Nb-Ta-REE mineralization associated with the Crevier alkaline intrusion

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1. Introduction

The Crevier alkaline intrusion is in the Grenville Province, north of the Lac Saint-Jean region of Québec (Fig. 1). It covers ~25 km^2 (Bergeron, 1980) and intrudes charnockitic suites in the allochthon belt defined by Rivers et al. (1989). This intrusion has a U-Pb zircon age of 957.5 ± 2.9 Ma (Groulier et al., 2014) and is oriented 320°, along the axis of crustal weakness known as the Waswanipi-Saguenay corridor (Bernier and Moorhead, 2000). This corridor is related to the Saguenay graben, which hosts the Saint-Honoré (Niobec) Nb-Ta-REE deposit and Montviel REE deposit. The age of the Saint-Honoré carbonatite was estimated at 584 to 650 Ma (K-Ar whole rock; Vallée and Dubuc, 1970; Boily and Gosselin, 2004). The Montviel intrusion has a U-Pb zircon age of 1894 ± 3.5 Ma (David et al., 2006; Goutier, 2006). These crystallization ages are very different and cannot be related to a single event for the injection of alkaline intrusions. As mapped by Bergeron (1980), the Crevier alkaline intrusion is broadly composed of syenite and carbonatite rocks (Fig. 2). The Nb-Ta mineralization consists of pyrochlore hosted by a nepheline syenite dike swarm in the centre of the intrusion. The highest REE concentrations, up to 729 ppm La and 1465 ppm Ce, are at the edge of the Crevier alkaline intrusion (Niotaz sud showing; Fig. 2).

2. Geology of the Crevier alkaline intrusion

Bergeron (1980) divided the Crevier alkaline intrusion into four units (Fig. 2): 1) a main unit of massive nepheline syenite with variable textures and characterized by the presence of igneous carbonates; 2) a banded syenite formed by the injection of dikes of different facies (ijolite, nepheline syenite, biotite syenite, carbonate-biotite syenite, and carbonatite); 3) a late alkaline syenite; and 4) dike swarms of pegmatitic nepheline syenite containing mineralization.

Crosscutting relationships observed in the field indicate that the second and third units were emplaced into the first, and that dike swarms cut the first two units. These dikes, which constitute the principal hosts for the Nb-Ta mineralization, are in the centre of the complex and parallel the Waswanipi-Saguenay corridor. Mineralization consists of two types: disseminated magmatic mineralization represented by small grains of pyrochlore (≤1 mm), and late magmatic mineralization that cuts the dikes (Groulier et al., 2014). The latter type is associated with networks of veins and veinlets rich in sodalite, cancrinite, zircon, sulphides and larger grains of pyrochlore (≥1 mm).

3. Geochemistry

3.1. Whole rock analysis

Based on 41 whole rock analyses, the Crevier alkaline intrusion, similar to the St Honoré complex (Currie, 1976), is miaskitic. It has an agpaitic index that ranges from 0.8 to 1 and low zirconium content (mean value 650 ppm). Baddelyite is rare and no other zirconium silicates, such as eudialyte, were observed. Two-differentiation trends are visible on total alkali silica (TAS) diagrams (LeBas et al., 1992; Fig. 3) and Harker diagrams. The first trend, which shows an increase in SiO_2 from ijolite to pegmatitic nepheline syenites, is interpreted to reflect a fractional crystallization process. The second trend represents rocks containing carbonate minerals such as calcite or ankerite. In the TAS diagram (Fig. 3), ijolite is interpreted as the starting point for both trends, and corresponds to the most mafic rock found in the Crevier alkaline intrusion. This rock is probably the best candidate for the original magma composition. The two trends that start from ijolite can be explained by an immiscibility process that may have led to the separation of silicate and carbonatitic melts. Field observations, petrographic study, and immiscibility textures between a carbonated and silicate liquids observed at macroscopic scale, support this hypothesis. Trace elements, in particular REE, are generally enriched in the carbonatite compared to the silicate phase.

