

Kwyjibo, a REE-enriched iron oxides-copper-gold (IOCG) deposit, Grenville Province, Québec



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1. Introduction

Iron oxide-copper-gold (IOCG) refers to a group of ore deposits that contain more than 10% low-Ti Fe oxides (mainly magnetite and hematite) and have elevated Cu, Au, REE, P, U, Ag or Co (Barton, 2014). This term excludes sedimentary iron deposits, magmatic iron-titanium oxide deposits, and members of the porphyry copper clan. They tend to be structurally or stratigraphically controlled and are temporally and spatially associated with intense and pervasive Na-Ca-K metasomatism. They are usually magmatic-hydrothermal deposits, commonly associated with large-scale continental A- to I-type granitic suites, and are found in late-or post-orogenic, extensional, shallow- to mid-crustal intracratonic, intra-arc, or back-arc settings (Barton, 2014), although metamorphic-affiliated deposits appear to be related to compressional settings (Corriveau, 2007; Groves et al., 2010; Barton, 2014). Some qualify as giant deposits such as the Olympic Dam Cu-Au-U deposit in Australia (Groves et al., 2010 and Barton, 2014). Total REE content in IOCG is commonly in the range of 0.2 to 3%, mostly enriched in light REEs (Barton, 2014). In magnetite-rich deposits, such as Kiruna (Sweden), the Fe-oxides – apatite end-member of the IOCG group, the main REE-bearing minerals are apatite, titanite and allanite. In the Kiruna district, the average REE-content of iron ore-type deposits ranges from 3275 ppm to 6560 ppm, and most of the REEs are associated with apatite (Parak, 1973). In hematite-rich deposits, such as Olympic Dam, REE occur in apatite and a variety of minor phases of REE-bearing phosphates (monazite, xenotime, britholite), REE-bearing fluorocarbonates (bastnasite, synchysite) and silicates (allanite) (Barton, 2014).

Kwyjibo is a Mesoproterozoic Fe-Cu-REE-(Au) deposit of IOCG type in the northeastern part of the Grenville Province, on the north shore of St-Lawrence Gulf, in the Province of Québec (Fig. 1). It consists of 10 known polymetallic mineralized zones over a strike length of 4 kilometres. The main mineralized zones (Malachite, Josette, Andradite, Fluorine, Grabuge and Gabriel) were discovered between 1993 and 1995 during regional follow-up of regional geochemical lake-bottom sediment anomalies spatially associated with a

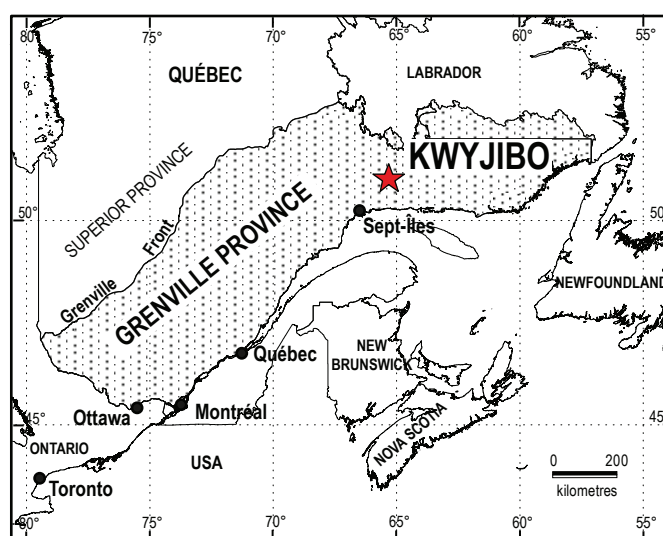


Fig. 1. Location of the Kwyjibo deposit.

regional curvilinear magnetic anomaly. Most of the zones consist of low-grade copper and REEs, except in the Josette horizon, a deformed hydrothermal iron formation (referred to as a magnetitite) metamorphosed to upper amphibolite metamorphic grade that extends for more than 1.2 kilometres (Fig. 2). High grade REE-mineralization, mainly of Nd, Y, Dy and Tb, has been delineated by both surface work at the Josette showing (2.95% total rare earth oxide [TREO] and 1.44% Cu over 10 m) and by close-spaced diamond drilling along the Josette horizon (reported weighted average intervals from 0.84% TREO over 65 m to 3.64% TREO over 33 m).

