Columbitization of fluorcalciopyrochlore by hydrothermalism at the Saint-Honoré alkaline complex, Québec (Canada): new insights on halite in carbonatites

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Abstract

Niobium (Nb) in carbonatite is mainly hosted in fluorcalciopyrochlore and columbite-(Fe). Information related to Nb petrogenesis is useful for understanding the processes related to Nb mineralization and carbonatite evolution. The Saint-Honoré, Quebec, alkaline complex offers a rare opportunity for studying these processes as the complex is not affected by post-emplacement deformation, metamorphism nor weathering. Columbite-(Fe) is shown to be an alteration product of fluorcalciopyrochlore (columbitization). Columbitization is characterized by the leaching of Na and F from the A- and Y-sites of the pyrochlore crystal structure. As alteration increases, Fe and Mn are slowly introduced while Ca is simultaneously leached. Leached Ca and F then crystallize as inclusions of calcite and fluorite within the columbite-(Fe). A-site cations and vacancies in the crystal structure of fresh and altered pyrochlores demonstrate that pyrochlore alteration is hydrothermal in origin. Moreover, halite is a ubiquitous mineral in the Saint-Honoré alkaline complex. Petrographic evidence shows that halite forms in weakly altered pyrochlores, suggesting halite has a secondary origin. As alteration increases, halite is expelled by the hydrothermal

fluid and is carried farther into the complex, filling factures throughout the carbonatite. The hydrothermal hypothesis is strengthened by significant enrichments in Cl and HREEs in columbite-(Fe). Chlorine is most likely introduced by a hydrothermal fluid that increases the solubility of REEs. A HREE rim is observed around magmatic apatite associated with fluorcalciopyrochlore and columbite-(Fe), suggesting a late magmatic event related to hydrothermal activity.

Keywords

Pyrochlore; Columbite-(Fe); Halite; Niobium; Carbonatite; Saint-Honoré

1. Introduction

Carbonatites are important rocks for understanding the Earth's evolution as they provide a window into the mantle and its dynamics. As such, they have been abundantly studied (Chakhmouradian et al., 2015; Decrée et al., 2015; Le Bas, 1981; Mitchell, 2015; Wyllie, 1966; among many others). However, the crustal evolution of carbonatites, either by fractional crystallization, hydrothermalism, carbothermalism or weathering can obliterate or modify much of the initial information recorded by these rocks. Thus, an understanding of the evolution of carbonatites is essential to better constrain any interpretation of their formation. Moreover, carbonatites are important economic rocks as they host strategic metals such as rare earth elements (REEs) (Chakhmouradian and Wall, 2012; Giebel et al. 2017), niobium (Mariano, 1989; Wall et al., 1999) and, in some cases, base metals (e.g. Cu; Heinrich, 1970). A rapidly increasing demand for Nb (Roskill, 2017) in emerging countries (Mackay and Simandl, 2014), requires a better understanding of the mineralization processes within carbonatites to develop avenues of possible exploration.

The petrography and chemistry of columbite and pyrochlore are often key for understanding the genesis of Nb mineralization.

Within carbonatites, minerals from the pyrochlore group host Nb mineralization and act as recorders of carbonatite petrogenesis (Atencio et al., 2010; Hogarth et al., 2000; Lumpkin and Ewing, 1995). The pyrochlore mineral group contains more than a dozen species although fluorcalciopyrochlore [$(Ca,Na)_2(Nb,Ti)_2O_6(O,OH,F)$] (Hogarth, 1977) is the end-member that is usually exploited for Nb. A second economically important mineral in carbonatite is columbite-(Fe) [$(Fe,Mn)(Nb,Ti)_2O_6$]. Columbite is generally found as a primary mineral in granites and pegmatites (e.g. Cerný, 1989; Lumpkin, 1998). It is generally uncommon in carbonatites except for a few occurrences as a secondary mineral (Mackay and Simandl, 2015; and references therein); its presence as a primary mineral is rare (Mariano, 1989). Columbite can be a primary or an alteration product from pyrochlore through an igneous or hydrothermal event (Chakhmouradian et al., 2015; Heinrich, 1966; James and McKie, 1958; Mariano, 1989). James and McKie (1958) were the first to describe the alteration process from pyrochlore to columbite in carbonatite, later named columbitization (Heinrich 1966). Alteration of pyrochlore has been studied recently (Chakhmouradian et al., 2015; Cordeiro et al., 2011; Lumpkin and Ewing, 1995; Nasraoui and Bilal, 2000; Mitchell, 2015; Wall et al., 1996) in lateritic and relatively fresh carbonatites. These works highlight an origin of columbite from the alteration of pyrochlore, although none of the studies showed the conservation of all major elements between pyrochlore and columbite-(Fe), minus the release of Na.

The economic viability of a Nb exploitation is influenced by the variation in size, shape and chemistry of Nb-bearing minerals as well as by the distribution of different Nb-bearing phases within a deposit. Therefore, a thorough understanding of the mechanisms that control Nb-hosting phases and their alteration are crucial for a comprehension of mineralization associated with carbonatites and potential causes of metallurgy issues, such as the alteration of minerals that can hinder economic exploitation.

The Saint-Honoré alkaline complex is an ideal setting for the study of carbonatites and their related Nb-hosting minerals as it is currently exploited and accessible to a depth of 808 m (2650 feet). Studies regarding mineralization (Fortin-Bélanger, 1977; Thivierge et al., 1983) have been conducted in the weathered upper portion of the carbonatite and more recent studies of the Saint-Honoré carbonatite focused on REE mineralization (Fournier, 1993; Grenier et al., 2013; Néron, 2015; Néron et al., 2013) or the origin of ubiquitous halite (Kamenetsky et al., 2015). The main minerals exploited for Nb are fluorcalciopyrochlore (using the pyrochlore classification of Atencio et al. (2010)) and columbite-(Fe). There are four other pyrochlore species (e.g. Sr, Th or U-rich) present in the Saint-Honoré carbonatite (Belzile, 2009; Clow et al., 2011), but they are of minor importance.

Columbite from the Saint-Honoré carbonatite is part of the iron end-member and hence is classified as columbite-(Fe) (Burke, 2008) (previously named ferrocolumbite). With depth, columbite-(Fe) increases in abundance, becoming a major Nb-bearing mineral. This pattern with depth provides new insights on the genesis of carbonatites, but also presents extractive

metallurgy issues for exploitation. In this study, the petrogenesis of pyrochlore and columbite-(Fe) is investigated. The puzzling presence of halite grains observed in minute cavities of weakly altered pyrochlores provides clues about sodium remobilization in carbonatites and the contribution of halite to fenitization.

1.1 Geological setting

The Saint-Honoré alkaline complex is located in the Saguenay region, Quebec (Canada). The regional bedrock is the Canadian Shield and is mainly composed of Mesoproterozoic rocks of the Grenville Province (Dimroth et al., 1981; Higgins and van Breemen, 1996). Dimroth et al. (1981) divided the geological province into three units: 1) a gneiss complex that was deformed and migmatized during the Hudsonian Orogeny (1735 Ma); 2) anorthosite and charnockite-magnerite batholiths dating from pre- to post-Grenville orogeny (935 Ma); and 3) calc-alkaline intrusions that cross-cut the host rocks. This late stage, the Iapetan rift system, is related to alkaline activity (Kumarapeli and Saull, 1966) and includes the intrusion of the Saint-Honoré alkaline complex.

The alkaline complex is composed of a crescent-shaped carbonatite surrounded by alkaline silicate rocks. The host rocks were fenitized by the emplacement of the complex and the fenitization is characterized by sodic-amphiboles, aegirine, sericitized plagioclases as well as green and red carbonate veins (Fortin-Bélanger, 1977). Silicate rocks are represented by three types of syenites: alkaline syenite, nepheline-bearing syenite and syenite foidolites (ijolite-urtite). The presence of xenoliths of altered syenites in the carbonatite suggests

118 silicate rocks are older than the carbonatite. K-Ar dating of the alkaline complex gave an
119 age of 565 Ma (Doig and Barton, 1968). McCausland et al. (2009) report an Ar-Ar age of
120 571±5 Ma from phlogopite and Kamenetsky et al. (2015) report a two-point Rb-Sr model
121 age of 564±8 Ma. More recently, baddeleyite from lamprophyre dikes associated with the
122 Saint-Honoré suite yielded a U-Pb age of 582.1±1.8 Ma (Michael Higgins, UQAC,
123 personal communication, 2015). The carbonatite is covered by Ordovician black shale and
124 limestone.
125
126 The carbonatite complex is generally composed of concentric, subvertical layers of various
127 carbonate types, ranging from calcite in its external portion to dolomite and ankerite toward
128 its core (Fortin-Bélanger, 1977; Thivierge et al., 1983) (Fig. 1). The ankerite facies is
129 known to host an economic REE mineralization (Fournier, 1993; Grenier et al., 2013;
130 Néron et al., 2013). The calcitic outer rim is barren of Nb and REE mineralization and is
131 characterized by the presence of amphiboles. Underground, it is possible to observe several
132 calcite-bearing dikes, lenses of semi-massive to massive magnetite and xenoliths of
133 syenitic rocks throughout the dolomitic facies. Our textural observations, such as hydraulic
134 fracturing and the presence of unaltered calcite grains, suggest the calcitic injections to be
135 from a younger episode of magmatism. The calcitic rocks within the dolomite facies are
136 also younger than the calcitic rocks of the external portion of the carbonatite. This
137 assumption is based on the comparison of accessory minerals, textures and alterations. In
138 other words, the different carbonatitic layers of the Saint-Honoré complex are
139 homogeneous at a regional scale (calcitic, dolomitic and ankeritic carbonates), but are very
140 heterogeneous at the local scale. The complex patterns involving multiple generations of

carbonatitic units and alteration fronts suggest a complicated history of multiple injections of differing composition and variable alteration fronts (Fig. 2).

1.2 Mining overview

The Saint-Honoré alkaline complex was discovered in 1967 and mining operations began in 1976. Reserves were recently estimated at 416 Mt grading 0.41% Nb_2O_5 (Vallières et al., 2013). Exploitation is currently at a depth of 808 meters (2650 feet) and mineralization is open at depth. Production at the mine accounts for ~8–10% of the global production of Nb_2O_5 (Papp, 2015). Phosphorus (Savard, 1981) and LREE in the Saint-Honoré complex (Grenier et al., 2013; Néron et al., 2013) are also being considered for future exploitation.

