



Fugacité de l'oxygène et contenu en éléments volatils des magmas syntectoniques du secteur de Chibougamau, Sous-province d'Abitibi

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RÉSUMÉ

La Sous-province d'Abitibi est l'une des ceintures de roches vertes (CRV) Néoarchéennes les plus enrichies en or. Les nombreuses études sur la mise en place des gisements aurifères de la CRV de l'Abitibi ont permis d'établir une relation spatiale, structurale et/ou génétique entre les magmas de la période syntectonique et une partie des minéralisations aurifères (gisement de type or orogénique et *intrusion related gold system*). La relation génétique entre le magmatisme et la minéralisation reste très débattue, ce qui est problématique car cela ne permet pas d'évaluer précisément le rôle que joue le magmatisme syntectonique dans le transport et la concentration de l'or dans les CRV. Documenter le cycle de l'or dans ces systèmes magmatiques est également important pour l'exploration.

La présente maîtrise utilise la fugacité de l'oxygène (fO_2) et le contenu en éléments volatils (p.ex., S, CO_2 , H_2O) de cinq intrusions syntectoniques et synvolcaniques de la région de Chibougamau-Chapais afin de mieux contraindre le potentiel aurifère de cette région. Ces facteurs peu étudiés dans les CRV archéennes sont essentiels au transport de l'or par les magmas. En effet, l'or et les métaux de base ne sont transportés par un magma puis transférés à un fluide d'origine magmatique que dans des conditions d'oxydo-réduction particulières et seulement si certains ligands (p.ex., S, Cl) sont présents. L'objectif de ce projet est donc de mesurer ces paramètres afin de déterminer la quantité maximale d'or que les systèmes magmatiques de la région étudiée ont pu transporter, en utilisant la chimie de l'apatite, du zircon et de l'amphibole. L'apatite et le zircon sont des minéraux résistants et riches en éléments traces à variances variables. Leur contenu en Ce, Eu et Mn permet de caractériser la fO_2 des magmas syntectoniques. L'amphibole et l'apatite sont, enrichies en Cl, S et F, et permettent d'accéder au contenu en volatils des magmas.

Les travaux de terrains, les datations U-Pb ainsi que les analyses géochimiques montrent que l'intrusion d'Anville s'est mise en place durant la première phase de construction de la CRV de l'Abitibi aux environs de $2796,5 \pm 3,8$ Ma. Cette intrusion typiquement synvolcanique appartient à la suite des tonalites-trondhjemites-granodiorites (TTG) riche en potassium et fait partie des plus anciennes roches observées dans la Sous-province d'Abitibi. L'intrusion du Lac Line s'est mise en place durant les premières phases de déformation à la transition entre les périodes synvolcanique et syntectonique, et correspond à une suite TTG de haute pression. Enfin, les intrusions de Chevrillon, Saussure et Opémisca se sont mises en place vers la fin de la période syntectonique et correspondent respectivement à des granitoïdes de type high-K calc-alkaline (HKCA), des syénites et des sanukitoïdes.

Le paramètre fO_2 déterminé à partir de la chimie des zircons et des apatites indique une augmentation de la fO_2 entre les périodes synvolcanique (pluton d'Anville) et syntectonique (autres intrusions étudiées). En effet, au moment de la cristallisation du zircon et de l'apatite, le magma à l'origine de l'intrusion d'Anville était plus réduit que les magmas modérément oxydés des intrusions syntectoniques.

Le contenu en éléments traces des apatites montre que les magmas à l'équilibre avec les apatites analysées contenaient entre 10 et 30 ppm de soufre pour les intrusions d'Anville, de Chevrillon et d'Opémisca et entre 20 et 100 ppm de soufre pour les intrusions de Saussure et du Lac Line. Les données obtenues indiquent que les magmas à l'origine des intrusions du Lac Line et de Saussure offraient des conditions idéales pour le transport de l'or à travers la croûte au Néoarchéen, et que les autres intrusions étudiées ont un potentiel minéralisateur moindre.

MOTS-CLÉS : fugacité de l'oxygène, volatil, intrusion syntectonique, gisement d'or, ceinture de roches vertes de l'Abitibi

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LISTE DES ABRÉVIATIONS

Divers

ΔFMQ	<i>Fayalite - magnetite -quartz buffer</i>	LA-MC-Q-ICP-MS	<i>Laser Ablation Multicollector- Quadrupole-based Inductively Coupled Plasma Mass Spectrometer</i>
ΔQFM	Quartz - fayalite -magnétite - buffer	LOI	<i>Loss on ignition</i>
BSE images	<i>Back-scattered electrons images</i>	LREE	<i>Light rare earth elements</i>
CRV	Ceinture de roches vertes	MEB	Microscope électronique à balayage
CL images	<i>Cathodoluminescence images</i>	MERC-IGL	<i>Mineral Exploration Research Centre - Isotope Geochemistry Laboratory</i>
EMPA	<i>Electron Microprobe Analysis</i>	MERN	Ministère de l'Énergie et des Ressources Naturelles
fO₂	Fugacité de l'oxygène	P	Pression
HKCA	<i>High-K calc-alkaline granitoid</i>	REE	<i>Rare earth element</i>
HREE	<i>Heavy rare earth elements</i>	T	Température
IRGS	<i>Intrusion related gold system</i>	TTD	Tonalite-trondhjemite-diorite
Kd	Coefficient de partage	TTG	Tonalite-trondhjemite-granodiorite
LabMaTer	Laboratoire des Matériaux Terrestres	VMS	<i>Volcanogenic Massive Sulphide</i>
LA-ICP-MS	<i>Laser Ablation Inductively Coupled Plasma Mass Spectrometer</i>		

Minéraux

Alu	Alunite	Ilm	Ilménite
Ap	Apatite	Kfs	Feldspath potassique
Aug	Augite	Mag	Magnétite
Bt	Biotite	Pl	Plagioclase
Cb	Carbonate	Qz	Quartz
Ep	Épidote	Ttn	Titanite
Hbl	Hornblende	Zrn	Zircon

Nomenclature en accord avec les travaux de Whitney et Evans (Whitney et Evans, 2010)

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CHAPITRE 1

INTRODUCTION GENERALE

1.1 INTRODUCTION

Ce mémoire s'inscrit dans le cadre du programme d'étude 1666 intitulé Maîtrise recherche en géologie et génie géologique volet recherche de l'Université du Québec à Chicoutimi. Ce projet de recherche porte sur la fugacité de l'oxygène (fO_2) et le contenu en éléments volatils des magmas syntectoniques de la Sous-province d'Abitibi. L'ensemble des résultats est présenté sous la forme d'un article rédigé en anglais et publié par la revue scientifique en accès libre *Minerals*. Ce projet a été mené sous la direction de la Professeure Lucie Mathieu dans le cadre de la chaire institutionnelle sur les processus métallogéniques archéens et financé par le programme de recherche *Metal Earth* (Université Laurentienne, Sudbury). Le but de ce programme de recherche est de déterminer les caractéristiques et les processus clés ayant un impact sur la distribution des métaux dans les ceintures de roches vertes archéennes, en comparant des ceintures qui présentent des caractéristiques géologiques similaires et des quantités de gisements très différentes.

Au sein de la Sous-province d'Abitibi, qui est une ceinture de roches vertes enrichie en métaux précieux et de base, plusieurs minéralisations

aurifères sont associées à des systèmes magmato-hydrothermaux syntectoniques. Ces minéralisations, qui sont principalement localisées à proximité de la faille Cadillac dans la partie sud de la Sous-province, sont difficiles à étudier car elles sont souvent remobilisées par les processus ayant formés des gisements de type or orogénique. Ainsi, le rôle que les intrusions syntectoniques ont joué pour fertiliser la croûte supérieure est encore largement débattu. Le camp minier de Chibougamau-Chapais situé dans le coin nord-est de la Sous-province d'Abitibi contient une grande quantité de systèmes magmato-hydrothermaux qui n'ont pas ou peu été remobilisés. Ce camp minier pourrait permettre de préciser le rôle des intrusions syntectoniques dans le transport des métaux.

Ce projet de maîtrise a donc pour objectif de quantifier avec précision la fO_2 et le contenu en éléments volatils des magmas syntectoniques archéens du coin nord-ouest de la Sous-province d'Abitibi.

1.2 PROBLEMATIQUE GENERALE

Les roches étudiées sont des roches métamorphiques et, par souci de simplification, le préfixe « méta » est omis pour toutes les roches mentionnées dans le texte.

Les ceintures de roches vertes archéennes sont des ensembles de roches supra-crustales recoupées par des intrusions qui appartiennent, pour

la plupart, à la suite tonalite-trondhjémite-granodiorite (TTG) (Laurent et al., 2014b; Moyen et Laurent, 2018). Les ceintures de roches vertes sont majoritairement métamorphisées au faciès des schistes verts et les roches mafiques qui les composent sont riches en chlorite-actinote-épidote (Burke et al., 1977). Les roches supra-crustales se sont mises en place sur (ou font partie intégrante) des planchers océaniques et sont dominées par des ensembles de roches volcaniques souvent mafiques, mais aussi ultramafiques à felsiques et par des roches sédimentaires (Beakhouse, 2011; Thurston et al., 2008).

L'évolution tectono-magmatique des ceintures de roches vertes comprend généralement deux périodes principales : synvolcanique et syntectonique (Beakhouse, 2011; Laurent et al., 2014a; Mathieu et al., 2020a). La phase synvolcanique, plus ancienne, est une phase de construction qui a permis la mise en place de grands volumes de roches volcaniques de la série tholéiitique dans lesquels se mettent en place des complexes intrusifs appartenant aux suites TTG et TT-diorite (TTD) (Martin et Moyen, 2002). Cette période est généralement associée à la mise en place des gisements de type sulfures massifs volcanogènes et de type porphyre (Mathieu et Racicot, 2019).

La période synvolcanique est suivie par la période syntectonique qui est définie par la présence d'une forte activité tectonique (raccourcissements N-S principalement pour l'Abitibi) comprenant plusieurs phases de déformation, d'érosion et de sédimentation (Laurent et al., 2014a; Thurston et al., 2008).

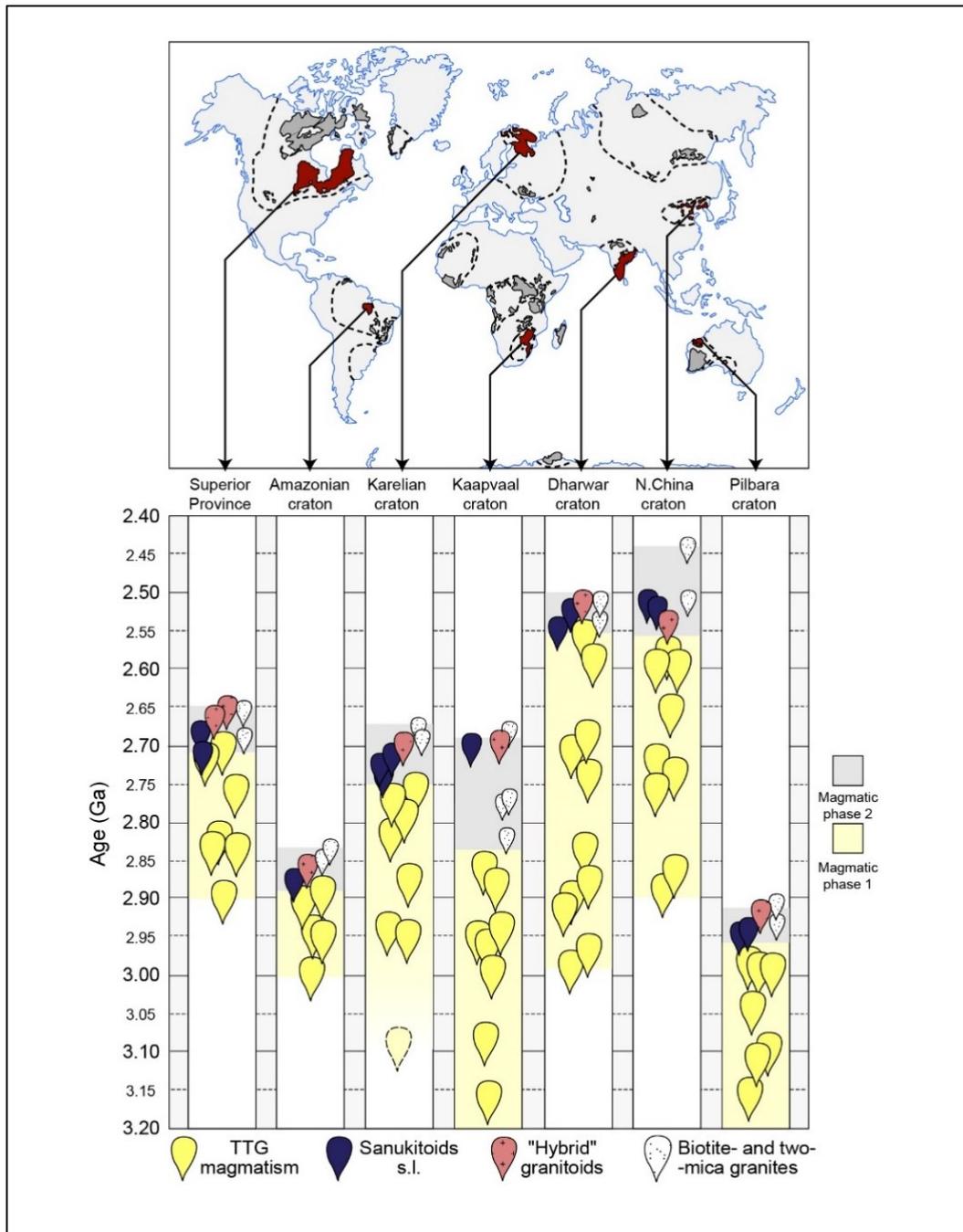


Figure 1.1. Haut : carte montrant en gris la croûte Archéenne et en rouge les cratons d'intérêts. Bas : figure de synthèse présentant les âges simplifiés des quatre groupes de granitoïdes tardi-archéens. La même séquence se répète dans chaque craton de manière diachrone : (1) longue période de mise en place de TTG suivi (2) d'une période plus courte pendant laquelle se met en place trois nouveaux types de granitoïdes (Huguet, 2019; Laurent et al., 2014b)

Durant cette phase, le volume de magma émis est plus faible que pendant la période précédente et ce magmatisme est généralement de type calco-alcalin à alcalin (Figure 1.1). Ce magmatisme comprend des TTG tardives, des granites riches en potassium, des magmas de la série alcaline des sanukitoïdes et des *high-K calc-alkaline granitoids* (HKCA) (Moyen, 2019). Les magmas de la période syntectonique sont associés à des styles de minéralisation de type or orogénique et IRGS (Legault et Goutier, 2014; Robert, 2001). Le lien entre magmatisme et minéralisations reste très débattu et pourrait être soit important (les magmas sont la source de l'or) soit limité (les intrusions sont de simples hôtes de la minéralisation).

1.3 PROBLEMATIQUE SPECIFIQUE

Le secteur de Chibougamau-Chapais est situé dans le coin nord-est de la Sous-province d'Abitibi et est délimité au nord par la Sous-province d'Opatika et à l'est par le front de déformation orienté NE de la Province du Grenville (Daigneault, 1991; Leclerc et al., 2011). Dans le secteur de Chibougamau comme dans le reste de la Sous-province d'Abitibi, les roches sont principalement métamorphisées au faciès des schistes verts.

L'activité magmatique est divisée entre la période de construction synvolcanique et de la période de déformation syntectonique qui s'étendent respectivement de > 2730 à 2710 Ma et de 2704 à 2690 Ma (Daigneault et

Allard, 1990; Leclerc et al., 2017). Les roches les plus anciennes de la période synvolcanique, dans la région de Chibougamau, correspondent aux formations de Des Vents ($2798,7 \pm 0,7$ Ma) (Davis et al., 2014) et de Chrissie ($2791,4 \pm 2,9$ Ma) (David et al., 2011; Leclerc et al., 2017; Potvin, 1991). Ces deux formations sont recouvertes par les roches des cycles volcaniques 1 et 2 du Groupe de Roy (Figure 1.2). Le cycle volcanique 1 est composé dans sa majeure partie par des laves mafiques et non datées de la Formation d'Obatogamau et par les laves intermédiaires à felsiques de la Formation de Waconichi ($2729,0 \pm 1,1$ Ma) (Boucher, 2020; Boucher et al., 2020; David et al., 2012; Leclerc et al., 2011). Le cycle volcanique 2 est quant à lui composé des unités mafiques de la Formation de Bruneau ($2724,4 \pm 1,2$ Ma) (Davis et al., 2014), des roches felsiques de la Formation du Blondeau ($<2724,4 \pm 1,2$ Ma) (Leclerc et al., 2012) et des unités volcanoclastiques felsiques à intermédiaires et sédimentaires non datées de la Formation de Bordeleau (Figure 1.2) (Leclerc, 2001; Leclerc et al., 2017). Pendant la période synvolcanique, plusieurs intrusions appartenant à des suites TTG (p. ex., pluton de la Dauversière) et TTD (Complexe à l'Eau Jaune, Pluton de Chibougamau) se mettent en place dans les roches du Groupe de Roy (Kieffer, 2019; Mathieu et al., 2020a).

Dans le secteur de Chibougamau, la période syntectonique est caractérisée par la présence de bassins ayant une extension limitée et remplis par les sédiments clastiques du Groupe d'Opémisca (Daigneault et Allard, 1990). Dans le centre du secteur d'étude, ce groupe est subdivisé entre les

formations de Stella et d'Haüy (Figure 1.2), alors que dans le nord et l'ouest du secteur, il est composé des formations de Chebistuan et de Daubrée (Allard et Gobeil, 1984). Durant la période syntectonique, plusieurs intrusions, généralement de faible volume, se sont mises en place (p.ex., pluton de Muscocho) (Mathieu et al., 2020b; Piché, 1985). Ce magmatisme syntectonique comprend des intrusions alcalines (syénite), calco-alcalines (granodiorite) et des sanukitoïdes (Leclerc et al., 2012; Moyen, 2019; Robert, 2001).

Les intrusions alcalines sont de faible volume. Ces magmas sont majoritairement représentés par des syénites, des syénites quartzifères et des granites alcalins (Legault et Goutier, 2014). Les magmas sont métalumineux ou faiblement peralumineux (enrichis en Na_2O et/ou K_2O vis-à-vis de leur contenu en SiO_2 et/ou Al_2O_3). Ces intrusions sont aussi riches en éléments incompatibles et notamment en *High Field Strength Elements* (HFSE). Cependant, ces magmas étant peu volumineux et relativement rares, leur chimie est peu documentée. De ce fait, ils sont souvent décrits comme étant potassiques ou sodiques et sont également majoritairement magnésiens (Charbonneau et al., 1991; Mathieu, 2015; Moyen, 2019).

Les sanukitoïdes sont définis comme étant des magmas plus ou moins différenciés comprenant des granodiorites, ainsi que des diorites ou des enclaves mafiques. Les sanukitoïdes sont des intrusions calco-alcalines, métalumineuses, potassiques avec un contenu en SiO_2 très variable ($45 \leq \text{SiO}_2$

≤ 70 wt.%) et un Mg# élevé (Martin et al., 2010; Stern et al., 2011). Le patron des éléments traces normalisés au manteau primitif de ces intrusions est similaire à celui des TTG, avec une anomalie Nb-Ta marquée et une concentration en éléments incompatibles (p.ex., LILE), notamment en Ba-Sr, plus élevée qu'observé dans les suites TTG. Le patron en terres rares de ces intrusions est fortement fractionné avec un contenu élevé en terres rares légères et faible en terres rares lourdes (Fayol et Jébrak, 2017).

Le magmatisme syntectonique comprend aussi les HKCA aussi nommés high Ti-sanukitoïde. Ces magmas sont mal définis et sont souvent regroupés avec les sanukitoïdes sur la base de leurs caractéristiques géochimiques (Halla, 2005). D'un point de vue pétrographique, ces magmas sont majoritairement des granites et monzogranites riches en Mg-K et en phénocristaux de feldspath potassique. Ces magmas sont métalumineux avec un Mg# de 0,5 (Moyen, 2019). Ils sont généralement plus riches en K₂O et plus pauvres en Na₂O que les sanukitoïdes. De plus, les HKCA présentent des concentrations élevées en LILE et terres rares légères ($(La_N = 300)$, avec N indiquant une normalisation au manteau primitif (McDonough et Sun, 1995), et relativement élevées en HREE. Ces magmas ont un ratio de fractionnement $(La/Yb)_N$ similaire à celui des sanukitoïdes (Huguet, 2019; Laurent et al., 2014b).

