

**The Nucleus deposit: superposed Au-Ag-Bi-Cu mineralization systems at Freegold
Mountain, Yukon, Canada with constraints from titanite U-Pb dating**

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Abstract

In this paper we present titanite U-Pb (both single crystal CA ID-TIMS and *in situ* LA ICP-MS) data, coupled with ore and gangue mineralogy and geochemical (both litho-geochemistry and microanalysis) data from the Nucleus Au-Ag-Bi-Cu deposit, in the Yukon (Canada) portion of the Tintina Au province. Arsenic-bearing Au-Ag-Bi-Cu mineralization at Nucleus consists of two distinct styles of mineralization including: (i) reduced Au skarn and sulfide replacement; and (ii) a relatively shallow-emplaced (as supported by textures and temperature of formation), vein-controlled mineralization occurring mainly as veins and veinlets of various shapes (sheeted, single, stockworks, and crustiform), breccias, and disseminated. Whereas Au, Bi, and Cu mineralization from skarn is associated with hydrous retrograde alteration phases (actinolite, ferro-actinolite, hastingsite, cannilloite, and hornblende), numerous alteration types are associated with the vein-controlled style of mineralization and these include: potassic (biotitization), phyllic, argillic, propylitic, carbonate, and quartz (silicification) alterations. The mineralization-alteration processes took place over a wide temperature range that is bracketed between 340-568 °C, as indicated by chlorite and arsenopyrite geothermometers. The Au-rich Nucleus deposit is characterized by anomalously high content of As and Bi (as much as 1%), and whereas Au moderately correlates with Bi ($r = 0.40$) in the skarn mineralization style (where native Au is spatially associated with native Bi and Bi-bearing sulfides), the two elements poorly correlate ($r = 0.14$) in the vein-controlled type, in which native Bi- and Bi-sulfide-bearing veins are locally observed. Sphalerite from the vein-controlled mineralized type is Fe-rich (9.92-10.54 mol % FeS), indicative of low sulfidation conditions, as well as high temperature, with the latter further supported by arsenopyrite geothermometry (up to 491 °C), low Ag content (3-7 wt %) in Au, and the high gold fineness (926-964). Whereas molybdenite Re-Os ages from quartz-

molybdenite veins range from 75.8 to 76.2 ± 0.3 Ma, titanite from the skarn type mineralization recorded CA ID-TIMS and LA ICP-MS U-Pb ages of 182.6 ± 2.4 Ma and 191.0 ± 1.5 Ma, respectively, thus precluding any genetic link between the two spatially associated styles of mineralization from the Nucleus deposit area. The Au-Ag-Bi-Cu Nucleus deposit is therefore regarded as a superposed system in which two mineralization types, without any petrogenetic relationship, overlapped, possibly with remobilization of early formed mineralization.

Keywords: gold, skarn, vein-controlled, titanite, geochronology, Nucleus, Yukon.

1. Introduction

The Nucleus deposit, in the central Dawson Range, west central of Yukon is within the Dawson Range Cu-Au-(Mo) Belt portion of the Tintina Au Province that spans from Alaska into the Yukon, NWT, and BC and hosts significant Intrusion-Related Gold (IRG) deposits (see Hollister, 1992; Sillitoe & Thompson, 1998; Thompson *et al.*, 1999; Lang & Baker, 2001; Maloof *et al.*, 2001; Marsh *et al.*, 2003; Hart, 2007), such as Fort Knox (proven and probable reserves of 314.669 Mt at 0.43 g/t Au, Kinross Gold Corp, 2012), Donlin Creek (proven and probable reserves of 504.8 Mt at 2.09g/t Au, http://www.novagold.com/_resources/donlin_gold), and Pogo (total reserve and resource of 12.332 Mt at 12.5 g/t Au, Sumitomo Metal Mining Co, Ltd., 2012) in Alaska, and Dublin Gulch (probable reserves of 92 Mt at 0.78 g/t Au, Victoria Gold Corp., May 29, 2015 news release) and Brewery Creek (indicated mineral resources of 14.1 Mt at 1.27 g/t Au, Golden Predator, November 12, 2014, News) in Yukon.

The Nucleus deposit has an indicated resource of 1.31 M ounces of gold, within 74.7 Mt at 0.55 g/t Au with a cutoff grade of 0.3 g/t (NFR, March 25, 2015 news release) and it is characterized by two distinct styles of mineralization including: (i) skarn and sulfide replacement bodies and; (ii) vein-controlled mineralization style. The petrogenetic age from the latter was constrained at 75.9 ± 0.3 to 76.2 ± 0.3 Ma (molybdenite Re-Os ages, Bineli Betsi *et al.*, 2013), whereas the age from the skarn mineralization style was unknown. Considering the wide age discrepancy (68 to 190 Ma, Bineli Betsi & Bennett, 2010) of magmatic rocks spatially associated with mineralization across the Freegold Mountain area, the two contrasting styles of mineralization may be related to different magmatic events and consequently it is necessary to

constrain the temporal and by inference the genetic relationship between the two types of mineralization.

In this paper the mineralization styles, mineral parageneses, alteration patterns, ore mineral chemistry, and geochemical data of the two contrasting types of mineralization are presented. This paper also includes titanite U-Pb geochronology (both ID-TIMS and LA ICP-MS) data, which are compared with previously published molybdenite Re-Os data in order to constrain the genetic relationship between the two styles of mineralization from the Nucleus deposit. Textural observations are combined with geochemical anomalies to properly characterize the Nucleus deposit. Micro-analytical results and pertinent experimental and thermodynamic data are used to determine physico-chemical features of mineralizing fluids and to constrain Au-Bi-Cu deposition processes.

2. Geological Setting

The Nucleus deposit is located within the NW-trending interior mountain belt of the Dawson Range, which is part of the Intermontane Belt of the Northern Canadian Cordillera (Gabrielse *et al.*, 1991). The Dawson Range is bounded by two major NW-trending fault systems, i.e., the Tintina Fault to the northeast and the Denali Fault (Shakwak) to the southwest (Fig. 1; after Colpron & Nelson, 2011). The geology of the Nucleus Deposit is thoroughly presented in Bineli Betsi & Bennett (2010) and Sexton *et al.* (2013). As a summary, the Nucleus deposit is underlain by strongly deformed, locally mylonitic, metasedimentary, and meta-igneous schistose and gneissose rocks of probable Devonian to Mississippian and older ages of the pericratonic Yukon-Tanana terrane (YTT), which represents a composite of terranes that were accreted to the North

American continent during early Mesozoic time (Colpron *et al.*, 2006). Regional metamorphic grade varies from greenschist to amphibolite facies (Payne *et al.*, 1987). Within the Nucleus main ore zone, the Yukon-Tanana terrane had been intruded by numerous plutonic bodies that in turn are crosscut by dike swarms mostly oriented east-west (Fig. 2). Both plutons and dikes are mostly of granitic and locally of granodioritic compositions, essentially peraluminous, and were classified as ilmenite and S-type granitoids (Bineli Betsi & Lentz, 2009; 2011). Plutonic bodies are mainly composed of: (i) medium-grained, and equigranular leucogranite; (ii) fine-grained, foliated and unfoliated, locally porphyritic leucogranite (microgranite of Sexton *et al.*, 2013), and; (iii) rare medium-grained biotite-hornblende granite. Dike swarms include: (i) Middle Cretaceous (104-105 Ma, Bineli Betsi & Bennett, 2010) that probably belong to the Middle Cretaceous Whitehorse Plutonic Suite of Gordey & Makepeace (2000) and (ii) Late Cretaceous (ca 76 Ma, V. Bennett personal communication, 2011) porphyritic and aplitic bodies that belong to the Casino Plutonic Suite (see Johnston, 1995).

The Big Creek Fault is the major structure in the study area (Fig. 2), a prominent northwest-trending topographic and aeromagnetic feature of regional scale that extends across the Freegold Mountain area. The Big Creek Fault is considered as an important structure controlling the distribution of numerous copper porphyry and related epithermal deposits and structurally hosted gold deposits, as well as associated placer gold across the region (Carlson, 1987).

