To Marcos
Thanks for all
your help.
Lesley.

STABLE ISOTOPE (O, H, S, AND C) AND GEOCHEMICAL STUDY OF THE KEMPT SNARE LAKE MINERAL PROSPECT, SOUTHWESTERN NOVA SCOTIA

by

Lesley Dinnett

Submitted in partial fulfilment of the requirements
for the degree of Master of Science
at
Dalhousie University,
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DALHOUSIE UNIVERSITY

DEPARTMENT OF EARTH SCIENCES

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DEDICATION

To all those who listened, understood and helped,

my heartfelt appreciation,

For those of who didn't, will never and wouldn't,

"Pogue ma hone".

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ABSTRACT

Kempt Snare Lake Pb-Zn mineral prospect is hosted within a small greisenised granite cupola that intrudes metasediments of the Goldenville Formation. Major oxide, trace element, REE, and stable isotopes studies (O, H, C, and S) reveal the fluid sources, sequential alteration, greisenising, graphite precipitation, and mineralisation stages. Trace element and REE analyses show all the Kempt Snare Lake lithologies are related through magmatic differentiation. The greisenised units have increased ΣREE, reflecting REE complexing in the alteration fluids. Alteration has affected all the units and resulted in high K, Na, and Fe contents, albitic plagioclase, phengitic muscovite, and secondary K-feldspar. Stable isotope signatures for silicate minerals from all lithological units (least altered leucomonzogranite to highly altered greisen), and vein silicate minerals have similar isotopic compositions with quartz ($\delta^{18}O$ = 9.9-11.1 ‰), and muscovite ($\delta^{18}O$ = 6.7-8.0 ‰). Hydrogen isotopes from granitoid and vein muscovite have δD = -39.80 to -58.8 ‰. Geothermometry carried out on these samples suggests temperatures of equilibration ~500 °C with a fluid of mixed igneous / metamorphic origin responsible for these isotopic compositions. K-feldspar signatures from the host units have values out of equilibrium with the other minerals, and reflect continued reequilibration with the alteration fluids to lower temperatures. Carbon values from graphite from lithological units vary in composition from $\delta^{13}C$ = -17 to -27 ‰ with carbon probably entering the cupola from the carbonate-bearing Goldenville Formation and from the hydrocarbon-bearing Halifax Formation. Mixing of the CO_2 fluid with the CH_4 fluid resulted in the formation of graphite with variable isotopic signatures. Brittle deformation followed graphite precipitation and fO_2 increased, resulting in the oxidation of wall-rock graphite and fluid CH_4, forming vein siderites ($\delta^{13}C$ = -15 to -18 ‰; $\delta^{18}O$ = ~9.5 ‰). Sulphides from the veins show a narrow range ($\delta^{34}S$ = 6.9-10.5 ‰) consistent with H_2S being the dominant sulphide species and the sulphur originating within the Meguma Group metasediments. A later, restricted influx of meteoric water reequilibrated some of this siderite to low-temperature oxygen isotopic composition ($\delta^{18}O$ = 27 ‰).

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CHAPTER 1 - INTRODUCTION

1.1 General Statement

Stable isotope geochemistry has become a necessary component in the study of the genesis of ore deposits. When used in conjunction with other geological and geochemical data, i.e., petrography and whole rock geochemistry, carbon, sulphur, oxygen, and hydrogen isotopic data may reveal information on the source, temperature and physicochemical conditions of the mineralising fluids. By understanding the mineralising history of a deposit, constraints may be placed on further exploration.

In this study, carbon, sulphur, oxygen, and hydrogen isotopic signatures obtained from the Kempt Snare Lake mineral prospect in southwestern Nova Scotia have yielded information on the sources and temperatures of the fluids responsible for the alteration and mineralisation found at this deposit. In addition, detailed geochemistry, major and trace element, and rare earth element (REE) data collected allow a more thorough interpretation of the fluid composition, enabling the examination of the relationships and inter-relationships of the host lithologies.

1.2 Stable Isotope Studies

Stable isotope geochemistry originated in the mid 1940's, with one of the first applications in geothermometry carried out by Urey (1947); however, reliable stable isotope geothermometry only became possible after the development of accurate methods of measuring samples, and the determination of accurate fractionation factors. These techniques were unavailable until the late 1960's - early 1970's. During the intervening years, advances were made on the isotopic variations in natural systems. Thode et al. (1949) showed the natural variations in the isotopic content of sulphur and the possible significance of these variations. Thode et al. (1961) suggested that meteorite sulphur could be used as the reference for all sulphur samples. In the 1950's work established that the isotopic composition of fluids was related to their origin. Freidman (1953) researched the deuterium content of natural waters and other fluids and related the variations to different sources, and Epstein and Mayeda (1953) discussed the variations in oxygen isotope content from natural waters. Craig (1953) studied the naturally occurring variation in carbon isotope signatures. Taylor and Epstein (1962) discussed the oxygen isotope relationships between coexisting minerals in igneous and metamorphic rocks. Their study established the natural enrichment patterns for minerals within a rock that has maintained equilibrium.

In the 1970's understanding of the use of stable isotopes as fluid tracers and geothermometers continued to advance. New analytical techniques allowed Bottinga and Javoy (1973) to present fractionation factors that were considerably different from previously published data. Taylor (1974) showed how variations in oxygen and deuterium isotopes are related to source and applied these isotopes to hydrothermal alteration and ore deposit studies. In his study, Taylor (1974) showed how different stages of hydrothermal alteration, when caused by different fluids, could be distinguished by their isotopic signature.

In 1969, Bachinski presented data showing the enrichment patterns that should occur between coexisting sulphides that formed at, and have remained in, equilibrium. This work allowed the testing and identification of equilibrium assemblages, enabling a more accurate interpretation of sulphides minerals as indicators of fluid composition and temperature. Further work carried out by Ohmoto (1972) and Rye and Ohmoto (1974) showed that the isotopic signatures of carbon and sulphur are related not only to the source, but also to the oxygen and sulphur fugacity and the pH of fluids.

Investigation of the stability of minerals under different fluid conditions, pH, salinity, dissolved gas contents, and under varying physical conditions, temperature and pressure, is important in understanding fluid conditions, and many have researched the effect of changing the physical and chemical parameters (Craig and Scott 1974; Barnes 1979; Barton and Skinner 1979; Holland and Martin 1979; Burt 1981; D'amore and Gianelli 1984; McKenzie and Hegelson 1985). This work, used in conjunction with the information on the fluid conditions derived from stable isotopes, may provide a thorough understanding of the formation of a mineral deposit.

The identification of the origins and conditions of fluids responsible for a mineral deposit has become an intergral part of ore deposit studies for many years (White 1974). As a result, the type of information that stable isotopes reveal makes them a common tool in studying ore geology in many world class deposits (Bluebell, British Colombia, Ohmoto and Rye 1970; El Salvador, Chile, Sheppard and Gustafson 1976; Yankee Fork, Idaho, Criss et al. 1985; Keno Hill Ag-Pb-Zn district, Yukon, Lynch et al. 1990; JC tin deposit, Yukon, Layne et al. 1991; Olympic Dam, Australia, Oreskes and Einaudi 1992; Loulo, Mali, Fouillac et al. 1993).

1.3 Regional Geology of Nova Scotia

Mainland Nova Scotia consists of two main lithotectontic units separated by the Cobequid-Chedabucto fault system. The suture that separates the Meguma Terrane and the Avalon Terrane is the Cobequid-Chedabucto Fault System (Keppie and Dallmeyer 1987). To the north of this fault lies the Avalon Terrane that represents a composite of microcontinental fragments (Zen and Palmer 1981). To the south of the Cobequid-Chedabucto fault system lies the Meguma Zone, composed of the metasedimentary rocks of the Cambrian - Ordovician Meguma Group, the peraluminous granites of the South Mountain Batholith and lower Carboniferous sediments (Schenk 1983) (Figures 1.1 and 1.2). The Avalon and Meguma Terranes have distinct faunal and tectonic characteristics that suggest these two terranes were not brought together until the Late Devonian (Schenk 1981; Keppie 1977; Keppie and Dallmeyer 1987).

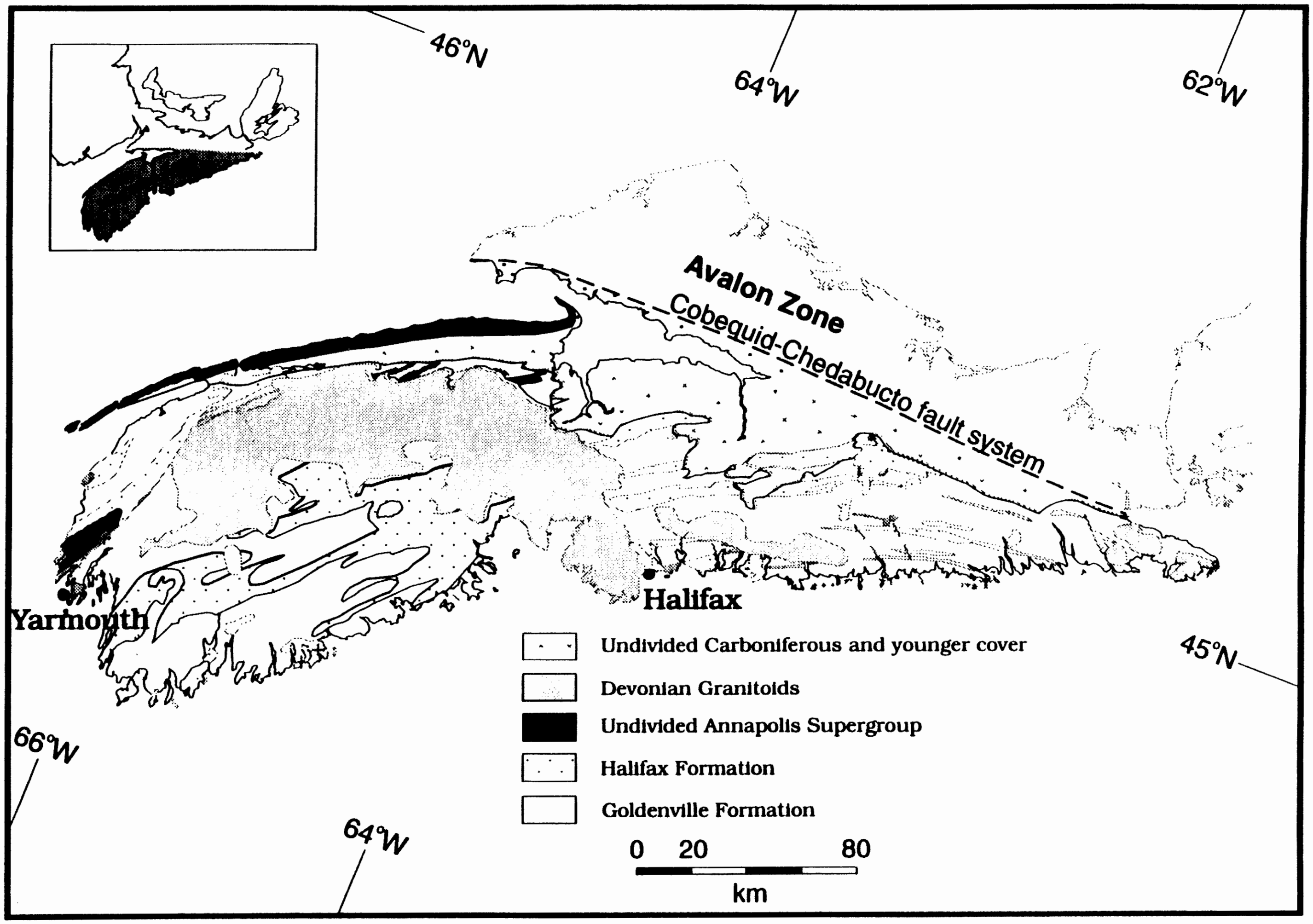


Figure 1.1. Regional geological map for southwestern Nova Scotia, from Tate (1995)

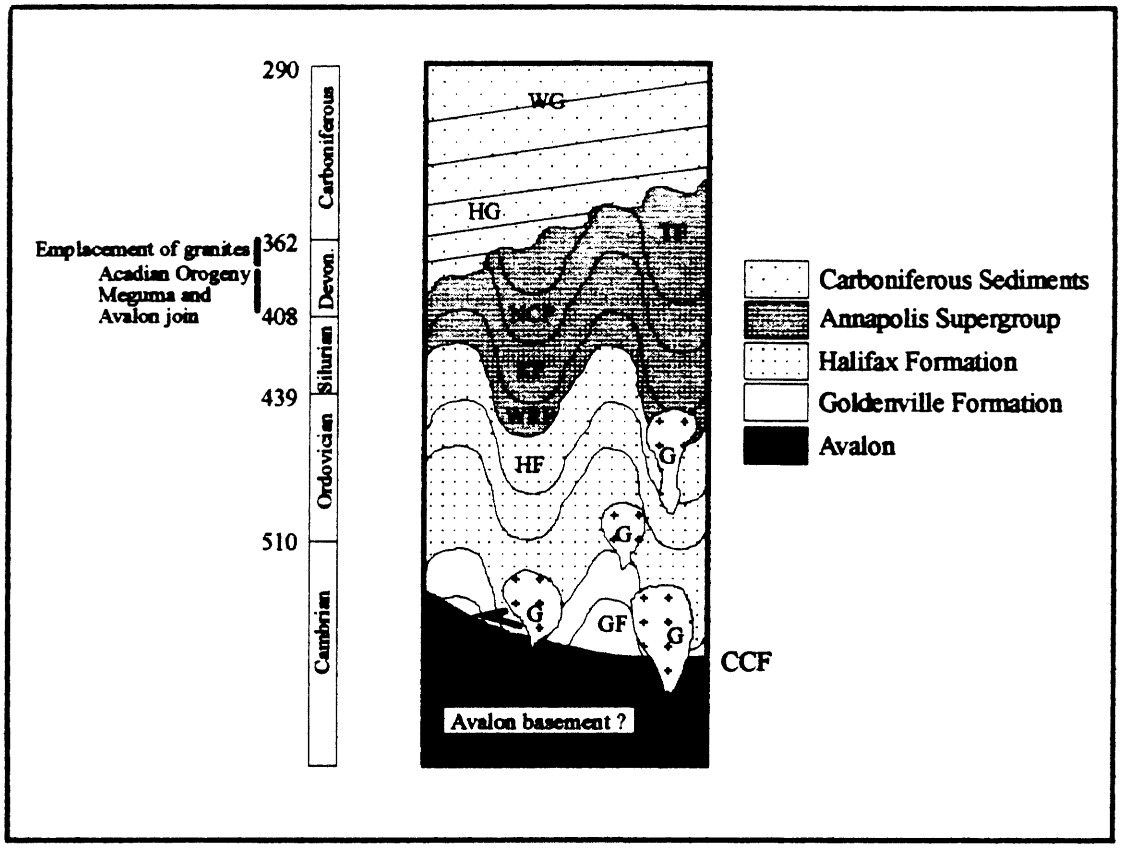


Figure 1.2. Schematic stratigraphic section showing the main geological events. GF-Goldenville Formation, HF- Halifax Formation, G-Devonian-Carboniferous Granites,WRF- White Rock Formation, KF- Kentville Formation, NCF- New Canaan Formation, TF- Torbrook Formation, HG- Horton Group, WG- Windsor Group and CCF- Cobequid-Chedabucto Fault. Time Scale- Harland et el. (1989) Stratigraphy compiled from Schenk (1978) and MacDonald (1994).

The Avalon Terrane is characterised by Late Precambrian volcanic and sedimentary rocks. Overlying these lithologies is a sequence of Cambrian-Ordovician shallow-water sediments (Schenk 1978). Eberz et al. (1991) studied the Nd isotopic composition of the lower crust beneath the Meguma Zone and found that granulite xenoliths within the Tangier dykes have isotopically "young" ages compared to the overlying Meguma Zone lithologies. Similarly, Clarke et al. (1993a) indicated the Nd model ages of the gneisses of Liscomb Complex were younger than those for the surrounding lithologies. These workers suggested that these ages may be the result of material younger than Meguma Zone lithologies lying beneath the Meguma Group. Eberz et al. (1991) and Clarke et al. (1993a) suggested that this younger lower crustal component may be Avalon Terrane, with the Meguma Terrane thrusted on top during the suturing event now represented by the Cobequid-Chedabucto Fault System.

The Meguma Group consists of two formations. The Goldenville Formation is composed of massive, fine-grained quartzitic rocks and interbedded slates with restricted occurrences of carbonaceous and sulphide-rich argillite. The overlying Halifax Formation consists of dark, massive to thinly laminated carbonaceous, pyrrhotitic argillite (Sangster 1992), siltstones, and minor quartzites. The Goldenville Formation resembles modern-day channel deposits in the mid-fan areas of deep-water fan systems, whereas the Halifax Formation resembles modern overbank turbidites, and slope and outer shelf environments (Schenk 1983). In southwestern Nova Scotia, the stratigraphic relationships of the two formations suggest that they represent part of a prograding turbidite fan, progressing upwards from a distal to a suprafan environment (Chatterjee and Strong 1985).

The boundary between the two Meguma Group formations is termed the Goldenville-Halifax Transition zone (GHT). This zone is characterised by black organic-rich metasediments with high manganese and arsenic contents, and highly variable sulphur isotopic compositions (Sangster 1993). Carbonates and calcareous argillites from the GHT have Mn-rich compositions and isotopic temperatures indicating diagenetic equilibration at 25 to 200 °C (MacInnes 1986).

Above the Meguma Group lies the 3 km thick conformable package of shelf sediments of the Annapolis Supergroup (Schenk 1978). Schenk (1978) proposed that this group of Ordovician to Lower Devonian sediments were deposited as a result of glacial eustatic changes in sea level. During the Acadian orogeny (395-388 Ma, Hicks and Jamieson (1995)) the entire group of Cambrian to Devonian sediments was deformed and regionally metamorphosed. This deformation resulted in the Meguma sediments being metamorphosed to greenschist - amphibolite facies (Reynolds et al. 1981; Muecke and Keppie 1979), with the increasing grade of metamorphism marked by the progressive development of chlorite - biotite - garnet - andalusite - staurolite- cordierite and sillimanite (Clarke and Muecke 1980).

In the Late Devonian - Early Carboniferous (Clarke et al. 1988), peraluminous granites of the South Mountain Batholith intruded the Meguma Terrane at ca. 372 Ma (Clarke et al. 1993b). Duration of the intrusion was short (ca.6 Ma), and occurred by two processes, diapirism and stoping (Horne et al. 1989). The granites vary in composition from biotite granodiorite to muscovite-biotite monzogranite and finally to a late suite of leucogranite porphyries and aplites (Clarke et al. 1993b). Intrusion of the South Mountain Batholith granites had a significant thermal metamorphic effect on the surrounding Meguma Terrane metasediments (Reynolds et al. 1987). The intruding plutons are surrounded by contact aureole characterised by the development of porphyroblastic chlorite, biotite, cordierite, staurolite, andalusite +/- sillimanite (Dallmeyer and Keppie 1988). In southwestern Nova Scotia, the contact metamorphism caused assemblages characteristic of hornblende-hornfels facies (Cullen 1983). Heat from the Devonian - Carboniferous granitoids also caused resetting of argon-bearing minerals in the aureoles, thus permitting indirect dating of the plutons (Dallmeyer and Keppie 1988).

From the Middle Devonian until the Early Permian, fluvial to laucustrine conditions prevailed, forming locally thick (up to 13 km) accumulations of sediments (Schenk, 1978). In Nova Scotia these sediments are generally unmetamorphosed (Schenk 1978), and they rest unconformably on the underlying metamorphic rocks. Locally, Upper Carboniferous sediments contain important coal reserves.

1. 4 Previous Work in Nova Scotia

Within Nova Scotia, many mineral prospects and deposits that have been studied by whole-rock geochemistry. For example, Richardson (1988), and Richardson et al. (1989) studied the Davis Lake Pluton; Clarke et al. (1993a and b) studied parts of the South Mountain Batholith; Kontak (1988 and 1990a), Kontak et al. (1988 and 1990a) researched the geochemistry of the East Kemptville leucogranite; and Corey and Chatterjee (1990) studied the REE and trace element variations within the South Mountain Batholith. These studies provide a broad data base for this investigation of the Kempt Snare Lake mineral prospect.

The amount of conventional geochemical data contrasts with the lack of stable isotope work on deposits within Nova Scotia. Stable isotopic work in Nova Scotia has tended to be restricted to known base metal deposits and to known and possible gold prospect areas; however, some detailed studies on the Meguma Zone lithologies do exist. Stable isotopic signatures for the Meguma Group rocks show values of $\delta^{34}S = -5$ to $+30$ ‰ (Sangster 1989 and 1992) and $\delta^{13}C = -14$ to -18 ‰ (Graves et al. 1988) (where $\delta = (((R_{sample}-R_{standard})/R_{standard})* 10^3)$, R = the ratio of the heavy/light isotope of the element in question, expresed in parts per thousand (‰)). Sulphur values for the South Mountain Batholith, established by Poulson et al. (1991), indicated $\delta^{34}S = +1.6$ to $+15$ ‰. Longstaffe et al. (1980) obtained ranges in value for the $\delta^{18}O$ content of the South Mountain Batholith that vary from $\delta^{18}O = 10.1$ to 12 ‰, and from Meguma Group clastic

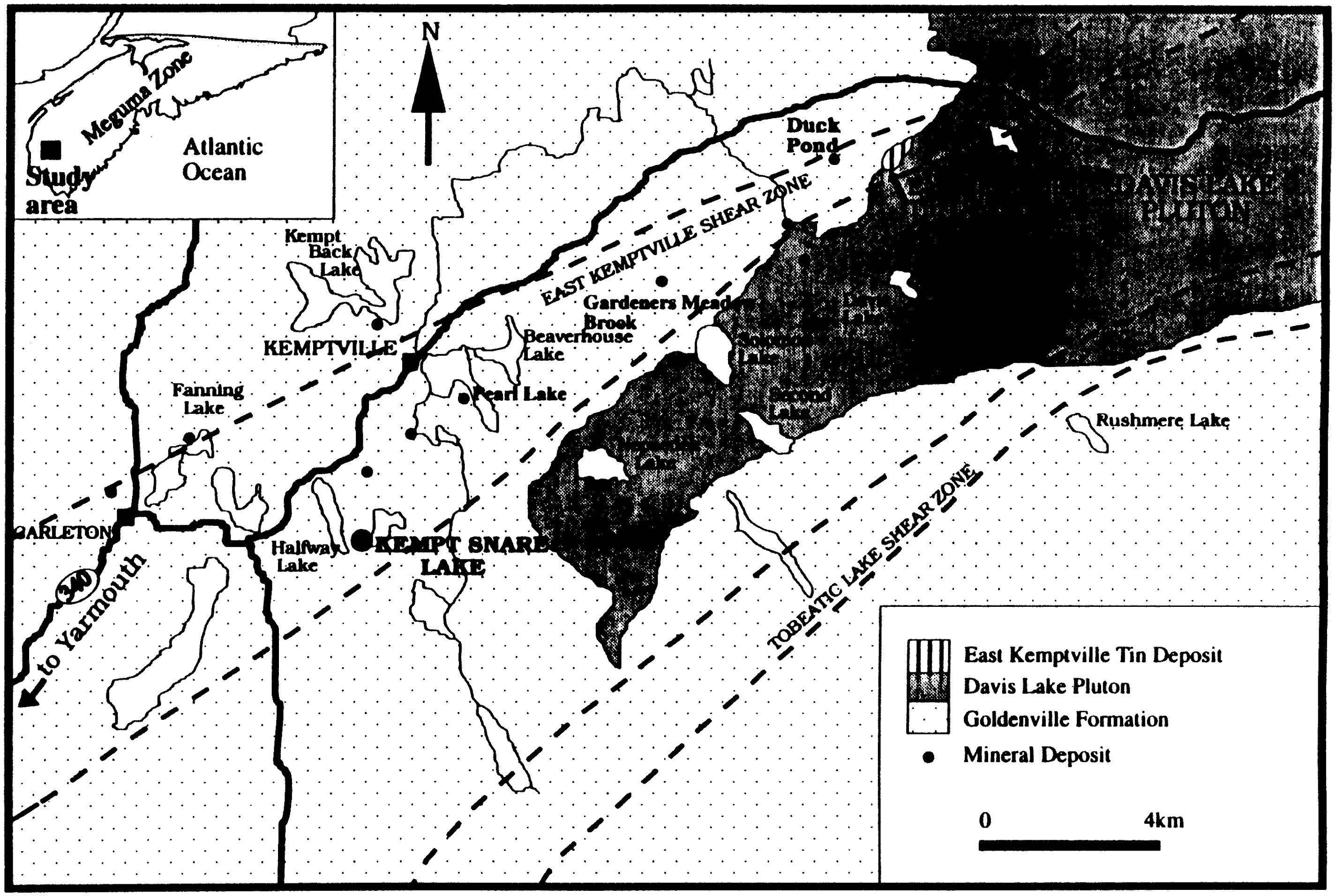


Figure 1.3 Location of Kempt Snare Lake mineral deposit and surrounding deposits, adapted from Soehl (1988).

metasedimentary rocks which host the granitoids that vary from $\delta^{18}O = 10.1$ to 12.9 ‰. Leucogranites from the eastern South Mountain Batholith vary from $\delta^{18}O = 10.2$ to 12.7 ‰ (Clarke et al. 1993b).

Available stable isotope data on mineral deposits consist of oxygen and sulphur data obtained from East Kemptville (Kontak 1988, 1990a, and 1993; Kontak et al. 1988, 1990a and b), and unpublished hydrogen isotope data also exist. Oxygen and carbon isotopic values from some Meguma Group hosted gold deposits are published (Kontak et al. 1987; Kontak and Smith 1989; Sangster 1992). These gold deposit studies have concentrated on the oxygen, carbon, and sulphur content of the vein minerals associated with the gold. Detailed studies have been carried out on gold deposits in the Eastern Meguma Terrane, for example, Beaver Dam and Miller Lake (Kontak and Smith 1989). Isotopic studies of carbonate-hosted lead-zinc deposits within Nova Scotia include Gays River (Ravenhurst et al. 1987 and 1989), Pembroke deposit (Ponsford 1983), and Smithfield deposits (Ravenhurst et al. 1989).

1.5 Previous Work in Southwestern Nova Scotia

The Kempt Snare Lake prospect lies about 40 km northeast of Yarmouth in the southwest Nova Scotia tin domain (O'Reilly and Kontak 1992). This area is host to many deposits and prospects of different sizes and origins (Figure 1.3). These deposits include Duck Pond, a Sn-Cu-Zn deposit hosted by greenschist facies argillaceous and arenaceous sediments of the Goldenville Formation (Pitre and Richardson 1989); Pearl Lake, a Sn-Cu-Zn-Fe sulphide deposit hosted by slates and quartzites of the Meguma Group; Dominique Sn-Zn-Cu deposit, located 4-5 km east of Yarmouth within Goldenville Formation calcareous wackes and black slates (O'Reilly and Kontak 1992); and East Kemptville, the largest tin deposit in Nova Scotia, and at one time North America's only producer of primary tin. Kontak (1988, 1989, and 1990a) has studied East Kemptville greisenised muscovite-topaz leucogranite host extensively using geochemistry (major and trace elements and REE's) and isotopes (O, S, H and radiogenic isotopes). This work suggests magmatic origins for the mineralising fluids, with meteoric or fluids of mixed origin playing a role in the latter stages of mineralisation (Kontak et. al 1989). Kontak's work contrasts with the work of Pitre and Richardson (1989) who classified Duck Pond according to the alteration state of the host rocks, and showed that the mineralisation is associated with the chloritic alteration assemblage. Pitre and Richardson (1989) proposed that, based on the texture of chlorites and garnets at Duck Pond, this deposit is hydrothermal in origin, with the chlorite and garnet formation accompanying the mineralisation.

1.6 Previous Work at Kempt Snare Lake

Work on the Kempt Snare Lake deposit started in 1927, with the discovery of galena- and sphalerite-bearing quartz-diorite boulders on the lake shore. In 1928, a 23 m (75 ft) shaft was sunk on a 2 m wide mineralised quartz vein. Extraction of some wall rock occurred at the 20 m (66 ft) level, but work ceased one year after the project began. Combined grades of Pb and Zn were typically 2 %, with Cu at 0.5 %, and up to 61 ppm Au and 153 ppm Ag (as reported by Jensen 1987). Various unsuccessful attempts were made to pump water out of the trenches and shafts during the 1930's to 1950's. In the 1960's, regional mapping surveys were undertaken and tailings from Kempt Snare Lake examined. Reports at this time stated that mineralisation at Kempt Snare Lake occurred in quartz veins in a diorite porphyry (cited in Soehl 1988). A re-evaluation of the Kempt Snare Lake deposit occurred with the discovery of East Kemptville in the late-1970's. Using geophysical anomalies, Falconbridge Ltd. diamond-drilled three holes to test the mineralised centre at Kempt Snare Lake, and intersected mineralisation with a top grade of 1.12 % Sn over 3m. Soehl (1988) and Soehl et al. (1989) studied these cores, along with dump samples, to provide information on the mineralogy, chemistry, and fluid inclusion composition of the mineralised granite cupola. G. O'Reilly (Nova Scotia Department of Natural Resources) undertook more detailed lithogeochemical studies (unpublished). The samples for this study come from the Falconbridge core and from dump samples collected at the site. In addition, samples from the Meguma Group host rocks were obtained from three holes Falconbridge Ltd. drilled on the north side of Kempt Snare Lake in 1990.

1.7 Objectives

The three main objectives of this study are:

1) To gain information about the relationships among the different granites and greisens, and the interrelationships within the greisens and within the granites. This part of the investigation relies on major, trace elements and REE geochemistry of the five different rock units (described in Chapter 2) present at Kempt Snare Lake.

2) To obtain C, S, O, and H isotopic signatures for the alteration and mineralisation at Kempt Snare Lake, to permit the identification of the numbers, sources, and temperatures of fluids. This research represents the first stable isotope study using four systems on a mineral deposit in the polymetallic tin domain of Nova Scotia. This study will allow assessment of the connections between the formation of this deposit and others in the region.

3) To assess the influence that the Meguma Group rocks have played in the mineralisation at Kempt Snare Lake. This assessment involves comparison of sulphur and carbon isotopic signatures from the Kempt Snare Lake deposit with surrounding Goldenville Formation rocks.

1.8 Claim

This research shows that the mineralising fluids responsible for the Kempt Snare Lake prospect are of mixed origin. The first phase of alteration was carried out by a igneous/metamorphic fluid, inheriting carbon and sulphur isotopic signature from the surrounding Meguma Group country rocks. A carbon-rich fluid (possibly a petroleum fluid) mixed with the igneous fluid and caused the precipiation of the graphite. The sulphur species dominant in this fluid was H_2S, and the fluid was also enriched in K, Na, and Fe. At some later time, a limited input of meteoric water, restricted to one location, re-equilibrated existing hydrothermally deposited siderite to values more consistent with a diagenetic source.

1.9 Organisation

Chapter 2 of this thesis contains a summary of the geology surrounding Kempt Snare Lake, and descriptions of the lithologies occurring at Kempt Snare Lake. Chapter 2 also discusses possible relationships between the host lithologies, and possible sources for the fluids and mineralisation. Chapter 3 contains the petrography and mineral chemistry of the Kempt Snare Lake lithologies, and presents an interpretation of thin section and the paragenesis of the deposit. The results of the whole-rock geochemistry from Kempt Snare Lake occur in Chapter 4, together with a discussion of the results in comparison with other deposits of the region. Chapter 5 presents the results and a brief discussion of the stable isotope work. Chapter 6 contains the discussion of the results from the entire project and relates Kempt Snare Lake to other deposits within the region. Conclusions and recommendations for future work are in Chapter 7.

CHAPTER 2 - GEOLOGY

2.1 Introduction

This chapter summarises the local geology at Kempt Snare Lake in southwestern Nova Scotia. It also outlines the lithologies comprising the Kempt Snare Lake cupola, describes the rock units in core samples, and suggests possible genetic relationships between the lithologies.

2.2 Geology at Kempt Snare Lake

Plutons of the Davis Lake Suite (Figure 2.1) represent the South Mountain Batholith in southwestern Nova Scotia. Richardson et al. (1989) used Rb-Sr isotopic data to suggest that the Davis Lake Complex is at least 35 Ma younger than the South Mountain Batholith. Richardson et al. (1989) indicated that, although whole-rock geochemical trends exist between the Davis Lake Complex and the South Mountain Batholith, detailed investigation of some elements and oxides, i.e., Ti, Zr, P_2O_5 and Fe_2O_3 suggest that the Davis Lake may not be derived from, nor be cogenetic with the South Mountain Batholith; however, Kontak and Chatterjee (1992) used to Pb isotopic data for whole-rock and mineral separates to obtain a secondary lead isochron age of 366 Ma for both unaltered leucogranite and mineralised greisen, suggesting that the leucogranite and the hydrothermal fluids had the same origin. This conclusion is supported by the oxygen isotope data obtained from the same samples which showed leucogranite with $\delta^{18}O = 8.2$ to 10.5 ‰ and greisens having similar values at $\delta^{18}O = 7.9$ to 10.9 ‰.

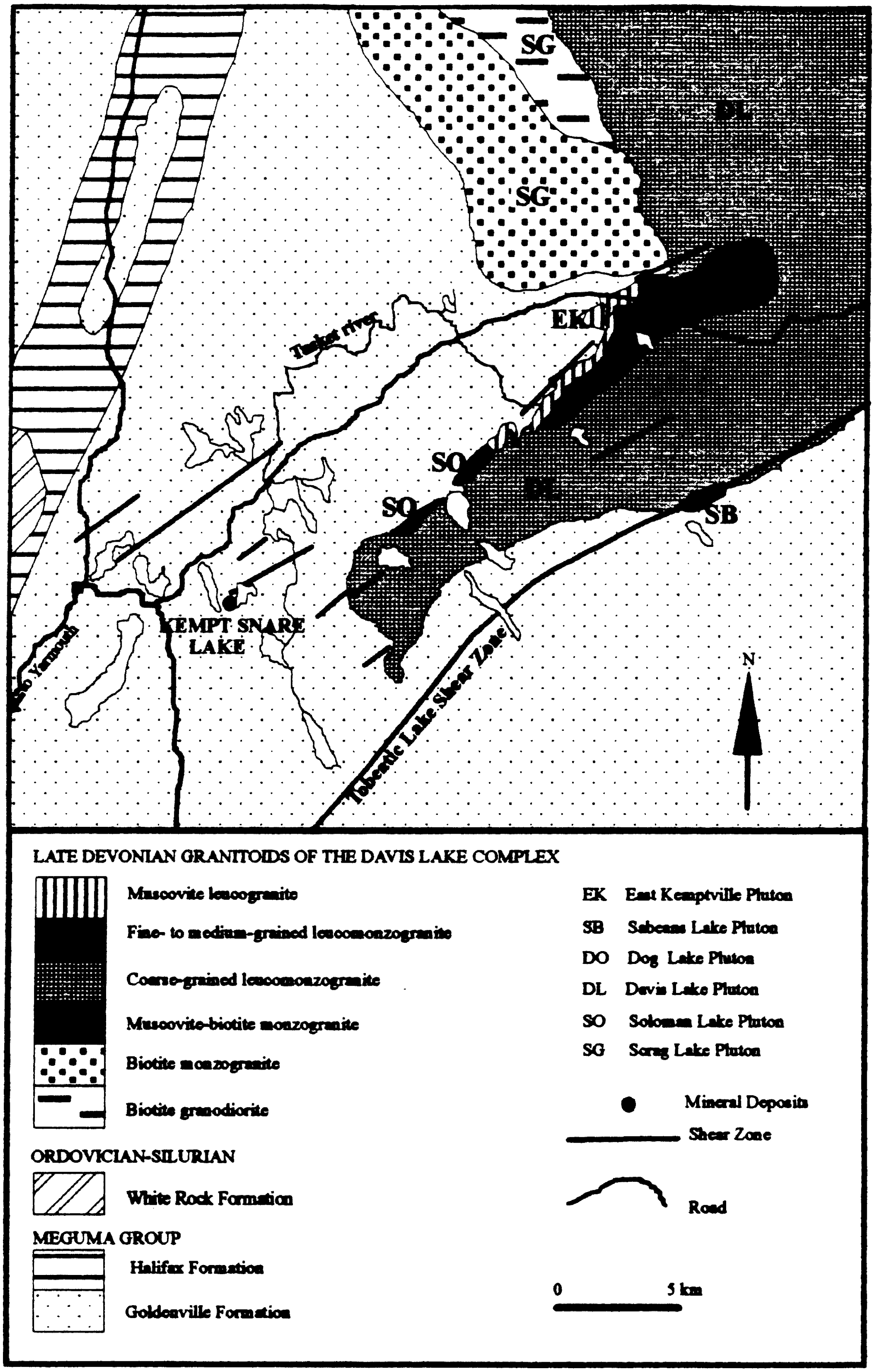


Figure 2.1. Regional geology surrounding Kempt Snare Lake. Modified from MacDonald (1994) and Ham and MacDonald (1994).

The Kempt Snare Lake W-Pb-Zn-Cu-As-Ag mineral prospect (Jensen 1987) is located on the southwestern shore of Kempt Snare Lake (Figure 1.3). At Kempt Snare Lake, a small greisenised granite cupola has intruded the metasediments of the Goldenville Formation (Kontak et al. 1990a). According to the definition of Shcherba (1970), greisen means a hydrothermally altered granitic rock, rich in quartz and muscovite, that probably formed at temperatures above 350 °C. The term greisenised granite used in this thesis refers to a lithological unit that has been through the process of greisenisation but still maintains some original igneous features. The Kempt Snare Lake rock units also contain several mineralised quartz veins (described in detail in Chapter 3). During the cooling phases of the granites of Nova Scotia, northeast sinistral shear joints and faults formed (Chatterjee and Strong 1985). In addition, C-S fabrics which are related to fault movement during time of emplacement occur along the south contact of the Davis Lake Pluton and at Rocky Shore Lake, near East Kemptville (O'Reilly 1988). Late-stage plutons, localised along the shear zones, suggest that the faults were active at the time of emplacement (Horne et al. 1990). Rocks within the shear zones vary from relatively undeformed granitoid rocks to granites containing C-S to C-C'-S structures also indicating active movement of the faults during the time of emplacement (Smith 1985). Retrograde alteration, localised shearing, and mineralisation are associated with these shear zones, leading Chatterjee and Strong (1985) to suggest the northeast trending shear zones acted as fluid pathways resulting in the present polymetallic mineral domain. East Kemptville, located approximately 12 km northeast of Kempt Snare Lake, is hosted within such a shear zone. The Kempt Snare

Lake cupola occurs near a 20 km long southwest-trending, zone of metasediment-hosted tin mineralisation (O'Reilly and Kontak 1992).

2.3 Lithologies

Samples for this study come from core drilled at Kempt Snare Lake by Falconbridge Ltd. in 1986. Falconbridge drilled three boreholes, KS-86-1, KS-86-2, and KS-86-3 producing ca. 200 meters of core from the Kempt Snare Lake prospect. Figure 2.2 shows the location of the three boreholes, and figures of the boreholes, showing the distribution of the five lithologies and samples location forms Appendix A. The lithological names for the rock units at Kempt Snare Lake are similar to those used in previous publications (Soehl 1988; Soehl et al. 1989). However, the units numbers applied to the litholgies are different. The units numbers are arranged so that Unit 1 is the least altered rock unit at Kempt Snare Lake, and Unit 5 the most altered. The core contains five lithologies, based on mineralogy, grain size, and colour, called Unit 1 to 5 as follows:

Unit 1- Coarse-grained, grey, porphyritic leucomonzogranite
Unit 2- Medium- to coarse- grained, light grey porphyritic leucogranite
Unit 3- Medium-grained, grey, porphyritic greisenised granite
Unit 4- Fine-grained, dark grey greisen
Unit 5- Medium-grained, dark grey, porphyritic greisen

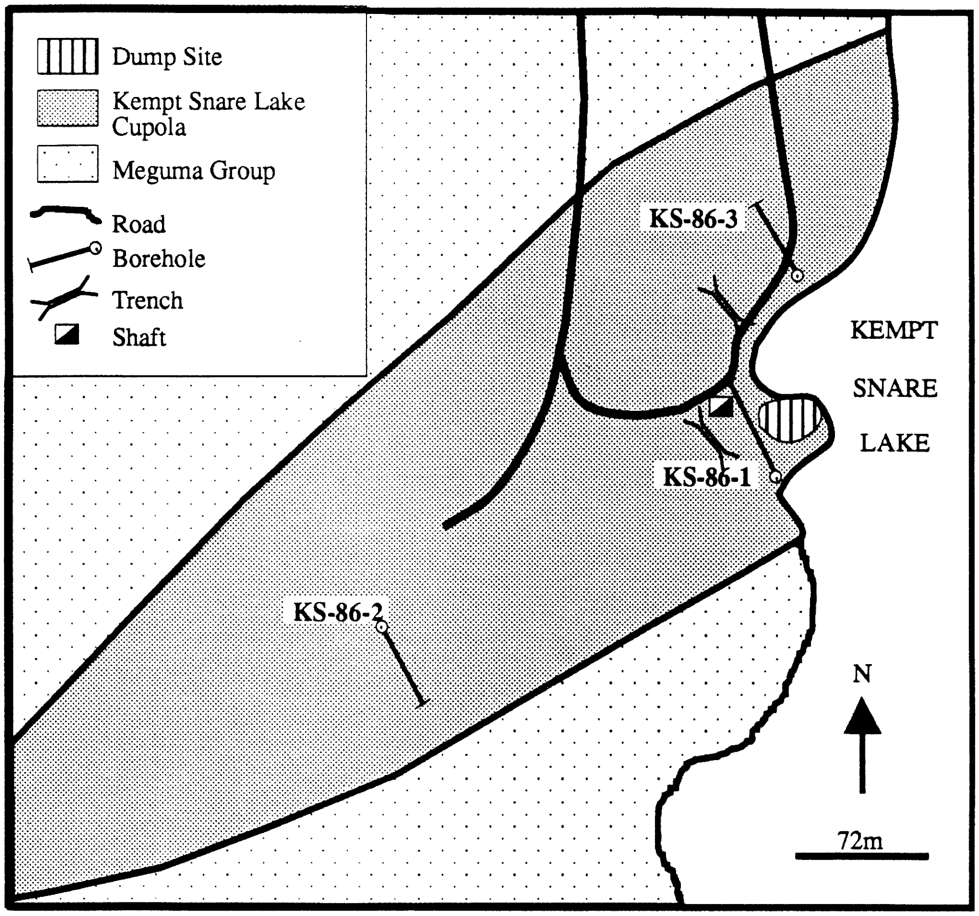


Figure 2.2 Location of boreholes at Kempt Snare Lake. Outline of KSL cupola identified by diamond drilling and chargeability anomaly (from Soehl 1988).

2.3.1 Unit 1- Coarse-Grained, Grey Porphyritic Leucomonzogranite

Unit 1 comprises ~ 16% of the total core and occurs midway through borehole KS-86-3, and at the bottom of borehole KS-86-2. This monzogranite is darker and coarser grained (~5mm) than the leucogranite (Unit 2), but is lighter in colour than any of the three greisens. Large K-feldspar phenocrysts (5 to 8mm in longest dimension), containing a small amount of graphite, are clearly visible in hand specimen. Quartz, plagioclase, muscovite, and biotite make up the remainder of the unit.