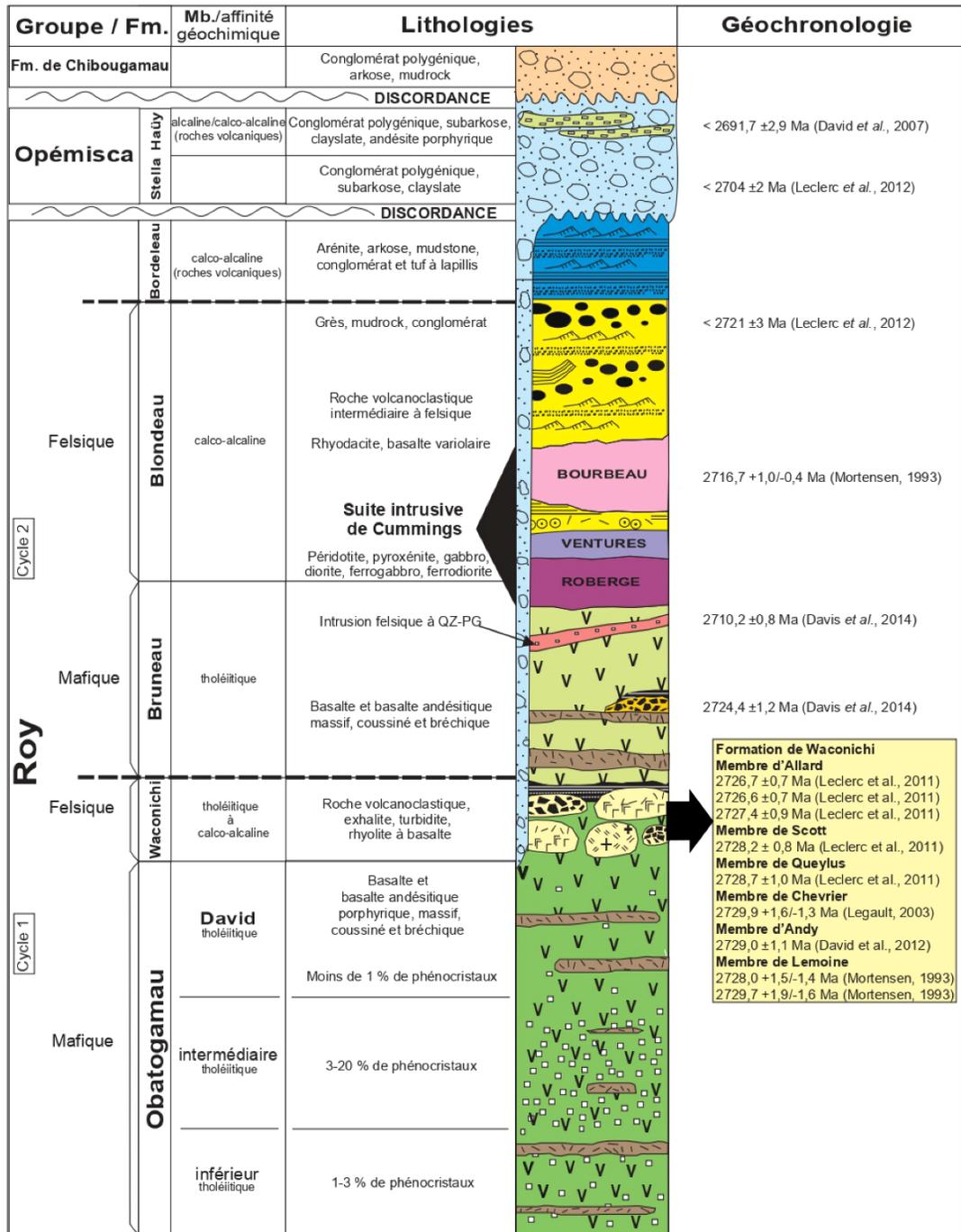


Figure 1.2. Colonne stratigraphique de la région de Chibougamau (Leclerc *et al.*, 2017)

Au sein de la Sous-province d'Abitibi, deux principaux types de systèmes minéralisateurs opèrent durant la période syntectonique, c.-à-d., les IRGS et les gisements de type or orogénique (Mathieu, 2015; Robert, 2001). Il peut être difficile de classer un gisement donné dans l'une ou l'autre de ces catégories (Mathieu, 2021). Ces styles de minéralisation, répandus le long de faille Cadillac, se recoupent et sont fréquemment déformés, p.ex., Canadian Malartic (Helt et al., 2014). La déformation tend à oblitérer, les textures associées à chacun des événements minéralisateurs et rend difficiles l'identification de la source de l'or (c.-à-d., magmatique ou autre) (Bigot et Jébrak, 2015; Mathieu, 2021). La région de Chibougamau-Chapais présente une concentration anormale de systèmes magmato-hydrothermaux. Les styles de minéralisation n'étant pas forcément surimposés et les phases de déformation moins intenses que dans le sud de la Sous-province d'Abitibi, l'étude des systèmes minéralisateurs de cette région pourrait permettre de préciser le lien entre les intrusions syntectoniques et les gisements aurifères.

A Chibougamau et dans le reste de la Sous-province d'Abitibi, les gisements de type IRGS sont définis comme étant des systèmes magmato-hydrothermaux polymétalliques (Cu, Bi, Te, As, W, etc.) enrichis en or (Figure 1.3). Ces gisements sont généralement centrés sur une intrusion syntectonique associée à une altération hydrothermale d'étendue et d'intensité limitées (Bigot et Jébrak, 2015; Robert, 2001). De plus, la distribution spatiale des métaux est zonée et la minéralisation consiste principalement en des veines de quartz aurifères, des skarns, des dykes minéralisés et des sulfures

disséminés (Figure 1.3) (Bigot et Jébrak, 2015; Lang et al., 2000). Le lien entre l'intrusion et la minéralisation est encore mal compris et pourrait être soit spatial (intrusion et minéralisation qui se mettent en place successivement au même endroit), structural (l'intrusion est l'encaissant de la minéralisation) et/ou génétique (l'intrusion est la source des fluides et des métaux). Ce dernier lien reste le plus controversé et le modèle métallogénique reste à préciser pour de nombreux gisements.

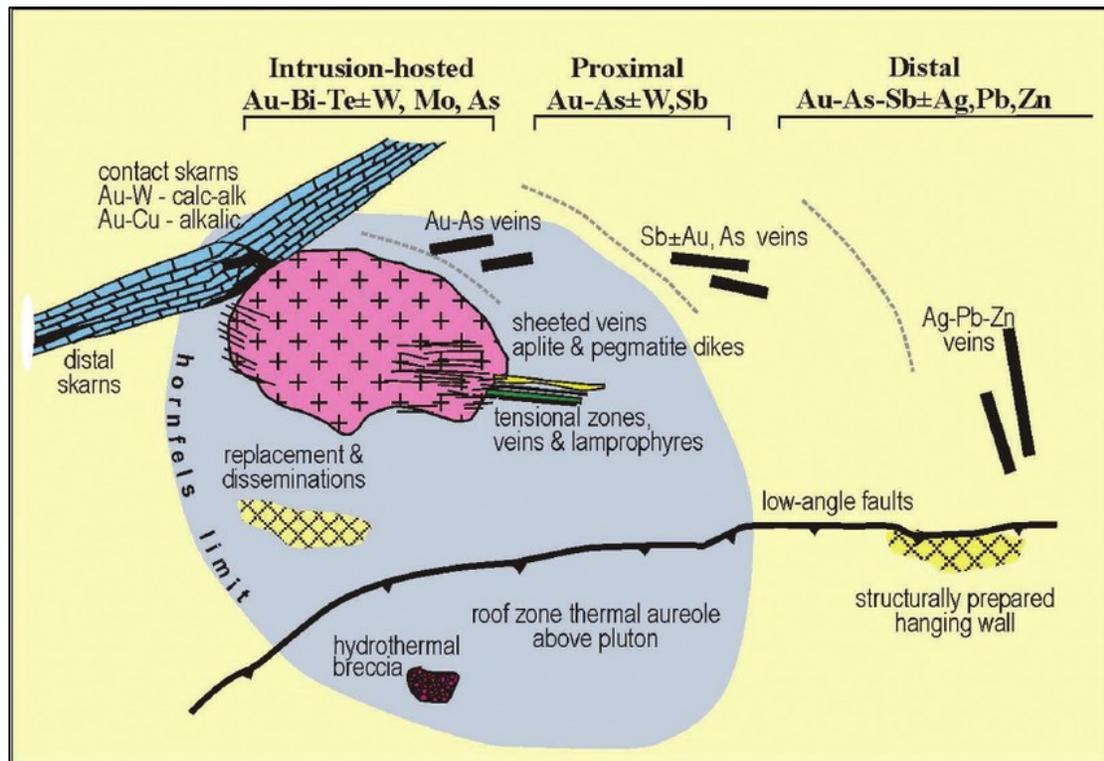


Figure 1.3. Modèle métallogénique des gisements de type IRGS (Hart et Goldfarb, 2005; Hart, 2007)

Dans le cas d'un lien génétique entre magmatisme et minéralisation, l'or est transporté à travers la croûte par le magma. Les conditions favorables à ce transport sont peu étudiées dans la Sous-province d'Abitibi. Les études ont

montré que la capacité d'un magma à transporter de l'or et des métaux de base augmente en fonction du contenu en Cl et S du magma et de la spéciation de ces éléments (de S notamment) (Botcharnikov et al., 2011; Botcharnikov et al., 2010). En effet, si la fO_2 est comprise entre $\Delta FMQ + 0,5$ et $+ 1,5$, alors S et Cl peuvent former des complexes sulfurés et/ou chlorés avec les métaux, ce qui permet au magma riche en volatils de transporter une plus grande quantité d'or et de métaux de base qu'un magma dépourvu de Cl et de S.

En résumé, la pétrogenèse des magmas de la période syntectonique de la Sous-province d'Abitibi est peu documentée pour un grand nombre d'intrusions. De plus, bien que plusieurs études mettent en avant un lien possible entre magmatisme et gisements de type IRGS, le contenu en or des magmas reste débattu. Ce qui nous amène à nous poser les questions suivantes :

- Quelles sont les sources des magmas syntectoniques du secteur de Chibougamau ?
- Ces magmas ont-ils participé à des processus minéralisateurs ?
- Est-ce que la fO_2 et le contenu en éléments volatils des magmas Archéens sont mesurables et est-ce que la mesure de ces paramètres permet de mettre en avant des conditions de transport favorables à la formation de gisements aurifères ?

1.4 OBJECTIF DE L'ETUDE

L'objectif principal de cette étude est d'utiliser la chimie des magmas syntectoniques afin de déterminer la nature de leurs liens avec les minéralisations aurifères. Pour ce faire, cette étude se concentre sur la caractérisation de la fO_2 et du contenu en éléments volatils de quatre types d'intrusions syntectoniques ainsi que d'une intrusion synvolcanique (suite TTG) du coin nord-est de la Sous-province d'Abitibi. Afin de répondre à la problématique exposée ci-dessus, plusieurs objectifs ont été déterminés :

- Caractériser le type de magma à l'origine des intrusions étudiées ;
- Réaliser des datations U-Pb sur les intrusions étudiées afin de valider leur appartenance à la période syntectonique ou synvolcanique ;
- Déterminer si les zircons et les apatites étudiés reflètent bien les conditions magmatiques et non les événements postérieurs, p.ex., altération hydrothermale et métamorphisme ;
- Déterminer quelles sont les méthodes qui permettent d'estimer et/ou de quantifier avec précision la fO_2 et le contenu en éléments volatils des magmas archéens.

1.5 METHODOLOGIE

Cette partie présente une revue succincte des méthodes qui ont été employées afin de répondre aux objectifs fixés. Une description détaillée des

méthodes employées ainsi que des résultats obtenus est fournie dans le second chapitre de ce mémoire.

1.5.1 Échantillonnage

Cinq intrusions calco-alcalines et alcalines ont été échantillonnées dans la région de Chibougamau au cours de deux campagnes de terrain effectuées au cours des étés 2019 et 2020. Les intrusions ciblées sont non-minéralisées (p.ex., Pluton de Chevrillon) et minéralisées (p.ex., stock du Lac Line), et ont été sélectionnées afin d'évaluer si ces différents types d'intrusions ont des pétrogenèses, fugacité de l'oxygènes ou autre qui diffèrent. Des échantillons d'environ 10 kg ont été collectés à la masse. Les échantillons récoltés sont ceux qui contiennent le moins de minéraux d'altération.

1.5.2 Caractérisation pétrologique des intrusions

Dans un premier temps, les intrusions échantillonnées ont été caractérisées macroscopiquement, de manière à définir les proportions modales. Une étude pétrographique à partir de lames minces polies a ensuite été réalisée au microscope optique de manière à caractériser les assemblages minéralogiques, les altérations éventuelles et les textures. Les lames minces ont aussi permis de caractériser la quantité d'apatites présentes dans les échantillons. Les zircons n'étaient pas visibles au microscope optique. Enfin, des analyses de type roche totale ont été réalisées dans le but de classer les roches sur la base de leurs chimies.

1.5.3 Etude texturale des minéraux

Les apatites observées en lame mince ont fait l'objet d'analyses chimiques in-situ. Afin d'analyser une plus grande quantité de zircons, des séparations minérales ont été effectuées par un consultant (ODM – Overburden Drilling Management Ltd.) et les grains de zircons ont été assemblés dans une matrice d'époxy. Les minéraux étudiés ont été imagés et caractérisés pétrographiquement au microscope optique puis au microscope équipé de cathodoluminescence et enfin au MEB (microscope optique à balayage) de manière à caractériser les zonations et les textures des minéraux d'intérêts.

Les analyses des minéraux observés en lames minces et des concentrés de zircons ont permis d'obtenir des informations texturales détaillées sur les zircons, les apatites et leurs relations avec les autres phases minérales. L'origine des apatites et des zircons sera évaluée sur la base des textures et des zonations observées. Les images obtenues au MEB vont permettre de déterminer la morphologie des grains de zircons. Dans le cas de l'apatite (Figure 1.4), cette étude permettra de déterminer s'il s'agit d'apatite primaire ou secondaire. Les apatites primaires (non-altérées) seront sélectionnées sur la base de leurs textures (grains automorphes et, présence de zonations oscillatoires).

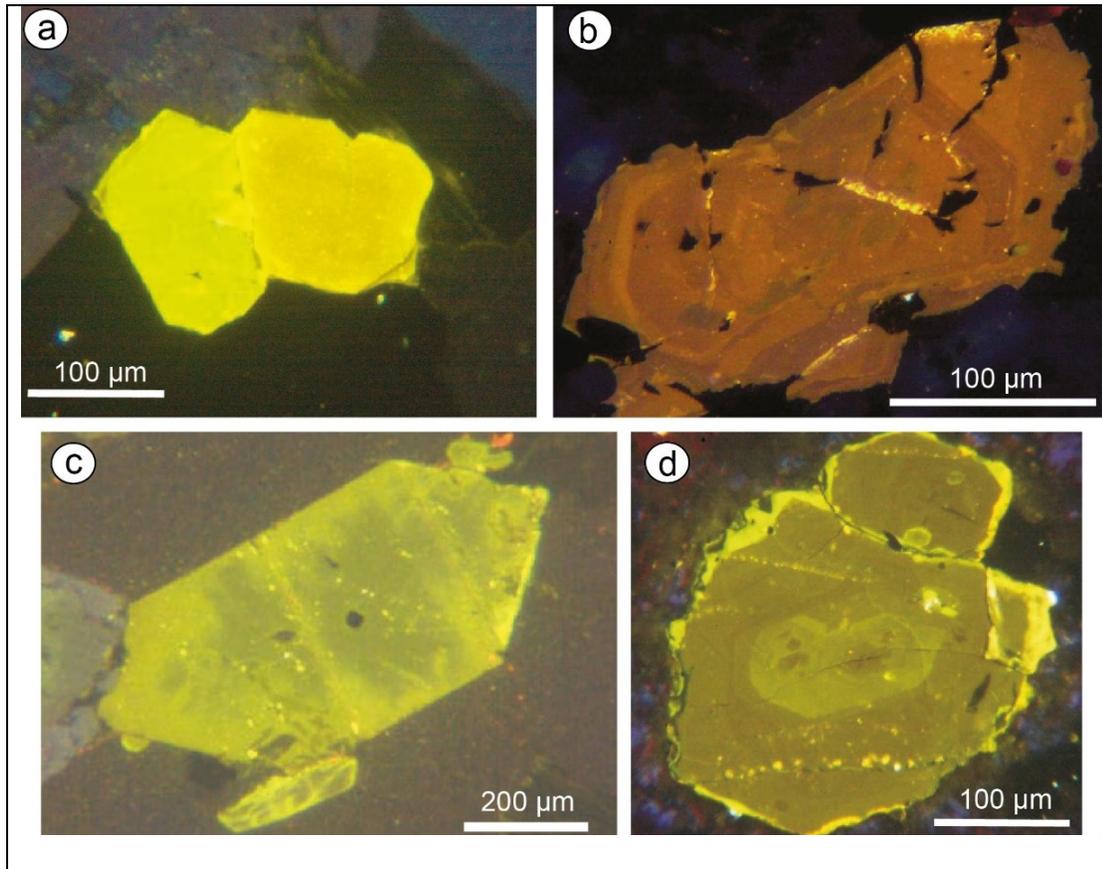


Figure 1.4. Images prises avec un microscope équipé de cathodoluminescence et présentant (a) deux apatites magmatiques non altérées, (b) une apatite avec des zonations de croissance et (c-d) des apatites altérées avec (c) un cœur poreux et (d) des bordures recristallisées (Bouzari et al., 2016)

Les zircons sont des minéraux prismatiques qui peuvent développer des zonations oscillatoires en cristallisant (Figure 1.5). Ces zonations indiquent que le minéral est possiblement d'origine magmatique et qu'il n'a pas été fortement altéré. Ces zonations sont définies par des variations du contenu en éléments traces. En résumé, les images obtenues au MEB, permettront de caractériser les étapes de cristallisation (étude de la relation entre les phases minérales) et

l'origine (magmatique, métamorphique ou hydrothermale) des apatites et des zircons.

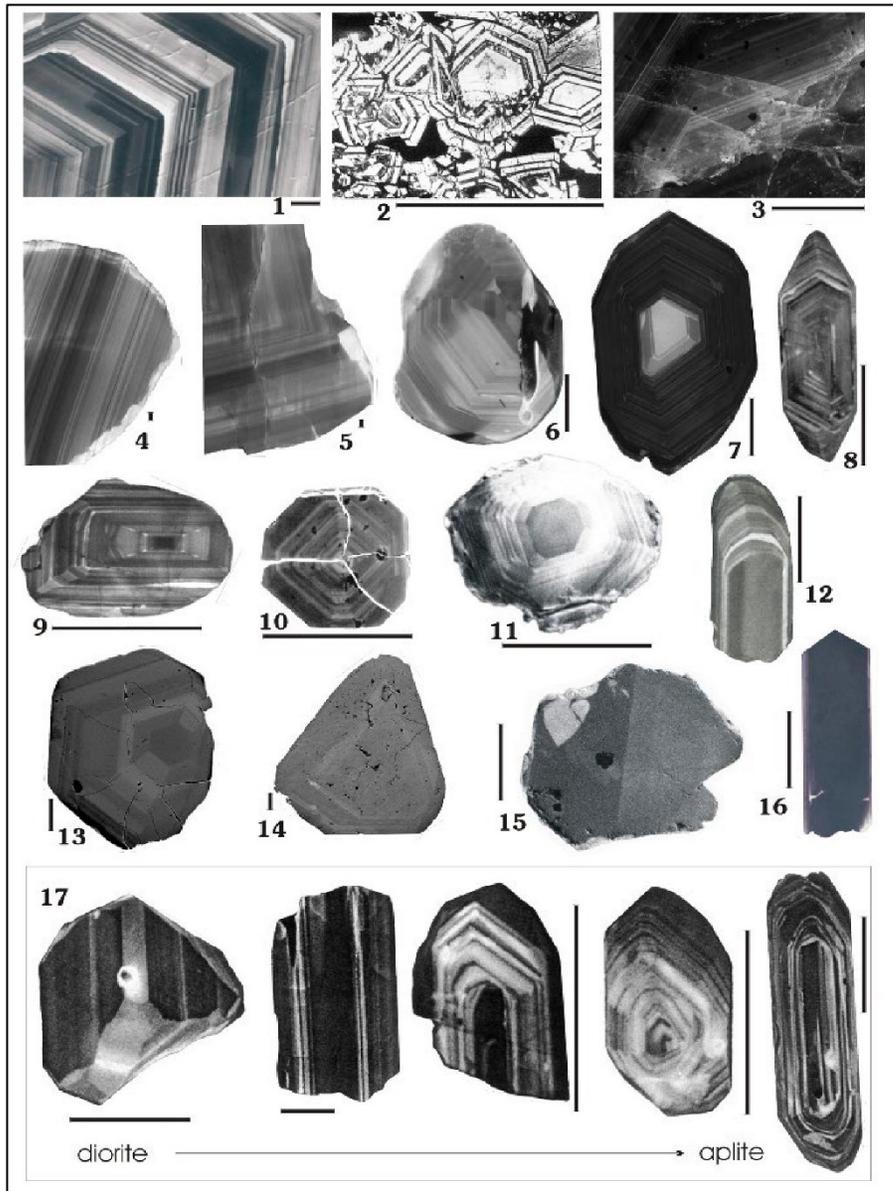


Figure 1.5. Images prises avec un microscope équipé de cathodoluminescence et présentant plusieurs types de zonations de croissance observées dans des zircons magmatiques. Les échelles correspondent à 100 μm (Corfu et al., 2003)

1.5.4 Etude géochimique des minéraux

La détermination de la fugacité de l'oxygène nécessite la caractérisation et la quantification d'éléments à valences variables (p.ex., Fe, Ce, Eu, etc.) au sein des minéraux traceurs. Ces paramètres seront étudiés à partir de la chimie de l'apatite et du zircon, car il s'agit d'oxy-thermomètres bien documentés. En effet, de nombreuses études (Burnham, 2012; Ryabchikov et Kogarko, 2009; Smythe et Brenan, 2016; Trail et Wang, 2018) utilisent ces deux minéraux afin de caractériser la fO_2 des magmas modernes.

La quantification de la fO_2 nécessite l'utilisation d'éléments tels que le Fe, le Ce ou le Mn (Burnham, 2012). Il s'agit toujours d'éléments à variance variable. En effet, selon son coefficient de partage (K_d), un élément intègre plus ou moins facilement la structure d'un minéral. Le K_d permet de décrire l'affinité d'un élément, dans certaines conditions de P, T, et fO_2 , pour une phase solide ou liquide donnée. Par exemple, en condition réductrice, l'Eu à une valence de +2 et est compatible avec les feldspaths car il se substitue au calcium (Ca^{2+}). Alors qu'en conditions oxydantes, Eu^{3+} entre difficilement dans la structure des feldspaths. Les analyses seront effectuées soit par LA-ICP-MS soit par microsonde électronique selon le contenu en éléments traces des minéraux étudiés.