2. Methods

2.1 Sample collection and preparation

Two drill holes at the 1600’ level (~490 m) were selected; one facing north and one facing south. These drill holes were selected to cover a wide spectrum of mineralogical assemblages and to allow for study of the dolomitic and calcitic mineralized zones. Furthermore, mineralogy and textures in rocks at this depth are not affected by supergene alteration. During sampling, we ensured that mineralization samples were collected from different facies to best represent the carbonatite. Niobium mineralization in the different Nb-bearing minerals is not evenly distributed in the deposit. The southern portion of the carbonatite is characterized predominantly by pyrochlore mineralization whereas the northern portion contains a higher proportion of columbite-(Fe). The north-facing drill hole length is 235 m and is inclined downwards at 6 °. The length of the south-facing drill hole

is 115 m and dips at 31 °. A third drill hole was selected at the 2100-foot level (~640 m) to ensure representability at depth.

From the cores recovered from the upper two drill holes, 73 polished thin sections were produced. Twenty-three polished thin sections were prepared from the lower drill hole. Nine additional polished thin sections of mineralized lenses from the three drill holes were prepared with a water-free lubricant (acetone) to preserve water-soluble chlorides.

2.2 Sample analysis

We conducted macroscopic observations and selected samples under the supervision of mine geologists. Thin sections were studied at the Université du Québec à Chicoutimi (UQAC) with a Nikon polarizing microscope and cathodoluminescence using a CITL Mk5-1 coupled with a cathodoluminescence stage (Cambridge Image Technology Ltd, Cambridge, UK) and an optical microscope. Most analyses were obtained under the settings of 0.003 mbar, 12 kV and 150 μA. However, voltage and current were often increased to 18 kV and 200 μA, respectively, to observe more discrete colors and zonings.

A scanning electron microscope (SEM) (JEOL JSM-6480LV) equipped with energy dispersive spectroscopy (EDS) (Oxford x-act) based at UQAC was used to produce back-scattered electron (BSE) images. Analysis parameters were 15 kV and a working distance of 12 mm. The EDS-SEM was used to identify Nb-bearing minerals and undetermined inclusions as well as to confirm the presence of chlorides on thin sections prepared with acetone.

Major elements were analyzed using a microprobe (JEOL JXA-8900 L) at McGill University (Montréal, Quebec, Canada) having the parameters set at 15 kV, 20 nA and a beam size of 10 μm. Multiple analyses used a beam size of 5 μm to characterize thin zoning and to identify micrometric inclusions within pyrochlore. We applied the ZAF method for matrix corrections.

Trace elements in pyrochlore and columbite-(Fe) were analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Our analyses used an UP-213 laser ablation system (213 nm) from New Wave Research coupled with an Agilent 7700x ICP-MS. Calibration was performed by using NIST SRM-610 for pyrochlore with ^{44}Ca as internal standard and GSE-1G for columbite-(Fe) analysis with ^{57}Fe as internal standard. The beam diameter was 100 μm with a pulsing rate of 20 Hz.

3. Results

3.1 Petrography of the niobium-bearing units

The niobium mineralization is predominantly distributed within the dolomitic portion of the carbonatite although it may also be found in minor amounts within the calcitic facies. There is no significant Nb mineralization in the ferro-carbonatite central core. This study focuses solely on the Nb-bearing units comprising the dolomitic facies and younger mineralized calcitic units enclosed within the dolomitic facies.

The carbonatite is strongly banded at a centimeter to meter scale (Fig. 2). Mineral proportions are highly variable both between and within the bands. Niobium mineralization appears in the form of elongated subvertical lenses varying from a few millimeters to several meters in width and having a complex geometry. These lenses are also visible within the calcitic units enclosed within the broad dolomitic assemblage. Other petrological units are also observed, including xenoliths of syenites, glimmerites and cumulates of magnetite.

3.1.1 Dolomitic rocks

The dolomitic facies is characterized by the same mineralogical assemblage throughout the complex, composed mainly of medium-grained, hypidiomorphic dolomite free of cleavage with accessory phlogopite, magnetite, pyrite and several types of apatite. Ilmenite, hematite, sphalerite, chlorite, amphibole, quartz, zircon, barite and REE minerals (e.g. bastnäsite and monazite) are also present in trace amounts. Accessory minerals appear disseminated within the carbonatite or concentrated in bands (flowbanding?) forming economic lenses (Fig. 3). The dolomite is generally equigranular and shows no apparent zoning (Fig. 4A). Dolomite does not show any obvious calcitization nor replacement by a secondary mineral. Mineralization is composed of fluorcalciopyrochlore and columbite-(Fe). The dolomitic rocks are usually weakly to moderately altered and are characterized under polarized light by grayish dolomite grains, a light chloritization of phlogopite and a darkening of pyrochlore grains. Rare lamellae of calcite are also observed within some phlogopite grains.

3.1.2 Enclosed calcitic units

Enclosed calcitic units are subvertical across the dolomitic units. Hydraulic fracturing of the dolomite rocks near the margins of the calcitic rocks also confirms the interpretation of later calcitic injections (Fig. 4D). They are mineralized and are—from a mineralogical point of view—different from the outer barren calcitic unit of the carbonatite. For example, the outer calcitic unit holds amphiboles and has a green pervasive tint, features not observed in the calcite injections. Unlike the dolomitic rocks, calcitic rocks are medium- to coarse-grained and are idiomorphic with apparent cleavages (Fig. 4B). A mosaic polygonal texture is often visible, but grains are not deformed as is often observed in many other carbonatites (Chakhmouradian et al., 2016). Accessory minerals (Ap, Mag, Phl, Py) are the same as those found in the dolomitic facies, however they are mostly disseminated. The calcitic injections are not altered suggesting they crystallized during or after the alteration event. Furthermore, pyrochlores found in this facies are idiomorphic, often zoned, unaltered and hence light brown. Columbite-(Fe) grains observed in the calcitic injections are heavily fractured and are interpreted as antecrysts from the dolomitic facies.

3.2 Nb mineralization

At the 1600’ (~485 m) level, the petrography of the mineralization shows that fluorcalciopyrochlore and columbite-(Fe) account for approximately 65% and 35%, respectively, of Nb mineralization. As fluorcalciopyrochlore and columbite-(Fe) are the most abundant and main minerals exploited for Nb at the Saint-Honoré carbonatite, only these two minerals are considered for the remainder of this study.

3.3 Fluorcalciopyrochlore

For our purposes, fluorcalciopyrochlore will be referred to as pyrochlore (Pcl) given that other pyrochlore species are much less abundant and have not been as extensively studied. Fluorcalciopyrochlore (pyrochlore) has been the main mineral exploited for Nb at the Saint-Honoré deposit since 1971. Unaltered pyrochlore grains are usually euhedral, typically 0.01–2 mm in size, but are up to a centimeter in size in a few samples. They are usually light brown to gray with a greenish tint. A few grains are zoned (Fig. 5) and are usually inclusion-free, excepting a few apatite or rare pyrite inclusions. Most of the economic pyrochlore mineralization is associated with magmatic apatite (AP1) in bands, lenses or clusters within the dolomitic unit (Fig. 6). Pyrochlore grains are also distributed randomly in the carbonatitic matrix, but at a much lower proportion. Coarser and zoned pyrochlores are also observed in the calcitic units. The geochemistry of unaltered pyrochlores shows the expected major elements: Ca, Na, Ti and F. In contrast, altered pyrochlores show leaching of most of the Na, F, Ca and Sr as well as the addition of Fe and Mn (Table 1). Fresh, weakly and moderately altered pyrochlores are distinguished by the proportion of pores, their color (from brown to blackish) and their shapes, varying from octahedral to anhedral.

3.4 Columbite-(Fe)

In hand samples, columbite-(Fe) can easily be misidentified as magnetite. It is black with varying shapes and sizes (ranges from 10 μm–1 mm). Under cathodoluminescence, inclusions of calcite and fluorite are easily distinguished by orange and blue colors, respectively (Fig. 5D). The inclusions are irregular in shape and may account for up to 50%

of a columbite-(Fe) grain. Calcite and/or fluorite inclusions are a discriminating characteristic of columbite-(Fe). As with pyrochlore, columbite-(Fe) is observed to be disseminated within the dolomitic matrix, but is in a higher proportion within magmatic apatite (AP1). In general, a dark orange microcrystalline apatite (AP2) is associated with columbite-(Fe) (Fig. 6B). AP2 is orange in hand samples, but is dark orange unless under intense light under the microscope. Where columbite-(Fe) is present rather than pyrochlore, darkened dolomite grains and partly chloritized phlogopite are present. A few grains of columbite-(Fe) are observed in the calcitic rocks as xenocrysts with no inclusions of calcite or fluorite. Nevertheless, unlike pyrochlore, columbite-(Fe) grains show no zoning and are generally observed in association with altered dolomite intersected by very fine-grained orange apatite (AP2). Unlike unaltered pyrochlore, columbite-(Fe) has an insignificant content of Ca, Na and F, but a considerable amount of Fe and Mn (Table 2).

3.5 Trace elements in Nb mineralization

To characterize the trace elements in both minerals, LA-ICP-MS analysis was performed on five pyrochlore and five columbite-(Fe) samples (Table 3). Elements including Al, Si, K, Zr, Ta and Hf do not show any significant difference between pyrochlore and columbite-(Fe). These elements, except for K that is undocumented in the pyrochlore crystal structure, are generally found in the B-site and are therefore immobiles (Atencio et al., 2010). Pyrochlore has a very high Th content compared to columbite-(Fe). On the other hand, columbite-(Fe) is enriched in U and it does not follow the same trend as Th as normally expected (both are recognized as being held in the A-site). Transitional metals such as V

298 are surprisingly high in columbite-(Fe), up to 100× higher than in the pyrochlore samples
299 (Fig. 7).
300
301 REEs also display large variations in abundance between pyrochlore and columbite-(Fe)
302 samples. LREE abundance in pyrochlore is nearly ten times greater than in columbite-(Fe)
303 whereas HREE and Y abundance is significantly higher in the columbite-(Fe) (Table 3,
304 Fig. 7 & 8). A comparison of the median content of REEs in pyrochlore from the Aley
305 carbonatite (Chakhmouradian et al., 2015) and pyrochlore from the Saint-Honoré
306 carbonatite shows the latter to have lower or similar REE amounts. Major elements (e.g.
307 Na, Ca, F) are, however, found at higher amounts in pyrochlores from Saint-Honoré than
308 found in the Aley carbonatite.
309

310 ***3.6 Crystallization of halite***

311 Sodium is a major cation in fluorcalciopyrochlore at the Saint-Honoré carbonatite. While
312 Ca and F are both observed as inclusions of calcite and fluorine within columbite-(Fe), Na-
313 bearing minerals are not observed as inclusions. However, halite is ubiquitous in the Saint-
314 Honoré carbonatite (Guillaume Matton, Niobec Inc., personal communication, 2015) and
315 is either observed disseminated or filling fractures. Its proportion is difficult to estimate
316 underground as it is leached during mine operations, such as drilling and logging. Halite
317 was always observed in pores of moderately altered pyrochlore (Fig. 9A & B) in those
318 samples with a decreased Na content. Kamenetsky et al. (2015) described halite crystals in
319 pyrochlore melt inclusions (a conclusion that relies heavily on interpretation), but we could
320 not find any halite in fresh pyrochlore nor within columbite-(Fe) grains.

