A STUDY OF THE TIN MINERALIZATION AND LITHOGEOCHEMISTRY

IN THE AREA OF THE WEDGEPORT PLUTON,

SOUTHWESTERN NOVA SCOTIA

by

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Submitted in partial fulfillment

of the requirements for the degree of Master of Science at

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DALHOUSIE UNIVERSITY

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ABSTRACT

Cassiterite and base metal sulphides have recently been discovered in Yarmouth County, southwestern Nova Scotia, in an area of folded and metamorphosed Cambro-Ordovician turbidites of the Meguma Group intruded by the monzogranitic Wedgeport pluton.

Several kinds of tin mineralization occur:

1. rare detrital cassiterite grains in a pelitic 'microscour'.
2. stratiform sulphide-cassiterite replacement bodies in calcareous layers.
3. sulphide-cassiterite veinlets in metasediments with restricted chlorite alteration.
4. rare sulphide-cassiterite veinlets in pluton with restricted greisen alteration.

Cassiterite occurs in several habits:

1. equant - in detrital, stratiform replacement bodies and veins.
2. prismatic - in stratiform replacement bodies.
3. acicular - in veins.
4. botryoidal - in stratiform replacement bodies(rare) and veins.

Geochemical analysis of drill core show that most background values in the metasediments and pluton are low compared to lithologies in the Cornish tin district and specialized ore-bearing granitoids. The sulphide-cassiterite veinlets exhibit a mineralogical and therefore geochemical variation with distance from the pluton: from Mo and W within 2 km of the pluton, to Sn about 3 to 4 km distant, to Pb and Zn about 4 to 7 km distant.

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ACKNOWLEDGEMENTS

CHAPTER ONE

INTRODUCTION

1.1 General Statement

Cassiterite mineralization was discovered in the
Wedgeport area in 1976 to 1977 by Millmor Syndicate and Shell
Canada Resources Limited. It consists of a veinlet stockwork
in the margin of the Wedgeport monzogranite, and both vein
and stratiform styles in the surrounding turbidite sequences
of the Goldenville Formation. The study area is situated
along the coast of southwestern Nova Scotia in Yarmouth
County, about 10 km southeast of the town of Yarmouth (Fig.
1.1). It covers an area of approximately 240 km^2. Access is
gained by provincial highway 103 from Halifax to Yarmouth,
and secondary paved and dirt roads. Yarmouth is also linked
to Halifax by the CNR railway line and by daily air service.
Generalized geology of the area is shown in the map in the
back pocket of the thesis.

1.2 Physiography and Surficial Geology

The study area is part of the Atlantic Uplands, a
low-lying region with rolling hills of up to 50 m relief

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Figure 1.1   Location of the study area in southwestern Nova Scotia.
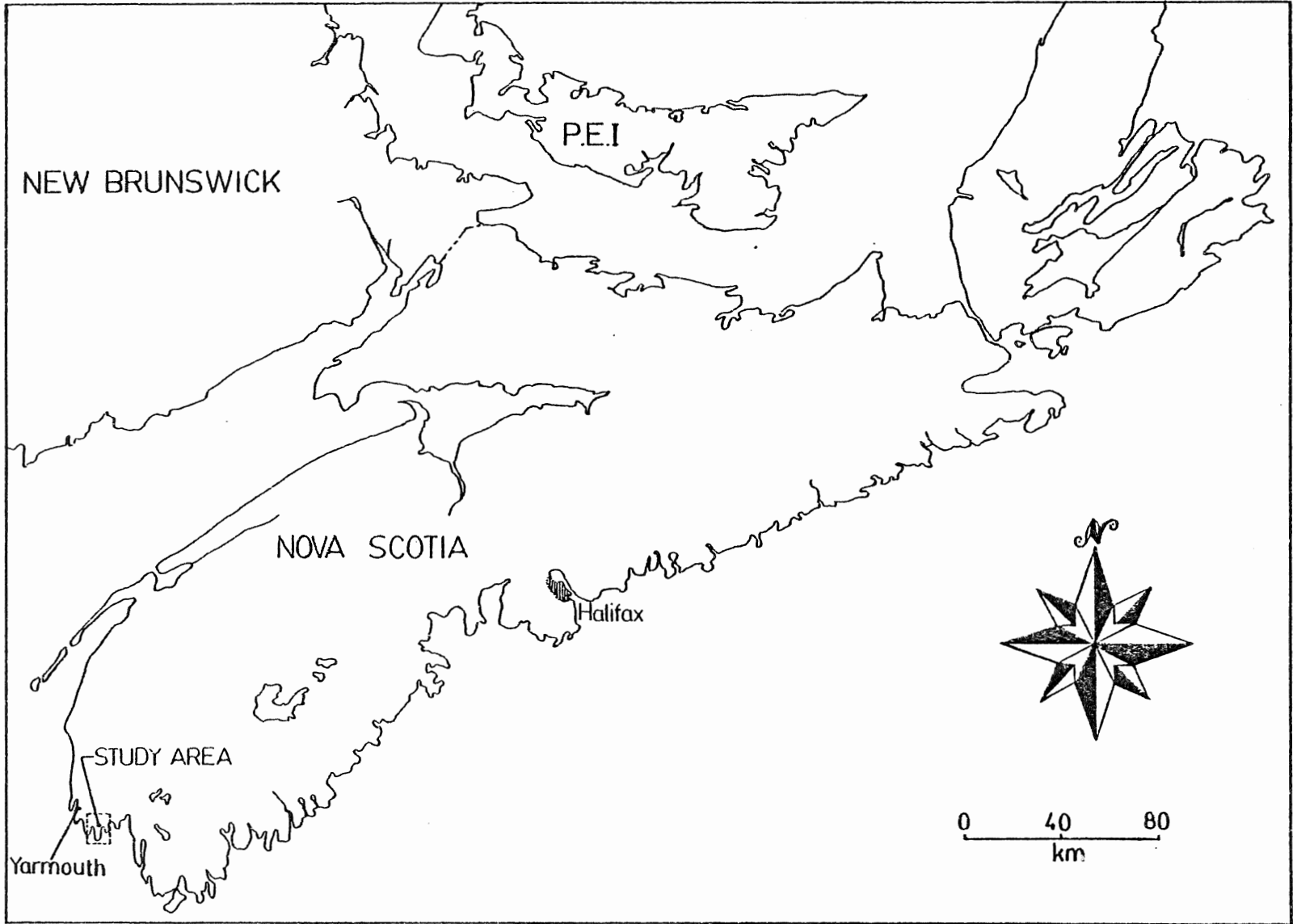
(Sinclair, 1978); small lakes, swamps and streams occur in
between. The coast is a submergent one and is characterized
by salt marshes, tidal flats, bays, peninsulas and islands.

Drainage toward the south is controlled by the Tusket
River to the east and the Chebogue and Little Rivers to the
west (Taylor, 1967).

Bedrock exposure is limited to the coastline, rivers and
lakeshores, with minor occurrences along road and railway
cuts. Most of the region is covered by Pleistocene deposits
of the Wisconsinan glaciation. Sandy till (up to 18 m in
thickness), with boulders (up to 7 m across) of the
underlying bedrock is the main type of drift; stratified
outwash and ice contact deposits of sand and gravel occur
locally (Sinclair, 1978). Two ice lobes may have existed in
this area, one moving south-southeast, the other
south-southwest (Cant et al., 1978; Taylor, 1967).

1.3 Regional Setting

Tin mineralization is found in both the Goldenville
Formation of the Cambro-Ordovician Meguma Group and the
Wedgeport pluton. The sediments are part of a thick sequence
(at least 10 km; Schenk, 1975) of turbiditic wackes and
slates, partly interfingered with, and partly overlain by,
the pelitic Halifax Formation. Rare graptolites in both

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formations indicate an Early Ordovician period of sediment
deposition.   K-Ar ages from detrital muscovite in sandstone,
provide ages of 476 ± 19 Ma and 496 ± 20 Ma (Harris and
Schenk,1975). The sediments are believed to have been derived
from a large, low-lying continental mass of granodioritic and
metasedimentary composition; they were deposited by
channelized turbidites ('contourites'), overflow turbidites
and bottom currents (Schenk and Lane,1982).

The Meguma Group is overlain, mostly conformably, by
Late Ordovician to Early Devonian volcanic rocks and detrital
sedimentary rocks of the White Rock, Kentville, New Canaan,
and Torbrook Formations (Schenk,1975).

The Paleozoic strata were subsequently tightly folded
and regionally metamorphosed to greenschist, locally
almandine-amphibolite facies, during the mid-Devonian Acadian
Orogeny (Taylor,1967). These folds were offset by northwest-
trending, mainly sinistral, faults with horizontal
displacements of up to 6 km (Harris and Schenk,1975).

Following these events, the South Mountain batholith and
related satellite stocks were emplaced at relatively shallow
depths in the crust (about 4 to 10 km;McKenzie and
Clarke,1975), causing local thermal metamorphism (Reynolds et
al.,1981).   The batholith covers 1/3 to 1/2 of western Nova
Scotia, outcropping over about 10 000 km^2. The batholith is

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predominantly of granodioritic to monzogranitic composition, but parts of it may range from norite and tonalite to syenogranite in composition (McKenzie and Clarke,1975; Clarke et al., 1980). Stratigraphic relationships indicate that the batholith was emplaced after the Acadian Orogeny, from the mid-Devonian to Early Carboniferous. Age dating of 28 mica samples from the batholith and various northern satellite stocks by K-Ar and $^{40}Ar/^{39}Ar$ yield a mean age of 367 Ma (Reynolds et al.,1981). Clarke and Halliday (1980), constructing Rb-Sr isochrons from whole rocks and mineral separates, estimated the age of granodiorite emplacement at 371.8 ± 2.2 Ma and that of adamellite emplacement at 364.3 ± 1.3 Ma. Dating of 14 mica samples from southern satellite stocks (including the Wedgeport pluton) yield younger ages (258-353 Ma). This may be due to either actual intrusion during the Late Carboniferous or to a thermal or tectonic event(s) which partially degassed the rocks or, less probably to protracted cooling to argon blocking temperatures (Reynolds et al.,1981). The Brenton pluton near the study area is a cataclastic granite with foliation parallel to regional schistosity and was believed intruded before or during the Acadian Orogeny; 6 analyses of both biotite and muscovite yield apparent Ar ages of from 314 to 328 Ma, suggesting emplacement during the Late Carboniferous before or during a period of deformation ('Maritime Disturbance').

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Analysis of chloritized biotite from the Wedgeport pluton
reveals apparent ages of 258 to 175 Ma (Permian to Jurassic)
and may be associated with a mineralizing event; the younger
ages are probably due to resetting (degassing) by Triassic
mafic dykes. Muscovite and biotite from mineralized greisen
and pegmatite of the Davis Lake pluton yield ages from 335 to
267 Ma (average of 290 Ma). Biotites from a granitoid body
near this pluton give an average age of 272 Ma. These young
ages again imply some kind of intrusive, tectonic, or
hydrothermal event in the Late Carboniferous to Permian
(Reynolds and Zentilli, in prep; Reynolds et al.,1981).

1.4 Previous Work

Prior to 1950, preliminary mapping was carried out by
such geologists as C.T. Jackson and F. Alger in 1828, A.
Gesner in the first half of the nineteenth century, L.W.
Bailey in 1898, E.R. Faribault in the early twentieth
century, and S. Powers in 1915 (Taylor,1967).

Gravity and aeromagnetic maps of southwestern Nova
Scotia have been produced by G.D. Garland, and the Geological
Survey of Canada in the nineteen fifties (Taylor,1967); the
Nova Scotia Department of Mines and the G.S.C. in 1977
produced airborne gamma ray spectrometric maps covering the
South Mountain batholith of southern Nova Scotia (Chatterjee

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and Muecke,1982; Sinclair,1978).

R.W Boyle and others in the late fifties analysed water and sediment samples from streams, rivers and lakes of the southwestern part of the province for Cu, Pb and Zn (Taylor,1967).

A more detailed investigation of the geology of the study area was made by Taylor (1967), in which he described the sedimentary Meguma Group, the volcano-sedimentary White Rock Formation, and the various intrusive felsic and mafic rocks; he made a preliminary study of the area's structure and metamorphic characteristics and assembled a list of metal and industrial mineral locations.

Further refinement of the geology was accomplished in the fields of: the Meguma Group (Schenk and Lane,1982; Schenk,1975; Harris and Schenk,1975); the White Rock Formation (Lane,1975; Sarkar,1978); structural geology by Fyson in 1966 and Keppie in 1977 (Cullen,1983); geochronology of intrusions (Reynolds and Zentilli,in prep; Reynolds et al.,1981; Clarke and Halliday,1980) and Meguma Group slates (Reynolds et al.,1973); and metamorphic petrology by Taylor and Schiller in 1966, Muecke in 1973, Keppie and Muecke in 1979, Clarke and Muecke in 1980 (Cullen,1983), and J. Cullen (1983). Pleistocene glacial history has been described by Grant and Gravenor (Sinclair,1978).

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1.5 Economic Geology

Only minor exploration took place in the region before 1975. Three small gold occurrences were worked in the late nineteenth and early twentieth centuries. Beryl- and spodumene-bearing pegmatites and veins are found at several localities (e.g. Brazil Lake, Port Joli and Shelburne granodiorites). One very small molybdenite occurrence is near the Jordan River, within a series of quartz veins. Granodiorite, hornblende diorite and quartz diabase were once quarried for building stone. From 1945 to 1960, quartzite beds of the White Rock Formation at Cheggogin Point were quarried for the production of silica brick (Taylor,1967).

Prior to 1977, prospecting for Cu, Pb, Zn, Sn, W, Ag, and Mo was performed by Chib-Kayrand Copper Mines, Cuvier Mines, Quebec Uranium Mining Corporation and Lacana Mining Corporation (Sinclair,1978). Discovery of sulphide-bearing boulders in gravel pits by Millmor Syndicate in 1976 resulted in staked claims and subsequent optioning of the property to Shell Canada Resources Limited. In 1978 a tin deposit was discovered about 35 km northeast of Yarmouth, near East Kemptville. Tin, in the form of cassiterite, occurs with various sulphides within a 100 m thick, 500 by 1500 m zone of sericitized and greisenized rocks of the Davis Lake pluton, a part of the South Mountain batholith. By 1982, reserves were

estimated at 38 million tonnes with a grade of 0.2 % Sn and a
0.1 % Sn cutoff grade (Richardson et al., 1982).

Shell Canada Resources Limited undertook an exploration
program in the study area, performing airborne and ground
geophysical surveys, geologic mapping where possible,
geochemical sampling (soil and rock), mineralized boulder
tracing, and overburden and diamond drilling. Most diamond
drill holes were located over geophysical anomalies. From
1977 to 1978, 80 holes were drilled for a total of about
10 600 m; in 1979 only 8 holes were drilled for a total of
about 650 m; and 1980, 3 holes were drilled, totalling about
280 m. The anomalies were found to be due to pyrrhotite and
graphite in the metasediments, sulphide stringers in both the
metasediments and pluton, and to magnetic mafic dykes.
Because of the unsatisfactory results, the company decided
against further work in the area (Cant et al.,1978;
Cant,1979; Sarkar,1980). This area and the East Kemptville
deposit are currently owned by Rio Algom Limited.

1.6 Purpose and Methods of Study

Tin and base metal mineralization have only recently
been discovered within southwestern Nova Scotia. Subsequent
exploration for these metals may be aided by a knowledge of
their mode of formation. In an attempt to understand the

genesis of tin and associated metals, the thesis had several basic objectives.

1. To determine the type of tin mineralization. In what form does it occur with respect to veins, sedimentary and igneous host rocks? With what minerals is tin associated? What is its relationship with the pluton?

2. To determine the general type and extent of alteration associated with mineralization.

3. To determine the distribution of a selected group of metals in the metasediments and pluton, and establish background and threshold values for these lithologies.

Because of the limited exposure of both the pluton and country rock (mainly along part of the western shoreline), the thesis is based upon the study of about 11.5 km of drill core. Core logs, drill hole cross-sections and plan maps of all 91 drill holes in the area were studied in order to select core with such features as: vein systems, stratabound mineralization, unmineralized zones, and various structures like foliations, fractures and breccias.

Four weeks were spent sampling the core stored at the base camp of Shell Canada Resources Limited near East Kemptville. Core and reference samples(122 in total) were cleaned, powdered and sent for geochemical analysis to X-Ray

Assay Laboratories Limited in Toronto. Thin and polished sections(almost 200 in total) of relevant samples were made, described and analyzed by microprobe.

This detailed study of tin mineralization in and around the Wedgeport pluton should contribute to the overall understanding of tin genesis in Nova Scotia and assist in subsequent exploration programs.

CHAPTER TWO

LOCAL GEOLOGY AND PETROLOGY

2.1 Introduction

The study area comprises about 240 square km of part of the Lower Paleozoic Meguma Group metasediments with later intrusive monzogranite and basic dykes. Because of the paucity of outcrop, the petrologic study was performed on sections of diamond drill core, using a combination of microscope, microprobe and geochemical methods. All microprobe and chemical analyses are tabulated in the Appendices. Modal compositions were visually determined with the aid of percent comparison charts (Terry et al.,1955).

The core consists of a monotonous metamorphosed sequence of interbedded wackes, siltstones and argillites of the upper members of the Goldenville Formation flysch. Black carbonaceous pelitic layers are also present and may represent coeval, interfingered parts of the Halifax Formation (Schenk,1975; Harris and Schenk,1975). Bedding contacts are usually sharp, with minor gradational sequences.

Bedding thickness varies, from less than 1 cm to about 7 m (Taylor,1967); similar lithologies found along the eastern

shore of Nova Scotia have maximum thicknesses greater than 50 m (Harris and Schenk,1975). The core generally has thin to medium bedding (3-30 cm).

The meta-wackes and meta-siltstones are commonly structureless, with minor graded bedding, cross-bedding, flutes (Fig. 2.1), and argillaceous rip-up clasts. Minor slump features occur within the pelitic units (Fig. 2.2). Calcareous concretions, metamorphosed to calc-silicate nodules occur within particular psammitic layers and are described by Cullen (1983).

Because the study is based on drill core, continuity of individual layers is unknown. One sample of drill core exhibits a facies change in an open fold (sedimentary slump?), from carbonaceous argillite to biotite meta-wacke (Fig. 2.3).

This sedimentary package was affected by low grade greenschist facies regional metamorphism (Cullen,1983), folding, intrusion by the Wedgeport pluton (with associated thermal metamorphism to the hornblende hornfels facies), faulting, and intrusion by a series of mafic dykes. Airborne and ground geophysical surveys performed by Shell Canada Resources (electromagnetic, magnetic and induced polarization) plus dip orientations of core and outcrop indicate the presence of several northerly-plunging synclines and anticlines in the study area (Cant et al., 1978).

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Figure 2.1   Contact of scoured meta-argillite with
upper meta-wacke. Note light coloured
current marks rich in ilmenite(altered
to leucoxene and rutile) and zircon.
Note silver white angular arsenopyrite.

Sample 77-34-86.13

Figure 2.2   Meta-argillite exhibiting contorted soft
sediment deformation and linear clusters
of pyrrhotite and pyrite.

Sample 80-03-118

15

5 cm

5 cm

Figure 2.3   Facies change within an open fold(sediment-
                  ary slump?). Graphitic meta-argillite and
                  central meta-wacke(with green blades of
                  ?) grade laterally to the right into
                  biotite meta-wacke.

                  Sample 77-31-105.38

5 cm

IW-098

The meta-pelitic rocks usually possess two foliations: the first is parallel or at low angles (up to about 40 degrees, depending on location of sample in the folded metasediments) to bedding planes and manifests itself by parallel orientation of phyllosilicate minerals or elongate blebs of pyrrhotite (Fig. 2.4); the second foliation occurs as a set of crenulations which in many places develop into cleavages, and are usually oriented at high angles (50-90 degrees) to the first foliation. Pre-existent veinlets are kinked, ptygmatically folded or broken (Fig. 2.5). Meta-psammitic lithologies exhibit the first foliation in the same manner as the meta-pelites but the second foliation is either absent or manifested as quartz-calcite-filled tension fractures (but may be of later origin), also at high angles to the first foliation.

The metasediments are in sharp, sometimes parallel contact with the Wedgeport pluton and exhibit thermal metamorphic features such as hornfelsic texture and development of biotite, cordierite, andalusite and garnet. The intrusion dips steeply under the metasediments.

Both metasediments and pluton are faulted, exhibiting narrow (up to about 1 metre wide) shear and breccia zones with associated late stage veins(calcite-quartz-arsenopyrite ± pyrite). Minor displacement, on the order of several cm is observed in drill core (Fig. 2.6); aeromagnetic maps show a

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Figure 2.4   Carbonaceous meta-argillite and meta-
                    argillite with metamorphic biotite in
                    bedding planes. Foliated pyrrhotite
                    blebs occur at an angle to bedding.

                    Sample 77-31-111.97

5 cm

Foliation

Bedding

Figure 2.5   Meta-argillite cut by early quartz-
                    calcite veinlets, which are both
                    ptygmatically folded and cut by
                    crenulation cleavage.

                    Sample 78-10-10

Figure 2.6   Blue mineralized zone in meta-wacke
                    containing fine sulphide hair veinlets
                    and cut and displaced by a late calcite
                    vein.

                    Sample 77-25-197.8

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shift in the position of a pyrrhotite-bearing sedimentary
member (Cant et al., 1978) by several hundreds of metres
(Cullen,1983). Pre-existent veins are stretched; sulphides
are smeared along phyllosilicate grain boundaries.

The lithologies are also cut by northeast- and
northwest-, rarely north-trending lamprophyre and olivine
diabase dykes. They have roughly the same orientations as
the previously described faults and may have intruded along
these pre-existent planes of weakness. They were mapped by
Shell Resources by airborne electromagnetic surveys and by
drill intersections.

The upper 20 to 30 m of the core are weathered,
resulting in oxidation of sulphides and dissolution of
calcite in veinlets and tension fractures, leaving vuggy
zones.

2.2 Metasedimentary Lithologies

2.2.1 Meta-pelitic Lithologies

In drill core, the meta-pelites range in colour from
pale greenish grey and greyish green to bluish green to
greyish blue to black; this is a manifestation of the
concentrations of chlorite, muscovite, quartz, feldspar and
carbonaceous material (graphite;Cullen,1983).

Pelitic rocks generally consist of medium to coarse,

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silt-sized (averaging 0.03 mm) aggregates of chlorite,
muscovite, quartz and feldspar (albitic; in places,
potassic), with minor amounts of coarser ilmenite (about 0.1
mm), pyrite and pyrrhotite, finer anhedral to euhedral zircon
and sphene (about 0.01 mm), and variable concentrations of
extremely fine-grained graphite (≤0.003 mm). Several whole
rock geochemical analyses are tabulated in Appendix II.

Flakes and needles of chlorite and muscovite are usually
tightly intergrown with their long axes defining the
foliation. They may be intergrown with roughly equant
subangular to subrounded grains of strained quartz and
feldspar. Grain contacts range from straight to curved; less
commonly they are embayed to sutured lobate. Other pelitic
samples have the tectosilicates segregated into silty
partings (Fig. 2.7).

Subhedral laths of ilmenite are ubiquitous and are
usually partially to wholly altered to rutile or leucoxene,
giving the laths a poikilitic appearance (see Stendal,1982).
They parallel foliation and are usually reoriented by
crenulation. Ilmenite is a minor constituent of the
argillites, but may comprise up to 15 modal percent of some
thin layers.

Pyrrhotite is less common in meta-pelitic lithologies.
It occurs as elliptical blebs usually oriented parallel to
foliation; stress caused pyrrhotite elongation by translation

Figure 2.7   Crenulated meta-argillite with silty
                    partings and ilmenite blebs reoriented
                    by crenulation. In places crenulation
                    develops into cleavage.

                    Crossed nicols.

                    Long axis of photograph measures 5 mm.
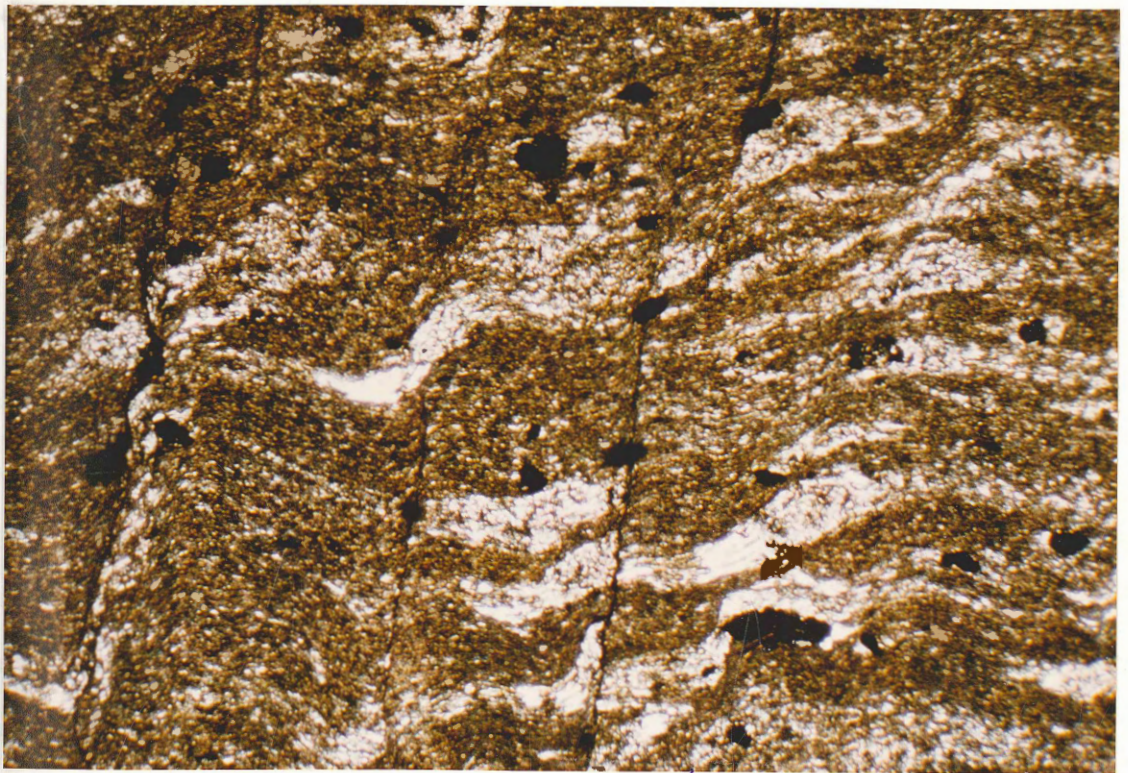
gliding along (0001) crystal planes (Ramdohr,1980; Spry,1969; Graf et al., 1970).

Darker varieties of meta-pelites contain less chlorite and muscovite, more quartz, carbonate and graphite. Graphite is found as extremely fine disseminations or as linear clusters, forming 'wispy' sheaf aggregates intergrown with the phyllosilicates.

The meta-pelites may become siltier, with decreased phyllosilicate content, and increased concentration of equigranular quartz, forming fine-grained siltstones.

Thermal metamorphism caused overprinting of foliation by such poikiloblastic minerals as: euhedral garnet; subhedral chiastolite retrograded to assemblages of muscovite-quartz-carbonate (Fig. 2.8); euhedral to subhedral blades of carbonate (calcite,dolomite,ankerite); biotite; and chlorite. Round to elliptical aggregates of quartz-chlorite-carbonate are also found, discontinuously rimmed by opaques such as leucoxene and pyrite, and may be altered cordierite 'spots'. One carbonaceous argillite sample contains green poikiloblastic blades of a mineral that has a retrograde assemblage of quartz-chlorite-carbonate; it is not known what the original mineral was (amphibole?).

The most common sulphide mineral within the meta-argillites is pyrrhotite, usually found as blebs, but

Figure 2.8   Slightly sheared carbonaceous meta-
argillite containing contact
metamorphic andalusite(var. chiastolite)
retrograded to muscovite, quartz and
calcite.

Sample 77-31-87.30

IW-0β7

1   5 cm
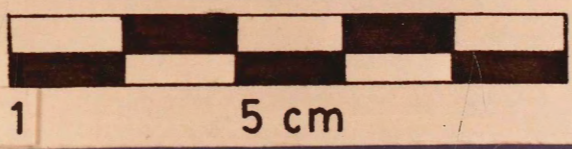
may occur as stratiform layers several cm thick and very slightly foliated. More discussion of this and other sulphides is found in chapter 3.

2.2.2 Meta-psammitic Lithologies

Interbedded with the meta-pelites are pale greenish-grey to greyish-green meta-psammites. They are a fine-grained, massive, indurated rock with rare graded bedding, scours and argillaceous rip-up clasts. These lithologies have both bimodal and unimodal grain size assemblages. The coarser fractions (up to 20 modal percent) of the bimodal samples consist of medium sand-sized (averaging 0.5 mm) quartz and feldspar (usually albitic plagioclase with albite and Carlsbad twinning; less potassium feldspar). They are distributed in a finer (averaging 0.04 mm) silty matrix of quartz, feldspar (up to 25 modal percent), chlorite and muscovite with minor ilmenite, pyrrhotite and carbonate with trace amounts of biotite, zircon, sphene, apatite, chalcopyrite, arsenopyrite and graphite (e.g., Fig. 2.9). Most of the geochemically analysed meta-psammites fall within 'typical' greywacke compositions (Fig. 2.10).

The coarser grains are angular to subrounded and roughly equant; quartz grains are strained.

The matrix (and unimodal meta-psammites) consists of tightly intergrown minerals with embayed to sutured lobate

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Figure 2.9   Typical meta-wacke.

                    PPL

                    Long axis of photograph measure 8 mm.
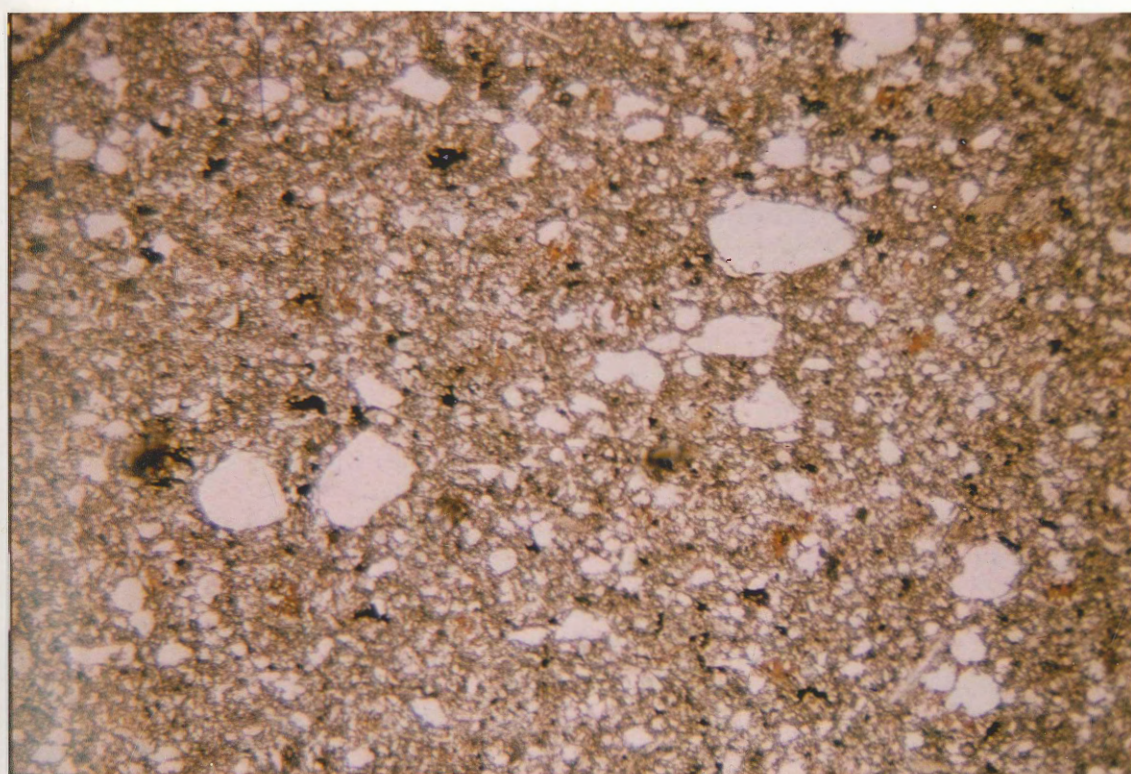
Figure 2.10 Na_2O : K_2O contents in metasediments.

Most meta-wackes plot in the greywacke
field; 2 samples have greater amounts
of sericite and so plot in the other
field.
Meta-argillite which plots near the
origin is mineralized.

+   meta-wacke

⊙   meta-argillite

⊕   carbonaceous meta-argillite
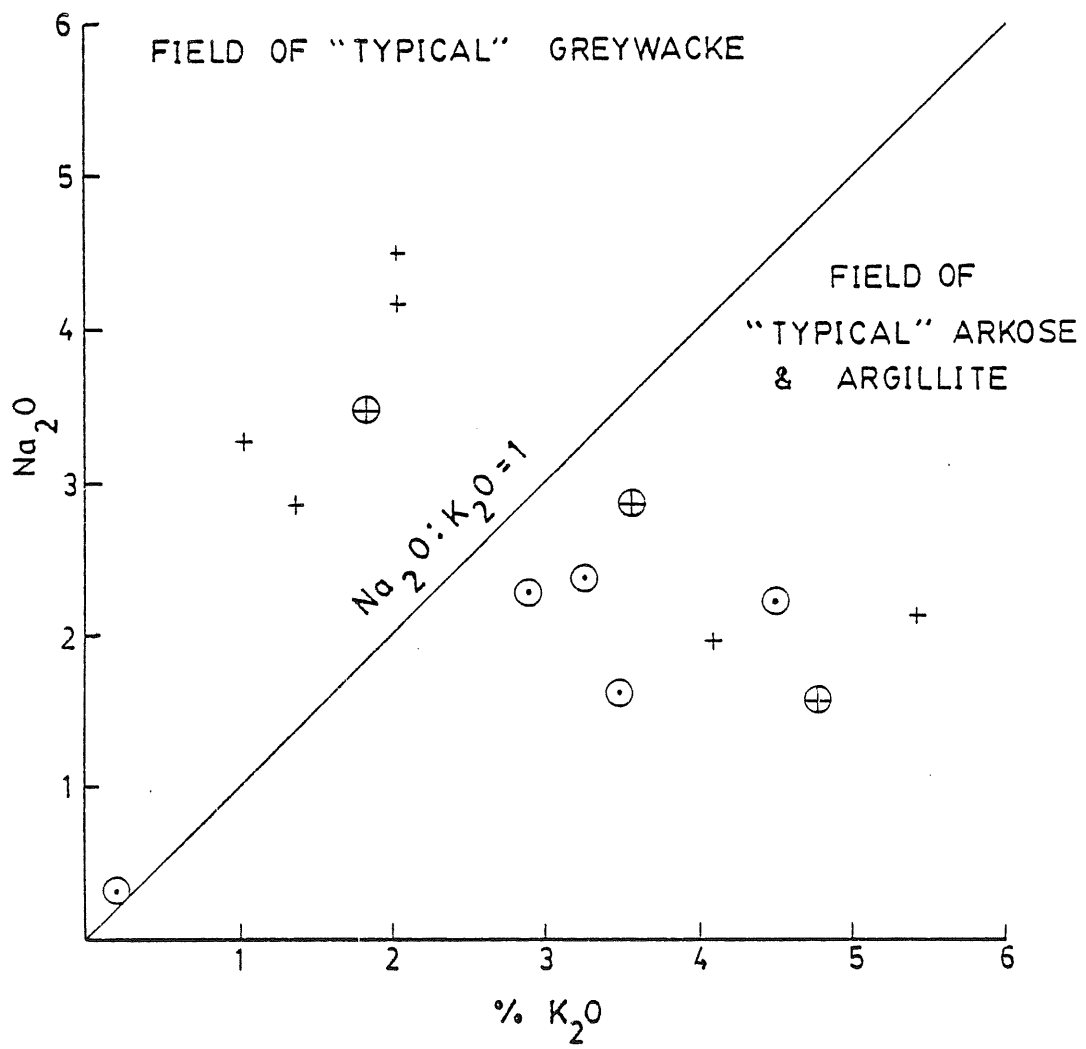
grain contacts. Tectosilicates are anhedral, tabular to
equant, and are separated by chlorite-muscovite
intergrowths. Subparallel orientation of the phyllosilicates
and tabular feldspar grains define the linear fabric.

A few meta-psammitic samples appear 'spotted', due to
subrounded aggregates of either more (appearing darker) or
less (appearing lighter) chlorite and graphite. These may
have once been individual clay-rich pellets rolled around by
currents and incorporated into sandy layers (Pettijohn,1975).

Calc-silicate layers also occur throughout the core
(Fig. 2.11). They generally have a fine-grained (averaging
0.05 mm) matrix of quartz, with lesser feldspar, biotite and
chlorite. This is overprinted by such thermal metamorphic
minerals as euhedral garnet, biotite, granoblastic epidote
and actinolite, euhedral to embayed carbonate (calcite,
dolomite, ankerite) and poikilitic, colloform and massive
pyrite.

Several interesting features are found within the
meta-psammitic layers:

1. Layers of manganese-rich garnet (Cullen,1983) in fine sand-
sized meta-psammite (Fig. 2.12); this may reflect metamor-
phosed, originally manganiferous sediments. These may have
formed by concentration of manganese carbonates or
oxides/hydroxides or both during diagenesis or by accumulation

Figure 2.11   Contact metamorphic zones paralleling
                     original layering.

            Green zone: actinolite-epidote-garnet-
                         carbonate-biotite-sphene.

            Brown zone: quartz-biotite-epidote-
                         garnet-sphene-chlorite-
                         plagioclase-carbonate.

            Sample 77-10-44.6

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near submarine vents (Whitehead,1973; Germann,1973; Duurama et al., 1976). Apparently, there is a calcareous manganese-rich zone within the upper part of the Goldenville Formation sediments throughout Nova Scotia, and may have formed in response to some widespread synsedimentary, diagenetic or mineralizing event (Zentilli, pers. comm.,1983; Jenner,1982).

2. Calc-silicate layers previously discussed; and calc-silicate nodules (Fig. 2.13) - elliptical to amoeboid metasomatised calcareous concretions within meta-psammitic lithologies. They appear similar to altered limestone nodules in pelitic hornfels of the CanTung tungsten deposit (Dick and Hodgson,1982). Original calcium carbonate may have derived from dissolution of shelly material by acidic intrastratal water and subsequently reprecipitated elsewhere in a less acidic environment within psammitic layers (Schenk,1975; Pettijohn et al.,1972). Additional calcium may have been obtained by albitization of plagioclase (Blatt et al.,1980) during diagenesis. These nodules have been studied in detail by M.F. Purves (cited in Cullen, 1983).

3. Stratiform sulphide zones; these will be discussed in a later chapter.

Figure 2.12   Layered manganiferous garnet in meta-
                     wacke. They possibly represent
                     metamorphosed manganiferous
                     sediments.

                     Sample 77-34-10

Figure 2.13   Metasomatic concretion in meta-wacke.
                     It is an amoeboid body with a white
                     core and rim of quartz, muscovite
                     and zoisite, with a middle green
                     zone of quartz, zoisite and chlorite
                     (Cullen, 1983).
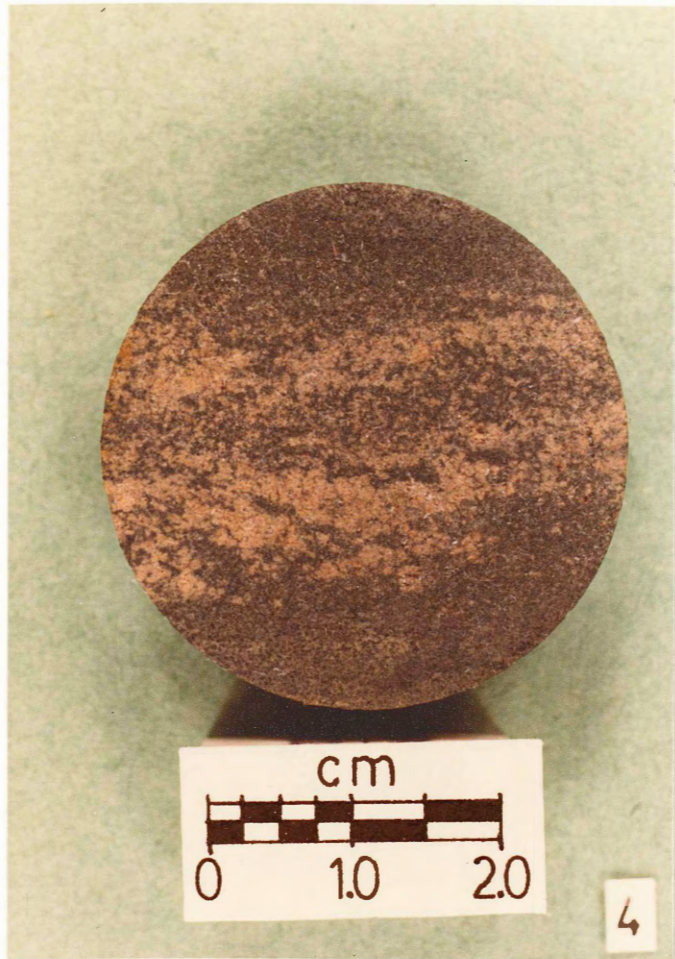
2.3 Plutonic Lithologies

2.3.1 Wedgeport Pluton

The Wedgeport pluton is exposed along a part of the shoreline. It is in sharp contact with the metasediments, which contain minor injections of granitic material (Fig. 2.14). Most of the shoreline comprises monolithic boulders weathered from till.

Samples from the pluton have a modal mineralogy corresponding to monzogranite of Streckeisen's (1976) classification (Fig. 2.15). The samples have normative and oxide contents similar to those of adamellites of the South Mountain batholith (Figs. 2.16 and 2.17). A high ferrous to ferric iron ratio (Fig. 2.18) plus scarcity of opaque minerals, of which ilmenite is the most common, may possibly characterize the pluton as an 'ilmenite series' type (Ishihara,1981; Takahashi et al.,1980; Ishihara et al.,1979). Geochemically, the pluton appears to be an 'I-type' granite (Chappell and White, cited in Plimer,1980); mineralogically, it resembles the 'S-type' variety (Table 2.1). Attempts to characterize the pluton geochemically as either potentially ore-bearing or barren have proved disappointing. Selected trace and major element ratios (e.g. Table 2.2, Fig. 2.19) exhibit both 'specialized' (at the margin of the pluton) and 'normal' (the interior of the

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Figure 2.14   Wedgeport pluton(left) in sharp
                     contact with metasedimentary
                     country rock. A thin granitic dyke
                     (centre) is injected into
                     hornfelsed meta-wackes.

43
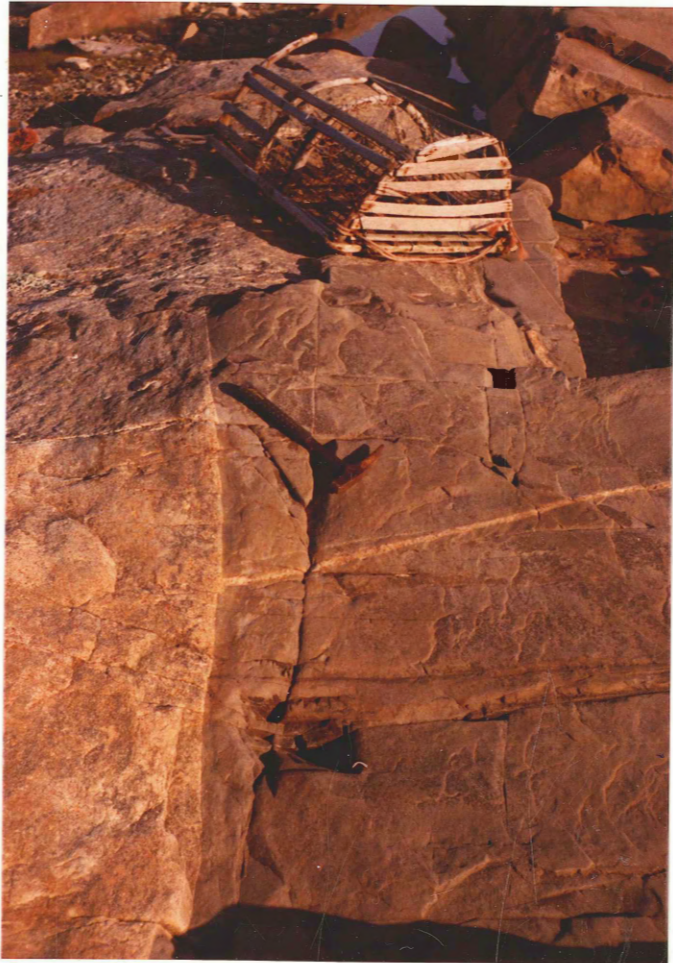
Figure 2.15   Modal QAP composition of plutonic
lithologies. All plot within the
monzogranite field.

+   Wedgeport pluton

⊙   .South Mountain batholith
adamellites(McKenzie and
Clarke, 1975)
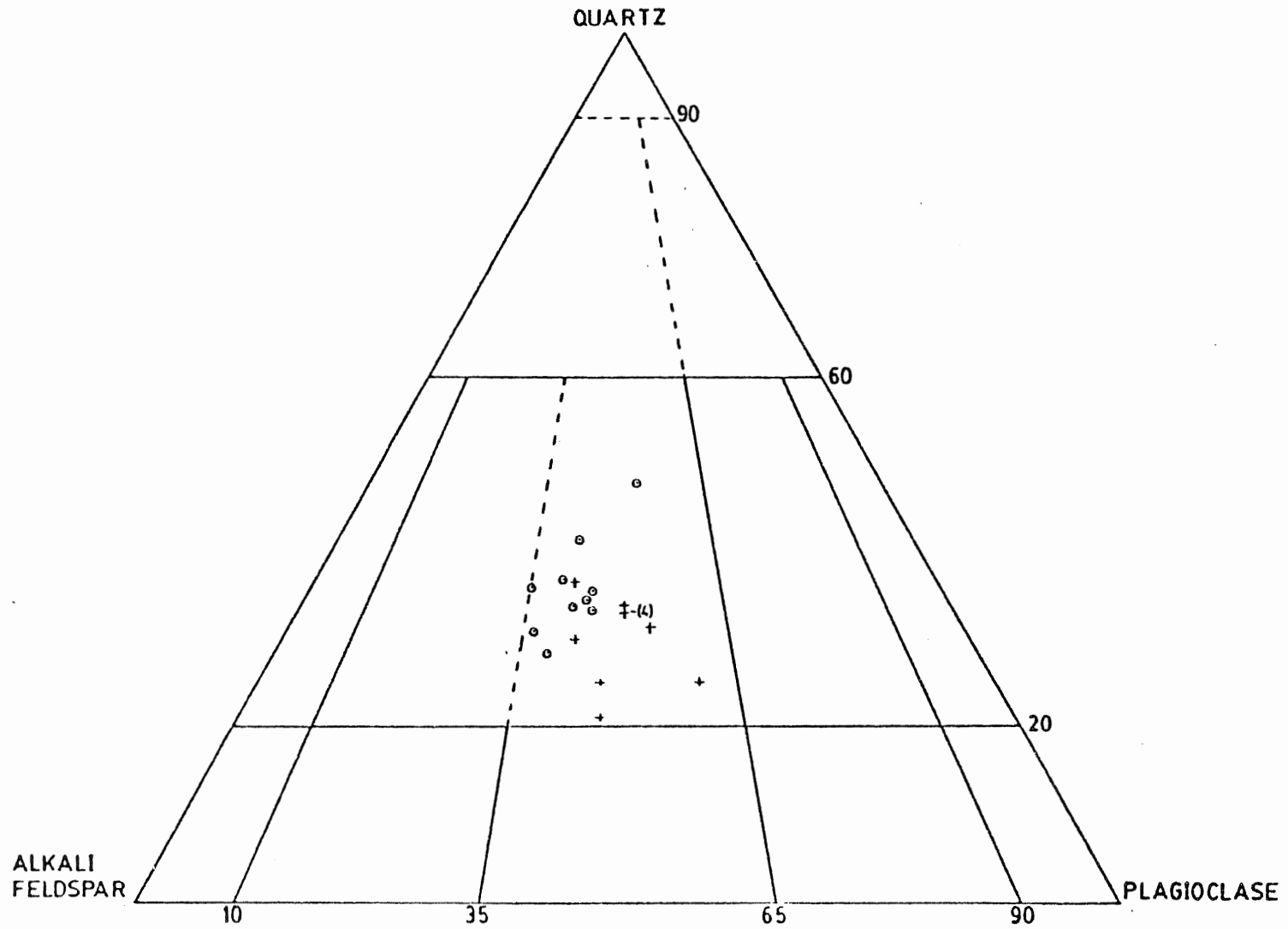
Figure 2.16   Normative quartz-albite-orthoclase
diagram. Parallelogram approximately
denotes field for adamellite and
granodiorite lithologies of the
SMB(McKenzie and Clarke, 1975).
Greisen sample near the orthoclase
apex contains white mica and fluorite
with little quartz.

+   monzogranite and greisen samples,
this study.

●   2 biotite granites, 1 muscovite-
quartz greisen from the Davis
Lake pluton, East Kemptville
(Chatterjee, 1980).