Dans le cas du zircon, le cérium (Ce) et l'euporium (Eu) seront utilisés pour évaluer le paramètre fO_2 . L'amplitude des anomalies positives en Ce dans

le zircon est corrélée à la fO_2 du magma (Trail et al., 2011a). En effet, en condition oxydante, le Ce sera sous forme Ce^{4+} et il sera compatible ($K_d > 1$) avec le zircon. Une augmentation progressive du ratio Ce^{4+}/Ce^{3+} dans le zircon peut être interprétée comme une augmentation de l'état d'oxydation du magma pendant, par exemple, son refroidissement (Trail et al., 2012). La concentration en Ce et en Eu du zircon est fonction de la concentration de ces éléments dans le magma et des ratios Ce^{4+}/Ce^{3+} et Eu^{2+}/Eu^{3+} . Les zircons analysés seront ceux qui présenteront le moins d'inclusions fluides et solides (p.ex., apatite) pour éviter l'obtention de résultats incohérents.

Dans le cas de l'apatite, plusieurs éléments à valence variable sont présents dans la structure du minéral (p.ex., Mn, Eu, S). La fO_2 sera estimée grâce au Ce ou au Mn. Ce sont les éléments les mieux corrélés à la fO_2 selon plusieurs études (Miles et al., 2014; Vaughn, 2016).

1.5.5 Documentation du contenu en éléments volatils

La caractérisation du contenu en éléments volatils se fera à partir d'analyses réalisées avec le LA-ICP-MS du LabMaTer (Laboratoire des matériaux terrestres) sur des apatites et des amphiboles magmatiques. La composition en éléments volatils de ces minéraux varie en fonction de divers paramètres (p.ex., P, T, et fO_2).

L'analyse de la chimie de l'apatite va permettre de déterminer le contenu en volatils (F, Cl et S) du magma, ce qui est important puisque ces éléments permettent le transport des métaux via la formation de complexes ioniques. A partir de ces analyses, on pourra estimer le contenu en éléments volatils du magma, au moment de la cristallisation de l'apatite et en utilisant les K_d reportés dans la littérature. L'analyse des amphiboles va apporter des données supplémentaires sur le contenu en F et Cl des magmas (Chambefort et al., 2013; Li et al., 2018).

Aucune étude des inclusions fluides ne sera réalisée car, dans les roches étudiées, la majorité des inclusions fluides sont secondaires, ce qui signifie qu'elles renseignent sur le fluide (fluide exsolvé du magma ou fluide d'origine métamorphique) et non sur la composition du magma. L'analyse des inclusions vitreuses pourrait apporter des indications précises sur le contenu en or des magmas étudiés. Ces inclusions n'ont cependant pas été identifiées dans le cadre de ce projet et n'ont donc pas pu être analysées.

CHAPITRE 2

FUGACITE DE L'OXYGENE ET CONTENU EN ELEMENTS VOLATILS DES MAGMAS SYNTECTONIQUES DU SECTEUR DE CHIBOUGAMAU, SOUS-PROVINCE D'ABITIBI

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2.1 CONTRIBUTION DES AUTEURS

Premier auteur : Baptiste Madon

- Echantillonnage des zircons
- Observation macroscopique et microscopique des lames minces et des minéraux d'intérêts
- Analyses des minéraux d'intérêts au LA-ICP-MS
- Traitement des analyses de roche, des zircons, des apatites, des amphiboles
- Interprétation des données
- Rédaction de l'article et du mémoire

Deuxième auteur : Lucie Mathieu

- Direction du projet
- Réalisation des images MEB des apatites et des zircons
- Aide à l'interprétation générale des données
- Aide à la rédaction et correction des manuscrits

Troisième auteur : Jeffrey Marsh

- Préparation et analyses des zircons pour les datations U-Pb
- Interprétation des données géochronologiques pour les intrusions de Saussure, Opémisca, Chevrillon
- Aide à l'interprétation générale des données
- Aide à la rédaction et correction de l'article

2.2 RESUME TRADUIT

Dans le secteur de Chibougamau, Sous-province d'Abitibi, les intrusions néoarchéennes syntectoniques, peuvent être génétiquement associées aux minéralisations de type *intrusion related gold systems*. Ces systèmes magmato hydrothermaux possèdent des caractéristiques communes avec les gisements de type or orogénique comme par exemple, une association spatiale et temporelle avec les intrusions syntectoniques. Cependant, le lien génétique avec le magmatisme est encore fortement débattu pour de nombreux gisements d'or présent au sein des ceintures de roches vertes archéennes. Afin d'identifier avec précision le lien entre le magmatisme syntectonique et les minéralisations aurifères de la Sous-province d'Abitibi, les contenus en éléments majeurs et traces des roches, ainsi que des zircons, apatites et amphiboles de cinq intrusions syntectoniques du secteur de Chibougamau ont été mesurés. La chimie des plutons Anville, Saussure, Chevrillon, Opémisca et Lac Line est représentative de la diversité du magmatismes synvolcanique (TTG) et syntectonique (p.ex., sanukitoïde, intrusion alcaline). Les données géochimiques récoltées grâce à une microsonde électronique et un spectromètre de masse plasma à couplage inductif par ablation laser vont permettre de calculer la fugacité de l'oxygène et le contenu en éléments volatils des magmas étudiés. La chimie du zircon et de l'apatite ont permis d'évaluer la fugacité de l'oxygène et de montrer que les magmas les plus récents sont les plus oxydés. De plus, le pluton de Saussure et l'intrusion minéralisée du Lac Line possèdent des contenus en éléments volatils et des fugacités de

l'oxygène comparables, ce qui signifie que le pluton de Saussure pourrait être associé à un système minéralisé.

Mot clefs : fugacité de l'oxygène ; contenu en éléments volatils ;

Géochronologie ; IRGS ; intrusions syntectoniques ; ceinture de roches vertes de l'Abitibi.

2.3 ABSTRACT

Neoproterozoic syntectonic intrusions from the Chibougamau area, northeastern Abitibi Subprovince (greenstone belt), may be genetically related to intrusion related gold mineralization. These magmatic-hydrothermal systems share common features with orogenic gold deposits, such as spatial and temporal association with syntectonic magmatism. Genetic association with magmatism, however, remains controversial for many greenstone belt hosted Au deposits. To precisely identify the link between syntectonic magmas and gold mineralization in the Abitibi Subprovince, major and trace-element compositions of whole rock, zircon, apatite, and amphibole grains were measured for five intrusions in the Chibougamau area: the Anville, Saussure, Chevrillon, Opémisca, and Lac Line Plutons. The selected intrusions are representative of the chemical diversity of synvolcanic (TTG suite) and syntectonic (e.g., sanukitoid, alkaline intrusion) magmatism. Chemical data enable calculation of oxygen fugacity and volatile content, and these parameters were interpreted using data collected by electron microprobe and laser ablation inductively coupled plasma-mass spectrometry. The zircon and apatite data and associated oxygen fugacity values in magma indicate that the youngest magmas are the most oxidized. Moreover, similar oxygen fugacity and high volatile content for both the Saussure Pluton and the mineralized Lac Line intrusion may indicate a possible prospective mineralized system associated with the syntectonic Saussure intrusion.

Keywords: Oxygen fugacity; Volatile content; Geochronology, IRGS,
Syntectonic intrusions; Abitibi greenstone belt.

2.4 INTRODUCTION

The Abitibi Subprovince (greenstone belt), Superior craton, is a gold-endowed greenstone belt where gold is mostly concentrated within volcanogenic massive sulfide (VMS) and orogenic gold systems. In addition, intermediate to felsic alkaline intrusions, such as monzonite and syenite, may provide fluids and metals to intrusion related gold system (IRGS) (Lang et al., 2000). As IRGS and orogenic gold deposits formed during the syntectonic period and display some similarities (e.g., mineralized quartz veins), the influx of magmatic fluid in many gold systems is debated. For example, the Canadian Malartic deposit was first interpreted as an IRGS, re-interpreted as an orogenic gold system (Hart, 2007; Lang et al., 2000) and was then described as a complex association of both genetic models (Souza et al., 2015). Thus, Archean IRGS and orogenic gold systems may be hard to distinguish (Hart et Goldfarb, 2005), rendering difficult the application of a single, mutually exclusive exploration model.

IRGS are generally polymetallic and gold-dominated magmatic-hydrothermal systems centered on intrusions, e.g., Beattie syenite (Bigot et Jébrak, 2015; Mathieu, 2016). Metals distribution is generally zoned with hydrothermal alteration having a limited extent and potentially including K-metasomatism. Mineralization generally consists of sheeted auriferous quartz veins (W, Cu, Zn, Au), skarns (Au, Bi, Cu, W), mineralized dykes and disseminated sulfides (Hart, 2007; Lang et al., 2000). Moreover, in the IRGS

metallogenic model, magma is envisaged to carry metals through the crust. Experimental studies on silicate magmas show that Au solubility and the melt capacity to transport gold increases as the Cl and/or S-content of the melt increases. Moreover, the formation of Au bearing Cl- and/or S-complexes, in magmas, is linked to a narrow range of oxygen fugacity, i.e., $\Delta\text{FMQ} +0.5$ to $\Delta\text{FMQ} +1.5$, where FMQ refers to the fayalite-magnetite-quartz buffer (Botcharnikov et al., 2013; Botcharnikov et al., 2011; Botcharnikov et al., 2010). In summary, the volatile and metal contents, as well as the $f\text{O}_2$ of the magma, need to be constrained to determine whether syntectonic magmatism can transport Au and fertilize the upper crust, and whether the IRGS metallogenic model is realistic.

Most of the gold deposits (orogenic Au, IRGS) in the Abitibi Subprovince are present along the Cadillac fault; however, these systems generally have complex overprinting relationships, rendering hard the study of early IRGS. For that reason, this study focuses on the Chibougamau area, where a variety of syntectonic magma types (sanukitoid, alkaline intrusions, granitoid) are observed, and gold deposits are not overprinted by features characteristic of orogenic gold systems – a mineralizing style that is not abundant in the study area. Furthermore, magmatic-hydrothermal systems are unusually abundant in the Chibougamau area (e.g., Central camp, MOP-II, Lac Line mineralization) (Côté-Mantha, 2009; Lépine, 2009; Mathieu et Racicot, 2019), although the tectonic processes causing this remain unclear (Mathieu et al., 2020a; Mathieu et al., 2020c). The abundance of such mineralizing systems in this area offers

a unique opportunity to study the chemistry of 'fertile' magma intrusions. This contribution will mainly focus on constraining the fO_2 parameter and the volatile content for a variety of syntectonic magmas.

To address these issues, this work presents a detailed study of the geochemical characteristics of one synvolcanic and four syntectonic intrusions. Uranium-Pb dating was conducted to validate the syntectonic age of undated intrusions. The trace elements chemistry of zircon and apatite is used to evaluate the fO_2 of the melts and this study provides a basis for a systematic measurement of this parameter in Neoproterozoic intrusions. Moreover, the data are used to evaluate the economic potential of the studied intrusions.

2.5 GEOLOGICAL SETTINGS

2.5.1 Abitibi Subprovince and Chibougamau area

The Abitibi Subprovince, southern Superior Province, Canada, is a Neoproterozoic granitoid-greenstone belt composed of 40% intermediate to felsic intrusions and 36% volcanic rocks with the remaining 24% composed of sedimentary rocks, gneisses with undocumented protoliths and mafic to ultramafic intrusions (Mathieu et al., 2020a). In greenstone belts such as the Abitibi Subprovince, magmatic activity mostly occurs in two main stages, during the synvolcanic (pre-2750 Ma to 2704 Ma) and the syntectonic periods (2704 Ma to 2690 Ma) (Laurent et al., 2014b; Thurston et al., 2008). The synvolcanic period is the main period of magmatism and is characterized by large volume volcanism, as well as tonalite-trondhjemite-granodiorite (TTG) and TT-diorite

(TTD) intrusive suites (Mathieu et Racicot, 2019). This is followed by the syntectonic period, which is characterized by deformation, erosion-sedimentation, and orogenic gold style of mineralization (Bleeker, 2015; Dubé et Gosselin, 2007). Syntectonic magmatism is typically K-richer and has a limited volume (plutons, plugs and subordinate volcanism) compared to TTG and TTD suites (Moyen, 2019; Robert, 2001). The main magma types of the syntectonic period are K-rich TTG, alkaline series, sanukitoids, biotite and two-mica granitoids, as well as high-K calc-alkaline (HKCA) intrusions (Moyen, 2019; Stern et al., 2011). The petrogenetic evolution of these magmas is debated (Moyen, 2019). Intermediate to felsic alkaline magmas (mainly monzonite and syenite) may actively participate in generating fluids and metal budgets to gold mineralizing systems of the syntectonic period, i.e., IRGS (Lang et al., 2000).

Syntectonic magmatism is ubiquitous in the Abitibi Subprovince. This study focuses on the Chibougamau area because (1) it displays a variety of magma types (sanukitoid, alkaline intrusions, granodiorite, shoshonite lava flows) and (2) magmatic-hydrothermal mineralizing systems are not significantly overprinted by orogenic gold systems, which are not abundant in the study area (Côté-Mantha, 2009; Lépine, 2009; Mathieu et Racicot, 2019). These characteristics offer a unique opportunity to study the fO_2 of mineralized and un-mineralized intrusive systems that we assume representative of synvolcanic and syntectonic magmatism.

In the Chibougamau area, as in the rest of the Abitibi Subprovince, rocks have been metamorphosed to greenschist facies or higher grade, although the prefix 'meta-' is omitted from rock names. The Chibougamau area is located in the north-eastern corner of the Abitibi Subprovince and is bounded by the Opatica Subprovince to the north and the Proterozoic Grenville orogeny to the east (Figure 2.1). In the Chibougamau area, the synvolcanic and syntectonic periods extend from > 2730 to ca. 2710 Ma and from 2704 to 2690 Ma, respectively (Leclerc et al., 2017). The oldest volcanic rocks belong to the Des Vents (2798.7 ± 0.7 Ma (Davis et al., 2014) and Chrissie (2791.4 ± 2.9 Ma (David et al., 2011)) formations. These rocks are overlain by volcanic cycles 1 and 2 of the Roy Group (Leclerc et al., 2017). Volcanic cycle 1 consists mostly of undated mafic lava flows of the Obatogamau Formation (Mortensen, 1993) and intermediate to felsic lava flows of the Waconichi Formation (2729.0 ± 1.1 Ma (David et al., 2012; Mortensen, 1993)). Volcanic cycle 2 is characterized by mafic rocks of the Bruneau Formation (2724.4 ± 1.2 Ma (Davis et al., 2014)), felsic rocks of the Blondeau Formation ($< 2724.4 \pm 1.2$ Ma (Leclerc et al., 2012)) and by the intermediate to felsic volcanoclastic and sedimentary units of the undated Bordeleau Formation (Mathieu et Racicot, 2019). The synvolcanic period is also characterized by large volume TTG suites (e.g., La Dauversière pluton) (Chown et al., 1992) and TTD suites such as the Eau Jaune Complex (Kieffer, 2019; Legault, 2003) and the Chibougamau pluton (Mathieu et Racicot, 2019) (Figure 2.1).

During the syntectonic period, basin-restricted sedimentation formed the Opémisca Group. This group is mostly made of clastic sedimentary rocks (conglomerate, sandstone). The Opémisca Group comprises the Stella Formation and the lava flow-bearing (shoshonite) Haüy Formation ($< 2691.7 \pm 2.9$ Ma (David et al., 2007)). The maximum deposition age for the Stella Formation is 2704 ± 2 Ma, according to dating (ID-TIMS on zircon) performed on a conglomerate (Leclerc et al., 2012). In the northern and western part of the study area, the Opémisca Group comprises the Chebistuan (Caty, 1978; Leclerc et al., 2017) and Daubrée (Charbonneau et al., 1991; Simoneau, 1986) formations, respectively. Several intrusions, such as the Muscocho pluton (2701.2 ± 1.7 Ma (Mortensen, 1993)), formed during the syntectonic period (Figure 2.1).

2.5.2 Syntectonic magmatism in the Chibougamau area

The Chibougamau area contains a variety of syntectonic intrusions such as alkaline, calc-alkaline and sanukitoid plutons. Representative intrusions for each category are selected for the need of this study. The selected intrusions are emplaced within either the sedimentary rocks of the Opémisca Group – granodiorite of the Chevrillon pluton and alkaline Saussure intrusion – or within the volcanic rocks of the Roy Group – Opémisca pluton (sanukitoid), Anville pluton (TTG suite) and the Au-Cu-Ag mineralized Lac Line intrusion.

The undated **Saussure intrusion** is located in the western part of the northern Opémisca basin (Figure 2.1). This 9 by 3.5 km intrusion is elongated in the NE-SW direction. It cuts, and is therefore younger than, the sedimentary rocks of the 2693.6 ± 0.6 Ma Daubrée Formation (McNicoll et Goutier, 2008), as well as undated diorite sills.

The **Opémisca pluton** is located west of the Chibougamau pluton and corresponds to a 25 by 11 km intrusion elongated in the WNW-ESE direction (Figure 2.1). The Opémisca pluton is emplaced in volcanic, volcanoclastic and sedimentary rocks, including the Blondeau and Bruneau formations (Davis et al., 2014; Leclerc et al., 2011). The pluton has an age of 2697 ± 2 Ma (Frarey et Krogh, 1986) and is coeval with the other sanukitoid pluton of the Chibougamau area, i.e., the 2697 ± 3 Ma Barlow pluton (Gariépy et Allègre, 1985) (both are zircon U-Pb ID-TIMS ages).

The **Lac Line intrusion** is a small volume felsic to intermediate intrusive stock emplaced into the volcanic and volcanoclastic rocks of the Blondeau Formation (Figure 2.1). This intrusion has a zircon U-Pb TIMS age of 2707.6 ± 1.4 Ma (Côté-Mantha, 2009) and formed during the transition between the synvolcanic and syntectonic periods (Côté-Mantha, 2009).

The **Chevillon pluton** is located 6 km south of the Opatoca Subprovince. This pluton is a 11 to 8 km intrusion elongated in the N-S direction (Figure 2.1). The pluton is emplaced into felsic to mafic volcanic rocks of the Bruneau and

Bordeleau formations (Allard et al., 1985; Moisan, 1992) and sedimentary rocks of the Chebistuan Formation (Leclerc et al., 2012). The pluton records a limited amount of deformation and likely formed toward the end of the syntectonic period, as shown by underdeveloped foliation and the lack of deformation of the quartz grain (Huguet, 2019).

The **Anville intrusion** is 25 by 8 km long and is elongated in the E-W direction. It is intruded into the tonalite gneisses of the Lapparent massif (2714 ± 2.5 Ma, ID-TIMS on zircon) (Mortensen, 1993) and into mafic volcanic rocks of the Chrissie and Obatogamau formations (Figure 2.1). The Anville intrusion is, locally, relatively undeformed compared to the Lapparent massif and the pluton may correspond, at least in part, to a syntectonic intrusion. However, recent geochronological investigations estimate that the Anville intrusion crystallized at 2714.8 ± 0.6 Ma (Thurston et al., 2008). The area mapped as the Anville pluton may consist of several intrusions emplaced during the synvolcanic and syntectonic periods (Gervais, 1986; Midra et al., 1992).

2.6 METHODOLOGY

2.6.1 Sampling

Eight samples were collected in the Chibougamau area from the Saussure, Opémisca, Lac Line, Chevrillon and Anville intrusions during summer 2018 (Figure 2.1, Table 1). Only fresh rocks were sampled to avoid secondary processes that may affect the trace element chemistry of zircon and

apatite. Alteration minerals, however, are observed in samples from the Lac Line intrusion that is entirely composed of hydrothermally altered rocks. A review of the literature about the petrography of the selected samples is proposed in the following section.

The Saussure intrusion is made of three fractionated and concentrically organized intrusive phases. From the margin towards the core, these phases are a granite, a quartz-rich syenite and a pegmatitic syenite (Thiboutot et Rouillard, 1981). The granite phase is made of 60% to 70% of K-feldspar and plagioclase, 15 to 20% of quartz and 10 to 15% of mafic mineral (Figure 2.2c). The quartz-rich syenite is made of 85% of sodic plagioclase and microcline with strong oscillatory zoning, 5 to 10% of quartz and 2 to 7% of mafic minerals (mostly biotite, magnetite, hematite, and amphibole). The pegmatitic syenite consists of 90% of zoned sodic plagioclase and potassic feldspar, 5% of mafic minerals (biotite and amphibole) and 5% of quartz (Figure 2.2a). Accessory minerals include titanite, zircon, apatite and magnetite.

Lac Line is a multiphase intrusion mostly made of a porphyritic and equigranular tonalite. The other intrusive phases are a porphyritic syenite and a diorite observed in contact with tonalite dykes. The Lac Line stock is associated with polymetallic mineralization (Au-Cu-Ag \pm Mo) (Pilote, 1986) observed in the eastern part of the tonalite phase. The mineralization is characterized by quartz-sulphide-bearing veins associated with sericitisation (Côté-Mantha, 2009; Pilote, 1986). The studied tonalite (Figure 2.2b) is made

of 40 to 65% of phenocrysts of plagioclase, 20 to 30 % of quartz, as well as 5 to 10 % of biotite and amphibole. Plagioclase is strongly sericitized, whereas hornblende recrystallized into an assemblage of carbonate, chlorite and actinolite (Côté-Mantha, 2009). Accessory minerals include zircon, apatite and up to 5% of disseminated pyrite.