4. Discussion

The study of the mineralization highlighted a strong association of pyrochlore and columbite-(Fe) with the accessory minerals. An intrinsic relationship between pyrochlore and columbite-(Fe) was also identified by the presence of calcite and fluorite inclusions under cathodoluminescence and, under SEM analysis, grains showing ongoing alteration from pyrochlore into columbite-(Fe). Alteration appears to be hydrothermal and the enrichment of Cl in columbite-(Fe) reinforces this interpretation. Chloride, along with leached Na from pyrochlore, could be involved in the formation of halite.

4.1 Petrology of the Nb-bearing units and mineralization

Within the dolomitic units, apatite and other accessory minerals (Phl, Mag, Py) are agglomerated in lenses. Considering the post-Grenvillian geological setting, this foliation-like pattern is interpreted as an igneous texture (flowbanding) induced by the low viscosity of the carbonatitic magma (Treiman, 1989). Alternatively, accessory minerals in the calcitic units are generally disseminated and lenses are less frequent. It suggests that the magma chamber was less turbulent in the late magmatic stage. These calcitic units are thought to be derived from a later event given their coarser grain size, the presence of well-developed cleavages and the absence of alteration. Pyrochlores in these calcitic units are euhedral and mostly unaltered. A few columbite-(Fe) grains are also visible, but they are highly fractured without calcite and fluorite inclusions. These columbite-(Fe) grains are likely antecrysts from the dolomitic facies. Antecrysts refer to crystals that did not crystallize from the calcitic magma, but still have a relationship with the magma (as described in Charlier et al., 2005).

Both columbite-(Fe) and fluorcalciopyrochlore are intimately associated with apatite, a common characteristic in carbonatites (Hogarth et al., 2000; Knudsen, 1989). The first type of apatite (AP1) is translucent, euhedral and zoned as described by Chakhmouradian et al. (2017). Primary textures suggest this apatite to be of magmatic origin. A few inclusions of AP1 were observed within pyrochlore grains suggesting it is syngenetic. AP1 and pyrochlore might have crystallized earlier in the magmatic evolution as Nb was probably transported with phosphate and fluorine complexes resulting in the co-precipitation of apatite and fluorcalciopyrochlore (Hogarth et al., 2000; Knudsen, 1989). As proposed by Jago and Gittins (1991), fluorine might lower melting temperatures, thereby precipitating pyrochlore. To have pyrochlore crystallized instead of other Nb-bearing minerals, the liquid must have more than 1% F (Mitchell and Kjarsgaard, 2004). Magmatic apatites (AP1) appear to be in equilibrium with the second type of apatite (AP2, fine-grained, anhedral and orange) as they are unmodified when cross-cut by AP2. However, AP1 produces a thin outer white rim under cathodoluminescence (Fig. 6D). The AP2 follows random patterns in the carbonatite. Most of the pyrochlores are altered by the AP2: pyrochlore darkens, develops pores and tips are truncated.

4.2 Alteration of pyrochlore

Although some replacement of pyrochlore by columbite-(Fe) from Saint-Honoré has been documented (Mitchell, 2015), a lack of proper samples has previously hindered a complete interpretation. Our study provides more complete evidence for the removal of A-site

366 cations and the transitional sequence of alteration of fluorcalciopyrochlore to columbite-
367 (Fe).
368
369 According to the published literature (e.g. Lumpkin and Ewing, 1995), the first stage of the
370 alteration of pyrochlore is the leaching of Na. When Na is completely leached, minor Fe
371 and Mn begin filling vacancies in the A-site. At the same time, F is slowly leached from
372 the Y-site and Cl is suspected to replace F. Alteration then leaches Ca and Sr with Fe and
373 Mn partly filling this vacancy leading to crystals having a composition of $(Fe,Mn)Nb_2O_6$,
374 referred to as columbite. Moreover, if alteration persists, tiny pores, as small as 1 μm, may
375 be left. The smallest pores are orientated (Fig. 10A) and are related to zoning, crystal
376 structure weaknesses or fractures. The larger pores containing halite, calcite and fluorite
377 are irregular in shape, angular and never spherical (Fig. 9A & B) as it would be expected
378 for melt inclusions. Inclusions of altered pyrochlore to columbite-(Fe) are also visible (Fig.
379 10A).
380
381 The alteration of pyrochlore correlates with the alteration level of the carbonates and other
382 accessory minerals, such as phlogopite to chlorite. Thus, alteration of pyrochlore depends
383 on its physical properties (fractures or any other crystal weaknesses) and corrosion along
384 the alteration front. For the Saint-Honoré samples, microprobe (Fig. 10A, C & D) and BSE
385 imagery (Fig. 10B) clearly show the columbitization process along margins and fractures.
386 Pyrochlore is altered stepwise into columbite-(Fe) as the fluid weakens the structure
387 through leaching of the major cations. Pyrochlore is clearly not in equilibrium with the

388 fluid; a pyrochlore in contact with a fully altered pyrochlore to columbite-(Fe) will tend to
389 transform as well (Fig. 10).
390
391 In addition to the leaching of Na, Ca and Sr and their replacement by Fe and Mn on the A-
392 site, other trace element levels are modified during alteration. Our microprobe and LA-
393 ICP-MS analyses showed an enrichment of Cl, transition metals (Cr, V, Y) and HREEs as
394 well as a decrease in LREEs in columbite-(Fe) relative to pyrochlore (Fig. 7 & 8). A loss
395 in LREEs in columbite-(Fe) might be due to lower compatibility of LREEs than HREEs in
396 common rock-forming minerals (Linnen et al., 2014) and are therefore leached out during
397 alteration. These LREEs are found as fine needles of bastnäsite in immediate vicinity of
398 weakly altered pyrochlore. Columbite-(Fe) had an average of 510±155 ppm Cl (Table 2)
399 whereas pyrochlores had Cl concentrations below detection limit (70±160 ppm Cl; Table
400 1). A Cl enrichment during alteration (Fig. 11) is therefore evident and a Cl-rich fluid
401 suggests hydrothermal activity. Weathering can be dismissed as we observed no
402 petrographic evidence, such as gypsum or karst, at the sampled levels. Geodes, karsts and
403 highly altered carbonates are observed in the upper 120 m of the Saint-Honoré carbonatite
404 (Thivierge et al., 1983), but not any deeper. Thus, supergene alteration (weathering) as the
405 source of Cl is less likely. Unfortunately, Cl in pyrochlore is poorly documented and its
406 position in the crystal structure remains unclear. However, based on its chemical
407 similarities with F, it is assumed to be replacing F in the Y-site.
408
409 In pyrochlore, the mean value of Y_2O_3 is below detection limit (850±761 ppm) while its
410 content in columbite-(Fe) exceeds 3920±754 ppm. Yttrium behaves similarly to other

411 HREEs and is therefore considered as a heavy rare earth element sensu lato. It replaces A-
412 site cations (Atencio et al., 2010). A HREE enrichment of a magnitude of ~5 is observed
413 in columbite-(Fe) (Table 3; Fig. 7). This is similar to results from the Aley carbonatite
414 where pyrochlore and fersmite were compared (Chakhmouradian et al., 2015). This also
415 agrees with the results of Néron (2013, unpublished data) who observed a HREE-rich rim
416 around apatite and suggested a hydrothermal event for the REE mineralization in the Fe-
417 carbonatite of the Saint-Honoré complex. No other primary mineral in the carbonatite has
418 shown a considerable Y content. This suggests that Y and HREE did not originate from an
419 earlier magmatic stage but from a later event.
420
421 The enrichments of Y, HREEs or any other metals could arguably have been related to a
422 volume change due to columbite-(Fe) collapsing during alteration. A gain of roughly 10%
423 Nb_2O_5 is observed in columbite-(Fe) compared to unaltered pyrochlore. On the other hand,
424 heavy REEs (including Y) increase 4 to 6× in columbite-(Fe). Considering Nb is immobile
425 and varies much less than any other enriched element, this hypothesis of an enrichment by
426 a volume change is unlikely.
427
428 An intriguing transitional alteration state was also observed. The mineral is called
429 “ferropyrochlore” by the mine geologists, although it does not fit the classification of
430 Atencio et al. (2010). Geochemically, this pyrochlore has completely lost its Na, but only
431 half of its Ca. As Ca is leached, it is replaced by Fe±Mn. Analyses have shown a pyrochlore
432 with 7% of FeO and 7% CaO. The sum of major divalent oxides (FeO+MnO+CaO+SrO)
433 during alteration is stable at approximately 17% and increases above 21% when Ca is

completely leached out and the alteration to columbite-(Fe) is complete. Fersmite is known as a transitional state of alteration of pyrochlore to columbite-(Fe) or as an alteration product of columbite-(Fe) (Lumpkin and Ewing, 1995). However, fersmite is not observed anywhere in the carbonatite.

4.3 Origin of alteration

Based on Lumpkin and Ewing (1995), the ternary diagram of A-site monovalent and divalent cations and vacancies can be used to define the origin of the alteration. Alteration can be either a late magmatic alteration, a hydrothermal event or a supergene alteration (Nasraoui and Bilal, 2000; Zurevinski and Mitchell, 2004). At the Saint-Honoré carbonatite, the use of the ternary diagram is fairly straight-forward considering: (1) there are only two major A-site cations in the pyrochlore, which are respectively monovalent and divalent (Na and Ca); (2) various samples show various stages of alteration of pyrochlore; and (3) more than 800 microprobe analyses were used. This includes 543 microprobe analyses from 1978 (SOQUEM) and 136 from 2011 (SGS Canada). To ensure reproducibility, we added 145 new microprobe analyses performed on pyrochlore and columbine-(Fe).

Apfu (atoms per formula unit) of the A-site were calculated with a structural formula based on the assumption that B-site anions are immobile and therefore have a sum of two. Results were plotted into the triangular (A-site monovalent and divalent cations and vacancy) plot to provide an alteration trend (Fig. 12). Fe and Mn introduced during alteration were calculated as A-site cations to evaluate more precisely the vacancy in the A-site. Otherwise,

fully transformed pyrochlore to columbite-(Fe) would have plotted in the upper part of the vacancy field implying an origin by supergene alteration, although our observations clearly show that this is not the case for the Saint-Honoré complex. This is a false assumption considering that Fe and Mn are divalent cations (as are Ca and Sr) and are therefore required in the calculations. Moreover, this method was developed solely for pyrochlore and not for columbite-(Fe). However, plotting columbite-(Fe) with pyrochlore fits the purpose in the diagram as it reinforces the alteration trend. Figure 12 clearly shows a transitional trend from a primary pyrochlore to a hydrothermally-altered pyrochlore into columbite-(Fe). This is in accordance with the higher Cl content of columbite-(Fe) and the HREE rim around AP1.

