The application of gas chromatography in characterizing bulk fluid inclusion hydrocarbons in the footwall of the Sudbury Igneous Complex and other magmatic, hydrothermal and surficial ore-forming environments

By
Mitchell James Kerr

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Approved: Dr. Jacob Hanley
Supervisor
Department of Geology
Saint Mary's University

Approved: Dr. Doreen Ames
Supervisory Committee
Geological Survey of Canada

Approved: Dr. Jason Clyburne
Supervisory Committee
Department of Chemistry – Environmental Science
Saint Mary's University

Approved: Dr. Yana Fedortchouk
External Examiner
Department of Earth Science
Dalhousie University

Approved: Dr. Lucie Kocum
Faculty of Graduate Studies Representative
Saint Mary's University

Abstract

The application of gas chromatography in characterizing bulk fluid inclusion hydrocarbons in the footwall of the Sudbury Igneous Complex and other magmatic, hydrothermal and surficial ore-forming environments

By*:* Mitchell James Kerr

The North Range of the Sudbury Igneous Complex hosts footwall-style Cu-Ni-platinum group element-rich sulfide deposits of predominantly magmatic origin but that have been influenced by multiple hydrothermal events. The composition of hydrocarbon phases (unsaturated and saturated, C1 to C6) in fluid inclusions within the matrix of Sudbury breccia, a rock unit permeable to circulating volatiles and that commonly hosts footwall-style Cu-Ni-PGE deposits, has been investigated by in-line rock-crushing gas chromatography (GC). Zones of breccia that are known to contain economic footwall sulfide deposits and zones barren of such deposits were investigated. Subtle but strategically significant differences have been found in the composition and abundance of bulk hydrocarbons that are released from mineralized and barren breccias when fluid inclusions are opened. These findings strongly suggest that fluid hydrocarbon signatures should be taken into consideration when exploring for Cu-Ni-PGE-rich footwall-style ore bodies as a supplemental criterion to traditional visual and geochemical approaches.

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Table of Contents

List of Figures

In Chapter 2

In Chapter 3

List of Tables

In Chapter 1

In Chapter 2

In Chapter 3

Chapter 1: Introduction

1.0 Structure of thesis

This study is comprised of four chapters: Chapter 1 offers a brief outline of the thesis structure and key objectives. Chapter 2 describes the bulk hydrocarbon chemistry of rocks associated with the Sudbury Igneous Complex (SIC) and its ore-forming environments, and represents a stand alone manuscript for submission to *Economic Geology*. Combining rock crushers (to release fluid inclusion volatiles) in-line with high-resolution gas chromatography (GC), the bulk hydrocarbon chemistry of volatiles trapped in Sudbury breccia (the main host rock type to footwall Cu-Ni-platinum-group element [PGE] sulfide mineralization styles) was investigated from barren and mineralized environments. The goal of this work was to determine if any systematic differences in hydrocarbon abundance and/or speciation in these two environments could be identified as a means to explore for footwall deposits. Chapter 3 describes a comprehensive comparison of the volatile (fluid inclusion) bulk hydrocarbon chemistry of a variety of rock types from magmatic, hydrothermal and surficial environments world-wide, and respresents a stand alone manuscript for submission to Chemical Geology. Since Chapters 2 and 3 are prepared as separate and independent manuscripts for journal submission, there is a certain amount of duplication of introductory and methods details between the two chapters. Chapter 4 provides a brief summary of the key findings of both Chapters 2 and 3, and outlines future work needed to resolve outstanding issues raises from these studies.

1.1 Primary objectives of thesis

The primary objective of this thesis was to investigate hydrocarbons in Sudbury breccia, the primary host rock for Cu-Ni-platinum group elements (PGE) deposits in the Archean-age country rocks along the northern range of the Sudbury Igneous Complex. Zones of breccia known to host economic mineralization were compared to those considered/presumed/proven barren of economic mineralization. Hydrocarbon speciation, abundances, and spatial distribution were characterized in order to determine if statistically significant differences between the two environments exist. The investigation: (i) improves our understanding of the origin of hydrocarbons in the Sudbury ore-forming environment, with application to other mafic-ultramafic Ni-Cu-PGE deposit settings where hydrocarbons/carbonic fluids have been documented (e.g., Lac des Iles: Hanley and Gladney, 2011; Bushveld Complex: Ballhaus and Stumpfl, 1986; Skaergaard Intrusion: Larsen et al., 1992; Stillwater Complex: Hanley et al., 2008); (ii) speculates on potential abiogenic chemical mechanisms responsible for the generation of the unsaturated and saturated hydrocarbon species in the Sudbury ore-forming environment; and (iii) describes a set of criteria that may be used during routine exploration to improve footwall ore detection efficacy. This portion of the study was funded by Quadra FNX Mining Ltd. (now KGHM International Ltd.) with the intention of supplementing their exploration program with an unconventional vectoring tool in a chemically and physically complex ore-forming environment where appropriate techniques for exploration are limited. Although cursory studies of the hydrocarbon chemistry of fluids in igneous and hydrothermal systems have been performed in the past (see Chapter 2: *Introduction*), a detailed study designed develop an exploration tool is unique. This study has an exploration-oriented purpose supplemented by a preliminary scientific interpretation, reflecting the priorities in any mineral exploration setting: the development of cost effective exploration methods that improve the likelihood of discovery and enhance and ore deposit model.

1.2 Secondary objective of thesis

The secondary objective of this thesis was to compare the bulk hydrocarbon chemistry of fluids from a variety of geological environments (i.e., differing in their formation conditions, tectonic and mineralogical complexity, both ore bearing and non-ore-bearing), in order to determine if any systematic classification scheme can be developed based on hydrocarbon chemistry alone. The data presented in this chapter represents a combination of new data collected by direct analysis of samples using gas chromatography at Saint Mary's University (see Chapter 3) with data compiled from published literature sources.

1.3 List of acronyms and abbreviations

The following table summarizes acronyms and abbreviations that are commonly used throughout the thesis (following page):

Table 1.1: List of acronyms and abbreviations used throughout this thesis

Acronym/abbreviation	**Meaning**
BGB	Barberton Greenstone Belt
C2	total abundance of all 2 carbon-bearing hydrocarbons unless otherwise stated. Also for C3, C4, etc.
CAVZ	Central Andean Volcanic Zone
CMB	Central Metamorphic Belt (of Grenville Province)
FID	flame ionization detector
FLNR	felsic norite
FT	Fischer-Tropsch synthesis
FWBX	footwall breccia
GC	gas chromatography
GDGN	granodiorite gneiss
GN	gneiss
GR	granite
GRBX	granite breccia
HC	hydrocarbon(s)
IOCG	iron oxide copper gold (deposit)
ISS	intermediate solid solution
KAIC	Khibiny Alkaline Igneous Complex
KSZ	Kapuskasing Structural Zone
MAR/MOR	Mid-Atlantic Ridge/mid-ocean ridge
MFNR	mafic norite
MGMT	migmatite
MSS	monosulfide solid solution
msul	massive sulfide(s)
MVP	magmatic volatile phase
NR	norite
PIC	Palabora Igneous Complex
PGE	platinum group element(s)
PGM	platinum group element mineral(s)
sat.	saturated hydrocarbon(s)
SIC	Sudbury Igneous Complex
SLNR	sublayer norite
SMB	South Mountain Batholith
SSGS	Salton Sea geothermal system
SUBX	Sudbury breccia
REE	rare earth element(s)
RLS	Rustenburg Layered Suite
TB	Tarim Basin
TOC	total organic carbon
unsat.	unsaturated hydrocarbon(s)
qtz	quartz
WGD	Wawa Gneiss Domain

Chapter 2: Preliminary evaluation of trace hydrocarbon speciation and abundance as an exploration tool for footwall-style sulfide ore associated with the Sudbury Igneous Complex, Ontario, Canada

Mitchell Kerr*[1], Jacob Hanley[1], Gord Morrison[2], John Everest[2], and Colin Bray[3]
[1]*Department of Geology, Saint Mary's University, Halifax, Nova Scotia, Canada*
[2]*KGHM International Ltd. (QuadraFNX Mining Ltd.), Sudbury, Ontario, Canada*
[3]*Department of Earth Science, University of Toronto, Toronto, Ontario, Canada*
*corresponding author email address: mitchjkerr@gmail.com

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Abstract

The North Range footwall of the Sudbury Igneous Complex (SIC) hosts footwall-style Cu-Ni-platinum group element (PGE)-rich sulfide deposits of predominantly magmatic origin that have been influenced chemically, mineralogically and texturally by multiple syn-magmatic and post-magmatic hydrothermal events. The composition of reduced carbonic phases (unsaturated and saturated hydrocarbons, C1 to C6) in fluid inclusions within the matrix of Sudbury breccia, a rock unit permeable to circulating volatiles, has been investigated by in-line rock crushing gas chromatography (GC). This was done on samples from zones of breccia that are known to contain economic footwall sulfide deposits and zones barren of such deposits (to the most current knowledge available from the exploration industry). A fundamental limitation of this work is that this technique,

intended for application in routine exploration, represents a bulk sampling method which samples all generations of fluid inclusions present in the rock. In the rock units analyzed in this study, however, samples were chosen that were relatively simplistic in their fluid inclusion complexity. Therefore, variation in bulk hydrocarbon speciation and abundance in volatiles released from crushed breccia samples can be correlated to a few key events associated with the development of the ore-forming environment.

Trace hydrocarbons occur ubiquitously throughout all SIC, footwall and country rocks investigated. However, there are subtle but strategically significant differences in the composition and abundance of bulk hydrocarbons that are released from mineralized and barren breccias when fluid inclusions are opened. The following hydrocarbon species were detected and quantified in the Sudbury footwall using this technique: (i) the saturated hydrocarbon species: methane, ethane, propane, *n*-butane, *i*-butane, 2,2-dimethylpropane, 2-methylbutane, n-pentane, 2,2-dimethylbutane, 2-methylbutane, 3-methylbutane, and n-hexane; and (ii) the unsaturated hydrocarbon species: ethylene, propylene, t-2-butene, c-2-butene, 1-butene, isobutylene, 1,3-butadiene, t-2-pentene, c-2-pentene, 1-butyne, t-2-hexene, c-2-hexene, and 1-hexene. Bulk hydrocarbon analysis of volatiles released from samples of Sudbury breccia from sulfide mineralized and sulfide barren embayments demonstrates: (i) statistically higher abundances of *average light saturated* hydrocarbons (C1-C4) and approximately 2x higher *total* abundance of hydrocarbons (mol/g basis) associated with samples from mineralized embayments compared to samples from barren environments in the footwall; and (ii) no statistically significant differences between *average unsaturated* hydrocarbon abundances of the two environments are present (two-tailed t-test of unsaturated/saturated hydrocarbon ratios: $\alpha = 0.05$, $P = 0.36$), yet a significant difference is present between the breccia environments when considering the total range of values collected. Differences in light saturated hydrocarbon abundances between the breccia environments is the result of: (i) more fluid being trapped in mineralized breccia than barren breccia (i.e., more fluid inclusions); (ii) the presence of a different, more hydrocarbon-rich fluid that charged the mineralized breccia environment and not the barren environment; and/or (iii) modifications to an initially identical fluid by influencing factors present in the mineralized breccia environment but absent in the barren environment (i.e., mineral catalysts, elevated temperatures, etc.). These factors cannot be fully resolved in the breadth of this study. Breccia proximal to the region in which the footwall-hosted ore is physically connected to contact-style ore has elevated unsaturated hydrocarbon abundances (specifically propylene). This demonstrates that, although when considering the mineralized versus barren embayment breccia packages as a whole, no statistically significant difference is present in unsaturated hydrocarbon abundances, these abundances locally vary within the mineralized embayment package itself.

Gas chromatographic analysis of quartz from 5 PGE-rich and 1 PGE-poor quartz + massive sulfide ± epidote assemblages collected from the North Range footwall environment of the SIC was performed to determine if the presence of PGE/PGM influence the hydrocarbon signatures. Samples from PGE-rich environments showed a significant increase in the abundance of unsaturated hydrocarbons (i.e., elevated unsaturated to saturated hydrocarbon fluid ratios, particularly the propylene to propane ratio) compared to a quartz sample from a PGE-poor environment. It is suspected that the presence of PGE and/or PGM catalyze reductive coupling and dehydrogenation reactions, effectively increasing higher order hydrocarbon (C_{2+}) and unsaturated hydrocarbon abundances, respectively. Additional experiments are required to quantify the contribution of these reactions to the fluid's hydrocarbon budget under various geological conditions.

A Schultz-Flory distribution between the hydrocarbon abundance versus carbon number strongly suggests that the hydrocarbon phases present in the fluid associated with the SIC and its footwall rocks are abiogenic in origin. Consistent and linear trends between the C2 hydrocarbons and methane and the C3 hydrocarbon and methane present in the SIC rocks, country rocks and Sudbury breccia populations suggests a genetic and/or chemically related relationship between the hydrocarbon species in the system. This suggests that a single volumetrically dominant generation of carbonic fluid equilibrated early prior to charging the system with a fluid of uniform composition, or that separate fluids unrelated temporally or by origin equilibrated under similar chemical pathways in different regions of the SIC yielding very similar bulk hydrocarbon signatures. Samples from PGE-rich environments and a number of breccia samples from the mineralized embayment were found to deviate from these expected light hydrocarbon trends. We foresee two potential causes for these local hydrocarbon deviations: (i) the presence of PGE complexes or PGM phases associated with the hydrocarbon-rich fluid chemically modifies the hydrocarbon speciation through catalytic dehydrogenation reactions prior to entrapment, or (ii) post entrapment alteration/hydrothermal events increased the oxygen fugacity of the external environment altering the CH_4-CO_2 proportions inside the inclusions (i.e., respeciation). A combination of both factors is likely responsible for the anomalous hydrocarbon signatures seen in these samples.

Discrimination diagrams display some degree of clustering between mineralized and barren breccia populations; however, a significant amount of overlap is always present between the two populations. To effectively employ hydrocarbon signatures for sulfide ore body exploration it is necessary to analyze a large number of samples and compare them against a barren breccia background field (also sufficiently populated). Preliminary spatial analysis of hydrocarbon signatures with respect to footwall-hosted massive sulfide mineralization shows total hydrocarbon abundance of the fluid within breccia does not statistically change with respect to ore body proximity. However, it was determined that regions of breccia near the top of the sulfide body (proximal to where the footwall-style and contact-style ore is physically connected) were enriched in propylene. We have determined that elevated unsaturated hydrocarbon abundances, C3/C1 ratios and propylene to propane ratios correlate with elevated levels of PGE in samples of Sudbury breccia and in assemblages of quartz + sulfide ± epidote. Thus, fluid hydrocarbon signatures should be taken into consideration when exploring for Cu-PGE-rich footwall-style ore bodies.

2.0 Introduction

It is well documented that carbonic volatiles (CO_2, hydrocarbons) may play direct (as ligands, or as hosts for ligands) and indirect (promoting unmixing/immiscibility triggering metal precipitation, or precipitation of ore metals during fluid-rock interaction) roles in ore formation (Ypma and Fuzikawa, 1980; Sisson et al., 1981; Ballhaus and Stumpfl, 1986; Read and Meinert, 1986; Walsh et al., 1988; Naden and Shepherd, 1989; Ballhaus et al., 1994; Wood, 1996; Pettke et al., 2000; Yang and Scott, 2002; Hanley et al., 2005; Hanley et al., 2008; Hanley and Gladney, 2011). While present as trace species in the vast majority of high-temperature magmatic-hydrothermal environments (due to their decreasing stability with increasing temperature) hydrocarbons can occur as major components in some igneous environments of alkalic-agpaitic affinity (e.g. Strange Lake, Canada: Salvi and Williams-Jones, 1992, 1997a, 1997b; Khibiny and Lovozero, Russia: Nivin, 2002, Potter and Konnerup-Madsen, 2003 and references therein, Potter et al., 2004, Ryabchikov and Kogarko, 2009; Ilimaussaq, South Greenland: Konnerup-Madsen et al., 1985, Graser et al., 2008). Such hydrocarbons may originate from respeciation of exsolved inorganic gases, originally introduced by graphite or carbonate assimilation, at lower temperatures and oxygen fugacities around QFM (Lyutkevich, 1967; Petersilie and Sorensen, 1970; Gerlach, 1980; Kogarko et al., 1987; Konnerup-Madsen et al., 1988). Alternately, abiogenic reactions such as the Fischer-Tropsch process (FT) can significantly contribute to the hydrocarbon budget of a hydrothermal system, in which carbon dioxide undergoes catalytic reductive polymerization via reaction with hydrogen gas to yield CH_4 (and higher order hydrocarbons) and H_2O (Abrajano et al., 1990; Sherwood-Lollar et al., 1993, 2008; Salvi and Williams-Jones, 1997a, b; Charlou et al., 1998; Potter and Konnerup-Madsen, 2003; Potter et al., 2004; Nivin et al., 2005; Taran et al., 2007; Ryabchikov and Kogarko, 2009).

Hydrocarbons have been recognized as important ore fluid constituents associated with the magmatic Ni-Cu-platinum-group element (PGE) deposits of the Sudbury Igneous Complex (Hanley et al, 2005), an igneous system that assimilated carbon-rich sediments at the time of impact melting (Ames, 1999; Mungall et al., 2004; Ames et al., 2006, 2008; Wright et al., 2010). Whereas the chemical signature of Sudbury-related ore-forming *aqueous* hydrothermal fluids has been extensively documented and can be recognized at a strategic (in the exploration sense) distance from ore (Farrow, 1994; Farrow and Watkinson, 1992; Li, 1992; Li and Naldrett, 1993; Molnar et al., 2001; McCormick et al., 2002; Hanley et al., 2003; Pentek et al., 2011; Marshall et al., 1999; Hanley et al., 2004; Hanley and Bray, 2009; Tuba et al, 2010; Stewart, 2010), the chemical "fingerprint" associated with non-polar species (e.g. CO_2, hydrocarbons) has not been investigated. With the increased sensitivity of analytical methods such as gas chromatography (GC) for analyzing trace hydrocarbon species, the ability for more subtle and spatially extensive geochemical signatures to be recognized in the vicinity of ore-forming environments is approaching a potentially competitive level with other routine geochemical or geophysical methods for ore exploration. Understanding of the fluid assemblages likely transporting volatile species generated by or associated with the metal precipitation process through rocks in ore forming environments allows for the potential application of this method not only to characterize fluids in mineralized and alteration veins but also the variably permeable host rocks surrounding ores.

In this study, in-line rock crushing gas chromatography (Andrawes and Gibson, 1979; Andrawes et al., 1979; Bray et al., 1991; Bray and Spooner, 1992; Salvi and Williams-Jones, 1997a, 1997b) was used to investigate the speciation and concentrations of hydrocarbon fluids trapped in a Sudbury breccia, igneous rocks of the Main Mass, and country rocks, from ore-bearing and non-ore-bearing environments of the Sudbury Igneous Complex (SIC), Ontario, Canada. Footwall-style magmatic Cu-Ni-PGE deposits at Sudbury are hosted in Sudbury breccia (SUBX), a pseudotachylite (pseudo-cataclastite) formed via the shock melting of Archean-age country rock along the North Range of the SIC (Coats and Snajdr, 1984). Aside from the presence or absence of mineralization, there are few differences in the chemistry of barren and mineralized packages of Sudbury breccia that can be recognized through routine geochemical analysis. A study of this nature is challenging due to the complexity of the SIC and its footwall environment, which is host to number of ore styles with unique metal tenors and a large diversity of country rocks and magmatic rocks with very complex and controversial magmatic-hydrothermal history. As a result, there is a diversity of fluid inclusion generations associated with pre-, syn- and post-ore processes all of which presumably have specific chemistry tied to the thermochemical conditions at the time of entrapment. This technique is also limited to bulk analysis, careful sample selection allowed the interpretation of data to be tied to the dominant fluid inclusion assemblages in the samples. Although being limited to bulk analysis, this technique has significant advantages: (i) it is quick and cost effective, and (ii) the hydrocarbon signature of fluids in rock proximal to ore can indicate its presence in the area despite mineralization not necessarily being physically present in the samples investigated. These factors make this tool an attractive and easily implemented criterion to supplement currently employed exploration programs. The current study is a preliminary evaluation of the effectiveness of GC bulk fluid inclusion gas analysis for hydrocarbons as an exploration method in an ore-forming environment (Sudbury) where hydrocarbons are closely associated with structures that now contain magmatic-hydrothermal sulfide ores. The main goals of this study are to: (i) characterize abundances and variations in light aliphatic hydrocarbons present in secondary fluid inclusions within mineralized and barren breccias that are known to host ore, and (ii) speculate on the potential mechanisms that influenced their abundance and speciation in this ore forming environment, and (iii) work to develop simple discrimination diagrams to illustrate fundamental differences at a strategic scale between mineralized and barren breccias.

2.1 Geological Setting

2.1.1 Regional Geology

The Ni-Cu-PGE sulfide deposits at the Levack and McCreedy West mines occur entirely within the footwall zone north of the SIC contact in the North Range (Farrow and Watkinison, 1992; Morrison et al., 1994; Watkinson, 1999; Hanley et al., 2005) and are often spatially associated with Sudbury breccia, a pseudotachylite formed via the impact-brecciation and shock-melting of country rocks distal to the SIC contact (Morrison et al., 1994; Ames et al., 2008; Hanley et al., 2011). The SIC is a large (roughly 60 km by 25 km), differentiated, hypabyssal igneous body of Proterozoic age (~1850 Ma) (Dressler, 1984; Krough et al., 1984). The main mass of the SIC is composed of noritic and gabbroic mesocumulates overlain by a thick granophyric residuum (~800 – 1000 m). The

SIC is considered to be the product of meteorite impact-induced melting of carbonaceous shale and marine sediments as well as upper and lower crust (Dietz, 1964; Faggart et al., 1985; Naldrett et al., 1986; Walker et al., 1991; Grieve, 1994; Mungall et al., 2004; Hanley et al., 2005; Hanley et al., 2011). The rocks of the Archean Superior Province constitute the footwall of the North and East Ranges of the SIC. The Levack Gneiss Complex of granulite and amphibolite facies (2711+/- 7 Ma; Krogh et al., 1984) occurs immediately north of the SIC contact mainly in Levack and its neighbouring townships, whereas migmatites are the dominant rock type at distances greater than ~2 km from the SIC (Dressler, 1984; Coats and Snajdr, 1984; Card, 1994; Ames et al., 2008; Hanley et al., 2011). The Archean footwall is mainly comprised of orthogneiss with a granitic to monzodioritic composition with lesser amounts of mafic orthogneiss, metapyroxenite, metagabbro, amphibolite and migmatite that occur as isolated and discontinuous rafts and layers (Hanley et al., 2011). Later hydrothermal alteration associated with the formation of Cu-Ni-PGE sulfide deposits is marked by zones abundant in secondary hydroxysilicate minerals including chlorite and amphibole, and halogen-rich haloes that surround ore bodies for distances up to ~200 m. Large-scale alteration and geochemically anomalous zones are related to areas containing Sudbury breccia and Cu-rich mineralization in the footwall contact (Farrow and Watkinson, 1992; 1997; Farrow, 1994; Jago et al., 1994; Morrison et al., 1994) and in the hanging wall contact (Ames and Gibson, 1995; Ames et al., 1998, 2006). These hydrothermal phases overprint the footwall rocks that were previously modified by contact and shock metamorphism (Hanley and Mungall, 2003; Hanley et al., 2011).

The SIC and its footwall are host to three main magmatic sulfide deposit types: (i) contact-style deposits (high Ni, low PGE with a Ni/Cu > 1). These deposit types occur near the basal contact of the SIC within footwall breccia or a basal igneous unit of the SIC ('sublayer') and primarily consist of pyrrhotite-rich disseminated to massive sulfides with minor amounts of pentlandite and trace chalcopyrite (Naldrett, 1984); (ii) offset-type deposits hosted in radial or concentric quartz diorite offset structures that are physically connected to the main mass of the SIC and may extend up to 30 km or more away from the base of the SIC (Ames and Farrow, 2007). These deposits are also pyrrhotite-rich but possess a higher proportion of pentlandite and chalcopyrite and a Ni/Cu ratio of about 1 (Grant and Bite, 1984; Jago et al., 1994; Farrow and Lightfoot, 2002); and (iii) footwall-style deposits hosted entirely within the footwall of the SIC in zones of Sudbury breccia. These Cu- and PGE-rich deposits are characterized by chalcopyrite-rich assemblages occurring mainly in sheet-like massive sulfide veins (up to 1.5 m thick) and low-sulfide, PGE-rich vein stockworks (Naldrett, 1984; Jago et al., 1994; Farrow and Lightfoot, 2002; Farrow et al., 2005; Hanley et al., 2005). At the Levack and McCreedy mines, footwall-style deposits are mined for their high Cu and PGE content. This region of the footwall is characterized by complex networks of veins and pods of chalcopyrite ± cubanite with more minor amounts of pyrrhotite, pentlandite, millerite, bornite and magnetite with PGM occurring ubiquitously as discrete minerals (commonly <150 μm in diameter; bismuthides and tellurides are most predominate) in either sulfide or silicate hosts and very often along grain boundaries. Variably developed amphibole + epidote + quartz ± chlorite ± titanite alteration selvages are also present in areas affected by fluid alteration

(Farrow and Watkinson, 1992; Jago et al., 1994; Farrow and Lightfoot, 2002 and references therein; Farrow et al., 2005).

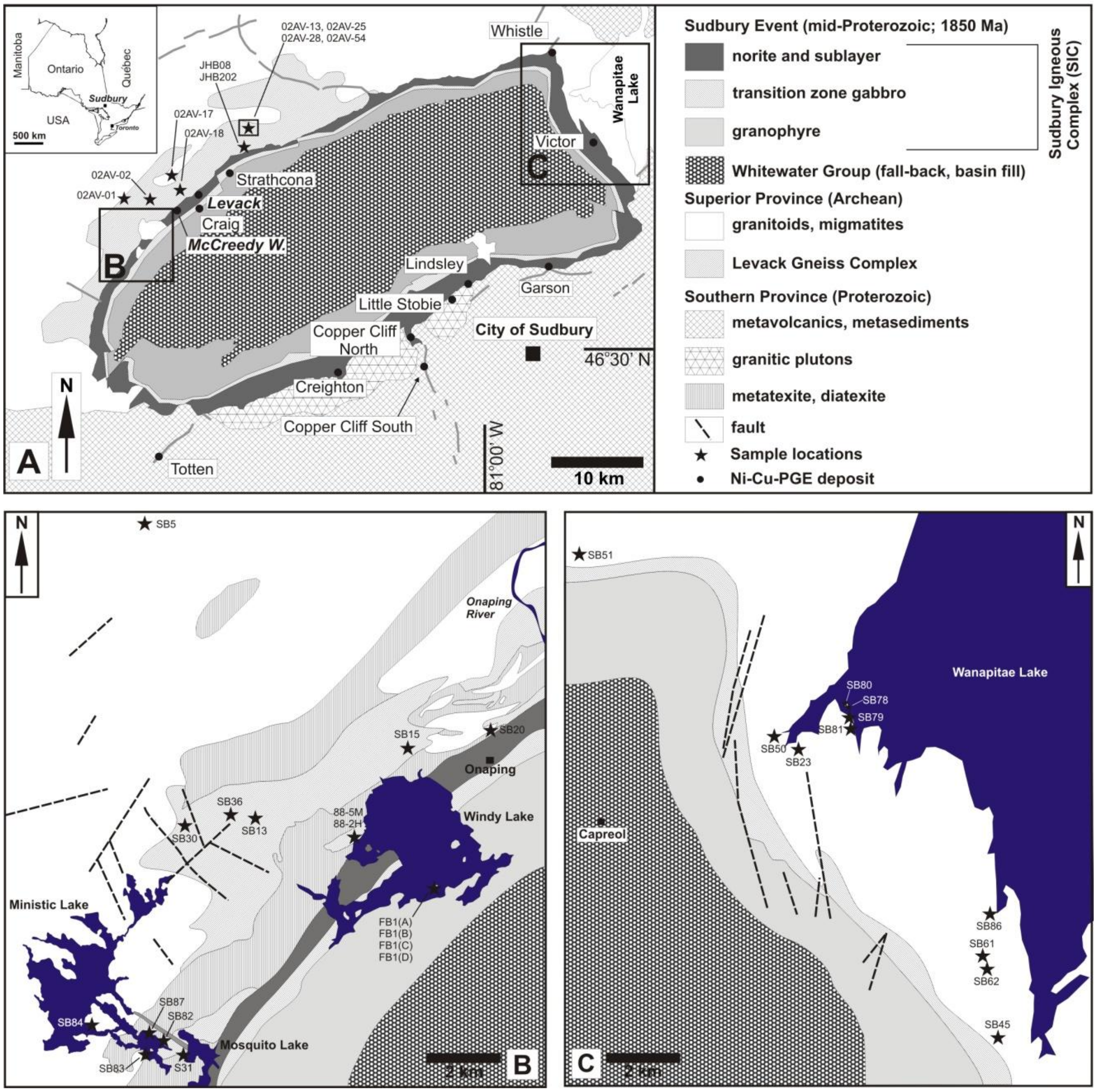


Figure 2.1: ***A* – Geological map of the Sudbury Igneous Complex.** A number of Sudbury breccia samples (SUBX) have been acquired from the North Range near the Barnet Showing (box with star) and from northwest of Levack (stars). The remainder of barren SUBX samples were collected from areas distal to sulfide mineralization west of Levack at near Windy Lake and from the East Range SIC at Wanapitae Lake. ***B* – Windy Lake barren SUBX samples locations.** Samples were collected from areas around Windy and Ministic Lakes. No sulfide mineralization is present in this region either as footwall-style veins or contact-style embayment mineralization. ***C* – Wanapitae Lake barren SUBX sample locations.** Samples were collected from the East Range of the SIC near Wanapitae Lake. Samples other than SB51 are ≥2 km from known footwall- or contact-style deposits (i.e. Capre). Sample SB51 is ≤1 km from contact-style mineralization along the North Range.

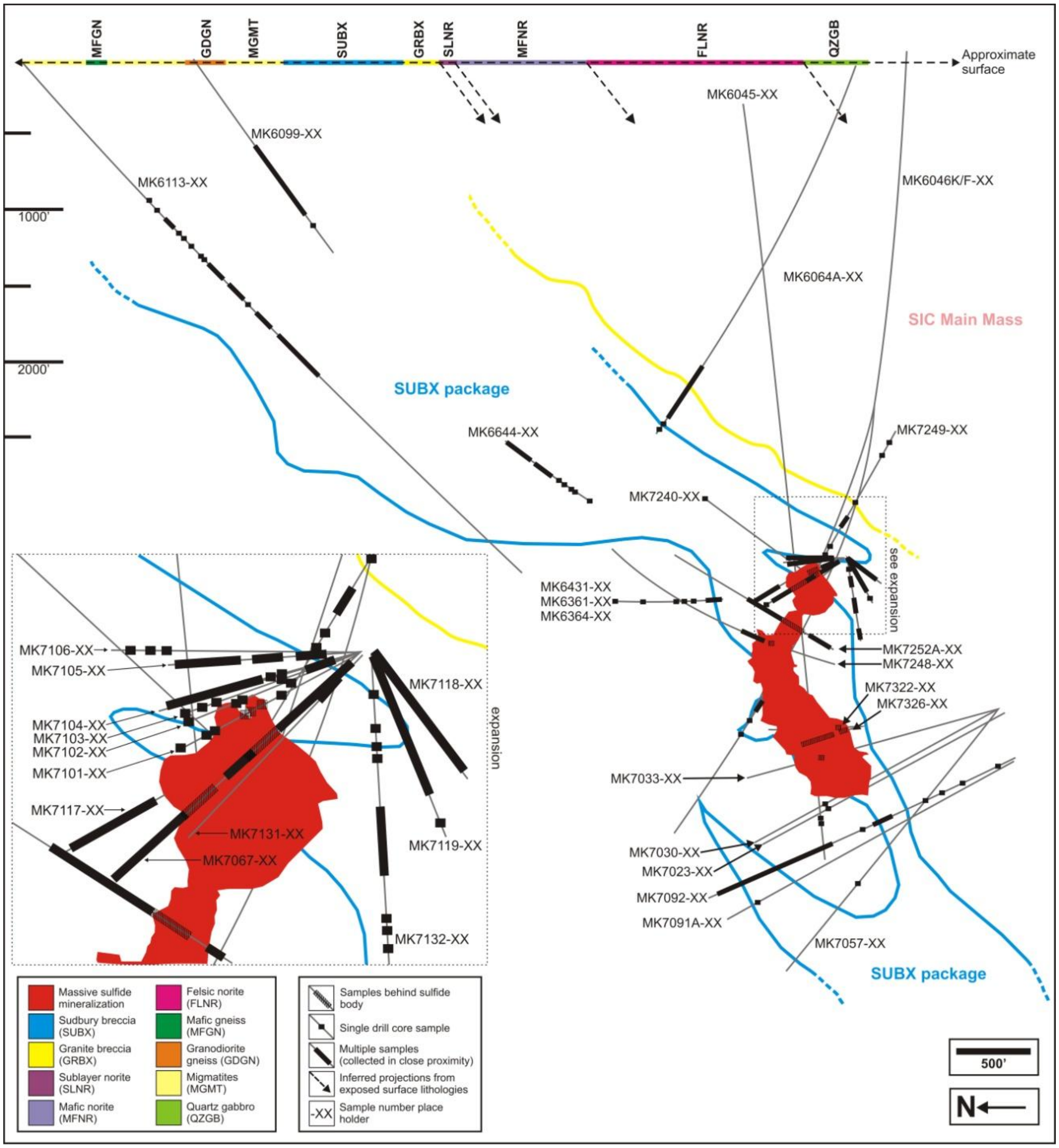


Figure 2.2: Cross-sectional view of the Cu-Ni-PGE footwall deposit at Levack with drill core sample locations. (Crosssection at approx. +319250E) Multiple names associated with what appears to be a single core is due to the presence of multiple cores made with one collar (via shimming the drill head) and/or because of the fixed viewing angle. Sample drill core MK7067 (in expansion) cuts in front of and behind sulfide mineralization, which is why some samples are collected from in front of the body (solid black bars) and from behind the body (hatched bars). The view shown in the expansion is from a lower depth looking slightly upwards for clarity of showing drill cores. Blue and yellow lines represent SUBX and GRBX contacts, respectively (i.e. yellow line is contact between GRBX and SLNR). Hatched lines along lithological contacts indicate implied projections from limited data. Drill core FNX7093 (from which MK7093 samples were collected) could not be shown in this Figure.

2.1.2 Footwall hosted ore deposits and associated hydrothermal fluids

Footwall-style deposits are widely distributed and can occur up to 2 km from the footwall contact of the SIC. They are primarily found in zones of Sudbury breccia within the Levack Gneiss Complex (commonly found along clast boundaries). Although footwall-style deposits are smaller than contact-style deposits and generally harder to locate, they possess significant importance owing to their high contents of Cu, Pd, Pt and Au (Watkinson, 1999; Farrow and Lightfoot, 2002; Hanely et al., 2005). Cu/Ni ratios are generally >6, the Pt+Pd+Au contents exceed 7 g/ton and the ratio of Pt/(Pt+Pd) is between 0.45 and 0.5 in most of the economical zones (Morrison et al., 1994; Farrow and Lightfoot, 2002; Farrow et al., 2005). Footwall-style deposits can be subdivided into two physically and chemically distinct ore types: (i) sharp-walled, "high-sulfide" vein deposits of a controversially magmatic-hydrothermal origin that formed via primary differentiation and/or fractional crystallization of sulfide liquid at the lower contact of the SIC, which underwent secondary remobilization and re-deposition of ore metals by saline fluids, hydrocarbons and salt melts. These systems are physically connected to the Ni-rich "contact-style" sulfide deposits along the base of the SIC (Farrow and Watkinson, 1992; Li et al., 1992; Li and Naldrett, 1994; Morrison et al., 1994; Farrow and Watkinson, 1997; Molnar et al., 2001; Farrow and Lightfoot, 2002; Hanley et al., 2004; Farrow et al., 2005; Hanley et al., 2005, 2011); and (ii) disseminated, stringer and blebby sulfides that constitute "low-sulfide" ores. Low-sulfide ores have bulk PGE/S ratios an order of magnitude higher than in high-sulfide ores (Farrow et al., 2005). Recent findings suggest that low-sulfide ore types are predominantly hydrothermal and paragenetically pre-date the emplacement of the high-sulfide footwall deposits (Farrow et al., 2005; Hanley et al., 2005; Hanley et al., 2011).

Although most researchers agree that the emplacement of magmatically fractionated sulfide liquid into the footwall rocks of the SIC introduced the Ni, Cu, PGE and Au into the system (Naldrett and Kullerud, 1967; Li, 1992; Hanley et al., 2011), it is also recognized that high salinity magmatic hydrothermal fluids (driven by the heat of the cooling SIC) may have leached and redistributed Cu, PGE and Au from contact-style deposits into ore bodies within the footwall (Farrow and Watkinson, 1992; Farrow, 1994; Farrow et al., 1994; Everest, 1999; Hanley et al., 2005). Extensive fluid inclusion, O and H isotope and petrographic evidence suggests that hydrothermal volatiles played an important role in the emplacement and redistribution of base and precious metals (i.e., PGE, Au), in the compositional modification of magmatic sulfides and the generation of halogen enriched haloes encompassing the ore bodies (Li, 1992; Farrow, 1994; Jago et al., 1994; Farrow and Watkinson, 1997,1999; Marshall et al., 1999; Molnar et al., 2001; Hanley and Mungall, 2003; Hanley et al., 2004, 2005; Ames, 2007; Hanley and Bray, 2009; Hanley et al., 2011). Evidence that supports a hydrothermal model/origin for low-sulfide footwall ore deposits includes: (i) the occurrence of high salinity fluid inclusions in sulfide and silicate alteration minerals that host ore metals (i.e., Ag, Cu; Farrow, 1994; Hanley et al., 2005); (ii) the occurrence of metal halide minerals in PGE-Au-rich sulfide vein assemblages (i.e., unnamed Pd-Bi-Cl phase; Li, 1992); (iii) the occurrence of primary, low temperature Pt- and Pd-bearing minerals hosted in Cl-rich, hydroxysilicate mineral assemblages along the boundaries of massive sulfide veins rather than within the veins themselves (Li, 1992; Farrow, 1994; Farrow and Watkinson, 1997); and (iv) the presence of altered, oxidized zones (i.e., “epidote zone”) characterized by the presence of Ni- and PGE-bearing bismuthides and tellurides but depleted in Cu, Ag and Au (Farrow, 1994; Farrow and Watkinson, 1999; Hanley et al., 2005). Recent investigations of low-sulfide footwall-style deposits (Farrow et al, 2005) have suggested that ore metals in these particular systems possess a largely fluid-derived component and were emplaced in the footwall prior to the emplacement of the sharp-walled magmatic sulfides due to the cross-cutting relationship of the low-sulfide disseminated mineralization by the dominantly magmatic high-sulfide veins. Previous research has suggested that ore-fluids associated with footwall-style deposits were mixtures of deeply sourced saline groundwaters and high temperature “magmatic” fluids derived from the mineralized contact region or the main igneous mass of the SIC itself (Hanley et al., 2011).

In addition to aqueous saline fluids being pervasive in the North Range of the SIC, carbonic fluids phases have also been reported (Farrow and Watkinson, 1999; Molnar et al., 2001; Hanley et al., 2005). Microthermometric and gas chromatographic analyses of fluid inclusions trapped within quartz from a quartz + sulfide + epidote “alteration” vein spatially associated with typical Cu-PGE rich footwall-style sulfide veins indicate the presence of a methane dominant reduced carbonic fluid (hydrocarbon fluid) that occurs with high salinity aqueous inclusions (brine) as a coeval primary assemblage in the quartz (Hanley et al., 2005). Inclusions in the assemblage often contain both hydrocarbon and brine phases within the same inclusion with significantly variable phase ratios indicating the heterogeneous entrapment of coexisting fluids in the system. Although some research has noted the presence of CO_2 as the dominant carbonic phase in quartz associated with the North Range systems (Farrow and Watkinson, 1999; Molnar et al., 2001), the aforementioned investigations of Cu-PGE associated quartz assemblages by Hanley et al. (2005) determined that CH_4 was the dominant carbonic phase and CO_2 was essentially absent from all inclusions investigated. It has been noted that CO_2-bearing fluids more commonly occur in the South Range where rocks have been strongly deformed and metamorphosed during and after the Penokean Orogeny (Card et al., 1984; Peredery and Morrison, 1984; Watkinson, 1999). A number of higher order hydrocarbon species (i.e., C_2H_6-C_2H_2, C_3H_8, C_4H_{10}) have also been identified coexisting with methane and have been found to constitute a significant volumetric contribution to the carbonic fluid phase budget (i.e., ~64% CH4, 29% C_2H_6-C_2H_2, 3% C_3H_8) (This study; Hanley et al., 2005). A growing body of research suggests that these hydrocarbon-rich fluids play an important role in the uptake and redistribution of ore metals including Cu and Au (Wood, 1996; Hanley et al., 2005; Williams-Jones et al., 2009; Hanley and Gladney, 2011) and may be chemically altered via the interaction with certain metals. As a result, it is important to understand the origins and chemical characteristics of these fluids in order to better constrain how these fluids chemically interact, redistribute and/or concentrate particular ore metals.

2.2 Sampling and analytical methods

2.2.1 Sample description

Samples were obtained from drill cores from the Levack and McCreedy West properties and outcrops around the SIC. Samples of Sudbury breccia were the main analytical focus of this study; samples of SIC rocks, country rocks were also investigated. Quartz from quartz + sulfide ± epidote ± amphibole assemblages (often referred to as simply quartz + sulfide assemblage for brevity) was investigated. Quartz from these samples is characterized by the presence of primary and secondary fluid inclusion assemblages that have been extensively discussed in the literature as synchronous to or spatially-associated with the emplacement of footwall-style Cu-Ni-PGE ore bodies (Farrow & Watkinson, 1992, 1999; Li & Naldrett, 1993; Marshall et al., 1999; Molnar et al., 2001; Hanley et al., 2005). Thus the fluid present in footwall quartz + sulfide assemblages constitutes the most representative sample of the volatiles present in mineralizated structures before and/or during footwall mineralization. Bulk analysis of volatiles may therefore be used as a tool for detecting particular characteristic signatures of fluids genetically related to mineralization. Sudbury breccia from a mineralized package (hosting the Morrison deposit; n=410; Figure 2.2) known to contain footwall sulfide mineralization along with samples of breccia from barren environments in the footwall (n=41+4 repeat crushes; ~2km from any footwall mineralization and distant from SIC contact-style mineralized embayment structures; Figure 2.1B,C) were collected. Additional samples from SIC-associated lithogies include: norite (NR) proximal to a contact-style mineralized embayment structure (n=13), norite distal to contact-style mineralization (n=3; Windy Lake region), footwall breccia (FWBX; n=4; distal to mineralization, Windy Lake region), gneiss (GN) from the Leveck Gneiss Complex (n=5), and granite (GR) from the footwall (n=3) (GN and GR from various locations around Levack). Quartz from PGE-rich quartz + sulfide assemblages (n=5; UG3750(#0), UG3750(#5), UG3750(#6), ROM1158 and MK4209-1; see Figure 2.6 for images of

UG3750(#0) and MK4209-1) was manually extracted, prepared and crushed. The 'UG' samples were collected from quartz-bearing sulfide veins visible at the 3750 level of Levack underground (Morrison deposit) associated with primarily chalcopyrite ± millerite mineralization. The ROM sample is a sample from the Broken Hammer deposit in the North Range footwall (8.19 ppm Pt, 2.14 ppm Pd). This sample is an example of a high-sulfide/low-sulfide environment hybrid that contains disseminated and blebby sulfide with unusual sperrylite-quartz-epidote assemblages. The MK4209-1 sample was collected from KGHM International Ltd./Quadra FNX Mining Ltd. drill core from Levack (core ID: FNX4209; 3.14 ppm Pt, 0.88 ppm Pd) at a distance of 240 feet from the drill collar. This sample contains blebby chalcopyrite and quartz adjacent to a vuggy quartz veinlet. An additional sample of quartz (A2-2) from a PGE-poor quartz + sulfide ± epidote assemblage from the North Range footwall of the SIC was analyzed as comparison to the PGE-rich assemblages. Samples of inclusion-free Brazilian quartz (n=8; 2 trails per crusher) were used to acquire a background to account for any volatiles that may be generated as a result of the mechanical action of the crush (i.e., o-ring rubbing, sample fracturing, possible volatiles released from carbon-bearing steel, etc.). Blank crushes only yielded small amounts of methane and an unknown impurity peak located at approximately 32.2 minutes (Figure 2.3 - inlay).

A group of 8 samples of Sudbury breccia (02AV–## samples; Figure 2.1A) were collected and analyzed as a preliminary trial to gauge the effectiveness of this technique to aid in the location of sulfide ore bodies. The samples were collected from various areas across the North Range of the SIC footwall. Samples 02AV-01, 02AV-02, 02AV-

17, and 02AV-18 were collected from areas north of the Levack and McCreedy West mines, outside of contact-style mineralized embayment structures and distal to any significant surface exposed sulfide mineralization. Samples 02AV-13, 02AV-25, 02AV-28 and 02AV-54 were collected on surface from an area near the Barnett Showing, north of Strathcona mine. These samples were fragmented, prepared and crushed identically to all other samples in this study and analyzed on Method 2.

2.2.2 Gas chromatography

This technique was based on the original work by Andrawes and Gibson (1979) and Andrawes et al. (1979) in which samples were crushed in stainless steel, hydraulically driven, sealed crushers under dynamic helium carrier gas flow, passing the liberated volatiles directly into an analytical column to be separated and analyzed. Significant advances were made to this technique by Bray et al (1991), Bray and Spooner (1992) and Salvi and Williams-Jones (1997b) who were first to characterize fluid inclusion gas species in detail through further development of inline crushing systems. Gas chromatographic analyses of mineral samples (i.e., quartz, tourmaline) by Bray et al. (1991) and Bray and Spooner (1992) were able to separate and detect a number of saturated and unsaturated hydrocarbon species ranging from C1-C4 by employing an 11.7 eV photoionization detector (PID) in series with a micro-thermal conductivity detector (TCD). However, their technique was unable to effectively resolve hydrocarbons larger than C4 as well as unsaturated C4 hydrocarbon species. Also, since methane ionizes at ≥12.98 eV, it does not produce a linear response on the PID and thus had to be quantified using the TCD, which possesses higher limits of detection (Salvi and Williams-Jones, 1997b). Unlike various ‘off-line’, gas analysis techniques of the past including *in vacuo* thermal decrepitation (Piperov and Penchev, 1973; Smith et al., 1984; Barker and Smith, 1986; Kesler et al., 1986) and *in vacuo* mechanical crushing gas liberation in an inert atmosphere (Petersilie and Sørensen, 1970; Piperov and Penchev, 1973; Ikorskiy and Voloshin, 1982; Whelan, 1988; Potter and Siemann, 2004; Beeskow et al., 2006), the ‘in-line’ technique allows for the transfer of all extracted volatiles to the analytical column without significant complications due to thermal degradation of the compounds or gas loss due to inefficient transferring techniques. Direct injection of liberated volatiles at lower operating temperatures under dynamic He flow effectively improves detection levels for trace volatiles in fluid inclusions and minimizes issues such as adsorption and chemical reactions upon crushing (Bray et al., 1991; Bray and Spooner, 1992; Salvi and Williams-Jones, 1997b,2003; Potter and Longstaffe, 2007). Previous studies employing this technique can identify and quantify saturated hydrocarbons (as well as the unsaturated hydrocarbon ethene in a few cases) up to at least C4 (Bray et al., 1991; Bray and Spooner, 1992; Salvi and Williams-Jones, 1997; Channer et al., 1999; Hanley et al., 2005) or C5 (Potter and Longstaffe, 2007). The technique used in this study has been refined to separate and detect trace saturated and unsaturated hydrocarbons (and various conformational and structural isomers thereof; e.g. trans-2-butene, cis-2-butene, 1-butene, etc.) down to a lower limit of approximately 10^{-12} moles per gram of crushed sample. Analysis was performed using an Agilent 7890 series gas chromatograph at Saint Mary’s University adapted with the appropriate valve and injection systems by Wasson-ECE Instrumentation. A custom adapted chromatograph was required in order to be able to select between the 4 separate crushers and GC injection port. The GC was equipped with a micro-thermal conductivity detector (TCD) along with 2, H_2-burning flame ionization detectors (FID), one of which was installed in series with the TCD and one installed on a separate, valve controlled assembly. An assembly of this nature is required since the GC possesses 2 distinct separation methods. The first method (Method 1) employs all three detectors and can be used to detect and quantify both inert and non-combustible compounds (i.e., CO_2, CO, H_2O) as well as hydrocarbons (i.e., CH_4, C_2H_6, etc.) through the use of the TCD and FIDs respectively. The second method (Method 2) only employs one FID in series with the analytical column and is thus only suitable for analyzing combustible compounds such as hydrocarbons (i.e., olefins, paraffins, thiols, etc.). The analytical column employed for Method 2 possesses the power to separate and resolve saturated (paraffinic) and unsaturated (olefinic) hydrocarbons and various structural isomers (i.e., pentane, 2-methylbutane, 2,2-dimethylpropane, etc.) and conformational isomers (i.e., cis-2-butene, trans-2-butene, 1-butene, etc.) thereof, making this the method of choice when determining the detailed hydrocarbon signature of any given sample (Method 1 does not possess this level of hydrocarbon separation; Figure 2.5). The raw data (sample chromatograms) was collected and integrated with the aid of the PC-operated software, Agilent Chromatographic ChemStation®. Integrated data was converted to 'moles/g of rock' by comparing the sample data to predetermined calibration curves made using standard gas mixtures (Matheson Tri-gas Standards) and normalized to the mass of rock crushed.