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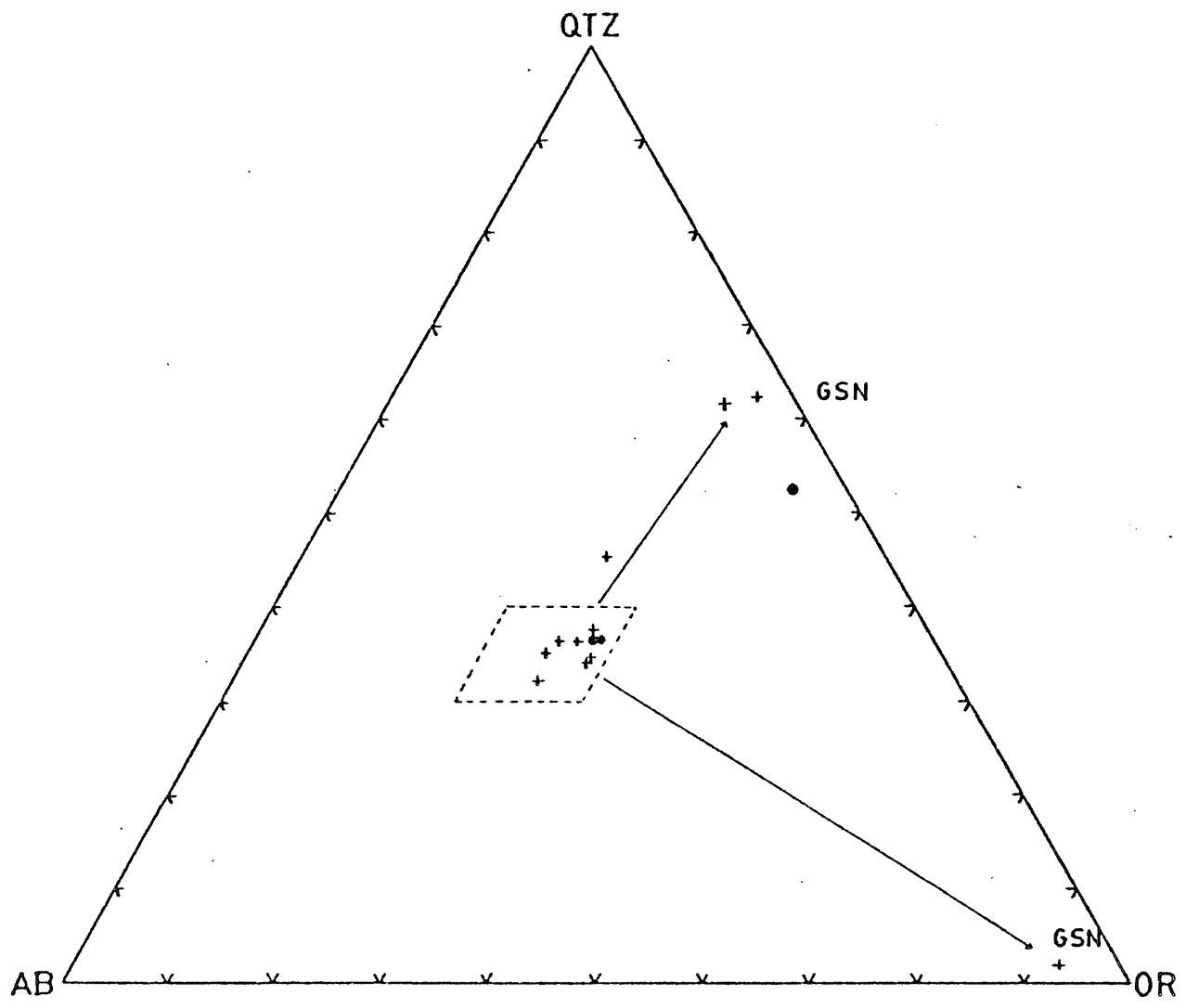
Figure 2.17 K_2O-Na_2O-CaO variation diagram
                   of 11 samples from the pluton. Dotted
                   parallelogram approximately denotes
                   the adamellite field of the SMB;
                   shaded parallelogram approximately
                   denotes the granodiorite field of
                   the SMB(McKenzie and Clarke, 1975).
                   Arrows point to 3 greisen samples
                   adjacent 3 unaltered monzogranite
                   samples, indicating loss of Na_2O
                   and relative increase of K_2O.

        +   monzogranite and greisen
                   samples, this study.

        ●   2 biotite granites, 1 muscovite-
                   quartz greisen from the Davis
                   Lake pluton, East Kemptville
                   (Chatterjee, 1980).
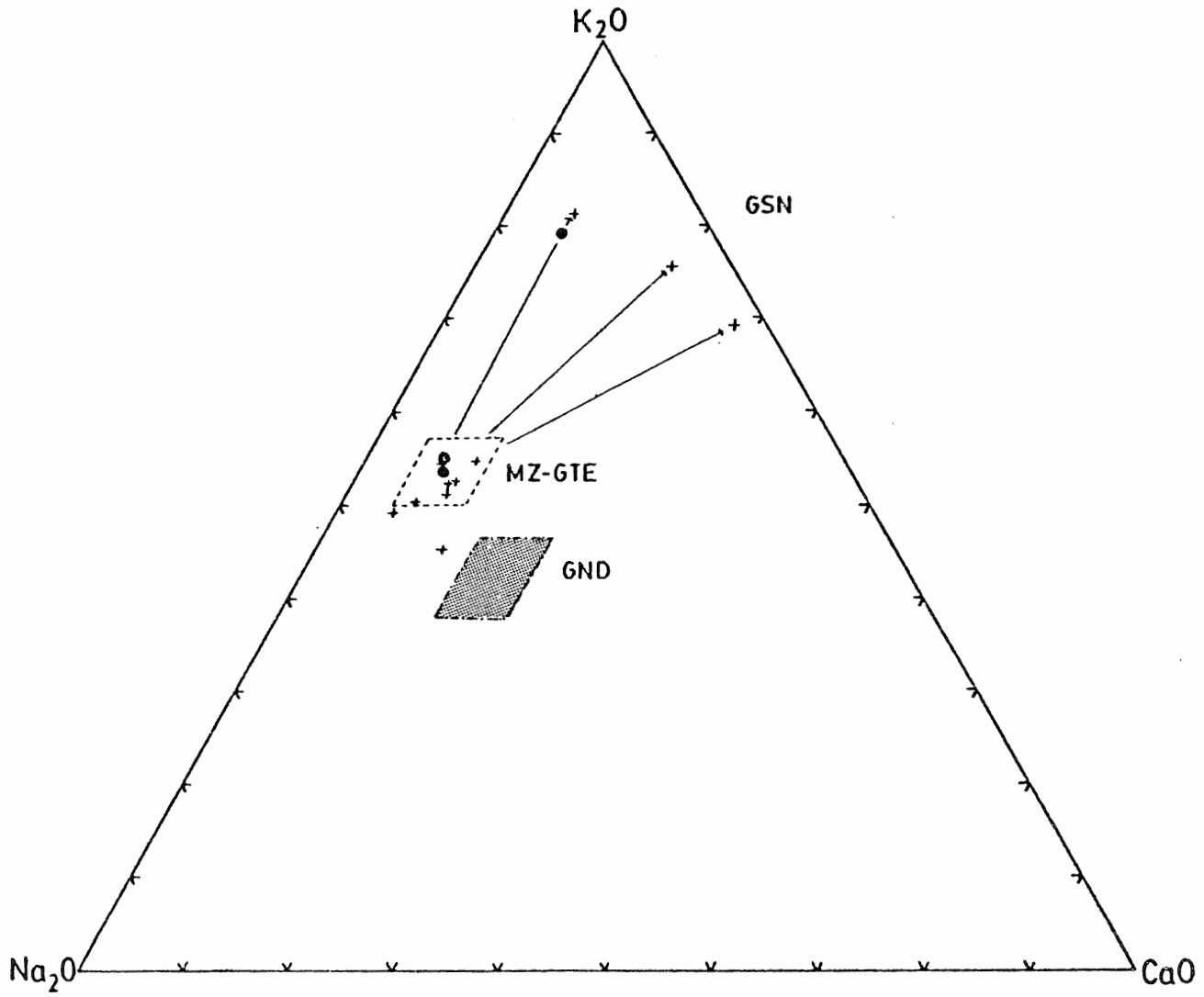
Figure 2.18   Ferrous/Ferric ratio of monzogranite
                   samples. Broken line separates
                   magnetite- and ilmenite-series
                   granitoids of Japan. FeO/Fe_2O_3
                   is roughly 1 to 2 on granite
                   compositions(DI=95-80) and is
                   roughly 2 to 3 on granodiorite
                   (DI=80-60) and tonalite and
                   quartz diorite(Ishihara et al.,1979).

FeO/Fe$_2$O$_3$

(ILMENITE SERIES)

(MAGNETITE SERIES)

Thornton-Tuttle Differentiation Index (wt.%)
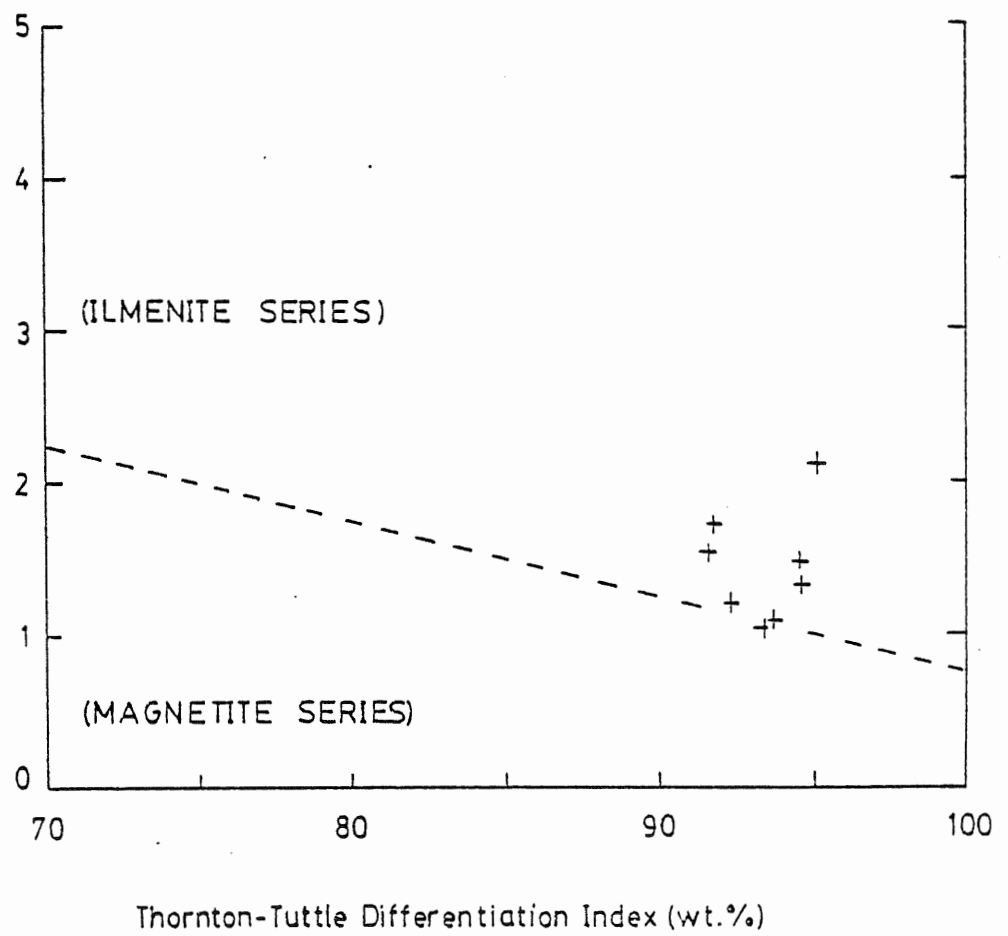
Table 2.1   Properties Of Monzogranite, S- and I-type granites
              (from Chappell and White, quoted in Plimer,1980)

Wedgeport Monzogranite (n=8)	S-type Granite	I-type Granite
Na2O 2.86-4.28% K2O 4.25-5.07%	Na2O < 3.2% in rocks with ~ 5% K2O < 2.2% in rocks with ~ 2.2% K2O	Na2O > 3.2% in felsic types > 2.2% in mafic types
	Molecular Al2O3 / (Na2O+K2O+CaO)	
0.93-1.06	>1.1(peraluminous)	<1.1
	norm corundum	
0.00-0.45%	> 1%	<1%
	norm diopside	
0.00-1.74%	-	norm di present
Biotite common	Muscovite and Biotite common	Hornblende common

Table 2.2   Major Element Ratios Typical Of 'Normal' and
              'Specialized' Granites

	K/Na	K/Rb	Mg/Li
'Normal'	1.2	> 100	270
'Specialized'	1.6	< 100	75
This Study			
Monzogranite (n=8)	1.18-1.78	120-180	14.7-40.97
Greisen (n=3)	7.53-25.5	60-70	4.75-17.5

Values for normal and specialized granites are from various
authors in Boissavy-Vinau and Roger(1980).

Figure 2.19   Proportions of F, Li and Sn in
                     samples from the Wedgeport pluton
                     (n=25) and the Davis Lake pluton
                     (n=3).
                     There is a large scatter of data,
                     but there appears to exist a trend
                     towards the Sn axis in altered,
                     sheared and greisenized samples.
                     Samples are grouped according
                     to their positions in the pluton
                     or to their states of alteration.
                     The 3 arrows join barren monzo-
                     granite to their adjacent
                     greisenized zones.

         +   monzogranite and greisen
                     samples, this study.

         ●   2 biotite granites, 1 muscovite-
                     quartz greisen from the Davis
                     Lake pluton(Chatterjee,1980).
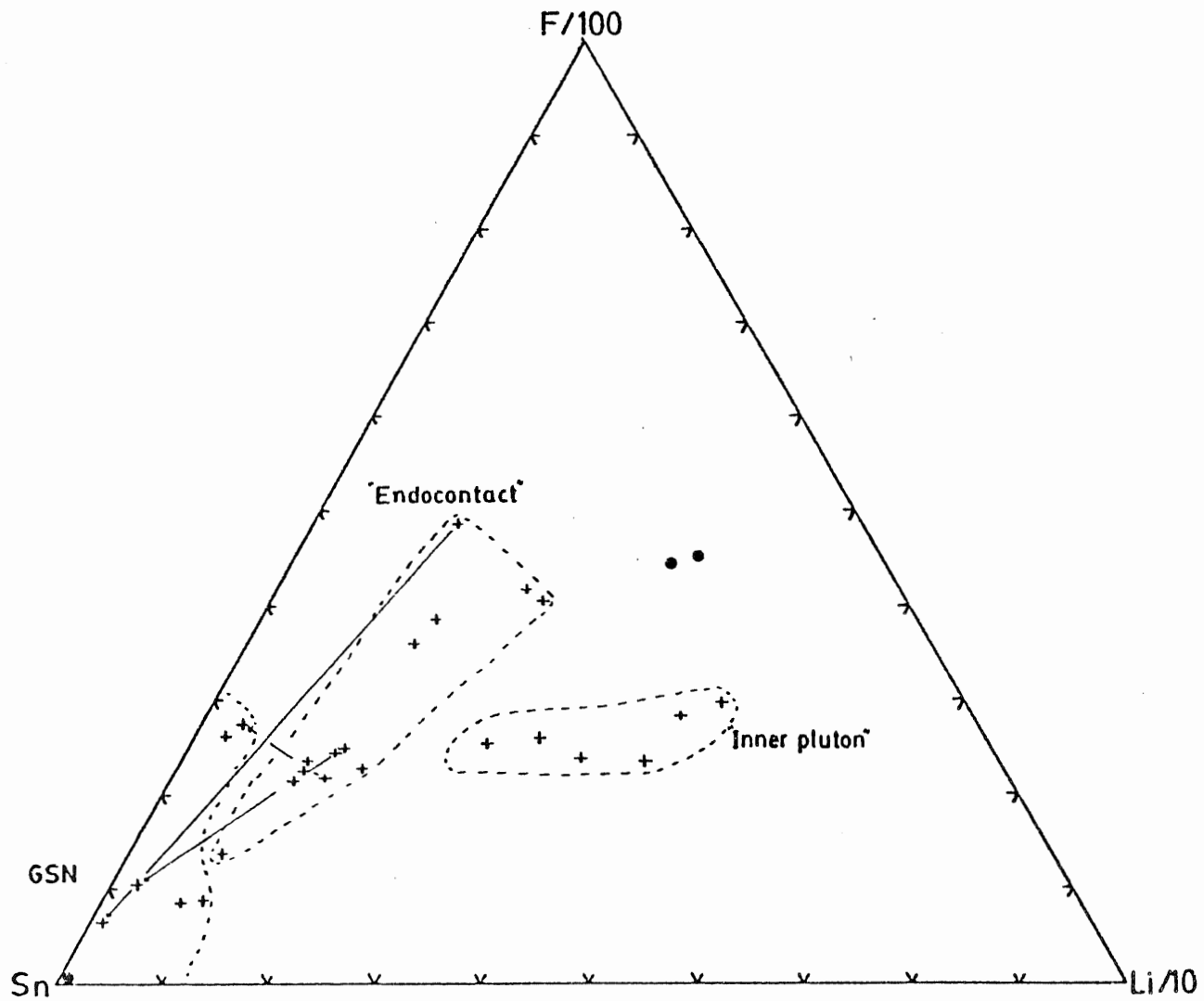
pluton) features. Airborne gamma ray spectrometric
measurements (Chatterjee and Muecke, 1982) indicate high
total radioactivity and high thorium values within the pluton
and these appear associated with mineralized intrusions found
elsewhere in Nova Scotia (e.g. the tin mineralized Davis Lake
pluton).

The samples display a variety of textures throughout the
pluton. Fresh material ranges from greyish white with black
flecks to a mottled white, grey and black combination. It
has a hypidiomorphic granular (granitic) texture, from fine
grained equigranular to porphyritic with medium, rarely
coarse grained phenocrysts. The endocontact exhibits this
diversity of colours and textures - there are no contacts
among the different types, rather each type grades into one
another. Figure 2.20 shows some examples of this diversity.
Samples from the interior of the pluton are less
heterogeneous and are generally medium grained with minor
coarse phenocrysts.

The monzogranite consists of roughly equal amounts
(about 30 modal percent) of fine grained translucent grey
(light brown in weathered exposures) quartz, greyish-white
(rarely pinkish) microcline and pale greenish-white (rarely
pinkish) plagioclase of albite to oligoclase composition.
Fine grained black, ragged flakes of biotite comprise up to
10 modal percent; they contain minor inclusions of euhedral,

Figure 2.20   Diversity of monzogranite textures
                     in one drill hole(78-27). Depth
                     increases from left to right:
                     31.15 m, 68.37 m(near a mafic dyke),
                     and 78.55 m.

Figure 2.21   Effects of mafic dyke intrusion upon
                     monzogranite.

                     Top: 78-31-30.18   Coarse monzo-
                             granite. Pink coloration of
                             microcline; plagioclase
                             remains greenish white.

                     Bottom: 78-27-70.71   Chloritization
                             of biotite.

zoned zircon prisms, euhedral to subhedral needles of apatite
and subhedral laths of ilmenite. Rare fine grained anhedral
purplish fluorite, pinkish scheelite, molybdenum, pyrite and
pyrrhotite occur throughout the core.

Phenocryst abundances range up to about 15 modal percent
and consist of medium (1-5 mm), rarely coarse (up to about 9
mm) grained, round translucent pinkish quartz 'eyes' and
subhedral white equant blocks of microcline; subhedral pale
greenish-white plagioclase laths are less common.

Quartz is usually slightly strained, showing undulose
extinction. Near areas of shear, it exhibits minor subgrain
and new grain development. Quartz phenocrysts have minor
inclusions of both the feldspars and biotite. Irregular
quartz is interstitial to the feldspar crystals.

Microcline occurs as anhedral blocks, rarely as anhedral
laths. It is slightly perthitic with bleb and ribbon albitic
plagioclase. Cross-hatched or 'tartan' twinning is common.
Phenocrysts are poikilitic with quartz and plagioclase
inclusions. Rarely, embayed microcline is mantled by
plagioclase. It is usually slightly sericitized; near veins
microcline is more altered and has a greyish turbid
appearance due to the presence of microscopic to
submicroscopic fluid inclusions. Near dykes it may take on a
rust-brown turbid appearance (presence of iron oxides or
hydroxides?) and look pinkish in hand sample (Fig. 2.21).

Plagioclase is found as subhedral to anhedral laths of albite to oligoclase composition. It usually has albite twinning; some phenocrysts have vague normal zoning. Minor microcline and quartz are included within the phenocrysts. Plagioclase suffers a greater degree of alteration, changing to sericite with variable amounts of calcite and rarely epidote, usually within crystal cores. Near dykes it usually becomes a turbid rust brown, appearing pink in hand specimen, although it may remain greenish white.

Biotite occurs as clear brown ragged individual flakes or aggregates of flakes. It usually contains inclusions of zircon, apatite, ilmenite and epidote(?); rarely subhedral pyrite and arsenopyrite crystals and rutile(?) needles. Biotite alters readily to clear, dark green chlorite, even where no alteration is evident in adjacent minerals. Near veins, shears and contact with the metasediments, biotite is altered to a 'shredded' tan aggregate of vermiculite(?) with disseminated iron oxides or hydroxides; included ilmenite is generally altered to blue anatase.

Rare vugs (miarolitic cavities?) are found in some of the core. They are round to elliptical, and up to 3 mm diameter with drusy quartz coatings.

Monzogranite is readily weathered, as seen by the pinkish to rust-brown coloration of both exposed country rock

and upper portions of the drill core, some to 22 m depth (Fig. 2.22).

The core is cut by several stages of veins, several mm to several cm width. Many are of quartz-calcite composition with variable sulphides, fluorite (both purple and green), scheelite, white mica, kaolinite and cassiterite. Alteration envelopes range from slight 'bleaching' immediate the vein (sericitization of feldspars) to greisen zones up to 20 cm in drill core. These vein types will be discussed in a later chapter.

Rare aplite dykes are observed in both core and outcrop. They are thin (several cm), greyish white and aphanitic with assimilated mineral fragments. They are in sharp contact with the monzogranite with no observable alteration effects.

Shears cut the pluton with or without accompanying veins of quartz ± arsenopyrite ± scheelite ± molybdenite ± pyrite. Widths vary from centimetres to several metres over the length of the drill core. In places one may observe a progressive reduction of grain size, destruction of feldspars, orientation of elongate quartz 'eyes' and development of saccharoidal quartz and parallel planes of pale silvery green sericite. Within endocontact samples, euhedral sulphides (principally pyrite; minor chalcopyrite) overprint the shear planes. In shoreline exposures, these

Figure 2.22   Effect of monzogranite weathering.
                     Sample 78-33

                     Left: Hematite-stained at 13.73 m.

                     Right: Unweathered at 46.6 m.

sulphides weather to form iron oxides, producing 'rusty' shear zones (Fig. 2.23).

2.3.2 Mafic Dykes

A series of northeast- northwest- and rare north-trending mafic dykes intrude both the pluton and the metasediments. They are fresh, black, aphanitic with minor vitreous crystals, and are tens of cm thick. Contacts are sharp and reddish brown; little alteration or assimilation of the host rock is observed. Several dykes appear composed of two phases, as if the magma had reintruded planes of weakness. Two types of dykes occur - one a lamprophyre, the other an olivine diabase. Relationships between the two are not known. Such dykes have been described and analysed by Cullen (1983), so will only be given a brief description here.

Lamprophyre dykes (monchiquite?) have a glomeroporphyritic texture, with up to 25 modal percent of clusters of medium grained clinopyroxene and olivine phenocrysts in a fine grained matrix of clinopyroxene, olivine, plagioclase(?), hornblende (kaersutite?), biotite and either a zeolite or feldspathoid (Fig. 2.24a).

Euhedral, zoned and sometimes twinned titaniferous augite laths occur (about 1.5 mm), and may include olivine and magnetite; some have mantles of hornblende. Subhedral to

Figure 2.23   Part of a 'rusty shear' from the
western margin of the Wedgeport
pluton. The altered monzogranite
has a saccharoidal texture; feldspars
are completely destroyed. Develops
(to the right) into pyrite-(minor
chalcopyrite) bearing end of shear,
altered to iron oxides.

anhedral olivine phenocrysts (about 1 mm) group with augite;
they range from fresh, to totally altered to serpentine,
calcite and talc, edged with magnetite. Fine brown laths of
hornblende (about 0.15 mm) comprise 10 to 15 modal percent of
the lamprophyre. Rare flakes of dark brown and dark green
biotite, and fine needles of plagioclase(?) are disseminated
throughout. The matrix also contains round amygdales(?) (up
to 1.5 mm in diameter) filled either with a feldspathoid or a
zeolite (analcite?). Matrix minerals are oriented around
these forms; some minerals appear to grow into them.

As the contact with the country rock is approached, the
matrix becomes glassy and reddish brown. Adjacent
metasediments appear slightly altered (sericitization of
feldspars). Within the monzogranite feldspars may be turned
pink and biotite may be chloritized (Fig. 2.21).

Trace element analyses (Appendix II) include high
fluorine (about 1000 ppm) which probably substitutes for the
hydroxyl component of both hornblende and biotite. See
Cullen (1983) for their whole rock chemistry.

One sample of an olivine diabase dyke was observed in
thin section (Fig. 2.24b). It is relatively unaltered and
consists of a fine grained holocrystalline assemblage of
euhedral labradorite laths (about 60 modal percent) with
undulatory extinction, euhedral augite laths (about 25 modal
percent) and minor anhedral olivine altered to serpentine and

talc (about 5 modal percent). Disseminated throughout are
fine magnetite and skeletal ilmenite (about 10 modal percent)
and a trace amount of brown needles of hornblende(?).

Figure 2.24a   Glomeroporphyritic lamprophyre
dyke. Solitary biotite flake
occurs in centre. Brown hornblende
occurs throughout.

PPL

Long axis of photograph measures 3.23 mm

Figure 2.24b   Plagioclase-rich olivine diabase
dyke.

Crossed nicols

Long axis of photograph measures 8.0 mm
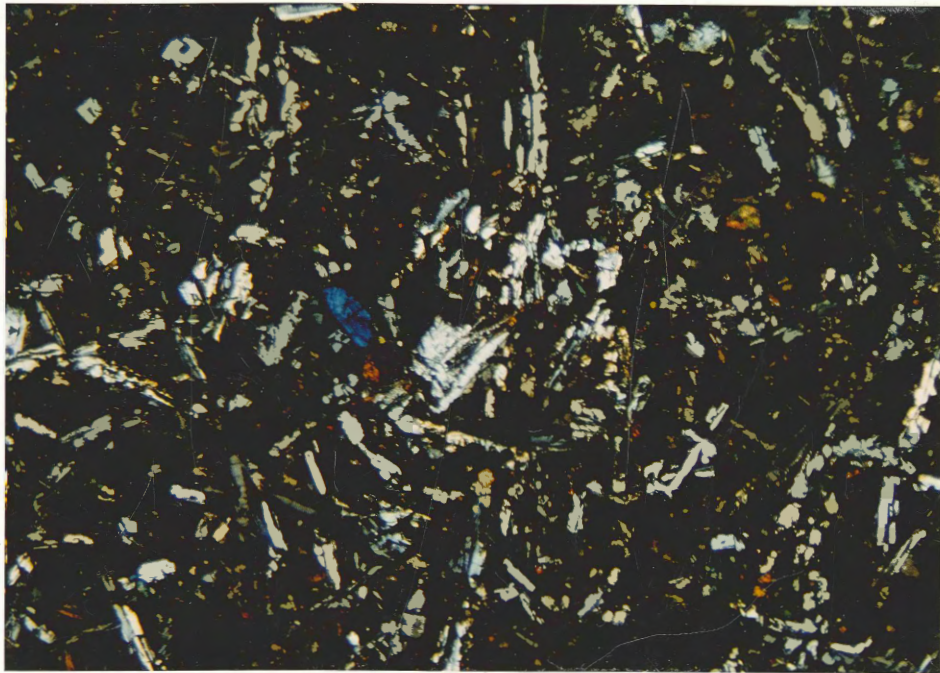
CHAPTER THREE

ORE PETROLOGY

3.1 Introduction

Both the metasediments and the Wedgeport pluton are cut
by a variety of vein systems of variable orientation and
mineralogy, reflecting stress and fluid regimes before and
during mineral transport and deposition. A detailed analysis
of fracture and vein system orientations is beyond the scope
of the thesis; however, their positions with respect to
bedding and foliation within drill core have been noted.

Cassiterite mineralization occurs both in veins (mainly
within the metasediments) and in thin, sulphide-rich
stratiform blue grey to brown 'patches' or zones within the
metasediments. The mineralogy, textures and possible modes
of genesis of the mineralization will be discussed.

3.2 Vein Systems

Because the vein systems within the metasediments and
pluton have somewhat different mineralogies and effects on
the host rock, and because relationships between the systems
in the two lithologies are not well known, they will be
treated separately. Each lithology appears to contain three

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main stages of veins: pre-tin, tin, and post-tin. Each stage
will be described in terms of its mineralogy and alteration
effects on the wall rock. Cassiterite will be described in a
later section, incorporating these descriptions in an attempt
to develop a possible genetic interpretation of tin
mineralization.

3.2.1 Veins Within Metasediments

Relationships among the different veins are not clear as
only a small segment of each vein is obtained in drill core.
Crosscutting relationships are rare, therefore comparisons
were made between the vein and structures within the host
i.e., bedding, foliation, crenulation and fractures.

Pre-mineralization veins may parallel bedding, are
commonly affected by crenulation (see Fig. 2.5) and cause
little, if any alteration of adjacent host rock.

Veins associated with main-stage mineralization crosscut
bedding and foliation - some parallel crenulation cleavage -
and may have thin, slightly perceptible alteration haloes.

Post-mineralization veins appear related to a late
shearing event, which caused fracturing, bleaching,
'smearing' and some displacement of pre-existent veins and
mineralized 'patches', concentrations of thin veinlets
('crackle breccia') and minor brecciation infilled with

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quartz and calcite.

3.2.1.1 Pre-mineralization Veins

Pre-mineralization veins within meta-argillite are
usually affected by crenulation. They are kinked,
ptygmatically folded or boudinaged (Fig. 3.1). This vein type
within the meta-wackes is at most, slightly offset.

They are usually less than 1 cm wide, and planar in
drill core; finer veinlets appear to be anastomosing. Some
veins occur at bedding contacts. Intergrown quartz, calcite
and chlorite are the principal constituents; muscovite and
sulphides (arsenopyrite, chalcopyrite, pyrite, pyrrhotite,
sphalerite(?)) are minor or rare. The quartz is commonly
strained, forming sub- and new grains. The immediate host
rock is bleached(on the order of <1 mm), usually adding
sericite and carbonate $\pm$ quartz.

At least two stages of this vein type occur, at times
crosscutting each other.

3.2.1.2 Main Stage Veins

This type comprises a variety of widths, orientations,
mineral assemblages, and alterations. Widths vary from less
than 1 mm to several tens of cm of drill core length
(commonly barren quartz);they are usually 0.5 cm or less.

Alteration haloes vary, from slightly perceptible with slight bleaching, to about ten times the vein width. The main alteration types are:

1. Bleaching(common) - destruction of biotite to chlorite(to vermiculite?); sericitization of feldspar; addition of silica, sericite, chlorite and carbonate.

2. Biotitization(uncommon) - development of biotite porphyroblasts adjacent outer selvedge of quartz-calcite-sulphide veinlets (Fig. 3.2); the biotite is later than the regional metamorphic biotite.

3. Chloritization(minor) - development of chlorite ± rare cassiterite around sulphide veinlets (Fig. 3.3).

Main stage veins consist mainly of quartz, carbonate (calcite, siderite), chlorite, pyrite, pyrrhotite and white mica with variable amounts of other sulphides, cassiterite and scheelite. Table 3.1 lists the common vein mineral assemblages. Vein mineralogy changes with distance from the pluton. Near the intrusion (up to about 2 km from its surface projection), rare scheelite, molybdenite and epidote are found. At greater distances, cassiterite and base metals predominate; scheelite is not observed. Cassiterite is a major mineral between 2 and 4 km from the pluton, after which sphalerite and galena become prominent. Arsenopyrite and chalcopyrite are common throughout the study area. This mineral zonation roughly follows that of greisen stockworks above an intrusion, and sulphide-cassiterite deposits described by Shcherba (1970) and Grigoryan (1974),

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Figure 3.1   Early quartz-arsenopyrite veinlets
                   in meta-argillite, cut by crenulation
                   cleavage.

                   Sample 78-10-83.55

Figure 3.2   Vein types.

                   Left: IW-005(77-27-57.7)
                           Biotite developed around
                           quartz-chlorite-carbonate-
                           pyrrhotite-pyrite-chalcopyrite-
                           galena veinlet in silty meta-
                           argillite.

                   Right: IW-054(78-11-97.84)
                           Arsenopyrite-galena(+ Ag/Bi)-
                           chalcopyrite-pyrite-marcasite-
                           carbonate veinlet parallel
                           crenulation cleavage with no
                           major wallrock alteration.
                           A few fine veinlets of
                           rust brown material(iron
                           oxides/hydroxides?) offshoot
                           the veinlet into foliation.

IW-005   IW-054

2
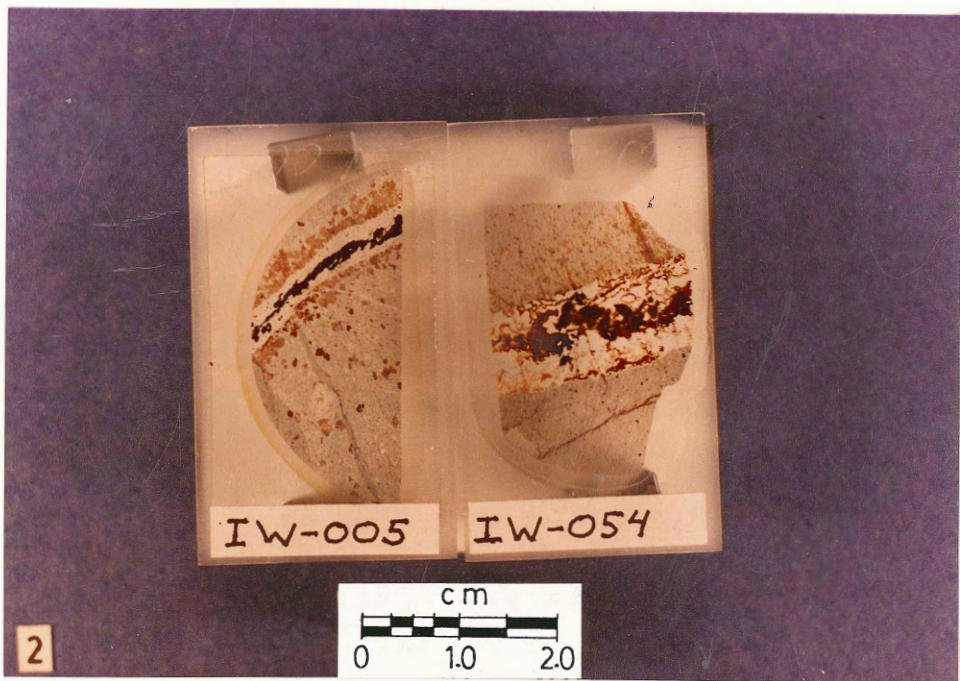
Figure 3.3a   Sulphide-cassiterite veinlets with
                     a green chloritic alteration zone
                     within blue-grey meta-wacke.

                     Sample 77-25-164.77

Figure 3.3b   Thin section of the above sample,
                     showing detail of sulphide-cassiterite
                     veinlet and green alteration halo of
                     chlorite and cassiterite(fine dark
                     brown spots).

IW-176

Table 3.1. Mineralogy of Vein Systems

| | Metasediments | | | | Pluton | |
	Pre-Crenulation	Main Stage	Post-Mineralization	Pre-Greisen	Greisen	Post-Greisen
Quartz	X	X	X	X	X	X
Carbonate*	X	X	X			x
Chlorite		X				
White Mica**		x		x	X	x
Pyrophyllite(?)			x			
Pyrite	x	X	.	.	X	x
Marcasite		x			.	.
Pyrrhotite	x	X		.	x	x
Arsenopyrite	x	x	x		x	x
Chalcopyrite	x	x	.			x
Sphalerite	x?	x				
Galena		x				
Silver/Bismuth		.				
Scheelite		.		.	.	.
Epidote		.				
Garnet+		.				
Cassiterite		x			.	
Fluorite				x	X	x
Molybdenum		.		x	x	x
Kaolinite						x

* Includes calcite, siderite, dolomite

** may be lithium- or fluorine-bearing

+ appears incorporated from matrix

? uncertain

X major vein mineral

x minor vein mineral

. trace or rare

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respectively.

Textures among cassiterite, sulphides and gangue
minerals are relatively straightforward. The habits,
associations and genesis of cassiterite in this vein type and
other settings will be discussed in a later section.
Generally, the fine grained sulphides (averaging ≤ 0.5 mm) and
cassiterite are found in the middle of the vein within a
matrix of quartz, carbonate (usually calcite; minor
siderite), chlorite and white mica. Other veins may have
sulphides at the selvedges instead; others may consist of a
patternless intergrowth of all minerals. Mineral contacts
are usually straight to curved.

Arsenopyrite occurs as subhedral rhombs and blades, and
as massive anhedral grains. It has minor inclusions of
pyrrhotite, galena and chalcopyrite. Fine cracks may be
filled, and crystal boundaries may be discontinuously rimmed
by irregular massive galena, chalcopyrite, pyrrhotite, pyrite
and sphalerite. Arsenopyrite may also be rimmed by fine
druses of calcite. This sulphide is usually in the middle of
the veinlet, but some rhombs are found at vein edges and
within the the immediate host rock, grown around phyllo- and
tectosilicates.

Pyrite is commonly anhedral and massive, grown around
other sulphides, cassiterite and gangue minerals (Fig. 3.4);
it also occurs as angular blocks (Fig. 3.5). Gangue and minor

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anhedral chalcopyrite and sphalerite may be included in pyrite. Minor pyrite hair veinlets may traverse the earlier sulphide-cassiterite veinlets, crosscutting vein minerals (Fig. 3.6) and the cleavages of phyllosilicates in the wallrock. This is believed to be a later part of the main-stage vein system.

Weathered or altered samples contain round to elliptical, concentric intergrowths of blocky pyrite, marcasite and gangue ('graphic pyrite') (Fig. 3.5). This is a result of pyrrhotite conversion to pyrite and marcasite by loss of iron during low temperature alteration (stoichiometric $2FeS \rightarrow FeS_2 + Fe$; Stanton,1972); cell volume decreases (from roughly 180 $\overset{\circ}{A}^3$ for stoichiometric hexagonal pyrrhotite to 160 $\overset{\circ}{A}^3$ for cubic pyrite using cell dimensions from Berry and Mason,1959), causing the structure to shrink and form cracks. Liberated iron may form oxides, hydroxides or magnetite, staining the surrounding rock (Stanton,1972). Much of the 'primary' pyrite may in fact be completely altered pyrrhotite.

Pyrrhotite is found as irregular, lobate grains growing around other sulphides (principally arsenopyrite) and gangue minerals. It is rarely observed altering to an assemblage of pyrite (see above description).

Marcasite is rare, and is found as subhedral blades and massive amorphous zones in altered pyrrhotite. Several

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Figure 3.4   Part of veinlet containing pyrite,
                      sphalerite and cassiterite
                      intergrowth, with minor chalcopyrite
                      inclusions.

                      Reflected light, oil immersion.

                      Long axis of photograph measures 1.08 mm

Figure 3.5   Concentric graphic pyrite(after
                      pyrrhotite) in weathered vein
                      sample.

                      Reflected light, oil immersion.

                      Long axis of photograph measures 1.08 mm
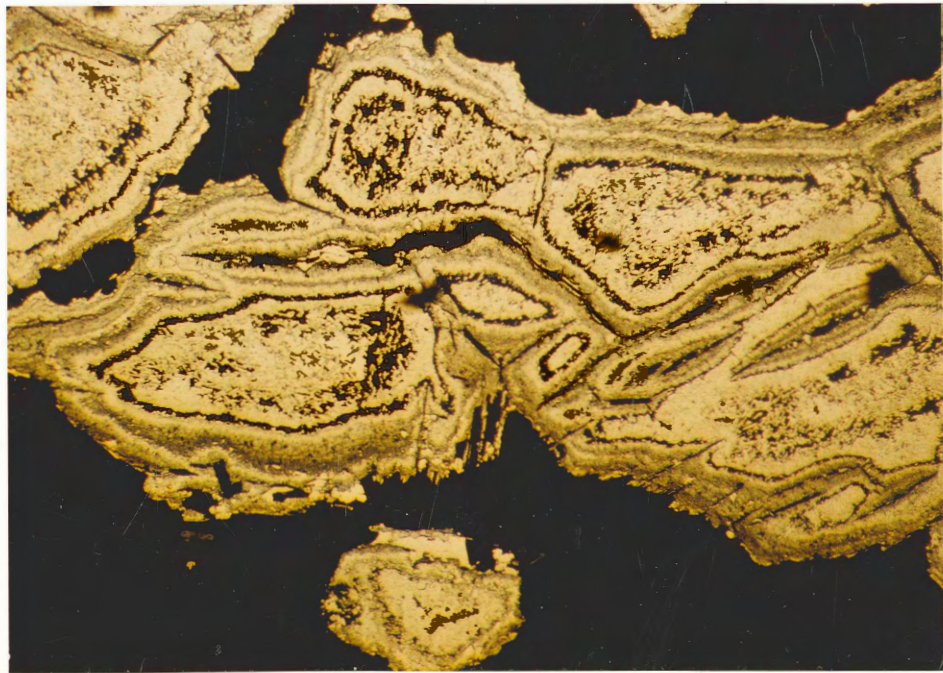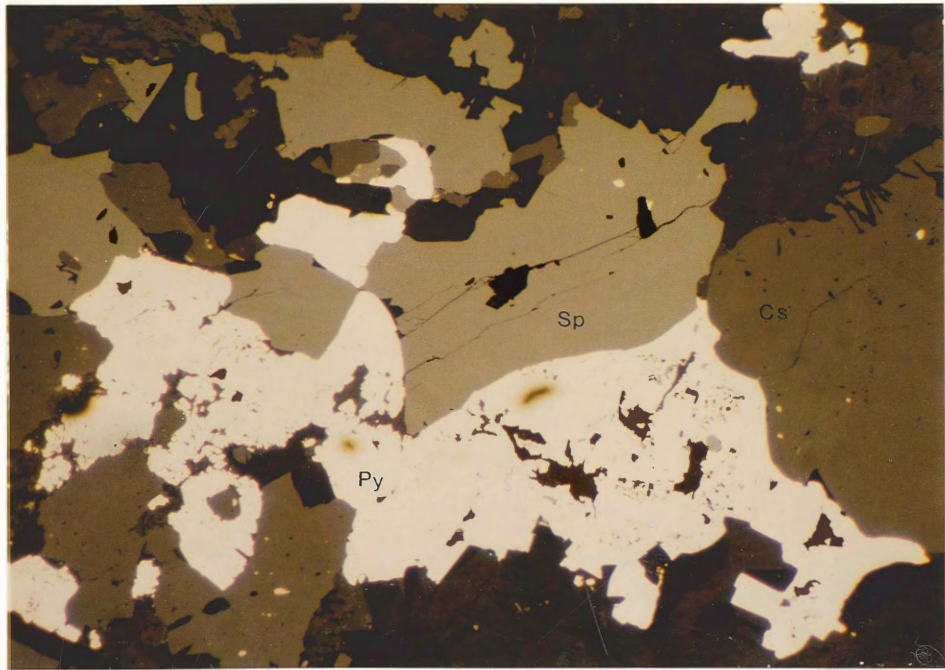
Figure 3.6a   Later pyrite veinlet crosscuts
                 main stage sulphide-cassiterite
                 vein(IW-174); it cuts a sphalerite
                 grain and travels around a
                 cassiterite grain.

                 Reflected light.

                 Long axis of photograph measures 0.54 mm

Figure 3.6b   Later pyrite veinlet cuts pyrite
                 and marcasite grains(altered from
                 pyrrhotite) in a stratiform
                 sulphide layer.

                 Reflected light, oil immersion.

                 Long axis of photograph measures 1.08 mm
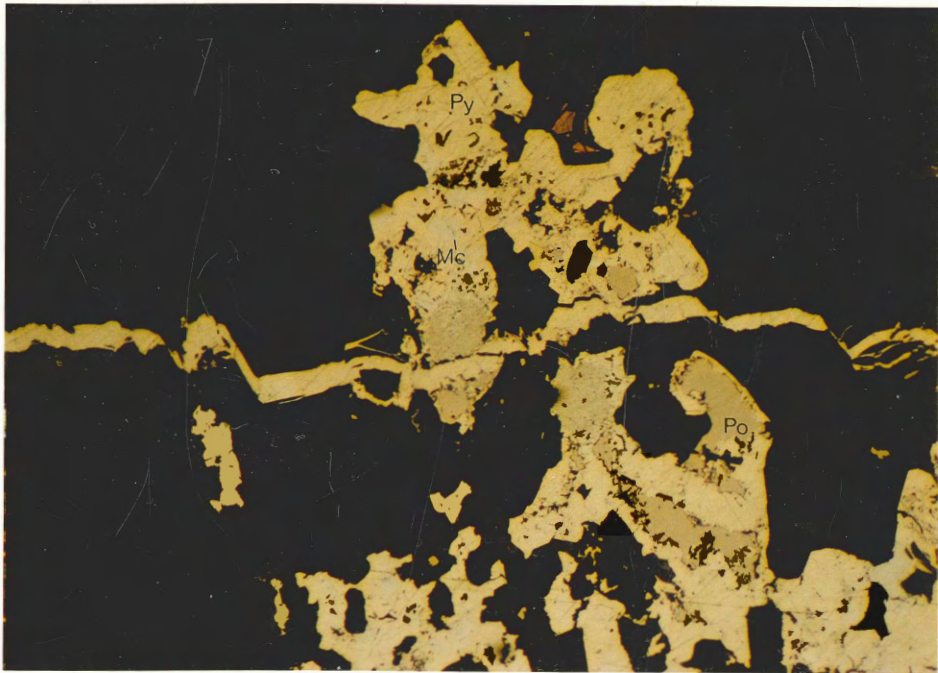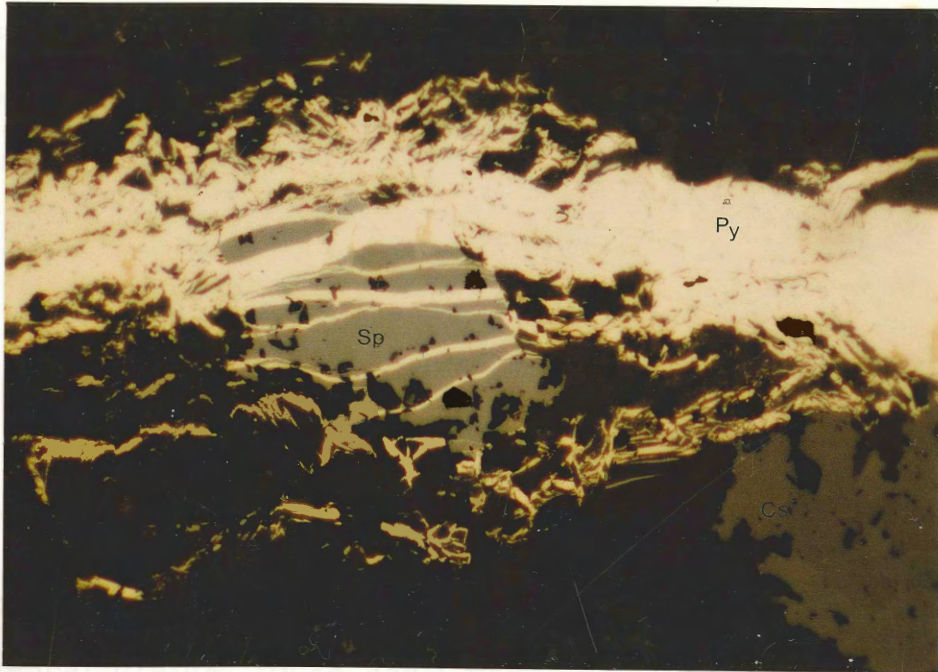
sulphide veins in drill core contain 'vuggy' zones lined with marcasite blades which appear to be a later weathering product.

Sphalerite is a rare to common constituent in the veins. It occurs as anhedral, equant to rectangular grains. The mineral may infill fractures in arsenopyrite and form discontinuous margins around both arsenopyrite and pyrrhotite.

Chalcopyrite is a ubiquitous minor sulphide. It occurs as anhedral grains, forms small exsolution blebs in sphalerite, and is intergrown with pyrite, pyrrhotite, marcasite, sphalerite, galena and gangue; it also mantles pyrrhotite, pyrite, and sphalerite grains.

Galena occurs as anhedral blebs and subhedral to euhedral blocks. It is included in arsenopyrite, fills the fractures of that sulphide, and rims and incorporates arsenopyrite, pyrrhotite, marcasite, sphalerite, and chalcopyrite. A very fine grained, highly reflective mineral is commonly included within galena and may be native silver or native bismuth. Attempts to microprobe several of these grains failed as they were too small.

Scheelite is rare, and is found in quartz-carbonate veinlets near the pluton as flesh-coloured, rectangular anhedral grains.

The gangue consists of granular intergrowths of quartz, carbonate, iron-rich chlorite (see Fig. 3.7) and white mica (muscovite and probably F- and Li-bearing varieties). Two stages of carbonate emplacement are observed in several samples: a minor encrustation of drusy carbonate around sulphides, followed by pyrite and massive carbonate. White mica commonly occurs as discrete flakes, but is also found as radiating spherules intergrown with chlorite and sulphides. Rare garnet is incorporated into the vein.

A possible depositional sequence within the vein system is given in Table 3.2.

Later movement along veins (i.e., along pre-existing planes of weakness) caused elongation of pyrrhotite (parallel to phyllosilicates), strain in quartz (undulatory extinction to formation of sub- and new grains) and incorporation of low temperature acicular cassiterite into new quartz grains. One sample appears to have had regrowth of chlorite into random aggregates and overgrowth of garnet.

3.2.1.3 Post-Mineralization Veins

Identification of this vein type is difficult. The best examples occur where they cut mineralized veins or zones (e.g., Fig. 2.6), but this is relatively uncommon. Brecciated core is tentatively identified as post-mineralization because breccias cut all sedimentary

Figure 3.7   Chlorite compositions of samples
                    in veins and metasediments. Upper
                    field A contains microprobe
                    analyses from 16 chlorite samples
                    in and adjacent to sulphide veinlets.
                    Lower field B contains analyses
                    from 13 chlorite samples in meta-
                    wacke and in stratiform mineralized
                    zones.

