



A petrographic study of Nb-bearing minerals at the Saint-Honoré niobium deposit

J. Tremblay^{1, a}, L.P. Bédard¹, and G. Matton²

¹ Sciences de la Terre, Université du Québec à Chicoutimi, Chicoutimi, QC

² Niobec Inc., Saint-Honoré-de-Chicoutimi, QC

^a corresponding author: jonathan.tremblay11@uqac.ca

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1. Introduction

Carbonatites are currently the focus of many studies to improve understanding of their petrogenesis and mineralization (e.g., Chen and Simonetti 2013; Chakhmouradian et al., 2015; Kamenetsky et al., 2015). Carbonatites are exploited for niobium (Nb); however they are also mined for Cu, P, and rare earth elements (REE). They tend to be enriched in Ba, F, Mn, Sr, V, Th, U, and Zr (Le Bas, 1981). Niobium is a strategic metal used in a broad range of applications, including superconducting magnets and steel alloys. Production of Nb has increased rapidly over the last decades (Roskill, 2013), driven by its use in modern equipment and for building pipelines in emerging countries such as China and India (Mackay and Simandl, 2014). However, only three mines currently produce most of the world's Nb. The Araxá and Catalão-II mines in Brazil (supergene deposits) account for more than 90% of the annual worldwide production, and the Saint-Honoré mine in Canada (magmatic-hydrothermal deposit) accounts for 8%. Other minor sources account for the remaining 2% (Papp, 2015).

This study examines mineralization at the Saint-Honoré Nb deposit. Initial studies that addressed mineralization of the Saint-Honoré carbonatite (Fortin-Bélanger, 1977; Thivierge et al., 1983) were conducted several decades ago, and recent studies that considered REE mineralization (Fournier, 1993; Grenier et al., 2012; Néron et al., 2013) did not treat the Nb-rich zone. Hence the relationships between the different Nb-bearing mineral phases remain poorly understood. Recent drilling in the deeper parts of the carbonatite offers an opportunity for new observations and improved interpretations. Herein we present the preliminary results of a petrographic study of Nb mineralization in the Saint-Honoré carbonatite.

2. Geology of the alkaline complex

The Saint-Honoré alkaline complex is in the Saguenay-Lac-Saint-Jean region, Québec (Fig. 1). It was discovered by airborne radiometric survey in 1967; exploitation began in 1976 and continues to the present. The Saint-Honoré deposit is an alkaline complex with a carbonatitic core comprising

concentric zones of varying composition, with calcite in its external portion to dolomite and ankerite towards its core (Fortin-Bélanger, 1977; Thivierge et al., 1983). The carbonatite is surrounded by a nepheline syenite envelope. Syenite xenoliths are observed within the carbonatite units. The carbonatite and syenite complex was intruded into Grenvillian diorite and gneiss, which was subsequently fenitized (Fig. 1). The carbonatite is covered by Paleozoic rocks of the Trenton Group (limestone) and Utica Formation (shale). Doig and Barton (1968) reported a K/Ar age of 565 Ma for the alkaline complex; more recently, baddeleyite from lamprophyre dikes associated with the Saint-Honoré suite yielded a U-Pb age of 582.1 ± 1.8 Ma (Michael Higgins, personal communication, 2015).

The crescent-shaped orebody is hosted entirely by dolomite and calcite units that surround the ferro-carbonatite (ankerite) core. It is currently mined to a depth of 850 metres and is open at depth. Most recent reserves estimates are 416 Mt grading 0.41% Nb (Vallières et al. 2013). Mineralization decreases gradually toward the margins of the carbonatite. The silicate rocks lack significant mineralization.