2.3.2 Unit 2- Medium-Coarse-Grained, Light Grey, Porphyritic Leucogranite

Unit 2 occurs in boreholes KS-86-1 and KS-86-3, and represents 8% of the total core recovered. This unit is light grey, with large K-feldspar phenocrysts (3-6mm in longest dimension) that are less altered than those found in the greisens. Quartz comprises ca. 40% of the unit, with muscovite and minor amounts of biotite comprising the remainder of the unit.

2.3.3 Unit 3- Medium-Grained, Grey Porphyritic Greisenised Granite

Unit 3 occurs in all three boreholes, and comprises 30% of the total core recovered. This grey unit is lighter in colour than Units 4 and 5, and has a greenish tinge attributable to several, fine chloritic veins. K-feldspar phenocrysts, 3 to 8 mm in longest dimension, comprise up to 25% of the unit and are set in a groundmass of ~1mm in size crystals. The feldspars contain less graphite than those of Units 4 and 5, resulting in a lighter overall colour to this unit. Altered biotite also occurs and chlorite occurs in small veins with arsenopyrite. Arsenopyrite occurs disseminated throughout the rock.

2.3.4 Unit 4- Fine-Grained, Dark Grey Greisen

Unit 4 occurs in boreholes KS-86-1 and KS-86-3, and comprises less than 1% of the total core recovered. Although the mineralogy of the greisen is similar to Unit 5, this greisen is easily distinguished by its finer grain size (<1mm) and much darker colour. Except for rare quartz phenocrysts (3 to 5 mm in longest dimension), which comprise ~ 10% of the rock unit, this unit is homogeneous in grain size and appearance. The feldspars contain a high percentage of fine-grained, black graphite, and disseminated arsenopyrite also occurs throughout the unit.

2.3.5 Unit 5- Medium-Grained, Grey Porphyritic Greisen

Unit 5 occurs in all three boreholes and comprises the largest single unit (39%) of the total core length recovered. Quartz represents ~ 40% of the total rock. Phenocrysts (3 - 6mm in longest dimension) of quartz and feldspar in a groundmass of ~1 mm are clearly visible in hand specimen and give the rock a "mottled" appearance. K-feldspar and plagioclase, which correspond to ~ 45% of the rock, are altered to sericite and replaced by graphite. Small (<1mm) altered biotite and muscovite are present. Disseminated arsenopyrite occurs throughout this unit.

2.4 Veining and Lithological Relationships

Total core recovery varies from ~ 80 % in borehole KS-86-3 to ~ 90 % in borehole KS-86-1. The length of core samples varies from broken fragments (2-3 cm) to lengths ~ 1 m. The contacts between the units are unclear and are mostly transitional. Slickensides and planar faults are visible in certain parts of the core, but at no location do these structures coincide with a change of lithology. The small diameter of the core, however, restricts the amount of information about the types of contacts that occur. Veins of varying mineralogy occur throughout the core, although they are more common in Units 3 to 5. The veins are dominated by quartz, with muscovite, arsenopyrite, pyrite, chalcopyrite, galena, sphalerite, siderite, and minor fluorite.

2.5 Relationship Among the Granites, Greisens and Veins

Three possible explanations for the relationships among the five lithologies at Kempt Snare Lake (Figure 2.3) are:

a) The leucogranite and leucomonzogranite are related to each other through a differentiation process, and the mineralising fluids, represented by the veins, caused the progressive alteration of the granitic rocks to the greisens.

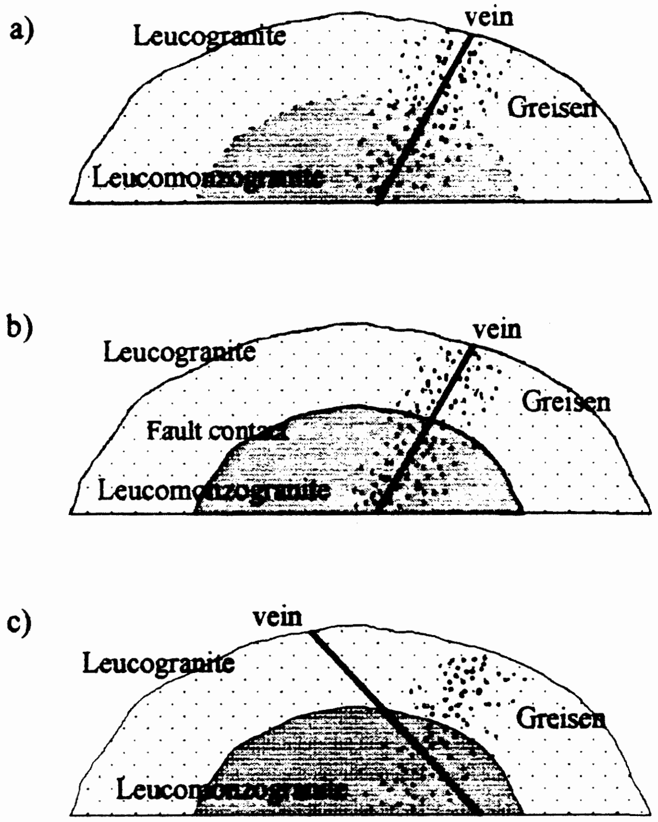


Figure 2.3. Possible relationships between the granites, greisens and veins.
a) The granites and greisens are related by differentiation, and the veins now present formed from the greisenising fluids. b) The leucogranite and leucomonzogranite are not related to the vein formed from the mineralising fluids. c) The granites are not related to each other and the veins are not related to the greisenising fluids.

b) The leucogranite and leucomonzogranite are unrelated and were altered by the passage of the mineralising fluids to form the greisens. The mineralising fluids are again represented by the mineralised veins.

c) The leucogranite, leucomonzogranite, and the greisens are completely unrelated.

Chapters 3 and 4 use, respectively, petrography and major, trace, and REE geochemistry to examine the relationships among the five rock units and the veins more closely.

2.6 Possible Sources for the Mineralising Fluids

Several possible sources exist for the mineralising fluids and metals at Kempt Snare Lake. These sources are the Kempt Snare Lake cupola, the Meguma Group country rocks, overlying or underlying metasediments, Avalon Group, the South Mountain Batholith granites or a mixture of these sources. Possible mechanisms of the involvement of these fluid sources are:

1) The fluids and metals are solely derived from within the Kempt Snare Lake cupola. In this explanation, the mineralisation results from the partitioning of metals into the late-stage fluids of a differentiating granite. The mineralisation occurs with a change in the P-T-X conditions within the Kempt Snare Lake cupola. Other possible igneous sources for the fluids and metals are the South Mountain Batholith or the Davis Lake Pluton. The

South Mountain Batholith and the Davis Lake are much greater volumes of magma, and would produce a much higher volume of water that may have "flooded" the Kempt Snare Lake site.

2) The fluid and metals are solely derived from the Meguma Group country rocks, or from lithologies lying above or below the Meguma Group. In this explanation, the heat from the intrusion drives convective circulation that results in waters and metals being brought into the Kempt Snare Lake cupola, eventually resulting in the mineralisation. The source for the fluids and the metals may be any one of the sedimentary units or a mixture.

3) The fluids and metals have mixture of sources, inheriting components from the meta-sedimentary units, the surrounding granites, and the Kempt Snare Lake cupola itself.

Chapter 5 presents the results of stable isotope work, and provides more detailed information about the mineralising fluid sources.

2.7 Summary

This chapter has reviewed the local geology for the Kempt Snare Lake mineral prospect. The region surrounding Kempt Snare Lake is host to several granitoid bodies, which were emplaced over a short period of time, when shearing and tectonic movement was occurring throughout southwestern Nova Scotia. Many of the mineral prospects in this region contain structures suggesting that they formed during this period of shear zone formation. Five granitoid and greisen lithologies with transitional contacts between them occur at Kempt Snare Lake. Although tectonism has affected the rock units, resulting in the faults occurring in the Kempt Snare Lake core, the lithologies have transitional contacts suggesting that they are related through magmatic and hydrothermal alteration. Possible explanations for the origin of the Kempt Snare Lake lithologies and the mineralising fluids responsible for the formation of this deposit are the subjects of the following chapters.

CHAPTER 3 - PETROGRAPHY AND MINERAL CHEMISTRY

3.1 Introduction

This chapter presents generalised results from petrographic inspection and microprobe analysis on samples from the Kempt Snare Lake site. Detailed descriptions of each lithology form Appendix A. Appendix B contains the microprobe operating conditions and the method of establishing modal percentages.

3.2 Mineralogy of Units 1 to 5

As discussed in Chapter 2, five lithologies at Kempt Snare Lake can be distinguised in hand specimen. Although the granites and greisens have similar mineral assemblages, they differ in their mineral proportions (Table 3.1). The greisens (Units 3 to 5) are characterised by high modal proportions of muscovite, up to 18 %, <1 to 4 % biotite and ~ 40 % quartz. K-feldspar (~ 30 %), is the dominant feldspar, and plagioclase (~ 12 %) is a minor component. This composition varies from the leucogranites (Unit 2), where the muscovite and biotite content are lower at only 3 % each (Figure 3.1). Similar amounts of quartz and K-feldspar, 40 % and 35 % respectively, occur within the leucogranites, however, the plagioclase content is greater at 18 %. The leucomonzogranite (Unit 1) differs from the leucogranite in that it has higher muscovite and biotite contents, each 7 %, a smaller proportion of K-feldspar, 24 %, and a plagioclase content of 11 %. The muscovite content of the leucomonzogranite, although higher than the leucogranite, is still less than any of the greisens. Petrography shows that similar textures and minerals occur

		Modal%				
Lithology	Unit	Quartz	K-feldspar	Plagioclase	Muscovite	Biotite
Leucomonzogranite	Unit 1	45-51	20-26	9–16	6-7	7-8
Leucogranite	Unit 2	36-43	32-40	17-18	2-3	2-4
Greisenised granite	Unit 3	37-44	26-40	11–14	5-12	5-6
Fine-grained greisen	Unit 4	41-42	26-35	10-20	6-16	2-4
Porphyritic greisen	Unit 5	31-47	22-39	9-20	10-20	<1

Table 3.1. Modal % of Kempt Snare Lake rock units.

in each of the five lithologies and microprobe analyses carried out on polished thin sections showed that all the rock units have similar mineral compositions. Therefore, a summary of the petrography and mineral compositions is shown here.

Quartz Quartz, the major constituent in all five units, comprises 31-51 % of the rocks. The quartz grains are commonly subhedral in shape, with phenocrysts 3-6 mm in longest dimension. Quartz grains are also a major constituent in the groundmass of all five units. Undulose extinction (Figure 3.2) is common in the quartz of all units, suggesting they have undergone tectonic strain and deformation. Recrystallised quartz (Figure 3.3), and highly fractured quartz grains (Figure 3.2), are also present in Unit 3, again suggesting deformation.

Alkali Feldspar Alkali feldspar grains are euhedral, 2 - 7mm in longest dimension and comprise ~30 % of the rocks. The K-feldspar, with a composition of Or_{94-100} (Table 3.2A), commonly has exsolution lamellae (Figure 3.2). Inclusions of plagioclase and patchy alteration to albite is common, as is a patchy alteration to sericite (Figure 3.5). Graphite is present along the cleavage planes and disseminated within alkali feldspar grains in Units 3 to 5.

Table 3.2A K-feldspar compositions from Kempt Snare Lake.

Sample	LD-7/3	LD-44/1	LD-42/1	LD-21/1	LD-25/6
Unit	1	2	3	4	5
SiO2	66.22	64.89	65.37	65.37	64.19
TiO2	0.02	0.06	0.05	0.05	0
Al2O3	18.82	18.64	18.56	18.56	18.6
FeO	0.08	0	0.09	0.09	0.09
MnO	0.04	0.03	0	0	0
MgO	0	0	0	0	0.07
CaO	0.03	0	0.03	0.03	0.04
Na2O	0.8	0.31	0.23	0.23	0.31
K2O	15.78	16.64	16.62	16.62	16.37
BaO	0.07	0	0.2	0.2	0.24
Total	102.42	100.47	101.08	101.08	99.78

Table 3.2B Plagioclase compositions from Kempt Snare Lake.

Sample	LD-7/3	LD-34/5	LD-42/3	LD-23/4	LD-25/7
Unit	1	2	3	4	5
SiO2	69.5	68.34	69.56	68.24	68.15
TiO2	0.09	0.04	0	0.09	0
Al2O3	19.72	19.87	19.77	19.98	20.65
FeO	0.1	0	0.05	0.12	0
MnO	0.06	0.04	0.03	0	0
MgO	0	0.03	0.02	0.04	0.13
CaO	0.08	0.13	0	0.17	0.91
Na2O	11.83	11.27	10.86	10.57	10.57
K2O	0.05	0.03	0.01	0.2	0.08
Cr2O3	0	0	0.11	0	0.26
Total	101.05	99.61	100.31	99.42	100.66

Figure 3.1. Medium- to coarse-grained, light grey, porphyritic leucogranite, Unit 2, KS-86-1. Typical igneous texture of the granites at Kempt Snare Lake, with intergrowing feldspar crystals present, all of which have undergone some alteration. Scale = 1 mm.

Figure 3.2. Coarse-grained leucomonzogranite, Unit 1, Hole KS-86-2. A large undulose quartz grain (Q) is visible in the lower left corner. Running across the quartz are fractures which post date the formation of the undulose extinction. A highly altered biotite grain (Bt) occurs in the middle. The biotite is altering to form muscovite, chlorite and Fe-Ti oxides. Scale = 1 mm

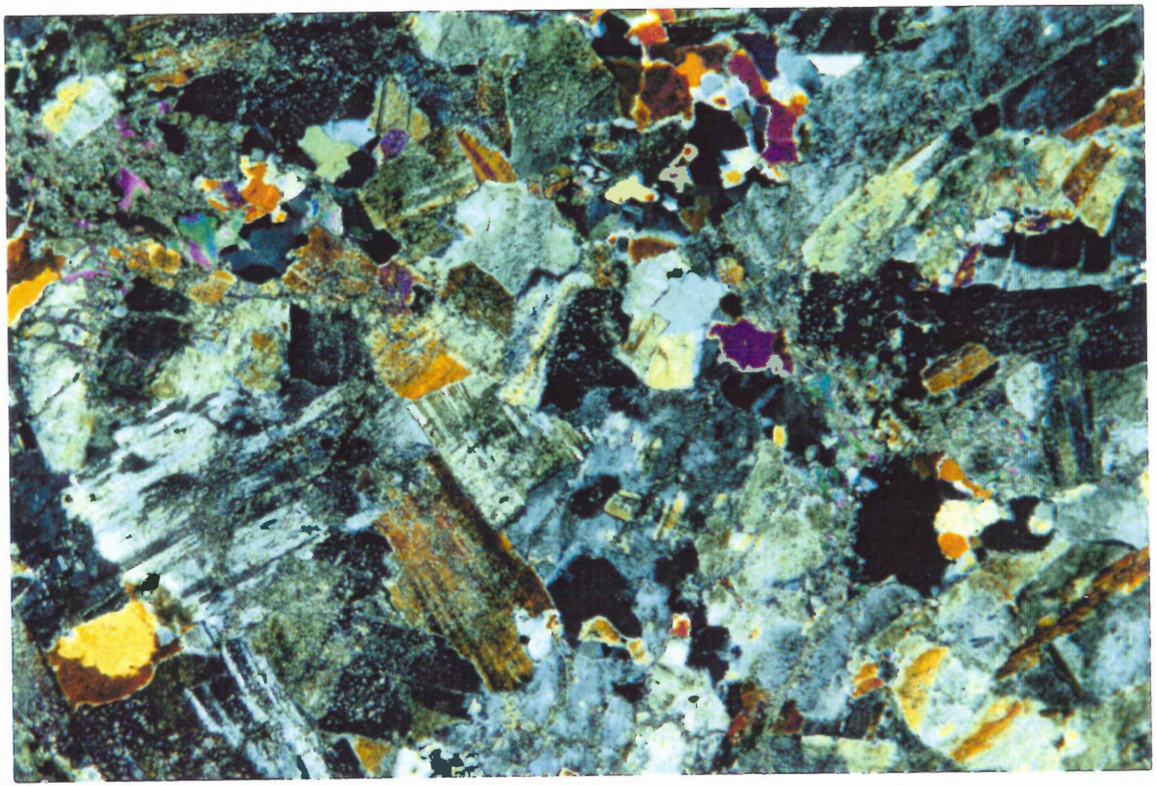


Figure 3.1

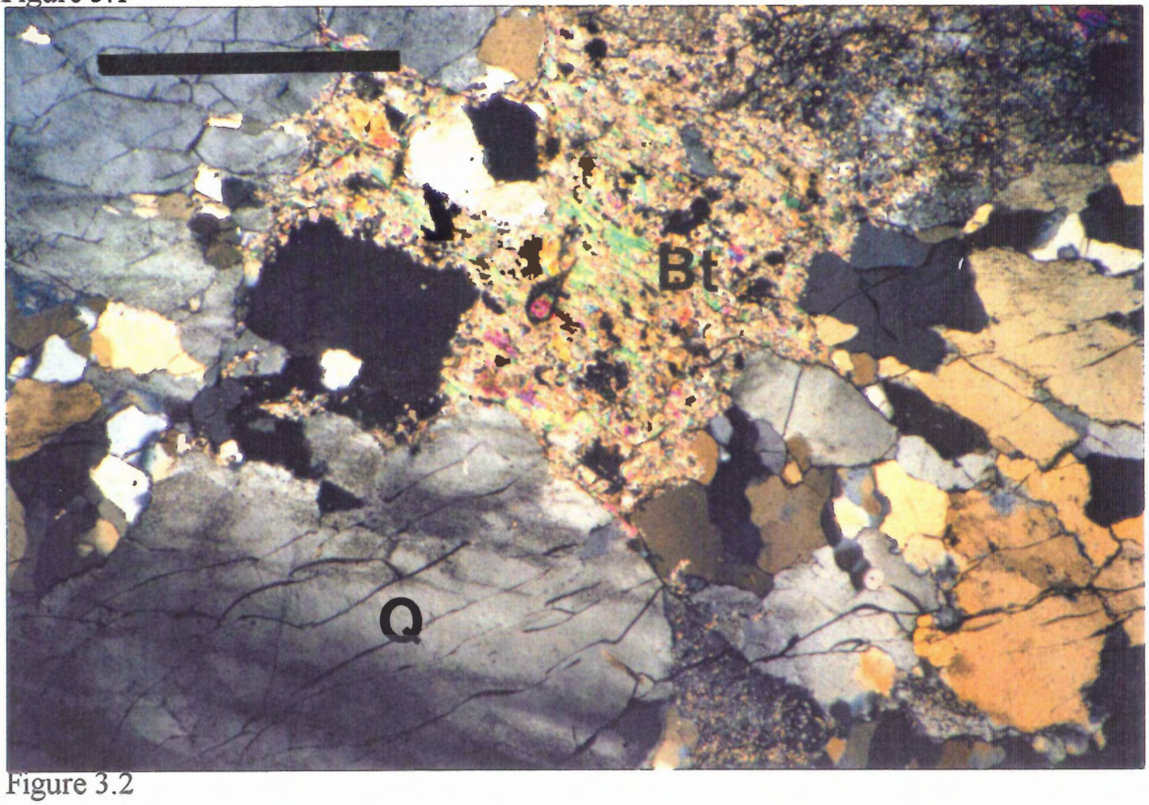


Figure 3.2

Plagioclase Plagioclase makes up a smaller proportion of the units, varying between 12 and 20 % of the units. Phenocrysts are typically unzoned, subhedral, and 1-4mm in longest dimension, with an albite composition (Ab_{92-100}) (Table 3.2B). Most of the plagioclase in the five units is highly altered to sericite, and some grains have K-feldspar inclusions. Commonly the plagioclase grains show kinked and bent twinning patterns, suggesting deformation (Figure 3.3).

Muscovite The muscovite content of the units varies greatly from 18 % in the highly altered greisens (Unit 5) to only 3 % in the leucogranite (Unit 2). Muscovite is anhedral to subhedral in shape, and may be both primary (magmatic), large, clear crystals, and secondary (hydrothermal), small and cloudy crystals. Some secondary muscovites have formed through the alteration of biotite, and in these cases relict halo spots, zircon, and Fe-Ti oxides are common (Figure 3.2). The muscovite has phengite composition with a Fe_2O_3 (T) content of 4-8 wt% (Table 3.3). Deformation textures (kinked cleavage planes) occur in some muscovite grains (Figure 3.6).

Biotite Biotite is a minor constituent of all five units, varying from <1 to 7 %, and is most common in Unit 4, the leucogranite. In the greisens, the biotite crystals are completely altered to muscovite and chlorite. In the granites the alteration of biotite to chlorite varies from 60 - 80 %, although relict halo spots, zircon, and Fe-Ti oxides are common (Figure 3.2).

Table 3.3 Muscovite compositions from Kempt Snare Lake.

Sample	LD-7/4	LD-34/1	LD-36/3	LD-23/3	LD-24/3	LD-60/2
Unit	1	2	3	4	4	Vein
SiO2	48.44	46.84	47.08	47.18	47.87	45.3
TiO2	0.13	0.22	0.74	0.16	0.19	0.22
Al2O3	27.55	31.85	27.41	30.6	30.41	31.33
FeO	5.66	4.23	7.78	4.88	4.18	5.57
MnO	0.06	0.02	0.15	0	0.1	0.08
MgO	0.87	0.4	0.7	0.64	0.45	0.33
CaO	0.17	0.03	0	0	0.03	0
Na2O	0.42	0.32	0.16	0.08	0.11	0.28
K2O	9.87	8.75	10.02	9.42	9.49	9.55
Cr2O3	0.01	0.06	0	0	0.07	0
Total	92.98	92.57	93.54	93.96	92.95	92.6

Figure 3.3. Coarse-grained leucomonzogranite, Unit 1, Hole KS-86-2. A kinked and bent plagioclase feldspar (Pl), with an irregular, corroded, margin. This feldspar shows some evidence of alteration to sericite. An area of recrystallised quartz (RQ) is present at the top right of the photograph. Scale = 1 mm.

Figure 3.4. Coarse-grained leucomonzogranite, Unit 1, Hole KS-86-2. A large alkali feldspar (Kf), with exsolution lamellae. Scale = 1 mm.

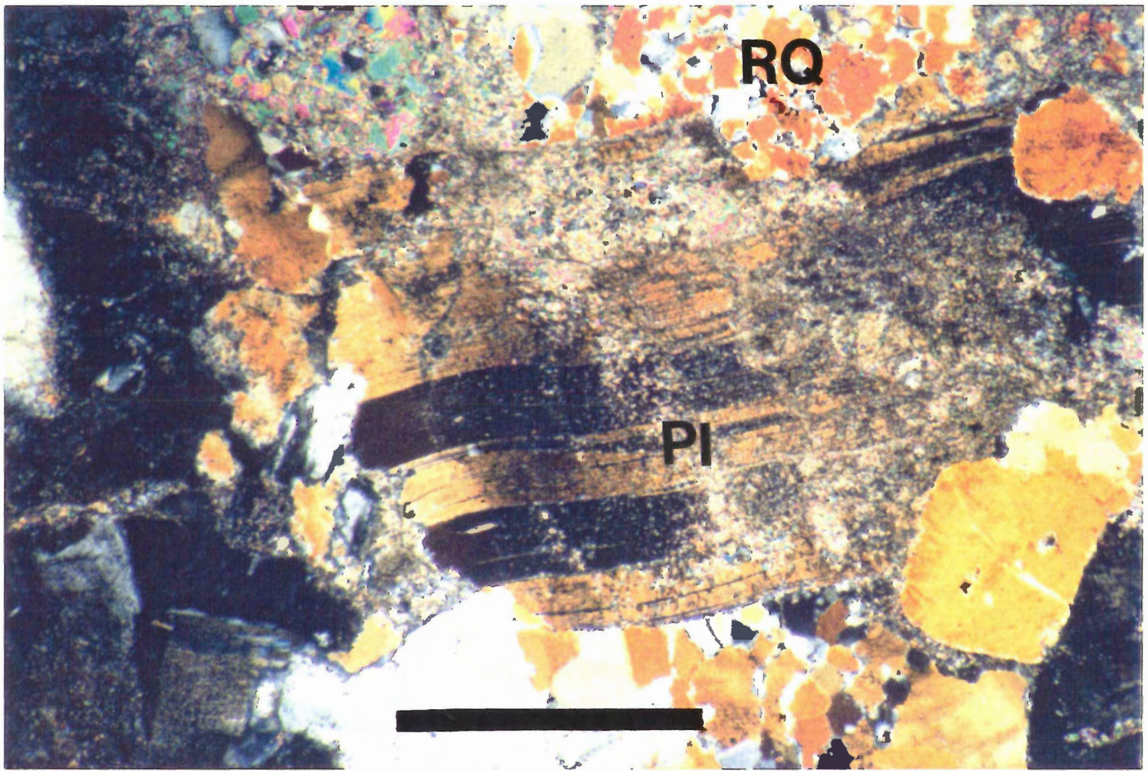


Figure 3.3

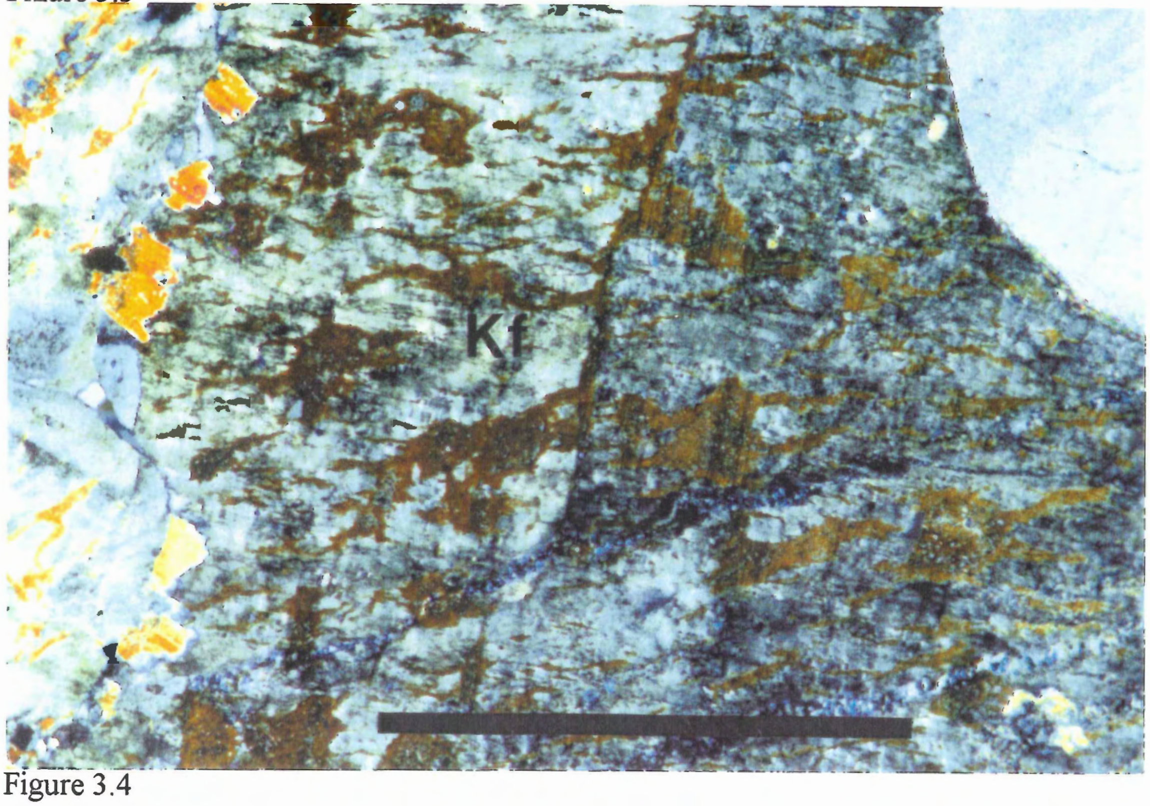


Figure 3.4

Graphite Graphite occurs in all units, but is most common in Units 3 to 5. Graphite is precipitated within K-feldspar, plagioclase, and muscovite, where it occurs disseminated within them and along the cleavage planes (Figure 3.7). Textures similar to a carbon-rich (petroleum ?) fluid having permeated the rock, along grain boundaries are common (Figure 3.7). X-ray diffraction on carbon separates completed by G. O'Reilly (NSDNR) showed poor mineral profiles, suggesting this mineral was non-crystalline and and for the purposes of this thesis the amorphous carbon is referred to as graphite.

3.3 Interpretation of Mineralogy

The mineralogy of the Kempt Snare Lake rocks (high muscovite content, albitic plagioclase) suggests that they have undergone extensive interaction with fluids. Table 3.4 shows the mineralogical reactions occurring at Kempt Snare Lake. All five units show perthitic alteration of K-feldspar, and have high albite contents in plagioclase. These features suggests that all units have undergone processes such as K-feldspathisation and albitisation. The high degree of alteration of the biotite to chlorite and muscovite is also consistent with hydrothermal alteration. All units show some evidence of graphite precipitation, however, the greisenised units have been affected more.

The amount of alteration is greater in the greisens than in the granites and increases from Unit 3 to Unit 5. The greisenised lithologies have greater proportions of muscovite and

Figure 3.5. Unit 3, greisenised granite, Hole KS-86-2. A K-feldspar with sericite stringers and veinlets (Se). A small inclusion of plagioclase (Pl) occurs at the middle right of the photograph. Scale = 1mm.

Figure 3.6. Medium-grained, grey, porphyritic greisen, Unit 5, Hole KS-86-1 Large primary (?) muscovite (M) grain with bent cleavage planes. Scale = 0.5 mm.

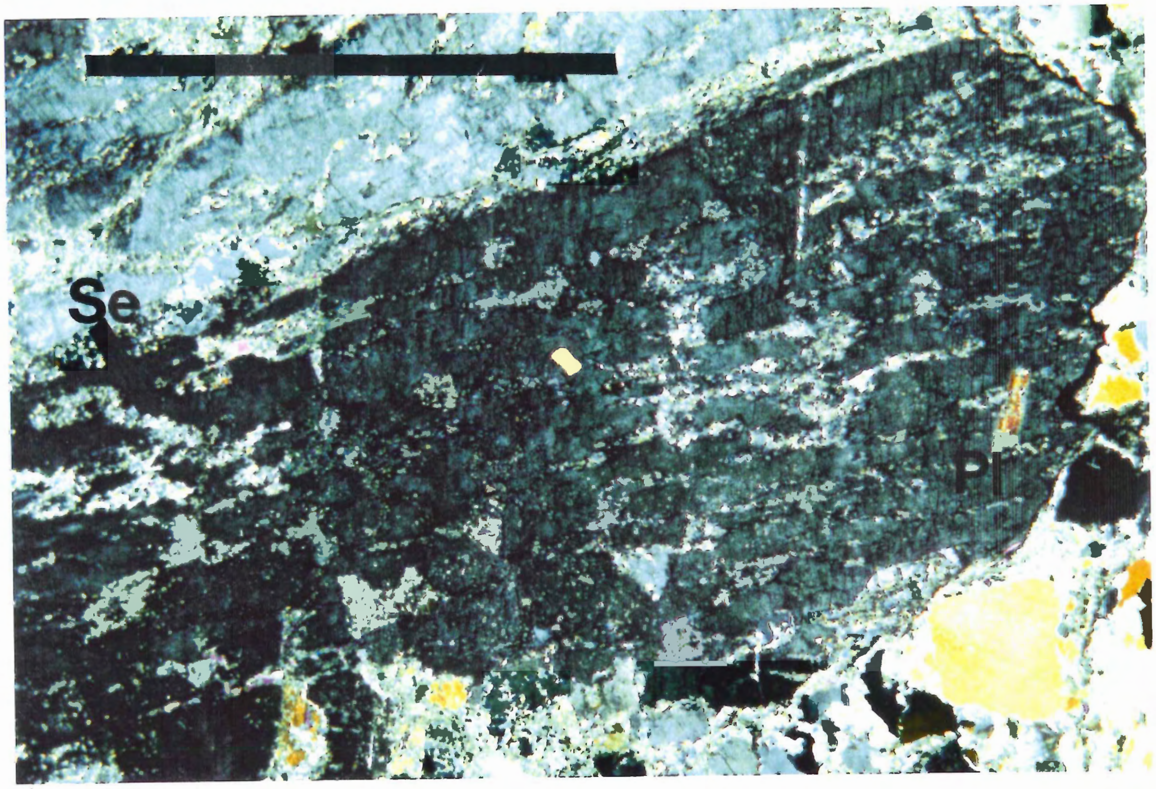


Figure 3.5

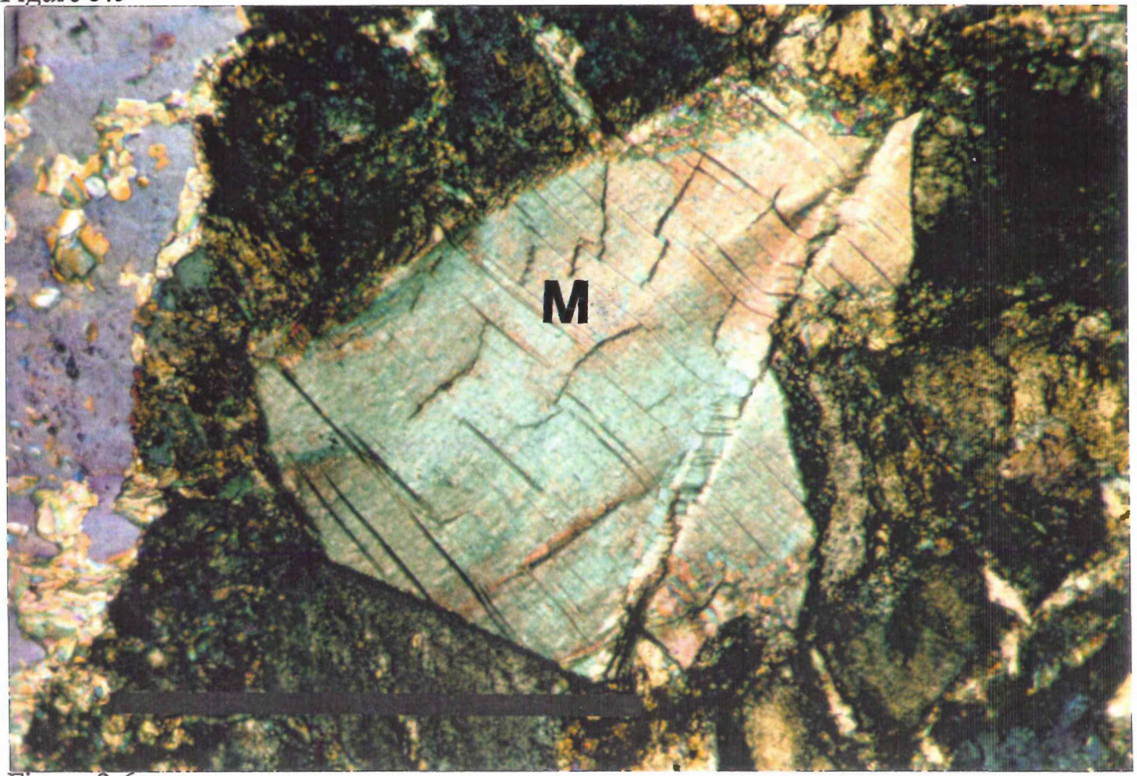


Figure 3.6

Figure 3.7. Medium-grained, grey, porphyritic greisen, Unit 5, Hole KS-86-1. The dark colour of the greisens is caused by the amount of graphite present. In the top centre of this photograph are clear quartz grains which have no trace of graphite. The feldspars, however, are black, with graphite (g) precipitated along grain boundaries and within cleavage planes. The blackend grain boundaries suggest a carbon-rich fluid flowed along these boundaries. Scale = 1mm.

Figure 3.8. Vein within Unit 5, sample KS-86-DP-1. Galena (G) rims a euhedral arsenopyrite (As) grain. Scale = 0.25 mm

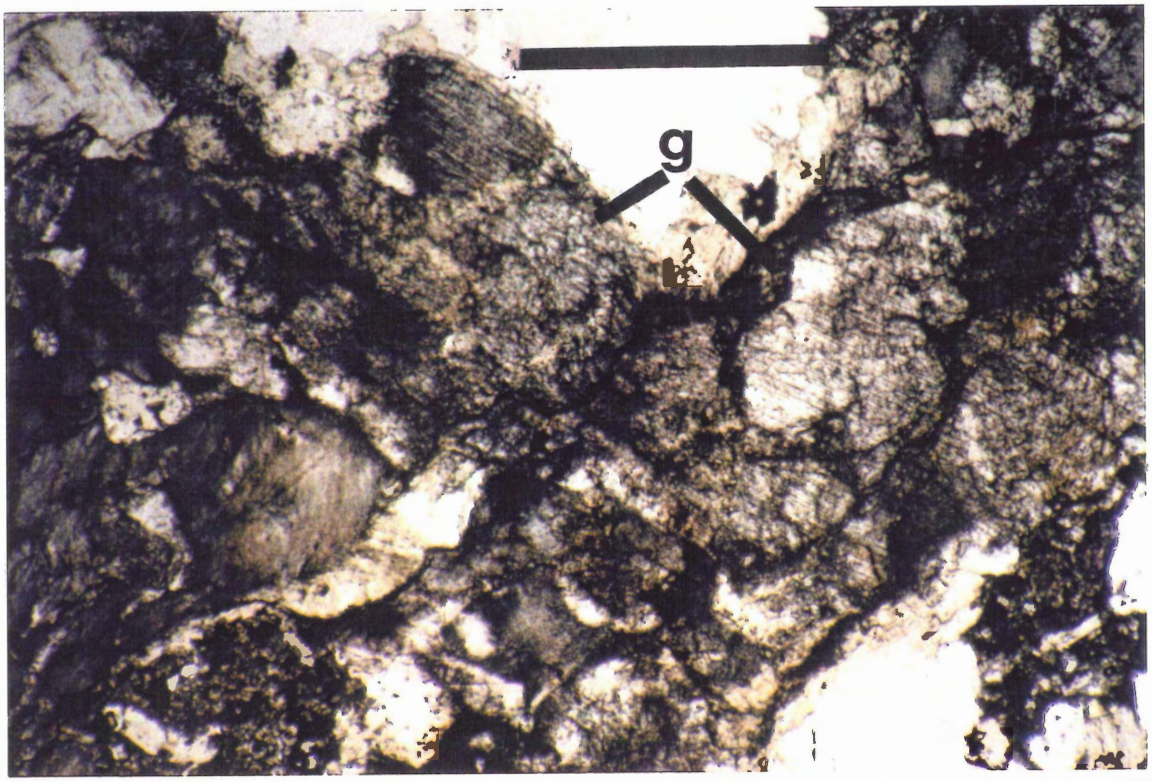


Figure 3.7

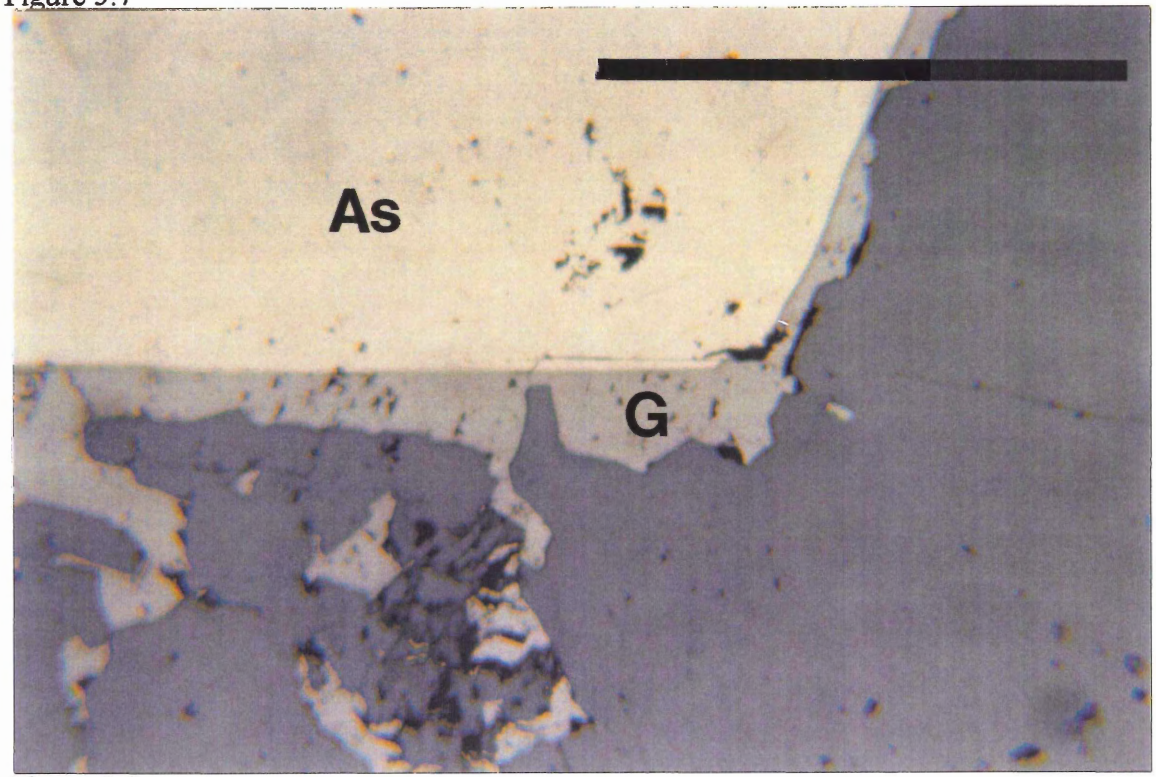


Figure 3.8

Process	Occurrence	Reaction	Textures and evidence
K-feldspathisation	Units 1-5	Plag. → K-feldspar (perthite)	Patchy alteration of plagioclase by K-feldspar.
Albitisation	Units 1-5	K-feldspar → Albite	Albitic patches and veins in K-feldspar.
		Ca-Plag → Na-Albite	Chemicaly altered Na-rich plag after Ca-rich magmatic plag.
		Biotite → Muscovite	Biotite breaking down to form muscovite and chlorite.
Graphite Precipitation	Units 3-5, and present in Units 1 & 2, but to a lesser extent.		Graphite precipitated along cleavage planes of feldspars and muscovite, and along grain boundaries.
Greisenisation	Units 3-5	Feldspars → Muscovite and Quartz	Muscovite patches and veinlets within feldspars.

Table 3.4. Mineral reactions occurring in Kempt Snare Lake lithologies.

graphite, possibly because of the greisenisation process. The presence of graphite within the cleavage planes of some muscovite grains, and the absence of graphite within other muscovites, may suggest at least two fluids are responsible for the mineralisation at Kempt Snare Lake. Graphite does not occur within veins and this absence may suggest that graphite precipitation preceded the main veining event, and occurred during a pervasive stage of alteration.

All Kempt Snare Lake lithologies show extensive evidence of ductile deformation with bent cleavage planes in muscovite grains and kinked twinning patterns within plagioclase crystals in both greisens and granite lithologies. Undulose extinction within quartz grains is also common within all the lithologies, again suggesting that all the Kempt Snare Lake rocks underwent strain. Soehl (1988) reported boudinage textures within the Kempt Snare Lake rocks and suggested that they represent ductile deformation; however, the boudinage features are also highly fractured, indicating that the lithologies experienced brittle deformation subsequent to the ductile period. Planar faults, crosscutting the lithologies and veins, suggest a second, later, period of brittle deformation affected the cupola. The highly fractured quartz grains that have an undulose extinction (Figure 3.2) may also suggest that the rock units experienced both dutile and brittle periods of deformation.