The Opémisca pluton is made of quartz-bearing monzonite in his inner parts and quartz-bearing syenite in his outer parts. The monzonite phase (Figure 2.2d) on which this study is focused is made of 50 to 60% of albite and oligoclase, 15 to 25% of perthitic K-feldspar, 13 to 18% of quartz, 2 to 10% of hornblende and minor amount of biotite (Wolhuter, 1971, 1984). Accessory minerals include zircon, apatite, titanite, oxide minerals and epidote.

The Chevrillon pluton is mostly made of K-feldspar phenocryst-bearing granodiorite. The matrix is made of 35 to 40% of plagioclase, 25 to 30% of microcline and 10 to 15% of quartz (Figure 2.2e). It also contains 15% of mafic minerals including biotite, chloritized hornblende and epidote with allanite core. Accessory minerals correspond to titanite, zircon, apatite and Fe-oxides (Huguet, 2019).

The Anville intrusion is mostly made of tonalite transitioning gradually into granodiorite to the west. This study focuses on the granodiorite phase (Figure 2.2f), which is made of 25% of quartz, 40 to 45% of albite-oligoclase and 10 to 15% of microcline, as well as 10% of biotite and hornblende (Augland et al.,

2016; Caty, 1978). Accessory minerals include zircon, apatite, epidote, allanite and ilmenite.

For each intrusion, petrographic observations were performed on standard (30 µm thick) polished thin sections to document the texture of accessory phases and the contact relationships between apatite and silicates. Modal proportions were estimated visually on the microscope by counting 200 points (Table 2). Apatite was then imaged using a petrographic microscope equipped with cathodoluminescence (CL), i.e., CL8200 Mk5-1 Optical instrument.

For each intrusion, zircon separates were obtained from 5 to 10 kg samples. The rocks were disaggregated (1 mm grains) using the electric pulse method at the ODM (Overburden Drilling Management Ltd) laboratory. Zircons were then separated using a shaking table and heavy liquids with densities of 3.0 and 3.3. Zircon grains of various shape and size (up to 300 µm) were then hand-picked dry using a binocular microscope. The most representative grains were selected and mounted using epoxy resin and the mounts were polished to expose the cores of the zircons. Prior to analysis, CL and back scattered electron (BSE) images were obtained using a Tescan Vega 3 scanning electron microscope (SEM) at the Mineral Exploration Research Centre, Laurentian University. Inherited cores and porous grains were avoided during the analyses.

2.6.2 Whole rock analyses

Whole rock chemical analyses were performed on all the samples collected in the field (Table 1). The whole rock analyses were performed by ALS Canada Ltd laboratory. Major elements were determined by inductively coupled plasma (ICP) atomic emission spectroscopy (AES) after Li-borate fusion. Trace elements concentrations were quantified using an ICP- mass spectrometer (MS). Loss on ignition (LOI) was measured after heating samples at 1000°C. A duplicate performed on a sample from the Anville intrusion shows precision of 1% for all major elements and of 10% for trace elements, including rare earth elements (REE). Analytical accuracy and precision were monitored using the standard materials: OREAS-105 (Harmon et al., 2019), SRM88B (Gladney et Roelandts, 1987), AMIS0304 and AMIS0085 (Loader et al., 2017) for major and trace elements. An additional 30 whole rock chemical analyses were compiled from the SIGEOM dataset (Québec et Ministère des ressources naturelles, 2018).

2.6.3 Mineral chemistry

Electron microprobe analyses (EMPA) were performed on apatite and amphibole, using a fully automated CAMECA SX-100 electron microprobe equipped with five wavelengths dispersive spectrometers at the Laboratory of Microanalyses of the Geology Department of Laval University (Québec). Time of acquisition for the analysed elements are presented in the supplementary material S1. The microprobe was set to a current of 20 nA and to a voltage of

15 kV. Apatite and amphibole grains were analyzed with a 5 μm diameter focused beam. Natural and synthetic standard materials were used for calibration including the Durango apatite that was used for Ca, P, and F calibration (Chew et al., 2016) (supplementary material S1).

Apatite and zircon were then analyzed for trace elements using the laser ablation (LA) ICP-MS system at the LabMaTer (Earth's Material Laboratory) laboratory of UQAC. The LA-ICP-MS instrument used is a ArF Resolution M-50 Excimer (193 nm) laser coupled with a Agilent 7900X Q-ICP-MS. Apatite and zircon were analyzed using spots with diameters of 25–33 μm and 11–25 μm , respectively. Masses and time of acquisition for the analysed elements are presented in the supplementary material S1. The analyzed areas were carefully selected to avoid inclusions, inherited cores (zircon), and altered cracks. Laser repetition rate of 15 Hz and a fluence of 5 $\text{J}\cdot\text{cm}^2$ (measured) were used. Data were recorded for 60 s after 30 s of gas analysis (blank). Data quality (precision and accuracy) was monitored using the NIST 610, NIST 612, GSE, Durango, GSD and 91500 zircon reference materials (Jochum et al., 2011). The results are in good agreement with expected values except for Li (Durango), P, K, Fe, Ni (NIST standards and GSE) and Pt (GSD, NIST 610, NIST 612) (supplementary material S1).

Ablation data for apatite and zircon were then reduced using the LADR 1.1.01 (<http://norris.org.au/ladr>) and Iolite softwares (<https://iolite-software.com>), respectively. The internal standards are Ca (average value for

each sample measured using EPMA) and stoichiometric Si-content (15.28 wt.% Si) for apatite and zircon, respectively. The internal standard for apatite has a value of 37.1 to 39.5 wt.% Ca according to EPMA analyses. For apatite grains lacking EPMA data, a median value of 38.7 wt.% Ca was used as an internal standard.

Prior to data processing, pristine and non-pristine zircons are identified using a preexisting method, proposed by Zeh and collaborators (Zeh et al., 2014); Turlin and collaborators (Turlin et al., 2019); and Groulier and collaborators (Groulier et al., 2020). The pristine and non-pristine grains are distinguished using CL and BSE imaging. Trace element chemistry was then used to confirm this classification. Altered zircon commonly appears as white or dark grey in CL. These altered grains are also enriched in non-formula elements, e.g., Sr, Fe, LREE (Geisler-Wierwille et al., 2007). In the study area, altered zircons are enriched in Fe, Sr and LREE (mostly La). Zircon grains defined as pristine fulfill the following criteria: (1) zircon are homogeneously grey (light or dark) in CL, with or without oscillatory or banded zoning; (2) fracture, visible inclusion and porosity are absent, except for the one that can be avoided during LA-ICP-MS analysis; and (3) Sr and La contents are low, with Sr < 6 ppm and LaN < 1 (Figure 2.3a,b), and the LREE content has to be under 100 ppm.

2.6.4 Uranium-Th-Pb Isotopic Ratios

Uranium-Th-Pb isotopic ratios and trace element analyses were performed on ~50 zircons from the Anville, Saussure and Chevrillon intrusions, using split stream LA-MC-Q-ICP-MS at the Mineral Exploration Research Centre – Isotope Geochemistry Laboratory (MERC-IGL) at Laurentian University. The details of analytical setup, reference materials used, and data quality control are described in supplementary material S1. Data quality was monitored using the reference materials NIST 610, NIST 612, OG1, OGC and 91500. The results are in good agreement with expected values (supplementary material S3).

2.6.5 Data processing

Mineral chemistry data were processed to obtain intensive parameters for the studied intrusions, including temperature and oxidation state (oxygen fugacity – fO_2). Temperatures were obtained using the Ti-in-zircon thermometer of Ferry and Watson (Ferry et Watson, 2007). To apply this method, data from the LabMaTer and MERC-IGL were used and bulk rock chemistry was assumed to be representative of melt composition and was used to calculate the FM parameter (Ferry et Watson, 2007). Furthermore, the activities of SiO_2 and TiO_2 (α_{TiO_2} and α_{SiO_2}) were estimated as follows. The bulk of the studied intrusions contains primary magmatic quartz and the α_{SiO_2} parameter is thus 1. The main Ti-bearing mineral is titanite and α_{TiO_2} is < 1 .

The αTiO_2 parameter is estimated with the method of Hayden and Watson (Hayden et Watson, 2007), using a temperature of 850 °C and a FM parameter of 2.65, 3.19, 2.98 and 1.96 for the Saussure, Opémisca, Chevrillon and Anville intrusions, respectively. The αTiO_2 parameter is 0.3, 0.5, 0.6 and 0.7 for the Saussure, Opémisca, Chevrillon and Anville intrusions, respectively. The FM parameter could not be calculated for the altered rocks of Lac Line intrusion and αTiO_2 is assumed to be 0.6 for this intrusion, which is a reasonable value for felsic magmas (Hayden et Watson, 2007; Shen et al., 2015).

Four methods based on the chemistry of different minerals were used to determine the oxidation states of the studied magmas and to evaluate which method is most suitable for the estimation of the $f\text{O}_2$ of these Archean magmas. Redox conditions during crystallization were estimated from the trace element contents of apatite and zircon. These methods were only applied to pristine grains to constrain the redox conditions of the parental melt. Cerium and Eu anomalies in apatite are dependent on $f\text{O}_2$, bulk rock composition, temperature, pressure as well as co-existing mineral assemblage (e.g., plagioclase fractionation modifies Eu/Eu*) (Cao et al., 2011; Drake, 1975; Sha et Chappell, 1999). For apatite, Ce and Eu anomalies were displayed and interpreted using the binary diagram of Azadbakht (Azadbakht et al., 2018).

In zircon, oxidation state was estimated using the Ce/Ce* vs Eu/Eu* oxybarometer of Loader and collaborators (Loader et al., 2017), the (Ce/(Ce*))_CHUR oxybarometer of Trail and collaborators (Trail et al., 2012;

Trail et al., 2011b), and the REE-independent $\left[\frac{X_{Ce^{4+}}^{Melt}}{X_{Ce^{3+}}^{Melt}}\right]$ oxybarometer of Smythe and Brenan (Smythe et Brenan, 2015; Smythe et Brenan, 2016). These methods are based on the incorporation of Ce in zircon and on the lattice strain model (Zou et al., 2019).

The $\left(\frac{Ce}{Ce^*}\right)_{CHUR}$ oxybarometer (Equation ()) is a redox-sensitive method used to determine the oxidation state of magmas based on the partition coefficients ($D_{zircon/chondrite}$) of Ce, La and Pr for zircon (Li et al., 2019; Trail et al., 2012; Trail et al., 2011b).

$$\left(\frac{Ce}{Ce^*}\right)_{CHUR} = \frac{D_{Ce}^{zircon/chondrite}}{\sqrt{(D_{La}^{zircon/chondrite} * D_{Pr}^{zircon/chondrite})}} \quad (1)$$

The equation was put forward by Trail and collaborators and was further simplified by Zou and collaborators (Trail et al., 2012; Trail et al., 2011b; Zou et al., 2019) Equation (2).

$$\left(\frac{Ce}{Ce^*}\right)_{CHUR} = \frac{\left(\frac{Ce}{\sqrt{(La * Pr)}}\right)^{zircon}}{4.17} \quad (2)$$

Using this oxybarometer Equation (2), oxygen fugacity is then calculated after Trail and collaborators (Trail et al., 2011b) Equation (3).

$$\ln\left(\frac{Ce}{Ce^*}\right)_{CHUR} = (0.1156 \pm 0.0050) \times \ln(fO_2) + \frac{(13860 \pm 708)}{T(K)} - (6.125 \pm 0.484) \quad (3)$$

with K the temperature in Kelvin.

The Ce/Ce* vs Eu/Eu* oxybarometer is based on the REE content of zircon but due to low concentration of La and Pr in zircon (usually < 0.1 ppm) and the abundance of LREE-rich micro-inclusions such as apatite or titanite (Loader et al., 2017) that can lead to a mis-estimation of the fO_2 parameter, the method was reformulated Equation (4) (Loader et al., 2017).

$$Ce^* = \frac{Nd_N^2}{Sm_N} \quad (4)$$

with N the normalisation to the chondrite (McDonough et Sun, 1995).

Smythe and Brenan (Smythe et Brenan, 2015; Smythe et Brenan, 2016) formulated a REE-independent $\left[\frac{X_{Ce^{4+}}^{Melt}}{X_{Ce^{3+}}^{Melt}}\right]$ oxybarometer (6) based on the partition coefficients of Ce in zircon ($D^{zircon/chondrite}$) Equations (5-6).

$$\ln \left[\frac{X_{Ce^{4+}}^{Melt}}{X_{Ce^{3+}}^{Melt}} \right] = \frac{1}{4} \ln(fO_2) + \frac{13136 (\pm 591)}{T} - 2.064 (\pm 0.011) \frac{NBO}{t} - 8.878 (\pm 0.112) * H_2O - 8.955 (\pm 0.091) \quad (5)$$

where T is the temperature in kelvin calculated using a Ti-in-zircon thermometer, H₂O is the water content of the melt estimated using the empirical amphibole formulation (Mair et al., 2011; Ridolfi et al., 2009) and NBO/t is the proportion of non-bridging oxygen where NBO = 2O – 4T and t = Si + Ti + Al + P (in atomic percent), as Al < Na + K + 2Ca + 2Mg (Virgo et al., 1980).

Moreover, the REE-independent $\left[\frac{X_{Ce^{4+}}^{Melt}}{X_{Ce^{3+}}^{Melt}} \right]$ oxybarometer is estimated with Ce_{melt} and Ce_{zircon} which are the Ce-content in ppm of the melt and of zircon, respectively. Equations (5-6):

$$\left[\frac{X_{Ce^{4+}}^{Melt}}{X_{Ce^{3+}}^{Melt}} \right] = \frac{\Sigma Ce_{Zircon} - \Sigma Ce_{melt} * D_{Ce^{3+}}^{zircon/whole\ rock}}{\Sigma Ce_{Melt} * D_{Ce^{4+}}^{zircon/whole\ rock} - \Sigma Ce_{Zircon}} * 1.04877 \quad (6)$$

where the Ce_{melt} parameter is estimated by assuming that whole rock analyses are representative of melt composition.

2.7 RESULTS

2.7.1 Whole Rock Chemistry

The studied intrusions (n = 5) are intermediate to felsic, with Si contents ranging from 62 to 77 wt.% SiO₂ (Table 3, Figure 2.4a). Moreover, they tend to be peraluminous (Figure 2.4b) alkaline to subalkaline granite, syenite, and monzonite according to their Si- and Na and K-contents (Figure 2.4). The alkaline Saussure intrusion is the most enriched in Na and K (Figure 2.4a).

Except for the Anville intrusion, the intrusions display similar trace element contents. The bulk of the studied intrusions display negative Ta, Nb, Ti and Rb anomalies (Figure 2.4d). The Anville intrusion also displays strong negative Sr, V and P anomalies and flat Eu anomaly (Figure 2.4c).

The bulk of the studied intrusions displays a strong fractionation of the LREE over the HREE on the chondrite-normalized REE patterns (Figure 2.4c), with (La/Yb)_N ratio of 15 to 30 for the Anville and Opémisca intrusions and 40 to 70 for the Chevrillon, Lac Line and Saussure intrusions (Figure 2.4c). Three samples from the Anville intrusion display a positive Eu anomaly possibly due to local plagioclase accumulation, while the other intrusions show no to slight positive Eu anomalies. Moreover, the syenite sample from the Saussure intrusion contains more REE (up to 500 ppm Σ REE for Saussure) than rocks from the other intrusions (from 80 to 200 ppm Σ REE).

2.7.2 Petrography

The studied samples are mostly composed of feldspar (plagioclase and alkali feldspar), quartz, biotite and green hornblende (Table 2). Except for the rocks of the Anville intrusion, which are dominated by quartz, the studied intrusions are mostly made of K-feldspar and plagioclase. Plagioclase from each sample is recrystallized, with overgrowth texture and saussuritization in the core. The Saussure and Chevrillon intrusions contain K-feldspar phenocrysts. Accessory phases are apatite, zircon, epidote, titanite, magnetite

and pyrite. In the Lac Line and Anville intrusions, amphibole and biotite have been replaced by chlorite, actinolite and carbonate. Amphiboles are observed in the samples from the Chevrillon, Opémisca and Saussure intrusions. Amphibole grains are mostly subhedral to euhedral and are in contact with feldspar. Some amphiboles from the Opémisca intrusion are resorbed. Moreover, some amphiboles from the Saussure intrusion are altered and/or partly replaced by accessory minerals such as albite, chlorite and, epidote. Most inclusions observed in amphibole are apatite, magnetite and titanite.

Apatite is generally observed as inclusions in amphibole and feldspar and is generally abundant, except in the Anville intrusion. Apatite is euhedral to subhedral and grain-size varies from coarse-grained (up to 1 mm long in the Saussure intrusion) to finer-grained, i.e., <200 μm in the Opémisca and Chevrillon plutons, < 100 μm (Lac Line intrusion) and < 30 μm (Anville intrusion). Apatite displays oscillatory zoning (Figure 2.5a), with resorbed cores and overgrowth textures that indicate complex crystallization history. Oscillatory zoning is typical for minerals with a magmatic origin (Corfu et al., 2003; Scherer et al., 2007). Some apatites from the Opémisca, Anville, Saussure and Chevrillon intrusions are more homogeneous, indicating more continuous crystallization and/or less recrystallization. Cracks are common in the studied apatite and most grains from the hydrothermally altered Lac Line intrusion and the Opémisca intrusion are porous, unzoned and display corroded rims.

Zircons are translucent to light brown in natural light and are generally subhedral to euhedral. Grain size varies between 100 and 150 μm in most samples, except for some $> 200 \mu\text{m}$ long grains observed in the Opémisca, Lac Line and Anville intrusions. In the bulk of samples, part of the zircon grains display cracks and corroded rims. Multiple concentric growth zoning and resorbed cores are observed (Figure 2.5b–f), which is common for magmatic zircons. Zircon displays tabular (1:1 aspect ratio for the Saussure and Anville intrusions - Figure 2.5b, Figure 2.5e) to elongated prismatic morphology (1:2 to 1:4 aspect ratio for the Anville, Opémisca, Lac Line, and Chevrillon intrusions, Figure 2.5c, Figure 2.5d, Figure 2.5f). Zircons from the Anville, Saussure and Chevrillon intrusions are strongly altered and metamict. The most common inclusion observed in zircon is tabular apatite.

According to the calculation of the structural formula (Hawthorne et al., 2012), amphiboles are calcic B($\text{Ca}/(\text{Ca}+\text{Na}) \geq 0.75$ apfu) with low-Al content (≤ 10 wt.% Al). In the bulk of intrusions, amphiboles are all magnesio-hornblende, tremolite and pargasite (supplementary material S2). Amphiboles from the Chevrillon pluton are the most enriched in Al, Fe, and K, and these from the Opémisca intrusion are the most enriched in Mg and Cl (Table 4).

Apatites are fluorapatites, containing 2.6 to 4.6 wt.% F, and < 0.03 wt.% Cl except for the apatites from the Lac Line intrusion that contain 0.05 to 0.1 wt.% Cl (supplementary material S1). Fluorapatites are common in felsic

magma (Piccoli et Candela, 2002). Major constituents are close to stoichiometric values with 37.1 to 39.5 wt.% Ca and 17.2 to 19.1 wt.% P. Most apatites are S-poor, with < 0.08 wt.% S, except for the apatites of the Lac Line and Saussure intrusions that contain > 0.1 to 0.2 wt.% S. Silica and Na generally vary from 0.01 to 0.3 wt.% for all the samples. Titanium, Al, K, Mg and Mn-contents are generally < 0.1 wt.% and iron is generally < 0.1 wt.% Fe to up to 0.5 wt.% Fe in the bulk of the analyzed apatites (Table 4).

The Sr and Y contents of apatite range from 60 ppm to 1 wt.% Sr and from 70 to 5000 ppm Y. Also, three main types of apatite (groups 1, 2 and 3) are distinguished on the basis of their chondrite-normalized REE patterns (Figure 2.6). Group 1 apatite is observed in the Anville intrusion and is characterized by limited fractionation of the LREE over the HREE on their chondrite-normalized REE patterns (La/YbN ratio of 0 to 2), with convex-upward LREE profile and strong negative Eu anomaly. Group 2 apatite is from the Lac Line intrusion and is characterized by weak fractionation of the LREE over the HREE on their chondrite-normalized REE patterns, (La/YbN ratio of 16 to 50) and a small negative Eu anomaly. Group 3 apatite is from the Opémisca, Chevrillon and Saussure intrusions and is characterized by strong fractionation of the LREE over the HREE on their chondrite-normalized REE patterns (La/YbN ratio of 30 to 250) and no significant Eu anomaly. Apatite from the Saussure, Lac Line and Opémisca intrusions is the LREE richest with 10,000 to 30,000 ppm Σ LREE and up to 50,000 ppm for some apatites from the Saussure intrusion.

The Zr-content of zircon is close to stoichiometric value (58 wt.% ZrO₂), except near cracks and apatite inclusions, where it can range from 53 to 61 wt.% ZrO₂ (supplementary material S1). Hafnium, which is the most abundant trace element in zircon, has a concentration of 0.70 to 1.40 wt.% HfO₂. Trace elements such as P and Ti range from a few to thousands of ppm and from below the LOD to hundreds of ppm, respectively (Table 5). Yttrium contents range from 1000 to 10000 ppm Y. Zircon from the Anville intrusion contains more Y (1000s of ppm Y) than zircon from other intrusions (<1000 ppm Y). Tantalum in zircon is between 0.05 and 1 ppm for the bulk of intrusions, except for the Anville intrusion where zircon contains 1 to 3.5 ppm Ta. Also, Ta is positively correlated with Nb (LOD to 5 ppm Nb for the bulk of intrusions and up to 15 ppm for the Anville intrusion).