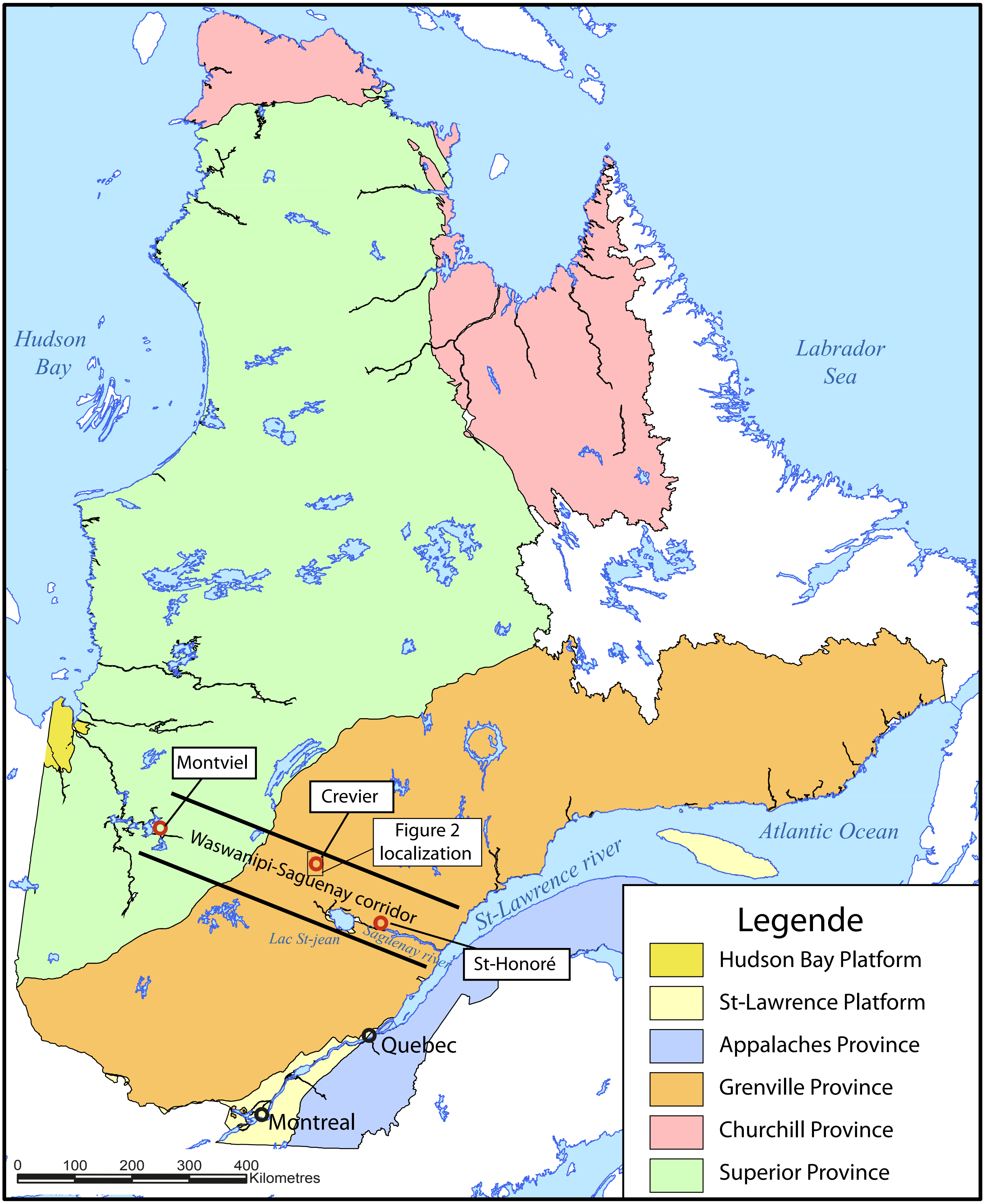

Fig. 1. Geological provinces of Quebec. Note the alignment of the principal alkaline intrusions along the Waswanipi-Saguenay corridor.