The alteration stages can be linked to different types of deformation. K-feldspathisation and albitisation occur in all five units and are not restricted to sections of the core that are highly veined. This pattern of alteration suggests that the rocks were pervasively altered by the passage of fluids though the entire rock mass. The most graphite-rich units (Units 3 to 5) are more closely associated with the greisens, and the greisens are, in turn, more closely associated with areas of the core that are highly fractured and veined. The location of the greisenised units would, therefore, suggest that during greisenisation the deformation pattern changed from a ductile to a brittle phase, resulting in fractures, which caused the fluids to be focused along certain fluid pathways that are now represented by the veins. The fluids flowing along these pathways may have caused the alteration of the wall rock to form the greisens.

3.4 Mineralogy of Veins

The core from Kempt Snare Lake consists of five lithologies, crosscut by many veins. The veins vary from <1 mm to 20-25 cm in width. Although present throughout the core, veins are more common in the greisenised sections of the core as shown in the borehole sections of Appendix A. The veins contain a number of different minerals, but are dominated by quartz. Other common minerals are sulphides (arsenopyrite, pyrite, chalcopyrite, galena, and sphalerite), carbonate (siderite), muscovite, and fluorite. Petrographic and microprobe investigations of the vein samples are as follows:

Arsenopyrite Euhedral arsenopyrite commonly occurs disseminated within the greisens and is the only sulphide occuring within the granitoids. Arsenopyrite also commonly occurs within veins, often at the boundary between the vein and the wallrock (Figure 3.8). Rare inclusions of pyrite and chalcopyrite occur. The arsenic content varies from 31.2 to 33.9 As atomic %.

Pyrite Pyrite occurs as small euhedral grains, but also forms rims around sphalerite (Figure 3.9). Pyrite is also commonly present in association with chalcopyrite (Figure 3.10) and occurs as inclusions in arsenopyrite and sphalerite.

Chalcopyrite Chalcopyrite is yellowish brown in reflected light and is present as subhedral grains, also rimming pyrite, arsenopyrite and sphalerite (Figures 3.10 and 3.11). Chalcopyrite commonly occurs as inclusions in sphalerite.

Galena Galena, present as massive grains with poor crystal habit, also occurs as rims on vein arsenopyrite (Figure 3.8). Galena occurs in close association with sphalerite (Figure 3.12) where the sphalerite rims the galena.

Sphalerite Sphalerite varies from dark brown to light reddish brown, with poor crystal shape. Inclusions of chalcopyrite, pyrite, and less commonly pyrrhotite, occur in some larger sphalerite grains. Sphalerite also rims galena and pyrite in some veins (Figure 3.12) and in close association with chalcopyrite, where sphalerite rims chalcopyrite (Figure

Figure 3.9. Vein within Unit 3, sample KS-86-DP-2 In the centre of the photograph pyrite (Py) rims a section of a large sphalerite (Sp) grain. Scale = 0.25 mm.

Figure 3.10. Vein within Unit 5, sample KS-86-DP-1. Pyrite (Py) in contact with subhedral chalcopyrite (Ch) grains sitting in quartz (Q) vein. Fractures cut across the sulphides giving evidence for a later brittle deformation period. Scale = 0.5 mm.

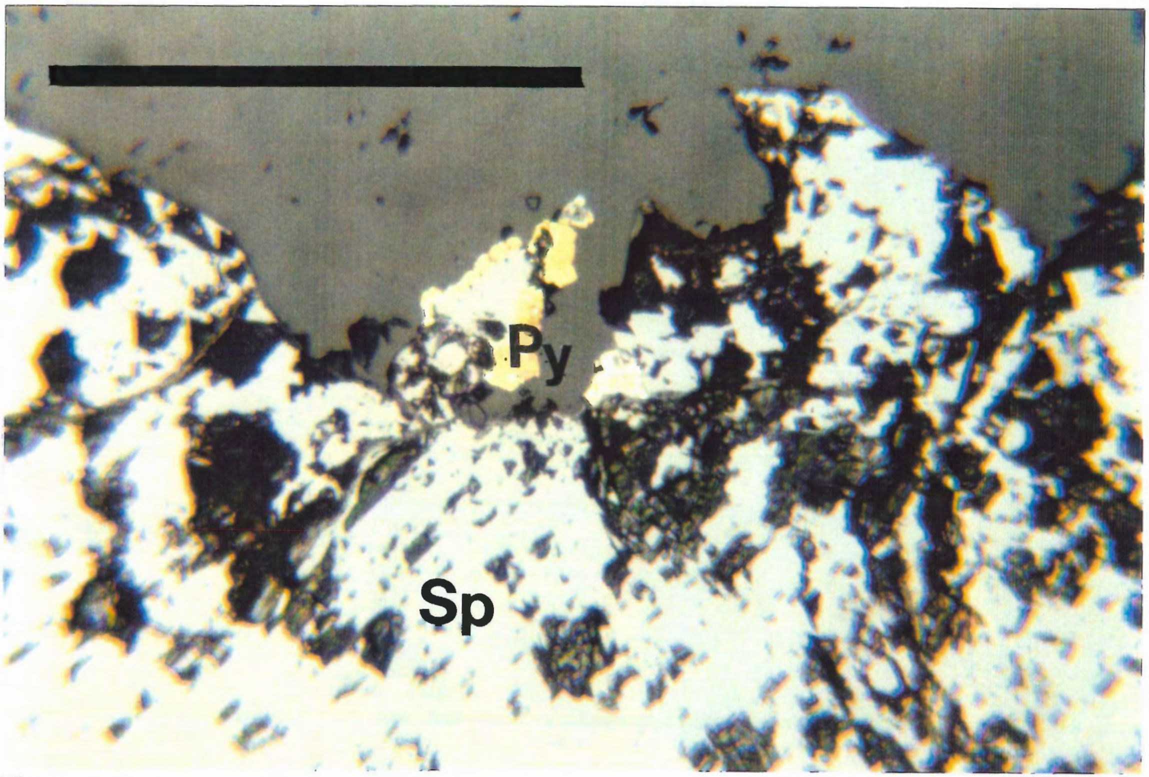


Figure 3.9

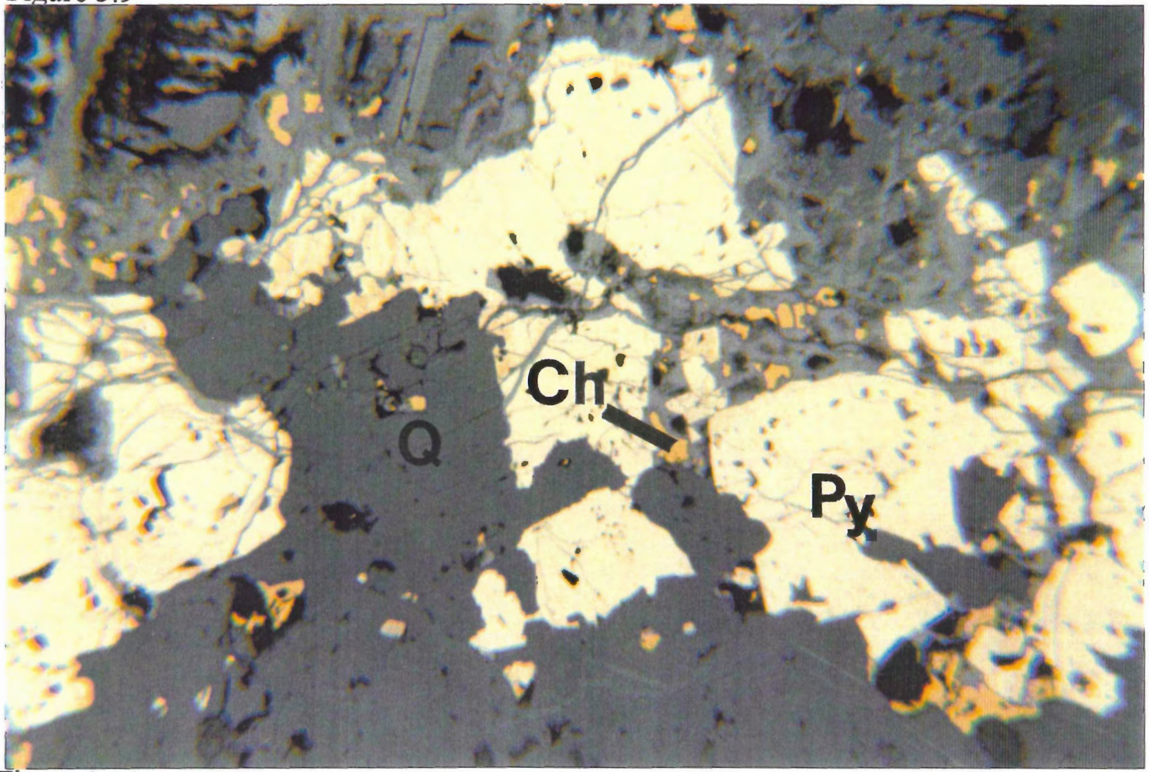


Figure 3.10

Figure 3.11. Vein within Unit 5, sample KS-86-DP-3. Large chalcopyrite (Ch) grain with lighter coloured pyrite (Py) crystals surrounding it. An arsenopyrite (As) crystal occurs in the centre of the photograph. Scale = 0.5 mm.

Figure 3.12. Vein within Unit 5, sample KS-86-DP-4. Galena (G) in the bottom left corner of the photograph occurs in contact with pyrite (Py) in the centre and has a rim of sphalerite (Sp). A sphalerite grain is also present in the bottom right. Quartz (Q) surrounds the sulphides. Scale = 0.5 mm.

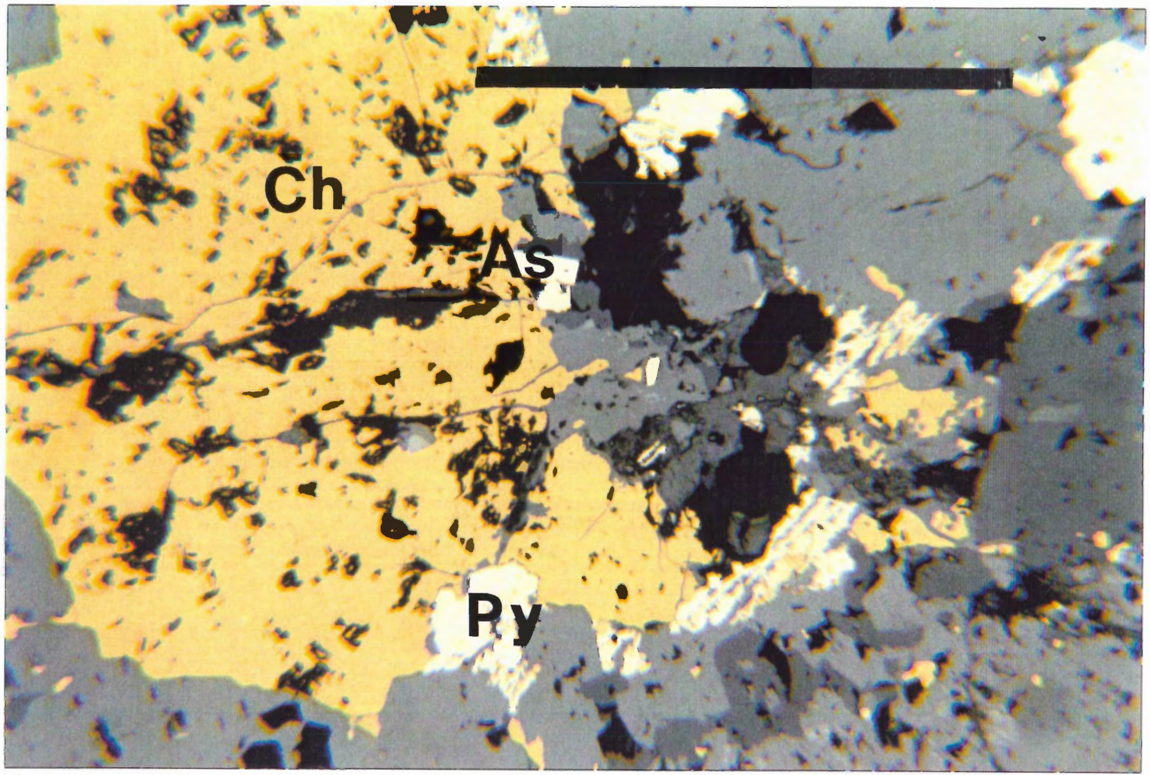


Figure 3.11

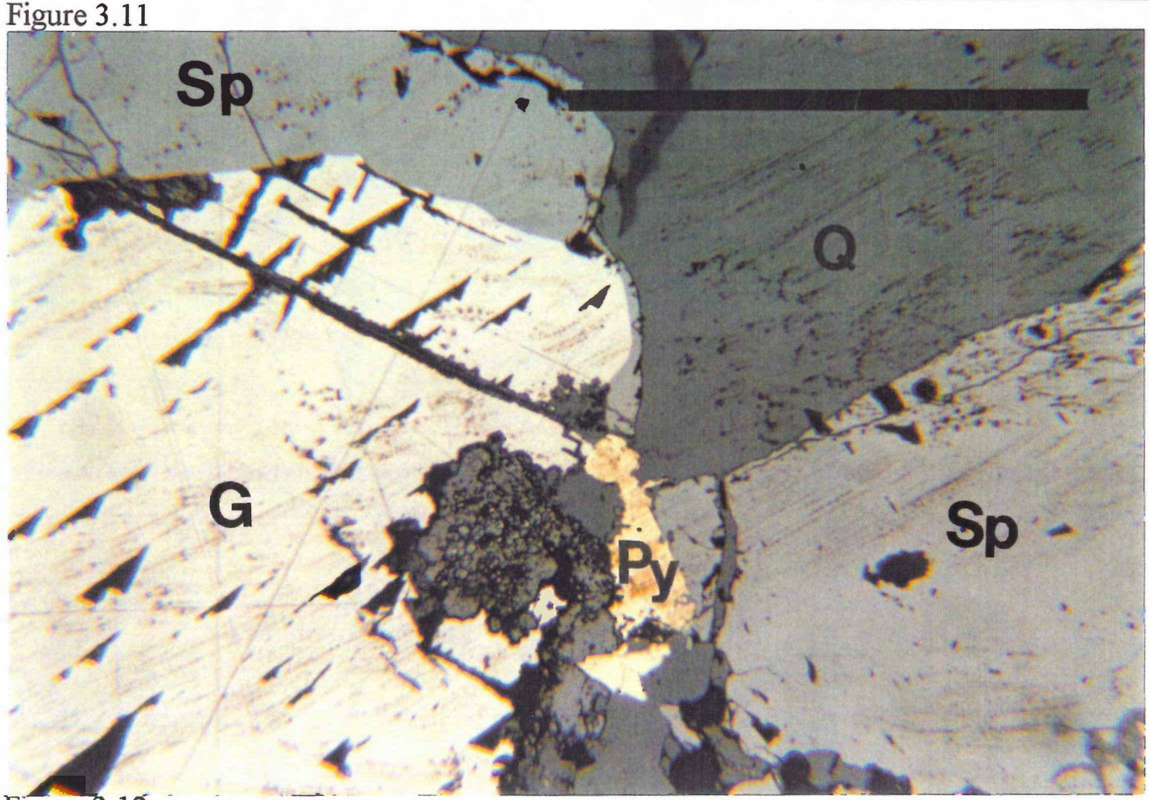


Figure 3.12

Figure 3.13. Vein within Unit 5, sample KS-86-DP-4. Chalcopyrite (Ch) and sphalerite (Sp) intergrown within a quartz (Q) vein. Scale = 0.5 mm.

Figure 3.14. Vein within Unit 5, Hole KS-86-1, sample LD-46. Hydrothermal (HM) muscovite which grows out from the vein boundary. Scale = 1 mm.

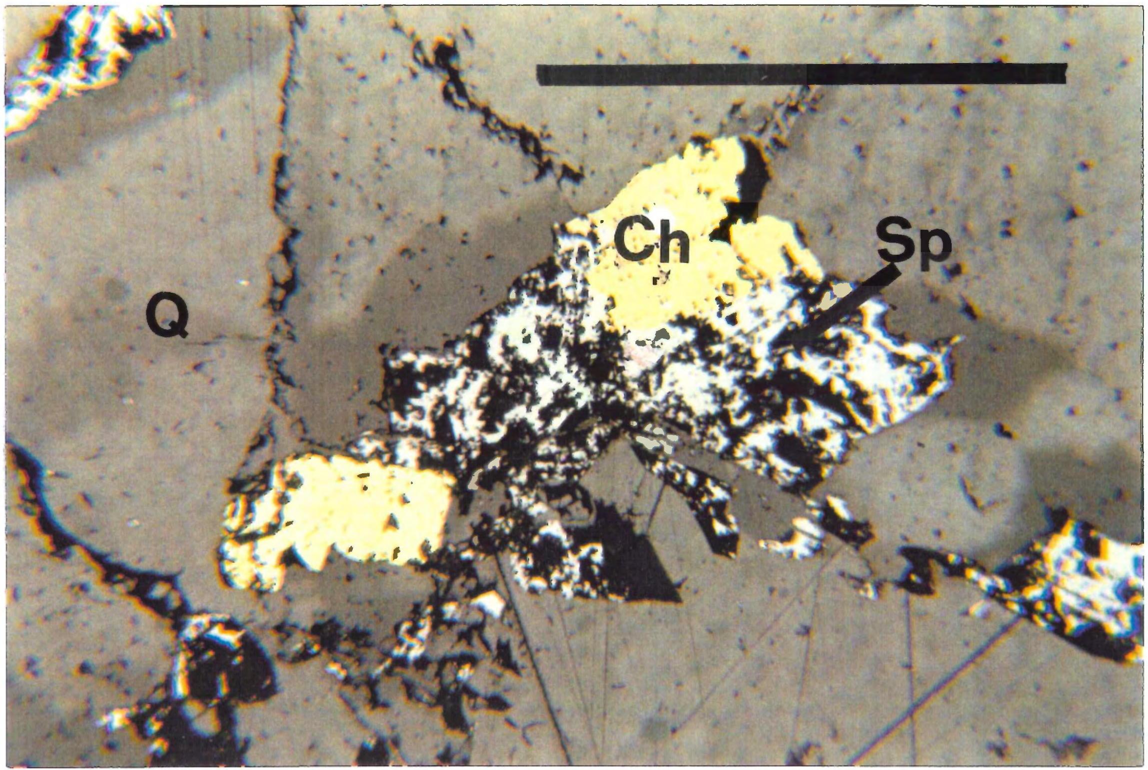


Figure 3.13

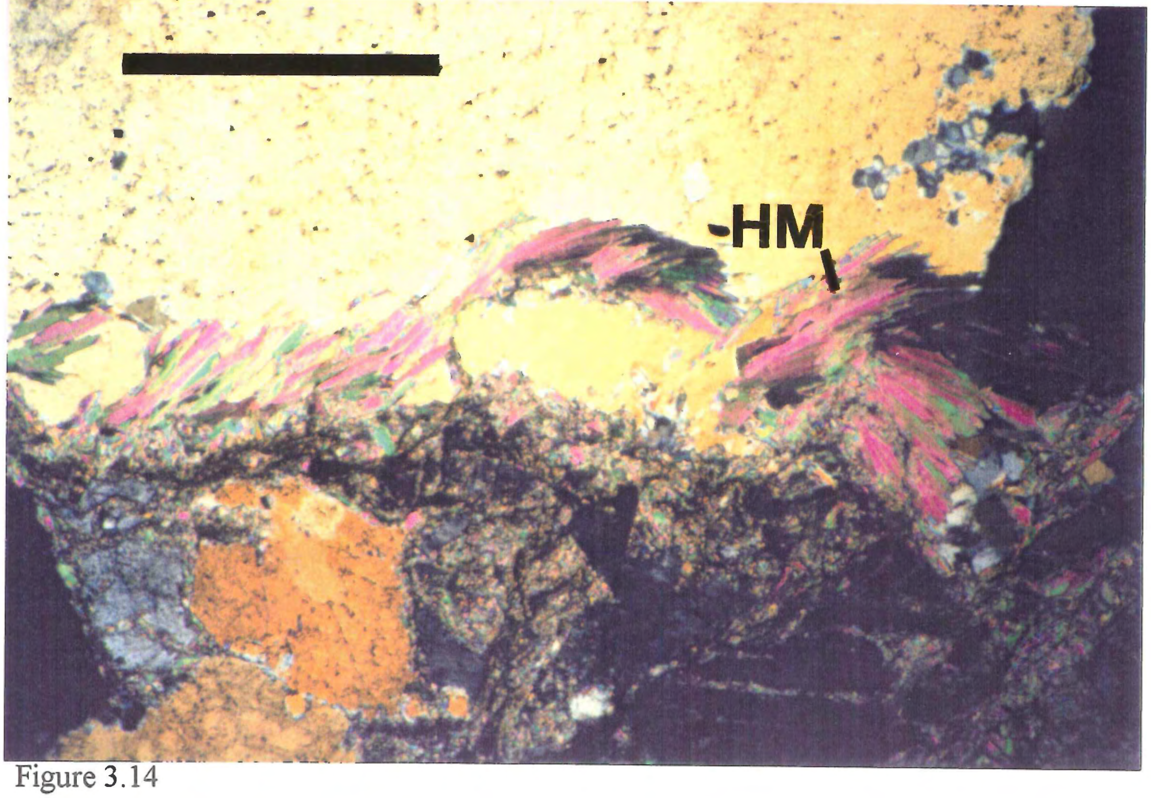


Figure 3.14

3.13). The iron content of the sphalerite at Kempt Snare Lake varies from 6.5 to 7.25 Fe atomic %.

Quartz Quartz is the dominant vein mineral and occurs in contact with all the other vein minerals. Primary and secondary fluid inclusions occur in many vein samples.

Muscovite Small elongate muscovite grains are present in the veins. Commonly the muscovites have hydrothermal flow textures, whereby the orientation of the muscovite changes (Figure 3.14), that occur not only at the boundary of the vein with the wall rock, but also in the centre of the vein.

Siderite Buff-coloured siderite is present in many veins and occurs in contact with sulphide minerals including galena, chalcopyrite, pyrite, and sphalerite. Two types of siderite can be distinguished optically and chemically. One type of siderite forms small blackened and "corroded" crystals with anhedral crystal shape (Figure 3.15). Samples such as these have a Fe:Mn ratio of ~ 5:4. The second type of siderite has visible cleavage planes, high birefringence colours, and euhedral crystal shape (Figure 3.16). In some places, siderite appears as a later generation of vein mineral, filling gaps (Figure 3.17). The Fe:Mn ratio of the second type of siderite is near 4:1.

Fluorite Pale purple fluorite occurs in veins in contact with siderite, and as fine, less than 1 mm wide monomineralic veins.

Figure 3.15.Vein within Unit 1, Hole KS-86-1, sample LD-35. In the centre of the photograph a large siderite (HS) crystal, with a corroded outline and blackened colour, occurs. Scale = 1 mm.

Figure 3.16. Vein within Unit 3, Hole KS-86-2, sample LD-56. Second form of siderite (DS) with high birefringence colours and subhedral crystal shape occurs at the bottom right of the photograph. Scale = 1 mm.

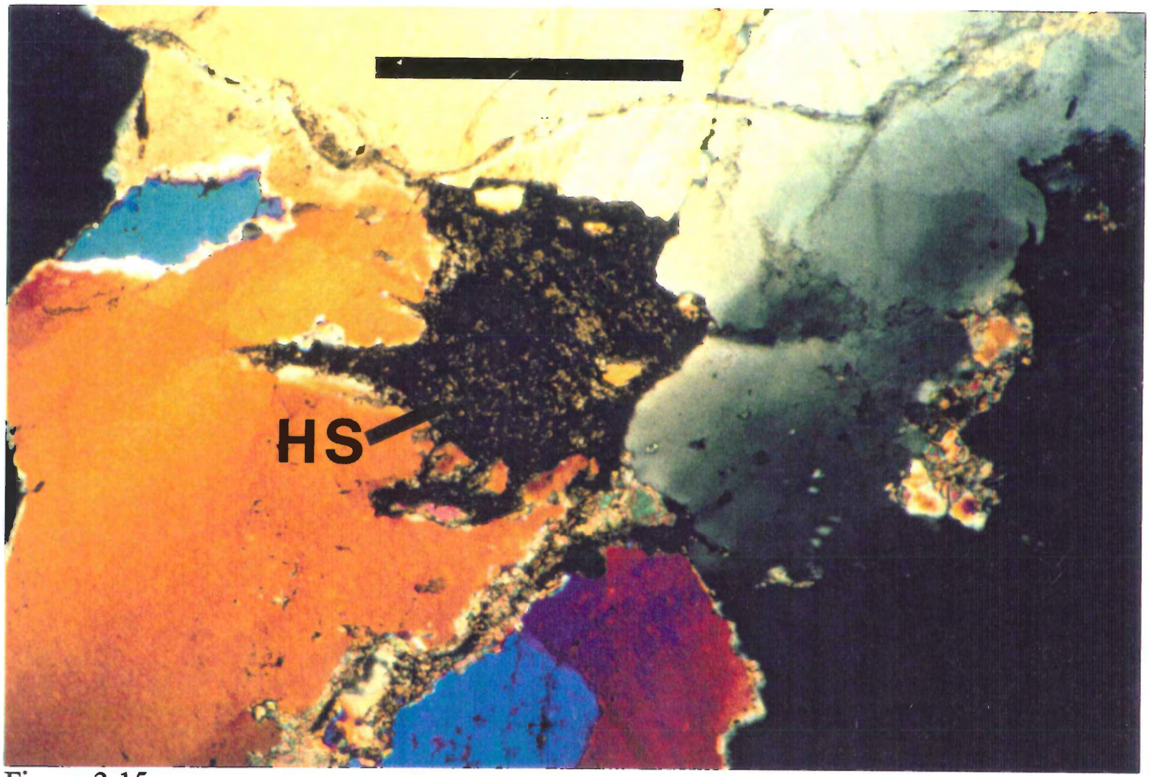


Figure 3.15

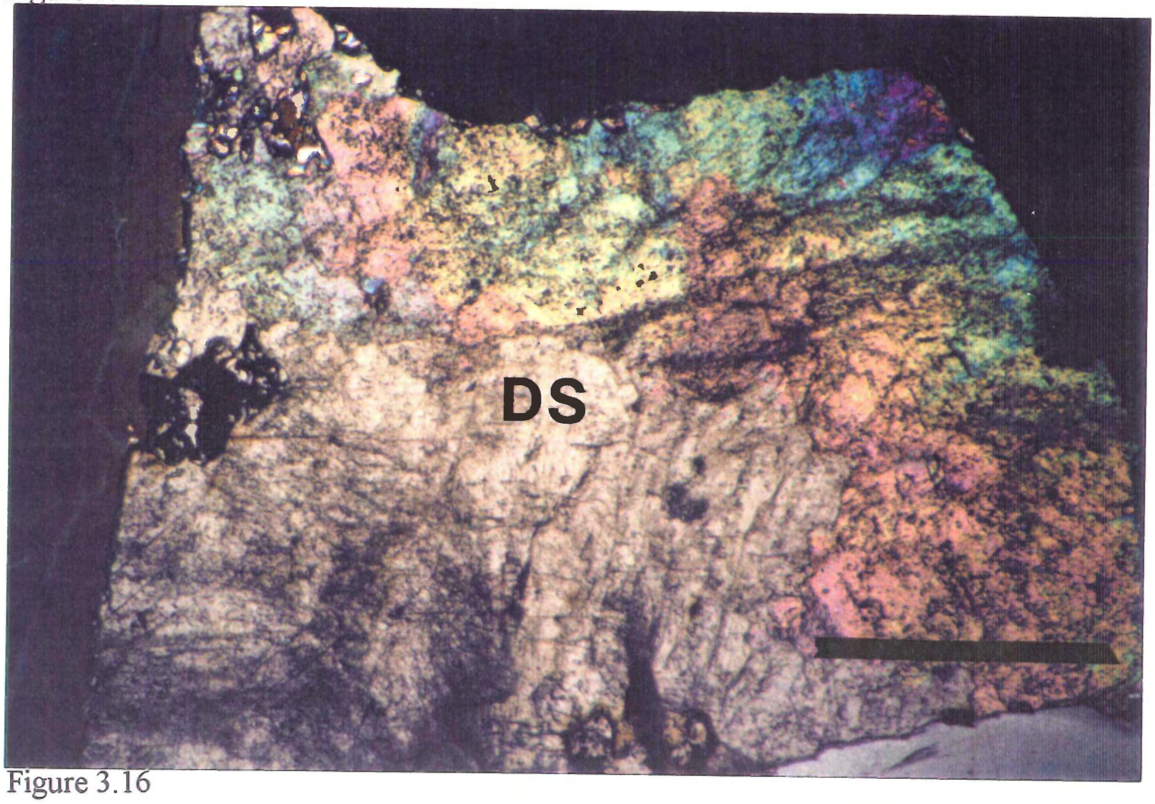


Figure 3.16

Figure 3.17. Vein within Unit 3, Hole KS-86-2, sample LD-56. The second form of siderite (DS) (as in Figure 3.16) seen in PPL. Here the siderite is filling in gaps and veins. This siderite has a clearer outline and form than the siderite in Figure 3.15. Scale = 1mm.

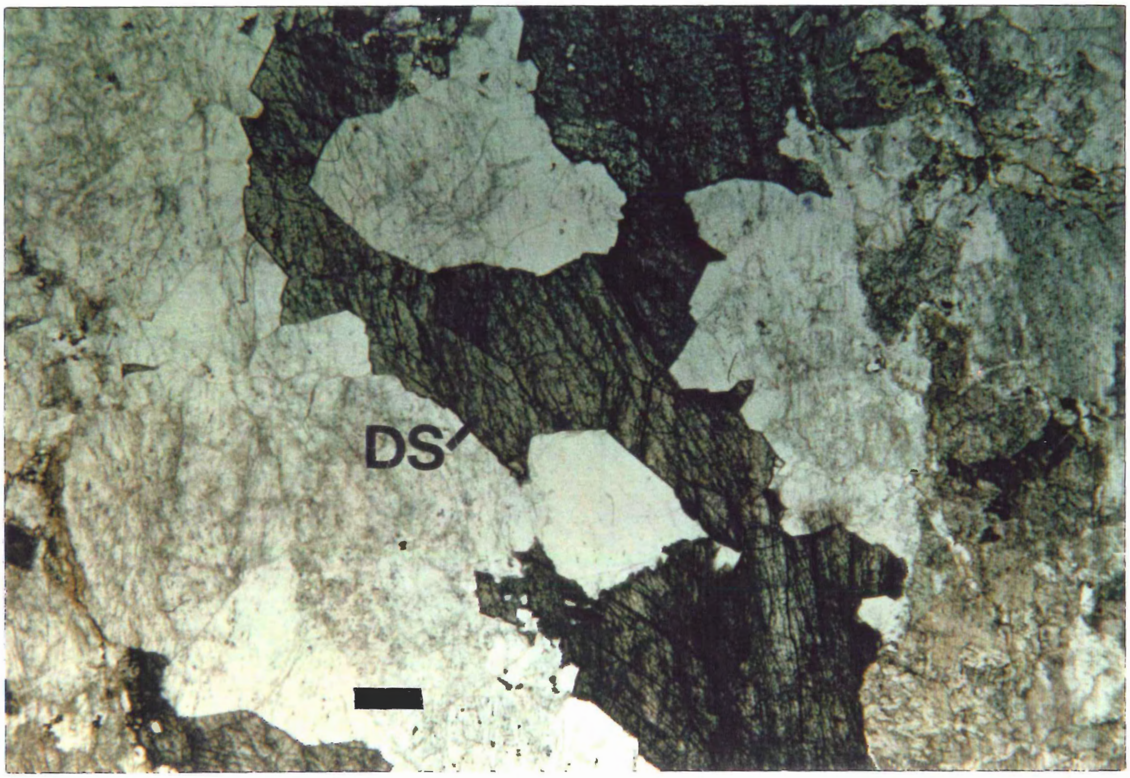


Figure 3.17

3.5 Paragenetic Sequence at Kempt Snare Lake

The mineral relationships described above define a paragenetic sequence (Figure 3.18). Graphite occurs within the units but does not occur with the veins, restricting the timing of graphite precipitation to a period before the brittle deformation and veining. As arsenopyrite is the only sulphide disseminated within the greisenised lithologies, arsenopyrite was also precipitated during a pervasive phase of alteration, and was the first sulphide formed. The presence of arsenopyrite at vein boundaries suggests that it continued to be precipitated during the main veining event. Rare inclusions of pyrite and chalcopyrite within arsenopyrite suggest that pyrite and chalcopyrite are closely related to the time of arsenopyrite precipitation, and probably started to crystallise from the mineralising fluid shortly after arsenopyrite crystallisation started. Pyrite and chalcopyrite also occur as crystals within the veins. Chalcopyrite rims pyrite, but pyrite does not rim chalcopyrite. This relationship suggests that pyrite started to crystallise before chalcopyrite, and the precipitation of chalcopyrite continued after the period of pyrite formation had ended. Pyrite and chalcopyrite occur in close association with sphalerite, with chalcopyrite rimming sphalerite, and sphalerite rimming pyrite. The start of the precipitation of sphalerite must, therefore, be after the initiation of pyrite precipitation and must have continued after pyrite formation had ended. Sphalerite precipitation must have ended before chalcopyrite precipitation ended, enabling chalcopyrite to have rimmed the sphalerite. Pyrrhotite only occurs as inclusions within sphalerite, and crystallisation of pyrrhotite must, therefore, be restricted to the timing of sphalerite precipitation. Galena

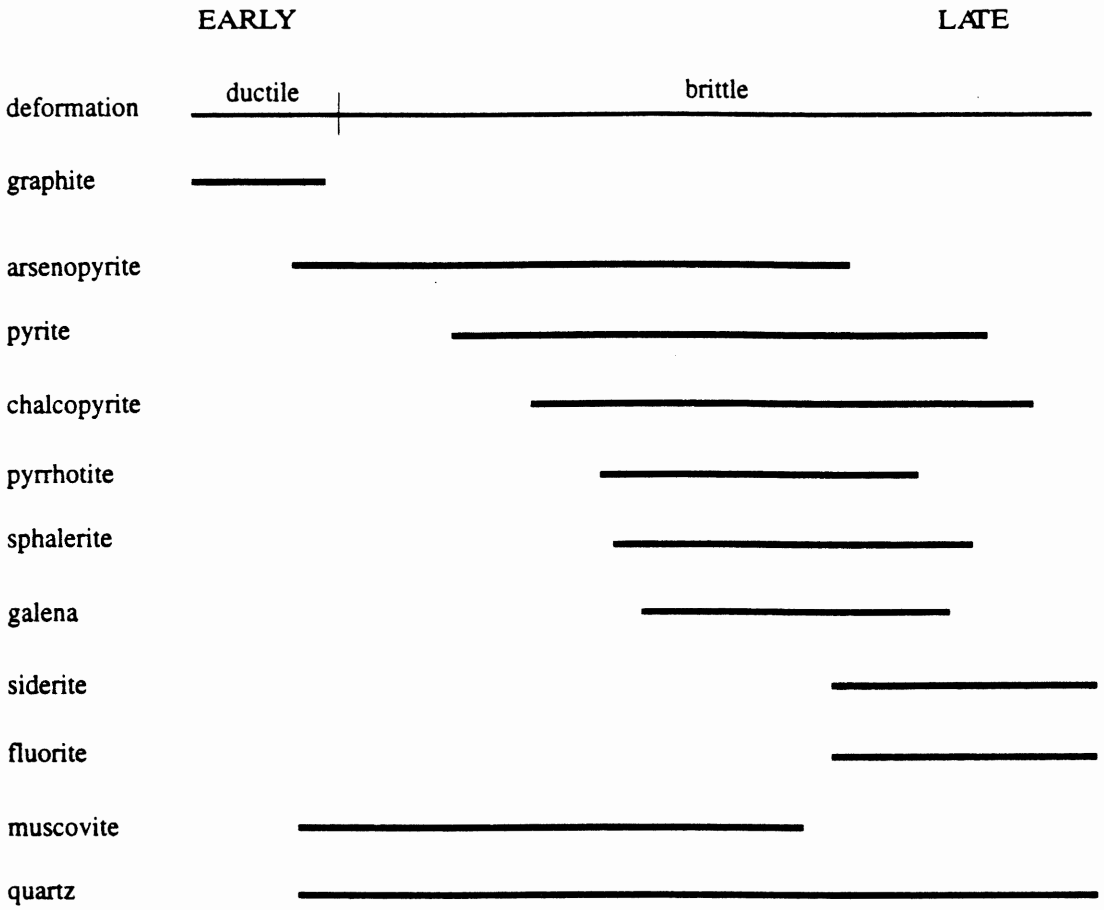


Figure 3.18 Paragenetic sequence at Kempt Snare Lake.

occurs in close association with sphalerite, suggesting that the timing of the start of galena formation is similar to sphalerite; however, sphalerite rims galena, and therefore, must continue after galena formation had ceased. Galena also occurs rimming arsenopyrite, suggesting a later timing of precipitation of galena relative to arsenopyrite.

Quartz is the dominant vein mineral and occurs in contact with all the vein minerals and must have precipitated throughout the mineralisation. Muscovite occurs in veins with quartz and sulphides, but is not present in contact with siderite, suggesting that muscovite precipitation stopped before the siderite precipitation started. Siderite occurs in contact with pyrite and chalcopyrite, suggesting that the precipitation of siderite overlapped with the sulphide mineralisation phase. Pure siderite veins, however, and siderite-quartz-fluorite veins where no sulphides also occur, suggest that siderite, fluorite, and quartz precipitation continued after the sulphide mineralisation. No variation between the vein mineralogy and the two types of siderite identified earlier occurs. Fluorite occurs in many monomineralic veins, and in veins with siderite and quartz.

3.6 Summary

This chapter summarises the mineralogy, and mineral textures present at Kempt Snare Lake. The five lithologies have similar mineral compositions but differ in their modal percentage of the minerals: greisens are characterised by a greater abundance of muscovite and quartz than the granites; the leucogranite is characterised by a higher plagioclase content and low muscovite and biotite content relative to the leucomonzogranite K-feldspar modal percentage but more muscovite and biotite than the leucogranite. The greisens contain a high proportion of graphite, that readily distinguishes them from the granites.

All the units have undergone some hydrothermal alteration, with abundant K-feldspathisation and albitisation occurring in all lithologies. Graphite precipitation has also occurred in all the units, but has more severely affected the greisens. Graphite may, therefore, be more closely associated with the greisenisation process than with the other alteration stages. Evidence of both pervasive alteration, K-feldpathisation and albitisation, and alteration associated with brittle deformation and veining, occurs within the Kempt Snare Lake units. The alteration reactions taking place with the Kempt Snare Lake lithologies are discussed in greater detail in Chapter 4, with the results of the whole-rock geochemistry.

A clear, paragentic sequence for the mineralisation occurring within the host lithologies and the veins has been established, with arsenopyrite being the first-formed sulphide and the pyrite, chalcopyrite, sphalerite, and galena following. Quartz precipitation occurred throughout mineralisation, and siderite and fluorite formed during the later veining event. Possible sources for these vein minerals are discussed in Chapter 5.

CHAPTER 4 - GEOCHEMISTRY

4.1 Introduction

This chapter presents the results of whole-rock geochemical analyses of the five lithologies at Kempt Snare Lake. The geochemical samples were prepared according to the methods outlined in Appendix B. The analytical work was undertaken to establish any genetic links among leucomonzogranite, leucogranite, and greisens, and the variations resulting from the hydrothermal alteration. Also examined in this chapter are the relationships between the granites at Kempt Snare Lake, and those of the Davis Lake Pluton, Wedgeport Pluton, and the South Mountain Batholith. To accomplish these goals, fifteen samples from Kempt Snare Lake were analysed for their major and trace element content, and ten were analysed for their rare earth element content (REE). The samples chosen and their location within the core are shown in Table 4.1. The results of the major and trace element analyses are presented first, with the REE results following. Discussion of the results in relation to other studies completed at Kempt Snare Lake and surrounding plutons and South Mountain Batholith samples follows.

4.2 Major, Trace, and Rare Earth Element Analyses

Fifteen samples were analysed for major oxides and some minor elements (Ba, Rb, Sr, Y, Zr, Nb, Th, Pb, Ga, Zn, Ni, Cu, V, and Cr) by X-ray fluorescence spectroscopy at the Regional XRF laboratory at St. Mary's University, Halifax, Nova Scotia. In addition, Ta and Hf contents were reported within the REE data obtained from Memorial University of

				Whole Rock			Stable Isotopes			
Borehole and depth	Sample	Unit	Vein	Major	Trace	REE	Silicates	Graphite	Siderite	Sulphides
KS-86-1 10.12m	LD-47		x						x	
KS-86-1 13.30m	LD-46		x				x			
KS-86-1 28.70m	LD-38	U2		x	x					
KS-86-1 32.13m	LD-44	U2		x	x	x	x			
KS-86-1 38.00m	LD-42	U3		x	x	x	x	x		
KS-86-1 47.00m	LD-35		x				x		x	
KS-86-1 47.23m	LD-34	U2		x	x	x	x	x		
KS-86-1 66.28m	LD-37	U3		x	x					
KS-86-1 66.58m	LD-36	U3		x	x	x	x	x		
KS-86-2 26.52m	LD-1	U5		x	x					
KS-86-2 29.13m	LD-12		x				x		x	x
KS-86-2 29.57m	LD-52		x						x	
KS-86-2 33.13m	LD-49		x						x	x
KS-86-2 37.49m	LD-56		x						x	
KS-86-2 39.75m	LD-16		x				x			x
KS-86-2 58.21m	LD-58		x							x
KS-86-2 66.97m	LD-18		x						x	
KS-86-2 70.60m	LD-7	U1		x	x					
KS-86-2 77.81m	LD-11	U1		x	x	x	x	x		
KS-86-2 78.85m	LD-10	U1		x	x	x	x	x		
KS-86-2 89.70m	LD-64		x						x	
KS-86-3 10.30m	LD-50		x				x		x	
KS-86-3 13.54m	LD-21	U4		x	x	x				
KS-86-3 13.60m	LD-22	U4		x	x		x	x		
KS-86-3 14.24m	LD-24	U4		x	x	x	x	x		
KS-86-3 17.48m	LD-51		x						x	
KS-86-3 21.44m	LD-29		x				x		x	
KS-86-3 26.08m	LD-30		x							x
KS-86-3 27.43m	LD-25	U5		x	x	x	x	x		
KS-86-3 28.57m	LD-27	U5		x	x	x	x	x		
KS-86-3 36.80m	LD-60		x				x			
KS-86-3 42.84m	LD-32		x						x	

Table 4.1. Samples selected and analyses obtained.

Newfoundland, St John's, Newfoundland. In Newfoundland, ICP-MS analyses were carried out for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, and Lu, following the procedure of Longerich et al. (1990). ICP-MS analysis was then completed using the method of internal standardisation.