                    (Classification by H.M. Hey, in
                    Deer, Howie and Zussman, 1974)

Nomenclature for oxidized chlorites

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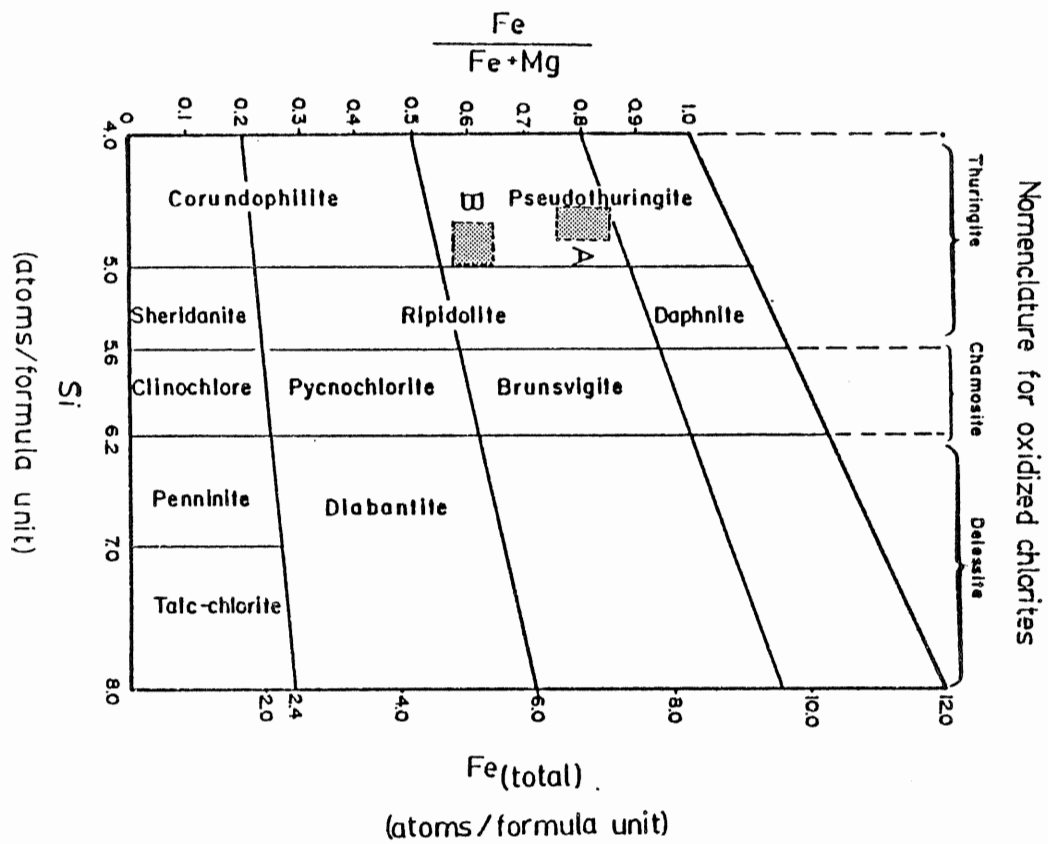
Table 3.2　　　　Mineral Paragenesis in Main Stage Veins

	Early		Late
Scheelite	- - -		
Molybdenite	- - -		
Arsenopyrite	———		
Pyrite	- - ———————————— - -		
Pyrrhotite	- - ——————— - -		
Cassiterite	- - equant ———————————— acicular - -		
Sphalerite	- - ————— - -		
Chalcopyrite	- - ————— - -		
Galena	- - ——		
Silver / Bismuth	- -		
Druse Carbonate	——		
Main Carbonate	- - ——————		
Marcasite			- - -
Gangue (qtz+chl+mica)	———————————————————		

weathered po   - - -

structures and contain only trace amounts of sulphides and no cassiterite; they also are associated with the greatest displacement observed (up to several cm), which is not found in other vein stages.

Widths vary from less than 1 mm to several cm. Veins may occur either singly or in fine networks ('crackle breccia'). Some quartz-calcite tension fractures cut mineralized zones, and therefore belong to this stage; it is not known how these relate to other tension gashes (pre-mineralization?).

Quartz and calcite are the main components; minor arsenopyrite, pyrite and chalcopyrite are disseminated throughout. Several veinlets contain tan spherulitic intergrowths of pyrophyllite(?) and are possibly altered fragments of pelitic wallrock or rock 'flour' formed during brecciation.

Wallrock alteration is variable. Restricted assemblages ($\leq$ 1 mm wide) of muscovite, chlorite and quartz may occur adjacent to the vein and fine hair veinlets may branch from the main vein. Other samples have wide, light hued 'bleached' zones several m in core length, containing intergrown quartz and muscovite aggregates. Several sheared core samples are cut by later quartz-calcite veinlets.

3.2.2 Veins Within Pluton

The endocontact of the Wedgeport pluton is cut by a
myriad of thin veinlets; the interior contains minor
veining. In contrast with veining in the metasediments,
crosscutting relationships are common, and it is sometimes
difficult to resolve the various vein stages. As with the
metasediments, three main stages of veins exist. Early,
pre-greisen quartz veins are usually thin with minor
concentrations of other minerals and do not perceptibly alter
the adjacent wallrock. Main stage tin-bearing greisen veins
are of variable thicknesses and alter the monzogranite
country rock from mm to several tens of cm of core length.
Late stage quartz veins cut the previous veins, may contain
kaolinite and cause little, if any alteration. Later shears
may cut any of these veins, and in places have associated
quartz-arsenopyrite ± scheelite veining.

3.2.2.1 Pre-Greisen Veins

This type of vein is usually thin ($\leq$0.5 cm) and is
composed of quartz with variable, but minor amounts of white
mica, scheelite, purplish fluorite, molybdenum, pyrite and
pyrrhotite. Several of these veins usually crosscut each
other. Alteration is minimal and comprises fine (several mm)
assemblages of quartz and white mica in the adjacent
wallrock.

They are not otherwise notable except for their role as

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physical barriers to later greisenizing fluids: greisen alteration zones abruptly halt at these pre-existent veins (Fig. 3.8).

3.2.2.2 Greisen Veins

This interesting vein type varies from <1 mm to about 1 cm thick veinlets. A typical greisen vein contains major quartz and minor fluorite, white mica, chalcopyrite, pyrite $\pm$ arsenopyrite $\pm$ molybdenum $\pm$ scheelite $\pm$ sphalerite $\pm$ a rust brown phyllosilicate (vermiculite??) $\pm$ cassiterite.

Alteration is extensive, affecting a zone many times the width of the vein itself. The greisen halo is predominantly a quartz-white mica aggregate containing variable amounts of purplish (in places greenish) fluorite and minor calcite, chalcopyrite, pyrite, pyrrhotite and cassiterite.

Quartz is fine grained (0.25-0.75 mm), commonly anhedral (rarely euhedral), slightly strained and appears to comprise relict quartz 'eyes' of the monzogranite plus silica introduced by greisenization. Fine grained (0.1-0.5 mm) white mica clusters are intergrown with the quartz grains. This phyllosilicate may be lithium-bearing, as evidenced by high lithium concentrations in geochemical analyses of greisen samples. Attempts to identify the mica by X-ray powder diffraction proved disappointing as the d-spacings of muscovite and the lithium-bearing micas (e.g., zinnwaldite,

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lepidolite) are very similar.

Anhedral purplish fluorite (usually up to 2 mm in size)
has grown around the quartz muscovite aggregate, following
their crystal outlines. It comprises from 1 to 10 modal
percent of the greisen; rarely it grades into massive
fluorite.

Minor anhedral chalcopyrite, pyrite and pyrrhotite (up
to about 5 modal percent) are found throughout the greisen
and are usually enveloped by or in contact with fluorite. A
few opaques are overgrown by calcite.

Minor relict euhedral to subhedral prisms of zircon are
disseminated throughout the greisen.

Subhedral cassiterite is rare, both within the greisen
vein and its halo, and is usually in close association with
fluorite.

Contact between the greisen and monzogranite may be
sharp (Fig. 3.9), due either to rapid equilibration
('neutralization') of the greisen fluid with the wallrock or
to the presence of a pre-existing quartz vein barrier. The
greisen may also be diffuse, changing from a 'true' greisen
(quartz-white mica-fluorite assemblage) to an altered
('greisenized') monzogranite, where matrix minerals and their
textures are progressively destroyed. Feldspar phenocrysts
become rounded and are gradually broken down into mica-rich

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Figure 3.8   Leucocratic monzogranite with
                    greisen alteration which stops
                    at pre-existent quartz veinlet
                    barrier.

                    Sample 79-07-70.66

Figure 3.9   Veinlet with greisen alteration
                    in relatively sharp contact with
                    slightly phenocrystic monzogranite.

                    Sample 79-08-72.93

aggregates, leaving dark 'ghost' rectangular forms. Quartz phenocrysts appear unaltered and remain as round pinkish 'eyes' in the greisen. This progressive alteration of monzogranite is rarely seen in drill core; usually only individual greisen or slightly altered zones are observed. Fortunately, one such specimen was obtained (Fig. 3.10). It exhibits a gradual change from unaltered material to a 'tan' alteration zone to a 'white' alteration zone to a greisen. The changes which take place during greisenization will be discussed in the cassiterite section.

3.2.2.3 Post-Greisen Veins

Both greisens and unaltered monzogranite are cut by thin (≤1 cm) veinlets. They consist of quartz and kaolinite with minor calcite, dolomite and trace molybdenum, pyrite, marcasite, pyrrhotite, arsenopyrite, fluorite, scheelite, chalcopyrite and white mica. Quartz is commonly euhedral and terminated, and is intergrown with the sulphides; kaolinite and the carbonates overgrow these minerals (Fig. 3.11).

Sheared monzogranite may be unmineralized, may cut pre-existent mineralization, or may be mineralized itself. Widths range from < 1 cm to tens of cm (up to 1 m) in drill core. Pre-existent greisens and quartz-scheelite-molybdenite veins may be sheared, although this pre-existence is usually only establised in thin section: mineralized quartz veins

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Figure 3.10   Phenocrystic monzogranite with
                     alteration zones from 'fresh'
                     to 'tan' to 'white' to greisen
                     proper. Core is cut by later
                     kaolinite veinlets; note
                     displaced feldspar phenocryst
                     (arrow).

                     Sample 79-08-70.70

Figure 3.11   White and tan altered slightly
                     phenocrystic monzogranite cut
                     by a fine greisen veinlet
                     and a later kaolinite veinlet.
                     Although the latter veinlet
                     appears truncated by a thin
                     veinlet, it actually changes
                     course, following this pre-
                     existent veinlet to the top
                     right.

                     Sample 79-07-26.30

Gsn   Wt   Tan ↓

1   10 cm

5 cm

100

contain strained quartz and are cut by parallel aggregates of
white mica. Some shears have associated quartz veins with
variable concentrations of arsenopyrite, scheelite, pyrite
and chalcopyrite (Fig. 3.12); others have sulphides (pyrite,
pyrrhotite, sphalerite, chalcopyrite) overgrowing the shear
planes. Contact with the monzogranite is gradational,
exhibiting changes in grain size, orientation and
mineralogy. Feldspar and quartz phenocrysts are broken down;
newly formed phyllosilicates are oriented in parallel
planes.

3.3 Stratiform Mineralization

Many sulphide zones are found throughout the drill core
and consist of individual pyrrhotite blebs through to
concentrated sulphide disseminations in cm thick beds. They
occur in both pelitic and psammitic lithologies (Fig.3.13)
within discrete layers, usually in sharp contact with
adjacent beds. The thicker, tin-bearing sulphide-rich beds
are commonly a distinctive dark blue grey and hence have been
termed 'blue mineralized patches'. Description of these
concordant zones has been divided into tin-barren and
tin-bearing sections.

Figure 3.12   Sheared monzogranite with
                   quartz-arsenopyrite vein.

                   Sample 79-07-33.36

10 cm

Figure 3.13   Anhedral pyrrhotite disseminated
                   throughout meta-wacke.

                   Sample 78-26-117.54

                   PPL

                   Long axis of photograph measures 8 mm
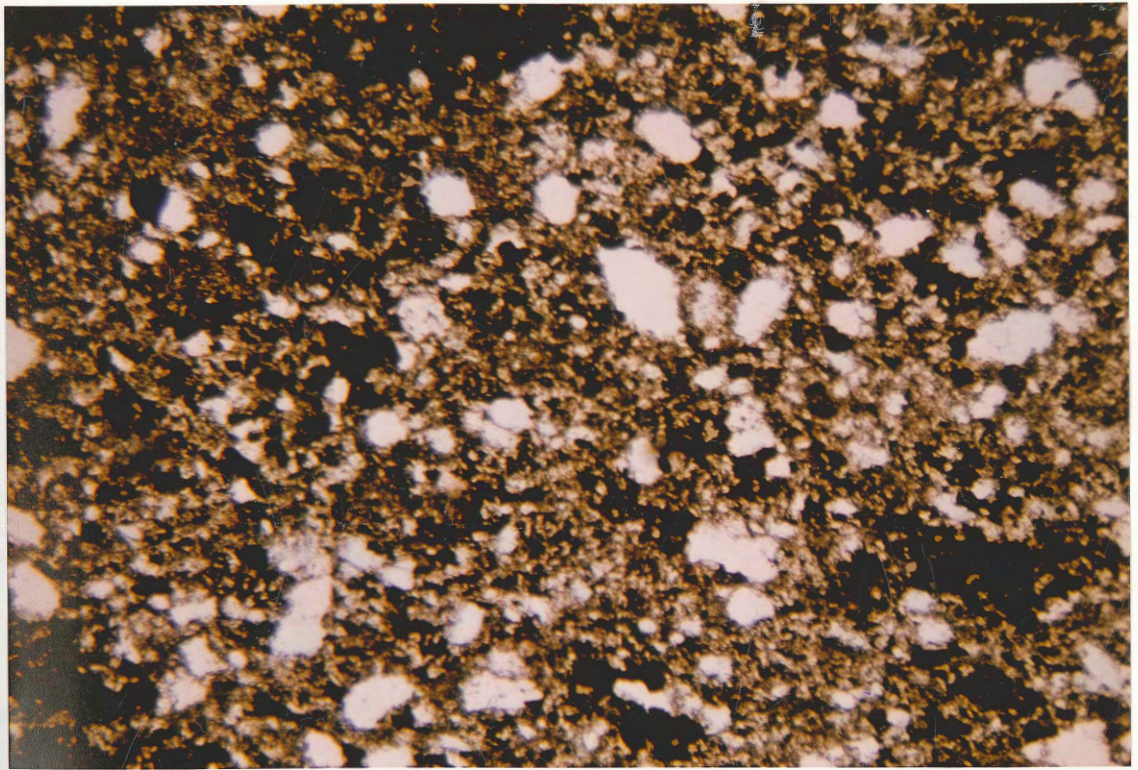
3.3.1 Tin Barren Sulphide Zones

This type of mineralization is commonly found as fine-grained elongate blebs of pyrrhotite oriented parallel to foliation; in places they are crenulated. Rarely, layers of almost massive sulphides (pyrrhotite, minor chalcopyrite and arsenopyrite) of several cm thickness occur(Fig. 3.14).

These sulphides consist of anhedral, granoblastic pyrrhotite altering to spotted and massive aggregates of marcasite and pyrite (Fig. 3.15). The sulphides grow around and include all gangue. These larger sulphide layers may in fact represent part of the mineralized sequence, but do not contain any cassiterite.

A number of samples contain 'shredded-textured' sulphides subparallel to the enclosing phyllosilicates (Fig. 3.16); this may indicate an episode of stress after sulphide formation, possibly metamorphic or sheer related.

Various authors (e.g., Krauskopf,1979; Rickard,1969a,b; Saxby,1976; and Stanton,1972b) suggest iron sulphide formation is due to reaction of biogenic sulphur with iron from the sediments. Anaerobic bacteria within organic-bearing sediments reduce seawater sulphate in marine pore water to hydrogen sulphide, and in so doing, produce water and carbon dioxide (Krauskopf,1979). Iron may become soluble in this reducing environment from detrital iron minerals or iron hydroxides (e.g. goethite) found alone, adsorbed to clays and organic material or coated to clastic

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Figure 3.14   Slightly crenulated stratiform
pyrrhotite layer in carbonaceous
meta-argillite. Minor chalcopyrite
and arsenopyrite also occur.

Sample 77-34-233.35

5 cm
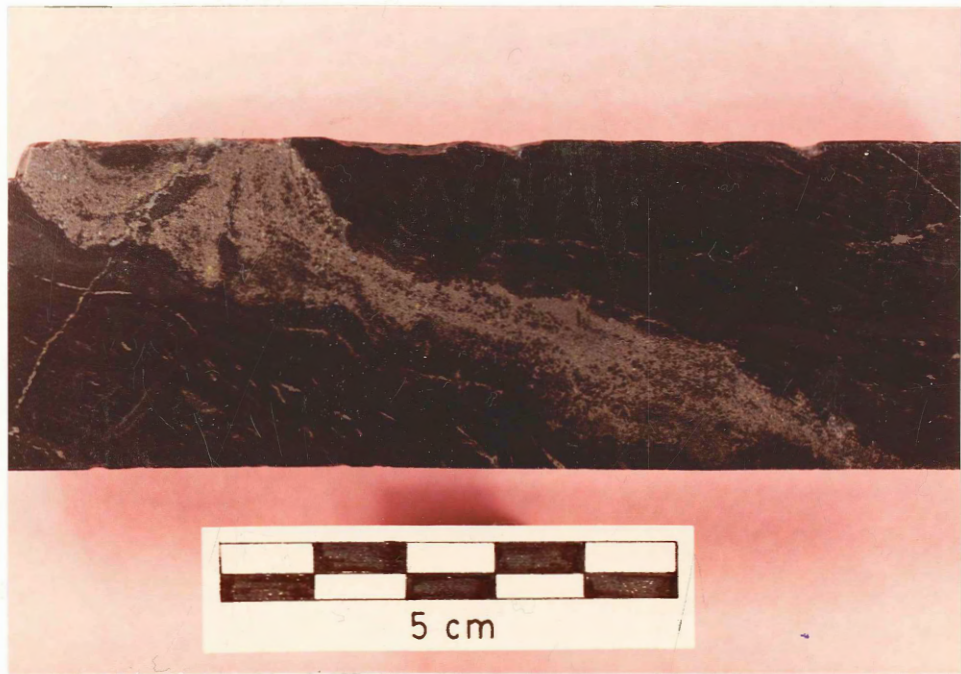
Figure 3.15a   Anhedral grains of graphic pyrite
                    and marcasite altered from pyrrhotite
                    within mineralized 'patches'.

                    Sample 78-12-93.60

                    Reflected light, oil immersion.

                    Long axis of photograph measures 1.08 mm

Figure 3.15b   Low temperature alteration of
                    pyrrhotite to a 'speckled'
                    assemblage of marcasite and
                    pyrite to homogenous pyrite.

                    Sample 77-08-31.45

                    Reflected light, oil immersion.

                    Long axis of photograph measures 1.08 mm
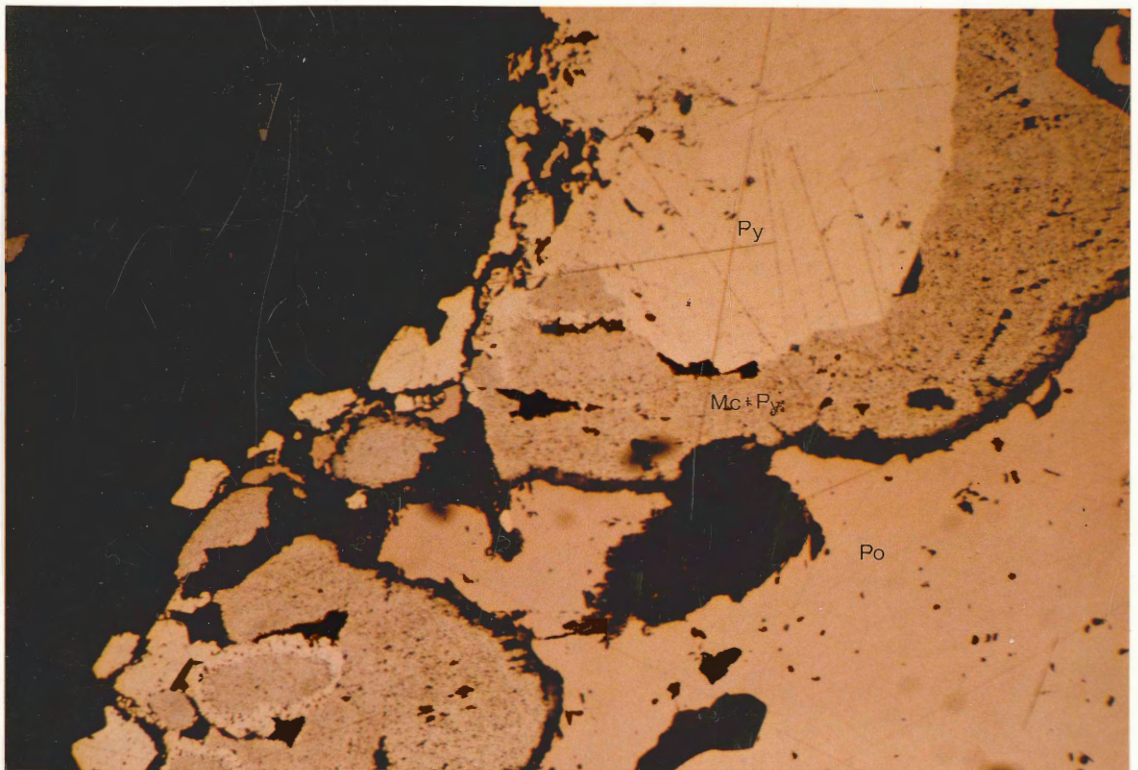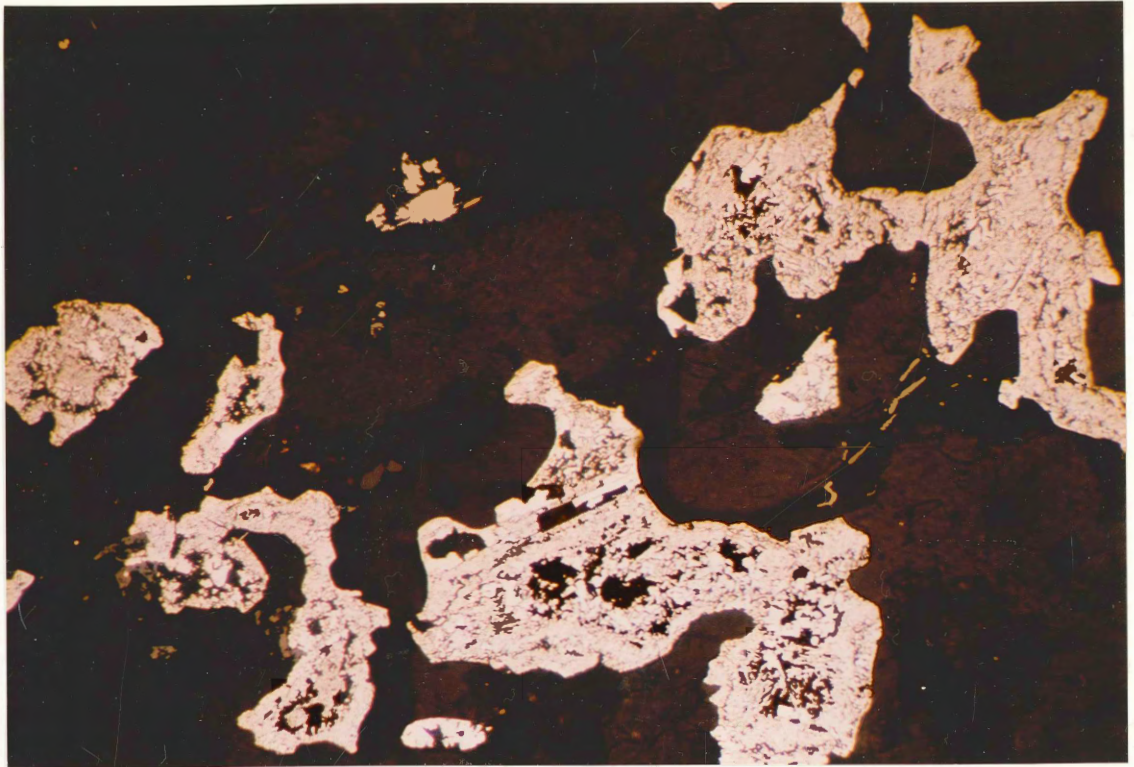
Figure 3.16   Elongate, 'shredded-textured'
                     pyrrhotite in a biotite meta-
                     wacke.

                     Sample 77-05-74.75
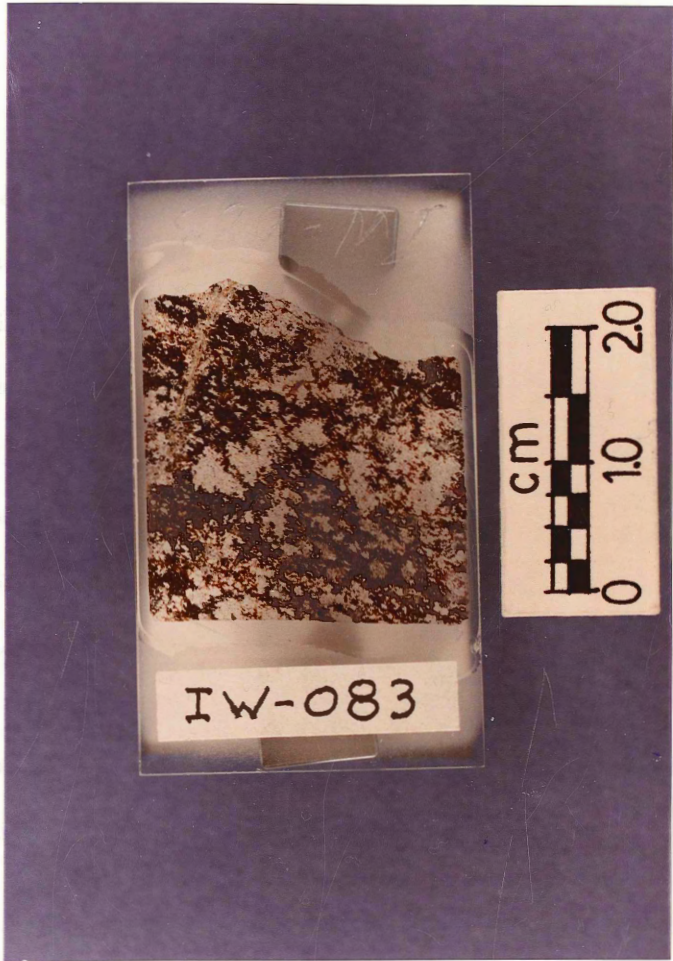
IW-083

grains (Love,1969). The first products are soft, dark iron

sulphides (e.g. mackinawite, greigite) which may equilibrate

to pyrrhotite or incorporate more sulphur from biogenic H_2S

or elemental sulphur to form pyrite (Rickard,1969a).

Sulphides may form in place in the organic-bearing sediments;

the mobile sulphide and metal ions may also be expelled

upward during compaction and diagenesis into porous beds to

combine there (Vaughan,1976).

An increase in temperature, by compaction, diagenesis

and metamorphism may lead to a decrease in sulphur content of

pyrite and subsequent conversion to pyrrhotite

(Stanton,1972a). Pyrrhotite responds to directed pressure by

translation gliding along (0001) crystal planes and thus

forms elongate bodies parallel to foliation. The released

sulphur from the pyrite may combine with existent iron oxides

or hydroxides, iron carbonates or calc-silicates to form

'replacement' or 'sulphidized' iron sulphides (Rose and

Burt,1979; Gamble,1982; Love,1969; Kullerud and Yoder,1965;

Mookerjee,1981).

Minor chalcopyrite, sphalerite and arsenopyrite found

with these pyrrhotite-rich layers may also have formed by the

combination of bacterial action, diagenesis and metamorphism

(Saxby,1976; Mercer,1976; Love,1969).

Rare samples contain arsenopyrite grains which appear

detrital (Fig. 3.17); these angular grains are disseminated

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Figure 3.17   Diagenetic(?) arsenopyrite and
                  other sulphides(black) in a
                  coarse meta-wacke in contact with
                  a meta-argillite scour. Current
                  laminations consist of ilmenite
                  and zircon. Steeply dipping
                  lines within meta-argillite are
                  crenulation cleavages.

                  Sample 77-34-86.13

thoughout coarser layers of meta-wackes. Closer examination
reveals arsenopyrite to be subhedral with overgrowths of
anhedral pyrrhotite, minor chalcopyrite and rare galena;
these softer sulphides are compressed around the arsenopyrite
and detrital gangue grains. One arsenopyrite grain
incorporates a detrital ilmenite lath. This evidence
suggests arsenopyrite and the other sulphides formed in situ
after sediment deposition and before compression (regional
metamorphism?). Little work has been done on arsenopyrite
(e.g. Kretschmar and Scott,1976; Barton and Skinner, 1979)
and much of that at high temperatures ($>400^{\circ}$C) so it is not
known if this can occur. However, stratabound arsenopyrite
has been described within a sandstone layer in Late
Precambrian sediments of the East Greenland Caledonides
(Ghisler et al.,1980); euhedral crystals had grown across the
laminae, implying a diagenetic to metamorphic(greenschist
facies) origin.

3.3.2 Tin Bearing Sulphide Zones

The mineralized 'patches' are usually dark greyish green
to dark greyish blue bands (Fig. 3.18). Less commonly they
are green, dark and light brown amorphous masses. Rarely,
they form dark brownish red and white bands (Fig. 3.19). In
drill core the 'patches' have a varied appearance: felty
masses rich in phyllosilicates; saccharoidal in the more
psammitic zones; or mottled, with light grey, white and

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Figure 3.18a   Blue mineralized zone in
                      meta-wacke.

                      Sample 77-34-113.73

Figure 3.18b   Two mineralized zones with
                      thin chloritic haloes.

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5 cm

IW-049   IW-051

cm

0   1.0   2.0

Figure 3.19a   Sphalerite-pyrite-chlorite
layers in quartz-carbonate
meta-wacke.

Sample 78-12-13.88

Figure 3.19b   Thin section of above sample.
Elongate sphalerite and pyrite
(opaque) are intergrown with
chlorite and quartz, and are
overgrown by white mica laths.

PPL

Long axis of photograph measures 5 mm

119
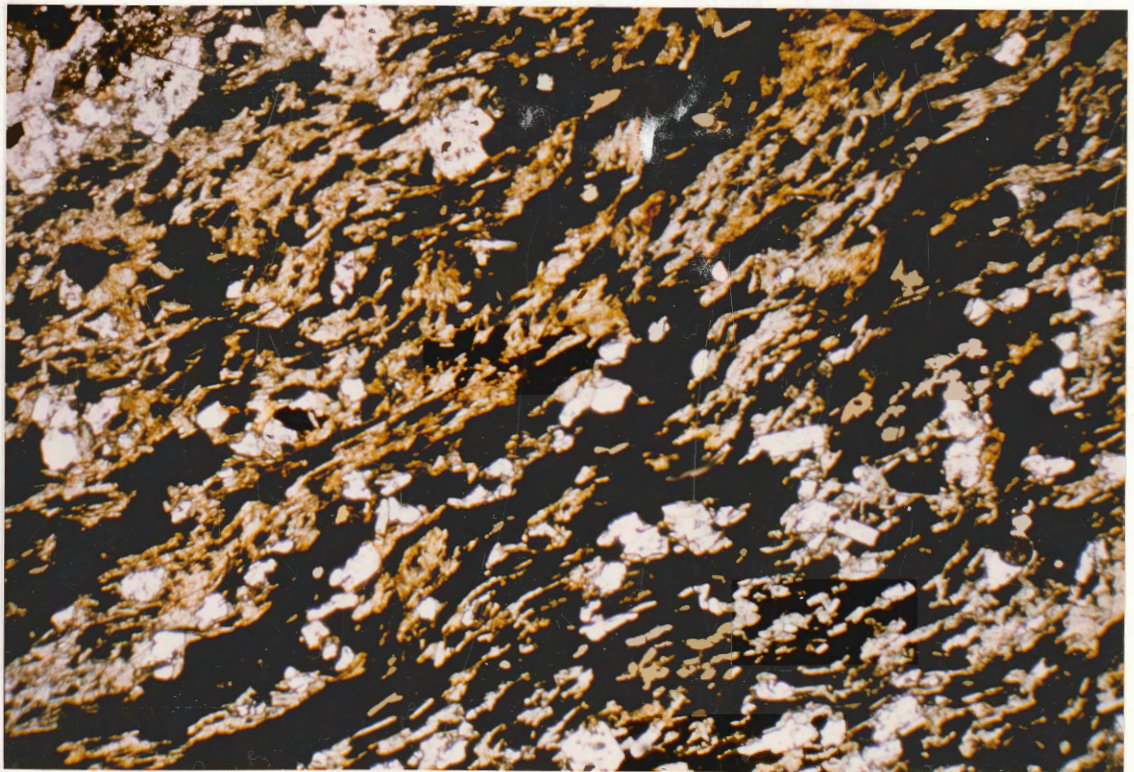
orange stained blebs of carbonate, and irregular

disseminations and veinlets of sulphides. They are thin (<1

cm) but rarely attain up to 12 cm length in drill core. The

zones are concordant with bedding, with sharp to gradational

contacts. Some 'patches' have chlorite and white mica haloes

up to 0.5 cm width; one such sample has chlorite that,

crosscuts the foliation, implying a post-foliation

development of these mineralized layers. Their lateral

continuity is not known; areas which contain much of this

mineralization have these 'patches' at all stratigraphic

levels (e.g.,see section A in Fig. 5.12). They are

pre-faulting, as is evidenced by the crosscutting and

displacement of one such zone (Fig. 3.20); therefore they may

have formed at the same time as the mineralized veins.

The dark coloration is mainly due to less chlorite and

muscovite, and more quartz with disseminated graphite.

Mineralization is found in both pelitic and psammitic

lithologies, so the gangue mineralogy reflects the host

rock. It usually consists of tightly intergrown chlorite,

muscovite, quartz, feldspar, and trace amounts of zircon,

rutile, sphene and ilmenite. The tectosilicates are

granoblastic with lobate to triple point boundaries. The

minerals are commonly homogeneously intergrown, although

there are 'patchy' growths of: felted chlorite masses;

chlorite and quartz; and carbonate. Foliation is defined by

parallel orientation of white mica, or vague parallel

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Figure 3.20   Blue mineralized zone displaced
by a fine veinlet, and cut by a
quartz-pyrite veinlet.

Figure 3.21   Carbonaceous calcite layer
containing cassiterite
aggregates(arrow).

IW-132

IW-068

orientation of graphite.

Graphite occurs as <0.003 mm disseminations to about 0.1 mm needles and wispy aggregates, usually near chlorite. One sample (IW-068) contains vaguely foliated and crenulated graphite wisps and blades in a calcite matrix. It makes up <1 to about 15 modal percent of the mineralized zones. The boundary between mineralized and barren layers is defined, in part, by the concentration of graphite.

Chlorite makes up from 1 to 30 modal percent of the zones, and is found as 0.01 to 0.15 mm anomalous blue needles. It can concentrate at the boundary with unmineralized layers. White mica has about the same form and concentration as chlorite; larger flakes (about 0.45 mm) overprint the matrix.

Carbonate, in the form of calcite, siderite, dolomite or ankerite, occurs throughout the 'patches'. It may form 0.06 to 0.1 mm amorphous blebs intergrown with the matrix, or may form subhedral, equant to tabular, lobate rhombs overprinting the matrix. Inclusions of quartz, muscovite and cassiterite are found. It makes up <1 to 20 (rarely up to 50) modal percent of the zone (Fig. 3.21).

In the more psammitic 'patches' near the pluton, biotite, tremolite (only 1 grain observed) and epidote are also found. Epidote varies from rare to 25 modal percent,

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intergrown with, and overprinting the matrix.

Cassiterite and the sulphides comprise from 1 to 30
modal percent of the mineralized zone and occur as clots of
grains and fine veinlets. The grains range up to 0.9 mm in
size and veinlets are about 0.09 mm wide. Most veinlets are
found near the contact with the unmineralized zone, with the
graphite and chlorite. They are subparallel to the
foliation, following phyllosilicate grain boundaries. The
opaques overprint, grow around, or replace the silicates and
carbonates.

Pyrite is the major sulphide and appears to have been
derived from pre-existing pyrrhotite; seen by remnant
pyrrhotite within the pyrite (Fig. 3.15). Pyrite is found as
anhedral to subhedral, massive to skeletal and graphic
textured grains with straight to embayed grain boundaries,
following gangue boundaries. Other grains overprint and
replace tectosilicates, phyllosilicates (along cleavage
planes) and carbonates (from the rim, inwards); see Figure
3.22 for some examples of replacement textures. Many of the
grains are on or adjacent to pyrite veinlets, exhibiting a
paternoster pattern. This sulphide is intergrown with and
replaced by minor chalcopyrite and sphalerite.

Pyrite is also found as individual or bundles of hair
veinlets, cutting or outlining silicate and carbonate
grains.

Figure 3.22   Replacement Textures in Stratiform Sulphide
               Zones. All are reflected light, oil
               immersion.

               A. Detail of poikilitic pyrite(altered from
                  pyrrhotite) inundating cleavage planes of
                  a phyllosilicate, probably biotite.
                  Long axis of photograph measures 0.21 mm.

               B. Pyrite 'atolls' rimming and replacing gangue
                  minerals, probably carbonates. Long axis of
                  photograph measures 1.08 mm.

               C. Detail of partial pyrite replacement of a
                  gangue grain. Long axis of photograph
                  measures 1.08 mm.

               D. Detail of partial pyrite replacement of a
                  phyllosilicate along cleavage planes. Long
                  axis of photograph measures 0.21 mm.
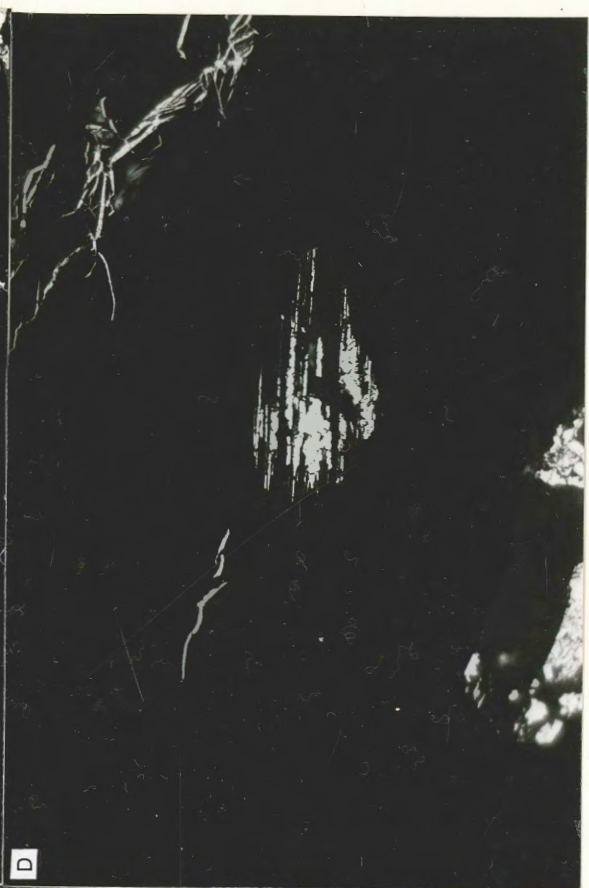
Pyrrhotite varies from less than 1 modal percent in the tin-bearing zones, up to about 40 modal percent in the tin-poor layers. It occurs as anhedral, embayed, polygonal granular and poikilitic grains. This sulphide is intergrown with cassiterite and gangue minerals; it rarely occurs within chalcopyrite, and is partially to completely replaced by pyrite.

Sphalerite is a rare mineral within tin-rich layers (1-2 modal percent), but can attain up to 60 modal percent in tin poor zones. It is usually disseminated, and surrounded by chlorite and white mica. In the richer zones, massive, anhedral sphalerite is intergrown with pyrrhotite partially altered to pyrite; these sulphides are interlayered with chlorite and quartz and are overprinted with white mica (Fig. 3.19). Sphalerite may replace pyrite and may be replaced by chalcopyrite.

Chalcopyrite is a minor sulphide, ranging up to about 1 modal percent. It is associated with pyrite and sphalerite grains. It is grown around, and may replace pyrite, pyrrhotite and sphalerite.

Arsenopyrite is rare, occurring as sub- to euhedral grains surrounded by pyrrhotite.

Cassiterite will be described in detail in the next section, but generally is rare (<1 modal percent), and is

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closely associated with the sulphides. It overprints the matrix, and incorporates pyrite, graphite and the phyllosilicates.

A few of these mineralized 'patches' have an adjacent halo of tightly intergrown chlorite and white mica with trace amounts of pyrite, pyrrhotite, chalcopyrite and arsenopyrite.

3.4 Cassiterite - Description

Cassiterite is found in a variety of mineral associations and crystal habits. This diversity appears to be due to the different modes and temperatures of cassiterite formation, and will be discussed further in a later section of the chapter. A summary of the habits and associations of cassiterite is found in Table 3.3.

3.4.1 Stratiform Association

Cassiterite occurs as 0.01 to 0.3 mm sized equant subangular to subrounded grains; several are subhedral (square combination prisms) and have simple twins. The grains are commonly sharply zoned, although the zoning is not always symmetrical: several grains have ragged or broken edges, which may imply a possible detrital origin (Fig.

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3.23). One zoned cassiterite grain has a rounded core, a
possible relict from an earlier origin (Fig. 3.24).

The grains have a variegated brown coloration, either
associated with zoning, or completely random. The core is
usually dark brown, lightening outward. Approximately
one-half of the grains have colourless ragged rims of
cassiterite (Fig. 3.25).

In the only thin section where this particular habit is
observed, about 15 modal percent cassiterite occurs in
granular aggregates in a pelitic unit. The unit consists of
two layers of white mica, chlorite, quartz, minor rutile,
graphite and rare chalcopyrite. The aggregates parallel the
layering; in one place cassiterite appears to be in a
microscour (Fig. 3.26). Cassiterite has also been noted
within crossbeds of a Goldenville Formation meta-wacke (A.K.
Chatterjee, pers. comm.,1983).

3.4.2 Stratiform Sulphide Association

This type of association is more common, and occurs in
the blue to dark green pelitic 'patches'. Cassiterite occurs
in two habits: subequant anhedral grains and the more common
botryoidal clusters of grains (the so-called 'wood-tin'). The
anhedral grains are 0.01 to 0.5 mm in size, of irregular
shape with rounded to serrate edges. They are dark brown in

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Figure 3.23   Broken zoned cassiterite crystal.
                   Part of detrital aggregate of
                   cassiterite.

                   Sample 78-11-112.4(IW-056)

                   PPL

                   Long axis of photograph measures 1.44 mm

Figure 3.24   Zoned euhedral cassiterite with
                   round core. Part of detrital
                   aggregate of cassiterite.

                   Sample 78-11-112.4

                   PPL

                   Long axis of photograph measures 0.39 mm
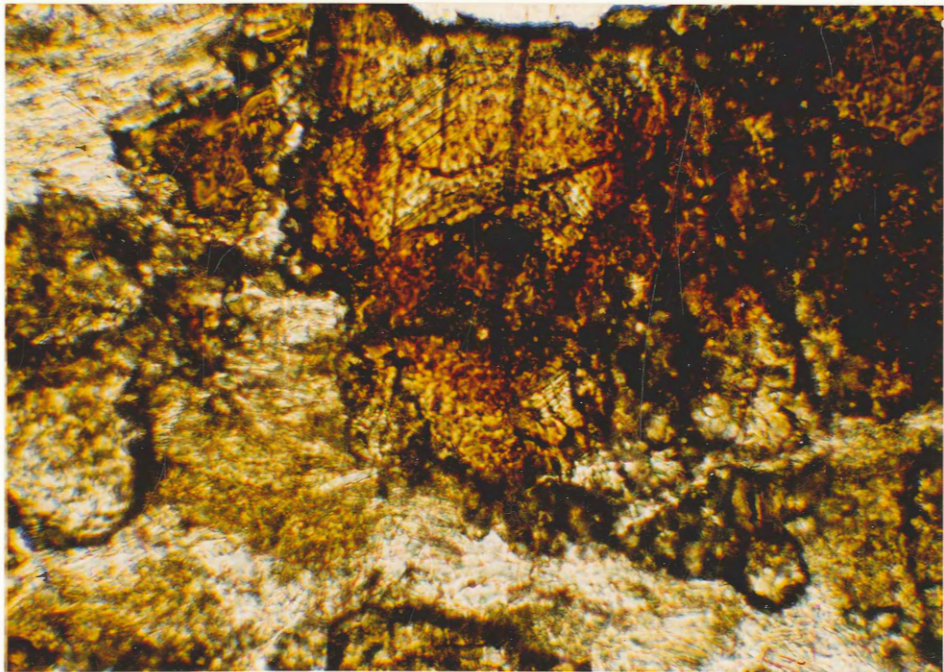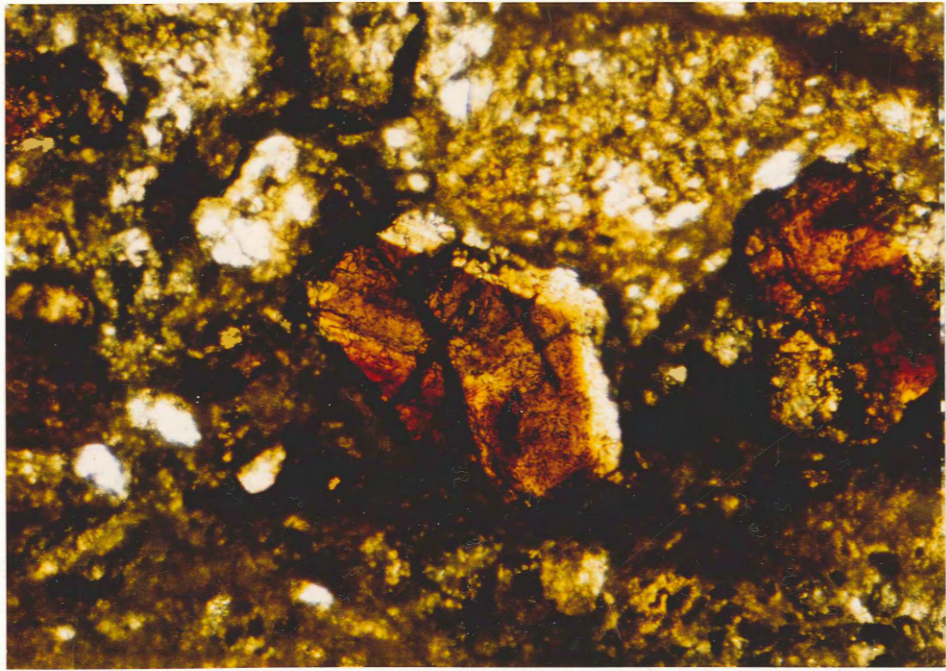
Figure 3.25   Zoned twinned cassiterite with
                  ragged colourless overgrowth.

                  Sample 78-11-112.4

                  PPL

                  Long axis of photograph measures 0.39 mm
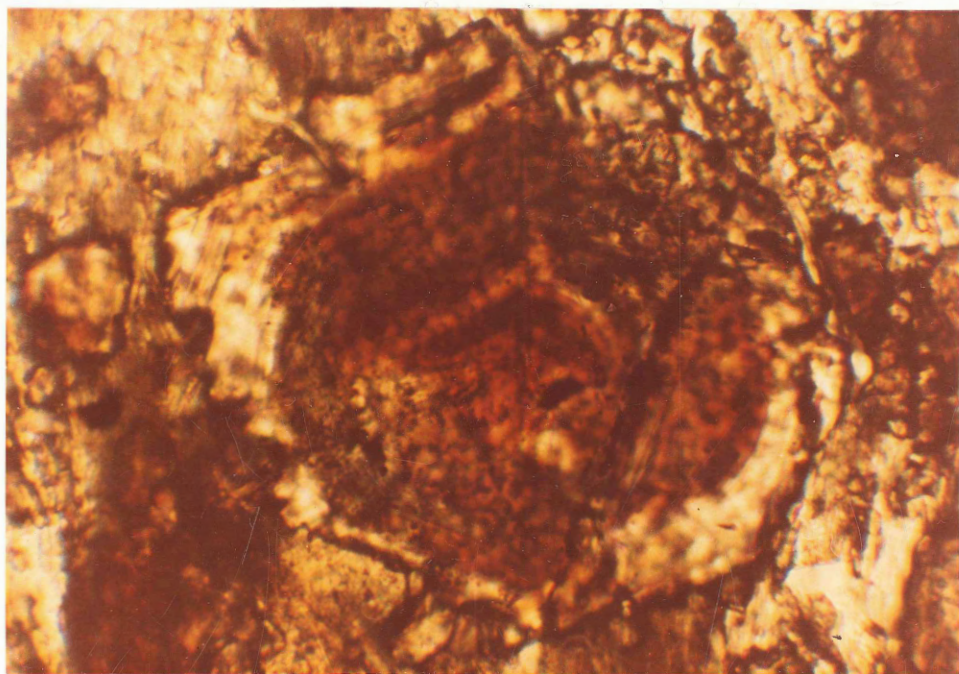
Figure 3.26   Detrital cassiterite in a
                     siltstone scour. Opaques in
                     lower layer are ilmenite.

                     Sample 78-11-112.4

                     PPL

                     Long axis of photograph ~ 6.25 mm

the centre, lighten toward the edges, and vary from clear to turbid.

Cassiterite is closely associated with sulphides (pyrite, pyrrhotite, chalcopyrite and sphalerite), ilmenite, rutile, zircon and chlorite. It occasionally partially to completely encloses the sulphides, ilmenite and chlorite. Rarely, it is found without sulphides, within a quartz-biotite-clinozoisite meta-siltstone (Fig. 3.27).

Botryoidal cassiterite occurs as irregular-shaped, rounded or slightly prismatic clusters of grains from 0.003 to 0.2 mm in size, and is dark brown. They usually occur within a groundmass of chlorite and white mica, with or without carbonate, either alone or adjacent the sulphides mentioned previously. They occasionally enclose pyrite, chlorite and white mica, and overprint the groundmass.

Both habits in this association usually comprise less than 1 modal percent in the 'patches', but can attain a maximum of 5 modal percent.

3.4.3 Stratiform Calcareous Sulphide Association

This is an uncommon association, observed in only two thin sections. Cassiterite occurs as 0.05 to 0.1 mm euhedral tetragonal prismatic crystals. They have a variegated coloration: neutral to light brown, with darker brown along

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Figure 3.27   Granular cassiterite in biotite-
quartz-clinozoisite meta-wacke.

PPL

Long axis of photograph measures 0.84 mm
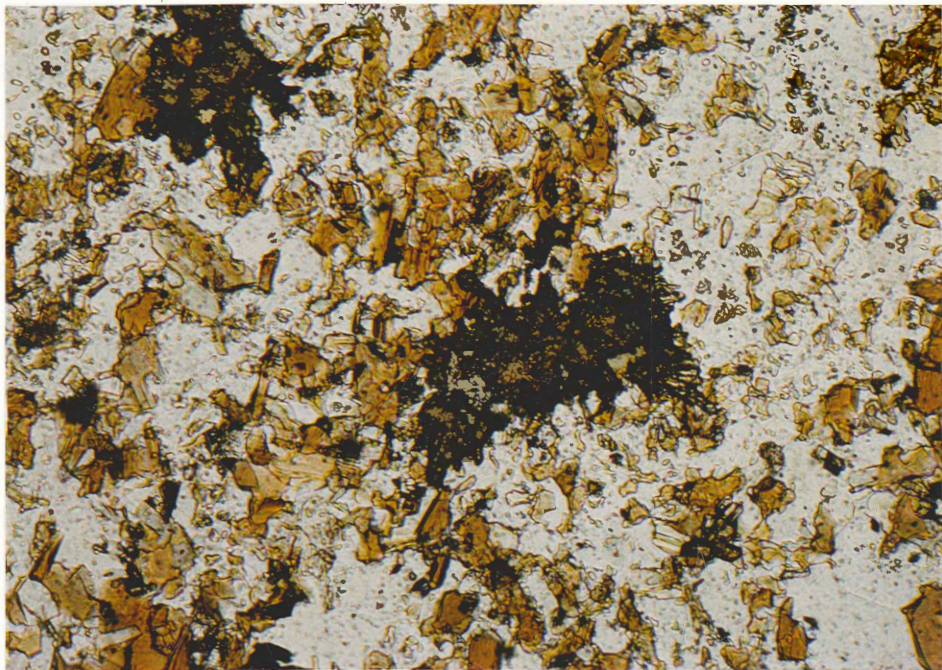
crystal edges and microfractures.