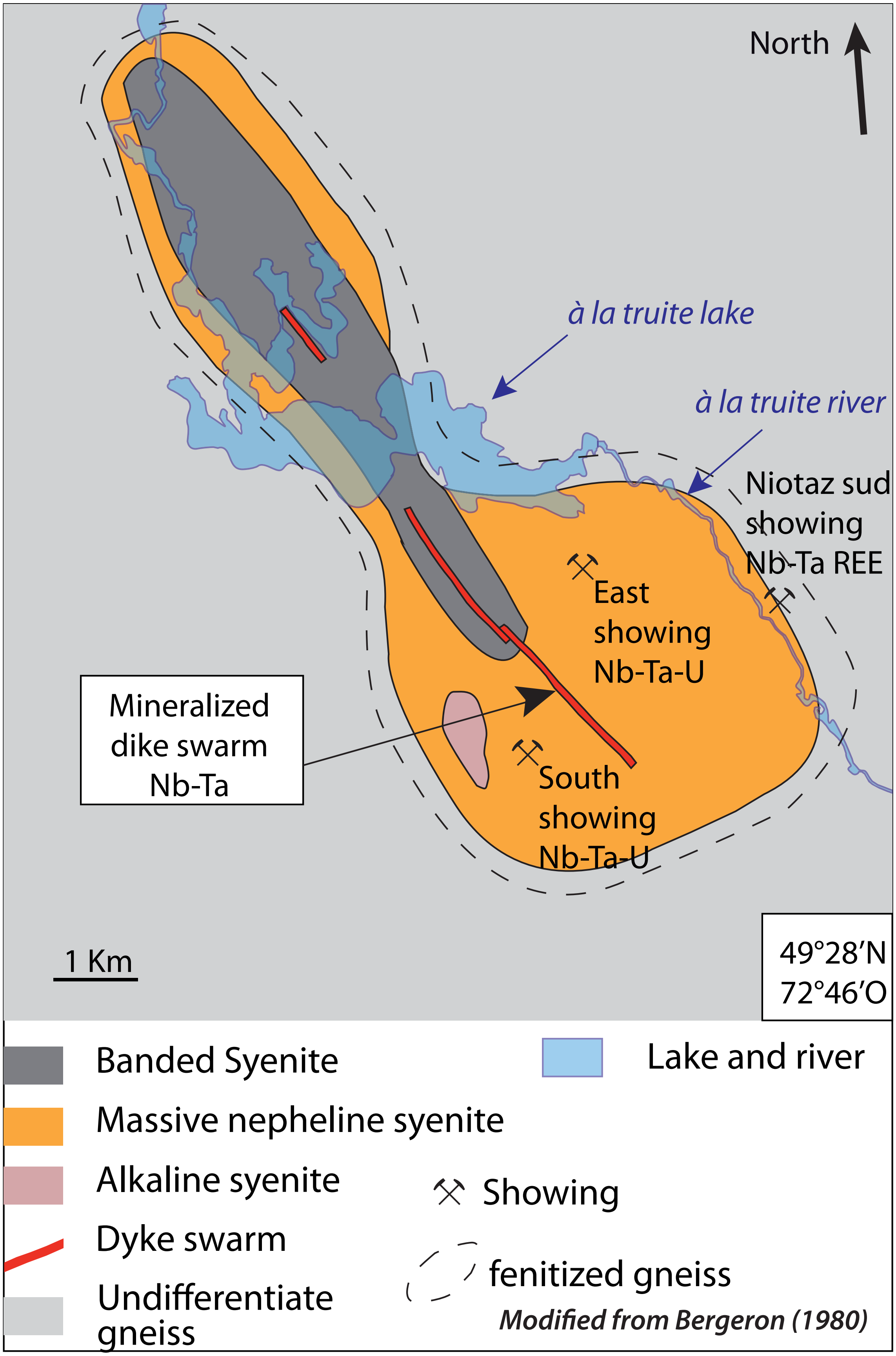

Fig. 2. Geological map of the Crevier alkaline intrusion. Modified from Bergeron (1980).