Helium carrier gas was employed at a flow rate of 7.0 ± 0.5 ml/min to drive volatiles into a 30m x 0.53mm x 5μm DB-1 capillary column prior to a 25m x 0.53mm x 10μm

Porabond-Q capillary column for Method 1. A flow rate of 8.5 ± 0.5 ml/min was used with a 50m x 0.53mm x 10μm Alumina-PLOT capillary column for Method 2. The columns employed in both methods have the capability to separate both polar and non-polar compounds; however, Method 2 is incapable of detecting non-combustible compounds due to the method's detection technique (i.e., FID). Crushing is carried out at elevated temperature (~105-110^{o}C) in order to ensure that instantaneous volitization of the entrapped fluids (including H_2O) is achieved. Calibration was performed using a number of standard gas mixtures supplied by Matheson Tri-Gas.

Stainless steel, hydraulically driven rock crushers (Figure 2.3) were custom made by the University of Toronto Machine Shop using schematics outlined by Bray and Spooner (1992) and Bray *et al.* (1991), which are adapted from original designs by Andrawes and Gibson (1979) and Andrawes *et al.* (1984). A crusher consists of a basal block in which the upper portion of the crusher is inserted. The basal unit houses two cartridge heaters. The upper unit of the crusher consists of a cylinder and piston assembly. Upon crushing, the piston is driven downward into the sample cavity through the use of an Enerpac$^{®}$ hydraulic ram pressurized by a manually driven hand pump. Viton$^{®}$ fluoroelastomer o-rings seal the sample cavity from the external atmosphere and allow the upper portion of the crusher apparatus housing the piston to be pressurized to a slightly lower pressure with the same gas used as the carrier gas. This provides extra protection from atmospheric contamination of the sample cavity, especially when the piston is in motion (i.e., during a crush).

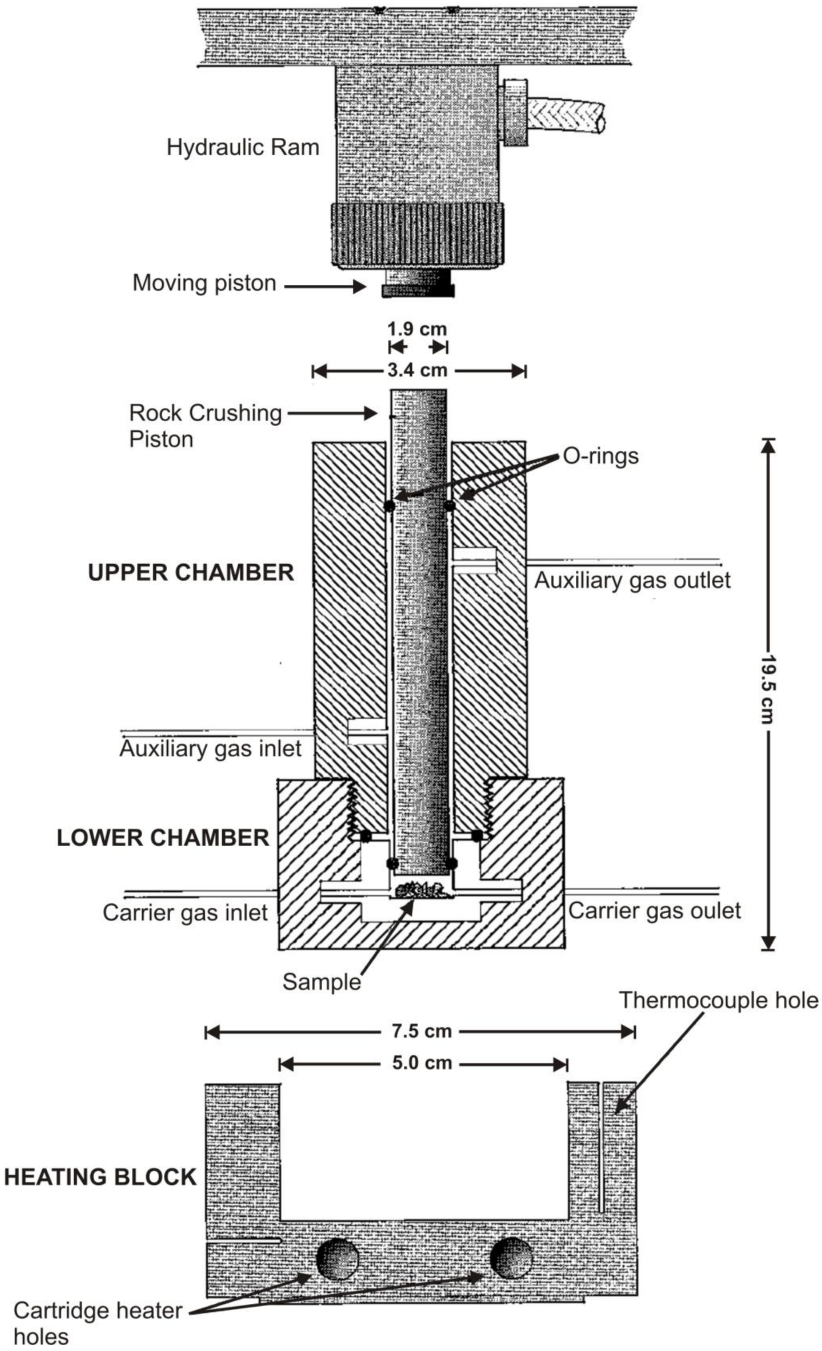


Figure 2.3: Schematic of the rock crushing apparatus used in the gas chromatographic system at Saint Mary's University. Crusher schematic image was adapted from original image made by Salvi and Williams-Jones (1997b, 2003). Original designs developed by Andrawes and Gibson (1979), Andrawes et al. (1984) and Bray et al. (1991).

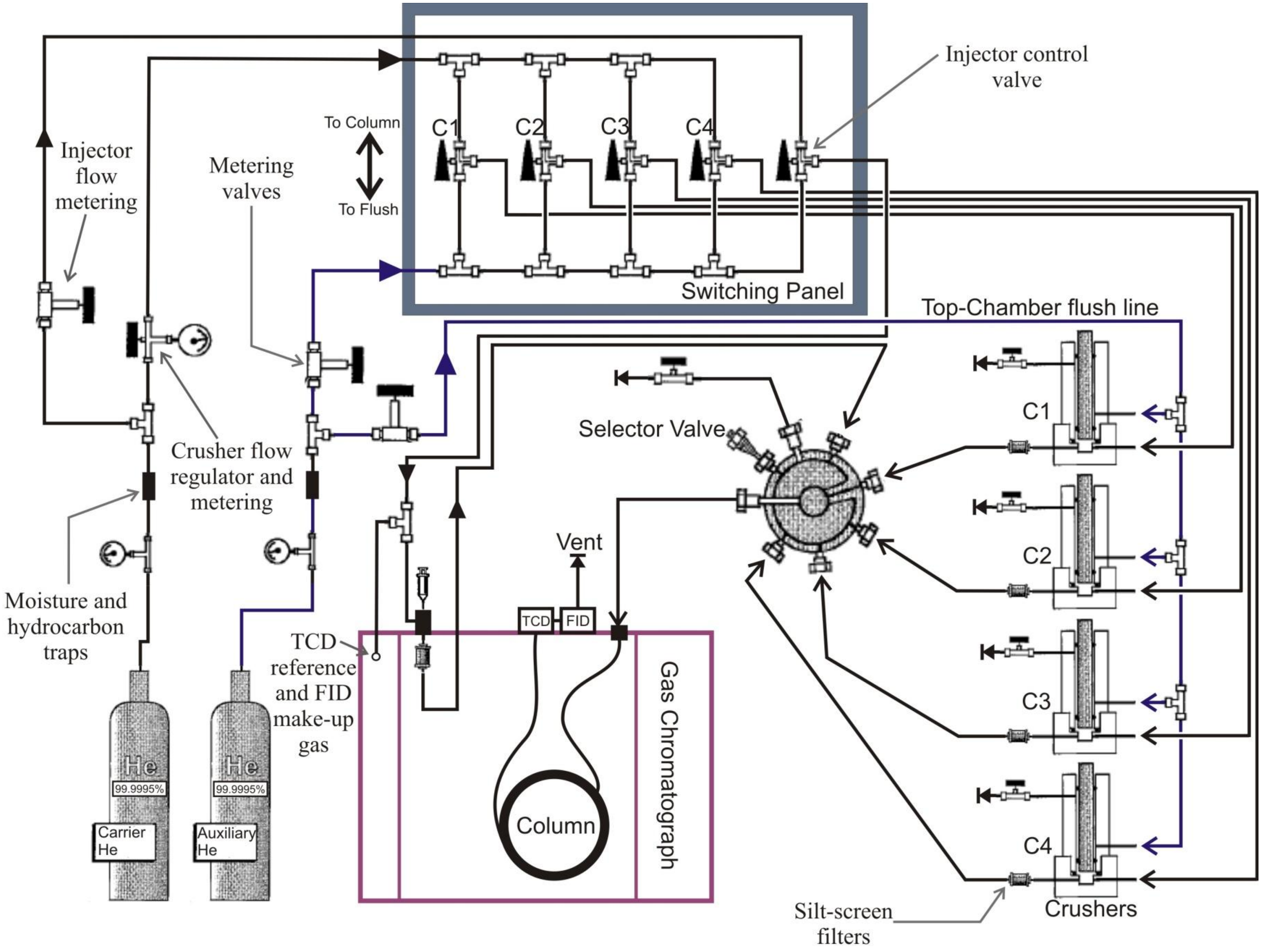

Injector flow metering
Metering valves
To Column
To Flush
C1
C2
C3
C4
Injector control valve
Switching Panel
Top-Chamber flush line
Crusher flow regulator and metering
Selector Valve
Moisture and hydrocarbon traps
Vent
TCD
FID
TCD reference and FID make-up gas
He
99.9995%
Carrier He
He
99.9995%
Auxiliary He
Column
Gas Chromatograph
C1
C2
C3
C4
Crushers
Silt-screen filters

Figure 2.4 (previous page): Schematic of the in-line rock crushing gas chromatographic system at Saint Mary's University employed in this study. Schematic was adapted from designs by Salvi and Williams-Jones (1997b, 2003), which was in turn developed from designs from Bray et al. (1991) and Andrawes et al. (1979).

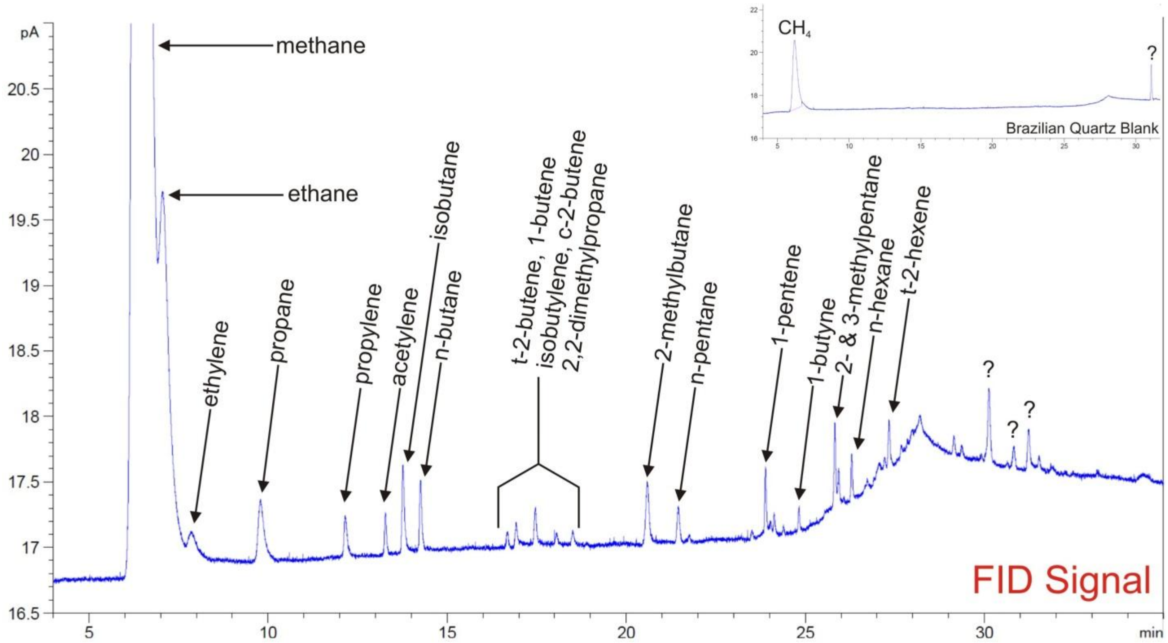


Figure 2.5: Sample gas chromatogram from crushed quartz sample illustrating high level of hydrocarbon speciation. Sample characteristics and identity is beyond the scope of this study but was used due to its high level of hydrocarbon speciation. Blanks were acquired from identically prepared inclusion free Brazilian quartz (see inlay). Peaks labelled with question marks are not yet identified. Collected with Method 2.

2.2.3 Sample preparation

Rock samples were prepared by first fragmenting the rocks into chips approximately 1-3 mm in maximum dimension using a jaw crusher. The rock fragments were weighed (~0.7 grams) and sonicated in de-ionized water for ~30 minutes. The samples were washed 2 times after sonication with additional de-ionized water to ensure the removal of all adsorbed acids and organic solvents. The samples were then dried on a hot plate (~50-60^{o}C) and inserted into the pre-cleaned crushers. Crusher sample chambers were cleaned with acetone and crusher pistons were cleaned with isopropynol since the fluorocarbon o-rings used on the piston are sensitive to acetone. Crushers were thoroughly dried with compressed air after solvent cleaning. A small amount of inert and volatile-free silicone grease was placed around crusher o-rings and the crushers were then sealed and heated overnight (~10-15 hours; ~100-110^{o}C) under dynamic He flow (≤ 2 ml/min) in order to remove any adsorbed compounds including water and cleaning solvents. Brazilian quartz blanks were fractured, hand-picked and cleaned in the same way as all other samples. This background was averaged and subtracted from the collected chromatograms.

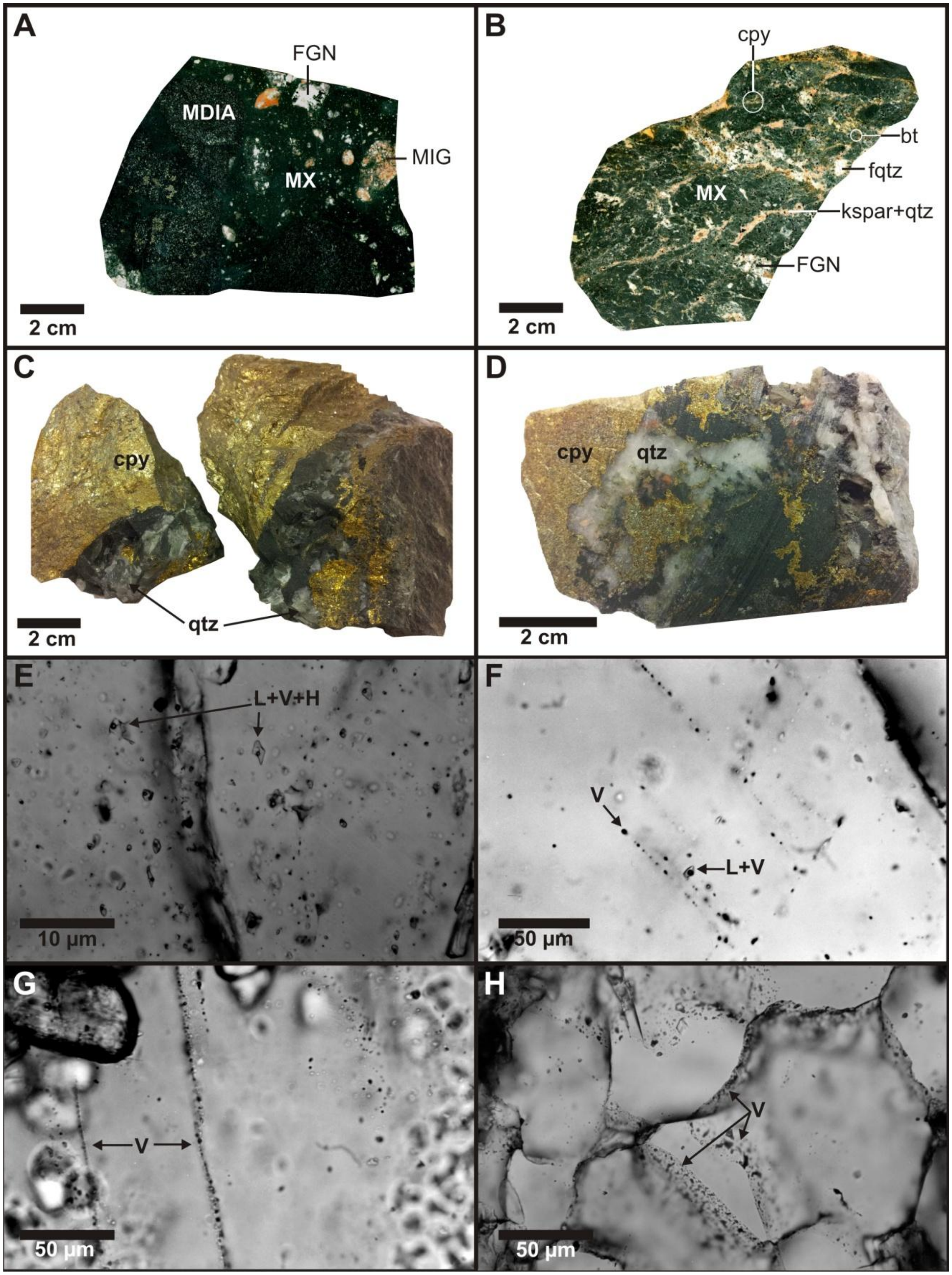
2.2.4 Methodology for the evaluation of the effects of sample preparation on GC analyses

Experiments were performed to determine if the pre-crush sonication and heating practices has any effect on the volatile hydrocarbon abundances and speciation in the samples. Four aliquots of quartz, from hydrocarbon-bearing quartz + sulfide assemblages weighing 0.7 grams each were prepared. This quartz sample is unrelated to the scope of this study but was chosen to be used for this experiment based on the large trace hydrocarbon speciation it possesses, allowing us to more clearly determine what effect, if any, heating and sonication has on the hydrocarbon signature. Of these 4 samples, 2 (MK-full) were prepared and analyzed in the standard fashion of sonicating and heating prior to crushing. One sample was employed to investigate the effects of sonication and another to investigate the effects of heating on the hydrocarbon signature. All four samples are prepared in an identical manner to all other samples prior to sonication and heating (i.e., fragmented and placed into glass vials and pre-washed twice with de-ionized water). (1) Sonication trial: rather than any sonication, sample ‘MK-nosoni’ was simply washed twice with de-ionized water. The sample was placed in a cleaned crusher and heated to ~110^{o}C overnight (~10-15 hours) prior to analysis. (2) Heating trial: sample MK-noheat was identically washed and sonicated for ~30 minutes. This sample was dried on a hot plate at a low setting (~50^{o}C) and placed in an un-heated cleaned crusher overnight.

2.3 Results

2.3.1 Petrographic characterization of samples

Characteristic samples of Sudbury breccia from mineralized and barren environments were investigated petrographically. Characteristics of mineralized and barren Sudbury breccia hand samples are illustrated in Figure 2.6. Petrographic investigation of quartz-hosted fluid inclusions within clasts in Sudbury breccias was performed. Analysis of breccias samples demonstrated that there is no visibly discernable difference in the abundance of fluid inclusions in breccia from mineralized versus barren environments. However, intensive petrographic investigation (i.e point counting) of many samples from each breccia environment must be performed to fully confirm this conclusion. Also, this conclusion relies on the assumption that the abundance and characteristics of fluid inclusions hosted in the matrix of the breccias is similar to that present in the corresponding clasts. The quartz within quartz-rich clasts in Sudbury breccia from mineralized and barren environments is host to three distinct fluid inclusion assemblages (Figure 2.6): (i) Three-phase aqueous inclusions (V+L+H) of unclassified origin (i.e., do not possess clear characteristics of either primary or secondary origin) containing a small vapour bubble, a halite cube and brine. These inclusions are very rare (< ~1% of total visual inclusions) and do not occur in the same inclusion trails as other fluid inclusion assemblages of noted secondary origin; (ii) two-phase, low salinity aqueous inclusions (V+L) of secondary origin that are found along healed fractures. This inclusion type represents approximately 10% of total visible fluid inclusions in breccia clasts; and (iii) one-phase vapour-only inclusions (V) of secondary origin that are found ubiquitously throughout breccia clasts (~ 90%) and in association with the less abundant two-phase inclusions. One-phase vapour-only inclusions also commonly occur in significant abundance along quartz grain boundaries (Figure 2.6H). Quartz within breccia-hosted clasts from barren environments does not possess the same degree of recystallization as that from mineralized environments and the quartz grains are generally larger in barren locations. Gas chromatographic analysis of breccia samples only used portions of extracted matrix material, which is presumably enriched with the same fluids entrapped within quartz along grain boundaries and microscopic pockets in the breccia matrix.


A
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2 cm
D
cpy
qtz
2 cm
E
L+V+H
10 µm
F
V
L+V
50 µm
G
V
50 µm
H
V
50 µm

Figure 2.6 (previous page): Representative hand samples of Sudbury breccia and PGE-rich quartz + sulfide assemblages, and fluid inclusion images from residual, quartz-bearing Sudbury breccia clasts. ***A* –** A hand sample of fresh, unaltered SUBX sampled from study area SB15 (see Figure 1B). The breccia matrix (mx) is very fine grained and glassy with little to no evidence of metamorphic alteration/events (i.e., no contact metamorphic evidence). Clasts include felsic gneiss (FGN), migmatite (MIG), meta-diabase (MDIA) and all display sharp contact with matrix. ***B* –** A hand sample of SUBX from a mineralized environment showing evidence of thermal metamorphism. Sampled from a study area adjacent to JHB08 and JHB202 from the Barnet Showing (see Figure 1A). The matrix is lighter in colour than barren breccia counterparts and shows clear evidence of having been recrystallized. Evidence of biotite (bt), fluidal patched of "flood" quartz (fqtz) and symplectic intergrowths of quartz and potassic feldspar (kspar+qtz) is found in the matrix. FGN clasts display fluidal contacts with host matrix. Disseminated chalcopyrite (cpy) replaces clasts and matrix material via the replacement of felsic material, feldspar and quartz. Figure samples and details adapted from work done by Hanley et al. (2004). ***C*** – UG3750(#0) hand specimen (constitutes a PGE-rich quartz + massive sulfide assemblage). Texturally, quartz post-dates the emplacement of the massive sulfides. UG samples were collected directly from underground at the Levack Mine. ***D*** - MK4209 (MK4209-1) hand specimen was collected from drill core (drill core ID: FNX4209; constitutes a PGE-rich quartz + massive sulfide assemblage). Texturally, quartz post-dates the emplacement of the massive sulfides. Only 2 of the 5 PGE-rich quartz + sulfide assemblage samples are illustrated in this image. ***E* –** Three-phase (L+V+H; H represents halite) inclusions of unknown origin (no conclusive evidence of primary or secondary origin) in quartz. Three-phase assemblages are very rare and occur in an abundance >1%. ***F*** – Secondary fluid inclusion trails of one- and two-phase inclusions in quartz. One-phase inclusions dominate representing approximartly 90% of total visible fluid inclusions. ***G*** – Secondary inclusion trails of one-phase, vapour-only fluid inclusions in quartz. ***H*** – One-phase, vapour-only inclusions hosted along quartz grain boundaries.

2.3.2 Hydrocarbon abundances and fluid characteristics

All samples analyzed contain detectible amounts of hydrocarbon fluid but the abundance of this fluid and the abundance of individual hydrocarbon species contained in it was found to vary between sample populations. Analysis of Sudbury breccia from a mineralized embayment footwall package (KGHM International Ltd./Quadra FNX Mining Ltd. Levack and McCreedy West properties) known to contain sharp-walled high-sulfide and low-sulfide hydrothermal vein stockworks (Farrow and Watkinson, 1992; Morrison et al., 1994; Farrow and Watkinson, 1997; Farrow and Watkinson, 1999; Watkinson, 1999; Farrow and Lightfoot, 2002; Legault et al., 2003) were found to be statistically more abundant in hydrocarbons than samples of barren Sudbury breccia distal to footwall sulfide mineralization (Windy Lake region, North Range and Wanapitae Lake region, East Range). This result was most pronounced between the saturated hydrocarbons methane, ethane, propane and butane (Figure 2.7). Two-tailed t-tests illustrate that statistically significant differences are present between the populations of Sudbury breccia from mineralized and barren environments. This result indicates that the average total abundance of light volatile hydrocarbons trapped in breccia from a mineralized package/environment is higher than that in breccia from distal, non-mineralized environments.

Table 2.1: T-test results from mineralized (n=410) versus barren (n=45) Sudbury breccia populations. Alpha value (α) set at 0.05.

	Methane CH_4	**Ethane** C_2H_6	**Propane** C_3H_8	**Butane** C_4H_{10}
P(two-tailed) $\alpha = 0.05$	1.93E-28	5.62E-28	8.05E-24	3.67E-13

No statistical difference was observed between the average unsaturated to saturated hydrocarbon ratios (unsat:sat HC; two-tailed t-test: $\alpha = 0.05$, $P = 0.36$) of the Sudbury breccia populations (Figure 2.8). A very distinct and statistically significant increase in this ratio is observed in fluid from samples of quartz from PGE-rich environments. A small distinction is present when observing the ratio of average propylene to propane ratios between mineralizated and barren breccia populations (two-tailed t-test: $\alpha = 0.05$, $P = 0.022$). Similarly, a statistical difference is present between the average propylene to propane ratio of samples from PGE-rich environments and the breccia populations. Although no statistically significant distinction is present between the *average* unsaturated to saturated hydrocarbon and propylene to propane ratios between the Sudbury breccia populations, a statistical difference is present when considering the *range* of values present in each population. Ratios are more variable (i.e., data covers a larger breadth) in mineralized breccia and PGE-rich quartz populations than the barren breccia population.

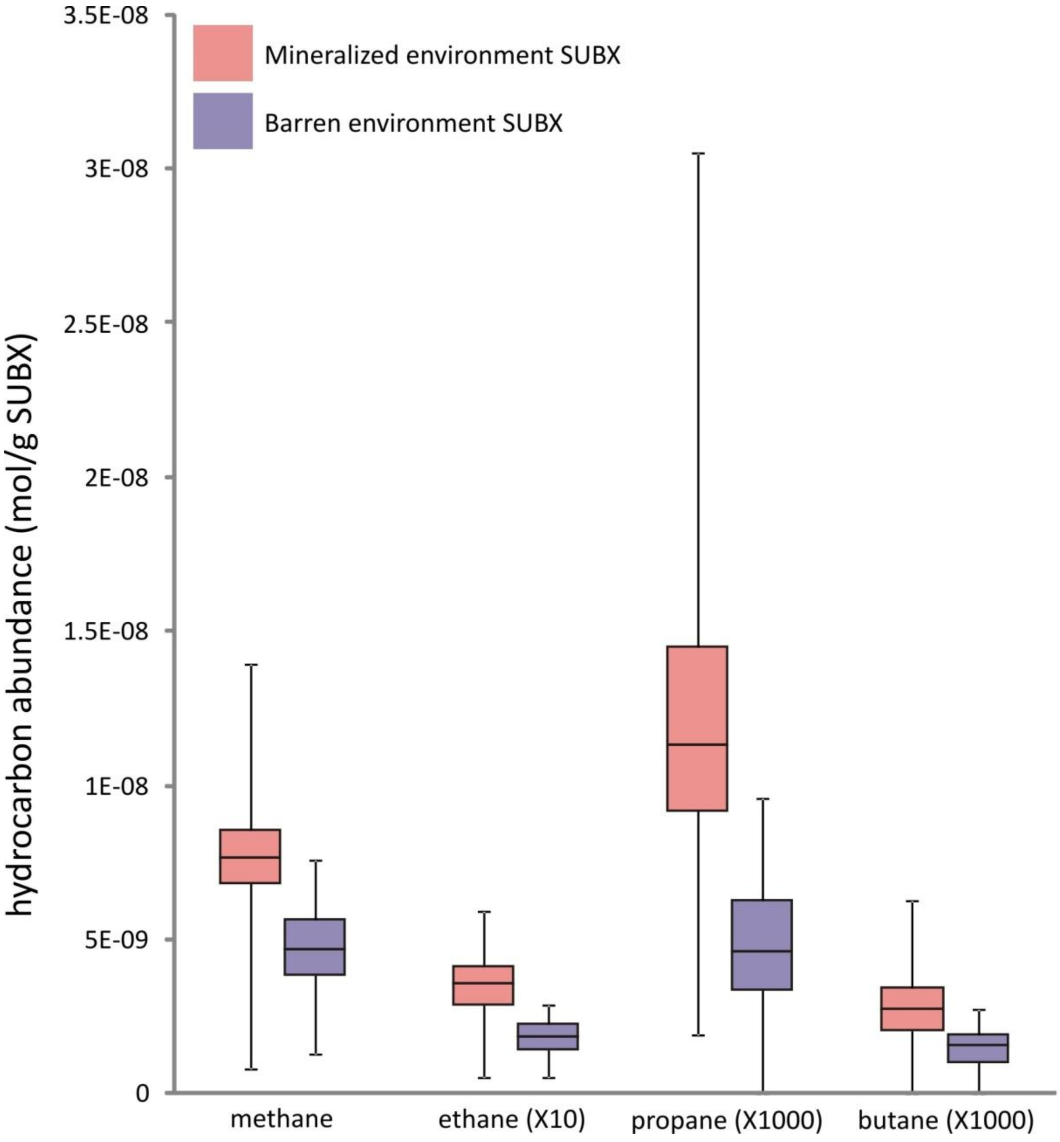


Figure 2.7: Box and whisker plot of hydrocarbon abundances for methane, ethane, propane and butane of fluid trapped in Sudbury breccia (SUBX) from mineralized (n=410) and barren (n=45) environments. Hydrocarbon abundances from sulfide mineralization associated SUBX populations consistently show statistically higher abundances than barren SUBX populations. Also, mineralized SUBX populations have larger ranges of HC abundances than barren SUBX populations.

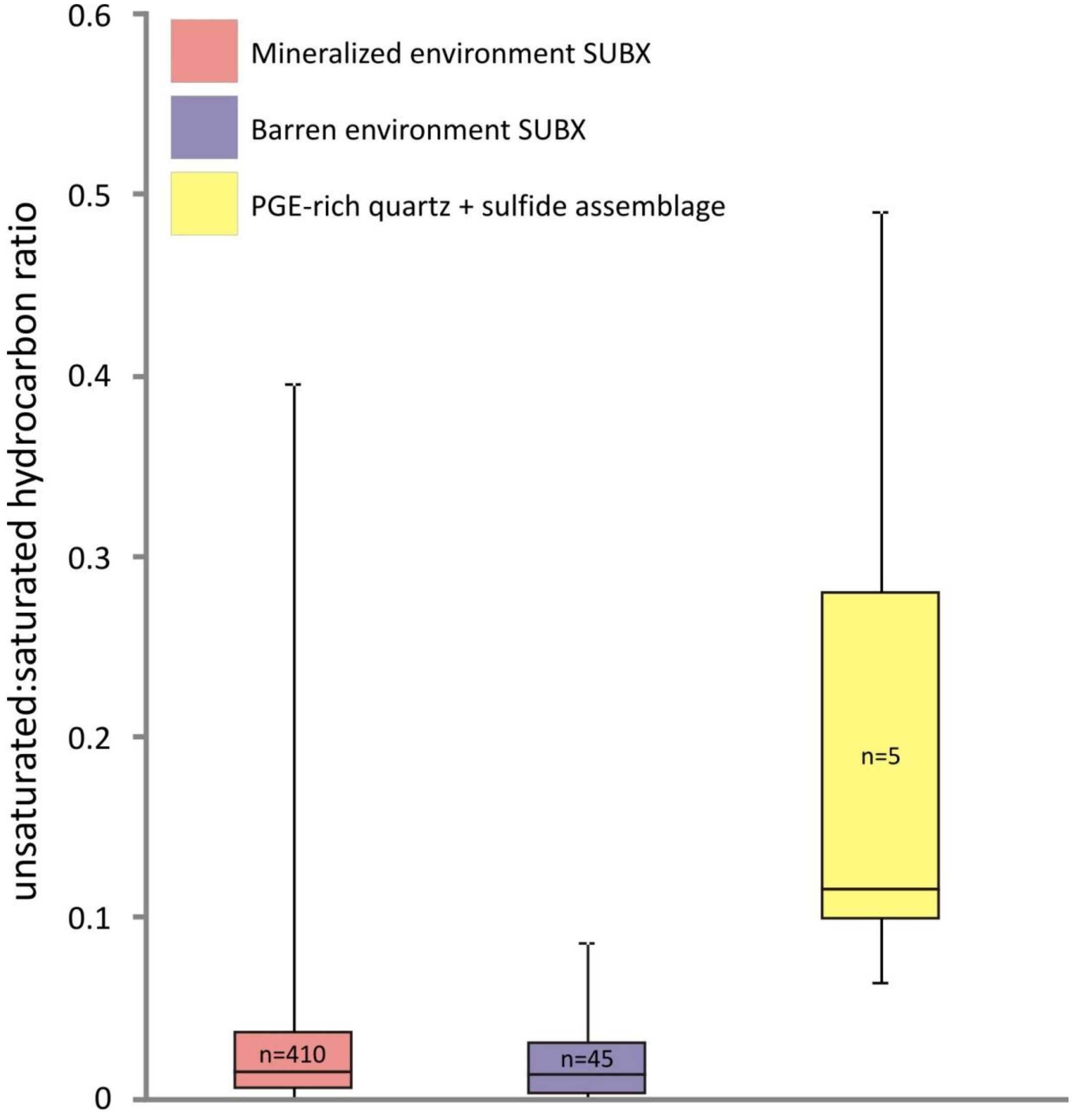


Figure 2.8: Box and whisker plot of the unsaturated to saturated hydrocarbon ratios of Sudbury breccia (SUBX) from mineralized and barren environments, and quartz from PGE-rich quartz + massive sulfide alteration assemblages. SUBX populations possess very similar average ratios to one another. No statistically significant difference between the populations is present, but the range of values for the mineralized SUBX is larger than that of barren SUBX. Unsaturated to saturated HC ratios of fluid from PGE-rich quartz assemblages are on average significantly higher than that of both SUBX environments.

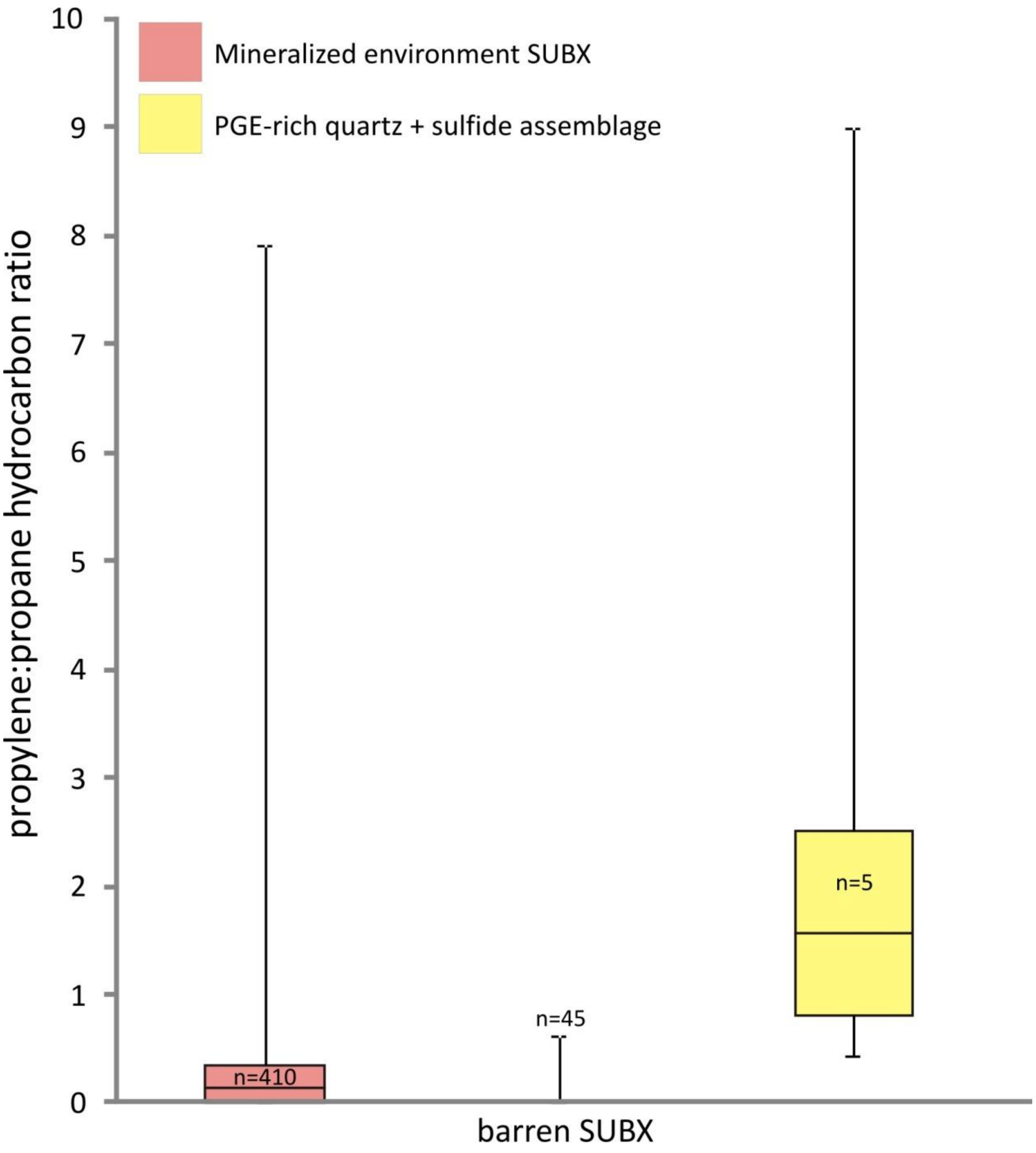


Figure 2.9: Box and whisker plot of the propylene to propane hydrocarbon ratios of Sudbury breccia (SUBX) from mineralized and barren environments and quartz from PGE-rich quartz + massive sulfide alteration assemblages. The ratios from SUBX associated with sulfide mineralization has a higher average value and a much larger range of values than barren SUBX samples. Propylene to propane ratios of fluid from PGE-rich quartz assemblage samples are on average significantly higher than that of both SUBX environments.

2.3.3 Genetic relationships and trends in light hydrocarbon abundances

Upon normalization to total hydrocarbon abundance, a consistent and linear trend is present between the mole% of methane (C1) and the C2 hydrocarbons (i.e., ethane ± ethylene ± acetylene) in the hydrocarbon fluids in all of the rock types associated with the Sudbury Igneous Complex and its footwall lithologies. As the mole% of methane in the system decreases, the mole% of the C2 hydrocarbons increases proportionally, suggesting a potential genetic relationship between methane and the higher order hydrocarbons (namely the C2 hydrocarbons in this case). This trend is also present to a lesser degree between methane and the C3 hydrocarbons (i.e., propane ± propylene). As the mole% of methane decreases, the mole% of the C3 hydrocarbons increases. Deviations from these trends are present in samples from PGE/PGM-rich environments and from a number Sudbury breccia samples from mineralized environments (Figure 2.10, labelled 1-4). Core logs report that the 4 mineralized Sudbury breccia samples found to deviate the most are either enriched in PGE themselves (Pt and Pd), very close (within 20’) to areas of PGE enrichment (i.e., massive sulfide veinlets or disseminated sulfides; assays acquired from KGHM International Ltd./Quadra FNX Mining Ltd. core logs), or have been subjected to recrystallization or secondary alteration events. No samples from barren Sudbury breccia or samples from SIC rocks or its country rock lithologies are found to deviate from the trends.