4.3 Relationship Among the Granites and Greisen Protoliths

The relationships between the leucomonzogranite and leucogranite can be established by immobile elements, which have not been changed by subsequent hydrothermal alteration. At Kempt Snare Lake these elements include, TiO_2, Ta, Nb, Zr, and the REE's. Once the relationship between the granites is established, determination of the protoliths for the greisen samples is discussed.

4.3.1 Major and Trace Element Results

The results of the major and trace element analyses are shown in Table 4.2. Table 4.3 shows the average compositions of the most immobile elements for the five rock units, and Figures 4.1 to 4.4 show some of these elemental variations.

SiO_2 vs. TiO_2 Figure 4.1 shows the variation in silica and titania between unaltered South Mountain Batholith rocks and those of Kempt Snare Lake. Data for this figure come from this study, McKenzie and Clarke (1975), and Richardson (1988). This plot clearly shows that if magmatic fractionation is dominant, a clear trend, with increasing silica content and

Table 4.2. Geochemical results for Kempt Snare Lake.

Sample	LD-7	LD-10	LD-11	LD-34	LD-38	LD-44	LD-36
Unit	1	1	1	2	2	2	3
			MAJOR	ELEMENTS			
SiO2	70.71	69.15	74.35	69.98	70.69	71.96	70.78
Al2O3	15.32	16.38	14.15	16.61	15.56	15.54	16.38
Fe2O3 (T)	2.02	1.73	1.59	1.29	1.57	1.60	1.86
MgO	0.07	0.07	0.01	n.d.	0.04	0.03	0.01
CaO	0.68	1.06	0.75	0.99	1.01	1.09	0.62
Na2O	3.15	3.34	2.71	3.33	3.37	3.63	3.50
K2O	4.54	5.50	4.78	5.78	5.13	4.70	5.24
TiO2	0.16	0.13	0.13	0.04	0.09	0.10	0.10
MnO	0.06	0.11	0.09	0.06	0.07	0.07	0.05
P2O5	0.10	0.09	0.09	0.12	0.11	0.10	0.11
LOI	1.40	1.70	1.30	1.40	1.70	1.40	1.20
Total	98.20	99.26	99.96	99.61	99.34	100.23	99.86
A/CNK	1.35	1.23	1.30	1.21	1.20	1.18	1.23
			TRACE	ELEMENTS			
Ba	17	46	<5	55	52	48	34
Rb	687	710	628	694	655	615	731
Sr	35	56	33	44	65	73	41
Y	55	59	54	22	29	51	25
Zr	132	108	107	63	86	90	84
Nb	21	17	17	15	17	18	24
Th	37	29	29	23	35	30	32
Pb	15	65	38	52	19	18	16
Ga	29	30	27	30	31	30	31
Zn	53	180	313	60	33	43	37
Cu	12	<5	<5	5	9	7	<5
Ni	<5	6	6	<5	<5	5	5
V	11	10	9	5	10	8	9
Cr	11	12	12	7	<5	7	11
Hf	-	3.34	2.63	2.98	-	3.58	2.94
Ta	-	3.48	3.41	4.19	-	6.58	5.06
				REE			
La	-	24.39	13.95	7.23	-	14.18	7.54
Ce	-	59.46	34.23	19.29	-	37.17	20.13
Pr	-	7.08	4.28	2.32	-	4.56	2.51
Nd	-	25.66	16.38	8.32	-	16.63	9.17
Sm	-	7.14	4.85	3.09	-	5.45	3.12
Eu	-	0.17	0.11	0.03	-	0.08	0.40
Gd	-	7.74	5.61	3.13	-	5.86	3.46
Tb	-	1.56	1.18	0.79	-	1.33	0.80
Dy	-	11.06	8.70	5.60	-	9.21	5.66
Ho	-	2.34	1.87	1.12	-	1.90	1.18
Er	-	7.28	1.23	0.59	-	0.71	0.68
Tm	-	1.23	0.99	0.68	-	1.03	0.70
Yb	-	8.29	6.83	5.44	-	7.41	5.19
Lu	-	1.15	0.97	0.74	-	1.05	0.71

n.d.= not detected - = not analysed

Sample	LD-37	LD-42	LD-21	LD-22	LD-24	LD-1	LD-25	LD-27
Unit	3	3	4	4	4	5	5	5
				MAJOR	ELEMENTS			
SiO2	71.81	70.53	67.16	69.87	68.58	68.03	57.12	66.16
Al2O3	15.86	16.97	19.01	17.08	17.07	16.84	23.15	18.53
Fe2O3 (T)	1.51	1.49	2.12	1.34	1.59	3.02	3.89	2.13
MgO	0.04	0.04	0.07	0.01	0.01	0.09	0.19	0.06
CaO	0.71	0.93	0.25	0.25	0.48	0.13	0.15	0.16
Na2O	3.34	3.15	2.24	2.94	3.11	2.46	0.38	2.08
K2O	4.99	5.12	6.06	5.31	5.60	5.69	10.07	6.81
TiO2	0.08	0.10	0.05	0.03	0.05	0.07	0.11	0.07
MnO	0.03	0.06	0.03	0.03	0.27	0.04	0.06	0.07
P2O5	0.11	0.12	0.13	0.12	0.12	0.11	0.12	0.11
LOI	1.10	1.20	1.80	1.50	1.90	2.10	3.50	2.20
Total	99.57	99.70	98.92	98.48	98.78	98.58	98.75	98.38
A/CNK	1.32	1.41	1.89	1.59	1.44	1.61	1.86	1.69
				TRACE	ELEMENTS			
Ba	22	61	61	39	46	27	155	87
Rb	670	657	870	674	674	756	1406	866
Sr	44	44	17	20	37	23	16	21
Y	20	27	<5	6	34	36	46	21
Zr	72	85	68	63	75	72	113	85
Nb	23	24	18	14	15	14	26	17
Th	26	30	24	25	26	24	37	23
Pb	17	50	23	47	19	37	70	17
Ga	28	33	38	31	32	31	52	35
Zn	35	40	92	64	131	297	204	110
Cu	<5	<5	<5	6	<5	41	6	<5
Ni	5	5	5	5	<5	5	6	<5
V	8	7	<5	<5	6	<5	9	5
Cr	13	<5	7	<5	6	5	<5	6
Hf	-	3.44	2.53	-	2.99	-	4.7	2.14
Ta	-	6.58	4.37	-	4.69	-	6.71	4.88
					REE			
La	-	6.11	2.03	-	5.35	-	9.76	8.64
Ce	-	16.03	5.71	-	14.79	-	27.21	21.34
Pr	-	1.99	0.76	-	1.98	-	3.74	2.55
Nd	-	7.50	3.00	-	7.64	-	14.87	8.83
Sm	-	2.76	1.50	-	3.34	-	5.56	2.82
Eu	-	0.07	0.04	-	0.06	-	0.18	0.09
Gd	-	3.12	1.75	-	3.82	-	6.80	2.89
Tb	-	0.77	0.42	-	0.92	-	1.67	0.69
Dy	-	5.57	3.21	-	6.75	-	12.34	5.04
Ho	-	1.18	0.63	-	1.41	-	2.59	1.01
Er	-	0.70	0.10	-	0.37	-	0.81	1.42
Tm	-	0.71	0.37	-	0.81	-	1.42	0.59
Yb	-	0.55	2.94	-	5.88	-	10.04	4.55
Lu	-	0.76	0.45	-	0 .78	-	1.40	0.61

Element/Oxide	Leucomonzogranite Unit 1	Leucogranite Unit 2	Greisenised granite Unit 3	Fine-grained greisen Unit 4	Porphyritic greisen Unit 5
Ta	3.4	4.3	5.8	4.6	5.8
Nb	18	18	24	16	19
Zr	115	80	80	69	90
TiO2	0.14	0.07	0.09	0.04	0.08
REE(total10)	110	56	36	33	65
Eu/Eu*	0.02	0.01	0.07	0.02	0.03
La/Sm	1.98	1.50	1.45	0.09	1.50
La/Lu	1.85	1.21	1.00	0.59	1.08
Gd/Yb	0.70	0.53	0.50	0.50	0.51

Table 4.3. Variations in the average compositions of the Kempt Snare Lake rock units.

decreasing TiO_2 occurs. However, data from the Davis Lake Pluton and the East Kemptville leucogranite plot on an intersecting line, with silica decreasing as a function of increasing alteration. The Kempt Snare Lake leucomonzogranite plots close to the area identified by the magmatic trend of MacKenzie and Clarke (1975), suggesting the Kempt Snare Lake leucomonzogranite formed as part of the fractional crystallisation process occurring within the South Mountain Batholith, and represents an evolved unit of the MacKenzie and Clarke (1975) sequence. The trend of the leucogranite and greisens suggests a different process occurred. The leucogranite and greisens follow the trend of the East Kemptville leucogranites, which has been interpreted to be caused by fluid interaction (Richardson 1988). The compositions of the leucogranite and greisen units at Kempt Snare Lake are not controlled by normal fractionation processes, and are likely the products of fluid interaction.

TiO_2 vs. Zr Figure 4.2 shows the variation in titania with zirconium. Variations in Ti and Zr are often used to identify relationships between magmas. Within the South Mountain Batholith a decrease in both Ti and Zr is expected with increasing fractionation. The low abundances of TiO_2 (0.03 to 0.16 wt%) and Zr (63 to 132 ppm) suggest that all the Kempt Snare Lake lithologies are highly evolved. Figure 4.2 shows the Kempt Snare Lake leucogranite (Unit 2) with lower titania and zirconium contents, that probably represents a more evolved lithology than the leucomonzogranite (Unit 1). The well defined TiO_2 vs. Zr trend may be the result of fractional crystallisation of zircon and biotite.

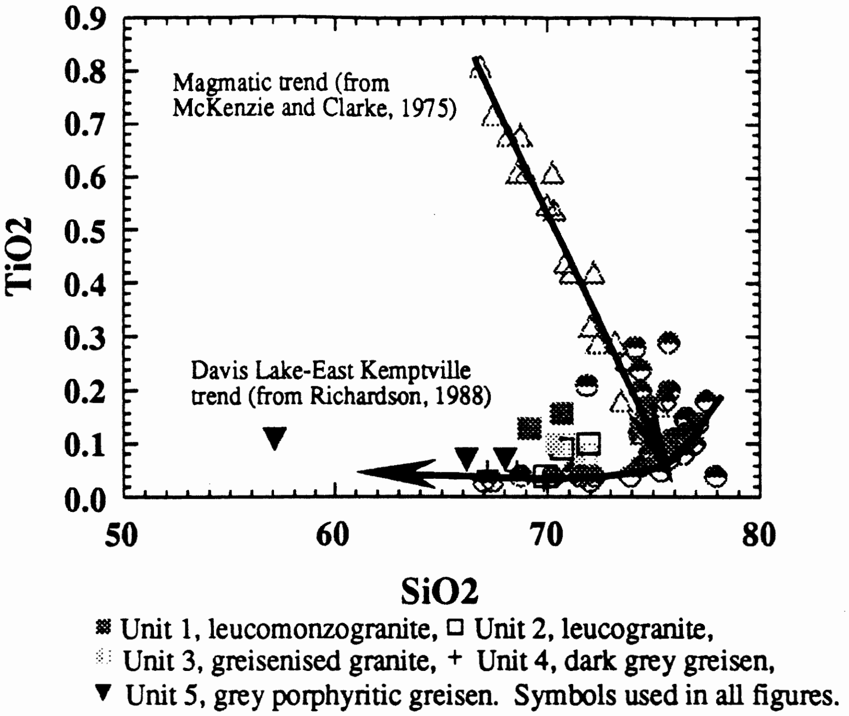


Figure 4.1 Relationship among the granites of Kempt Snare Lake and surrounding granites. As shown here the KSL leucomonzogranites fall close to the magmatic trend, whereas the remaining lithologies more closely follow the Davis Lake - East Kemptville trend. △ McKenzie and Clarke (1975), ● Richardson (1988).

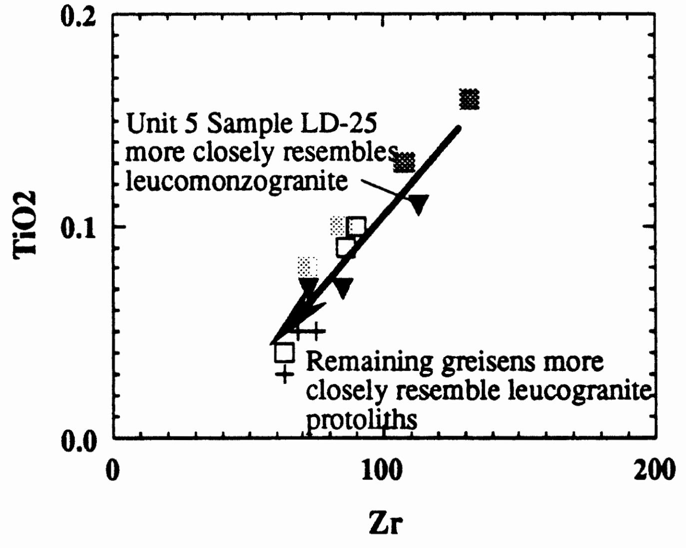


Figure 4.2 More evolved units usually have lower TiO2 and Zr contents. This plot suggests that some of KSL greisens are more closely related to the leucomonzogranite and some related to the leucogranite.

Figure 4.2 also suggest that some Unit 5 rocks (sample LD-25) have higher TiO_2 and Zr contents, more closely resembling leucomonzogranite protoliths, whereas, the remainder of the greisen samples plot in the area nearer the leucogranite, suggesting these samples have leucogranite protoliths.

Zr vs. Nb, Ta vs. Zr, Nb vs. Ta, and Zr vs. Rb Figure 4.3 presents four binary plots, Zr vs. Nb, Ta vs. Zr, Nb vs. Ta, and Zr vs. Rb, to examine the possible relationships between the host units. In this series of diagrams, the variation in the two least altered units, Unit 1 and Unit 2, are clear. Under magmatic processes, more differentiated units have higher values of both Nb and Ta, and lower contents of Zr. These plots show that the leucogranite (Unit 2) has higher Ta, equal Nb content, and lower Zr content, compared to the leucomonzogrante (Unit 1), suggesting that the leucogranite is a more evolved relative of the leucomonzogranite. Charest (1976) reported that the Nb content of the South Mountain Batholith remained constant throughout differentiation, whereas Ta contents increased and Zr contents decreased. Plot C shows a poor linear relationship among all the units. The average Nb/Ta ratio for all the Kempt Snare Lake lithologies is 4.1+/- 0.9. The variation in Zr, Ta, and Nb between the leucomonzogranite and the leucogranite may be the result of crystallisation and fractionation of zircon.

The plot of Zr vs. Rb shows that the less altered units have similar Rb contents, whereas, the more altered Units, 4 and 5, have a variable Rb content, extending to higher Rb values

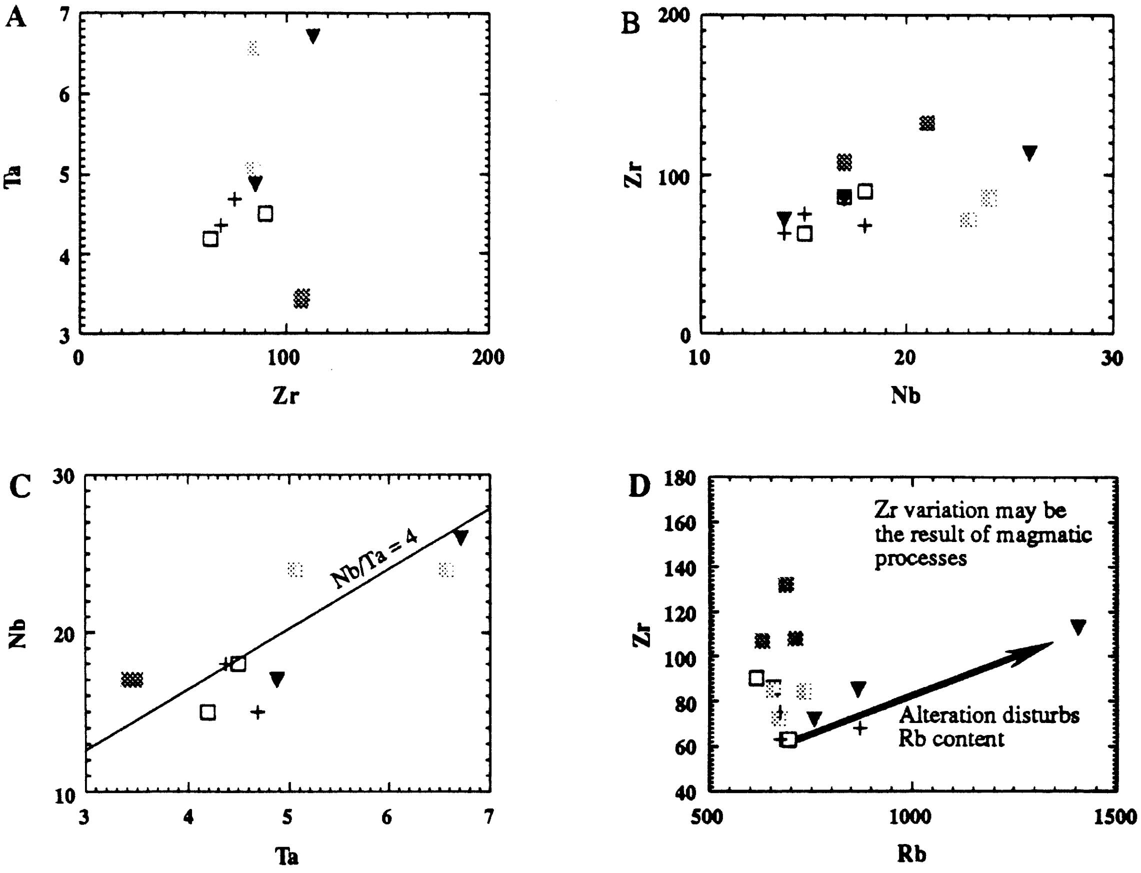


Figure 4.3 The relationship between the leucogranite and leucomonzogranite. A) The leucogranite has higher Ta content, whereas the leucomonzogranite has a higher Zr content. B) The leucomonzogranite has a higher Zr contents, but the average Nb value for both the leucomonzogranite and the leucogranite are equal. C) the Nb/Ta ratio for all KSL rocks. D) the decrease in Zr content between the three least altered units is seen, however, the more altered units have disturbed Rb values.

with the degree of alteration. This plot again suggests that Zr may be used to define magmatic processes within the least altered Units (the leucomonzogranite, leucogranite, and the greisenised granite). The figure suggests that the leucogranite is more differentiated than the leucomonzogranite, and may be the result of fractionation of zircon. However, the Rb contents have been affected by hydrothermal alteration. The higher and more variable Rb content of the most altered greisens, compared to the less altered units, suggest that Rb is more stable in the altered, muscovite-rich units.

4.3.2 REE Results

The REE contents of the five units is dominated by magmatic processes and are not greatly affected by hydrothermal alteration. Therefore, the REE profiles for the five units at Kempt Snare Lake should give information of the relationship between the granites, and the probable protoliths for the greisen samples. Figure 4.4 presents chondrite-normalised REE patterns for all five Kempt Snare lake lithologies. As shown in this figure, all the rocks have similar patterns, showing flattened profiles with slight concave trends to the HREE portion of the plot, however, some distinctions occur.

Leucomonzogranite (Unit 1) The leucomonzogranite is characterised by a $La_N = 38\text{-}66$, $La_N/Yb_N = 1.5\text{-}2.2$, and $Gd_N/Yb_N = 0.67\text{-}0.75$. The europium anomaly for the leucomonzogranites is very low and is similar to all the lithologies at Kempt Snare Lake with $Eu/Eu^* = 0.02$, where $Eu^* = ((Sm_N * Gd_N)^{1/2})$. The gradient of the profile, $La_N/Lu_N =$

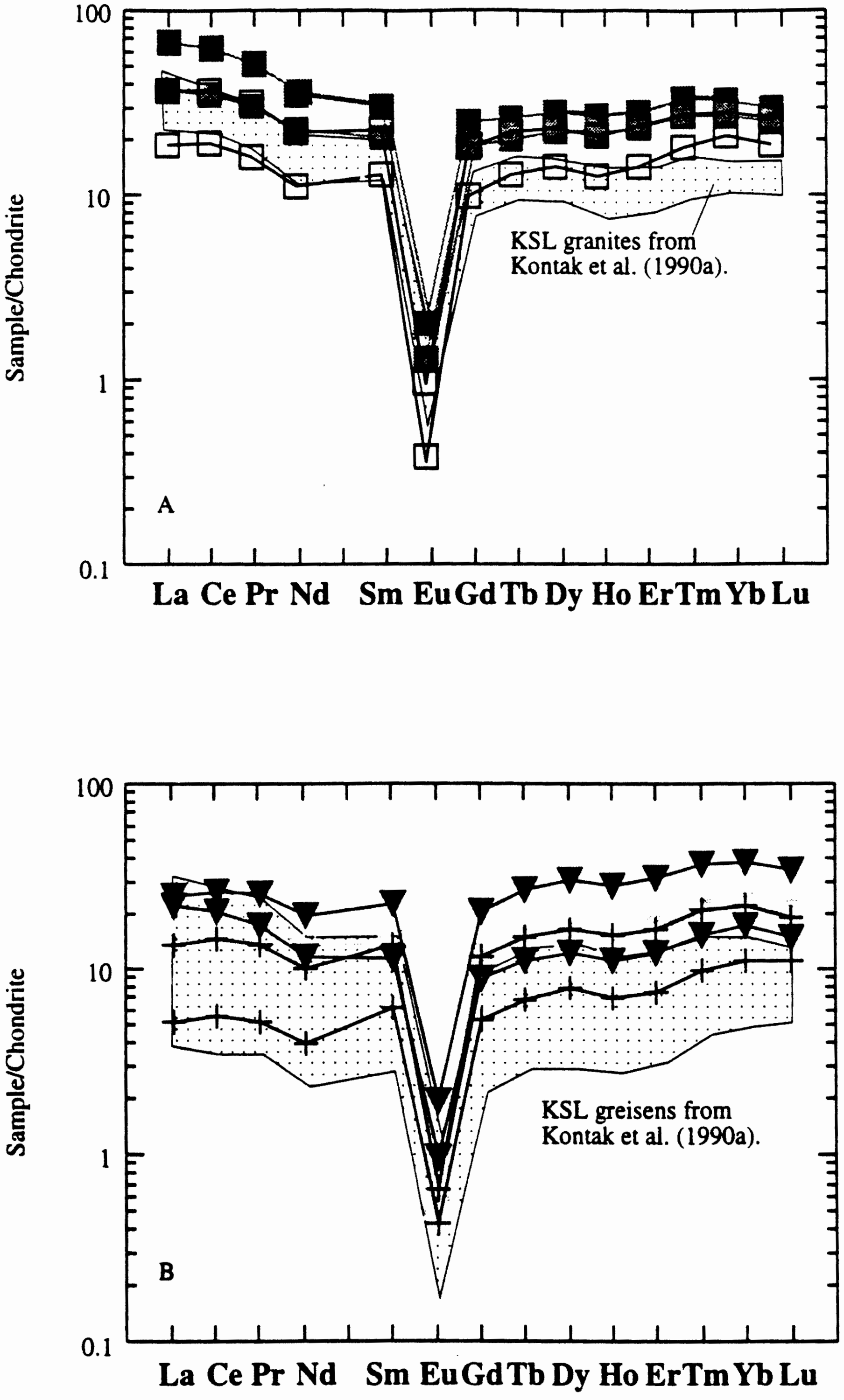


Figure 4.4 The REE for A) the granites and B) the greisens at KSL. Shaded areas represent the REE profile obtained for KSL from Kontak et al. (1990a).

1.5-2.2, is steeper than the other lithologies. The leucomonzogranites are also richer in total REE with ΣREE(10) = 85-137.

Leucogranite (Unit 2) The leucogranite has a lower La_N = 19 - 38, and lower ratios of La_N/Yb_N = 0.9-1.3, and Gd_N/Yb_N = 0.46-0.66. The europium anomaly is similar to the other units at Kempt Snare Lake with Eu/ Eu* = 0.01. The gradient of the whole profile is La_N/Lu_N = 1.0-1.4, and the ΣREE(10) = 21-90.

Greisens (Units 3, 4, and 5) The greisens at Kempt Snare Lake have similar trends to the other units with La_N = 5.5-26.6, La_N/Yb_N = 0.46-1.28 and Gd_N/Yb_N = 0.46-0.54. The europium anomaly is Eu/Eu* = 0.02 -0.12. These units have slightly flatter profiles than either of the granites with La_N/Lu_N = 0.46-1.12; however, the ΣREE(10) =18-78, overlaps with the lower ranges of the granites.

The similarity in the profiles of the leucogranite and leucomonzogranite suggests that these two units are closely related, with the general lowering of the ΣREE content, decreasing La_N/Yb_N and Gd_N/Yb_N consistent with the leucogranite being a more evolved unit of the leucomonzogranite. The similar trend of all five units suggests that all the units at Kempt Snare Lake are related by magmatic processes. The greisens show lower ΣREE contents, with the smallest totals generally found in the more altered units. This trend does not correspond to Unit 5, however, where this unit has a higher ΣREE content than the other greisenised units. These variations in REE contents of the greisens suggest that individual greisen samples have different granite protoliths.

4.3.3 Greisen Protoliths

Figure 4.2 shows that the majority of the greisen units have similar TiO_2 compositions to the leucogranite, however, sample LD-25 has significantly higher TiO_2 content. The REE profiles for the two Unit 5 lithologies (LD-25 and LD-27) are higher than the other greisen samples. The differences in these samples suggest that these Unit 5 samples have leucomonzogranite protoliths, whereas all the Unit 2 and Unit 3 greisens have leucogranite protoliths.

4.4 Hydrothemal Alteration Affects

The effect of alteration on the five lithologies was indicated in Figure 4.3, where the Rb content of the greisens was higher than the less altered units. The hydrothermal effect will now be discussed.

A/CNK vs. SiO_2 Figure 4.5 shows the A/CNK ratio varying with SiO_2, of all five lithologies at Kempt Snare Lake. This figure clearly shows that the granites plot towards the more evolved end of the magmatic trend, but the greisenised units extend above this line, with considerably higher A/CNK ratios. This plot may suggest fluid interaction, where the fluid is responsible for higher Al contents while removing silica.

Al_2O_3 vs. SiO_2 Al_2O_3 is plotted versus SiO_2 in Figure 4.6. This plot suggets that with increasing grade of alteration, the Al content of the units increases at the expense of silica. A tieline between pure muscovite and quartz is also plotted on this figure. The mixing line is consistent with the trend identified for the Kempt Snare Lake lithologies, demonstrating that, at least for these components, greisenisation is the process responsible for the trend.

K vs. Rb Figure 4.7 shows the K/Rb ratios for the Kempt Snare Lake lithologies. Taylor (1965) and Shaw (1968) suggested that K/Rb ratios <160 are not produced by crystal-melt equilibria, but are controlled by fluid phases which result in the precipitation of muscovite. The K/Rb values in the Kempt Snare Lake rocks show strong evidence of hydrothermal alteration. Tbis conclusion is supported by the actual lithologic types (greisens), numerous veins, and albitic composition of plagioclase (as shown in Chapter 3). The K/Rb ratio suggests that the fluids responsible for the alteration at Kempt Snare Lake were either rich in K allowing the production of the secondary muscovite and K-feldspar seen in the Kempt Snare Lake lithologies, or the fluids removed elements other than K from the rock units resulting in the appearance of higher K values. In either case, the covariation of K with Rb suggests that the fluids responsible for the alteration at Kempt Snare Lake stabilised muscovite with a low K/Rb content.

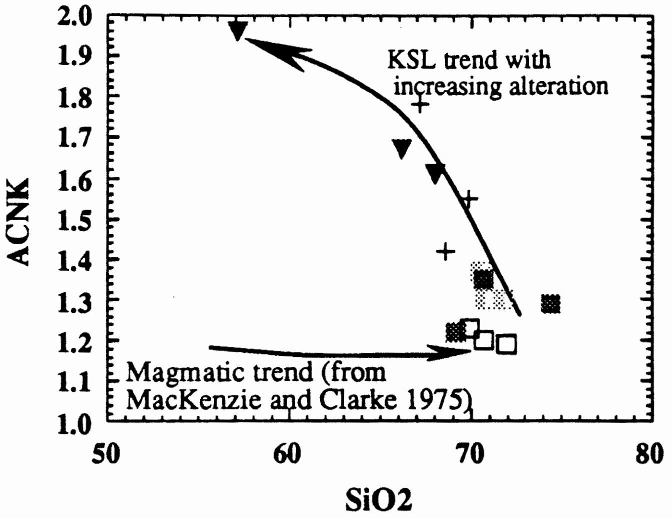


Figure 4.5 A/CNK vs. SiO2 at KSL. As the A/CNK ratio increases the silica content in decreases.

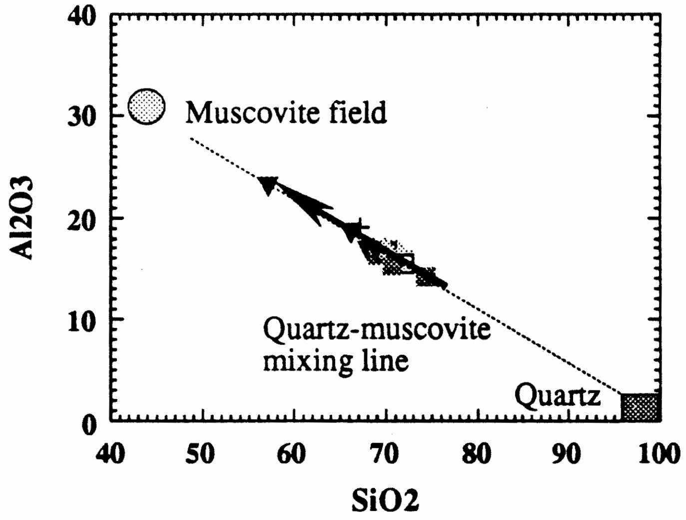


Figure 4.6 Al2O3 vs. SiO2 at KSL. A clear trend is present between the Al content of the KSL lithologies and the silica content suggesting silica breakdown to form muscovite.

Rb vs. Ba Figure 4.8 shows the variation of Rb with Ba, occurring in the lithologies at Kempt Snare Lake. This plot shows that the first part of the trend is flat, with the less altered units having a constant Rb content with higher Ba contents. However, this trend steepens in the more altered units, resulting in the upward turn towards higher Rb contents. This trend suggests that within the more altered units the fluid responsible for the alteration, stablised Rb in muscovite and Ba in secondary K-feldspar.

K vs. Na_2O and CaO Figure 4.9 shows how K varies with Na_2O content and Figure 4.10 how K varies with CaO. These two plots suggest that a small increases in K content results in the almost total removal of Na_2O and CaO from the system. This variation is consistent with the alteration of plagioclase to form K-feldspar.

Figures 4.9 and 4.10 show the CaO and Na_2O content of the Kempt Snare Lake lithologies falling with increasing alteration. However, the CaO is more greatly affected, being reduced to almost zero, whereas, the Na_2O content is halved. This variation is consistent with the alteration of Ca-rich magmatic plagioclase to Na-rich albite during the hydrothermal alteration phase. As discussed previously, plagioclase feldspars from Kempt Snare Lake have a composition of $Ab_{92\text{-}100}$. The higher K contents of greisenised units are consistent with production of secondary K-feldspar.The Ca removed from the lithologies may now be forming the carbonates occurring within the veins.

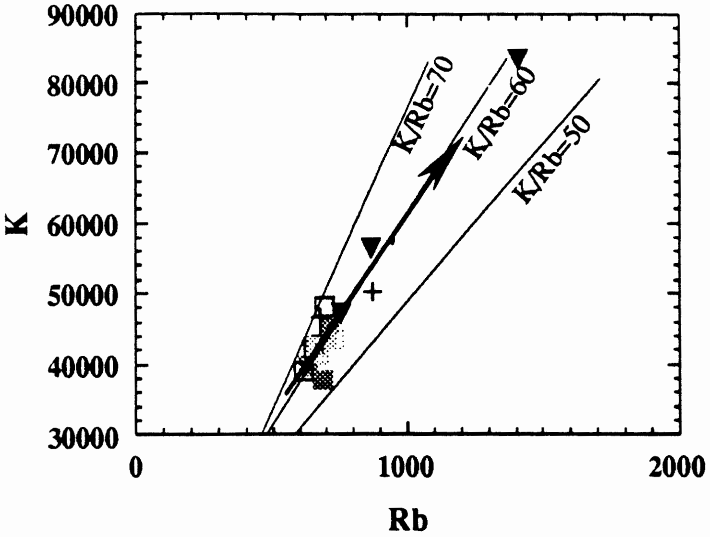


Figure 4.7 K vs. Rb at KSL. With increasing grades of alteration the K and Rb content on the KSL lithologies increases.

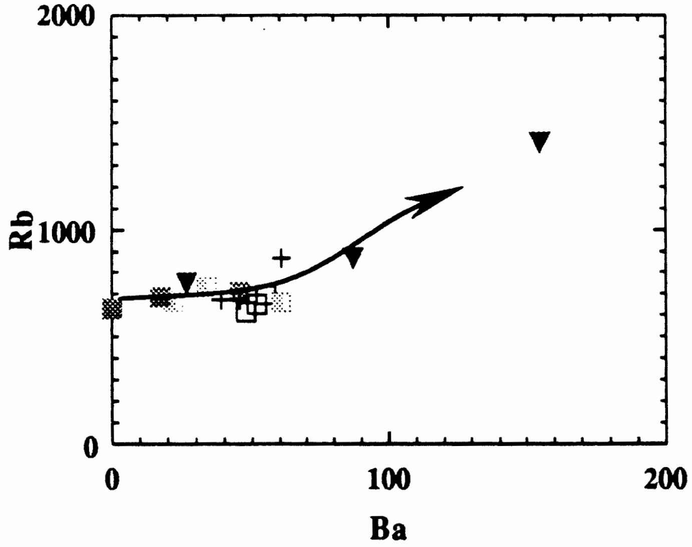


Figure 4.8 Rb vs. Ba at KSL. The Ba content of the KSL lithologies increases greatly in the most altered units.

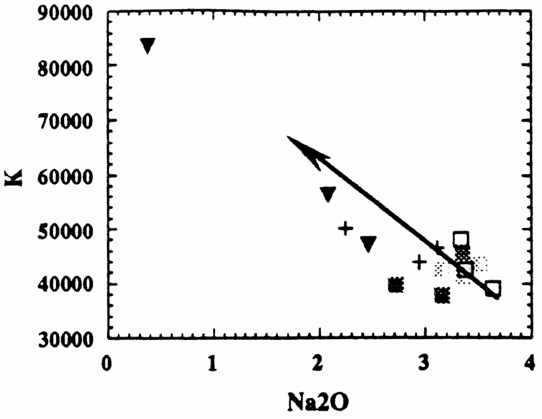


Figure 4.9 K vs. Na2O at KSL.With increasing alteration the KSL lithologies are depleted in Na2O and enriched in K.

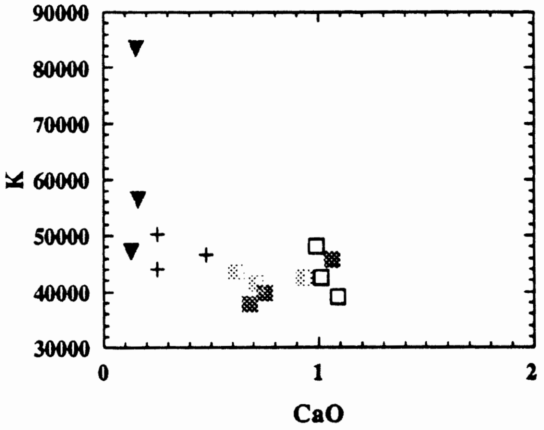


Figure 4.10 K vs. CaO at KSL. With increasing alteration the CaO content on the KSL lithologies is reduced to almost zero.

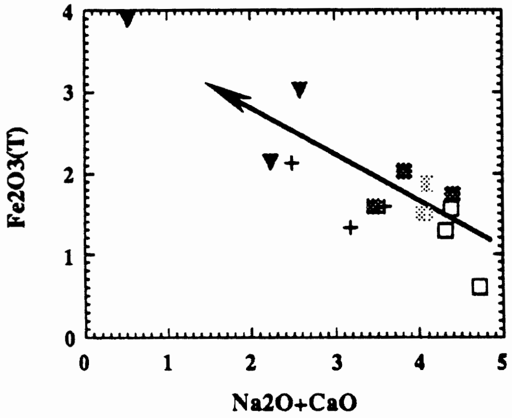
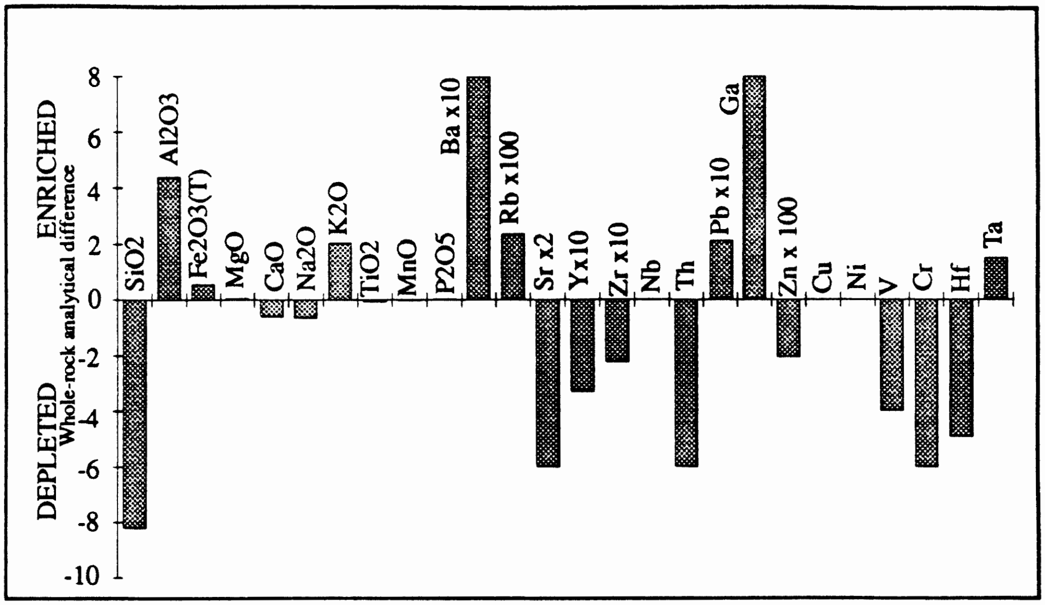


Figure 4.11 Fe2O3 vs. Na2O + CaO at KSL. With increasing grade of alteration the Na2O and CaO content of the lithologies is reduced while the total Fe2O3 content increases.

Fe_2O_3 vs. Na_2O and CaO Figure 4.11 shows Fe_2O_3 (T) content varying with Na_2O and CaO. This plot suggests that with increasing alteration grade, the Fe_2O_3 (T) content increases. This increase can be explained by the greater modal percentage of muscovite occurring in the greisenised units than in the fresher leucogranite and leucomonzogranite. As mentioned in the previous chapter the muscovite at Kempt Snare Lake is Fe rich, and the high number of Fe-bearing sulphides, also suggests that Fe was an important constituent in the mineralising fluid.

The variation in K_2O, Fe_2O_3(T), Rb, and A/CNK shown in Figures 4.5 to 4.11 suggest that the lithologies at Kempt Snare Lake may all be related by common fluid interaction processes.The upturn in the heavy REE (HREE) of all the REE profiles may be the result of fluid interaction, whereby HREE are brought into the system via ionic complexing. The similarity in geochemistry of sample LD-27 with the leucomonzogranites, and LD-22 with the leucogranite allow any enrichments and depletions to the host rock during the alteration process to be identified. Figure 4.12 shows the oxide and element enrichments and depletions that are present among these units. In this figure, Unit 4 and Unit 5 clearly have similar alteration profiles and are enriched in Al_2O_3, Fe_2O_3(T), K_2O, Ba, Rb, and Pb relative to the less altered leucomonzogranite and leucogranite. This enrichment suggests that the fluids responsible for the alteration and mineralisation in both units were similar in fluid composition. Unit 4 and Unit 5 are depleted in SiO_2, Na_2O, CaO, Sr, and Zr.

A) Enrichments and depletions between a greisen (LD-27, Unit 5) and average leucomonzogranite (Unit 1).



B) Enrichments and depletions between greisen (LD-22, Unit 4) and average leucogranite (Unit 2)

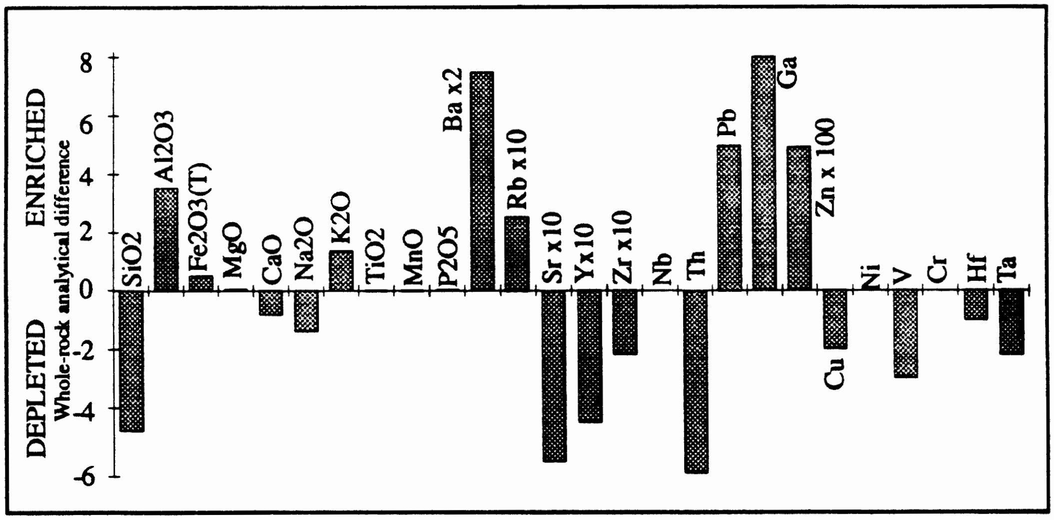


Figure 4.12 The enrichments and depletions occuring between different units at KSL. A) This figure shows the variation between a leucomonzogranite and a greisen that has a leucomonzogranite protolith. B) This figure shows the variation between a leucogranite and a greisen that has a leucogranite protolith.

Oxides and elements that have remained relatively unaltered during fluid interaction are TiO_2, MnO, and P_2O_5.

4.5 Mineralogical Explanation for Geochemistry

The effect of the hydrothermal fluids on the mineral composition and the mineralogy of the five units and a summary of the important reactions which may be taking place within the units, are shown below.