Except for the non-pristine zircon from the Anville, Saussure and Chevrillon intrusions that display elevated LREE contents (Figure 2.7), the bulk of zircon generally displays similar chondrite-normalized REE patterns (Figure 2.7). On chondrite-normalized REE patterns, LREE are strongly fractionated over HREE and display strong positive Ce anomalies (from 10s to 100s) and negative Eu anomalies. Non-pristine grains from the Saussure, Chevrillon and Anville intrusions display chondrite-normalized REE patterns with LaN > 1 and LREE enrichment (Table 5). Lanthanum enrichment in pristine zircon points either to La-rich inclusions (apatite), coprecipitation of coeval phases and may locally be a consequence of alteration. The temperatures calculated for the

pristine zircon range from 650 °C to 750 °C, except for few zircons for which temperatures over 800 °C were obtained (Table 5).

2.7.3 Volatile content of the melt

The volatile content (mainly Cl, S and H₂O) of a magma is an essential factor for the formation of IRGS, as it permits the formation of Cl- and S-complexes that transport metals, such as Au and Cu, through the crust (Botcharnikov et al., 2010). In this section, apatite and amphibole chemistry is used to estimate the volatile content (H₂O, S, Cl) of the studied magmas.

As the Anville and Lac Line intrusions lack amphiboles, only the H₂O concentration of the Saussure, Chevrillon and Opémisca intrusions is estimated using an empirical amphibole formulation (Mair et al., 2011; Ridolfi et al., 2009). The melt in equilibrium with the Saussure, Chevrillon and Opémisca amphiboles yield H₂O concentrations of 3.7 to 4.5 wt.%, 5.4 to 5.5 wt.% and 3.7 to 4.1 wt.%, respectively.

Apatite from the Chevrillon, Opémisca and Anville intrusions display low sulfur content (< 0.1 wt.% SO₃). These low values may reflect low S concentration in the melt. In a reduced magmatic environment (Anville intrusion), S is mostly dissolved in the magma as sulfur (S²⁻), which is more incompatible than sulfate (S⁶⁺) in apatite (Sha et Chappell, 1999). On the other hand, the moderate to elevated S content (0.2 to 0.5 wt.% SO₃) observed in

the apatite from the Saussure and Lac Line intrusions may indicate that S was introduced in the structure of apatite by secondary processes. To comment on the S-content of the melt, the empirical partitioning relationship of S between apatite and rhyolitic/andesitic melt is applied Equation (7) (Parat et al., 2011).

$$S_{apatite} = 0.0629 * \ln S_{melt} + 0.4513 \quad (7)$$

with $S_{apatite}$ and S_{melt} the S content in ppm in apatite and melt, respectively.

For the Chevrillon, Opémisca and Anville intrusions, this method points to magmas with low S- contents of about 10 to 30 ppm S. On the other hand, the Saussure and Lac Line intrusions return values ranging from 20 to 100 ppm S and up to 350 ppm S, respectively.

The studied apatites are also Cl-poor (<0.1 wt.% Cl) and there are no significant differences between altered and unaltered apatite, which mean that it could be a pristine value. To estimate the Cl concentration of the melt, we used a thermodynamic apatite/melt chlorine partitioning model (Equations (8) and (9) (Li et Hermann, 2017):

$$Cl_{melt} = \frac{X_{Cl}^{ap}}{X_{OH}^{ap}} \frac{1}{Kd_{Cl-OH}^{ap-melt}} * 10.79 \quad (8)$$

where X_{Cl}^{ap} and X_{OH}^{ap} are the mole fractions of chlorapatite and hydroxylapatite estimated by calculating the structural formula of apatite (Li et Hermann, 2017)

$$Kd_{Cl-OH}^{ap-melt} = e^{(25.81 + (X_{Cl}^{ap} - X_{OH}^{ap}) * 17.33) * \frac{10^3}{8.314 * T}} \quad (9)$$

with T the temperature in K [88].

Using this method, we obtain Cl melt concentrations that range from less than 0.01 to 0.1 wt.% Cl. Only three apatite grains from the Lac Line and Saussure intrusions return values of 0.1 wt.% Cl in the melt. The studied magmas present H₂O, S and Cl values within the range expected for felsic magmas (Chelle-Michou et Chiaradia, 2017; Ridolfi et al., 2009). Only the Saussure and Lac Line intrusions show S-content anomalously elevated, but these values need further validation.

2.7.4 Oxidation state

Redox conditions at the time of crystallization were estimated using the trace element chemistry of apatite and zircon (supplementary material S2). Three types of apatite are distinguished on the basis of their respective Eu anomalies (Figure 2.8), which is a proxy for the fO_2 parameter (Loader et al., 2017). According to apatite chemistry, the Anville intrusion crystallized under the lowest fO_2 conditions (type 1 apatite; Figure 2.8). The Lac Line apatites point to slightly higher fO_2 conditions (type 2 apatite). The Saussure and

Chevriillon intrusions crystallized under the highest fO_2 conditions (type 3 apatite). Variation of fO_2 values is limited in individual intrusions, except for the Opémisca pluton that displays a range of Eu anomalies values (types 2 and 3 apatites observed; Figure 2.8).

The Eu/Eu^* vs Ce/Ce^* in zircon oxy-barometer (Loader et al., 2017) has been used on pristine zircon to further evaluate the fO_2 parameter. Two zircon populations are observed on the basis of their Eu anomalies (Figure 2.9). Both populations display a wide range of Ce anomalies (0.9 to 100). Population 1 zircon is composed of zircon from the Anville intrusion and displays a generally lower Eu anomaly (up to 0.1), except for two grains that display high Eu anomaly. Population 2 is composed of zircons from the Lac Line, Saussure, Chevriillon and Opémisca intrusions and displays a moderate Eu anomaly (0.1 to 0.3) except for few grains from the Anville, Chevriillon and Saussure intrusions with Eu anomalies up to 1. Results of zircon from the Saussure, Chevriillon, Lac Line and Opémisca intrusions suggest that they crystallized under more elevated fO_2 conditions than zircons from the Anville intrusion, which crystallized under the lowest fO_2 conditions.

The $\left(\frac{Ce}{Ce^*}\right)_{CHUR}$ oxybarometer (Trail et al., 2012; Trail et al., 2011b) and the REE-independent $\left[\frac{X_{Ce^{4+}}^{melt}}{X_{Ce^{3+}}^{melt}}\right]$ oxybarometer (Smythe et Brenan, 2016) have been applied to the studied zircons to calculate the fO_2 parameter (Figure 2.10a).

These methods provide distinct results. The $\left(\frac{Ce}{Ce^*}\right)_{CHUR}$ oxybarometer returns, at similar temperatures, a wide range of fO_2 values for individual intrusions, e.g., ΔFMQ from -0.2 to $+9.3$ for the Opémisca intrusions at $750^\circ C$ (Figure 2.10b). There is a discrepancy between these results and the results obtained with the other methods applied to the studied samples, which returned a narrow range of fO_2 values for individual intrusions.

The REE-independent $\left[\frac{X_{Ce^{4+}}^{melt}}{X_{Ce^{3+}}^{melt}}\right]$ oxybarometer (Figure 2.10b) returns a narrow range of fO_2 values for individual intrusions. According to this method, the synvolcanic Anville intrusion crystallized under the lowest and highest fO_2 conditions with mean ΔFMQ of -1.4 . The Lac Line, Chevrillon zircons point to intermediate fO_2 values with mean ΔFMQ values of -0.3 and -0.7 , respectively. The Saussure and Opémisca Intrusions show higher fO_2 values with mean ΔFMQ values of 0.7 .

2.7.5 Geochronology results

The U-Pb ratios and trace element composition were measured on zircon from the Anville, Saussure and Chevrillon intrusions (supplementary material S3). Overall, the zircons from each sample display characteristics of moderate to severe alteration-related Pb-loss, a feature common to Archean zircons that have experienced significant radiation damage accumulation. Additionally, there is a slight overdispersion in the $^{238}U/^{206}Pb$ due to variable ablation rates

relative to the OGC primary reference material (also a byproduct of variable damage).

Analyses within the filter criteria yielded intercept ages of 2697 ± 11 Ma for the Chevrillon (MSWD = 1.9; Sr < 8 ppm) and 2688 ± 8 Ma for the Saussure (MSWD = 0.2; Sr < 12 ppm) intrusions, respectively (Figure 2.11). Zircons from the Anville intrusion have mostly concordant ages with an intercept age of 2796.5 ± 3.8 Ma (Figure 2.11), which we interpret as recording the timing of primary crystallization (Augland et al., 2016).

2.8 DISCUSSION

2.8.1 Magma type

The studied intrusions are alkaline to subalkaline and correspond to differentiated magmas according to their alkali and silica contents (Table 3). In this section, magma types are characterized using a recent classification of plutonic rocks (Moyen, 2019).

The Anville and Lac Line intrusions have the chemical composition of TTG suites, as defined by Moyen (Moyen, 2019). The Lac Line intrusion has the characteristics of a high pressure (HP) TTG suite, with $K_2O/Na_2O < 0.2$ wt.%, high Na_2O content, lack of K-feldspar (Figure 2.4, Table 2) and a strong fractionation of the LREE over the HREE (Figure 2.4c). However, the Fe, Mg,

and Al contents (for 70 wt.% SiO₂) of the Lac Line intrusion are higher than these of HP TTG suites (Table 3). Classification of the Lac Line intrusion remains uncertain, as extensive hydrothermal alteration likely modified its major element chemistry. The Anville intrusion resembles a K-rich TTG as it displays chemical characteristics of TTG suites, as well as these of ordinary biotite granite, such as relatively elevated K content (K₂O/Na₂O = 0.56) and elevated HFSE content (e.g., 35 ppm Y, Figure 2.4).

The Opémisca intrusion has a spotted macroscopic aspect that is common in sanukitoid intrusions (Moyen, 2019; Wolhuter, 1971). This intrusion is also Na-K-rich (4.80 wt.% Na₂O and 3.16 wt.% K₂O) with a K₂O/Na₂O ratio of 0.66 and has elevated Sr (1165 ppm) and La (30 ppm) contents (Table 3). The Opémisca intrusion thus has the whole-rock composition of a sanukitoid intrusion (Martin et al., 2010; Mondal et Raza, 2013; Moyen, 2019) to the exception that it is slightly peraluminous (ASI = 1.0 – 1.1) while sanukitoids tend to be metaluminous (ASI < 1, Figure 2.4) (Moyen, 2019). This Al-enrichment and Ca-depletion may be the results of alteration that induced the saussuritization observed in calcic plagioclase. This alteration could be due to sub-solidus reactions between intrusive rocks and tardi-magmatic fluids.

The Chevrillon intrusion is a high-K calc-alkaline (HKCA) granitoid intrusion (Huguet, 2019) with large phenocrysts of K-feldspar (Figure 2.2e) and elevated K₂O (3.1 wt.% K₂O) and Sr contents (1200 to 1400 ppm). The intrusion also has sanukitoid chemical characteristics, with a K₂O/Na₂O ratio of

0.6 and high contents of LREE (200 ppm sum LREE). Moreover, the HKCA group has been defined recently (Moyen, 2019) and its chemical definition likely requires refinement. This intrusion is also slightly peraluminous (ASI = 1.0-1.1), but that may be a consequence of secondary processes.

The Saussure intrusion is a typical quartz-bearing alkali syenite. This intrusion has elevated alkali ($\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO} = 9 \text{ wt.}\%$) and incompatible elements contents (up to 200 ppm Rb, up to 1300 ppm Sr, 550 ppm ΣREE , Table 3), which is typical of alkaline magmatism of any geological period (Moyen, 2019).

2.8.2 Zircon U-Pb geochronology

The results reported here indicate that the age ($2796.5 \pm 3.8 \text{ Ma}$) reported for the Anville intrusion (Figure 2.11a) is similar to that of the Chrissie and Des Vents formations, which formed in the early stage of the synvolcanic period. This age is also much older than the previous synvolcanic age ($2714.8 \pm 0.6 \text{ Ma}$) reported for the Anville intrusion (Augland et al., 2016). The Anville intrusion is likely an assemblage of synvolcanic and syntectonic intrusions emplaced in a restricted area throughout the evolution of the Chibougamau area. The syntectonic component was likely emplaced in the highly deformed southern part of the pluton that remains undated (McNicoll et Goutier, 2008). This intrusion is covered by quaternary material and the paucity of exposed outcrops prevents detailed investigation of crosscutting relationships.

For the Saussure and Chevrillon intrusions, the larger proportion of zircon that have undergone alteration and Pb-loss has resulted in slightly higher age uncertainty. The Chevrillon intrusion crystallization age of 2697 ± 11 Ma (Figure 2.11b) is in good agreement with recent yet unpublished TIMS age for the intrusion of 2693.1 ± 1.7 Ma (Huguet, 2019). This and the intrusion's crosscutting relationships with the Chebistuan Formation confirm that the intrusion is syntectonic (Figure 2.1). Also, the Saussure intrusion has likely an age of crystallization of 2688 ± 8 Ma (Figure 2.11c), which is in good agreement with stratigraphic relationships. Indeed, the Saussure intrusion emplaced in the Daubrée Formation (Figure 2.1), which formed during the syntectonic period.

In summary, the studied intrusions formed within about 10 Ma during the syntectonic period. Only the sample from the Anville intrusion is older and may be representative of synvolcanic magmatism.

2.8.3 Impact of alteration on mineral chemistry and fO_2 estimates

One of the main objectives of this study is to determine how the fO_2 parameter of Archean magmas can be evaluated using rocks that have generally been hydrothermally altered within magmatic-hydrothermal mineralizing systems. Apatite and zircon from the studied intrusions are more or less altered, as indicated by textural changes and heterogeneous chemistry (as discussed below).

Apatite from the Lac Line and Opémisca intrusions is strongly altered according to textural observations, i.e., porous texture, abundance of cracks, lack of oscillatory zoning and resorption texture. This alteration is accompanied by variation of the Na, Si, Fe, K, Al and S content of apatite and by REE remobilisation that is likely a consequence of hydrothermal alteration (Azadbakht et al., 2018; Cave et al., 2018; Exley, 1980) and/or of the co-crystallization of accessory minerals such as monazite and feldspar (Harlov et al., 2002; Panina et al., 2016).

As shown by the CL and BSE images (Figure 2.5) as well as the Sr- and LREE-contents (Figure 2.3), most zircon from the Chevrillon and Saussure intrusions and some zircon from the Anville intrusion are strongly altered. Alteration is manifested by corroded rims, porous textures, lack of oscillatory zoning, porosity of the core, as well as concentric and non-concentric cracks. Preserved oscillatory zoning (Figure 2.5) and resorption in other grains, point to complex crystallization history. Altered zircons may be enriched in trace (e.g., Ca, P, Al, Fe, Sr and Ti) elements compared to unaltered zircons (Groulier et al., 2020; Turlin et al., 2019; Zhong et al., 2018). Gain of trace elements may also be due to coupled substitution of non-formula elements (Geisler-Wierwille et al., 2003; Yang et al., 2013) and to inclusions of feldspar, quartz or apatite (Hoskin, 2005; Hoskin et Schaltegger, 2003; Nutman et al., 2014). Local decrease of the Zr, Pb, Hf and Si content may also be due to intense metamictization (Geisler-Wierwille et al., 2003).

Modification of apatite and zircon chemistry also impacts the results of Ti-in-zircon thermometry and fO_2 estimations. In felsic and intermediate intrusions, the Ti-content of zircon is generally less than 20 ppm, which corresponds to average crystallization temperatures of 653 ± 124 °C and 758 ± 98 °C, respectively (Fu et al., 2008). Alteration (Geisler-Wierwille et al., 2003; Hoskin et Schaltegger, 2003) or the entrapment of co-precipitated phases (Groulier et al., 2020; Turlin et al., 2019) may explain Ti enrichment (up to 150 ppm Ti), which lead to unreliable temperature estimates (Watson et al., 2006).

The fO_2 values obtained from REE dependent method (Azadbakht et al., 2018; Loader et al., 2017; Trail et al., 2011b) provide significantly different results when applied to pristine and non-pristine apatite and zircon grains, as was also noted for the Muscocho pluton (Mathieu et al., 2020b). For example, the apatites from the Opémisca intrusion provide a wide range of $\log(fO_2)$ estimates from -17.2 to -18.3 at 700 °C. The lowest fO_2 values are likely due to LREE-rich inclusions. Apatites from the Lac Line intrusion are strongly and evenly altered, which induced REE depletion and lead to underestimation of the fO_2 parameter.

2.8.4 Oxidation state and magma temperature

As discussed in the previous section, most apatites from the Lac Line and Opémisca intrusions and most zircons from the Saussure and Chevrillon intrusions are non-pristine. For this reason, the fO_2 parameter may be best

estimated by comparing results obtained from two minerals, i.e., apatite and zircon. In this section, non-pristine grains are no longer considered, and results obtained from pristine apatite and zircon are compared.

Zircon crystallization temperature estimated using the Ti-in-zircon method [61] returned median temperatures of crystallization of 650 to 720 °C for the pristine zircon (Figure 2.10). These are reasonable temperatures for the last stage of magma crystallization (Blundy et Cashman, 2001; Blundy et Cashman, 2008). Note that the alkaline intrusion (Saussure) contained only four least-altered zircons and temperature estimates are the least reliable for this intrusion.

The CHUR oxybarometer (Trail et al., 2011b) uses the La content of zircon and seems to be the least reliable method, as results cross many buffers and are uncorrelated with results obtained using other methods. The CHUR-method is strongly dependent on the quality of the La measurement and to La-increase induced by alteration and La-rich inclusions (Groulier et al., 2020; Turlin et al., 2019; Zeh et al., 2014), as is observed in the studied zircons. This method is likely unreliable in hydrothermally altered contexts.

While the Eu/Eu^* vs. Ce/Ce^* ratio method provides an estimation of the $f\text{O}_2$ parameter, results are comparable with the other methods. This method may be reliable, and its results will be compared to results obtained from the other zircon oxybarometer. Elevated oxygen fugacity corresponds to low

values of the $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratio in magma, leading to a low Eu negative anomaly in apatite and zircon. The Eu/Eu^* vs. Ce/Ce^* ratio points to oxidizing to moderately oxidizing conditions for most intrusions, except for the synvolcanic Anville intrusion that records reduced conditions.

According to the $\left[\frac{X_{\text{Ce}^{4+}}^{\text{melt}}}{X_{\text{Ce}^{3+}}^{\text{melt}}}\right]$ oxybarometer (Smythe et Brenan, 2016), zircon containing < 0.1 ppm La crystallised in reduced conditions (ΔFMQ of -1.4) for the Anville intrusion and moderately reduced conditions (ΔFMQ of -0.3 to -0.7) for the Lac Line and Chevrillon intrusions. Zircons from the Opémisca and Saussure intrusions return even more elevated values (ΔFMQ of 0.7), which correspond to moderately oxidizing conditions. These values are correlated with Eu/Eu^* vs. Ce/Ce^* ratio. The $\left[\frac{X_{\text{Ce}^{4+}}^{\text{melt}}}{X_{\text{Ce}^{3+}}^{\text{melt}}}\right]$ oxybarometer (Smythe et Brenan, 2016) is more accurate as it is independent of the REE, and especially La-content of zircon.

These methods also use factors that are additional sources of uncertainty. The $\left[\frac{X_{\text{Ce}^{4+}}^{\text{melt}}}{X_{\text{Ce}^{3+}}^{\text{melt}}}\right]$ oxybarometer (Smythe et Brenan, 2016) requires melt composition. As melt inclusions are lacking in the study area, whole rock analyses are used as rough approximation of magma composition. However, the studied rocks contain large euhedral plagioclase and amphibole that likely crystallized prior zircon and whole rock chemistry is unlikely representative of the composition of the residual melts in equilibrium with the studied zircons. In order to evaluate

the uncertainty associated with a poor estimate of residual melt composition, the Si- and K- and Ca-contents of the melt were arbitrarily increased prior recalculating the fO_2 parameter. These modifications have little effects on the fO_2 . For example, a decrease of the Si-content from 60 to 70 wt%, will cause a diminution of 0.05 of the fO_2 .

These methods also require insights into the H_2O content of the melt, the NBO/T parameter, and the temperature of the zircon-saturated melt. To test the sensitivities of the method to these parameters, the H_2O content of the melt was arbitrarily increased from 3 to 5 % and this induced a decrease of 1 log unit of the fO_2 parameter. In addition, a 0.1 increase of the NBO/T parameter induces a 0.3 log unit increase of the fO_2 parameter. Ideally, these parameters should be constrained using melt inclusions, which are lacking in the studied samples. Results of this study thus provide an approximation of the fO_2 parameter that is, to date, the best available estimation of this parameter for Neoproterozoic magmatism in the Chibougamau area.

In summary, depending of the quantity of pristine and non-pristine zircon, the $\left[\frac{X_{Ce^{4+}}^{melt}}{X_{Ce^{3+}}^{melt}} \right]$ oxybarometer seems to be the most reliable method to estimate the fO_2 parameter. If no pristine zircons are available, we recommend using the Eu/Eu* vs. Ce/Ce* ratio in apatite that provides a general estimation of the fO_2 parameter. Moreover, this study shows that synvolcanic magmas (Anville

intrusion) are more reduced than syntectonic magmas and that syntectonic magmas display similar oxidation states.

2.8.5 Consequences for IRGS Exploration

Among the studied intrusions, only the Lac Line stock is associated with a magmatic-hydrothermal system (IRGS possibly), i.e., Au-Ag-Cu \pm Mo mineralization (Côté-Mantha, 2009; Pilote, 1986). To evaluate potential Au deposit fertility, the geochemical characteristics (whole rock analyses, fO_2 , volatile content) of the mineralized Lac Line intrusion will be compared to the other studied intrusions. The synvolcanic Anville intrusion is not included in this comparison as IRGS only form in syntectonic settings.