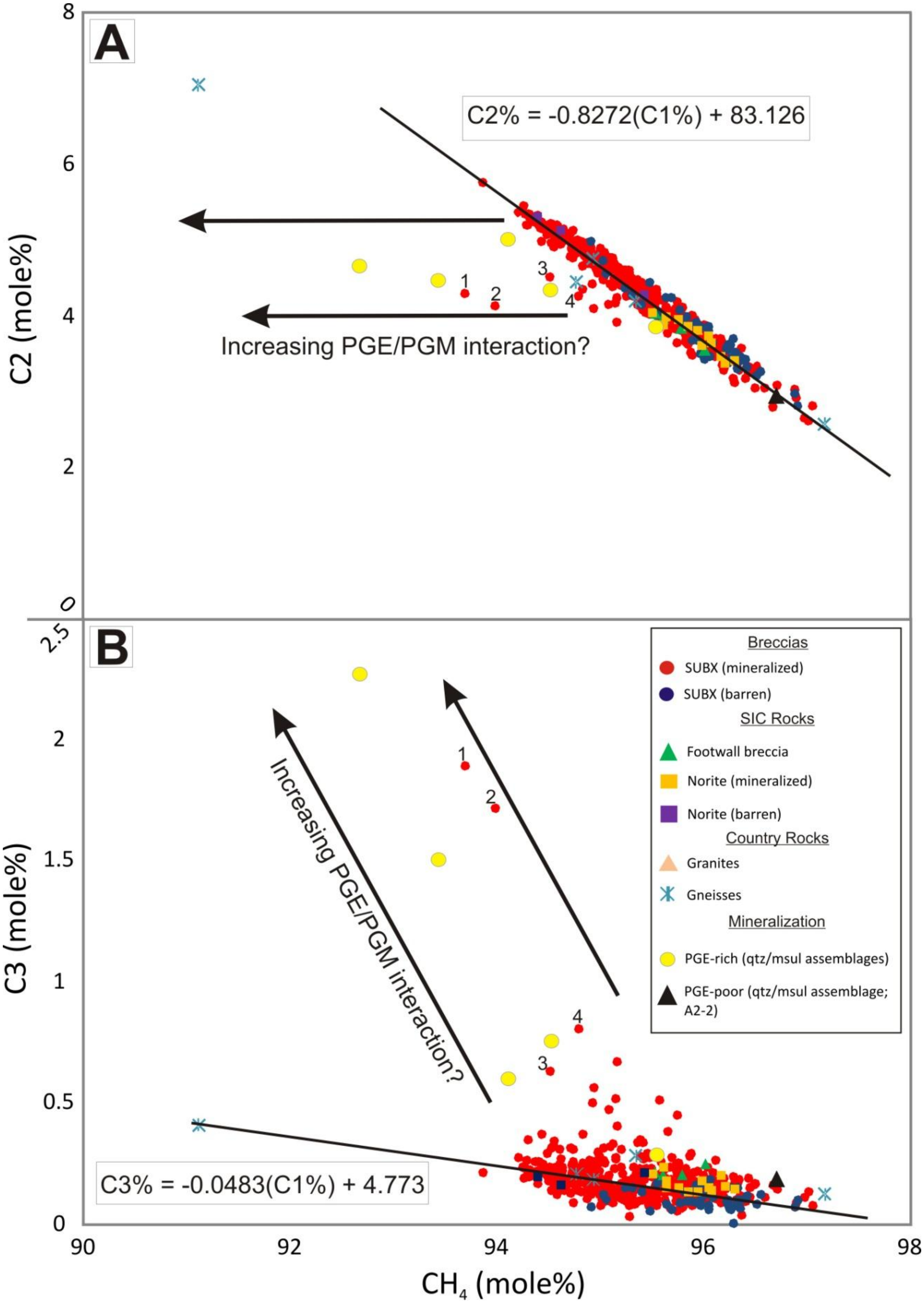
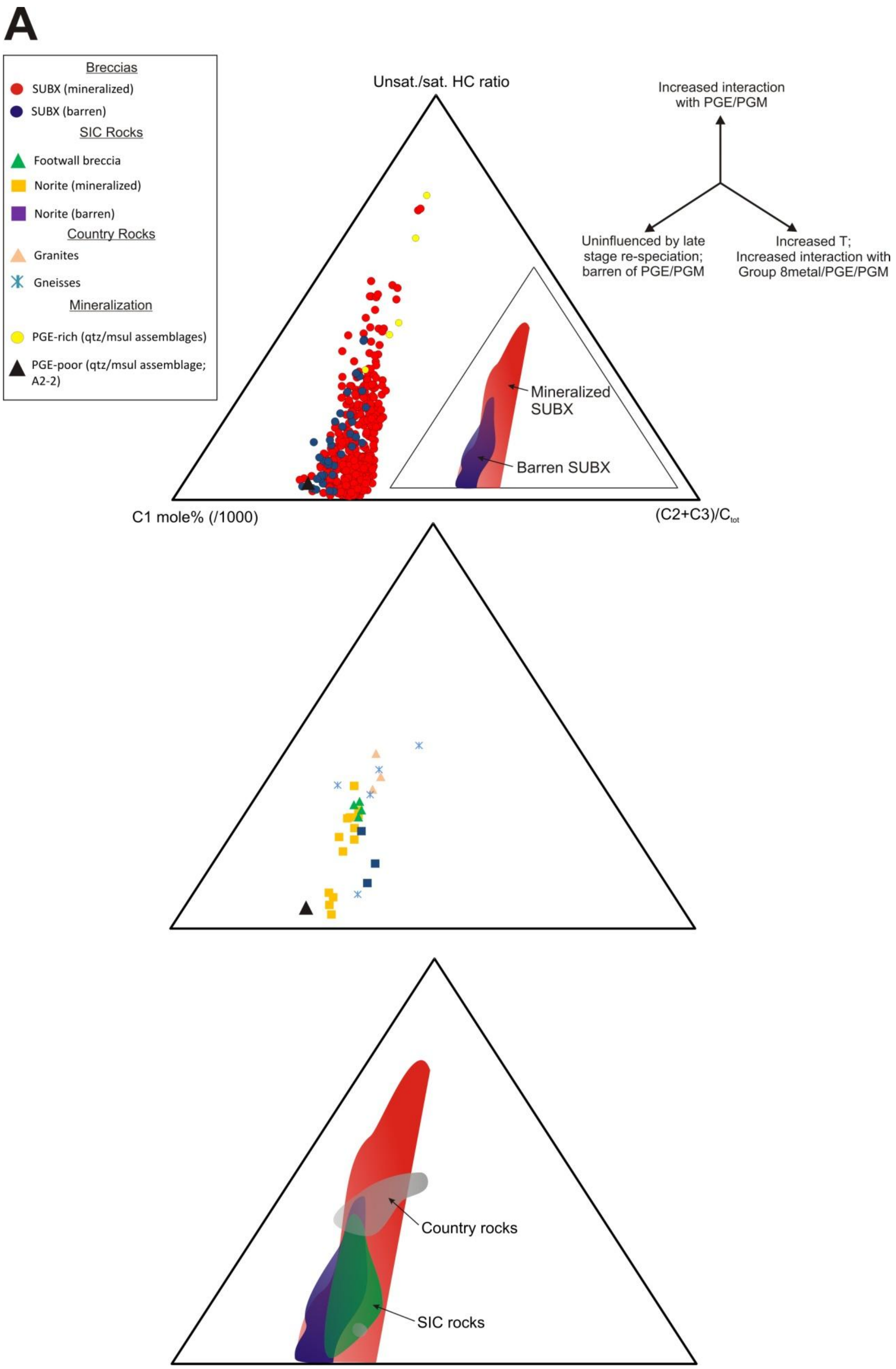
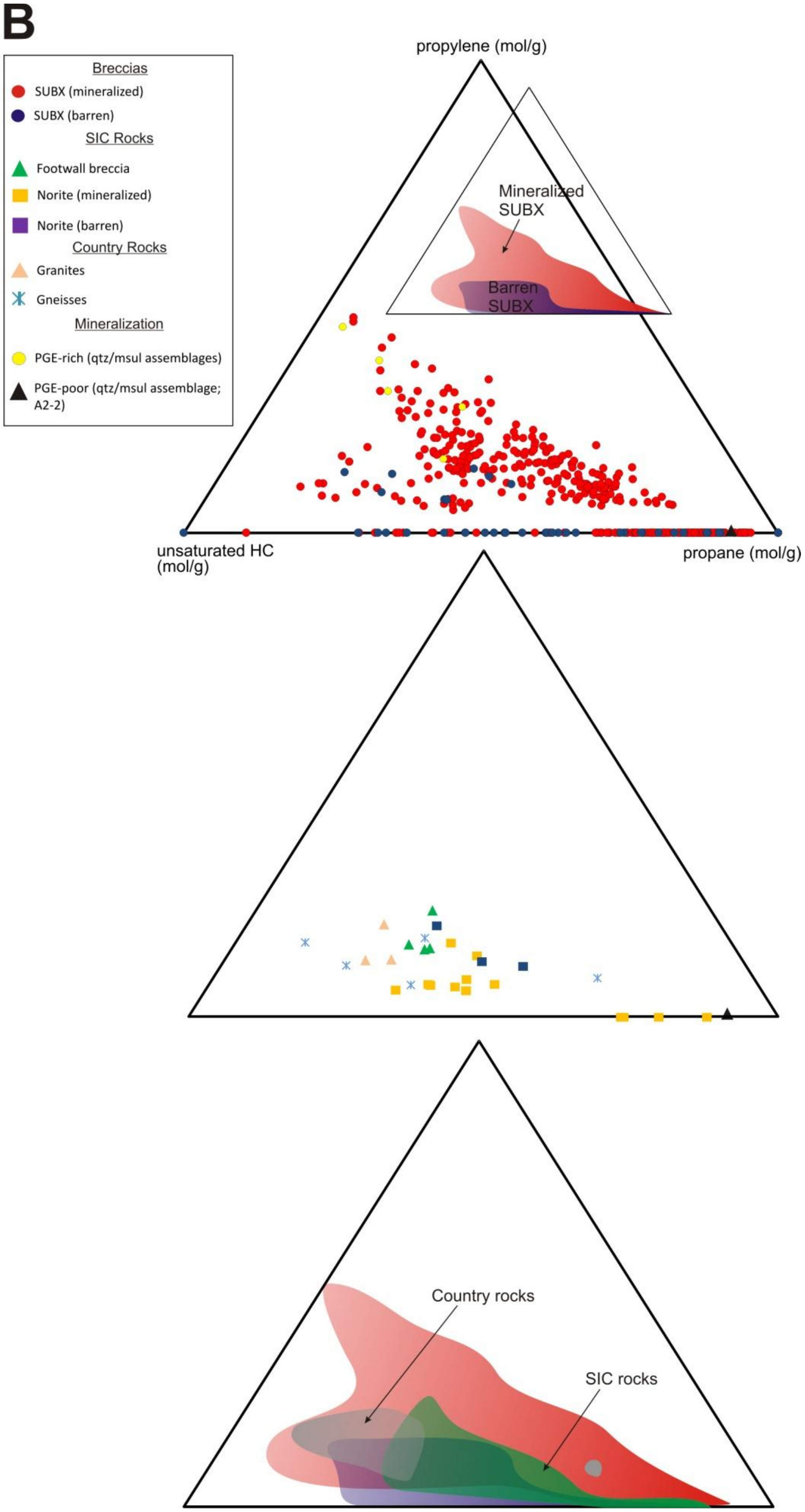

A
C2% = -0.8272(C1%) + 83.126
Increasing PGE/PGM interaction?
1
2
3
4
C2 (mole%)
8
6
4
2
0
B
C3% = -0.0483(C1%) + 4.773
Increasing PGE/PGM interaction?
1
2
3
4
C3 (mole%)
2.5
2
1.5
1
0.5
0
90
92
94
96
98
CH$_4$ (mole%)
Breccias
● SUBX (mineralized)
● SUBX (barren)
SIC Rocks
▲ Footwall breccia
■ Norite (mineralized)
■ Norite (barren)
Country Rocks
▲ Granites
✳ Gneisses
Mineralization
● PGE-rich (qtz/msul assemblages)
▲ PGE-poor (qtz/msul assemblage; A2-2)

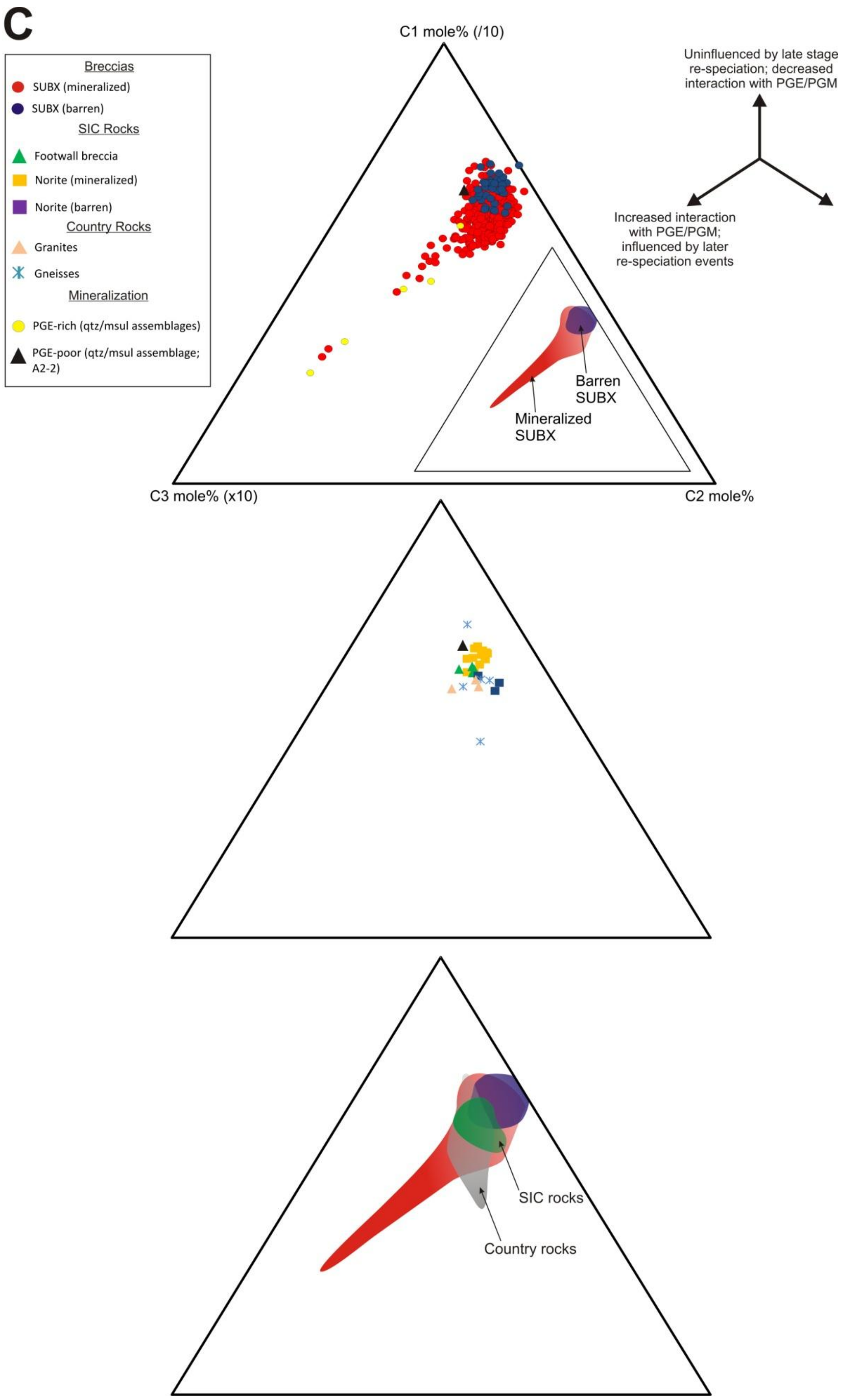
Figure 2.10: (previous page): ***A*** **- C1 versus C2 hydrocarbon molar% of analyzed samples from all environments.** ***B*** **– C1 versus C3 hydrocarbon molar% of analyzed samples.** Note that C2 and C3 represent total abundances of all 2-carbon, and 3-carbon containing species, respectively. Normalized to total hydrocarbon abundance. Sample A2-2 is a quartz sample from a PGE-poor quartz + massive sulfide + epidote assemblage. PGE-rich samples represent quartz from quartz + massive sulfide ± epidote assemblages. Samples that have been found to possess elevated PGE concentrations deviate from the trend as illustrated by the arrows. Four samples of SUBX from the mineralized sample set have been identified as most prominently in the region suspected to represent the either presence of elevated PGE concentrations or secondary respeciation of CH_4 to CO_2, effectively reducing the CH_4 concentrations. KGHM International Ltd./Quadra FNX Mining Ltd. core logs of these samples show the following: Sample 1: FNX7249, sampled at 868 ft., weak pervasive K-feldspar alteration, assay 865-870 ft: 0.04 gpt Pt & 0.04 gpt Pd (~20’ away from enrichment of 0.12 gpt Pt and 0.17 gpt Pd); Sample 2: FNX7119, sampled at 84.5 ft., ~20 ft away from reported moderate pervasive epidote alteration, adjacent to disseminated cpy veinlets, assay 82.6-84 ft: 0.15 gpt Pt & 0.08 gpt Pd; Sample 3: FNX7067, sampled at 418 ft., strong pervasive epidote alteration and recrystallization texture, calcite veinlets present, 411-424 ft disseminated cpy and mlt at 3% and 5% respectively, assay 416.5-419.5 ft: 0.11 gpt Pt & 0.13 gpt Pd; Sample 4: FNX6113, sampled at 1126 ft., SUBX veins partially recrystallized, assay 1124.7-1129.7 ft: 0.02 gpt Pt & 0.02 gpt Pd (structurally related to Pt & Pd enrichment not noted in drill core?).

2.3.4 Hydrocarbon ternary plots for use as exploratory/discriminatory criteria

The quartz samples from PGE-rich environments and the PGE-enriched Sudbury breccia samples that deviate from the expected trends in hydrocarbon abundance binary plots were also found to deviate from expected clustering in a number of ternary plots. These particular samples possess elevated unsaturated hydrocarbon abundances and C3/C1 ratios. Figures 2.11A and 2.11B show the consistent enrichment of total unsaturated hydrocarbons and propylene in fluid hosted in quartz from PGE-rich environments, respectively. Additionally, figures 2.11C and 2.11D show consistent deviation toward the C3%(x10) and C3/C1 apices of the aforementioned samples. The best distinction between the mineralized and barren Sudbury breccia fields was found in Figures 2.11B and 2.11C and to a lesser extent in Figures 2.11A and 12D. The best distinction is achieved when taking into account the C3 hydrocarbons either as the molar% or C3/C1 hydrocarbon ratio. This is supported by the data illustrated in the hydrocarbon abundance box and whisker plot (Figure 2.7) in which the difference in propane abundance between breccia populations is most pronounced. In all instances the analyses of SIC rocks and country/footwall rocks overlapped with the breccia fields. The country rocks (Levack Gneiss, granite) were found to possess a larger abundance of unsaturated hydrocarbons than the SIC lithologies (norite, footwall breccia) (Figures 2.11A and 2.11B).


A
Breccias
SUBX (mineralized)
SUBX (barren)
SIC Rocks
Footwall breccia
Norite (mineralized)
Norite (barren)
Country Rocks
Granites
Gneisses
Mineralization
PGE-rich (qtz/msul assemblages)
PGE-poor (qtz/msul assemblage; A2-2)
Unsat./sat. HC ratio
C1 mole% (/1000)
(C2+C3)/C$_{tot}$
Increased interaction with PGE/PGM
Uninfluenced by late stage re-speciation; barren of PGE/PGM
Increased T; Increased interaction with Group 8metal/PGE/PGM
Mineralized SUBX
Barren SUBX
Country rocks
SIC rocks


B
Breccias
SUBX (mineralized)
SUBX (barren)
SIC Rocks
Footwall breccia
Norite (mineralized)
Norite (barren)
Country Rocks
Granites
Gneisses
Mineralization
PGE-rich (qtz/msul assemblages)
PGE-poor (qtz/msul assemblage; A2-2)
propylene (mol/g)
Mineralized SUBX
Barren SUBX
unsaturated HC (mol/g)
propane (mol/g)
Country rocks
SIC rocks


C
C1 mole% (/10)
C3 mole% (x10)
C2 mole%
Breccias
● SUBX (mineralized)
● SUBX (barren)
SIC Rocks
▲ Footwall breccia
■ Norite (mineralized)
■ Norite (barren)
Country Rocks
▲ Granites
✳ Gneisses
Mineralization
● PGE-rich (qtz/msul assemblages)
▲ PGE-poor (qtz/msul assemblage; A2-2)
Uninfluenced by late stage re-speciation; decreased interaction with PGE/PGM
Increased interaction with PGE/PGM; influenced by later re-speciation events
Barren SUBX
Mineralized SUBX
SIC rocks
Country rocks

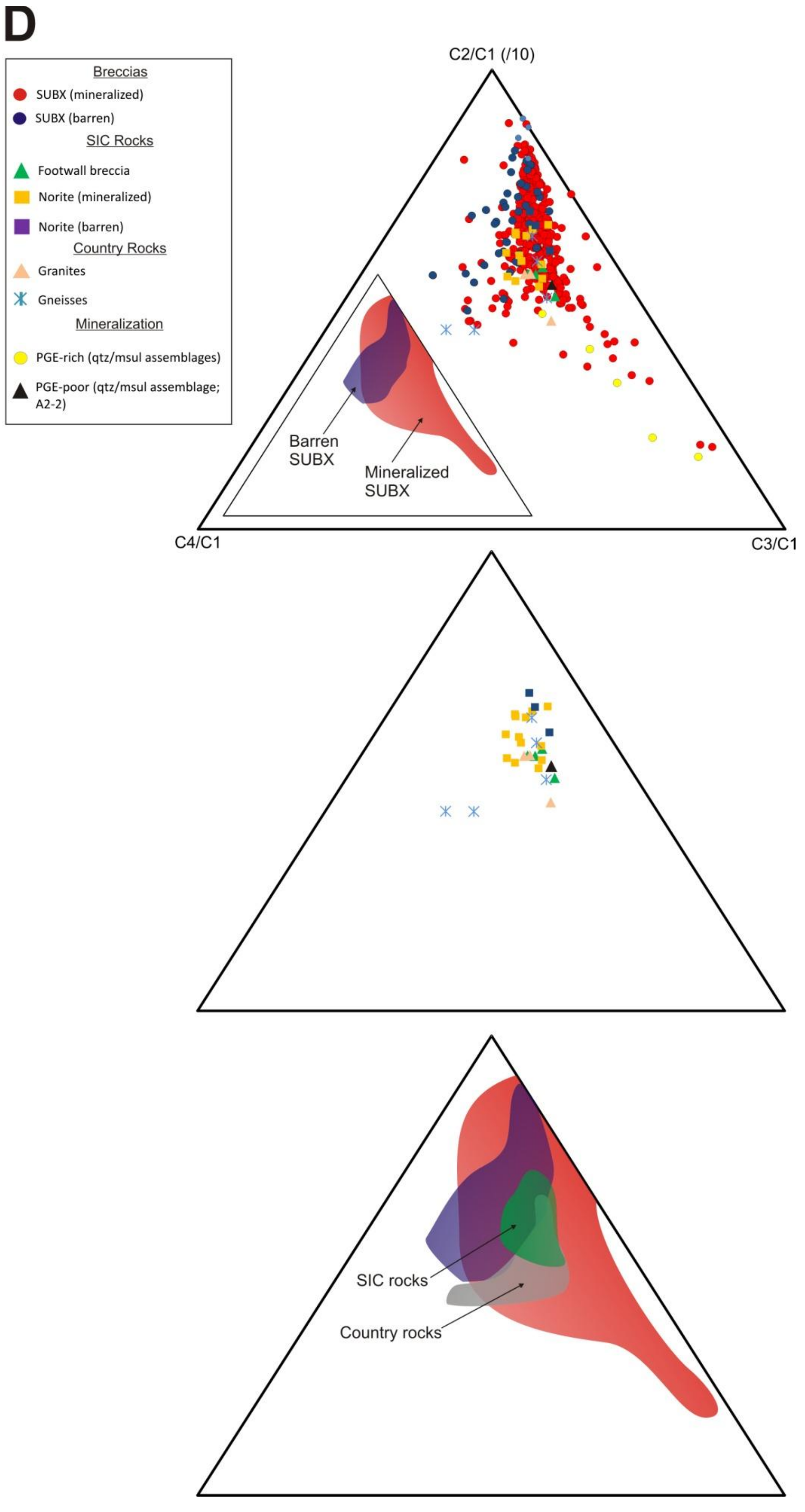

D
Breccias
SUBX (mineralized)
SUBX (barren)
SIC Rocks
Footwall breccia
Norite (mineralized)
Norite (barren)
Country Rocks
Granites
Gneisses
Mineralization
PGE-rich (qtz/msul assemblages)
PGE-poor (qtz/msul assemblage; A2-2)
C2/C1 (/10)
C4/C1
C3/C1
Barren SUBX
Mineralized SUBX
SIC rocks
Country rocks

Figure 2.11: (pages 58-62) Hydrocarbon ternary diagrams showing analyzed samples from all environments. Fields were made by tracing the full extent of sample distribution. Variable field shading is used to clearly show each field. Note that C2, C3 and C4 represent total abundance of 2-carbon, 3-carbon and 4-carbon containing species, respectively. ***A* -** unsaturated to saturated hydrocarbon ratio versus methane mole% (C1%) divided by a factor of 1000 versus (C2+C3)/C_{tot} (C2 and C3 hydrocarbons divided by the total hydrocarbon abundance. ***B* -** propylene abundance versus the propane abundance versus the total unsaturated hydrocarbon abundance (all in mol/g of rock). ***C* -** hydrocarbon abundance in mole% of methane (C1) versus the C2 hydrocarbons versus the C3 hydrocarbons (multiplied by a factor of 10). ***D* -** hydrocarbon ratios C2/C1 (divided by a factor of 10) versus C3/C3 versus C4/C1. Note that C2, C3 and C4 represent total abundances of all detected hydrocarbons possessing 2, 3 and 4 carbon atoms, respectively.

2.3.5 Evaluation of the effects of sample preparation on GC analyses

Sample preparation variation trials showed that sonication has no distinctly noticeable effect on the hydrocarbon signature of the samples. Total hydrocarbon abundances were very close in both the sonicated (2.36×10^{-8} mol/g) and non-sonicated (2.29×10^{-08} mol/g) samples, differing by only 6.64×10^{-10} mol/g. Additionally, the hydrocarbon speciation was identical in the sonicated and non-sonicated samples, indicating that sonication does not alter the original hydrocarbon signature of the samples, at least when used for brief periods of time. The unheated sample was found to vary from heated samples. The speciation of this sample had a lower abundance of unsaturated hydrocarbon species and was slightly less abundant in total hydrocarbon content. Heated samples possessed an average unsaturated hydrocarbon abundance of 4.09×10^{-11} mol/g, while the unheated sample was found to have 1.35×10^{-11} mol/g of unsaturated hydrocarbons. The unheated sample had a lower abundance of hydrocarbons in general at 1.67×10^{-8} mol/g compared to 2.36×10^{-8} mol/g for heated samples. However, despite the differences in hydrocarbon abundances, hydrocarbon ratios were found to remain fairly constant regardless of preparation technique (Figure 2.19). The 4 experimental trials are plotted with the 5 quartz samples from PGE-rich quartz + sulfide assemblages described earlier in this work for spatial comparison. The average propylene/propane, unsaturated/saturated and $(C_2+C_3)/C_{tot}$ ratios for preparation variation trials are 1.033 ± 0.253, 0.0756 ± 0.0227, and 0.0228 ± 0.0011, respectively.

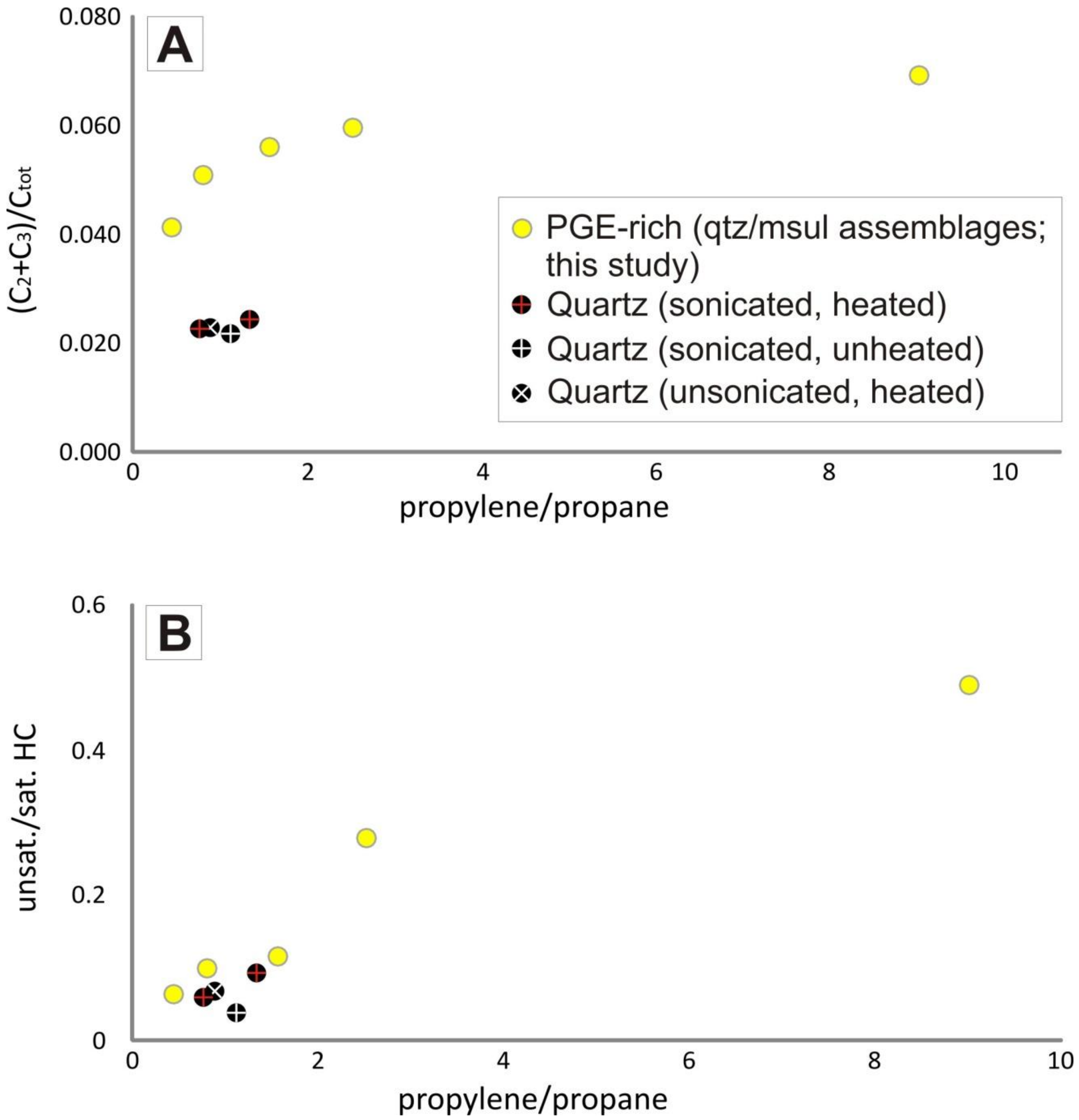


Figure 2.12: Effects of sample preparation variation on hydrocarbon signatures from GC analysis. The quartz sample from a quartz + sulfide assemblage used for sample preparation variation trials is not related to the scope of this study but was used due to the high abundance and speciation of hydrocarbons in the sample to aid in determining whether the preparation method used has an influence on the hydrocarbon signature. Heating and sonication practices were investigated in these trials. For the sake of comparison, the 5 quartz samples from quartz + sulfide ± epidote assemblages investigated in this study are plotted. All analyses were performed with a crush size of ~0.7 grams. ***A*** **–** binary plot of the (C2+C3)/C_{tot} hydrocarbon ratio versus the propylene to propane ratio. ***B*** **–** binary plot of the unsaturated to saturated HC ratio versus the propylene to propane ratio.

2.4 Discussion

2.4.1 Fundamental limitations of hydrocarbon based ore exploration via GC

The technique of volatile hydrocarbon analysis via in-line rock crushing gas chromatography is a bulk technique. Thus, in a single sample crush, all fluid generations (primary and secondary fluid phases) will be liberated and analyzed as constituting a single bulk rock fluid. It would be likely in vain to attempt extracting accurate information about the ore system from the fluid alone, such as the crystallization history, temperature and pressure of fluid entrapment and timing of secondary fluid phases. Rather, this study was performed to determine if any systematic bulk fluid change was clearly distinguishable in Sudbury breccia from regions containing high- and/or low-sulfide mineralization versus barren environments. Nonetheless, this technique can still be employed as a potential tool for sulfide ore body exploration given that a statistically significant population of samples from both environments is investigated. In this paper we outline possible mechanistic and genetic interpretations for the origin of the hydrocarbon species, particularly the higher order species; however, it is important to note that this is not the goal of the study. This study works to generate a set of criteria that may be preliminarily used to aid in the exploration of sulfide mineralization based on the hydrocarbon signature of entrapped fluid within the rocks. Additional studies must be performed to investigate the potential chemical mechanisms and geological conditions responsible for these hydrocarbon signatures – this is beyond the scope of this investigation.

2.4.2 Potential fluid origin and factors influencing hydrocarbon fluid variations

Hydrocarbon abundances between Sudbury breccia from barren versus sulfide mineralized environments were found to be statistically distinct from one another. Specifically, the abundances of the light hydrocarbons (methane, ethane, propane, and butane) were markedly higher in breccia from mineralized environments (Figure 2.7). The most noticeable distinction between the two populations of breccia is present in the abundance of propane. Propane abundance averages are 1.176×10^{-11} mol/g versus 4.803×10^{-12} mol/g for mineralized versus barren breccia populations, respectively. The average increase in hydrocarbon abundance in the mineralized Sudbury breccia over the barren breccia may be the result of: (i) breccia from mineralized environments being overall richer in fluid (i.e., higher abundance of fluid inclusions and/or occluded gas); (ii) the presence of a different, more hydrocarbon-rich fluid that charged the mineralized breccias environments but not the barren one; and/or (iii) the fluid phase itself trapped in the breccia from mineralized environments is richer in hydrocarbons than the fluid from barren breccias due to chemical modifications to an initially identical fluid. It is impossible to determine which of these factors, if not both, is responsible for the varying hydrocarbon signatures without individually, detailed petrographic investigation of many breccias samples. Investigation of representative samples of breccia from both environments (Figures 2.6) it appears as though the first factor is not a main control on the hydrocarbon abundance. This is evident through the investigation of breccia-hosted residual quartz clasts from barren and mineralized environments, which were found to possess an approximately equal abundance of fluid inclusions, suggesting that the fluid trapped in mineralized breccia samples is richer in hydrocarbons than that from barren samples of breccia in order to account for the higher hydrocarbon abundances in mineralized breccia samples. Additionally, the presence of clear Schultz-Flory distributions between the average abundances of saturated hydrocarbon from the investigated environments versus the carbon number is a strong indication that the hydrocarbons in these systems have been abiogenically generated. The average abundances of saturated hydrocarbons in the Sudbury breccia, SIC rocks, country/footwall rocks and the quartz from both PGE-rich and -poor environments show a clear log linear decrease from C2 (ethane) to C5 (pentanes) in which the abundance decreases from 10^1 to 10^{-2}, respectively (mole%; Figure 2.12). This is consistent with a Schultz-Flory distribution with the production of a light hydrocarbon dominated mixture with low ethane/methane ratios (this study: C2/C1 = 0.031 – 0.052) and higher order hydrocarbons ratios less than 0.6 (Szatmari, 1989; Salvi and Williams-Jones, 1997a; this study: C4/C3 and C5/C4 ratios between 0.14 – 0.47). This suggests that volatile hydrocarbons in the fluids trapped in rocks of the SIC and its footwall environment, including quartz + massive sulfide assemblages, are of abiogenic origin such as those produced by Fischer-Tropsch or reductive coupling reactions (Potter and Konnerup-Madsen, 2003, and references therein). Biogenically derived hydrocarbon mixtures, such as those formed in oil and gas fields and geothermal (thermogenic) springs by the decomposition of organic hydrocarbon molecules, possess significantly larger concentrations of higher order hydrocarbons including propane, butane and pentane (grey field; Figure 2.12) than abiogenically formed hydrocarbon mixtures. Whereas biogenic hydrocarbons are often a result of the thermal cracking and decomposition of larger

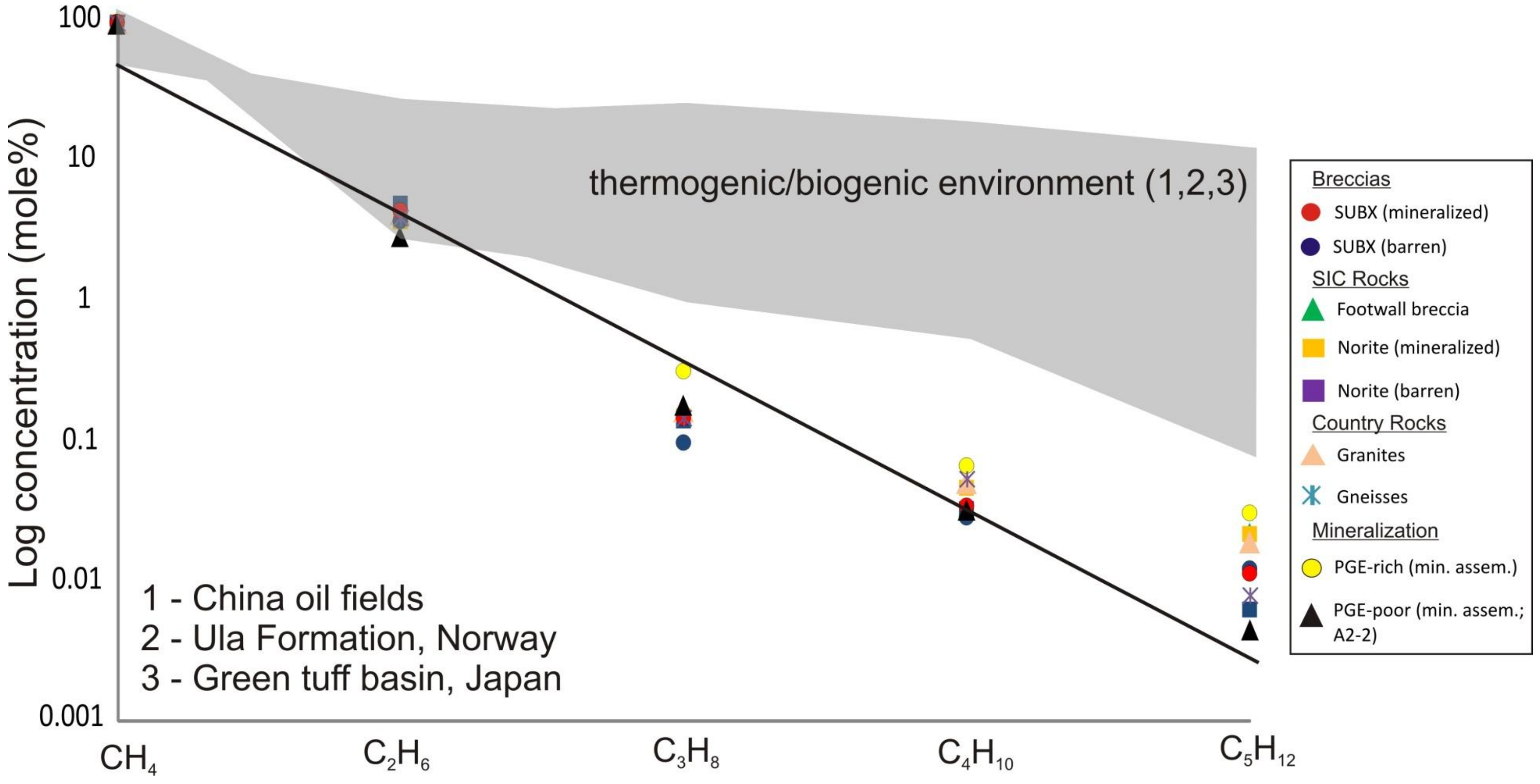

Log concentration (mole%)
100
10
1
0.1
0.01
0.001
CH_4
C_2H_6
C_3H_8
C_4H_{10}
C_5H_{12}
thermogenic/biogenic environment (1,2,3)
1 - China oil fields
2 - Ula Formation, Norway
3 - Green tuff basin, Japan
Breccias
SUBX (mineralized)
SUBX (barren)
SIC Rocks
Footwall breccia
Norite (mineralized)
Norite (barren)
Country Rocks
Granites
Gneisses
Mineralization
PGE-rich (min. assem.)
PGE-poor (min. assem.; A2-2)

Figure 2.13 (previous page): Shultz-Flory distribution of analyzed samples plotting average molar abundance (log scale) versus carbon number of saturated hydrocarbon species. Each data point represents the average value of the given sample population. The exponential equation of the line of best fit is expressed in the boxed inlay. The biogenic field is represented by data from China oil fields (Chen et al., 2000), the Ula formation in Norway (Potter and Konnerup-Madsen, 2003 references therein) and the Green buff basin in Japan (Sakata et al., 1997). Thermogenic/biogenic field adapted from Potter and Konnerup-Madsen (2003). The thermogenic/biogenic field has a significantly flatter Schultz-Flory distribution than the samples analyzed in this study. This data suggests that the hydrocarbons in all the Sudbury related samples analyzed in this study are likely the result of abiogenic processes. Note: min.assem. – quartz-bearing mineralized assemblage carbon based molecules to yield lighter ones, abiogenically synthesized hydrocarbons are generated by the coupling of light hydrocarbons (methane and ethane predominantly) to yield higher order hydrocarbon species leading to an exponential decrease in the concentration as the carbon number increases.

Studies investigating the hydrocarbon fluid present in the peralkaline granite at Strange Lake have suggested that hydrocarbon fluids (predominantly methane) in that environment are most likely of magmatic origin based on the presence of coevally entrapped aqueous fluid inclusions determined to be of magmatic origin (Salvi and Williams-Jones, 1992, 1997a). Reports of magmatic fluids from activity related to the cooling Sudbury Igneous Complex on the other hand are largely focused on the presence and interpretation of aqueous inclusions (Farrow and Watkinson, 1992; Marshall et al., 1999; Molnar et al., 2001; Farrow and Lightfoot, 2002; Hanley et al., 2004, 2011) with very few studies investigating the nature of hydrocarbon-rich inclusions associated with the SIC. A study performed by Hanley et al. (2005) noted the presence of methane dominated hydrocarbon inclusions in quartz from a quartz + sulfide + epidote assemblage spatially associated with Cu-rich, PGE-poor, “hybrid-style” footwall mineralization, but went on to express that a hydrocarbon dominated, CO_2-free fluid would only be stable at late-stage magmatic temperatures (~500-700^{o}C) in unrealistically reducing conditions (QFM-4; iron-wustite buffer; Mathez et al., 1989). With this being said, it seems unlikely that a hydrocarbon dominated fluid was exsolved directly from the cooling SIC or cooling sulfide liquid. It may be the case that a [CO_2 + CH_4] or CO_2 dominated fluid exsolving from cooling sulfide liquid in the footwall was locally reduced/respeciated upon interaction with a source of hydrogen (Huizenga, 2001; Potter and Konnerup-Madsen, 2003 and references therein), group VIII metal catalysts (F-T synthesis; Anderson, 1984; Sherwood Lollar et al., 1993, 2002; Salvi and Williams-Jones, 1997a; Potter et al., 2004; McCollom and Seewald, 2006; Taran et al, 2007, 2010) or PGE (reductive coupling reactions) in the sulfide melt, simultaneously generating higher order hydrocarbons and endowing the SUBX proximal to sulfide mineralization with an increased abundance of hydrocarbon-enriched fluid (relative to barren SUBX). However, isotopic investigations (H, C and Sr isotopic analysis; Hanley et al., submitted) of hydrocarbon fluids and coevally entrapped brine inclusions in quartz from the SIC footwall quartz + sulfide + epidote assemblage A2-2 (also investigated in this study) shows very strong evidence that methane associated with the SIC and its footwall environments was sourced directly from the deep crust/upper mantle and is not a result of late stage CO_2 respeciation/reduction (i.e., methane endowment is a primary feature). The $\delta^{13}C$ signature of methane was found to be approximately -10‰, suggesting an abiogenic and likely mantle origin, as biogenic $\delta^{13}C$ signatures tend to be below -30‰ (Schoell, 1988; Welhan, 1988; Potter and Konnerup-Madsen, 2003; Potter and Longstaffe, 2007; Hanley et al., submitted). Additionally, it was found that the $\delta^{13}C$ signatures of heavier hydrocarbons from the methane dominated fluid become more depleted as the carbon number increased. Depletion of ^{13}C with increasing carbon number strongly suggests that the higher order hydrocarbons are the result of abiogenic chemical processes and not of biogenic or thermogenic processes, which become progressively more enriched in ^{13}C with increasing carbon number (Sassen et al., 1999; Lorant et al., 1998; Potter and Konnerup-Madsen, 2003; Sherwood Lollar et al., 2002, 2006; Beeskow et al., 2006; Potter and Longstaffe, 2007) Strontium and hydrogen isotope analysis also suggests a mantle provenance of the hydrocarbon fluid (Hanley et al., submitted). Therefore, it appears highly plausible that a methane dominated hydrocarbon fluid associated with the SIC and its footwall quartz + sulfide assemblages has origins in the mantle. Evidence has also been reported of the occurrence of apparently detrital carbon as heterogeneous, microscopic spherules in Ni-Cu-PGE sulfides that have been determined to represent the integration of pre-impact carbonaceous material into the igneous melts upon impact (Wright et al., 2010). The spherules dominantly occur in chalcopyrite suggesting the carbon behaved as a chalcophilic element and their heterogeneity suggests they did not form via precipitation from a single carbonic fluid phase. Thus, it is also possible that large volumes of carbon were introduced into the Sudbury melt by this means, significantly influencing the carbon budget of the system and possibly playing an important role in the sulfide mineralization process (Wright et al., 2010).

Four of the five samples of quartz from PGE-rich sulfide assemblages were shown to possess significant enrichments in CO_2, accounting for up to 88 mole% of total carbonic volatiles (UG3750(#5)). Upon plotting the mole% of CO_2 versus CH_4 of quartz samples from PGE-poor and PGE-rich environments, an inverse approximately 1:1 ratio is present between the 2 carbonic species (Figure 2.14). This is what would be expected if the abundance of the 2 species were controlled through the reaction:

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \qquad \textbf{Eq. 2.1}$$

in which fluids initially dominated by methane can evolve towards a more oxidized, CO_2-rich fluid by reaction with oxygen. Although it has been shown that in situ fluid re-equilibration can occur within single $CH_4+CO_2+H_2O$ inclusions altering the volatile carbonic abundances over time (Cesare, 1995), a source of oxygen is needed for this reaction to proceed. Oxygen can be readily generated at hydrothermal temperatures and oxygen fugacities by the dissociation of water in situ via the reaction (Seewald, 1994):

$$2H_2O \leftrightarrow O_2 + 2H_2 \qquad \textbf{Eq. 2.2}$$

A post entrapment increase in fO_2 in the environment outside of the inclusions causes water inside of the inclusions to dissociate to generate H_2 that can migrate outside of the inclusions reacting with oxygen in the external environment regenerating water (i.e., Le Chatlier’s Principle; Smith et al., 1984; Mavrogenes and Bodnar, 1994; Hanley et al., 2011). This leaves free oxygen in the inclusions to oxidize methane to carbon dioxide.

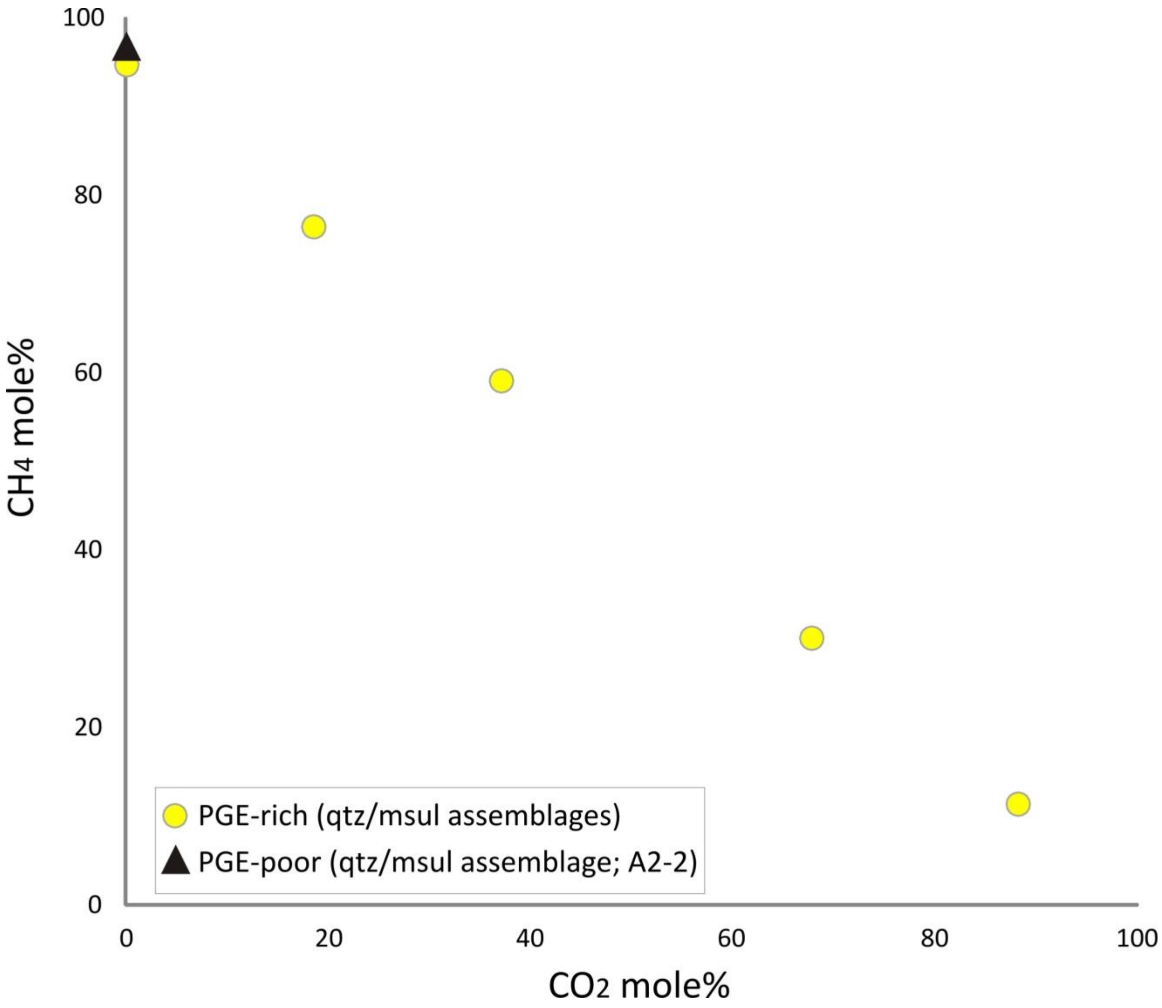


Figure 2.14: CO_2 versus CH_4 mole% of carbonic fluid within quartz from PGE-rich and PGE-poor quartz + sulfide ± epidote assemblages. An inverse, approximately 1:1 ratio is present between the molar abundance of CH_4 and CO_2, indicating they are the dominant volatile carbonic species in the trapped fluids and suggests they are likely genetically related through the re-speciation reaction: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$. Molar percentages of CO_2 and CH_4 were calculated out of total carbonic fluid concentration.

Sample A2-2 was found to be highly depleted in CO_2 (Hanley et al., 2005; Hanley et al., submitted; This study). Isotopic investigation of trace CO_2 associated with methane dominated hydrocarbon inclusions from A2-2, accounting for only 0.003 mol% of total volatile content (Hanley et al., 2005), showed that the CO_2 is more depleted in ^{13}C than methane (approximately -25‰ in CO_2; Hanley et al., submitted). If the CO_2 is the result of post entrapment in situ methane re-speciation, than this difference in the $\delta^{13}C$ signatures of the two species must be accounted for. Reports have noted that during the re-speciation of CH_4 to generate CO_2, kinetic isotopic fractionation produces CO_2 that is more depleted in ^{13}C than its CH_4 precursor (Kiyosu and Krouse, 1989; Beeskow et al., 2006; Potter and Longstaffe, 2007). This would imply that methane-rich fluid was the initial carbonic phase to endow the SIC and its footwall, preceding F-T type reactions involving magmatic CO_2 as a source of methane, and that the presence of CO_2 in these fluids are likely the result of post entrapment re-speciation reactions from external increases in fO_2 from late stage hydrothermal events (Potter and Longstaffe, 2007). The re-speciation of methane to form CO_2 would by extension be most prevalent in areas showing evidence of alteration or secondary fluid generations. Figure 2.10B shows that the majority of these quartz samples tend to be slightly reduced in methane and enriched in propane relative to the majority of the breccia, SIC and country rocks. This is also evident in a number of Sudbury breccia analyses from mineralized environments (Figure 2.10; labelled samples 1-4). Drill core logs from the intervals in which the anomalous SUBX samples were collected (core logs by KGHM International Ltd./Quadra FNX Mining Ltd.) show that they have been affected by later stage alteration (i.e., epidote or K-feldspar alteration), underwent recrystallization or have been crosscut with late stage hydrothermal veins/veinlets (i.e., calcite veinlets). Thus, it may be the case that later hydrothermal or recrystallization events in these areas altered the external fO_2 of the system, in turn altering the CH_4/CO_2 ratios in the fluid inclusions. PGE assay data (reported in drill core logs) shows that the majority of the samples displaying trendline deviation in Figure 2.10 are moderately enriched in PGE, which likely catalyze the production of higher order hydrocarbons at the expense of methane. Therefore, it seems likely that methane is removed from hydrocarbon-rich fluid by a combination of two key processes: (i) the re-speciation of CH_4 to CO_2 due to external fO_2 increase, and (ii) the reductive coupling of CH_4 to generate higher order hydrocarbons (Figure 2.20). It is important to keep in mind that this GC technique is a bulk method that unavoidably detects the presence of all fluids released during a crush, from all generations. However, due to the very strong inverse, approximately 1:1 ratio between CH_4 and CO_2 (Figure 2.14), these species are most likely genetically related through re-speciation reactions.