K-feldpathisation

Plagioclase $\longrightarrow$ K-feldspar (perthite)

$$Ca\,Al_2\,Si_2\,O_8 + 4\,SiO_2 + 2\,KCl \longrightarrow 2\,K\,Al\,Si_3\,O_8 + CaCl_2$$

Albitisation and Muscovitisation

K- feldspar $\longrightarrow$ Albite

$$K\,Al\,Si_3\,O_8 + NaCl \longrightarrow Na\,Al\,Si_3\,O_8 + KCl$$

Plagioclase $\longrightarrow$ Albite

$$Ca\,Al_2\,Si_2\,O_8 + 4\,SiO_2 + 2\,NaCl \longrightarrow 2\,Na\,Al\,Si_3\,O_8 + CaCl_2$$

Biotite $\longrightarrow$ Muscovite

$$K_2\,(Fe_5)\,Al\,Si_6\,Al_2\,O_{20}\,(OH)_4 + H_2O + 3\,NaCl + 2\,1/2\,F_2 \longrightarrow$$

$$K_2\,(FeAl)_5\,Al\,Si_6\,O_{20}\,(OH)_4 + AlCl_3 + 3\,NaF + FeO + 2\,HF$$

These equations summarise the alteration processes that occurred at Kempt Snare Lake during albitisation. The final reaction also shows how HF could be liberated during the process of albitisation and how this may alter the fluid conditions to a more acidic pH.

Greisenisation

K-feldpar ⟶ Muscovite and Quartz

$$3\,K\,Al\,Si_3\,O_8 + 4\,HF + 2\,Fe_2O_3 \longrightarrow$$

$$K_2\,(FeAl)_5\,Al\,Si_6\,O_{20}\,(OH)_4 + 3\,SiO_2 + KF + AlF_3$$

Plagioclase ⟶ Muscovite and Quartz

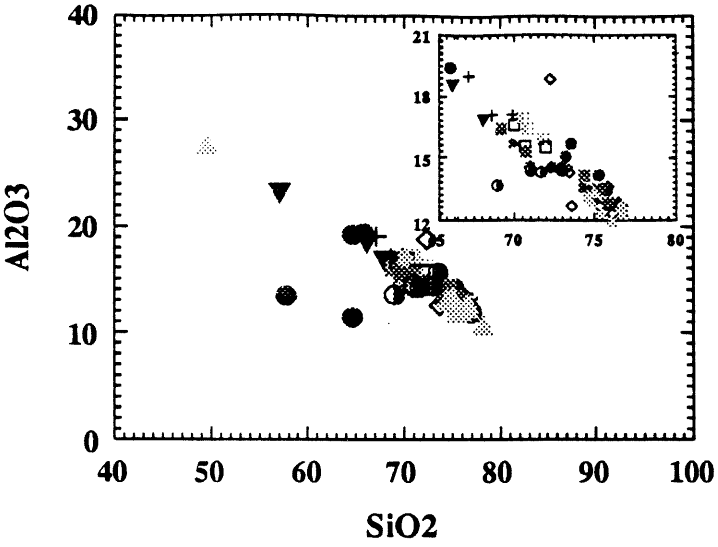
$$3\,Ca\,Al_2\,Si_2\,O_8 + 2\,KCl + 2\,Fe_2O_3 + 16\,HCl \longrightarrow$$

$$K_2\,(FeAl)_5\,Al\,S_6\,O_{20}\,(0H)_4 + 3\,CaCl_2 + 4\,AlCl_3 + 6\,H_2O$$

These reactions show how the whole-rock geochemistry may be explained in terms of the petrography. The alteration assemblages and the whole-rock geochemistry suggest that the fluids at Kempt Snare Lake contained a large percentage of K and Na in the form of dissolved salts. Preliminary observations completed by Soehl (1988) confirmed the presence of salts in fluid inclusions of vein samples from the Kempt Snare Lake lithologies. The equations show how, with time and albitisation, the fluids may have liberated HF producing a more acidic fluid, and this evolved fluid may be responsible for the greisenisation event.

4.6 Comparison of Kempt Snare Lake data with other Plutons from Nova Scotia.

When plotted with data from East Kemptville (Kontak et al. 1988 and 1990; Chatterjee and Strong 1984), South Mountain Batholith (Kontak et al. 1988), Davis Lake Pluton (Richardson 1988), Wedgeport Pluton (Wolfson 1983), other data from Kempt Snare Lake (Soehl 1989; Kontak et al. 1988) and the eastern South Mountain Batholith (Clarke et al 1993b), Kempt Snare Lake plots in similar field to those for other southwestern Nova Scotia (SWNS) plutons (Figures 4.13 and 4.14) These graphs show how the granites of this area have similar trends, probably as a result of similar alteration processes. The granites and greisens of SWNS are characterised by wide La+Ce range and restricted Th content and differ greatly from the leucogranites from the eastern South Mountain Batholith (Fig. 4.15). Figure 4.16 shows the Kempt Snare Lake samples fall on an extension of the Wedgeport sample TiO_2 vs. Zr trend, below the trend produced by Davis Lake Pluton samples, suggesting Kempt Snare Lake samples are depleted in Ti compared to Davis Lake Pluton and East Kemptville samples. However, the granites and greisens from Kempt Snare Lake are distinguished from all the other granites in SWNS by their K/Rb (Fig. 4.17) and Rb/Ba (Fig. 4.18) content where the Kempt Snare Lake samples show a distinct trend. Kempt Snare Lake K/Rb =~60, whereas, the other granites and greisens of this region show a range in value from K/Rb= ~100 to 25. However, as discussed previously, these K/Rb values suggest interaction with fluids, and Kempt Snare Lake may just be unusual in the amount of fluid interaction. Similarly the Rb/Ba ratios of the least altered units at Kempt Snare Lake plot in the region defined by the other granites



Symbols used in the all following figures
● East Kemptville - Chatterjee and Strong, (1984) and Kontak et al., (1988)
◇ East Kemptville - Kontak et al., (1989) ◁ Davis Lake - Sangster, (1990)
◑ SMB - Sangster, (1990) ▲ Wedgeport - Wolfson, (1983)
➤ KSL- Soehl, (1988) × KSL - Kontak et al., (1989)
KSL symbols as in Figure 4.1

Figure 4.13 Al2)3 vs. SiO2 from KSL and Nova Scotia. KSL data define a clear trend.

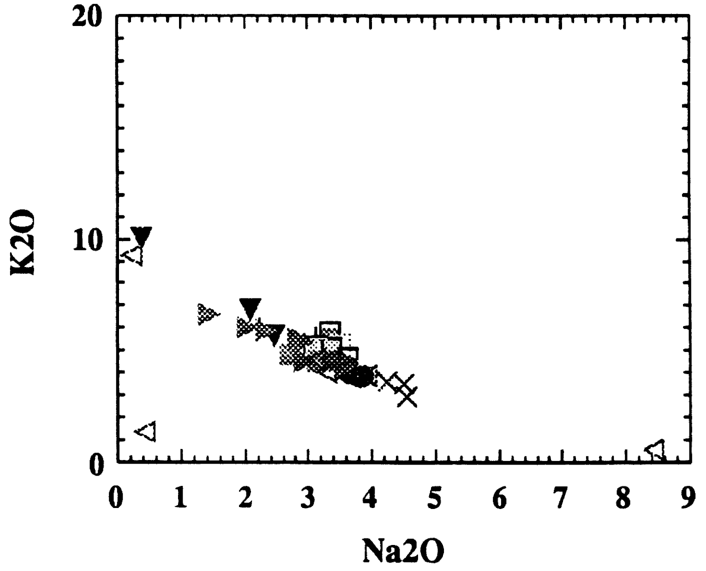


Figure 4.14 K2O vs. Na2O from Nova Scotia and KSL. KSL samples plot along a distinct trend.

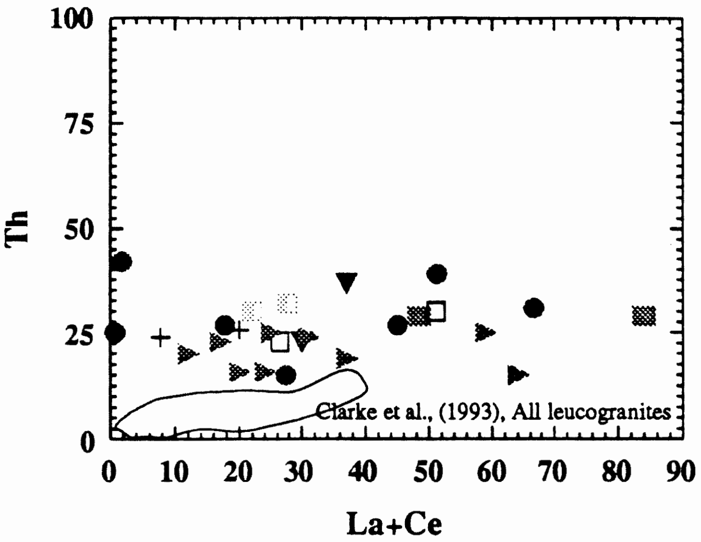


Figure 4.15 Variation of Th/ (La +Ce) at KSL. The southwestern plutons and KSL: have a significantly different profile from the eastern SMB.

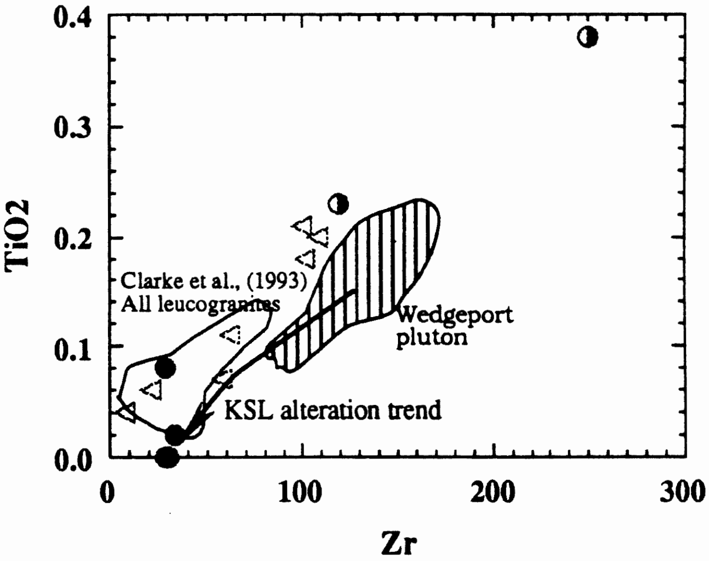


Figure 4.16 TiO2 Vs. Zr from Nova Scotia and KSL. KSL (arrow) plots under the trend observed for the Davis Lake KSL is similar to the Wedgeport and South Mountain Batholith samples.
Pluton trend.

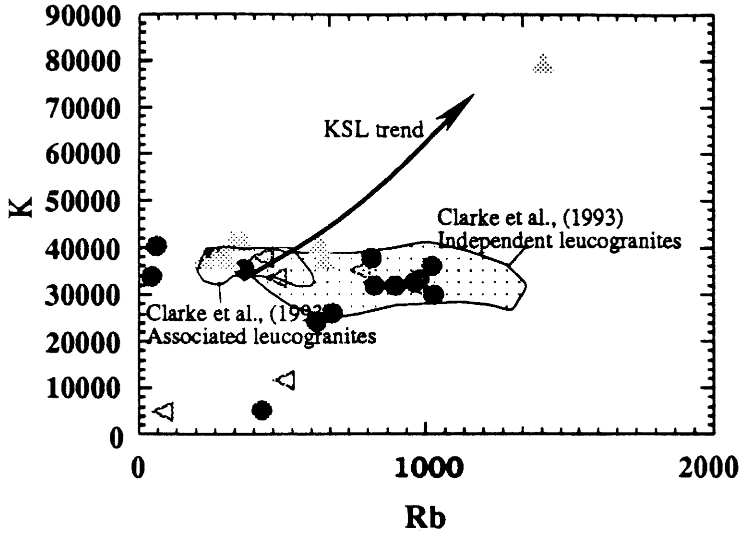


Figure 4.17 K vs. Rb from Nova Scotia and Kempt Snare Lake. KSL samples have a different trend from other plutons in the area and the South Mountain Batholith.

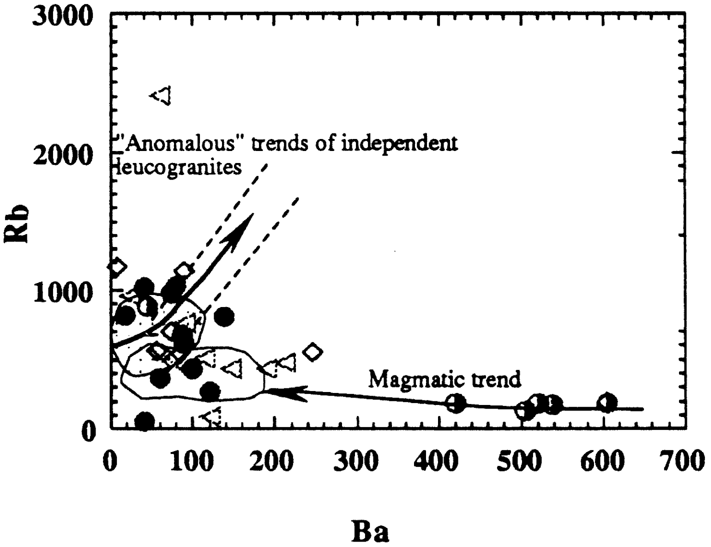


Figure 4.18 Rb vs. Ba from Nova Scotia and Kempt Snare Lake. KSL differs from most of the surrounding plutons, and more closely resembles "anomalous" independent leucogranites from the eastern SMB.

of this area, whereas the greisenised units clearly deviate from this grouping, extending to more Ba-rich compositions, which correspond to the "anomalous independent leucogranites" from Clarke et al (1993b).

Table 4.4 shows the content of the most reliable magmatic chemical signatures for Kempt Snare Lake, with data from the New Ross area in the South Mountain Batholith, and the eastern South Mountain Batholith leucogranites. Kontak et al. (1988) identified two types of leucogranites within the New Ross area. The first type of leucogranite is dominated by crystal-melt equilibria, and formed during a continuing sequence granodiorite-monzogranite-leucogranite. The second type of leucogranite is associated with pegmatite occurrences and formed during fluid interaction. Clarke et al (1993b) identified two types of leucogranite: associated leucogranites, with greisen type mineralisation, produced by hydrothermal alteration of leucomonzogranites; and independent leucogranites, with pegmatite veining, formed by fluid-magma interaction.

Leucogranites at Kempt Snare Lake have higher Zr and ΣREE than the average leucogranite compositions from East Kemptville. The Ta and Zr content of the Kempt Snare Lake leucogranite resembles the associated type, whereas the Nb, ΣREE, La/Yb, Eu/Eu*, and Gd/Yb ratios are similar to the Type 1 leucogranites. The TiO_2 content and La/Sm fall between the Type 1 leucogranites, associated and independent fields. The Nb/Ta ratio of Kempt Snare Lake is Nb/Ta = 4.1+/-0.9. The leucogranites from Kempt

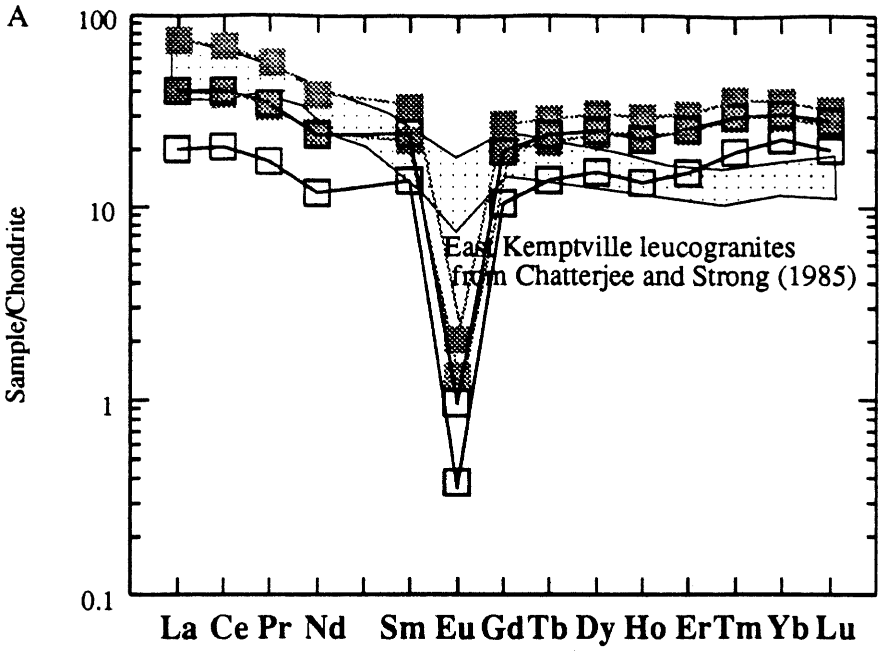
Element/Oxide	Leucogranite KSL	Leucogranite 1 New Ross	Leucogranite 2 New Ross	Associated Eastern SMB	Independent Eastern SMB
Ta	4.3	2.4	16.2	2.9	7.1
Nb	18	19.5	37.2	12.8	23.4
Zr	80	37	28	52	31
TiO2	0.07	0.04	0.005	0.09	0.05
REE(total 10)	56	38	12	34.1	19.9
Eu/Eu*	0.01	0.01 to 0.46	0.07 to 0.11	0.1 to 0.38	0.05 to 0.25
La/Sm	1.5	1.3 to 4.9	2.1 to 4.8	1.54 to 2.22	1.02 to 2.06
La/ Yb	1.1	5 to 22	0.5 to 9.2	6.3 to 9	2.9 to 12.4
Gd/Yb	0.53	2.4 to 6	0.37 to 7.9	1.3 to 2.7	2.4 to 6.8

Table 4.4 Comparison of Kempt Snare Lake leucogranite with those of surrounding plutons. Data for New Ross from Kontak et al. (1988), and Eastern SMB data from Clarke et al. (1993b).

Snare Lake, therefore, do not clearly fall into either of the catagories suggested by either Kontak et al. (1988) or Clarke et al. (1993b).

The REE patterns of the five units at Kempt Snare Lake are similar to those from East Kemptville (Chatterjee and Strong 1985)(Figure 4.19) and Kontak et al. (1990)(Figure 4.4). The REE profile of the Kempt Snare Lake plotted with the leucogranite fields of Clarke et al (1993b) is shown in Figure 4.20. At all these locations the Kempt Snare Lake REE profiles show general depletion in ΣREE compared to their host lithologies, "flattened" overall REE profile, and some enrichment in of the HREE in comparison to the LREE. The patterns at Kempt Snare Lake, however, differ significantly from those of the East Kemptville quartz-topaz greisen (Kontak et al. 1990a; Chatterjee and Strong 1985).

Therefore, on the basis of this study it is possible that although some geochemical similarities exist with the Type 1 leucogranites, associated and independent leucogranites, Kempt Snare Lake samples do not clearly fall in any one category. This difference may be the result of a hybrid (?) type of fluid interaction forming Kempt Snare Lake, with late stage fluid-magma interaction (as seen in independent leucogranite) and suggested by the SiO_2/TiO_2 data, and a later hydrothermal interaction with the Kempt Snare Lake granites (forming greisens as in associated leucogranite). The possible numbers and sources for the fluid are discussed in more detail in Chapter 5.



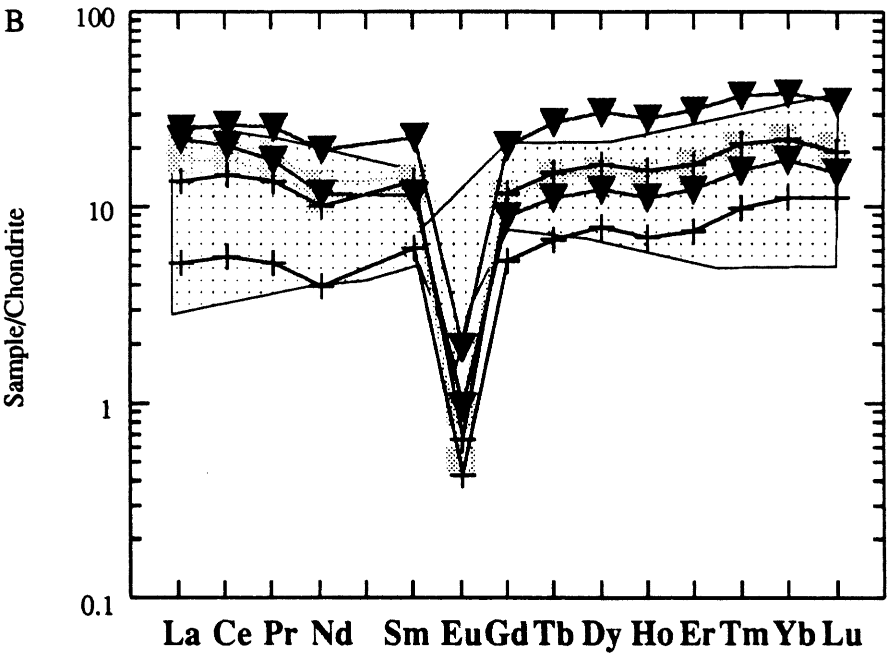


Figure 4.19 The KSL REE from A) granites and B) greisens compared to East Kemptville data from Chatterjee and Strong (1985). The similarity in the REE profiles from the two deposits is clear.

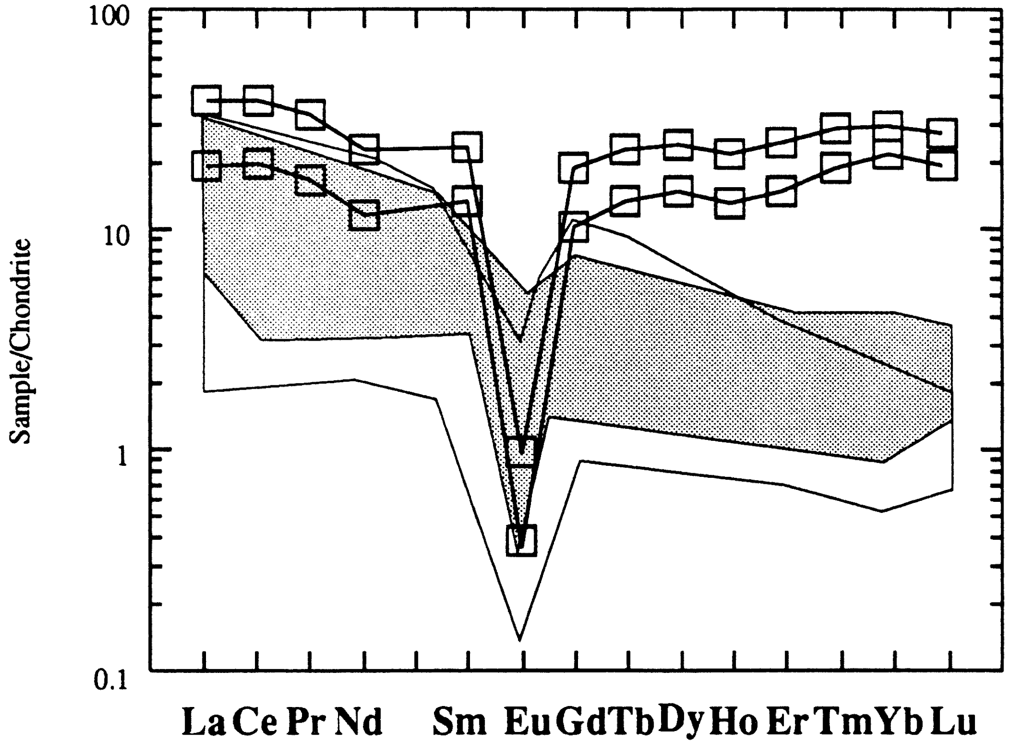


Figure 4.20. REE profiles for KSL and SMB granites. The associated (clear) and the independent (shaded) leucogranites from Clarke et al. 1993b differ from KSL, having lower ΣREE and greater slope to their profiles.

4.7 Summary

With respect to some chemical trends, Kempt Snare Lake lithologies form a distinct grouping within the Meguma Zone granites. Kempt Snare Lake lithologies show enrichments of Al, K, Rb, and Ba which may be explained by the production of muscovite and secondary K-feldspar during the K-feldspathisation and greisenisation processes. Similarly, reductions in Na_2O, and CaO may be caused by the processes of albitisation of magmatic plagioclase and K-feldspar. Kempt Snare Lake appears to be unique, with a distinctive K/Rb trend. The trends noted previously in conjunction with the mineralogy indicate the alteration fluid at Kempt Snare Lake was enriched in K and CO_2. The REE patterns from Kempt Snare Lake and other greisens of SWNS suggest that the hydrothermal fluids were capable of either carrying HREE, or preferentially stripping LREE resulting in the REE profiles found at Kempt Snare Lake. The style of mineralisation and the relationship between the least and most altered units at Kempt Snare Lake suggest that a late stage fluid-magma interaction took place, resulting in the leucogranite (Unit 2) being evolved from the leucomonzogranite (Unit 1). Geochemically the TiO_2 vs. Zr content of Kempt Snare Lake more closely resembles the Wedgeport Pluton than the Davis Lake or South Mountain Batholith granites. There is extensive evidence for hyrothermal fluid interaction, which may been produced by the same fluid as the magmatic interaction or may be the result of a later fluid pulse. These options are discussed in more detail with the results of the stable isotope analyses.

CHAPTER 5 - STABLE ISOTOPES

5.1 Introduction

Stable isotopes can provide information on the sources, numbers, and temperatures of mineralising fluids that form mineral deposits. In this study, sulphur, carbon, oxygen, and hydrogen isotopic signatures of minerals occurring at Kempt Snare Lake were measured to gain an understanding of the mineralising history at Kempt Snare Lake. Appendix B contains the mineral separation and stable isotope analytical techniques.

5.2 Stable Isotope Analyses

All the stable isotope analyses were carried out in the stable isotope laboratory at the University of Western Ontario, London, Ontario, under the direction of Dr. Fred Longstaffe and Mr. Paul Middlestead. For the purposes of this thesis, the results from all rock and vein samples are discussed separately. Analytical error for all stable isotope analyses is +/- 0.2 per mil. The samples for this study were run with internal laboratory standards from the University of Western Ontario laboratory, and internationally recognised standard samples. Results for the international standards were within +/- 0.1 per mil for carbon analyses and +/- 0.2 per mil for other isotopic systems. The isotopic results are presented relative to the international reference standards. For oxygen and hydrogen isotopic results the reference used is Standard Mean Ocean Water (SMOW), for carbon isotopic results the Pee Dee Belemnite (PDB), and for sulphur analyses the reference standard is the Cañon Diablo Troilite (CDT).

5.3 Results from Silicate Minerals

5.3.1 Oxygen from Granite and Greisen Silicates

Table 5.1 shows the results of the isotopic analyses of mineral samples from the five lithological units at Kempt Snare Lake. Little variation occurs within the quartz values of the different units ($\delta^{18}O$ = 10.5 to 10.9‰, n =10), within the feldspar values ($\delta^{18}O$ = 9.3 to 10.3 ‰, n =10), or within the muscovite samples ($\delta^{18}O$ = 6.9 to 8.0‰, n = 7) (Figure 5.1). Regardless of the degree of alteration, the isotopic composition of the minerals is similar, indicating that all units have been affected by similar fluids under similar conditions. The amount of oxygen enrichment ($\delta^{18}O$ quartz- $\delta^{18}O$ feldspar = $\Delta_{q\text{-}f}$), that occurs between quartz and K-feldspar within granitoids which are in equilibrium under magmatic conditions, is $\delta^{18}O$ = 2 +/- 0.4 ‰ (Longstaffe 1982). All the units within Kempt Snare Lake show a smaller $\Delta_{q\text{-}f}$, varying from 0.5 to 1.3 ‰. The $\Delta_{q\text{-}m}$ that is expected to occur under magmatic conditions between quartz and muscovite in granitoids is 3.8 +/- 0.3 ‰ (Longstaffe 1982). At Kempt Snare Lake, the $\Delta_{q\text{-}m}$ = 2.7 to 3.7 ‰.

Tables 5.3 and 5.4 show the temperatures calculated from quartz-K-feldspar pairs and quartz-muscovite pairs. The results from the quartz-feldspar pairs from all rocks average approximately 730 °C, and these are significantly higher than the quartz-muscovite pairs, which average at 480 °C. These temperatures indicate that all the minerals are not in equilibrium with each other. As described in Section 3.2, the feldspars show evidence of

	Quartz	K-feldspar	Muscovite		Graphite
Sample	δ180	δ180	δ180	δD	δ13 C
Unit 1 LD-10	10.9	9.9	7.2	-43.1	-17.2
LD-11	10.8	10.3			-20.3
Unit 2 LD-34	10.6	9.6			-20.6
LD-44	10.6	10.0	7.5	-39.8	
Unit 3 LD-42	10.6	9.6	7.3		-21.4
LD-36	10.6	9.6	6.9	-46.4	-20.6
Unit 4 LD-22	10.7	9.9	7.6		-27.0
LD-24	10.7	9.4	8.0	-58.1	-26.6
Unit 5 LD-25	10.5	9.3	7.3	-53.8	-27.0
LD-27	10.7	9.8			-25.9

Table 5.1 Results of stable isotope analyses on granitoid mineral samples.

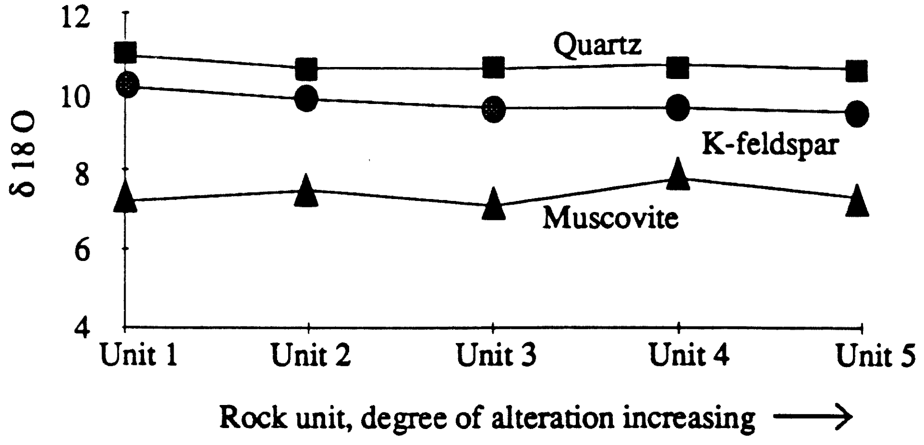


Figure 5.1 The variation in oxygen signature from silicate minerals in the five units occurring at Kempt Snare Lake. The isotopic composition of all the lithologies is very similar suggesting that all units have undergone the same processes.

Table 5.2 Oxygen and hydrogen isotope geothermometric equations.

Mineral Pair (a-b)	Equation Coefficient	T Range °C	Reference
OXYGEN			
1 Quartz-muscovite	A= 2.2 B= - 0.6	>500	Bottinga and Javoy 1973
2 Quartz-K-feldspar	A = 1.19 B = -0.29	500-800	Bottinga and Javoy (1973) Quartz-water, and K-feldspar -water.
3 Quartz-calcite	A= 1.32 B = -0.3	500-800	From Quartz-water, Bottinga and Javoy (1973) and Calcite -water, O'Neil et al. (1969))
HYDROGEN			
4 Muscovite - water	A = -22.1 B = +19.1	400 - 850	Suzuoki and Epstein (1976)

$$\text{Where } T(K) = \left[\frac{A * 10^6}{\Delta_{a-b} - B}\right]^{1/2}$$

For an analytical precision (P) of 0.2 per mil, the temperature errors can be calculated by

$$\pm T\,(^\circ C) = \frac{T(K)^3 * P}{A * 10^6 * 2}$$

Table 5.3 Geothermometric calculations from granitoid quartz and feldspar.

Sample	Quartz δ180	K-feldspar δ180	$\Delta_{q\text{-}f}$	Temp °C (Table 5.2, eq 2)	δ180 fluid in equilibrium with Qtz. at 730°C
Unit 1 LD-10	10.9	9.9	1.0	687 ±74	10.4
LD-11	10.8	10.3	0.5	954± 155	10.8
Unit 2 LD-34	10.6	9.6	1.0	687±74	10.1
LD-44	10.6	10.0	0.6	883±130	10.5
Unit 3 LD-42	10.6	9.6	1.0	687±74	10.1
LD-36	10.6	9.6	1.0	687±74	10.1
Unit 4 LD-22	10.7	9.9	0.8	771±96	10.4
LD-24	10.7	9.4	1.3	592±96	9.9
Unit 5 LD-25	10.5	9.3	1.2	620±60	9.8
LD-27	10.7	9.8	0.9	727±84	10.3

Results of geothermometry for quartz-K-feldspar pairs. The oxygen isotopic composition of a fluid in equilibrium with quartz at the temperature indicated is also calculated.

Table 5.4 Geothermemetric calculations from granitoid and vein quartz and muscovite.

Sample	Quartz δ180	Muscovite δ180	$\Delta_{q\text{-}m}$	Temp °C (Table 5.2, eq 1)	δ180 fluid in equilibrium with	
					Muscovite	Quartz
Unit 1 LD-10	10.9	7.2	3.7	442 ±17	6.9	6.6
Unit 2 LD-44	10.6	7.5	3.1	498±21	7.3	7.4
Unit 3 LD-42	10.6	7.3	3.3	478 ±19	7.1	7.0
LD-36	10.6	6.9	3.7	442 ±17	6.6	6.3
Unit 4 LD-22	10.7	7.6	3.1	498±21	7.4	7.5
LD-24	10.7	8.0	2.7	543±25	7.8	8.2
Unit 5 LD-25	10.5	7.3	3.2	487± 20	7.1	7.1
Vein LD-50	11.1	7.1	3.0	508 ±22	6.9	8.1
LD-60	10.5	6.7	3.8	434 ±16	6.4	6.0

Results of geothermometry carried out on quartz-muscovite pairs from Kempt Snare Lake.

alteration, with cloudy, weathered appearance, high graphite content and albite and sericite alteration. In addition, some of the K-feldspars suggest they are secondary in origin and did not form at the same time as the quartz and muscovite; therefore, this evidence suggests that the isotopic composition of the feldspar is also not in equilibrium with the other minerals.

The greater resetting of the $\delta^{18}O$ of the feldspar compared to the other minerals is a result of their different interaction with fluids. Quartz is exceptionally resistant to reequilibration, even at high temperatures, and muscovite is also likely to retain its original isotopic composition when in contact with alteration fluids. The $\Delta_{q\text{-}m}$ at Kempt Snare Lake suggests equilibrium with high temperature fluids. The $\Delta_{q\text{-}f}$ values from Kempt Snare Lake are smaller than those usually found in unaltered granitoids (Longstaffe 1980). These small values gives the impression of high temperature magmatic processes, however, the low closing temperature of feldspars (~100 °C) means that reequilibration of the isotopic composition of feldspars is very common, and they rarely reflect equilibrium with other minerals (Longstaffe 1980). The quartz values from Kempt Snare Lake probably reflect high temperature environments, whereas the feldspar values are the result of continued reequilibration of the feldspars with the alteration fluids to lower temperatures, which resulted in an increase of the feldspar isotopic signatures. This increase in values caused the $\Delta_{q\text{-}f}$ to become smaller than usually present in granitoids, and resulted in temperatures higher than for the $\Delta_{q\text{-}m}$ pairs from Kempt Snare Lake.

The similarity of all the oxygen values from all the units suggests that, even in the least altered units, the quartz- K-feldspar values do not reflect magmatic temperatures and are the result of continued reequilibration of the feldspar as the fluids and the magma cooled. A temperature of 480 °C reflects subsolidus conditions, and is not representative of magmatic processes. This lower temperature is expected because of the formation and reequilibration of the minerals during the cooling of the pluton, and reflects a minimum temperature for the fluids which entered the cupola.

Aqueous fluids in equilibrium with the quartz and muscovite minerals at 480 °C have a $\delta^{18}O = 6.0$ to 8.2 ‰ . A fluid with this composition falls within the range normally attributed to primary magmatic fluids (range $\delta^{18}O = 5.5$ to 9.5 ‰, Sheppard 1986; Sheppard et al. 1969; Taylor 1974); however, this range also overlaps with fluids of metamorphic origin (Taylor 1974).

5.3.2 Oxygen from Vein Silicates

As shown in Table 5.5, the values for vein quartz range from $\delta^{18}O =$ +9.9 to +11.1 ‰, with a mean value of $\delta^{18}O = 10.6$ ‰ (n=8). The values from three vein muscovite samples are $\delta^{18}O = 6.7$, 7.1, and 7.4 ‰. The $\Delta_{q\text{-}m}$ for two vein samples is similar to all the unit samples at 4.0 and 3.8 per mil, reflecting samples that are approximately in equilibrium with hot fluids. Geothermometry carried out on these two samples revealed temperatures of 508 +/- 22 °C and 434 +/-16 °C, respectively. These temperatures are

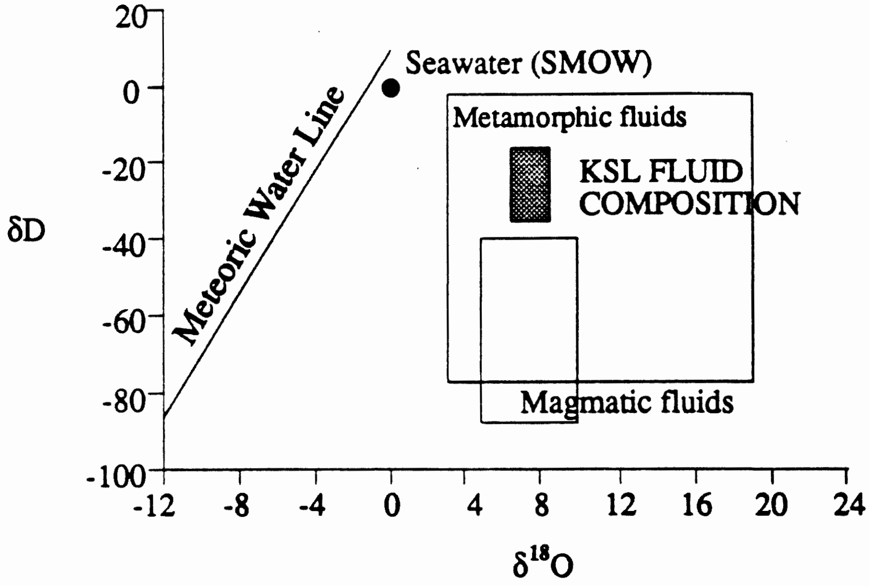


Figure 5.2 Composition of fluids in equilibrium at 480℃ with from quartz and muscovite samples from Kempt Snare Lake.

Vein	Quartz	Muscovite		Siderite	
Sample	δ180	δ180	δD	δ180	δ13C
LD-12	10.6			26.2	-14.1
LD-16	11.0				
LD-18				9.5	-15.4
LD-29	10.6			12.8	-15.8
LD-32	9.9				
LD-35	10.5			9.5	-16.1
LD-46		7.4	-40.4		
LD-47				9.3	-16.2
LD-49				26.5	-14.0
LD-49R	10.6			26.4	-14.1
LD-50	11.1	7.1		9.5	-17.6
LD-52				9.5	-17.9
LD-52R				9.2	-18.0
LD-56				27.5	-15.9
LD-60	10.5	6.7			
LD-64				10.4	-15.2

Table 5.5 Results of isotopic analyses from vein mineral samples.

consistent with those derived from quartz-muscovite pairs in the host units. The composition of a fluid in equilibrium with these vein samples at 480 °C would have had a value of $\delta^{18}O$ ~ 7.5 ‰. These fluid values also overlap the magmatic and metamorphic fields outlined by Taylor (1974).

5.3.3 Hydrogen from Granite, Greisen, and Vein Muscovite

The results of hydrogen analyses completed on 6 muscovite samples are shown in Tables 5.1 and 5.5. These values are similar to other muscovite samples found within granitoid rocks (Taylor 1974). All the samples, regardless of type, have similar hydrogen values and represent a relatively narrow range (δD = -39.8 to -59.1‰). Using the hydrogen equilibration equation of Suzuoki and Epstein (1976) a fluid in equilibrium with muscovites of this composition at a temperature of 480 °C would have a δD ~ -35 to -16.5 ‰. Figure 5.2 shows the fields usually applied to magmatic, metamorphic, meteoric, and ocean water calculated by Taylor (1974). The Kempt Snare Lake fluids fall outside the range usually applied to magmatic fluids.

5.4 Results from Carbon-Bearing Minerals

5.4.1 Graphite from Granite and Greisen Samples

Graphite from 9 of the 10 unit samples ranged from $\delta^{13}C$ = -27.0 to -17.2 ‰. A spatial relationship exists in which the highly altered units have values around $\delta^{13}C$ = -27‰, the

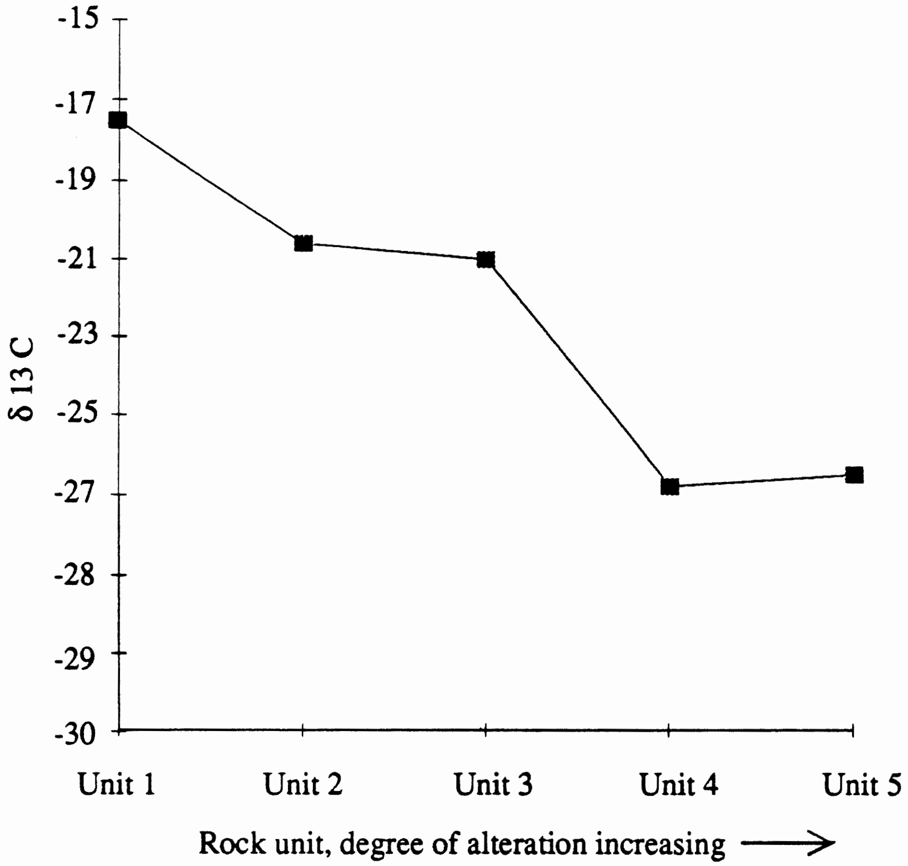


Figure 5.3 The variation in graphite composition with the degree of alteration. The more altered greisens have an organic isotopic signature, very different from the less altered granitic units, which have a mixed organic/carbonate isotopic signature.

middle stage of alteration has values around $\delta^{13}C$ = -20 ‰, and the least altered unit has a value of $\delta^{13}C$ = -17 ‰ (Figure 5.3 and Table 5.1).