To provide magmatic-derived fluids to a mineralizing system, an intrusion must likely be volatile-rich. Deuteric alteration, in the Saussure intrusion, is indicated by amphibole pseudomorphosed by chlorite. This points to significant fluid exsolution and circulation in this intrusion, which is essential for IRGS mineralization (Mair et al., 2011). In addition, the H₂O concentration of the Saussure, Chevrillon and Opémisca intrusions, as estimated using the empirical amphibole formulation (Mair et al., 2011; Ridolfi et al., 2009), is within the range of values for hydrated magmas. Magmas of the Chevrillon, Saussure, and Opémisca intrusions, with which apatite and zircon may have equilibrated, yield oxygen fugacity of ΔFMQ -0.7 to 0.7 and H₂O concentration of 5.4 to 5.5 wt.%, 3.7 to 4.5 wt.%, and 3.7 to 4.1 wt.%, respectively. Magmas associated

with porphyry mineralization display comparable water contents and fO_2 (Li et al., 2018), except for the Chevrillon intrusion, which display a lower fO_2 (Botcharnikov et al., 2013; Botcharnikov et al., 2011; Botcharnikov et al., 2010).

A magma also has to contain a significant amount of S and/or Cl to dissolve and retain Au, as there is a strong linear correlation between Au solubility and the amount of Cl and S dissolved in a magma (Botcharnikov et al., 2011; Botcharnikov et al., 2010). The studied intrusions are Cl-depleted according to apatite chemistry. However, the Lac Line and Saussure intrusions may contain significant amount of S. With 0.03 wt.% S dissolved in the melt, the maximum amount of Au that can be dissolved in a felsic melt is 1.2 ppm (Botcharnikov et al., 2010). In addition, S speciation has a strong impact on Au solubility. For felsic melts, maximum Au solubility is reached for fO_2 ranging from FMQ + 0.5 to FMQ + 1.5 (Botcharnikov et al., 2011). In the studied syntectonic intrusions, the fO_2 measured from zircon of the Saussure intrusion allows optimal Au solubility, meaning that, if Au was available, the magmatic system, may have accumulated Au.

2.8.6 Melts sources and oxygen fugacity

In this study, the intrusions are mostly generated from TTG and alkaline to subalkaline melts. The source of TTG is an enriched and hydrated mafic rock and partial melting occurred at high pressure, i.e., within the stability field of garnet (10–12 kbar) (Martin et al., 2014; Moyen, 2011). These mafic rocks are

likely hydrated on the sea floor and then retain part of their water during metamorphism.

The petrogenesis of syntectonic magmatism remains controversial (Moyen, 2019). Alkaline magmas likely come from low degree partial melting of an enriched ultramafic component, which generally corresponds to a metasomatized mantle (Morris et Pasteris, 1987). The sources of calc-alkaline and other magmas of the syntectonic period likely display a range of crustal and mantle components (Moyen, 2019). These magmas also evolve through several processes, such as fractional crystallization, assimilation or mixing, and differentiate to intermediate to felsic oxidized magmas such as HKCA and sanukitoid (Moyen, 2019). The relative importance of source composition and differentiation process in producing the chemical diversity observed in syntectonic intrusions remains debated (Laurent et al., 2014b). However, and regarding source composition, the elevated fO_2 measured in the studied alkaline and subalkaline syntectonic magmas gives additional support to Neoproterozoic metasomatized mantle as a possible source of at least part of syntectonic magmas.

2.9 CONCLUSIONS

The aim to this study was to estimate the under-measured geochemical parameters (fO_2 , volatile content) of syntectonic magmas. For this reason, the oxygen fugacity and volatile contents of the melt were measured using both

apatite and zircon chemistry to determine which method is more suited for the study of Archean magmas. This study reveals that:

- Apatite and zircon are useful to estimate the oxygen fugacity depending on the mineral quality, but further investigations are needed to efficiently measure the fO_2 parameter of a melt using apatite chemistry;
- There is an increase of the fO_2 parameter between the synvolcanic and syntectonic periods of the Abitibi Subprovince;
- The studied part of the Anville intrusion was emplaced during the same period as the Chrissie and Des Vents formations, which makes it the oldest subvolcanic complex of the Abitibi Subprovince. Moreover, geochronological analyses of the undated Saussure and Chevrillon intrusions, as well as their stratigraphic relationships with syntectonic sedimentary basins, confirms that they are both syntectonic intrusions;
- Magmas from the Saussure intrusion have the optimal fO_2 for Au transportation. Moreover, the magma from the Saussure and Lac Line intrusions may have contributed S-rich mineralizing fluids to magmatic-hydrothermal systems. As such, further investigations are needed to evaluate the Au-content of the melt and the size of the magmatic system, and to evaluate the economic potential of the studied intrusions.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Table S1: containing the microprobe and LA-ICP-MS analysis of amphibole, apatite and zircon. Table S2. containing the different

calculations used in this study. Table S3: containing the process used for the geochronology.

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FIGURES

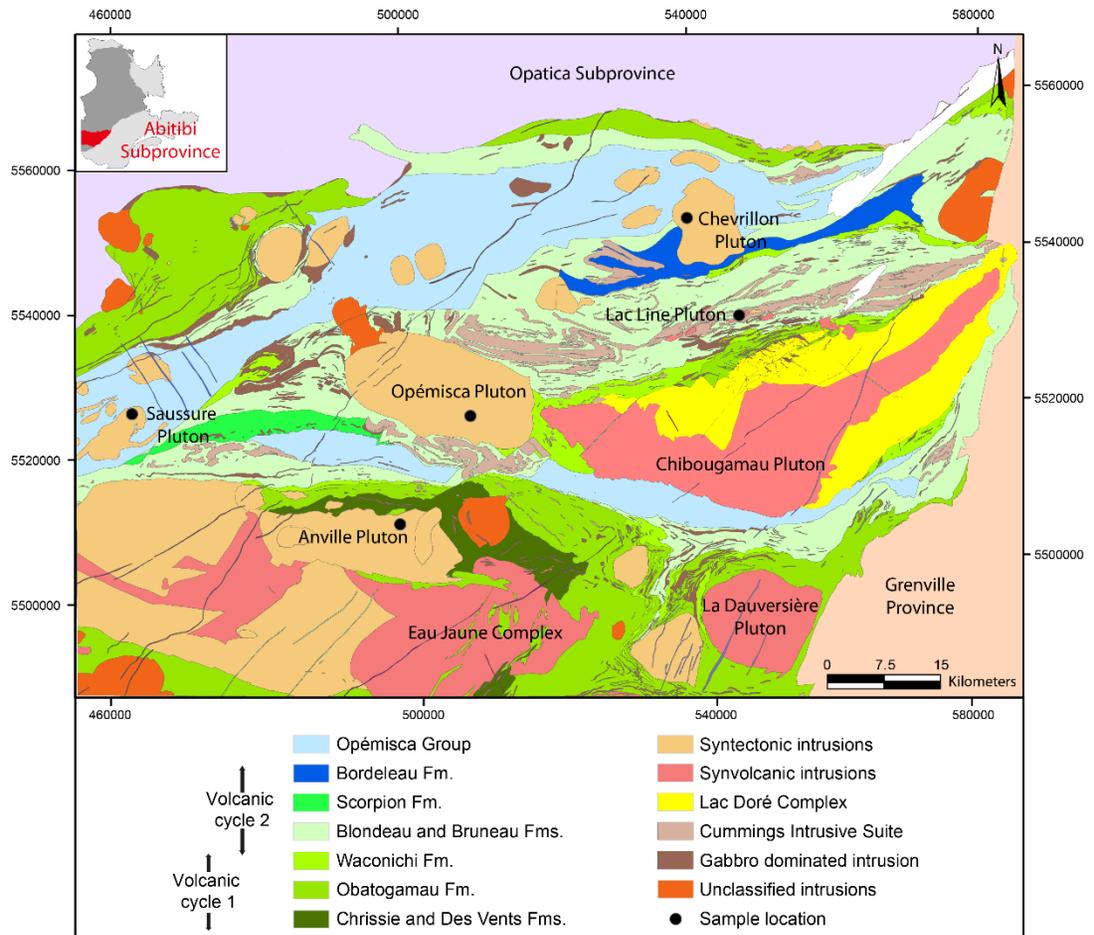


Figure 2.1. Geological map of the Chibougamau area showing the studied intrusions and the main volcanic and sedimentary sequences. The geological map is modified from the ministère de l'Énergie et des Ressources Naturelles (MERN), Québec (Québec et Ministère des ressources naturelles, 2018).

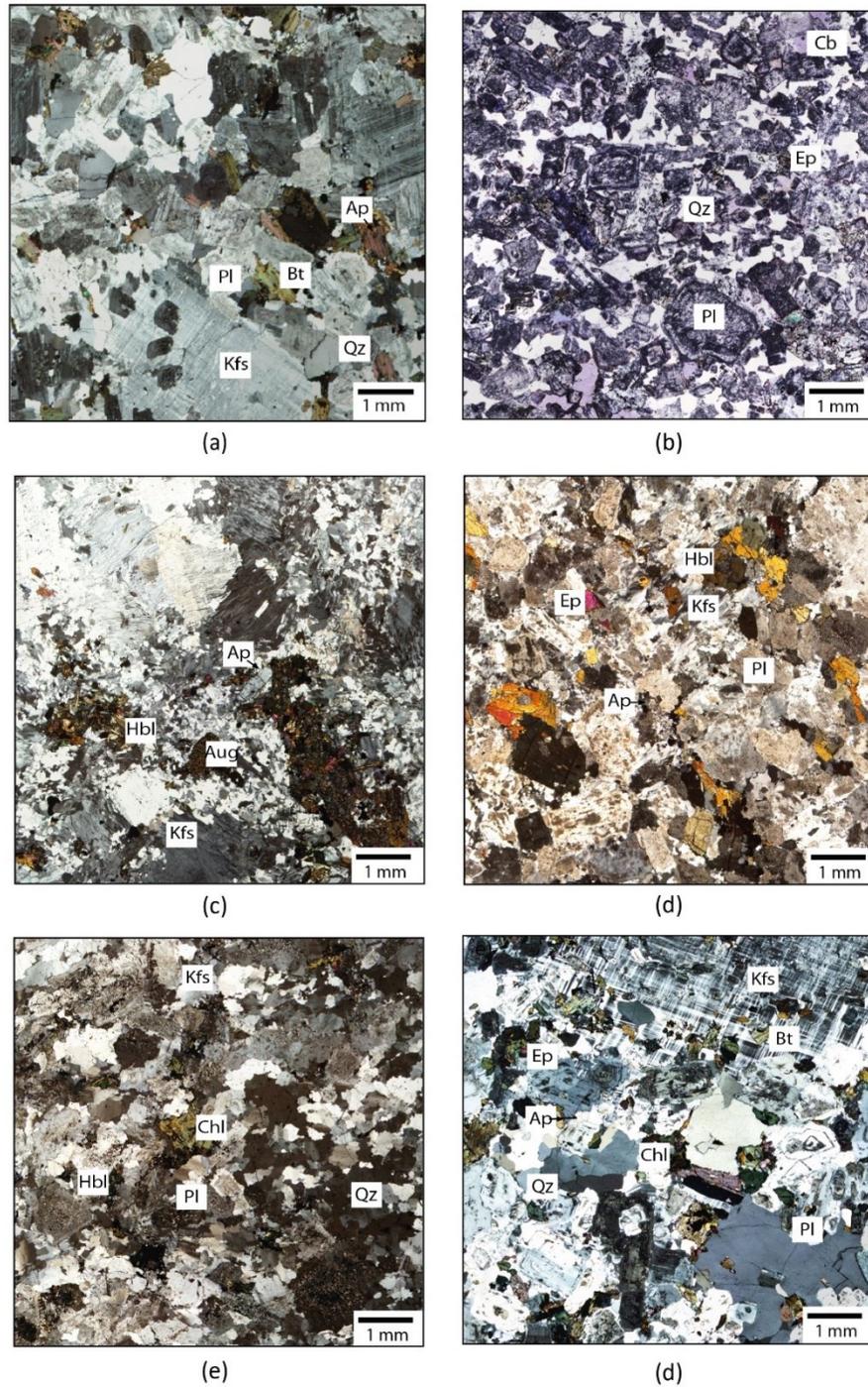
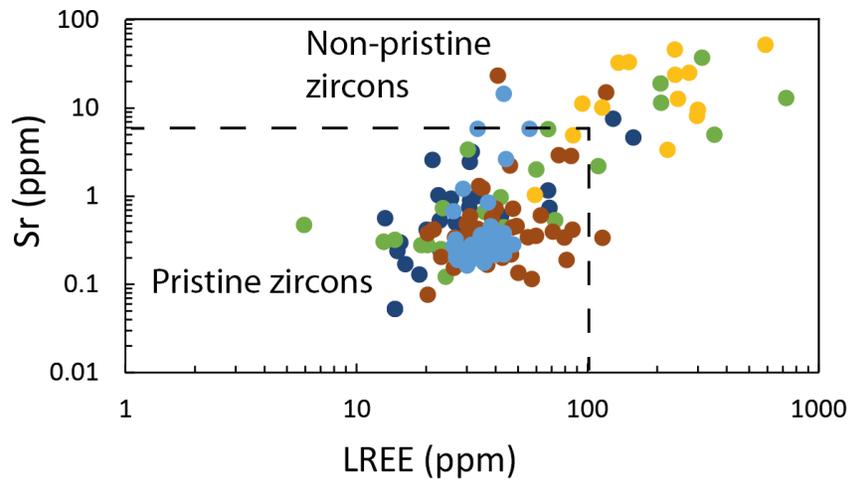
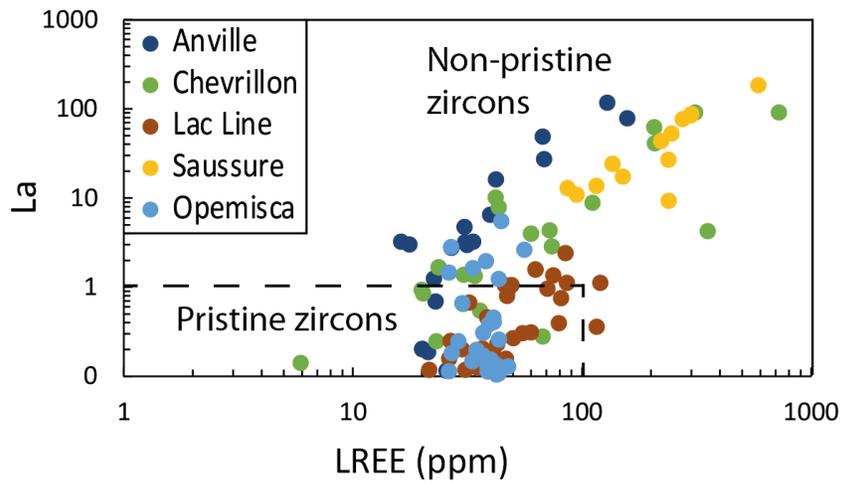


Figure 2.2. Photography of samples observed under polarized light and showing the main paragenesis of the (a–c) Saussure, (b) Lac Line, (d) Opémisca, (e) Chevillon, and (f) Anville intrusions. Abbreviations are from Whitney and Evans (Whitney et Evans, 2010).



(a)



(b)

Figure 2.3. Discrimination diagrams for magmatic (pristine) and non-pristine zircons (metamict zircons and/or zircons modified by secondary processes), showing the (a) Sr vs. light rare earth elements (LREE); and (b) La vs. LREE contents of zircon. Black dashed lines locate the pristine zircon and non-pristine zircon fields. La data are normalized to chondrite (McDonough et Sun, 1995).

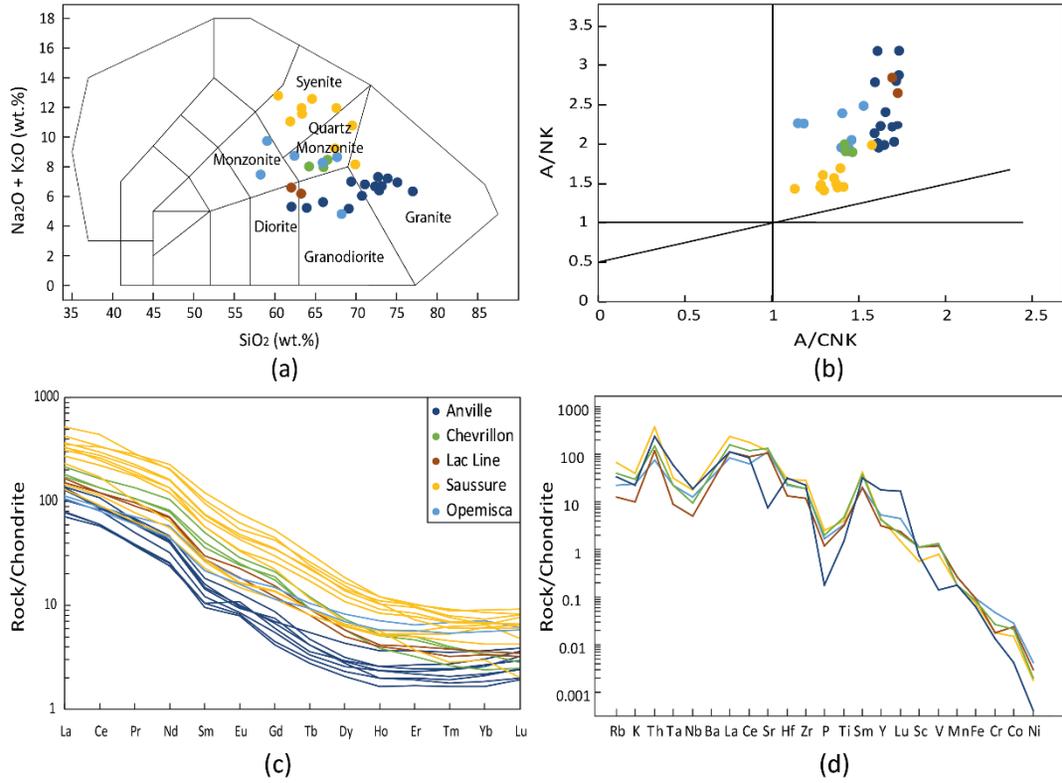


Figure 2.4. Whole rock ($n = 38$) analyses displayed on the (a) the total alkali silicate (TAS) diagram for intrusive rocks [77,78]; (b) A/NK vs. A/CNK diagram with A, N, K and C standing for Al, Na, K, and Ca, respectively [79], (c) chondrite normalized rare earth elements (REE) pattern (McDonough et Sun, 1995); and (d) multi-element diagrams for immobile elements displaying data acquired during this study.

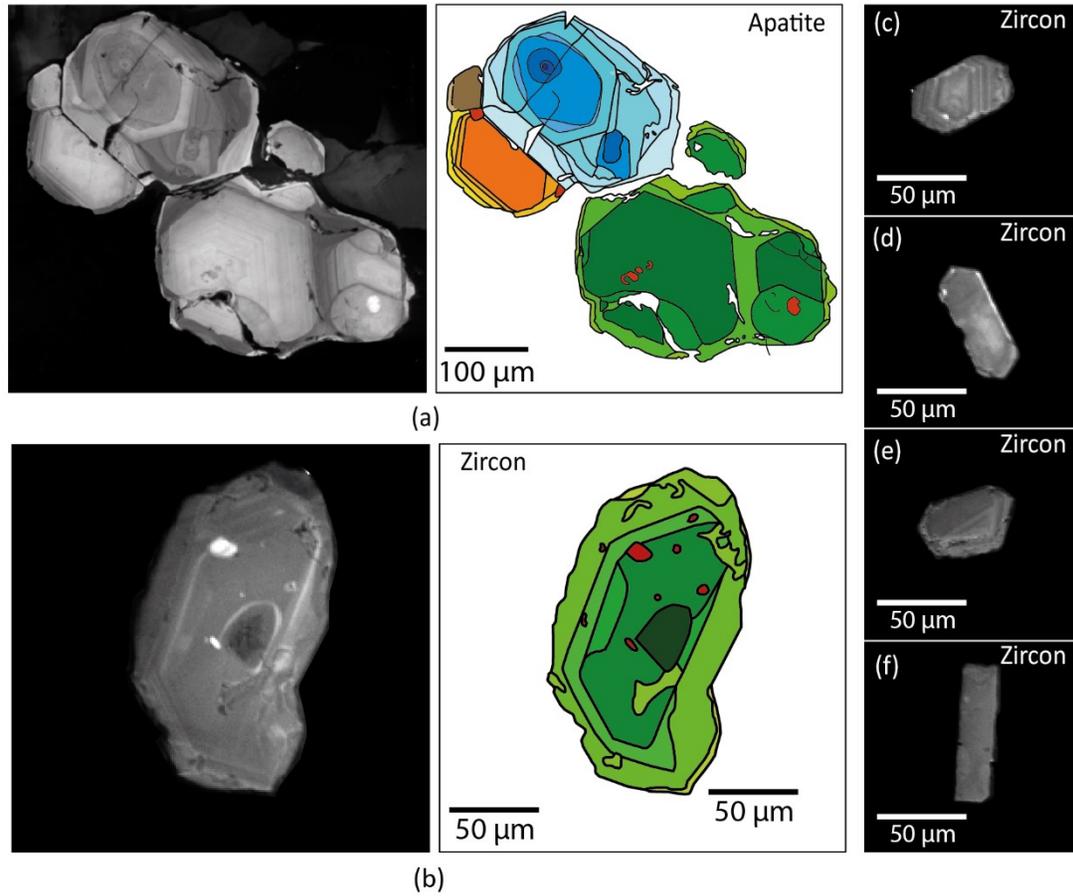


Figure 2.5. Cathodoluminescence imagery and drawing of zoned (a) apatite, and (b) zircon from the Anville, (c) Chevrillon, (d) Opémisca, (e) Saussure, and (f) Lac Line intrusions. Red color is used to highlight inclusions in apatite and zircon, distinct colors are used to distinguish grains, and shade of colors correspond to growth stages.