There is no statistical difference in the relative abundance of total unsaturated to saturated hydrocarbons between Sudbury breccia from mineralized versus barren environments (Figure 2.8), but a small difference is present when observing only the propylene to propane ratios of the two breccia populations (Figure 2.9). A very large statistical difference is present in both the unsaturated/saturated and propylene/propane ratios of the fluid from quartz inclusions from PGE-rich quartz + sulfide assemblages. This result is suspected to be directly related to the presence of PGE/PGM associated with these environments to catalytically dehydrogenate saturated hydrocarbon species (i.e., propane) into their unsaturated counterparts (i.e., propylene). Similarly high ratios are not present in the majority of mineralized SUBX samples because of 2 potential factors: (i) the distance of the SUBX from PGE-rich mineralization and (ii) the degree of interaction of hydrocarbon-rich fluid with PGE/PGM. Firstly, SUBX samples collected from “mineralized environments” are not necessarily in direct contact with, or do not necessarily contain sulphide mineralization. Rather, mineralized SUBX represent samples collected from a footwall environment containing footwall-style mineralization that is associated with an embayment structure (Figure 2.2). These units can be quite large and so, although “mineralized” SUBX samples may be from the same ore-containing SUBX package, many samples may lie some distance away from actual sulfide mineralization. Therefore, we would expect that hydrocarbon-rich fluid that has been chemically affected by localized PGE-rich sulfide mineralization would not be uniformly distributed through the whole of the SUBX unit. Secondly, the crystallization/precipitation of both the quartz and PGM in quartz + sulfide ± epidote assemblages is spatially associated and temporally synchronous (Farrow et al., 2005; Farrow and Lightfoot, 2002). By extension, the fluid circulating within these PGE-rich hydrothermal systems would likely have a great deal of direct interaction with solid PGM phases and/or dissolved PGE complexes, altering the fluid’s hydrocarbon chemistry prior to becoming entrapped as fluid inclusions. Conversely, a hydrocarbon-bearing fluid migrating within the less PGE-rich SUBX matrix or along SUBX contacts may not be as chemically affected and would in turn possess a lower unsaturated to saturated hydrocarbon ratio, although the fluids may be locally affected by areas of local PGM abundances (i.e., areas of disseminated sulfides or ‘low-sulfide’ vein stockworks; Farrow et al., 2005). All of the quartz samples from PGE-rich assemblages showed elevated abundances of unsaturated hydrocarbons with an average unsaturated to saturated HC ratio of 0.211, whereas quartz from a PGE-poor assemblage (A2-2) has a ratio of only 0.005. This difference is even larger when considering only the propylene:propane ratios of PGE-rich versus PGE-poor assemblages, with average values of 2.86 and 0.004, respectively. This supports the theory that the presence of PGE/PGM is an important factor in the unsaturated hydrocarbon speciation and abundance in carbonic fluids. Additionally, the mineralized SUBX population covers a larger range of values for hydrocarbon ratios and abundances than barren SUBX (i.e., long whiskers in the box and whisker plots; larger breadth of data) with some samples displaying a more barren hydrocarbon signature in regions of minimal PGE-rich sulfide mineralization or fluid abundance while other samples, more locally enriched PGE and entrapped fluid, display more anomalous hydrocarbon signatures (Figures 2.8-2.10, 2.11A-D).

Rock units associated with the Sudbury Igneous Complex (i.e., footwall breccia, norite) and its country rocks (i.e., gneiss and granite) were also found to contain significant abundances of methane and trace amounts of higher order hydrocarbons. Hydrocarbon abundances from these samples were found to follow the same trends observed for SUBX populations in binary plots (Figure 2.10). Ternary plots (Figure 2.11) show that fields constituted by SIC rocks and country rocks overlap significantly with both SUBX populations. It seems likely from these results that the entire SIC and its adjacent footwall and country rocks were endowed with a common fluid that pervaded the whole system. It is possible that a mantle derived hydrocarbon-rich fluid that equilibrated early, with respect to its light hydrocarbon abundances (i.e., C1-C4), was injected throughout the entire SIC and its footwall environments, albeit non-uniformly. This fluid was further locally affected by PGE-rich hydrothermal fluids or mineralization associated with ‘high-sulfide’ and/or ‘low-sulfide’ ore emplacement and post entrapment re-equilibration reactions due to the late stage hydrothermal activity. Hydrocarbon fluid trapped within country rocks including gneisses and granites may represent a mix of two potential end members: (i) the hydrocarbon-rich fluid that pervaded the SIC and its footwall during the formation and cooling of the SIC and its sulfide ore bodies, and (ii) a more ancient hydrocarbon-bearing fluid that was present as trapped fluid in the granite and gneiss prior to the formation of the SIC and its ore bodies (i.e., ancient groundwaters or pre-SIC fluids from inclusions in country rocks). There are two complications with the latter interpretation. First, the meteorite impact that subsequently formed the SIC would have likely ruptured a large percentage of inclusions in the gneiss and granite proximal to the impact site and secondly, the similarities in the hydrocarbon relationships and abundances between the SIC rocks, Sudbury breccia and country rocks suggest that the fluids present in these rocks share a common origin and/or genetic relationship.

2.4.3 Spatial relationships between mineralization and hydrocarbon abundance

Hydrocarbon data from analyses of fluid trapped in the investigated breccia samples collected from drill cores were plotted to constrain the spatial relationship of breccia hydrocarbon signatures with massive sulfide mineralization in the footwall. Total C1-C6 hydrocarbon abundance is not preferentially enriched in areas proximal to ore as many above average total hydrocarbon signatures (i.e., $>8.03\times10^{-9}$ mol/g) were found at distance from massive sulfide mineralization (Figure 2.15). Averages were calculated based on all samples analyzed from the mineralized footwall breccia package. Above average propylene/propane ratios (C_3H_6/C_3H_8; i.e., >0.27) were found in samples both distal and proximal to massive sulfide mineralization; however, it is clear that a number of Sudbury breccia samples in the region toward the top of the footwall-hosted sulfide body are characterized by highly elevated C_3H_6/C_3H_8 ratios (i.e., >1). This region is spatially associated to where the Ni-rich, embayment-hosted, contact-style massive sulfide bodies are physically connected to the Cu-PGE-rich, footwall-hosted, footwall-style sulfides (Dr. Jacob Hanley, personal communication), suggesting the fluids may be related to the injection of Cu-PGE-rich ISS into the footwall from fractionated MSS hosted in the SIC embayment structures, which went on to develop Ni-Fe-rich contact-style deposits (Naldrett, 1984; Morrison et al., 1994; Watkinson, 1999; Farrow and Lightfoot, 2002; Hanley et al., 2005). To investigate the spatial relationships between volatile hydrocarbon signatures and the presence of sulfide ore, particularly PGE-rich sulfide ore, drill core logs were investigated and areas of PGE enrichment (Pt and Pd considered here) and S enrichment were plotted along the studied cores (Figure 2.17 – 2.18). A lower value of 0.1 wt% sulfur was used as it roughly represents the amount of sulfur (present in sulfide minerals) visible to the unaided eye in a segment of core in routine drill core logging. An upper value of 0.8 wt% used as it represents the approximate abundance at which a systematic increase in PGE is observed when all drill core assay data is considered (all KGHM International Ltd./Quadra FNX Mining Ltd. Levack drill core). A sulfur abundance of 0.8 wt% corresponds with approximately 1 ppm Pt+Pd. A lower value of Pt+Pd-enrichment of 0.05 ppm represents the highest concentration of Pt+Pd observed in barren breccia samples from unmineralized footwall environments in the West, North and East Ranges of the SIC. Platinum and palladium enrichments greater than 0.05 ppm (determined via drill core assays) were most prevalent toward the top portion of the footwall sulfide body; however, enrichments greater than 1 ppm occur ubiquitously, dominantly in the region around massive sulfide mineralization.

As the total C1-C6 hydrocarbon abundance is relatively uniform throughout the investigated region of the footwall, the localized propylene-enriched breccia region is not simply the result of an anomalous area of hydrocarbon fluid enrichment. Assuming PGE/PGM have a catalytic effect on the unsaturated hydrocarbon abundance of a hydrocarbon-bearing fluid, elevated C_3H_6/C_3H_8 ratios in this region are likely the result of two potential causes: (i) hydrocarbon-bearing fluid migrating from depth interacted with zones of PGE-enrichment in the footwall prior to being trapped in breccia at shallower depth near the top-most portion of the sulfide body, or (ii) volatiles dissolved in the fractionated Cu-PGE-rich ISS melt interacted with PGE in the melt prior to being exsolved and trapped in breccia during ISS injection into the footwall. Two samples displaying elevated C_3H_6/C_3H_8 ratios were found at distance away from the footwall-hosted massive sulfide ore body, which may represent the interaction of fluids in that region with local PGE-rich veins or stockworks. Core logs report no Pt+Pd-enrichments >0.05 ppm are present along the drill core from which the two anomalous samples displaying C_3H_6/C_3H_8 ratios >1 were collected; however, a local area of Pt+Pd-enrichment is present approximately 1000 feet away.

Although more detailed sampling is required to better resolve zones of propylene-enrichment relative to the sulfide body, these results illustrate the potential of employing hydrocarbon-based criteria to aid in footwall-style ore body exploration. The location of sulfide mineralization in the footwall is limited primarily to the lithological interpretation of drill core. This technique is significant in that sulfide mineralization does not necessarily need to be visually present in the drill core in order to detect the presence of nearby mineralization. Elevated abundances of propylene in breccia-hosted fluid appear to be an indication of mineralization hosted deeper in the footwall.

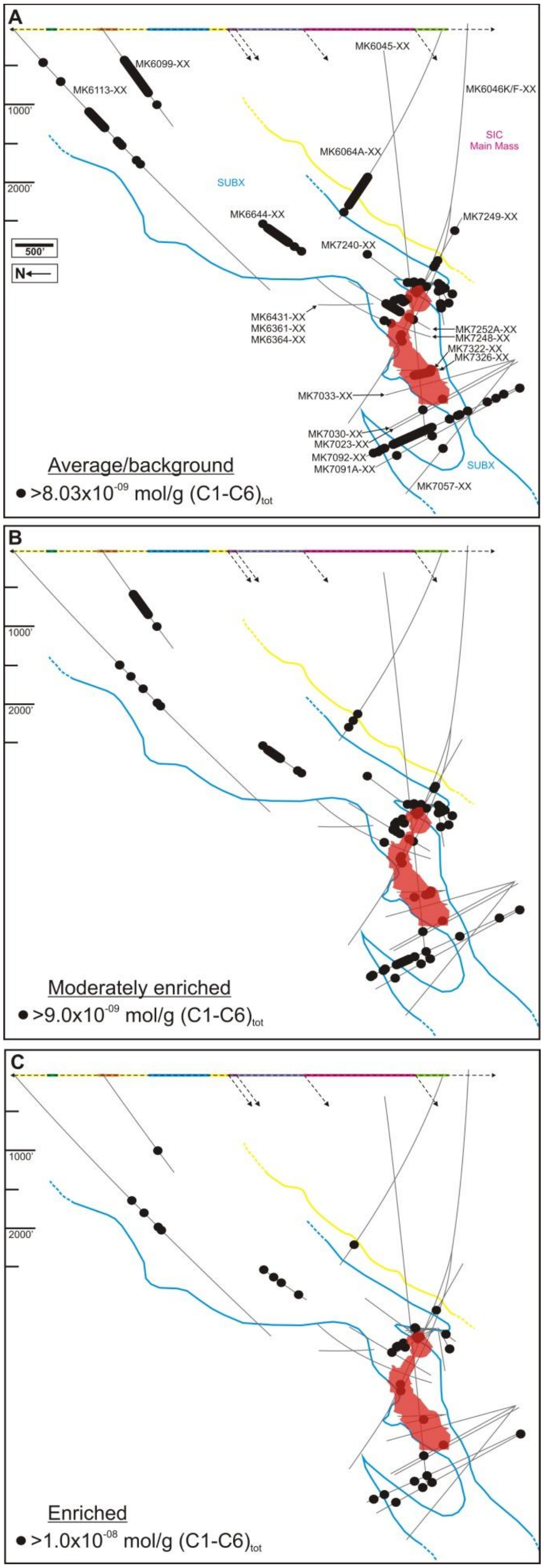
A
MK6099-XX
MK6113-XX
MK6045-XX
MK6046K/F-XX
1000'
2000'
SIC
Main Mass
MK6064A-XX
SUBX
MK6644-XX
MK7249-XX
500'
N
MK7240-XX
MK6431-XX
MK6361-XX
MK6364-XX
MK7252A-XX
MK7248-XX
MK7322-XX
MK7326-XX
MK7033-XX
MK7030-XX
MK7023-XX
MK7092-XX
MK7091A-XX
SUBX
MK7057-XX
Average/background
● >8.03x10-09 mol/g (C1-C6)tot
B
1000'
2000'
Moderately enriched
● >9.0x10-09 mol/g (C1-C6)tot
C
1000'
2000'
Enriched
● >1.0x10-08 mol/g (C1-C6)tot

Figure 2.15 (previous page): Total C1-C6 hydrocarbon (HC) abundace (mol/g of breccia) variation with respect to footwall mineralization along sampled drill cores. (Crosssections at approx. +319250E). **A** – Total HC abundance > 8.03×10^{-9} mol/g. This value represents the average total HC abundance of all breccia samples collected from the mineralized footwall embayment package; thus, any value higher than 8.03×10^{-9} represents an above average HC abundance. **B** – Moderately enriched in hydrocarbons; total HC abundance > 9.0×10^{-9} mol/g. **C** – Enriched in hydrocarbons; total HC abundance > 1.0×10^{-8} mol/g. Black strips rather than points indicate that the samples are too close together to resolve in this image. Note that this is a crosssectional view with the mineralized body and drill cores projected to the surface of the section. The sulfide body is shown translucent to indicate that the drill cores samples pass behind the body in this view. Refer to Figure 2 for a broader view of these regions relative to all samples drill cores.

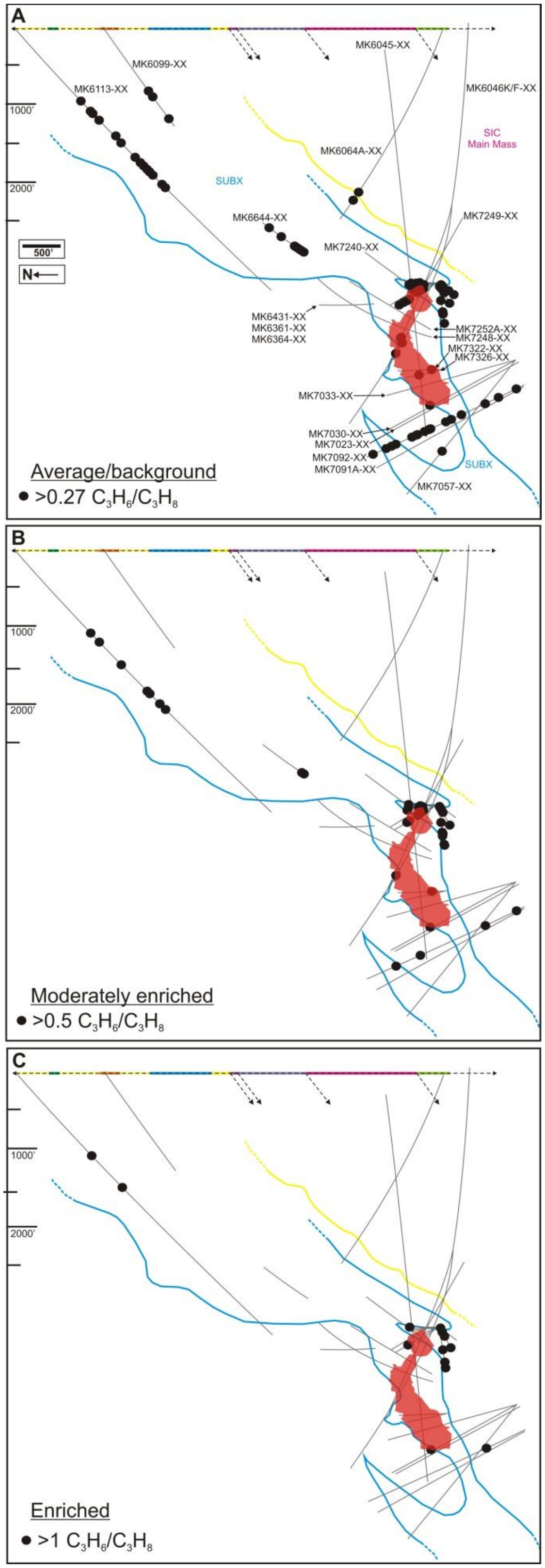

A
MK6045-XX
MK6099-XX
MK6113-XX
MK6046K/F-XX
1000'
SIC
Main Mass
MK6064A-XX
SUBX
2000'
MK7249-XX
MK6644-XX
500'
MK7240-XX
N
MK6431-XX
MK6361-XX
MK6364-XX
MK7252A-XX
MK7248-XX
MK7322-XX
MK7326-XX
MK7033-XX
MK7030-XX
MK7023-XX
MK7092-XX
MK7091A-XX
SUBX
MK7057-XX
Average/background
● >0.27 C_3H_6/C_3H_8
B
1000'
2000'
Moderately enriched
● >0.5 C_3H_6/C_3H_8
C
1000'
2000'
Enriched
● >1 C_3H_6/C_3H_8

Figure 2.16 (previous page): propylene/propane ratio (C_3H_6/C_3H_8) variation with respect to footwall mineralization along sampled drill cores. (Crosssections at approx. +319250E). **A** - C_3H_6/C_3H_8 ratios > 0.27. The ratio 0.27 represents the average of all breccia samples collected from the mineralized footwall embayment package; thus, any value higher than 0.27 represents an above average C_3H_6/C_3H_8 ratio. **B** – Moderately enriched in propylene; C_3H_6/C_3H_8 ratio > 0.5. **C** – Enriched in propylene; C_3H_6/C_3H_8 ratio > 1. No statistically significant difference was seen in any other explored hydrocarbon abundances or ratios to the same degree as the C_3H_6/C_3H_8 ratio. Black strips rather than points indicate that the samples are too close together to resolve in this image. Note that this is a crosssectional view with the mineralized body and drill cores projected to the surface of the section. The sulfide body is shown translucent to indicate that the drill cores samples pass behind the body in this view. Refer to Figure 2 for a broader view of these regions relative to all samples drill cores.

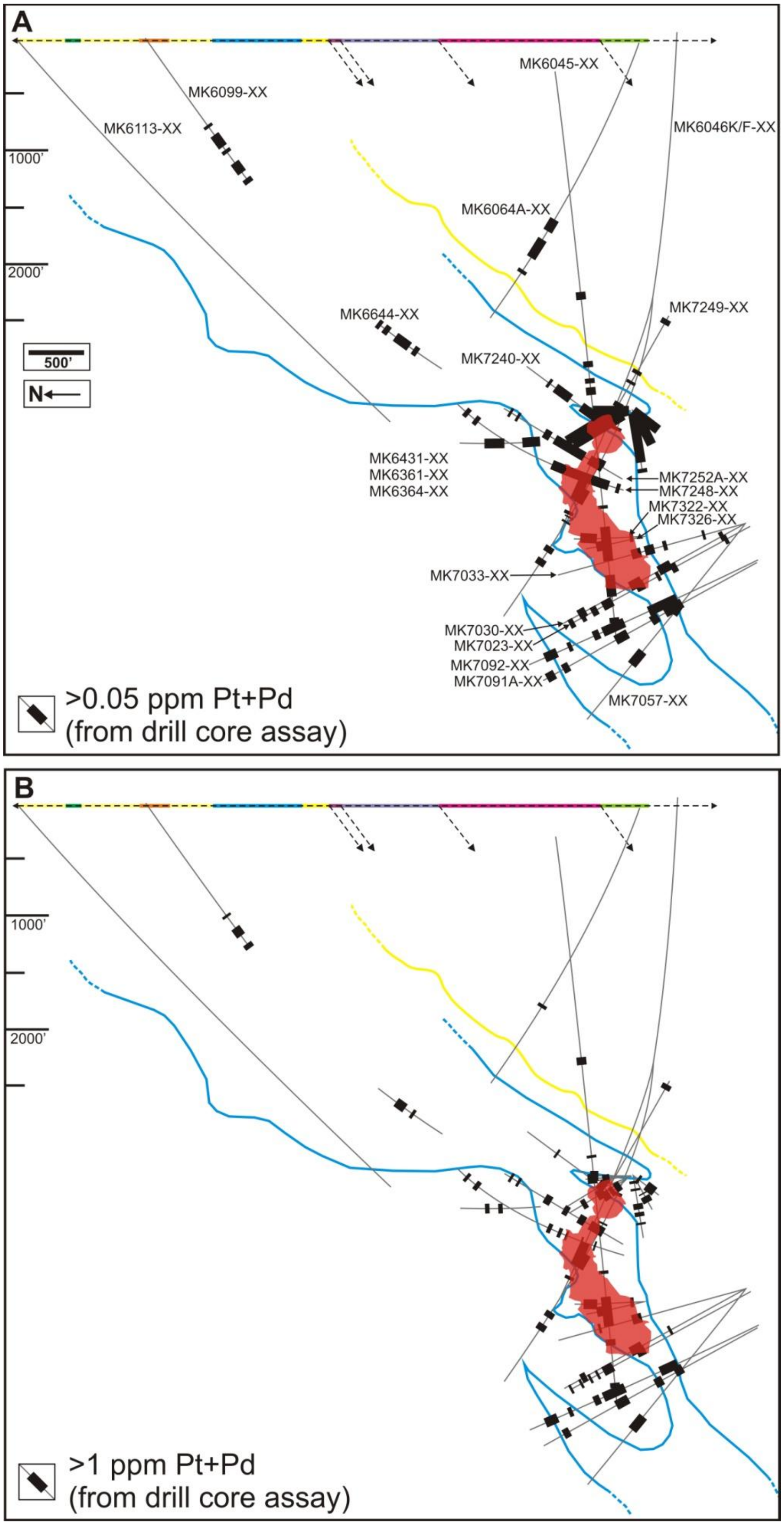

A
1000'
2000'
500'
N
MK6099-XX
MK6113-XX
MK6045-XX
MK6046K/F-XX
MK6064A-XX
MK7249-XX
MK6644-XX
MK7240-XX
MK6431-XX
MK6361-XX
MK6364-XX
MK7252A-XX
MK7248-XX
MK7322-XX
MK7326-XX
MK7033-XX
MK7030-XX
MK7023-XX
MK7092-XX
MK7091A-XX
MK7057-XX
>0.05 ppm Pt+Pd
(from drill core assay)
B
1000'
2000'
>1 ppm Pt+Pd
(from drill core assay)

Figure 2.17 (previous page): Platinum and palladium (Pt+Pd) assay data (ppm) along sampled drill cores from study area. (Crosssections at approx. +319250E). **A** – Areas of Pt+Pd-enrichments of >0.05 ppm. **B** – Areas of Pt+Pd-enrichments of >1 ppm. Black bars were used to indicate the presence of assay points too close together to resolve. Only minor areas of Pt+Pd enrichment >1 ppm occur at distance from massive sulfide mineralization. Much of the enrichment is localized in or near the footwall sulfide mineralization.

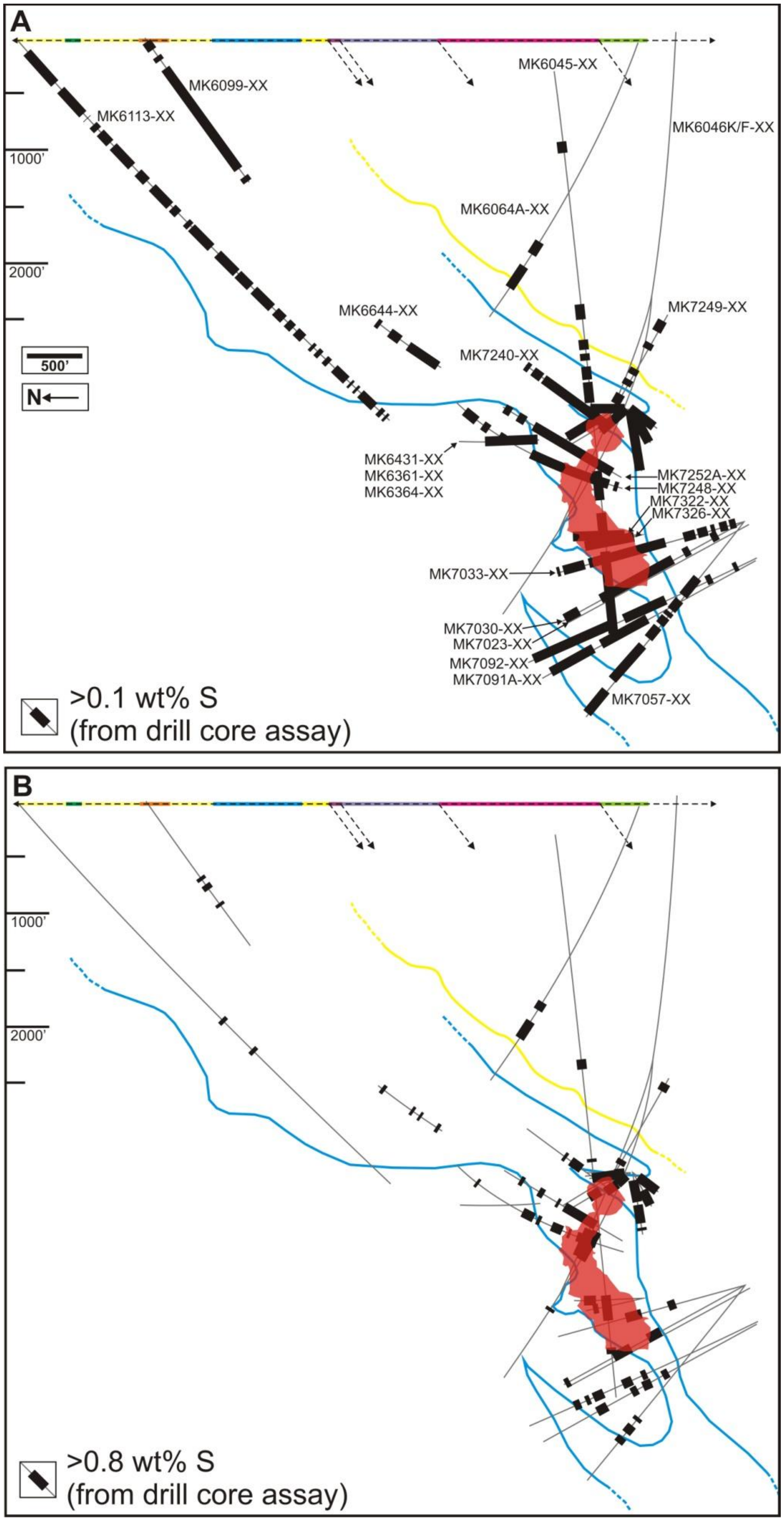

A
MK6113-XX
MK6099-XX
MK6045-XX
MK6046K/F-XX
MK6064A-XX
MK6644-XX
MK7249-XX
MK7240-XX
MK6431-XX
MK6361-XX
MK6364-XX
MK7252A-XX
MK7248-XX
MK7322-XX
MK7326-XX
MK7033-XX
MK7030-XX
MK7023-XX
MK7092-XX
MK7091A-XX
MK7057-XX
1000'
2000'
500'
N
>0.1 wt% S
(from drill core assay)
B
1000'
2000'
>0.8 wt% S
(from drill core assay)

Figure 2.18 (previous page): Sulfur (S) assay data (wt%) along sampled drill cores from study area. (Crosssections at approx. +319250E). **A** – Areas of >0.1 wt% S. **B** – Areas of >0.8 wt% S. Black bars were used to indicate the presence of assay points too close together to resolve. Elevated concentrations of sulfur indicate the presence of sulfide mineralization, either disseminated or massive.

2.4.4 Potential thermochemical controls on hydrocarbon abundance and speciation

Comparing the Schultz-Flory distribution of the hydrocarbons associated with the SIC and its footwall and country rocks with the abundances of biogenic hydrocarbons from oil and gas fields and geothermal (thermogenic) springs (Figure 2.13; thermorgenic/biogenic field; Potter and Konnerup-Madsen, 2003 and references therein), the two groups are clearly different. The biogenic hydrocarbon distribution has a flatter trend as the carbon number increases whereas the SIC associated hydrocarbons decrease in a log linear fashion with increasing carbon number. The thermogenic/biogenic hydrocarbons are generated primarily by the thermogenic decomposition of large biogenically formed hydrocarbon molecules into smaller ones producing a flatter Schultz-Flory distribution (i.e., larger concentrations of heavier hydrocarbons). Elevated abundances of higher order saturated hydrocarbons is expected in thermogenically derived fluids, where C2+ hydrocarbons can account for up to approximately 15% (by volume) of the total gas phase, becoming progressively more C2+ depleted with fluid maturity (Schoell, 1980; Lorant et al., 1998; Sherwood Lollar et al., 2008).

Although the gases CO_2, H_2S and H_2O are often the most dominant volatile species in magmatic and hydrothermal fluids, CH_4 and higher order hydrocarbons are also common (i.e. seafloor: Welhan, 1988; ophiolites: Abrajano et al., 1990; SIC footwall stringers: Hanley et al., 2005). Previous studies have reported the presence of abiogenic hydrocarbons in igneous rocks associated with peralkaline (Salvi and Williams-Jones, 1992, 1997a,b) and silica undersaturated alkaline rocks (Konnerup-Madsen et al., 1979, 1985; Konnerup-Madsen and Rose-Hansen, 1982) and have interpreted them as having a magmatic origin based on both textural and isotopic evidence. Work by Salvi and Williams-Jones (1992, 1997a) interpreted the hydrocarbon-rich fluid from the Strange Lake peralkaline granite as possessing a magmatic origin based on the interpretation of coevally entrapped aqueous inclusions. The magmatic origin of hydrocarbons envisions the exsolution of a C-O-H fluid from the magma that will eventually evolve to become hydrocarbon-enriched through respeciation and reductive coupling reactions (Salvi and Williams-Jones, 1997a; Huizenga, 2001). It has been shown that a CH_4-rich fluid can evolve in equilibrium in a closed system from a primary, more oxidized fluid under geologically reasonable conditions (i.e., equation 2.1; below about 500-600^{o}C and a fO_2 between QMF and QMF-3; Gerlach, 1980; Huizenga, 2001; Potter and Konnerup-Madsen, 2003 and references therein). However, these studies are only feasible in significantly reducing environments for particular alkaline melt compositions and fail to address the origin of the heavier hydrocarbon species in these environments. It thus seems likely that the methane and higher order hydrocarbons associated with the SIC and its footwall environments are not simply the result of re-equilibration of a CO_2-rich fluid.

$$CO_2 + 2H_2O \leftrightarrow CH_4 + 2O_2 \qquad \textbf{Eq. 2.3}$$

A study (Salvi and Williams-Jones, 1997a) of the hydrocarbon signature of the Strange Lake peralkaline granite found that the proportions of hydrocarbon species in various samples from the area were very similar, showing a decrease in abundance with increasing molecular weight and the predominance of saturated hydrocarbons over unsaturated ones, leading them to the conclusion that the hydrocarbon fluid in these samples represents a single fluid generation. This trend is also present in the hydrocarbon signatures of the samples analyzed in this study. All investigated samples show a log linear decrease in hydrocarbon abundance with molecular weight and a higher abundance of saturated hydrocarbons over unsaturated ones indicating that the entire SIC and its footwall systems was probably charged, un-uniformly, with a single generation of hydrocarbon-rich fluid or with pulses of a fluid from a common source. It is still unclear as to exactly how the higher order hydrocarbon species were introduced into the system. The presence and concentration of higher order hydrocarbons cannot be the result of thermodynamic equilibrium of a C-O-H bearing fluid. It has been shown that at temperatures between 200-500^{o}C at various oxygen fugacities (QFM, QFM-2 and QFM-5), the dominant carbonic species is either carbon dioxide or methane (at a lower temperature and oxygen fugacity). A maximum equilibrium ethane abundance of 0.06 mole% is acquired at 350^{o}C and a fO_2 of QFM-2 with no other higher order hydrocarbons present in any significant abundance (Salvi and Williams-Jones, 1997a). It could be the case that the higher order hydrocarbons were generated through non-equilibrium reactions (i.e., F-T synthesis, catalytic reductive coupling reactions) prior to being introduced into the SIC and its footwall systems, subsequently becoming trapped. Conversely, the fluid initially introduced into the system could have been quite hydrocarbon depleted dominated by varying proportions of CO_2 and CH_4 that later respeciated and polymerized to form higher order species in situ under similar geological conditions. Although the temporal relationship between the generation of the higher order hydrocarbons and their entrapment is not necessarily evident, their abiogenic production can be described as the probable result of two key processes: (i) Fischer-Tropsch style reactions in which carbon dioxide or carbon monoxide react with hydrogen gas in situ forming methane and some higher order hydrocarbons (equations 2.4 and 2.5), and (ii) PGE and/or PGM catalyzed reductive coupling reactions between methane and short chain hydrocarbons yielding longer chained species (equations 2.8 and 2.9; Figure 2.19).

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \qquad \textbf{Eq. 2.4}$$

$$2CO_2 + 7H_2 \rightarrow C_nH_{2n+2} + 2nH_2O \qquad \textbf{Eq. 2.5}$$

The Fischer-Tropsch (F-T) synthesis is an abiogenic hydrocarbon forming reaction that has been extensively characterized (Anderson, 1984; Bertole et al., 2004a, 2004b; McCollom and Seewald, 2006; Taran et al, 2007, 2010; McCollom et al., 2010) and has been reported as a probable abiogenic hydrocarbon generating process in a number of geological environments (Lancet and Anders, 1970; Szatmari, 1989; Salvi and Williams-Jones, 1992, 1997a; Sherwood-Lollar et al., 2002; Potter and Konnerup-Madsen, 2003; Proskurowski et al., 2008; Taran et al., 2010). F-T reactions tend to favor the production of shorter chain saturated species (i.e., C2-C3 alkanes/paraffins) over unsaturated ones (i.e., alkenes/alkynes/olefins) (Anderson, 1984), especially at elevated temperatures and pressures (Krishna and Bell, 1993; Salvi and Williams-Jones, 1997a; Liu et al., 2007), although Liu at al. (2007 and references therein) noted that small amounts of catalytic Mn can enhance the formation of olefin species. F-T reactions can be effectively catalyzed by group VIII metals in their native form, as an oxide such as wustite or magnetite or as an Fe-bearing silicate, but metal sulfides are not effective in this respect (Lancet and Anders, 1970; Anderson, 1984; Szatmari 1989; Salvi and Williams-Jones, 1992,1997a; Potter and Konnerup-Madsen, 2003 and references therein; Housecroft and Sharpe, 2005;

Sivaramakrishna et al., 2010). The length of the carbon chain produced by F-T synthesis is governed by the probabilities of addition to the chain by either another carbon moiety (propagation) or a hydrogen atom (termination). Therefore, a mixture of straight chain and branched hydrocarbons will be produced but light, shorter chain species will always be favoured (Anderson, 1984; Salvi and Williams-Jones, 1997a and references therein; Liu et al., 2007; McCollom et al., 2010). We can express these factors via the following equations. The mole fraction of a product having ‘n’ carbons is given by the expression:

$$Mn = (1-p)p^{n-1} \qquad \textbf{Eq. 2.6}$$

Where ‘p’ is the chain growth probability, defined as:

$$P = \gamma_p/(\gamma_p + \gamma_t) \qquad \textbf{Eq. 2.7}$$

where γ_p and γ_t are the rates of propagation and termination, respectively (Ushiba and De Deken, 1984). For the sake of argument, assuming that the probabilities of propagation and termination are equal (i.e., a hydrocarbon molecule is just as likely to react with another hydrocarbon molecule propagating the carbon chain or with a hydrogen molecule, terminating the chain), as the carbon number of the product increases, the mole fraction of that product decreases exponentially (Shultz-Flory trend; Figure 2.13). This is a strong indication of an abiogenic hydrocarbon origin either via Fischer-Tropsch or catalytically enhanced reductive coupling reactions in which larger hydrocarbons are produced by the ‘polymerization’ of smaller molecules with one another.

$$2CH_4 = C_2H_6 + H_2 \qquad \textbf{Eq. 2.8}$$

$$CH_4 + C_2H_6 = C_3H_8 + H_2 \qquad \textbf{Eq. 2.9}$$

Four (ROM1158, MK4209-1, UG3750#0 and UG3750#6) of the five samples of quartz from PGE-rich quartz + sulfide assemblages show significant deviation from the expected trends of saturated and unsaturated hydrocarbon abundances. These samples show a stark increase in the unsaturated hydrocarbon abundance, particularly in propylene, with the abundance of propylene exceeding, or comparable to that of propane. This trend seems to be prevalent in samples, including a number of mineralized Sudbury breccia samples that are enriched in PGE or associated with PGE/PGM enrichment in the vicinity. For instance, drill core assay information for sample MK4209-1 (Levack Property, KGHM International Ltd./Quadra FNX Mining Ltd. drill core ID: FNX4209) show a Pt and Pd enrichment of 3.14 and 0.88 gpt (grams per ton of ore), respectively. The propylene/propane ratio in this sample is 1.56, which is significantly higher than the average ratio from the Sudbury breccia of both mineralized (0.273) and barren (0.056) environments. The average propylene/propane ratio from all 5 samples of crushed quartz from PGE-rich quartz + massive sulfide alteration assemblages yields a value of 2.86, approximately an order of magnitude higher than the average ratio of the mineralized Sudbury breccia samples. This trend is also evident in the unsaturated to saturated hydrocarbon ratio with the PGE-rich samples possessing an average ratio of 0.211 while the mineralized and barren Sudbury breccia samples average 0.026 and 0.021, respectively (Table 2.2). A number of Sudbury breccia samples from the mineralized package also deviate from expected hydrocarbon trends in a similar fashion to the PGE-rich samples (Figure 2.10 – labelled points 1-4). The Pt and Pd assay values for these samples can be found in the Figure 2.10 caption.

Table 2.2: Unsaturated/saturated hydrocarbon ratio and propylene/propane ratio from investigated environments.

	SUBX (mineralized environment)	**SUBX (barren environment)**	**PGE-rich mineralized alteration veins**	**PGE-poor mineralized alteration vein (A2-2)**
Sample number	410	45	5	1
unsaturated/saturated hydrocarbon ratio	0.026	0.021	0.211	0.005
propylene/propane ratio	0.273	0.056	2.859	0.004

It has been documented that Pt and Pd metal, minerals bearing these elements as well as other transition metal-bearing minerals can catalyze dehydrogenation reactions of light saturated hydrocarbons (i.e., propane) at elevated temperatures and pressures (Figure 2.19; Cavani and Trifiro, 1995; Housecroft and Sharpe, 2005; Virnovskaia et al., 2008; Czuprat et al., 2010; Ziaka and Vasileiadis, 2011) and promote skeletal rearrangements (Sivaramakrishna et al., 2010).

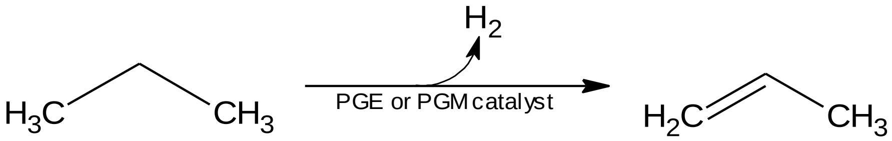


Figure 2.19: Propane dehydrogenation to propylene by means of PGE or PGM catalysis.

This seems to suggest that the presence of PGE/PGM will chemically alter the hydrocarbon signature of the fluid with which it interacts, catalytically dehydrogenating saturated hydrocarbons. Figure 2.20 displays how a carbonic fluid originally endowed with methane or carbon dioxide can evolve to form a fluid richer in higher order saturated and unsaturated hydrocarbons in a PGE/PGM-rich environment.

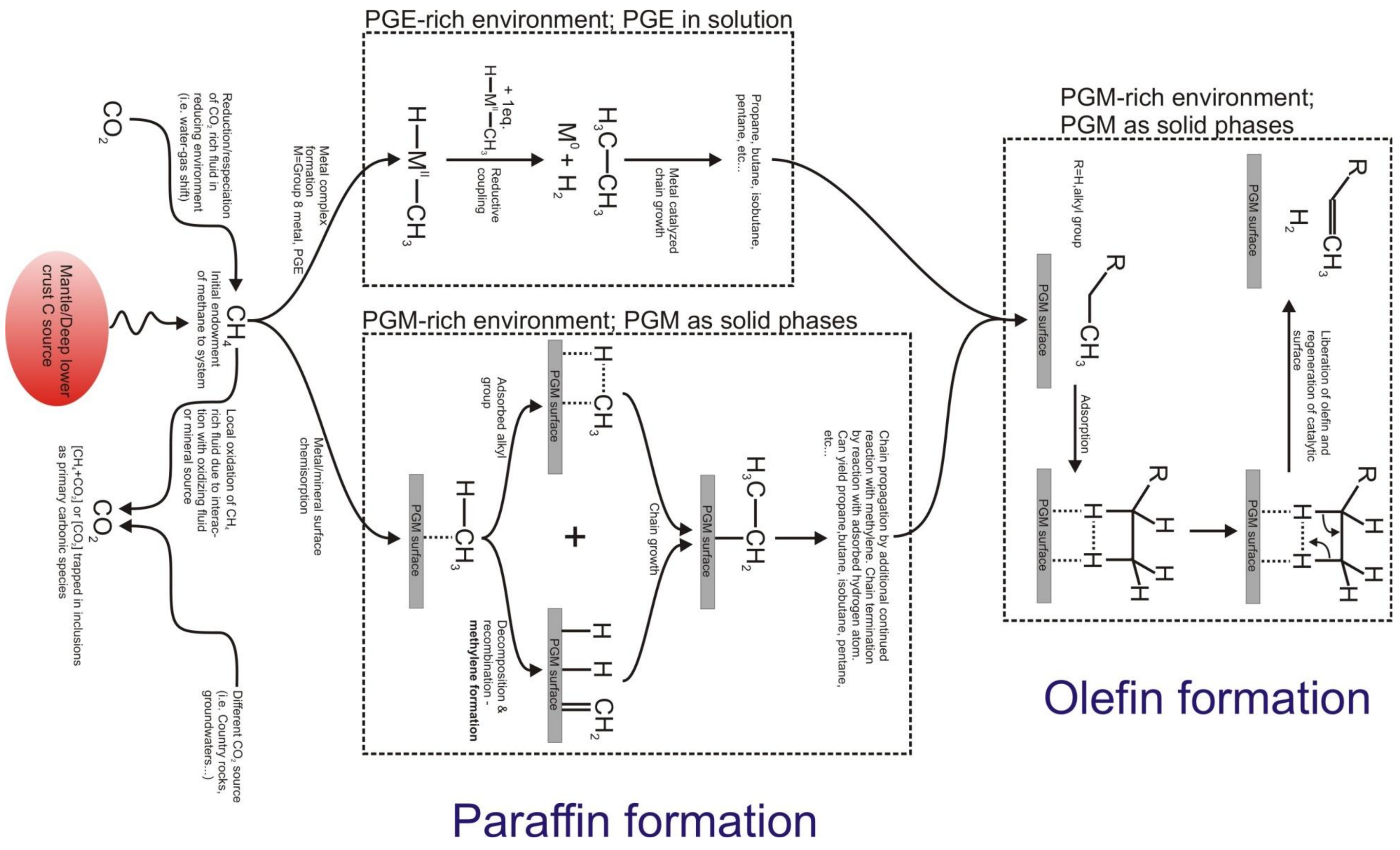
PGE-rich environment; PGE in solution
PGM-rich environment; PGM as solid phases
PGM-rich environment; PGM as solid phases
Olefin formation
Paraffin formation
Mantle/Deep lower crust C source
CO_2
Reduction/respeciation of CO_2 rich fluid in reducing environment (i.e. water-gas shift)
CH_4
Initial endowment of methane to system
Local oxidation of CH_4 rich fluid due to interaction with oxidizing fluid or mineral source
Different CO_2 source (i.e. Country rocks, groundwaters...)
CO_2
$[CH_4+CO_2]$ or $[CO_2]$ trapped in inclusions as primary carbonic species
Metal complex formation M=Group 8 metal, PGE
Metal/mineral surface chemisorption
$H—M^{II}—CH_3$
+ 1eq. $H—M^{II}—CH_3$
Reductive coupling
$M^0 + H_2$
$H_3C—CH_3$
Metal catalyzed chain growth
Propane, butane, isobutane, pentane, etc...
PGM surface
$H—CH_3$
Adsorbed alkyl group
Decomposition & recombination - **methylene formation**
H····CH_3
+
H H CH_2
Chain growth
$H_3C—CH_2$
Chain propagation by additional continued reaction with methylene. Chain termination by reaction with adsorbed hydrogen atom. Can yield propane,butane, isobutane, pentane, etc...
R=H,alkyl group
R
CH_3
Adsorption
H H H
H····H
Liberation of olefin and regeneration of catalytic surface
H_2
CH_3

Figure 2.20: (previous page): Condensed and simplified model outlining the various PGE/PGM catalyzed reactions that may occur in geological environments. The formation of paraffinic species (saturated hydrocarbons; alkanes) can occur through metal-ligand complexation or surface catalyzed pathways from which olefinic species (unsaturated hydrocarbons; alkenes, alkynes) can be generated from surface catalyzed reactions yielding hydrogen gas as a by-product.

2.4.5 Comparison to other studies environments

To our knowledge, this is the most comprehensive study of the hydrocarbon signatures from igneous rock-hosted fluid and of the SIC and its footwall environment. An appreciable number of hydrocarbon investigations have been performed on various igneous/crystalline bodies around the world (Petersilie and Sorensen, 1970; Konnerup-Madsen et al., 1985; Kogarko et al., 1987; Salvi and Williams-Jones, 1992,1997a,1997b; Channer and Spooner 1994a,1994b; deRonde et al., 1997,2003; Nivin, 2002; Potter and Konnerup-Madsen, 2003 and references therein; Potter et al., 2004; Hanley et al., 2005; Graser et al., 2008; Savelieva et al. 2008; Ryabchikov and Kogarko, 2009). Salvi and Williams-Jones (1992,1997a) report several in-depth hydrocarbon studies on a REE-rich peralkaline granite (1.3% REE oxides near the center of the complex; Strange Lake, Quebec/Labrador, Canada) where hydrocarbons up to C5 were detected in quartz from pegmatitic veins within the granitic complex. Hydrocarbons were interpreted as abiogenic in origin due to their presence in crystalline basement rock with no access to organic carbon sources. Three possible mechanisms put forth to explain the abiogenic synthesis of hydrocarbon species in this granitic body include: (i) the reaction between an aqueous fluid and graphite, (ii) the re-equlibration/re-speciation of oxidized carbonic fluids (i.e., CO_2, CO) to methane in a significantly reducing C-O-H bearing system (water-gas shift reaction - equation 2.2; Potter and Konnerup-Madsen, 2003), and (iii) Fischer-Tropsch style reactions (equations 2.4 and 2.5). The very low abundance of graphite in the North Range lithologies of the SIC suggest that the hydrocarbons present there are unrelated to the re-speciation of elemental carbon. Thus, the hydrocarbons related to Sudbury may be in part related to CO_2/CO respeciation or F-T reactions as described by Salvi and Williams-Jones (1992,1997a), or the result of PGE/PGM catalyzed reductive coupling reactions.