The hypothesis that the alteration is of a hydrothermal origin is strengthened by the enrichment of Cl and HREEs in columbite-(Fe) (Tables 1 & 2). Chloride suggests an aqueous fluid whereas the presence of HREE follows a similar description of hydrothermal enrichment in the ferro-carbonate core of the carbonatite (Néron, 2015). However, the presence of fluorite suggests that F was probably a component of the hydrothermal fluid.

4.4 Origin of halite

The presence of ubiquitous halite in the Saint-Honoré carbonatite is intriguing. Sodium is certainly magmatic in the Saint-Honoré carbonatite as it is a major constituent of fluorcalciopyrochlore (up to 8% Na_2O), one of the first minerals with apatite to crystallize in a carbonatitic magma (Hogarth et al., 2000; Knudsen, 1989; Hogarth et al., 2000). The

strong relationship of pyrochlore to apatite and the textural evidence also argue for a magmatic origin.

The origin of chlorine is, however, enigmatic. From the spatial distribution of halite in and around magmatic minerals from the Saint-Honoré carbonatite, Kamenetsky et al. (2015) proposed halite, and specifically chlorine, to be mantle-derived, based on the presence of halite in melt inclusions found in pyrochlore, apatite, phlogopite and pyrite. Although we did not study phlogopite, apatite and pyrite, our study of the Nb-bearing minerals of the carbonatite offers a slightly different understanding of the petrogenesis of halite. Petrographic observations and geochemical analyses of pyrochlore and columbite-(Fe) demonstrate that Na was leached during alteration whereas Cl was related to hydrothermal fluid. Thus, the Na is considered to be magmatic in origin and some Cl as hydrothermal (Tremblay et al., accepted). Although it is possible that some halite in the carbonatite is indeed magmatic, given the observation of halite in pyrochlore, halite crystals were all produced by the release of Na during the alteration of pyrochlore. Interestingly, the only units showing halite are those having more radiogenic Sr (Kamenetsky et al., 2015). As such, these observations confirm that Na has a magmatic origin, but that some of the Cl is fluid-related. A portion of the halite has therefore a magmato-hydrothermal origin. The absence of Cl in other magmatic minerals (e.g. apatite and phlogopite) reinforces the hypothesis of Cl being from a hydrothermal fluid and not from a primary origin. It does not preclude that some halite might have crystallized from a magmatic event, but none of our observations can confirm this hypothesis.

A mass balance study determined whether the alteration of pyrochlore was an important source of Na for post-magmatic activity such as fenitization. We based our calculations on the Na content of 51,600 whole rock analyses. It is important to specify that these results come from various rock types of the mine property, including units having little halite. Values follow a log-normal distribution and range from below the detection limit to 5.77% with a log-normal mean of 0.329%. Cl is a readily soluble element and is quite likely lost during drilling, mine operations, sample preparation, etc. Thus, results from whole rock analysis are considered to be less reliable. Therefore, we used the Cl content from an unpublished environmental study of mine effluents, as we consider that it offers a better overall sampling of Cl content for the complete carbonatite complex. However imperfect, it offers quantitative limits to the model. Analyses of 119 samples produced a Cl content of 0.008 to 1.88% and an arithmetic mean value of 0.429%, with a standard deviation of 0.337%. As the Cl/Na ratio is 1.54 in halite, and 0.429%/1.54 <0.329%, then it is apparent that Na is the limiting factor. Since there are no other major Na-bearing minerals in the carbonatite other than pyrochlore and halite, a maximum proportion of 0.622% halite could be formed if all Na was used. Other chlorides were also observed, however only in anecdotal proportions; a few grains of sylvite (KCl), hydrophilite ($CaCl_2$) and chloromagnesite ($MgCl_2$) were identified by SEM. It is possible they may have recrystallized during the preparation of the thin sections.

To quantify the amount of Na leached during the alteration of pyrochlore, the amount of pyrochlore in the carbonatite must be constrained. Historic whole rock analysis shows a mean Nb_2O_5 of 0.427% throughout the carbonatite, including holes drilled in barren units.

Considering fluorcalciopyrochlore accounted for more than 95% of the Nb-bearing minerals (Nb-rutile and other minor phases account for less than 5%) before alteration, we calculate a disseminated 0.615% pyrochlore in the carbonatite. This is based on pyrochlore containing approximately 66% Nb_2O_5. Hence, 0.615% pyrochlore at 5.42% Na (mean value of microprobe analysis) gives a weight percentage of 3.33% Na. Therefore, if all pyrochlore is indeed altered into columbite-(Fe), this limits the quantity of halite at 0.085%.

Based on the logarithmic mean content of Na (as Na has a log-normal distribution) in the carbonatite and the possible output of Na during alteration, pyrochlore alteration might contribute up to 10% of the necessary Na to form halite. Our results show that it is unlikely the Na needed to crystallize halite comes entirely from the alteration of pyrochlore; it was demonstrated, however, that it does contribute to some degree. The remaining Na needed to form the halite is thought to come from a Na-rich late magmatic event that was affected by hydrothermal activity, solubilizing Na and forming halite as soon as the parameters had changed. Furthermore, current resource estimates at the mine suggest that the proportion of pyrochlore increases with depth. If confirmed, the presence of Na would be higher and hence contributing even more to the mass balance. At even greater depths, it is possible that with the increased proportion of pyrochlore, Na from these pyrochlore units could have been released during hydrothermalism and, because Na is easily soluble, it could have been transported upwards in the carbonatite to form halite. This would reinforce the interpretation that the alteration of pyrochlore is a major contributor of Na.

5. Conclusion

548 The Saint-Honoré carbonatite offers a significant opportunity to study carbonatites:
549 sampling is available down to ~640 m deep and samples are devoid of weathering below
550 ~120 m. Samples are also easily accessible and very abundant. The petrological study of
551 the main Nb-bearing minerals, fluorcalciopyrochlore and columbite-(Fe), shed light on
552 their genesis and the alteration process. Grains of varying alteration levels showed
553 transitional states of alteration beginning at the crystal margins or within fractures. Na, Ca
554 and F are gradually leached out, creating a vacancy as the crystal structure changes. During
555 this process, inclusions of calcite and fluorite are formed within columbite-(Fe). A few
556 weakly altered pyrochlores had preserved halite in their pores. The Cl, Y and HREE
557 enrichments in columbite-(Fe) and the leaching of LREEs suggest this is a possible source
558 of crystallization of halite and a HREE-bearing, water-rich fluid. This refines the
559 interpretation of Kamenetsky et al. (2015): not all halite is magmatic, as some has a
560 hydrothermal origin.
561
562 Considering that most carbonatites are studied from outcrop samples or through shallow
563 drilling where weathering is prevalent, this study provides much needed insight into the
564 deeper evolution of carbonatites. We also provided new information regarding the
565 columbitization process and its contribution in the formation of halite in the Saint-Honoré
566 carbonatite. Chloride could have played an important role in the transport of REEs in
567 ankeritic rocks. The presence of Cl along with HREEs within columbite-(Fe) suggest that
568 the chlorine complex is an excellent carrier for REE as proposed by Migdisov and
569 Williams-Jones (2014).
570

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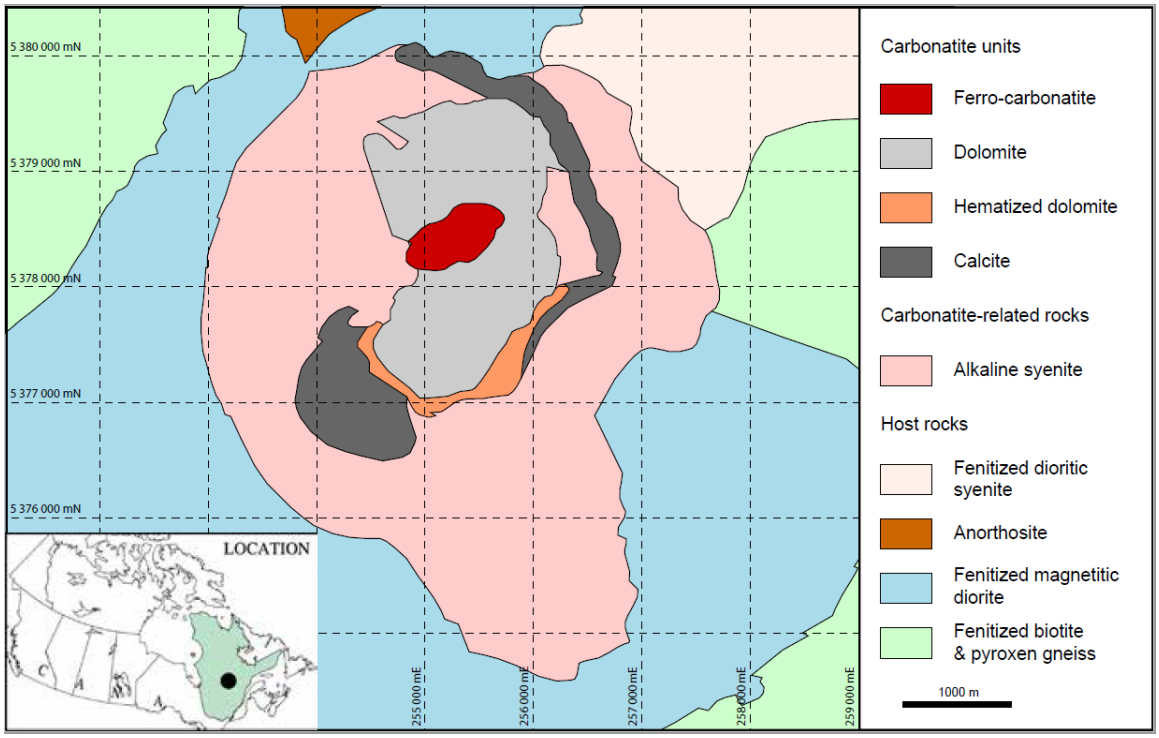
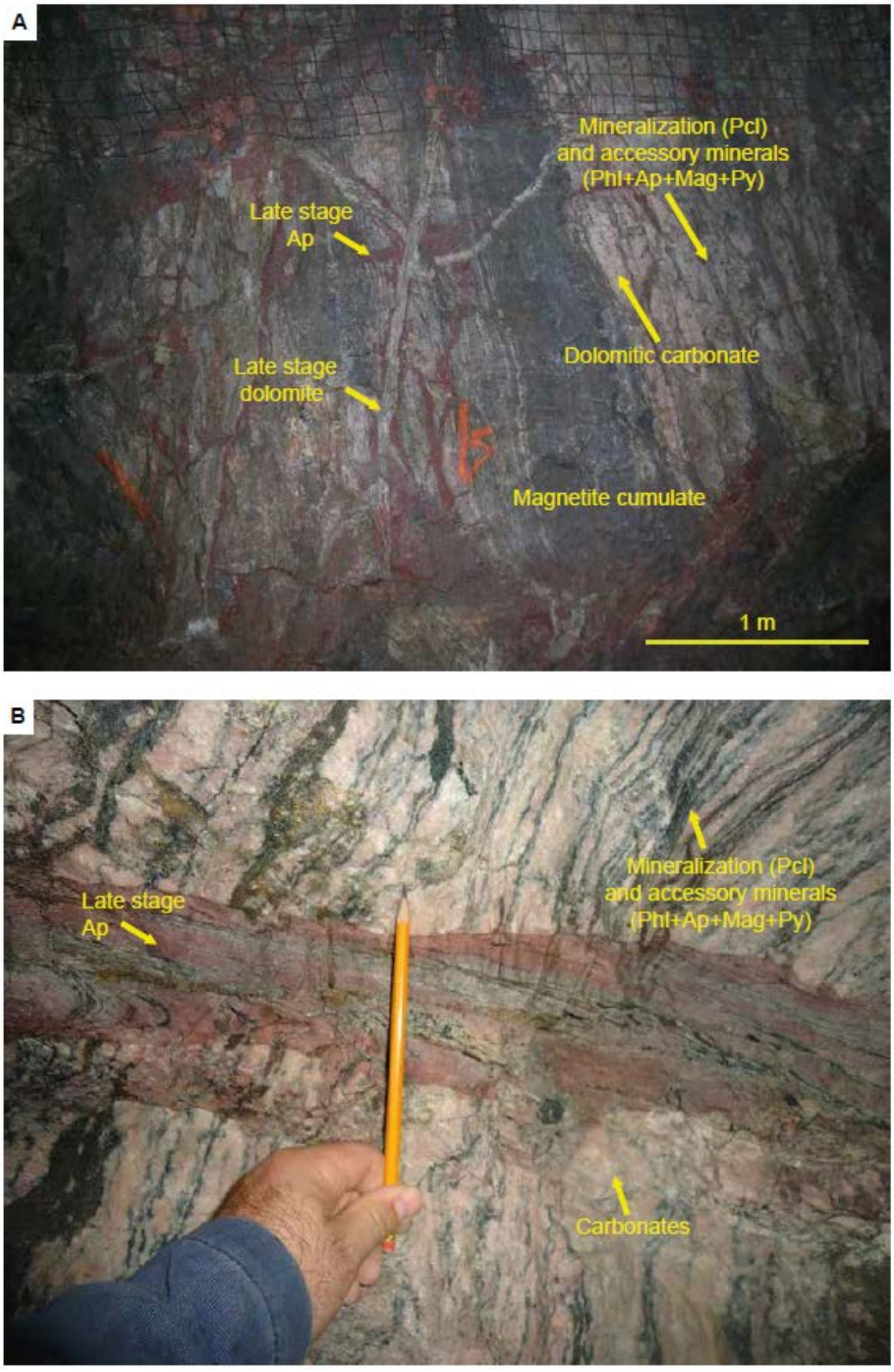
729

