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MAGNETITE COMPOSITION AS PETROGENETIC AND PROSPECTIVITY INDICATOR FOR FE-TI-V-P MINERALIZATION IN ARCHEAN MAFIC-ULTRAMAFIC INTRUSIONS WITHIN THE SUPERIOR PROVINCE, ONTARIO AND QUEBEC

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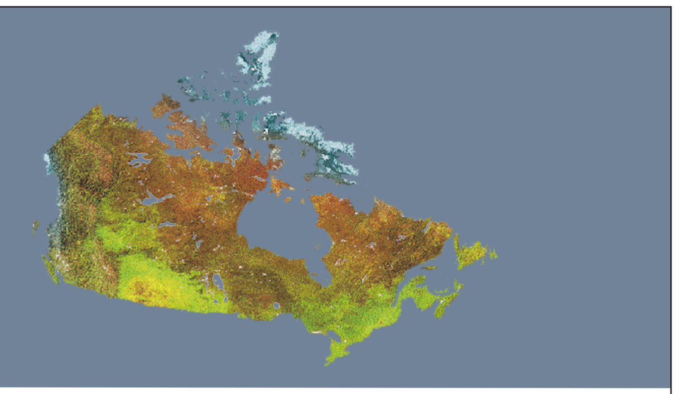

Summary

The mineral chemistry of magnetite from various Archean mafic to ultramafic intrusions within the Superior Province (**Fig. 1**) was characterized in order to identify the most prospective areas to host Fe-Ti-V and Fe-Ti-P mineralization, but also to be used as a petrogenetic indicator. The composition of magnetite is influenced by the presence of exsolutions and inclusions, the type of parental melt, and the element partitioning with co-crystallized minerals or previously crystallized minerals. The overall composition of magnetite, however, appears to be mainly independent of the host-rock type. The composition of magnetite in compatible (e.g., Mg, Co, V, Ni, and Cr) and incompatible (e.g., Al, Ga, Mn, Ti, and Zn) elements provides useful information regarding the degree of fractionation and the internal stratigraphy of each host intrusion. In addition, the V and Ni+Cr contents of magnetite can be used as a prospectivity indicator for Fe-Ti-V-P mineralization.

Overall, magnetite signatures from these Archean intrusions are characterized by lower Ti+V values than expected, with magnetite compositions plotting within fields for hydrothermal deposits rather than within fields for Fe-Ti-V and Fe-Ti-P deposits, as shown in Ni/(Cr+Mn) versus Ti+V, Ca+Al+Mn versus Ti+V, and Ni+Cr versus Ti+V discrimination diagrams. Considering that the Fe-Ti-V-P deposit fields in these diagrams were mainly defined based on Fe-oxides hosted within Proterozoic and Phanerozoic Fe-Ti deposits, the preliminary results presented here suggest there may be a specific signature for magnetite from Archean Fe-Ti-V-oxide-bearing intrusions. However, further investigations are required to corroborate this distinct signature to the Archean.

1. Location

Names of the host intrusions of the deposits and occurrences:

1 = Croal Lake
2 = Big Mac
3 = Butler West and East
4 = Highbank-Fishtrap
5 = Oxtoby Lake and Wabassi Main
6 = Baie Chapus Pyroxenite
7 = Rivière Bell
8 = Lac Doré