In one thin section crystal aggregates occur in a layered graphitic, micaceous calcite-sulphide 'patch' (Fig. 3.28a). The other thin section hosts cassiterite crystals in a linear distribution (boundary layer?) between two calcareous siltstone layers. This type of cassiterite comprises about 1 modal percent of the thin section.

The accompanying sulphides include up to 10 modal percent of pyrrhotite, plus rare pyrite, chalcopyrite and arsenopyrite. They occur throughout the sections and have curved to embayed boundaries (Fig. 3.28b).

3.4.4 Vein Association in the Metasediments

Three habits of cassiterite are displayed within and adjacent to the veinlets of quartz-carbonate-sulphides(pyrite, pyrrhotite, chalcopyrite, ± galena, arsenopyrite, sphalerite). Most cassiterite in the study area is found with this association.

i.   Subhedral to anhedral equant crystals(square prisms) up to 1.0 mm in size occur either alone or adjacent to the sulphides in veinlets. They commonly have diffuse colour zonation, defined by a gradual colour change from dark brown in the core to colourless in the rim; few have

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Figure 3.28a   Aggregate of prismatic cassit-
                      erite in carbonaceous calcite-
                      rich layer(IW-068).

                      PPL

                      Long axis of photograph measures 3.23 mm

Figure 3.28b   Pyrrhotite intergrown with
                      cassiterite in IW-068. Darker
                      hued patches are remnants of
                      graphite coating.

                      Reflected light.

                      Long axis of photograph measures 0.54 mm
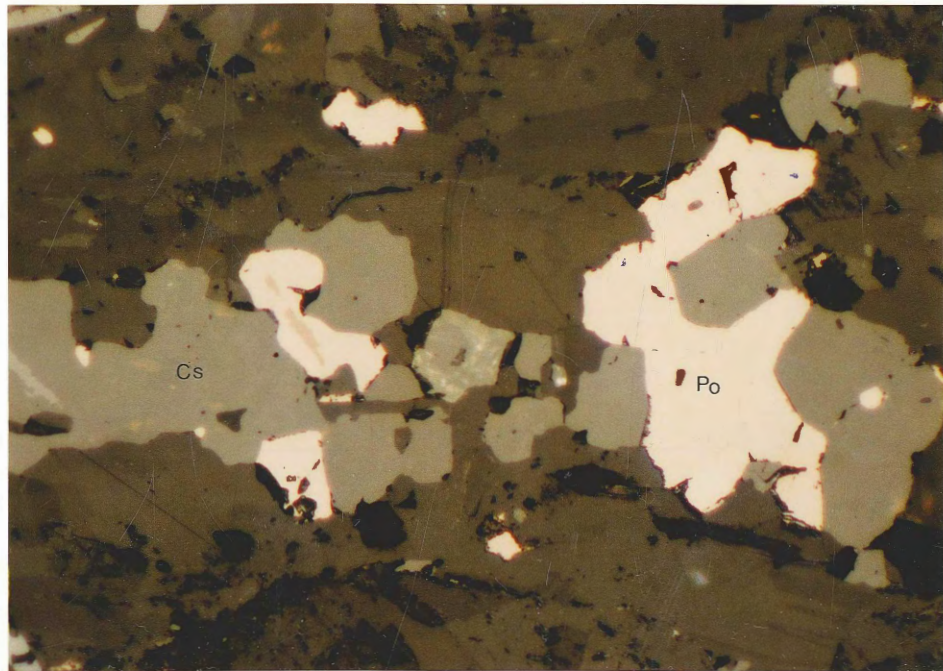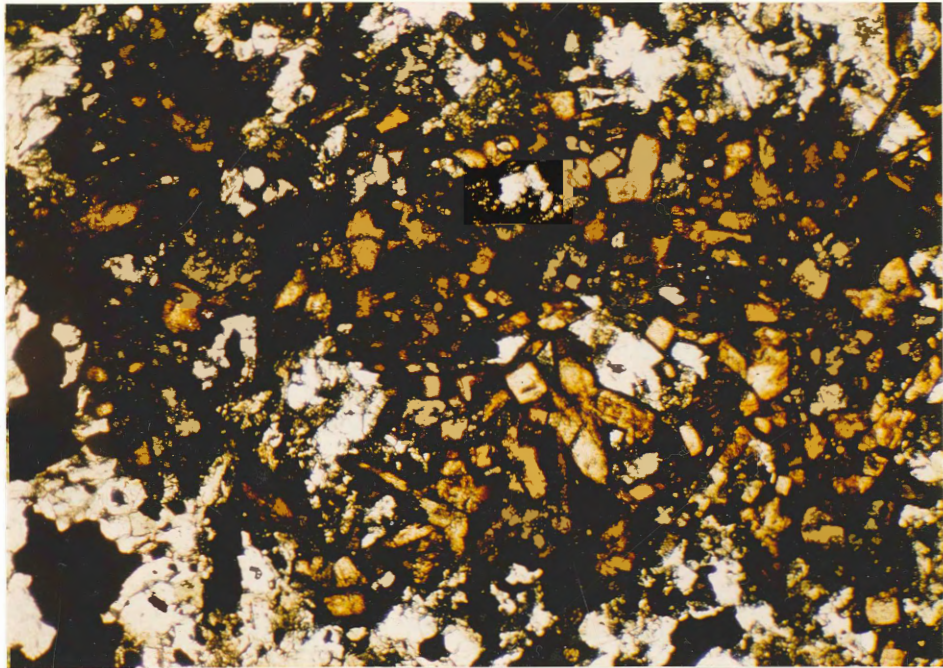
oscillatory zoning (Fig. 3.29). Dark to light brown variegated coloration also exists in other crystals.

ii. Pale to dark brown botryoidal cassiterite up to 0.25 mm in size is disseminated throughout the green chloritic halo surrounding the sulphide veinlets (Fig. 3.30). It is intergrown with chlorite, muscovite, ilmenite and zircon, and occasionally incorporates ilmenite.

iii. Radial clusters of orange brown to dark brown acicular cassiterite up to 1.25 mm in diameter occur in the veinlets adjacent to late stage carbonate (Fig. 3.31). They form whole or partial spherules and contain variable amounts of inclusions, notably ilmenite, with minor pyrite, pyrrhotite and chalcopyrite. Some form acicular druses on pyrite and pyrrhotite.

3.4.5 Greisen Association

Cassiterite rarely occurs in this association. It is found as light to dark brown, equant, sub- to anhedral crystals up to 0.25 mm in size. It is intergrown with quartz, white mica, fluorite, ± pyrite, pyrrhotite, chalcopyrite. One crystal occurs within a fluorite grain in a greisen zone (Fig. 3.32) and one is found within a greisen veinlet.

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Figure 3.29   Subhedral zoned vein cassiterite.

                     PPL

                     Long axis of photograph measures 0.84 mm

Figure 3.30   Botryoidal cassiterite in
                     chlorite alteration halo
                     adjacent sulphide-cassiterite
                     vein.

                     PPL

                     Long axis of photograph measures 0.39 mm
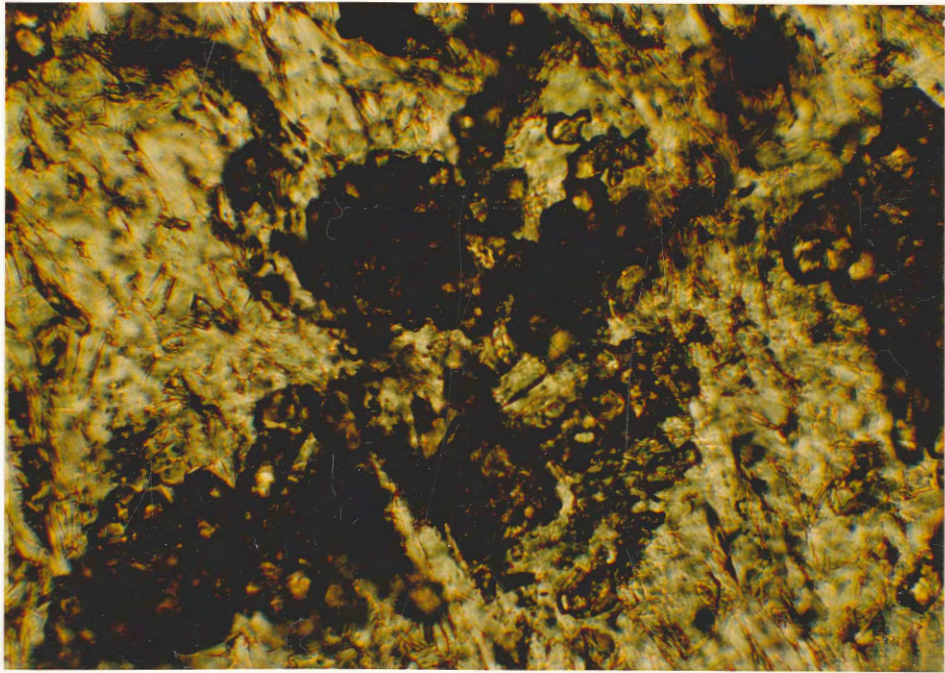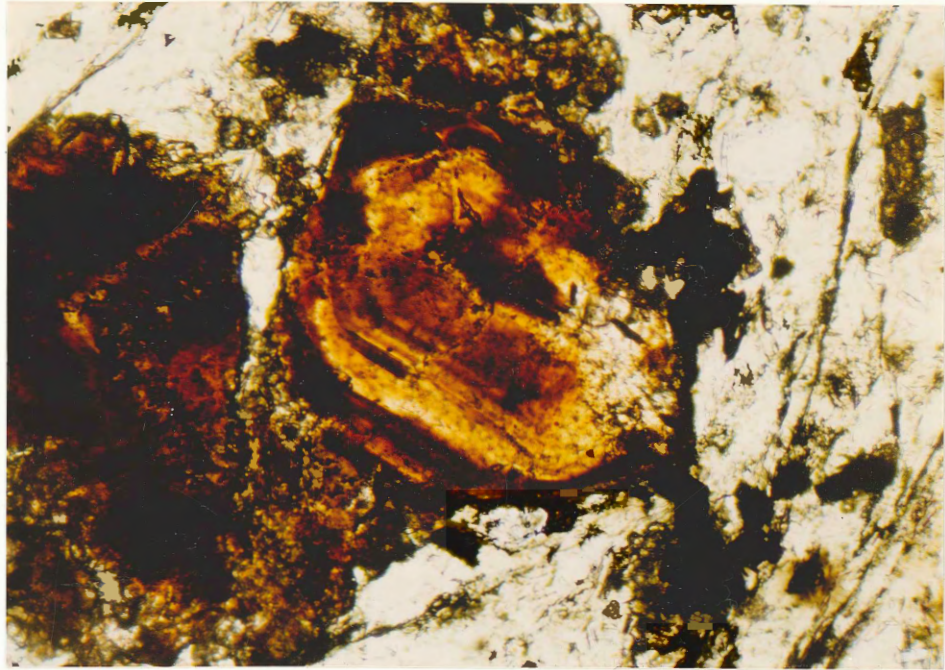
Figure 3.31a   Late stage spherulitic vein
                      cassiterite.

                      PPL

                      Long axis of photograph measures 2 mm

Figure 3.31b   Late stage acicular vein
                      cassiterite grown around
                      pyrite.

                      PPL

                      Long axis of photograph measures 0.84 mm
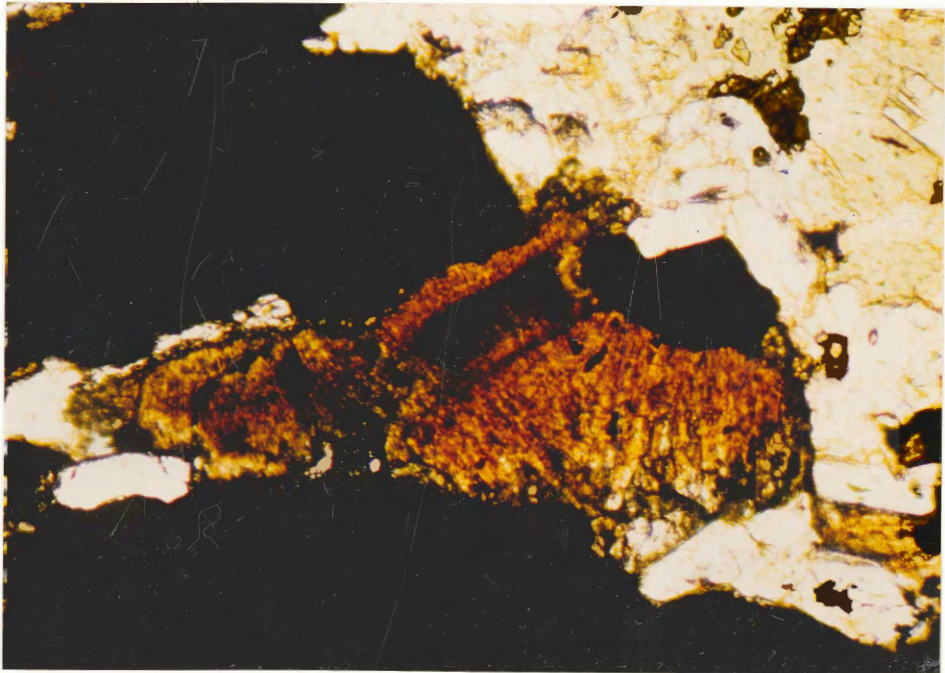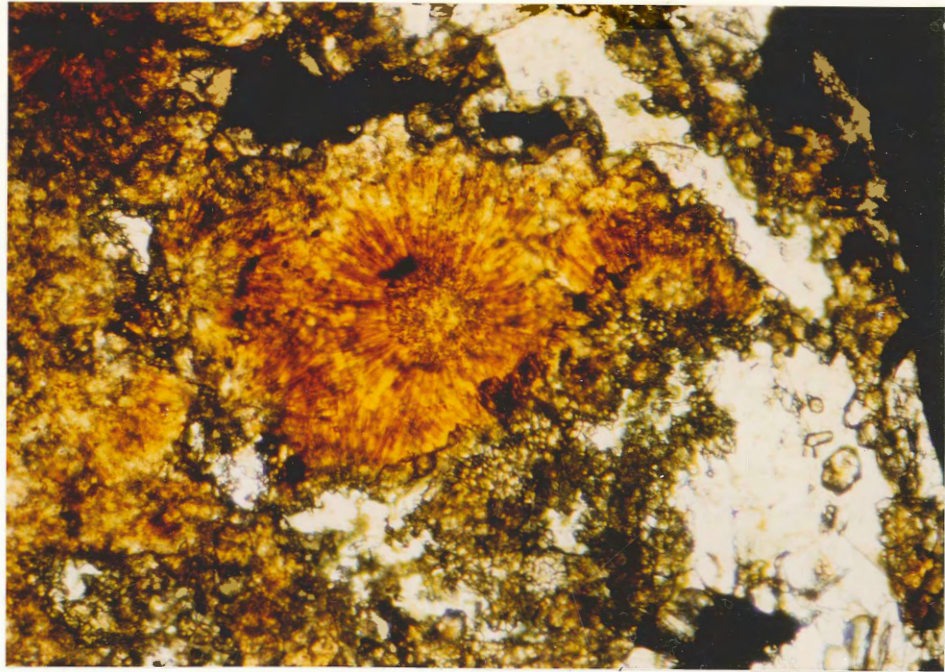
Figure 3.32   Subhedral cassiterite
                      associated with fluorite,
                      pyrite and chalcopyrite in
                      a quartz-white mica greisen.

                      PPL

                      Long axis of photograph measures 2 mm
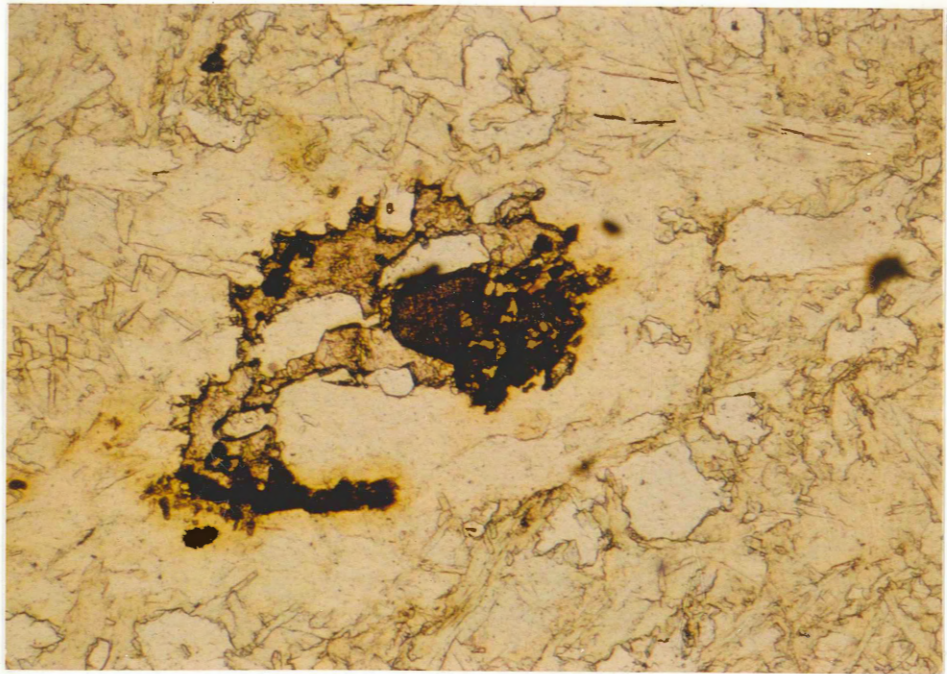
3.5 Cassiterite - Temperature of Formation

Studies of the formation of cassiterite have shown it to
form in the range of approximately $150°-600°C$ (Taylor,1979a;
Pan and Ypma,1974; Shneider,1937). The crystal forms of
cassiterite can be related to its temperature of formation
(Miyahisa,1968; Shneider,1937) and are not influenced by
trace element contents (although trace element substitution
of Sn^{4+} can change the cell volume; Taylor,1979a).

Cassiterite belongs to the tetragonal crystal system and
the ditetragonal dipyramidal class. It occurs in a variety
of forms, including combinations of prisms, with pyramids,
dipyramids without prisms, acicular fibers and botryoidal
grains ('wood tin') (Berry and Mason,1959; Taylor,1979a).

In any given deposit, cassiterite characteristically
occurs in more than one generation, and in more than one
habit, and this diversity serves to assign the minimum
relative temperatures of cassiterite formation (Taylor,1979a;
Hosking, 1979).

Shneider (1937) and Miyahisa (1968) have measured
cassiterite from different deposits and found that cell
parameters change with decreasing temperature. This change
is manifested by a change from more equant, dipyramidal
forms, to more prismatic, acicular forms (Table 3.3).

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Table 3.3 Cassiterite Crystal Habits and Related Temperatures of Formation

	Habit [1,2]	Temperature[1] and Environment[2] of Formation	Cell Parameters[2]		Habits in Study Area
			a	c	
	Obtusely bipyramidal or octahedral (short c axis) with a columnar bipyramidal subtype	> 600°C	–	–	Equant grains in stratiform association
	Tabular	> 500°C	–	–	?Subequant grains in stratiform sulphide association?
	"Isometric" (italics this author)	500°C High temperature type	4.736–4.739	3.187–3.190	
	Acutely bi- or monopyramidal	450°C Meso-xenothermal type	4.738–4.742	3.184–3.187	
	Columnar-prismatic (includes acicular)	< 450°C Bolivian volcanic type	4.738–4.741	3.186–3.190	Square prisms in stratiform calcareous sulphide association. Late stage spherulites in sulphide veins
	Botryoidal, colloform, globular, oolitic	= at least 150°C	–	–	Botryoids in chloritic haloes adjacent vein and in stratiform sulphide association

1. Shneider, 1937
2. Miyahisa, 1968

N.B. Shneider reports that at high temperatures, the c-axis is compressed and lengthens with decreasing temperature. This is roughly true, although data from Miyahisa show that a also increases. Data from Goncharov and Filatov (1972) roughly indicate an increase in both a and c axis lengths with depth (due to temperature or pressure?).

Botryoidal forms ('wood tin') occur in late stage, high
level, lower temperature deposits, and are believed to form
by rapid nucleation from highly saturated, possibly colloidal
solutions (Taylor,1979a; Hosking,1979; Lufkin,1977; Pan and
Ypma,1974; Lebedev,1967; Roedder,1968), flocculating in zones
of rapid chemical change, such as in wall rocks adjacent
veins (Doucet, quoted in Taylor,1979a).

3.6 Cassiterite - Genesis

The variety of cassiterite crystal habits appears to
reflect the temperature and environment of its formation.
There appear to be three main stages of genesis: detrital,
vein and replacement.

3.6.1 Detrital

The anhedral, equant grains which occur within the
pelitic layers have several features which serve to
characterize their detrital nature.

1. In the one sample (IW-056), aggregates of cassiterite
are restricted to the bottoms of two thin pelitic layers; one
layer is a possible scour infill (Fig. 3.26).

2. Many grains in this sample have sharp growth zoning
and several such grains have broken edges (Fig. 3.23). These
grains could not have grown and been broken in place. No
evidence of cataclasis exists, only slight fracturing of the
cassiterite with development of brown coloration along the
fractures.

One zoned grain has a rounded core (Fig. 3.24), a
possible nucleus around which subsequent layers grew. Such
zoning is indicative of relatively free growth into
fluid-filled spaces with slight changes in the
physico-chemical environment (Craig and Vaughan,1981;
Ramdohr,1980;). The equant habit is indicative of high
temperature formation, which could not have occurred under
conditions of low grade greenschist facies metamorphism.

3. The cassiterite grains are not associated with any
sulphides usually found in the stratiform sulphide

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association; there is no evidence of alteration of surrounding host minerals as in all the other associations. There is a slight wrapping of phyllosilicates around the cassiterite, suggesting the grains had existed before or during regional metamorphism (Spry,1969).

This type of cassiterite does not appear to have formed in place; rather it originated in a high-temperature open space (a vein?). Subsequent uplift and erosion liberated the grains and they were transported to a basin. Harris and Schenk (1975) have suggested that the sediments of the Meguma Group were derived from a deeply eroded, cratonic terrain, later sorted on a continental shelf and alluvial plain, and then transported by turbidity currents down submarine channels. It is therefore possible that the cassiterite, eroded from the above terrain could have been winnowed on the continental shelf, transported and then deposited in or along these channels, in scours or on the abyssal plain.

There is no cassiterite in the only other scour infill (Fig. 3.17). This may be because of the scarcity of cassiterite in the first place; finding detrital cassiterite in any concentration would therefore be fortuitous, even in scours. A less likely explanation for the paucity of detrital cassiterite would be its dissolution by intrastratal solution in the more permeable wackes during diagenesis (Blatt and Sutherland,1969; Blatt et al.,1980). Although

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detrital cassiterite grains do have ragged edges (Fig. 3.25), the associated ilmenite and zircon (which theoretically should be corroded) do not.

It is beyond the scope of the present study to do more than speculate on the possible origins of detrital cassiterite. Schenk (1975) and Harris and Schenk (1975) have suggested that the source continent consisted of metasedimentary or meta-igneous material of Precambrian age, possibly the present Saharan Shield in northwestern Africa or even a Precambrian shield in northwestern South America. Although stratiform copper, manganese, lead, zinc and uranium mineralization occur in clastic and chemical sedimentary rocks of the 'Infracambrian superieur' of Morroco, no Precambrian tin occurrences have been documented by Michard (1976). Minor tin mineralization in quartz veins occurs in the Morrocan Hercynian Oulmés granite of El Karit in the Meseta with aplites, pegmatites and rare lamprophyres. Minor tin is associated with quartz veins and pegmatites of the Precambrian metamorphic shield of northeastern South America in Brazil; Lower Paleozoic tin deposits are documented in northwestern South America in Bolivia (Taylor,1979a). These tin occurrences may have either been too young to have been the source of the Meguma detrital cassiterite, or may have been too far removed spatially at the time of erosion (Strong,1980; Harris and Schenk,1975), although other resistant minerals such as diamonds have been known to travel

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by fluvial and marine processes hundreds of kilometers from
their primary source (Sutherland, 1982).

3.6.2 Main Stage Vein Genesis

The transportation and deposition of tin in vein systems
have been subject to much study and experimentation (e.g.
Smith, 1947; Shcherba,1970; Cuff in Taylor,1979a) and the
reader is referred to these authors for further details.

Because of the amphoteric nature of stannic oxide
(Smith, 1947), it is soluble as both alkali stannates and tin
halides and may therefore be transported in, and crystallized
from both alkaline and acid aqueous solutions. It is
tentatively suggested that both types of solutions played
roles in the transportation of tin in veins in both the
pluton and the metasediments.

Tin can form a variety of complexes in aqueous
solutions; those commonly described in the literature are
presented here.

Acid aqueous solutions - tin soluble as simple ions(Sn^{4+})
                    (Smith,1947).
                - chloride, fluoride and hydroxide
                  complexes of divalent tin under
                  conditions of acid pH(<7) and low oxygen
                  fugacity(< qtz-feld-musc buffer)
                  (Taylor,1979a; Patterson et al.,1981).

Alkaline aqueous solutions - if a high concentration of sulphide
                              ions exist, tin is soluble as an alkali
                              stannic sulphide complex(SnS_4^{4-})
                              (Smith,1947).
                            -alkali complexes of tetravalent tin,
                              such as $Na_2(Sn(OH)_6)$,
                              $Na_2(Sn(F)_6)$ and
                              $Na_2(Sn(OH,F)_6)$ in neutral to
                              alkaline solutions (Taylor,1979a).
                            -hydroxy-fluorostannate(Sn^{4+})
                              complexes of the type
                              $(Na,K)_2[Sn(OH)_x F_{6-x}]$ at
                              pH 6-11.75 (Taylor,1979a)

Changes in the ambient physico-chemical conditions (e.g.
P, T, pH, fO_2) lead to the destruction of the complex and
deposition of tin as cassiterite, either directly or as a
hydroxide, $Sn(OH)_4$ which then dehydrates to SnO_2.

A possible model for the transportation and deposition
of tin in the study area is presented.

3.6.2.1 Greisen Veins

According to Shcherba (1970), greisenization involves
the high temperature (300°-500°C) alteration of rocks by acid
aqueous ($\pm$ vapour) solutions, the residual fluids of a
crystallizing granitic intrusion. These fluids are rich in
water, silica and such volatiles as F, Cl, S, and C; the
concentration of F being much lower than that of H_2O, CO_2 and
Cl (Bailey,1977). They also contain Al, K, Na and Ca. Metals
which commonly occur in these fluids are: Sn, Li, W, Mo, B,

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Fe, Mg, Cu, Pb, Zn and As, and are transported as halogen
complexes.   Salinities, measured in fluid inclusions from
greisen deposits range up to about 10 wt. % NaCl equivalent
(Charoy and Weisbrod,1974; Kelley and Rye,1979;
Taylor,1979a).

Plutonic feldspars and micas are destroyed by these
fluids and replaced by variable amounts of muscovite,
fluorite, topaz, tourmaline, feldspar, cassiterite,
wolframite and sulphides (e.g. chalcopyrite, pyrite and
molybdenite).   Table 3.4 presents some of the major mineral
and element changes which occur during greisenization.

Prior to greisenization, alteration of primary magmatic
feldspars to secondary albite or microcline or both is
reported to occur (Shcherba,1970; Taylor,1979a). Microscopic
examination and microprobe analysis of the feldspars both
adjacent to greisens and in optically unaltered monzogranite
show the plagioclase to vary in composition from
oligoclase-andesine to albite, although there appears to be
no pattern to their flucuating An content.   Taylor (1979a)
cites from the literature several causes for this diverse
feldspar composition:

1. Removal of anorthite component from primary
   plagioclase.   by alkaline
                                                         solutions
2. Addition of Na_2O and removal of   (from residual
   K_2O from potassium feldspar.   fluids?)

3. Albite already primary magmatic.

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Table 3.4   Major Mineral and Element Changes During Greisenization

$(K_2O \cdot Al_2O_3 \cdot 6SiO_2) + 2Al_2O_3 + 4(F,OH) \longrightarrow [K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 4(F,OH)]$

   K - feldspar   Muscovite

$[CaO \cdot Al_2O_3 \cdot Si_2O_8] + 2HF \longrightarrow [CaF_2] + Al_2O_3 + 2SiO_2$

   An component of plag   Fluorite

$[K_2O \cdot 6(Mg,Fe)O \cdot Al_2O_3 \cdot 6SiO_2 \cdot 4(OH,F)] + 2Al_2O_3 \longrightarrow [K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 4(OH,F)] + 6(Mg,Fe)$
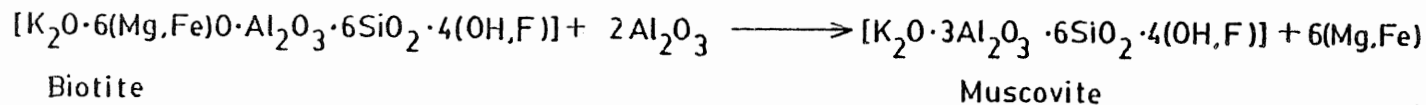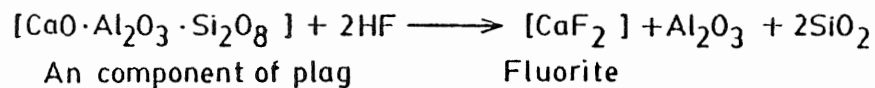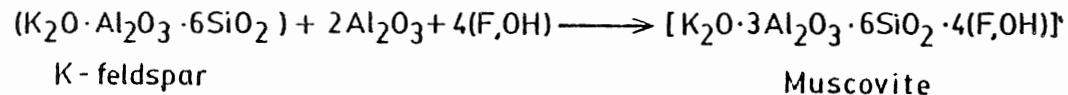
   Biotite   Muscovite

Biotite $\longrightarrow$ Chlorite + Magnetite $\longrightarrow$ Muscovite + Pyrite

Ilmenite $\longrightarrow$ Rutile + Pyrite

Elements brought to greisen zone - Sn W Li Mo Be Cu Pb Zn As Bi REE's Ta Nb P Th Zr
                                     - Si F Cl B H_2O S CO_2

Elements removed from wallrock - Ca Mg Al(in part) Na

Elements redistributed   - K Al Fe Ti

From Mulligan, 1975; Shcherba, 1970

According to these authors, feldspar alteration can be both pervasive and locallized, of irregular geometry, and may occur repeatedly, before and after greisenization, as the physico-chemical conditions of the fluid changes with time and location within the pluton. Shcherba (1970) explains that microclinization occurs by conversion of orthoclase to K-anorthoclase to twinned microcline, but not how it happens (possible conversion of monoclinic potassium feldspar to a lower temperature triclinic system during final stages of cooling of the pluton?). J. Logothetis (pers. comm., 1983) suggests that readjustments in major element contents by greisenizing solutions may cause albitization and microclinization. The only unequivocal optical evidence of alteration of the feldspars in the Wedgeport monzogranite is observed in the greisen zones and this is deemed to be caused by the greisenization episode and not by a prior 'alkaline stage feldspathization' episode described by Shcherba (1970). Localized alteration occurs adjacent later shears, mafic dykes and along weathered fractures.

Fresh unaltered monzogranite consists of quartz, slightly sericitized plagioclase and microcline, with accessory biotite containing inclusions of apatite, zircon and ilmenite (Fig. 3.33). In the early stages of greisenization, biotite flakes alter to chlorite($\pm$ vermiculite?; possibly $\pm$ potassium feldspar $\pm$ epidote? (J.

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Logothetis, pers. comm.,1983)) and magnetite (+ iron hydroxide?) aggregates, appearing rusty brown or tan in hand specimen. This is the indicator material of the 'tan alteration zone'. Ilmenite alters to anatase; apatite and zircon appear unaffected. Microcline shows slightly greater sericitization and begins to take on a turbid appearance due to a myriad of extremely fine (<0.001 mm) inclusions. Plagioclase is more sericitized, with larger white mica flakes and contains calcite, usually in the crystal cores. Fluorite rarely occurs in this zone.

As greisenization continues, the chlorite breaks down into a light rust-brown hydrous phyllosilicate (vermiculite with iron hydroxide staining?; Craw,1981; Kodama et al.,1982; or epidote grains with subsequent alteration to carbonate?; J. Logothetis, pers. comm.,1983). Plagioclase continues to alter to white mica (possibly lithium-bearing) and carbonate, while microcline becomes more turbid with diffuse grid-iron twinning. The hand specimen now appears a homogeneous milky white ('white alteration zone') with pinkish-grey quartz blebs. Minor fluorite and sulphides may occur in this zone.

In the greisen proper, both feldspars are destroyed, as is the vermiculite(?), possibly due to its instability at temperatures over 300°C (Deer et al.,1974). The zone consists primarily of white mica and quartz, with common to abundant fluorite, rare cassiterite and sulphides.

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Figure 3.33   Progression of alteration in
greisenized monzogranite.
Sample 79-08-70.70
All PPL; long axis of first
two photographs measures
3.23 mm; last one measures 4.9 mm.

A. Unaltered zone; biotite flakes
are clear and include apatite,
zircon and ilmenite. The
surrounding feldspars are
slightly sericitized.

B. 'Tan alteration zone'; biotite
flake has altered to a chlorite-
vermiculite(?) aggregate contain-
ing iron and titanium oxides
(ilmenite to anatase). Microcline
becomes turbid; plagioclase remains
clear.

C. 'White alteration zone'; biotite
flakes completely alter to oxide
and vermiculite(?) assemblages.
Microcline becomes more turbid;
grain boundaries become diffuse.
Plagioclase remains clear but
becomes sericitized.

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A

B

C

Ser

K-Spar

Plag
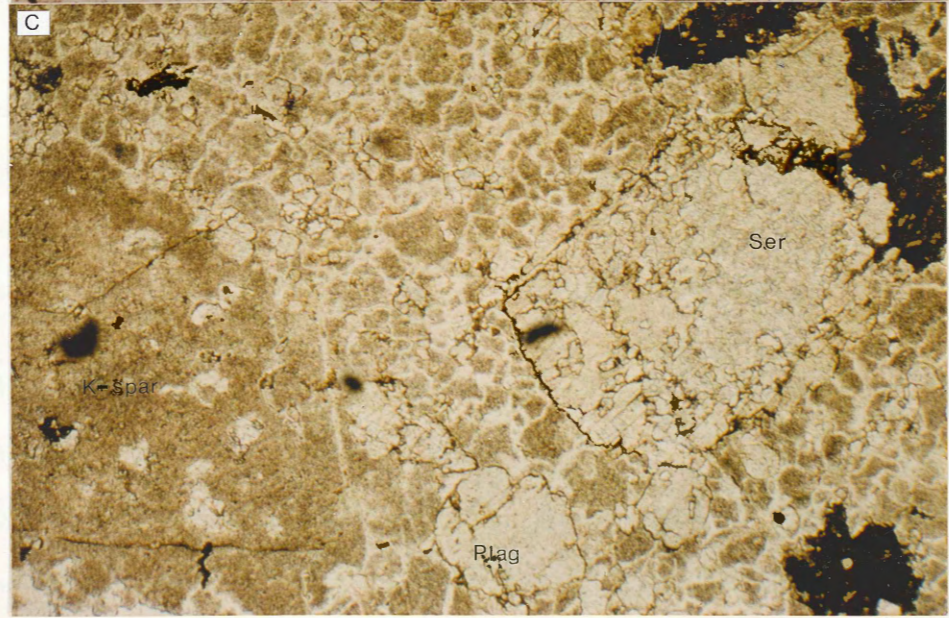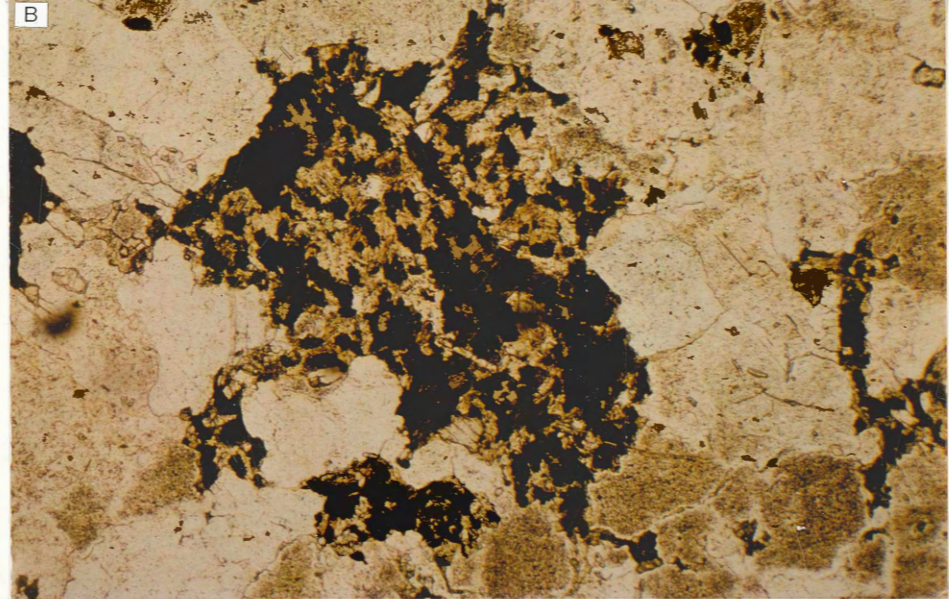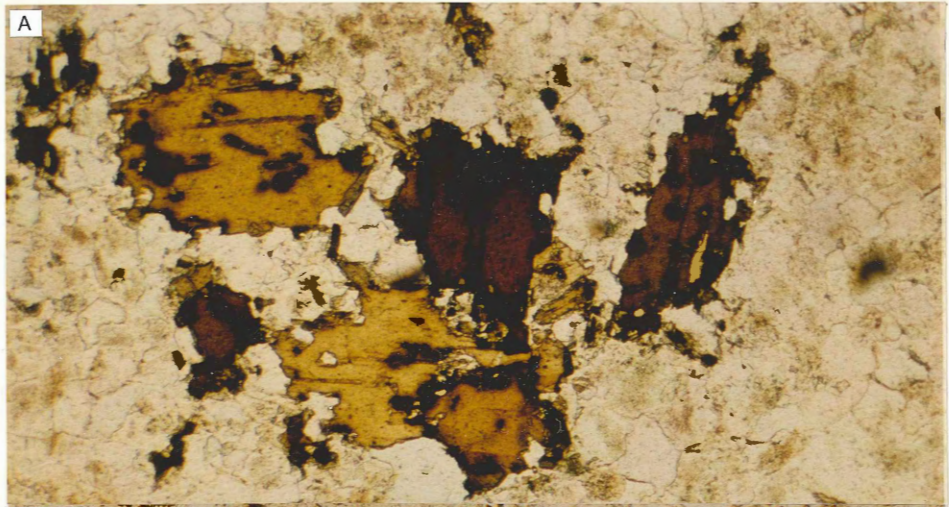
Greisenization begins with acid leaching of the granitic wallrock. The acid fluids may either be 'primary' residual solutions of a crystallizing granitic intrusion or may result from the breakdown of alkaline fluids: a rapid decrease in P or T or both destroys complexes, thereby freeing halogens and causing the pH to decrease (Shcherba,1970). These acid fluids break down the feldspars and biotite, adding and removing various constituents. Fluorine tends to react with calcium released from destroyed plagioclase, forming fluorite; F may also substitute for OH in the white micas of a greisen. Removal of F from the fluid destroys whatever complexes it held with tin and the tin may either precipitate as cassiterite or recombine to form other complexes. The close association of cassiterite and sulphides with fluorite (Fig. 3.32) suggests that fluorine probably aided in metal transport. Evidence for transport of tin by other complexes, such as chlorides or hydroxides, is more difficult to ascertain because such elements form few independent minerals, and are instead incorporated in other minerals or in fluid inclusions. The subhedral equant habit of cassiterite suggests it precipitated at a relatively high temperature ($\geq 450^{\circ}C$?) (Shneider,1937).

Removal of F also decreases the activity of the fluids, and this, in combination with the addition of alkali metals from the leached silicates, causes the fluids to become more alkaline (Shcherba,1970; Tischendorf,1973).

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The paucity of cassiterite within the greisens of the study area suggests either a low initial concentration of tin in the residual fluids, or the persistance of tin in solution by complexing with alkali metals ($\pm$ sulphide ions) introduced by greisenization. The greisen zones in the pluton are rather narrow (on the order of cm) and usually in sharp contact with fresh or incompletely altered monzogranite. This implies relatively rapid equilibration (neutralization) of acid fluids with the wallrock, removing large amounts of alkalies from the silicate minerals. As tin-halogen complexes break down and the halogens are incorporated in the greisen minerals (fluorite, white micas), tin may be able to form complexes with the now abundant alkali metals and remain in solution (now alkaline) instead of precipitating as cassiterite. It may also be possible that other halogen complexes would be more stable under these changing conditions (chloride complexes) and keep tin in solution (Patterson et al.,1981).

3.6.2.2 Metasediment Veins

These alkaline fluids may enter the metasediments via fracture systems and react with the wallrock. Metals may be carried in such alkali complexes as:

$(K,Na)_K[Metal_M(CO3)_N(OH,F,Cl)_P]$ or $(K,Na)_K[Metal(F,Cl)_N]$

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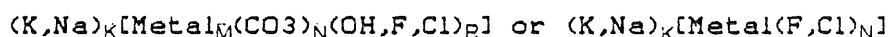
(Shcherba,1970), and, if enough sulphide ions are available, as alkali-metal-sulphide complexes (Smith,1947; Stanton,1972a; Barnes,1979). Shcherba (1970) and others believe that since Cl is more mobile than F, it is able to travel beyond the greisen in solution and is therefore the more important carrier of tin in complexes; F tends to be readily fixed within the greisen zones as F-bearing minerals. Geochemical analyses seem to bear this out: greisen vein samples in the pluton show enrichment of F relative to unmineralized monzogranite, while those of sulphide-cassiterite veins in the metasediments show F concentrations at or near background levels. Chlorine analyses were unusable as all values were below the detection limit of 50 ppm.

Changes in the physico-chemical conditions (e.g. decrease in P, T and pH, dilution of fluids, increase in the fugacity of oxygen) can result in destruction of the complexes and precipitation of metals and gangue minerals (Barnes,1979). Deposition of metal sulphides(in this case mainly pyrrhotite, pyrite and chalcopyrite) decreases the sulphide ion content of the alkali-thio-metal complex, leading to precipitation of tin as cassiterite with the sulphides. The subhedral, equant habit of this type of cassiterite may indicate a relatively high temperature of formation ($\geq 450^{\circ}$C??) (Shneider, 1937). Fluid inclusion studies, however, point to lower formation temperatures ($\sim 350^{\circ}$

C) of cassiterite-sulphide veins (Jackson et al.,1979).

Carbonate and later acicular cassiterite overgrow the

previous minerals as the fluid cools and complexes continue

to break down - the acicular habit indicates a lower

formation temperature ($<450°C$) (Shneider,1937). Quartz, minor

accessory white mica and chlorite form within the vein;

iron-rich chlorite and botryoidal cassiterite surround the

vein, forming a thin alteration halo, again implying rapid

equilibration of the fluids. Formation of the

phyllosilicates and quartz accounts for most of the other

constituents of the fluid; Na may enter feldspars in the

country rock, or remain in solution with Cl and other

material in fluid inclusions. Botryoidal cassiterite is

considered a late-stage, low-temperature (at least $150°C$;

Shneider, 1937) tin oxide, formed by rapid nucleation of

saturated solutions (Taylor,1979a).

The relationship of these fluids with cassiterite-absent

veins is not known. They exist farther from the pluton and

at shallower depths than the tin-bearing veins. They may be

extensions of the same vein system; fluids are depleted in

tin, but still contain such metals as Cu, Pb, and Zn in

complexes whose solubility products are exceeded at lower

pressures and temperatures.

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3.6.3 Stratiform Mineralization

A major problem in dealing with stratiform mineralization is the mode of its formation. Two schools of thought exist on this issue: this type of mineralization forms as a result of syngenetic or diagenetic processes; or, it forms as a result of epigenetic processes, in this case by replacement. This section will deal with these two genetic models in terms of formation of the stratiform zones.

To determine the possible origin of these 'patches', a number of questions must be answered, namely:

1. What was the original habit of tin and how was it mobilized?

2. Where is tin deposited (unconsolidated sediments, sediment-seawater interface, consolidated sediments)?

3. Under what conditions is tin deposited and does this process noticeably affect the surrounding host?

4. If the tin is indeed an early precipitate (i.e., synsedimentary or diagenetic) will it and its associated host rock be affected by subsequent metamorphic events?

An attempt will be made to qualitatively answer these questions for each genetic interpretation.

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3.6.3.1 Synsedimentary / Diagenetic Origin

In this model, tin is somehow mobilized from
pre-existing sediments, transported in a hydrothermal fluid
with other metals and ionic complexes, and deposited in
higher level unconsolidated sediments or onto the seafloor.

The most common form of tin within these sediments is
detrital cassiterite; it is possible that tin ions or their
complexes were adsorbed to clastics or organics, or had
formed organo-metallic complexes (Saxby,1976).

Mobilization of tin may prove difficult. If it is
adsorbed onto particles or forms organo-metallic complexes,
compaction and resultant dewatering of the fluid-rich
turbidites may be sufficient to strip the tin from its
substrate. Cassiterite is harder to deal with as it is
considered a stable resistate. However, another such
resistant mineral, zircon can be dissolved by intrastratal
solution (Blatt and Sutherland,1969). This may have occurred
with cassiterite, but evidence for this is poor - only one
sample contains detrital cassiterite, and it occurs within a
pelitic layer (detritus in less permeable shales may not be
subject to this process; Blatt and Sutherland,1969). The
cassiterite is subrounded with irregular edges and this may
be more due to abrasion during transport, rather than
solution by pore water. Zircon is found throughout the
metasediments and exhibits no demonstrable corroded edges,
even within coarser (and thus more permeable) psammitic

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layers. Mobilization of tin by dissolution is therefore not considered likely.

If, for the sake of argument, corrosion did take place, what conditions are necessary for this process? Most studies (see Cuff, in Taylor,1979a) deal with formation of cassiterite at high temperatures (> 250°C) and under various chemical conditions. Diagenesis is thought to take place at temperatures ranging from several degrees below 0°C to about 250-300°C (Hanor,1979). Smith (1947) determined that cassiterite was stable in, and crystallized from, sodium stannate(IV) solutions from room temperature up to at least 450°C. Barsukov and Kuril'chikova (quoted in Taylor,1979a) reported that tin can be transported as hydroxy-fluorostannate complexes in the temperature range of 25-400°C and pH range of 6-11.75. Patterson et al. (1981) calculated from thermodynamic data, dissociation equilibrium constants of divalent tin complexes of Cl, OH and F, at temperatures from 25° to 350°C. Tin concentrations in solutions containing such complexes would be small at low temperatures (< 10 ppm).

If cassiterite can precipitate from low-temperature solutions, it may be possible to dissolve cassiterite by such fluids. According to the above authors, tin is soluble in a variety of pH's (because of its amphoteric nature); at neutral pH, cassiterite is insoluble.

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Can sedimentary formation water dissolve cassiterite?
Various authors (e.g., Blatt et al.,1980; Mookerjee,1981;
Pettijohn et al.,1972; Hanor,1979; Bischoff et al.,1981) have
listed the diverse physico-chemical characteristics of
hydrothermal brines derived by sediment diagenesis and the
reader is referred to their works. Generally, pore water
chemistry changes in response to mineral-ion-fluid reactions
during diagenesis. Clay layers within shale units can act as
semi- permeable membranes and, driven by pressure
differentials with depth, can effectively 'salt sieve',
leaving certain ions behind in the pore fluid. Increase in
salinity is attributed to this process. Reaction of clay and
feldspar minerals to chlorite and calcite to dolomite
depletes pore fluid of magnesium and increases H^+ ion
concentrations for further reaction with host sediments.
Potassium, calcium, silica, CO_2 and metal concentrations
within interstitial water increase by dissolution of various
mineral species. The chlorinity of sandstone porewater
increases; shale pore water is dominated by HCO_3 and SO_4 ions
(Hanor,1979). Chlorine concentrations range up to 7.61 molal
with a median of 2.48 molal (compare to modern seawater of
0.535 molal Cl;Blatt et al.,1980). Seawater sulphate is
reduced to bisulphide ions by bacterial action.

Compaction of shales at shallow depths (0 to 100 m)
results in the expulsion of 75 percent of their pore water;
sandstone requires burial to about 3 km before this amount of

fluid is expelled. This compaction would displace shallower waters out of the basin and not produce hot saline brines (Hanor,1979). It is necessary for the fluid to remain at depth to heat up and react with coexisting sediments to form a brine capable of mobilizing and transporting metals. Large amounts of fluid within rapidly deposited turbidites may be trapped by overlying shale units of low permeability. As subsequent layers are deposited, the increased weight causes deeper fluids to be overpressured. Growth or block faulting provides a means of rapid egress (Morganti,1981); fluids may also migrate through more permeable strata laterally to a fault zone or angular unconformity (Cathles,1981).

Studies by Bischoff and others (1981) indicate hot brines (200°-350°C; 500 bars) are capable of leaching metals from greywackes with little change in bulk rock composition. Long and Angino (1982) found that low temperature (25°-90°C), low pressure (<400 atm) fluids are capable of leaching metals from shales. In both studies, increase of temperature or ionic strength of the fluid, or both effectively increases the leaching capability of the fluids. At low temperatures (25°C) tin is more chemically active than iron in a system with iron in excess (Krauskopf,1979) and so it is possible cassiterite may be leached in addition to iron and other base metals during reaction with low temperature brines.

The brines move rapidly up the fault conduits and cool;

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they may mix with shallower formation waters or may even
reach the sediment-seafloor interface before minerals
precipitate. In the study by Bischoff and others (1981),
metal-Cl complexes within high temperature brines (350°C)
dissociate below 200°C, at which temperature metal sulphides
precipitate and reaction of K-rich brines with sediment
produces extensive potassic or sericitic alteration. Lower
temperature, lower salinity fluids cause the same effects,
but at a lesser magnitude; at temperatures less than 200°C,
few sulphides coexist with metals unless the fluid has a low
pH (<7) (White,1981). Gross solution chemistry of brines
after reaction with greywacke samples appears similar to that
of hot submarine springs, namely hot acidic saline fluids
enriched in Ca, K, H_2S and metals (including tin) and
depleted in Mg and sulphate (Edmond,1982).