730 **Figure captions**

731 

732 Fig. 1. Simplified geological map of the Saint-Honoré alkaline complex (modified from

733 Vallières et al., 2013). The economically Nb-bearing unit is the dolomitic carbonatite unit.



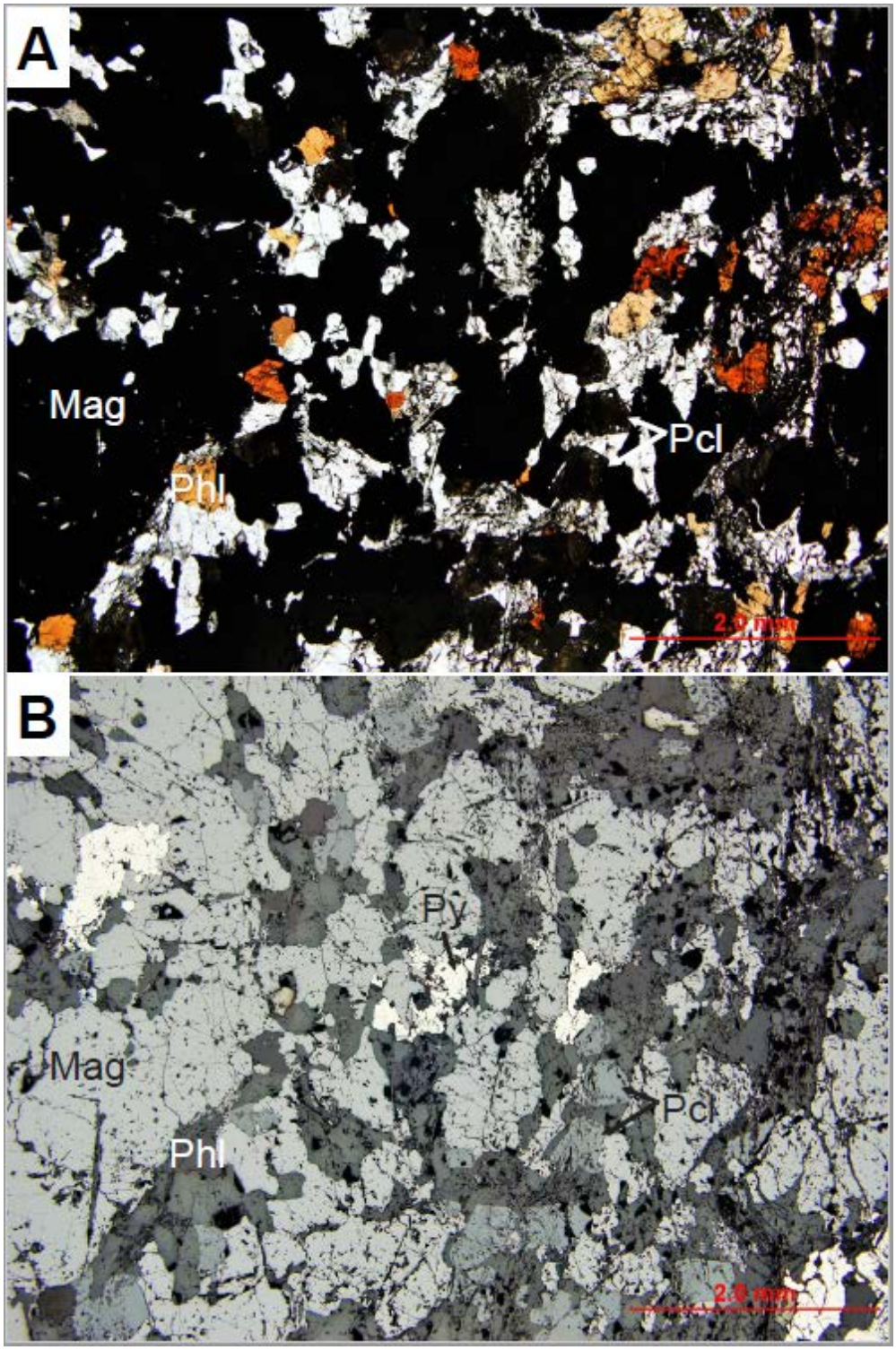
734

735 Fig. 2. Underground views of mineralized zones. (A) Dolomitic matrix with mineralized

736 bands of varying size. Late injections of dolomite with late stage apatite (red) cross-cut the

737 unit. (B) A late fine-grained apatite vein cross-cuts the banded mineralized carbonatite (AP:

738 apatite, Mag: magnetite, Phl: phlogopite, Py: pyrite, Pcl: pyrochlore).



739

Fig. 3. Polarized light (A) and reflected light (B) images of a lens of accessory minerals, including magnetite, phlogopite and pyrite in association with apatite and a few pyrochlore grains (Mag: magnetite, Pcl: pyrochlore, Phl: phlogopite, Py: pyrite).