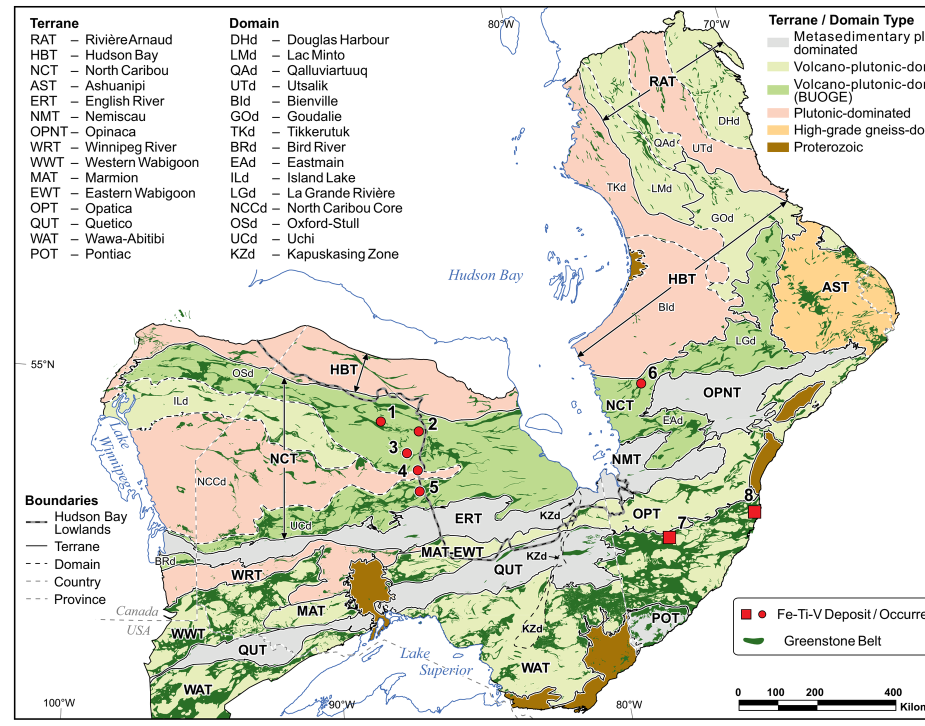

Fig. 1. Geological map showing the locations of the mafic to ultramafic intrusions that were studied across the Bird River–Uchi–Oxford-Stull–La Grande Rivière–Eastmain (BUOGE) domains and the Wawa-Abitibi terrane (after Houlé et al., 2020). Terrane and domain boundaries are modified from Stott et al. (2010), Percival et al. (2012), and SIGÉOM (2020).

2. Magnetite Composition from Mafic to Ultramafic Intrusions

The oxide-bearing mafic to ultramafic rock samples (<40% Fe-Ti oxides) were collected from the mafic-dominated Croal Lake, Big Mac, Butler (East and West), Highbank-Fishtrap, Oxtoby Lake, Wabassi Main, and Lac Doré intrusions and the Baie Chapus Pyroxenite, an ultramafic-dominated intrusion. In these rocks, the composition of magnetite varies from intrusion to intrusion (**Figs. 2A, 2C**). Magnetite from the Croal Lake, Big Mac, Butler, and Highbank-Fishtrap intrusions shows high Cr and locally high V contents. Magnetite from the Oxtoby Lake intrusion has low Mg contents, relatively low Cr, Al, and Mn contents, and the lowest Ti contents of the intrusions studied. Magnetite from the Wabassi Main intrusion has the highest Mg and Co contents and high V, Ni, Cr, Al, Mn, and Ti contents. Magnetite from the Lac Doré complex has low V contents, relatively low Mg and Cr contents, and the lowest Ni contents, but high Mn, Ti, and Zn contents. Pyroxenite from the Baie Chapus intrusion contains magnetite with the highest Ni contents, relatively high Mg contents, and low V, Cr, and Al contents.

The semi-massive and massive Fe-Ti oxide samples (40-80% and >80% Fe-Ti oxides, respectively) are from the mafic-dominated Croal Lake, Big Mac, Highbank-Fishtrap, and Rivière Bell intrusions, and the ultramafic-dominated Baie Chapus Pyroxenite. The chemical signature of the magnetite from these samples also varies by intrusions (**Figs. 2B, 2D**). Magnetite from the Croal Lake and Big Mac intrusions have relatively high Mg and Cr contents, whereas magnetite from the Highbank-Fishtrap intrusive complex has relatively low Mg contents but high Cr contents. In the Rivière Bell complex, the magnetite has been affected by regional and local metamorphism and most of its primary composition, with the exception of V and Cr contents, has been modified (Polivchuk, 2017). The Fe-oxides from this complex have relatively low V and Cr contents. Semi-massive to massive Fe-Ti oxides from the Baie Chapus Pyroxenite host magnetite with intermediate Ni contents, relatively high Mn contents, locally low Mg and Zn contents, and the lowest contents of Co, Cr, Al, and Ga.

