavities and vein margins. A) Chalcopyrite patches along the margins of irregular and discontinuous quartz veins where the host rock shows a strong pink color suggesting strong albite alteration. B) Chalcopyrite mass filling a space in a quartz vein with strong albite alteration. C) Molybdenite and intense red albite forming irregular ribbons in a milky quartz vein. D) Disseminated fine-grained molybdenite lining cavities in a pink albite altered rock with abundant chlorite disseminated. E) and F) show respectively chalcopyrite and molybdenite crystals lining the walls of submillimetric cavities in felsic dykes (Both reflected light - 5x). Ccp= Chalcopyrite, Ab=Albite, Mo=Molybdenite, Cav=Cavity, Py=Pyrite.



Figure 9. Examples of albite alteration type 1. Thin dashed lines represent margin of quartz veins whereas thicker lines indicate extension of albite 1 alteration. A) Irregular reddish albite halo mantling quartz veinlet and a narrower (mm) quartz stringer. Note the decreased abundance of mafic minerals within the proximal albite halo; in every case the distal halo is richer in chlorite. B) Quartz vein with a light pink albitization halo only on its top margin. These albite haloes are in many cases absent. C) Light pink albite halo mantling a quartz vein stockwork zone. D) Intense red albite halo around an irregular quartz vein. E) Narrow parallel quartz-carbonate stringers with pink-red albite envelopes. F) Photomicrograph of a quartz vein with associated tourmaline crystals and two different textural varieties of albite: AbA represents large irregular crystals with "chessboard twinning" and  $Ab<sub>B</sub>$  consists on aggregates of very fine crystals formed in a small embayment at the margin of the vein (Sample MI-AL-PET-11 (2.5X – crossed nicols). Qz=Quartz, Ab=Albite, Chl=Chl, Tur=Tourmaline.



**Figure 10.** Examples of albite alteration type 2. A) shows a dark red equigranular dyke with strong presence of albite replacing primary feldspars; this dyke is being intruded by a darker porphyritic dyke. B) The zones labelled  $Ab<sub>1</sub>$  represent two proximal albite alteration haloes around quartz veins (not observed in the photo) and the white dashed line marks the limit with the distal  $Ab<sub>2</sub>$  zone where albite is replacing feldspar phenocrysts and it is generally accompanied by chlorite and calcite. C) Comparison of two porphyritic dykes with different degrees of hematite alteration associated with the albite alteration; in both cases the feldspars are dominantly  $Ab_{100}$ . The sample on the left shows a very light red colour in phenocrysts and groundmass whereas the one on the right shows white feldspars and dark grey groundmass with hematite only associated to fractures. D) Back scattered electron image showing abundant micro-porosity in secondary sodic plagioclase (Ab<sub>100</sub>) with cross-cutting fractures controlling Kfeldspar alteration. E) and F) show the same sample in PPL and CPL respectively; a porphyritic

dyke is shown where the primary feldspar phenocrysts have been replaced by  $Ab<sub>100</sub>$  with cloudy-rusty appearance ( $Ab<sub>A</sub>$ ), when the larger crystals are observed under CPL abundant bright sericite inclusions are observed. Every rusty albite grain is rimmed by a lighter colored generation of albite Ab<sub>100</sub>, labelled as Ab<sub>B</sub> (Sample MI-AL-PET-28 2.5X PPL and CPL). Ab=Albite, Hem=Hematite, Chl=Chlorite, Str=Strong, Mod=Moderate, Tr=Trace.



**Figure 11.** Details of sodic altered dykes showing the development of episyenite texture. A) and B) show the general appearance of dyke hand samples with high irregularly distributed porosity. Note the shape of the pores or cavities varies from sub-rounded to elongated. In B) can be noticed how most of the cavities show a green colour caused by the presence of chlorite C) shows a close-up of the texture with two variations of habit in albite;  $Ab<sub>1</sub>$  represents a primary subhedral feldspar crystal replaced by reddish albite whereas Ab2 is very fine-grained

albite precipitated around crystals as well as lining some of the cavities. Ab<sub>2</sub> is occasionally accompanied by K-feldspar. Pyrite crystals are observed in some of the cavities. D) Thin section of a strongly altered dyke where subhedral feldspar crystals were replaced by albite  $Ab<sub>1</sub>$  where polysynthetic twinning can be appreciated; cavities or pores with semicircular shape are partially lined by a second generation of albite Ab<sub>2</sub> which is fine grained and forms irregular aggregates. Occasionally K-feldspar might be part of the fine-grained feldspar aggregate. Both Ab<sub>1</sub> and Ab<sub>2</sub> are sodic end member feldspar Ab<sub>100</sub> (2.5x – CPL). Cav=Cavity, Ab=Albite, Py=Pyrite, Kf=K-Feldspar. E) SEM image of chlorite and apatite crystals filling a cavity with both albite and K-feldspar forming the walls.