Salvi and Williams-Jones (1997a) were able to detect the presence of H_2 gas as a significant gas fluid phase in many of the samples analyzed (up to 35 molar% in fluid from quartz extracted from fresh pegmatite). The presence of hydrogen and varying levels of carbon dioxide in the fluid lends support to the Fischer-Tropsch synthesis being responsible, at least in part, to the hydrocarbon budget of the fluid phase. The abundance of ethane and propane detected in the peralkaline granites of Strange Lake were found to range between 0.9 – 9% and 0.2 – 1.9%, respectively (mole% normalized to total hydrocarbon volatiles and thus excludes water and CO_2; Salvi and Williams-Jones, 1997a). Ethane abundances in the Sudbury breccia populations are moderately lower, averaging 3.8% and 4.4% for barren and mineralized breccia populations, respectively. The analysis of quartz from PGE-rich quartz + sulfide assemblages showed similar ethane abundances, averaging 4.4%. Propane abundances in the Sudbury breccia were found to average 0.15% and 0.1% for barren and mineralized breccia populations, respectively; this value averages 0.31% in the quartz samples. The elevated levels of light hydrocarbons (i.e., ethane and propane) in the peralkaline granite from Strange Lake compared to Sudbury breccia and quartz samples from the SIC footwall environment may be attributed to the predominance of F-T reactions as the main hydrocarbon control in the peralkaline system. This theory is supported by the widely distributed F-T synthesis iron-based catalysts magnetite and hematite (Anderson, 1984; Salvi and Williams-Jones, 1990; Potter and Konnerup-Madsen, 2003 and references therein; McCollom and

Seewald, 2006; McCollom et al., 2010) present in the peralkaline granite as by-products of alteration caused by the introduction of late stage orthomagmatic fluid into the system released during the crystallization of subsolvus granite (Salvi and Williams-Jones, 1997a). Magnetite is present in Sudbury as only a minor phase in 'high-sulfide' veins or found associated with alteration assemblages in sulfide vein margins and as a late stage phase in epidote altered zones (Farrow and Watkinson, 1992, 1999; Farrow and Lightfoot, 2002 and references therein; Farrow et al., 2005). Therefore, the absence of magnetite in the Sudbury breccia, its scarcity in massive sulfide assemblages and its emplacement in epidote assemblages as a late stage suggests that magnetite did not play a significant role in catalyzing in situ F-T reactions within early circulating fluids. Rather, it seems more likely that catalytically active PGE/PGM played a more significant role than magnetite in generating the abiogenic hydrocarbons associated with the SIC and its footwall lithologies. However, this cannot be confirmed until additional experiments have been performed to determine the activity of PGE/PGM in producing higher order hydrocarbons from methane in geological systems.

The occurrence of hydrocarbons has been reported in alkaline rocks (Nivin, 2002; Potter and Konnerup-Madsen, 2003 and references therein; Potter et al., 2004; Ryabchikov and Kogarko, 2009), peralkaline granites (Salvi and Williams-Jones, 1992,1997a) as well as carbonatites (Ting et al., 1994). Additionally, complex hydrocarbons have been found in garnet phenocrysts in the Mir kimberlite, Siberia (Krot et al., 1994) and were interpreted as being magmatic in origin. This would imply that methane and higher order hydrocarbons are stable at the high pressures (~10 GPa) and high temperatures (>1000 K) and were preserved in the Mir kimberlite due to their rapid ascent to the surface. This is in agreement with theoretical (Ancilotto et al., 1997; Spanu et al., 2011) and diamond anvil experiments that replicate upper mantle pressures and temperatures (Kolesnikov et al., 2009; Shinozaki et al., 2010) and show that the production of higher order hydrocarbons is thermodynamically preferable in these conditions and is thus available to migrate to more shallow crustal environments via deep faults and conduits. Extending this concept to Sudbury, it may be the case that the entire SIC, and the adjacent brecciated and ductile footwall environment, was initially endowed with an influx of light hydrocarbons (dominated by methane) that was introduced into the system from the lower crust and/or upper mantle, liberated by the 1.85 Ga impact event and later chemically modified in situ (Hanley et al., submitted). Geophysical modelling has suggested that an impactor the size of that which struck the Sudbury area (~10 km in diameter) would have possessed sufficient energy to penetrate deep into the crust, shock melting a large volume of the lower crust and potentially breaching the upper mantle (Mungall et al., 2004), which would allow for the release of large volumes of carbonic volatiles that could migrate into the upper crust through deep penetrating conduits. The upper-mantle is a significantly reducing environment with oxygen fugacities at or below FMQ (Frost & McCammon, 2009; Ryabchicov & Kogarko, 2010; Cottrell & Kelly, 2011; Goncharov and Ionov, 2012), however, thermodynamic calculations (Huizenga, 2001) and fluid inclusion studies (Hidas et al., 2010; Yamamoto et al., 2011; Berkesi et al., 2012) indicate that the dominant carbonic phase at oxygen fugacities and temperatures associated with the upper mantle is CO_2. Other work (Shinozaki et al., 2010) has shown that in deeper regions of the mantle and at regions near the base of the lithospheric mantle (~90km, 2.5GPa, 1150°C & fO_2 of -3.0 log units below QFM; Goncharov & Ionov, 2012), methane is the dominant carbonic phase. This result has also been determined by GC analysis of mantle xenolith olivine that showed the presence of methane but no CO_2 or water (unpublished data from Kerr and Hanley – Chapter 3).

2.4.6 Evaluation of the effects of sample preparation on GC analyses

Sample preparation variation trials indicate that the sonication and heating of samples prior to analysis does not have a significant effect on the hydrocarbon ratios and relative abundances (i.e., the molar percent of hydrocarbon species remains constant). The unheated sample was found to yield less total hydrocarbons and less unsaturated hydrocarbons than heated samples. This is potentially due to issues involving gas adsorption and gas dissolution at low temperatures. At low temperatures (room temperature) hydrocarbons more readily adsorb to surfaces including stainless steel and mineral surfaces, effectively reducing the volume of hydrocarbon volatiles passed into the GC for analysis. Also, at lower temperatures gas is more soluble in water. Thus, the potential for increased gas dissolution in the aqueous phase of the inclusions increases. Since the crusher is not heated past the boiling point of water, this gas may remain dissolved in the non-volatalized water and not passed into the GC. Previously performed studies employing GC suggest that heating at temperatures slightly over 100°C is best for the most complete release of hydrocarbons for GC analysis. In addition, temperatures around 100°C are sufficiently low to not cause hydrocarbon decomposition or undesired side reactions (Bray et al., 1991; Bray and Spooner, 1992; Potter and Longstaffe, 2007). Unsaturated hydrocarbons are especially susceptible to surface adsorption due to the presence of a carbon-carbon double bond that can coordinate to the metal/mineral surface (Bond, 1966; Housecroft and Sharpe, 2005 and references therein). This would explain the lower abundances of unsaturated hydrocarbons detected in the unheated sample analysis. Even though the relative hydrocarbon abundances and ratios remain fairly constant regardless of preparation technique, it is evident from Figure 2.12 that the lowest unsaturated to saturated HC ratio is present in the unheated sample. In the unheated sample the abundance of propylene is reduced yet still detectible in appreciable concentrations while trace amounts of higher order unsaturated species are absent in the chromatogram. Since propylene is always found in higher abundances than other unsaturated species (in all analyses performed in this study) it constitutes the main control over the unsaturated to saturated HC ratio of the fluid. This explains why the unsaturated:saturated ratio of the fluid from the unheated sample is not drastically lower than that of heated samples even though there are fewer unsaturated hydrocarbon species detectable in the unheated sample.

Results from preparation variation experiments indicate that sonication does not have any noticeable effect on either the hydrocarbon speciation or abundances from samples analyzed using this gas chromatographic technique. On the other hand, heating was found to be very important for complete volatilization of both saturated and unsaturated hydrocarbon species. Both the total hydrocarbon and unsaturated hydrocarbon abundances were markedly lower in the unheated sample than in heated samples most likely due to surface adsorption and dissolution effects.

2.4.7 Test of hydrocarbon-based exploration criteria on a "blind" sample set

A selection of 8 Sudbury breccia samples collected from outcrops from the North Range footwall environment were analyzed to determine if their hydrocarbon signatures display predicted hydrocarbon discrimination based on their location relative to sulfide mineralization. Of these 8 samples, the 4 acquired from footwall environments distal to surface exposed mineralization or contact-style embayment structures displayed hydrocarbon signatures that one would expect, falling within the field outlined for the barren Sudbury breccia environment (Figure 2.21). The other 4 samples were collected from an area proximal to the Barnet Showing adjacent to the Strathcona Mine, which is characterized by Cu-PGE-rich, high-sulfide vein exposure that crosscuts Sudbury breccia and Levack gneiss and represents the surface expression of the Strathcona Mine ore body (Legault et al., 2003). Two of the four samples collected from the area proximal to the Barnet Showing (02AV-28 and 02AV-54) show significantly elevated abundances of propane and propylene and lie within the 'mineralized' Sudbury breccia field in the discrimination diagrams investigated, while the other 2 lie within the 'barren' Sudbury breccia field, despite there being considerable overlap between the two fields. The Barnet Showing is a surface exposed high-sulfide, Cu-Ni-PGE sulfide vein that crosscuts the Sudbury breccia package from which the 4 samples were acquired. The presence of PGE-enriched ore near the collected samples may be the cause of the elevated propylene abundance in these samples. However, without detailed mapping of the vein stockwork systems and an understanding of the temporal relationship between the emplacement of the sulfide ore and associated Sudbury breccia, it is difficult to determine the definite cause of the anomalous hydrocarbon signatures. Nonetheless, this method of analysis possesses the potential to determine the presence of nearby sulfide mineralization considering that 2 of the 4 Sudbury breccia samples taken from an area proximal to Cu-Ni-PGE sulfide mineralization were found to significantly deviate from background hydrocarbon abundances. A much larger number of samples must be collected and analyzed in order to yield more conclusive results, yet tentative findings illustrate the potential of this technique to aid in the exploration of footwall-style ore bodies.

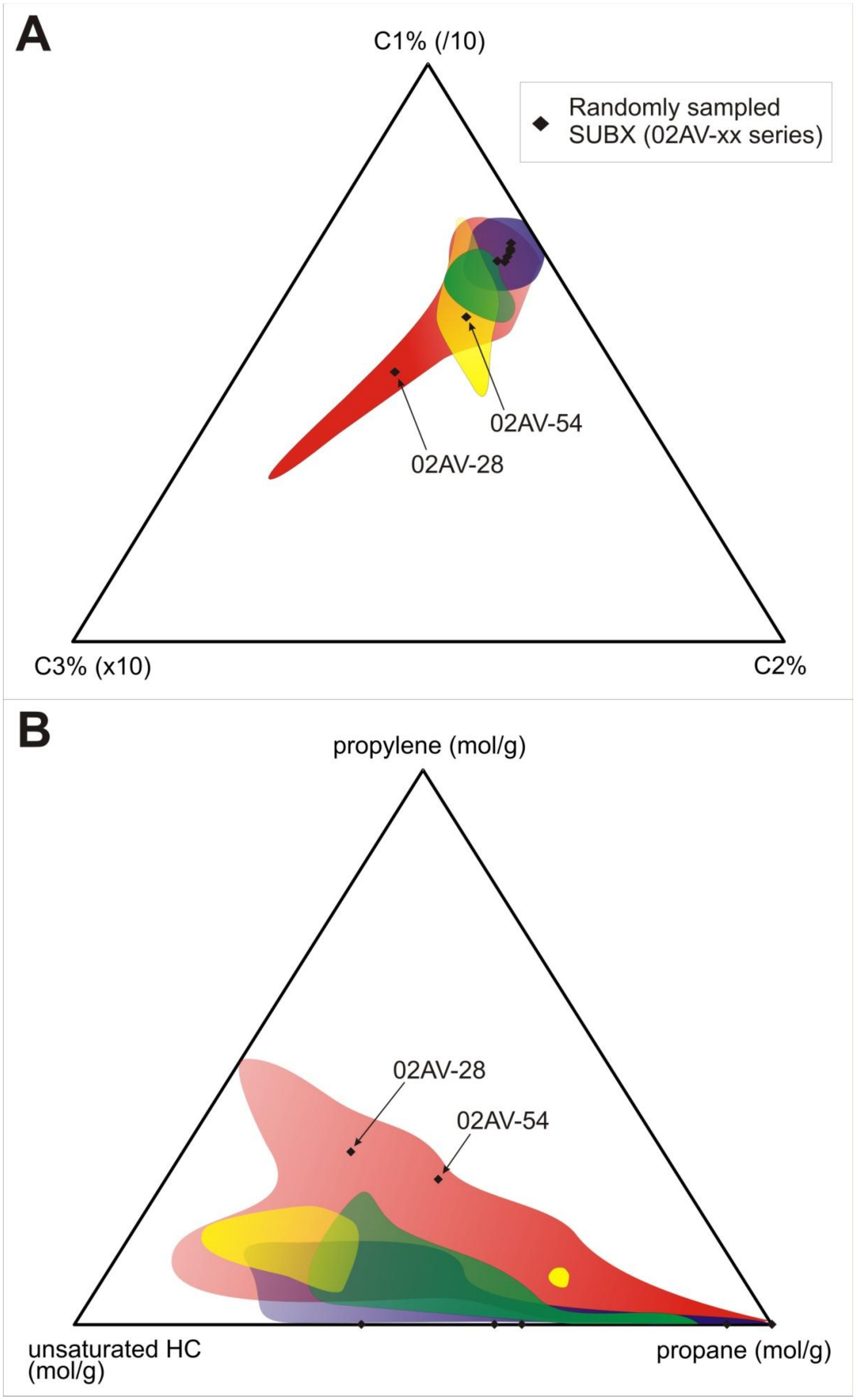

A
C1% (/10)
◆ Randomly sampled SUBX (02AV-xx series)
02AV-54
02AV-28
C3% (x10)
C2%
B
propylene (mol/g)
02AV-28
02AV-54
unsaturated HC (mol/g)
propane (mol/g)

Figure 2.21 page): Hydrocarbon discrimination diagrams displaying the potential of the hydrocarbon signature of Sudbury breccia for exploration of footwall Cu-Ni-PGE sulfide mineralization. Eight SUBX samples from the North Range (see Figure 2.1) were analyzed and plotted in 2 hydrocarbon discrimination diagrams. Of the 8 samples, 4 (02AV-01, 02AV-02, 02AV-17, and 02AV-18) were collected from a barren environment distal from any embayment structure or surface exposed mineralization. The other 4 samples (02AV-13, 02AV-25, 02AV-28 and 02AV-54) were taken from an area close to the Barnet Showing, a Cu-PGE footwall-style surface exposed sulfide vein. Of the 4 samples taken from nearby mineralization, 2 samples (02AV-28 and 02AV-54; labelled in diagrams) possessed anomalous hydrocarbon signatures. *A* – Ternary discrimination diagram of C1 mole% (/10) versus C2 mole% versus C3 mole% (x10). *B* – Ternary discrimination diagram of propylene abundance versus propane abundance versus unsaturated hydrocarbon abundance (mol/g of rock).

2.4.8 Implications and limitations for routine exploration

This study was performed in order to determine if the hydrocarbon signature of Sudbury breccia could be employed as an exploration tool for the location of footwall-style sulfide mineralization. Thus, understanding the genetic, mechanistic and temporal characteristics of the hydrocarbons in these systems is not of paramount importance to this study. Two key factors may be useful in aiding sulfide ore exploration. First, the average abundance of the light saturated hydrocarbons is markedly higher in breccia from mineralized environments than barren breccia. For this factor to be used effectively, a sufficiently large number of samples must be analyzed against sulfide-barren Sudbury breccia samples in order to yield a statistically significant separation between the two populations (i.e., clustering). The most effective way in which this exploratory tool could be brought into fruition is performing gas chromatographic analysis in the field, in which one could portably crush and analyze samples of Sudbury breccia (or other footwall-associated rocks) to determine, to a particular degree of certainty, whether sulfide mineralization is nearby. The saturated hydrocarbon abundance criteria for use in exploration possesses some limitations: (i) a large number of samples must be collected and analyzed in order to produce statistically significant results, (ii) samples of breccia collected only from surface exposures may not be necessarily representative of breccia at depth. This would mean drill core, and thus drilling operations, would still be required to effectively explore for sulfide mineralization, and (iii) elevated saturated hydrocarbon abundances from samples of breccia is not necessarily a function of sulfide proximity but rather would suggest the presence of sulfide mineralization somewhere in the embayment-associated footwall breccia package.

A more robust hydrocarbon based exploratory tool is the unsaturated to saturated hydrocarbon ratio, specifically the propylene to propane ratio, and the abundance of the C3 hydrocarbons in general. Through the use of the unsaturated hydrocarbon signatures (particularly propylene), it appears possible to locate the presence of footwall-style Cu-PGE-rich massive sulfide deposits based on elevated propylene/propane ratios in hydrocarbon-bearing, breccia-hosted fluids toward the upper region of the sulfide body. This tool may be best suited for the exploration of PGE/PGM-rich sulfide ore and not just base metal sulfide deposits in general. The abundance of propylene detected in quartz from PGE-rich quartz + massive sulfide alteration assemblages is distinctly higher than that of either Sudbury breccia environment. Additionally, a number of samples of breccia from mineralized environments display similar C3 and unsaturated hydrocarbon deviations from expected trends and clusters in a number of discrimination plots. These samples of Sudbury breccia were found to be enriched in Pt and Pd themselves or within 20 feet or less of an area of PGE enrichment. These findings suggest that the presence of PGE or PGE-bearing minerals promotes the increase in C3 hydrocarbon abundance and the dehydrogenation of saturated hydrocarbon species, effectively altering the unsaturated to saturated HC ratio. Employing the unsaturated to saturated HC ratio in PGE-rich ore exploration appears more promising than using average hydrocarbon abundances for two main reasons: (i) a smaller sample size is likely needed as illustrated by the consistent deviation from expected hydrocarbon trends by 4 of the 5 PGE-rich quartz samples and 2 of the 4 Sudbury breccia samples from very close to the Cu-Ni-PGE mineralization of the Barnet Showing, and (ii) the deviations to the hydrocarbon signatures from the presence of PGE-rich mineralization are easily recognizable and distinguishable from background signatures. Drilling projects would still be required to in order to determine the presence of potential PGE-rich ore bodies not necessarily expressed at surface via the GC analysis of rocks taken from depth. Work by Hanley et al., (2004) determined that Sudbury breccia bulk rock concentration of Cl and Br increases as the proximity to Cu-Ni-PGE sulfide ore decreases. The combination of ion and gas chromatography (Channer and Spooner, 1994) for the analysis of Cl, Br and hydrocarbon pathfinders would bolster the effectiveness and level of confidence in sulfide ore exploration associated with the SIC. With that being said, a multifaceted exploration approach seems a likely necessity.

To summarize, in order for hydrocarbon signatures to be effectively used in sulfide ore exploration, 3 factors must be considered: (i) a large enough sample size is obtained in order to acquire sufficient statistical distinction between mineralized and barren hydrocarbon signatures, (ii) rock crushing gas chromatography must be readily available (e.g. in core chack or field truck), as trace level higher order hydrocarbons are undetectable optically and analysis by techniques such as Raman or mass spectrometry can prove to be more time consuming, expensive and not necessarily compound selective (i.e., Raman analysis is functional group selective; Burke, 2001; Scoog et al., 2007; Kolesnikov et al., 2009), and (iii) drilling projects will still be required in order to collect a comprehensive set of samples from depth.

2.5 Conclusions

The hydrocarbon signature of the fluid phase contained in Sudbury breccia from the North Range footwall of the Sudbury Igneous Complex was detected and characterized through the use of in-line rock crushing gas chromatography. A population of Sudbury breccia samples from barren and Cu-PGE-fertile environments were to determine if any systematic differences are present in the hydrocarbon signatures of the two populations (i.e., speciation, abundances). Additionally, rock samples from the SIC main mass units, country rocks and footwall-hosted mineralized alteration veins have also been investigated. The key findings of this study are:

(i) Fluids trapped in Sudbury breccia from mineralized embayments (n=410) are characteristically more enriched in C1-C4 *saturated* hydrocarbons (more than 2x more abundant [for propane for instanct] on the basis of mol per gram of crushed host rock) compared to fluids in barren breccias (n=45). The size of the sample population required to detect this difference does not have to be large and can be obtained from surface outcrop (e.g. population size of 5-10; Figure 2.21), not necessarily drill core. Analysis of a blind sample set of 8 Sudbury breccia samples (4 from barren footwall, 4 from within 200 meters from footwall-style mineralization) showed that 2 of the 4 samples from the mineralization-proximal environments were anomalous with respect to hydrocarbon abundance, whereas the 4 samples from a barren footwall environment were not anomalous.

(ii) Within the mineralized embayment, unsaturated hydrocarbon abundance in SUBX matrix shows a spatial association with a footwall-style sulfide ore body. However, the average abundance of total *unsaturated* hydrocarbons does not differ by a statistically significant amount between the two breccia environments. A region of anomalously high propylene/propane ratios (i.e., >1) occurs in the narrow region (150 – 200 meter thickness) of Sudbury breccia between the SIC contact area (mineralized with contact-style Ni-Fe-rich ore) and the upper-most portion of the footwall-style Cu-Ni-PGE ore body nearest the contact. While the PGE are suspected as the catalytic mechanism for the formation of unsaturated hydrocarbons, it is still unclear as to whether the elevated levels of unsaturated hydrocarbons in this area are the result of localized chemical alteration of pre-existing saturated hydrocarbons due to locally higher temperatures and PGE concentrations or a physical mechanism responsible for concentrating unsaturated hydrocarbons in this region.

(iii) A Schultz-Flory distribution for hydrocarbons C1-C6 in the trapped fluid is present in all investigated samples from all environments (including analyzed mineralized alteration veins) suggesting an abiogenic hydrocarbon origin. Additionally, there is a strong linear relationship between the molar abundances of methane and ethane, and methane and propane to a lesser degree, in the trapped fluid associated with the SIC and its footwall environment. This suggests the presence of common chemical mechanisms/controls responsible for the generation of hydrocarbons in these environments. Analysis of a sample of quartz from a PGE-poor mineralized alteration vein that is spatially and structurally coeval with footwall-style magmatic ore also consistently follows the aforementioned hydrocarbon trends indicating that the fluids present in Sudbury breccia and in quartz-bearing mineralized alteration veins share a common source or have been influenced by identical chemical and physical factors (i.e. mineralogical regime, temperature, etc.).

(iv) In contrast to the aforesaid hydrocarbon relationships followed by all samples from the SIC main mass units, country rocks, Sudbury breccia and PGE-poor mineralized alteration veins, significant deviations to these relationships in quartz-hosted fluid from PGE-rich mineralized alteration veins are present. This finding suggests that PGE/PGM likely play an important role on the hydrocarbon speciation and abundances of fluid circulating through the Sudbury ore environments via catalytic dehydrogenation of saturated to unsaturated hydrocarbons. However, additional high temperature and pressure experiments are required to fully elucidate the effects of metal and mineral catalysts on fluid hydrocarbon signatures.

The analysis of breccia-hosted fluid by GC is a potentially important criterion to consider when exploring for footwall-hosted sulfide ore. Exploration of footwall-style sulfide mineralization in the North Range of the SIC through the use of hydrocarbons is most effective using the total abundances of light saturated hydrocarbon species and unsaturated hydrocarbons, with specific attention to propylene abundance. Our results show that light saturated hydrocarbon abundances are statistically higher in regions of the footwall that are host to sulfide mineralization relative to breccia environments barren of such mineralization. Within a mineralized footwall embayment environment itself, unsaturated hydrocarbon abundances can be effectively used to aid in ore exploration. Results illustrate that the Sudbury breccia near upper-most region of a footwall-hosted ore body is significantly enriched in unsaturated hydrocarbon, specifically propylene. This result can be employed as a down hole tool to supplement drilling programs. Samples of breccia can be systematically analyzed as one drills into the footwall, where elevated unsaturated hydrocarbon abundances would suggest the presence of a nearby ore body, one of which is likely more deeply hosted in the footwall. Additionally, significantly elevated fluid unsaturated hydrocarbon abundances and deviations from light hydrocarbon abundance relationships (i.e., methane mole% versus ethane mole%) is present in samples from PGE-rich mineralized alteration veins. This is also possesses important implication to exploration as a cheap and viable chemical tool to determine whether a system of hydrothermal veins and stockwork is PGM mineralized. Platinum group elements are effective catalysts in dehydrogenation reactions in which saturated hydrocarbons are converted to their unsaturated derivatives. Thus, anomalous levels of unsaturated hydrocarbons (i.e., predominantly propylene) can be used as an effective criterion for the exploration of low-sulfide Cu-Ni-PGE-rich footwall-style ore bodies.

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Chapter 3: Preliminary investigation of the light hydrocarbon compositions of fluids associated with various geological environments and regimes: A first comparision

Mitchell Kerr*, Jacob Hanley
Department of Geology, Saint Mary's University, Halifax, Nova Scotia, Canada
*corresponding author email address: mitchjkerr@gmail.com

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Abstract

The light, saturated hydrocarbon signatures (C1-C4 saturated species) of trapped fluid (in fluid inclusions and/or occluded gas) have been analyzed directly via gas chromatography and collected from a number of published literature sources in order to investigate how light hydrocarbon abundances compare and contrast in a variety of different geological environments. Environments investigated are represented by samples from various sedimentary, metamorphic and igneous terranes, both ore-bearing and non-ore-bearing. Although gas chromatographic studies investigating the hydrocarbon signatures of trapped fluids from certain environments has been performed previously, a study comparing the hydrocarbon signatures from a comprehensive variety of geological environments has yet to be compiled. Even though this study is limited to using bulk analytical gas chromatographic techniques and relying in part on the past

research of others, some important findings have been identified. Hydrocarbon-bearing fluids of known thermogenic origin are well known to be markedly richer in C3+ hydrocarbon species relative to hydrocarbons of suspected abiogenic origin. Fluids from various igneous environments (i.e., mantle, porphyry-epithermal, alkali-agpaitic, mafic-ultramafic associated Ni-Cu-PGE sulfide deposits, Phanerozoic/Proterozoic rare metal pegmatitic environments) share very similar hydrocarbon signatures, suggesting similar origins and genetic controls likely abiogenic in nature due to their magmatic, organic-compound-free setting of entrapment (i.e., Fischer-Tropsch synthesis or abiogenic reductive coupling reactions). Fluids from complex geologic environments with multiple fluid generations (i.e., magmatic fluids in metamorphosed terranes), have very scattered and inconsistent hydrocarbon signatures, which is what would be expected from said environments due to the presence of multiple fluid generations and a large degree of post-entrapment modification effects. This study presents a number of binary and ternary discrimination diagrams comparing the hydrocarbon signatures from various geological environments and offers a number of potential chemical controls and mechanisms responsible for the hydrocarbon signatures of the trapped fluids observed.

3.0 Introduction

Hydrocarbons are ubiquitous in many geological environments as volatile fluids trapped in fluid inclusions and/or as occluded gases in rocks. These hydrocarbons are present as trace phases in igneous environments as aqueous and carbonic (i.e., CO_2-dominated) fluid inclusions yet have been recognized in igneous crystalline rocks as important ore fluid constituents in Ni-Cu-platinum group element (PGE) deposits in the Sudbury mining district (Hanley et al., 2005), in igneous environments of alkali-agpaitic affinity (Konnerup-Madsen et al., 1985; Salvi & Williams-Jones, 1997a; Nivin, 2002; Potter and Konnerup-Madsen, 2003), and in quartz-carbonate and pegmatitic veins in Archean terranes (Bray & Spooner, 1992; Channer & Spooner, 1994b) for example. Hydrocarbons are also prevalent fluid constituents in many basinal/sedimentary (Sassen et al., 1999; Chen et al, 2000; Mazzini et al., 2011) and metamorphic environments (Channer & Spooner, 1994a; de Ronde et al., 1997). Hydrocarbons present in these systems can be the result of multiple chemical processes, both biogenic and abiogenic. Biogenically derived carbonaceous material in basinal (Sassen et al., 1999; Chen et al., 2000), geothermal (Mazzini et al., 2011) and fumarolic/bubbling pool environments (Botz et al., 2002; Tassi et al., 2010) can undergo thermogenic decomposition yielding short chain, primarily aliphatic, hydrocarbons (Schoell, 1980; Lorant et al., 1998; Sherwood Lollar et al., 2008). Conversely, hydrocarbons present in certain igneous environments may originate from respeciation of exsolved inorganic gases (i.e., CO_2) or via fluid re-equilibration in a graphite- or carbonate-bearing system at lower temperatures and oxygen fugacities around QFM (Lyutkevich, 1967; Petersilie and Sorensen, 1970; Gerlach, 1980; Kogarko et al., 1987; Konnerup-Madsen et al., 1988). Abiogenic reactions contribute factor to the hydrocarbon budget of igneous and hydrothermal systems through processes such as the Fischer-Tropsch synthesis (FT) in which carbon dioxide can react with hydrogen in catalytic reductive polymerization reactions yielding methane and higher order hydrocarbon species (Abrajano et al., 1990; Sherwood-Lollar et al., 1993, 2008; Salvi and Williams-Jones, 1997a, 1997b; Charlou et al., 1998; Potter and Konnerup-Madsen, 2003; Potter et al., 2004; Nivin et al., 2005; Taran et al., 2007; Ryabchikov and Kogarko, 2009).

Biogenic and abiogenic hydrocarbons are differentiated from one another primarily based on compound specific isotopic analysis, which has been extensively documented as being a robust provenance indicator of bacterial, thermogenic, mantle and atmospheric hydrocarbon (methane) origin (i.e., δD and $\delta^{13}C$ of methane and higher order species; Welhan & Lupton, 1987; Schoell, 1988; Welhan, 1988a; Botz et al., 1996, 2002; Sassen et al., 1999; Potter & Konnerup-Madsen, 2003; McCollom and Seewald, 2006; Tassi et al., 2007, 2010; Sherwood Lollar et al., 2008); however, this technque can be time consuming and requires the use of expensive equipment (i.e., mass spectroscopic techniques). There is little known about distinctive characteristics between the abundances and speciation of hydrocarbons (light aliphatics C1-C4) present in various geological environments. This may be useful in the quick and efficient identification of fluid provenance and equilibration conditions. To the best of our knowledge, no systematic investigation of fluid inclusion hydrocarbon characteristics has been performed on a variety of geological environments (i.e., biogenic and abiogenic hydrocarbons in sedimentary, metamorphic and igneous suites, ore-bearing and non-ore-bearing). Many factors can influence hydrocarbon abundances and speciation in geological environments, including temperature, oxygen and hydrogen fugacities, pressure, and the presence of organic compounds and mineral catalysts. A better understanding of the hydrocarbon fluid characteristics will help determine how these fluids are chemically affected under a variety of unique geological regimes, which can in turn have important exploratory and provenance implications and aid in the determination of fluid equilibrium conditions. However, it is important to note that a study of this nature is challenging for a few main reasons: (i) gas chromatography (the technique used in this study) is a bulk technique such that all fluid inclusions from all assemblages are simultaneously ruptured and analyzed thus constituting a bulk rock fluid, (ii) the use of data from published literature sources raises issues of reliability and consistencey (i.e., methodological concerns), and (iii) the very complex geological histories of many of the investigated environments makes it challenging to draw viable comparisions to other environments.

The main goals of this paper are to: (i) investigate the hydrocarbon signatures of fluid released from fractured fluid inclusions (and occluded gases) from a wide variety of geological environments via gas chromatography performed in this study and from a number of literature sources, (ii) determine whether the light aliphatic hydrocarbon signatures of trapped fluids can be used to differentiate between biogenically versus abiogenically derived fluids and/or equilibration/entrapment conditions, and (iii) offer a number of potential chemical pathways responsible for the presence of hydrocarbon species in trapped rock fluids.

3.1 Geological settings and sample characteristics

This study investigates the volatile hydrocarbon signature of fluids associated with a number of geological environments. This section will work to describe each geological environment investigated in this study and the characteristics of the samples that constitute each environment.

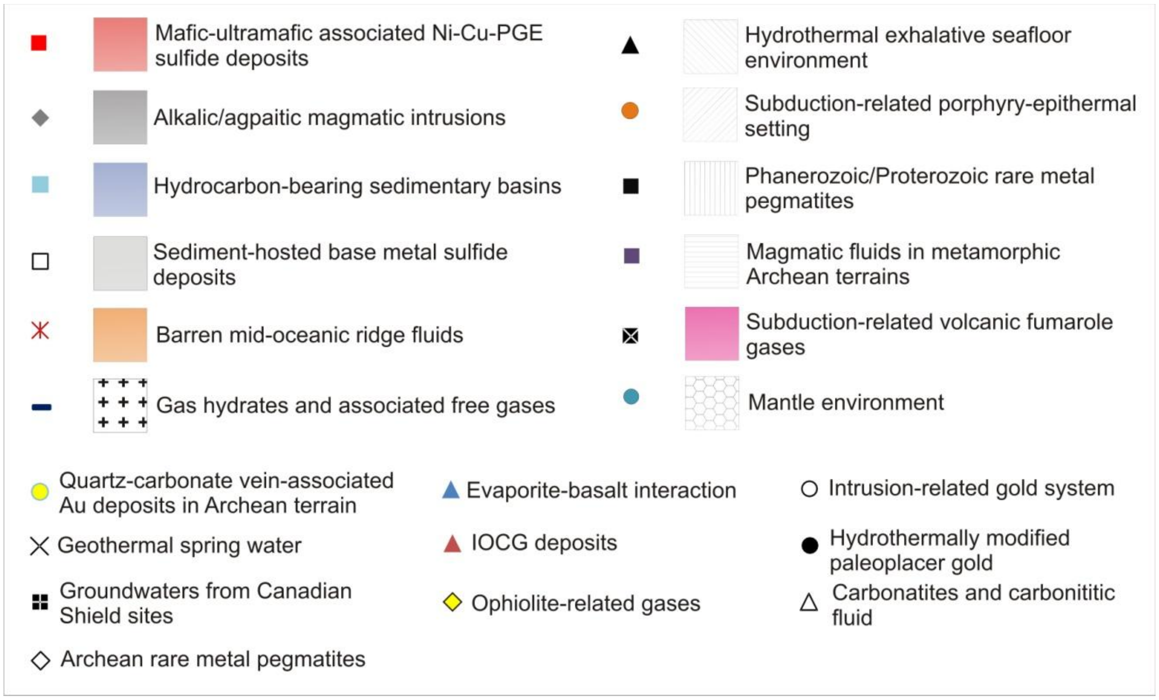


Figure 3.1: Sample environments investigated in this study. Some environments do not have distinct fields associated with them due to the paucity of samples for that particular environment and/or the inability of those environments to be clearly encompassed by a field.

3.1.1 Mafic-ultramafic associated Ni-Cu-PGE deposits

Two world-class Ni-Cu-PGE environments at Sudbury, Canada and Bushveld, Republic of South Africa, yielded data from quartz extracted from quartz + massive sulfide ± epidote ± accessory phase assemblages collected from locations around the Sudbury Igneous Complex (SIC; n=27) and the Bushveld Complex (n=2). The SIC is a large (roughly 60 km by 25 km), differentiated, hypabyssal igneous body of Proterozoic age (~1850 Ma) (Dressler, 1984; Hanley et al., 2005; Hanley et al., 2011). The SIC and its footwall are host to significant Cu-Ni-PGE sulfide mineralization in 'contact-style', 'offset dyke-style' and 'footwall-style' deposits (Naldrett, 1984; Morrison et al., 1994; Ames and Farrow, 2007). Sulfide ore associated with the SIC footwall can be divided into two main types: 'low-sulfide' and 'high-sulfide' styles. Low-sulfide style deposits are Cu-PGE rich, S-poor and interpreted as hydrothermal in origin, hosting low-sulfide minerals such as bornite and PGM (Farrow et al., 2005; Hanley et al., 2005), whereas high-sulfide style deposits are Cu-rich, PGE-moderate, S-rich and are magmatic in origin representing a late stage magmatic residuum post-dating the early hydrothermal activity responsible for low-sulfide, PGE-rich deposits (Naldrett, 1984; Watkinson, 1999; Farrow et al., 2005). Samples were collected from quartz + sulfide mineralized alteration vein assemblages associated with the footwall ore bodies of the SIC which are often always spatially associated with Sudbury breccia, a pseudotachylite/pseudocataclastite formed via the impact-brecciation and shock-melting of country rocks distal (Coats and Snajdr, 1984; Ames et al., 2008).

The Bushveld Complex is a 2055-2060 Ma mafic-ultramafic igneous intrusive body and is host to the Rustenburg Layered Suite (RLS), the largest known layered igneous body in the world (van der Merwe et al., 2012, references therein). The RLS is host to three major PGE-mineralized horizons: UG2, Merensky reef and Platreef, which are hosted in olivine gabbros and troctolites (Kinnaird and McDonald, 2005). Quartz samples were collected from quartz + sulfide assemblages collected from late-stage pegmatite veins, crosscutting mineralized reefs.

3.1.2 Alkalic/agpaitic magmatic intrusions

The peralkaline granite environment is represented by samples of quartz (n=4) in pegmatite veins associated with the Strange Lake peralkaline granitic body in Quebec/Labrador, Canada and whole rock samples (n=7; nepheline-syenites, foidolites and apatite ores) associated with the Khibiny Alkaline Igneous Complex (KAIC) of the Kola Peninsula, Russia. Hydrocarbon data from Strange Lake reported by Salvi and Williams-Jones (1997a, 1997b), and an additional geological description of this environment can also be found in Salvi and Williams-Jones (1992). The Strange Lake pluton occurs in the Rae tectonic Province of the Canadian Shield at the contact between the Archean basement rock and Elsonian quartz monzonite. The 1189 ± 32 Ma granitic body is about 6 km in diameter and is comprised of roughly concentric units of hypersolvus, subsolvus and transsolvus granites. The hypersolvus granite is comprised mostly of perthite, quartz and late arfvedsonite whereas the subsolvus granite is composed of quartz, arfvedsonite, albite and microcline. Pegmatites are present primarily within the subsolvus granite forming thin (10-50 cm) bodies and veins. It is reported that most of the subsolvus granite units have undergone at least 2 episodes of alteration. The first is characterized by the replacement of arfvedsonite by aegirine with magnetite and quartz and is thought to be associated with orthomagmatic fluids released from the crystallizing subsolvus granite. The second stage is characterized by pervasive hematisation and enrichment in calcium. At the center of the igneous body, a potential ore body is present with enrichments of 3.25% ZrO_2, 1.3% REE-oxides, 0.66% Y_2O_3, 0.56% Nb_2O_5 and 0.12% BeO (Salvi and Williams-Jones, 1997a). Hydrocarbon analyses of quartz from “fresh” pegmatites (n=7) that did not display calcic metasomatism were averaged to represent the sample ‘Fresh peg. (avg)’, whereas analyses of quartz from “altered” pegmatites (n=6) displaying calcic metasomatism were averaged to represent the ‘Alt. peg. (avg)’ sample. Averages were calculated based on hydrocarbon data presented in Salvi and Williams-Jones (1997a). An additional 2 sample analyses from Salvi and Williams-Jones (1997b) were used in this study that represent identical samples of fresh pegmatite that differ only by amount of sample crushed (i.e., two separate trials using the same sample but different amounts).

Samples from Khibiny (the KAIC) were collected and analyzed by Nivin et al. (2005) from within the Central Arch zone of the KAIC. The KAIC is of late Devonian age (377 – 362 Ma) and was intruded at the contact of Archean gneisses and Proterozoic sedimentary-volcanic rocks. The KAIC is theorized to be related to a deep mantle plume that drove alkaline magmatism in the area and data indicates a depleted mantle source for the parental magmas of the KAIC with limited crustal fluid contamination. The KAIC is comprised primarily of nepheline-syenites, foidolites and carbonatites (hosts Ba-REE-Sr mineralization), and is host to several economic apatite-nepheline deposits in the Central Arch zone of the complex. The Central Arch zone runs through the center of the otherwise nepheline-syenite based complex and is composed of rocks including urtites, ijolites, melteigites, rischorrites (up to 11% K_2O) and juvites. Unusually high levels of hydrocarbon gases have long been known to be associated with the complex with HC enrichments seemingly linked to Na-carbonate-bearing veins. Carbon is also present in the KAIC in the form of dispersed bitumens, to a lesser degree, as well as solid biogenic matter and graphite, which is even rarer. The 7 samples of interest from this environment represent collected gas samples from boreholes within the Central Arch zone.

3.1.3 Hydrocarbon-bearing sedimentary basins

Hydrocarbon signatures from this environment (n=26) were reported by Chen et al., (2000). Samples were collected from the Tarim basin (TB), located in northwest China that covers an area of about 560,000 km^2. The TB is a cratonic basin that developed on metamorphosed continental crust basement rock. The basin is comprosed of thick layers of marine sedimentary rocks that can be subdivided into three units based on age, sedimentary characteristics and tectonic and thermal evolution: the Sinian-lower Paleozoic unit, the upper Paleozoic unit and the Mesozoic-Cenozoic unit. The basin is an important source of oil and gas, as a series of oil and gas wells with an approximate 1:1 oil to gas ratio have been discovered. The Sinian-lower Paleozoic rocks are important oil and gas source rocks consisting primarily of marine carbonate and clastic rocks and possessing a total organic carbon (TOC) level of 0.92 – 3.4%. The upper Paleozoic (Carboniferous-Permian) source rocks contain an even higher level of TOC of 0.6 to greater than 5%. For a complete and comprehensive description of the rock units and their characteristics, refer to Chen et al. (2000).

3.1.4 Quartz-carbonate vein-associated Au deposits in Archean terrains

Hydrocarbons in quartz and scheelite mineral samples (n=11) from 4 Archean, epigenetic, Au-bearing quartz vein systems: 9 from the Hollinger-McIntyre and Kerr-Addison deposits located in northern Ontario that were collected and analyzed by Channer and Spooner (1994a), 1 from the Lupin Mine, Northwest Territories and 1 from the Red Lake mining district, Ontario. The Kerr-Addison Au-quartz vein system is hosted in mafic and ultramafic volcanics and is closely spatially and temporally related to a hydrothermally altered mafic dyke system. In this comparative study, only sample '89-KA-15-2' is from the Kerr-Addison system. The remaining 7 samples are from the Hollinger-McIntyre Au-quartz vein system that is hosted in mafic to intermediate volcanic rocks as well as carbonaceous horizons and strained felsic porphyries in the southwestern part of the Abitibi greenstone belt, which consists of metamorphic volcanic, sedimentary and intrusive rocks of Archean age (Smith et al., 1984). This vein system is situated in a brittle-ductile shear system and structural analysis indicates that vein formation and deformation occurred synchronously. However, more than one period of deformation and alteration have affected the area (Smith et al., 1984). Adjacent to the veins, the wall rock consists of pyrite-sericite-ankerite-quartz-muscovite assemblages with most of the gold occurring as inclusions in the wall rock pyrite (Wood et al., 1986; Channer and Spooner, 1994a) characterized predominantly by disseminated auriferous pyrite and quartz veins and stringers occurring with carbonaceous material (Smith et al., 1984). [CO_2 + CH_4]-rich inclusions and CH_4-dominated inclusions were found in a vein in massive graphite with interpreted pseudosecondary and secondary origins, respectively, with the pseudosecondary inclusions predating the secondary ones (Smith et al., 1984).

The Lupin deposit is hosted in the Archean Yellowknife Supergroup of supracrustal metasedimentary and metavolcanic rocks in the Slave province, Northwest Territories. The Lupin deposit itself is hosted in an Archean metaturbidite sequence of the Contwoyto Formation and has undergone both contact and regional metamorphic events, 3 phases of deformation, plutonism and all Archean rocks in the area are crosscut by Proterozoic diabase dykes. Ore zones of the Lupin deposit are localized to a continuous sulfide-rich, amphibolitic iron-formation in the Contwoyto Formation, with gold and sulfides in close relationship with quartz veining (Bullis et al., 1993; Geusebroek and Duke, 2004).

The Red Lake gold mine occurs with the Archean Red Lake greenstone belt in the Uchi Sub-province of northwestern Ontario, Canada. The greenstone belt is comprised of mafic-ultramafic to felsic volcanic rocks with lesser amounts of sedimentary rock units surrounded by granitoid units. The gold deposit contains many barren to low-grade banded iron-carbonate ± quartz veins and breccia, which have since been overprinted by silicification and sulfidation temporally related with gold mineralization. The gold mineralization has been noted to be related to the second deformation event in the area occurring between 2723 – 2712 Ma, which has been affected further by later deformation events and dyke emplacement (Dubé et al., 2004; Liu et al., 2011)

3.1.6 Sediment-hosted base metal sulfide deposits

This environment is represented by two samples (n=2), one of quartz and one of calcite originating from the Fundy National Park, New Bruswick, Canada and the Pillara Mine, Western Australia, respectively. The Fundy National Park situated in the Coldbrook Group of late-Precambrian age contains intensely deformed flows, tuffs and abundant volcanogenic sediments of dominantly arkosic composition (Giles and Ruitenberg, 1977; Barr et al., 1994). Sulfides including covelite, chalcocite, chalcopyrite and bornite are commonly found in association with quartz-carbonate veins and stringers crosscutting volcanogenic sediments and tuffs.

The Pillara Mine is an epigenetic Mississippi Valley Type (MVT) deposit hosted in 354 – 378 Ma carbonate rocks of the Lennard Shelf in the Canning Basin, Western Australia. The Pillara Mine is a fault-hosted deposit characterized by open-space filling, breccia and colloform replacement textures of sphalerite, galena, marcasite, calcite and lesser amounts of pyrite and barite. Barite and iron sulfides are interpreted as exhalative in origin (Symons and Arne, 2005).

3.1.7 Barren mid-ocean ridge fluids

The modern seafloor mafic/ultramafic environment (n=9) is represented by 6 samples of whole rock, 1 sample of amphibole and 1 sample of ore minerals that have been collected and analyzed by Savelieva et al. (2008) by dredging at the Mid-Atlantic Ridge (MAR) rift valley and the slopes at 5^{o} – 6^{o} N. The rocks exposed at the seafloor surface where the samples were collected include mantle ultramafic varieties including peridotites and dunites, gabbro, as well as fresh and greenschist facies basalts. Whole rock samples from this environment analyzed via GC include plagiogranite (as veinlets in harzburgites and gabbros), granodiorite, gabbronorite, gabbro and serpentinized lherzolite. It is also noted that the harzburgites and plagiogranites are quite enriched in REE as well as Zr, Hf and Y (Savelieva et al., 2008).

3.1.8 Hydrothermal exhalative seafloor environments

The Archean seafloor mafic/ultramafic environment is represented by samples of quartz (n=11) and barite (n=2) from the 'Ironstone Pods' of the Fig Tree Group rocks of the Barberton greenstone belt (BGB). These samples were collected and analyzed by de Ronde et al. (1997). The massive, Fe-rich Ironstone Pods are the result of seafloor hydrothermal activity during the Archean (~3230 Ma) and occur in conjunction with Cu-Pb-Zn-Ba-rich volcanogenic massive sulfide deposits. This system has been noted to represent the oldest oceanic hydrothermal venting yet recorded on Earth. Features such as chimney-like structures indicate that the pods formed on the Archean seafloor from a fluid of modified seawater composition. The Ironstone Pod assemblages are comprised mainly of hematite and goethite with more minor amounts of quartz, clays and magnetite, and are hosted in Fe-rich, carbonaceous shales with minor sandstone horizons (Hofmann, 2005). No sulfide minerals are present in the pods examined by de Ronde et al. (1994). Altered foliated green chert (silicified ± talc-carbonate ± fuchsite-rich) underlie the pods which are in turn underlain by pervasively altered ultramafic rocks (i.e., serpentinites). The metasomatism present in this system is evident by the pervasive carbonate, silica and iron alteration assemblages throughout most of the central parts of the BGB. A more comprehensive description of the BGB and Ironstone Pod geology can be found in de Ronde et al., (1994,1997).