5.4.2 Vein Carbonates - Siderite

As discussed in Chapter 3, the two different phases of siderite at Kempt Snare Lake are distinguished by their appearance and composition (Table 5.6). The two different groups of siderite are also isotopically distinct (Figure 5.4), with Type 1 having much higher $\delta^{18}O$ than Type 2. The results of the carbon and oxygen analyses on the carbonate samples are discussed separately.

Carbon The carbon values for all the siderites range from $\delta^{13}C$ = -14.1 to -18.0 ‰, suggesting that during siderite formation, irrespective of type, the carbon reservoir and fluid conditions remained relatively constant. Values around $\delta^{13}C$ = -15 ‰ may reflect carbon of mixed origin, inheriting one portion from organic matter (values around -25‰) and another portion from freshwater/seawater carbonates (values between +5 and -14 ‰). Carbon values from Kempt Snare Lake carbonates have $\delta^{13}C$ similar to Meguma Group carbonate nodules ($\delta^{13}C$ = -14.8 to -22.2 ‰, Graves et al. 1988), suggesting that they may be a possible source for the carbon. The shaly organic-rich Halifax Formation of the Meguma Group has also been proposed as a source rock for hydrocarbons (Zentilli

Table 5.6 Characteristics of the two siderite types.

	Petrographic	Chemical	Isotopic		Formation
		Fe:Mn	Oxygen	Carbon	
Type 1	anhedral, blackened, corroded crystals	5:4	~ 9.5	~ -15.0	High temp
Type 2	euhedral, clean crystals	4:1	~ 26.5	~ -14.5	Low temp

et al. 1992) and could, therefore, provide carbon with an organic signature, but no isotopic results from this material is available.

Oxygen The oxygen values from siderites suggest a more complicated history. Type 1 siderites have $\delta^{18}O = 9.2$ to 9.5 ‰ (n = 6). Oxygen values such as these represent high temperature environments (Lynch et al. 1990). Quartz-siderite pairs for Type 1 siderite show that quartz is enriched by 1.0 to 1.6 per mil, suggesting equilibrium assemblages. No high-temperature fractionation factors exist for siderite, but if the fractionation is assumed to be similar to other carbonates, the temperatures of formation for these siderites vary from 875 to 560 °C . Type 2 siderites have $\delta^{18}O = 26.2$ to 27.5 ‰ (n = 4), which is more characteristic of diagenetically formed siderites (MacInnis 1985; Kontak et al. 1988). Assuming the same fractionation equation for these samples as Type 1 siderites, Type 2 temperatures are negative (°C), indicating that the oxygen of these samples was not in equilibrium with coexisting quartz. Two samples have oxygen values between these two fields with $\delta^{18}O = 10.4$ and 12.8 ‰ These samples may represent slight mixing of the two types of siderite, as the Type 1 siderite was reequilibrating to form Type 2 siderite. These isotopic differences suggest that the Type 1 siderite formed during the initial veining event from a hot fluid, and that the Type 2 siderite generation, either as new mineral growth, or as reequilibration of preexisting siderite, occurred during a low-temperature event.

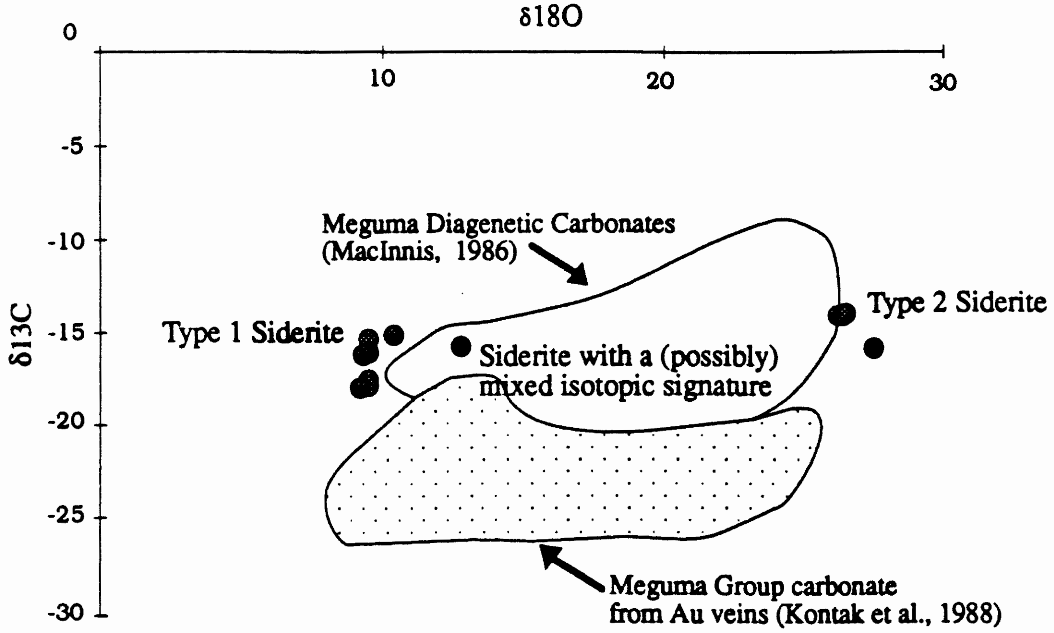


Figure 5.4 The variation in siderite values from Kempt Snare Lake. Two distinct groups of siderite can be distinguished by their isotopic composition.

5.5 Results of Sulphur Analyses

The results of the sulphur analyses are shown in Table 5.7. The sulphide values obtained at Kempt Snare Lake range from $\delta^{34}S = 6.9$ to 10.5 ‰. According to Ohmoto and Rye (1979) this spread of values represents a narrow range for variations in $\delta^{34}S$ in minerals of one deposit, as well as for different locations and times during the paragenetic sequence. Values from three pyrrhotites from the Goldenville Formation rocks surrounding Kempt Snare Lake are $\delta^{34}S = 8.7$, 9.4, and 9.9 ‰.

Bachinski (1969) established the order of $\delta^{34}S$ enrichment that occurs in natural systems. The sulphide minerals at Kempt Snare Lake correspond to the pattern established by Bachinski (1969), and suggest that the Kempt Snare Lake samples record crystallisation conditions. Geothermometry carried out on coexisting sulphide pairs indicates temperatures between 430 - 600 °C. These temperatures are higher than those suggested by preliminary fluid inclusion work completed by Soehl (1988).

5.6 Summary

The similarity in the fluid composition of all the veins and granite and greisen silicate mineral samples suggests that one fluid dominates the main alteration, greisenisation, and mineralising stages at Kempt Snare Lake. The graphite compositions suggest a carbon-rich fluid or carbon from the Meguma Group lithologies entered the cupola during certain stages. The fluid entered early in the cooling history of the cupola and remained until the

Table 5.7 Results of sulphide stable isotope analyses and geothermometry from veins and Meguma.

Sample	Sphalerite δ34S	Galena δ34S	Pyrite δ34S	Chalco δ34S	Arseno δ34S	Pyrrhotite δ34S	$\Delta_{a\text{-}b}$	Temp °C
KSL								
LD-12			9.2	8.3			0.9^{1}	433 ± 40
LD-16		6.9		7.8			0.9^{2}	518 ± 50
LD-30	10.0				10.2			
LD-49			9.3	8.7			0.6^{1}	593 ± 50
LD-51					10.5			
LD-58	8.2	7.1					1.1^{3}	542 ± 45
MEGUMA								
M-7						8.7		
M-3						9.9		
M-9						9.4		

Results of sulphide isotopic analyses, where temperatures were calculated using the equation from Ohmoto and Rye (1979),

$$T\,(K) = \frac{A * 10^{3}}{\Delta_{a\text{-}b}^{1/2}}$$

where

1 Δ pyrite-chalcopyrite — $A = 0.67 \pm 0.04$

2 Δ chalcopyrite- galena — $A = 0.76 \pm 0.05$

From galena-H_2S and chalcopyrite-H_2S
(Ohmoto and Rye 1979)

3 Δ sphalerite - galena — $A=0.85 \pm 0.03$

last veining stages. The dominant fluid has an igneous / metamorphic composition and remained relatively constant in composition throughout all the alteration and mineralising stages.

CHAPTER 6 - DISCUSSION

6.1 Introduction

This chapter presents a discussion of the results from the investigation carried out at Kempt Snare Lake, and a comparison with other stable isotope data from the region. A model for the formation of Kempt Snare Lake is proposed on the basis of these results.

6.2 Silicate Stable Isotope Results

6.2.1 Interpretation of Silicate Results from Kempt Snare Lake

If the present isotopic mineral signatures result primarily from magmatic processes, with a later overprinting by fluids, the amount of reequilibration can be assessed through the isotopic variation between the same mineral pairs in different rock units that show different degrees of alteration. If the units at Kempt Snare Lake primarily have igneous values that have been altered by later fluids, the more altered units would be expected to show a greater amount of feldspar $\delta^{18}O$ enrichment. The mineral separates from Kempt Snare Lake do not show such a pattern, and greisenised units have similar values to the granite units. The consistency of the quartz, feldspar, and muscovite isotopic values, irrespective of the degree of alteration, suggests that all the units have been affected by similar fluids and similar magmatic and alteration processes.

The similarity in the oxygen isotopic signature of both the vein and granitoid samples suggests the isotopic compositions of the granitoid samples were produced by the same fluid that the veins now represent. The isotopic signature of the minerals, both granitoid and vein samples, corresponds to the a fluid value, $\delta^{18}O$ ~ 7.5 per mil and δD ~ -35 per mil, for fluids at 480°C.

The oxygen composition of this fluid falls within the range usually applied to magmatic (mantle) origin. The hydrogen values, however, are more consistent with metamorphic fluids. The Kempt Snare Lake fluids plot in the metamorphic region described by Talyor (1974) (Figure 5.2), and could suggest that the fluids were totally derived from metamorphic rocks; however, the nearby cooling South Mountain Batholith could provide a large source of igneous fluids to enter the polymetallic region (~ 2 x the volume of Lake Ontario has been calculated as a being dissolved within the granitic magma of the South Mountain Batholith (Clarke 1992). Clarke et al. (1993b), Poulson et al. (1991) and Longstaffe et al. (1980) have all suggested that the South Mountain Batholith is partly composed of Meguma and other metasedimentary material. The interaction of Meguma Group metamorphic rocks to modify the South Mountain Batholith magma would be likely to affect the isotopic composition of the fluids derived from the magma to more metamorphic signatures. This assimilation of crustal, metamorphic lithologies, therefore, provides an explanation for the mixed metamorphic/magmatic oxygen and hydrogen signatures for the Kempt Snare Lake deposit.

6.2.2 Comparison with Other Studies in Nova Scotia

Whole-rock $\delta^{18}O$ values for the South Mountain Batholith range from $\delta^{18}O = +10.1$ to +12 ‰, whereas some discrete plutons in southern Nova Scotia have lower $\delta^{18}O = 7.8$ to +10.4 ‰ (Longstaffe et al., 1980). Clarke et al. (1993b) established the oxygen isotope signatures from leucogranites within the eastern South Mountain Batholith at $\delta^{18}O = 11.2$ +/- 1.2 ‰ for "associated " leucogranites and $\delta^{18}O = 11.4$ +/- 0.5 ‰ for "independent" leucogranites (Figure 6.1). The data of Clarke et al. (1993b) therefore, fall within the range for the South Mountain Batholith established by Longstaffe et al. (1980). Mineral separate analyses were carried out in this study, and when the individual minerals are taken together a rough comparison to whole-rock data can be made. The weighted averages for the Kempt Snare Lake lithologies are: Unit 1, leucomonzogranite $\delta^{18}O = 10.1$ ‰; Unit 2, leucogranite $\delta^{18}O = 10.1$ ‰; Unit 3, greisenised granite $\delta^{18}O = 9.6$ ‰; Unit 4, fine-grained greisen $\delta^{18}O = 9.8$ ‰; and Unit 5, porphyritic greisen $\delta^{18}O = 10.0$ ‰. The Kempt Snare Lake granites fall at the lower end of the range established by Longstaffe et al. (1980) for the South Mountain Batholith, but are within the range identified for other discrete plutons in southern Nova Scotia. The greisens fall within the range for the discrete plutons. Longstaffe et al. (1980) interpreted the isotopic difference between these two types of plutons to be the results of slightly different processes. The South Mountain Batholith samples were thought to be the result of anatexis involving ^{18}O-rich clastic

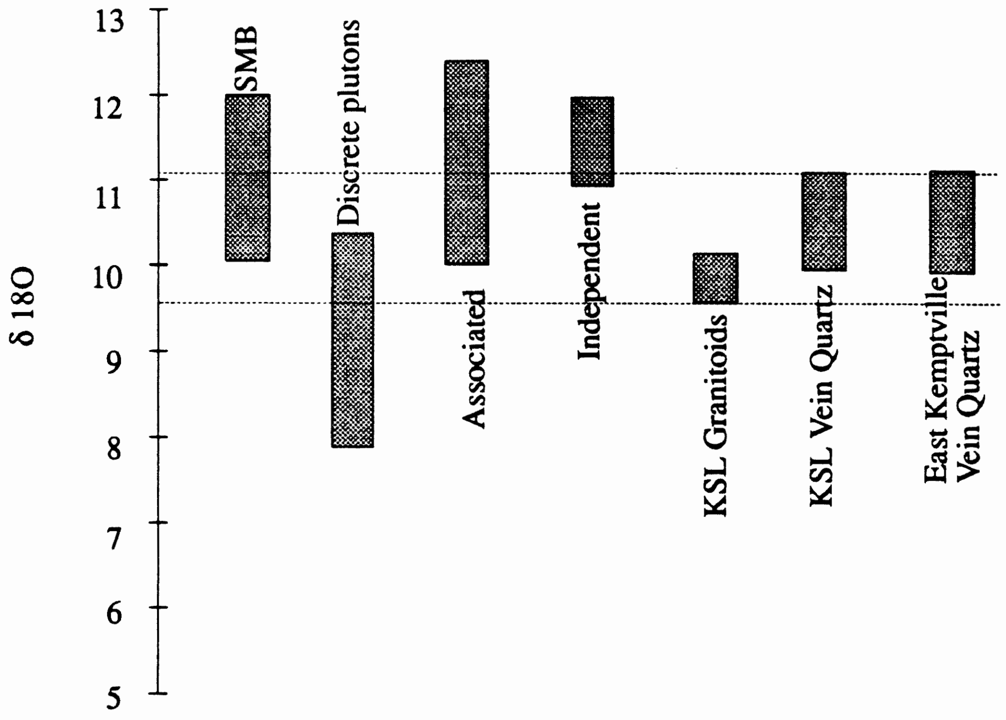


Figure 6.1 The variation in whole-rock oxygen isotope compositions among the granites of southwestern Nova Scotia. Data for Kempt Snare Lake- this study, South Mountain Batholith -Longstaffe et al. (1980) and Clarke et al. (1993b), and East Kemptville - Kontak (1988).

metasedimentary units, whereas the distinct southern plutons indicate interaction with a low ^{18}O source, possibly, mafic magmas (Longstaffe et al. 1980).

The oxygen values from vein samples closely correspond to those obtained by Kontak (1988) for the East Kemptville deposit, where vein quartz from the sulphide stage of mineralisation ranges from $\delta^{18}O = 9.9$ to 11.1 ‰. Kontak (1988) interpreted these values to suggest a magmatic fluid was responsible for the veining at East Kemptville. This interpretation is similar to that obtained for the Kempt Snare Lake mineral prospect, located around 20 km southwest of East Kemptville.

The mixed metamorphic/magmatic signature for the oxygen and hydrogen isotopic data corresponds to other geochemical data which show crustal components within the Nova Scotia granitoids. On the basis of strontium-neodymium isotopic relationships, Clarke et al. (1995) and Tate (1995) distinguished two major divisions in the granitoids, the Central plutons, and the Peripheral plutons. They proposed that the Central plutons (e.g., South Mountain Batholith) formed from the partial melting of lower crustal units (Tangier felsic source) with Meguma Group contamination, whereas, the Peripheral plutons (e.g., Shelburne pluton, Barrington Passage pluton) are hybridised products of crustal Tangier felsic and sources and mantle-derived Tangier mafic sources, and Late Devonian mafic intrusion magmas. Kempt Snare Lake cupola falls on the boundary of these two types of plutons.

6.3 Sulphur Isotopic Results

6.3.1 Interpretation of Sulphur from Kempt Snare Lake

Sulphur from a mantle source has $\delta^{34}S = 0$ ‰ (Ohmoto 1972). A large deviation from $\delta^{34}S = 0$ ‰ (ca. 7 per mil deviation) was inferred to be the result of biologic processes (Jensen 1967); however, work completed by Sakai (1968), and Ohmoto (1972) suggested that the range of values and the average of these values may reveal more about the fluid conditions than just the source region. The narrow range of $\delta^{34}S$ sulphide values at Kempt Snare Lake suggests that H_2S was the dominant sulphur species, and in such environments, the $\delta^{34}S$ of the minerals is a good indication of the $\delta^{34}S$ of the fluids from which the sulphides crystallised (Ohmoto and Rye 1979). The narrow range of isotopic composition for the sulphides also suggests that, during sulphide precipitation, the fluid conditions remained constant. The similarity in sulphide mineralisation values and the Meguma sedimentary units, suggest that the country rocks may be the source region for the sulphur within Kempt Snare Lake.

Information on the composition of the mineralising fluids at higher temperatures can be established by the stability fields of chalcopyrite. McKenzie and Helgeson (1985) showed the effects of changing temperatures and activities of Fe^{2+} and Cu^{+} on the stabilities of Fe-Cu sulphides. Figure 6.2 shows the effect of temperature and fH_2S on the stability field of chalcopyrite. The stability field of chalcopyrite shrinks with higher temperatures and higher fH_2S. These figures also suggest that, even at higher temperatures, the pH of the

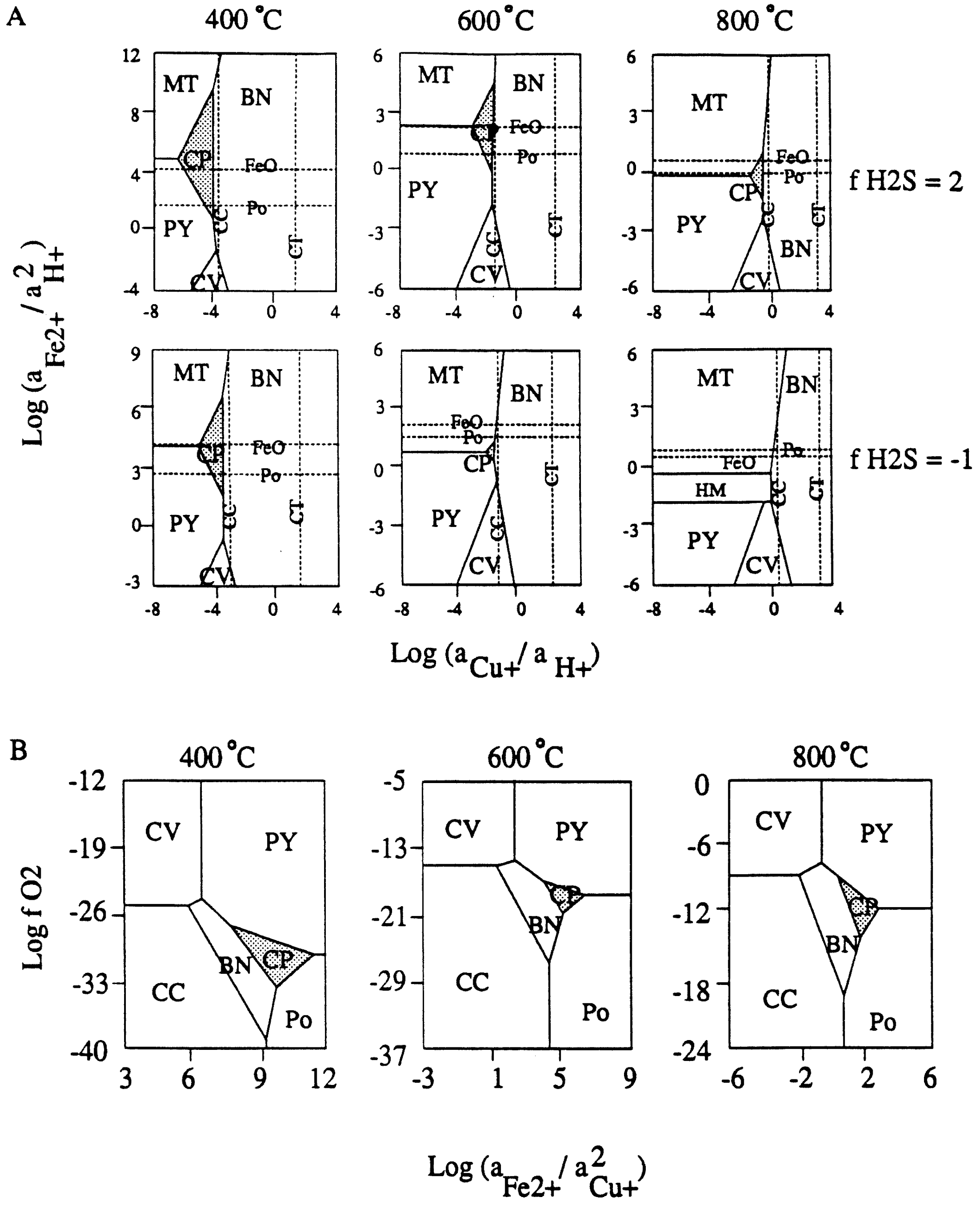


Figure 6.2 Logarithmic activity diagrams for the system Cu_2-FeS-H_2S-O_2-H_2O-HCl at 2 kb and 400, 600, and 800°C for (A) log activity H_2O = 0 and log f H_2S =2 and -1, and (B) log activity H_2O = 0 and log f H_2S = 2. The stability field of chalcopyrite is affected by the temperature and the H_2S fugacity of the fluid. BN = bornite, CP = chalcopyrite, PY= pyrite, CV = covellite, CC= chalcocite, Po = pyrrhotite MT= magnetite and HM = hematite, from McKenzie and Helgeson (1985).

solution can affect the sulphide mineral species present, with chalcopyrite and pyrite favouring more acidic conditions, and bornite more stable at higher values of pH. The absence of bornite and covellite from the Kempt Snare Lake assemblages restricts the fluid conditions to the left side of the figures, where the Cu^+/ H^+ ratio is lower and the pH is more acidic. The stability field of chalcopyrite is also larger if the $f\,H_2S$ is greater (Figure 6.2). The effect of $f\,O_2$ on the sulphide species formed at these higher temperatures (400 - 800 °C) is also shown by McKenzie and Helgeson (1985) where increasing temperatures cause the $f\,O_2$ to increase also, and the stability of pyrite and chalcopyrite are influenced by the $f\,O_2$ conditions. These figures show that chalcopyrite can be stable in fluids at high temperatures, if the $f\,H_2S$ is relatively high and the fluids are iron rich (McKenzie and Helgeson 1985).

The stability of the vein minerals (chalcopyrite, pyrite, and muscovite) as the mineralising fluid cooled also suggests low $f\,O_2$ conditions. Scott (1974) showed how the stability of Fe-bearing sulphides is affected by $f\,O_2$ and $f\,S_2$, and proposed, that for pyrite and pyrrhotite to form in preference to hematite and magnetite, the $f\,O_2$ and the pH must be low, suggesting that H_2S is the dominant sulphur species (Figure 6.3). Although the carbonates suggest that the $f\,O_2$ conditions of the fluid were higher than during graphite precipitation, if the fluids suddenly became highly oxidising, all the graphite from the wall-rock/ vein boundary would have formed carbonate, and a different sulphide mineralogy assemblage would occur. Barnes (1979) indicated that the absence of bornite + pyrite in

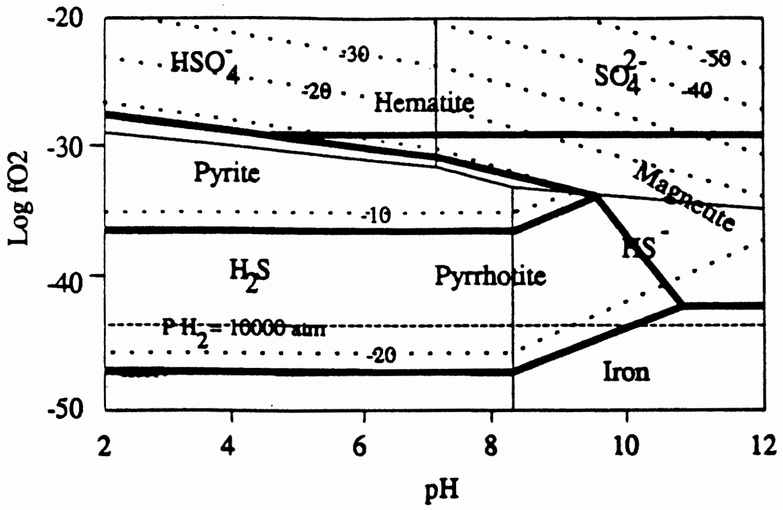


Figure 6.3 Distribution of solid phases of the Fe-S-O system and the predominant sulphur-bearing aqueous species as a function of oxygen fugacity and pH at 300℃. Contours show sulphur fugacity (from Scott 1974).

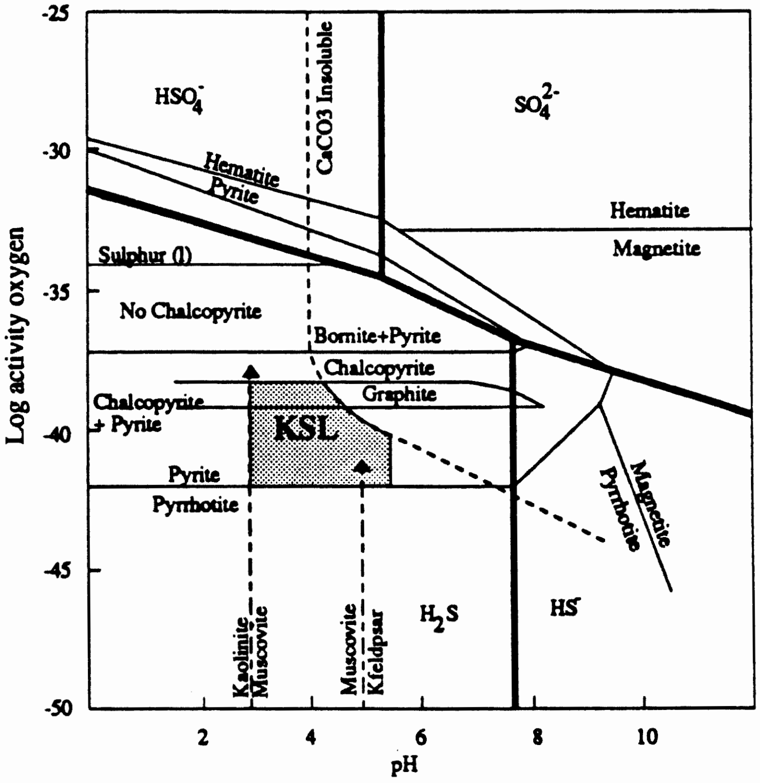


Figure 6.4 The stabilities of various minerals commonly found in ore deposits at 250°C. The absence of bornite, and presence of graphite and muscovite in the mineral assemblage at Kempt Snare Lake can be used to place restrictions on the fluid conditions (from Barton 1979).

the granitoid mineral assemblage and the presence of the mineral pair pyrite + chalcopyrite, with some occurrence of pyrrhotite, suggest that H_2S continued to be the dominant sulphur species even at lower temperatures (Figure 6.4). Barnes (1979) further demonstrated how the stability of wall-rock minerals such as graphite and muscovite are also enhanced by reduced sulphur species at lower temperatures. At Kempt Snare Lake, the presence of chalcopyrite, pyrite, graphite, and muscovite, therefore, suggests that H_2S is the dominant form of sulphur occurring. The lower temperature stability fields calculated by Scott and Barnes indicate that even when temperatures vary greatly, similar conditions must exist for similar assemblages of sulphides to remain.

6.3.2 Sulphur Isotope Studies in Nova Scotia

Regional South Mountain Batholith granite values range from $\delta^{34}S$ = +1.6 to +15.0 ‰, with granodiorite values varying from $\delta^{34}S$ = +5.4 to 8.4 ‰ (Poulson et al., 1991) (Figure 6.5). Sulphur values from Meguma Group sulphides range from $\delta^{34}S$ = +8 to +30 ‰ in the Goldenville Formation, to $\delta^{34}S$ = -5 ‰ in the transition zone between the Goldenville and Halifax Formations and values ranging from $\delta^{34}S$ = +22 ‰ in the base of the Halifax Formation to $\delta^{34}S$ = -5 ‰ at the top (Sangster, 1992). The values from the Kempt Snare Lake sulphides, therefore, overlap both the values from Goldenville Formation country rocks and the regional South Mountain Batholith values suggesting a mixed origin for the sulphur at Kempt Snare Lake. The closeness in values of the Meguma country rock sulphides and Kempt Snare Lake sulphide data and the average sulphur value suggests that

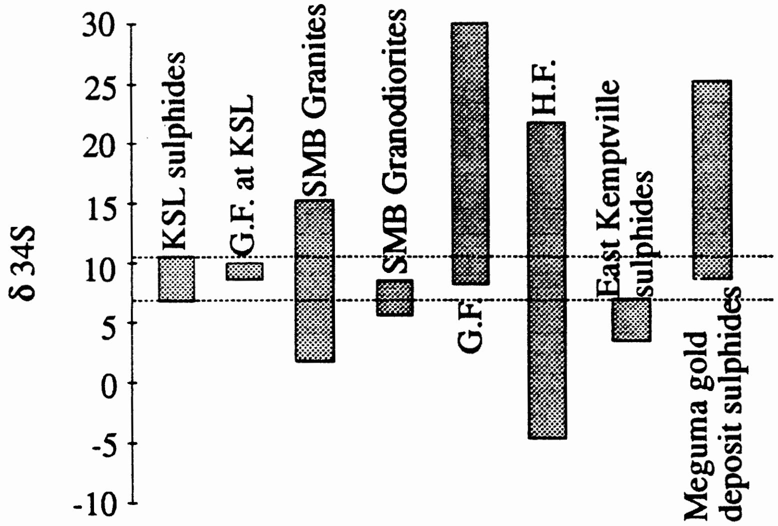


Figure 6.5 The variation in sulphur values from various rock suites found in Nova Scotia. KSL values determined during this study. Meguma Group values from Sangster (1992), granitic values from Poulson et al. (1991), East Kemptville from Kontak (1993), and gold deposits from Kontak et al. (1993). G.F. Goldenville Formation, H.F. Halifax Formation.

the sulphur at Kempt Snare Lake primarily originates from Meguma Group metasedimentary rocks, although some limited mixing with mantle sulphur may have occurred.

This explanation contrasts with that suggested by Kontak (1990) for the sulphur from East Kemptville. Kontak proposed that the narrow range in sulphide values for East Kemptville suggests that H_2S was the dominant form of sulphur, but unlike Kempt Snare Lake, the average value of $\delta^{34}S = 5$ ‰ for the fluid was interpreted as a magmatic source for the sulphur (Figure 6.5). The magmatic source for the sulphur at East Kemptville also contrasts with the sources of sulphur suggested for the Meguma Group gold deposits, where purely magmatic sources for that sulphur seem improbable. Kontak and Smith (1989) and Sangster (1992) suggested that metamorphogenic fluids originating within the Meguma Group or lithologies below the Meguma may be a more probable source for the sulphur found in these deposits.

6.4 The Carbon Problem

Unlike the silicates and sulphides, the graphite and siderite at Kempt Snare Lake show highly variable isotopic compositions, suggesting that the carbon history is more complicated than the other isotopic systems. The variable composition of the graphite $\delta^{13}C = -17$ to -27 ‰, may be functions of how the graphite or carbon entered the system, with carbon from different sources, or changing fluid conditions during graphite formation, or may have been altered by the passage of later fluids through the cupola. The siderite values ($\delta^{18}O$ = 27 ‰ and $\delta^{18}O$ = 9.5 ‰) represent either two different phases of siderite growth from different oxygen reservoirs , or the alteration of one type of siderite to form the second. The possible mechanism forming graphite and siderite, and the isotopic results are discussed below.

6.5 Methods of Graphite Entering System

The carbon responsible for the graphite formation may have become incorporated during the anatexis which may have formed the cupola magma, or may be the result of later interaction of the magma with either solid, liquid, or gaseous forms of graphite and carbon. The effect of incorporation of Meguma Group lithologies has previously been noted during this study and, therefore, this material may indicate that the graphite at Kempt Snare Lake may have been formed from carbon species already within the magma. However, the close association of the carbon-rich greisens to the later stages of alteration and veining suggests that a more likely source for the majority of the graphite may be the Meguma Group lithologies which now surround the cupola. The interaction of these Meguma Group lithologies with the magma may have brought carbon into the cupola as either a solid (previously formed graphite), liquid(hydrocarbon-bearing fluid /petroleum), or gaseous species (CO_2 +/-CH_4). Each of these options is discussed below.

6.5.1 Previously Formed Graphite Entered the Kempt Snare Lake Cupola

If the graphite were carried into the rock units as grains, the source of these isotopically different graphites must have had different carbon isotopic values. The graphite itself would then have to had to infiltrate cleavage planes within minerals, as well as along grain boundaries where it was then deposited. This method of emplacement seems unlikely as the space present along grain boundaries and within cleavage planes of minerals was probably unreasonably small to allow this to occur.

6.5.2 Petroleum Fluid Entered Cupola

The base of the Halifax Formation has been identified as a hydrocarbon generating and entrapment area (Zentilli et al. 1992). If fluids from this zone were to enter the Kempt Snare Lake site, the graphite may be the remains from this fluid interaction. Hydrocarbon-bearing fluids moving through the rock mass could produce the distribution pattern of graphite within the grain boundaries and cleavage planes and such fluid movement seems a more probable method of introducing graphite along cleavage planes than if it entered as solid grains; however, liquid petroleum does not exist at temperatures around 400-500 °C, making this material an unlikely source for the carbon. At these temperatures liquid hydrocarbons would become gasesous species, the option discussed below.

6.5.3 Gaseous Reactions Forming Graphite

Little information exists on the formation of graphite from hydrothermal fluids (Rumble and Hoering 1986); however, where hydrothermal graphite occurs, the precipitation of graphite usually happens as a result of mixing of magmatic and metamorphic fluids (Rumble and Hoering 1986; Weis et al. 1981). If petroleum fluids from the Halifax Formation were to release CH_4 as a result of heating and metamorphism, this methane could react with other gases to precipitate graphite. The reactions proposed by these workers are discussed here.

Weis et al. (1981) Metamorphic fluids in equilibrium with organic-rich pelitic rocks can produce CO and C, according to the following equations

Reaction 1 $C + H_2O \longrightarrow CO + H_2$

Reaction 2 $2\,CO \longrightarrow C + CO_2$

For these reactions to proceed, temperatures of 700 to 900 °C are required for Reaction 1, and 600 to 750 °C for Reaction 2. Whether the Kempt Snare Lake cupola intruded an organic-rich pelite layer of the Meguma remains unknown, but organic pelite layers within the Meguma are known to exist, and the presence of extensive shear zones (e.g., East Kemptville shear Zone, and Tobeatic shear zone) would enable metamorphic fluids to permeate the entire region. The temperatures of the reactions may indicate that, if this mechanism took place, the reactions occurred early in the cooling history of the cupola. Whether the temperature of the deposit was high enough during these periods of mineral formation for Reactions 1 and 2 to occur is unknown.

Rumble and Hoering (1986) A second mechanism for graphite precipitation may result from the mixing of two fluids one with a high CO_2/CH_4 ratio and one with a low CO_2/CH_4 ratio. Here the formation of graphite occurs in the reaction

Reaction 3 $$CO_2 + CH_4 \longrightarrow 2C + 2H_2O$$

This proposed method requires the mixing of a CO_2-rich fluid, in this case probably the igneous fluid, with a CH_4-rich fluid which could be formed from the metamorphism of organic-rich sediments, if low fO_2 conditions prevail. Similarly a CH_4 -rich fluid could be formed by the heating of a liquid petroleum, where CH_4 volatiles are driven off during the metamorphic reaction (Weis et al. 1981). If the CO_2 composition were heavier ($\delta^{13}C \sim -16$ ‰) and it mixed with a fluid with a CH_4 composition of around $\delta^{13}C = -45$ to -60 ‰, variations in the amount of each reservoir at various stages of alteration could deposit graphite with a variable carbon isotopic signature.

The pattern of graphite precipitation (along grain boundaries and along cleavage planes) suggests that a petroleum fluid, or hydrocarbon-rich fluid did interact with the Kempt

Snare Lake cupola, however, not by the method explained in Section 6.5.2. This interaction probably took the form of mixing of gaseous species (CH_4) with igneous CO_2 which resulted in the formation of the graphite.

6.6 Interpretation of the Graphite and Siderite Isotopic Signature

Variation in the graphite composition of the rock samples, from $\delta^{13}C = -17$ ‰ furthest from the veins to $\delta^{13}C = -27$ ‰ near the veins and within the greisens (Figure 6.6), may be the result of primary differences in the carbon reservoirs or fluid conditions during the time of graphite deposition. Primary variations in carbon values may result from variations in source region, temperature, or physicochemical conditions of the fluid, and each of these mechanisms for the graphite isotopic composition is discussed below. The close association of the graphite to areas of the drillcore that are highly veined suggests that the graphite may be related to the formation of the siderite. The variation in the siderite isotopic signatures is also discussed below.

6.6.1 Variation in Source Region

The variation in the graphite values shown in Figure 6.6 can be most simply explained through a variation in source region, with the lightest values being formed by an organic source region (or the CH_4-rich fluids of Rumble and Hoering 1986), and the heavier values formed by a mixture of organic material with a heavier carbon source (sedimentary carbonates). Studies of peraluminous leucogranites have shown that CO_2 may be a major

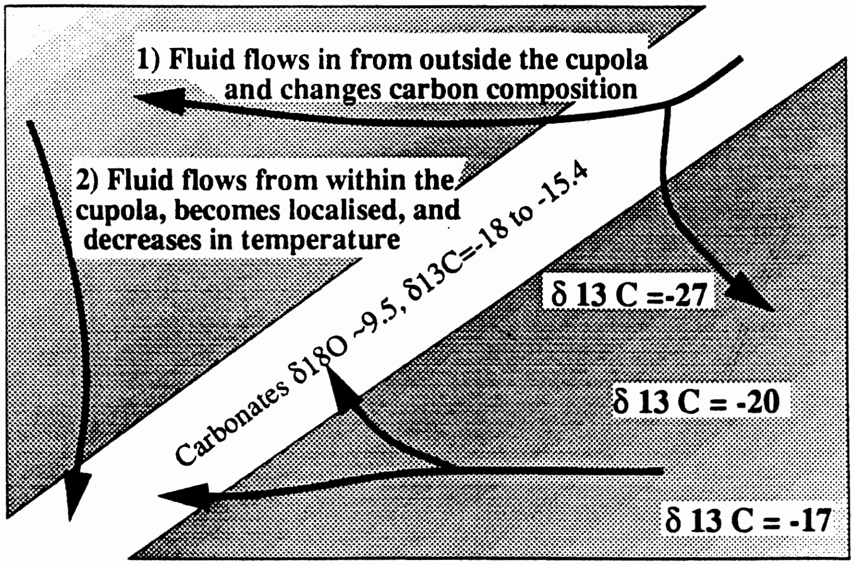


Figure 6.6 Possible fluid pathways which may have resulted in the formation of the graphite at Kempt Snare Lake. At the time of graphite precipitation no vein was present, however, a localised area of flow had developed. The vein represents a later period of brittle deformation.

component of the fluids evolved from them (Frezzotti et al. 1994). If this carbon is formed from a mantle source, its isotopic signature would be a second source for "heavy" carbon ($\delta^{13}C$ = -5 to -10 ‰). The spatial relationships of the different types of graphite suggest that, if the graphite precipitation was caused by fluids being localised along part of the magma body, the fluids which travelled the furthest from the localised flow, and the fluids that were first to pass throughout the units, were of a mixed origin precipitating graphite with an isotopic signature of $\delta^{13}C$ = -17 ‰. This value suggests a mixed organic and heavy carbon (mixing of organic CH_4 with CO_2 of mantle origin ($\delta^{13}C$ = -5 to -10 ‰) +/- carbonate carbon ($\delta^{13}C$ = +5 to -15 ‰)) source region for the fluid. With time this fluid changed to a more organic signature (higher CH_4 ratio within the fluid) precipitating graphite with $\delta^{13}C$ = -20 ‰ and finally $\delta^{13}C$ = -27 ‰. In the context of this model, the later-formed vein siderites with $\delta^{13}C$ = -15 to -18 ‰ would have formed from fluids which had returned to a fluid where the CO_2 content of the fluid had increased again. This simple model of changing CH_4/CO_2 ratios, although accounting for graphite variations, requires a reversal in carbon source during carbonate formation; therefore, this model does not explain all the carbon isotopes and other factors must also be causing the present isotopic signatures.

6.6.2 Variations in Physicochemical Conditions

Ohmoto (1972) showed the effect of changing physicochemical parameters on sulphur and carbon isotope values. Figure 6.7 shows the carbon isotopic composition of $H_2CO_{3(apparent)}$

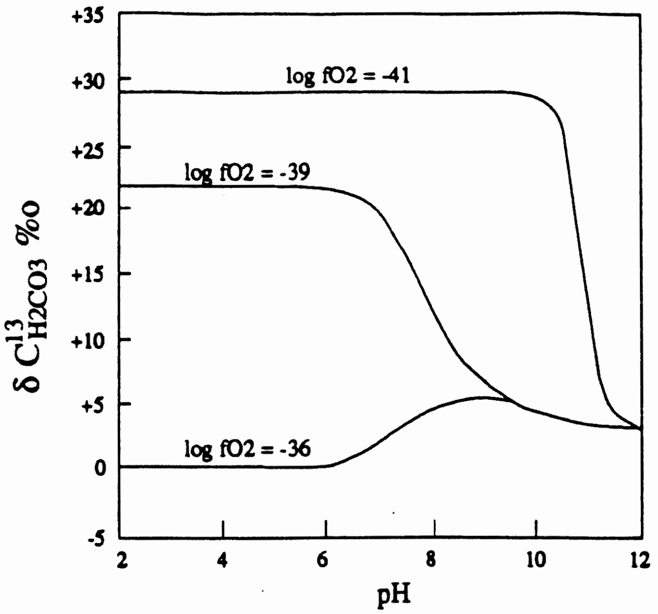


Figure 6.7 The effect of pH and oxygen fugacity on the isotopic composition of carbon-bearing species. Where H2CO3 = H2CO3 + CO2. δ 13 C H2CO3 = δ 13 C CO2 of the fluid for temperatures > 100 °C and pH <7, from Ohmoto (1972).