In the early 1990s, SOQUEM recognized that rocks of the Kwyjibo area share many similarities with IOCG type deposits (Perry and Raymond, 1996), including a regional linear magnetic anomaly and alteration patterns such as: iron enrichment, calcic and sodic-calcic alteration, potassic alteration with associated sodium depletion, anomalous content in F, P, REE, Y, Cu, Mo, Th, and locally U, silicification and quartz veins, hematization (specular hematite) and sodic-calcic alteration (Clark et al., 2005, 2010). Mineralized zones at Kwyjibo display a complex

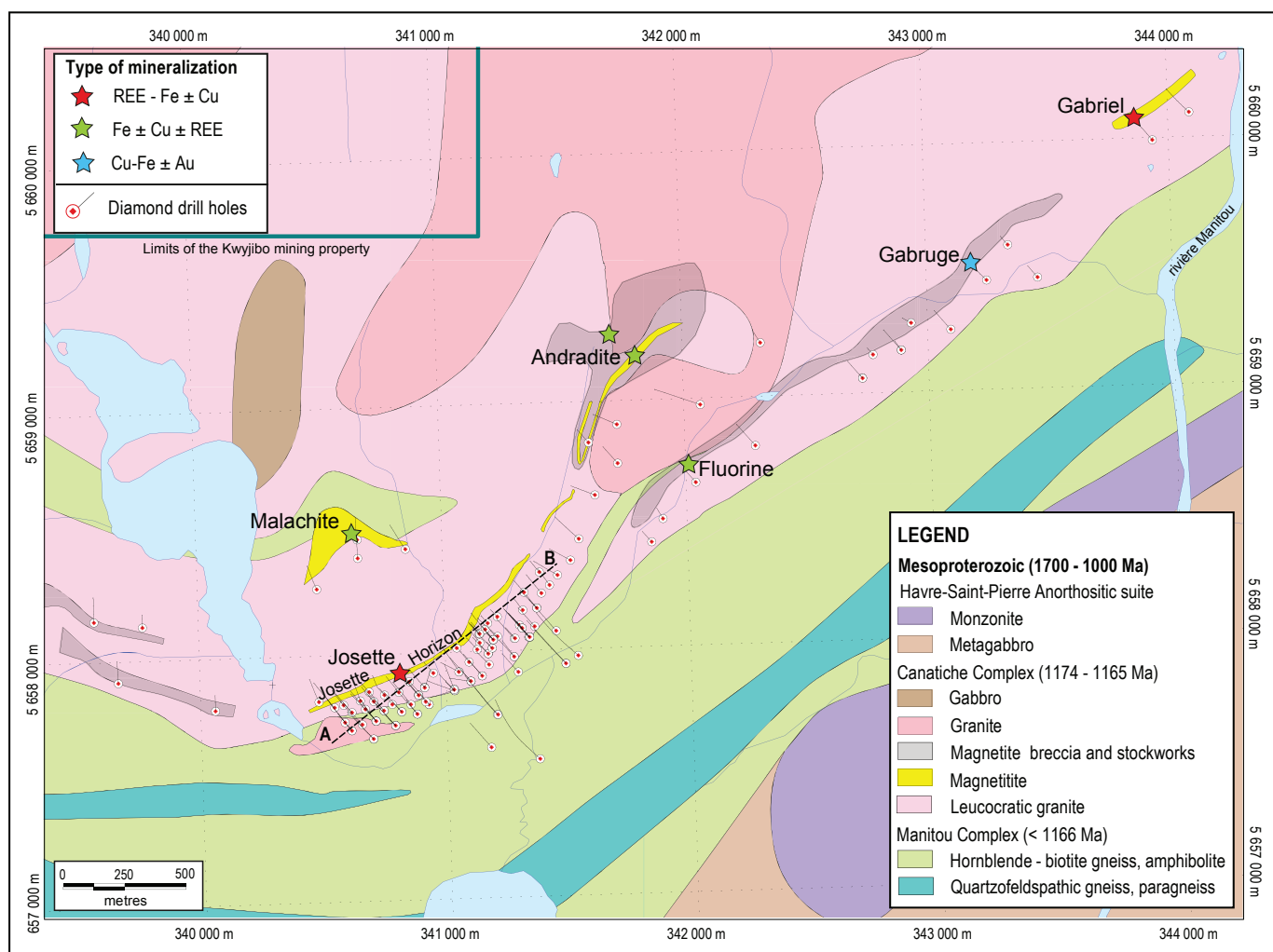


Fig. 2. Geological map of the Kwyjibo deposit showing the mineralized prospects, Josette horizon and the location of the diamond-drill holes. Coordinates are in UTM Zone 20 (NAD 83).

alteration history, resulting from mixed hydrothermal and meteoric fluids, and are strongly controlled by structures (Clark et al., 2005 and 2010). The mineralizing event forming the hydrothermal iron formation began during shortening related to the Grenville orogen, but most of the REE and Fe-Cu sulphide minerals were remobilized and deposited during the later extensional stages (Gauthier et al., 2004, Clark et al., 2005 and 2010). High-grade REE mineralization is found in the late apatite- allanite- britholite- kinosite-bearing calcsilicate (andradite-titanite-hornblende) veins and stockworks (with and without fluorite, biotite, and magnetite), with or without magnetite, that brecciated the magnetitite and its host gneissic leucogranite.