Stratabound tin deposits have been documented throughout
the world (e.g., Mulligan,1975; Lehmann and Schneider,1981),
but are usually associated with volcanic lithologies: e.g.,
Precambrian cassiterite-bearing Pressnitz Series of the
Erzgebirge and equivalent beds in the Izera Mountains in
Czechoslovakia and Poland; the polymetallic massive sulphide
deposits of Canada, including Kidd Creek and Brunswick Mining
with byproduct cassiterite and stannite; and possibly the
sedimentary complex of the Belitung district of Indonesia.
Hutchinson (1979,1980,1982) suggested that the Tasmanian
stratabound, stratiform tin deposits are of exhalative

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origin, one of the reasons being the close association of ore within submarine mafic volcanics. This idea has been disputed by Solomon (1980) and Patterson (1981,1982), who believe these deposits are of replacement type. Plimer (1980) describes a 'typical' stratiform submarine exhalative tin deposit as consisting of extremely fine cassiterite (<0.001 mm) associated with pyrrhotite ± carbonate or quartz-tourmaline rocks within a thick deep water sequence of pelites, carbonates, calc-silicates, cherts and mafic volcanics. Thermal energy, supplied by the volcanics, was sufficient for fluid circulation and associated leaching of tin from the sediments; cassiterite and other metals were deposited at the sediment-seawater interface. Below this deposit is a zone of K enrichment and Na depletion, whereas Mn is enriched in the sediments surrounding the deposit, all due to fluid-sediment interaction.

Stratiform tin-bearing deposits not associated with volcanic lithologies are less common, or are not recognized as such. The Sullivan Mine of British Columbia is a polymetallic base metal sulphide deposit within argillaceous meta-siltstones and quartzites. Cassiterite occurs near the outer edge of the orebody's pyrrhotite core. Mineralization occurred at the sediment-seawater interface, where hydrothermal brines were expelled from feeder conduits. Continued activity caused tourmalinization of footwall rocks and albitization of hanging wall rocks; the feeder zone

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itself suffered chloritic alteration.

Subsequent low grade regional metamorphism may readjust mineral assemblages in several ways in addition to general coarsening of grains and formation of 'typical' metamorphic mineral suites; this has been described in detail by Mookherjee (1981). The isograd of pyrite to pyrrhotite and sulphur is found within the chlorite zone of the greenschist facies; if the released sulphur cannot escape, sulphide-sulphide, sulphide- silicate, sulphide-carbonate or sulphide-oxide reactions may take place, forming new minerals. Softer minerals may flow into cracks and fractures. Metals within carbonaceous material may migrate into iron sulphide grains. Movement of material (except CO_2 and H_2O) across lithological boundaries is restricted to the higher metamorphic grades. Cassiterite is not affected by low grade metamorphism (Plimer,1980). Non-sulphide metal-bearing zones may be transformed into layers containing distinctive mineral species, e.g., Mn-carbonate-bearing layers metamorphosed to layers containing Mn-garnet.

This discussion is made in an attempt to show that tin may be of a syngenetic or diagenetic origin. However, applying this model to the mineralized zones in the study area meets with a number of difficulties:

1. Scarcity of cassiterite (only one sample obtained) exhi- biting unequivocal solution textures, plus no evidence of

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solution of other minerals in supposedly once permeable
psammitic layers. As cassiterite is believed to be the
major tin-bearing mineral, it does not appear likely tin
was mobilized in the first place.

2. No clearcut alteration zones attributable to this model
except for the layered Mn garnet. Other restricted
alteration zones can be attributed to metamorphism,
later veining and shearing.

3. Proximity of these mineralized 'patches' to a fold hinge,
which acts as a locus for structural weakness and can
therefore act as a conduit for epigenetic fluids.
Similar favourable layers(containing carbonate, calc-
silicate nodules) far from this hinge(100's of m) do
not show this type of mineralization, implying its
structural control. Limited study of this area does
not show any evidence of diagenetic growth or block
faulting.

4. Proximity of these mineralized zones to an intrusion
containing tin-bearing greisens and which produced the
tin-sulphide veins in the adjacent metasediments;
arguments have been made(Plimer,1980; Hutchinson,1979,
1980,1982) to the effect that existence of a granitic
body does not preclude a prior synsedimentary origin.

5. No volcanics within the sedimentary sequence which would

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have added thermal energy to drive the hydrothermal brine system. Evolution of a sedimentary basin with no additional heat source may not have been enough to provide the necessary temperatures($>200^{\circ}$C) for metal mobilization and transport (White,1981).

6. Existence of a chloritic alteration halo adjacent a mineralized zone in which chlorite and white mica needles crosscut pre-existent foliation, therefore implying a post-metamorphic event.

7. Sulphide replacement textures can be explained just as easily by an influx of ore fluids from the pluton, replacing pre-existent minerals. One does not have to resort to desulphurization of pyrite to produce sulphide minerals from gangue. Individual pyrrhotite blebs in the study area have been elongated, but do not show vein forms or replacement textures. Other 'shredded-textures' in the sulphides are attributed to late shearing of sulphides within ductile phyllosilicate layers.

3.6.3.2 Epigenetic Origin

In contrast to a syngenetic origin, these mineralized layers may form by reaction of magma-derived, ore-bearing fluids with chemically reactive host rocks. Tin may precipitate directly from the solutions as cassiterite, or form the oxide as a consequence of destruction of earlier

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tin-bearing calc-silicate minerals.

Skarn formation has been recently described by Einaudi and others (1981) and Rose and Burt (1979) and the reader is referred to these works for further information. Detailed description and interpretation of tin-bearing skarns have only been published in the past few decades (e.g.,Patterson and Solomon,1981; Lehmann and Schneider,1981; Dobson,1982; Nekrasov, 1971; Shcherba,1970; El Sharkawi and Dearmann,1966). The findings of these authors will be used to discuss the formation of tin-bearing skarns in relation to the stratiform mineralization of the study area.

According to Einaudi and others (1981), there are three main stages in the genesis of a skarn deposit:

1. Isochemical contact metamorphism in response to magma intrusion. Groundwater is expelled, local reaction skarns occur and a widespread (km scale) zoned thermal aureole (hornfels) is formed in the surrounding country rock. Calcareous shales are metamorphosed to their equivalent, unmineralized calcium aluminum silicate layers.

2. Metasomatism of calcareous country rock by reaction with high temperature ($400^{\circ}-650^{\circ}C$) magmatic hydrothermal fluids along permeable zones (e.g. beds along stock and fault boundaries; sedimentary contacts). This produces an 'igneous metasomatic skarn' and can affect up to hundreds of metres of host rock. The skarn may be conformable or

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crosscut bedding. The resultant calc-silicate mineralogy

depends on both the protolith and the fluid chemistry.

Sulphide mineralization is minor at this stage of skarn

development (usually pyrrhotite, bornite, chalcopyrite

and sphalerite). Metasomatism may also occur locally

('reaction skarn') on the order of mm to several metres,

and is concordant with bedding. It is due to reaction

between chemically incompatible layers (e.g. limestone

and shale) in moderate to high grade metamorphic terrains.

Ore is not usually found in this type of skarn.

3. Low temperature alteration and sulphide deposition. Early

   formed hornfels· and skarn(containing metals in silicate and

   carbonate crystal structures) are subject to hydrous

   alteration by lower temperature ($300°-450°C$) mixed fluids of

   magmatic and meteoric origins. Alteration patterns are

   influenced by local structure, and usually crosscut earlier

   skarns. Calc-silicate minerals are leached of their calcium,

   and are replaced by silicate-carbonate-oxide-sulphide

   assemblages. Neutralization of hydrothermal fluids by

   carbonate host rocks, decreasing temperature and

   increasing Eh cause sulphides to precipitate, replacing

   earlier minerals.

In this highly simplified evolution of skarn, tin may

precipitate in the last two stages, either as a major tin

mineral (e.g. cassiterite or stannite) or as a tin-bearing

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calc-silicate, sulphide or aluminoborosilicate (e.g. garnet, axinite, idocrase or epidote), possibly substituting for iron in the mineral structure.

Several types of tin-bearing skarns have been described (Einaudi et al.,1981; Nekrasov,1971) - magnesian skarns, calcic skarns, and replacement deposits. Their mineral compositions and stages of mineralization are a reflection of the changing physico-chemical conditions of the fluid (Eh, pH, T, activities of S, F, B, fO_2, fCO_2) as it reacts with the carbonate wallrocks. Primary minerals are destroyed and replaced by new minerals, which in turn are replaced by later phases. Tin-bearing phases which are destroyed release tin to the fluids. It may be reprecipitated as cassiterite or stannite in association with chlorite, carbonate, quartz and sulphides. The depositional sequence of tin and sulphide minerals is similar to that of cassiterite-sulphide vein deposits (Nekrasov,1971). Cassiterite, chlorite and quartz are deposited first, followed by arsenopyrite and pyrrhotite; these sulphides may be replaced by sphalerite, chalcopyrite, stannite, loellingite and valleriite. Bismuth minerals, galena and siderite are the last minerals deposited.

In contrast to this step by step development of contact metasomatism, reaction and magmatic hydrothermal metasomatism (skarn) and retrograde alteration with ore deposition, there is another way in which to form stratiform tin deposits.

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Contact metamorphic calcareous lithologies are replaced by relatively low temperature hydrothermal fluids from intrusions; there is no intermediate skarn formation (Einaudi et al.,1981). Oxides (principally magnetite) or sulphides (mainly pyrrhotite) predominate. In the sulphide replacement deposits, cassiterite occurs in a carbonate gangue with pyrrhotite and minor stannite, arsenopyrite and pyrite; this may be followed by calcite, fluorite, chalcopyrite, galena and sphalerite (Einaudi et al.,1981).

The Renison Bell cassiterite-sulphide deposit in Tasmania is considered a carbonate replacement type (Taylor,1979b; Patterson et al.,1981; Einaudi et al.,1981). Dolomite beds were replaced at about $350^{\circ}C$ at low fO ($\sim 10^{-31.5}$ atm; probably controlled by CO_2-CH_4 reaction), low fS_2(10^{-11}-$10^{-12.5}$ atm) and low pH (3.9-5.4). Tin was transported as a divalent chloride complex. Dolomite replacement resulted in pH increase, causing ore deposition. Replacement assemblages include cassiterite, massive pyrrhotite, arsenopyrite, minor chalcopyrite, iron oxides, quartz, tourmaline, talc, tremolite, magnesian siderite and fluorite. Layers of pyrrhotite parallel to bedding may represent original carbonate-rich layers in the siliceous sediments (Patterson et al.,1981).

Comparison of the blue 'patch' mineralogy (section 3.3.2) with the above descriptions shows this type of

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mineralization to be of the lower temperature replacement origin. There are none of high temperature calc-silicate minerals (e.g. calcium pyroxene, amphibole, garnet) indicative of skarn formation. Cassiterite and sulphides appear to have replaced original carbonates within thin calcareous layers. Carbonate and phyllosilicates are rimmed and corroded; later carbonate, muscovite and chlorite overgrow the sulphides. Fluids which caused this probably leached the immediate surrounding host of boron and some copper (see lithogeochemistry section) and formed restricted chlorite and muscovite haloes.

The layered sphalerite in one sample (Fig. 3.19) and higher zinc contents in 'patches' far from the pluton may be equivalent to the 'distal facies' zinc replacement skarn (Einaudi et al., 1981) - zinc may remain in solution over a greater range of conditions, and thus be precipitated far from its source, either in veins or in replacement layers.

According to A.H. Clark (pers. comm. 1983), these blue 'patches' resemble the replacement tin-bearing 'carbonas' of Cornwall.

CHAPTER   4

GENERALIZED MODEL OF TIN GENESIS

4.1 Introduction

The tin prospect of the study area comprises a variety
of styles of cassiterite mineralization.   Detailed
description of these styles, as presented in this thesis,
suggests both a syngenetic and an epigenetic origin: detrital
cassiterite deposited within turbidites, and cassiterite
precipitated in veins and associated replacement layers.

Based on these descriptions and a review of the current
literature, an interpretation of this mineralization will be
attempted.

4.2 Origin of Tin in Sediments and Magma

Cassiterite and other clastics were eroded from a
low-lying continental mass (Schenk,1975). Because of its
zoned, equigranular habit, cassiterite probably derived from
a relatively high-temperature source; possibly from
Precambrian tin-bearing veins.   Cassiterite was deposited
within scours and crossbeds.

Partial melting of these cassiterite-bearing
carbonaceous turbidites may lead to a melt of low oxygen

fugacity (below the quartz-magnetite-fayalite buffer)

(Lehmann,1982) and low SO_2 fugacity (Burnham and Ohmoto,1980).

In such a magma, tin may exist in its divalent state rather

than its tetravalent state (Lehmann, 1982). This is a

possible analogue of the reduction of iron by hydrolysis in a

felsic melt (Burnham, 1979) where,

$$1/2 \ H_2 + O^{2-} + Fe^{3+} \ \longleftrightarrow \ OH^- + Fe^{2+}$$

$$H_2 + 2(O^{2-}) + Sn^{4+} \longleftrightarrow \ 2(OH^-) + Sn^{2+}?$$
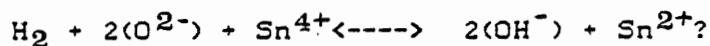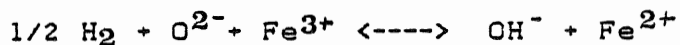
Divalent tin is larger than its tetravalent counterpart;

about 0.93 $\overset{o}{A}$ vs 0.69 $\overset{o}{A}$ respectively, for these

octahedrally-coordinated ions (Cotton and Wilkinson, cited in

Taylor,1979a). Because of its low oxidation state, relatively

large radius and relatively high electronegativity, Sn^{2+} tends

to be excluded from the crystal lattices of rock forming

minerals, becoming concentrated in residual fluids.

Mulligan (1975) states that Sn^{4+} may also exist in the

magma. It is a very minor network-forming element in a

silicate melt and can form three-dimensional bonds with

oxygen ions. However, the dominant network-forming elements,

silicon and aluminum, have much stronger bonds with oxygen,

thereby excluding tin from these complexes; it remains a free

ion to be concentrated in residual fluids. Tetravalent tin

may substitute for Ti^{4+} and Fe^{3+} in ferromagnesian minerals, and

is therefore concentrated in such accessory minerals as

ilmenite, rutile, magnetite, sphene, biotite and hornblende

(Mulligan,1975; Lehmann,1982).

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4.3 Magma Emplacement

According to McKenzie and Clarke (1975), the adamellites
(monzogranites) of the South Mountain batholith were emplaced
at pressures of about 1 to 2 kb, equivalent to about 4 to 8
km depth. Hornblende-hornfels thermal metamorphic
assemblages in the study area indicate P-T conditions of 1 to
3 kb (about 4 to 10 km depth) and 550° to $700^{\circ}C$ (Cullen,1983).

Marsh (1982) has discussed two theories of magma
emplacement. The magma body may rise buoyantly as a diapir;
wallrock flows plastically around the magma with minor
fracturing, giving rise to concordant contacts. Magma may
also ascend by stoping the wallrock. Because of the thermal
stresses set up, blocks can spall off and sink through the
magma. The country rock suffers little deformation, and the
magma may exhibit unassimilated xenoliths.

According to Shell Canada's mapping, the Wedgeport
pluton cuts several fold hinges of the metasediments. Its
contact with the country rock on the western shore outcrop is
concordant with bedding. There is no clear evidence of
xenoliths in the pluton. Accordingly, the pluton may have
been emplaced by either method, although such a high crustal
level of emplacement(4-10 km depth) implies ascent by
wallrock stoping.

4.4 Fluid Genesis

Burnham (1979) and Burnham and Ohmoto (1980) have discussed how an aqueous fluid evolves and is released from a cooling magma body.

In one of their examples, a granodioritic magma is emplaced and cools. The margin of the pluton has cooled and crystallized first, and has an inner coating of water saturated interstitial melt. As magma cools and crystallizes, the water remains in the melt. The water is of low diffusivity and will tend not to move any great distance, remaining in this lining. A further decrease in pressure and temperature oversaturates the melt, causing separation of volatile bubbles (known as 'second boiling'). Evolution of this vapour phase is accompanied by an increase in volume (of this phase), which can produce stress on the outer crystalline margin. This margin behaves in a brittle manner at shallow depths and will tend to be fractured by the expanding volatiles. At deeper levels, total pressure is greater, resulting in less volume expansion (and therefore less mechanical energy) of the volatiles. Less fracturing takes place, and few or no void spaces (miarolitic cavities) are formed.

Early fractures are lengthened by the fluid phase outward from the inner lining ('hydraulic fracturing'). This decreases the fluid pressure, causing crystallization of the

inner magma; the water saturated liner withdraws deeper into the magma body.

Mineral precipitation heals the fractures and isolates the melt system. Continued cooling of the magma begins the above process all over again. .

Initial water content of a magma influences its depth of crystallization, and therefore its depth at the stage of vapour separation and extent of subsequent wallrock fracturing. An initial melt with greater than 2 wt % water will be able to evolve enough vapour at second boiling to cause extensive fracturing at pressures less than 2 kb (~ 8 km depth). An 'ideal' magma to generate sufficient ore-bearing fluid would have an initial water content of 2 to 4 wt % ; this would result in vapour phase separation at 2 to 6 km depth before the magma becomes totally crystalline. Higher water contents restrict magma emplacement to deeper crustal levels which would not allow extensive wallrock fracturing. Lower water content restricts the amount of vapour released on second boiling, resulting in little or no fracturing of the wallrock.

Strong (1980) noted that biotite granites usually do not have enough initial water to concentrate lithophile elements, but are too water-rich to reach shallow crustal depths and leach metals from the country rock.

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According to Burnham and Ohmoto (1980), a granodioritic magma with an initial water content of 2.7 wt % will only cause sufficient wallrock fracturing at depths of less than 5 km. Shallow magma emplacement (< 10 km) appears to be one of the criteria for hydrothermal ore genesis.

The evolved aqueous phase contains lithophile elements and chloride complexes of alkalies, chalcophile metals, hydrogen and calcium. The chloride content of these fluids determines their ability to transport metals; a total chlorine content of greater than 0.3 molal is necessary. Ilmenite series magmas evolve fluids containing CO_2 and CH_4 in nearly equal proportions, low total sulphur content (SO_2 and H_2S) and low oxygen fugacity.

These fluids precipitate small amounts of sulphides (mainly pyrrhotite) and larger quantities of oxides, such as cassiterite. According to Patterson and others (1981), divalent tin may be transported as a chloride complex. Other authors (e.g. Barsukov, in Taylor,1979a) suggest tetravalent tin transport as a hydroxy-fluorostannate complex, although divalent tin could conceivably be carried in this way; i.e. $(Na,K)_2[Sn(OH)_x F_{4-x}]$. Smith (1947) also suggests divalent tin transport as a sulphide complex.

Reaction of such chloride-rich fluids with feldspathic wallrock results in potassium and hydrogen metasomatism (potassic and phyllic alteration), hydrolysis of SO_2 to H_2S

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and H_2SO_4 and production of HCl from metal chloride
complexes, leading to precipitation of the metals.

Reaction of these fluids with carbonate rocks leads to
destruction of HCl by decarbonation ($CaCO_3$+ 2HCl --> $CaCl_2$+
H_2O + CO_2). This results in destruction of the metal chloride
complexes and precipitation of metal sulphides and oxides,
replacing the carbonates (Burnham and Ohmoto,1980). For
example,
  $ZnCl_2$ + H_2S --> ZnS + 2HCl   and possibly,

  $SnCl_2$ + $4H_2O$ --> SnO_2 + 2HCl + $2H_2$ + $2(OH^-)$
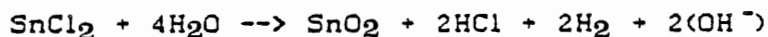
Study of the Wedgeport monzogranite reveals the western
shore contact margin (endocontact) to be porphyritic with
several generations of veinlets and some shear zones. This
may represent the chilled carapace described by Burnham
(1979) and Burnham and Ohmoto (1980). The pluton either did
not initially contain sufficient water or did not reach
shallow enough crustal depths(2-6 km?) to cause extensive
fracturing by an evolved aqueous phase. The endocontact was
breached by minor fractures, allowing formation of early
veinlets containing quartz and carbonate with rare scheelite
(fluid with high activity of CO_2?). Healing of fractures
began the process again, causing fracture formation either
along previous planes of weakness or in other orientations.
A mid stage in this evolution produced fluids of low oxygen
fugacity and low sulphur content which caused greisen
formation, sulphide-cassiterite veins and replacement zones

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within the country rock. Sulphide mineralogy is a reflection of the changing physico-chemical conditions outwards and upwards from the pluton. It may be possible that a later evolved fluid (containing radioactive elements ??) caused the shearing in the pluton and consequent movement in the country rock.

CHAPTER FIVE

TRACE ELEMENT LITHOGEOCHEMISTRY

5.1 Introduction

The lithogeochemical survey was performed to identify
those elements associated with tin mineralization and to
study their dispersion patterns to discover possible
indicator elements ('pathfinders') for use in subsequent
exploration programs in similar geological settings.

Specific drill core samples were analysed for a
selection of 13 elements typically associated with tin
deposits (Table II-1). Results of the 122 analyses are
tabulated in Appendix II.

Geochemical dispersion patterns are based upon a number
of factors which must be taken into account during any
lithogeochemical survey (Levinson,1974):

1.   Different mobilities of elements in solution.

2.   Porosity and permeability of country rock, be it primary
     (e.g. pore space) or secondary(e.g. fractures).

3.   Possibility of fluids reacting with the country rock.

     Certain elements remain in solution over a wide range of

Figure 5.1   General base map of study area
                    showing location of diamond drill
                    holes samples and 2 cross-section
                    lines A-A', B-B'.
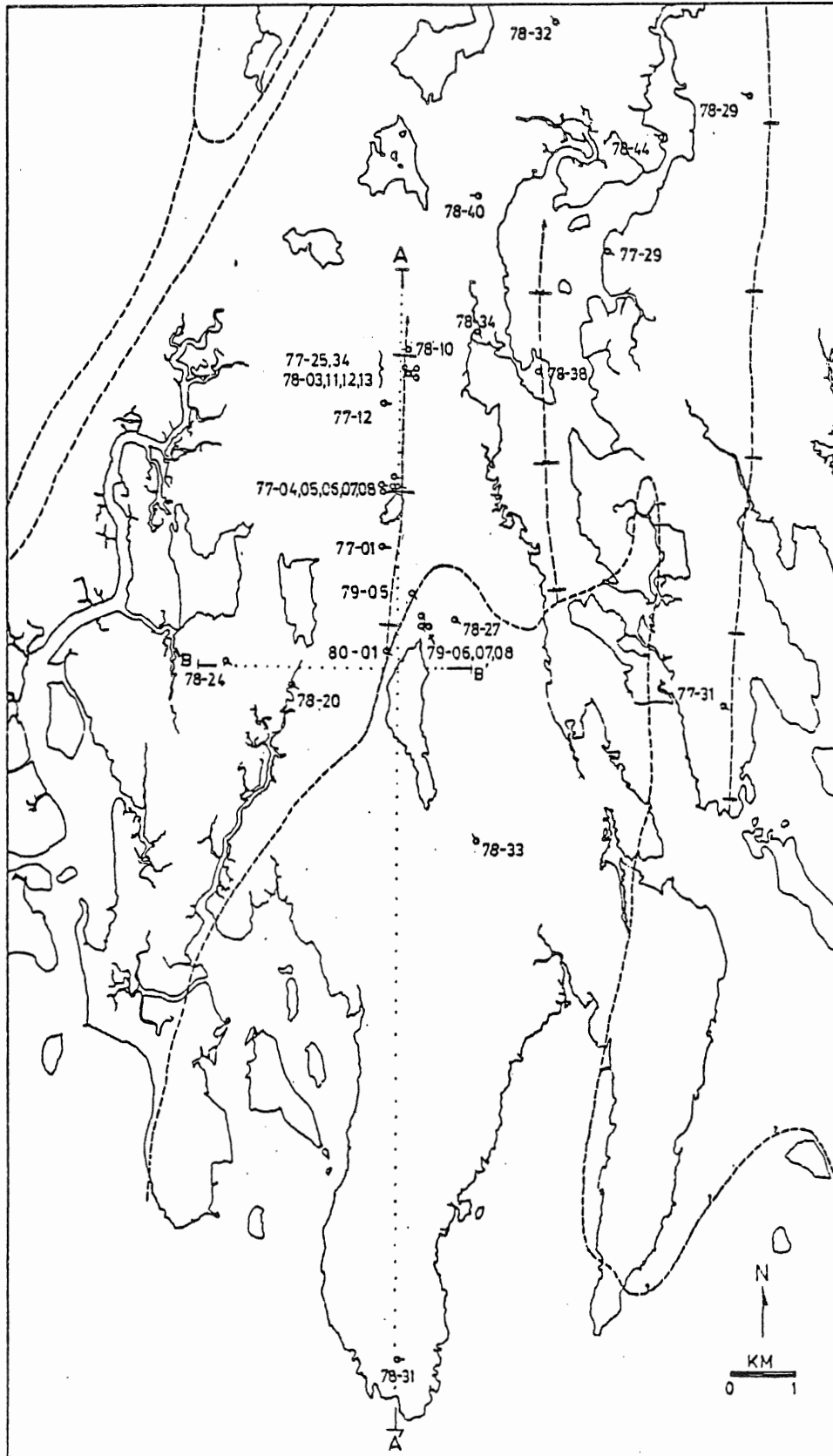
physico-chemical conditions (hence are 'mobile') and therefore are observed over a greater volume of rock than other, less mobile elements. These more mobile elements associated with mineralization may be used as pathfinders, as they may have a greater possibility of discovery than the element of economic interest.

For ore-bearing fluids to pass through the country rock, permeability must exist. Extensively fractured host rock enables these fluids to travel longer distances from their source, creating wider geochemical dispersion patterns.

Fluids reacting with the country rock may precipitate minerals characteristic of certain deposits and may be used as guides in exploration, e.g., reaction with calcareous rocks producing metalliferous skarns.

Levinson (1974) describes from Hawkes several geochemical patterns which may occur: extensive penetration of rock by fluids producing an areal pattern; migration of fluids from an ore body during or just after its formation, along fractures, creating leakage haloes; reaction and alteration of adjacent wallrock with solutions producing wallrock patterns.

One of the objectives of the geochemical study was to search for the existence of these patterns and try to relate them to the tin mineralization. The sampling procedure was

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established to select drill core with observable
mineralization as well as unmineralized ('barren') material
from a variety of locations and depths.   This was to
determine several characteristics of the study area:

1. Relationship of elements with respect to different
   lithologies (meta-argillites, meta-wackes, monzogranite) to
   compare their mean ('background') and anomalous (above
   'threshold') values.

2. Relationship of elements with respect to different styles
   of mineralization: greisens, sulphide veins and stratabound
   zones ('patches').

3. Extent of trace element dispersion from the mineraliza-
   tion; for this reason samples adjacent the mineralization
   were obtained, on the order of several centimetres to
   several metres distant.

4. Relationship of elements in the metasediments with respect
   to distance from the pluton. A series of samples were
   obtained at increasing distance from the surface projection
   of the pluton and at various depths.

   After the drill core samples were selected they were
cleaned, powdered and sent to X-Ray Assay Laboratories

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Limited (Toronto) for analyses. Appendices I, II and III describe sample preparation and analytical methods with their precision and accuracy estimates.

5.2 Population Partitioning

To adequately interpret the metal distribution in the mineralized samples, a comparison is made with that in the unmineralized core. The distributions are assumed to result from either the 'normal' processes of geochemical dispersion in the metasediments and the pluton (e.g. sedimentation, metamorphism, anatexis, diffusion in a melt) or the mineralizing event(s) and not from a secondary dispersion by later chemical weathering. Most samples were chosen free of relatively late fractures with recognizable oxidation products; all sample surfaces were ground to remove the effects of recent weathering.

Separation of the data set of each element in each lithology into background and anomalous populations was accomplished graphically by means of cumulative frequency plots, which depict the general form of each population. The graph is constructed in such a way that points of a single population will form a straight line; deviations from linearity represent combinations of populations (Sinclair,1974; Parslow, 1974). These populations are separated by the partition method explained by Sinclair (1974) and summarized in Appendix IV along with the

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cumulative frequency diagrams of the analysed samples. The
procedure arbitrarily chooses threshold values between
background and anomalous populations. Because other methods
of choosing threshold values are also arbitrary (see
Levinson,1974; Parslow,1974), this particular method is
believed to be just as satisfactory. Sinclair (1974) notes
that although a minimum of 100 values should be used to
construct a cumulative frequency graph, fewer values can be
dealt with using the plotting percentage technique of Koch
and Link (1970). Such computations were performed on the
small data sets (see Appendix IV for an example) and the
differences in the final values between the two methods were
not large enough to warrant the use of the latter technique.
Furthermore, the geochemical analyses were performed on a
selected sampling of lithologies, from known unmineralized to
known mineralized material, so as to estimate background and
anomalous populations. Manipulation of these small data sets
by Sinclair's method serves to define further the backgrounds
and thresholds.

Several attempts were made to obtain the best possible
groupings of metasedimentary sample data; e.g. group all
metasedimentary analyses together, all unmineralized sample
analyses together, etc. It became evident that grouping the
metasediments according to their lithologies
('pre-partitioning' into meta-pelitic and meta-psammitic
samples) facilitated interpretation of the cumulative

frequency graphs. It also established different background
and threshold values for several elements (e.g. Sn, Cu, Zn).
This is important if further exploration in the area is
planned, as an anomalous value in one lithology may only be
of secondary importance in another; more time, effort and
money would need to be expended to perform follow-up
examination (and possible rejection) of these spurious
anomalies. It is easier to first establish background and
threshold values of the two lithologies; it is also
relatively easy to distinguish the two lithologies in hand
sample so no extra effort need be expended.

Several difficulties were encountered in population
partitioning:

1. Values below the detection limit. To continue population
   partitioning with a large enough data set, values one order
   of magnitude lower than the detection limit were substituted
   during mathematical manipulations. This can cause erroneous
   cumulative frequency curves and therefore, inaccurate
   background and threshold values. An example of this is
   observed in molybdenum values in the metasediments; most are
   below the detection limit of 0.5 ppm. Use of 0.05 ppm instead
   results in one or two populations with an interpolated
   background of 0.4 ppm which is not a valid estimate. Care
   must be taken in the subsequent interpretation of such
   results.

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2. Gentle slopes of the cumulative frequency curves create difficulty in selection of inflection points and can cause inadequate partitioning of the data set.

3. Insufficient number of analyses to give a continuous (i.e. 'smooth') range of values. This can produce a rapid change in slope, giving the impression of the existence of two or three populations where in fact only one or two exist.

4. Existence of two inflection points (implying three populations) complicates partitioning as a limited number of data points are available for the partitioning equation. At least three points per population are desirable and this is not always possible when more than one inflection point occurs. When this happens, points are obtained from the cumulative frequency curve, which may produce errors in final background and threshold values.

    Once the background and threshold values were acquired, they were compared with the data set and their corresponding lithologies to determine possible causes for their trace element distributions. Background and threshold values of the elements in the three lithologies, average values in tin-bearing rocks of Cornwall, of the nearby Davis Lake pluton, and of the so-called 'specialized' and 'normal' granites, as well as the clarkes of shale, sandstone and

granite are listed in Table 5.1. A summary of the results of
analyses of each element in each lithology is found in Table
5.2. Plots of element distributions with respect to
lithologic type or mineralization type are found in Figures
5.2 to 5.4 and are discussed in the tabulated summary. It is
important to keep in mind the small sample sizes; even though
an adequate estimate of background and threshold values was
obtained, comparison of trace element contents among this
selection of lithologies is believed to be limited.

It is also necessary to realize the importance of
analytical control. Duplicate and reference standard samples
were included in the sample batch to evaluate the precision
and accuracy of the analyses performed by X-Ray Assay
Laboratories Limited. Details are shown in Appendix III.
Precision (reproducibility of analyses) ranged from poor to
excellent; accuracy (closeness to 'true' or accepted
concentrations) ranged from very poor to acceptable. The
analyses appear to be relatively precise, but not too
accurate. In other words, the results may be considered
'valid' within the data set but are not to be taken as
absolute ('true') values.

5.3 Discussion

Assuming the analyses and population partitioning are
valid, the following observations of geochemical distribution
can be made.

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Table 5.1 Background and Threshold values in the lithologies of the study area and average values in various other lithologies.

All values in ppm		Metapelitic Rocks (n = 23)	Metapsammitic Rocks (n = 51)	Monzogranite (n = 25)	Davis Lake 1 Biotite Granite (n = 2)	Cornish 2 Metasediments (Avg. min-max)	Granite	Plumasitic 3 Rare-Metal Granitoids	"Specialized" Granite	"Normal" 4 Granite	Shale	Clarkes 5 Sandstone	Granite
Sn	Background	3.5	18	8	16.5	10- 17	17-58	6.3	30 ± 15	1-8	4	0.X	3
	Threshold	100	180	48									
W	Background	7.5	5	12	-	4- 5	20-30	4.1	7 ± 3	1-2.7	2	1.6	2
	Threshold	60	19	65									
Mo	Background	0.4*	0.4*	4		-	-	1.4	4 ± 2	<1-2.5	3.	0.2	2
	Threshold	5	9	32									
As	Background	11.5	18	4.5	-	12-30	26-65	-	-	-	15	1	1.5
	Threshold	100	160	70									
Cu	Background	36	10	4.5	4.5	30-59	4- 9.5	-	-	-	50	X.	10
	Threshold	250	365	135									
Pb	Background	4.5	7	8.5	-	14-51	13-44	30	-	-	20	7	20
	Threshold	50	120	15.5									
Zn	Background	80	110	26	40	112-245	39-63	57	-	-	100	16	40
	Threshold	275	330	76									
Sb	Background	0.54	0.44	0.3	-	-	-	-	-	-	1	0.0X	0.2
	Threshold	2.0	1.45	0.6									
Bi	Background	0.42	1.65	5.4	-	-	-	-	-	-	0.18	-	0.1
	Threshold	3.5	10	100									
Li	Background	30	52	45	186	-	-	97	200 ± 100	36±5-150	60	15	30
	Threshold	100	100	80									
F	Background	410	470	730	4000	-	-	3000	3700±1500	250-1500	740	270	735
	Threshold	900	1000	1550									

Values from:

[1] Chatterjee, 1980

[2] Jackson, 1979

[3] Tauson, 1974

[4] Tischendorf, In Hosking, 1979

[5] Taylor In Levinson, 1974 and Turekian and Wedepohl, 1961 with order of magnitude estimates in form of X

*Background values unreliable; near or at detection limit

Dashes (-) denote unavailable data.

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Figure 5.2   Trace element variation with
                    lithology and mineralization
                    in meta-argillites.
                    Values in ppm unless otherwise noted.

                    Carb Argillite - carbonaceous argillite

                    Min'd "Patches" - stratiform mineralization

B

150

10

1

Detection Limit (10)

‒ ‒ ‒ ‒ ‒ (8) ‒ ‒ ‒ ‒ ‒

F

1000

100

Threshold (900)

Background (410)

Li

250
100

10

1

Threshold (100)

Background (30)

Mo

100

10

1

Threshold (5)

Background (< 0.5)

+(5)   ↓(5)   ↓(6)   ↓   <0.5

W

100

10

1

Threshold (60)

Background (7.5)

Sn 1.5 %

1000

100

10

1

(6)

Threshold (100)

Background (3.5)

•(5)

ARGILLITE	CARB ARGILLITE	MIN'D "PATCHES"	VEIN
(N = 6)	(N = 8)	(N = 8)	(N = 1)

Cu

1000

100 .... Threshold (250)

100

10 .... Background (36)

10

1

Pb 1000

1000

100 .... Threshold (50)

100

10

10 .... Background (4.5)

1

Zn

10 %

1 %

1000

.... Threshold (275)

100 .... Background (80)

10

ARGILLITE   CARB   MIN'D   VEIN
              ARGILLITE "PATCHES"
(N=6)   (N=8)   (N=8)   (N=1)

Bi

100

10 ⁺ (5)

Threshold (3.5)

1 ⁱ

(4)

Background (0.42)

(2)

0.1 ⁺ adj dyke

Sb

25
10 ⁺ ⁺

Threshold (2)

1 ⁱ(5) ⁺ (5L) ⁺

Background (0.54)

ⁱ(5)

0.1

As

1% ⁺ ⁺

1000 ⁺

100 ⁺ ⁱ Threshold (100)

⁺ ⁺

10 ⁱ(4) ⁱ(4) Background (11.5)

ⁱ(5)

1

ARGILLITE	CARB ARGILLITE	MIN'D "PATCHES"	VEIN
(N=6)	(N=8)	(N=8)	(N=1)

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Figure 5.3　　　　　　Trace element variation with
　　　　　　　　　　　　lithology and mineralization
　　　　　　　　　　　　in meta-wackes.
　　　　　　　　　　　　Values in ppm unless otherwise noted.

　　　　　　　　　　　　Unmin'd - unmineralized samples

　　　　　　　　　　　　Adjacent Min'n - barren samples adjacent
　　　　　　　　　　　　　　　　　　　　　mineralization

　　　　　　　　　　　　Min'd "Patches" - stratiform mineralization

　　　　　　　　　　　　Contact - refers to those samples in or
　　　　　　　　　　　　　　　　　near the contact with the
　　　　　　　　　　　　　　　　　pluton in DDH 79-05, 80-01

B

100
.(2)
.(2)
.(6)
.(11)
(4) ....(4) .... (2) ___ Detection Limit (10)
10   .(3)

F

2500
. Contact
1000 ____ .... Threshold (1000 ppm)
[(20)   [(11)   [(6) .... Background (470 ppm)
100

Li

250
. Contact
100 ____ .... Threshold (100)
[(17)   [(11)   [(8) .... Background (52)
10

1
.<1

Mo

20   .
10 ____ .... Threshold (9)
                                              .
[.(2)   .(2)   (3)
[(19)   [(7)   [(5)   [(2) _____ Background (<0.5)
1   < 0.5

W

1000
.
.
100   .
[(19)   [(5)   [(6) ____ Threshold (19)
10   [[[(6) ___ Background (5)
[(4)   [(2)   < 1
1

Sn

1%
[(5)
1000
[[(11)   [Threshold (180)
100   [(25)
Background (18)
10

1

UNMIN'D   ADJACENT   MIN'D   VEINS
            MIN'N   " PATCHES"

(N=25)   (N=11)   (N=8)   (N=7)

207

208

Bi

As rich			
Threshold (70)			
Sn rich			
Background (1.65)			

Sb

As rich

Sn rich — Threshold (1.45)

Background (0.44)

< 0.2

As

As rich
Sn poor

Sn rich — Threshold (160)
As poor

Background (18)

UNMIN'D	ADJACENT MIN'N	MIN'D "PATCHES"	VEINS
(N = 25)	(N = 11)	(N = 8)	(N = 7)

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Figure 5.4   Trace element variation with
                  lithology and alteration in pluton.
                  Values in ppm unless otherwise noted.

                  Non pheno - non-phenocrystic monzogranite

                  Sl. pheno - slightly phenocrystic monzo-
                              granite(1-5 modal %)

                  Pheno   - phenocrystic monzogranite
                              (>5 <75 modal %)

                  Tan alt'n - sample adjacent greisen with
                              tan-coloured alteration

                  Kaol. alt'n - sample with kaolinite vugs
                              and veinlets

                  Post gsn veining - samples with those
                              quartz veinlets which cut
                              greisen zone

                  Shear   - sheared monzogranite
                              containing a pre-shear quartz
                              veinlet containing scheelite,
                              molybdenite and chalcopyrite

                  Adj. mafic dyke - 2 samples(78-27)
                              adjacent a mafic dyke

Bi

250
100 — — — — — — — — — — — — — — Threshold (100)

10

Background (5.4)

1

< 0.1

Sb

15
10

1 — — — — — — — — — — — — — Threshold (0.5)
— — — — — — — — — — — — — Background (0.3)

0.1

< 0.2

As

1%

1000

100 — — — — — — — — — — — — Threshold (70)

10

— — — — — — — — — — — — Background (4.5)

| NON PHENO | SL. PHENO | PHENO | TAN ALT'N | GREISEN | KAOL. ALT'N | POST GSN VEINING | SHEAR | ADJ. MAFIC DYKE |
| (N=4) | (N=5) | (N=3) | (N=1) | (N=4) | (N=1) | (N=4) | (N=1) | (N=2) |
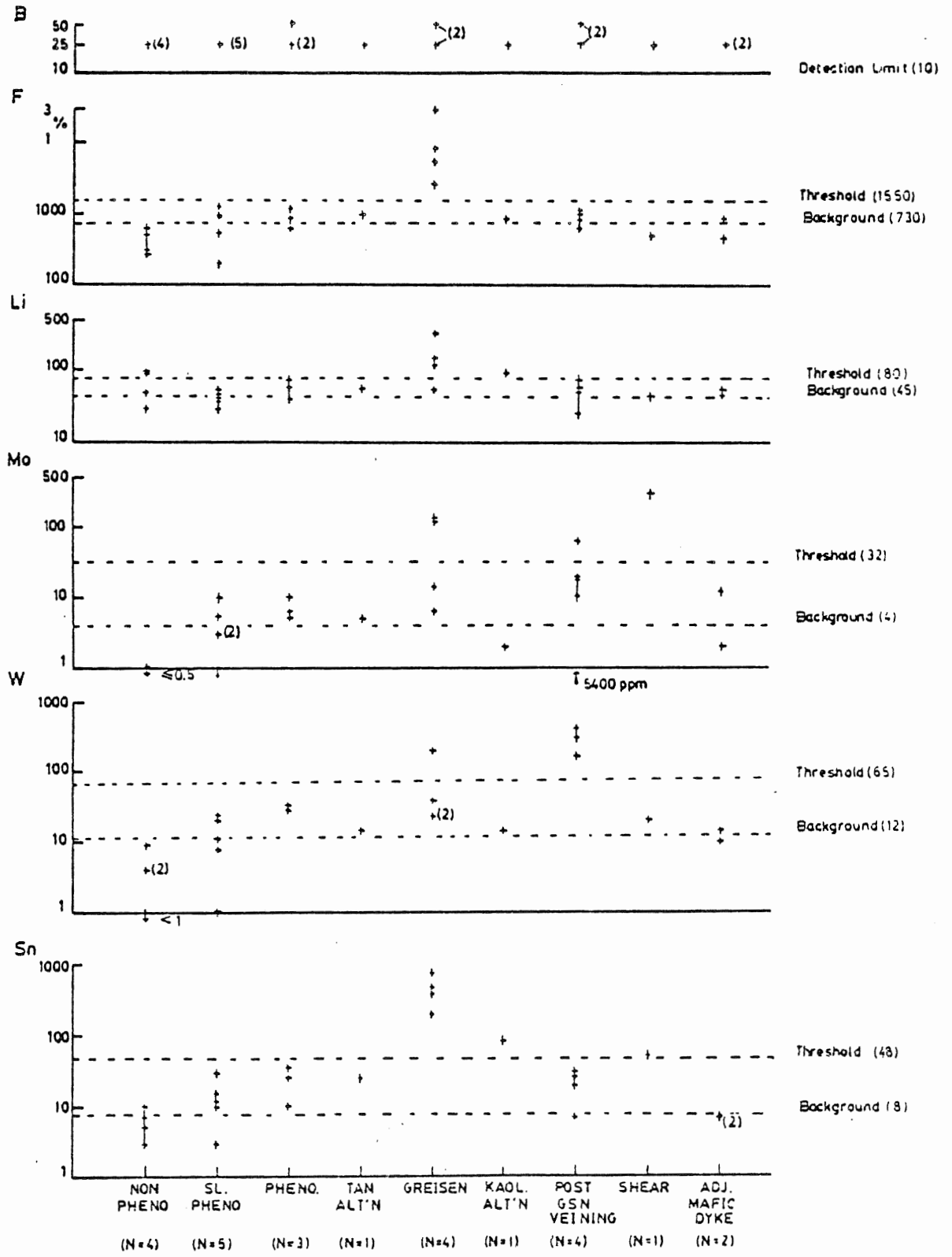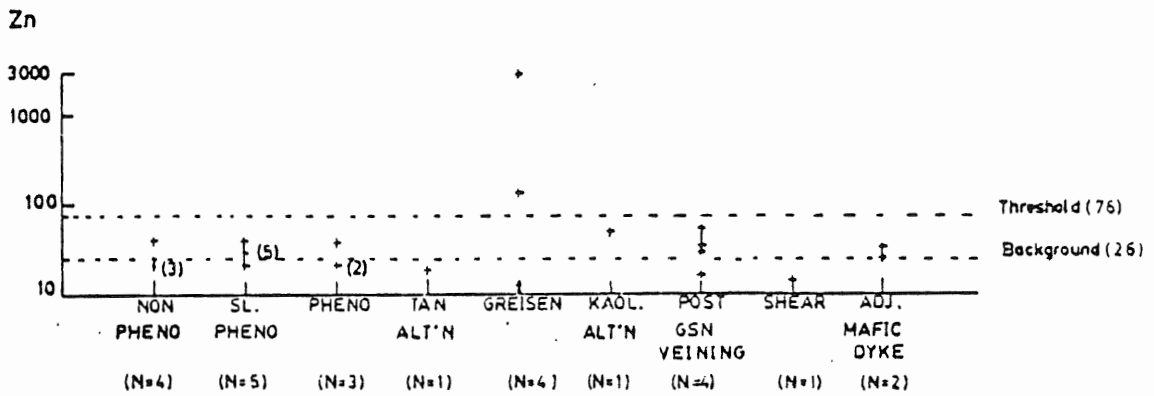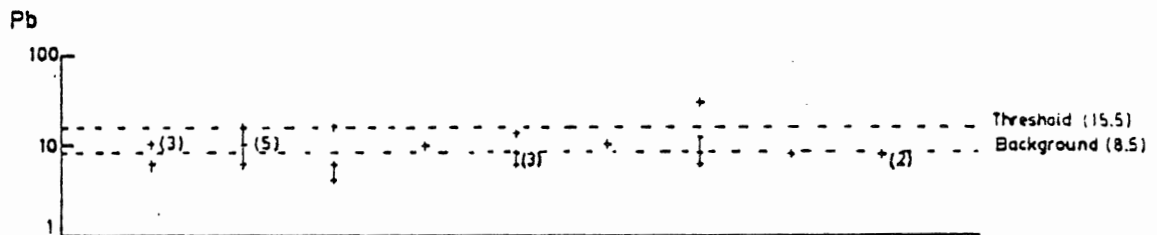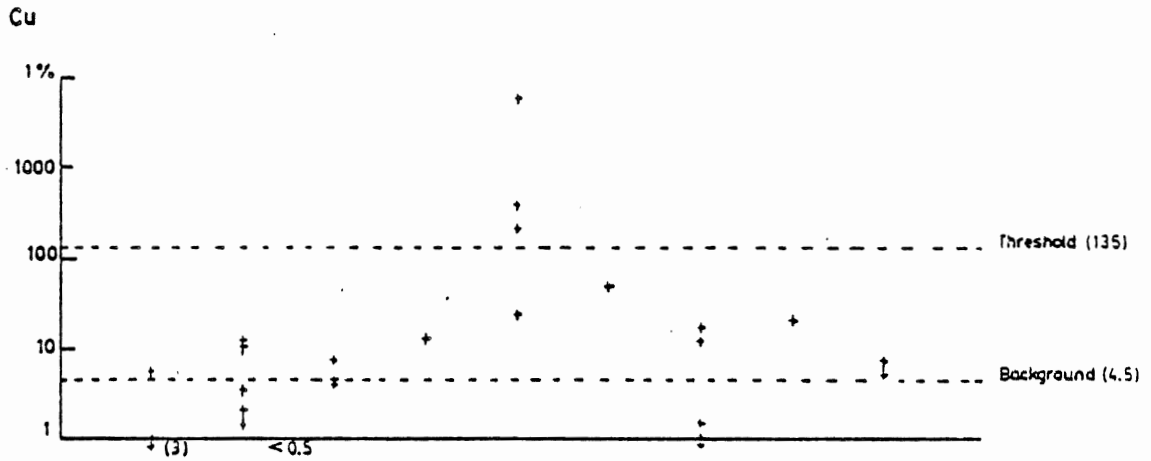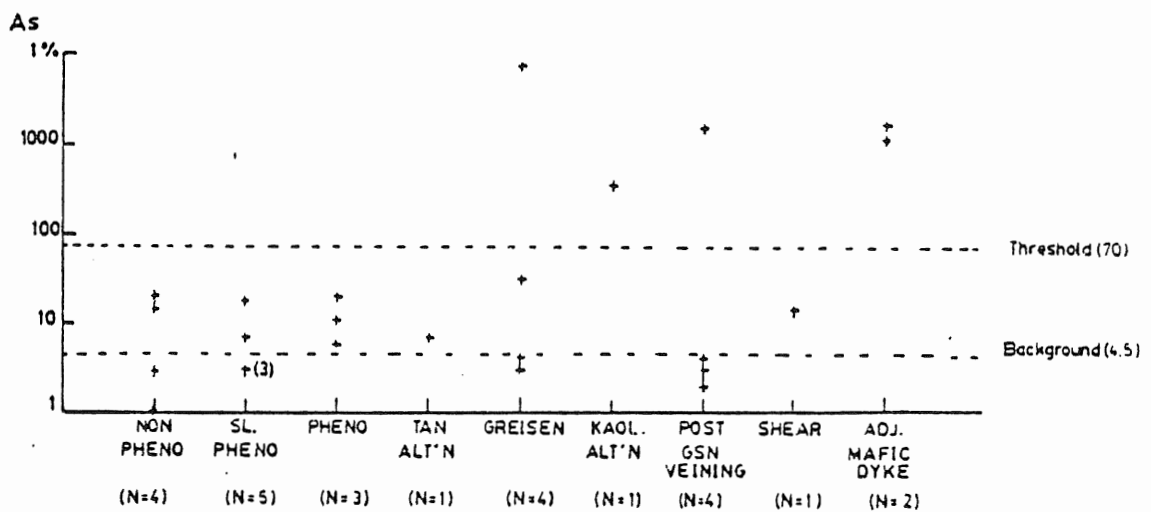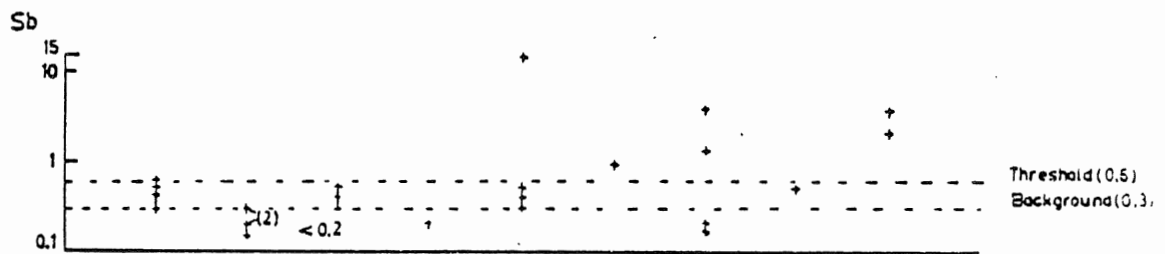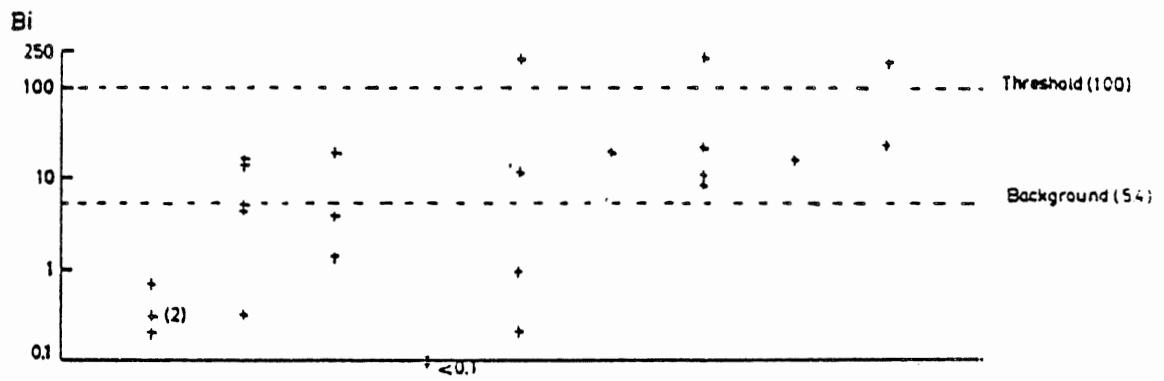
5.3.1 Relationship of Elements With Respect to Different Lithologies

Trace element distributions were compared within each lithology, i.e., among gross mineralogical types arbitratily established in each rock group. For example, meta-psammitic samples were classified on both mega- and microscopic features such as presence of biotite, feldspar and carbonate, as well as by grain size; meta-argillites were typed by presence of carbonaceous material; samples from the pluton were grouped arbitrarily by the presence of phenocrysts (none, 1 to 5 modal percent, greater than 5 modal percent), presence of greisens, alteration, veinlets, shears or mafic dykes. Obviously the meagre number of samples precludes any definite conclusions about trace element distribution within each lithology; however, a rough estimate of the ranges may be inferred. Accordingly, there appear to be no major differences in trace element contents among the various unmineralized meta-psammitic samples. Within meta-pelitic samples, wider ranges of metal contents are observed in the carbonaceous meta-argillites, due either to slightly greater number of samples or to primary sedimentological differences; organic-rich sediments appear relatively enriched in metals, by adsorption or by forming metallo-organic or chelate compounds (Krauskopf,1979). Both metasediment types have relatively high contents of molybdenum, tungsten, lithium and

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fluorine in samples close to the pluton, implying possible addition of these elements from the intrusion. Background values of both lithologies are similar except for those of tin, copper, zinc and bismuth; the meta-pelitic samples have a higher copper background, and the meta-psammitic samples have higher backgrounds in the other elements. This may be due to the presence of discrete metal-bearing particles, minerals with those metals in solid solution, or 'sorption of those metals or their complexes to particular mineral grains.