3. Objectives

Previous mineralogical studies of the Saint-Honoré alkaline complex focused primarily on the upper portion where minor interactions with surface water took place (Fortin-Bélanger 1977, Thivierge et al., 1983). Samples for this study were taken at greater depths to prevent any bias due to meteoric alteration, thus providing a clearer distinction between hydrothermal and magmatic processes. Several Nb-bearing carbonatite samples used in previous studies were degraded by weathering, and magmatic and/or hydrothermal features were only partially preserved. For example, it was recently demonstrated that the halite interpreted to be of magmatic origin is only in deep portions of the Saint-Honoré carbonatite (Kamenetsky et al., 2015).

For this study, rocks from two sub-horizontal diamond-drilled holes were considered representative of mineralization at the 490 m mine level. One hole (235 m long) plunges 6°

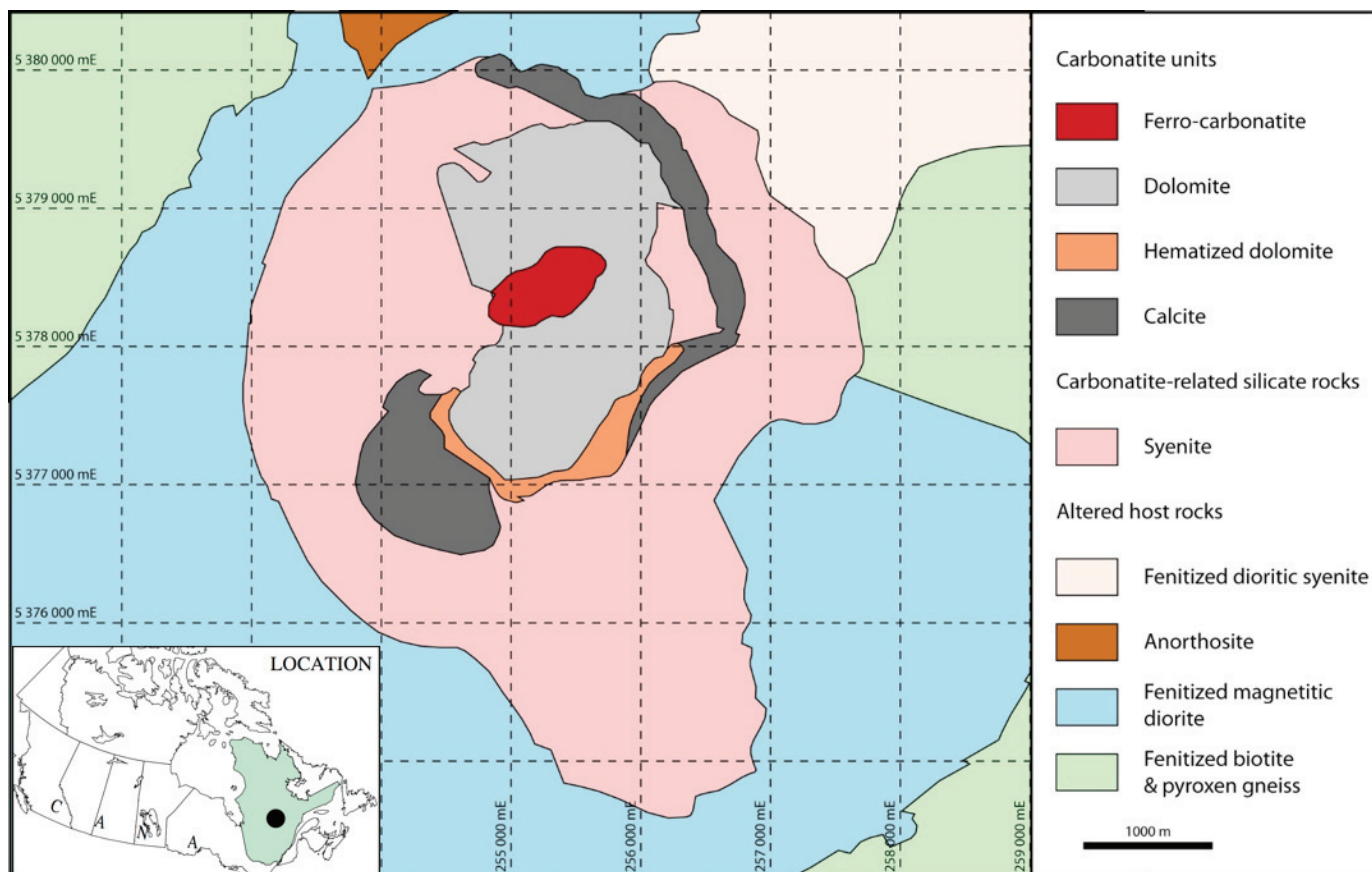


Fig. 1. Simplified geological map of the Saint-Honoré alkaline complex. Modified from Vallières et al., 2013.

north, the second (115 m long) plunges 31° south. They were selected because they provide a continuous view of mineralization from north to south in the mine. Twenty-one polished thin sections were prepared from the southern zone, 52 from the northern zone. These sections were examined using both polarized and reflected light microscopy as well as cathodoluminescence (CL) and scanning electron microscopy (SEM). Cathodoluminescence is particularly useful for detecting trace elements (activators), impurities, and growth textures (McLemore and Barker, 1987; Mariano, 1988, Götze, 2002; Götze et al., 2013). In carbonatites, magmatic zoning in apatite is clearly observed and provides critical information on geological evolution. Furthermore, zonation in pyrochlore may provide insight into the petrogenetic evolution of mineralization.