2. Geological setting

The property straddles two lithotectonic complexes separated by a major thrust fault: the Manitou complex, with mainly supracrustal rocks, in the south and the Canatiche complex, with mainly granitic rocks to the north (Fig. 2). The Canatiche complex, comprises undated orthogneiss, slivers of paragneiss,

undeformed to weakly-deformed biotite ± hornblende granite (1181 ± 2 Ma, U-Pb zircon, Clark et al., 2005) and leucogranites (1175 ± 5 Ma, U-Pb zircon, Clark et al., 2005, and $1165 \pm 4/-2$ Ma, U-Pb zircon, David, 2014, personal communication) that host most of the mineralized zones, gabbros and pegmatite. All units have been metamorphosed to amphibolite facies. The biotite ± hornblende granites are magnetite-bearing, metaluminous to peraluminous, anorogenic (A-type) intraplate granites (Clark et al., 2005). Both the Canatiche and Manitou complexes were affected by thrusting during the metamorphic peak at 1083-1076 Ma attributed to the Ottawa phase of the Grenville orogeny (Clark et al., 2005 and references therein). All these units are intruded by late-orogenic granite and pegmatite associated with the Rigolet event of the Grenville Orogeny (Gauthier et al., 2004 and Clark et al., 2005).

Field and diamond drill core observations indicate that the southern limit of the Canatiche complex corresponds to a major fault zone (Clark et al., 2005, and references therein). At mineralized outcrops, the leucogranite hosting the Josette horizon is well foliated to gneissic. Metasomatized

leucogranite with mylonitic bands are observed in drill core close to the thrust contact with the hornblende-biotite gneiss of the Manitou complex. Close to the mineralized zones, quartz phenocrysts in the leucogranite are commonly elongated. At the Malachite mineralized zone and in drill core of the Josette horizon, a breccia unit mapped and logged as fragmental granitic gneiss represents a marker lying structurally above the mineralized magnetitite. The significance of this breccia is unclear. It might indicate that the leucogranite is part of a felsic volcanic complex (Gauthier et al., 2004) and this unit represents a volcanoclastic rock; alternatively it may have originated by tectonic or hydraulic fracturing (Clark et al., 2005).

Folding and boudinage in the magnetitites and associated magnetite-rich breccias, are observed at all scales in most of the mineralized zones.

3. Age of the REE mineralization

The $1165 \pm 4/-2$ Ma (U-Pb zircon; David, 2014, personal communication) age of the quartz-phyric and magnetite-bearing leucogranite of the Canatiche complex that hosts the Josette horizon provides a maximum age for the Josette Horizon and other mineralized zones.

An age of 983 ± 6 Ma (David, 2014, personal communication) from REE-bearing titanites in the calcsilicate minerals veins that brecciated the magnetitite suggest a late Grenvillian age for REE enrichment at the Josette horizon. This age is in agreement with the 972 ± 5 Ma age on titanites reported by Gauthier et al. (2004) from magnetitite at the Josette mineralized zone. This late Grenvillian age for REE enrichment is supported by the minimal deformation observed in the apatite-allanite-britholite veins and veinlets and in the calcsilicate minerals veins, which commonly contain centimetre-scale euhedral crystals of apatite, allanite, andradite and hornblende.

An age of 947 ± 4 Ma (U-Pb zircon; David, 2014, personal communication) from a pegmatite cutting the mineralized zone in the Josette horizon and a similar age of 951 Ma (U-Pb titanite, perovskite and allanite; Gauthier et al., 2004) from a pegmatite cutting a Cu-bearing magnetite vein in a ductile shear zone at the Grabuge mineralized zone suggest that the late granitic magmatism is associated with the unroofing and cooling of both Canatiche and Manitou complexes during the Rigolet event of the Grenville Orogeny (Gauthier et al., 2004 and Clark et al., 2005).