Figure 12. Minerals observed in cavities. In most cases, two generations of albite are observed; Ab<sub>1</sub> is primary feldspar replaced by Ab<sub>100</sub> whereas Ab<sub>2</sub> is an agglomerate of fine-grained second albite grains formed in open spaces or cavities. A) A cavity around the margin of feldspar crystals almost filled by Ab<sub>2</sub> (CPL-2.5x). B) Chlorite and pyrite lining cavity with Ab<sub>2</sub> on the walls. (PPL-2.5x). C) Subhedral titanite and epidote in a cavity (PPL-5x). D) Relatively large cavity with elongate shape hosting a large titanite and smaller chlorite agglomerates (PPL-2.5x). E) Pyrite, chalcopyrite, and chlorite lining a cavity (Reflected light – 10x). F) Flakes of molybdenite and chlorite precipitated within a cavity (Reflected light – 5x). Ab=Albite, Chl=Chlorite, Py=Pyrite, Ep=Epidote, Ttn=Titanite, Ccp=Chalcopyrite, Mo=Molybdenite, Cav=Cavity.


**Figure 13**. A) Drill core sample of intensely altered (Fine Ab, Chl, Cal, Ser, Py) mafic volcanic rock close to the contact with a felsic dyke rock. B) Back scattered electron (BSE) image showing some of the fine-grained intergrown mineralogy of the mentioned alteration zone. Albite = Ab, Chlorite = Chl, Calcite = Cal, Pyrite= Py, Chalcopyrite = Ccp.



**Figure 14**. A) Irregular patches of skarn alteration in metavolcanic rock. B) Mineralogy of one of these alteration zones. (Grt=garnet; Ep=epidote; Ca=calcite). B) Core sample showing a quartz vein which has been broken and displaced by small fault zone lined by chlorite-clay. C). Photomicrographic image of a breccia zone showing a matrix of chlorite, clay and pyrite cementing clasts of quartz veins and plagioclase. E) Quartz vein truncated by a mm-scale zone of reddish quartz breccia. F). Quartz crystals lining fracture zones in strongly red altered plagioclase.



Figure 15. Plot of Zr/TiO<sub>2</sub> versus Nb/Y (Winchester and Floyd, 1977) with samples from the MDC.



**Figure 16**. Alkaline/subalkaline diagram based on plot of total alkali versus. silica (curve after Irvine and Baragar, 1971) for intrusive rocks from the MDC (n=21). The diagram is presented to illustrate and stress the particular situation of alkalinity of the MDC dykes due to Na enrichment of probably different original compositions.



Figure 17. Harker-like diagrams for Na<sub>2</sub>O, K<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>. Despite the mobility of major elements, the diagram is presented to illustrate the three groups of dykes.



**Figure 18**. Primitive mantle normalised extended spider diagram for intrusive rocks of the Miller project (normalising values from Wood et al., 1979). Mafic dykes are not included to simplify the diagram. Samples 12, 13, 17 and 28 are labelled to be tracked in following diagrams



**Figure 19**. Chondrite normalised REE diagram for intrusive rocks of the MDC (values from McDonough and Sun, 1989). Samples 17, 13 and 28 are labelled to be tracked in following diagrams



**Figure 20**. Concordia plot for U-Pb zircon geochronology of the felsic dykes. The analysed sample (MI-PL-DAT-01) is shown to the right side; a reddish equigranular dyke, medium-grained with abundant feldspar, minor quartz, biotite and hornblende which represents the least altered sample of the project. The inset shows an SEM image of the separated zircon grains for analysis.