In this study we: 1) identify the Nb minerals and describe Nb mineral transformations that occurred in the carbonatite complex; 2) describe the mineralogical associations of Nb minerals to understand their evolution and petrogenesis; and 3) define variations in mineralization from north to south. Geologists at the Niobec Mine propose a north-south variation in the distribution of Nb minerals, where columbite would be predominant in the northern section and Na-Ca pyrochlore in the southern and central portions (Guillaume Matton, personal communication, 2015). Variation in Nb mineralization with

increasing depth has yet to be demonstrated.

4. Ore mineralogy

The carbonatite-hosting the orebody is composed predominantly of dolomite, calcite, magnetite, pyrite, phlogopite, fluorapatite, Ca-Na pyrochlore $[(Ca,Na)_2(Nb,Ti)_2O_6(OH,F)]$ and columbite $[(Fe,Mn)(Nb,Ti)_2O_6]$. Minor alkali feldspar, pyroxene, chlorite, quartz, zircon, ilmenite, rutile, hematite, pyrrhotite, sphalerite, barite, fluorite, siderite, REE minerals and other species of the pyrochlore group (e.g. uranopyrochlore $[(U,Ca,Ce)_2(Nb,Ta,Fe,Ti)_2O_6(OH,F)]$) have been observed throughout the carbonatite (Fortin-Bélanger, 1977; Thivierge et al., 1983; Grenier et al., 2013). The carbonatite units are strongly banded on scales of a few centimetres to several metres. Some band contacts are gradual whereas others are sharp. Mineral proportions are highly variable both between and within the bands. Despite a relatively homogeneous background of uneconomic Nb grades throughout the orebody, Nb-enriched zones in the form of asymmetric and elongated, steeply plunging lenses are distributed in very complex patterns.

5. Main niobium minerals

Niobium mineralization in the Saint-Honoré alkaline complex consists primarily of Ca-Na pyrochlore and columbite-(Fe) (Table 1). Both minerals are found throughout the carbonate

Table 1. Average chemical analyses, in per cent, of representative ore minerals and inclusions (calcite) determined by EDS-SEM analysis (4 analyses per mineral).