Barite samples were collected from the Main Workings barite deposit that represent thin (<10cm) barite beds that occur stratigraphically about 50 meters above the Ironstone Pods associated with the Barberton greenstone belt. The barite occurs as coarse crystals, as fine-grained barite-rich sediments, or as the groundmass in sedimentary breccias and conglomerates. Minor sulfides are disseminated within the barite horizons (mainly pyrite; de Ronde et al., 1994,1997).

3.1.9 Subduction-related porphyry-epithermal settings

Samples from this environment (n=5; EB, 06943-110.5, BP, Wolfram, Mt.Wash) consist of quartz from quartz-bearing assemblages from five unique porphyry-epithermal environments. Sample 'EB' is from a quartz + sulfide ± K-feldpsar ± sericite vein from the Elatsite porphyry Cu-Au-PGE deposit in Bulgaria. This deposit is hosted in Palaeozoic granodiorite (314.8 ± 4.9 Ma) and diabase (443 ±1.5 Ma) as relatively young discontinuous porphyry dykes (92.1 ± 0.3 Ma – 91.84 ± 0.3 Ma) (U-Pb in zircon; von Quadt, 2005) cutting Paleozoic and Precambrian metamorphic rocks (Tarkian et al., 2003). Main ore minerals present in the porphyry dykes include bornite, chalcopyrite, sphalerite, molybdenite, magnetite, gold/electrum, and merenskyite. Hydrothermal K-feldspar, anhydrite, and sericite alterations overprint areas along fractures and faults.

Sample '06943-110.5' from Mount Milligan, in B.C., Canada represents quartz from a pyrite (Hg- and As-bearing) ± quartz ± carbonate ± chlorite assemblage that occurs in volumetrically minor, late-stage hydrothermal veins in hosted in volcanic and pyroclastic rocks adjacent to areas of Cu-Au porphyry mineralization and overprint porphyry-stage veins. These late-stage veins contain early and late stage electrum and PGE tellurides and have been interpreted to represent “transitional” (post-porphyry, pre-epithermal) veins in a characteristic calc-alkaline porphyry deposit (LeFort et al., 2011 and references therein).

Sample ‘BP’ represents quartz from a quartz + sulfide assemblage from the Berg porphyry copper molybdenum deposit also in the Canadian Cordillera of B.C, Canada. The mineralization in this deposit occurs in hydrothermal, multistage vein stockworks cutting through the pervasively altered and thermally metamorphosed Jurassic volcanic rocks and Tertiary quartz diorite. Molybdenite and chalcopyrite constitute the most significant ore minerals in the deposit. Molybdenite occurs primarily along the intrusive contact in areas the quartz vein stockworks are well developed whereas the chalcopyrite is abundant in areas displaying biotitic alteration (Brown and Hanley, 2009; Panteleyev, 1981 and references therein).

Sample ‘Mt.Wash’ represents quartz from the Mount Washington porphyry in the Canadian Cordillera of B.C., Canada. This deposit is host to porphyry Cu ± Mo ± Au and epithermal Au-Ag-Cu systems. A late-Eocene to early-Oligiocene quartz diorite stock intrudes older sedimentary and volcanic rock units of Upper Cretaceous and Upper Triassic ages, respectively. The entire area is cut by thrust faults that control mineralization in the system. The Mount Washington system is considered a porphyry-type deposit that has been superimposed by an epithermal Au-Cu-As event (Carson, 1960; BC Geological Survey, 1985).

To the best of our knowledge, there is an absence of peer-reviewed published literature describing the regional geology and petrology of the tungsten-molybdenum porphyry deposit located at Wolfram, Queensland, Australia. However, Queensland Ores Limited describes the site as one of Australia's richest W-Mo deposits characterized by quartz pipes and veins, often exceeding 5 modal% wolframite + molybdenite, hosted in country rock granites.

3.1.10 Phanerozoic/Proterozoic rare metal pegmatites

Samples from this environment (n=4; SQ, CCG, GQA1, GQA2) represent mineral samples (quartz - SQ and CCG; aquamarine beryl – GQA1 ; apatite – GQA2) from U-, Mo- and REE-enriched (± Sn, W and Nb) granitic pegmatitic veins. Samples 'SQ' and 'CCG' were collected from 2 different granitic pegmatite veins associated with the South Mountain Batholith (SMB) of Nova Scotia, Canada. The SMB is a peralumnious granitoid batholith dominated by granodiorites and monzogranites that covers much of southwestern Nova Scotia (~7300 km^2) and is host to number of U-, Sn-, Mo- and W-rich deposits (Clarke and Clarke, 1998). Pegmatite deposits commonly host Mo, Sn, W, Cu, Nb and Ta ore minerals (MacDonald, 2001 and references therein) Sample 'SQ' is from a sample of smoky quartz from crystals that had grown into a cavity/vug in the pegmatite along with large crystals of tourmaline. Sample 'CCG' is from a sample of massive quartz associated with pegmatite stockworks cutting through the often porphyritic granitoids of the SMB at Chebuco Head, N.S., Canada. Samples GQA1 and GQA2 are samples of aquamarine beryl and apatite, respectively, from U-, Mo-, and REE-bearing granite pegmatite veins cutting through the Central Metasedimentary Belt (CMB) of the Grenville Province in Ontario/Quebec, Canada. The Grenville Province is the term generally applied to the youngest portion of the Canadian Shield (~1 Ga) that covers ~1 million square kilometers and formed as the result of an orogenic event. The Grenville Supergroup is the name given to the stratified, now metamorphosed volcanic and sedimentary rocks running through the CMB of the Province as assemblages of quartzite, marble and sillimanite-garnet gneiss. The Grenville Province is underlain by highly deformed and metamorphosed rocks such as migmatites (Moore, 1986 and references therein; Lentz, 1991, 1996).

3.1.11 Archean rare metal pegmatites

Samples from this environment (n=15) were collected and analyzed by Bray and Spooner (1992) and Channer and Spooner (1994b). The Tanco granitic pegmatite occurs in the amphibolites of the English River subprovince in southeastern Manitoba. The Tanco pegmatite is a complex igneous body that can be divided into nine unique zones based on the mineralogical and textural criteria outlined by Crouse et al. (1979). Fluid inclusion studies of the Tanco pegmatite have led to multiple interpretations of when the crystallizing magma became fluid saturated, with some suggesting that fluid-magma immiscibility was present at a very early stage of crystallization (Thomas et al., 1988) while others suggest that the fluid phase did not separate until very late (not until the magmatic solidus; i.e., fluid inclusions in quartz were post-magmatic and secondary;

London, 1985, 1986). Two samples of tourmaline (‘SLE-20A(1)’ and ‘SLE-20A(2)’) were collected and analyzed as part of this environment. The inclusions in the tourmaline were determined to be primary with an estimated trapping temperature between 500-600°C. Two samples of quartz (‘PV-1-86c-1’ and ‘PV-2-86-1’) were collected from the Lower Intermediate Zone vug quartz. These quartz samples contain the evidence of the transition from a homogenous H_2O-CO_2 fluid to separated fluids with the inclusions having a mean trapping temperature of ~350°C and contain the only primary inclusions in quartz in Tanco formed from post-magmatic fluids during the sub-solidus stage. One sample of beryl (T-2-6A-1) was collected from the ‘beryl fringe’ and the remaining quartz samples from Channer and Spooner (1994b) are from the ‘quartz zone’. The beryl fringe and quartz zone show evidence of fluid phase separation at ~291°C and a mean trapping temperature of ~262°C. In the model put forth by London (1986), the quartz zone was magmatic in origin and only contains secondary inclusion due to the loss of all primary inclusions due to continual recrystallization. Samples of Ta104 quartz show increasingly greater numbers of strain related inclusions occurring in subgrain boundaries (Channer and Spooner, 1994b).

Bray and Spooner (1992) analyzed 2 samples of quartz (‘Ta104-qtz(1)’ and ‘Ta104-qtz(2)’) that represent 2 separate trials using the same sample. These samples are related to the Ta104 samples collected and described by Channer and Spooner (1994b).

3.1.12 Magmatic fluids in metamorphic Archean terrains

The magmatic fluids in metamorphic Archean terrains environment is represented by samples of quartz (n=7) and calcite (n=1; n_{tot}=8) from the Kapuskasing structural zone (KSZ) and the Wawa gneiss domain (WGD) of Northern Ontario, Canada. The hydrocarbon data for this environment as collected from fluid investigations by Channer and Spooner (1994c) using combined gas and ion chromatography. Both units (KSZ and WGD) lie within the Wawa Subprovince of the Superior Province. The KSZ is of predominantly granulite facies and contains a variety of rock types including orthogneiss and paragneiss, tonalities, and anorthosites and gabbros of the Shawmere anorthosite complex. To the west of the KSZ, the rocks of the WGD are amphibolites facies tonalities and granodiorites. Geochronology shows that high-grade metamorphism affected the area between 2.7 – 2.6 Ga (Krough et al., 1988) at conditions of 8-9 kbar and 700-800^{o}C. Refer to Channer and Spooner (1994c) and references therein for additional geological description of this environment.

3.1.13 Subducted-related volcanic fumarolic gases

Samples from this environment (n=23) represent gaseous samples from bubbling pools from the volcanic systems in the Arica-Parinacota, Tarapacá and Antofagast regions of northern Chile (Tassi et al., 2010), samples from the Calypso hydrocarbon field, New Zealand (Botz et al., 2002) as well as a sample of volcanic glass from the Coso volcanic field, California. The Arica-Parinacota, Tarapacá and Antofagast fumarolic systems lie on the western side of the Pliocene-Holocene Central Andean Volcanic Zone (CAVZ) that runs parallel to the Andean sedimentary chain. The area is relatively geologically homogeneous consisting of Miocene – Pleistocene ignimbrites and andesitic-rhyolitic volcanic rocks overlying Middle Cretaceous – Upper Miocene volcano-sedimentary formations. Additional geological description can be found in Tassi et al., 2010 and references therein. The 16 samples chosen to represent this environment are from the Puchuldiza-Tuja (n=12) and the Torta de Tocorpuri (n=4) hydrothermal systems. The Puchuldiza-Tuja hydrothermal system is located about 27 km SW of the active Isluga volcano and possesses permanent fumarolic activity as manifested by bubbling pools, thermal springs and geysers, while the Torta de Tocopuri system is about 20 km NE of the Putana volcano and is characterized by smaller bubbling pools with a lower flow than that of Puchuldiza-Tuja. From the water and gas geochemistry of these two systems, Tassi et al. (2010) suggest that the fluids associated with the Puchuldiza-Tuja system may have been derived from mixing between andesitic and meteoric waters equilibrating between 220-250^{o}C and the hydrocarbon gases present are compatible with thermogenic processes occurring within the hydrothermal reservoirs. Conversely, it was suggested that the waters associated with Torta de Tocorpuri are likely meteoric in origin and the hydrocarbons are likely derived from bacterial activity as indicated by the ^{13}C-depleated CO_2 in the fluid.

The Calypso hydrothermal field from the Bay of Plenty, New Zealand, represent submarine (under ~190 m of water) fumarolic fields near the active White Island and Motuhora adecite-dacite volcanoes. The Calypso vent site is characterized by extensive native sulfur and anhydrite deposits along with Au-Ag-As-Sb-Hg sulfide mineralization. Dredge hauls from the area recovered much oily/waxy material as well as a number of liquid hydrocarbons. Isotopic analysis (H and C from CH_4) strongly suggest a thermogenic origin for hydrocarbon gases present in the system (Botz et al., 2002).

The sample of volcanic glass analyzed at Saint Mary's University was collected from the Coso Pleistocene volcanic field on the eastern side of the Sierra Nevada and Owens Valley. The field is underlaid by pre-Cenozoic granitic plutons, dioritic to gabbroic plutons and metamorphic basement rock (Simon et al., 2009 and references therein).

3.1.14 Carbonatites

This environment is represented by samples of magmatic carbonate (n=2) from the Palabora carbonatite-hosted magnetite-copper sulfide deposit, South Africa and from carbonatitic lavas from Oldoinyo Lengai volcano in Tanzania. These samples were not sonicated due to potential decrepitation effects, but rather, were just washed with two extra aliquots of deionized water instead. The Palabora Igneous Complex (PIC) resulted from three cycles of magma emplacement and collectively represents a suite of rocks ranging from ultramafic to peralkaline in character. These units were emplaced in Archean gneiss country rocks. The first phase to constitute the PIC was an ultramafic vertical pipe composed of primarily pyroxenite. This was followed by the emplacement of an alkaline phase in which syenite bodies intruded various area along the edges of the ultramafic pipe-like body. The last phase to be emplaced in the area is known as the Loolekop carbonatite-foskorite assemblage. This body is an elliptically shaped pipe-like unit with carbonatitic rock constituting the center of the body and surrounded by a magnetite-olivine-apatite rock termed foskorite. The foskorite is host to copper sulfide minerals, apatite, and titaniferous magnetite, which represent the main economic ore minerals of the complex (Groves & Vielreicher, 2001).

Oldoinyo Lengai is an active peralkaline volcanic system located in the eastern region on the East African Rift System hosted in the Archean Tanzanian Craton. The system is characterized by predominantly phonolites and nepheline tuffs and lavas constituting the bulk of the volcanic cone and reach high levels of peralkalinity ((Na+K)/Al > 1). More recent natrocarbonatites are present toward the summit of the volcano and are volumetrically minor (Klaudius and Keller, 2006; Keller et al., 2006).

3.1.15 Geothermal springs

This environment is represented by a sample of calcite (sample 'HAS'; n=1) from adjacent to a geothermal spring on Axel Heiberg Island in the Candian Arctic Archipelago and samples of gases from geothermal gas seeps (n=21; n_{tot}=22) collected and analyzed by Mazzini et al. (2011) from the Salton Sea Geothermal System (SSGS) in California. The SSGS is characterized by surface apparent hydrothermal seeps in the Salton Trough where Quaternary magmatic intrusions are responsible for an elevated heat flux of up to 600 mW/m^2. Metasediments are present throughout the area and occur at depths greater than 3000 m (deepest drilled depth). The temperature at these depths reaches approximately 350^{o}C. It has been noted that the fluids released at surface may be mixtures of biotic gases due to the thermal maturation of kerogens (Welhan and Lupton, 1987) and abiogenically derived gases via late- to post-magmatic reactions (i.e., F-T synthesis; Mazzini et al., 2011 and references therein).

3.1.16 Mantle environments

This environment is represented by samples of olivine (n=3) hand-picked from fractured peridotite xenoliths and subsequently crushed and analyzed using the rock crushing GC at Saint Mary's University. Sample 'MantleXeno(1)' is from the Czech Republic. Samples 'MantleXeno(2)' and 'MantleXeno(3)' are from Queensland, Australia and Mortlake, Victoria, Australia, respectively.

3.1.17 Evaporite-basalt interactions

This environment is represented by a sample (n=1) of melted and recrystallized halite associated with the evaporate deposits of the Werra Mining District in Germany. Due to the nature of the sample, the halite samples could not be cleaned and prepared in the same way as other samples. No solvents were used to wash this sample due to either solubility or contamination effects, rather, this sample was subjected only to elevated heat (~110^{o}C). The Werra Mining District is characterized by extensive evaporate deposits (~1000 km^{2}) with numerous basalt dykes and magmatic fluids phases entrapped within the salt rocks. The evaporites in this area were deposited during the Upper Permian while most of central and western Europe were covered by the Zechstein sea. During the Tertiary, basaltic melts intruded into the evaporate beds as dykes and sills. Alteration and accumulation of gas in the evaporites has been determined to be related to the basaltic intrusions. Refer to Knipping (1989) for in depth geological detail of this sample and environment.

3.1.18 Iron-oxide copper gold deposits (IOCG)

This environment is represented by samples of quartz (n=2) from IOCG-style deposits from the Kiruna District, Sweden and the Wolf Lake region, Ontario. The IOCG type deposits of the Kiruna Porphyries are hosted in Paleoproterozoic metavolcanics and metasedimentary rocks. These rocks are broadly divided into the Karelian Greenstone Group (>1.9 Ga) and the Svecofennian Porphyry Group. The former consists of primarily tholeiitic to komatiitic volcanic rocks overlying Archean basement, whereas the later group consists of andesitic to syenitic and quartz-syenitic rocks (minimum formation age of 2050 Ma) and associated sediments. Country rocks have been noted to have undergone metamorphism to upper greenschist to lower amphibolites facies (Smith et al., 2012 and references therein).

The Wolf Lake region is characterized by the presence of two main IOCG deposits: the Scadding Mine and Cobalt Hill. These deposits are located in the Southern Structural Province and are hosted in the Huronian Supergroup. The Supergroup is comprised primarily of metasedimentary and volcanic rocks and believed to have been deposited 2.45 – 2.2 Ga. This area possesses a complex geological history including the Penokean Orogeny at 1.89 – 1.83 Ga, the emplacement of the Sudbury Igneous Complex at 1.85 Ga, the introduction of the Killarney magmatic belt between 1.75 – 1.73 Ga, the emplacement of olivine diabase dykes at 1.24 Ga and the Grenville Orogeny at 1.1 Ga. A number of magmatic events have since albitized much of the Huronian metasedimentary units. Primary and secondary inclusions have been identified in pyrite- and chalcopyrite-rich quartz veins with inferred fluid trapping temperatures of 340-390^{o}C and 230-360^{o}C, respectively (Schandl, 2004; Schandl & Gorton, 2007).

3.1.19 Intrusion-related gold systems

This environment is represented by a samples of quartz (n=1) collected from the Fort Knox Au-bearing pluton, Alaska. The pluton is emplaced in the Fairbanks schist, which is characterized by polymetamorphic micaceous-quartz schist and mica quartzite of Precambrian to mid-Paleozoic sedimentary origin. The Fort Knox pluton hosts gold-bismuth-tellurium sulfide mineralization associated with stockworks of sheeted veins. Fluid inclusion data from the pegmatitic quartz and quartz veins suggest a trapping temperature of approximately 300 ± 30^{o}C at a pressure of 1.25 – 1.50 kbar (~5 km depth). Dating of zircons and molybdenite by U/Pb and ^{187}Re/^{187}Os, respectively, indicated an age of the pluton of approximately 92.5 Ma (Symons and McCausland, 2006).

3.1.20 Hydrothermally-modified paleoplacer gold deposits

This environment is represented by a sample (n=1) of quartz from the Witwatersrand Supergroup located in South Africa. Quartz was extracted from a quartz pebble conglomerate. The 2.98 – 2.78 Ga Witwatersrand Supergroup is host to an enormous amount of Au (ore resources and reserves of 7.2 and 6.6 g/t respectively) contained in conglomerate beds. Petrographic investigations of the quartz conglomerates reveal the presence of organic matter within the cement, along fissures or as microscopic disseminations in quartz pebbles. Also, the Witswatersrand lithological section contains scattered carbonaceous layers (Kremenitsky and Maksimyuk, 2006) Current models of this environment suggest a hydrothermally modified paleoplacer source of the gold along with the associated pyrite and urnainite in the Supergroup (Koglin et al., 2010 and references therein). Homogenization temperature for a number of secondary fluid inclusions have a range between approximately 100 – 150^{o}C with pressure corrections suggesting that these values may be as high as 240^{o}C at 2kbar (Parnell, 2001 and references therein).

3.1.21 Groundwaters from the Canadian Shield

Samples from this environment (n=12) represent analyses of the dissolved gas content (via headspace analysis) of groundwaters from various sites within the Ontario Canadian Shield as reported by Sherwood-Lollar et al. (1993a, 2008). Gas extraction and analysis methodology can be found in Sherwood-Lollar et al., (1993b, 2008). Groundwaters were collected in copper tubes by downhole samplers and gases were extracted from the waters via vacuum degassing. Samples were collected from two sites in the Sudbury area (Ontario, Canada); one from the Copper Cliff South Mine ('Sudbury CCS') associated with a quartz diorite offset dyke sulfide mineralized environment and one from the Strathcona Mine in the North Range ('Sudbury N') associated with footwall-style mineralization. Two samples were collected from the Campbell and Dickenson mines of the Red Lake Archean metavolcanic belt ('Red Lake Dickenson' and Red Lake Campbell'), which is dominated by mafic and felsic volcanic piles and metasedimentary layers of 2960-2740 Ma. Six samples from the Kidd Creek Mine of Timmins, Ontario are associated with the Abitibi greenstone belt (2500-2700 Ma). This area is composed primarily of altered felsic volcanics and basaltic flows with smaller peridotitic and granitic intrusive bodies. The last samples considered for this environment is from the Elliot Lake region of Ontario ('Elliot Lake'). This area is dominated by sedimentary rocks consisting of quartz and feldspar-rich clastics of the Huronian sequence (2500-2150 Ma). A more comprehensive description of these environments can be found in Sherwood-Lollar et al. (1993a, 2008) and references therein.

3.1.22 Gas hydrates and associated gas seeps

This environment is represented by collected gas samples (n=11) from de-gassing gas hydrates and associated gas seeps on the Gulf of Mexico continental slope (offshore Louisiana; Sassen et al., 1999). The gas hydrate mounds are shallowly buried in marine sediments often outcropping. The study area is characterized by many sea-floor gas vents, oil seeps, gas hydrates and subsurface oil and gas fields. Isotopic studies of the methane and associated C2-C4 hydrocarbons indicated a thermogenic origin (Sassen et al., 1999 and references therein).

3.2 Methodology

3.2.1 Gas chromatography

Many of the samples investigated in this study were analyzed using an in-line rock crushing gas chromatograph (GC) at Saint Mary's University. This analytical GC system is similar to that described by Bray *et al.* (1991) and Salvi and Williams-Jones (1997b,2003). An Agilent 7890 series gas chromatograph at Saint Mary's University was adapted with the appropriate valve and injection systems by Wasson-ECE Instrumentation (Chapter 2 Figure 2.5 - GC schematic). A custom valve assembly allowed for the selection between 4 stainless steel rock crushers and the GC injection port. This GC system has two distinct separation methods that were used in this study. Method 1 is able to detect and quantify inert and non-combustible compounds (i.e., CO_2, CO, H_2O) as well as hydrocarbons (i.e., CH_4, C_2H_6, etc.) through the use of a thermal conductivity detector (TCD) and flame ionization detector (FID), respectively (assembled in series). Method 2 is able to detect and quantify only combustible compounds since only one FID is used in this method. The analytical column employed in Method 2 has the power to separate and resolve saturated (paraffinic) and unsaturated (olefinic) hydrocarbons and various structural isomers (i.e., pentane, 2-methylbutane, 2,2-dimethylpropane, etc.) and conformational isomers (i.e., cis-2-butene, trans-2-butene, 1-butene, etc.) thereof, making this the method of choice when determining the detailed hydrocarbon signature of any given sample (Method 1 does not possess this level of hydrocarbon separation; Figure 3.2 – sample chromatogram). Helium carrier gas at a flow rate of 7.0 +/- 0.5 ml/min was used to drive volatiles into a 30m x 0.53mm x 5µm DB-1 capillary column prior to a 25m x 0.53mm x 10µm Porabond-Q capillary column for Method 1. A flow rate of 8.5 +/- 0.5 ml/min was used with a 50m x 0.53mm x 10µm Alumina-PLOT capillary column for Method 2. The columns used in both methods can effectively separate both polar and non-polar compounds; however, Method 2 is incapable of detecting non-combustible compounds due to the method's detection technique (i.e., FID). Rock crushing is performed at elevated temperature (~105-110^{o}C) in order to ensure that instantaneous volitization of all entrapped fluid (including H_2O) is achieved. Standard gas mixture from Matheson Tri-Gas were used for calibrations.

Custom, stainless steel, hydraulically driven rock crushers (Chapter 2 Figure 2.4) were made by the University of Toronto Machine Shop using schematics outlined by Bray and Spooner (1992) and Bray *et al.* (1991), which are adapted from original designs by Andrawes and Gibson (1979) and Andrawes *et al.* (1984). The rock crushers used in this study consist of a basal block in which the upper portion of the crusher is inserted. This basal unit houses two cartridge heaters controlled by a variable voltage transformer. The upper unit of a crusher consists of a cylinder and piston assembly. Fluoroelastomer o-rings (Viton®) were used to seal the sample cavity from the external atmosphere and volatile contaminants, and allow the top chamber of the crusher housing the piston to be placed under dynamic He flow at a reduced pressure to the sample cavity. This ensures that if there were to be any gas leak within the crusher it would leak into the top chamber cavity rather than into the sample cavity (i.e., leaks from an area of higher pressure to an area of lower pressure). This prevents foreign contaminants/volatiles from entering the sample cavity upon crushing and analysis.

The raw data (sample chromatograms) was collected and integrated with the PC-operated software Agilent Chromatographic ChemStation®. Integrated data was converted to 'moles/g of rock' via calibration curves made using standard gas mixtures and then normalized to the mass of rock crushed.

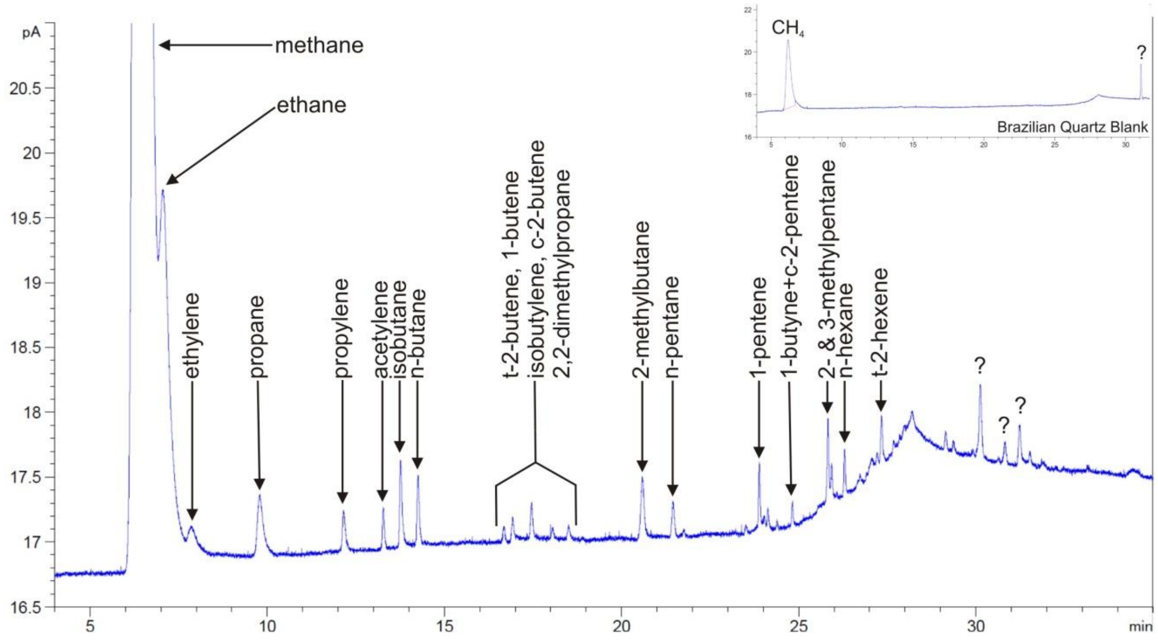


Figure 3.2: Sample gas chromatogram from crushed quartz sample (J9) illustrating high level of hydrocarbon speciation. Sample J9 represents a quartz + massive sulfide assemble from the mafic-ultramafic Ni-Cu-PGE sulfide deposit environment. Blanks were acquired from identically prepared inclusion free Brazilian quartz (see inlay). Peaks labelled with question marks are not yet identified. Collected with Method 2.

Hydrocarbon data was also collected from a number of literature sources. Only saturated hydrocarbon data was used in this study due to the limited unsaturated hydrocarbon data available in most studies. Some sources only analyzed hydrocarbons up to C2, in which case they could not be plotted in diagrams employing higher order hydrocarbon ratios (i.e., C3/C1 and C4/C1). Additional sample details and methodology used in these studies can be found in the referenced works.

3.2.2 Sample preparation and description

Rock samples that were analyzed at Saint Mary's University for use in this study were prepared by fragmenting the rocks into chips approximately 1-3 mm in maximum dimension using a jaw crusher then weighed (~0.7 grams) and sonicated in de-ionized water for ~30 minutes. The samples were then washed 2 times after sonication with additional de-ionized water, dried on a hot plate (~50-60^{o}C) and inserted into the pre-cleaned rock crushers. A small amount of inert and volatile-free silicone grease was placed around all crusher o-rings, sealed and heated overnight (~10-15 hours; ~100-110^{o}C) under dynamic He flow ($\leq$ 2 ml/min) to remove any adsorbed compounds including water and cleaning solvents. Blank samples of inclusion-free Brazilian quartz were crushed (n=8; 2 trials per crusher) in order to acquire a background. The Brazilian quartz was fractured, hand-picked and cleaned in the same way as all other samples. This background was averaged and subtracted from the collected chromatograms. Samples preparation techniques employed by those in cited literature sources can be located in said sources (see Table 3.1 in supplementary file for source references).

3.3 Results

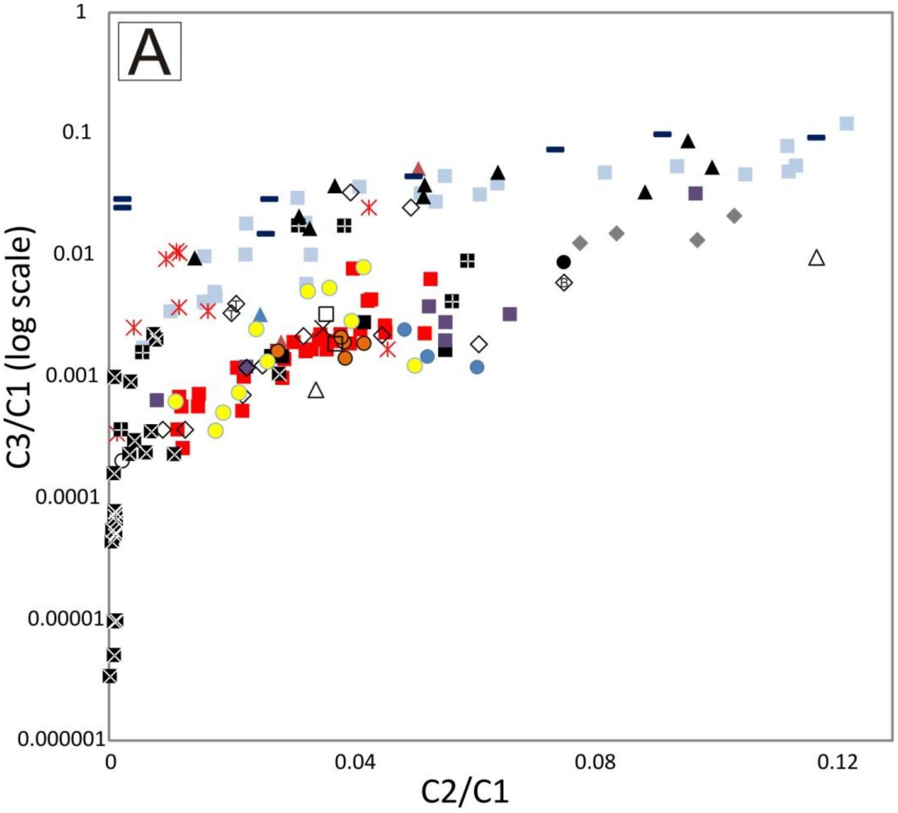
The results compiled in this section express the hydrocarbon data collected from literature sources and data collected directly via gas chromatographic analysis of various samples at Saint Mary's University (Tables 3.1 and 3.2 in supplementary file). Literature sources missing higher order hydrocarbon information (i.e., C3+) could not be plotted in particular hydrocarbon ratio plots (i.e., plots considering C3/C1 and C4/C1). Coloured or hatched environmental fields have been generated for samples that were found to cluster or follow a distinguishable trend. Some environments could not be made into coherent fields due to the large spatial variation of sample points or paucity of samples for that environment. Refer to Figure 3.1 for environmental legend.

3.3.1 Environmental discrimination – hydrocarbon ratios

Hydrocarbon ratios were calculated and plotted against each other in a number of ternary and binary plots. Two distinct fields appear to be present when considering the light saturated hydrocarbon ratios between C2/C1 and C3/C1 (Figure 3.3 A&B). Note that C3 represents propane and C2 represents ethane. Environments that contain hydrocarbons of thermogenic and/or biogenic origins possess an elevated C3/C1 ratio by approximately an order of magnitude. Volatile hydrocarbons from 'Hydrocarbon-bearing sedimentary basins' (Chen et al., 2000) and from 'gas hydrates and associated free gases' (Sassen et al., 1999) of thermogenic origin display this characteristic propane enrichment. All analyzed samples from the 'hydrothermal exhalatives seafloor environment' also display elevated propane enrichments suggesting a potential thermogenic and/or biogenic origin for the hydrocarbon phases present there. Environments associated with crustal igneous and metamorphic terrains containing hydrocarbons of suspected abiogenic origins possess characteristically lower C3/C1 hydrocarbon ratios. Unpublished data investigating the hydrocarbon chemistry of fluids from ‘mafic-ultramafic associated Ni-Cu-PGE deposits’ (Kerr et al. Chapter 2) illustrates a clear Shultz-Flory relationship between the molar abundance and carbon number of the hydrocarbon phase, strongly suggesting an abiogenic origin for the higher order hydrocarbons. In addition, compound specific H and C isotopic analysis of a sample from this environment also strongly suggest abiogenic origins (Hanley et al., submitted). Significant variation is present in the C2/C1 ratio in the majority of environments investigated. An exception being samples from subduction-related fumarolic environments, which seem to have a consistently depleted C2/C1 ratio (i.e., low ethane abundance) but vary by approximately two orders of magnitude when considering the their C3/C1 ratios.

Similar trends are present when considering the collective propane (C3) and butane (C4) abundances (shown in log scale for clarity) versus the methane abundance (mole%) (Figure 3.4 A&B). Molar percents are normalized to total hydrocarbon phase abundance (i.e., CO_2 not considered). Unsaturated species were not considered in these plots due to the lack of comprehensive hydrocarbon analyses present in many literature sources. Again it is clear that samples from a ‘subduction-related fumarolic’ environment are the most depleted in higher order hydrocarbons (propane and butane in this case), with the hydrocarbon phase dominated primarily by methane. The sample of volcanic glass (sample VG) from this geological environment is more depleted in methane than other samples in this environment possibly due to respeciation/oxidation of CH_4 to CO_2 at elevated temperatures. Thermogenically derived hydrocarbons from ‘Hydrocarbon-bearing sedimentary basins’ and ‘gas hydrate and associated free gases’ cover a wide range of methane abundances ranging from approximately 80 – 99 mole% and 72 – 95%, respectively, and are generally quite enriched in higher order hydrocarbons. Samples from the ‘mantle’, ‘subduction-related porphyry/epithermal’, and ‘Appalachian rare metal pegmatite’ environments cluster very closely are on average more depleted in higher order hydrocarbons than the majority of the other geological environments investigated. Samples from ‘qtz-carb associated Au deposits in Archean terrain’, ‘Archean rare metal pegmatites’ and ‘barren mid-oceanic ridge’ environments were quite variable and overlap with a number of other sample environments. Additionally, samples from ‘groundwater’ analysis also overlap quite extensively with other environments and do not localize themselves into a clearly definable field. A tightly clustered group of groundwater samples from Kidd Creek, Ontario is present at moderately elevated C3+C4, and depleted CH_4 abundances suggesting a commonality in the hydrocarbon fluid origin and/or chemical equilibration conditions in these samples. Samples from the ‘hydrothermal exhalative seafloor’ environment tend to be most depleted in methane on average while maintaining elevated higher order hydrocarbon abundances and overlap significantly with samples from the ‘hydrocarbon-bearing sedimentary basins’ environment.

A ternary discrimination diagram (Figure 3.5 A&B) investigating the higher order hydrocarbon ratios C2/C1, C3/C1 and C4/C1 demonstrate adequate clustering of a number of environments. Samples from ‘mafic-ultramafic associated Ni-Cu-PGE deposits’ containing hydrocarbons of suspected abiogenic origins cluster quite well and are relatively more enriched in ethane over propane and butane than samples of ‘hydrocarbon-bearing sedimentary basins’ and ‘gas hydrates and associated free gases’, which contain hydrocarbons of thermogenic origin. Samples from the ‘mantle’, ‘sudbuction-related porphyry-epithermal’, ‘Appalachian rare metal pegmatites’ and ‘sediment-hosted base metal sulfide deposits’ environments all overlap significantly with samples from ‘magmatic residue and hydrothermal veins from Ni-Cu-PGE sulfide deposits in mafic-ultramafic settings’, suggesting a potential abiogenic origin for the hydrocarbons in these environments. Samples from ‘groundwater’, ‘qtz-carb associated Au deposits in Archean terrain’ and ‘Archean rare metal pegmatites’ are quite variable and thus do not cluster into distinct fields. This is likely due to the presence of multiple fluid generations from varying sources/origins in these environments possessing chemically distinct fluid chemistry as well as potential post-entrapment metamorphic and metasomatic events likely altering the fluid chemistry. This is supported by the presence of the closely clustered analyses of tourmaline-hosted fluid from the ‘Archean rare metal pegmatites’ environment (open diamonds labeled with a T). The tourmaline in this environment is noted as metasomatic in origin, post-dating the emplacement of the pegmatite with which it is associated (Selway et al., 2000 and references therein). The hydrocarbon chemistry of ‘subduction-related fumaroles gases’ is variable depending on the environment from which they originate, suggesting that the hydrocarbon signatures of these fluids can be highly variable and likely influenced by factors such as temperature, pressure, oxygen fugacity and the presence of organics and microbial action. Fluid from a sample of volcanic glass from this environment (labeled VG) overlaps with fields characterized by samples with fluids of suspected abiogenic origins. This agrees well with environmental considerations of this environment (i.e., magmatic temperatures and the absence of organics). Other samples from this environment cluster into fields encompassing fluid analyses from the Puchuldiza-Tuja (labeled PT) and Torta de Tocorpuri (labeled TT) bubbling pools, which have been suggested as possessing hydrocarbons of thermogenic and bacterial origins, respectively (Tassi et al., 2010). Fumarolic hydrocarbon gases from the Calypso hydrothermal field of thermogenic origin were quite scattered and thus not encompassed by a field. However, many of the samples from Calypso are situated in the lower section of the ternary (i.e., higher abundances of propane and butane relative to ethane), overlapping with fields defined by fluids of suspected thermogenic and biogenic origins. This result is consistent with the presence of abundant oily long-chained saturated and aromatic organic compounds associated with the investigated samples from Calypso, suggesting that the volatile hydrocarbons present in this environment are the result of thermogenic decomposition of higher order, biogenically derived hydrocarbon species (Botz et al., 2002).


A
C3/C1 (log scale)
C2/C1
1
0.1
0.01
0.001
0.0001
0.00001
0.000001
0
0.04
0.08
0.12

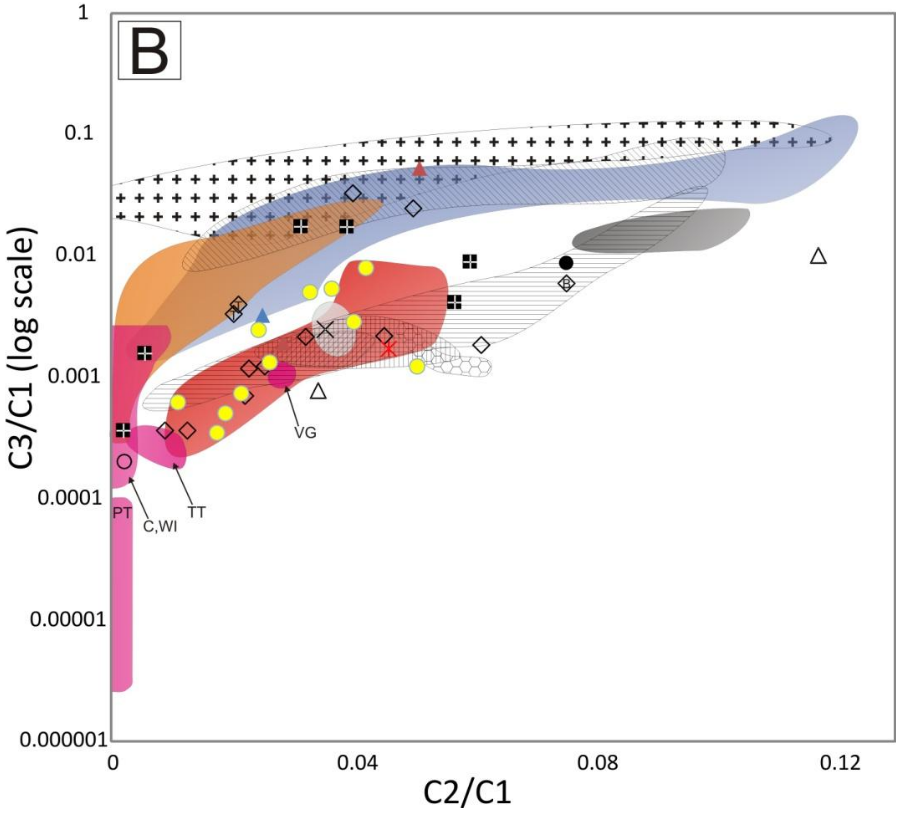

B
C3/C1 (log scale)
C2/C1
1
0.1
0.01
0.001
0.0001
0.00001
0.000001
0
0.04
0.08
0.12
VG
PT
C,WI
TT

Figure 3.3 (previous page): C2/C1 versus C3/C1 hydrocarbon based discrimination binary plots illustrating saturated hydrocarbon data from all environments studied. Ratio C3/C1 shown in log scale. C1 represents methane, C2 represents ethane and C3 represents propane. A – All data points are from analyses from this study and from literature. No fields. B – Shaded/hatched fields to illustrate environments. Samples that are too scarce or widely distributed to make into clear fields were left as data points. Some environments and particular samples from various environments could not be expressed in this diagram due to the absence of higher order hydrocarbon analyses (i.e., C3+) from the literature. The letter 'B' and the letter 'T' associated with particular samples from the 'magmatic fluids in metamorphic Archean terrains' environment represented crushed samples of beryl and tourmaline, respectively. 'Subduction-related volcanic fumaroles gases' fields ascribed with 'PT', 'TT' and 'VG' represent samples from the Puchuldiza-Tuja hydrothermal field, Torta de Tocorpuri hydrothermal field and from volcanic glass, respectively. Fumarole field ascribed 'C,WI' are those samples from the Calypso and White Island hydrothermal fields, New Zealand. Refer to 'Geological setting and sample characteristics' section for sample details.

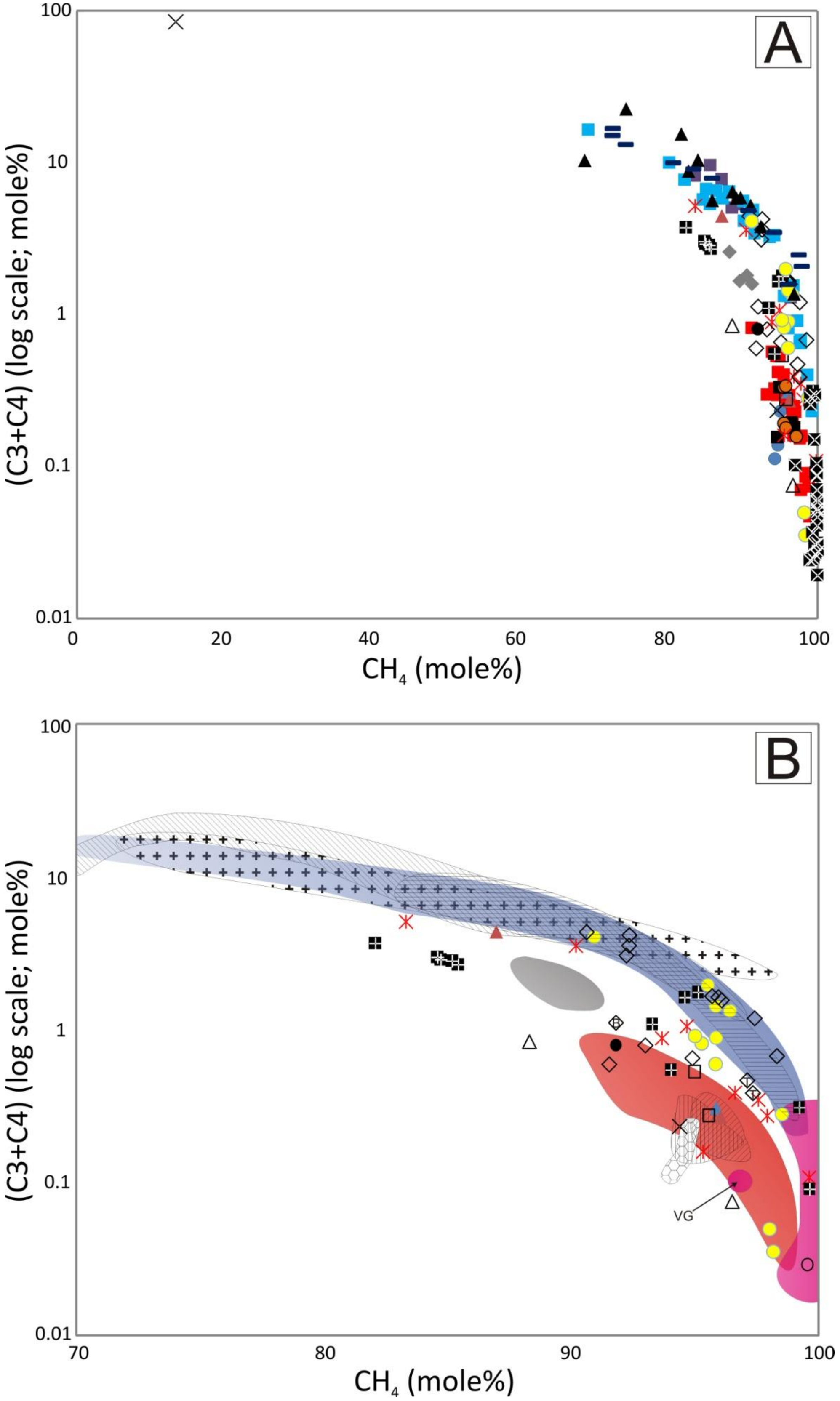

A
100
10
1
0.1
0.01
0
20
40
60
80
100
(C3+C4) (log scale; mole%)
CH$_4$ (mole%)
B
100
10
1
0.1
0.01
70
80
90
100
VG
(C3+C4) (log scale; mole%)
CH$_4$ (mole%)

Figure 3.4 (previous page): Methane abundance versus C3+C4 saturated hydrocarbon abundance (log scale) discrimination binary plots illustrating data from all environments studied. Units of mole% used. C3 represents propane and C4 represents butane; short forms are used for clarity. One sample from the 'geothermal spring water' environment (sample CA08-05A) is not included in the diagram since it fell well outside the range occupied by all other samples. A – All data points are from analyses from this study and from literature. No fields. B – Shaded/hatched fields to illustrate environments. Samples that are too scarce or widely distributed to make into clear fields were left as data points. Some environments and particular samples from various environments could not be expressed in this diagram due to the absence of higher order hydrocarbon analyses (i.e., C3+) from the literature. The letter 'B' and the letter 'T' associated with particular samples from the 'magmatic fluids in metamorphic Archean terrains' environment represented crushed samples of beryl and tourmaline, respectively. The 'subduction-related volcanic fumaroles gases' field ascribed with 'VG' represents a sample of volcanic glass; all other samples in this environment are grouped under a second, unlabeled field. Refer to 'Geological setting and sample characteristics' section for sample details.