**Figure 21**. Molybdenite samples selected for Re-Os geochronology. A) Sample MI-PL-DAT-12 from the Planet zone; felsic dyke with carbonate, molybdenite and chalcopyrite in fractures. B) Sample MI-AL-DAT-18, from the Allied zone; hydrothermal breccia with fragments of albite altered dyke and quartz veins, cemented by calcite and molybdenite. C) Sample MI-ME-DAT-17, from the Meilleur zone; quartz vein with ribbons of albite altered intrusive and molybdenite resembling crack and seal texture. Mo = molybdenite, Ab= albite, Qz= quartz



**Figure 22**. Details of sample MI-AL-PET-70, selected for in situ U-Pb geochronology of hydrothermal titanite. A) Hand sample before cutting the polished-thin section where two large titanite grains Ttn1 and Ttn2 are observed associated to cavities filled with pyrite - chlorite and calcite, respectively. The dyke hosting the cavities and titanites is strongly albitized. B) Scanned image of the thin section showing the same two crystals. C) Detail of Ttn1 in reflected light (2.5x) showing pyrite inclusions and chalcopyrite trace hosted in fractures (inset). D) Detail of the grain 2 Ttn2 in reflected light (2.5x). Ttn=Titanite, Py=Pyrite, Ccp=Chalcopyrite, Ab=Albite, Chl=Chlorite, Cal=Calcite



**Figure 23**. A) Concordia diagram for 20 analyses on Ttn1. Note that 9 of the measurements are not concordant presumably due to Pb loss. B) Cluster of the concordant data (n=11; shown in A) that yields an age of  $2069.3 \pm 6.0$  Ma.



**Figure 24**. Plot of quartz solubility versus water temperature from 0° to 900°C contoured with isobars from 200 to 1000 bars. The coloured arrows show four different mechanisms that increase quartz solubility and might trigger quartz dissolution. Diagram is modified from Fournier (1999).



**Figure 25**. Global distribution of some of the best-known ore bearing episyenites reported in the literature. Only three places, including this work, have reported Au-bearing episyenites in Canada, all of them associated with Archean intrusions in the Abitibi greenstone belt. Deposits included in the map taken from Ashton (2010); Boulvais (2007); Borges et al. (2009); Charoy & Pollard (1989); Jebrak & Doucet (2002); Lopez Moro (2013); Theodore et al.(1987); Wilde (2013).



**Figure 26**. Close spatial relationship between irregular shaped veins, episyenitic texture and Cu sulfides. A) Irregularly shaped quartz vein showing intense dissolution along its margins and albitization in the wall rock. Note internal formation of chlorite, albite, and pyrite. Chlorite is also forming an outer rim around the vein. B) Quartz vein, its alteration halo, and its wall-rock all showing evidence of dissolution cavities suggesting that episyenitisation is post quartz

veining. C) An early quartz vein is laterally truncated suggesting that quartz has been leached and the space filled by chlorite and calcite. D) A quartz vein that has been partially dissolved and re-filled by chlorite and chalcopyrite. E) Dissolved quartz veins where the original fracture has been sealed by secondary albite. The wallrock is intensely albitised with presence of episyenitic texture, where the cavities are lined by chlorite and albite. F) A laterally truncated quartz vein with chlorite filling the original fracture. Qz=Quartz, Chl=Chlorite, Py=Pyrite, Cal=Calcite, Cav=Cavity.



**Figure 27**. Different types of breccias and episyenite textural variations due to multiple episodes of fluid flow through sodic alteration zones. A) Crackle or mosaic breccia with intensely albitised clasts and a secondary feldspar matrix with abundant dissolution cavities. Note the presence of chalcopyrite (Ccp) in the porous area. B) Example of a hydrothermal matrix supported breccia with fragments of angular albitised material in a matrix of chlorite (Chl) – calcite (Cal) with locally abundant titanite (Ttn). C) Brecciated albitic (Ab) episyenite with quartz (Qz) and calcite filling centimetric dissolution cavities. D) Strongly albitised rock with fragmental and episyenitic texture and apparent grain size gradation. A curvilinear coarse-grain horizon (outlined by dashed white line) might represent the separation between two grain size domains. The texture is alike to those observed associated with dissolution and collapse in some karstic systems E) Intensely albitized dyke with irregular episyenitic texture and patchy red colouring. The sodic alteration and episyenitisation forms multiple zones with this bizarre texture. F) Hydrothermal breccia with quartz vein and albite-rich fragments in a matrix of molybdenite (Mo), trace chalcopyrite and calcite indicating that molybdenite is coeval with the brecciation process and post-dates the quartz veins. Ab=Albite, Ccp=Chalcopyrite, Chl=Chlorite, Cal=Calcite, Ttn=Titanite, Qz=Quartz, Hem=Hem, Mo=Molybdenite, Cav=Cavity, C. U= Coarsening Upwards.