3. Methods

Mineralized samples analyzed in this study were collected from Nucleus drill core, and investigations on different parageneses and alteration mineral assemblages were done using both transmitted and reflected light microscopy. In order to complement alteration-related investigations, some altered rock samples were analyzed by X-ray diffraction (XRD).

Chemical compositions of some of skarn gangue minerals (hornblende, epidote, and chlorite), sulfide, and native Au and Bi were assessed with electron probe micro-analysis (EPMA), using a JEOL JXA-733 microprobe, equipped with four wave length dispersive spectrometry (WDS) detectors at the University of New Brunswick. This was conducted on carbon-coated polished thin sections and the operating parameters for sulfide, Au and Bi analyses were 15 kV and 50 nA and both synthetic and natural standards were used. Quantitative scanning electron microscope-energy dispersive spectrometry (SEM-EDS) was used for determination of chemical composition of a fine-grained composite Bi-bearing mineral. Gangue minerals were analyzed on operating conditions that included an accelerating voltage of 15 kV, a probe current of 30 nA, counting times on peaks of 30s, except for epidote (90 s) and high and low backgrounds were each counted for 15 s.

Geochronological studies were carried out to constrain the absolute timing relationships between the vein-controlled mineralization type that was previously dated (see Bineli Betsi *et al.*, 2013) and the key skarn mineralization type. Titanite from the skarn deposit was dated using both U-Pb conventional abrasive isotope dilution thermal ionization mass spectrometry (CA ID-TIMS) and laser ablation inductively coupled plasma-mass spectrometry (LA ICP-MS) techniques. CA ID-TIMS was conducted at the Pacific Centre for Isotopic and Geochemical Research in the Department of Earth and Ocean Sciences, University of British Columbia, where

all sample preparation and isotope measurements were completed. Titanite grains were separated from the sample using conventional crushing, grinding, and Wilfley table techniques, followed by final concentration using heavy liquids and magnetic separations. Mineral fractions for analysis were selected on the basis of grain quality, size, magnetic susceptibility, and morphology. Masses were determined with a Sartorius SE2 ultramicrobalance to ± 1.0 micrograms. Grains were transferred into 300 μl PFA microcapsules (crucibles) and 0.1 ml subboiled 29N HF and 14N HNO_3 in a 10:1 mixture was added. Each fraction was spiked with EARTHTIME ET535 $^{233}\text{-}^{235}\text{U-}^{205}\text{Pb}$ tracer solution (typically 3 mg), capped and placed in a 125ml Teflon liner (8-13 microcapsules per liner), which in turn went into Parr-style stainless steel high pressure dissolution devices for 7-10 days at 240 $^{\circ}\text{C}$. Sample solutions were then dried to salts at 130 $^{\circ}\text{C}$ and residues were dissolved in 100 ml of sub-boiled 6.2 M HCl in oven in high pressure devices for 12 hours at 210 $^{\circ}\text{C}$. These solutions were again dried to salts and were again dissolved in 3.1 N HCl in high pressure devices for at 210 $^{\circ}\text{C}$ for 12 hours. Purification of Pb and U employed ion exchange column techniques modified slightly from those described by Parrish *et al.* (1987). Lead was eluted into PFA teflon beakers and U into a second set of beakers and further purified by passing through columns a second time. U was then eluted into beakers containing Pb. Elutants and dried in 7 ml screwtop PFA beakers on a hot plate at 120 $^{\circ}\text{C}$ in the presence of 2 μl of ultrapure 0.2N phosphoric acid (H_3PO_4). Samples were loaded onto degassed, zone-refined Re filaments in 2 μl of silicic acid emitter (Gerstenberger & Haase, 1997). Isotopic ratios were measured using a modified single collector VG-54R thermal ionization mass spectrometer equipped with an analogue Daly photomultiplier. Measurements were done in peak-switching mode on the Daly detector. Analytical blanks during the course of this study

were 0.2 pg for U and 5 pg Pb. Fractionation was determined directly on individual runs using the $^{233}\text{-}^{235}\text{U}$ tracer, and Pb isotopic ratios were corrected for fractionation of 0.23%/amu, based on replicate analyses of the NBS-982 Pb standard and the values recommended by Thirlwall (2000). Data reduction employed the Excel based program of Schmitz & Schoene (2007) and standard concordia diagrams were constructed and regression intercepts, weighted averages calculated with Isoplot (Ludwig, 2003). Unless otherwise noted, all errors are quoted at the 2σ or 95% level of confidence.

Laser Ablation Inductively Coupled Plasma-Mass Spectrometry (LA ICP-MS) was conducted using a Resonetics M-50-LR 193nm Excimer laser ablation system at the University of New Brunswick, Department of Earth Sciences. Samples and standards (520 Ma Khan Mine titanite age standard and NIST glass for tuning) were loaded together in a two-volume low-volume Laurin Technic Pty sample cell and ablation was conducted in a pressurized high-purity He atmosphere (~ 750 mL/min). Laser crater sizes were $44\ \mu\text{m}$ and ablation was carried out at a fluence of $\sim 3.5\ \text{J}/\text{cm}^2$ and a repetition rate of 5 Hz. Ablation products were combined with Ar (650 mL/min) and N_2 (2.8 mL/min) downstream of the ablation cell and carried to the ICP-MS using Nylon tubing. A Laurin Technic Pty ‘Squid’ smoothing device was placed between the ablation cell and the ICP-MS torch. Isotope abundances for ^{44}Ca , ^{49}Ti , ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th , and ^{238}U were collected with a total sweep time of 0.4 sec using an Agilent 7700x quadrupole ICP-MS. For U-Pb geochronology, the ICP-MS is tuned on either NIST 612 or 610 to achieve $^{248}\text{ThO}/^{232}\text{Th} < 0.3\%$, $^{238}\text{U}/^{232}\text{Th} \sim 1.05$, and doubly-charged production $\leq 1\%$. An ablation sequence is defined that includes a measurement of Khan Mine titanite after every three to four unknowns with NIST glass analyzed at the start and end of the sequence. Positioning of

craters was guided by backscattered electron images of the target grains, which were imported into the laser ablation software (Resonetics Geostar) as semi-transparent overlays on the optical image. A 30 second background collection was followed by a short 3 laser pulse cleaning step, a 10 second delay, and then 30 seconds of ablation. This ablation sequence is run semi-automatically (i.e., under user supervision for fine tuning crater locations) and the time-resolved intensity data are collected in a single ICP-MS file. Data are exported from the ICP-MS software as counts/second and isotope ratios and elemental abundances were calculated offline using Iolite version 2.15 (released October 21st, 2011) using procedures outlined in Paton *et al.* (2010).

4. Types of mineralization

The Nucleus deposit is comprised of two main gold mineralization types hosted by metasedimentary and plutonic rocks. The two spatially overlapping mineralization types (Fig. 3) include: (i) skarn and sulfide replacement bodies, and; (ii) a relatively shallow-emplaced, vein-controlled deposit type. Of note is that the spatial distribution of the two different styles of mineralization is beyond the scope of this manuscript and this may be the focus of an upcoming investigation.

4.1 Skarn and sulfide replacement bodies

Skarn bodies occur primarily as massive thick lenses (up to 35 m apparent thickness) that are rarely banded and locally vuggy. Massive skarn is essentially coarse grained and locally fine grained (where calc-silicate alteration overprints fine-grained dikes). Coarser grained massive skarn (Fig. 4A) formed after moderately calcareous amphibole-schist of the YTT basement rocks

and where the replacement is partial, the primary texture (foliation) of the protolith (amphibole-schist) is still recognizable. The transition from the partial to complete replacement is locally observed and appears gradual. Banded skarn (Fig. 4B) is locally observed within the Nucleus deposit and it occurs as monomineralic pyrrhotite-rich layers alternating with sulfide-poor and polymineralic calc-silicate layers. The thickness of pyrrhotite-rich layers varies from millimeter, up to 0.5 cm.