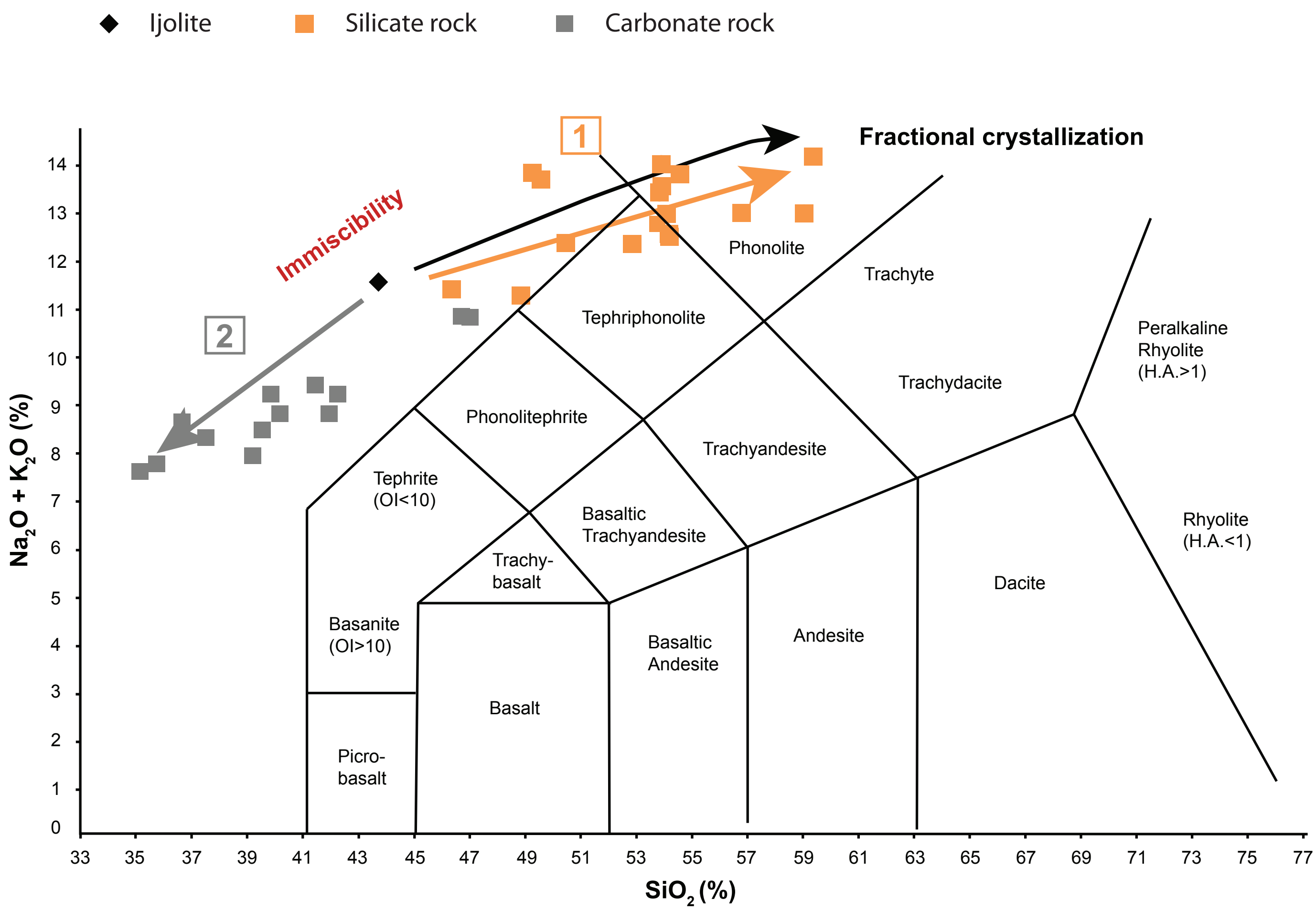

Fig. 3. TAS diagram (LeBas et al. 1992) showing composition of main rock types from the Crevier alkaline intrusion and two fractionation trends centred on ijolite.

3.2. Pyrochlore analysis

Niobium-tantalum mineralization in the Crevier alkaline intrusion is composed of oxides belonging to the pyrochlore supergroup of Atencio et al. (2010), defined by the general formula $A_{2-m}B_2X_{6-w}Y_{1-n}$. In the following, the most common elements in the formula are in bold.