**Figure 28**. A schematic illustration of the albitization of an earlier feldspar crystal via coupled dissolution-precipitation (CDP). The cartoon represents the ideal situation where perfect pseudomorphic replacement takes place. Figure modified after that of Ruiz-Agudo et al. (2014).





**Figure 29.** Two examples showing evidence of repeated replacement of feldspar by the CDP process at the MDC. A) Euhedral crystal of hydrothermal albite (Ab $_{100}$ ) with strong microporosity with an overgrowth of K-Feldspar (Kf). Note that chlorite (Chl) is filling fractures or dissolution zones in and around the K-feldspar. B) Fine-grained hydrothermal albite  $(Ab<sub>100</sub>)$ being replaced by later K-Feldspar.



**Figure 30**. Diagrams showing the behaviour of Na<sub>2</sub>O and K<sub>2</sub>O (in wt. %) in samples from the MDC. Inverted triangles represent felsic dyke rocks, which is the group most affected by sodic alteration. For comparative purposes, the grey dots shown represent the compositions of typical igneous rocks (Cox et al. 1979) and the composition of albite (Ab) is also shown to highlight the intensity of the alteration process. Bslt=Basalt, And=Andesite, Monz=Monzonite, Rhy=Rhyolite.



**Figure 31**. Isocon diagrams (after Grant, 1986) for four felsic dykes samples with different degrees of alteration (Table 6) showing the relative gains and losses and the relative mass

changes. Major elements are plotted as % of the oxides whereas trace elements are plotted as part per million (ppm). According to Grant (1986), elements are scaled to have a clearer view and to highlight the changes in some trace elements that otherwise would not be visible. For every case, the least altered sample is the same (MI-LGC-01), an equigranular dyke from the Planet area. Samples are organised according to the sodium content. A) Sample LGC-15, B) Sample LGC-12, C) Sample LGC-13, and D) Extremely altered sample LGC-28.



**Figure 32**. A summarized illustrative diagram showing the different scales at which the sodic alteration occurs at the MDC. A) simplified ideal cross section of the MDC, felsic dykes not wider than 500m have been emplaced along the strike of the CFS close to the contact between mafic and felsic volcanic rocks; sodic alteration zones are controlled by fault or fracturing zones. B) example of an structurally controlled alteration zone like the one circled in black color in A. The felsic dykes show albite – hematite alteration for several meters in core where the movement of fluids and precipitation of albite is controlled by fracturing. C) detail of an episyenitic texture like the one circled in B; the red arrows illustrate how alkaline fluids circulated through the cavities (yellow) generated by the dissolution of quartz and mafic minerals from the original felsic dyke, facilitating the CDP processes in single crystals. D) and E) two different ways how the crystal replacement can take place. In D, a single subhedral feldspar crystal was replaced inwards keeping the shape of the crystal (pseudomorphic replacement) with high porosity observed in the newly formed mineral, whereas in E, an anhedral K-Feldspar crystal is being replaced from its core outwards, the hydrothermal fluids entered to the centre of the grain using micro-porosity, in this case the replacement is partial and not pseudomorphic, the shape of the grain is modified and two different compositions are observed in the final product.

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**Figure 33**. A generalized paragenetic sequence for the evolution of the MDC. Six stages have been observed: magmatic, deuteric, mineralisation I, episyenitisation, mineralisation 2, and late mineral stage. Note that dashed bars denote uncertainties about the timing. Red bars are used to highlight ore minerals.

## **Appendices**

## **Appendix 1. Summary of petrographic examination of thin sections**


























## **Appendix 2. Geochemical results**















## **Appendix 3. Geochronological results**









U concentration uncertainty is ~20%; individual errors are given as 2sigma standard deviation and only reflect the random error; error are 206Pb/238U = 1.2%, 207Pb/206Pb = 0.6% (2s)