Skarn mineralogy at Nucleus is dominated by retrograde hydrous alteration phases including mostly amphibole and biotite, with minor chlorite, tourmaline, and epidote. Amphibole is typically calcic and displays a wide compositional range that includes tschermakite, actinolite, magnesio-hornblende, hastingsite, cannilloite, and ferro-actinolite (Table 1), whereas epidote group minerals are of Fe-Al-rich type and correspond to the pistacite end member (Table 2). Chlorite from skarn mineralization type is Fe-rich, Ti-poor (Table 3), and its Al (Al^{IV}) abundance was used to calculate the temperature at which, chlorite associated with skarn formed. The geothermometry data obtained are reported in Table 3 and discussed in section 7.3.1. Locally, coarse-grained prograde garnet was observed and in places it was overprinted by retrograde amphibole and pyrite (Fig. 4C). Garnet typically occurs as anisotropic and zoned crystals, which are locally fibrous and is typically of grossularite and andradite compositions (Table 4). Full data set of garnet composition can be found in digital appendix 1. Furthermore, some skarn facies from the Nucleus deposit are characterized by their elevated content (up to 60 vol. %) of euhedral quartz (Fig. 4D-F). The presence of euhedral hexagonal quartz, as well as excellent triangular texture of chalcopyrite around quartz crystals (Fig. 4D and 4E), is characteristic of open space filling (see Taylor, 2009). Open space filling features are further supported by

remaining void spaces (incomplete filling) locally observed in some skarn from Nucleus (Fig. 4F). This suggests both replacement (alteration) and infill processes led to formation of contact metasomatic skarn that formed the Nucleus deposit.

Ore minerals associated with both alteration and infill skarn include pyrrhotite, chalcopyrite, various unknown Bi-sulfides, native Bi and Au, and minor arsenopyrite. The mode of occurrence of skarn ore minerals is depicted from Figures 5 and 6. This paragenesis is similar to numerous gold skarn mineralization occurrences within the Tintina Au Province, such as at the Nixon Fork deposit (see Flanigan *et al.*, 2000). Of note is that pyrite and pyrrhotite at Nucleus are rarely spatially associated and where they locally occur together, skarn is sharply zoned and displays a pyrite zone and a pyrrhotite zone (Fig. 4J). Sulfide content in skarn is highly variable and ranges from < 4 vol. % to >70 vol. %, thus leading locally to massive pyrite and pyrrhotite (Fig. 4H and 4I). Magnetite skarn was also observed and consists of a magnetite (mostly)-amphibole-epidote-quartz-feldspar assemblage that is overprinted by stockwork veinlets.

In terms of the paragenetic sequence (Fig. 7), the gangue and ore minerals observed from the Nucleus skarn likely formed through three main stages including: (i) the prograde 1 stage; (ii) the prograde 2 stage; and (iii) the retrograde stage (Fig. 7). The prograde first stage silicate mineralogy consists mostly of garnet, whereas the prograde 2 stage mineralogy consists mostly of quartz, calcite, pyrite, pyrrhotite, native Au, minor feldspar and at lesser amounts of chalcopyrite occurring at the end of this stage (see Fig. 7). The retrograde stage silicates consist mostly of amphibole (actinolite, ferro-actinolite, hornblende, hastingsite, and cannilloite) and minor biotite, chlorite, quartz, carbonate, and epidote, whereas ore minerals related to this stage

comprise dominantly pyrrhotite and native Au and Bi, and subordinate chalcopyrite, Bi-bearing sulfide and sulfosalts, arsenopyrite, and magnetite.

Sulfide replacement bodies (Fig. 8) are observed within both foliated and unfoliated granitic plutons and felsic porphyries. Within the foliated bodies (Fig. 8A), replacement occurs mostly along the foliation plane with sulfides also randomly distributed and crosscutting the foliation. This may indicate that mineralization occurred after shearing and mineralized fluids used the foliation plane to focus fluid flow and precipitate metals. In unfoliated bodies (Fig. 8B and 8C), sulfide replacement is either pervasive (Fig. 8B) or selectively replaces the groundmass, whereas phenocrysts are the least altered (Fig. 8C). In both foliated and unfoliated rocks, replacement by sulfides grades from disseminated through semi-massive to massive with progressive replacement of the primary structure and mineralogy of the host rock. Gangue minerals associated with sulfidized rocks consist of the following assemblages: (i) carbonate + minor chlorite and muscovite, and relict quartz, and; (ii) biotite-carbonate \pm chlorite. In sulfide replacement zones, native Au occurs as spatially interlocked with pyrite as it can be clearly discerned from Figures 5 and 6.

4.2 Vein-controlled mineralization

Vein-controlled mineralization occurs as various styles including: (i) veins; (ii) breccias, and; (iii) disseminated types. Veins, disseminations and breccias mineralization styles are included in the same main deposit type, because of the similarities in terms of mineralogy and alteration patterns. Veins within the Nucleus deposit occur as numerous sets (Fig. 9) with variable mineralogy, shapes, and textures that cut and are crosscut by intrusions thus suggesting multiple

cycles of fluid flux from intrusion(s) (see Bineli Betsi & Lentz, 2011) and vein emplacements. The dominant vein/veinlet types identified at the Nucleus deposit, as reported in Table 5, are classified by mineralogy, and structure into the following groups: quartz-pyrite veinlets, quartz-sulfide veins, quartz-sericite veinlets, molybdenite veins, Au-bearing veins, Bi-rich veins, arsenopyrite-rich veins, and late carbonate veins (see Table 5). The mode of occurrence of vein-controlled mineralization is depicted in Figures 4 and 5, where native Au is observed to occur either enclosed in pyrite (Fig. 5C), or related to later Au-bearing silica veinlets cutting along an early-formed vein (Fig. 5D), suggesting multiple Au mineralization events. Of note also is that, whereas native bismuth is mostly associated with pyrrhotite in skarn deposit type, native Bi in vein-controlled mineralization type is mostly associated with Bi-sulfides (see Figs. 5, 6).

Breccias (Fig. 10) related to the vein-controlled mineralization types from the Nucleus deposit are of various styles as portrayed in Table 6. According to the classification of Laznicka (1989) and Jebrak (1997), these breccias can be classified into the following groups (Table 6): (i) fault-related; (ii) hydrothermal, and; (iii) intrusive breccias. Based on the nature of the infilling, mineralized fault-related breccias are subdivided into; (i) oxidized, and; (ii) sulfide-rich breccias. Oxidized fault-related breccias (Fig. 10A) that are Au enriched can also be subdivided into: polymictic clast-supported, crackled, and matrix-supported breccias. Sulfide-rich fault-related breccias (Fig. 10B-D) have been overprinted by hydrothermal fluid flow at a later stage with respect to tectonic brecciation and they are subdivided into 3 different groups including: (i) pseudotachylite; (ii) cataclasite, and; (iii) matrix- to clast-supported breccias (see Table 6). Hydrothermal breccias are rare, and mainly occur as stockwork breccias resulting from multi-directional quartz-sericite-bearing vein arrays that crosscut the host rocks in several areas, thus

leading to jigsaw clast-supported breccias (Fig. 10E). Intrusive breccias from Nucleus are discriminated into two subtypes: (i) sulfide-bearing intrusive breccias, and; (ii) chalcedony-bearing intrusive breccias (see Table 6). Ultra-fine quartz and chalcedony is diagnostic of high level epithermal environments (see Corbett, 2002) and this testifies to the relatively shallow emplacement of these breccias.

Whereas skarn and sulfide replacement mineralization types are typified by silicification and carbonatization, respectively, the vein-controlled mineralization at Nucleus is associated with numerous alteration types (Table 7) comprising in chronologic order of appearance (based on field crosscutting relationship): biotitization, phyllic alteration, silicification, propylitic alteration, carbonatization, and argillic alteration, with supergene weathering of these.

Compositions of chlorite associated with skarn, propylitic, and potassic (biotitization) alteration, as well as the calculated temperatures of formation of each alteration type are reported in Table 3. The gangue and ore minerals associated with each alteration type, as well as the mode of occurrences of the different alteration types are depicted in Table 7. Alteration mapping and therefore spatial distribution of alteration types is beyond the scope of the current investigation. The sericite mineral as stated in Table 7 refers to numerous white mica types as identified by XRD, which include: muscovite, vanadian muscovite, muscovite (3T), and phengite.