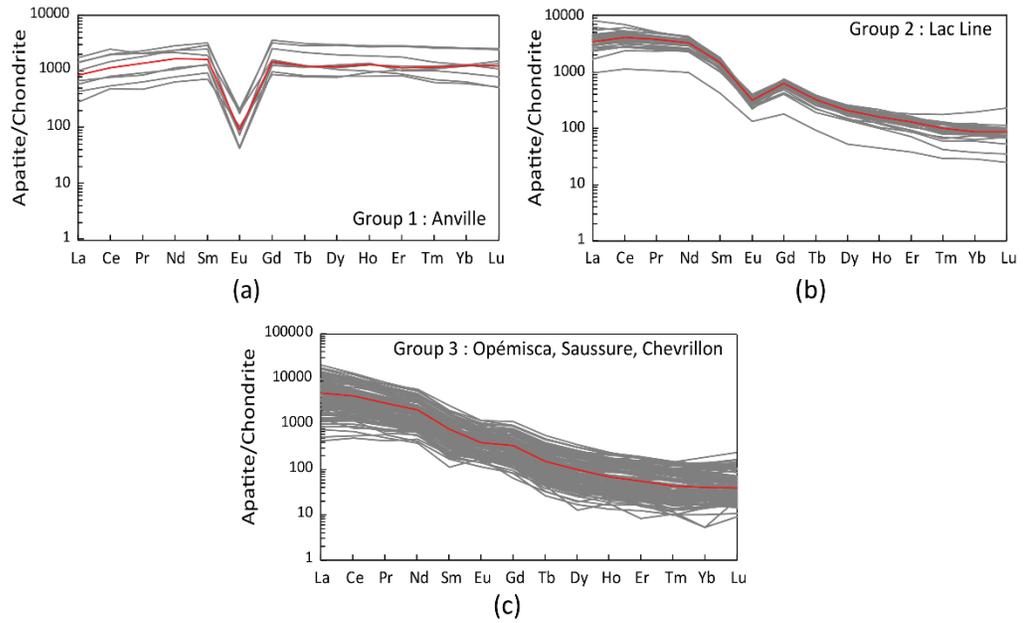


Figure 2.6. Chondrite-normalized REE pattern of apatites from the (a) Anville intrusion (Group 1); (b) Lac Line intrusion (Group 2); and (c) Opémisca, Saussure and Chevrillon intrusions (Group 3). Red lines correspond to mean values and data are normalized to chondrite (McDonough et Sun, 1995).

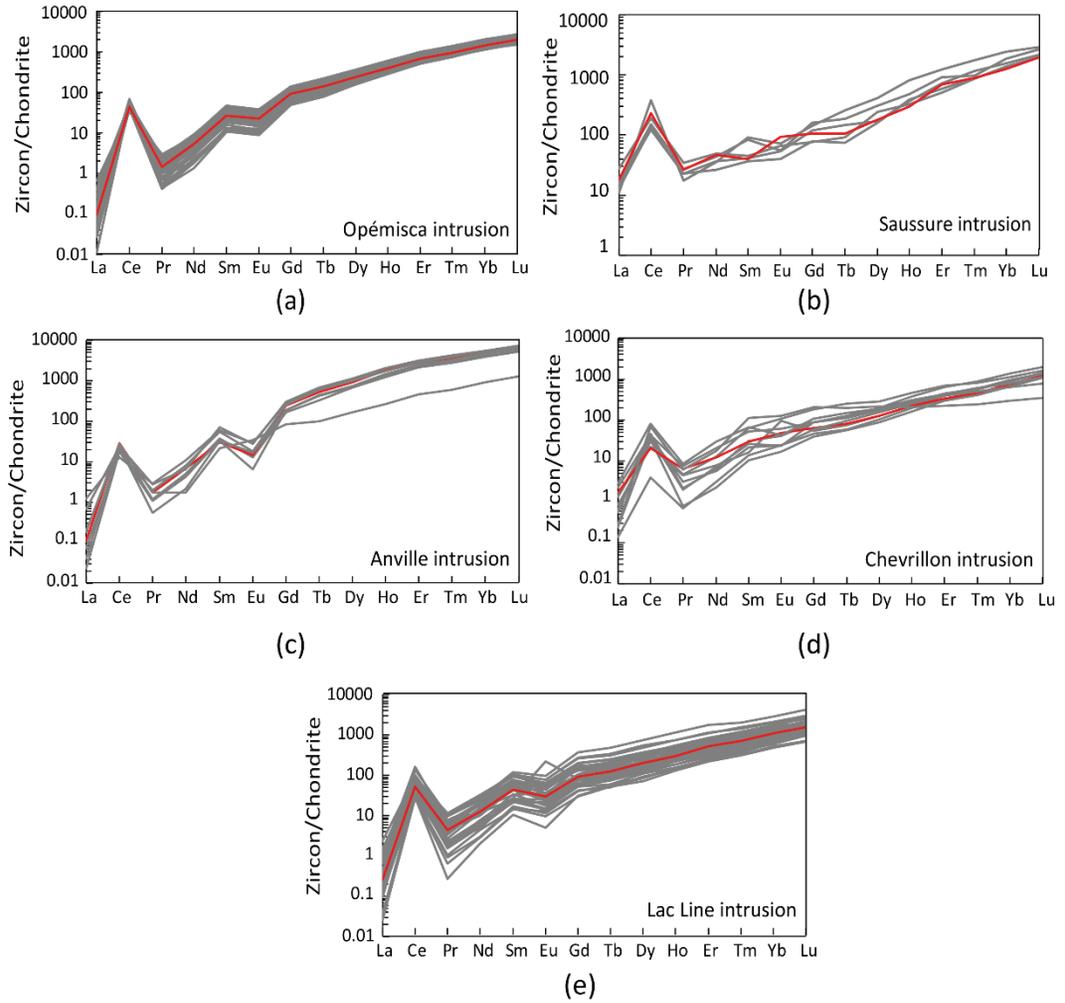


Figure 2.7. Chondrite- normalized REE pattern for the zircons of the (a) Opémisca, (b) Saussure, (c) Anville, (d) Chevrillon, and (e) Lac Line intrusions. Red lines correspond to mean values. Data are normalized to the chondrite (McDonough et Sun, 1995).

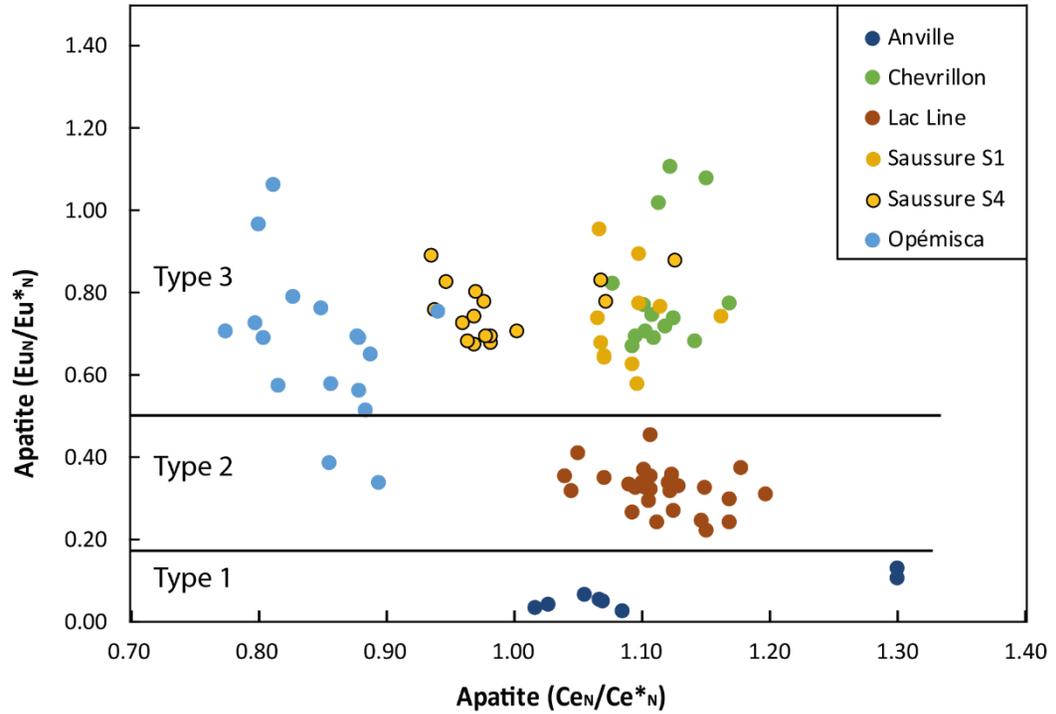


Figure 2.8. Diagram displaying the Eu anomalies (Eu/Eu^*) vs. Ce anomalies (Ce/Ce^*) of apatite ; with $\text{Eu}^* = 0.5 \cdot (\text{SmN} + \text{GdN})$, $\text{Ce}^* = 0.5 \cdot (\text{LaN} + \text{PrN})$. Limits between these three types are defined according to previous studies (Azadbakht et al., 2018; Cao et al., 2011). The S1 and S4 samples from the Saussure intrusion are from granite and syenite phases, respectively. Data are normalized to chondrite (McDonough et Sun, 1995).

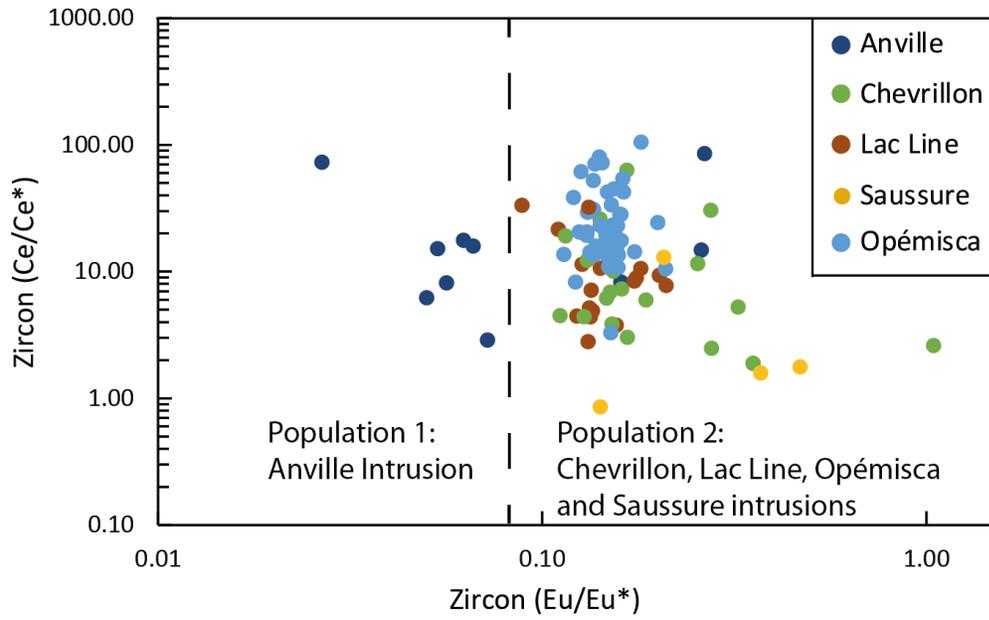
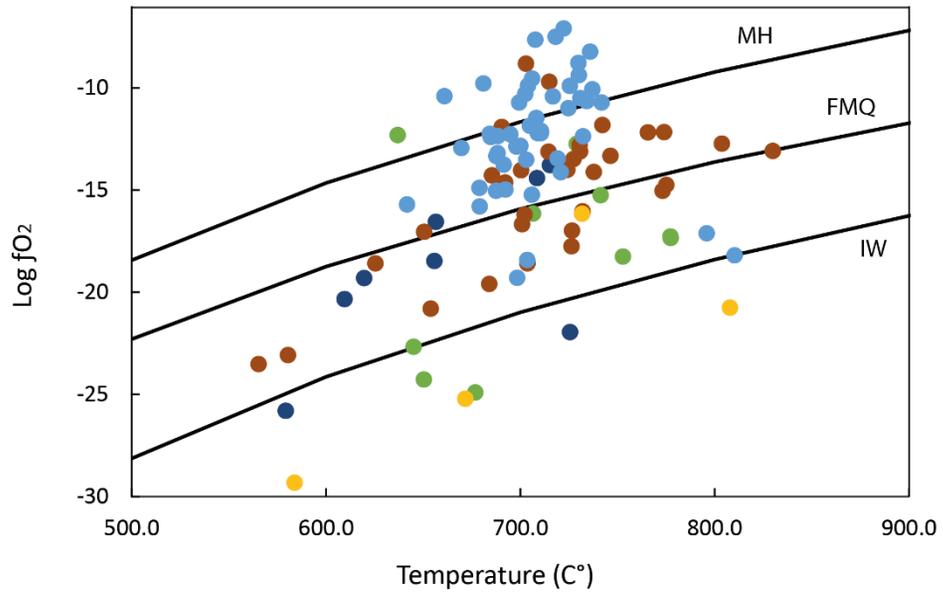
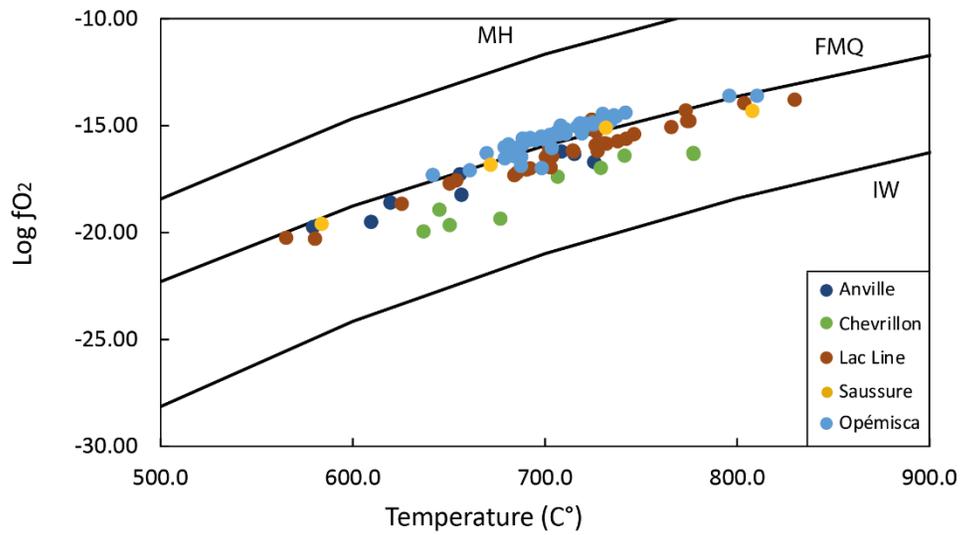


Figure 2.9. Diagram displaying the (Ce/Ce^*) vs. (Eu/Eu^*) in pristine zircon; with $Ce^* = (Nd)^2N/(Sm)N$; $Eu^* = 0.5^*(SmN + GdN)$. Data are normalized to chondrite (McDonough et Sun, 1995).



(a)



(b)

Figure 2.10. Diagram displaying the results of the (a) The $(\text{Ce}/(\text{Ce}^*))_{\text{CHUR}}$ oxybarometer [68,69] and (b) REE independent $[(X_{\text{Ce}^{4+}}^{\text{Melt}})/(X_{\text{Ce}^{3+}}^{\text{Melt}})]$ oxybarometer (Smythe et Brenan, 2016) for pristine zircons.

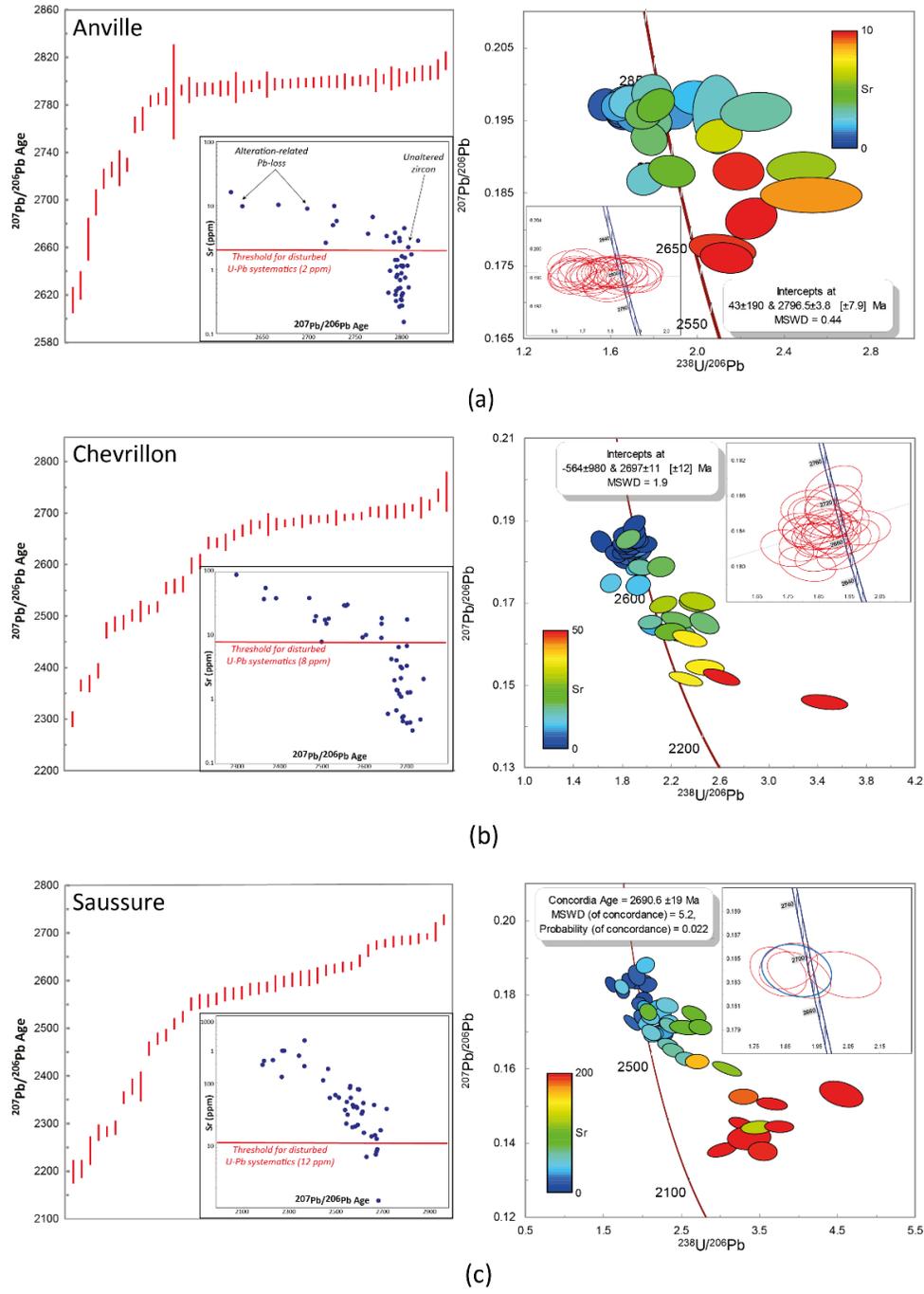


Figure 2.11. Zircon U-Pb age spectra (left) and concordia diagrams (right) for the (a) Anville, (b) Chevrillon and (c) Saussure intrusions. Age spectra inset shows relationship between individual $^{207}\text{Pb}/^{206}\text{Pb}$ dates and Sr concentration. Threshold value for data filtering defined by departure from vertical array. Ellipses in Concordia diagrams are colored for Sr concentration (ppm). Inset shows data conforming to filter criteria for each sample, from which sample crystallization ages are calculated.

TABLES

Table 1. Localization and lithology of the studied intrusions

Intrusions	UTME	UTMN	Zone	Sample	Whole-Rock Geochemistry	Apatite and Zircon Compositions	Dating U-Pb Geochronology
Saussure	467051	5526000	18	Granite	Figure 2	Figs. 5, 7 - Tables 2, 3	Figure 11
Saussure	466402	5526084	18	Quartz-rich syenite	Figure 2	Figs. 5, 7 - Tables 2, 3	Figure 11
Saussure	463895	5526093	18	Pegmatitic syenite	Figure 2	Figs. 5, 7 - Tables 2, 3	Figure 11
Chevillon	540371	5547339	18	Quartz-rich monzodiorite	Figure 2	Figs. 5, 7 - Tables 2, 3	Figure 11
Lac Line	548644	5533262	18	Tonalite	Figure 2	Figs. 5, 7 - Tables 2, 3	
Opémisca	511694	5520891	18	Qz-rich monzonite	Figure 2	Figs. 5, 7 - Tables 2, 3	
Anville	497685	5509637	18	Granodiorite	Figure 2	Figs. 5, 7 - Tables 2, 3	Figure 11

Table 2. Modal composition of the studied samples. Abbreviations are from Whitney and Evans (Whitney et Evans, 2010).