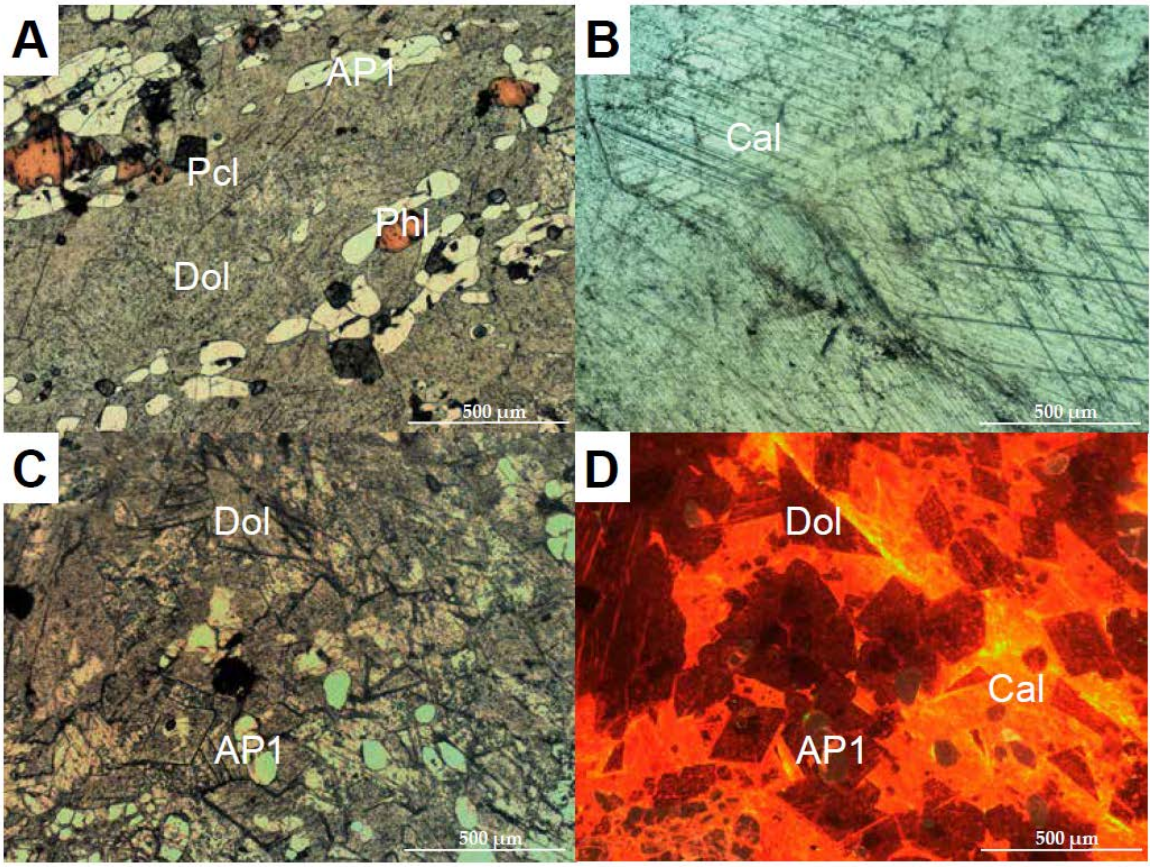
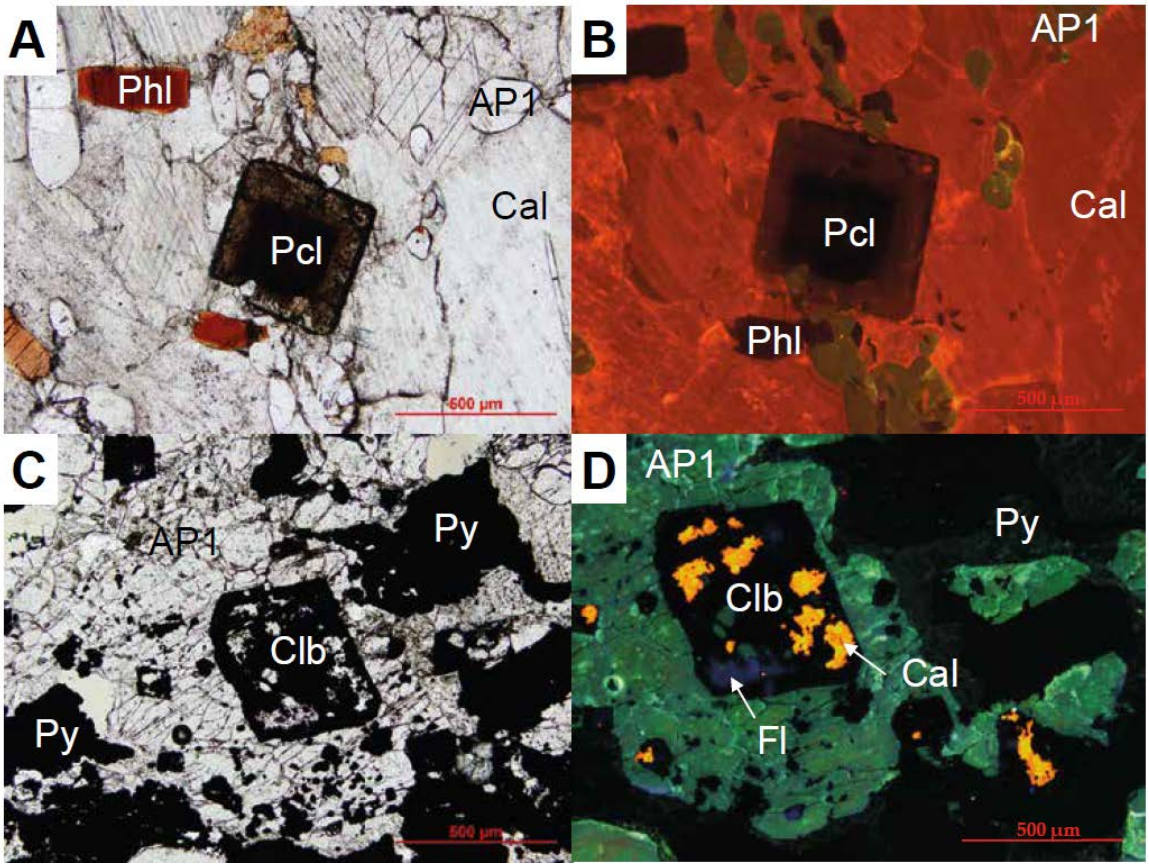


Fig. 4. A) Polarized light image of altered dolomite (Dol; grayish) with accessory minerals (AP1, Phl and Pcl). (B) Coarse-grained calcite (Cal) with apparent single and losangic cleavages. Polarized (C) and cathodoluminescence (D) images of hydraulic fracturing of dolomite by calcite. (Pcl: pyrochlore, Phl: phlogopite, AP1: apatite).

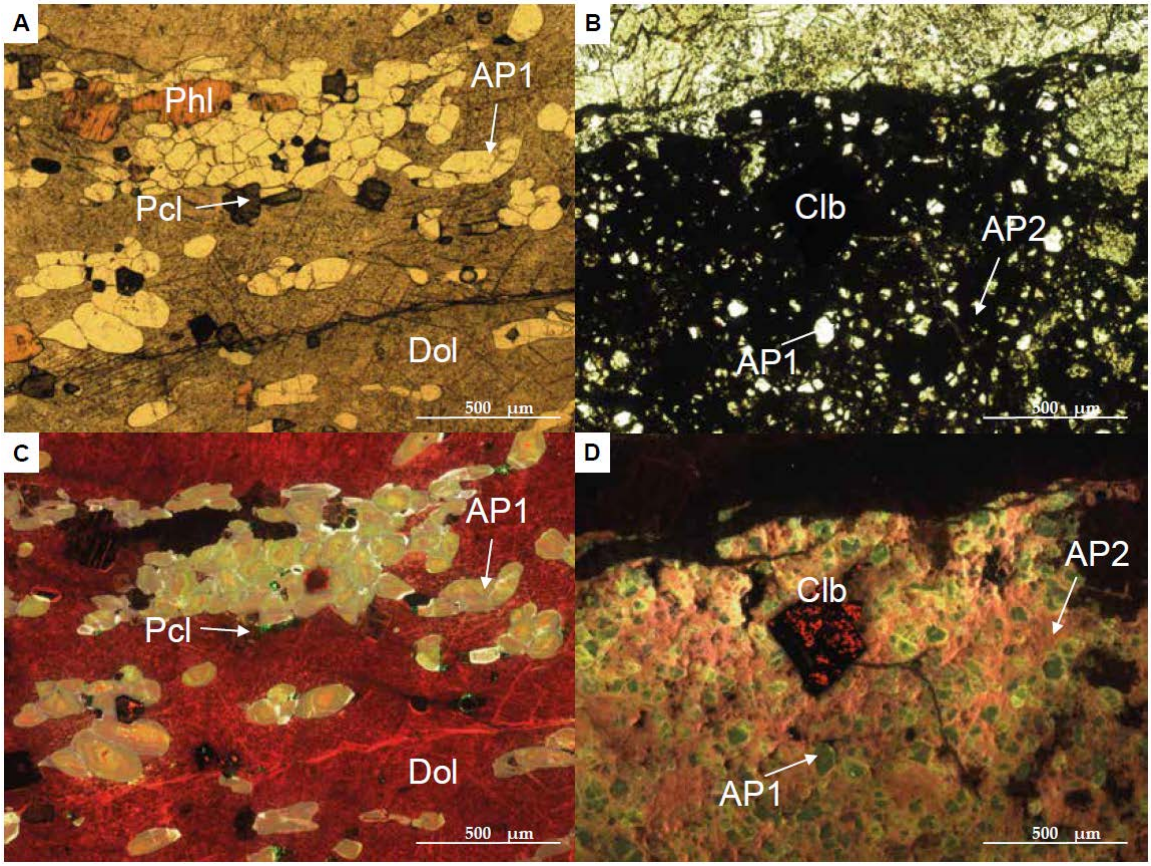


748

749 Fig. 5. Images of euhedral pyrochlore under polarized light (A) and cathodoluminescence

750 (B). Images of anhedral columbite-(Fe) with calcite and fluorite inclusions columbite-(Fe);

751 under polarized light (C) and cathodoluminescence (D).



752

753 Fig. 6. Euhedral pyrochlore associated with a magmatic apatite (AP1) cluster and accessory
754 minerals: under polarized light (A) and cathodoluminescence (C). Columbite-(Fe)
755 associated with dark orange apatite (AP2) altering carbonates: under polarized light (B)
756 and cathodoluminescence (D). (Dol: dolomite, Phl: phlogopite, Py: pyrite, Pcl: pyrochlore,
757 Clb: columbite-(Fe)).