Arsenic has a long paragenesis, occurring principally as arsenopyrite in sediment disseminations (detrital or diagenetic?), in pre-crenulation veinlets, in main-stage mineralization veins and patches, and in post-mineralization veins and breccias.

Determination of variations within plutonic samples is more difficult as consideration must be taken of sample location within the pluton (endocontact vs. the interior) and of the ubiquity of metal-rich veinlets which may go unnoticed but cause high trace element analytical results. Therefore, only general conclusions are made. No major differences in trace element contents exist in samples of different crystallinities, although the non-phenocrystic samples (of the interior of the pluton) usually have slightly lower ranges than those samples with phenocrysts. Two

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unmineralized samples adjacent a mafic dyke (DDH 78-27)
contain biotite with inclusions of arsenopyrite, causing high
concentrations of arsenic, antimony and bismuth. This has
not been observed in any of the other plutonic samples and
may due to the mafic dyke intrusion, although it is not known
how this occurs.

5.3.2   Relationship of Elements With Respect to Style of Mineralization

(i) Sulphide-Cassiterite Veins

Certain mineral assemblages are associated with the
sulphide-cassiterite veins in the metasediments and this is
reflected in the trace element distributions. Two main types
of veins exist: tin-rich (> 1000 ppm), arsenic-poor and
arsenic-rich (> 1000 ppm), tin-poor. Tin-rich veins have
relatively high concentrations of copper and bismuth due to
the existence of cassiterite and chalcopyrite; the high
bismuth content may be due to native bismuth, solid solution
within such minerals as native silver or galena, or to
presence of unobserved rare bismuth sulphides or
sulphosalts. Veins rich in arsenic have relatively high
contents of lead, zinc, antimony and bismuth. Bismuth
content within the two vein types is not clear - both types
have background and anomalous concentrations. A plot of
bismuth against arsenic (Fig. 5.5) appears to show a negative
correlation with several deviations, whereas that of bismuth

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against tin shows no correlation (Fig. 5.6). Bismuth
therefore seems to occur in other forms not associated with
arsenic or tin mineralization. Most of the arsenic-rich
veins have a higher range of fluorine content than the
tin-rich veins.

There appears to be a chemical and physical relationship
between the two vein types. Chemically, there is a positive
correlation between tin and copper, and a negative
relationship between tin and arsenic, lead, zinc and antimony
(Fig. 5.6). Physically, tin-copper-rich veins occur deeper in
the country rock and closer to the pluton than the relatively
shallow, more distant arsenic-rich veins with their more
'mobile' base metals and fluorine. Figure 5.7 gives a rough
metal pattern observed in this vein system. The two vein
types are not observed together in drill core, so their
relationship is only inferred; however, there is a
mineralogical (and therefore elemental) zonation in the major
veins in the metasediments surrounding the pluton. Veins
close to the pluton are relatively rich in tungsten and
molybdenum (in the form of scheelite and molybdenite,
respectively). Tin, zinc and lead become dominant farther
from the intrusion. Arsenic and copper, of variable
concentrations, are ubiquitous. Shallower and more distant
veins show a decrease in tin and an increase in the other
base metals. This type of zonation has been described by
Grigoryan (1974), and may be of use in exploration, to

Figure 5.5   Variation of Sb and Bi with As
content in veins in the
metasediments.
Sb is proportional to As
content. Bi, with a few
exceptions, shows a negative
correlation.

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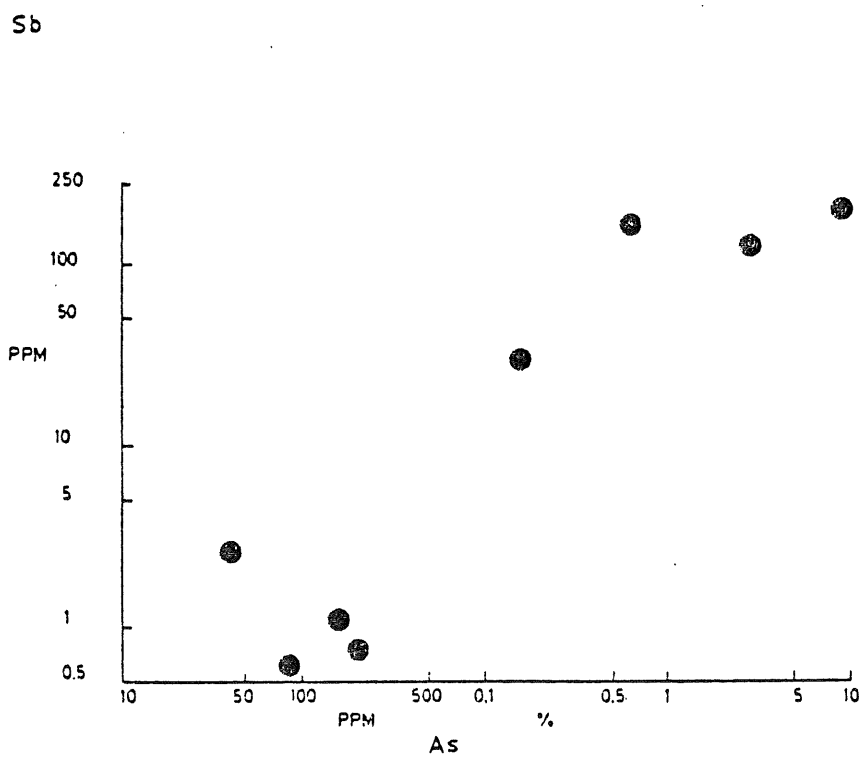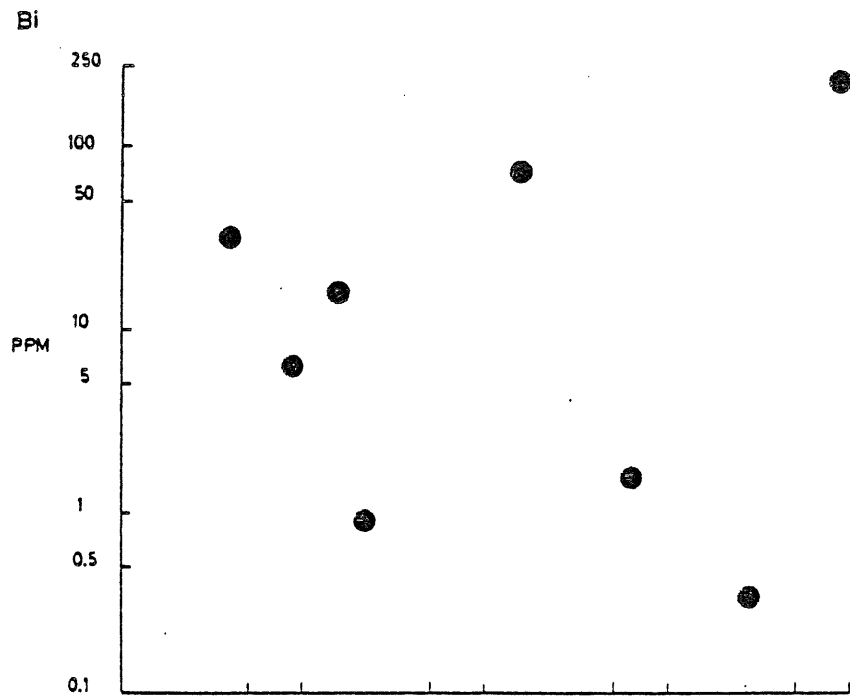
Figure 5.6   Variation of various metals with
Sn content in veins in the
metasediments.
Note the antipathetic relationship
of As, Pb and Zn(with one
exception) with Sn. Relationship
with Cu and Bi is not as clear.

221
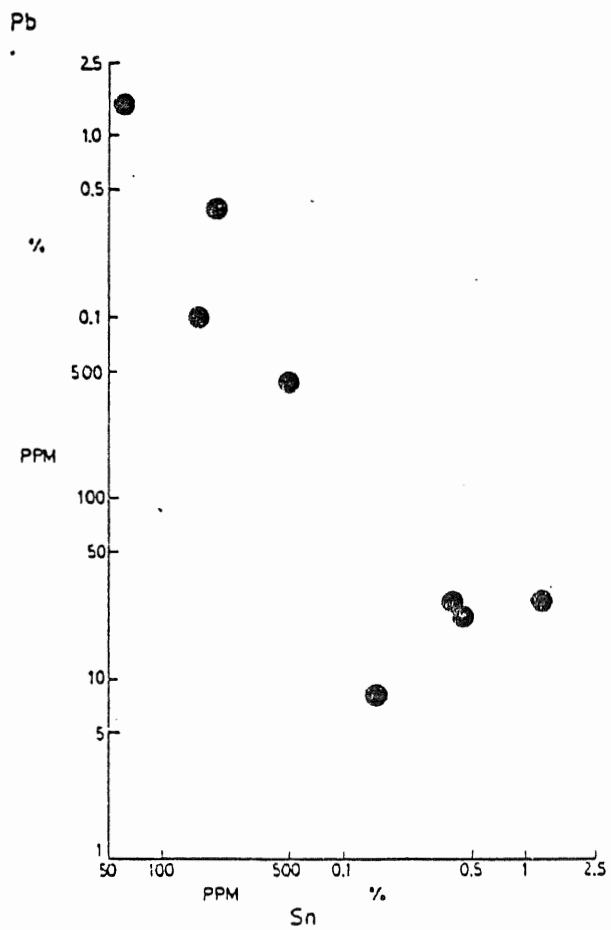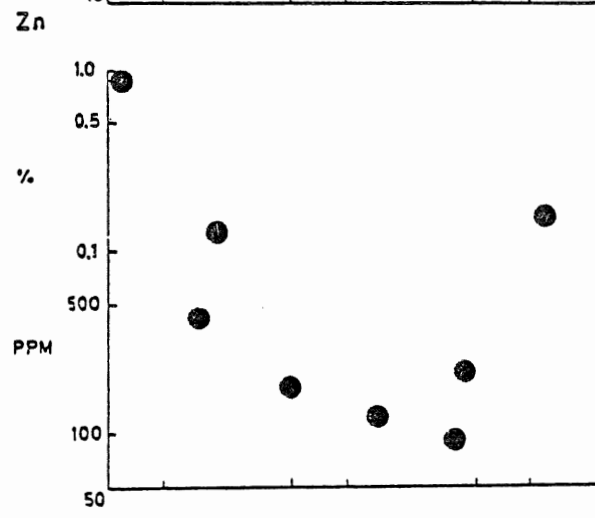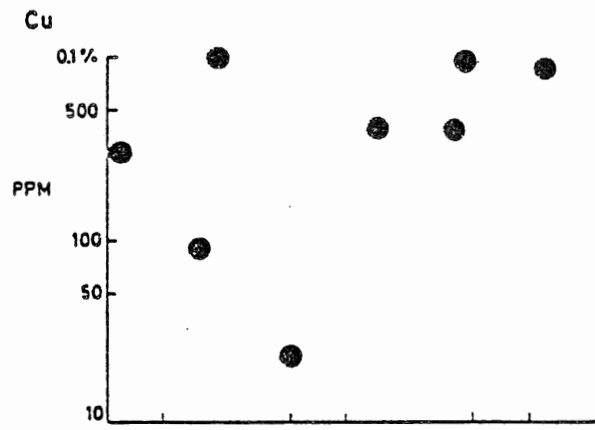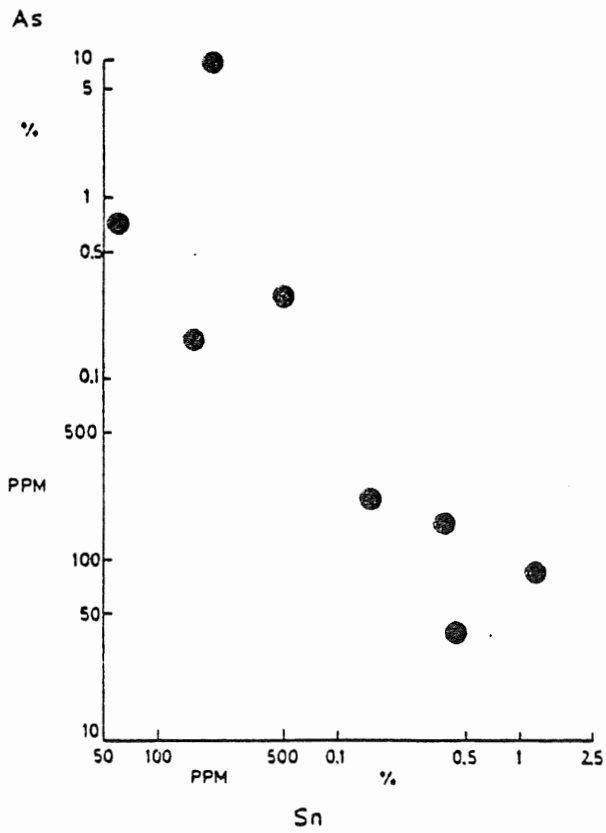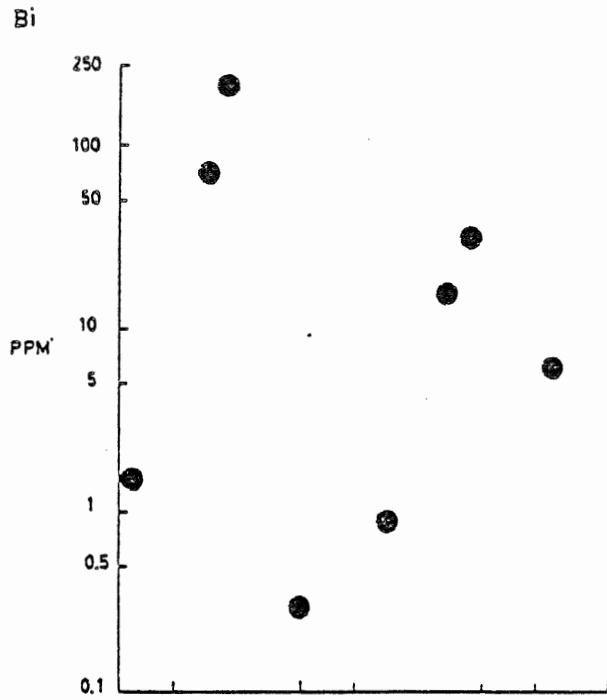
Figure 5.7   Plot of metals commonly
occurring in mineralized vein
systems in both the pluton and
surrounding metasediments.
There is a pattern of metal
concentration from the pluton
outwards and upwards, from
W and Mo to Pb and Zn; As and
Cu are ubiquitous; Sn has an
intermediate range(~ 3-5 km
from pluton).

Lower case metals have relatively
lower abundances.
"Mid" refers to those metals
occurring in veins at "middle"
depths of 50-100 m in DDH 78-34.
"Bottom" refers to those metals
occurring in veins at "bottom"
depths greater than 100 m in
DDH 78-34.

Cu Pb

C. As Pb Zn
Sb

Mid (As Pb Zn
Cu Sn Bi)
Bottom (Sn Cu As Bi)

Sn Cu Zn Bi
± As Sb Pb Ag

As Cu Zn Pb

Sn Cu As ± Pb Ag Sb W

W

Cu Sn As F
W Mo

Zn Pb

Sn

As Cu

W Mo

N

KM
0   1
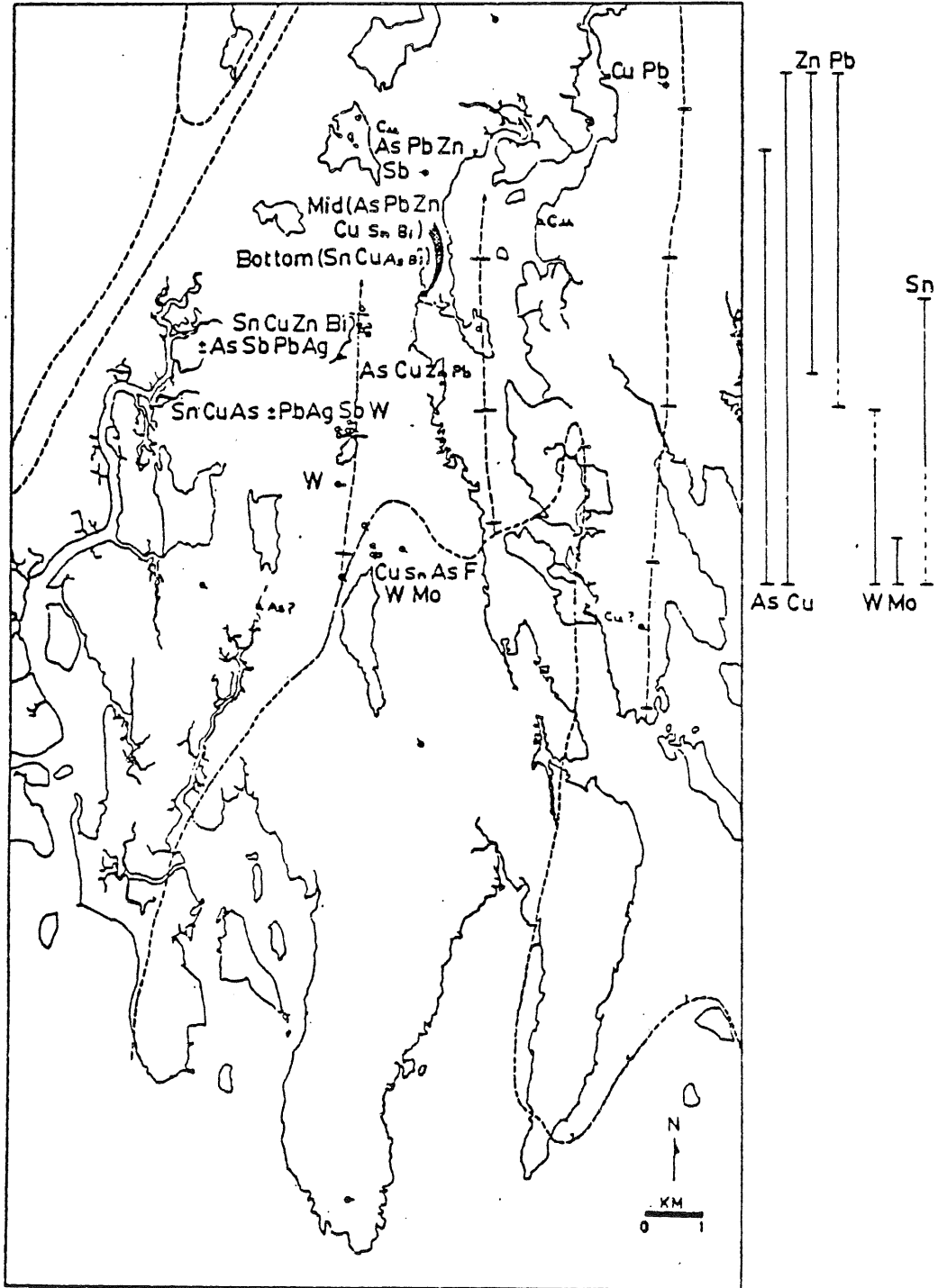
indicate possible directions and depths for further
geochemical or geophysical work.

The veins are rather thin (commonly on the order of mm)
and have relatively narrow alteration haloes (mm to several
cm). There has been no wide mineralogical or geochemical
response associated with these veins. If a stockwork of such
veins occurred within a small volume of rock, the geochemical
effects may be enhanced to such an extent as to produce a
broader, noticeable response, but this has not been
observed.

(11) Greisen Veins

Greisen veins and their associated haloes are relatively
high in tin (about 200-800 ppm) with respect to the rest of
the pluton, although low compared to sulphide-cassiterite
veins. The greisens are also relatively high in tungten,
copper, lithium, fluorine, total iron and rubidium; they have
wide ranges of molybdenum, arsenic, zinc and bismuth - this
is probably due to multiple-stage, cross-cutting veinlets
containing molybdenite, arsenopyrite,sphalerite and
scheelite. Both sodium and strontium are depleted in the
greisens (Fig. 5.8).

Contact of the greisen with the monzogranite varies from
sharp to gradational. Trace element contents of unaltered
samples adjacent greisens show either no change or a slight

Figure 5.8   Variation of several major
                    oxides(in %) and minor elements(in
                    ppm) in plutonic samples from study
                    area and two other granitoid bodies.

                    Greisens have higher concentrations
                    of Fe_2O_3(total) and Rb(addition
                    of sulphides and white mica); they
                    are relatively depleted in Na_2O,
                    Sr and K/Rb(destruction of feldspars).

                    Non pheno - non-phenocrystic monzogranite

                    Sl. pheno - slightly phenocrystic monzo-
                                granite(1-5 modal %)

                    Pheno   - phenocrystic monzogranite
                                (>5 <75 modal %)

                    *Biot gte - biotite granite and greisen
                    *Gsn   samples from the Davis Lake
                                 pluton, East Kemptville
                                 (Chatterjee, 1980)

                    **Adam   - adamellite from part of the
                                 South Mountain batholith
                                 (McKenzie and Clarke,1975)

Zr

Sr

Det
Lmt

Rb

K/Rb

NON PHENO — SL. PHENO — PHENO — GREISEN — BIOT. GTE — GSN — ADAM.

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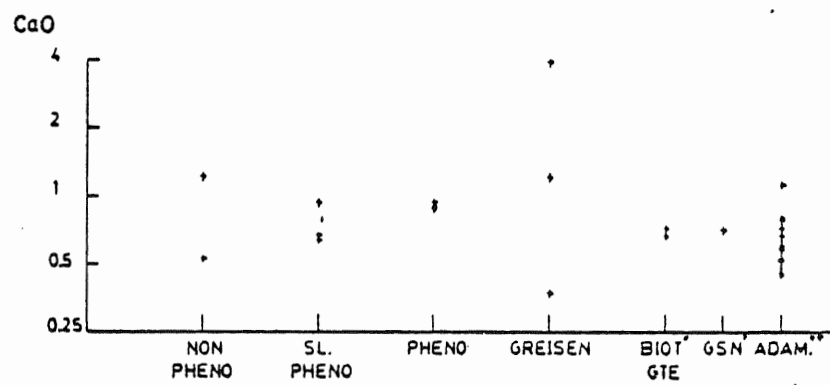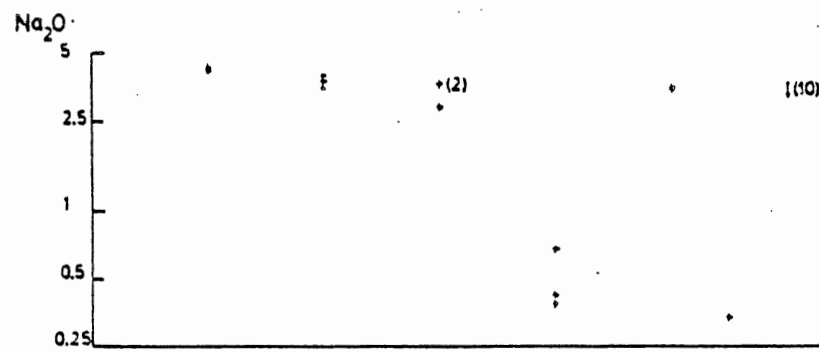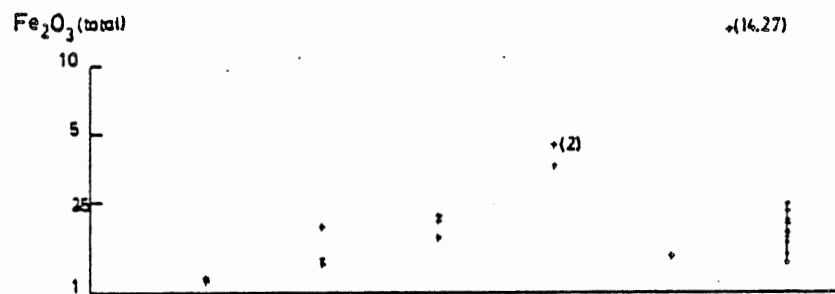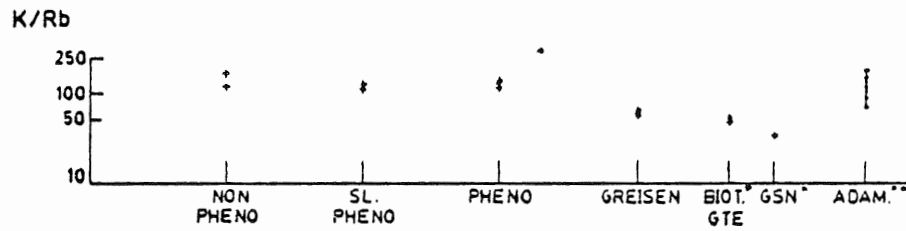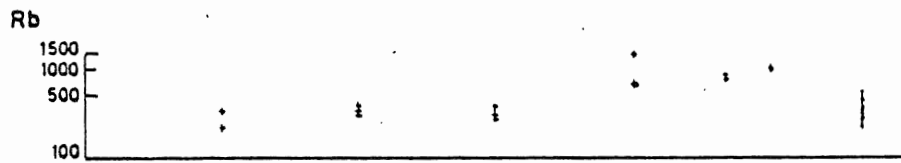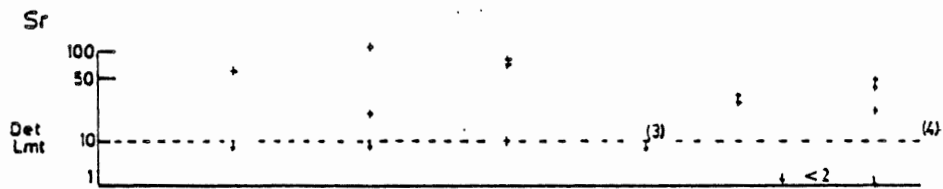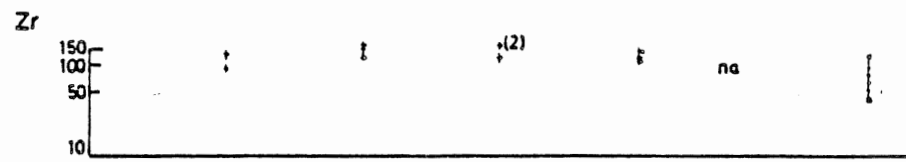
enrichment in tin and fluorine. One sample of slightly altered monzogranite (tan alteration adjacent greisen) is relatively enriched in copper and depleted in antimony and bismuth (addition of chalcopyrite, removal of arsenopyrite?).

As with veins in the metasediments, greisens do not have a wide zone of influence - usually several cm, rarely up to about 20 cm. Trace element contents have a narrow zone of enrichment around each greisen vein, e.g., see Figure 5.10 for variation of tin and copper in greisens and their adjacent country rock. Unless there is a concentration of such veins to produce a broad geochemical effect, they cannot be traced geochemically. If the overlying country rock had behaved in a more ductile fashion, with less fracturing, the ore-bearing 'greisen' fluids may have instead remained within the apical parts of the intrusion, 'ponding' against the country rock, forming broad greisen zones of economic interest.

(iii) Stratiform Mineralization

The stratiform patches are relatively enriched in tin, copper and bismuth, due mainly to the presence of cassiterite and chalcopyrite; bismuth may occur in the form of sulphides or sulphosalts, as submicroscopic inclusions in the other sulphides, or as solid solutions within native silver or galena. All boron analyses are below the detection limit (10

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ppm) (leaching effect?). Other element distribution patterns are not as distinct: tungsten contents have a slightly higher range, with larger values in samples close to the pluton; zinc contents are similar to those of unmineralized samples, with the exception of two samples containing much sphalerite; meta-psammitic samples have a higher range of antimony contents but they are not always directly related to arsenic content (Fig. 5.9) as observed in veins - perhaps Sb substitutes for other elements, e.g., Fe, Sn^{4+}, Ti^{3+4+} instead of existing as a sulphosalt within arsenopyrite. Sb analyses are also not very precise (see Appendix III for accuracy and precision estimates).

Samples adjacent psammitic mineralized zones show slightly elevated tin contents. Copper contents are ambiguous: seven of the eleven adjacent samples are in the upper ranges of the normal population; the other four samples are below the detection limit of 0.5 ppm (leaching effect?). Figures 5.10 and 5.11 show the variation of tin and copper, and tin and bismuth in mineralized patches and their adjacent zones. Other elements show no significant observable changes. Figures 12a,b show cross-sections of parts of the study area containing tin mineralization but show no clear-cut geochemical haloes.

Again, a restricted geochemical dispersion exists around the mineralization. No widespread halo occurs which would be

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Figure 5.9   Variation of Sb and Bi content
                  with As in mineralized 'patches'.
                  There is no apparent relationship
                  of the two elements with As(some
                  increase of Sb with As).

Sb

25

10

5

PPM

1

0.5

0.1

(2)

Bl

100

50

PPM

10

5

1

0.5

1   5   10   50   100   500   0.1   0.5   1

PPM   ‰

As
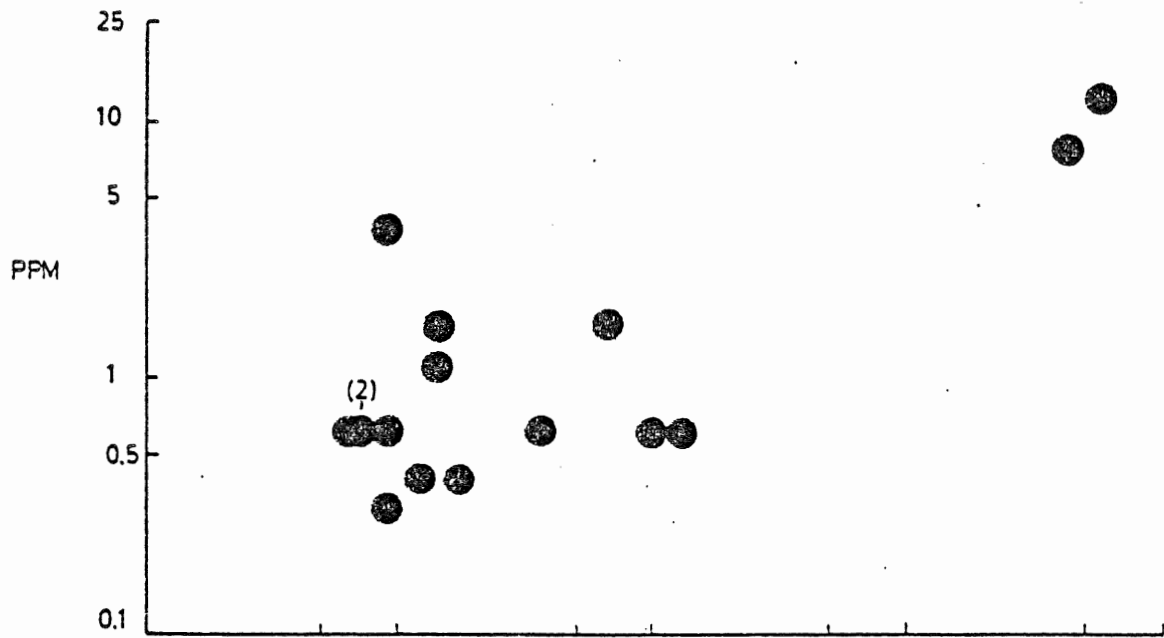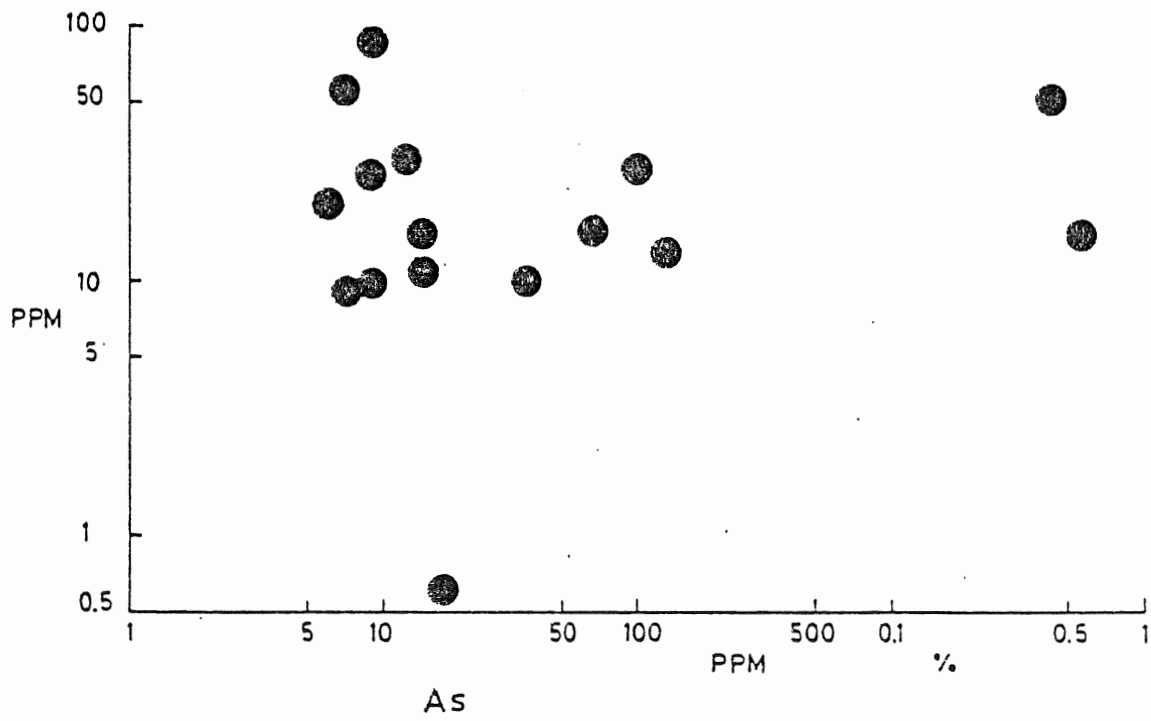
Figure 5.10   Variation of Sn and Cu within
mineralized 'patches' and greisens,
and their respective adjacent
unmineralized zones. The sharp
decrease in both elements indicates
their restricted ranges in both
mineralization types.

■   Mineralized 'patch'

□   Barren sample adjacent 'patch'
       (cm to m distant)

▲   Greisen

△   Barren sample adjacent greisen
       (cm to m distant)
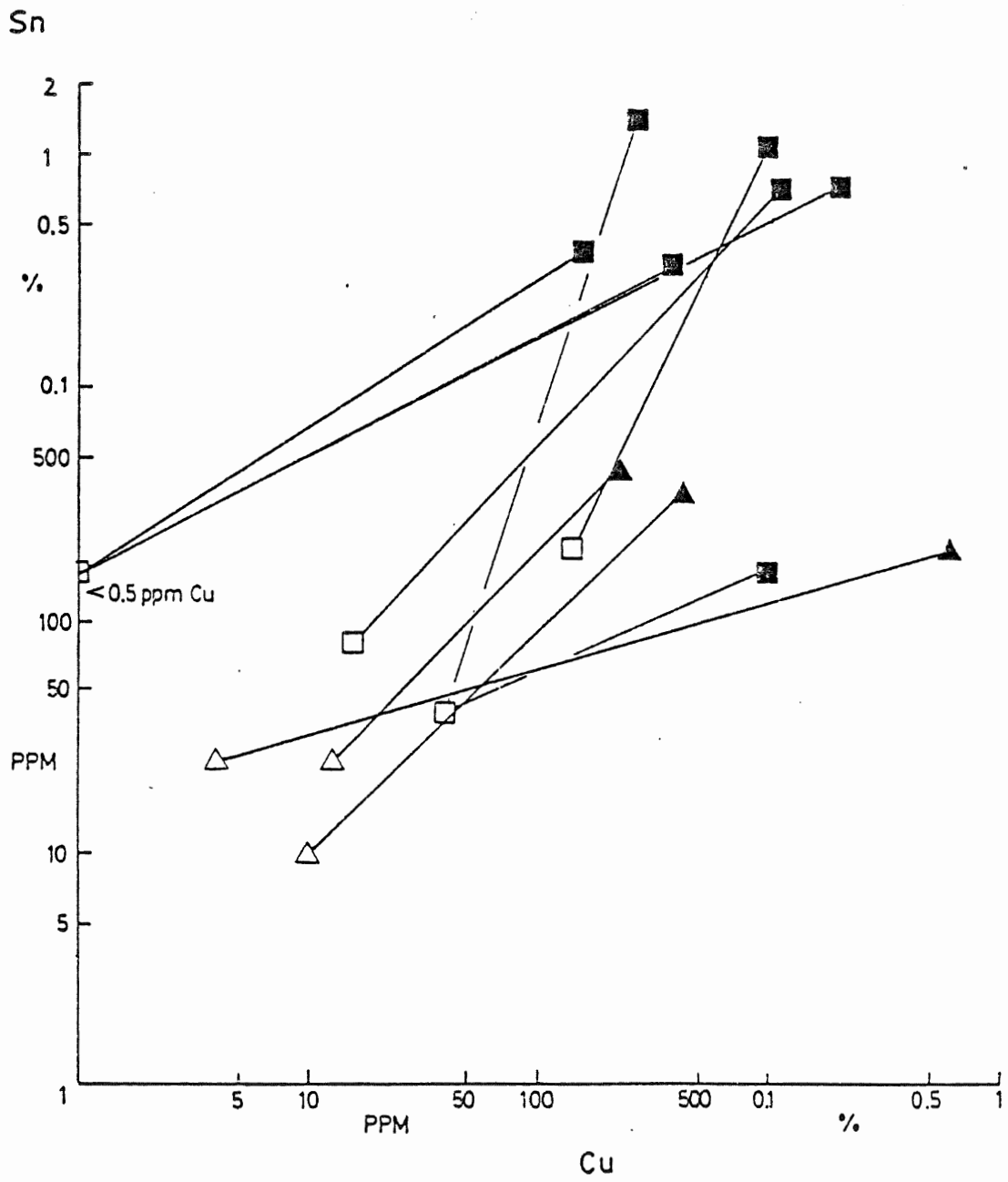
Figure 5.11   Variation of Sn and Bi within
                     mineralized 'patches' and their
                     adjacent unmineralized zones. There
                     is a sharp decrease in both elements
                     from mineralized to unmineralized
                     samples, indicating the restricted
                     extent of these elements.

                     ■   Mineralized 'patch'

                     □   Barren adjacent samples
                          (cm to m distant)
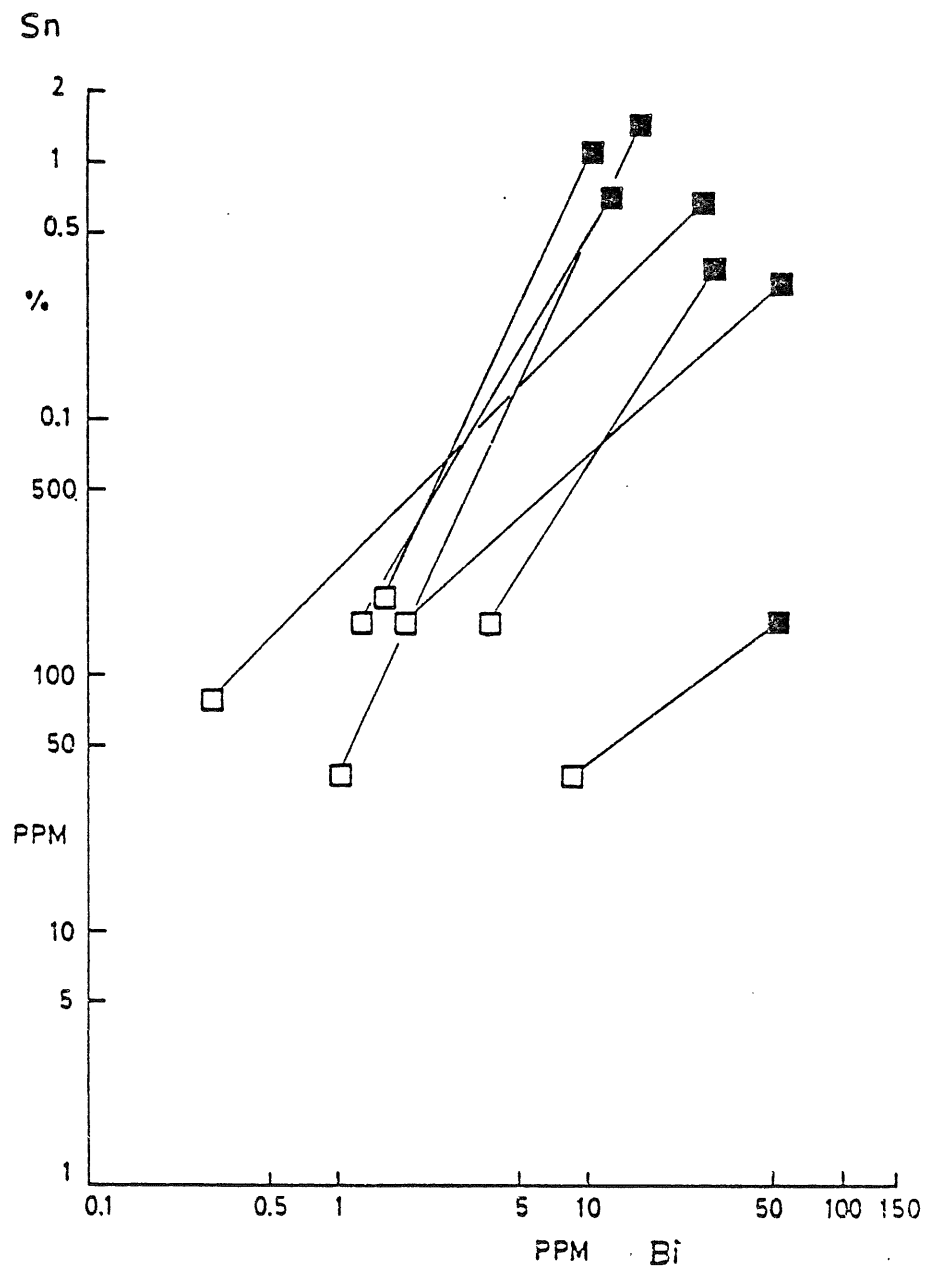
of use in a geochemical exploration program.

5.3.3 Relationship of Elements With Respect to Distance From the Pluton

Establishment of a trace element zonal pattern in any region can aid in subsequent geochemical exploration programs. Once position in any 'zone' is known, one can travel toward the ore-bearing zone with some degree of confidence.

Based on the present study, the mineralizing event(s) exerted no broad geochemical influence upon the country rock. Vein and stratabound mineralization are of limited lateral extent, with only a few cm of altered wallrock. Rarely, veinlets in the pluton have relatively wide greisen alteration haloes.

Because of the restricted nature of the mineralization, an attempt was made to investigate trace element distribution in mineralized samples at various distances from the pluton. Two cross-sections were made: one roughly follows a fold hinge from the metasediments to the pluton (A-A'); the second cuts regional foliation (B-B'). Sample point locations from each diamond drill hole were translated onto the plane of each cross-section. The cross-sections were arbitrarily divided into 'top', 'middle', and 'bottom' zones, representing depths of, respectively, 0 to 50, 50 to 100, and

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more than 100 metres. This was to look for trace element variation with depth. Several of these cross-sections are shown in Appendix 5. There appears to be little variation in trace element content in unmineralized metasedimentary samples, either with depth or with distance from the intrusion. Small variations in their concentrations may be due primarily to their lithology (pelitic vs. psammitic), so no definite conclusions can be made about geochemical dispersion in barren metasedimentary country rock. Relatively high contents of some trace elements in unmineralized samples occur close to or adjacent the pluton and appear caused by metalliferous veinlets (containing tungsten, fluorine, lithium and copper). Zinc decreases slightly with depth. Arsenic is ubiquitous, disseminated in the metasediments and within several stages of veins as arsenopyrite. Bismuth is erratic, and is related to both arsenic and tin.

Within the pluton, there is a slight decrease in trace element content in the interior. This may result from primary differentiation or the absence of metal-bearing veinlets found in the endocontact.

Few analyses were made of vein samples in areas of the cross-sections, so interpretation includes megascopic and microscopic presence of the metal-bearing minerals. There is a metal zonation within vein systems from the pluton into the

metasediments and this was discussed in a previous section of this chapter.

Trace element distribution within stratabound mineralized patches appears regular. There is little change with depth or distance from the pluton, except where cut by veinlets bearing tungsten, molybdenum, lithium and fluorine. Zinc content appears to increase with distance from the intrusion in two samples - possibly related to higher zinc content in distant parts of the vein system? Arsenic is erratic because of its common occurrence throughout the area.

5.3.4. Relationship of Elements With Respect to Other Variables

Trace element distribution may vary with other factors such as stratigraphy and secondary dispersion processes. Due to time and monetary constraints, it was not possible to perform a study of these types of element distribution.

It is conceivable trace element concentrations vary with depth or lateral extent in the sedimentary package. The geochemical study has been simplified by assuming there is little variation in trace element concentrations with depth or lateral extent.

Mafic dykes in the area do not change the trace element

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patterns in the host rock. Several samples adjacent the dykes were analysed and only the arsenic content in two monzogranite samples increased. Arsenopyrite was included in the biotite flakes — it is not known how this occurred, as arsenic contents in the dykes are low.

Chemical weathering of the country rock can disperse the trace elements at surface, along fracture systems, or through breccia produced by late shearing. Examination of some core proved difficult because of weathering effects from storage at surface — iron sulphides became oxidized. Clean core with fractures or breccia zones usually show little oxidation and it was assumed that little secondary dispersion took place; however as a precautionary measure these cores were not sampled. Some mineralized patches show elongate, 'shreddy'-textured sulphides, as if they had been stretched out by later movement, possibly the late-stage shearing event. It does not appear these chlorite- and sulphide-rich zones fractured cleanly with a minimum of rock powder ('gouge') to permit movement of fluids to disperse any elements. Other, more brittle, barren psammitic layers are well brecciated with later infillings by calcite, quartz and minor sulphides; a restricted bleached zone and rarely, a stockwork of veinlets ('crackle breccia') surrounds this breccia. Dispersion of elements appears limited.

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Figure 5.12   Pseudo-three-dimensional sections
                       of two mineralized area with tin
                       concentrations of sampled core
                       (in ppm except where noted). See
                       Fig. 5.1 for drill hole locations.

          A.   Intersecting drill hole grid

               ▓ Mineralized 'patch'

               + Unmineralized core

               ⊕ Mineralized vein

               adj -unmineralized sample
                       adjacent mineralization

               78-12 -diamond drill hole

               Boxes with two numbers indicate a
               mineralized 'patch'(higher value)
               with an adjacent sample. Inset
               depicts general bedding and
               crenulation(~) orientation.