	Ca-Na pyrochlore	Columbite-(Fe)	Apatite	Inclusions in Columbite-(Fe)
TiO ₂	3.47	2.25		
FeO		15.99		
MnO		2.96		
CaO	15.42	0.95	35.23	43.88
Na ₂ O	6.08			
P ₂ O ₅			48.88	
Nb ₂ O ₅	68.71	77.86		
CO ₂				56.12
F	6.32		15.89	
Total	100.00	100.00	100.00	100.00

Note: Determined with an EDS-SEM system ("standardless analyses")

units. Thorium±Ta pyrochlore is uncommon. Unaltered Ca-Na pyrochlore forms euhedral 0.01-2 mm crystals that are generally beige, light brown, greyish or reddish. Altered Ca-Na pyrochlore grains are darker and difficult to distinguish from magnetite and columbite-(Fe). Under polarized light, Ca-Na pyrochlores are commonly zoned and have darker cores (Fig. 2a). Ca-Na pyrochlore is inclusion free, except for rare apatite grains. Observations under reflected light allow the distinction between pyrochlore and magnetite (Fig. 2b). Considering that this type of pyrochlore shows little heterogeneity, CL was mainly used for identifying textures, mineral inclusions, and overgrowths. Figure 2c illustrates a brown Ca-Na pyrochlore under CL with minor apatite inclusions and no overgrowth. Backscattered electron imaging (BSE) was used to identify inclusion free regions of the grain (Fig. 2d). X-ray dispersive energy (EDS) analyses (four per sample) indicate a high Ca, Na, and F content (Table 1). Calcium content varies from 12-18% CaO, sodium from 5-8% Na₂O, and fluorine from 4-9% F.

Columbite-(Fe) is the second most abundant Nb mineral at the mine, although it is considered a minor Nb-bearing phase (Vallières et al. 2013). Columbite-(Fe) is commonly anhedral and fractured. Under plane polarized light (Fig. 3a), columbite-(Fe) ranges from dark brown or dark grey to opaque. In highly altered rocks, columbite-(Fe) grains are difficult to distinguish from magnetite. However, reflected light shows textures resembling a spider web (Fig. 3b). Reflected light was therefore used to distinguish columbite from magnetite, as both are opaque in polarized light and show no internal reflections in the Saint-Honoré carbonatite. Columbite-(Fe) shows surprising peculiarities under CL (Fig. 3c). Although columbite is quenched by Fe (no luminescence; Götze et al., 2013), mineral inclusions within columbite show orange luminescence. EDS-SEM analyses (Table 1, Fig. 3d) indicate that the orange inclusions are calcite.

Thorium±Ta pyrochlore is uncommon. Complete

characterization of this species of pyrochlore is outside of the scope of this study. Figure 4a illustrates one of the few grains observed in plane polarized light. It shows a characteristic pleochroism varying from translucent to pink and green. Oscillatory zoning is well developed having zones of similar thickness. Primary fractures (excluding those produced by secondary alteration) are only in the pinkish layers, suggesting radioactive damage. Reflected light analysis shows apatite inclusions (Fig. 4b). Apatite, magnetite, and pyrochlore crystals appear automorphous and moulded together suggesting a primary coeval origin. Cathodoluminescence shows multiple zonations (Fig. 4c) that are not visible under plane polarized light. The deep green suggests a strong activator. Using BSE imaging, Th±Ta pyrochlore appears brighter than Ca-Na pyrochlore (Fig. 4d). The composition of the dark halos has yet to be determined, but preliminary results show no Th or Ta values.

Calcium-Sodium pyrochlore and columbite grains are generally found in apatite bands and lenses, but rarely together. Apatite lenses in dolomitic units appear to be richer in Nb minerals than those in calcitic units. Furthermore, a few Ca-Na pyrochlore grains have a columbite-(Fe) rim, suggesting replacement. Unlike most Nb-bearing minerals, which are associated with apatite, Th±Ta pyrochlore grains occur in magnetite-rich lenses or syenite xenoliths in carbonatite.