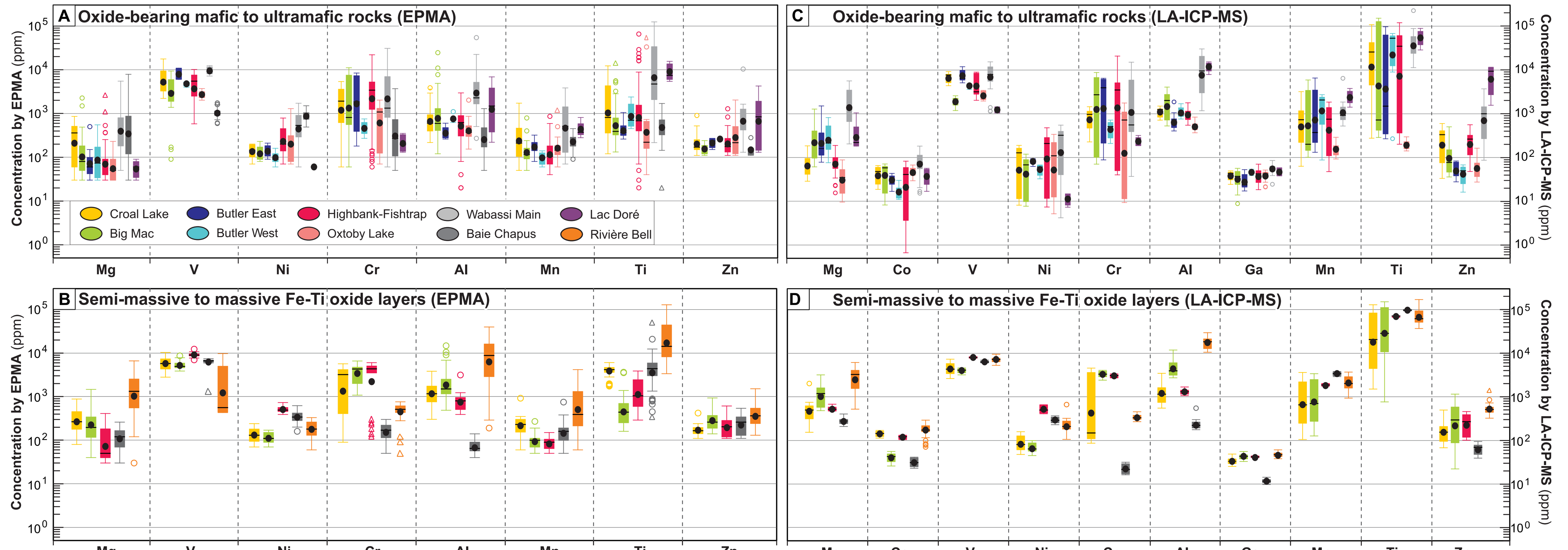

*Fig. 2. Box and whisker plots of selected minor and trace elements in magnetite **(A)** analyzed by EPMA in the oxide-bearing mafic to ultramafic rocks, **(B)** analyzed by EPMA in the semi-massive to massive Fe-Ti oxide layers, **(C)** analyzed by LA-ICP-MS in the oxide-bearing mafic to ultramafic rocks, **(D)** analyzed by LA-ICP-MS in the semi-massive to massive Fe-Ti oxide layers. The upper and lower margins of the box represent the upper 75% and lower 25% of the data. The whiskers represent the upper and lower threshold values (95% of the data). Median values are shown as solid black lines and mean values as solid black circles. Outliers are shown as open circles and far outlier as open triangles along the whisker.*