4. Mineralized zones

The main mineralized zones are Malachite, Josette, Andradite, Fluorine, Grabuge and Gabriel (Fig. 2), and have been described by Gauthier et al. (2004) and Clark et al. (2005 and 2010). Magnetite is omnipresent as an accessory mineral in the Canatiche granitoids, occurring as finely disseminated grains and clots locally associated with fluorite. However, significant magnetite accumulation (magnetitite) is generally restricted to individual mineralized zones, where it forms: 1) massive magnetitite and brecciated magnetitite, 1-30 m thick; 2) magnetite-rich breccias and pseudobreccias; 3) stockworks

of magnetite and calcsilicate veins; and 4) networks of anastomosing, centimetre- to decimetre-scale magnetite veins and veinlets, commonly containing apatite and allanite-bearing calcsilicate veins in the leucogranite.

The mineralized zones occur in three en-echelon zones that are concordant with the local structural grain. They consist of semi-massive to massive magnetite-bearing hydrothermal iron formation, or magnetitite, mineralized with copper and REE. Major differences between the Josette, Malachite, Andradite, Fluorine, Grabuge, and Gabriel mineralized zones involve the thickness and lateral extent of the magnetitite and its associated calcsilicate-bearing minerals veins and stockworks. Below we focus on Josette mineralization, which displays the highest grade in REE and Cu.

4.1. Josette mineralization

The mineralized zone at the Josette horizon is composed of massive and brecciated magnetitite and breccias and stockworks of magnetite, and calcsilicate veins hosted by a gneissic leucogranite. The mineralization outcropping in the central part of the horizon consists of massive and brecciated magnetitite, with stockworks of REE-bearing (apatite-britholite-allanite) calcsilicate minerals (with andradite, fluorite, blue-green hornblende) and late sulphides veins and veinlets (pyrite, chalcopyrite and pyrrhotite), hosted by a gneissic, quartz-phenocrysts bearing leucogranite. This central part displays a copper enrichment and higher U and Th content relative to the deep or lateral mineralized extensions of the Josette horizon. Analytical results of the channel samples assayed 2.95% TREO and 1.44% Cu over 10 m, including a high-grade sub-zone of: 4.59% TREO and 2.62% Cu over 2 m. The mineralized rocks are composed of magnetite, chalcopyrite, pyrite, pyrrhotite, bornite, molybdenite, apatite, and fluorite (Gauthier et al., 2004, Clark et al., 2005). The predominant REE-bearing minerals are allanite, apatite, britholite and kinosite. The mineralized zone is intruded by mafic rocks (gabbros and possibly lamprophyres), which are deformed and metamorphosed to amphibolite facies, and cut by late Grenvillian granite and pegmatite dikes.

Diamond drilling, indicates that REE mineralization is not only in the magnetitite but also in stockworks of magnetite and calcsilicate veins. The REEs and Cu mineralization in the Josette horizon occurs in three zones: upper breccia, magnetitite, and lower breccia.

The upper breccia zone is composed of magnetite veins with variable content of fluorite veinlets, locally associated with centimetre- to decimetre-scale veins of specular hematite, and centimetre- to decimetre-scale muscovite-rich bands replacing the leucogranite or the fragmental gneiss. The upper breccia zone is well developed in the fragmental gneiss (interpreted as a metamorphosed lapilli-block tuff). The thickness of the upper breccia zone varies from 1 metre to 10 metres. It generally contains very low grades in REEs.

The central magnetitite zone is a hydrothermal iron formation with more than 50% magnetite, and contains high-grade REEs, Cu, P and F. The magnetitite is a heterogeneous brecciated

rock with centimetre- to decimetre-thick lenses of fine-grained massive magnetite (>70%), and disseminated apatite, hornblende, quartz and chalcopyrite. The massive magnetite is brecciated by stockworks of decimetre-sized metasomatic veins of secondary magnetite and veins of usually coarse apatite-britholite-allanite±kainosite with andradite, blue-green hornblende, and titanite, and locally with clinopyroxene, scapolite, plagioclase, siderite, calcite and quartz (Fig. 3). Large euhedral crystals of andradite and allanite have been observed in some veins. Veins of apatite with crystals up to 5 cm, along with intergrown britholite are characteristically red and usually indicate high-grade REE. Locally, veins can totally replace the massive magnetite. The thickness of the magnetite zone varies from 1 metre to more than 40 metres due to large-scale boudinage and fold limb attenuation. Most of the REEs are found in the apatite, britholite allanite and kainosite in the calcsilicates veins. The massive magnetite contains lower grades.