The 'A' site is commonly occupied by a coordinating cation [8]; i.e. it is surrounded by eight other atoms with a large ionic radius (≈1 Å) or vacancy and, in some cases, H_2O. The A site preferably contains Na, Ca, Ag, Mn, Sr, Ba, Fe^{2+}, Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Y, Ce (and other lanthanides), Sc, U, Th, a vacancy or H_2O. The 'B' site is occupied by a coordinating cation [6]. This site typically contains high field strength elements (HFSE); more specifically, Ta, Nb, Ti, and Sb^{5+} and W; however, V^{5+}, Sn^{4+}, Zr, Hf, Fe^{3+}, Mg, Al and Si can also occupy this site. The 'X' site is mainly occupied by O but it may be replaced by OH or F. The 'Y' site commonly contains an anion but there may be a vacancy, H_2O or a very large (>>1 Å) monovalent cation (e.g.: OH^-, F, O, K, Cs and Rb). The parameters m, w and n in the chemical formula indicate occupancy values for the A, X and Y sites.

Minerals of the pyrochlore supergroup from the Crevier alkaline intrusion belong to the pyrochlore group sensus stricto (Nb+Ta≥2Ti and Nb>Ta). Previous pyrochlore analyses are given by Laplante (1980) and Hoggarth (1989). Laplante also described an uranopyrochlore in the carbonatite from the northern portion of the Crevier alkaline intrusion in the Lac à la Truite area.

Three pyrochlore populations may be distinguished in terms of crystal-chemical data on the diagram of Nasraoui and Bilal (2000; Fig. 4).Primary euhedral pyrochlore (Pcl I) has a Na or Ca cation that occupies the A site and no vacancies in this site. It is zoned and displays dissolution and recrystallization textures. In some cases an unidentified secondary silicate phase rich in Nb surrounds this type of pyrochlore. Secondary euhedral to subhedral non-zoned pyrochlore (Pcl II) has more vacancies in the A site than Pcl I, and is interpreted as its replacement. Late xenomorphic pyrochlore (Pcl III) contains more vacancies in the A site compared to Pcl I or Pcl II and is found in fractures that were open to circulation of late-magmatic fluids.

4. Geochronology

Uranium-lead and Lu-Hf analyses on zircon grains from the massive nepheline syenite were performed by LA-ICP-

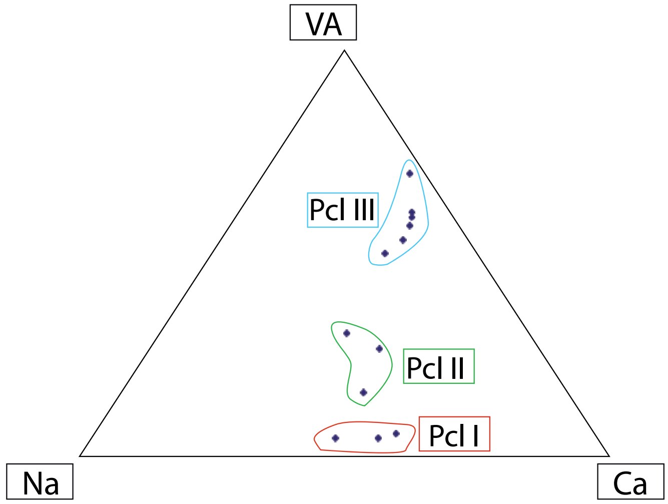

Fig. 4. Ternary (Na, vacancy (VA), Ca) plot (Nasraoui and Bilal, 2000) of three generations of pyrochlore (Pcl) from the Crevier alkaline intrusion indicating compositional differences between Pcl I, Pcl II and Pcl III.

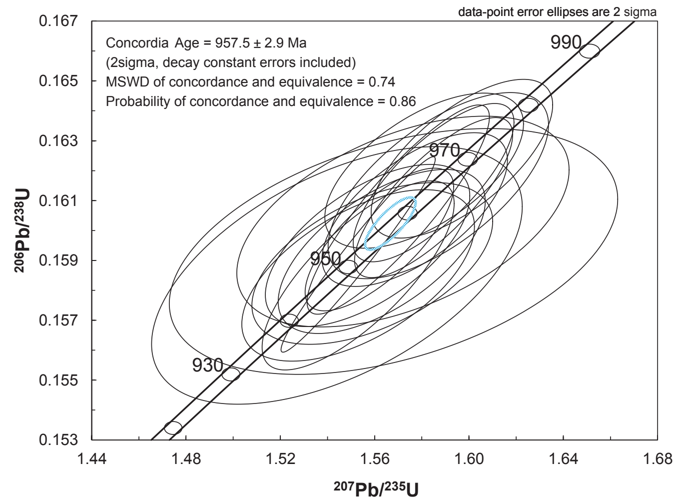

Fig. 5. Concordia diagram for U-Pb zircon data from the massive nepheline syenite.