3. Case Study: Big Mac Intrusion

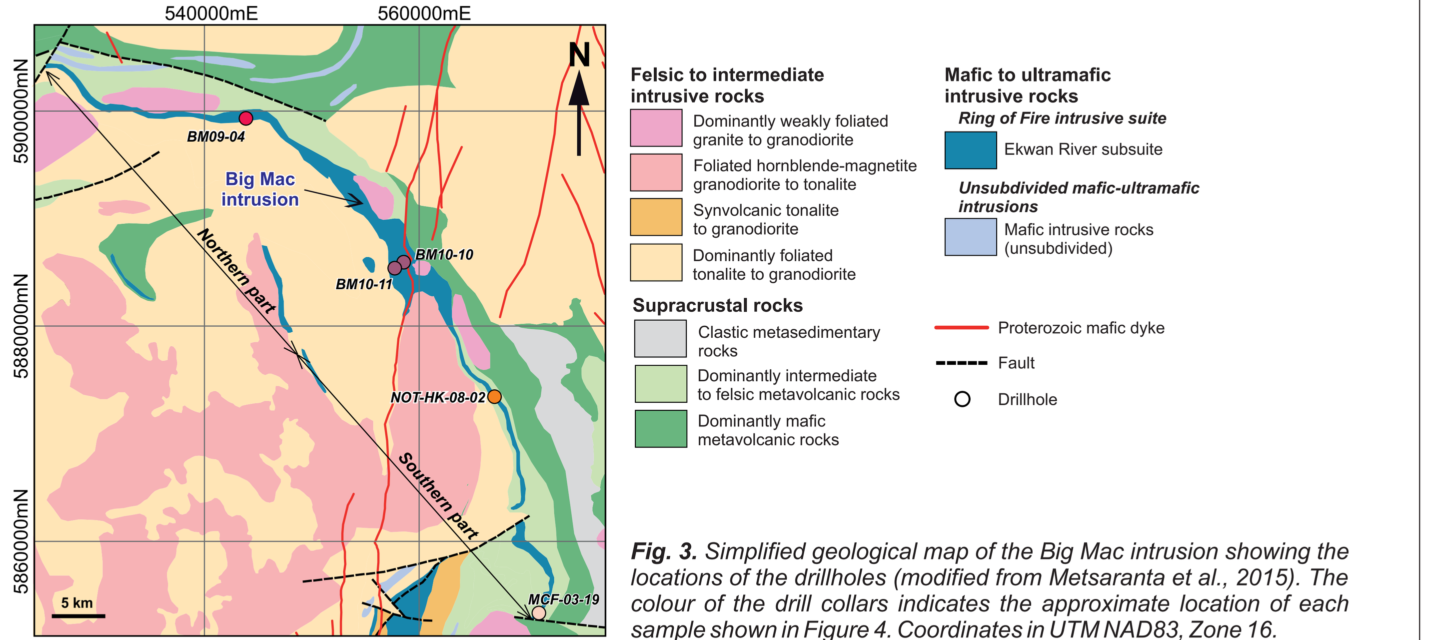

Fig. 3. Simplified geological map of the Big Mac intrusion showing the locations of the drillholes (modified from Metsaranta et al., 2015). The colour of the drill collars indicates the approximate location of each sample shown in Figure 4. Coordinates in UTM NAD83, Zone 16.

In the Big Mac intrusion, the chemical composition of Fe-oxides varies with location. Magnetite in the northern part of the intrusion is rich in elements that are compatible in mafic magmas (i.e. Mg, V, Ni, Cr), whereas to the south, the concentration of these elements is low and it is locally rich in elements that are incompatible during fractionation process (i.e. Mn, Ti, Zn; **Fig. 4**).