Intrusion	Lithology	Mineralogy	Accessory Minerals
Saussure	Qz-rich syenite	40% Kfs, 30% Pl, 10–12% Qz, 18% Bt-Hbl	Ttn, Zrn, Ap, Iox
Opémisca	Qz-rich monzonite	50–60% Pl, 15–20% Kfs, 10–15% Qz, 5–10% Hbl	Ep, Ttn, Mag, Ap, Zrn
Lac Line	Tonalite	>50% Pl, 30–35% Qz, 10–12% Cb, 5–7% Bt-Chl	Zrn, Ap,
Chevillon	Qz-rich monzodiorite	50–55% Pl, 10–20% Kfs, 10–20% Qz, 5–8% Bt-Hbl	Ep, Ttn, Mag, Ap, Zrn
Anville	Granodiorite	40–45% Qz, 30–40% Pl, 10–15% Kfs, < 5% Bt-Chl	Zrn, Ap, Ep, Ilm, Alu

Table 3. Whole-rock chemistry of the sampled intrusions

Intrusions	Saussure		Opémisca	Lac Line	Chevrillon	Anville
Elements	S101	S401	U139	LL01	CHV01	U140
SiO ₂ (wt %)	67.40	63.3	62.50	63.10	64.20	77.00
Al ₂ O ₃	15.55	17.3	17.10	17.60	16.00	12.30
FeO	1.38	1.26	1.47	1.64	1.50	1.45
Fe ₂ O ₃	1.66	1.84	2.29	2.15	1.94	1.12
CaO	1.96	1.82	3.44	4.28	3.21	1.30
MgO	1.24	0.86	2.37	2.19	1.78	0.22
Na ₂ O	5.04	5.91	6.32	5.17	5.03	4.03
K ₂ O	4.15	5.76	2.44	1.03	2.99	2.29
TiO ₂	0.40	0.35	0.34	0.32	0.48	0.15
MnO	0.04	0.05	0.06	0.06	0.04	0.04
P ₂ O ₅	0.29	0.21	0.19	0.14	0.23	0.02
BaO	0.20	0.150	0.10	0.06	0.18	0.05
LOI	0.31	0.21	0.56	1.92	0.60	0.44
TOTAL	99.62	99.02	99.18	99.79	98.18	100.41
C (ppm)	0.01	0.01	0.01	0.03	0.00	0.01
Ce	152.00	170.5	54.80	75.00	101.00	72.70
Cr	40.00	20	110.00	40.00	60.00	30.00
Cs	4.14	0.46	0.35	0.50	2.46	0.38
Dy	1.72	3.37	2.02	1.23	1.81	5.61
Er	0.60	1.54	1.03	0.59	0.80	3.78
Eu	1.88	2.59	1.02	1.04	1.63	0.91
Ga	22.10	20.9	20.10	20.90	24.10	16.20
Gd	4.45	6.88	2.97	2.41	4.21	5.58
Hf	5.80	5.7	4.20	2.50	4.60	5.90
Ho	0.31	0.56	0.39	0.22	0.29	1.18
La	79.80	77.8	26.90	36.00	51.00	36.80
Lu	0.05	0.12	0.15	0.08	0.07	0.58
Nb	9.90	15.2	6.90	2.80	5.40	10.30
Nd	62.20	73.7	26.50	31.90	47.60	28.80
Pr	17.00	19.95	6.63	8.36	12.50	7.83
Rb	124.00	110	42.90	24.20	75.30	61.70
Sm	8.48	10.95	4.07	4.08	7.47	6.25
Sn	1.00	1	1.00	1.00	2.00	3.00
Sr	1240.00	1285	1165.00	1140.00	1410.00	79.20
Ta	0.70	0.9	0.50	0.20	0.50	1.30
Tb	0.42	0.84	0.38	0.29	0.44	0.88
Th	14.70	4.62	3.03	4.71	6.12	9.58
Tm	0.07	0.19	0.17	0.08	0.10	0.57
U	1.72	0.96	0.55	0.67	1.06	1.82
V	38.00	47	60.00	59.00	67.00	7.00
Y	8.70	16.2	10.60	6.40	8.40	35.90
Yb	0.48	1.06	1.14	0.54	0.55	3.95
Zr	247.00	299	173.00	108.00	170.00	200.00

Table 4. Trace elements and REE composition of apatite from the studied intrusions.

Intrusions Elements	Anville			Chevrillon			Lac Line			Opémisca			Saussure		
	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max
Li	ND	25.8	152.4	ND	3.6	20.1	ND	4.2	18.9	ND	3.2	21.3	1.0	5.0	16.6
Na	414.2	876.8	1766.6	222.7	2432.9	29952.8	287.4	783.4	1816.4	194.7	816.8	2050.3	389.2	5195.3	117998.2
Mg	14.2	3617.9	26431.3	13.0	1053.0	8621.2	10.2	939.8	11077.4	13.7	871.0	13092.0	4.2	890.1	20498.0
Al	1006.1	17594.6	108042.4	32.4	3358.0	40388.3	222.0	1746.5	11838.2	36.8	973.2	8241.2	60.6	4860.8	133241.2
Si	2500.4	25923.9	117541.2	ND	8389.0	106053.2	ND	3241.3	38686.5	ND	2815.7	19774.3	781.4	19362.5	383624.1
S	ND	263.6	1038.6	ND	464.9	916.6	298.6	1371.4	2384.7	133.7	540.2	959.2	361.6	974.1	1645.5
Cl	ND	232.7	592.3	ND	180.4	1013.2	124.0	687.4	1064.2	ND	112.1	362.5	31.6	115.7	411.6
K	3.1	129.4	369.2	ND	151.7	990.5	ND	38.8	254.5	0.5	255.6	2429.0	ND	72.4	994.1
Ti	ND	1351.4	10356.4	ND	333.7	6667.4	1.3	27.7	535.6	0.2	164.2	3149.2	0.1	22.8	554.1
V	0.2	12.6	58.6	3.1	14.8	90.2	5.0	17.9	44.6	4.9	38.2	483.0	5.3	27.7	264.3
Mn	336.0	1173.6	6223.5	158.1	308.6	711.7	303.3	553.5	777.0	213.3	327.7	741.0	124.2	317.7	2723.0
Fe	108.8	9119.4	63402.0	56.2	1217.8	10177.3	855.7	1590.5	7864.7	43.0	4714.6	95786.4	49.8	624.3	14325.2
Rb	ND	2.6	28.9	ND	1.4	16.2	ND	0.1	2.6	ND	0.7	9.3	ND	2.1	17.9
Sr	55.2	73.5	118.9	887.7	1116.3	1779.2	338.2	398.4	506.9	830.9	905.5	986.0	723.9	1857.6	9637.5
Y	1382.8	2729.3	5129.2	44.1	97.4	156.0	81.3	250.4	340.4	72.8	199.7	334.1	45.5	189.6	494.1
Zr	0.2	158.1	1224.9	0.2	1.7	7.1	0.1	0.9	5.2	0.2	2.0	23.7	0.3	24.4	1203.2
Sn	ND	12.8	51.0	ND	0.4	3.0	0.0	1.0	5.7	0.0	3.6	40.7	0.0	10.0	131.9
La	66.0	226.5	413.6	100.3	367.2	819.4	244.7	880.5	1943.1	517.4	1374.7	2396.7	215.5	1773.9	5257.8
Ce	299.7	810.0	1515.9	288.3	999.4	1981.0	737.2	2529.5	4296.5	750.1	1997.5	3181.5	509.4	3486.8	9158.8
Pr	44.0	130.6	214.7	39.7	118.1	236.0	106.0	342.1	490.0	58.5	178.6	261.6	56.1	341.9	866.4
Nd	293.6	772.4	1317.8	187.6	504.4	972.9	482.7	1495.0	1994.0	271.8	678.8	1070.4	211.9	1228.4	3090.0
Sm	106.5	275.2	477.0	27.1	73.9	137.5	67.8	218.4	281.3	28.8	90.5	160.5	20.8	151.1	446.2
Eu	2.3	6.4	11.8	8.2	16.9	28.0	8.5	19.0	24.8	8.1	17.9	32.4	9.9	32.1	80.8
Gd	172.6	387.5	722.9	18.5	49.1	91.9	40.3	130.0	161.8	27.0	66.9	124.1	16.3	94.6	270.8
Tb	29.1	60.9	114.0	1.6	4.2	8.2	3.8	12.4	15.5	2.5	6.8	12.1	1.5	8.4	24.4
Dy	192.9	399.8	736.1	6.1	18.3	31.0	15.1	55.4	70.6	10.6	35.4	61.7	6.6	37.5	107.6
Ho	45.1	88.4	156.5	1.2	3.2	5.0	2.9	9.7	13.2	2.7	6.9	11.6	1.2	6.1	16.3
Er	133.2	250.9	461.3	2.8	7.6	11.1	7.2	22.4	32.4	7.6	19.0	30.3	3.5	14.3	38.0
Tm	15.7	35.8	68.1	0.4	0.9	1.6	0.9	2.7	4.9	0.8	2.5	3.6	0.4	1.7	4.6
Yb	96.9	225.6	424.5	2.0	5.9	8.3	5.5	16.5	35.2	3.9	17.0	29.7	2.9	9.7	26.0
Lu	12.7	33.2	63.0	0.5	1.0	1.4	0.7	2.4	6.4	1.1	2.9	5.9	0.5	1.4	3.3

CHAPITRE 3

CONCLUSION

Le présent mémoire porte sur la quantification de la fO_2 des intrusions syntectoniques du coin nord-est de la Sous-province d'Abitibi. La fO_2 a été documentée au sein d'intrusions fraîches à peu altérées afin d'éviter que des processus secondaires ne viennent affecter la chimie des roches et des minéraux accessoires comme le zircon et l'apatite.

Les objectifs de cette étude étaient (1) de caractériser la chimie et la minéralogie des intrusions syntectoniques étudiées et de déterminer la nature des magmas à l'origine de ces intrusions, (2) de dater les intrusions de Saussure, Anville et Chevrillon afin de déterminer ou de préciser leurs âges de mise en place, (3) d'estimer les paramètres physico-chimiques (contenu en éléments volatils, température de mise en place) des magmas étudiés, (4) de déterminer si la fO_2 des magmas archéens peut être estimée à partir de la chimie de l'apatite et/ou du zircon, (5) de quantifier cette fO_2 en utilisant la chimie du zircon et de l'apatite, et (6) d'évaluer le potentiel minéralisateur des intrusions étudiées.

Le premier objectif de cette étude est traité au sein des sections *Whole Rock Chemistry* et *Petrography* de la partie *Results* ainsi que dans la section *Magma type* de la partie *Discussion* du Chapitre 2. Cet objectif a été atteint

grâce à l'étude des lames minces, des images de type BSE et CL des concentrés de minéraux lourds, ainsi qu'à partir de l'analyse de la chimie des éléments majeurs et traces.

Le second objectif est traité au sein des sections *Geochronology results* des parties *Results* et *Zircon U-Pb geochronology* de la partie *Discussion*. Cet objectif a été atteint en mesurant, par LA-ICP-MS, le contenu en éléments traces du zircon et grâce à l'imagerie BSE et CL des différentes populations de zircons présentent dans chaque intrusion.

Le troisième objectif est traité au sein des sections *Volatile content of the melt* de la partie *Results* et des sections *Oxidation state and magma temperature* et *consequences for IRGS exploration* de la partie *Discussion* du Chapitre 2. Cet objectif a été atteint en analysant le contenu en éléments traces, obtenu au LA-ICP-MS et à la microsonde, des amphiboles, des apatites et des zircons.

Les objectifs 4 et 5 font références à la fO_2 et ont été traités au sein des sections *Oxidation state* de la partie *Results* et des sections *Impact of alteration on mineral chemistry and fO_2 estimates* et *Oxidation state and magma temperature* de la partie *Discussion* du Chapitre 2. Ces objectifs ont été atteint grâce à l'utilisation des imageries optiques, BSE et CL, ainsi qu'à partir de la chimie (éléments majeurs et traces) des apatites et des zircons.

Le dernier objectif, qui porte sur l'évaluation du potentiel minéralisateur des intrusions étudiées, a été traité au sein de la section *Consequences for IRGS exploration* dans la partie *Discussion* du Chapitre 2. Il a été atteint grâce à l'interprétation de l'ensemble des données acquises pour répondre aux objectifs listés précédemment et n'a pas nécessité l'acquisition de données supplémentaires.

Les principaux résultats de cette étude permettent d'apporter une réponse aux objectifs listés dans le Chapitre 1 et sont énumérés ci-dessous.

- En plus du caractère alcalin à subalcalin des intrusions, l'étude des éléments majeurs et traces a démontré que les intrusions étudiées correspondent à des magmas différenciés. Les intrusions d'Anville et du Lac Line appartiennent à la suite des TTG. Le contenu élevé en Na_2O , l'absence de feldspath potassique et l'important fractionnement des terres rares (enrichissement important des terres légères par rapport aux terres rares lourdes) indiquent que l'intrusion du Lac Line correspond au groupe des suites TTG de haute pression. L'intrusion d'Anville présente à la fois des caractéristiques similaires à celles des suites TTG et des granites à biotite (p.ex., contenu élevé en K et en HFSE), ce qui signifie qu'elle correspond à une suite TTG enrichie en K, ce qui est caractéristique des suites TTG de la période syntectonique. Dans le cas de l'intrusion d'Opémisca, sa texture macroscopique, son caractère faiblement peralumineux ainsi que son

contenu élevé en Na_2O et en certains éléments traces (Sr, La) semblent indiquer qu'il s'agit d'une sanukitoïde saussuritisée. L'intrusion de Chevrillon correspond majoritairement à un granite de type HKCA avec quelques caractéristiques qui la rapproche des sanukitoïdes. En effet, cette intrusion contient une grande quantité de phénocristaux de feldspath potassique, et a un contenu élevé en K, en Sr et en terres rares légères. Enfin, l'intrusion de Saussure est une syénite quartzifère, c.-à-d., une intrusion possédant un contenu élevé en éléments alcalins ($\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{CaO} = 9 \text{ wt.}\%$) et en éléments incompatibles.

- Les datations des différentes populations de zircons provenant des intrusions Anville, Chevrillon et Saussure ont révélé des âges U-Pb de $2796,5 \pm 3,8 \text{ Ma}$, $2697 \pm 11 \text{ Ma}$ et $2688 \pm 8 \text{ Ma}$, respectivement. Malgré la plus grande proportion de zircons non-frais au sein des intrusions de Chevrillon et de Saussure, les âges obtenus sont en accord avec les relations stratigraphiques observées, c.-à-d., la relation de recoupement entre ces intrusions et la Formation de Chebistuan pour l'intrusion de Chevrillon et la Formation de Daubrée pour l'intrusion de Saussure. De plus, les âges obtenus pour l'intrusion de Chevrillon sont similaires aux datations TIMS effectuées récemment, et qui indiquent un âge non-publié de $2693,1 \pm 1,7 \text{ Ma}$ (Huguet, 2019). L'âge obtenu pour l'intrusion d'Anville est similaire à ceux des formations de Chrissie et Des Vents, qui se sont formées au

début de la période synvolcanique. Cependant, les âges de $2796,5 \pm 3,8$ Ma obtenus pour l'intrusion d'Anville sont plus anciens que les datations obtenues précédemment ($2714,8 \pm 0,6$ Ma), ce qui signifie que ce pluton est probablement un assemblage de corps intrusifs d'âges synvolcaniques et syntectoniques. Les phases syntectoniques du pluton d'Anville se sont principalement mises en place dans la partie sud du pluton, qui est fortement déformée. L'âge du complexe intrusif d'Anville pourrait faire l'objet d'études plus poussées.

- Les analyses effectuées à la microsonde sur les amphiboles des intrusions de Saussure, de Chevrillon et d'Opémisca et les analyses LA-ICP-MS effectuées sur les apatites ont permis d'estimer le contenu en H₂O, Cl et S des magmas à l'origine de la mise en place des intrusions étudiées. Les magmas à l'équilibre avec les amphiboles ont des teneurs en H₂O comprises entre 3,7 et 4,5% pour Saussure et Opémisca et entre 5,4 et 5,5% pour Chevrillon. Le contenu en soufre du magma à l'équilibre avec les apatites analysées varie entre 10 et 30 ppm pour les intrusions d'Anville, de Chevrillon et d'Opémisca, et entre 20 et 100 ppm pour les intrusions de Saussure et du Lac Line. Des valeurs anormales allant jusqu'à 300 ppm ont été documentées au sein de ces deux intrusions. Le contenu en Cl de ces magmas est bas et varie entre 0,01% et 0,09% pour la plupart des apatites à l'exception de trois grains d'apatite provenant des intrusions de Saussure et du Lac Line et qui renvoient à des valeurs allant jusqu'à

0,1% Cl dans le magma. Les concentrations plus élevées en S ainsi que la fO_2 comprise entre + 0,5 et + 1,5 ΔQFM pour les magmas associés aux intrusions de Saussure et du Lac Line correspondent à des conditions idéales pour le transport de l'or par ces magmas. De ce fait, si de l'or était présent dans les roches sources (ce qui reste à déterminer), ces systèmes magmatiques auraient pu le transporter et ils auraient pu exsoler des fluides aurifères.

- L'emploi de différentes méthodes de quantification et d'estimation de la fO_2 des magmas archéens a permis de mettre en avant l'utilité du zircon et de l'apatite provenant des roches anciennes. En effet, la relative résistance de ces minéraux face à des événements secondaires comme l'altération et le métamorphisme local et régional en font des outils importants pour l'étude des systèmes magmatiques anciens. Cette étude a aussi permis de mettre en avant une relative augmentation de la fO_2 entre les périodes synvolcanique et syntectonique. En effet, l'intrusion d'Anville, qui est d'âge synvolcanique, est modérément réduite (-1,4 ΔQFM) alors que les intrusions du Lac Line et de Chevrillon présentent des fO_2 plus élevées, comprises entre -0,7 et -0,3 ΔQFM . Les intrusions de Saussure et d'Opémisca sont modérément oxydées (+0,7 ΔQFM), montrant que le paramètre fO_2 est variable dans les systèmes magmatiques de la période syntectonique.

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ANNEXES

ANNEXE 1 : PROCEDURE ANALYTIQUE DE DATATION DES ZIRCONS

Zircon U-Th-Pb isotope and trace element (TE) analyses were conducted at the Mineral Exploration Research Centre isotope Geochemistry Lab (MERC-IGL), at Laurentian University. Laser ablation sampling was performed using a Photon Machines Analyte G2 ArF excimer laser, with 193 nm wavelength, <5 ns pulse width, and HelEx II cell. Ablation durations were 30 seconds, with laser fluence of 2 J/cm² and 7 Hz repetition rate, leaving estimated ablation pit depths of <15 μm. Sixty seconds of background were measured at the beginning and end of the analytical session, with 30 seconds of background measured between each ablation. Helium carrier gas flows through the ablation cell was 0.95 l/min (cup) and 0.1 l/min (cell), with 1.1 l/min Ar and 9.5 ml/min N₂ makeup gas added downstream of the cell. The ablated aerosol was split downstream of the sample cell, so that U-Th-Pb and TE measurements could be conducted simultaneously (LASS; e.g. Kylander-Clark et al., 2013).

U-Th-Pb isotope measurements were conducted using a Thermo Scientific Neptune Plus multicollector (MC) ICP-MS, equipped with Jet interface and nine Faraday cups. All MC-ICP-MS analyses were conducted in low resolution, static mode to ensure maximum sensitivity and stability. All cups were coupled with 1011 Ω amplifiers, with the exception of L2, which was coupled with 1012 Ω amplifier for better precision on the low intensity ²⁰⁷Pb signal. Ion beam drift is typically <0.05 amu, with flat top peak width typically

~0.2 amu, ensuring stable on-peak measurements throughout long-duration analytical sessions. Cool gas and Ar auxiliary gas flows were set at 16 L/min and 0.85 L/min, respectively, and RF power was set to 1200 W. TE measurements were conducted using a Thermo Scientific iCap-TQ ICP-MS in single quad mode to ensure maximum sensitivity on the low to intermediate mass range. The masses measured and associated dwell times are shown in Table X. Cool gas, auxiliary gas, and RF power were set at 14 L/min, 0.8 L/min, and 1550 W, respectively.

The raw U-Th-Pb and TE data were synchronized in Lolite, along with the laser log file, prior to processing, so that the same timeslices (selections) for each analysis were used in the calculations. Baseline subtraction, instrumental drift, and downhole fractionation corrections were performed with the Vizual Age data reduction scheme (DRS) implemented within Lolite v3.6 (Petrus & Kamber, 2012), with U-Th-Pb isotope ratios normalized to the zircon reference material (RM) OGC (OG1; 3465 ± 1 Ma; Stern et al., 2009). OGC was analyzed three times at the beginning and end of the session, and once every ten unknowns throughout the session. Typically, 3 seconds at the beginning and 1 second at end of the ablation period were excluded from the selections in order to minimize potential fractionation effects, leaving ~26 seconds of signal for integration. Within run variance in the measured ratios for OGC (i.e. the additional percent error required to achieve MSWD = 1) was propagated into the 2SE uncertainty for all unknowns. Two verification RMs were analyzed during the session to ensure accuracy of the U-Pb ratios, with measured dates

shown in Table X. Trace element data were processed using the Internal Standard DRS within Lolite v3.6, and normalized to the synthetic glass NIST610 RM. An assumed stoichiometric concentration of 15.284 wt% Si was used for all zircon, to account for differing ablation characteristics between the glass and zircon. The synthetic glass NIST612 was used to verify the accuracy of TE analysis (Table X).

MATERIELS SUPPLEMENTAIRES

Le fichier Excel « ***Supplementary-material-S1*** » joint contient les résultats des analyses à la microsonde électronique et au LA-ICP-MS réalisées sur les apatites, les zircons et les amphiboles.

Le fichier Excel « ***Supplementary-material-S2*** » joint contient l'ensemble des calculs qui ont servi à estimer la température du magma, la fugacité de l'oxygène et les paramètres physico-chimiques estimés avec la chimie des amphiboles.

Le fichier Excel « ***Supplementary-material-S3*** » joint contient les paramètres analytiques et les résultats des analyses des zircons qui ont servi aux datations des intrusions.

Le fichier Pdf « ***Poster_Gac_Mac*** » joint contient un poster présenté durant le congrès du Gac Mac en 2019.