Carbonatization is probably one of the major alteration processes controlling the mineralization within the Nucleus deposit: it is visually correlated, i.e. spatially associated with native Au and Bi, as well as Bi-bearing minerals in both sulfide replacement bodies and in vein-controlled deposit types. For example, sulfidized bodies associated with carbonate alteration are locally highly Au-enriched (up to 402 g/t Au: GRD 08-99; 113.28-114.55 m). Oxidation may also

locally contribute to the Au budget from the Nucleus deposit as indicated by the Au content (up to 256 ppm (g/t): GRD 08-114; 22.67-23.63 m) of sulfide-free and oxidized bodies.

The interpreted paragenetic sequence from vein-controlled mineralized deposit, presented in Figure 11 was determined by careful observation and documentation of vein crosscutting relationships and overprinting textures. The early-phase paragenesis in vein-controlled mineralized type from the Nucleus deposit was a pyrite \pm magnetite \pm chalcopyrite \pm sphalerite \pm arsenopyrite assemblage from quartz-sulfides vein types (see Table 5). This was followed by molybdenite \pm pyrite \pm chalcopyrite assemblages from molybdenite-vein types, and then pyrite-chalcopyrite-sphalerite \pm arsenopyrite \pm native Au \pm Bi-Bi-sulfide \pm galena \pm pyrrhotite assemblage from the Au-bearing vein types; and arsenopyrite-(pyrite)-(chalcopyrite)-(tennantite/tetrahedrite) assemblage. Veins were reopened later, thus leading to additional deposition of Au and tennantite/tetrahedrite. The latest mineralization event is related to the weathering process that additionally concentrated Au (either by relative enrichment when sulfides are leached or by remobilization) and formed minor amount of secondary Cu-Fe sulfides, such as chalcocite, digenite, covellite, and bornite.

5. Chemical Composition of Ore Minerals

Chemical compositions of sulfide minerals from the Nucleus deposit are reported in Tables 8 and 9. Based on their chemical compositions (see Table 8), bismuth-bearing minerals from Nucleus can be discriminated into three main types: (i) Bi-sulfide; (ii) Bi-Te-(S-Se)-sulfide, and; (iii) Bi-Pb \pm Sb sulfide. Bi content of Bi-S sulfides is between 78.23-92.60 wt % Bi and the Pb content

of Bi-Pb \pm Sb sulfide is greatly variable (7.16 - 41.26 wt. %). Significant Pb variation is even reported between different species of a single minerals aggregation (7.16 and 40.99 wt. % Pb, see Table 8). Bi-Te-(S-Se) sulfide is composite and displays an S-bearing core composed on average (mean) of S (5.37 wt %), Te (30.33 wt. %), Bi (63.16 wt. %), Se (0.45 wt. %), and Fe (0.96 wt %), whereas the outer shell is S-free and composed on average (mean) of Te (31.19 wt. %), Bi (67.18 wt. %), Se (0.55 wt. %), and Fe (1.30 wt. %).

Sphalerite has >50 wt. % Zn, and is typified by its elevated Fe content (>10 wt. % Fe, equating to 9.92-10.54 mol % FeS). Sphalerite additionally contains Cu and Cd (1.10-1.53 and 0.53-0.64 wt. %, respectively). Arsenopyrite contains between 41.97- 47.12 wt. % As (equivalent to 29 15-33.20 at. %) and Fe (34.85-35.68 wt. %). The composition of arsenopyrite (at % As) in equilibrium with either sphalerite or pyrite was used to calculate the temperature at which, vein-controlled mineralization formed, as discussed in section 7.3.1. Tennantite exhibits >15 wt. % As and its Ag content is variable (mean: 0.57 wt. % Ag for late stage tennantite and 0.01 wt. % Ag for earlier formed tennantite). Late- and early-formed tennantite are further discriminated on the basis of their mean Zn content (0.12 wt. % and 0.00 wt. %, respectively) and mean Sb content (7.45 wt. % and 5.17 wt. %, respectively). The tennantite low Ag content is balanced by its elevated Cu content (mean: 40 wt. %) and Fe (7.04-8.14 wt. %), which substitute Ag in the structural formulae of fahlore [(Cu, Fe, Ag, Zn)₁₂(As, Sb)₄S₁₃]. Tetrahedrite, with 19.55 wt. % Sb, is Ag-poor as well (0.09 wt. %), and is characterized by a measurable Bi (0.26 wt. %). Like tennantite, Cu and Fe contents are high (38.61 and 5.64 wt %, respectively). Arsenic content is 7.61 wt. %, and unlike tennantite, Zn abundance is relatively elevated (1.19 wt. %).

Pyrite from the vein-controlled mineralization type is discriminated into As-poor (0.00-0.11 wt. %) and As-rich (1.00-1.40 wt. %) pyrite. The Fe contents of As-rich and As-poor pyrite overlap within the analytical error (44.55-45.47 and 45.84-46.15 wt. %, respectively). Native Au grains from both skarn and vein-controlled mineralization style are Bi, Te, and Hg-free, typically Ag bearing (3.18-7.36 wt. %) and Au content ranging from 92.60 to 98.20 wt. % (Table 10). The gold fineness is variable through the different mineralization styles: 966.5 for sulfide-carbonate replacement; 926.4 for skarn (massive pyrrhotite); and spans a narrow composition range (between 935.4 and 964.4) for veins. Native Bi grains from skarn and vein-controlled mineralization have Bi content of 99.10 and 99.5 wt. %, respectively, and in most cases, they are Au-Ag- and Te-free (Table 10). Exceptions, however, are rounded native Bi grains (Bi liquid?) associated with late carbonate veinlets crosscutting massive pyrrhotite that yielded up to 18.70 wt. % Au and 83.10 wt. % Bi. Also, whereas native Bi from skarn is totally sulfide-free, native Bi grains from veins contain up to 0.20 wt. %t Sb.

6. U-Pb Geochronology

Titanite from an amphibole-biotite skarn (TB 400-2: GRD 08-94, 259.15 m) was dated by both CA ID-TIMS U-Pb and LA ICP-MS U-Pb techniques. Titanite CA ID-TIMS U-Pb data are reported in Table 12. Of four analyzed titanite fractions three resulted in overlapping concordant points (Fig. 13A), giving a weighted mean $^{206}\text{Pb}/^{238}\text{Pb}$ age of 182.6 ± 2.4 Ma (Fig. 13B). This Early Jurassic age indicates the skarn mineralization formed prior to spatially associated Late Cretaceous vein-controlled mineralization of 75.9 ± 0.3 Ma (Bineli Betsi *et al.*, 2013).

Titanite LA ICP-MS U-Pb dating was carried out on four titanite grains (1, 2, 3, and 4) from the polished thin section shown in Fig. 14. Preliminary back scattered electron (BSE) imaging work was undertaken prior to laser ablation ICP-MS and SEM-BSE images show that apart from titanite grain 3 that displays distinct growth zones, the other grains are relatively homogeneous. Skarn titanite LA ICP-MS U-Pb data from 15 analyses are reported in Table 13 and the best estimate for the age of the titanite is 191.0 ± 1.5 Ma (Fig. 15), although three analyses (Ttn1-2, Ttn2-3, and Ttn3-2) that lie along a somewhat younger (e.g., 167 Ma) isochron. Of the three younger analyses, only one (Ttn3-2) was performed on obvious compositional zone.

7. Discussion

7.1 Nature and genesis of the skarn mineralization

The mineralogy and trace-element signature (Au-Ag-Bi-Cu) skarn, with Te and As, from the Nucleus deposit is typical of reduced gold skarns (cf. Einaudi *et al.*, 1981) and shares similarities with numerous reduced Au skarns, such as the Fortitude deposit, Battle Mountain District in Nevada (Myers & Meinert, 1991), and the Nickel Plate deposit in the Hedley District, British Columbia (Ray *et al.*, 1996; Ettliger *et al.*, 1992; Ray, 2013), as well as with intrusion-related pyrrhotite vein and reduced porphyry Cu-Au systems as described by Rowins (2000), such as the Rossland and 17 Mile Hill deposits in British Columbia and Western Australia, respectively. However, unlike most reduced Au skarns, where prograde alteration phases (pyroxene and

garnet) are associated with Au mineralization (see Meinert, 1995; Meinert *et al.*, 2003, 2005), Au-Bi-chalcopyrite-pyrrhotite mineralization from the Nucleus deposit is associated with actinolite and other hydrous retrograde alteration phases (actinolite, ferro-actinolite, hornblende, cannilloite, and hastingsite) that are the predominant alteration. Amphibole was also observed to be a primary alteration phase associated with mineralization at the Beal, Montana, reduced Au skarn deposit (Wilkie, 1996) and in the Marn property, Yukon (Brown & Nesbitt, 1987). Amphibole phases at the Nucleus deposit may have obliterated the prograde garnet, since garnet was observed being overprinted by amphibole (see Fig. 4C). Such an obliteration process was also observed in the Marn property, Yukon (Brown & Nesbitt, 1987) and in some shallow, porphyry copper-related skarn systems, where extensive retrograde alteration almost completely obliterates the prograde alteration phases (see Einaudi & Burt, 1982).