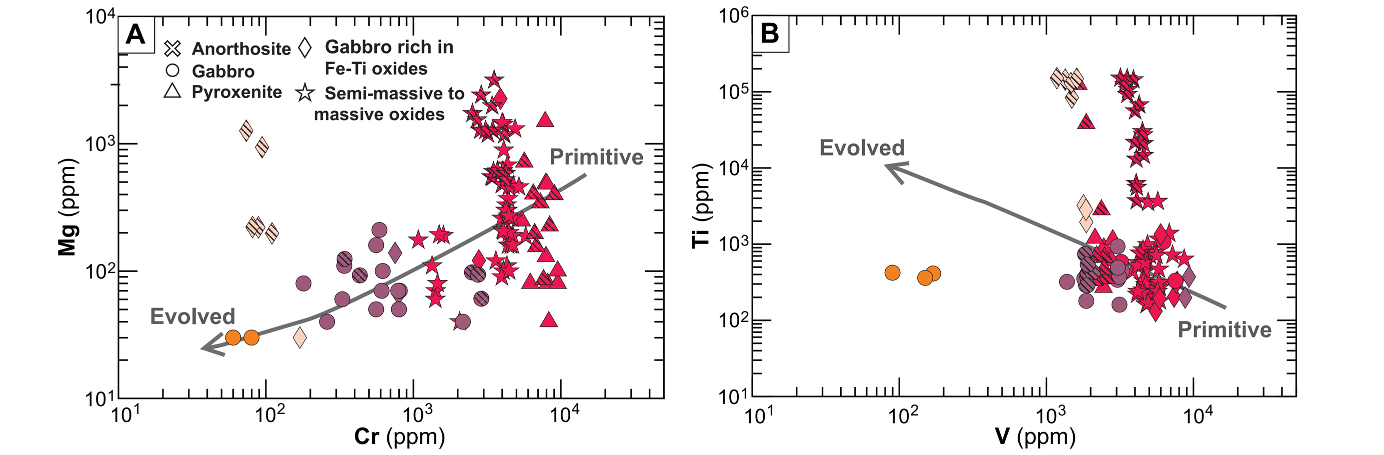

*Fig. 4. Composition of magnetite in anorthosite, gabbro, pyroxenite, and semi-massive to massive Fe-Ti oxide layers from the Big Mac intrusion. **(A)** Mg versus Cr and **(B)** Ti versus V. Each data point represents an individual magnetite grain analyzed by EPMA (nonhatched symbols) or LA-ICP-MS (hatched symbol). The fill colour of the symbols corresponds to the drill collars in Figure 3.*

4. Magnetite of Magmatic or Hydrothermal Origin

The vast majority of the magnetite grains in this study have low Ni/Cr ratios, regardless of analytical method, and plot within the magmatic field of the diagram (**Fig. 5**). However, the magnetite from the Baie Chapus Pyroxenite, which has the highest Ni/Cr ratios, has EPMA data that plot almost entirely within the hydrothermal field (**Fig. 5A**). Furthermore, based on EPMA data (**Fig. 5A**), most of samples contain magnetite with Ti contents that are less or equal to 1 wt%. However, the LA-ICP-MS data (**Fig. 5B**) indicate that the Croal Lake, Big Mac, Butler, Highbank-Fishtrap, Wabassi Main, Baie Chapus, Rivière Bell, and Lac Doré intrusions host some Ti-rich magnetite (1 wt% Ti), whereas the Oxtoby Lake intrusion only hosts Ti-poor magnetite (mostly <0.1 wt% Ti).