Two types of apatite are observed in the Saint-Honoré alkaline complex. Magmatic apatite is disseminated or concentrated in flow bands and lenses throughout the carbonatite units. Grains are translucent under plane polarized light, but are orange in hand specimen. Magmatic zoning is best observed under CL. Niobium mineralization is associated with this magmatic apatite. The second form of apatite is a fine-grained red hydrothermal alteration product (Néron et al. 2013) largely confined to apatite veins. These veins could easily be misidentified as hematite. The apatite veins crosscut the Nb

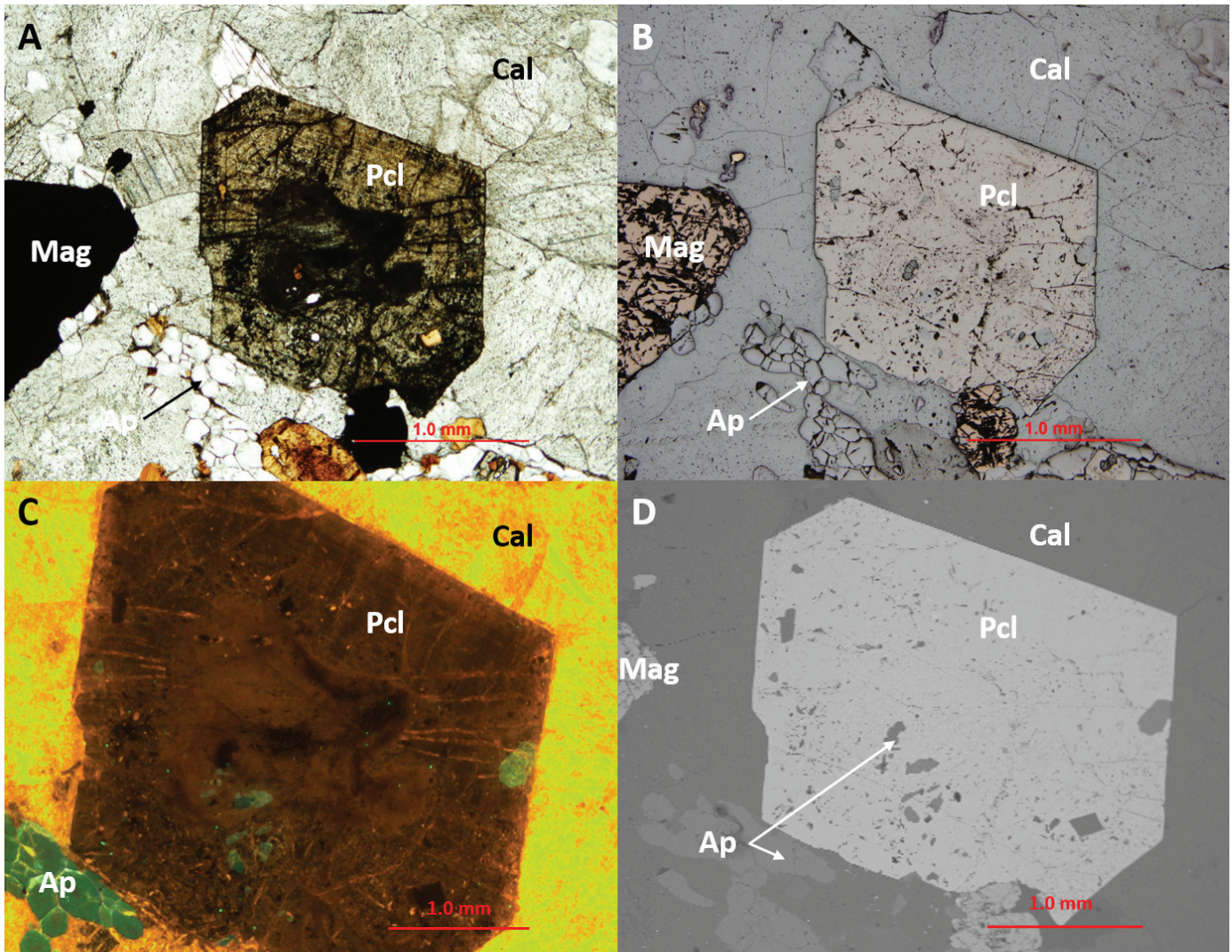


Fig. 2. Calcium-sodium pyrochlore (Pcl) morphology and mineralogical associations. **a)** Plane polarized light showing a fine zonation in a euhedral Pcl grain. **b)** Reflected polarized light showing distinction between magnetite (Mag) and Pcl. **c)** Cathodoluminescent image highlights inclusions of apatite (Ap; green) in Pcl and the calcite (Cal; orange). **d)** BSE image of apatite (Ap) inclusions in Pcl grain.