Skarn from the Nucleus deposit is primarily coarse-grained, suggesting a magmatic origin (cf. Meinert, 1983, 1992). In order to investigate the temporal relationship between the Nucleus mineralization and the spatially associated magmatic rocks, two molybdenite samples from molybdenite-vein types of the vein-controlled-mineralization type were dated by the Re-Os technique (Bineli Betsi *et al.*, 2013). This yielded similar ages of 75.9 ± 0.3 Ma (Bineli Betsi *et al.*, 2013), which were interpreted as the time whereby molybdenite-bearing veins and by inference vein-controlled mineralization formed within the Nucleus deposit. The study conducted by Bineli Betsi *et al.* (2013) therefore ascertained the temporal and/or genetic relationship between the vein-controlled mineralization type and the spatially associated Late Cretaceous magmatic rocks. In the present study, the age of skarn mineralization was investigated in order to quantify the absolute timing between the skarn and the vein-controlled

mineralization styles. Field crosscutting relationships, where skarn is observed to be crosscut and disrupted by the leucogranites as shown in Figure 12, may already suggest skarn is of relatively old age with respect to the non-dated leucogranite of probably Middle-to Late Cretaceous age, which in turn may be of the same age as the vein-controlled mineralization. Because of the suitability of titanite in dating skarn (see Romer & Soler, 1995) and various types of hydrothermal alteration (see Frost *et al.*, 2000), titanite from an amphibole-biotite skarn was dated by both CA ID-TIMS U-Pb and LA ICP-MS U-Pb techniques. Titanite CA ID-TIMS U-Pb dating yielded an age of 182.6 ± 2.4 Ma, suggesting the skarn mineralization formed prior to spatially associated Late Cretaceous vein-controlled mineralization and thus supporting the field crosscutting relationship mentioned above.

In order to make sure the Jurassic age obtained is not the effect of inherited cores, which titanite can contain (cf. Pidgeon *et al.*, 1996), titanite grains from the same sample were dated by LA ICP-MS, since this technique, with a robust common Pb correction, is likely to yield data that are as accurate as CA ID-TIMS data (see Storey *et al.*, 2006). The investigated polished thin section shows a close spatial relationship between sulfides (pyrite primarily and minor chalcopyrite) and titanite grains, suggesting concomitant precipitation between titanite and sulfides (and by inference the reduced Au-Bi skarn mineralization event). The obtained best estimate for the titanite LA ICP-MS age is of 191.0 ± 1.5 Ma, once more precluding any genetic relationship not only between Middle to Late Cretaceous magmatic rocks (primarily found in the Nucleus deposit main ore zone) and skarn mineralization, but also between skarn and the vein-controlled mineralization types. Therefore, the skarn's causative intrusion at the Nucleus deposit still needs to be clearly identified. However, the Early Jurassic age from the Nucleus deposit

skarn is consistent with Jurassic magmatism in many parts of the NFR Freegold Mountain project and of the YTT and of note is that similar Jurassic age was obtained 20 km south east of Nucleus from an aplitic dike from the NFR Tinta property (e.g., Bineli Betsi & Bennett, 2010) and was interpreted as inherited core ages. Likewise, calc-silicate alteration overprinting of fine-grained dike suggests an Earlier Jurassic or older dike event within the Nucleus Deposit. Similar Early Jurassic hydrothermal event was already reported within the Carmacks Copper Belt, and especially at the Minto Cu-(Au) deposit located to the east (Hood *et al.*, 2009), where coarse-grained muscovite yielded an Ar-Ar plateau age of 182 ± 1 Ma (see Tafti & Mortensen, 2004). Elsewhere in the northern Canadian Cordillera, Jurassic porphyry Cu-Au \pm Mo and epithermal Au \pm Ag mineralization are known in the Toodogone District of central British Columbia (Duuring *et al.*, 2009). It is reasonable to argue that the skarn's causative intrusion is a blind Jurassic magmatic body at depth nearby the Nucleus property. Meinert *et al.* (2005) however pointed out that pluton emplacement is not necessary required to form skarn, which also can form by metamorphism of pre-existing ore deposit (cf. Gemmell *et al.*, 1992) or along faults and major shear zones (Meinert *et al.*, 2005). . But our data (including the skarn mineralogy and texture and geochronology data) are in favor of skarn genesis process lead by a blind Jurassic magmatic body probably at depth, so there is considerable exploration potential for further Jurassic skarn and intrusion-related mineralization.

7.2 Nature of the vein-controlled mineralization

Recent technical reports (Sexton *et al.*, 2013, 2015) classified the Nucleus Deposit as “a low grade, bulk tonnage, intrusive related low sulfidation epithermal gold deposit, with a Au-Cu

massive sulfide component”, based on geology, styles of mineralization, and structure. In this study, the massive sulfide component is referred to as skarn and sulfides replacement, whereas the intrusive related low sulfidation epithermal gold deposit correspond to our vein-controlled mineralization type.. But the textures, styles of mineralization, alteration patterns, mineralogical association, geochemical anomalies, and metal distribution, as well as the composition of spatially associated igneous rocks, indicate the vein-controlled mineralization from Nucleus shares similarities with various classes of magmatic-hydrothermal deposits including: (i) porphyry system (see Seedorff *et al.*, 2005); (ii) Reduced Intrusion Related Gold Systems (see Hollister, 1992; McCoy *et al.*, 1997; Thompson *et al.*, 1999; 2000; Lang & Baker, 2001; Maloof *et al.*, 2001; Hart, 2007) and especially intrusion-related Au-Bi deposits (cf. Baker *et al.*, 2005), and; (iii) low sulfidation epithermal quartz-sulfide-gold \pm copper deposits (Corbett, 2002). Based on its textures (veins, breccias and locally colloform minerals as shown in Fig. 6 continued A), it is reasonable to assume that the vein-controlled mineralized component of the Nucleus deposit formed at relatively shallower crustal level compared to the skarn mineralization. However, arsenopyrite geothermometry (340-491 °C, obtained by superimposing phase relationship for Fe-Zn-S system and phase relationship Fe-As-S system (see Kretschmar & Scott, 1976; Scott, 1983)), as well as the native Au depletion in Ag (3.18-7.36 wt %) and the subsequent high gold fineness (935- 964.4), are consistent with mineralization formed at relatively greater depth and temperature with respect to epithermal deposits formed at temperatures < 300 °C and therefore at upper level crustal settings, typically <1 km (Heald *et al.*, 1987). Nevertheless, some deposits described as “epithermal” formed at relatively high temperatures and deep crustal levels (e.g., Kelian; Corbett and Leach, 1998), and some low sulfidation quartz-sulfide gold \pm copper formed

at deeper crustal levels are transitional to porphyry Cu-Au systems (e.g., the Cadia, Maricunga Belt; Corbett, 2002). Therefore, the vein-controlled mineralization type is reasonably classified here as low sulfidation deposit that formed at a transitional level between the classical porphyry deposit and epithermal deposit. The elevated Fe content of sphalerite further testifies to the low sulfidation conditions (see Hannington & Scott, 1999) that prevailed during the formation of the Nucleus vein-controlled mineralization type. The presence of sheeted veins may simply reflect the structural control of the hydrothermal fluid (Taylor, 2007), and especially along a strongly dilational structural setting. Because the vein-controlled mineralization type was later emplaced, with respect to the skarn mineralization type (as discussed in the section above), possible remobilization of metals from the earlier-formed skarn is not excluded .