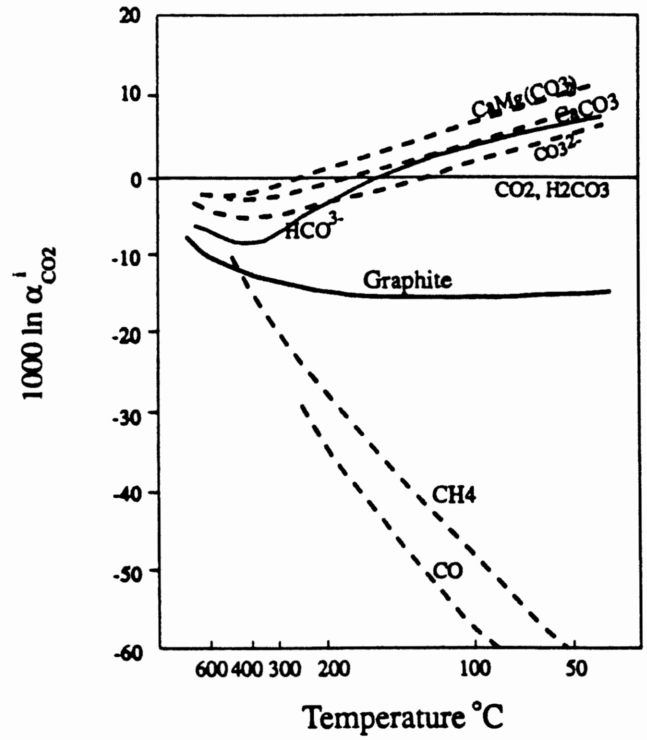


Figure 6.8 The effect of temperature on the fractionation factor among carbon compounds relative to H2CO3 (ap) where H2CO3(ap) = H2CO3 + CO2 (ap). From Ohmoto and Rye (1979).

which is assumed to equal $CO_{2\,(apparent)}$ composition of the fluid, is unaffected by changes in pH until alkaline pH values are reached. This figure shows that if the fluid has a starting composition of $\delta^{13}C_{CO2}$ = 0 ‰, for different oxygen fugacities the composition of carbon species can change by up to 30 per mil. The figure also shows, that for constant fO_2 conditions an increase in pH can alter the isotopic composition of the species formed. The pattern at Kempt Snare Lake may be the result of variations in fO_2, in which the fluid responsible for the graphite started in a more oxidised state, precipitating graphite with $\delta^{13}C$ = -17 ‰. Then, with time and the degree of alteration, the fluid became reduced (through a change in temperature or pH), the fO_2 decreased and the graphite became lighter in composition, i.e., graphite with $\delta^{13}C$ = -20 ‰ and $\delta^{13}C$ = -27 ‰. The fO_2 of the fluids then increased to higher values during the veining period, forming carbonates.

Another physicochemical explanation for the carbon isotopes of Kempt Snare Lake is that an increase in pH for stable fO_2 conditions resulted in the lowering of the isotopic signature of the graphite. The association of the occurrence of graphite and the greisenisation of the lithologies suggests that these two processes may be linked, and greisenisation is known to favour more acidic conditions (Burt 1981); therefore, an increase in pH in the Kempt Snare Lake system at this time seems improbable.

Although changing $f\,O_2$ to lower values during graphite precipitation, and then increasing during carbonate formation, could account for the isotopic composition of the carbon minerals, this model (as in the model in Section 6.6.1) requires a sudden reversal in fluid conditions; therefore, a simpler explanation is a combination of variable carbon sources and $f\,O_2$.

The variation in isotopic composition of graphite resulted from a continued change in the carbon source with an increase in the CH_4/CO_2 ratio. During this time, the $f\,O_2$ of the fluid remained constant. The brittle deformation of the cupola resulted in an increase in the fluid $f\,O_2$ and carbonates started to form. The isotopic composition of the siderites are now discussed.

6.6.3 Formation and Isotopic Composition of Siderite

Carbonate within the veins at Kempt Snare Lake suggests higher $f\,O_2$ fluid conditions than those present during graphite formation. If the fluids had higher $f\,O_2$, the source for the carbonate carbon may be the result of the oxidation of the carbon (CH_4) within the fluid (Reaction 4A) or from hydrolysis with wall-rock graphite (Reaction 4B) to form CO_2, which then forms the carbonates.

Reaction 4A $\quad CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

Reaction 4B $\quad C + H_2O \longrightarrow CO_2 + CH_4$

Table 6.1 Equilibrium fractionation factors for carbon compounds with respect to CO2.

Compounds	A	B	C	D	Temp Range °C
CaCO3	-8.914	8.557	-18.11	8.27	<600
C(graphite)	-6.637	6.921	-22.89	9.32	<700

According to equation from Bottinga (1968, 1969)

$$\Delta\, 13\, C_{i\text{-}CO2} = A * 10^{8}(T^{-3}) + B * 10^{6}(T^{-2}) + C * 10^{3}(T^{-1}) + D$$

If $f\,O_2$ continued to be high, the CO_2 could then be altered to form siderite, through a combined reaction with H_2S and Fe (Reaction 5).

Reaction 5 Increasing $f\,O_2$ conditions

Carbon dioxide + H_2S rich Fluid + Fe-rich Fluid $\longrightarrow$

Siderite + Sulphide + Water

$$1\,1/2\,O_2 + CO_2 + 2H_2S + 2Fe \longrightarrow FeCO_3 + FeS_2 + 2H_2O$$

At Kempt Snare Lake, at least four forms of carbon occur (graphite, carbonates, CH_4, and CO_2). The carbon isotopic composition of the fluid reflects the amounts of each of these reservoirs present within the fluid. The isotopic composition of the fluid during the last stages of alteration and mineralising history can be estimated through the measured compositions of the graphite and siderite, and the calculated compositions of CO_2 and CH_4 in equilibrium with these minerals.

Bottinga (1968, 1969) calculated the isotopic fractionation factors for various carbon species relative to CO_2 (Table 6.1). If the fractionation of siderite is assumed to be similar to other carbonates, and assuming a temperature of 480 °C (from sulphides and quartz-muscovite temperatures), the isotopic composition of CO_2 in equilibrium with siderite at this temperature would be around $\delta^{13}C = -16$ ‰.

If the CO_2 at Kempt Snare Lake is produced through reaction 4A and 4B, the isotopic composition of the CO_2 in equilibrium with the graphite can be calculated by the equations of Bottinga (1968 and 1969). According to these equations the isotopic composition of the CO_2 produced from oxidation or hydrolysis of the graphite at the boundary between the vein and the wall-rock ($\delta^{13}C$ = -27 ‰) would have an isotopic composition around $\delta^{13}C$ = -16 ‰, a value similar to the CO_2 composition in equilibrium with the measured values for the siderite, suggesting that carbon from the graphite could be a source for the carbon in the siderite. Similarly, if the carbon responsible for the graphite composition is still present within the fluid, this carbon could also be oxidised to form siderite of correct composition. Typically, CO_2 produced by the hydrolysis of graphite is heavier than the original graphite by 3 to 12 per mil (Ohmoto and Rye 1979; Anderson and Garven 1986). Ohmoto and Rye (1979) suggested that the $\delta^{13}CO_2$ - δ^{13} fluid = ~ 15 at ~500 °C; therefore, the δ^{13} Σ(total) C composition of the fluid is $\delta^{13}C$ ~ -31 ‰ , a value close to the composition of the graphite formed prior to the veining event, and suggesting an organic source for the carbon during the final stages of graphite precipitation and veining.

If CH_4 is also present (as suggested by Reaction 4B), and the total carbon signature $\delta^{13}C$ = -31 ‰, and a semi-quantitative balance is applied to the carbon isotopic signature, the CH_4 at Kempt Snare Lake, probably had a value of at least $\delta^{13}C$ ~ -46 ‰:

$$\delta^{13}\Sigma C \quad = \quad \text{graphite} \quad + \quad \text{siderite} \quad + \quad CO2 \quad + \quad CH4$$

$$\delta^{13}C = -31‰ \quad (-17 \text{ to} -27‰) \quad (-15 \text{ to } -18‰) \quad (-16‰) \quad (-46 \text{ to } -50‰)$$

6.6.4 Variation in Temperature

Temperature affects the fractionation factors of all isotopic systems (Figure 6.8). The variation in carbon isotopic composition of the graphite may be the result of temperature changes within the Kempt Snare Lake granite cupola (Figure 6.6) with graphite of isotopic composition $\delta^{13}C = -17$ ‰ forming first and, as the temperature of the fluid dropped, precipitating graphite with lighter signatures ($\delta^{13}C = -20$ ‰ then lastly $\delta^{13}C = -27$ ‰). This model requires a closed system, at least with respect to the carbon reservoir, where the carbon isotopes are fractionated as a function of falling temperature alone. This model seems unlikely as the igneous fluids are known to have altered the cupola prior to the graphite precipitation (altering the mineral chemistry) and after (forming the veins). These igneous fluids could have contributed carbon to the Kempt Snare Lake cupola and this additional carbon would have upset the temperature-driven fractionation process.

Temperature-driven fractionation, however, may have caused the variation in carbon isotopes occurring within the siderite. The isotopic compositions of the hydrothermal siderites range from $\delta^{13}C = -18$ to -15.4 ‰. As discussed previously the isotopic composition of the siderite formed in equilibrium with CO_2 is $\delta^{13}C = -18$ ‰ at 480 °C. Using the equations of Bottinga (1968 and 1969), and again assuming the isotopic fractionation of siderite is similar to other carbonates, as the temperature decreased the isotopic composition of the carbonate formed is expected to increase, causing the heavier siderite, carbon isotopic values.

6.6.5 Low Temperature Siderite Growth

The low temperature samples occur within a 10 m length of core within borehole KS-86-2, suggesting that some spatial control restricted this location to suitable alteration and reequilibration processes. Using the equilibration coefficient of Carothers et al. (1988), an aqueous fluid in equilibrium with siderite at temperatures ca. 20 °C (temperature of diagenetic siderite growth, used here because of the similarity of the oxygen values to diagenetic siderites) would have an oxygen isotopic signature of $\delta^{18}O \sim -6.8$ ‰, indicating meteoric water. This isotopic signature suggests that the low temperature siderites formed from meteoric waters, during a later, lower temperature event after the main mineralisation. The formation of this low temperature siderite probably occurred because of a localised input of meteoric water, through a number of small fractures and veinlets occurring in the core. Reequilibrium caused by dissolution and reprecipitation normally affects oxygen isotopes more than carbon (Ghazban et al. 1990), and may explain the greatly altered oxygen values, whereas the carbon values are only slightly higher than the hydrothermal siderites.

6.7 Carbon Isotope Studies in Nova Scotia

No values from Meguma Group organic matter were analysed during this study; however, Graves et al. (1988) and MacInnis (1986) obtained carbon values from carbonate within Meguma Group rocks, and Kontak et al. (1988) studied the isotopic composition of vein carbonates from the Meguma Gold deposits (Figure 6.9). The values reported by these workers are similar to those obtained in this study. The carbonates from these studies show carbon values that span the range found at Kempt Snare Lake; therefore, the Meguma could provide carbonate carbon with the suitable initial composition found at Kempt Snare Lake. The Kempt Snare Lake diagenetic samples fall near the field described by MacInnis (1986) for diagenetic Meguma carbonates and correspond to Meguma gold vein carbonates (Kontak et al. 1988).

6.8 Sources for Metals

The majority of the fluids which interacted with the Kempt Snare Lake cupola probably originated within the South Mountain Batholith. The fluids originating within the batholith could either carry the metals with them, or inherit them from the country rocks. Traditionally, a magmatic source has been inferred for mineralisation metals (Kontak 1990b). The close association of the South Mountain Batholith to many of the deposits in southwestern Nova Scotia suggests an igneous source for the metal; however, the source for the sulphur and carbon found with Kempt Snare Lake, are probably Meguma Group metasediments. The boundary between the organic-rich hydrocarbon-bearing Halifax

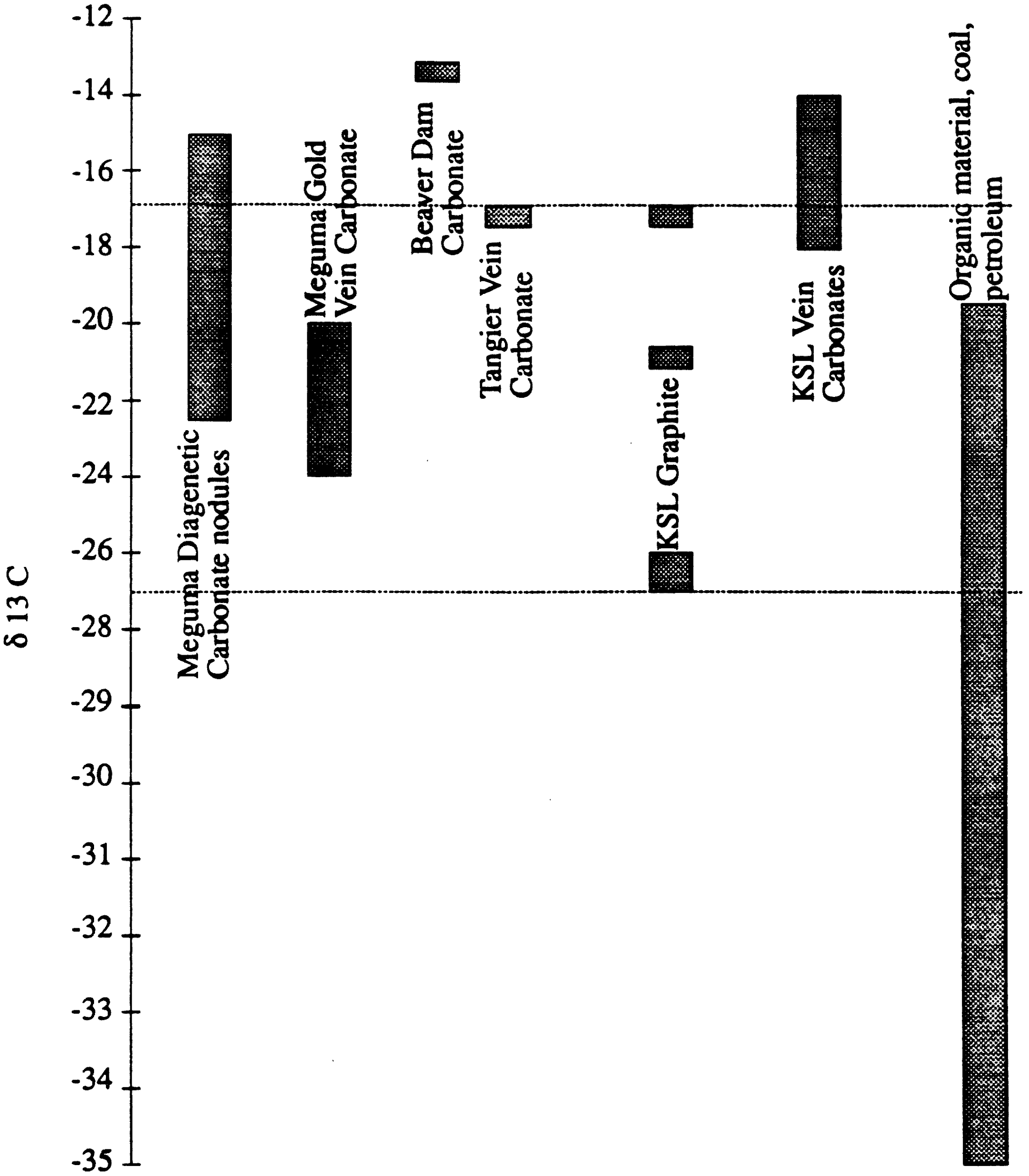


Figure 6.9 The variation in carbonate isotopic signatures found within the Meguma Group. Data for KSL- this study, Meguma Group carbonate nodules- Graves et al.(1988), Meguma gold deposits, including Beaver Dam and Tangier-Kontak et al. (1988), organic material, coal and petroleum- Hoefs (1986).

Formation with the Goldenville Formation (GHT) represents a carbon, sulphur, and metal source (Zentilli et al. 1992). The high arsenic and manganese contents of the sulphides and carbonates at Kempt Snare Lake correspond to the GHT, suggesting the GHT as a possible sulphur and metal source. The sources for the sulphides and metals at Kempt Snare Lake may, therefore, be mixed from within the South Mountain Batholith and the Meguma Group country rocks.

6.9 Water:Rock Ratio

Water:rock ratios are an important aspect of all mineral deposit studies. The two end-members of the system are: where the rock >> water, the isotopic content of the rock remains relatively unaltered and the isotopic composition of the fluid is modified; where the water >> rock, the isotopic content of the rock is modified and the fluid remains relatively unchanged. Equations calculating the water: rock ratio from the oxygen isotopic content have been proposed by Taylor (1977), however, knowledge of the isotopic composition of the rocks and fluid before and after alteration are required. At Kempt Snare Lake, all the units have been affected by fluid interaction, changing the original isotopic composition of the units; however, an estimation of the fluid rock ratio can still be made. The alteration of the units suggests that a significant amount of fluid was circulating through the cupola during its cooling history. The geological setting, near the cooling South Mountain Batholith, and intruding recently metamorphosed country rocks means a large volume of water may have been available in the region. The similarity in granitoid and vein isotopic composition suggests that either the rock completely reequilibrated all the fluid, and therefore, the rock dominates the system, or the fluids had a large enough volume and long enough time to alter the composition of the granitoid minerals. The abundant supply of fluids in the region, the extensive alteration of the lithologies, and the isotopic values suggests that the fluids dominate the system at Kempt Snare Lake and a moderate to high fluid: rock ratio can be inferred.

6.10 Geological History of Kempt Snare Lake Mineral Deposit

Chapter 5 identified three different fluids that entered the Kempt Snare Lake cupola at different times: a magmatic/metamorphic fluid, a methane-rich (hydrocarbon ?) fluid, and a late-stage restricted input of meteoric water. The magmatic/metamorphic fluid was responsible for the mineral alteration, evolved through time to cause the greisenisation and occurs as the dominant vein mineralising fluid. Figure 6.10 shows the possible sources for all these fluids.

The relative timing for the emplacement, alteration, and mineralisation of the Kempt Snare Lake are important in the possible sources for the fluids, metals, and the heat to drive the convective system. Age dating completed by Soehl (1989) suggested an age of 330-300 Ma years for the emplacement and alteration of the Kempt Snare Lake pluton. Similar ages of ~330 Ma, proposed for the other granites of southwestern Nova Scotia, have subsequently been redated at ~370 Ma. If the Kempt Snare Lake cupola was emplaced

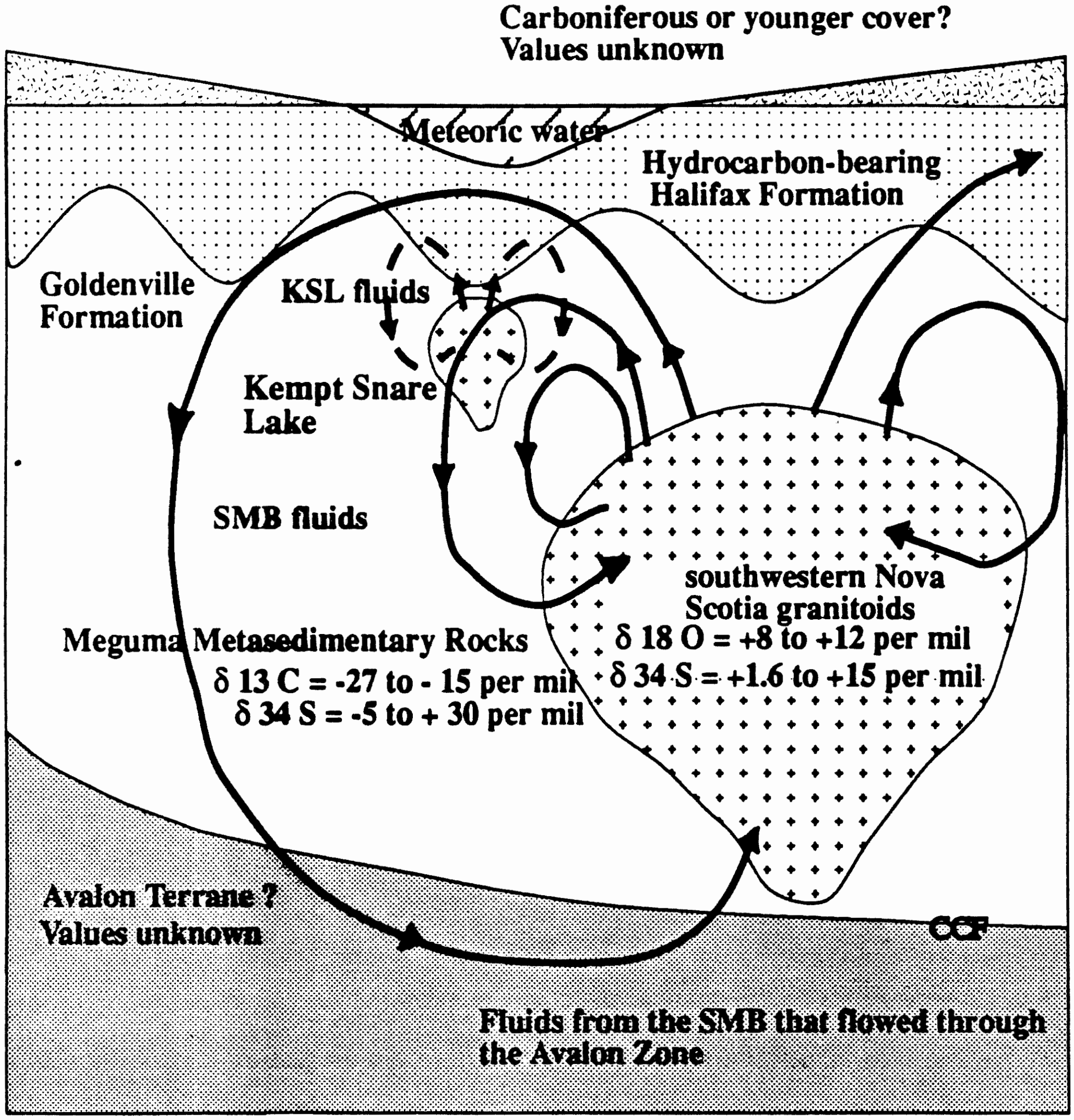


Figure 6.10 Schematic diagram of fluid sources and possible fluid paths. The fluids from the SMB or KSL could acquire the isotopic signature of any lithologies they flow though. Whether KSL is joined to the SMB does not restrict SMB fluids from entering the KSL cupola.

and altered at 300-330 Ma, the South Mountain Batholith could not provide the fluids or heat to drive the system. If the date of Soehl (1989) is correct, the hydrocarbon or methane source for the graphite at Kempt Snare Lake would also not be available, as this carbon source would have been metamorphosed during the Acadian Orogeny and the CH_4 would have subsequently been lost. The similarity in geochemistry and proximity of the South Mountain Batholith, however, suggests that Kempt Snare Lake may be related to this pluton, and therefore, the probable date of emplacement for Kempt Snare Lake is similar to the South Mountain Batholith at 370 Ma. This revised date of 370 Ma would also correlate with the lack of evidence for Carboniferous seawater ($\delta D \sim 0$ and $\delta^{18} O \sim 0$ per mil) within the isotopic signatures. If the younger date of Soehl (1989) was correct this fluid reservoir would be open to interact with the cupola. The 370 Ma age indicates that the intrusion of Kempt Snare Lake occurred prior to the Carboniferous, and therefore, rock units of this age or younger can be excluded from the geological history at Kempt Snare Lake.

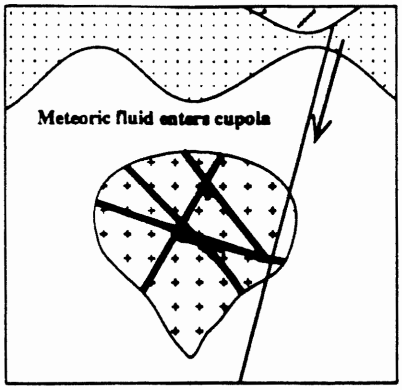
Few isotopic data exist for either the Avalon Zone or the Carboniferous or younger strata and, therefore, the role played (if any) by these groups can only be speculated. The isotopic composition of the Avalon Group probably is similar to other sedimentary and volcanic terranes, and therefore could have contributed sulphur and carbon of sedimentary origin if fluids circulated through the Group.

As mentioned in Chapter 3, core samples from Kempt Snare Lake are highly veined and fractured. Thin-sections from core samples show periods of both ductile and brittle deformation. The relationship between these two phases of deformation is closely linked to the alteration and mineralisation history at Kempt Snare Lake. Figure 6.11 and Table 6.2 show a schematic geological history.

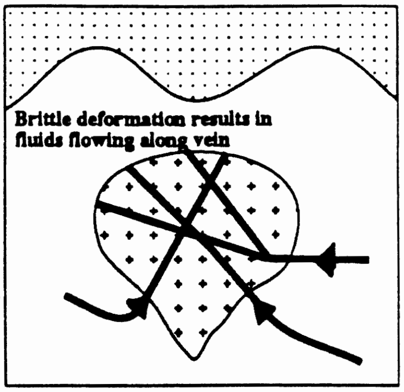
6.10.1 Pervasive Alteration and Ductile Deformation

The granites show the following evidence of alteration: clay alteration of feldspars; albitic plagioclase; and alteration of biotite to muscovite. The greisen lithologies clearly show extensive alteration of the granite protoliths, with high proportions of muscovite and albitic plagioclase. Textures caused by tectonic disturbance that may correlate with this period of alteration may be the ductile deformation features: undulose extinction of quartz; boudinage feldspar; bent twinning patterns of plagioclase feldspar; and bent cleavage plane of muscovite. This alteration, present within all units is a "pervasive" alteration, and is not restricted to veins and other specific fluid conduits.

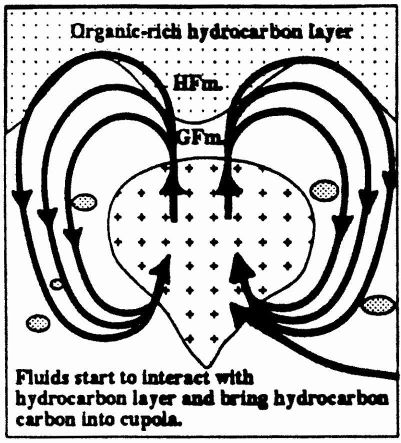
The fluid which entered the cupola, during the late crystal-melt stage and was responsible for the pervasive alteration, was igneous in origin (Kempt Snare Lake and South Mountain Batholith) with $\delta^{18}O$ ~7.5 ‰ and δD ~ -25 ‰ , and contained high contents of Na- and K- salts and Fe. The early entry of this fluid to the system allowed sufficient time for the composition of the minerals to be altered.



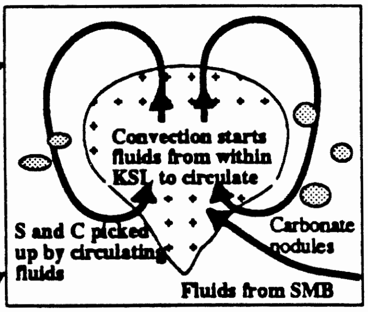
5) Much later brittle deformation allows meteoric water into cupola.



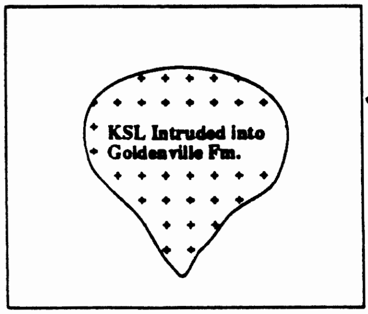
4) Brittle deformation occurs and veins form in the cooling cupola. Greisenising fluids and then mineralising fluids flow along the veins.



3) Convection brings carbon rich fluid into cupola. Cupola has cooled and formed restricted fluid pathways. Igneous fluid evolves to greisenising fluid.



2) Shortly after intrusion convection drives fluids out from and into KSL cupola. Fluids are igneous/metamorphic in origin, and cause alteration of minerals. Ductile Deformation.



1) KSL intrudes the Meguma Group.

Figure 6.11 Schematic geological history of Kempt Snare Lake.

ISOTOPIC RESULTS		GEOLOGICAL HISTORY	DEFORMATION
Siderite - δ18O ~ 27 per mil Meteoric Water		5 Much later meteoric water enters cooled cupola at restricted places and reequilibrates some hydrothermal siderite to low-temperature oxygen signatures. Reactions- Alteration of siderite to low-temperature form.	BRITTLE
Siderite δ18O 9.5 per mil Sulphides δ34S = 6 to 10 per mil Graphite δ13C= -17 to -27 per mil Fluid δ18O~7.5 per mil, δD ~-25per mil	MINERALISATION	4 Graphite precipitation ends and brittle deformation starts. Greisenisation is followed by mineralising fluids. Mineralising fluids have higher oxygen fugacity and result in alteration of wall-rock graphite and CH4 to react with Fe-rich fluid to form high temperature siderite . Reactions - Greisenisation, mineralisation, oxidation-reduction of graphite, CH4, and H2S, and formation of siderite.	
	GREISENISATION	3 Cupola continues to cool, and convection reaches organic-rich hydrocarbon layer. Igneous fluids with heavy carbon react with the CH4 rich fluid to form graphite. Igneous fluid evolves to higher pH and greisenisation starts Reaction-Greisenisation and muscovitisation.	DUCTILE
	ALTERATION	2 Convection of fluids starts and igneous fluids from the SMB and KSL start to circulate through the cupola and country rocks. S and C brought in from igneous fluids and country rocks. Reactions- K-feldspathisation, albitisation and muscovitisation	
		1 Intrusion of Kempt Snare Lake cupola (~ 370 Ma).	

Table 6.2 Geological history at Kempt Snare Lake (see Figure 6.11).

A second period of hydrothermal alteration may be the period relating to graphite precipitation. Graphite occurs in the greisens to a much greater extent than in the granites. The greisens are related to areas that have the highest density of veins. The pattern of graphite may suggest that the period of graphite precipitation is related to the veining event; however, although graphite is associated with areas of core that are veined, graphite does not appear within any of the veins indicating that the graphite did not flow within any of these veins. This methane-bearing fluid either used, or formed, selected fluid pathways, which later became the location of the veins. The restricted locations of graphite, compared to the universal plagioclase alteration and biotite breakdown, do suggest, however, that this period of alteration was not able to enter the rock mass as easily as those that occurred before. Therefore, the relative amount of solidification had probably increased during the time interval of the first and second stages of pervasive alteration.

As discussed earlier in this chapter, graphite precipitation is probably the product of a fluid mixing event. Therefore, during the period of graphite precipitation, a carbon-rich fluid entered the cupola. This fluid mixed with the igneous fluid that had previously entered the cupola, and this mixing resulted in the precipitation of graphite. Although graphite occurs in all units, its abundance is higher in the highly veined greisen units, although not in the veins. This pattern of deposition suggests that the entry of the carbon-rich fluid probably occurred just prior to the brittle deformation that caused the veins.

The close association of the greisens and graphite-rich units suggests that the greisenisation overlapped with the graphite stage. The association of greisens with the units that are more highly veined suggests that the greisens were formed either by fluids flowing along restricted pathways before fracturing had occurred, or altered the wall-rock as the greisenising fluids flowed along the veins; therefore, greisenisation may overlap the ductile and brittle stages of deformation. The $\delta^{18}O$ and δD composition of the greisenising fluid was the same as those with originally entered the pluton, however, the fluid had evolved to a more acidic pH.

6.10.2 Brittle Deformation and Alteration

Brittle forms of deformation (fractured quartz grains that have undulose extinction, where the fracture boundaries run across different crystals; broken, boundinaged feldspar) within the samples from Kempt Snare Lake indicate that a period of brittle deformation followed the period of ductile deformation. The association of the veins with the graphite-rich areas of the core suggest that the formation of veins and the brittle deformation followed the ductile and pervasive stage, and used features that had previously existed, i.e., the localised fluid pathways for the graphite alteration. The association of the greisens to areas of core that contain high number of veins suggests that the greisenising fluids flowed along these fluid pathways. The final stage of the brittle deformation was the veining event resulted in the precipitation of the vein minerals, the disseminated arsenopyrite, faults, and the final stage of alteration of wall-rock .

The presence of Na- and K-salts in fluid inclusions, the similarity of the vein and rock muscovite composition, and the similarity in isotopic composition of the vein minerals suggest that the vein fluids are the same as the igneous/ metamorphic fluid that first entered the cupola and caused the alteration. The vein mineralogy also indicates that the fluid was dominated by H_2S and acidic pH. The presence of arsenopyrite in the wall-rock and veins suggests that the vein fluid is a more evolved equivalent of the greisenising fluid. However, the fO_2 conditions of the fluid increased between the time of graphite precipitation of the carbonate formation. The increase fO_2 of the Fe-rich fluid oxidised the wall-rock graphite and fluid CH_4 to form vein siderites.

As previously discussed in Chapter 5, the sulphur and carbon compositions of the sulphides and carbon-bearing minerals do not suggest that the sulphur and carbon at Kempt Snare Lake had a primary magmatic/igneous source. Unlike the hydrogen- and oxygen-bearing minerals, the sulphides, carbonates, and graphite suggest a sedimentary origin. Therefore, the isotopic signature of the sulphides and carbonates suggest that the mixed igneous/metamorphic fluids inherited metasedimentary sulphur and carbon signatures during passage through them towards Kempt Snare Lake.

6.10. 3 Meteoric Fluid Input

A final period of restricted meteoric fluid input occurred after the mineralisation and cooling of the pluton. This fluid entered the cupola at one location, and caused the reequilibration of the hydrothermal siderite. This fluid probably entered the cupola using several small planar faults that occur within the core, suggesting that a phase of brittle deformation followed the earlier events; however, this fluid did not move pervasively through the cupola, preserving the earlier form of siderite. This meteoric water altered the $\delta^{18}O$ of the siderite more than the $\delta^{13}C$ content.

6.11 Summary

The isotopic compositions of the minerals at Kempt Snare Lake are similar to those of other granitoids within Nova Scotia. The carbon- and sulphur-bearing minerals within the cupola are more closely related to the Meguma Group country rocks, and these units are the source for the carbon and sulphur at Kempt Snare Lake.

The fluids responsible for the alteration, greisenisation, and mineralisation at Kempt Snare Lake have a mixed igneous/metamorphic signature, and probably originate within the Kempt Snare Lake cupola, the South Mountain Batholith, and the Meguma Group. The fluid evolved in composition and physicochemical conditions (pH and $f\,O_2$) to cause the subseqent alteration stages. The deformation styles within the cupola also changed from a ductile to brittle regime.

CHAPTER 7 - CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

1) The leucomonzogranite and leucogranite at Kempt Snare Lake are related through differentiation. Some greisen samples have leucomonzogranite protoliths, whereas others have a closer association with the leucogranite, although all five units at Kempt Snare Lake are clearly related. Whole-rock geochemistry shows that all the lithological units have been affected by fluids of similar compositions (high K, Na, and Fe content), resulting in albitic composition of all plagioclases and high contents of phengitic muscovite.

2) The fluids responsible for the alteration, greisenisation and mineralisation at Kempt Snare Lake were derived from within the cupola, the surrounding plutons, and mixed with some metamorphic fluids from the metasedimentary country rocks. The oxygen and hydrogen signature for the fluids is $\delta^{18}O = \sim 7.5$ ‰, and $\delta D = - \sim 26$ ‰. The sulphur and carbon isotopic compositions of the fluids are similar to the Meguma Group country rocks, with $\delta^{34}S = \sim 8$ ‰, and $\delta^{13}C$ (graphite) varying from $\delta^{13}C = -17$ to -27 ‰. Vein carbonates, formed from the oxidation of wall-rock graphite, have two distinct groupings reflecting alteration of high temperature siderite ($\delta^{18}O = 9.5$ ‰) by meteoric waters to form low-temperature siderite ($\delta^{18}O = 27$ ‰). The fluids remained the same isotopic composition throughout the alteration and mineralising events.

3) Kempt Snare Lake has been affected by two periods of deformation: ductile followed by brittle. The pervasive alteration and graphite precipitation stages reflect the ductile stage and the mineralisation reflects the brittle stages. The greisenisation stage, probably overlaps the two phases of alteration.

4) The fluids carried a number of dissolved species including H_2S, the dominant form of sulphur, CO_2 and CH_4. The fluids had low fO_2 and low pH. During the pervasive stage of alteration, the physicochemical conditions of the fluid remained constant; however, during the veining stages the fO_2 of the fluid increased.

7.2 Recommendations for Future Work

1) Detailed accurate age dating of the different stages of intrusion, formation, and alteration should be carried out at the Kempt Snare Lake site. As stated in Chapter 6, the 370 Ma age applied in the geological history of this deposit has not been established and further age dating in this area would provide a much clearer undertanding to the formation of this deposit.

2) Detailed fluid inclusion studies should also be undertaken at the Kempt Snare Lake site to determine the composition of the fluids. The work completed by Soehl (1988), although useful for a general comparison, was not pressure-corrected and samples from different mineral sets (quartz, carbonates, and fluorite) could provide information on the

interaction of metamorphic, hydrocarbon and igneous fluids at this location. This work would provide a clearer understanding of the fluid sources and mixing histories during the stages of alteration and mineralisation.

3) The term graphite used throughout this thesis, and used for other deposits in the region, needs clarification. The source for this carbon of organic origin may be petroleum liquid lost as a result of regional metamorphism, or may be from the gaseous carbon species produced from the metamorphism of organic material. More work on the nature, occurrence, source, and processes leading to the origin of this carbon material, and the subsequent alteration of this material, is required to fully understand the importance of this organic material in the formation of this and other similar deposits. The stable isotopes of this carbon material at Kempt Snare Lake, and other deposits, also requires further investigation. If the isotopic composition of the graphite is the result of variations in the CH_4/CO_2 ratio of the fluids, a continous variation from $\delta^{13}C = -17$ to -27 ‰ may be expected, unlike the three distinct groupings found during this study. These groupings however, may be function of the sample selection, and detailed sampling of the carbon material from a transect across the least to most altered unit is required before the complete isotopic story for Kempt Snare Lake is understood.

4) A regional stable isotope database would help the understanding of possible element and metal sources for the area. Little data on the carbon isotopic signature for carbonates

and organic material within the region exists, except for known ore deposits. Similarly hydrogen data are scarce for the entire region, making comparison and understanding of the fluid sources for the region unclear.

APPENDIX A

ROCK DESCRIPTIONS AND BOREHOLE LOGS

A.1 Rock Unit Descriptions

Table A.1 to A.5 contain detailed descriptions of the five lithologies present at Kempt Snare Lake, including modal percentage of the minerals, and the textures present within each unit. The modal percentages of the minerals were determined by point counting 250 points per thin-section with a minimum of five sections per unit counted. One thin section per unit was recounted to ensure reproducibility.

Table A.1. Unit 1- Coarse-grained leucomonzogranite

Mineralogy	Quartz	K-feldspar	Plagioclase	Muscovite	Biotite
Abundance	45-51%	20-26%	9-16%	6-7%	7-8%
Phenocrysts	Subhedral 1 - 3mm	Euhedral 3-6mm	Euhedral 2-5mm	Subhedral 1-2mm	
Groundmass	<1mm		Euhedral 0.5 - 1mm		
Textures	Undulose extinction Recrystallised quartz	Perthitic texture Exsolution lamellae Rare inclusion		Primary and secondary	
Alteration		Patchy alteration to sericite	Some alteration to sericite (<40%)		60% altered to chlorite/ muscovite Halo spots present, relict zircon
Deformation			Some kinked and bent plagioclase grains	Kinked	Kinked
Other	Some primary igneous textures still present, i.e., interlocking plagioclase grains.				

Table A.2, Unit 2- Leucogranite

Mineralogy	Quartz	K-feldspar	Plagioclase	Muscovite	Biotite
Abundance	36-43%	32-40%	17-18%	2-3%	2-4%
Phenocrysts	Euhedral - subhedral 1-3mm	Euheral 3-6mm	Euhedral 1-2 mm	Subhedral 0.5 - 1mm	Subhedral 0.5 -1mm
Groundmass	<0.5mm		<1mm	<0.5mm	
Textures	Undulose extinction and rare inclusions. Fluid inclusions clearly visible	Rare inclusions		Some primary(?) euhedral crystals present	
Alteration		Patchy alteration to sericite Plagioclase inclusions present.	Highly altered to sericite		60% altered to chlorite Halo spots present, relict zircon Fe-Ti oxides
Deformation			Some kinked and bent plagioclase grains	Kinked	Kinked
Other	Some primary igneous textures still present, i.e., interlocking plagioclase grains, but other areas show extensive recrystallisation				

Table A.3. Unit 3- Gresiened granite

Mineralogy	Quartz	K-feldspar	Plagioclase	Muscovite	Biotite
Abundance	37-44%	26-40%	11-14%	5-12%	5-6%
Phenocrysts	Subhedral 1- 3mm	6-7mm	Euhedral - subhedral 1- 3mm	Anhedral 1- 3mm	Subhedral 0.5 - 1mm
Groundmass	<0.5mm			0.5-1.5mm	
Textures	Fluid inclusion trails clearly visible Undulose extinction Fractured quartz	Rare plagioclase inclusion. Exsolution lamellae	Albite twins hard to see	Forms very fine grained patches	
Alteration		Patchy alteration to sericite. Small amounts of graphite	Highly altered to sericite		80% altered to chlorite Halo spots present, relict zircon
Deformation			Some kinked and bent plagioclase grains	Kinked	
Other	Little original igneous texture still present. Disseminated arsenopyrite present , and also present in veins				

Table A.4, Unit4- Fine-grained, dark grey greisen.

Mineralogy	Quartz	K-feldspar	Plagioclase	Muscovite	Biotite
Abundance	41-42%	26-35%	10-20%	6-16%	2-4%
Phenocrysts	Subhedral 1-3mm	Euhedal -subhedral 2-5mm	Subhedral		Anhedral 0.1 - 0.5mm
Groundmass	<0.5mm		<0.3 - 1mm	Interstitial <0.3mm	
Textures	Undulose extinction Recrystallised quartz Fractured quartz	Rare inclusions (plagioclase) Perthitic texture/exsolution			
Alteration		Highly altered to sericite Graphite present along cleavage planes	Some crystals are highly altered to sericite		Completely altered to chlorite
Deformation			Some kinked and bent plagioclase grains	Kinked	
Other	Very fine grained Graphite still present in cleavage planes of feldspars and along grain boundaries. Highly recrystalised, with little original igneous texture existing.				

Table A.5, Unit 5- Medium-grained, grey porphyritic greisen

Mineralogy	Quartz	K-feldspar	Plagioclase	Muscovite	Biotite
Abundance	31-47%	22-39%	9-20%	10-20%	<1%
Phenocrysts Groundmass	Subhedral 3-6mm <lmm	Euhedral - subhedral 2 -6mm	Subhedral 1-4mm	Subhedral -anhedral 0.5-1mm <0.5mm	Subhedral
Textures	Undulose extinction Recrystallisation-sutured boundaries	Plag. inclusions common	Inclusions of K-feld	Present as primary mineral and as a secondary replacement distinguished on the basis of size and clarity	
Alteration		Highly altered to sericite Graphite present along cleavage planes	Larger phenocrysts show extensive alteration to sericite		Totally altered to chlorite
Deformation	Highly fractured	Bent and show kinked twinning patterns		Kinked	
Other	Disseminated arsenopyrite common. Graphite seems to have "flowed' along grain boundaries, and occurs in the cleavage planes of the feldspars. No graphite found in quartz grains. Original igneous textures still visible.				

A.2 Schematic Core Logs from Kempt Snare Lake

Sketches of the core obtained from boreholes KS-86-1, KS-86-2, and KS-86-3 are shown in Figure A.1 to A.3. The location of the boreholes relative to the location of the greisenised cupola, as determined by chargeability is shown in Figure 2.2.