          B.   Parallel drill hole grid
               Same symbols as above, plus

               Sn -relatively high amount of
                       mineral containing this metal

               sn -relatively low amount of
                       mineral containing this metal

               •   sample location described but not
                    geochemically analysed

               •.ʼ general bedding orientation
               •

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N

77-06

cu

+60

77-04

Zn Pb
(As Cu) Pb Sb Ag (500)

+25

77-07   77-05

+50

Sn W Cu Pb Bi
(0.68%

80)

40 + Sn W Cu As Sb
Bi

77-08

Sn W Cu Zn Bi (0.58%)

Sn Cu As Pb Sb Bi (300)

120

(160)

Sn w Cu As (0.15%)

cu
+120 (adj min'n)

w 12

0m

50

100

150

200

0   50   100

m

0   50   100

m

0   50   100
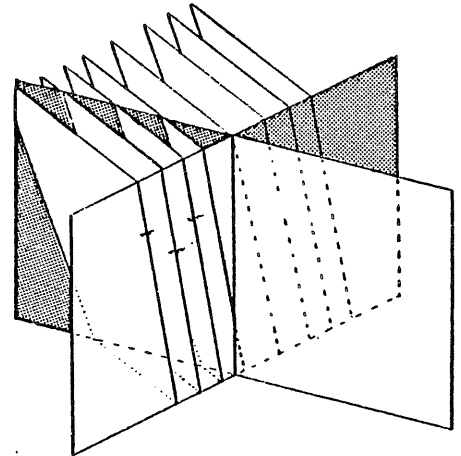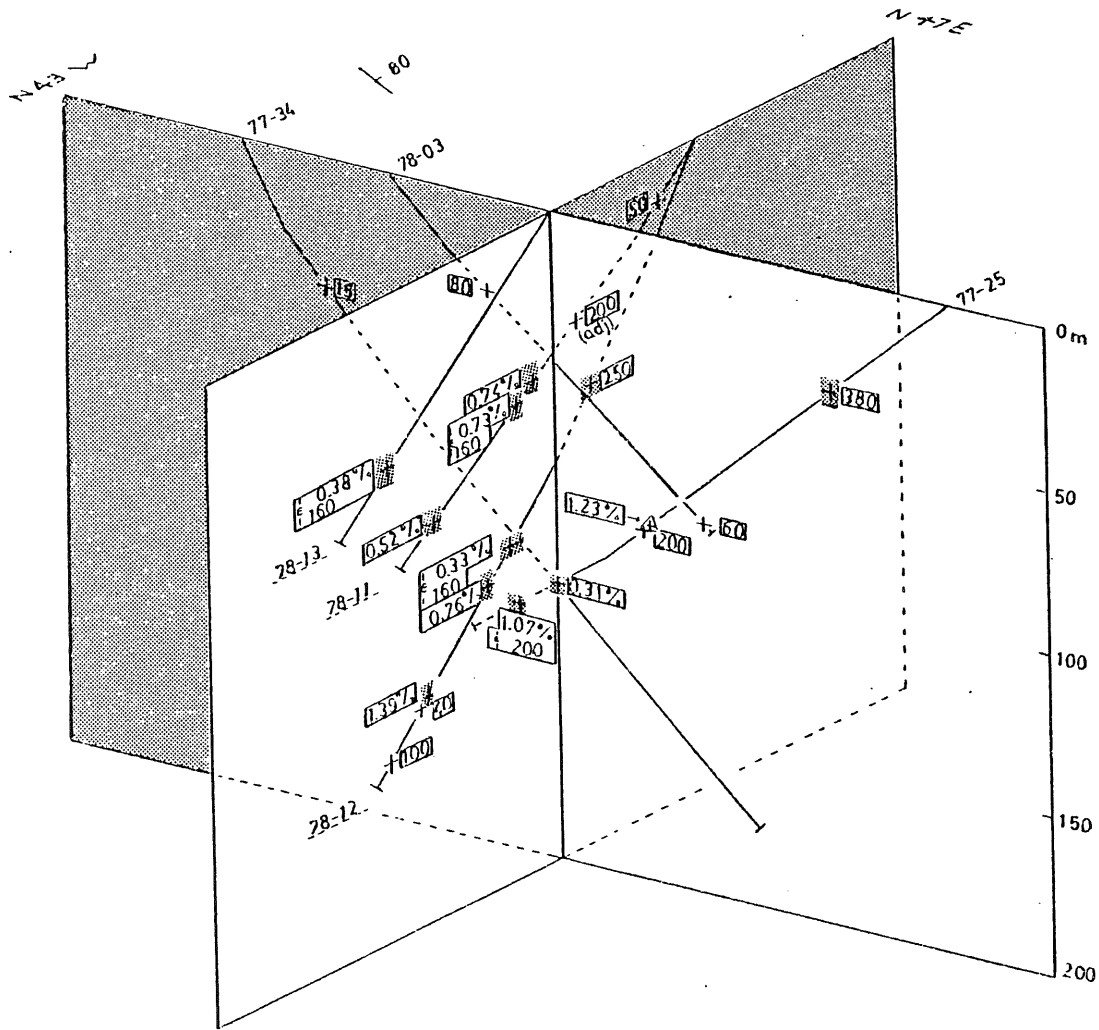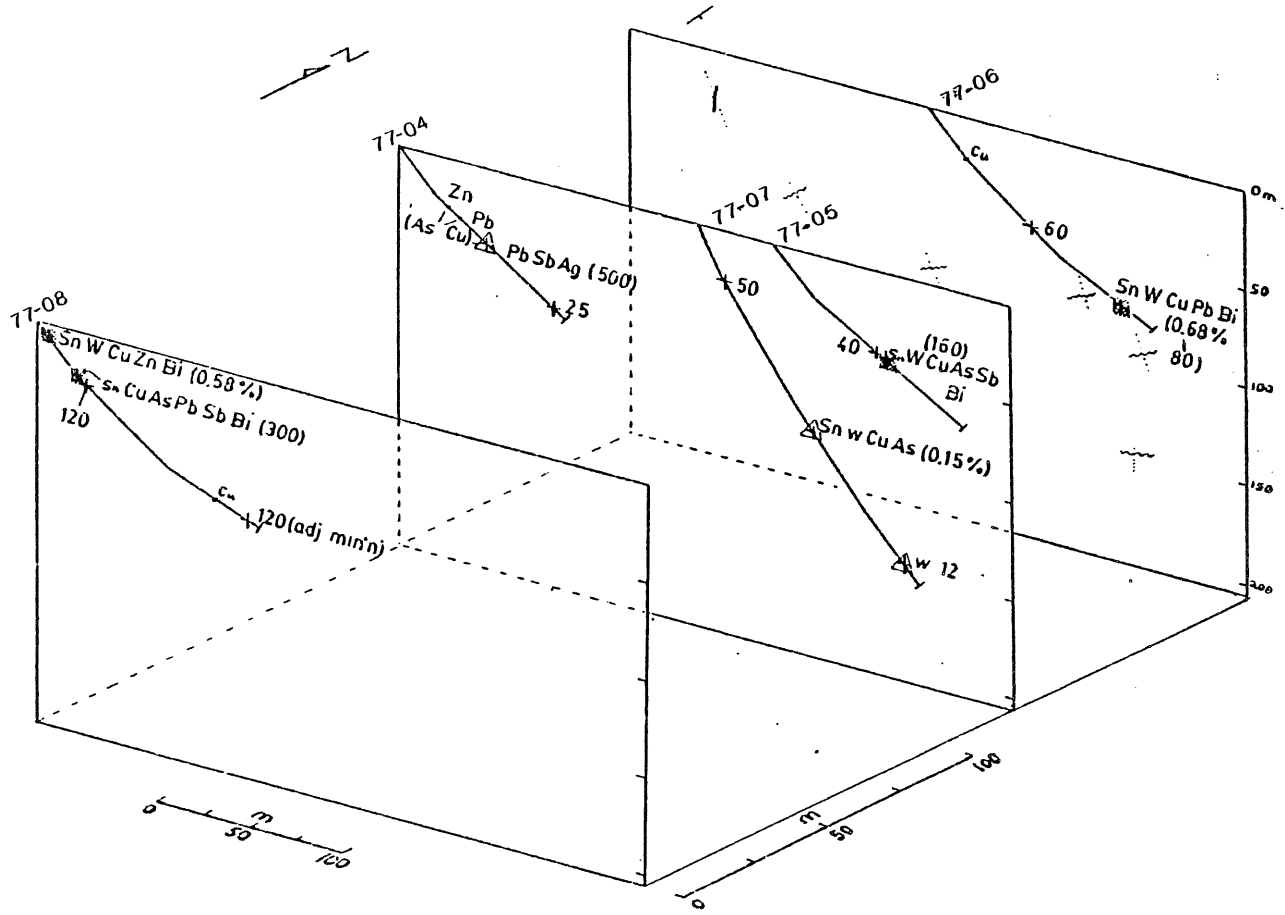
5.4 Summary

A group of barren and mineralized diamond drill core was analysed for 13 trace elements. Chlorine analysis was disappointing as most were below the detection limit (50 ppm). Boron analyses were not much use as the values were multiples of 10 and 25; however they proved useful in the mineralized samples, as all values were below the detection limit (10 pmm).

Analytical control was erratic: precision was adequate, but accuracy was not. The analyses may be useful for comparisons within the sample group, but are not to be considered 'true' values.

Background values between pelitic and psammitic samples are similar for most trace elements, with a few exceptions (Sn, Cu, Zn, and Bi). This may be due to primary sedimentologic factors. Element contents are similar to or lower than the average values found in Cornish tin-bearing metasediments, and the clarkes of shale and sandstone (Table 5.1). Trace element background values of plutonic samples are lower than those usually associated with 'specialized', tin-bearing granitoids. Accordingly, the Wedgeport pluton is not considered a major tin-bearing intrusion.

Alteration haloes around mineralization are limited (wallrock pattern of Hawkes, in Levinson,1974) and therefore lithogeochemical exploration is of little use in terms of

discovering trace element haloes. However, there is a metal zonation within the main-stage vein system, from the pluton, outwards. Accurate determination of the stage of a vein and its mineralogy may aid in tracing the more economic members of the system.

Table 5.1   SUMMARY OF LITHOGEOCHEMICAL SURVEY

ELEMENT	Meta-pelitic Samples (n=23)	Meta-psammitic Samples (n=51)	Monzogranite (n=25)

Sn

Meta-pelitic Samples (n=23)

2 Populations:

Anomalous(>100 ppm)
  All known mineralized
  samples

Background(<100 ppm)
  All known unmineralized
  samples

No significant differences
in background [Sn] between
meta-argillite and carbona-
ceous meta-argillite.
In mineralized patches a
positive correlation exists
among Sn, Cu, and Bi; all
B values at or below
detection limit(10 ppm).
Relationship with other
elements less clear.
Background and threshold
are lower than those of
meta-psammites. May be due
to small data set or to
primary sedimentological
differences, i.e., Sn as
cassiterite more likely
occurs in psammitic layers
(rarely in pelitic scours).

Meta-psammitic Samples (n=51)

3 Populations:

Anomalous(>180 ppm)
  Mineralized samples

Intermediate (<180 >128 ppm)
  Mineralized samples and
  samples adjacent mineral-
  ization

Background(<128 ppm)
  All known unmineralized
  samples, plus several sam-
  ples adjacent mineralization;
  1 in a mineralized patch;
  1 in a vein.

No significant differences in
background [Sn] among meta-
psammitic lithologies(wacke +/-
biotite, feldspar, carbonate).
In mineralized patches a +ve
correlation exists between
Sn and Cu;less so with W,Sb,
and Bi; most B values at or
below detection limit.
In veins a +ve correlation
exists between Sn and Cu; a
-ve correlation between Sn
and As,Pb,Sb and Zn. Other
relationships less clear.

Monzogranite (n=25)

3 Populations:

Anomalous(>48 ppm)
  Greisens; 1 sample with
  kaolinite alt'n; 1
  sheared sample

Intermediate(<48 >15 ppm)
  Samples adjacent
  greisens, cut by
  several vein stages;
  unmineralized samples

Background(< 15 ppm)
  Unmineralized samples
  and 1 adjacent greisen

No apparent distinction
in [Sn] based on presence
or absence of phenocrysts.
Endocontact background
samples have a higher
range(7-35 ppm) than
those in the interior
of the pluton(3-10 ppm).
May be due to: small data
set; presence of a myriad
of Sn-bearing veinlets
in endocontact; primary
differentiation of magma.

Table 5.1 cont'd.

ELEMENT	Meta-pelite	Meta-psammite	Monzogranite

W

Meta-pelite:

1 Population:usually
assume upper 2 1/2%
anomalous until
proven otherwise
(Sinclair,1974), i.e.,
60 ppm threshold.

Similar values occur
in min'd and barren
meta-pelites(2-23 ppm);
slightly higher [W]
in carbonaceous and
min'd meta-argillites.
Higher [W] near pluton.

Meta-psammite:

2 Populations:

Anomalous(>19 ppm)
10 min'd patches
and veins; 1 °
sample adjacent
min'n

Background(<19 ppm)
Mostly unmin'd
(22/40 samples);
11/40 adjacent
min'n;7/40 are min'd
patches and veins

Slightly higher values
occur in min'd patches
and zones adjacent
min'n. Higher values
occur in samples near
pluton-possibly cut
by scheelite-
bearing veinlets.

Monzogranite:

2 Populations:

Anomalous(>65 ppm)
1 greisen and all
samples with non-
greisen veining

Background(<65 ppm)
All other samples,
including 3/4 greisens

High W values appear rela-
ted to non-greisen schee-
lite bearing quartz vein-
lets. Similar values exist
for different phenocryst
concentrations;[W] increases
from non-phenocrystic
to phenocrystic samples.
W values in greisen slightly
higher than unmin'd samples;
23-38 ppm vs. <1-24 ppm
respectively.Endocontact
samples have higher values
than interior samples;
8-24 ppm vs.<1-9 ppm,
respectively.

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Table 5.1 cont'd.

| ELEMENT | Meta-pelite | Meta-psammite | Monzogranite |

Mo

| Mo | 2 Populations:

Anomalous(>5 ppm)
3 unmin'd carbona-
ceous meta-argil-
lites near the
pluton (1 is adja-
cent a mafic dyke)

Background(<5 ppm)
16/23 samples below
detection limit
(0.5 ppm)including
min'd patches and
vein; 4/23 are <5
and >0.5 ppm(3 are
min'd patches;1 is
barren)

In population partiti-
tioning, value of 0.05
ppm(1 order of magnitude
lower) was used for all
values below detection
limit, producing an
interpolated background
of 0.4 ppm. Use this
value with caution.
Mo content appears
related to pluton
proximaty. | 1 Population:
Most high Mo values
associated with veins,
either near pluton
with molybdenite
+/- scheelite, or
containing arsenopy-
rite and other sul-
phides(?). [Mo] in
min'd patches erratic
(<0.5-2.5 ppm) and
cannot be correlated
with [Sn]. 35/51 values
< 0.5 ppm, so 0.05
ppm was used in popu-
lation partitioning,
giving an interpolated
background of 0.4 ppm.
Use this value with
caution. Mo content
appears related to
pluton proximaty. | 2 Populations:

Anomalous(>32 ppm)
In samples cut by vein-
lets containing molyb-
denite +/- scheelite

Background(<32 ppm)
In unmin'd, altered,
and greisenized
samples.

Most low values are from
interior pluton samples;
endocontact samples are
higher in [Mo] and are
also cut by stockwork
hair veinlets bearing
molybenite +/- scheelite.
Greisen Mo values are
ambiguous-appear to
depend on presence of
non-greisen veinlets. |

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Table 5.1 cont'd.

ELEMENT	Meta-pelite	Meta-psammite	Monzogranite

===

As 3 Populations:

Anomalous(>100 ppm)
1 vein; 2 min'd patches;
1 barren sample with
disseminated arsenopyrite;
1 barren sample with pre-
crenulation arsenopyrite
veinlet.

Intermediate(<100 >16 ppm)
1 min'd patch; 3 barren
samples

Background(<16 ppm)
5 min'd patches; 9 barren
samples

Arsenic has erratic distri-
bution in metasediments,
patches and veins. Have to
know its stage in paragenetic
sequence before using As in
exploration.

2 Populations:

Anomalous(>160 ppm)
6 veins; 1 min'd
patch and 1 barren
sample with dissem-
inated arsenopyrite.

Background(<160 ppm)
Includes barren and
mineralized samples,
samples adjacent min'n
and 1 vein.

Appears to be an anti-
pathetic relationship
between Sn and As in
veins and patches.
Those veins with [As]
>7000 ppm have [Sn]
<500 ppm and are at
shallower depths
farther from the
pluton. Low [As] (<220
ppm)in veins have high
[Sn](>1500 ppm) and
are found closer to the
pluton at deeper levels.

May use Sn-As content in
veins as exploration guide.

2 Populations:

Anomalous(>70 ppm)
3 samples(barren;
greisen; kaolinite
alt'n) cut by
arsenopyrite-bearing
hair veinlets; 2 sam-
ples adjacent mafic
dykes contain biotite
with inclusions of
arsenopyrite(?).

Background(<70 ppm)
All other samples,
both barren and
mineralized;
actually all
<30 ppm.

Arsenic content ap-
pears related to syn-
& post-greisen
veining.

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Table 5.1 cont'd.

ELEMENT	Meta-pelite	Meta-psammite	Monzogranite

Cu	2 Populations:	2 Populations:	2 Populations:
	Anomalous(>250 ppm) All mineralized patches, 1 vein and 1 carbonaceous meta- argillite adjacent a mafic dyke and the pluton.	Anomalous(>365 ppm) 8 mineralized patches; 3 'high Sn', 1 'high As' veins.	Anomalous(>135 ppm) 3 greisens
	Background(<250 ppm) All barren samples; 1 carbonaceous meta- argillite (190 ppm) is near pluton and and contains chalco- pyrite within pyrrho- tite.	Background(<365 ppm) All barren samples; samples adjacent min- eralization; 3 mineral- ized patches and 3 'high As' veins.	Background(<135 ppm) All other samples, including 1 greisen
	There exists a definite gap between mineralized and unmineralized samples. Get interested in values >125 ppm.	No major differences be- tween unmineralized samples and those adjacent mineral- ization. In adjacent miner- alized samples there is a gap between very low values (<0.5 ppm) and those above background(possible leaching effect?).	Those samples adjacent to greisens, are greisen- ized, cut by non-greisen veinlets and are sheared, have high Cu values higher than the background. Interior pluton samples are on average lower than the endocontact samples;<0.5- 5.5 ppm vs. 1.5-35 ppm, respectively. May be due to ubiquity of veining in the endocontact. Both greisen and non-greisen vein samples have erratic Cu values, possibly because of low sample size.
		High [Cu] (<150 >70 ppm) may be due to chalcopyrite or Cu solid solution in the ubiqui- tous pyrrhotite blebs. Good correlation of Sn and Cu, but restricted range of Cu in patches precludes its use as a pathfinder. Try veins.	

Table 5.1 cont'd.

ELEMENT	Meta-pelite	Meta-psammite	Monzogranite

Pb   2 Populations:

Meta-pelite

2 Populations:

Anomalous(>50 ppm)
  2 mineralized patches;
  1 barren sample

Background(<50 ppm)
  All other samples

Pb distribution erratic;
gives a poor population
split.Higher values
(>15 ppm) associated
with mineralized patches,
1 vein,1 pre-crenulation
arsenopyrite veinlet and
1 barren sample. Pb
usually in galena, often
associated with arseno-
pyrite.

Meta-psammite

2 Populations:

Anomalous(>120 ppm)
  4 'high As-low Sn'
  veins, 1 barren
  sample

Background(<120 ppm)
  All other samples

Most values <23 ppm
(39/51 samples);higher
values(<90 >23 ppm)
include 3 mineralized
patches, 1 'high-Sn
low-As' vein and 3
barren samples(1 near
pluton with rare mo-
lybdenite on fracture
surface). 2 barren
samples from 1 drill
hole(78-29) contains
relatively high [Pb]
(40 & 170 ppm);not
known why. Not much
difference between
mineralized and un-
mineralized samples.
In veins, there is a
+ve correlation be-
tween Pb and As; a
-ve correlation
between Pb and Sn.

Monzogranite

2 Populations:

Anomalous(>15.5 ppm)
  1 sample adjacent a
  greisen; 1 cut by
  non-greisen veining;
  1 barren sample

Background(<15.5 ppm)
  All other samples

Pb values are erratic
with respect to litho-
logic types and miner-
alization; higher values
appear related to post-
greisen veinlets(contain-
ing arsenopyrite, molyb-
denite and scheelite).

Table 5.1 cont'd.

ELEMENT	Meta-pelite	Meta-psammite	Monzogranite
Zn	2 Populations:	2 Populations:	1 Population:
	Anomalous(>275 ppm) 3 mineralized patches and 1 vein	Anomalous(>330 ppm) 3 veins of 'high As-low Sn' type; 1 mineralized patch; 1 sample adjacent mineralization.	Most values(21/25) <41 ppm. 2 anomalous values exist in greisen zones(140 & 2900 ppm)
	Background(<275 ppm) All other samples		
		Background(<330 ppm) All other samples	Little difference among different granitold types. [Zn] in greisen erratic-may be due to cross-cutting post-greisen veinlets.
	Little difference among meta-argillites, carbonaceous meta-argillites and mineralized patches: Meta-argillite - narrow cluster of values (79-130 ppm) Carbonaceous meta-argillite - wider range of values (41-260 ppm) Mineralized patches-(54-680 ppm and 14.6%) Vein('high Sn-low As' type)- 1500 ppm	Little difference among various psammitic types or between mineralized and barren samples. Veins high in As have high Zn contents.	

Table 5.1 cont'd.

ELEMENT	Meta-pelite	Meta-psammite	Monzogranite

Sb   2 Populations:

Anomalous(>2.0 ppm)
   1 mineralized patch;
   2 carbonaceous meta-
   argillites with pre-
   crenulation arseno-
   pyrite; 1 meta-argil-
   lite

Background(<2.0 ppm)
   All other sample.17/23
   samples <1.0 ppm

[Sb] appears tied to
[As]; those samples with
arsenopyrite have higher
Sb contents.

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2 Populations:

Anomalous(>1.45 ppm)
   4 veins of 'high
   As-low Sn' type; 1
   'high Sn' type; 4
   mineralized patches.

Background(<1.45 ppm)
   All other samples.
   25/51 samples
   <0.5 ppm

No major observable
differences among
various psammitic
types; both wacke
and calcareous wacke
values are less than
background(<0.44 ppm)-
may be due to low sam-
ple size.High [Sb] in
mineralized patches
and veins tied to [As].

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2 Populations:

Anomalous(>0.6 ppm)
   1 greisen(with ar-
   senopyrite-bearing
   veinlet); 1 sample
   with kaolinite
   alteration; 2 with
   non-greisen veining;
   2 samples adjacent
   mafic dyke(with
   arsenopyrite in
   biotite flakes)

Background(<0.6 ppm)
   All other samples

Slightly phenocry-
stic samples have
lower Sb contents
than other unminer-
alized samples;not
known why. High [Sb]
tied to [As].

Table   5.1 cont'd.

ELEMENT	Meta-pelite	Meta-psammite	Monzogranite
Bi	2 Populations: Anomalous(>3.5 ppm) All mineralized patches & the Sn- rich vein Background(<3.5 ppm) All unmineralized samples There is a definite difference between mineralized and barren samples.	1 Population: Most(7/8) mineralized samples have higher Bi contents(>10 ppm) than the other samples. No observable differ- ences among various psammitic types or between unmineralized & adjacent mineralized samples(restricted range).[Bi] erratic with respect to 'high As' & 'high-Sn' type veins.	1 Population: Lower Bi content in non-phenocry- stic samples (interior pluton). Tan altered sample below detection limit(<0.1 ppm). Other samples have wide spreads of values. Bi does not appear related to Sn miner- alization as in the metasediments.

Table 5.1 cont'd.

ELEMENT	Meta-pelite	Meta-psammite	Monzogranite

Li — **Meta-pelite:**

2 Populations:
(Possibly 1)

Anomalous(>100 ppm)
    1 carbonaceous meta-
    argillite adjacent
    pluton

Background(<100 ppm)
    Rest of data set

Little difference
between pelitic types.
Tightly grouped(31-
70 ppm).
Exceptions:sample with
pre-crenulation arseno-
pyrite veinlet(89 ppm);
1 sample adjacent mafic
dyke(13 ppm). Mineralized
patches - values spread
out(8-59 ppm)

Meta-psammite:

1 Population:
Most values (35/51)
<60 ppm. High [Li]
usually occurs near
the pluton. One high
value(100 ppm) found
in a 'barren' sample
in a DDH with other
high trace element
contents(78-29).
Primary cause? Little
difference among
psammitic types, be
they barren or
mineralized.

Monzogranite:

2 Populations:

Anomalous(>80 ppm)
    3 greisens; 1 kao-
    linite alteration;
    2 non-phenocrystic
    barren samples
    from the interior
    pluton(78-31)(?).

Background(<80 ppm)
    Rest of data set.
    10/25 samples
    <49 ppm.

Restricted range of
Li in greisens.
Little difference
among non-greisen
samples;usually in
range of 26-80 ppm.

Table 5.1 cont'd.

ELEMENT	Meta-pelite	Meta-psammite	Monzogranite

F

Meta-pelite

1 Population:

Carbonaceous meta-
argillites have
wider spread(100-
820 ppm)than meta-
argillites(320-
630 ppm).
Mineralized patches
not different(360-
660 ppm)except for
2 samples(190 &
200 ppm); not
known why.
Highest value(820
ppm)found in barren
sample adjacent
pluton(80-01).

Meta-psammite

2 Populations:

Anomalous(>1000 ppm)
4 barren samples
and 1 mineralized
patch, all adjacent
the pluton(79-05;
80-01); 2 'high
As' type veins.

Background(<1000 ppm)
Rest of data set.
41/51 samples <760
ppm. Little differ-
ence among various
psammitic types or
mineralized patches.
[F] in veins not
clear cut: 3/4 'high
As' > 'high Sn'
types; 670-1500 ppm
vs. 280-530 ppm
respectively.

Monzogranite

2 Populations:

Anomalous(>1550 ppm)
All 4 greisens

Background(<1550 ppm)
Rest of data set

Slight differences
among various types
of non-greisen
samples. Interior
pluton samples have
a slightly lower
range than endo-
contact samples.
Greisens have
'classic' high F
contents, but are
of restricted range.

Table 5.1 cont'd.

ELEMENT

B   Population partitioning not performed as all values
             are multiples of 10 or 25(10, 25, 50, 75, 100 and
             150 ppm). This does not appear 'natural'.Little
             difference among meta-pelitic and meta-psammitic
             lithologies, except in mineralized patches of both
             rock types - at or below detection limit of 10 ppm.
             Due to leaching?

Cl   Not performed as most values below detection limit
             of 50 ppm.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS FOR

FURTHER WORK AND EXPLORATION

6.1 Conclusions

Mineral and geochemical study of the Wedgeport pluton
and adjacent metasedimentary host rocks has provided the
following impressions concerning the genesis of tin
mineralization in the area.

1. Tin as cassiterite, occurs in several habits and
mineral associations, reflecting variable conditions of its
formation. It is a rare detrital mineral within
Cambro-Ordovician Meguma metasediments; it rarely occurs
within greisen veins in the pluton; it occurs as a minor to
common mineral within sulphide veinlets and stratiform
sulphide replacement bodies in the metasediments.

2. Partial melting of carbonaceous, cassiterite-bearing
metasediments produced a low fO_2, ilmenite-series melt with
divalent tin(and other lithophile elements) concentrated
within a later evolved aqueous phase(s). Tin may have been
transported as chloride and fluoride complexes. Fracturing
of the pluton margin provided a means of escape for this
phase. Healing of the fractures by mineral precipitation and
refracturing by later aqueous phases resulted in several

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generations of veinlets. Sulphide-cassiterite precipitation
occurred in a 'middle' stage of vein formation, after barren
quartz veinlets and before quartz-kaolinite veinlets and
shears. These ore-bearing fluids caused limited
greisenization within the pluton margin. They then travelled
through fractures near or along an anticlinal fold hinge;
sulphides and cassiterite precipitated in veins and replaced
calcareous layers within the metasediments. Apparently there
was insufficient initial water in the melt to generate
economically significant amounts of ore-bearing fluid.

3. Mineralization is found in a zonal sequence away from
the pluton, reflecting the changing physico-chemical
conditions of the fluid(s) as it travelled through, and
reacted with the metasediments(e.g. P, T, fO_2, fS_2, pH, Eh,
wallrock chemistry).

4. Alteration effects associated with mineralization
within both the pluton and metasediments are restricted - no
broad geochemical or mineralogical halo is observed.

6.2 Possible Guides for Tin Exploration

1. Ilmenite series granitoids appear associated with tin
deposits (Ishihara,1981) and those containing biotite or
biotite-muscovite may have contained sufficient water to
evolve a separate aqueous phase of adequate volume to carry
ore metals. The characteristics used to recognize such

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intrusions are (Ishihara,1981):

- magnetic susceptibility below $1*10^{-4}$ emu/g

- low bulk Fe_2O_3/FeO ratio

- magnetite and ilmenite content < 1 vol. %

- contains accessory pyrrhotite(look for limonite staining on
  weathered surfaces)

Possibly look for these intrusions in carbonaceous sediments,
which were supposedly assimilated to produce such melts.

2. The Wedgeport pluton and granitic bodies associated
with known mineralization (e.g. East Kemptville deposit in
the Davis Lake pluton; New Ross-Vaughan Complex in the South
Mountain batholith) contain high total radioactivity and high
thorium values (Chatterjee and Muecke,1982). Airborne gamma
ray spectrometric measurements may serve to locate potential
ore-bearing intrusions (Yeates et al., 1982).

3. Mineralization within the study area is structurally
controlled - in fracture systems and replacement layers
within a fold hinge. Such axial structures may therefore be
of interest in the location of this type of mineralization.
Tin mineralization at the East Kemptville deposit is
controlled along an irregularly-shaped contact ('inflection
contact') of the Davis Lake pluton with the Goldenville
metasediments (Richardson et al.,1982). In European and some
Tasmanian deposits, mineralization is found in apical zones
('cupolas') of an intrusion, in contact with impermeable

country rock. Therefore, it would be of benefit to investigate any granite-country rock contacts.

4. Some of the tin mineralization occurs in sulphide-cassiterite replacement bodies of calcareous metasediments. It may be of interest to look for such beds adjacent relevant plutons in structurally prepared ground(e.g. fold hinges, intrusive contacts).

5. Pyrrhotite is the major sulphide in veins and replacement layers. It gives a good magnetic and electrical response and could be of use in geophysical exploration. Unfortunately, this mineral also occurs in tin-barren graphitic layers.

6. If mineralized veins and replacement layers have been found, it is possible to use the mineralogical and geochemical zonation of the vein systems to locate the tin-bearing sections.

6.3 Recommendations for Further Work

Much of the work accomplished within this thesis has been of a qualitative nature. A more quantitative investigation of the mineralization in this area would serve to define the parameters of ore genesis more rigorously. These include:

1. Fluid inclusion studies of the different vein stages

to obtain estimates of gross salinities and filling temperatures; possibly use the latest techniques (lasar?) to obtain fluid chemistry.

2. Age dating of unaltered and mineralized samples of the pluton to obtain better estimates of time of emplacement and time of mineralization. Studies of various mineralized plutons (Reynolds and Zentilli, in prep.) point to a Hercynian mineralizing event, which may have implications in future mineral exploration. Possibly dating of the lead in galena-bearing veins would further tighten age of mineralization.

3. A search for coexisting sulphide minerals in vein and replacement bodies to obtain estimates of temperatures of equilibrium.

4. A study of sulphur isotopes in veins and in mineralized and unmineralized layers; are there any differences?

5. A study of the tin concentrations in the ferromagnesian minerals of the pluton. Are there appreciable amounts in these minerals, as is indicated in other plutons (e.g. Nigerian Younger Granite, Erzgebirge plutons)? The microprobe can only analyse for elements in concentrations as low as 500 ppm, which is too high for tin in such minerals (more in the 10's ppm range).

6. A study of the reactions between ore-bearing fluids and wallrocks to get a better understanding of mass exchange.

7. A study of the 'rusty shears' within the pluton. They apparently contain radioactive minerals (Cullen pers. comm.,1982) and are the probable cause of the high values obtained in airborne gamma ray spectrometric measurements (Chatterjee and Muecke,1982). They are therefore an integral part of the evolution of mineralization in the study area.

APPENDIX I

SAMPLE PREPARATION

1. Remove surface drill marks and weathering effects by drill-mounted garnet paper. Blow away ensuing dust. Drill core should be of a lighter hue, with a clean smooth surface.

2. Split core into approximately 1 cm cubes. Discard any pieces with saw marks or marker labels. Clean the splitter with brush and air hose.

3. Reduce the sample further into mm-sized pieces by a ceramic jaw crusher. Preclean crusher with a portion of the sample and discard the crushed result. After crushing clean with nylon brush and air hose.

4a. Grind crushed sample in a ceramic shatterbox. Preclean sample holder with an aliquot(about 10 ml) of the sample. Run the machine for about 1 minute. Discard the powder and blow out holder with the air hose.

4b. Place a larger aliquot(about 30 ml) of the sample in the holder and run for about 8 minutes. Check resul-

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tant powder - if small granules are evident

(i.e. > 0.5 mm), sample must be ground a further 5

minutes. If in doubt, sieve a portion of powder to

check its size. For ease of acid digestion, sample

powders were -200 mesh.

4c. Transfer powder onto a clean folded sheet of paper.

Pour powder from sheet into a labelled 40 ml

polyethylene vial.

4d. Clean holder after use by these steps:

    i. Air blow holder.

   ii. Run an aliquot (about 10 ml) of silica gel for

       about 1 minute and discard powder. Air blow again.

  iii. Wash out shatter box - 5 rinses with tap water

                    - 1 rinse with distilled water

                    - 1 rinse with alcohol

   iv. Air blow dry inside and outside of holder. The

       steel rim will rust if left damp and can cause

       sample contamination.

Sources of Contamination:

1. Dust is a major problem during sample preparation and

may result in appreciable contamination. Rigorous

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cleaning between each stage may decrease this effect.

2. Remnant marker, drill and saw marks; remnant powder and chipped material from splitter jaws, jaw crusher and shatter box.

3. Excessive grinding may oxidize ferrous iron, producing decreased FeO contents (Jeffery and Hutchison, 1981).

APPENDIX II

ANALYTICAL METHODS

Powders of 122 samples were analysed for 13 trace elements by various methods (Table II.1) by X-Ray Assay Laboratories Limited in Toronto, Ontario. Of these, 13 were duplicate samples and 6 were reference samples. Powders of 30 additional samples were sent for whole rock analyses by XRF, and of these, 3 were duplicates and 2 were reference samples.

The following outlines the analytical methods used by the laboratory (J.H. Opdebeeck, X-Ray Assay Laboratories, written communication,1982).

Tin Determination by Emission Spectroscopy(EMS)

Low concentrations of tin are determined using a 0.1g sample, mixed with graphite and burned in a direct current arc. The spectrum is photographically recorded and interpreted using a densitometer. For small samples with greater than 50 ppm tin, 0.1g of sample is fused with 0.7g of lithium metaborate ($LiBO_2$) in a graphite crucible, and the melt is dissolved in 5% HNO_3. The solution is run on a direct-current plasma emission spectrometer. Calibration in both setups is done on synthetic standards. Larger samples with values above 50 ppm are determined by x-ray fluorescence

Table II-1 Elements Analysed, Methods and Detection Limits

Element	Method*	Detection Limit (ppm except where noted)
Sn (ppm)	EMS	3.000
Sn (%)	XRF	0.010%
W	NA	1.000
Mo	DCP	0.500
As	NA	1.000
Cu (ppm)	DCP	0.500
Cu (%)	XRF	0.010%
Pb (ppm)	DCP	2.000
Pb (%)	XRF	0.010%
Zn (ppm)	DCP	0.500
Zn (%)	XRF	0.010
Sb	NA	0.200
Bi	FAA	0.100
Li	AA	1.000
F	SIE	100.000
B	DCP	10.000
Cl	XRF	50.000
FeO (%)	Wet Chemical	0.100%
WRG-Major Oxides (%)	XRF	0.010%
WRG-Minor Elements (Cr,Rb,Sr,Zr)	XRF	10.000

*EMS - Emission Spectroscopy

XRF - Wavelength Dispersive X-ray Fluorescence Spectrometry

NA - Neutron Activation

DCP - Direct-Current Plasma Emission Spectrometry

FAA - Flameless Atomic Absorption Spectrometry

AA - Atomic Absorption Spectrometry

SIE - Selective Ion Electrode.

spectrometry using a Philips PW 1410 sequential x-ray
fluorescence spectrometer interfaced to a Digital PDP 11/40
computer.

Tungsten, Arsenic and Antimony Determination by Neutron Activation(NA)

Powders are irradiated in a high density neutron flux,
producing isotopes of elements contained in the sample. A
multi-channel gamma spectometer determines element
concentrations.

Molybdenum, Copper, Lead and Zinc Determination by Direct-Current Plasma Emission Spectrometry(DCP)

Samples are prepared by the acid soluble procedure.
Sample powders (0.25g) are digested with 2 ml of HNO_3 for 1/2
hour in a water bath, then 1 ml of HCl is added and digestion
continues a further 2 1/2 hours; test tubes are agitated at
regular intervals. Samples are made up to volume with a
lithium buffer. A high temperature argon plasma is used to
excite the elements in solution and the spectrum is analysed
by a direct-current Spectrametrics plasma emission
spectrometer using an echelle grating interfaced to a
microprocessor. Higher values (in the percent range) are
analysed by the XRF method.

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Bismuth Determination by Flameless Atomic Absorption Spectrometry

Samples are prepared by the acid soluble procedure and solutions are run on an atomic absorption spectrometer where the flame has been replaced by a heated quartz tube. Bismuth hydride is formed using sodium borohydride and is emplaced within the furnace containing the quartz tube.

Lithium Determination by Atomic Absorption Spectrometry

Sample powders are digested by HF and H_2SO_4 (total metal digestion method) followed by HCl to redissolve any residue. Solutions are run through the atomic absorption spectrometer.

Fluorine Determination by Selective Ion Electrode

Sample powders (0.25g) are fused with NaOH in a nickel crucible for 15 minutes at $650°C$. The resultant solid is dissolved in an ammonium citrate buffer solution. A fluoride-selective ion electrode determines the fluoride concentration in solution. The electrodes are used in association with reference electrodes and the reference samples are run with every batch.

Boron Determination by Direct-Current Plasma Emission Spectrometry

Sample powders (0.05g) are fused with KOH in a nickel crucible and the resultant solid is dissolved in 5% HCl. The solution is run on a direct-current emission spectrometer.

Chlorine Determination by X-Ray Fluorescence Spectrometry

Sample powders (4g) are mixed with 4 g of sand and 2 binder pellets and are pressed into pellets. The analysis is performed on a sequential x-ray fluorescence spectrometer. Peak and background readings are taken using a germanium crystal.

Whole rock major and minor element determinations are performed by x-ray fluorescence spectrometry; FeO, by wet chemical methods.

The analyses are calibrated on synthetic standards and reference samples; in house standards and previously analysed samples are run as controls of the digestion procedures.

Rock Coding for Lithogeochemistry

Explanation

Major rock classification; in ⌉ _____ 111 _____ ⌈Average grainsize; in
this case, a metasediment ⌋   ↑   ⌊this case, medium silt-sized
                Type of metasediment;
       in this case, a graphitic argillite

I   METASEDIMENTARY ROCKS 100 SERIES

(a) Type

   10_ Argillite

   11_ Graphitic Argillite

   12_ Calcareous Argillite

   13_ Siltstone

   14_ Biotite Argillite

   15_ Wacke

   16_ Feldspathic Wacke

   17_ Calcareous Wackes (±Feldspar)

   18_ Biotite Feldspathic Wacke

   19_ Biotite Wacke

(b) Size

   1_0 Fine Silt (0.004-0.0156 mm)

   1_1 Medium Silt (0.0156-0.0312 mm)

   1_2 Coarse Silt (0.0312-0.0625 mm)

   1_3 Fine Sand (0.0625-0.25 mm)

   1_4 Medium Sand (0.25-0.5 mm)

   1_5 Coarse Sand (0.5-2.0 mm)

II VARIATIONS IN METASEDIMENTARY ROCKS

   3__ Sulphide Vein Zone

   4__ Sulphide Disseminated Zone

                   } Type and size variations as above

- -

III MONZOGRANITE 500 SERIES

(a) Type

   50_ Nonporphyritic

   51_ Slightly Porphyritic
       (<5 modal % phenocrysts)

   52_ Porphyritic (>5, <75 modal %
       phenocrysts)

(b) Size (if porphyritic, 'size'
          indicates phenocryst size)

   5_0 Fine (<1 mm)

   5_1 Medium (1-5 mm)

   5_2 Coarse (>5 mm)

IV ALTERED MONZOGRANITE 600-900 SERIES

   6__ Tan Alteration

   7__ Greisen Alteration

   8__ Kaolinite Alteration

   9__ Sheared Monzogranite

                 } Type and size variations as above

   900 Mafic Dyke

Table II-2 Trace Element Contents of Selected Drill Core Samples (Metasediments)

DDH	78-32	78-29	78-29	78-44	78-44	78-44	78-40	78-40	77-29	77-29	78-38	78-38	78-38
Depth (m)	19.8	57.72	80.3	29.10	59.94	100.0	83.6	132.	68.30	99.50	30.18	68.5	129.82
Rock Type*	100	164	164	163	164	164	102	352	184	184	164	164	164

Values in ppm
except where noted

Sn	3	50	60	3	12	3	3	60	5	7	20	50	20
W	3	5	6	2	5	5	9	6	6	3	3	3	1
Mo	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	8.0	<0.5	2.0	<0.5	1.0	3.0
As	13	12	50	13	17	8	39	7100	19	12	10	23	19
Cu	29.0	31.0	9.0	84.0	7.5	44.0	23.0	310	33.0	5.0	15.0	2.5	1.0
Pb	6	40	170	<2	4	4	4	1.44%	10	4	6	16	8
Zn	110.	270.	230.	97.0	70.0	98.0	79.0	0.90%	86.0	80.0	57.0	61.0	55.0
Sb	7.9	0.7	0.6	0.6	0.2	0.6	1.5	280	0.4	0.3	0.2	0.2	0.5
Bi	0.9	1.0	9.1	0.4	0.2	0.2	0.2	1.5	0.2	0.1	0.7	1.3	0.7
Li	60	42	100	51	48	63	38	<1	65	54	27	36	60
F	470	460	720	480	400	480	420	190	320	300	360	500	540
B	50	25	25	25	10	50	75	<10	50	50	50	50	75
Cl	50	100	50	50	<50	<50	<50	<50	50	<50	<50	<50	<50

* Table of definitions on previous page.

Table II-2 (Cont'd) Trace Element Contents of Selected Drill Core Samples (Metasediments)

DDI	78-34	78-34	78-34	78-10	77-34	77-34	78-03	78-03	77-25	77-25	77-25	77-25	77.25
Depth (m)	72.16	75.61	109.24	93.5	48.30	154.90	44.18	132.0	53.88	132.19	135.58	186.25	186.35
Rock Type	354	364	364	110	110	422	100	164	455	301	163	412	173
Sn	200	160	0.33%	30	15	0.31%	80	60	380	1.23%	200	1.07%	200
W	550	<25	12	16	6	10	6	1	16	34	5	9	4
Mo	1.0	<0.5	1.0	<0.5	<0.5	2.5	<0.5	<0.5	<0.5	<0.5	1.5	<0.5	0.5
As	90000	15000	160	7500	2600	130	220	10	17	86	8	9	6
Cu	1000	89.0	400	48.0	24.0	400	41.0	140	160	860.	<0.5	95.0	140.
Pb	4000	1000	26	22	<2	26	9	<2	60	26	16	<2	4
Zn	1300.	440.	91.0	260.	120.	89.0	120.	120.	0.96%	1500.	220.	680.	480.
Sb	200.	29.0	1.1	16.0	5.8	0.6	0.7	0.7	0.4	0.6	0.3	0.6	0.2
Bi	220	72.0	16.0	1.3	0.9	13.0	0.6	0.2	0.6	6.2	1.1	9.7	1.5
Li	43	83.0	35	89	60	46	56	34	70	72	47	46	38
F	1200	1500	530	630	650	660	630	410	650	450	690	500	420
B	25	50	10	25	100	10	50	50	<10	<10	75	<10	10
Cl	<50	<50	<50	<50	<50	<50	<50	<50	50	150	50	50	<50

Table II-2(Cont'd)   Trace Element Contents of Selected Drill Core Samples (Metasediments)

DDH	78-11	78-11	78-11	78-11	78-11	78-11	78-12	78-12	78-12	78-12	78-12	78-12	78-12
Depth (m)	19.3	58.6	77.45	85.45	85.45	123.6	70.25	118	118	130.27	163.3	166.3	183.67
Rock Type*	164	163	432	432	132	452	423	422	153	453	423	164	164
Sn	50	200	0.74%	0.73%	160	0.52%	250	0.33%	160	0.76%	1.39%	40	100
W	10	19	21	19	13	15	4	14	11	25	19	11	7
Mo	<0.5	<0.5	<0.5	<0.5	<0.5	1.5	<0.5	1.0	0.5	<0.5	4.0	2.0	<0.5
As	34	6	66	14	7	36	9	7	25	6	14	6	7
Cu	<0.5	55	510	2000.	<0.5	670	670	430	<0.5	1000	260	41.0	140
Pb	6	<2	34	6	4	70	<2	22	4	18	18	8	2
Zn	170.	100.	98.	150.	85.0	93.0	14.6%	100.	100.	110.	54.0	90.0	77.0
Sb	0.6	0.9	1.6	1.6	0.3	0.6	0.3	0.6	<0.2	0.6	1.1	0.2	0.5
Bi	0.2	2.1	16.0	11.0	1.2	10.0	26.0	56	1.8	20.0	15.0	1.0	1.0
Li	40	46	45	63	31	27	8	40	39	30	18	53	42
F	440	540	460	740	450	490	190	560	570	550	430	610	680
B	25	25	10	<10	25	10	10	10	50	10	10	50	100
Cl	<50	<50	50	<50	<50	<50	<50	50	50	<50	50	<50	<50

Table II-2 (Cont'd) Trace Element Contents of Selected Drill Core Samples (Metasediments)

DDH	78-13	78-13	77-12	77-12	77-06	77-06	77-06	77-04	77-04	77-07	77-07	77-07
Depth (m)	81.40	31.57	135.70	135.77	74.7	127.5	128.14	62.1	105.9	31.85	106.75	183.10
Rock Type*	472	172	900	333	183	422	184	331	184	184	394	183
Sn	0.38%	160	15	0.45%	60	0.68%	80	500	25	50	0.15%	12
W	20	17	7	6	<1	64	1	<25	3	5	21	2
Mo	1.5	<0.5	2.0	4.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.0	<0.5
As	12	28	8	40	59	100	49	28000.	26	74	220	190
Cu	150.	<0.5	40.0	940.	27.0	1100.	16.0	23.0	38.0	15.0	410.	25.0
Pb	10	6	4	22	16	430	6	430.	4	<2	8	2
Zn	170.	150.	95.0	220.	240.	200	150.	180.	150.	89.0	120.	91.0
Sb	0.4	0.3	0.2	2.5	0.6	0.6	0.3	120.	<0.2	0.9	0.7	1.0
Bi	30.0	4.0	0.2	32.0	0.1	27.0	0.3	0.3	0.5	0.5	0.9	4.2
Li	41	38	30	65	41	40	35	75	60	37	29	51
F	240	680	1100	280	340	540	340	670	410	340	350	680
B	10	25	10	25	25	<10	50	10	25	25	50	100
Cl	<50	<50	50	<50	<50	100	<50	<50	50	50	<50	<50

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Table II-2(Cont'd)   Trace Element Contents of Selected Drill Core Samples (Metasediments)

DDH	77-05	77-05	77-08	77-08	77-08	77-08	77-08	77-01	77-01	78-24	78-24
Depth (m)	71.93	74.5	7.6	31.34	36.37	117 5	136.7	80.1	173.35	44.75	91.8
Rock Type*	183	433	422	403	183	Qtz vein	183	163	163	102	100
Sn	40	160	0.5%	300	120	3	120	20	17	3	3
W	1	250	20	8	<1	2	<1	10	2	3	3
Mo	<0.5	<0.5	<0.5	<0.5	<0.5	1.5	<0.5	<0.5	<0.5	<0.5	1.5
As	21	4200	7	5500	7	12	23	120	4	13	16
Cu	43.0	1000.	1100.	1000.	14.0	1.5	36.0	38.0	77.0	39.0	60.0
Pb	4	<2	24	460	70	14	16	<2	<2	4	100
Zn	68.0	110.	300	140.	130.	25.0	67.0	97.0	100.	110.	130.
Sb	0.6	7.8	0.6	12.0	0.4	0.3	0.7	0.4	0.2	0.7	0.9
Bi	8.2	52.0	9.1	15.0	9.0	3.4	1.0	0.3	8.2	0.4	0.7
Li	38	34	59	24	29	2	34	88	99	31	48
F	280	620	360	200	290	110	280	1000	700	320	420
B	50	<10	<10	10	25	50	25	75	50	50	25
Cl	<50	<50	50	<50	<50	200	<50	<50	<50	50	<50

Table II-2(Cont'd)   Trace Element Contents of Selected Drill Core Samples (Metasediments).