7.3 Physicochemical features of the mineralizing fluids and its evolution

7.3.1 Temperature and its evolution

Chlorite is a widespread mineral within the Nucleus deposit and it occurs both in the skarn and the vein-controlled deposits. In the latter, chlorite is associated with biotite alteration, propylitic alteration (chlorite-actinolite-tremolite), and quartz-carbonate-chlorite veins (propylitic alteration). Chlorite composition is known to reflect the physicochemical conditions under which it formed (Cathelineau & Nieva, 1985; Cathelineau, 1988; Kavalieris *et al.*, 1990; De Caritat *et al.*, 1993). In metamorphic environments, it has been demonstrated that the amount of Al substituting for Si in the tetrahedral site (Al^{IV}) increases with increasing temperature (Powell & Holland, 1990). The chlorite compositions from the Nucleus two types of mineralization were

measured in order not only to bracket the evolution of hydrothermal fluid temperatures, from biotitization to propylitization (in vein controlled-mineralization style), but also to investigate the temperature difference between the two types of mineralization.

The empirical calibration ($T(K) = -61.92 + 321.98 Al^V$; Cathelineau, 1988) was used to calculate temperatures at which chlorite from different alteration types formed (see Table 3), since the robustness of this temperature-sensitive substitution was confirmed from geothermal systems (formed in the temperature range of 130 to 310 °C, Bevins *et al.*, 1991), and lower and higher temperatures chlorite species (see Eaton & Setterfield, 1993; Panigrahi *et al.*, 2008). In the vein-controlled mineralization style, chlorite from quartz-(carbonate)-chlorite veins formed at the highest temperatures (481 to 568 °C), whereas chlorite associated with biotite alteration halo formed at average mean temperature of 459 °C and chlorite from actinolite-tremolite propylitic vein exhibits the lowest temperature (mean: 409 °C). Chlorite associated with skarn formed at average mean temperature of 441 °C, which is near equal to temperature of formation of chlorite in the biotitic alteration halo. The calculated temperatures are compatible with the known temperature ranges of potassic, skarn, and propylitic alterations (see Hemley *et al.*, 1980), and therefore can be confidently used to bracket the temperature of ore deposition within the Nucleus deposit.

Furthermore, arsenopyrite (grading about 30 at % As) coexisting with sphalerite (containing 10.54 mol % FeS), pyrite, and Au (sample TB 382) in the vein-controlled deposit type yielded an estimated temperature of 340 °C, obtained by superimposing phase relationship for Fe-Zn-S system and phase relationship Fe-As-S system (see Scott, 1983). Arsenopyrite (with 31.5 and 33 at % As) coexisting with pyrite in an arsenopyrite-rich breccia and in arsenopyrite-

rich veins, respectively (samples TB 396 and TB 094C) suggests temperatures between 363 and 491 °C (see Kretschmar & Scott, 1976), which are similar to temperatures obtained from chlorite geothermometry (see above). Even if the pressure dependence of arsenic composition (ignored here) was recognized (Clark, 1960a, b; Sharp *et al.*, 1985), the temperatures estimates are still meaningful, since the effect of pressure on arsenopyrite composition buffered by two phases is not large and can be ignored for low-pressure (as supported here by textures such as breccias and colloform minerals) hydrothermal deposits (see Sharp *et al.*, 1985). The arsenopyrite temperatures obtained here are similar within the error to those reported from intrusion-related Au deposits within the Tintina Au Province, such as Fort Knox (305 ± 25 °C; McCoy *et al.*, 1997), Illinois Creek (305 ± 25 °C; Flanagan, 1998), Cleary Hill (300 °C; Metz, 1991), Dublin Gulch (200-350; Smith *et al.*, 1996; Lang *et al.*, 2000), and Scheelite Dome (240-350 °C; Hulstein *et al.*, 1999).

Based on the discussion elaborated above, mineralization/hydrothermal alteration in the vein-controlled mineralization style took place at temperature range of between 568 and 340°C. The change in gold fineness (between 935.4 and 964.4) from vein-controlled mineralization further indicates changes in temperature during vein-controlled Au mineralization event, because temperature is the most important control on gold fineness (Corbett & Leach, 1998). In addition, the Fe-rich sphalerite, the elevated Cu content of fahlore and its subsequent low Ag abundance, and the lack of electrum are also consistent with a relatively high temperature. Furthermore, the precipitation of native Bi instead of bismuthinite is favored mainly by high temperatures (≥ 400 °C, Tooth *et al.*, 2008).

7.3.2 Fluid compositions and its evolution

Elemental Pearson Product correlation coefficients were used as the distribution of key elements in the mineralization is close to normal in that selected data population (Table 11). This was calculated from 3,229 samples (selected from 21,956 assayed drill core samples, which encompass results from up to and including the 2009 drilling campaign) grading ≥ 0.30 g/t Au (which is the cutoff grade of the Nucleus Deposit). Once geochemical data from the two types of mineralization are discriminated (based on the samples description from NFR data base), there is significant difference in elemental correlation between the two mineralization types (Table 11).

The difference in elemental correlation coefficients as well as the age difference (see sections above), between the skarn and the vein-controlled types of mineralization clearly suggests involvement of two different mineralizing fluids within the Nucleus Deposit. Mineralizing fluids from skarn were reduced and that can be ascertained by: (i) the non-negligible concentrations of Bi in skarn; (ii) the subsequent association of native Au and Bi, Bi minerals, and pyrrhotite, and; (iii) the presence of Bi-tellurosulfide phases with Bi:Te (+S, Se) > 1. The lack of native tellurium further precludes the involvement of oxidized fluids in the mineralizing process and the precipitation of native Bi instead of bismuthinite is favored mainly by reducing conditions ($f_{\text{CH}_4}/f_{\text{CO}_2} > 1$; pyrrhotite stable, cf. Tooth *et al.*, 2008). The hydrothermal fluids may be reduced by reaction with the Yukon Tanana metasedimentary complex or are related to S-type intrusive rocks.

Mineralizing fluids from the vein-controlled type interacted with the Yukon Tanana metasedimentary complex as well and were therefore somehow reduced, as testified by the Bi content and the presence of Bi-bearing mineral phases in the vein-controlled mineralization type.

But the scarcity of pyrrhotite (which is stable in reduced conditions) and the lack of spatial relationship between Au and Bi, and pyrrhotite suggest mineralized fluids were significantly less reduced in comparison with mineralizing fluid from skarn. The vein-controlled mineralizing fluids were also certainly CO₂-rich (and therefore oxidized), based on the ubiquitous presence of carbonate in all vein types (see Table 5) and its association with ore minerals. Involvement of fluids of characteristically meteoric origin, at a later stage of the mineralization/hydrothermal alteration process in the vein-controlled mineralization style is also envisaged as indicated by the significant overprint of phyllic alteration (see Guilbert, 1986).

Significant changes in fluid compositions with time is envisaged in both vein-controlled and skarn mineralization styles. In vein-controlled mineralization, this is ascertained by the great diversity or variability in the mineralogy of vein sets, suggesting changing P-T-X conditions with time. Changes in the compositions of the skarn mineralizing fluids is supported by the interpreted paragenetic sequence (Fig. 4), which clearly indicates an evolution from relatively reduced (grossular, actinolite, and pyrrhotite) to more oxidized conditions (epidote, magnetite) through time. This proposed evolution may be due to either predominantly reduced fluids interacting with wall rocks interaction, or by fluids mixing.

7.4 Gold and Bi transportation and precipitation mechanisms

In hydrothermal systems, Au is solubilized as Au + aqueous complexes, of which AuHS(aq), Au(HS)₂, and AuCl₂ are of particular importance, depending on the concentration of chloride and sulfur in the fluids (Stefansson & Seward, 2003, 2004). For example, Au bisulfide complexes

predominate in the low-salinity fluids with moderate sulfur contents), and Au chloride complexes are important in the sulfur-poor, saline to hypersaline fluids. Given the reduced nature of fluid and its low sulfidation state and high T (> 350 °C), and considering that low pH fluids are inferred to have exsolved from an intrusion, chloride complexes are most likely to have prevailed for Au transportation in the Nucleus hydrothermal system. Unlike Au, the aqueous solubility of Bi in hydrothermal system is not well constrained. However, there are indications based on thermodynamic data that thio-hydroxy complexes, such as $\text{Bi}_2\text{S}_2(\text{OH})\text{O}_2$ can transport significant amounts of Bi in reduced, weakly acid fluids, in the temperature range 350 to 275 °C (Skirrow & Walshe, 2002)..