MS in Frankfurt (University Goethe, Germany) to establish the crystallization age of the intrusion (U-Pb) and the mantle extraction age of the magma (Lu-Hf). The external shape and internal structure of zircons were imaged by combining cathodoluminescence (CL) and Scanning Electron Microscope (SEM; JEOL-6490 with Gatan MiniCL). Methods and instrumentation are described in Gerdes and Zeh (2006, 2009) and Zeh and Gerdes (2012).

4.1. U-Pb zircon analyses

Zircon observed in CL and SEM shows oscillations interpreted as magmatic zoning. Some zircons have altered edges that are white color under CL. These edges are interpreted to be a result of reaction between the zircon and a residual liquid enriched in uranium and were not analyzed. Analyses of 15 single zircons define an age of 957.5 ± 2.9 Ma, which we interpret as the age of the crystallization (Fig. 5). The mean square weighted deviation is 0.74 and the probability to find a point on the discordia is 0.86.

The 957.5 ± 2.9 Ma age corresponds to a late post-tectonic event (Gower and Krogh, 2002). Monzonitic-syenitic and granitic magmatism in the 975 to 955 Ma time interval was recognized in the eastern Grenville Province by Gower et al. (1991).

4.2. Lu/Hf zircon analyses

The model ages obtained by Lu-Hf analyses of zircon grains varies between 2.05 to 1.6 Ga. Rocks with the same model ages were also described in the central Grenville Province by Dickin and Higgins (1992) and Thomson et al. (2011) but from rocks that are generally granitic. The ages of 2.05 to 1.6 Ga are much older than the crystallization age. Two interpretations can be envisaged. In one, magma was extracted from the mantle and underplated the crust between 2.05 to 1.6 Ga, then, at the end of the Grenville orogeny, remelted to create the Crevier alkaline intrusion. Alternatively the age range may indicate magma contaminated by a heterogeneous continental crust of Archean or Paleoproterozoic age.

5. Conclusion

The Crevier alkaline intrusion is composed of rock types varying in composition from ijolite to carbonatite. The Nb-Ta mineralization is hosted in a pegmatitic nepheline syenite dike swarm. Highest REE concentrations are at the edge of the intrusion. Pyrochlore analyses indicate three types of pyrochlore and point to a possible remobilization of the primary mineralization by a late-magmatic fluid. Major and trace element geochemistry suggest that the Crevier alkaline intrusion formed by immiscibility process that resulted in silicate and carbonate phases. U-Pb geochronology on magmatic zircons from the nephelinic syenite gives a crystallization age of 957.5 ± 2.9 Ma. This age is similar to other alkaline intrusions in the eastern Grenville Province. The Lu-Hf age ranges between 2.05 to 1.6 Ga.

References cited

Atencio, D., Andrade, M.B., Christy, A.G., Giere, R., and Kartashov, P.M., 2010. The pyrochlore supergroup of minerals: nomenclature. The Canadian Mineralogist, 48, 673-698.

Boily, M., and Gosselin, C., 2004. Les principaux Types de Minéralisation en Métaux rares (Y-Zr-Nb-Ta-Be-Li-ETR) du Québec. Ministère de l'Énergie et des Ressources naturelles, Québec; ET 2004-01, 46p.

Bergeron, A., 1980. Pétrographie et géochimie du complexe igné alcalin de Crevier et de son encaissant métasomatisé. Master thesis, University of Chicoutimi, Canada, 129p.

Bernier, L., and Moorhead, J., 2000. Contrôles structuraux, caractéristiques pétrographiques et minéralogiques de la Kimberlite de d'Otish. Ministère des Ressources naturelles, Québec; MB 2000-14, 55p.