The lower breccia zone, 1 metre to more than 40 metres thick, consists of centimetre- to decimetre-thick stratabound, lenticular, fine-grained magnetite veins and boudins aligned along the regional gneissosity in the leucogranite. These rocks are cut, and locally replaced, by REE-bearing calcsilicate stockworks and veins, with or without magnetite (Fig. 4). The calcsilicate veins straddle the boundary between the massive magnetite and the host leucogranite and their mineralogy is the same as in the magnetite zone. The size of the stockworks and the number of veins decrease away from the magnetite.

Typically, the leucogranite shows intense potassic alteration and late hematization. At depth in the northeastern part of the Josette horizon, the REE-mineralization becomes more important in the lower breccia zone than in the magnetite zone.

4.2. Results of 2012 and 2013 drilling

Drilling in 2012 and 2013 was designed to evaluate the thickness, continuity, and REE content of the Josette horizon (Fig. 5). The Josette horizon was subdivided into two sectors: Josette Northeast and Josette Southwest. In the central part of the Josette horizon, the magnetite and the lower breccias are less than 5 metres thick; in some holes the magnetite is absent. Although similar in terms of rock types and mineralogy, the mineralized zone in the southwest sector shows greater thickness (locally up to 60 metres) but lower REE grades. Locally, copper reaches as much as 3% over a metre but continuity between holes is lacking.

The best REE mineralized intervals are in the northeastern sector of the Josette horizon as shown Figure 5 with higher REO factor (equivalent of the metal factor except this is the total rare earth oxides value multiplied by the length of the mineralized section of core). Some of the best weighted average intervals are 2.38% TREO over 48.8 metres (hole 11-58) in the upper part of Josette Northeast, predominantly the magnetite zone, and 2.12% TREO over 60 m (hole 13-112), including 12% TREO over 3 m, in the deeper lower breccia zone (Fig. 5). Neodymium-Eu-Tb-Dy and Y, the most sought