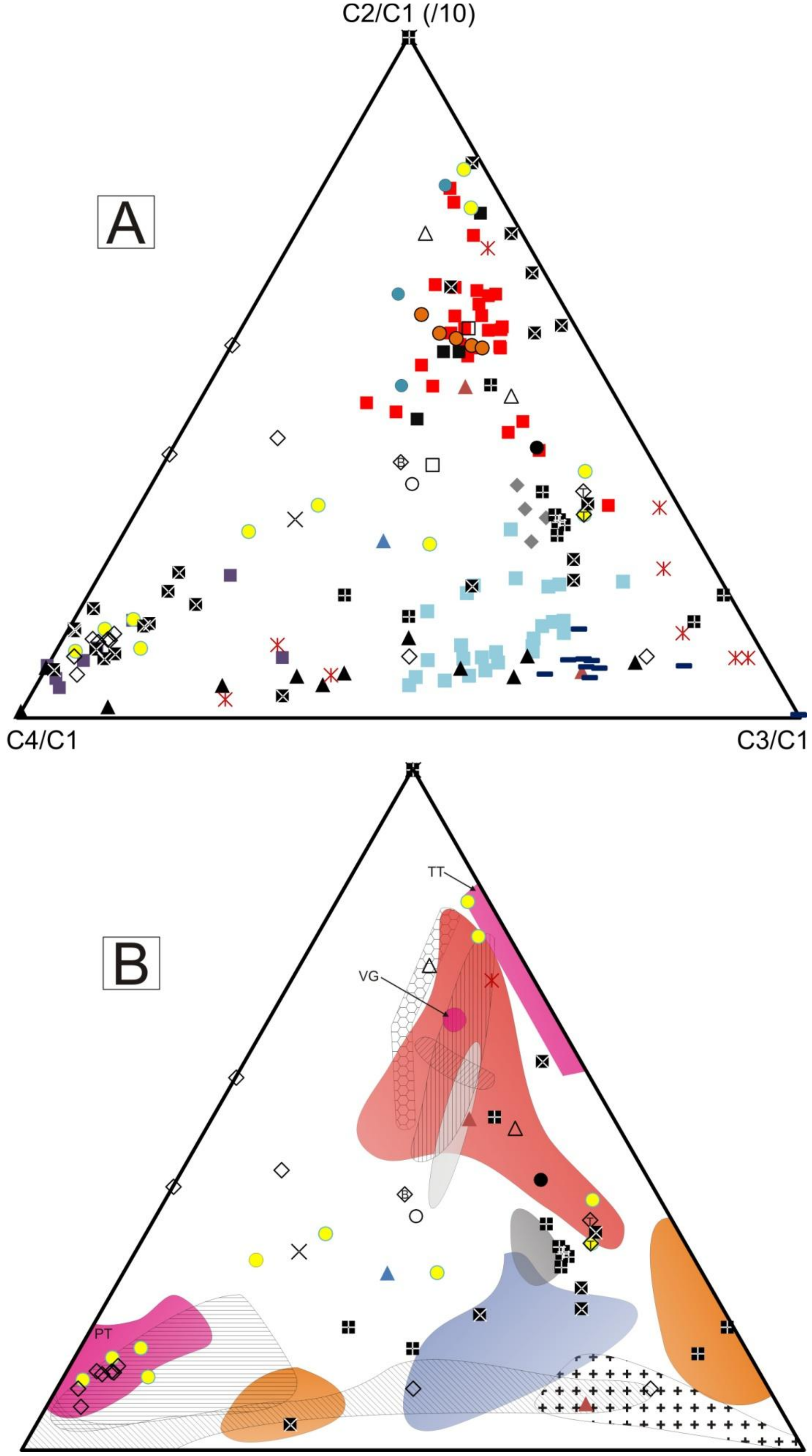

C2/C1 (/10)
A
C4/C1
C3/C1
B
TT
VG
PT

Figure 3.5 (previous page): C2/C1 versus C3/C1 versus C4/C1 saturated hydrocarbon ratio discrimination ternary plot illustrating data from all environments studied. Plotting C2/C1 (/10) versus C3/C1 versus C4/C1 showed the greatest degree of discrimination between the fields out of all variations investigated. A – All data points are from analyses from this study and from literature. No fields. B – Shaded/hatched fields to illustrate environments. Samples that are too scarce or widely distributed to make into clear fields were left as data points. Some environments and particular samples from various environments could not be expressed in this discrimination diagram due to the absence of higher order hydrocarbon analyses (i.e., C3+) from the literature. The letter 'B' and the letter 'T' associated with particular samples from the 'magmatic fluids in metamorphic Archean terrains' environment represented crushed samples of beryl and tourmaline, respectively. 'Subduction-related volcanic fumaroles gases' fields ascribed with 'PT', 'TT' and 'VG' represent samples from the Puchuldiza-Tuja hydrothermal field, Torta de Tocorpuri hydrothermal field and from volcanic glass, respectively. Additional fumarolic gas samples from the Calypso and White Island hydrothermal fields were left as sample points due to their wide spread across the ternary. Refer to the 'Geological setting and sample characteristics' section for sample/environmental details and the Discussion section for causal details.

3.3.2 Light hydrocarbon genetic relationships – Total hydrocarbon phases

The light hydrocarbons methane and ethane were plotted against each other to determine if a genetic relationship between the two species is present (Figure 3.6 A&B). Methane and ethane abundances in this plot are normalized to total hydrocarbon phase abundance (i.e., CO_2 not considered). A very strong linear relationship is present (trend 1: solid line in Figure 3.6B inlay) in which the abundance of ethane in the system is proportionally higher when methane abundances are lower, which is what would be expected if ethane was generated via methane combination. This trend is followed closely by samples from environments possessing hydrocarbon fluids of suspected abiogenic origins. Samples from 'ophiolite', 'sudbuction-related fumarolic' and 'geothermal spring' environments are very depleted in ethane and dominated by methane as its primary hydrocarbon phase, with proportionally elevated ethane abundances occurring in samples from 'sudbuction-related porphyry-epithermal', 'mantle', 'alkalic/agpaitic', 'Appalachian rare metal pegmatite' environments and in samples from 'mafic-ultramafic associated Ni-Cu-PGE deposits'. The majority of samples from 'qtz-carb associated Au deposits in Archean terrains' and 'Archean rare metal pegmatites' also consistently follow this trend, with a few notable exceptions. Quartz sample 2-S318 from the 'qtz-carb associated Au deposits' environment was collected from a high-grade tourmaline-bearing vein possessing a high degree of recrystallization (Channer and Spooner, 1994a). Quartz samples Ta64-1 and Ta64A-1 (sample split of the same quartz sample) and Ta104-qtz(1) and Ta104-qtz(2) (sample repeat analyses) from the 'Archean rare metal pegmatites' environment also deviate from this trend towards disproportionally depleted methane abundances. These samples are from what is known as the "quartz zone" of the Tanco granitic pegmatite which has been described as magmatic in origin but has since lost all primary inclusions through continual recrystallization, now containing almost exclusively post-magmatic secondary inclusions (London, 1986; Channer and Spooner 1994a). A quartz sample from the Kiruna IOCG deposit deviates from this trend as well. This sample was found to be highly enriched in higher order hydrocarbons (i.e., C3+) relative to methane, suggesting the methane was consumed to produce said higher order hydrocarbons *in situ*. In addition, a single sample of quartz (11-AV-01) from 'mafic-ultramafic associated Ni-Cu-PGE deposits' also deviates from this trend. This sample is unique in that is very enriched in PGE, displaying significant sperrylite mineralization. The significance of PGE/PGM to hydrocarbon speciation will be discussed in more detail in the following sections.

The majority of samples representing 'hydrocarbon-bearing sedimentary basins', 'magmatic fluids from metamorphic Archean terrains', 'hydrothermal exhalatives from a seafloor environment', 'barren mid-oceanic ridge fluids' and 'gas hydrates and associated gases' consistently fall off of trend 1 towards a more methane-depleted fluid (trend 2). Hydrocarbons present in the 'hydrocarbon-bearing sedimentary basins' and 'gas hydrates and associated gases' have been characterized as being thermogenic in origin (Sassen & MacDonald, 1997; Sassen et al., 1999; Chen et al., 2000), likely with minor contributions from bacterially derived phases. Fluids from a 'barren mid-oceanic ridge' environment were likely trapped at magmatic temperatures ($\geq 1000^{o}C$) as per their presence in ultramafic rocks (Savelieva et al., 2008). However, unlike fluids from 'mantle' environments and volcanic glass from a 'subduction-related fumarolic' environment, which were also trapped at magmatic temperatures, the fluids from the majority of samples from the 'barren mid-oceanic ridge' environment significantly deviate from the trend 1. The rock units hosting 'magmatic fluids from metamorphic Archean terrains' (Kapuskasing Archean crustal lithologies) and 'hydrothermal exhalatives from a seafloor environment' (Barberton Greenstone Belt lithologies) have been noted as having undergone multiple metamorphic events since there formation (Channer and Spooner, 1994c; deRonde et al., 1997). Rock units of the Kapuskasing Archean crust have undergone metamorphic events characterized by temperatures of up to 800^{o}C and have been determined to contain essentially no fluids that are related to high-grade Archean magmatic and metamorphic processes, suggesting that their current hydrocarbon fluid signature is unrelated to initial rock-forming events but has been respeciated and altered via secondary, post-entrapment processes. Rock units of the Barberton Greenstone Belt (BGB), hosting the Ironstone pods also display evidence of significant metamorphic and metasomatic events, have been overprinted by thermal anomalies of $\geq$200^{o}C. Carbonaceous shale horizons associated with the BGB may have also had an influence on the current hydrocarbon signature of the fluids present there (deRonde et al., 1994, 1997). The majority of samples from all environments fall in the range of 0-10% ethane and 80-100% methane. The two most ethane enriched samples are from 'alkalic/agpaitic magmatic intrusions' collected from the Khibiny Alkaline Igneous Complex with ethane abundances of 22.7 and 34.8 mole%.

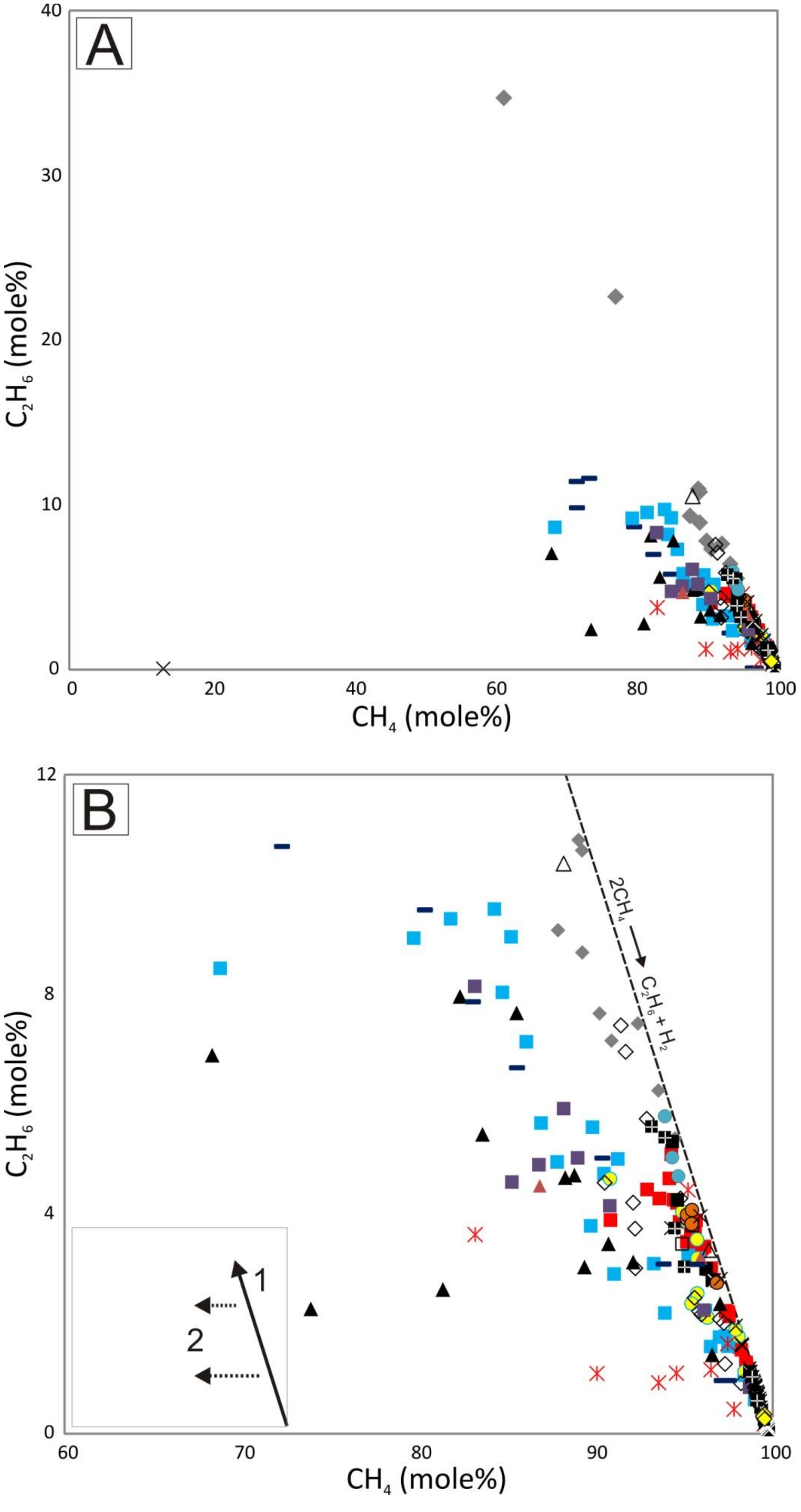
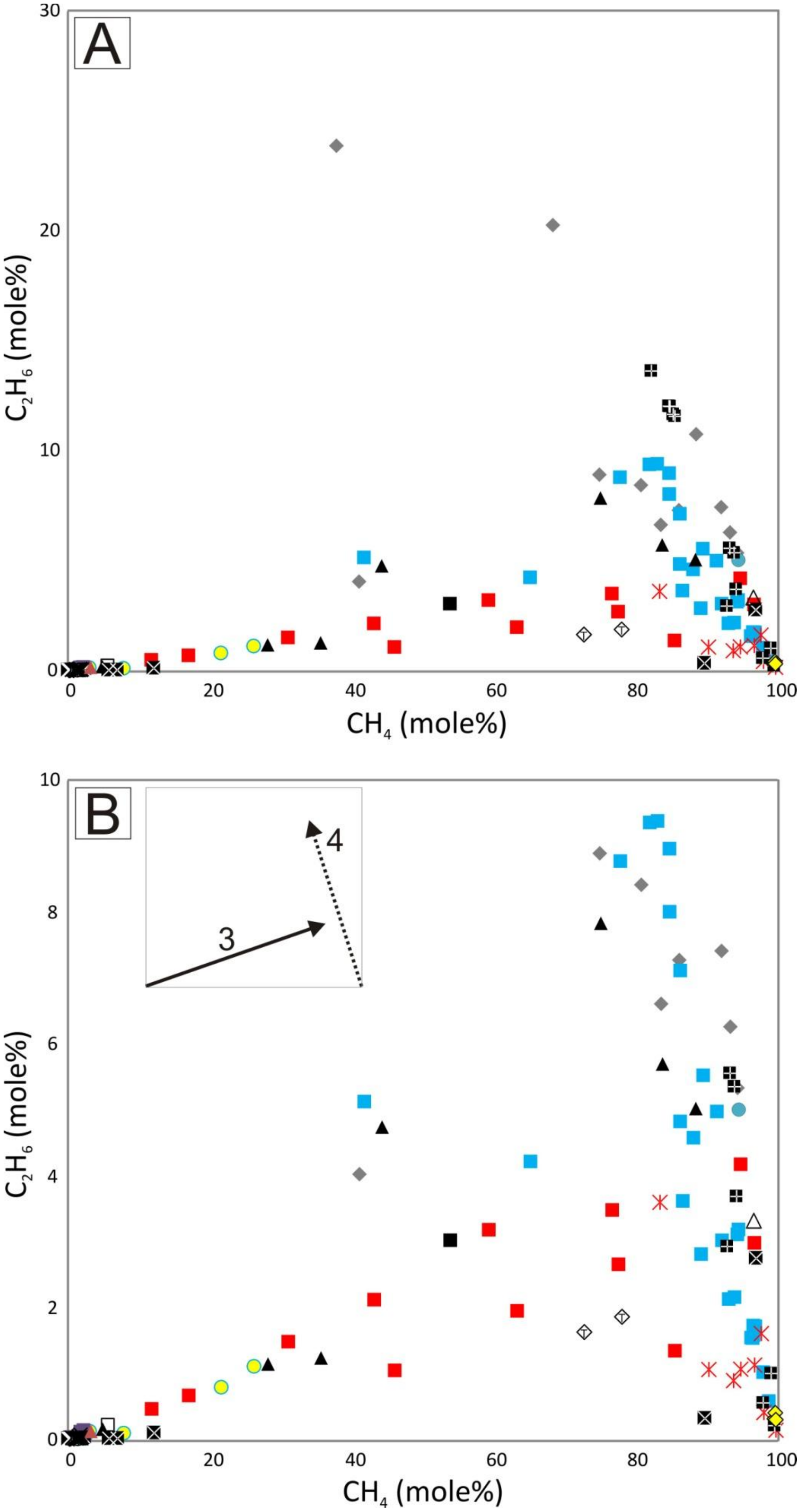

A
40
30
20
10
0
C_2H_6 (mole%)
0
20
40
60
80
100
CH_4 (mole%)
B
12
8
4
0
C_2H_6 (mole%)
60
70
80
90
100
CH_4 (mole%)
$2CH_4 \rightarrow C_2H_6 + H_2$
1
2

Figure 3.6 (previous page): Methane versus ethane (mole%) binary plots normalized to only hydrocarbon carbonic species (excludes CO_2). All data points are from analyses from this study and from literature are expressed here. A trend is present between the hydrocarbon species such that as the abundance of methane decreases, the abundance of ethane increases (inlay: solid line – trend 1). Deviations from this trend (i.e., disproportional decreases in methane abundance) are present in samples suspected of possessing hydrocarbons of biogenic and thermogenic origins or having underwent modification by post-entrapment respeciation events/reactions (inlay: dashed line – trend 2). A – All samples from all environments illustrated. B – An expanded view of the closely clustered samples in plot A for added clarity. The dashed line indicates the expected trend if ethane was the result of only methane polymerization (once CH_4 and C_2H_6 are re-normalized to total hydrocarbons).

3.3.3 Light hydrocarbon genetic relationships – Total carbonic phases

The light hydrocarbons methane and ethane were normalized to the total carbonic phase abundance (including CO_2) and plotted against one another (Figure 3.7 A,B&C) for various environments. Two distinct trends are present in this plot as indicated by the solid and dashed lines (Figure 3.7B inlay). Trend 3 (solid line) displays a tendency for fluids to have increased ethane abundances with higher methane abundances while trend 4 (dashed line) displays an tendency for fluids to be richer in ethane with lower methane abundances. Trend 4 is followed by samples from the following environments: (i) hydrocarbon-bearing sedimentary basins, (ii) groundwaters, (iii) alkalic/agpaitic magmatic intrusions (except for one outlier) and (iv) barren mid-oceainc ridge fluids. The remaining investigated environments fall on trend 3 or do not possess enough sample points to make a clear conclusion. The carbonic fluids associated with the majority of samples from 'subduction-related fumarolic' environments are very depleted in methane, lying near the origin. Five samples from this environment trend across the baseline to more elevated methane abundances while remaining consistently depleted in ethane. The sample of volcanic glass from this environment is the only sample displaying both elevated methane and ethane abundances of 96.9 and 2.7 mole%, respectively. All the samples from an 'Archean rare metal pegmatite' are depleted in methane expect the 2 analyses of fluids from tourmaline with methane abundances between 70-80 mole%, suggesting that the fluid present in these samples is from a distinctly different source or equilibrated under different conditions, consistent with descriptions by Channer and Spooner (1994a) and Selway et al. (2000). Environments falling near the origin (i.e., depleted methane and ethane abundances) may be the result of either: (i) the fluids associated with these environments were either initially CO_2-dominated, becoming slightly more enriched in methane, and subsequently ethane, due to minor CO_2 respeciation/reduction, or (ii) an initial hydrocarbon dominated fluid has become more enriched in CO_2 due to the its interaction with oxidizing fluids. Samples of ‘ophiolite-related gases’ are dominated by methane as its carbonic fluid phase and are very tightly clustered, which is to be expected in the reducing environment generated via the serpentinization of ultramafic rocks (Abrajano et al., 1988, 1990).


A
30
20
10
0
C_2H_6 (mole%)
0
20
40
60
80
100
CH_4 (mole%)
B
10
8
6
4
2
0
C_2H_6 (mole%)
3
4
0
20
40
60
80
100
CH_4 (mole%)

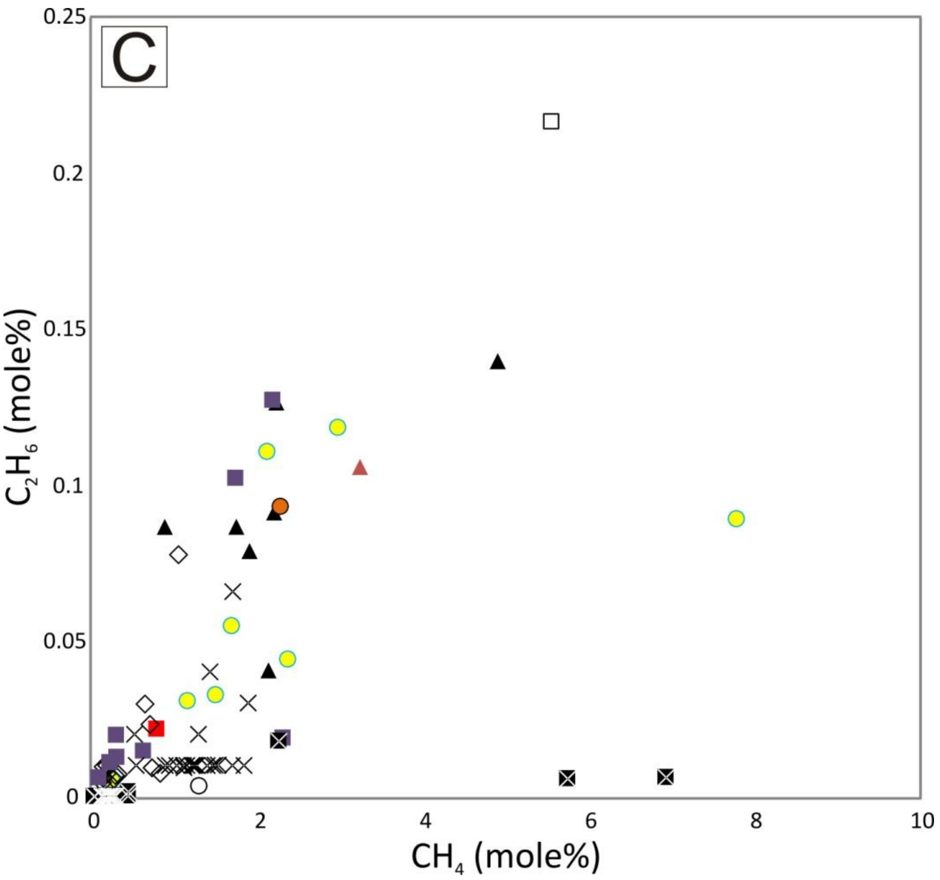


Figure 3.7 (pages 137-138): Methane versus ethane (mole%) binary plots normalized to only all carbonic species (including CO_2). All data points are from analyses from this study and from literature are expressed here. A – All samples from all environments illustrated. B – An expanded view. Two distinct trends are present (see inlay): (i) a positive trend in which ethane abundance increases as methane abundance increases (inlay: solid line – trend 3), and (ii) a negative trend in which ethane abundance increases as methane abundance decreases (inlay: dashed line – trend 4). C – A further expanded plot to clarify samples clustered near the origin (i.e., CO_2 dominant samples).

3.3.4 CH_4 and CO_2 genetic relationships

As indicated by the strong linear trend (Figure 3.8 A,B&C), the most abundant carbonic phases in all environments are methane and/or carbon dioxide. Environments near the CO_2-dominated end member include: ‘geothermal spring water’, ‘magmatic fluids from metamorphic Archean terrain’, ‘qtz-carb associated Au deposits in Archean terrain’, ‘IOCG deposits’, ‘intrusion-related gold system’, ‘sediment-hosted base metal sulfide deposits’, and the majority of samples from ‘Archean rare metal pegmatites’ and ‘subduction-related fumaroles gases’. Those near the CH_4-dominated end member include: ‘hydrocarbon-bearing sedimentary basins’, ‘groundwaters’, ‘carbonatites’ and most ‘alkalic/agpaitic magmatic intrusion’ samples. The remaining investigated environments have variable abundances of CH_4 and CO_2. Environments that deviate from a 1:1 inverse relationship include: ‘hydrocarbon-bearing sedimentary basinal’, ‘hydrothermal exhalative seafloor’ and ‘alkalic/agpaitic’ environments due to the presence of significant concentrations of higher order hydrocarbon phases in the fluids. This is most noticeable in fluids from ‘hydrocarbon-bearing sedimentary basinal’ environments in which the majority of samples possess CH_4 abundances between 75-99 mole% and CO_2 abundances below approximately 4 mole%.

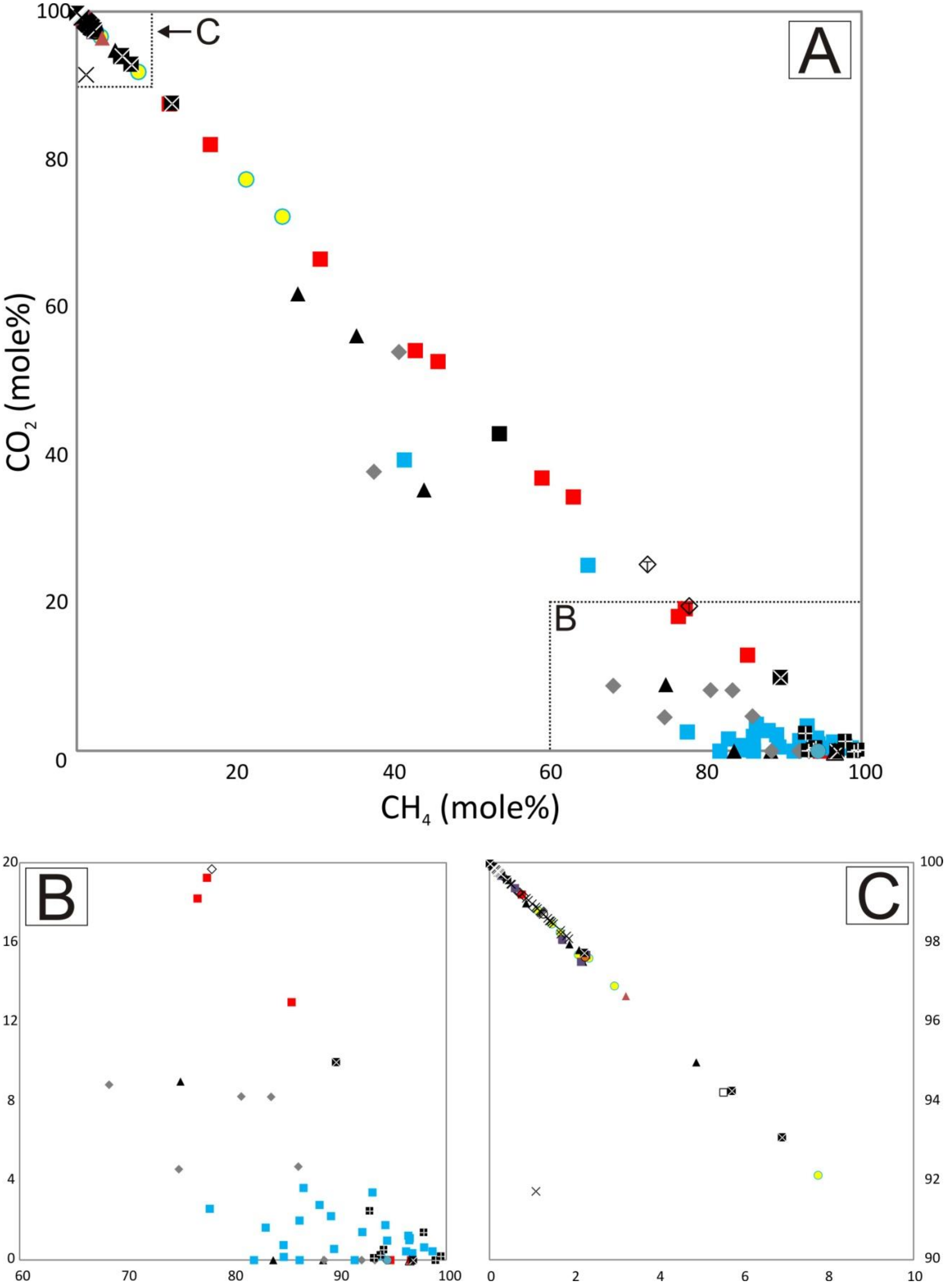

A
C
B
CO$_2$ (mole%)
CH$_4$ (mole%)
100
80
60
40
20
0
20
40
60
80
100
B
20
16
12
8
4
0
60
70
80
90
100
C
100
98
96
94
92
90
0
2
4
6
8
10

Figure 3.8 (previous page): CH_4 versus CO_2 abundances (mole%). Due to the lack of CO_2 data in some literature sources and for a number of samples analyzed in this study, some environments and data points are excluded from this graph. A – Full view. B – An expanded view of CH_4-rich domain (reduced fluids). The majority of samples from the ‘hydrocarbon-bearing sedimentary basins’ and ‘gas hydrates’ environment cluster between approximately 0-4 mole% CO_2 and 80-98 mole% CH_4. C – An expanded view of the CO_2-rich domain (oxidized fluids). All samples from the ‘geothermal spring water’ and ‘subduction-related fumaroles gases’ environments plot in this domain.

3.4 Discussion

3.4.1 Limitations and potential applications

Volatile hydrocarbon analysis by gas chromatography is a powerful tool to distinguish fluid signatures from various environments. New techniques such as in-line rock crushing GC (This study; Bray et al., 1991; Bray and Spooner, 1992; deRonde et al., 1997; Salvi and Williams-Jones, 1997a, 1997b; Channer and Spooner 1999; deRonde et al., 2003), allow for the detection and quantification of trace hydrocarbon phases, which has been difficult previously due to the potential for contamination and gas loss with other gas chromatographic techniques. Older, less reliable techniques including *in vacuo* thermal decrepitation (Piperov and Penchev, 1973; Smith et al., 1984; Barker and Smith, 1986; Kesler et al., 1986) and *in vacuo* mechanical crushing gas liberation in an inert atmosphere (Petersilie and Sørensen, 1970; Piperov and Penchev, 1973; Ikorskiy and Voloshin, 1982; Whelan, 1988b; Potter and Siemann, 2004; Beeskow et al., 2006). Despite improvements to gas liberation and detection techniques, fluid analysis via GC still has fundamental limitations. GC analysis is an unavoidably bulk-fluid technique in that upon crushing a rock sample for analysis, all fluid generations (primary and secondary fluid inclusions and occluded gases) are liberated to constitute a 'bulk' rock fluid (Bray et al., 1991; Salvi and Williams-Jones, 1997b). Careful sample selection must be considered when performing analysis of this nature. Environments that have been subjected to multiple hydrothermal alteration and metamorphic events would likely contain a variety of entrapped fluids from a number of sources and/or equilibration conditions chemically distinct from those associated with primarily entrapped fluids. For example, analyzed samples from the 'Archean rare metal pegmatite' environment (Tanco pegmatite, Manitoba, Canada) vary significantly in carbonic fluid composition, which is to be expected since the region has undergone extensive metamorphic and metasomatic events since its formation (Channer and Spooner, 1994a). Additionally, when comparing the hydrocarbon fluid chemistry from various studies problems arise with the consistency and quality of data resulting from the use of various gas chromatographic techniques. For instance, particular studies may or may not consider unsaturated hydrocarbon phases in the total hydrocarbon content of the fluid, yielding hydrocarbon abundances normalized to a carbonic fluid phase that considers a different assortment hydrocarbon species. Thermogenically-derived hydrocarbons can also yield variable and continuously changing abundances and the C2+ hydrocarbon content of a gas is sensitive to many secondary processes that may lead to erroneous interpretations (Schoell, 1980). Therefore, it is necessary to understand the geological environment, conditions of entrapment and the potential for disequilibrium reactions to occur (i.e., Fischer-Tropsch synthesis) to fully and effectively employ hydrocarbon signatures in geological interpretations.

Regardless of these potential limitations, preliminary investigation of hydrocarbon signatures from various geological environments demonstrates the potential to differentiate fluids from different sources and identify hydrocarbon origins (i.e., abiogenic versus thermogenic/biogenic). Results addressing the saturated hydrocarbon and carbon dioxide abundances for a number of geologically distinct environments are considered in this study.

3.4.2 Environmental hydrocarbon characteristics, variations and relationships

Understanding the hydrocarbon fluid chemistry of various ore-bearing and non-ore-bearing, magmatic, hydrothermal and surficial environments is an important, and potentially revealing, factor that is not often considered. Hydrocarbons such as methane, ethane and ethene, are sensitive to environmental factors such as oxygen and hydrogen fugacities, temperature and the presence of catalysts such as native metals, magnetite and PGM (Channer and Spooner, 1994a; Seewald 1994; Berndt et al., 1996; Salvi and Williams-Jones, 1997a; Horita and Berndt, 1999; Liu et al., 2007; Taran et al., 2007; Virnovskaia et al., 2008; Kolesnikov et al., 2009; Czuprat et al., 2010; Tian et al., 2010; Ziaka and Vasileiadis, 2011). Compound specific isotopic analysis of hydrocarbon species (i.e., C and H isotopic analysis of CH_4) are a robust provenance indicators in identifying hydrocarbons from bacterial, thermogenic, mantle and atmospheric origins (Schoell, 1988; Welhan, 1988; Botz et al., 1996; Sassen et al., 1999; Chen et al., 2000; Sherwood Lollar et al., 2002; Potter and Konnerup-Madsen, 2003; McCollom and Seewald, 2006; Taran et al., 2007, 2010; Sherwood Lollar et al., 2008). This latter technique can be expensive and often quite time consuming. A simpler technique employing hydrocarbon abundances to identify environmental characteristics such as fluid origin and the presence or absence of ore mineralization has previously not been identified. To this end, for a technique of this nature to be accurately employed for environmental differentiation, two key criteria must be met: (i) a statistically sufficient number of samples must be complied to constitute fields of geologically similar environments, and (ii) the background hydrocarbon chemistry of the fluids from these environments must be thoroughly understood such that alterations in hydrocarbon speciation and/or abundance related to specific processes (i.e., alkane dehydrogenation via PGE/PGM catalysis, catalyzed CO_2 reduction, etc.) can be readily identified.

3.4.2.1 Variation in light saturated hydrocarbon ratios

Geological environments with hydrocarbon fluids of interpreted abiogenic origin have a distinctly different fluid signature from those environments containing fluids of thermogenic origin. Abiogenic hydrocarbon signatures of are characteristically more depleted in the saturated higher order species propane and butane as opposed to their thermogenic counterparts (Figures 3.4 & 3.5). Hydrocarbons from mafic-ultramafic associated Ni-Cu-PGE deposits have been determined to be of an abiogenic origin due to the presence of a Schultz-Flory distribution between the hydrocarbon abundance and carbon number (Figure 3.9). A Schultz-Flory distribution is a bulk fluid hydrocarbon distribution that is governed by the probabililty of chain growth in abiogenic, stepwise polymerization-style reactions (Anderson, 1984; Taran et al., 2007, 2010; Sherwood Lollar et al., 2008). This distribution is a strong indication that the higher order hydrocarbon species have been generated via the abiogenic polymerization/oligomerization of shorter chained species (Eq. 3.7 – 3.8). This trend also demonstrates that the hydrocarbon fluid composition is not controlled by chemical equilibrium (Anderson, 1984; Potter and Konnerup-Madsen, 2003; Taran et al., 2007;

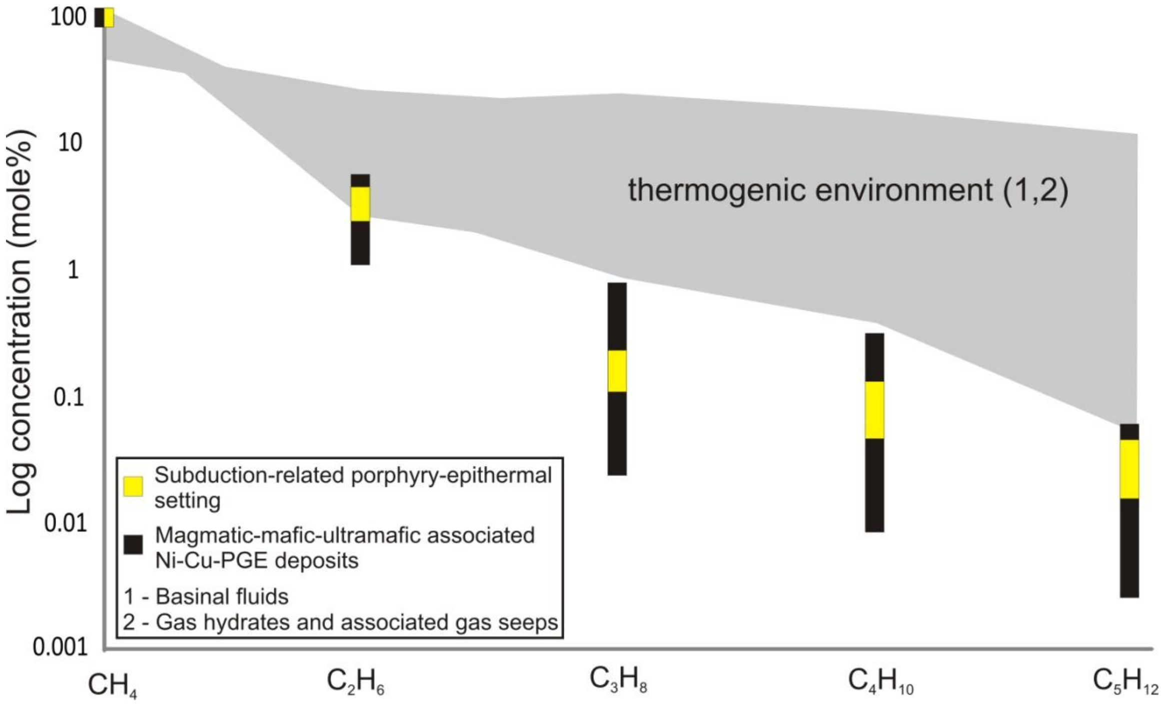


Figure 3.9: Shultz-Flory distribution of samples from mafic-ultramafic associated Ni-Cu-PGE deposits and subduction-related porphyry-epithermal setting. The coloured bars represent the total coverage of all samples from these environments. A log linear trend is strong indication of an abiogenic origin for higher order hydrocarbon species. Thermogenic hydrocarbons from the 'hydrocarbon-bearing sedimentary basins' and 'gas hydrates and associated gas seeps' are displayed for comparative purposes.

Proskurowski et al., 2008; Sherwood Lollar et al., 2008). Additionally, compound specific H and C isotopic analysis of hydrocarbon-rich fluid from a sample (A2-2) from the North Range of the Sudbury Igneous Complex (SIC; Hanley et al., submitted) also presents strong evidence of an abiogenic origin for hydrocarbons in this environment. Abiogenically derived hydrocarbons are generally characterized by elevated saturated light hydrocarbon abundances (i.e., methane, ethane) over heavy ones due to their preferential formation during abiogenic reactions such as Fischer-Tropsch (FT) synthesis (Anderson, 1984), especially at elevated temperature (Krishna and Bellm, 1993; Salvi and Williams-Jones, 1997a; Liu et al., 2007). Mantle, sudbuction-related porphyry-epithermal, Phanerozoic/Paleozoic rare metal pegmatitic and sediment-hosted base metal sulfide deposit environmental fields significantly overlap with fields constituted by samples from mafic-ultramafic associated Ni-Cu-PGE deposits in all discrimination diagrams investigated (Figures 3.3 - 3.5). This suggests that hydrocarbon species present in fluids associated with these aforementioned environments are also likely abiogenic in origin.

It is expected that a mantle derived hydrocarbon-bearing fluid would be of an abiogenic origin due to its organic-free environment of equilibration and entrapment. The upper-mantle is a fairly reducing environment with reported oxygen fugacities at or below QFM (Frost & McCammon, 2009; Ryabchicov & Kogarko, 2010; Cottrell & Kelly, 2011; Goncharov & Ionov, 2012). Thermodynamic calculations (Huizenga, 2001) and fluid inclusion studies (Hidas et al., 2010; Yamamoto et al., 2011; Berkesi et al., 2012) indicate that the dominant carbonic phase at oxygen fugacities and temperatures associated with the upper mantle is CO_2. Other work illustrates that fluids associated with deeper regions of the mantle (Shinozaki et al., 2010) and regions near the base of the lithospheric mantle (~90km, 2.5GPa, 1150^{o}C & fO_2 of -3.0 log units below QFM) contain CH_4 as the dominant carbonic phase (Goncharov & Ionov, 2012). The GC analysis of bulk volatiles in a sample of olivine from a mantle xenolith from this study also determined that CH_4 is the dominant carbonic phase, with no CO_2 being detected in this sample. Experimental evidence (Kolesnikov et al., 2009) and thermodynamic simulations (Ancilotto et al., 1997; Spanu et al., 2011) show that methane and ethane (and propane and butane to a lesser degree) can stably exist at upper-mantle pressure and temperature conditions, with increases in oxygen fugacities not substantially affecting hydrocarbon formation (Kolesnikov et al., 2009). Further physical evidence for the presence of abiogenic hydrocarbons in mantle environments was illustrated by Sugisaki and Mimura (1994), in which hydrocarbons were detected in mantle derived peridotites but were absent in peridotites formed via magmatic differentiation, suggesting a mantle carbon origin. Thus, in the mantle environments investigated, hydrocarbons C2-C4 were likely synthesized through P-T-governed, kinetically-controlled polymerization-style reactions in a carbonic fluid that evolved to a progressively more methane-dominated composition at upper mantle oxygen fugacities and cooling temperatures (Gerlach, 1980; Huizenga, 2001; Kolesnikov et al., 2009). Bulk fluids in samples from subduction-related porphyry-epithermal settings, Phanerozoic/Paleozoic rare metal pegmatites and mafic-ultramafic associated Ni-Cu-PGE deposits, which contain variable proportions of CO_2 and hydrocarbons, are of a dominantly magmatic-hydrothermal origin and have not interacted or equilibrated with organic-rich and/or carbonaceous horizons (as far as current knowledge suggests; Farrow & Watkinson, 1992; Watkinson, 1999; Molnar et al., 2001; Hanley et al, 2004, 2005; Lentz, 1991, 1996; LeFort et al., 2011). Samples from these environments were also found to follow a Shultz-Flory distribution (porphyry-epithermal samples also shown on Figure 3.9), coinciding with hydrocarbon distributions present in samples from mafic-ultramafic associated Ni-Cu-PGE deposits containing hydrocarbons of interpreted abiogenic origin.

Samples of thermogenically-derived hydrocarbon fluids from hydrocarbon-bearing sedimentary basinal environments and continental slope gas hydrate fluids are characteristically enriched in C3-C4 hydrocarbons (Figures 3.4 & 3.5). These fluids were determined to be of thermogenic origin based primarily on interpretation of compound specific C isotopic signatures (Chen et al., 2000; Sassen and MacDonald, 1997; Sassen et al., 1999), in which light hydrocarbons (C1-C2) derived from biogenic and thermogenic sources are notably more depleted in ^{13}C than analogous abiogenically derived species (Welhan, 1988; Botz et al., 1996; Berner & Faber, 1993; Sherwood Lollar et al., 1993, 2002; Horita and Berndt, 1999; Potter and Konnerup-Madsen, 2003; Ikorsky & Avedisyan, 2007). Additionally, it has been documented that during abiogenic hydrocarbon synthesis, higher order hydrocarbons become progressively more depleted in ^{13}C, whereas the opposite is true for biogenic and thermogenic reactions (Sassen et al., 1999; Lorant et al., 1998; Sherwood Lollar, 2002, 2006; Potter and Konnerup-Madsen, 2003; Potter and Longstaffe, 2007). However, this is not always the case, as noted in abiogenic reactions such as Fischer-Tropsch synthesis (Fu et al., 2007; Taran et al., 2007; Sherwood Lollar et al., 2008). Hydrocarbon fluids from these environments possess

C3/C1 and C4/C1 ratios markedly higher than in fluids of abiogenic origin. Hydrocarbons from thermogenic environments were not found to follow a Schultz-Flory distribution trend (flatter distribution; gray field, Figure 3.9), possessing elevated abundances of hydrocarbons C3-C5 (and C2 to a smaller degree). Elevated abundances of higher order saturated hydrocarbons is to be expected in thermogenically derived fluids (Welhan, 1988), in which C2+ hydrocarbons can account for up to approximately 15% (by volume) of the total gas phase, becoming progressively more C2+ depleted with fluid maturity (Schoell, 1980; Lorant et al., 1998; Sherwood Lollar et al., 2008). However, it has been noted that hydrocarbon fluids produced from thermogenic decomposition of organic matter can yield variable and continuously changing abundances (Schoell, 1980). Total average C2+C3+C4 saturated hydrocarbon abundances in hydrocarbon-bearing sedimentary basinal environments and gas hydrates are approximately 8.7% and 19%, respectively (Sassen et al., 1999; Chen et al., 2000), which are in good agreement with compositions expected from thermogenically derived fluids. Interpretation of the saturated hydrocarbon signatures from abiogenic and thermogenic environments, yields the following discrimination ternary diagram (Figure 3.10):

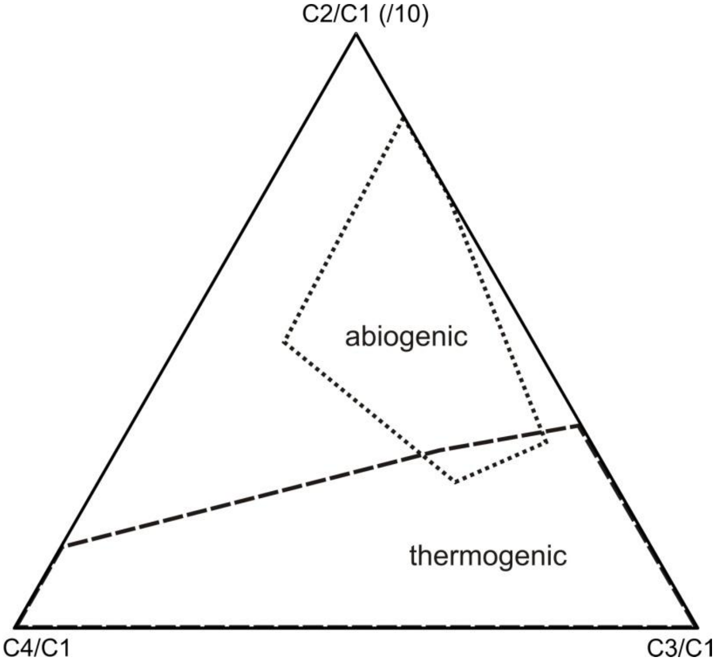


Figure 3.10: Thermogenic versus abiogenic hydrocarbon discrimination diagram based on results acquired directly and from literature. Fields are based on the interpretation of hydrocarbon origin based on the geological environment of fluid entrapment, saturated hydrocarbon distributions (i.e., Schultz-Flory) and literature δ^{13}C results (Sassen et al., 1999; Chen et al., 2000). Fluids from fumarolic environments and from metamorphosed/metasomatized terrains were more widely distributed, yet a large majority of samples from these environments possessed elevated C4/C1 ratios. Note that as the maturity of thermogenic fluids increases, it becomes more depleted in higher order hydrocarbons and will trend more towards the C2/C1 apex (Schoell, 1980; Lorant et al., 1998; Sherwood Lollar et al., 2008).