Currie, K.L., 1976. The alkaline rocks of Canada. Geological Survey of Canada Bulletin, pp. 239-228.

David, J., Dion, C., Goutier, J., Roy, P., Bandyayera, D., Legaut, M., and Rhéaume, P., 2006. Datations U-Pb effectuées dans la Sous-province de l'Abitibi à la suite des travaux de 2004-2005. Ministère de l'Énergie et des Ressources naturelles, Québec; RP 2006-04, 22p.

Dickin, A., and Higgins, M., 1992. Sm/Nd evidence for a major 1.5 Ga crust-forming event in the central Grenville Province. Geology, 20, 137-140.

Gerdes, A., and Zeh, A., 2006. Combined U-Pb and Hf isotope LA-(MC)-ICP-MS analyses of detrital zircons: comparison with SHRIMP and new constraints for the provenance and age of an Armorican metasediment in Central Germany. Earth and Planetary Science Letters, 249, 47-61.

Gerdes, A., and Zeh, A., 2009. Zircon formation versus zircon alteration- new insights from combined U-Pb and Lu-Hf in situ LA-ICP-MS analyses and consequences for the interpretation of Archean zircon from the Central Zone of the Limpopo Belt. Chemical Geology, 261, 230-243.

Goutier, J., 2006. Géologie de la région du Lac au Goéland (32/F15) Ministère de l'Énergie et des Ressources naturelles, Québec; RG 2005-05, 39p.

Gower, C.F., Heaman, L.M., Loveridge, W.D., Schärer, U., and Tucker, R.D., 1991. Grenvillian magmatism in the eastern Grenville Province, Canada. Precambrian Research, 51, 315–336.

Gower, C.F., and Krogh T.E., 2002. A U-Pb geochronological review of the Proterozoic history of the eastern Grenville Province. Canadian Journal of Earth Sciences, 39, 795-829.

Groulier, P.A., Ohnenstetter, D., Andre-Mayer, A.S., Zeh, A., Solgadi, F., Moukhsil, A., and El Basbas, A., 2014. Étude des minéralisations en Nb-Ta de l'Intrusion alcaline de Crevier. Ministère de l'Énergie et des Ressources naturelles, Québec; MB 2014-33, 66p.

Hoggarth, D.D., 1989. Pyrochlore, apatite and amphibole: distinctive minerals in carbonatite. In: Bell, K. (Ed.), Carbonatites Genesis and Evolution. Unwin Hyman, London, pp. 105-148.

Laplante, R., 1980. Étude de la minéralisation en Nb_Ta_U du complexe igné alcalin du canton Crevier, comté Roberval, Lac St-Jean, P.Q. M. Sc. Thesis, Université de Montréal, 51p.

LeBas, M.J., Le Maitre, R.W., and Woolley, A.R., 1992. The construction of the Total alkali-Silica Chemical Classification of Volcanic Rocks. Mineralogy and Petrology, 46, 1-22.

Nasraoui, M., Bilal, E., 2000. Pyrochlores from the Lueshe carbonatite complex (Democratic Republic of Congo): a geochemical record of different alteration stages. Journal of Asian Earth Sciences, 18, 237-251.

Rivers, T., Martignole, J., Gower, C.F., and Davidson, A., 1989. New tectonics division of the Grenville Province, southeast Canadian Shield. Tectonics, 8, 63-84.

Thomson, S., Dickin, A., and Spray, J., 2011. Nd isotope mapping of Grenvillian crustal terranes in the vicinity of the Manicuagan Impact Structure. Precambrian Research, 191, 184-193.

Vallée, M., and Dubuc, F., 1970. The St-Honoré carbonatite complexe, Quebec. Transactions of the Canadian Institute of Mining and Metallurgy and of the Mining Society of Nova Scotia, 73, 346-356.

Zeh, A., and Gerdes, A., 2012. U-Pb and Hf isotope record of detrital zircons from gold bearing sediments of the Pietersburg Greenstone Belt (South Africa) – Is there a common provenance with the Witwatersrand Basin. Precambrian Research, 204-205, 46-56.