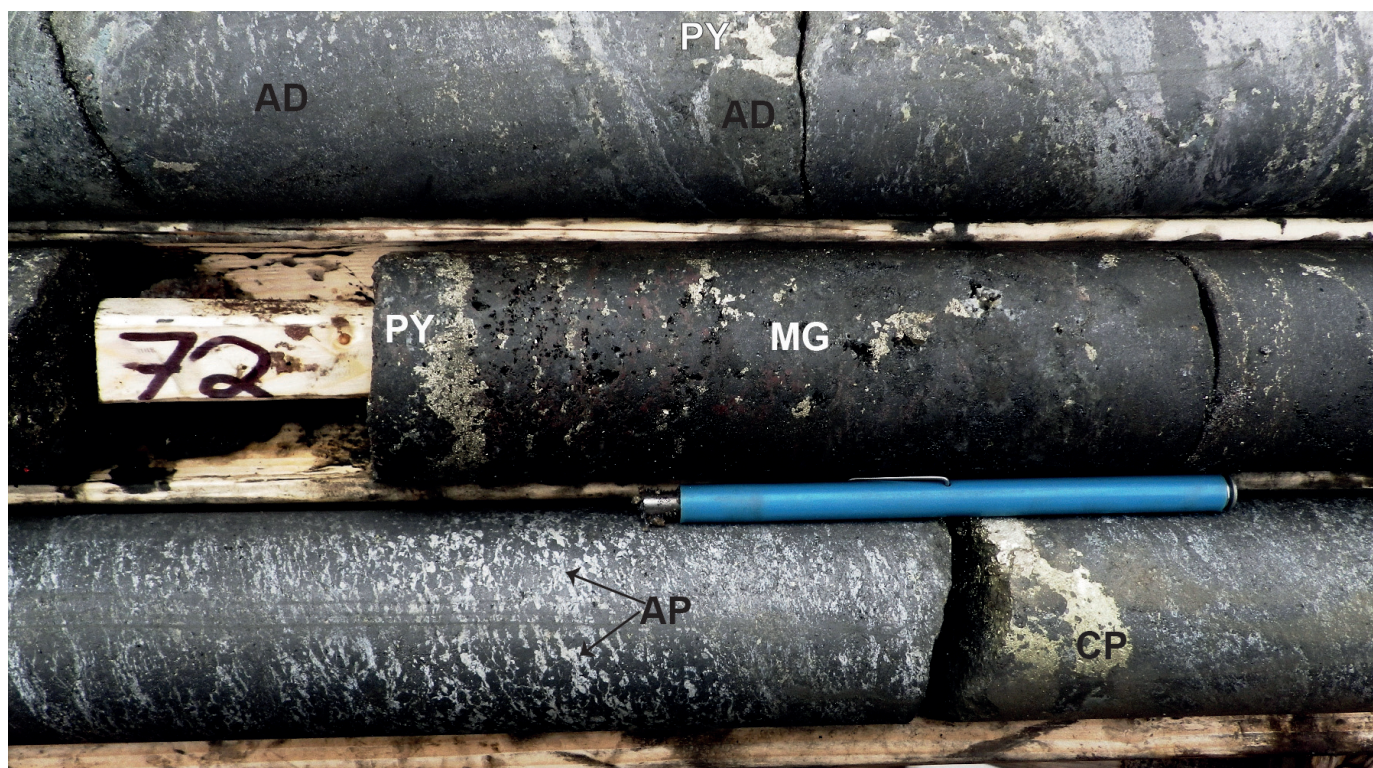


Fig. 3. Magnetite zone with massive fine-grained magnetite, locally porous, cut by apatite (AP)-britholite-andradite (AD) veins and veinlets (upper and lower part of the photo) and by pyrite (PY) –chalcopyrite (CP) veins, from hole 10885-12-63. The magnet is 15 cm long.

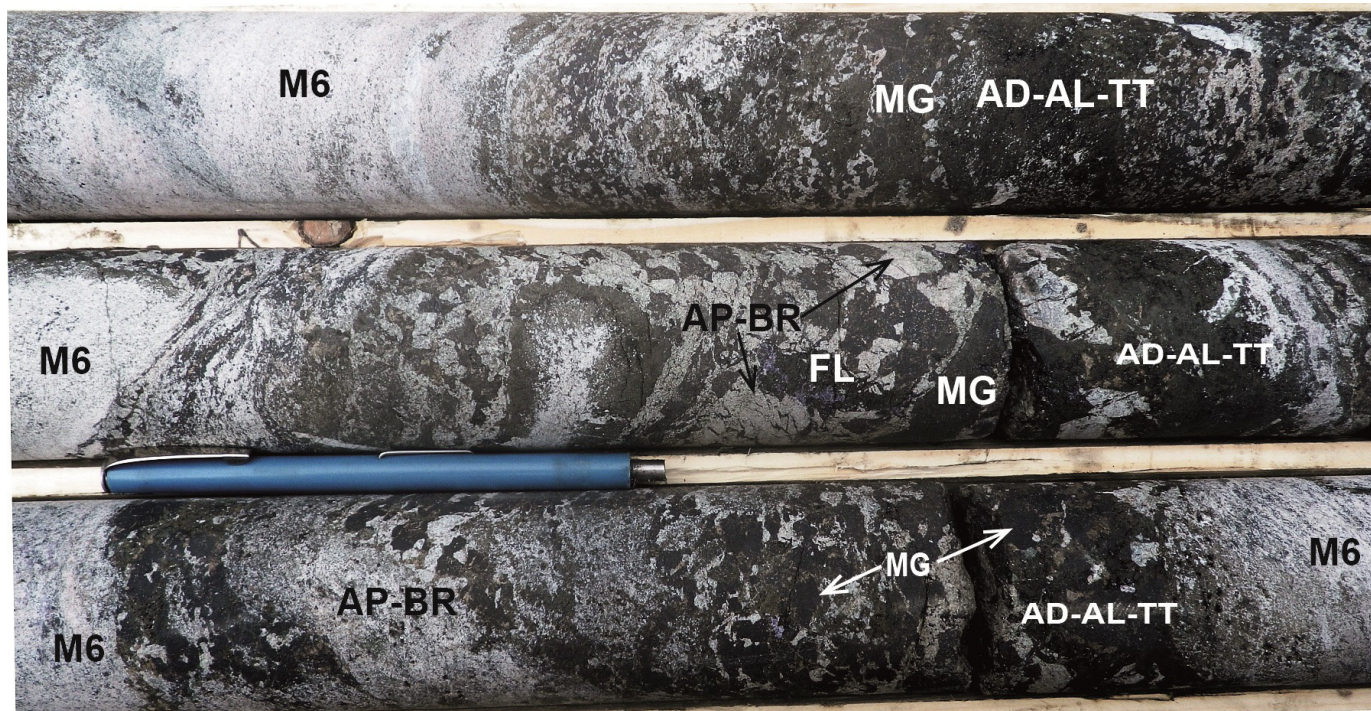


Fig. 4. Apatite (AP), britholite (BR)- and allanite (AL)-andradite (AD)-titanite (TT)-magnetite (MG) bearing calcisilicate minerals zones (in greenish grey tint with large green-black andradite crystals), locally with fluorite (FL) (blue-violet crystals in the central part of the photo) that brecciated older magnetite veins (MG); black fine-grained magnetite fragments) and the host metasomatized gneissic leucogranite (M6; in white pink).