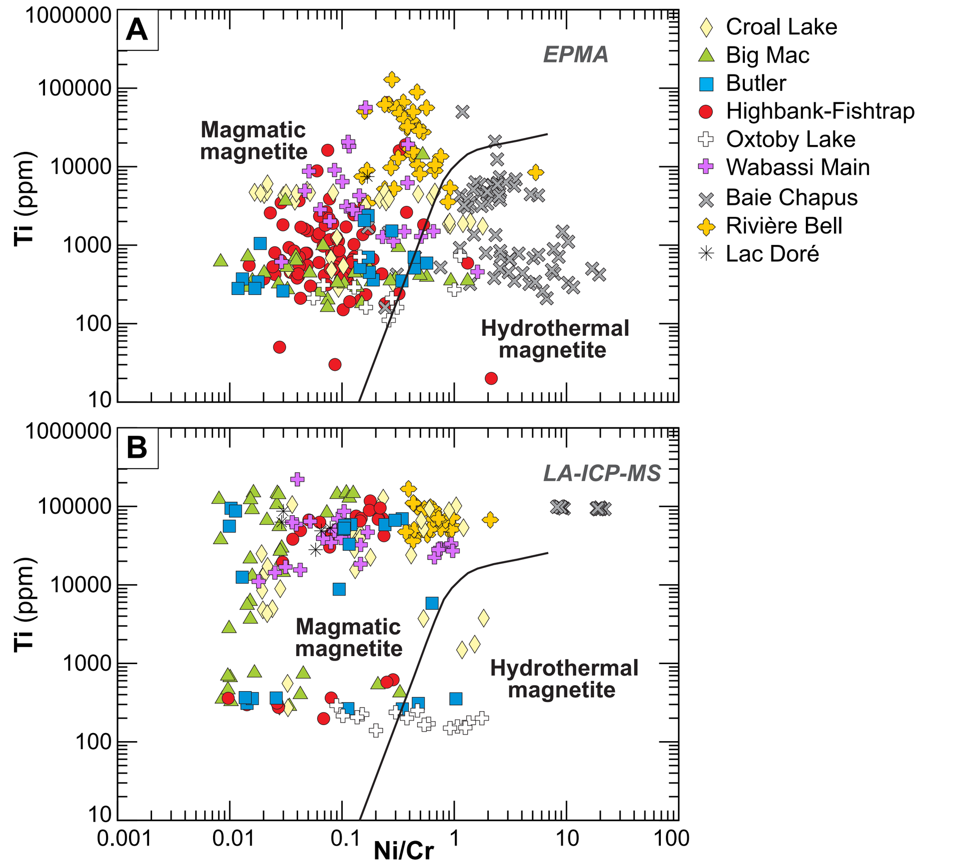

*Fig. 5. Ti versus Ni/Cr discrimination diagram of Dare et al. (2014) for differentiating magmatic and hydrothermal magnetite plotting data from the oxide-bearing mafic to ultramafic rocks and the semi-massive to massive Fe-Ti oxide layers of the studied intrusions. **(A)** Magnetite composition determined by EPMA. **(B)** Magnetite composition determined by LA-ICP-MS. Each data point represents an individual magnetite grain.*

5. Discrimination Diagrams of Magnetite Composition

In all the discrimination diagrams used to distinguish magnetite associated with hydrothermal deposits from those associated with Fe-Ti-V deposits, the EPMA data for the magnetite from the samples of the studied Archean intrusions have significantly lower Ti+V contents than expected and plot predominantly within the field for hydrothermal deposits rather than within the field for Fe-Ti-V and Fe-Ti-P deposits (**Figs. 6A, 6C, 6E**). An exception is the Rivière Bell magnetite, which plots predominantly within the Fe-Ti-V deposit field (**Figs. 6A, 6C, 6E**).Interestingly, the LA-ICP-MS data for the magnetite grains generally plot within the Fe-Ti-V and Fe-Ti-P deposit fields in the three discrimination diagrams (**Figs. 6B, 6D, 6F**). However, significant LA-ICP-MS analyses from many of the intrusions of this study still plot within the hydrothermal field, in particular those for magnetite from the Oxtoby Lake intrusion (**Figs. 6B, 6D, 6F**), which also shows similar results to those determined by EPMA (**Figs. 6A, 6C, 6E**).