Douglas *et al.* (2000) presented preliminary experiments in which Au was scavenged from hydrothermal solutions at temperature of ~300 °C by Bi melt; a process they termed the ‘liquid bismuth collector model’. Thermodynamic modeling (Wagner, 2007; Tooth *et al.*, 2008; Marshall, 2008) further demonstrated the effectiveness of the process of Au and Ag incorporation into Bi melt, and stipulated that Au concentrations in the melt are several orders of magnitude higher than in the coexisting fluid, indicating the possible formation of economic gold deposits from undersaturated aqueous fluids, in which mineralization would not be expected in the absence of a bismuth melt. This model has been considered for interpreting Au-Bi deposits across the magmatic-hydrothermal spectrum, including: (i) intrusion-related gold (IRG) veins at Pogo and Fort Knox (Tintina Belt, Alaska; McCoy, 2000); (ii) epithermal-porphyry transition at Larga (South Apuseni Mountains, Romania; Cook & Ciobanu, 2004); (iii) Au skarns as in the Ortosa and El Valle in the Rio Narcea Gold Belt (Asturias, Spain; Cepedal *et al.*, 2006), and; (iv) volcanic massive sulfide (VMS) system in the Escanaba Trough (Southern Gorda Ridge;

Toermanen & Koski, 2005) to name a few. This model is based on the fact that the native bismuth melting point at 1 atmosphere pressure is relatively low (271 °C, Okamoto and Massalski, 1983) and Au–Bi–Te–(S) and Ag–Bi assemblages are molten at temperatures that overlap the formation conditions of a large range of precious metal deposits. However, given the geochemical affinity between Au and Bi (e.g., Spooner, 1993) and Te, the Au-Bi-Te signature observed in the skarn mineralization component from the Nucleus deposit may simply reflect the partitioning of Au and Bi from the magmatic source. Thus, investigations of phase relationships among minerals, as well as textural evidences, are essential for assuming a melt scenario. Apart from the Au-Bi spatial association, the additional fact that can be in favor for a Bi melt model in Nucleus skarn is the occurrence of a Bi grain that yielded a composition of 83.07 wt. % Bi and 18.70 wt. % Au. This corresponds to the 271.4 °C eutectic point of the Au-Bi system, where native Bi can incorporate up to 19 wt. % Au (Fig. 16). However, the absence of maldonite (Au_2Bi), likely to be observed at the 241.1 °C eutectic point (Fig. 16) may preclude the Bi melt model, although one may argue for its complete transformation into Au + Bi when the system cooled down up to 116 °C (Fig. 16). In the absence of microscopic textural evidences of Au scavenging by Bi, such as symplectites of native Au and Bi or gold blebs within native Bi, we favor the strong partitioning of both Au and Bi in the exsolving high temperature hydrothermal fluid as a mechanism of their initial enrichment. Additional Bi may be ascribed to the extensive interaction of hydrothermal fluids with the Yukon-Tanana terrane metasediments complex. Such Bi enrichment by hydrothermal fluid-metasediment interaction has also been evoked to explain the Bi-Au association in the pyrrhotite-rich massive sulfide deposits, Escanaba Trough, Southern Gorda Ridge (Tormanen & Koski, 2005).

In high temperature hydrothermal systems, several processes are likely to induce Au precipitation. These include neutralization, saturation, cooling, and boiling. The close association of Au with pyrite and pyrrhotite in skarn might well be the result of Au precipitation by means of a pH increase (see Wood, 1998) and (or) decreasing temperature (see Gammons and Williams Jones, 1997). The lack of Au in magnetite skarn may therefore indicate Au precipitated at near neutral pH conditions and was exhausted before the magnetite stability field (high pH) was reached. In vein-controlled mineralization style, and in the absence of textural evidences of boiling, as well as the absence of fluid inclusions study, we submit that Au, Ag, and Cu deposition was promoted by neutralization and fluid cooling of exsolved magmatic hydrothermal fluids. Also, since the vein-controlled mineralization component of the Nucleus deposit obviously shows a structural control, a drop of pressure (due to the enhancement of fracture permeability) as the structural system evolved (transition from ductile to brittle behavior) may have also contributed to base and precious metal precipitation.

8. Summary and conclusions

In summary, the Nucleus deposit displays two types of juxtaposed, overlapping, and non cogenetic mineralization styles, including an Early Jurassic reduced Au-Ag-Cu-Bi skarn and a Late Cretaceous vein-controlled quartz-sulfide Au-Ag-Bi-Cu mineralization type, which are however similarly Bi-rich. The presence at Nucleus of features, such as: (i) later sulfide-bearing quartz veins overprinting skarn bodies, and; (ii) explosive products containing blocks of altered and mineralized rocks as the ones observed in Nucleus intrusive breccias may be indicative of telescoping hydrothermal systems (see Sillitoe, 1994). However, the two overlapping mineralization types are not genetically linked and the Nucleus hydrothermal system is better

referred to as a superposed mineralized system, possibly with remobilization. The overprinting process may have led to the observed complexity of the mineral assemblage throughout the Nucleus deposit. Additional overprinting evidence includes variation in mineral chemistry (e.g., Ag in gold, Sb and Pb in Bi-Pb sulfide), as well as the presence of Bi-bearing minerals that typically occur as combinations of several distinct species within a given patch of Bi-bearing minerals. Bierlein *et al.* (2004) reported in the Maldon deposit a similar complexity of the mineral assemblage and assigned that to the overprinting of two distinct mineralizing systems. We therefore propose that the Nucleus deposit is a structurally controlled Au-Ag-Cu-Bi deposit, in which later formed quartz-sulfide Au-Ag-Bi \pm Cu veins, of relatively shallow emplacement, overprinted the earlier formed and deeper reduced skarn environment during multiple protracted mineralization events. Base and precious metal skarn mineralization precipitated by cooling and neutralization, like Cu, of magmatic hydrothermal fluids, whereas in the vein-controlled deposit type, Au deposition was likely promoted by cooling of the mineralizing fluids.

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Figure captions

Fig.1 Terrane map of Yukon showing the location of the study area, which is located west of Teslin Fault, within the Yukon-Tanana terrane (adapted from Colpron and Nelson, 2011).

Fig. 2 Geological map of the Nucleus deposit also showing its adjacent Revenue prospect (adapted from Northern Freegold Resources Ltd).

FIG. 3. Photographs showing the spatial and relative temporal relationship between the type of mineralization from the Nucleus deposit. (A) Quartz-carbonate-chalcopyrite vein (with an outer biotitic alteration halo) from the vein-controlled style deposit overprinting the amphibole-rich skarn mineralization type (GRD.08-94, 258.88 m). (B) Quartz (qz)-(carbonate)-pyrite (py)-chalcopyrite (cpy)-hematite (hm) sheeted veins from the vein-controlled deposit crosscutting an amphibole skarn (GRD 08-94, 259.52 m). GRD refers to diamond drill hole labels.

Fig. 4 Representative skarn facies at the Nucleus deposit. (A) Massive and coarse-grained amphibole (am)-biotite (bt) skarn (GRD 08-94; 245.24 m). (B) Banded skarn typically occur as pyrrhotite-rich almost monomineralic layers alternating with sulfide-poor polyminerallc layers (GRD 08-73; 111.8 m). (C) Coarse-grained garnet (grt) is also locally observed in the alteration phases from Nucleus skarn. In most of cases, grt is overprinted by later formed minerals, such as amphibole and pyrite (py), with the latter that in places pseudomorphs grt (sample TB 19: GRD 08-71; 180.8 m). GRD refers to as diamond drill hole labels.