The logs show the different lithologies that occur through the length of core, and the location of the whole-rock and stable isotopes samples. Hole KS-86-1 was drilled to test the known mineralisation beneath the shaft, and was spotted at 0 + 13 E/ 0 + 42 S, and drilled towards 330° azimuth at -47° dip for a total of 70.12 m. Holes KS-86-2 and KS-86-3 were designed to cut the highest chargeability readings. KS-86-2 was spotted at 1 + 64 W/ 1 + 40 S, drilled towards 150° azimuth at a dip of -47°. The total length drilled was 82.32 m. Hole KS-86-3 was spotted at 0 + 1 - E/ 0 + 60 N, drilled towards 330° azimuth at -45 ° dip, for 50.00 m (Jensen 1987).

Abbreviations in Figure A.1 to A.3 from Kretz (1983): apy-arsenopyrite; ccp-chalcopyrite; gn,-galena; ms-muscovite; py-pyrite; qtz-quartz; sd-siderite; and sp-sphalerite.

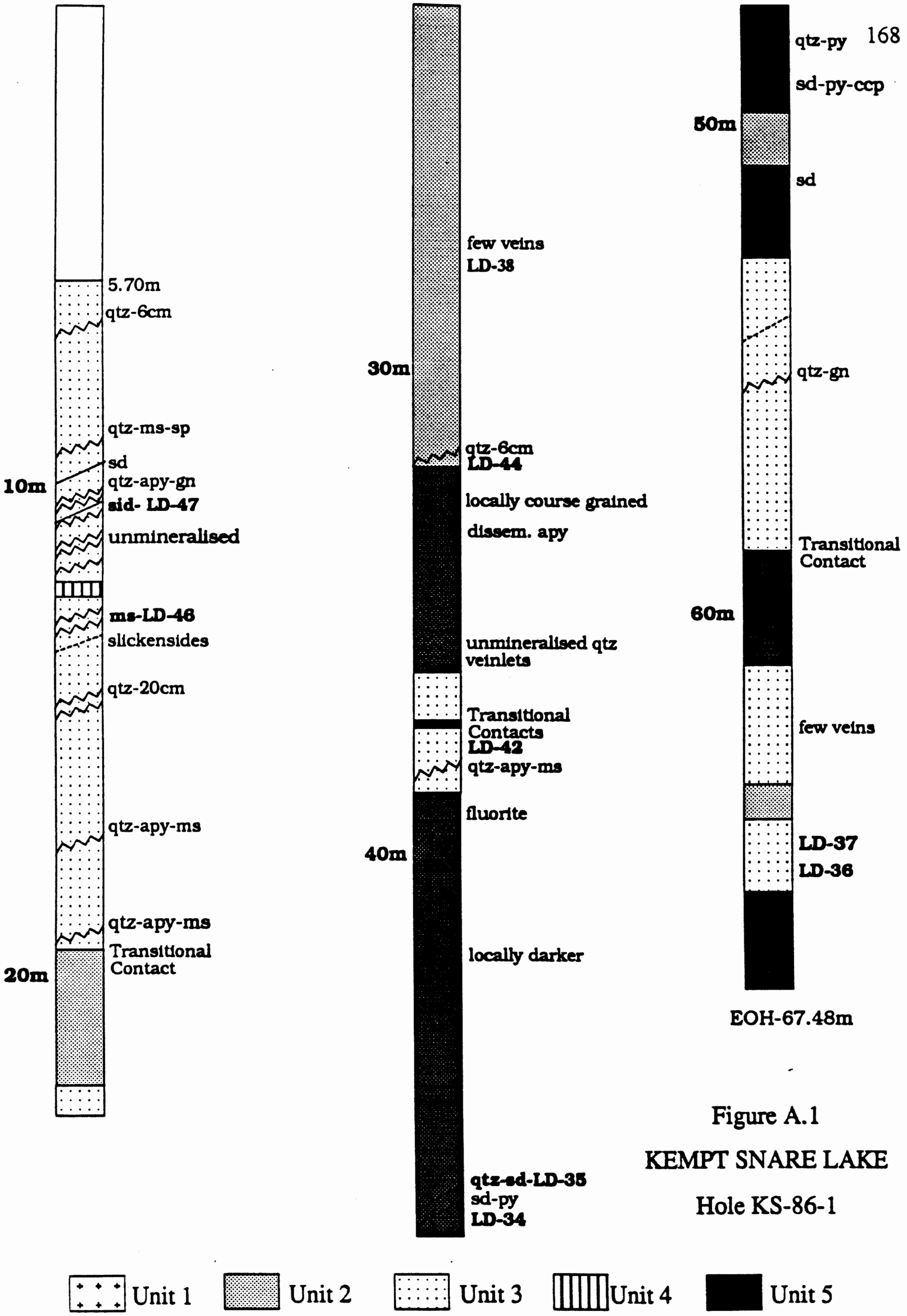


Figure A.1

KEMPT SNARE LAKE

Hole KS-86-1

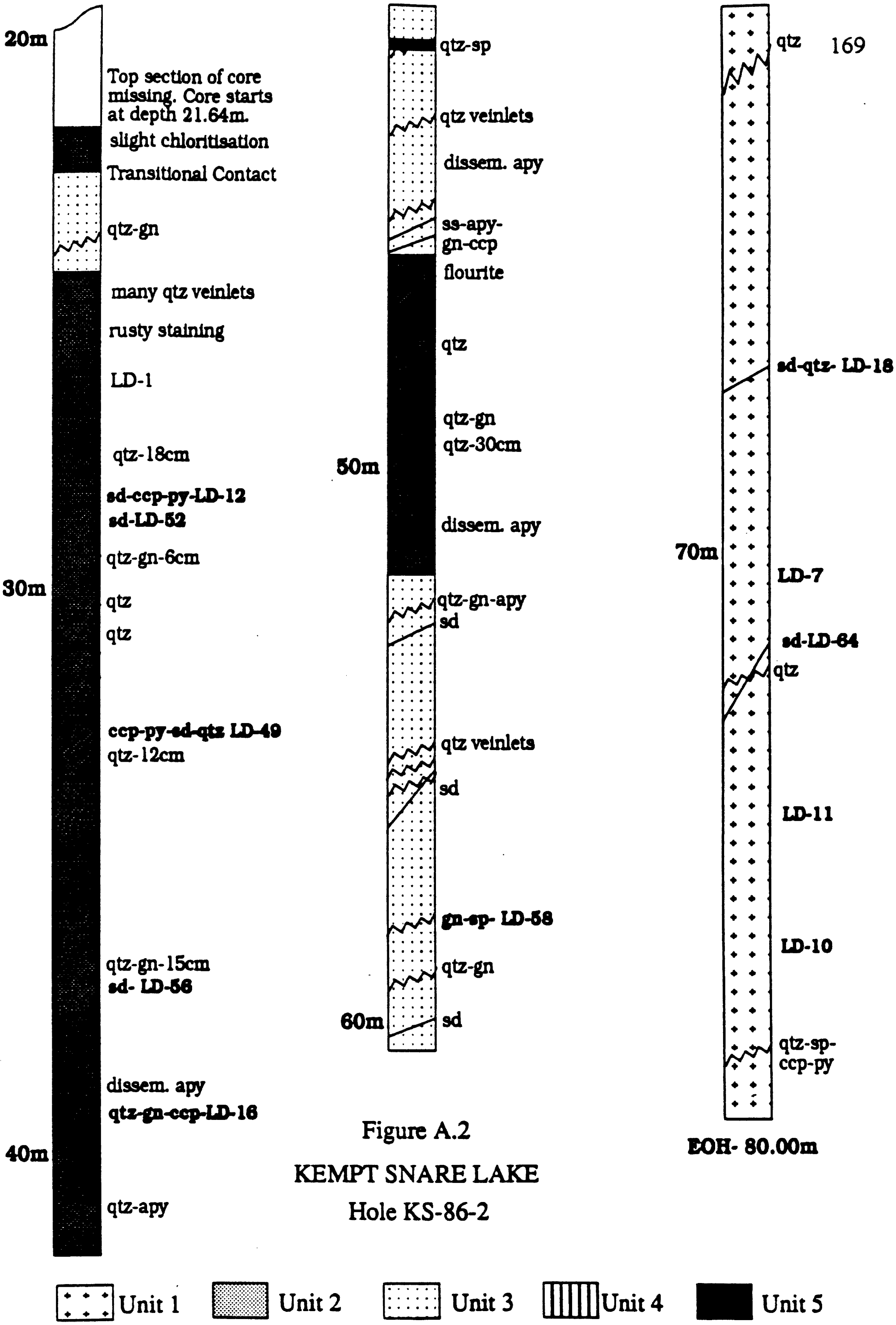


Figure A.2

KEMPT SNARE LAKE

Hole KS-86-2

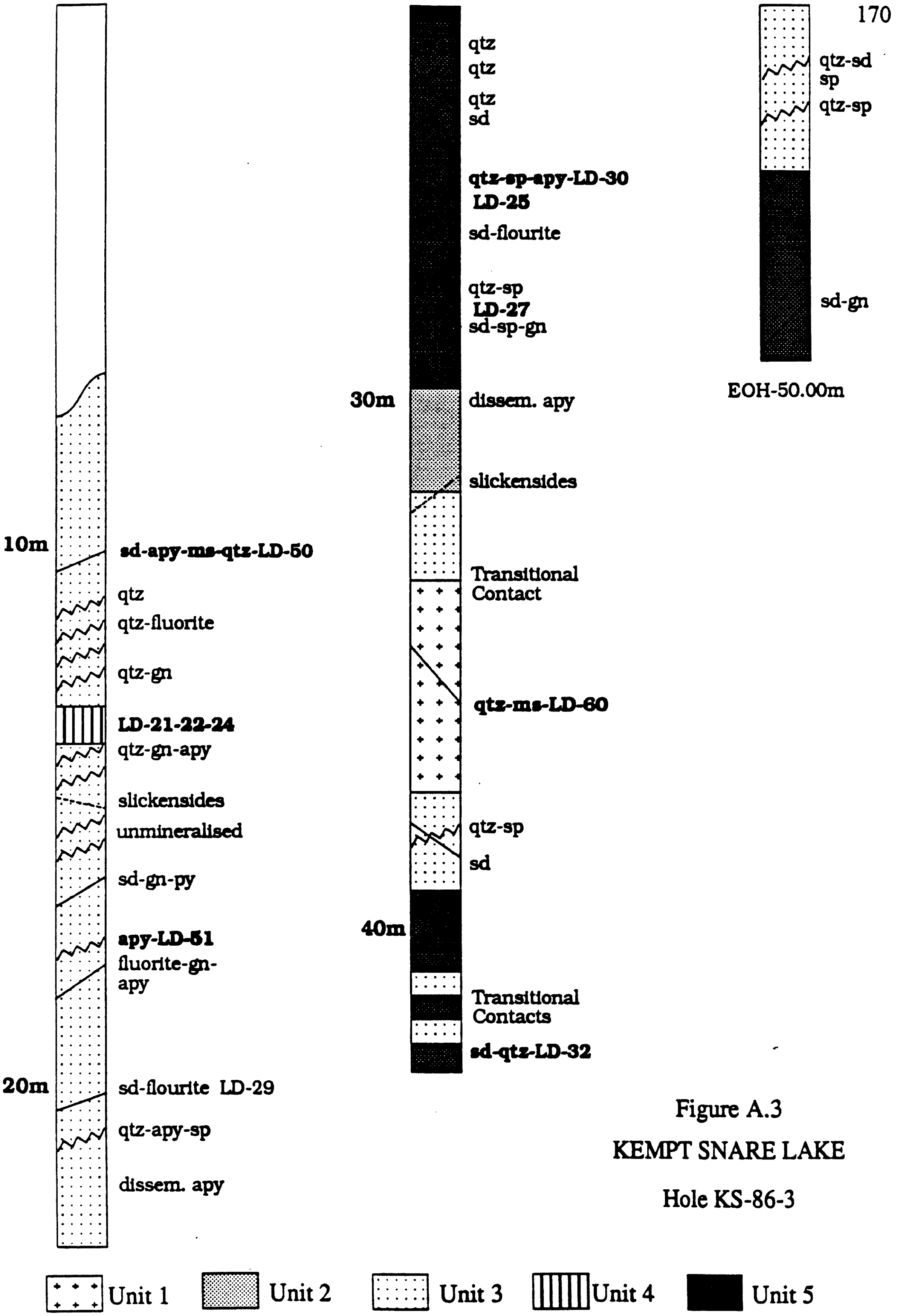


Figure A.3

KEMPT SNARE LAKE

Hole KS-86-3

APPENDIX B

SAMPLE PREPARATION AND ANALYTICAL METHODS

B.1. Microprobe Operating Conditions

Mineral analyses were obtained from polished thin sections using the Dalhousie Link eXL system and the JEOL 733 electron microprobe. Operating conditions were 15kV accelerating voltage, 13 nA probe current, and 12 μm beam diameter. The counting time was 40 seconds, at approximately 7600 total counts per second. Calibration used geological standards and a ZAF matrix correction program was employed in the reduction of raw data. Data recalculation and mineral classification used the MINPET data processing program by Richard (1994). Representative microprobe analyses for the muscovite, K-feldspar, plagioclase, sulphides, and siderite are shown in Tables B1 to B5.

B.2. Whole-Rock Geochemistry Sample Preparation

Whole-rock geochemistry samples were cut from the Kempt Snare Lake core with a copper-bladed rotary saw. Core samples were then broken with a hammer, and then broken to gravel-sized material in a ceramic rock crusher in a clean crushing room. Gravel-sized fragments were then placed in a ceramic pulveriser and crushed until a powder of -70 mesh was obtained. The powder was stored in inert plastic containers prior to analysis. This powder provided samples for major oxide, trace element, and rare earth element analyses.

B.3 Major, Trace Element, and Rare Earth Element Analytical Procedures

Samples were analysed according to the methods outlined in Tate (1995). Powdered samples were analysed for the major and minor elements Saint Mary's University. Oxide determinations were made from ca. 5 grams fused glass disk, and trace elements were analysed from pressed powder pellets. Analyses were completed on the Phillips PW 1400 sequential X-ray fluorescence spectrometer, which is equipped with a Rhenium anode tube. Loss of ignition (LOI) was determined for each sample, by heating a 1 gram of the sample at 1050 °C in an electric furnace for 90 minutes, prior to fusion. International standards (Govindaraju 1989) and in-house standards were used as instrument calibration. Duplicate analyses were also completed.

Rare earth element contents were determined by Beverly Chapman using ICP-MS analysis at the Memorial University of Newfoundland, following the procedure of Longrich et al. (1990). Aliquots (0.2 gram) of all samples were sintered with sodium peroxide. After dissolution of the sinter cake, REE's were separated in a hydroxide-bearing precipitate. Internal standards and pure quartz reagent blanks were employed to check and correct ICP-MS analysis for instrument drift and matrix effects.

B.4. Stable Isotope Sample Preparation

Stable isotope vein samples were cut from their host rocks by a copper rotary saw, and crushed by a hand iron anvil until -60 mesh size. Any iron filings that may have contaminated the samples were removed with a magnet. The crushed vein material was then washed with distilled water to remove any clay sized material and left to dry in air for three days, prior to storage in inert plastic containers.

Stable isotope granitoid mineral separates were cut from the Kempt Snare Lake core by a copper bladed rotary saw. The samples were then crushed firstly by a ceramic jaw crusher, then placed in a ceramic pulveriser until they were -60 mesh size. Samples were then again washed with distilled water and then left to dry in air for three days, before storage in plastic containers prior to analyses.

B.5. Mineral Separation for Stable Isotope Analyses

Mineral separates were obtained through several techniques (Figure B.1), where the light fraction minerals have a density less than the fluid and, therefore, float at the top of the liquid, and the heavy mineral fractions have a density greater than the liquid and sink. After passing through heavy fluids each sample was washed thoroughly. The Franz magnetic separator split siderite samples and mixed sulphide samples, i.e., chalcopyrite-galena. Once the mineral separation was complete all samples were checked under a binocular microscope and any remaining impurities were removed by hand. The samples were analysed by XRD at the University of Western Ontario (UWO) to confirm the identification and purity of the sample.

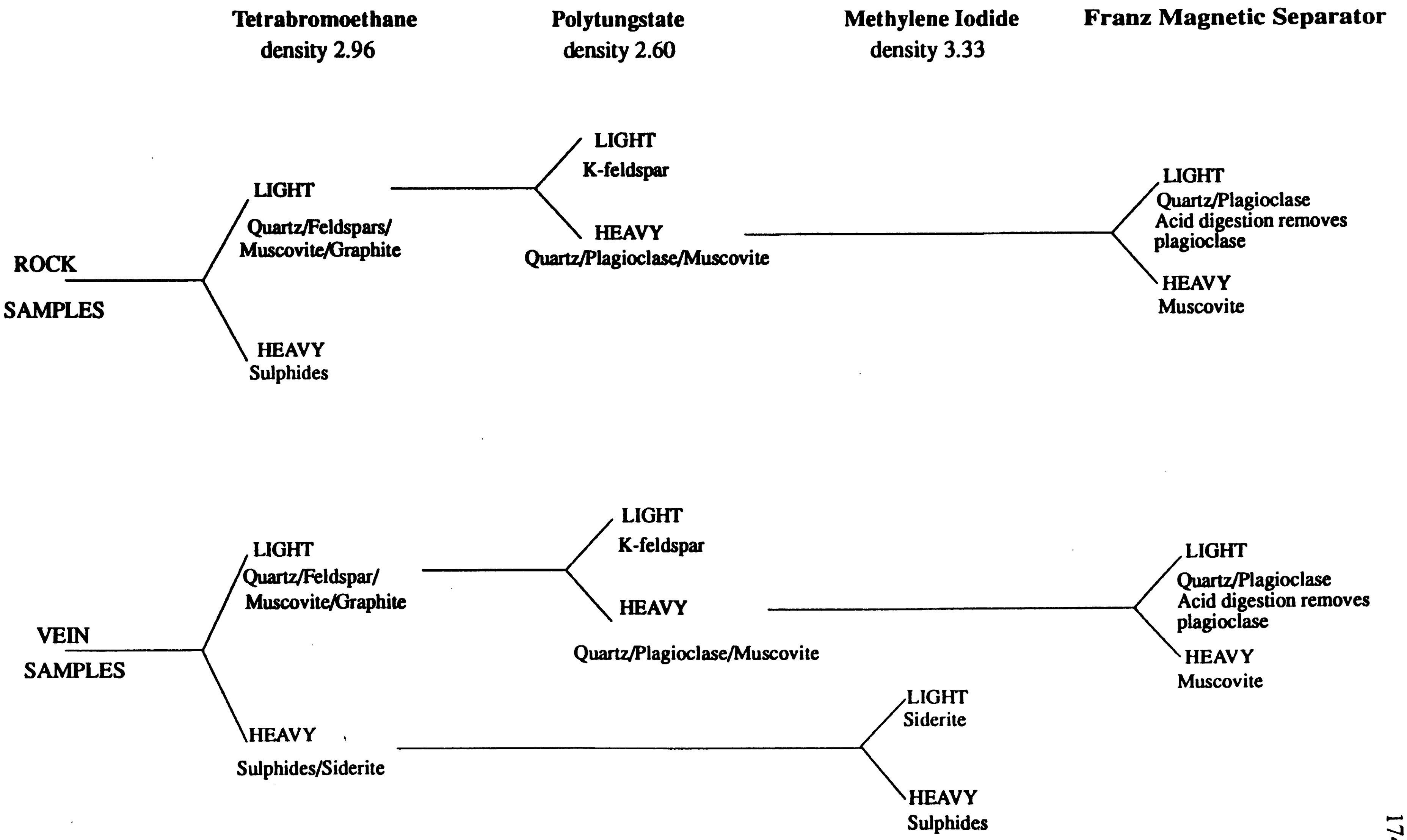


Figure B.1 Mineral Sparation Flow Chart.

B.6. Stable Isotope Analyses

B.6.1 Sulphides

Pure sulphide samples were analysed by two methods. 1) Samples were burned using a modification of the Fritz et al. (1974) method, 2) Some samples were burned on an Elemental Analyser. The SO_2 gas collected in both these methods was analysed on a Fisons OPTIMA mass spectrometer. Each of these methods is outlined below.

1) Fritz et al., (1974)

Samples are weighed out and the ground to a powder with 100 mg cuprous oxide (after Robinson and Kusakabe 1975) rather than the cupric oxide used by Fritz et al. (1974). This powder is then placed inside a quartz glass tube, that is placed into the sample tube. A copper wire plug is placed at the mouth of the sample tube, to ensure reduction of excess oxygen which may allow the production of SO_3. This tube is then attached to the extraction line as shown in Figure B.2. A collection tube is placed on the line and all valves are opened (except V1) and the line is allowed to pump out on full vacuum for 10 minutes. After 10 minutes V2 and V3 are closed and the oven at 1000 °C is placed over the sample tube to start combustion of the sulphide. The oven remains in place for 15 minutes while the remainder of the line pumps out to ensure a complete vacuum. After 15 minutes liquid nitrogen is placed over Trap 1, V4 and V5 are closed and V3 is opened to allow any gas produced to flow in to Trap 1 where it freezes. The oven remains in place for a further 5 minutes to ensure complete combustion of the sample. After 5 minutes V3,

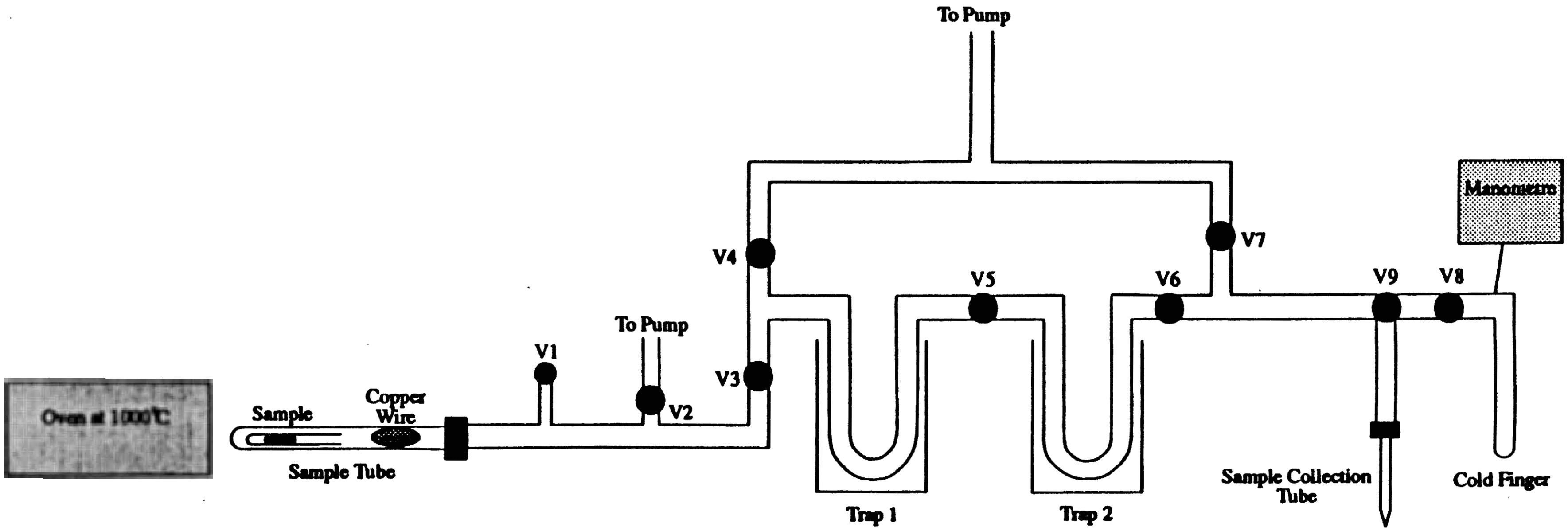


Figure B.2. SO2 Combustion and extraction line used at UWO.

V6 and V7 are closed and the oven is removed, and V4 is opened to allow any uncondensible gases to be pumped away. V4 is then closed and the liquid nitrogen on Trap 1 is replaced with a 'slurry' of liquid nitrogen and ethanol at -80°C, and liquid nitrogen is placed on Trap 2, V5 is then opened. Trap 1 is now freezing any water vapour and the SO_2 and CO_2 are moving into Trap 2. After 5 minutes, V5, V8, and V9 are closed, and the slurry on Trap 2 is replaced by a slurry at -120°C. This allows any CO_2 to become gaseous while the SO_2 remains frozen. Valves V7 and V6 are then opened for 30 seconds to pump away any CO_2. Liquid nitrogen is placed on the cold finger, the slurry on Trap 2 is removed and the SO_2 moves to the cold finger. After 5 minutes all the SO_2 has moved to the cold finger, and V6 and V8 are closed. A manometer reading is taken, liquid nitrogen is placed on the collection tube and then V9 and V8 are opened to transfer the SO_2 to the collection tube. Valve V9 is closed and the collection tube, filled with purified SO_2 is sealed by the breakseal method, and stored until analyses on a Fisons OPTIMA mass spectrometer.

2) Elemental Analyser

The Elemental Analyser used is known as the Carlo Erba, EA 1108 and Pella, (1990) gives a detailed description of the Elemental Analyser and its history. Briefly, the sulphide samples are sealed in small tin cups and then placed in the elemental analyser. The samples are then combusted at 1050 °C by the flash combustion method, whereby, the sample is instantaneously converted into combustion gases of the samples element composition. The combustion chamber is flooded with helium with up to 50% oxygen. The oxygen reacts with the tin sample containers and oxidises the tin. This reaction results in a local temperature increase from 1050°C to 1700 - 1800°C, which accelerates the combustion. The SO_2 gas is then purified on an extraction line attached to the Elemental Analyser. The method of purification is similar to that previously discussed. The pure SO_2 is then sealed into a glass breakseal ready to be placed on the Fisons OPTIMA mass spectrometer.

B.6.2. Carbonates

Carbon dioxide was released from siderite samples according to the method of Rosenbaum and Sheppard (1986). Pure siderite samples were placed inside a reaction vessel and 100% phosphoric acid was placed in the arm of the reaction vessel. The vessel was then placed on the carbonate combustion line and pumped for 20 minutes. The vessel was then heated to enable the acid to degas. The sample remained on the line for a further 20 minutes to ensure the sample containers were completely degassed. The reaction vessel was then closed and placed in an oven at 150°C for 30 minutes. After this time, the acid was reacted with the siderite and the sample was returned to the oven for a further 90 minutes. Once the samples had completely reacted the vessels were once again attached to the extraction line. The CO_2 was frozen in the sample collection tube by placing the tube in liquid nitrogen. A 'slurry' at -80° C froze any water vapour, and any uncondensible gases were pumped off.

B.6.3. Oxygen from Silicates

The method used was that of Clayton and Mayeda (1963). Briefly, this entails the silicate minerals undergoing a reaction with BrF_5 at high temperatures- 600°C for quartz, ~400°C for feldspars and 300°C for muscovite. The F substitutes into the crystal structure, releasing oxygen. This oxygen is then passed over hot graphite to produce CO_2 which is purified on the line to remove any uncondensible gases and any water. This purification is accomplished by passing the CO_2 gas through a sequence of traps that freeze the water (slurry at -80°C) and CO_2 (liquid nitrogen), allowing any uncondensible gases to be pumped away. The CO_2 remains frozen while any water is heated and pumped from the line, leaving only pure CO_2 which is frozen into a sample collection tube and was analysed on a Fisons OPTIMA mass spectrometer.

B.6.4 Hydrogen from Silicates

Hydrogen isotope composition was determined using the method of Vennemann and O'Neil (1993), using the uranium reagent of Godfrey (1962). Weighed amounts of hydrous minerals were loaded into quartz tubes. Coarse-grained quartz chips, which had previously been decrepitated at 1100 ° C was added to each tube, followed by a quartz wool plug. The tubes are then attached to the extraction line and degassed at 150 ° C. At the same time Pyrex collection tubes, with weighed amounts of uranium reagent are attached to the line and evacuated. The sample in the quartz tube is heated using a fuel-gas-oxygen torch to temperatures > 1400 °C. Water released during this heating is collected in a trap by liquid nitrogen, while hydrogen released during the reaction is oxidised by CuO at 700 °C, and condensed to form H_2O in a second liquid nitrogen trap. Once the sample is completely dehydrated and the H_2O frozen, uncondensible gases in the different sections of the extraction line are pumped off, and the sample transferred into the Pyrex collection tubes and analysed on the Fisons Prism Series II mass spectrometer.

Table B.1 Representative analyses of muscovite samples from Kempt Snare Lake

Sample	LD-7/4	LD-7/7	LD-7/9A	LD-7/9B	LD-10/7	LD-11/2	LD-34/1
Unit	1	1	1	1	1	1	2
SiO2	48.44	47.2	46.85	47.08	47.09	47.69	46.84
TiO2	0.13	0.2	0.91	0.38	0.65	0.08	0.22
Al2O3	27.55	29.47	27.53	27.89	27.48	30.86	31.85
FeO	5.66	6.77	7.56	7.42	7.49	5.4	4.23
MnO	0.06	0.05	0.11	0.07	0.11	0.07	0.02
MgO	0.87	0.76	0.91	0.88	1.01	0.85	0.4
CaO	0.17	0.05	0	0	0.04	0.01	0.03
Na2O	0.42	0.09	0.14	0.08	0.13	0.11	0.32
K2O	9.87	9.4	10.1	9.92	9.93	9.66	8.75
Cr2O3	0.01	0.1	0	0.08	0	0.04	0.06
Total	92.98	94.06	93.61	93.56	93.66	94.9	92.57

Sample	LD-38/4	LD-38/6	LD-44/3	LD-4/1	LD-4/4	LD-36/3	LD-42/6
Unit	2	2	2	3	3	3	3
SiO2	46.66	47.45	46.44	47.89	47.61	47.08	47.6
TiO2	0.12	1.02	0.58	0.05	0.28	0.74	0.12
Al2O3	31.02	28.56	26.99	31.26	31.55	27.41	30.86
FeO	5.83	6.63	8.25	5.03	4.93	7.78	4.68
MnO	0.09	0.1	0.9	0.14	0.11	0.15	0.11
MgO	0.85	1.29	1.07	0.53	0.46	0.7	0.76
CaO	0	0	0	0	0	0	0.03
Na2O	0.13	0.18	0.2	0.15	0	0.16	0.1
K2O	9.59	9.52	9.72	9.18	10.05	10.02	9.54
Cr2O3	0.14	0	0	0	0	0	0
Total	93.95	94.65	93.19	94.03	94.88	93.54	93.88

Table B.1 Continued

Sample	LD-21/3	LD-23/2	LD-23/3	LD-24/3	LD-1/4	LD-1/5	LD-25/1
Unit	4	4	4	4	5	5	5
SiO2	46.56	45.62	47.18	47.87	48.38	46.6	47.78
TiO2	0.21	0.03	0.16	0.19	0.07	0.24	0.15
Al2O3	33.3	32.05	30.6	30.41	30.12	31.45	30.31
FeO	4.05	5.23	4.88	4.18	5.59	5.25	5.57
MnO	0.1	0.06	0	0.1	0.01	0.02	0.08
MgO	0.36	0.048	0.64	0.45	0.63	0.73	0.33
CaO	0	0	0	0.03	0	0	0
Na2O	0.45	0.31	0.08	0.11	0.19	0.34	0.28
K2O	9.77	8.99	9.42	9.49	9.41	10.22	9.55
Cr2O3	0.06	0	0	0.07	0	0	0
Total	94.75	92.68	93.96	92.95	94.33	94.84	92.6

Sample	LD-25/2	LD-25/5	LD-27/3	LD-27/5	LD-27/7	LD-46/3	LD-46/5
Unit	5	5	5	5	5	Vein	Vein
SiO2	47.07	47.91	46.94	48.69	46.9	46.39	46.36
TiO2	1.53	0.15	0.74	0.14	0.18	0.1	0.16
Al2O3	27.8	30.03	29.79	28.62	31.06	32.45	32.09
FeO	5.97	5.68	6.25	6.17	4.75	4.62	5.8
MnO	0.14	0.01	0.03	0.12	0.05	0.04	0.03
MgO	0.73	0.55	0.52	0.58	0.42	0.65	0.45
CaO	0.03	0	0.02	0.03	0	0	0
Na2O	0.18	0.22	0.12	0.12	0.19	0.18	0.11
K2O	9.63	9.01	9.33	9.17	9.37	10.1	9.84
Cr2O3	0.06	0.02	0	0	0	0	0.1
Total	93.43	93.45	93.56	93.23	92.69	94.3	94.54

Table B.2. Representative analyses of K-feldpsar from Kempt Snare Lake.

Sample	LD-7/1	LD-7/3	LD-11/1	LD-11/7	LD-7/9	LD-34/3	LD-34/9
Unit	1	1	1	1	1	2	2
SiO2	65.77	66.22	64.66	64.87	65.07	61.57	63.58
TiO2	0	0.02	0.13	0.01	0.04	0	0
Al2O3	18.66	18.82	18.87	19.49	8.49	17.73	18.76
FeO	0.03	0.08	0.01	0	0	0	0.13
MnO	0.1	0.04	0	0	0	0	0
MgO	0.01	0	0.02	0.1	0.4	0.04	0.1
CaO	0	0.03	0	0	0	0	0.09
Na2O	0.44	0.8	0.44	0.31	0.41	0.45	0.24
K2O	16.54	15.78	16.2	19.92	16.53	15.74	16.46
BaO	0.06	0.07	0	0.15	0.01	0.15	0
Total	101.41	102.42	100.15	99.73	100.44	95.41	99.28

Sample	LD-34/11	LD-44/1	LD-44/5	LD-4/2	LD-4/3	LD-36/6	LD-42/1
Unit	2	2	2	3	3	3	3
SiO2	64.8	64.89	65.17	65.08	65.36	65.1	65.37
TiO2	0	0.06	0	0	0	0	0.05
Al2O3	18.58	18.64	18.68	18.63	18.81	18.53	18.56
FeO	0.8	0	0.03	0	0.07	0	0.09
MnO	0.01	0.03	0.07	0	0.02	0	0
MgO	0.04	0	0	0.15	0.04	0.07	0
CaO	0.03	0	0	0.09	0	0	0.03
Na2O	0.74	0.31	0.29	0.36	0.42	0.44	0.23
K2O	15.53	16.64	16.41	16.67	16.45	16.5	16.62
BaO	0.22	0	0	0.07	0.24	0.02	0.2
Total	99.93	100.47	100.59	100.88	101.24	100.59	101.08

TableB.2 Continued

Sample	LD-21/1	LD-24/1	LD-24/4	LD-24/4B	LD-1/1	LD-25/3	LD-25/6
Unit	4	4	4	4	5	5	5
SiO2	65.37	64.13	62.92	64.16	65.02	64.22	64.19
TiO2	0.05	0	0.03	0	0	0.05	0
Al2O3	18.56	18.22	17.87	18.42	18.66	18.53	18.6
FeO	0.09	0	0.04	0	0	0	0.09
MnO	0	0	0.04	0.09	0	0	0
MgO	0	0	0.07	0.03	0	0.1	0.07
CaO	0.03	0.03	0.02	0	0	0	0.04
Na2O	0.23	0.18	0.35	0.33	0.3	0.28	0.31
K2O	16.62	16.54	15.18	16.67	16.44	16.55	16.37
BaO	0.2	0.16	0.09	0.05	0.13	0	0.24
Total	101.08	99.08	96.61	99.64	100.42	99.45	99.78

Table B.3 Representative analyses of plagioclase feldspar from Kempt Snare Lake.

Sample	LD-7/3	LD-7/3B	LD-7/6	LD-11/4	LD-11/5	LD-34/4	LD-34/5
Unit	1	1	1	1	1	2	2
SiO2	69.5	69.22	66.88	67	66.94	67.51	68.34
TiO2	0.09	0.06	0.18	0	0.11	0	0.04
Al2O3	19.72	19.91	21.08	20.67	21.65	20.07	19.87
FeO	0.1	0.05	0.04	0.18	0.29	0.09	0
MnO	0.06	0.07	0	0	0	0.02	0.04
MgO	0	0	0	0	0.05	0	0.03
CaO	0.08	0.08	1.47	1.29	0.81	0.35	0.13
Na2O	11.83	11.61	10.63	11.02	9.41	11.2	11.27
K2O	0.05	0	0.1	0.01	0.85	0	0.03
Cr2O3	0	0.05	0	0	0	0.09	0
Total	101.05	100.74	100.15	100.03	100	99.25	99.61

Sample	LD-38/3	LD-44/6	LD-44/4	LD-4/7	LD-36/4A	LD-36/4B	LD-36/5
Unit	2	2	2	3	3	3	3
SiO2	68.61	67.95	68.02	67.42	68.23	68.44	67.42
TiO2	0	0	0.03	0	0.01	0	0
Al2O3	20.11	20.3	20.43	20.55	19.59	19.63	20.55
FeO	0	0	0	0.05	0.06	0	0.05
MnO	0	0	0	0	0.05	0	0
MgO	0	0.17	0	0.07	0	0	0.07
CaO	0.55	0.49	0.84	1.07	0.14	0.15	1.07
Na2O	10.75	11.5	10.98	11.16	11.42	10.35	11.16
K2O	0	0.04	0.04	0.01	0.04	0.03	0.01
Cr2O3	0	0	0	0.03	0	0.03	0.03
Total	100.36	10.23	100.25	100.66	99.7	98.56	100.66

Table B.3 Continued

Sample	LD-42/3	LD-42/3R	LD-42/5	LD-21/1	LD-21/5A	LD-21/5B	LD-23/4
Unit	3	3	3	4	4	4	4
SiO2	69.56	68.96	67.95	69.34	68.63	68.92	68.24
TiO2	0	0	0.05	0	0	0.04	0.09
Al2O3	19.77	20.09	20.65	19.68	19.62	19.74	19.98
FeO	0.05	0	0.02	0.03	0.06	0.08	0.12
MnO	0.03	0	0.03	0	0	0.08	0
MgO	0.02	0	0.06	0	0	0.08	0.04
CaO	0	0.14	0.96	0	0.09	0	0.17
Na2O	10.86	11.73	10.33	11.01	11.51	11.7	10.57
K2O	0.01	0.02	0.07	0.09	0	0.02	0.2
Cr2O3	0.11	0.24	0	0.22	0.03	0	0
Total	100.31	101.05	99.98	100.24	99.84	100.44	99.42

Sample	LD-23/5	LD-23/5R	LD-1/3	LD-25/2	LD-25/7	LD-27/4	LD-27/8
Unit	4	4	5	5	5	5	5
SiO2	68.3	68.02	67.17	67.39	68.15	69.02	68.16
TiO2	0.11	0	0.04	0	0	0	0
Al2O3	20	19.88	19.81	20.62	20.65	19.84	19.82
FeO	0.06	0	0	0	0	0	0
MnO	0	0	0	0.03	0	0.09	0
MgO	0.9	0	0.05	0.03	0.13	0.03	0.09
CaO	0.29	0.2	0.39	1.11	0.91	0	0.44
Na2O	11.25	11.27	11.41	10.24	10.57	12.01	10.8
K2O	0.01	0.04	0.08	0.3	0.08	0.07	0
Cr2O3	0	0.15	0	0	0.26	0.2	0
Total	99.85	99.37	98.85	99.23	100.66	100.88	98.93

Sample	LD-7/3	LD-34/5	LD-42/3	LD-23/4	LD-25/7
Unit	1	2	3	4	5
SiO2	69.5	68.34	69.56	68.24	68.15
TiO2	0.09	0.04	0	0.09	0
Al2O3	19.72	19.87	19.77	19.98	20.65
FeO	0.1	0	0.05	0.12	0
MnO	0.06	0.04	0.03	0	0
MgO	0	0.03	0.02	0.04	0.13
CaO	0.08	0.13	0	0.17	0.91
Na2O	11.83	11.27	10.86	10.57	10.57
K2O	0.05	0.03	0.01	0.2	0.08
Cr2O3	0	0	0.11	0	0.26
Total	101.05	99.61	100.31	99.42	100.66

Table B.4 Representative analyses of sulphides from Kempt Snare Lake.

Mineral- Galena

Sample	LD-38/3	LD-38/5	DP-1/1	DP-3/1	DP-3/2	DP-3/3	DP-3/6
Zn						0.58	0.59
Pb	86.23	87.10	86.30	87.82	87.91	87.88	86.56
S	12.78	12.65	12.76	12.81	12.93	13.14	12.88
Total	99.09	100.16	99.06	100.63	101.15	101.88	100.31

Mineral-Sphalerite

Sample	DP-3/9	DP-3/12	DP-3/15	DP-3/17	DP-4/4	DP-4/8
Fe	8.18	8.21	8.08	8.13	7.71	7.65
Zn	59.35	59.22	59.34	58.44	59.51	59.34
S	33.06	32.94	33.29	33.01	33.16	31.37
Total	102.88	102.40	102.15	102.06	102.55	99.63

Mineral- Arsenopyrite

Sample	LD-25/1	LD-27/2	LD-32/13	LD-33/1	LD-33/4	LD-38/1	LD-38/2
Fe	35.26	35.27	34.99	35.29	34.47	35.23	35.15
As	46.45	45.44	46.43	45.42	47.29	45.57	46.53
S	20.20	20.60	19.80	20.97	19.49	20.72	20.24
Total	102.02	101.60	100.84	102.36	101.25	101.52	101.93

Mineral- Arsenopyrite

Sample	LD-50/3	LD-A4/1	DP-1/1
Fe	35.34	34.92	34.63
As	45.28	47.38	46.22
S	21.12	19.42	20.21
Total	101.87	102.05	101.06

Mineral-Pyrite

Sample	DP-3/11	DP-3/13
Fe	46.20	47.63
As	2.94	0.70
S	52.65	54.10
Total	101.88	102.69

Table B.4 Continued

Mineral-Pyrrhotite

Sample	DP-3/14	DP-3/15
Fe	44.39	47.16
As	2.88	0.98
Zn	1.43	0.52
S	48.83	54.11
Total	99.40	103.10

Mineral-Chalcopyrite

Sample	LD-27/1	DP-1/1	DP1/2	DP-1/3	DP-4/7
Fe	30.42	31.69	32.04	31.37	30.40
Cu	34.52	35.11	34.51	34.92	34.55
Zn					0.72
S	35.04	35.12	34.91	35.16	34.81
Total	100.86	102.67	102.89	102.08	100.48

Table B.5 Representative analyses of siderites from Kempt Snare Lake.

Mineral - Siderite (Atomic %)

Hydrothermal

Sample	LD-13/3	LD-13/5	LD-13/9	LD-56/2	LD-56/3	LD-56/4
Fe	47.84	39.03	39.04	40.52	49.28	37.34
Mn	37.31	42.85	44.54	40.14	35.80	40.77
Ca	8.80	9.21	10.43	10.40	7.01	10.19

Low temperature

Sample	LD-13/10	LD-18/1	LD-18/3	LD-18/4	LD-35/1	LD-35/3	LD-35/6
Fe	69.24	76.57	75.74	72.45	69.44	70.80	70.80
Mn	26.46	19.60	20.53	22.96	23.48	24.20	24.30
Ca	3.08	1.87	2.07	2.54	3.79	3.32	3.23

Low temperature

Sample	LD-47/2	LD-47/4	DP-1/4	DP-1/8	DP-1/9	DP-2/3	DP-2/4
Fe	78.67	71.23	64.43	81.04	68.40	79.88	83.22
Mn	17.75	24.69	31.00	15.44	27.46	16.35	11.89
Ca	2.15	3.01	3.54	2.41	3.02	2.80	3.37

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