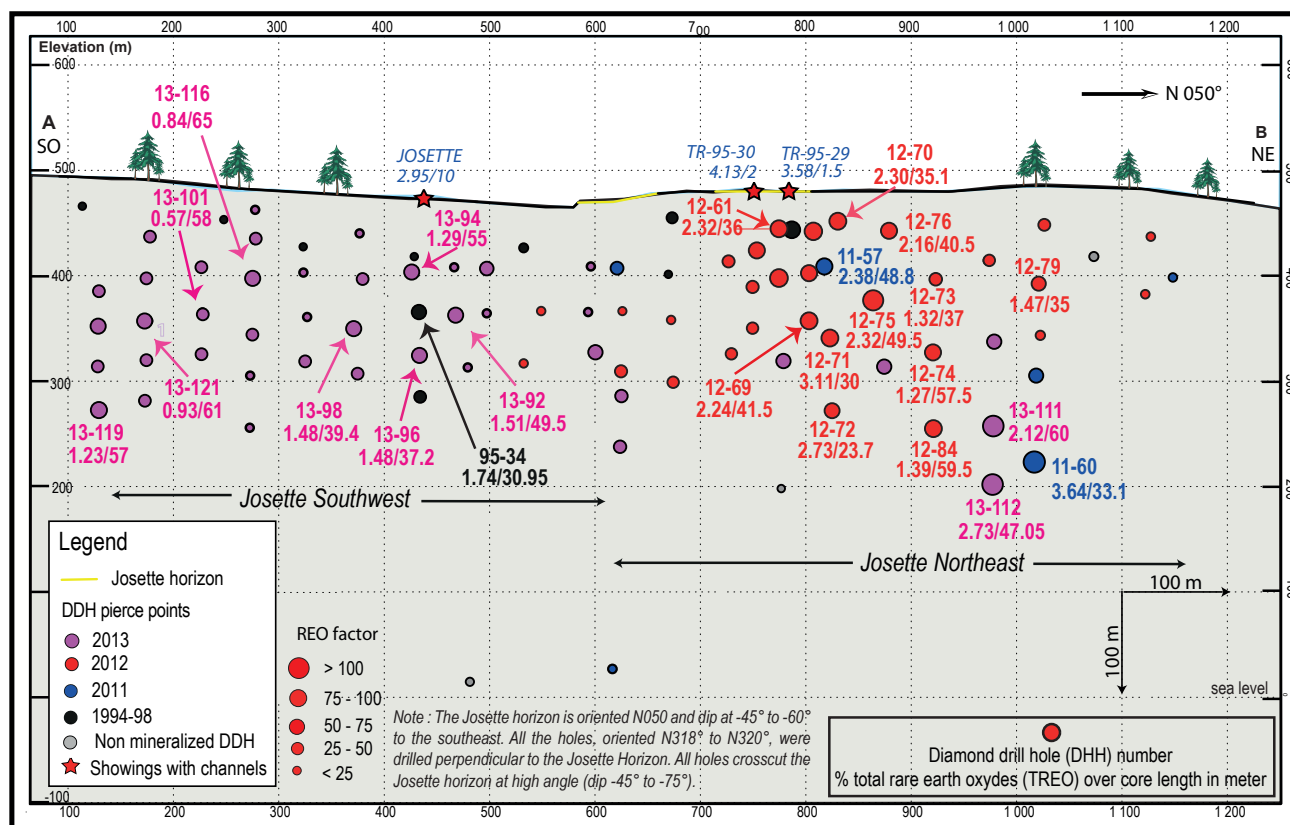


Fig. 5. Vertical longitudinal section of the Josette horizon, looking northeast with pierce points for the 1994 to 2013 diamond-drill holes. The size of the circles shows the range of the REO factor. The REO factor = % TREO multiplied by the core length (not the true thickness) in metres. Circle colours represent drilling year.

REE under current market conditions, represent 35 to 45% of the total REO's.

4.3. Mineralogy and distribution of REE

Apatite, britholite, and allanite are the main sites for REE in the Josette horizon (Wilhelmy, 2014; Laflamme, 2015). Kainosite ($\text{Ca}_2(\text{Y,Ce})\text{SiO}_4\text{O}_{12}(\text{CO}_3)\cdot(\text{H}_2\text{O})$), monazite ($\text{Ce, La, Nd, Th})\text{PO}_4$), bastnaesite ($(\text{Ce,La,Y})\text{CO}_3\text{F}$), gadolinite ($\text{Y}_2\text{Fe}^{2+}\text{Be}_2\text{Si}_2\text{O}_{10}$), synchysite ($\text{Ca}(\text{Ce,La})(\text{CO}_3)_2\text{F}$) and keilhauite ($(\text{Ca,Ti})(\text{Al}_2\text{Fe}_2\text{Y}_2)\text{SiO}_5$) have been locally identified but are rare. Chemical analyses of apatite have shown an average REE and Y of more than 2.5%, with Y, Ce, Nd and Gd as the main REE. It was selected as an attractive economic target for REE, Y and phosphate.