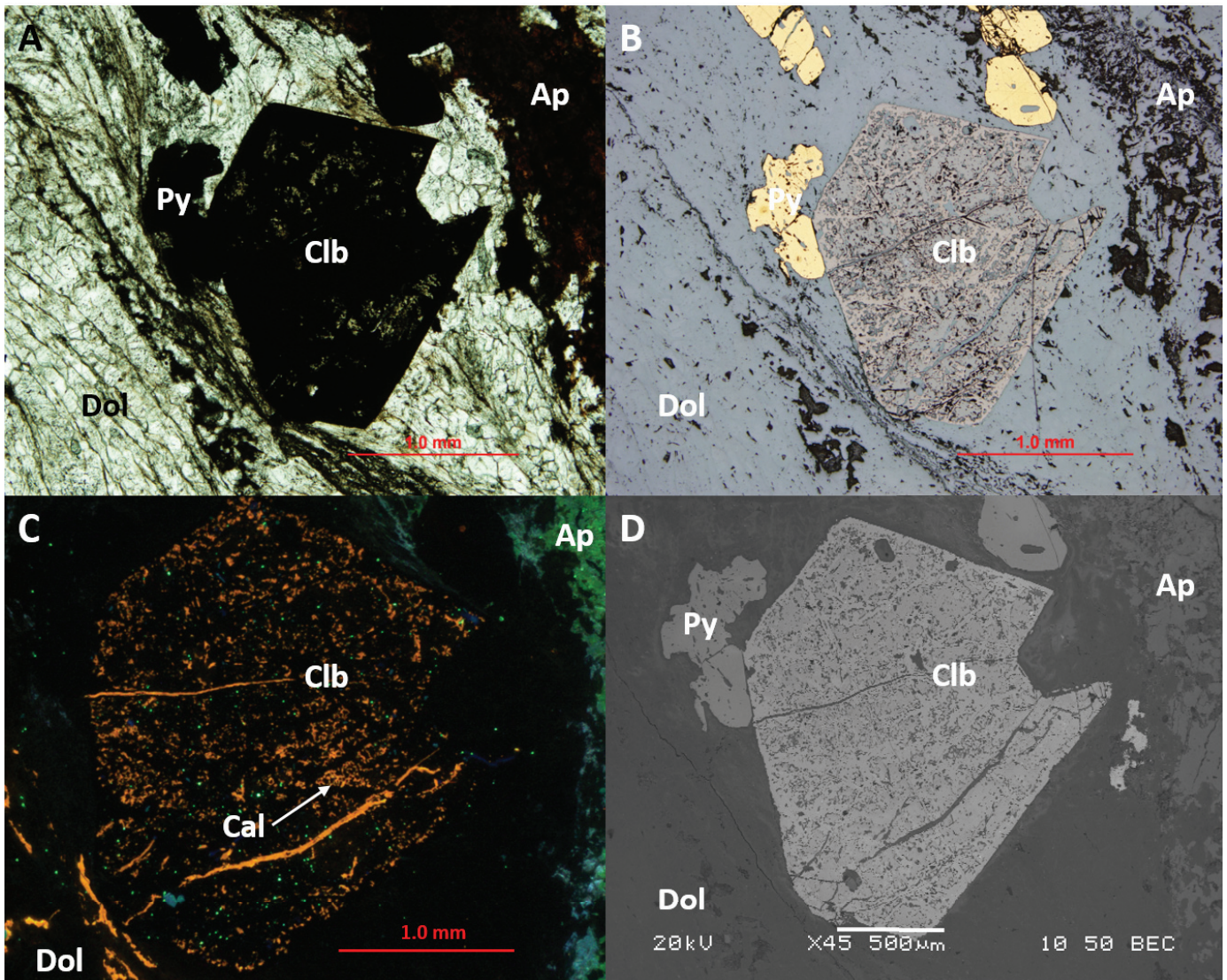


Fig. 3. Columbite-(Fe) (Clb) morphology and mineralogical associations. **a)** Dark brown to almost opaque Clb grain in contact with anhedral pyrite (Py); plane polarized light. **b)** The Clb grain contains multiple inclusions; reflected light. **c)** The cathodoluminescence activator signal (orange) suggests that inclusions in this Clb grain are composed of calcite (Cal). **d)** BSE image; SEM confirms the opaque matrix is columbite-(Fe) and the orange, under cathodoluminescence, is calcite.