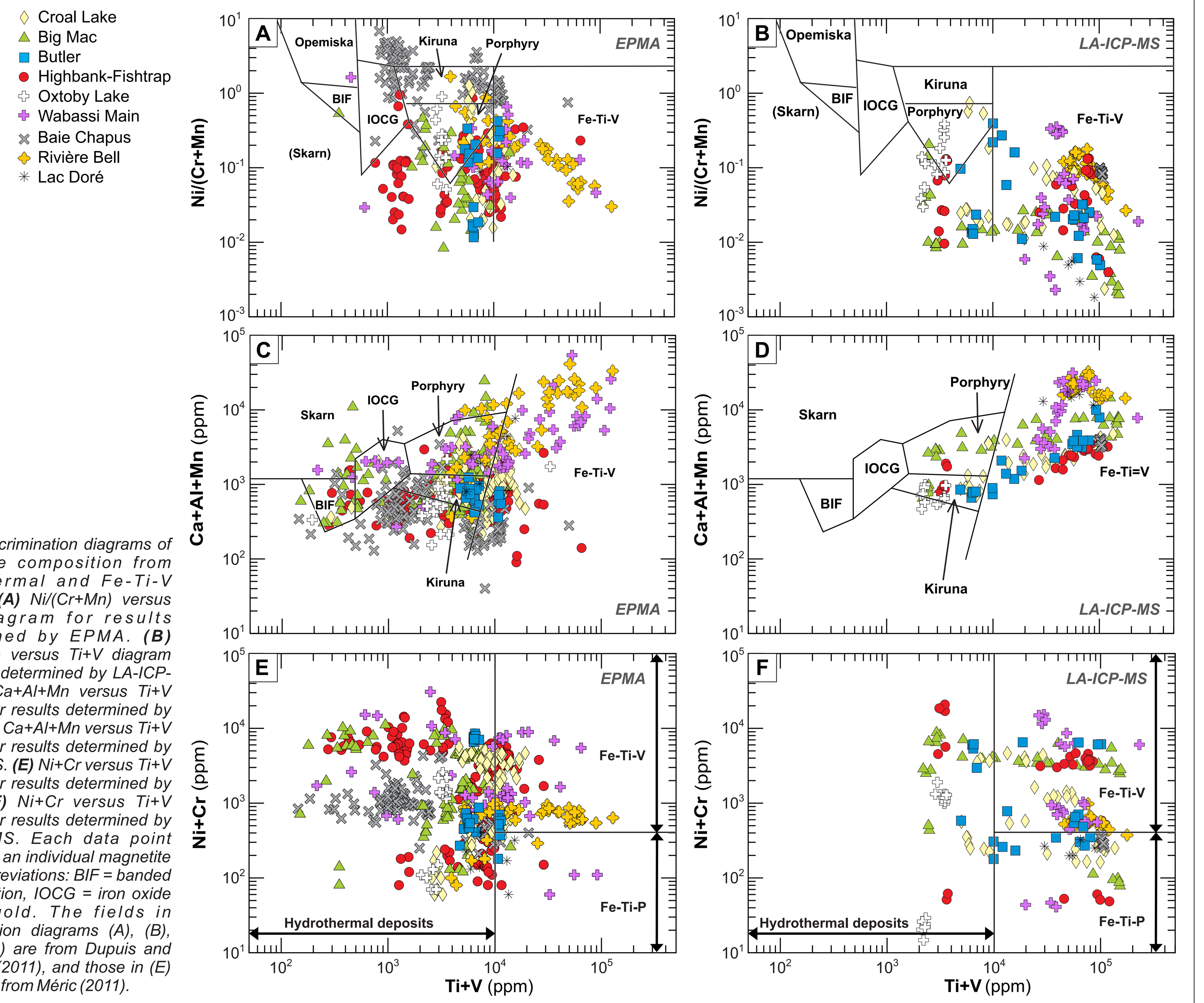

*Fig. 6. Discrimination diagrams of magnetite composition from hydrothermal and Fe-Ti-V deposits. **(A)** Ni/(Cr+Mn) versus Ti+V diagram for results determined by EPMA. **(B)** Ni/(Cr+Mn) versus Ti+V diagram for results determined by LA-ICP-MS. **(C)** Ca+Al+Mn versus Ti+V diagram for results determined by EPMA. **(D)** Ca+Al+Mn versus Ti+V diagram for results determined by LA-ICP-MS. **(E)** Ni+Cr versus Ti+V diagram for results determined by EPMA. **(F)** Ni+Cr versus Ti+V diagram for results determined by LA-ICP-MS. Each data point represents an individual magnetite grain. Abbreviations: BIF = banded iron formation, IOCG = iron oxide copper-gold. The fields in discrimination diagrams (A), (B), (C),and (D) are from Dupuis and Beaudoin (2011), and those in (E) and (F) are from Méric (2011).*