Two types of apatite have been observed. A fine-grained primary apatite, that forms small anhedral grains in contact with, and included in, magnetite, and a secondary coarse-grained apatite variably replaced by britholite. Britholite appears as fine inclusions in apatite, as crystals along the boundaries of apatite grains, and as veinlets that replace apatite. Due to complex textural relations with apatite, britholite contents may have been underestimated during mineralogical study. Allanite forms irregular clusters of anhedral grains or centimetre-scale euhedral crystals in the calcsilicate veins.

The modal apatite content varies between 8 and 12% in the mineralized zone. The average content of REE in the apatite is 7.9 wt.%, with a maximum of 12.5 wt.% REE in a breccia zone sample. The Y content varies from 37 to 45% of the total REE of the apatite. Varieties of Y-britholite, Ce-britholite and Ce-Nd-britholite have been detected by chemical analyses of a mixture of apatite and britholite during thin section studies of the magnetitite and breccia zones. Britholite is the main carrier of Y in the mineralized zone of the Josette horizon. Its Y content is variable depending of the subspecies of britholite. The average Y_2O_3 content is 10.7 wt.% and ranges from 9 to 19 wt.%. Britholite hosts a significant Nd_2O_3 , with an average of 8.5 wt.%. Allanite averages 28 wt.% REE and hosts most of the light REE (La, Ce, Nd). It is the main carrier of Nd_2O_3 , with an average of 5.1 wt.%. Kainosite is a source of Y but it is a minor component. In the mineralized zone, andradite averages 4.26 wt.% REE (with 70% of Y) and titanite 5.49 wt.% REE (with 35% of Y). In the breccia zone, andradite is an important component, comprising up to 15% of the mineral proportion of the head grade of the metallurgical samples.

5. Metallurgical tests

Two phases of metallurgical tests were done at COREM's facilities in Quebec City in 2013 and 2014. The second phase was more extensive and included physical separation tests of the iron concentrate, grindability and abrasion tests, and flotation and leaching tests. The final flow sheet includes magnetic separation, sulphide flotation, flotation of REE-bearing phosphates and silicates to ultimately produce one or two concentrates (one of REE-bearing phosphates and a second one of REE-bearing silicates), and subsequent lixiviation of

the concentrates to produce solutions that contains the rare earth elements (Laflamme, 2015). Results of Low Intensity Magnetic Separation (LIMS) show that the magnetic iron concentrate contains a high concentration of deleterious elements (phosphate, silica or sulphide) that do not meet steel industry requirements. On the other hand, the magnetic separation is essential in the ore treatment as it eliminates up to 50% of the total mass that has to be processed by flotation with a very low loss of REE (less than 10%) for the ore from the magnetitite. Flotation results show that 84% to 90% of the REE-bearing minerals are recovered in the concentrates, the traditional phosphate flotation with a fatty acid collector returning the highest recoveries. Acid (HCL) lixiviation of the different concentrates allows recovery of 80% to 94% of REE

6. Conclusion

Zones of the Kwyjibo deposit are examples of IOCG-type mineralization enriched in REE. Nedymium, Tb, Dy and Y, and the extent of mineralization are of economic interest. The best mineralized section lies in the northeastern part of the Josette horizon, where high REE content is found in the magnetitite and the lower breccia zone. In the southwestern part, the magnetitite and the lower breccia zones are thicker but the REE content is lower. Most of the REE are contained in apatite, allanite, and britholite. Light REE are mostly concentrated in allanite and, to a lesser extent, in Ce-britholite and Ce-Nd britholite. Heavy REEs are concentrated in apatite and britholite and, to a lesser extent, in kainosite, andradite and titanite. Metallurgical tests show that most of the REE-bearing minerals can be recovered by traditional phosphate flotation. Lixiviation (with HCl) of the concentrates allows high recoveries by dissolving most of the REE-bearing minerals. Further tests are mandatory to optimize the flow sheet, maximize the recovery of REE-bearing minerals during the flotation process, and to evaluate the best methods of lixiviation and recovery of Nd-Eu-Dy-Tb-Y after the lixiviation.

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