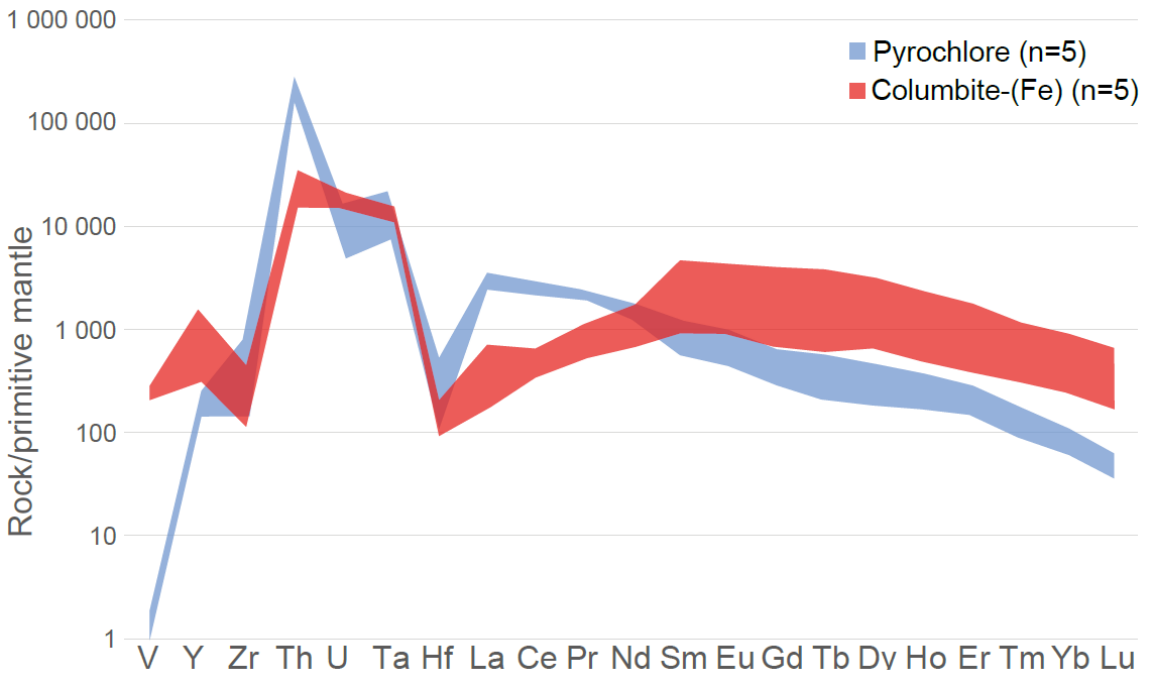
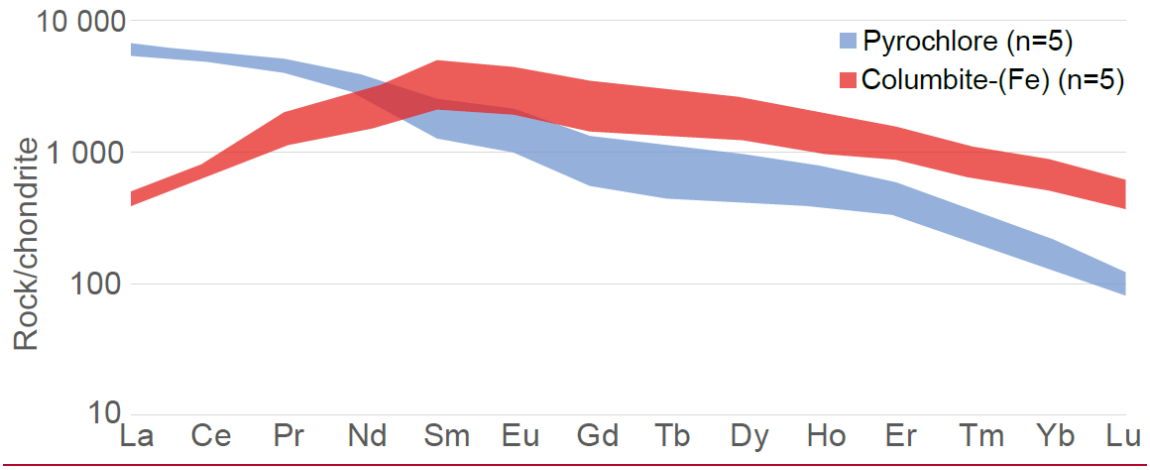
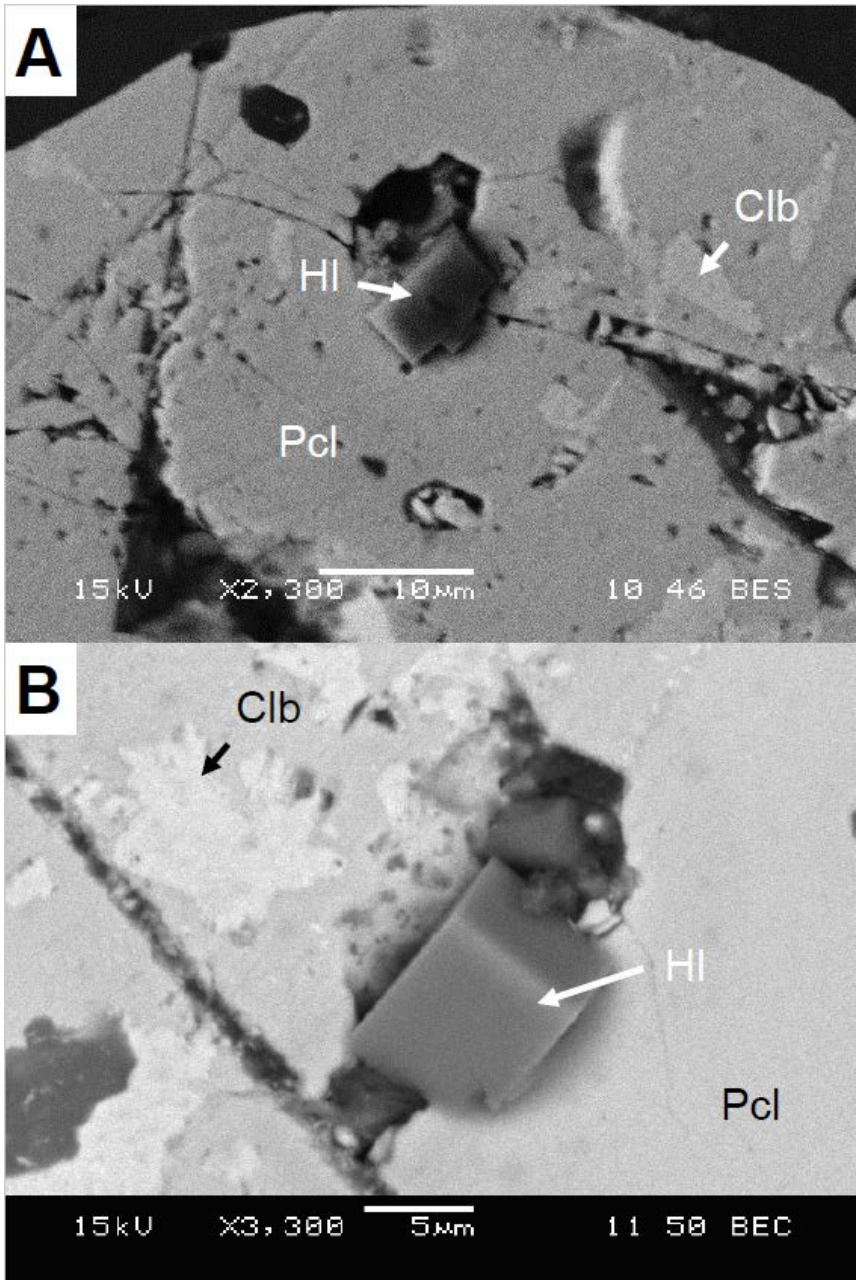


Fig. 7. Primitive mantle-normalized trace elements in pyrochlore and columbite-(Fe) from the Saint-Honoré carbonatite. A considerable increase in V and Y is apparent. Data obtained from LA-ICP-MS analysis.



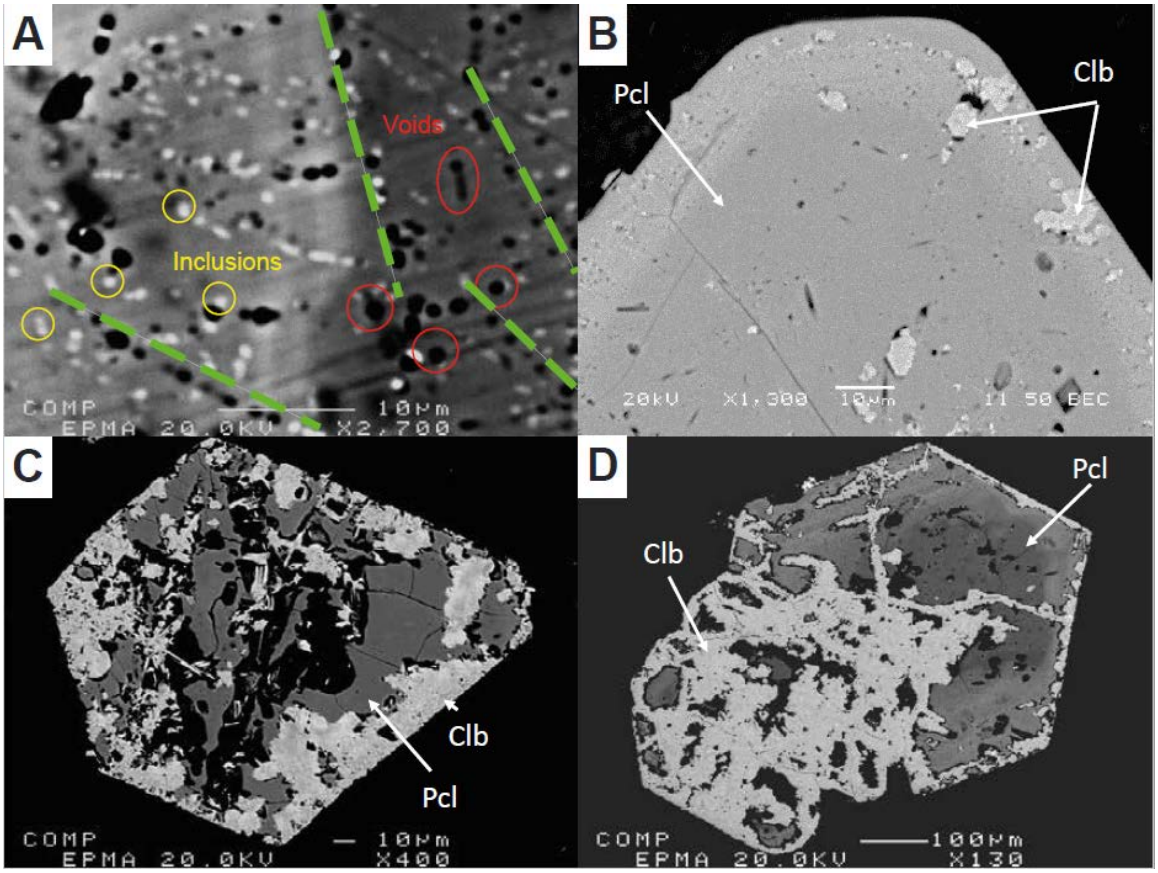
764 Fig. 8. Chondrite-normalized REE contents in pyrochlore and columbite-(Fe) from the
765 Saint-Honoré carbonatite. Columbite-(Fe) have a decreased content in LREEs, but is
766 enriched in HREEs compared to pyrochlore. Data obtained from LA-ICP-MS analysis.



767

768 Fig. 9. Microprobe (A) and SEM (B) images of halite (Hl) grains in weakly altered
769 pyrochlores (Pcl). Note that halite is crystallizing within irregular-shaped pores. Halite was

770 only observed in weakly altered pyrochlore (having lost some Na) and was not observed
771 in strongly altered pyrochlore or in columbite-(Fe). Clb: columbite-(Fe).



772

773 Fig. 10. Stages of pyrochlore alteration. (A) Microprobe image of microscopic pores in
774 weakly altered pyrochlore (Pcl). (B) SEM backscatter image of columbitization of a
775 pyrochlore on grain margins. (C) and (D) microprobe images of pyrochlores altering into
776 columbite-(Fe) (Clb) along fractures and grain margins.