6. Discussion and Concluding Remarks

1) Unlike the electron microprobe, the LA-ICP-MS uses larger beam sizes that could incorporate some exsolutions/inclusions during analyses. As a result, the EPMA and LA-ICP-MS data show small discrepancies for some of the minor and trace element contents of the magnetite (e.g., **Figs. 2, 5**). In particular, the LA-ICP-MS analyses include ilmenite exsolutions that form during the subsolidus exsolution-oxidation processes and provide an estimate of the initial magnetite composition (e.g., Dare et al., 2012, 2014). The higher Ti contents of the Baie Chapus magnetite when determined by LA-ICP-MS (**Fig. 5B**) could be the result of numerous Ti-enriched ilmenite exsolutions being present in the magnetite. This could explain the hydrothermal signature in **Fig. 5A** for the Baie Chapus magnetite, which was analyzed by EPMA.

2) Most of the intrusions studied contain some original Ti-rich magnetite (≥1 wt% Ti; **Fig. 5B**), suggesting that they were associated with high-Ti parental magmas. In contrast, the low-Ti contents of the Oxtoby Lake magnetite as determined by EPMA and by LA-ICP-MS (mostly <0.1 wt% Ti, **Fig. 5**) indicate that these Ti-poor Fe-oxides likely crystallized from low-Ti parental magmas.

3) The lower Cr and V contents than expected of the primitive magnetite from the Baie Chapus Pyroxenite could be explained by the nature of the minerals that crystallize with magnetite. The low Cr contents (**Figs. 2A, 2B, 2D**) could result from the fractional crystallization of chromite at depth. The depletion in V of magnetite from the ultramafic rocks (**Fig. 2A**) relative to magnetite from the oxide layers (**Figs. 2B, 2D**) could be explained by the high proportion of clinopyroxene in the pyroxenite, in which V also partitions.

4) Based on the magnetite of the mafic-dominated intrusions and its composition in compatible and incompatible elements (**Fig. 2**), it appears that the Rivière Bell and Lac Doré complexes have the most evolved composition, whereas the Croal Lake, Big Mac, Butler, Highbank-Fishtrap and Wabassi Main intrusions are the most primitive. Identifying the most primitive and evolved intrusions may help identifying which intrusions in the Superior are most likely to host Fe-Ti-V-P mineralization.

5) The composition of magnetite, in terms of compatible and incompatible elements, efficiently tracks the magmatic fractionation and indicates the way-up of intrusion. In the Big Mac intrusion, the more vent-proximal facies appear to be located to the north (**Fig. 4**). These data help to target the most prospective areas to host Fe-Ti-V mineralization within intrusions.

6) Magnetite with high V contents and Ni+Cr values >400 ppm (**Figs. 6E, 6F**) have a composition favourable to the formation of Fe-Ti-V deposits. In contrast, magnetite with low V contents and Ni+Cr values <400 ppm (**Figs. 6E, 6F**) are more compatible with Fe-Ti-P mineralization.

7) In the discrimination diagrams for results determined by EPMA (**Figs. 6A, 6C, 6E**), magnetite from the studied Archean intrusions has lower Ti+V contents than magnetite from the Proterozoic and Phanerozoic Fe-Ti deposits used to construct the diagrams. The distinct chemical signature of the Rivière Bell magnetite (higher Ti+V contents; **Figs. 6A, 6C, 6E**) could be due to ubiquitous fine ilmenite exsolutions in the Fe-oxide grains and/or late Ti remobilization during metamorphism (Polivchuk, 2017). The dichotomy between the Archean and Proterozoic magnetite composition does not appear to be related to an analytical error. One explanation could be that there is lower Ti and/or V contents in magnetite from Archean Fe-Ti deposits than from younger deposits.

8) In the discrimination diagrams, the LA-ICP-MS data appear better at correctly predicting the deposit type as the Ti contents determined by LA-ICP-MS are often higher than those determined by EPMA (**Figs. 6B, 6D, 6F**). However, a fair amount of the LA-ICP-MS data points still fall into other hydrothermal deposit types.

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