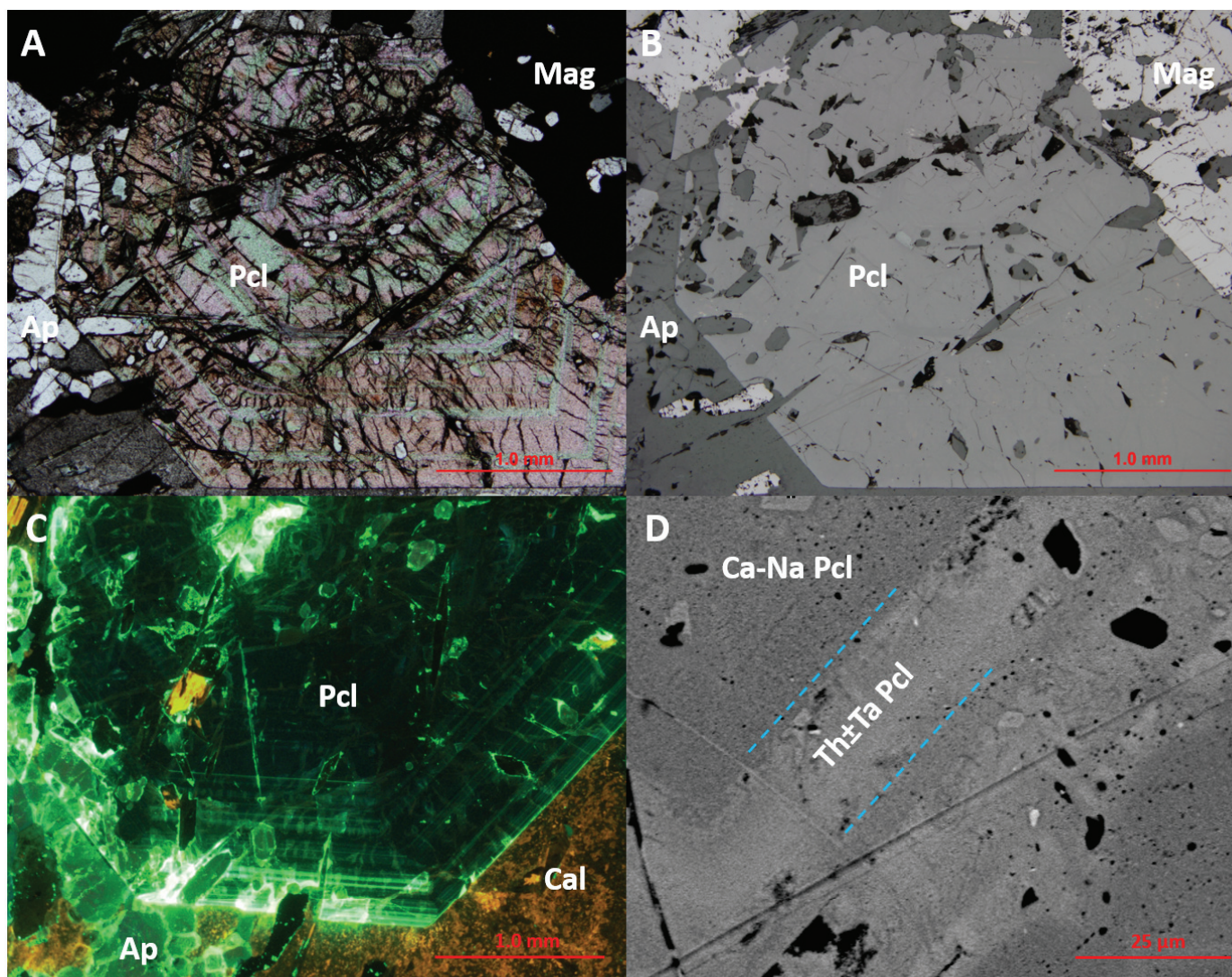


Fig. 4. Thorium±Ta pyrochlore (Pcl) morphology and mineralogical associations. **a)** Pyrochlore shows strong pleochroism and oscillatory zoning under plane polarized light. **b)** Apatite inclusions in pyrochlore displaying sharp contacts; reflected light. **c)** Unusual deep green observed in Pcl under cathodoluminescence. **d)** BSE image; SEM confirms the light halos are of Th±Ta and the dark halos refer to Ca-Na pyrochlore with trace elements (precise composition to be determined).

mineralization and are not associated with Nb mineralization.

The mineralogical observations presented in this study suggest four main forms of Nb mineralization: 1) euhedral and unaltered brown Ca-Na pyrochlore; 2) opaque columbite-(Fe); 3) replacement of pyrochlore by columbite; and 4) brown Ca-Na pyrochlore that was hydrothermally altered by red apatite-forming fluid.

6. Summary

Ca-Na pyrochlore is the main Nb ore mineral at Saint-Honoré. Columbite-(Fe), previously considered only a minor phase, was observed in a large number (30%) of our mineralized samples. Both columbite-(Fe) and Ca-Na pyrochlore are associated with apatite-rich magmatic layers in dolomite, however a few apatite lenses in calcite are also mineralized. No mineralization is related to red hydrothermal apatite veins. P- and F-complexes likely transported Nb during the early stages of carbonatite magmatism (Knudsen, 1989; Hogarth et al., 2000; Cordeiro et al., 2011). This could explain the strong relationship between the Nb minerals and apatite and the presence of F in pyrochlore in the Saint-Honoré carbonatite complex. It can be assumed that Ca-Na pyrochlore grains are of magmatic origin. Columbite-(Fe) rims around Ca-Na pyrochlore strongly suggest a chemical disequilibrium. Another important observation is that calcite inclusions are visible within the columbite-(Fe) grains. It is possible that the columbite-(Fe) expelled incompatible elements, such as Na and F, whereas Ca formed calcite suggesting a phase transformation from pyrochlore to columbite as the magma evolved.

The Th±Ta pyrochlore type needs further study using SEM to confirm absence of U. Oscillatory zoning and radial fractures in the pinkish zonations are consistent with the idea that the green zonations are relatively Th-rich; this Th is likely the cause of the radial fractures (Fig. 4a).

Both Ca-Na pyrochlore and columbite-(Fe) are visible in the northern and southern part of the orebody. Textural observations suggest that columbite is a replacement for pyrochlore. Variation in Nb mineralization with increasing depth has yet to be demonstrated.

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