Hydrocarbon fluid composition in fumarolic and metamorphosed terrains including subduction-related fumarole gases, qtz-carb associated Au deposits in Archean terrain, and Archean rare metal pegmatites, are quite variable and do not cluster well in most discrimination diagrams investigated. This result likely represents highly variable geological conditions (i.e., temperature, organics, mineralogy, etc.) and the presence of multiple fluid generations within individual environments that effectively alter the bulk fluid hydrocarbon signature (recall a bulk fluid signature is acquired via GC analysis through the crushing of *all* entrapped fluid inclusions). Hydrocarbon fluids from fumarolic environments were especially variable. Three different fumarolic gas seeps were investigated in this study: (i) the Torta de Tocorpuri hydrothermal system, Chile (TT; Tassi et al., 2010); (ii) the Puchuldiza-Tuja hydrothermal system, Chile (PT; Tassi et al., 2010); and (iii) the Calypso and White Island hydrothermal fields, New Zealand (CWI; Botz et al., 2002), with fluids from all three environments being CO_2-dominated (99.80, 99.99 and 80.41 mole%, respectively). The hydrocarbon fluids of the TT hydrothermal system were extremely depleted in C2+ hydrocarbons relative to the PT and CWI fluids. Water and gas geochemistry and C and H isotopic analysis of CH_4 determined that hydrocarbons in this system (overwhelmingly CH_4) are the result of bacterial activity in fresh, meteoric waters (i.e., enzymatic CO_2 reduction; Schoell, 1980; Tassi et al., 2010). This result is supported by the fact that biogenic/microbial gases are dominated by CH_4 and highly depleted in C2+ hydrocarbons (Schoell, 1980, 1983; Chen et al., 2000; Sherwood Lollar et al., 2002; Taran et al., 2010). Hydrocarbon fluids from the PT system are up to two orders of magnitude richer in CH_4 than TT fluids and have been determined to be of a predominantly thermogenic source, characteristically richer in higher order hydrocarbons (Figure 3.5). CWI hydrocarbon fluids, although still CO_2-dominated, possess the most hydrocarbon variance and are relatively depleted in the total higher order hydrocarbon abundance (C3+C4) compared to fluids from hydrocarbon-bearing sedimentary basinal and gas hydrate environments (Figure 3.4). However, these samples were found to possess elevated C3/C1 and C4/C1 ratios, characteristic of fluids of thermogenic origin (Figure 3.5). This is confirmed by H and C isotopic analysis and the abundance of oily, long-chained hydrocarbon species typically impregnating rocks from this area, strongly suggesting a thermogenic origin for these fluids (Botz et al., 2002). Fluid contained in volcanic glass from the Coso volcanic field in California was also analyzed to constitute the subduction-related fumarolic gases environment. This sample plotted within the domain of suspected abiogenic hydrocarbon signatures, overlapping with the field defined by samples from mafic-ultramafic associated Ni-Cu-PGE in each discrimination diagram investigated (Figures 3.3 – 3.5). This is to be expected seeing as the relatively low levels of CH_4-dominated fluid in this sample were trapped in an igneous, organic-free environment at magmatic temperatures and low oxygen fugacities (~QFM from study of MORB; Cottrell & Kelly, 2011). To add, it has been shown that a fluid rich in CO_2 at magmatic conditions will evolve to a CH_4-dominated fluid at temperatures below ~600^{o}C if allowed to maintain equilibrium with QFM (equation 3.1; Gerlach, 1980; Salvi & Williams-Jones, 1997a), which may be the process responsible for the CH_4-enrichment and CO_2-depletion in this sample. Thus, a magmatic source for the volcanic glass fluid (either CH_4 directly or due to the re-equilibration of CO_2) seems likely (Welhan, 1988).

$$CO_2 + 2H_2O \leftrightarrow CH_4 + 2O_2 \qquad \textbf{Eq. 3.1}$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O \qquad \textbf{Eq. 3.2}$$

Fluids from qtz-carb associated Au deposits and Archean rare metal pegmatites have variable hydrocarbon ratios that can likely be attributed to fluid alteration due to metamorphic and metasomatic post-entrapment events and the presence of multiple secondary fluid inclusion assemblages. The Archean rare metal pegmatite investigated in this study (Tanco Granitic Pegmatite, Manitoba, Canada) is a complex igneous body with multiple mineralogical and texturally unique zones with a controversial crystallization history (Crouse et al., 1979; London, 1986; Thomas et al., 1988, Channer and Spooner, 1994a). The significant variation in hydrocarbon ratios in this environments is most likely due to the presence of multiple fluid generations entrapped under drastically different conditions (i.e., ~500-600^{o}C trapping temperature for primary inclusions in wall-zone tourmaline versus ~260^{o}C for primary inclusions in quartz-zone quartz; Channer and Spooner, 1994a; Selway et al., 2000). This is supported by the very consistent hydrocarbon ratios between two separate analyses of tourmaline from the same assemblage (cluster very tightly in Figures 3.3 – 3.5), which suggests that large variations in the bulk hydrocarbon fluid chemistry from this environment is significantly influenced by the presence of separate fluid generations. Additionally, evidence for significant wall rock influence on fluid composition was seen in CH_4-rich inclusions in the metasomatized boarder zone and adjacent wall rock zone (Thomas et al., 1988; Channer and Spooner, 1994a). The qtz-carb associated Au deposits investigated in this study (McIntyre-Hollinger & Kerr Addison gold-quartz vein systems; Smith et al., 1984;

Channer and Spooner, 1994a) are hosted in metamorphosed volcanics of Archean age and are associated with multiple fluid inclusions types, both primary and secondary. Similarly, it has been suggested that the process most likely governing relative CH_4-enrichments (and N_2-enrichments) in secondary fluid inclusions in this environment are fluid-rock interactions, specifically involving graphitic material present in host rocks (Smith et al., 1984; Channer and Spooner, 1994a and references therein). Thermodynamic computations by Smith et al. (1984) demonstrated that the compositions of the inclusion fluid present in the McIntyre-Hollinger Au-quartz vein have changed significantly since their entrapment, either by reaction between constituent gases or due to the loss or introduction of components. Smith et al. (1984) went on to conclude that the CH_4-rich fluid present in this system was in equilibrium with graphitic material at temperatures between 296-350^{o}C. In contrast, the quartz sample collected from the Kerr Addison Au-quartz vein is hosted in altered komatiites devoid of graphite; this sample was markedly less rich in CH_4 (dominated in CO_2) than those samples from the McIntyre-Hollinger environment. Therefore, it has been determined that an initially CO_2-dominated, high temperature fluid, responsible for gold mineralization in the system, was altered by varying degrees via post-entrapment re-equilibration events and fluid-graphite interactions (Smith et al., 1984; Channer and Spooner, 1994a).

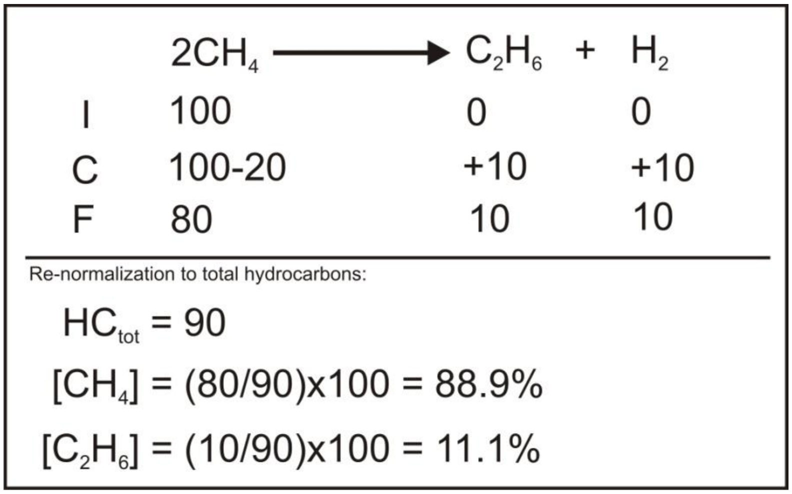
Groundwaters from Canadian Shield sites (Sherwood Lollar et al., 1993, 2008) also possess variable hydrocarbon ratios in all discrimination diagrams investigated. The majority of the samples from this environment (except one) plot in the region expected of thermogenically-derived fluids (Figure 3.10). Compound specific C and H isotopic analysis of groundwater gas samples have suggested a predominantly abiogenic origin for the hydrocarbon species detected. However, it was suggested that the bulk of these fluids, particularly those from Red Lake, Elliot Lake and Timmins, Ontario, represent the result of regional scale mixing of minor but significant bacterially-derived hydrocarbon gases and abiogenic gases with no reported evidence of a thermogenic contribution (Sherwood Lollar, 1993, 2006, 2008). Sherwood Lollar et al. (1993) favour a scenario in which isotopically distinct abiogenic CH_4 is generated at each site depending on the isotopic compositions of available carbon and local geochemical conditions. The variability in light saturated hydrocarbon ratios observed in this study is likely the result of these aforementioned mixing events and variable contributions from unique sources (i.e., bacterial and abiogenic). In addition, it is important to note the possibility for alterations in hydrocarbon abundances without significant changes to the isotopic signatures of said hydrocarbons.

3.4.2.2 Light carbonic species genetic relationships

The majority of samples show a strong genetic relationship between the light hydrocarbons methane and ethane (abundances normalized to total hydrocarbon content). In all investigated sample environments excluding magmatic fluids from metamorphic Archean terrains, hydrocarbon-bearing sedimentary basinal, barren mid-ocean ridge, hydrothermal exhalative seafloor and gas hydrate environments, the presence of ethane appears to be the result of methane oligomerization/coupling, as indicated by the close proximity of these samples to the trend expected from the reaction:

$$2CH_4 \leftrightarrow C_2H_6 + H_2 \qquad \textbf{Eq. 3.3}$$

once a re-normalization to total hydrocarbon phases is performed. A sample calculation illustrating this point can be found in Figure 3.11. This would suggest that ethane abundance, and presumably other higher order hydrocarbon abudances, in fluids from environments falling near this trendline is governed primarily by the reaction expressed in equation 3.3. As a corollary, it is also possible for this reaction to move in the opposite direction, generating methane via the breakdown of ethane. However, considering the characteristics of these environments (primarily igneous and organic-free) it seems unlikely that this is the case. Thermodynamic calculations by Salvi & Williams-Jones (1997a) have demonstrated that chemical equilibrium alone in a C-O-H system at various temperatures and oxygen fugacities do not account for the significantly elevated abundances of ethane and propane. They calculated a maximum ethane abundance of 0.06 mole% at 350^{o}C and QFM-2, which is much less than even the most ethane depleted samples from fumarolic (PT and TT environments) and ophiolite environments of 0.24 and 0.26 mole%, respectively (Abrajano et al., 1990; Tassi et al., 2010). This would imply that the hydrocarbon abundances present in these systems are the result of nonequilibrium processes (i.e., FT synthesis; Salvi & Williams-Jones, 1992, 1997a). It might be expected that fluids from ophiolite environments would display more elevated abiogenic ethane and higher order hydrocarbon abundances due to the absence of organics and the very reducing conditions produced as a result of the serpentinization of ultramafic rocks in this environment (Abrajano et al., 1990; Berndt et al., 1996; McCollom & Seewald, 2001). During abiogenic reactions, it has been shown that carbon



	$2CH_4 \longrightarrow$	C_2H_6	+ H_2
I	100	0	0
C	100-20	+10	+10
F	80	10	10

Re-normalization to total hydrocarbons:

$HC_{tot} = 90$

$[CH_4] = (80/90)x100 = 88.9\%$

$[C_2H_6] = (10/90)x100 = 11.1\%$

Figure 3.11: Sample calculation of hydrocarbon re-normalization. Expected molar abundances of methane and ethane if governed by the reaction: $2CH_4 \leftrightarrow C_2H_6 + H_2$. I – initial, C – change, F – final.

chain growth is preferable at lower temperatures (published experiments have employed temperatures no lower than ~240^{o}C to the best of our knowledge; Krishna & Bell, 1993; Ji et al., 2001; Liu et al., 2007; Tian et al., 2010). Through H_2-CH_4 isotopic equilibrium calculations, Abrajano et al. (1990) determined an equilibrium temperature range of 110-125^{o}C, which is significantly less than temperatures employed in abiogenic hydrocarbon generation experiments (i.e., FT synthesis; Krishna & Bell, 1993; Ji et al., 2001; Bertole et al., 2004a, 2004b; Liu et al., 2007; Taran et al., 2007, 2010) and thus a potential cause for the low levels of higher order hydrocarbon speciation.

A number of samples do not lie on trend 1, including those from magmatic fluids from metamorphic Archean terrains, hydrocarbon-bearing sedimentary basinal, barren mid-ocean ridge, hydrothermal exhalative seafloor and gas hydrate environments, but rather are disproportionally depleted in methane (i.e., trend 2, Figure 3.6 inlay). Fluids from these environments have been shown to be the result of thermogenic processes (Sassen et al., 1999; Chen et al., 2000) and/or have been chemically modified due to post-entrapment alteration effects (Channer and Spooner, 1994c; deRonde et al., 1997). The presence of methane-rich fluids from mid-ocean ridge environments have been suggested as being the result of either direct magmatic degassing or the result of abiogenic, high-temperature reactions within a hydrothermal fluid (Welhan, 1988). Thus we would expect these fluids to follow trend 2. Deviations from this trend may be the result of complex re-equilibration processes and late-stage alterations in fluid chemistry seeing as a number of rock samples from this environment display evidence of having been strongly tectonized and hydrothermally altered (Savelieva et al., 2008). It is not completely clear why samples from qtz-carb associated Au deposits in Archean terrain and from Archean rare metal pegmatites, which also display significant evidence for having undergone post-entrapment modifications (Crouse et al., 1979; Smith et al., 1984; Bray & Spooner, 1992; Channer & Spooner, 1994a), do not deviate to the same degree. However, one sample (2-S318) from the qtz-carb associate Au deposits setting and 4 (2 sets of sample repeats; Ta104-qtz samples and Ta64 samples) from the Archean rare-metal pegmatites setting, do display deviation from trend 1. Sample 2-S318 is from a high-grade, tourmaline-bearing vein surrounded by areas of significant recrystallization (Channer & Spooner, 1994a). Sample Ta104 displays the highest abundance of strain-related fluid inclusions occurring in sub-grain boundaries while sample Ta64 displayed relatively low total fluid inclusion abundance, dominated by saline, secondary inclusions

(Bray & Spooner, 1992; Channer & Spooner, 1994a). With this being said, hydrocarbon deviation in these samples is likely related to the presence of chemically distinctly fluids that originate from a different source, modification due to water-rock equilibration and reactions (Welhan, 1988) and/or post-entrapment metamorphic and metasomatic alteration effects. Additionally, one sample from a mafic-ultramafic associated Ni-Cu-PGE deposit setting was found to deviate from trend 1. Petrographic investigation of the quartz + sulfide + epidote assemblage from which the sample was acquired, displayed an unusually elevated modal abundance of sperrylite (PtAs) and other PGM. The fluid from this sample is propane-rich relative to the other samples from this environment (0.71 mole% versus 0.16 mole%, respectively) and was found to be extremely rich in unsaturated hydrocarbon abundance (not considered in this study). Unsaturated hydrocarbons have been noted to occur in significantly higher abundances in fluids of abiogenic origin, with thermogenically-derived fluids being characteristically depleted in unsaturated species (Welhan & Lupton, 1987). Also, a number of studies have illustrated the catalytic activity of PGE and PGE-containing compounds in dehydrogenation reactions (Cavani and Trifiro, 1995; Housecroft and Sharpe, 2005; Virnovskaia et al., 2008; Czuprat et al., 2010; Ziaka and Vasileiadis, 2011). The characteristics of these reactions will be discussed in a later section.

When methane and ethane abundances were normalized to total carbonic fluid (i.e., HCs + CO_2) and plotted against one another, two distinct trends manifest (Figure 3.7 - inlay). Trend 3 illustrates a propensity for fluids to be more enriched in ethane as the mole% of methane increases, opposite to that observed when normalized to only hydrocarbon phases. Trend 4, on the other hand, displays an increase in ethane with decreasing methane abundances, similar to that observed when normalized to hydrocarbon phases. The two distinctly different trends may reflect differences in initial fluid compositions. A starting fluid dominated initially by CO_2 may undergo reduction in situ (Gerlach, 1980, Huizenga, 2001; Salvi & Williams-Jones, 1992, 1997a) yielding variable amounts of methane, which can then go on to react with itself abiogenically generating ethane (and higher order species). Therefore, with increasing amounts of methane available to react with itself, the abundance of ethane would also increase, as illustrated by trend 3. On the other hand, a trend that displays increasing ethane abundance with decreasing methane abundance may be the result of two key processes: (i) thermogenic decomposition in which higher order hydrocarbons breakdown to yield smaller ones (Des Marais, 1981; Schoell, 1983; Sherwood Lollar et al., 2006), and/or (ii) Fischer-Tropsch synthesis in which available CO and CO_2 undergo reductive polymerization/oligomerizaton to form methane and higher order species (Anderson, 1984; Taran et al., 2007, 2010; Salvi & Williams-Jones, 1997a). It has been demonstrated that the monotonic distribution of polycondensation products generated via FT synthesis is the same as the distribution one would expect due to polymer decomposition (i.e., thermogenic HC production; Flory, 1936; Taran et al. 2007), with methane almost always as the most dominant product (Anderson, 1984). This agrees well with the findings by Salvi & Williams-Jones (1997a, 1997b) from the chemical analysis of the hydrocarbon fluid associated with the alkali/agpaitic rocks of Strange Lake, Quebec/Labrador, Canada (i.e., the data used in this study). The presence of dis-equilibrium hydrocarbon concentrations and the abundance of H_2 gas in the system due to mineral alterations highly suggest the hydrocarbon species in the system were the result of FT reactions. In addition, the ratios of the mole fractions of pairs of progressively heavier hydrocarbons (i.e., $C_{n+1/}C_n$), were found to level off at a value of approximately 0.34, which is consistent with a typical value of 0.38 – 0.6 for light hydrocarbons generated via FT reactions (Szatmari, 1989; Salvi & Williams-Jones, 1997a; McCollom & Seewald, 2006). For comparison, typical values of ~0.12 are typically exhibited for alcohols and heavy hydrocarbons (McCollom & Seewald, 2006).

3.4.3 Discussion of potential mechanisms responsible for hydrocarbon occurrence

The principal sources of methane, and in effect the higher order hydrocarbons (C2+) in hydrothermal systems are: (i) the thermal breakdown of long chain hydrocarbon species (i.e., thermogenic hydrocarbons; Sassen et al., 1999; Chen et al., 2000; Botz et al., 2002; Tassi et al., 2010; Mazzini et al., 2011); (ii) the biological/microbial generation of hydrocarbons at relatively low temperatures (Schoell, 1980, 1983, 1988; Galimov, 1988; Chen et al., 2000; Sherwood Lollar et al., 2002; Taran et al., 2010); (iii) direct outgassing of CH_4, and lesser amounts C2+ species, from mantle (Welhan, 1988; Potter & Konnerup-Madsen, 2003); and (iv) the abiogenic/inorganic synthesis of hydrocarbons via the oligomerization of shorter chained hydrocarbon with one another or the reductive oligomerization of CO and CO_2 through Fischer-Tropsch reactions (Salvi & Williams-Jones, 1997a, 1997b; Potter & Konnerip-Madsen, 2003; Potter et al., 2004; McCollom & Seewald, 2006; Taran et al., 2007, 2010).

Thermogenic hydrocarbons are generated by the thermal "cracking" of heavy hydrocarbons of biogenic origin (i.e., oils, kerogen, bitumen; Schoell, 1983; Sherwood Lollar et al., 2006). Although it may not possible to determine whether hydrocarbon fluids are of a thermogenic origin based on their geological location alone (i.e., due to fluid migration), hydrocarbon abundance and isotopic signatures are very useful in differentiating thermogenic from abiogenic and bacterially derived fluids (Welhan & Lupton, 1987; Schoell, 1988; Welhan, 1988; Botz et al., 2002; Tassi et al., 2010). A thermogenically derived hydrocarbon fluid can be distinguished from its abiogenic counter-part based primarily on the following criteria: (i) elevated CH_4 and C2+ concentrations; (ii) the distribution of C1-C5 hydrocarbon gases and the tendency of alkanes to predominate over alkenes; and (iii) compound specific C and H isotopic compositions (Welhan & Lupton, 1987). Isotopic signatures and Shultz-Flory distributions are very useful for determining whether hydrocarbons possess an abiogenic origin; however, the principal mechanisms and their characteristics in various geological systems remain poorly understood. There are two main abiogenic pathways for higher order hydrocarbon formation that need be considered: (i) Fischer-Tropsch synthesis and (ii) PGE/PGM catalyzed reductive coupling reactions.

Fischer-Tropsch synthesis (FT) is an abiogenic reaction that can occur under hydrothermal conditions (~150-500^{o}C, 0-500+ bar) and yields methane and higher order hydrocarbons via the reductive oligomerization of oxidized carbonic species (CO, CO_2; equations 3.4 – 3.5). FT synthesis tends to favour the production of shorter chained saturated species (CH_4 & C2-C3 alkanes), especially at elevated temperatures and pressure (Anderson, 1984; Krishna & Bell, 1993; Salvi & Williams-Jones 1997a; Ji et al., 2001; Liu et al., 2007; Tian et al., 2010).

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \qquad \textbf{Eq. 3.4}$$

$$2CO_2 + 7H_2 \rightarrow C_nH_{2n+2} + 2nH_2O \qquad \textbf{Eq. 3.5}$$

FT reactions are catalyzed by group VIII metals either in their native form, as an oxide (i.e., magnetite, wustite) or as a Fe-bearing silicate; however, metal sulfides have been demonstrated to be ineffective FT catalysts (Lancet & Anders, 1970, Anderson, 1984, Szatmari, 1989; Salvi & Williams-Jones, 1997a, Potter & Konnerup-Madsen, 2003, Taran et al., 2007). Hydrogen gas can be generated *in situ* via the hydrothermal alteration of minerals such as arfvedsonite to aegirine (Sugisaki & Mimura , 1994; Salvi & Williams-Jones, 1997al; Potter and Konnerup-Madsen, 2003), by the serpentinization of mafic-ultramafic rocks (Abrajano et al., 1988; Berndt et al., 1996; McCollom & Seewald, 2001;), or by the water-gas shift reaction. A simplified model of Fischer-Tropsch synthesis in geological systems under hydrothermal conditions is expressed in Figure 3.12. It has also been shown that catalyst modifications can have drastic effects on the product speciation, such as the addition of Mn in a 3:1, Fe:Mn ratio which was shown to enhance the formation of alkenes (Liu et al., 2007). Reaction products (light saturated hydrocarbons) yielded from FT reactions follow a Schultz-Flory distribution. This is evident when one considers the factors controlling chain growth, namely the rates of propagation versus termination. The mole fraction of a product having *n* carbons is given by the expression (Ushiba & De Deken, 1984):

$$Mn = (1\text{-}p)p^{n\text{-}1} \qquad \textbf{Eq. 3.6}$$

in which ‘p’ is the the probability of chain growth that can in turn be defined by the following expression:

$$P = \gamma_p/(\gamma_p + \gamma_t) \qquad \textbf{Eq. 3.7}$$

Where γ_p and γ_t are the rates of propagation and termination, respectively. Thus, the presence of Schultz-Flory distribution is a good indication of an abiogenic origin, although this factor should not be relied on exclusively (Flory, 1936; Sherwood Lollar et al., 2008). Under hydrothermal conditions in the presence of magnetite (or another catalytically active mineral/metal), FT synthesis is likely a very important factor to the hydrocarbon budget of a system.

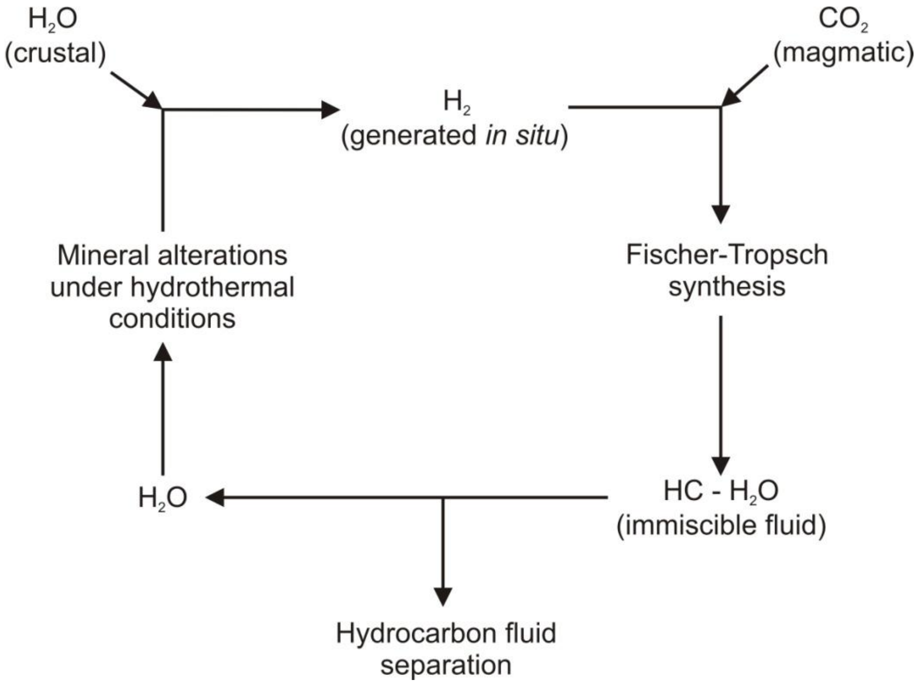


Figure 3.12: Simplied model for hydrocarbon formation under hydrothermal conditions through Fischer-Tropsch synthesis. Adapted from Nivin et al., (2005) and Potter et al., (1999).

In addition, a potential mechanism for the generation of higher order hydrocarbons is the reductive polymerization/oligomerization of smaller molecules to form larger ones.

$$2CH_4 = C_2H_6 + H_2 \qquad \textbf{Eq. 3.8}$$

$$CH_4 + C_2H_6 = C_3H_8 + H_2 \qquad \textbf{Eq. 3.9}$$

Methane already present in the fluid, either as the result of fluid respeciation in reducing environment (equations 3.1 & 3.2; Gerlach, 1980; Holloway, 1984; Potter and Konnerup-Madsen, 2003), as a result of FT synthesis, from thermogenic or biogenic sources or otherwise, can react with itself yielding hydrogen gas as a byproduct (equations 3.8 &

3.9). If these reactions were responsible for the abiogenic production of higher order hydrocarbons then one would expect to detect traces of hydrogen gas as well. However, this is not always the case. Hydrogen gas is small enough to diffuse from within fluid inclusions through the mineral crystal lattice, lowering the fH_2 in the inclusion to essentially zero over geologically short periods of time (Ponov and Kupryazhkin, 1979; Roedder, 1979; Holloway, 1981; Smith et al., 1984; Mavrogenes & Bodnar, 1994; Hanley et al., 2011). It has been well documented that PGE (and PGE-bearing compounds) can catalytically dehydrogenate saturated hydrocarbons at elevated pressures and temperatures yielding alkenes (Cavani and Trifiro, 1995; Housecroft and Sharpe, 2005; Virnovskaia et al., 2008; Czuprat et al., 2010; Ziaka and Vasileiadis, 2011) and promote dyhydrocylizations and skeletal rearrangements (Sivaramakrishna et al., 2010). Additionally, chain propagation can occur via alkene-metal complexation in which hydrocarbons can rapidly react and combine while coordinated to the metal (PGE, Ni) with subsequent reductive elimination yielding higher order alkenes (Figure 3.13; Cossee, 1964; Sivaramakrishna et al., 2010). Metal-hydrocarbon complexation may have significant implications on metal uptake and redistribution in hydrothermal systems, thus understand the characteristics and relevance of the aforemened reactions under geologically relevant conditions must be better understood. Figure 3.14 illustrates various chemical alterations/processes that can generate methane and hydrogen, and the abiogenic mechanisms that can potentially occur under hydrothermal conditions between carbonic volatile phases.

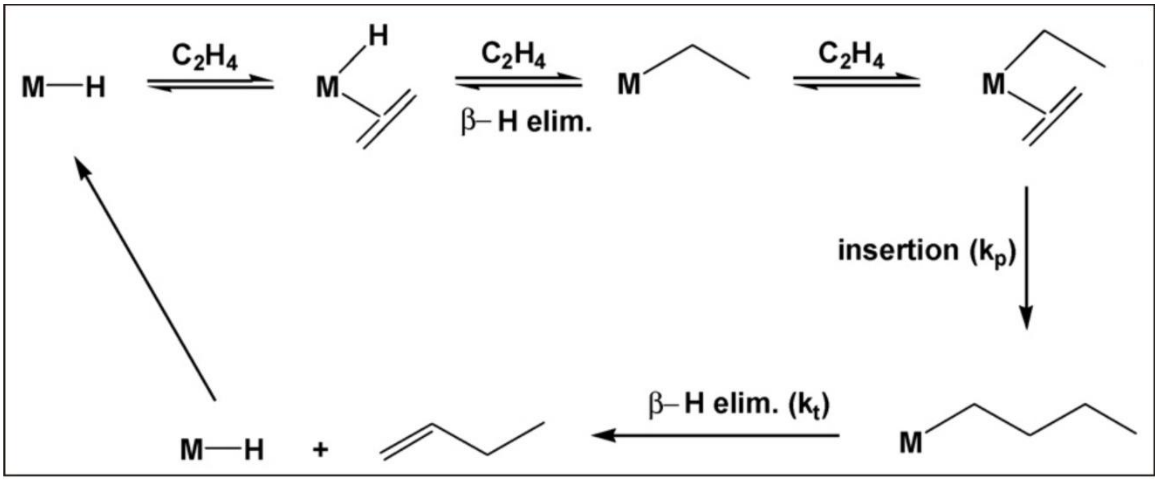


Figure 3.13: Cossee mechanism. An example of a catalytically mediated reaction resulting in carbon chain growth of alkenes. Taken from Sivaramakrishna et al. (2010), which was in turn adapted from Cossee (1964).

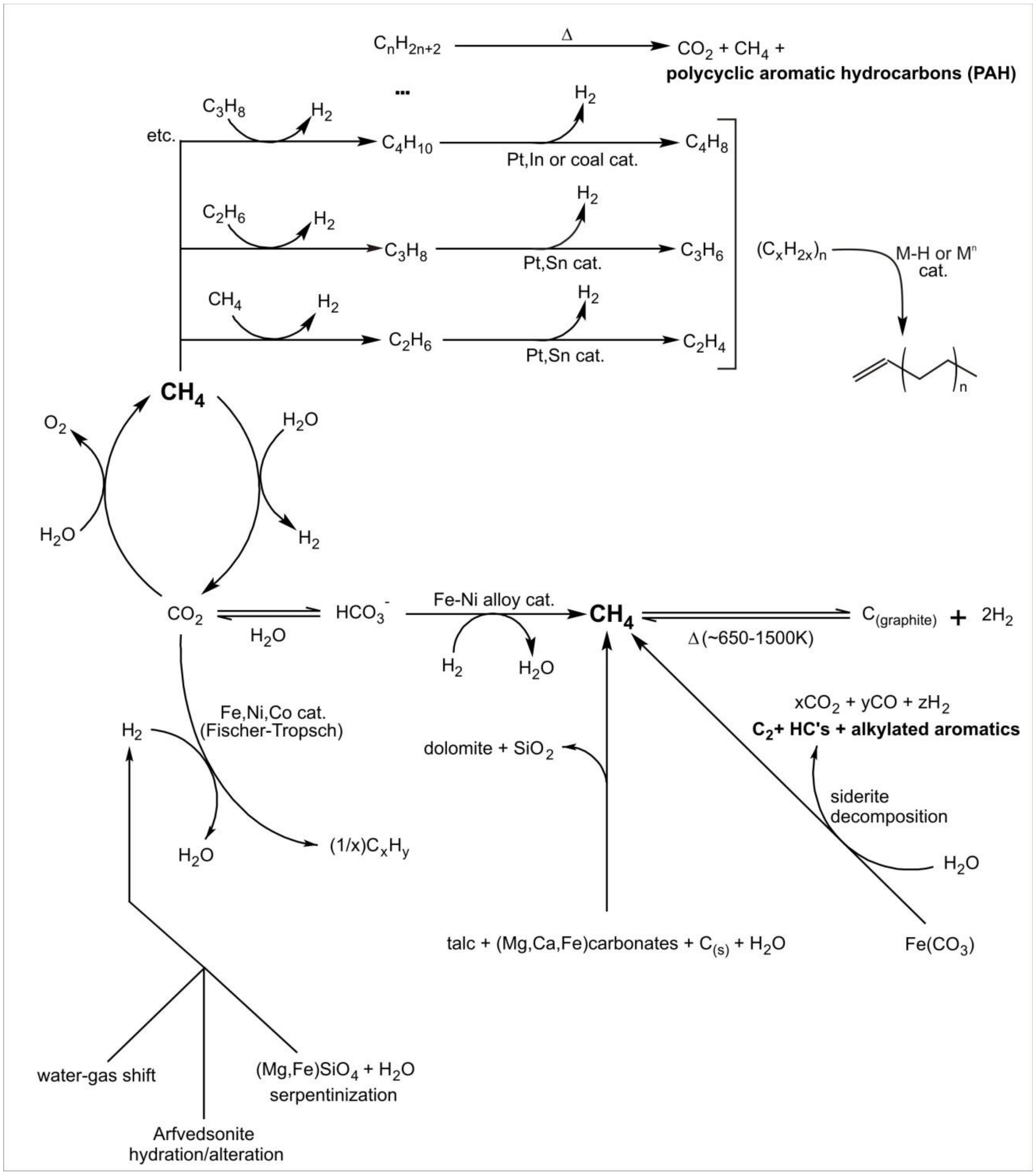


Figure 3.14 (previous page): Abiogenic process, alterations and mechanism that can potentially occur under hydrothermal conditions. This Figure outlines a number of processes responsible for the production of important volatile phases such as CH_4 and H_2, as well as a number of mechanisms responsible for the generation of higher order saturated and unsaturated hydrocarbons. Compiled using reactions presented by: Ramboz et al., 1985; Salvi and Williams-Jones, 1997a; Horita and Berndt, 1999; Maldonado-Hodar et al., 1999; Huizenga, 2001; Bertole et al., 2002,2004a; Potter and Konnerup-Madsen, 2003; McCollom, 2003; McCollom and Seewald, 2006; Taran et al, 2007; Virnovskaia et al., 2008; Czuprat et al., 2010; Sivaramakrishna et al., 2010.

3.4.4 Future work

Employing hydrocarbon signatures to differentiate between geological environments and determine fluid origin is a rather nascent area of study and thus much work still needs to done. Firstly, it is necessary to analyze a much larger number of samples and compile all available literature sources to generate a comprehensive database to better understand how hydrocarbon signatures vary between geological environments. With this being said, additional ore-bearing and non-ore-bearing envirnonments must also be considered to better understand the influence, if any, of particular ore-forming systems on hydrocarbon speciation and abundance. To better gauge the effect of particular ore minerals themselves on hydrocarbon signatures, high temperature and pressure furnace experiments will be performed. Controlled aliquots of carbonic gases (i.e., CO_2 or CH_4) can be placed in these high T and P aqueous environments with small amounts of ore minerals (i.e., magnetite, chalcopyrite, bornite, PGM, etc.) which allows one to investigate the changes in carbonic fluid speciation over time. These experiments are potentially very important in the creation of hydrocarbon-based mineral exploration criteria. Future studies will also consider a more comprehensive range of hydrocarbon species (alkanes, alkenes and alkynes) as previously unconsidered trace hydrocarbon species may prove very important.

3.5 Conclusions

The light, saturated hydrocarbon signatures of trapped fluid within rocks and minerals from a variety of geological environments have been quantified and compared to determine if any systematic differences are present. Data has been collected by direct GC analysis of samples at Saint Mary's University and by compiling data from literature sources presenting hydrocarbon data from various environments. The results of this study help to bolster some important aspects of the existing knowledge of fluid chemistry in various geological environments by (i) offering a detailed investigation of the light, saturated hydrocarbon signatures of trapped fluids from a variety of new geological environments, and (ii) presenting a comprehensive comparison of these hydrocarbon signatures within a large variety of different geological environments, both ore-bearing and non-ore-bearing, to help to better constrain and more readily identify hydrocarbon fluid origins and equilibration history.

This study has determined: (i) samples from environments containing hydrocarbons of thermogenic origins (i.e., hydrocarbon-bearing sedimentary basins, gas hydrates; thermal decomposition of biogenic material) are enriched in propane and butane; (ii) samples from environments containing hydrocarbons of suspected abiogenic origins (i.e., mafic-ultramafic Ni-Cu-PGE deposits, mantle, alkali-agpaitic magmatic fluids, volcanic glass, porphyry-epithermal setting) are relatively depleted in propane and butane but are rather more enriched in the light hydrocarbons methane and ethane; (iii) samples from fumarolic and ophiolite environments are enriched in CO_2 and CH_4, respectively, while both being very depleted in C2+ hydrocarbon species; (iv) samples from metamorphosed environments and from environments with complex geological histories show significant variation in their trapped fluid hydrocarbon signatures likely due to the presence of multiple fluid generations and post-entrapment fluid modification effects; (v) thermogenic and Fischer-Tropsch processes yield similar methane to ethane relationships when normalized to all inclusion-hosted carbonic species detected; and (vi) that there is potential to differentiate between hydrocarbons generated by biogenic and thermogenic versus abiogenic processes via the light, saturated hydrocarbon signatures.

From the data available, it is difficult to consider the differences in the hydrocarbon signatures due to temperature effects and the presence of organic compounds and ore metals for a few key reasons. Firstly, gas chromatography is a bulk analytical technique that simultaneously analyzes fluids from all fluid generations present in trapped inclusions. In environments with complex geological histories containing fluids trapped under various temperature and pressure regimes, analysis via bulk GC can be problematic. Additionally, considerations of this nature are limited to what is described in the employed literature (i.e., comprehensive petrography and microthermometry), which can often be lacking. In order to better constrain the effects of temperature, and the presence of ore minerals and organic compounds on the hydrocarbon signature of a C-O-H-bearing fluid, controlled laboratory experiments must be performed (i.e., high T and P furnace experiments). More comprehensive analysis of hydrocarbon signatures including the quantification of C4+ hydrocarbons (saturated and unsaturated) may also reveal potentially significant discriminatory factors. Also, additional work needs to be performed investigating a more comprehensive selection of environments bearing exclusively thermogenic and abiogenic hydrocarbon fluids to better constrain fluid origin end members. Despite certain limitations, this technique possesses the potential to determine the origin and chemical pathways responsible for hydrocarbon generation in certain geological systems. Most importantly, this study puts forth an initial investigation of how light saturated hydrocarbon signatures of trapped fluids (in fluid inclusions) vary in a number of geologically distinct environments.

3.6 References

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Chapter 4: Key conclusions and future work

4.0 Key conclusions

The results of the study described in Chapter 2 show that fluid inclusion volatiles, analyzed on a bulk basis, throughout the entire SIC environment (SIC main igneous mass units, mineralized alteration veins and country rocks and their brecciated equivalents; i.e., Sudbury breccia) contain trace quantities of both saturated and unsaturated aliphatic hydrocarbons. The key findings of this study are:

(i) Fluids trapped in Sudbury breccia from mineralized embayments (i.e., sulfide-mineralized footwall rock package associated with a mineralized embayment structure) are characteristically, based on bulk analyses of 410 mineralized and 45 barren Sudbury breccia samples, more enriched in C1-C4 *saturated* hydrocarbons (more than 2x more abundant [for propane for instanct] on the basis of mol per gram of crushed host rock) compared to fluids in barren breccias. The size of the sample population required to detect this difference does not have to be large and can be obtained from surface outcrop, not necessarily drill core. Analysis of a blind sample set of 8 Sudbury breccia samples (4 from barren footwall, 4 from within 200 meters from footwall-style mineralization) showed that 2 of the 4 samples from the mineralization-proximal environments were anomalous with respect to hydrocarbon abundance, whereas the 4 samples from a barren footwall environment were not anomalous.

(ii) In contrast to this, the average abundance of total *unsaturated* hydrocarbons does not differ by a statistically significant amount between the two breccia environments. However, within the mineralized embayment, unsaturated hydrocarbon abundance shows a spatial association with a footwall-style sulfide ore body. Specifically, a region of anomalously high propylene/propane ratios (i.e., >1) occurs in the narrow region (150 – 200 meter thickness) of Sudbury breccia between the SIC contact area (mineralized with contact-style Ni-Cu-PGE ore) and the upper-most portion of the footwall-style Cu-Ni-PGE ore body nearest the contact. While the PGE are suspected as the catalytic mechanism for the formation of unsaturated hydrocarbons, it is still unclear as to whether the elevated levels of unsaturated hydrocarbons in this area are the result of localized chemical alteration of pre-existing saturated hydrocarbons due to locally higher temperatures and PGE concentrations or a physical mechanism responsible for concentrating unsaturated hydrocarbons in this region.

(iii) A Schultz-Flory distribution for hydrocarbons C1-C6 in the trapped fluid is present in all investigated samples from all environments (including analyzed mineralized alteration veins) suggesting an abiogenic hydrocarbon origin. Additionally, there is a strong linear relationship between the molar abundances of methane and ethane, and methane and propane to a lesser degree, in the trapped fluid associated with the SIC and its footwall environment. This suggests the presence of common chemical mechanisms/controls responsible for the generation of hydrocarbons in these environments. Analysis of a sample of quartz from a PGE-poor mineralized alteration vein that is spatially and structurally coeval with footwall-style magmatic ore also consistently follows the aforementioned hydrocarbon trends indicating that the fluids present in Sudbury breccia and in quartz-bearing mineralized alteration veins share a common source or have been influenced by identical chemical and physical factors (i.e. mineralogical regime, temperature, etc.).

(iv) In contrast to the aforesaid hydrocarbon relationships followed by all samples from the SIC main mass units, country rocks, Sudbury breccia and PGE-poor mineralized alteration veins, significant deviations to these relationships in quartz-hosted fluid from PGE-rich mineralized alteration veins are present. This finding suggests that PGE/PMG likely play an important role on the hydrocarbon speciation and abundances of fluid circulating through the Sudbury ore environments via catalytic dehydrogenation of saturated to unsaturated hydrocarbons. However, additional high temperature and pressure experiments are required to fully elucidate the effects of metal and mineral catalysts on fluid hydrocarbon signatures.

This study has potential significant applications to routine exploration practices. Firstly, exploration for footwall-hosted Cu-Ni-PGE deposits can be initially guided via the analysis of light, saturated hydrocarbon abundances of fluid trapped in Sudbury breccia. Our results show that light, saturated hydrocarbon abundances are statistically higher in regions of the footwall that are host to sulfide mineralization relative to breccia environments barren of such mineralization. Within a mineralized footwall embayment environment itself, unsaturated hydrocarbon abundances can be effectively used to aid in ore exploration. Results illustrate that the Sudbury breccia near upper-most region of a footwall-hosted ore body is significantly enriched in unsaturated hydrocarbon, specifically propylene. This result can be employed as a down hole tool to supplement drilling programs. Samples of breccia can be systematically analyzed as one drills into the footwall, where elevated unsaturated hydrocarbon abundances would suggest the presence of a nearby ore body, one of which is likely more deeply hosted in the footwall. Additionally, significantly elevated fluid unsaturated hydrocarbon abundances and deviations from light hydrocarbon abundance relationships (i.e., methane mole% versus ethane mole%) is present in samples from PGE-rich mineralized alteration veins. This is also possesses important implication to exploration as a cheap and viable chemical tool to determine whether a system of hydrothermal veins and stockwork is PGM mineralized.

Gas chromatographic results collected from samples analyzed directly and from literature sources has characterized the bulk, light saturated hydrocarbon signatures (C1-C4; from fluid inclusions and gas seeps) of an assortment of geologically unique environments. Hydrocarbon fluids of interpreted abiogenic origin are enriched in ethane and depleted in the higher order hydrocarbons propane and butane relative to fluids of thermogenic origin. Thermogenic fluids from basinal environments and gas hydrates cluster closely in all discrimination diagrams investigated. Similarly, interpreted abiogenic fluids in samples from igneous magmatic-hydrothermal-related environments including subduction-related porphyry-epithermal, mantle, Phanerozoic/Paleozoic rare metal pegmatite and magmatic-mafic-ultramafic associated Ni-Cu-PGE deposit settings, are also closely related in discrimination diagrams. Fluids from Archean terrains that have been subjected to various metamorphic and metasomatic events since their formation (i.e. qtz-carb associated Au deposits, Archean rare metal pegmatites, hydrothermal seafloor exhalatives) and fluids related to fumarolic environments have variable hydrocarbon signatures. This can be likely attributed to presence of multiple fluid generations being trapped and modified by post-entrapment re-equilibration processes. Methane and ethane in the majority of environments investigated appear to share a genetic relationship with one another, either through abiogenic polymerization-style reactions or thermogenic decomposition, as indicated by linear relationships in CH_4 versus C_2H_6 binary plots.

Research involving the characterization of bulk fluid inclusion hydrocarbons in the footwall of the Sudbury Igneous Complex and other magmatic, hydrothermal and surficial environments found that hydrocarbon signatures can vary substantially as a function of: (i) geological conditions (i.e. fO_2, fH_2, temperature); (ii) proximity to ore (i.e. unsaturated hydrocarbon enrichments in regions around footwall-style Cu-Ni-PGE and low-sulfide, PGE-rich deposits); (iii) the presence of catalytic minerals such as magnetite (FT catalysis) and PGM (reductive coupling & dehydrogenation catalyst); and (iv) the presence of organics and biologically derived hydrocarbons (i.e. thermogenic decomposition). To this end, fluid inclusion hydrocarbon signatures can effectively: (i) aid in the understanding of fluid provenance, genetic and post-genetic histories, and conditions of equilibration (or shifts from theorized equilibration due to the presence of catalytic compounds), and (ii) be used as supplemental set of criteria for sulfide ore exploration (particularly PGE-rich ore).

4.1 Future work

Additional work must be performed in order to better constrain fluid provenance, the chemical processes affecting hydrocarbon speciation and abundance and the bulk fluid signatures of various geological environments. Compound specific C and H isotopic analysis has been performed for hydrocarbons C1-C3 (from hydrocarbon-dominated fluid inclusions in quartz associated with a quartz + sulfide + epidote assemblage in the footwall of the SIC) and is currently being processed and analyzed for future publication. This work will better constrain hydrocarbon origin as it can differentiate between hydrocarbons of biogenic and thermogenic origin (^{13}C enrichment as carbon number increase) versus those abiogenically derived (^{13}C depletion as carbon number increases). Isotopic analysis of Sr (in brines from coevally entrapped aqueous fluid inclusions) and of noble gases (He, Ne, Kr, Xe; from aqueous and hydrocarbon fluid inclusions) will help to further constrain fluid origin and its potential influence of footwall-style Cu-Ni-PGE mineralization. This work is currently being performed and results are pending. In addition, Raman spectroscopy will also be performed to determine the fluid chemistry of individual fluid inclusions (and thus individual fluid generations) in the Sudbury footwall environment. Gas chromatography, although a very powerful tool, is limited in its use for determining *bulk* fluid chemistry. Raman spectroscopy avoids this issue in that it can probe individual fluid inclusions and can thus be used to differentiate between multiple fluid generations.

To better constrain the chemical mechanisms responsible for the generation of saturated and unsaturated hydrocarbon species under various geological conditions (T, P, mineralogy, etc.), high T and P furnace experiments will be performed. Experiments will be performed investigating the affects of T, P, starting fluid C-O-H composition and mineral/catalyst content on the hydrocarbon speciation and abundances in hydrothermal environments. Gaseous aliquots will be removed from the system and analyzed via gas chromatography at Saint Mary's University. The GC system employed at Saint Mary's still requires refinement in order to accurately identify and quantify higher order hydrocarbon species (C6+; aromatics). A number of unidentified hydrocarbons that elute late (25-35 minutes on method 2; see Chapter 2) remain unidentified until sufficiently comprehensive standard gas mixtures can be analyzed. Additionally, there are a number of "impurity" peaks of unidentified origin in both GC method 1 and 2 (see Chapter 2 methodology) that need to be addressed.