Fig. 4 continued. (D-E-F) Infill process-related skarn displaying euhedral hexagonal quartz (qtz) crystals, which in turn are locally surrounded by chalcopyrite (cp). Carbonate infill and remaining empty voids are also observed (D: GRD 08-71; 214.6 m. E: GRD 08-73; 128.8 m, F: GRD 08-71; 151.8 m). (G) Actinolite (act) is the dominant calc-silicate mineral associated with ore minerals such as pyrrhotite (po) (GRD 08 71. 156 m). (H) Skarn from Nucleus is also observed as Au-bearing massive pyrite (py)-(qtz) bodies (GRD 08-99; 114.55m). (I). Massive po + minor cp lenses are observed as well (GRD 08-68; 75 m). (J) Locally, pyrrhotite and pyrite occur together, but the mineralized body is typically zoned, and exhibits a pyrite zone and a pyrrhotite zone (GRD08-71; 161.12 m). GRD refers to as diamond drill hole labels.

Fig.5. Photomicrographs (XPL) of representative native gold (Au) occurrences from both the vein-controlled and the skarn mineralization styles within the Nucleus deposit. (A) In skarn, native Au is spatially associated with pyrrhotite (Po) + chalcopyrite (cp) + native bismuth (Bi) (sample TB 309: GRD 08-68, 75 m). (B) In sulfide replacement bodies native Au is closely associated with pyrite (py) (sample TB 352: GRD 08-75; 144 m). (C-D) In the vein-controlled mineralization type, native Au occurs either enclosed in pyrite (py) (sample TB 355: DN 04-12; 94.88 m) or is related to later silicate veinlet cutting along previous sulfide-bearing quartz vein (sample TB 382: GRD 06-16; 137 m). GRD and DN refer to as diamond drill hole labels.

Fig. 6. Photomicrographs (XPL) of exemplary Bi-ore minerals from both vein-controlled and skarn mineralizations within the Nucleus deposit. (A-C) In veins, Bi-bearing sulfide display native Bi occurring as either dense tiny inclusions or big patches within Bi-sulfide. A and C are from sample TB 398 (GRD 08-94; 300 m), while B is from sample TB 504 (GRD 09-145; 115 m). In skarn (D-F), native Bi is strongly associated with pyrrhotite and occurs either as isolated rounded to subrounded crystals (D, sample TB 309: GRD 08-68; 75 m), or anhedral crystals occurring at pyrrhotite grain boundaries (E, sample TB 309), or enclosed in pyrrhotite where it occurs as trail of anhedral Bi (E, sample TB 309). GRD refers to as diamond drill hole labels.

Fig. 6 continued. Photomicrographs (XPL) of representative mineral assemblages in vein-controlled mineralization from the Nucleus deposit. (A) Chalcopyrite (cp)-pyrite (py) assemblage, with py exhibiting colloform texture (sample TB 508: GRD 09-129; 158 m). (B) py-cp-sphalerite (sph)-arsenopyrite (apy) assemblage, where mineral phases are in perfect textural equilibrium (sample TB 382: GRD 06-16; 137 m). (C) sph most often exhibits cp exsolutions (?) or replacement (?), and cp within sph is either crystallographically oriented, or randomly distributed (sample TB445: GRD 08-73, 135.4 m). (D) Early-formed cp veins crosscut by later tennantite (tn) veinlets (sample TB 401: GRD 08-87; 130.48 m). (E) cp is locally partially replaced by digenite (dg) through weathering processes

(sample TB 396: GRD 07-51; 114.4 m). (F) Molybdenite (mo) more often occurs in sulfide-poor quartz veins (sample TB 510: GRD 09-143, 95.9 m). GRD refers to as diamond drill hole labels.

Fig. 7 Interpreted paragenetic sequence of the skarn mineralization from the Nucleus deposit. Dashed lines represent minor phases, whereas solid lines represent major phases.

Fig. 8 Representative sulfide replacement mineralization from the Nucleus deposit. (A) Sulfide replacement in foliated granitoids mostly takes place along foliation planes but also across the foliation (GRD 08-73; 88.2-89 m). (B) Pervasive sulfides replacement in unfoliated granitoids (GRD 08-73; 140.22 m). (C) In unfoliated granitoids, sulfides also selectively replace the groundmass, whereas phenocrysts remain least altered (GRD 08-73; 77.8 m). GRD refers to as diamond drill hole labels.

Fig. 9 Representative veins from the vein-controlled mineralization style at the Nucleus deposit. (A) Quartz-chalcopyrite single vein type hosted by a rhyolitic porphyritic dyke (GRD 08-97; 231.3 m). (B) Single chalcopyrite-bearing quartz-(carbonate) vein with a sericite halo (GRD 08-68; 168.2 m). (C) High density quartz-chalcopyrite sheeted veins wholly overprinting leucogranite (GRD 09-136; 351 m). (D) Quartz-(carbonate)-pyrite chalcopyrite sheeted vein crosscutting limonite-overprinted foliated leucomicrogranite (GRD08-58; 38.5 m). GRD refers to as diamond drill hole labels.

Fig. 10. Representative breccias mineralization styles from Nucleus. (A) Jig-saw clast-supported fault-related oxidized breccias displaying angular clasts of various sizes, setting in a limonitic matrix (GRD 09-125; 120 m); oxidized breccias are commonly Au-enriched. (B) Mineralized pseudotachylite with sulfide both on the clasts and in the black glassy matrix (GRD 09-127; 131.5 m). (C) Sulfide-bearing cataclasite (GRD 09-127, 131.6 m). (D) Sulfide-enriched fault related breccias exhibiting chalcopyrite (yellow) patches (GRD 09-126; 239.6 m). (E) Sub surface sample from a Jig saw clast-supported hydrothermal stockwork breccia with quartz-sericite infilling (sample TB 450). (F) Intrusive breccias made up of mainly rounded to subrounded clasts set in extremely fine-grained siliceous and dark matrix (DN 04-12; 109.5 m). GRD and DN refer to as diamond drill hole labels.

Fig. 11 Interpreted paragenetic sequence of the vein-controlled mineralized deposit from Nucleus. Bolded lines indicate important mineral phases from each stage, whereas regular lines represent the least abundant mineral phases.

Fig. 12 Field crosscutting relationship between leucogranite and skarn. (A) Leucogranite intrudes the skarn at several points (GRD08-94, 259.08-263.47). (B) and (C) are zoom in on the insects in (A). GRD refers to diamond drill hole labels.

Fig. 13. Nucleus Titanite CA ID-TIMS plots. (A) $^{207}\text{Pb}/^{235}\text{U}$ versus $^{206}\text{Pb}/^{238}\text{U}$ plot (concordia diagram) showing that titanite U-Pb data from Nucleus skarn yielded 3 overlapping concordant analysis points. (B) $^{206}\text{Pb}/^{238}\text{U}$ plot exhibiting a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 182.6 ± 2.4 Ma for titanite from Nucleus skarn.

Fig. 14 Reflected full thin section annotated image of the biotite (bt)-amphibole (am) skarn (sample TB 400-2) dated by LA ICP-MS technique that clearly shows a close spatial relationship between pyrite (py) and chalcopyrite (cp) and titanite grains (1, 2, 3, and 4) dated.

Fig. 15. Nucleus titanite LA ICP-MS plots. (A). $^{238}\text{U}/^{206}\text{Pb}$ versus $^{206}\text{Pb}/^{206}\text{Pb}$ plot anchored at $^{206}\text{Pb}/^{207}\text{Pb} = 0.82$ that yielded a skarn titanite age of 191.0 ± 1.5 Ma. (B) $^{238}\text{U}/^{206}\text{Pb}$ plot exhibiting a free regression age of 189.4 ± 3.4 Ma for titanite from Nucleus skarn.

Fig. 16. Au-Bi alloy phase diagram modified from Okamoto and Massalski (1983). Pure liquid bismuth crystallizes at 271.4 °C. Native bismuth with gold concentrations of < 13 wt. % precipitates in the temperature range 271° to 241 °C. Liquid bismuth containing > 13 wt. % Au will precipitate maldonite upon cooling. At the eutectic

temperature of 241 °C, native bismuth and maldonite precipitate together, but maldonite has not been observed in Nucleus. The decomposition of maldonite to gold and native bismuth is predicted to occur at 116 °C.