777

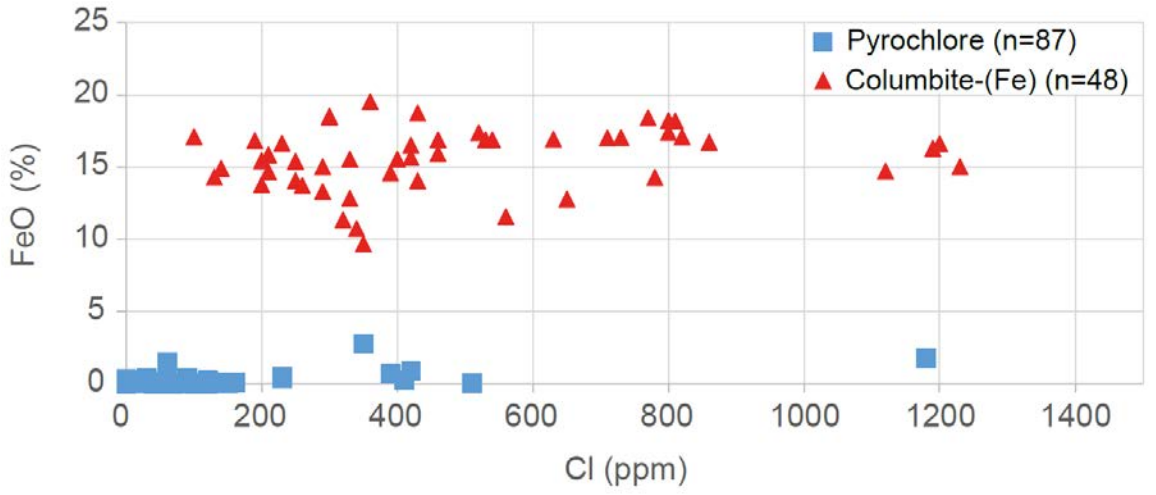
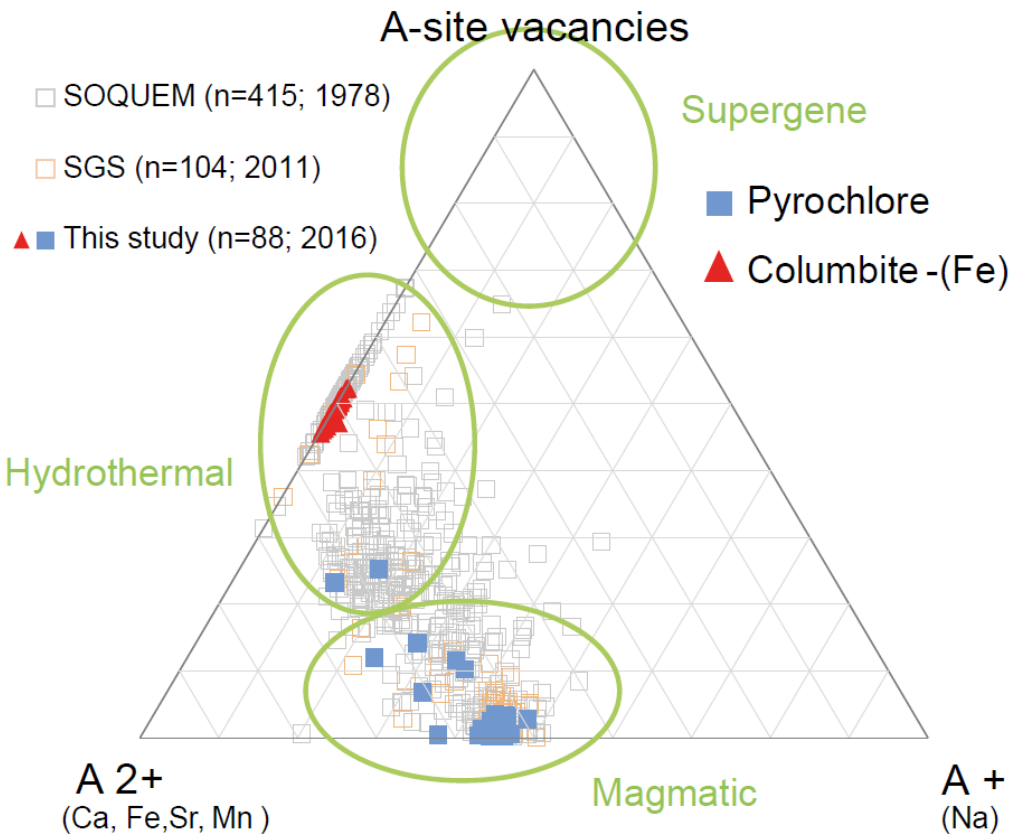


Fig. 11. Microprobe results showing the relationship between % FeO/Cl (ppm) content of pyrochlore and columbite-(Fe) from the Saint-Honoré carbonatite. The iron content is used to discriminate the pyrochlore from columbite-(Fe).



783

784 Fig. 12. Representation of pyrochlore and columbite-(Fe) within a ternary diagram of major
785 A-site cations (monovalent and divalent) and vacancies, based on 607 samples. Unaltered
786 pyrochlores are distributed in the magmatic field whereas strongly altered pyrochlores and
787 columbite-(Fe) are in the hydrothermal field.

Table 1: Representative major elements (wt%) of unaltered and altered fluorcalciopyrochlore from the Saint-Honoré carbonatite.

	Unaltered pyrochlore				Altered pyrochlore		
Wt.%	S11-C2-core	S01-C2	S07-C2	S07-C3	S21-C10	S05-C2-rim	S05-B
Na_2O	7.549	7.274	7.952	7.956	0.031	0.033	0.035
CaO	16.503	16.973	16.162	16.372	4.833	9.229	7.013
SrO	0.690	0.769	0.868	0.864	0.049	0.015	0.062
FeO	0.012	n.d.	0.005	0.102	11.570	6.177	9.671
MnO	n.d.	n.d.	0.008	n.d.	3.585	1.657	2.907
ThO_2	0.236	0.164	n.d.	0.049	0.289	0.217	0.132
UO_2	0.010	n.d.	0.029	0.031	n.d.	n.d.	0.032
Y_2O_3	0.069	0.083	0.083	0.094	0.290	1.165	0.302
TiO_2	2.036	2.827	1.197	1.595	2.304	4.553	2.182
Ta_2O_5	n.d.	n.d.	n.d.	0.029	0.040	0.012	n.d.
Nb_2O_5	69.840	67.697	71.525	70.472	75.896	70.588	75.678
Cl	n.d.	n.d.	0.010	0.008	0.056	0.051	0.035
F	2.753	3.023	3.242	3.348	0.090	n.d.	0.018
-O	1.159	1.273	1.365	1.410	0.038	n.d.	0.008
Total	98.539	97.537	99.716	99.514	98.995	93.697	98.059
Atoms per formula unit calculated on the basis of B=2 cations							
Na	0.884	0.862	0.928	0.933	0.003	0.004	0.004
Ca	1.068	1.111	1.042	1.061	0.287	0.560	0.419
Sr	0.024	0.027	0.030	0.030	0.002	-	0.002
Fe^{2+}	0.001	-	-	0.005	0.537	0.292	0.451
Mn	-	-	-	-	0.168	0.079	0.137
Th	0.003	0.002	-	0.001	0.004	0.003	0.002
U	-	-	-	-	-	-	-
Y	0.002	0.003	0.003	0.003	0.009	0.035	0.009
ΣA	1.983	2.005	2.004	2.034	1.010	0.973	1.024
Ti	0.092	0.130	0.054	0.073	0.096	0.194	0.092
Ta	-	-	-	-	0.001	-	-
Nb	1.908	1.870	1.946	1.927	1.903	1.806	1.908
ΣB	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Cl	-	-	0.001	0.001	0.005	0.005	0.003
F	0.526	0.584	0.617	0.640	0.016	-	0.003

Note: n.d. = not detected

Table 2: Representative major elements (wt%) of columbite-(Fe) from the Saint-Honoré carbonatite.

	Columbite-(Fe)					
wt.%	005-C1	011-C3	S11-C1	N47-C1	N22-C3	S21-C3
Na_2O	0.041	0.009	0.023	0.006	n.d.	n.d.
CaO	1.490	0.423	1.222	0.636	0.717	0.876
SrO	0.060	0.044	0.040	0.047	0.047	0.032
FeO	16.299	18.421	16.904	17.396	19.540	15.870
MnO	2.702	2.588	3.347	3.407	1.345	4.128
ThO_2	0.639	0.700	0.453	0.725	0.463	0.130
UO_2	n.d.	n.d.	0.024	n.d.	0.042	n.d.
Y_2O_3	0.648	0.235	0.111	0.230	0.209	0.191
TiO_2	2.902	3.652	2.731	2.487	3.405	3.081
Ta_2O_5	0.392	0.178	0.000	0.344	0.155	n.d.
Nb_2O_5	71.714	72.228	73.620	71.089	72.570	74.180
Cl	0.119	0.077	0.046	0.052	0.036	0.021
F	0.000	0.038	0.000	0.070	0.000	0.000
-O	0.000	0.016	0.000	0.029	0.000	0.000
Total	97.006	98.577	98.521	96.460	98.529	98.509
Atoms per formula unit calculated on the basis of six oxygen atoms						
Na	0.005	0.001	0.003	0.001	-	-
Ca	0.092	0.026	0.074	0.040	0.043	0.052
Sr	0.002	0.001	0.001	0.002	0.002	0.001
Fe	0.785	0.869	0.800	0.853	0.923	0.740
Mn	0.132	0.124	0.160	0.169	0.064	0.195
Th	0.008	0.009	0.006	0.010	0.006	0.002
U	-	-	-	-	0.001	-
Y	0.020	0.007	0.003	0.007	0.006	0.006
ΣA	1.044	1.037	1.048	1.082	1.045	0.996
Ti	0.126	0.155	0.116	0.110	0.145	0.129
Ta	0.006	0.003	0.000	0.005	0.002	0.000
Nb	1.868	1.842	1.884	1.885	1.853	1.871
ΣB	2.000	2.000	2.000	2.000	2.000	2.000
Cl	0.012	0.007	0.004	0.005	0.003	0.002
F	-	0.007	-	0.013	-	-

Note: n.d. = not detected

Table 3: Trace elements (in ppm) from fluorcalciopyrochlore and columbite-(Fe) samples collected from the Saint-Honoré carbonatite

	Fluorcalciopyrochlore					Columbite-(Fe)				
ppm	004-C4	004-C3	004-C3	004-C2	004-C1	021-C1	021-C2	021-C3	021-C4	021-C5
Cr	n.d.	n.d.	n.d.	n.d.	1	151	328	250	215	42
V	122	75	68	65	74	15 960	19 490	19 560	18 490	18 780
Al	990	1 302	1 341	751	1 310	990	1 120	1 720	2 490	610
Si	2 060	2 090	2 360	3 140	2 480	2 100	1 390	2 590	2 930	926
K	123	92	82	126	44	96	67	108	134	66
Y	623	482	461	817	592	1 016	2 190	5 090	1 530	1 407
Zr	2 040	709	486	3 260	2 970	399	1 557	1 696	536	1 083
Th	12 480	15 340	15 560	13 690	10 450	922	1 849	1 977	1 469	2 115
U	87	95	81	98	248	256	301	253	355	196
Ta	238	325	300	312	629	321	415	435	233	455
Hf	66	30	23	119	106	20	57	66	22	42
La	1 309	1 567	1 589	1 408	1 277	106	92	87	113	324
Ce	3 124	3 376	3 490	3 433	2 974	471	512	546	477	783
Pr	422	451	462	474	371	104	169	208	149	205
Nd	1 503	1 530	1 582	1 780	1 258	652	1 268	1 681	1 003	1 280
Sm	284	257	265	375	188	311	738	1 360	511	540
Eu	89	78	81	120	56	108	249	512	166	179
Gd	189	163	168	263	110	286	691	1 560	476	457
Tb	29	24	24	40	16	47	106	274	77	64
Dy	171	137	138	237	102	302	641	1 650	480	370
Ho	32	25	25	43	21	53	108	274	82	62
Er	71	55	53	94	53	133	249	596	188	140
Tm	7	5	5	9	6	16	27	61	22	16
Yb	30	22	20	36	30	91	142	303	114	82
Lu	3	2	2	3	3	11	15	32	12	9

Note: n.d. = not detected