DDH Depth (m) Rock Type*	78-20 53.88 110	78-20 86.67 110	78-20 104.68 194	77-31 55.61 900	77-31 55.61 110	77-31 59.90 900	77-31 60.16 110	77-31 78.94 112	77-31 115.79 141
Sn	5	10	5	3	7	3	3	3	3
W	4	3	<1	4	2	3	6	11	5
Mo	<0.5	<0.5	<0.5	4.5	0.5	3.5	55.0	23.0	<0.5
As	8	8	21	4	9	12	3	4	10
Cu	34.0	44.0	39.0	62.0	270.	64.0	8.5	45.0	21.0
Pb	<2	6	<2	2	4	46	<2	6	6
Zn	43.0	68.0	57.0	88.0	42.0	190.	32.0	45.0	120.
Sb	0.3	0.2	0.2	0.7	0.3	0.3	0.2	0.4	0.8
Bi	1.0	0.3	0.1	0.2	0.1	5.4	0.1	0.3	0.7
Li	52	61	41	32	13	51	32	50	70
F	350	550	440	820	230	820	260	370	360
B	100	150	25	10	10	10	50	75	50
Cl	<50	<50	<50	100	<50	50	<50	<50	50

Table II-2(Cont'd)   Trace Element Contents of Selected Drill Core Samples (Contact and Endopluton)

DDH	79-05	79-05	79-05	79-05	79-05	79-05	79-05	80-01	80-01	80-01	80-01	80-01	80-01	80-01
Depth (m)	15.07	51.60	53.48	54.0	63.08	63.09	81.54	24.3	37.2	47.68	51.25	52.0	76.0	85.85
Rock Type*	183	183	154	511	611	700	521	110	433	193	194	920	522	521
Sn	40	15	15	15	25	460	10	5	50	7	80	50	35	20
W	<1	9	19	8	15	24	34	23	430	3	16	21	29	5400
Mo	<0.5	4.5	17.0	3.0	5.0	6.5	10.0	65.0	2.5	1.5	<0.5	280.	5.0	10.0
As	16	13	17	3	7	4	6	42	9	71	9	14	11.0	2
Cu	18.0	7.0	6.5	2.0	13.0	220.	4.0	190	340	11.0	80.0	20.0	4.5	17.0
Pb	<2	<2	6	10	10	6	16.	6	<2	82	<2	8	6	30
Zn	170.	97.0	110.	21.0	18.0	11.0	38.0	41.0	47.0	220.	250.	14.0	21.0	30.0
Sb	0.4	0.3	0.2	<0.2	0.2	0.3	0.3	0.8	3.7	0.9	0.3	0.5	0.5	1.3
Bi	2.6	0.5	6.8	4.4	<0.1	0.9	1.4	1.4	88.0	4.3	0.7	16.0	20.0	210.
Li	160	150	120	23	59	150	76	130	76.	190	170	46	41	50
F	2400	2500	2300	520	1000	5400	1200	820	1500	2000	2200	500	620	830
B	10	10	10	25	25	50	50	50	25	25	25	25	25	50
Cl	<50	<50	<50	<50	<50	<50	<50	<50	50	<50	<50	<50	<50	<50

Table II-2(Cont'd) Trace Element Contents of Selected Drill Core Samples (Endopluton)

DDH	79-06	79-06	79-06	79-06	79-07	79-07	79-08	79-08	79-08	79-08	78-27	78-27	78-27	
Depth (m)	10.45	48.24	52.0	85.30	70.66	70.66	36.22	55.62	72.93	72.93	68.19	68.37	73.55	
Rock Type*	521	500	700	511	511	711	511	800	521	721	501	501	511	
Sn	25	30	760	7	10	360	12	80	25	200	7	7	30	15.4
W	170	390	38	300	24	23	11	14	18	190	14	10	20	13.4 (787)
Mo	3.5	19.0	14.0	63.0	5.5	130.	10.0	2.0	6.5	120.	12.0	2.0	3.0	
As	3	1500	3	4	3	30.	3	370	20	7400.	1600	1100	18	
Cu	<0.5	12.0	23.0	1.5	10.0	430.	3.5	46.0	4.0	0.60%	7.0	5.0	12.0	
Pb	12	8	8	6	16	8	19	10	4	14	8	8	6	
Zn	54.0	35.0	13.0	16.0	30.0	2900.	31.0	49.0	21.0	140.	25.0	35.0	39.0	31
Sb	0.2	3.8	0.5	<0.2	0.3	0.4	0.3	0.9	0.4	14.0	3.7	2.2	0.2	
Bi	8.7	22.0	0.2	11.0	16.0	12.0	5.0	19.0	4.0	210	24.0	190.	14.0	
Li	74	57	330.	26	37	55	40	93	57	120	56	47	53	49
F	960	1100	2.80%	610	1300	2500	900	850	860	8100	440	840	960	880
B	25	25	25	50	25	50	25	25	25	25	25	25	25	
Cl	<50	50	<50	<50	<50	<50	<50	<50	<50	<50	50	100	<50	

Table II-2 (Cont'd) Trace Element Contents of Selected Drill Core Samples (Endopluton)

DDH	78-33	78-33	78-33	78-31	78-31
Depth	13.73	46.6	73.33	9.4	71.75
Rock Type*	501	501	511	501	501
Sn	5	3	3	10	7
W	9	4	1	<1	4
Mo	0.5	<0.5	0.5	1.0	<0.5
As	15	20	7	3	1
Cu	5.5	<0.5	1.5	<0.5	<0.5
Pb	6	10	10	10	10
Zn	21.0	21.0	29.0	40.0	25.0
Sb	0.4	0.6	0.2	0.5	0.3
Bi	0.7	0.3	0.3	0.3	0.2
Li	30	49	48	97	92
F	270	310	230	620	500
B	25	25	25	25	25
Cl	<50	<50	<50	<50	<50

Table II-3   Whole Rock Geochemistry (Meta-argillites)

DDH Depth (m) Rock Type	77-25 132.10 301	77-34 48.30 110	78-24 92. 100	77-31 78.94 112	77-31 115.79 141	78-10 93.5 110	77-31 60.16 110	78-20 53.88 110
Values in wt.%								
SiO_2	31.8	55.8	57.5	52.3	60.4	46.5	66.6	61.9
TiO_2	0.76	1.02	0.95	1.22	0.83	1.21	0.68	1.00
Al_2O_3	14.3	19.4	18.0	19.6	17.1	23.4	16.4	15.7
Fe_2O_3*	3 2	2.04	1.64	2.07	1.71	3.4	0.88	1.84
FeO	31.8	7.5	6.8	5.5	5.9	7.2	1.1	5.5
MnO	0.42	0.17	0.14	0.06	0.14	0.24	0.02	0.12
MgO	3.98	3.88	3.14	2.42	3.33	4.31	1.18	2.92
CaO	0.19	0.52	2.88	0.42	2.19	1.08	0.39	3.17
Na_2O	0.26	1.63	2.28	2.22	2.37	1.56	2.85	3.46
K_2O	0.20	3.49	2.90	4.51	3.26	4.79	3.57	1.83
P_2O_5	0.09	0.14	0.14	0.18	0.13	0.18	0.11	0.15
L.O.I.	7.08	4.16	4.23	10.00	2.54	5.62	6.77	1.62
TOTAL	94.08	99.75	100.60	100.5	99.90	99.49	100.55	99.21

Trace Elements
(in ppm)

Rb	0	140	110	140	120	170	120	120
Sr	0	90	200	130	240	100	150	280
Cr	130	130	140	160	100	170	100	120
Zr	110	180	140	260	170	220	210	230

*Fe_2O_3 = Fe_2O_3 (total) - FeO

Table II-3   (Cont'd) Whole Rock Geochemistry (Meta-wackes)

DDH	78-29	77-25	77-06	77-04	78-20	79-05
Depth (m)	80.3	135.08	74.70	105.9	104.68	51.60
Rock Type	164	163	183	184	194	183
SiO_2	42.6	65.3	66.4	46.9	66.7	69.3
TiO_2	1.21	0.78	0.85	1.54	0.86	0.71
Al_2O_3	23.0	13.6	14.3	21.5	13.9	13.6
Fe_2O_3*	2.6	1.61	1.40	4.73	0.92	1.24
FeO	9.5	6.6	5.0	4.9	4.9	3.8
MnO	0.22	0.19	0.11	0.20	0.14	0.09
MgO	5.93	2.28	2.36	2.91	2.40	2.00
CaO	2.54	1.83	1.68	2.79	3.56	2.19
Na_2O	1.96	2.85	4.16	2.11	3.26	4.49
K_2O	4.08	1.36	2.04	5.43	1.03	2.03
P_2O_5	0.19	0.13	0.14	0.22	0.13	0.13
L.O.I.	5.47	2.70	1.39	5.31	1.16	0.85
TOTAL	99.3	99.23	99.83	98.54	98.96	100.5

Trace Elements (in ppm)						
Rb	220	110	140	220	50	220
Sr	110	150	250	240	310	290
Cr	180	120	110	180	110	100
Zr	190	140	170	210	140	110

Table II-3 (Cont'd) Whole Rock Geochemistry (Monzogranites)

DDH Depth (m) Rock Type	79-06 85.30 511	79-07 70.66 511	78-27 78.55 511	78-33 46.6 501	78-31 72.0 501	79-05 81.45 521	80-01 85.85 521	79-08 72.93 521
SiO_2	76.60	76.70	75.40	76.70	75.00	74.60	78.20	74.80
TiO_2	0.14	0.12	0.20	0.09	0.20	0.22	0.17	0.23
Al_2O_3	12.60	12.30	12.40	12.30	13.40	13.20	10.7	12.9
$Fe_2O_3^*$	0.60	0.54	0.95	0.38	0.75	0.76	0.83	0.84
FeO	0.8	0.8	1.0	0.8	0.9	1.3	0.9	1.3
MnO	0.02	0.02	0.04	0.03	0.03	0.03	0.04	0.03
MgO	0.11	0.09	0.36	0.14	0.29	0.23	0.16	0.27
CaO	0.64	0.67	0.93	0.52	1.21	0.93	0.89	0.90
Na_2O	3.92	3.49	3.73	4.16	4.28	3.60	2.86	3.59
K_2O	4.60	4.98	5.07	4.51	4.51	4.99	4.54	4.69
P_2O_5	0.04	0.03	0.06	0.03	0.07	0.09	0.05	0.07
L.O.I.	0.77	0.93	0.70	0.62	0.23	0.77	1.00	1.23
TOTAL	100.84	100.67	100.84	100.78	100.87	100.72	100.34	100.85

Trace Elements
(in ppm)

Rb	300	370	330	320	220	360	270	300
Sr	20	0	110	0	60	70	10	80
Cr	40	30	30	40	50	30	40	40
Zr	150	120	160	90	130	160	120	160

CIPW Norms

Quartz	34.37	35.54	31.97	33.45	29.79	31.82	42.35	33.32
Orthoclase	27.19	29.53	29.95	26.63	26.51	29.53	27.03	27.85
Albite	33.14	29.60	31.51	35.14	35.98	30.47	24.36	30.49
Anorthite	2.91	3.14	2.10	2.38	4.00	4.03	2.96	4.02
Diopside	0.00	0.00	1.74	0.00	1.25	0.00	0.98	0.00
Hypersthene	1.05	1.09	0.83	1.41	0.85	2.03	0.67	2.05
Magnetite	0.87	0.78	1.38	0.55	1.08	1.10	1.21	1.22
Hematite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ilmenite	0.27	0.23	0.38	0.17	0.38	0.42	0.33	0.44
Apatite	0.09	0.07	0.14	0.07	0.16	0.21	0.12	0.16
Corundum	0.10	0.02	0.00	0.20	0.00	0.40	0.00	0.45

Table II-3   (Cont'd) Whole Rock Geochemistry (Greisens)

DDH	79-05	79-06	79-07	Biot. porphyritic gte from
Depth (m)	63.08	52.0	70.66	Pine Hill - Renison Bell area,
Rock Type	700	700	711	Tasmania (Patterson et al, 1981) (avg. 6 analyses)
SiO_2	76.10	49.60	75.30	73.04
TiO_2	0.14	0.13	0.13	0.36
Al_2O_3	12.0	27.5	11.9	13.34
Fe_2O_3*	2.58	2.42	2.05	⎫ 2.14 Total iron as FeO
FeO	1.0	2.0	2.4	⎭
MnO	0.03	0.06	0.04	0.08
MgO	0.16	0.26	0.16	0.66
CaO	1.20	3.85	0.37	1.98
Na_2O	0.38	0.42	0.67	2.76
K_2O	4.88	9.59	4.51	5.23
P_2O_5	0.05	0.07	0.04	0.11
L.O.I.	2.08	4.54	2.62	1.05
TOTAL	100.6	100.44	100.19	100.75

Trace Elements (in ppm)				
Rb	630	1410	650	
Sr	0	0	0	
Cr	40	30	40	
Zr	120	110	140	

CIPW Norms				
Quartz	53.31	1.31	53.33	30.79
Orthoclase	29.30	59.15	27.34	30.88
Albite	3.26	3.71	5.81	23.91
Anorthite	5.71	19.44	1.61	7.80
Diopside	0.00	0.00	0.00	0.82
Hypersthene	0.40	2.31	3.05	4.57
Magnetite	2.96	3.66	3.05	
Hematite	0.58	0.00	0.00	
Ilmenite	0.27	0.26	0.25	0.68
Apatite	0.12	0.17	0.10	0.26
Corundum	4.09	10.00	5.47	0.00

APPENDIX III

GEOCHEMICAL REFERENCE MATERIALS AND

DETERMINATION OF ANALYTICAL ACCURACY AND PRECISION

In an attempt to assess the accuracy of the analytical
results a set of 5 samples of known trace element content and
a set of 2 samples of known major oxide content were randomly
placed in the sample batch (Tables III-1 and III-2).

Problems exist with such reference materials in that a
wide range in values exists in the analyses among
laboratories. Because of this uncertainty the values
obtained by such laboratories are termed 'usable' or
'recommended', meaning they may be used with caution and not
as exact concentrations. Most of the variability in the
analyses appears to stem from inter- laboratory bias and a
set of guidelines is used to determine the 'usefulness' of a
laboratory's results (Abbey,1980).

The reference samples used for trace element analysis
include:

1. Silica gel - this was essentially used as a 'blank' sample
                on the premise that it contained insignificant
                trace element concentrations and this is shown

in the results. Actual trace element contents
are not known.

2. GSE - one of a series of 4 artificial glass reference
standards containing 46 trace elements and made by
Corning Glass Works. This sample contains the 46
elements at concentration levels of about 500 ppm
each. The 'accepted values' are defined as the
medians of the analyses by different laboratories
(Meyers et al.,1976). Because analyses for Mo, Cu,
Pb, Zn and Bi involve acid digestion, these elements
were not totally liberated in the digestion process
and therefore give low values. These were not used in
accuracy calculations.

3. NIM-L - one of a set of 6 igneous rocks from South Africa,
this sample is a lujavrite (a coarse-grained
nepheline syenite) from the Pilanesberg Alkaline
Complex. The means and medians of the sets of
results are used in the published values (Abbey,
1980; Steele et al.,1978). This sample was
submitted in duplicate to assess the precision
of the analysis.

4. SY-2 - a syenite sample from the Canadian Certified
Reference Materials Project (Abbey,1980).

5. TLG-1 - a scheelite ore sample that is useful only for

   the analysis for tungsten.

   Two reference samples used for the whole rock
geochemical analysis are:

   .

1. NIM-G - a granite from the Bushveld Complex in the

   Transvaal, South Africa (Abbey,1980; Meyers

   et al.,1978).

2. QMC-M2 - a pelite from the Queen Mary College, United

   Kingdom (Abbey,1980).

   The accuracy of an analysis is a measure of the
'correctness' of a result or how close the observed result is
to the 'true' or recommended result. Put another way, it
reflects the absolute error of a measurement and is the
difference between the measured value and the true value of
the element being analysed, where

Accuracy = [1-|((X-T)/T)|] * 100%   where X = observed value
                                           T = 'true' value

In this study, accuracy was determined graphically by
obtaining the vertical difference between the sample value
furthest from the ideal value (slope = 1);these graphs are
shown in Figures III-1 and III-2. Results are plotted on
log-log graph paper, where results of analyses are plotted

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against the recommended or 'usable' values documented in various publications(e.g. Abbey, 1980). A 45° line is drawn - if the analyses were carried out satisfactorily, the points should lie on or very near this line (analysed values = recommended values). Minor deviations may be expected due to procedural errors. Limits of ± 10% (and in some graphs, ± 25%) are marked off on the graph parallel the 45° line.

Of the 13 trace elements analysed, 2 were not plotted: chlorine, because all values were below the detection limit of 50 ppm, and bismuth, because no reliable 'usable' values could be obtained from the literature for the above samples. Of the remaining 11 elements, analytical control ranged from acceptable to poor (e.g. Mo accuracy for 3 samples ranged from +117% to +183%).

Analytical control of whole rock analyses of the 2 samples fares much better, as most are within ± 10% . The graphs do not include those samples which have no known element content. 'Known' values include those with question marks, which are considered by the originating laboratories to be inadequate to recommend as usable values; however, because of the low number of samples, they were included for comparison purposes.

The precision (reproducibilty) of the analyses was checked by sending duplicate samples for both trace element and major oxide analyses (Tables III-2 and III-3). Duplicate

sample values for each element and oxide are plotted (Figs. III-3 and III-4) and precisions are determined graphically as well. Precision of trace element and whole rock analysis ranged from fair to excellent. Poor analytical results may be due to inadequate homogenization of sample powder prior to analysis (causing fluccuating results), inadequate analytical technique, or low element concentration within the samples.

Table III-1 Trace Element Reference Standard Analyses*

Sample	Silica Gel "Blank"	GSE	Recommended Value	SY-2	Recommended Value	NIM-L	Duplicate	Recommended Value	TLG-1 for W only	Recommended Value
Values in ppm.										
Sn	<3	300	440	5	4	3	3	7?	20	–
W	3	510	420	1	–	8	9	<20??	890	830
Mo	<0.5	12.0	500	6.5	3?	7.0	8.5	3?	54.0	–
As	6	490	450	19	18	4	3	<15??	25	–
Cu	<0.5	16.0	500	2.0	5	10.0	11.0	13	330.	–
Pb	<2	16	500	92	80	56	62	43	100	–
Zn	1.0	15.0	500	110	250	360	350	400	140.	–
Sb	0.3	490	470	0.5	0.2	0.3	0.3	0.3?	3.7	–
Bi	0.3	1.2	480	1.0	–	0.5	0.7	<3??	24.0	–
Li	<1	470	480	83	93	45	39	48?	15	–
F	140	260	300	3600	5100	2800	2600	4400	480	–
B	25	400	500	75	85?	10	10	<20??	10	–
Cl	<50	NSS	800	NSS	130?	NSS	NSS	1300	<50	–

GSE — Trace element glass standard from the USGS. Low values of some elements due to insufficient dissolution from their glass matrix.

SY-2 — Syenite, from Canadian Certified Reference Materials Project.

NIM-L — Lujavrite (a trachytic eudialyte-bearing nepheline syenite from the Pilanesberg Alkaline Complex), from the National Institute of Metallurgy, South Africa.

TLG-1 — Scheelite ore; used for tungsten only.

Recommended values are tabulated in Abbey (1980), Meyers et al. (1976) and Steele et al (1978). Values with question marks are considered by the original laboratories to be inadequate to recommend as usable values.

Table III-2 Whole Rock Duplicate and Reference Standard Analyses

DDH Depth (m) Rock Type	78-10 93.5 110	Duplicate	79-06 85.30 511	Duplicate	79-08 72.93 521	Duplicate	NIM-G (gran-ite)	Rec-ommended Value	QMC-M2 (Pelite)	Recommended Value
Values in wt.%										
SiO_2	46.3	46.5	76.6	76.0	74.8	74.8	76.2	75.70	48.9	48.86?
TiO_2	1.22	1.21	0.14	0.15	0.24	0.23	0.10	0.09	0.68	0.72 .
Al_2O_3	23.3	23.4	12.6	12.8	13.0	12.9	12.2	12.08	23.7	23.97?
Fe_2O_3* ·	3.2	3.4	0.6	0.58	0.73	0.84	0.75	0.6?	3.08	2.31?
FeO	7.4	7.2	0.8	1.0	1.4	1.3	1.2	1.30	6.2	6.30?
MnO	0.24	0.24	0.02	0.02	0.03	0.03	0.01	0.02	0.24	0.26
MgO	4.22	4.31	0.11	0.23	0.26	0.27	0.01	0.06?	2.37	2.45
CaO	1.08	1.08	0.64	0.68	0.89	0.90	0.80	0.78	1.72	1.75
Na_2O	1.57	1.56	3.92	3.88	3.59	3.59	3.72	3.36	1.38	1.40
K_2O	4.80	4.79	4.60	4.64	4.66	4.69	5.07	4.99	8.13	7.90
P_2O_5	0.18	0.18 ·	0.04	0.04	0.08	0.07	0.01	0.01	0.54	0.50?
L.O.I.	5.62	5.62	0.77	0.77	1.00	1.23	0.47	-	3.08	-
TOTAL	99.13	99.49	100.84	100.79	100.68	100.85	100.54	-	100.02	-

Trace Elements (in ppm)										
Rb	150	170	300	330	300	300	310	320	270	-
Sr	110	100	20	30	60	80	0	10	180	-
Cr	170	170	40	40	40	40	40	12	60	-
Zr	210	220	150	140	180	160	270	300	90	-

*Fe_2O_3 = Fe_2O_3 (Total)-FeO

NIM-G - Granite from the Bushveld Complex in the Transvaal (Steele et al., 1978)

QMC-M2 - Pelite, from Queen Mary College, U.K. (Abbey, 1980)

Question marks are used for values considered uncertain or inadequate by the original laboratories.
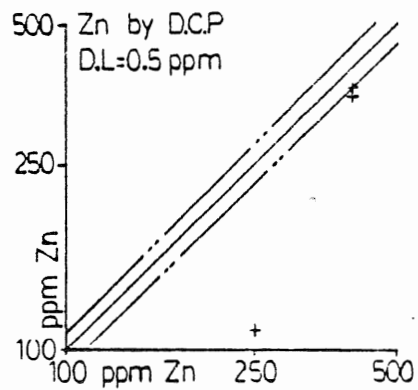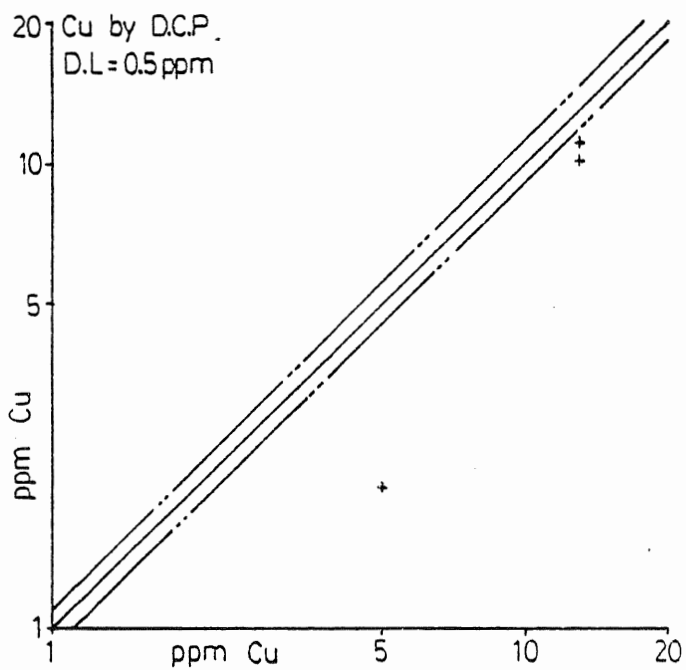
Table III-3 Trace Element Duplicate Analyses.

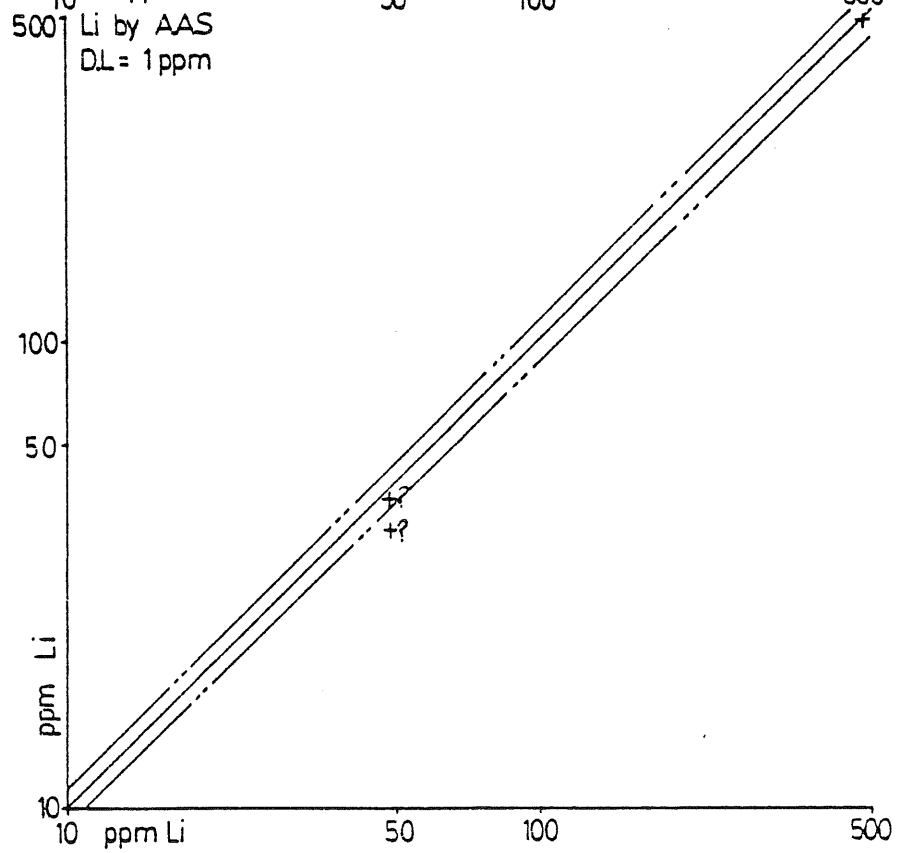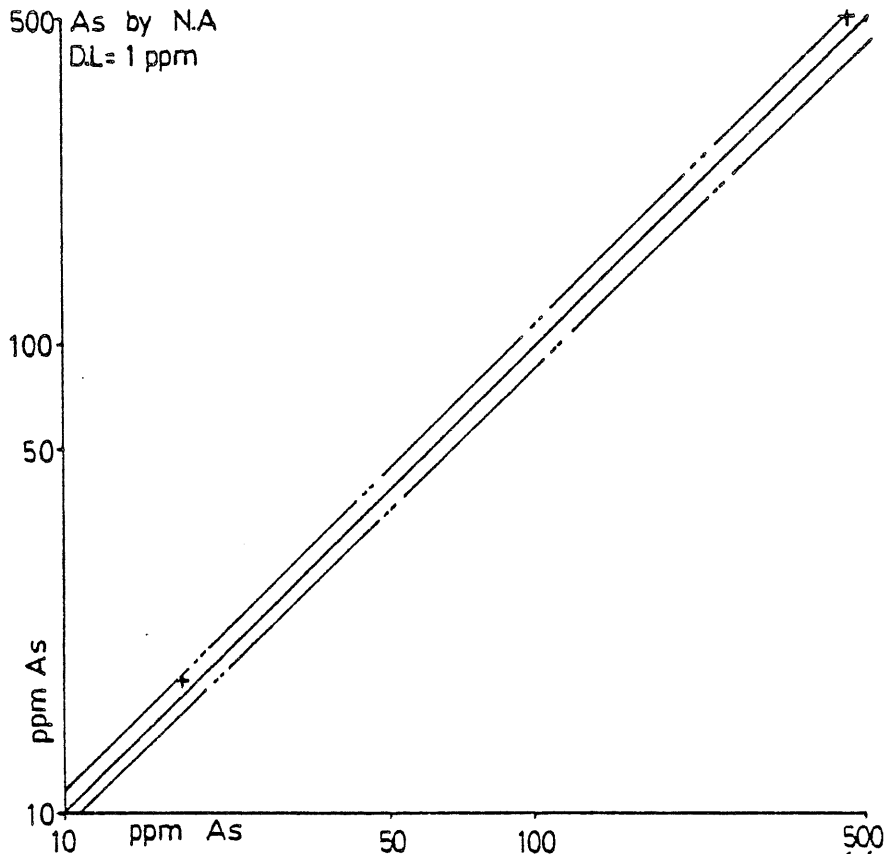| DDH Depth (m) Rock Type	78-44 100 164	Duplicate	78-29 57.72 164	Duplicate	77-25 132.10 301	Duplicate	78-10 93.5 110	Duplicate	78-11 85.45 432	Duplicate	78-12 118 153	Duplicate
Values in ppm except where noted												
Sn	3	3	50	50	1.23%	1.30%	30	25	0.73%	0.74%	0.33%	0.36%
W	5	6	5	6	34	35	16	16	19	17	14	10
Mo	<0.5	<0.5	<0.5	1.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.0	1.0
As	8	9	12	12	36	81	7500	8500	14	15	7	7
Cu	44.0	50.0	31.0	30.0	860.	960.	48.0	36.0	2000.	2000.	430	450.
Pb	4	2	40	42	26	28	22	28	6	16	22	22
Zn	98.0	100.	270	290	1500	1500	260	230	150	160	100	83
Sb	0.6	0.2	0.7	0.7	0.6	0.9	16.0	19.0	1.6	1.7	0.6	0.6
Bi	0.2	0.2	1.0	1.0	6.2	8.2	1.3	2.0	11.0	15.0	56.0	70.0
Li	63	62	42	51	72	81	89	61	63	42	40	51
F	480	560	460	480	450	420	630	670	740	590	560	610
B	50	50	25	25	<10	<10	25	25	<10	25	10	10
Cl	<50	50	100	<50	150	<50	<50	50	<50	<50	50	100

Table III-3 (Cont'd) Trace Element Duplicate Analyses

DDH Depth (m) Rock Type	73-24 44.6 102	Duplicate	78-24 92 100	Duplicate	78-20 53.88 110	Duplicate	79-05 51.60 183	Duplicate	79-07 70.66 711	Duplicate	79-08 72.93 521	Duplicate	79-06 85.30 511	Duplicate
Values in ppm except where noted														
Sn	3	5	3	5	5	5	15	25	360	340	25	20	7	5
W	3	<1	3	3	4	5	9	14	23	23	18	17	300	320
Mo	<0.5	<0.5	1.5	3.5	<0.5	<0.5	4.5	4.5	130.	120.	6.5	6.5	63.0	69.0
As	13	12	16	12	8	7	13	12	30	24	20	21	4	7
Cu	39.0	44.0	60.0	84.0	34.0	34.0	7.0	6.5	430.	410.	4.0	4.0	1.5	2.0
Pb	4	2	100	90	<2	<2	<2	2	8	8	4	4	6	6
Zn	110	110	130.	100.	43.0	72.0	97.0	96.0	2900.	2800.	21.0	22.0	16.0	17.0
Sb	0.7	0.5	0.9	0.2	0.3	0.4	0.3	0.4	0.4	0.3	0.4	0.8	<0.2	0.2
Bi	0.4	0.3	0.7	0.3	1.0	0.5	0.5	0.3	12.0	9.0	4.0	0.2	11.0	6.3
Li	31	37	43	52	52	55	150	130	55	170	57	57	26	25
F	320	310	420	420	350	480	2500	2200	2500	3500	860	1100	610	510
B	50	25	25	25	100	25	10	10	50	50	25	25	50	25
Cl	50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	50

Figure III-1   Accuracy of trace element analyses
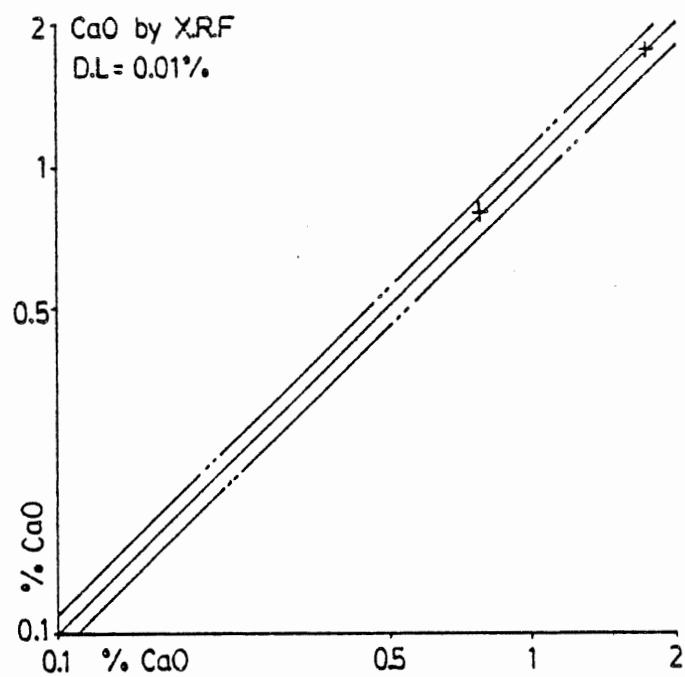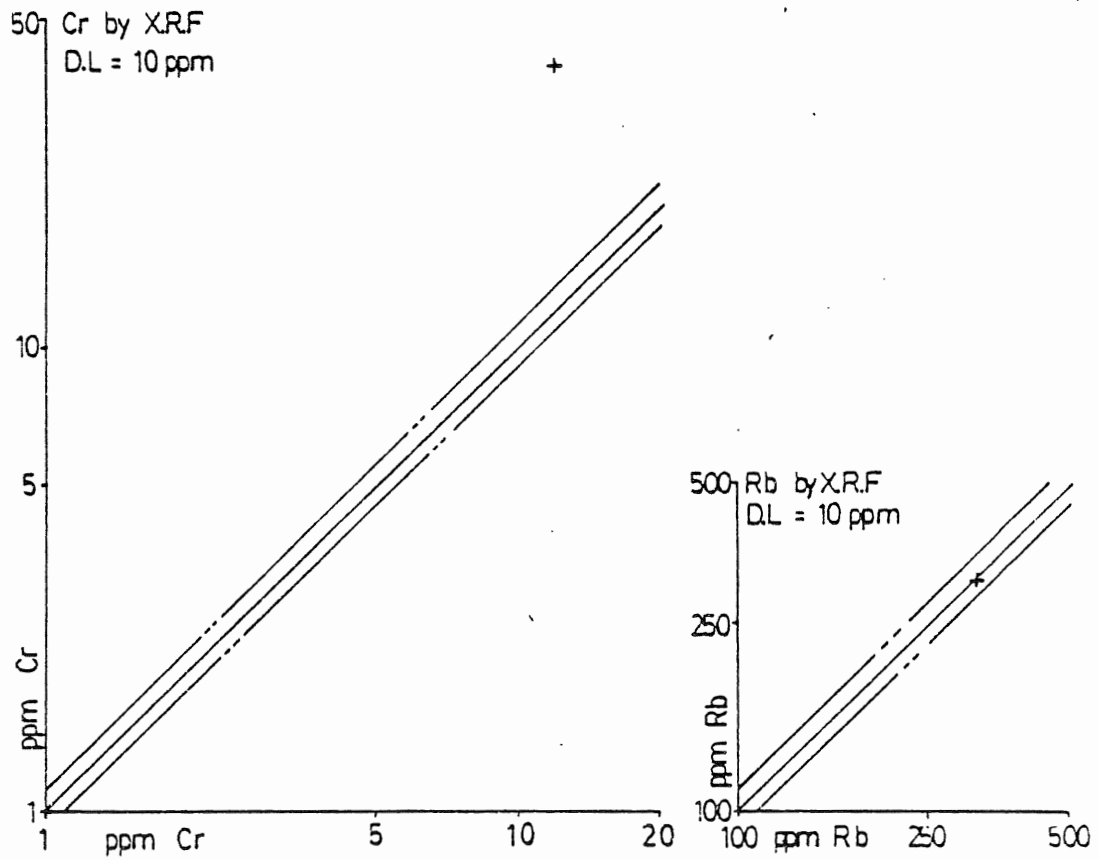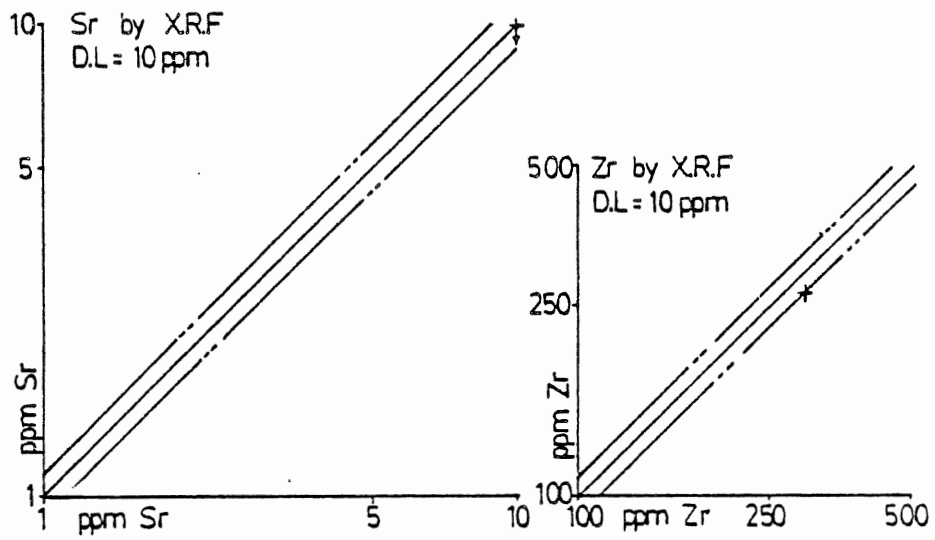   using reference samples. Results of
                        analyses are plotted against
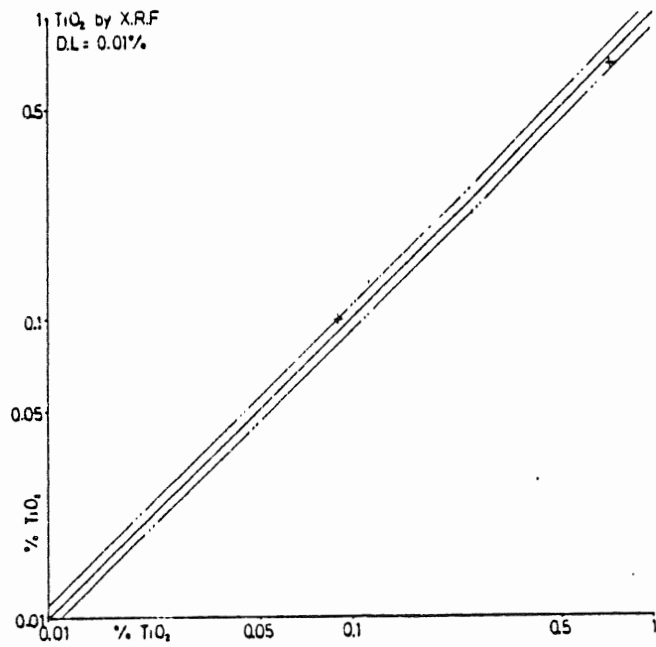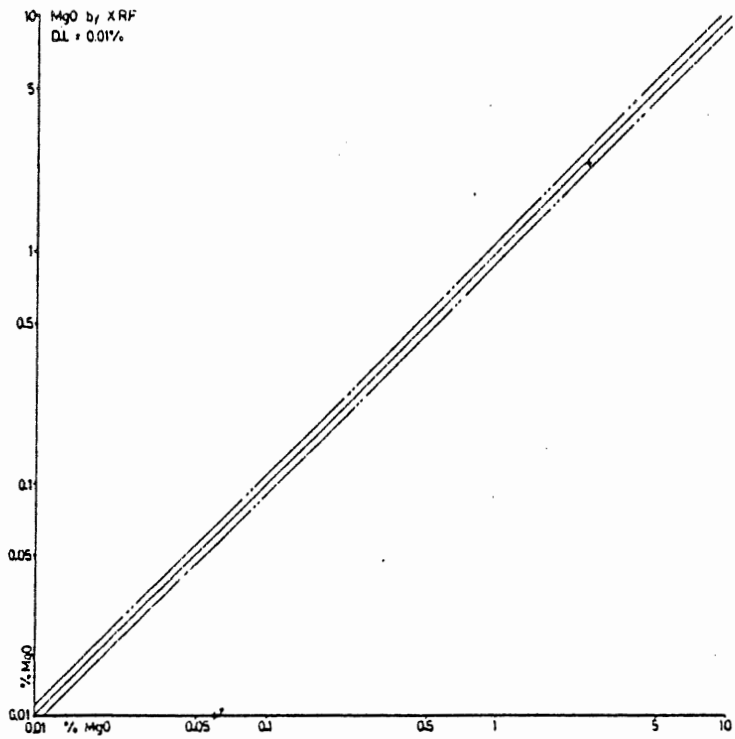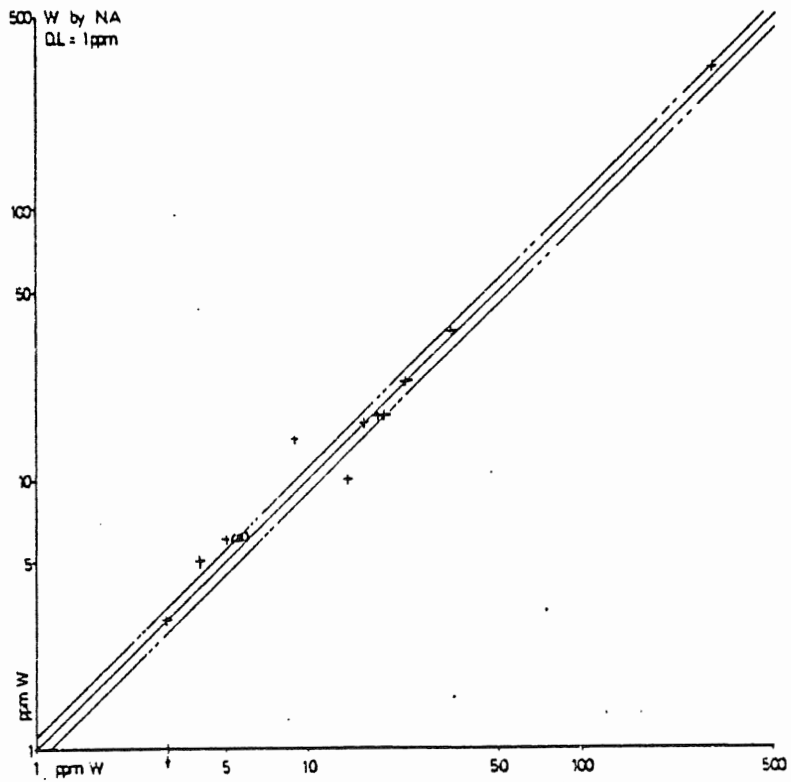   'usable' values. Precision limits
                        of ± 10% are marked. Bi is not plotted
                        as recommended values are unreliable
                        or, in the case of GSE, Bi was not
                        totally digested.

Sn by EMS
DL = 3 ppm

ppm Sn

ppm Sn

W by NA
DL = 1 ppm

ppm W

ppm W

As by N.A
D.L= 1 ppm

Li by AAS
D.L= 1 ppm

F by S.I.E
D.L = 100 ppm

ppm F

ppm F

B by D.C.P
D.L = 10 ppm

ppm B

ppm B
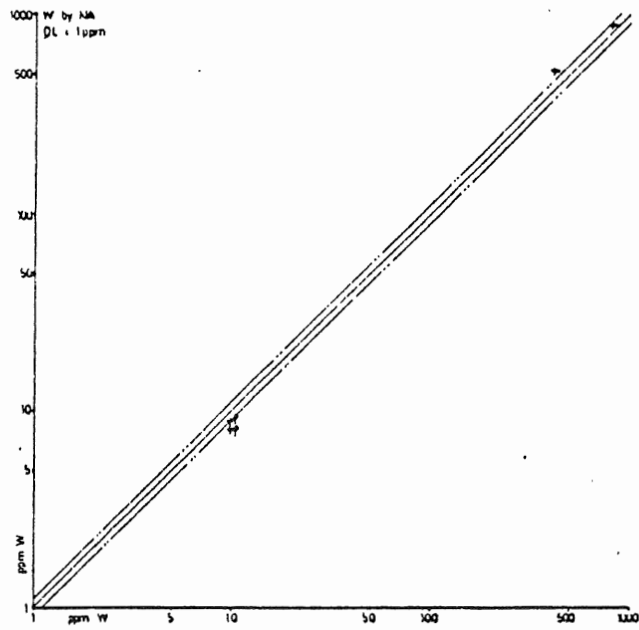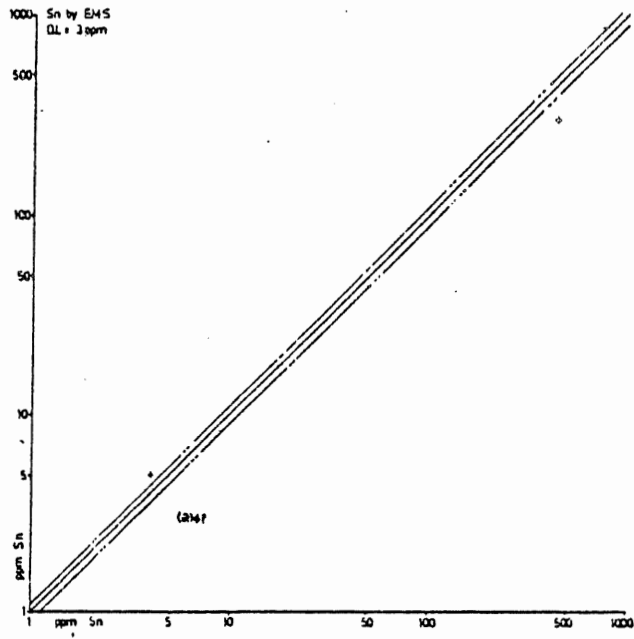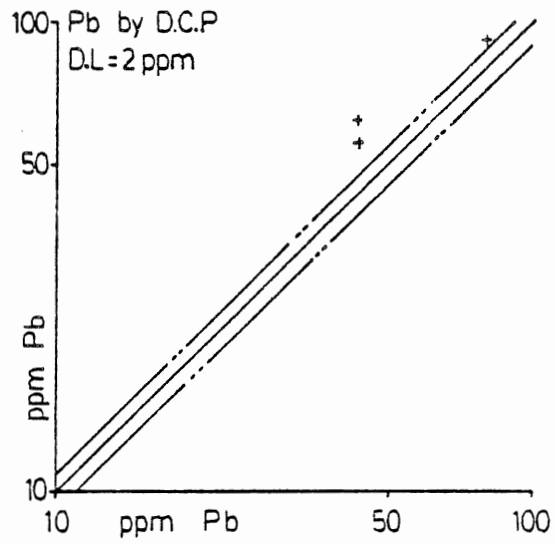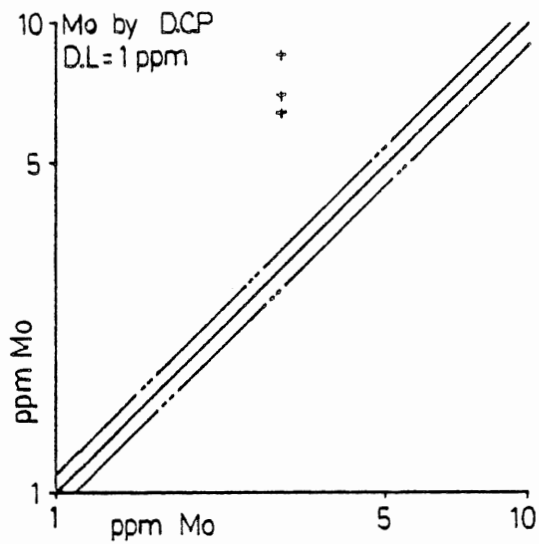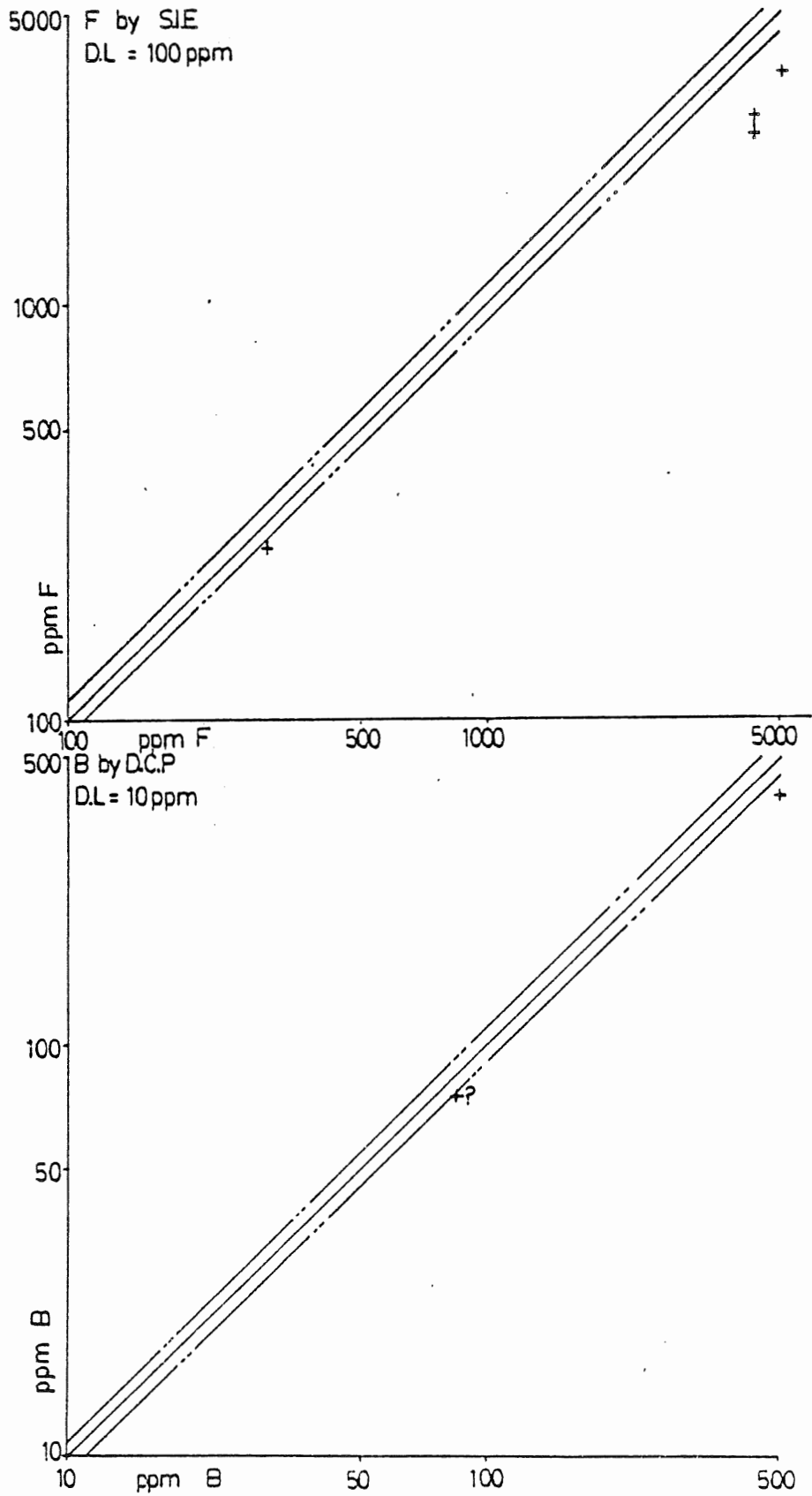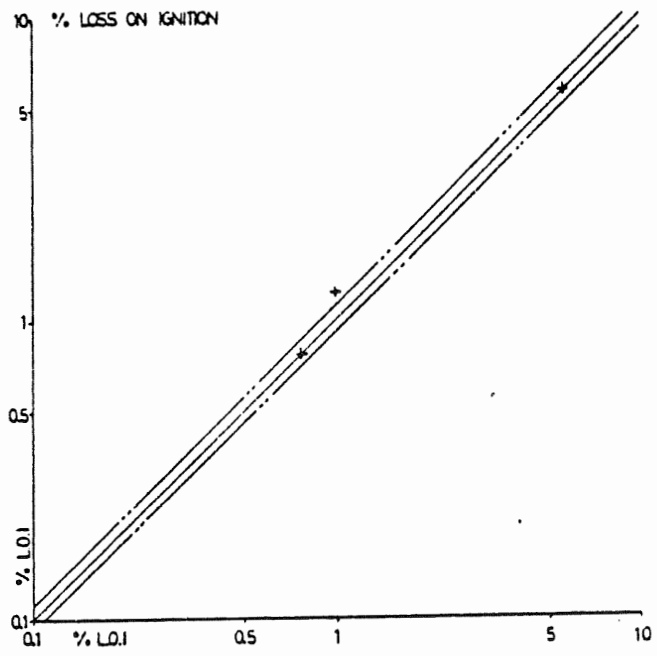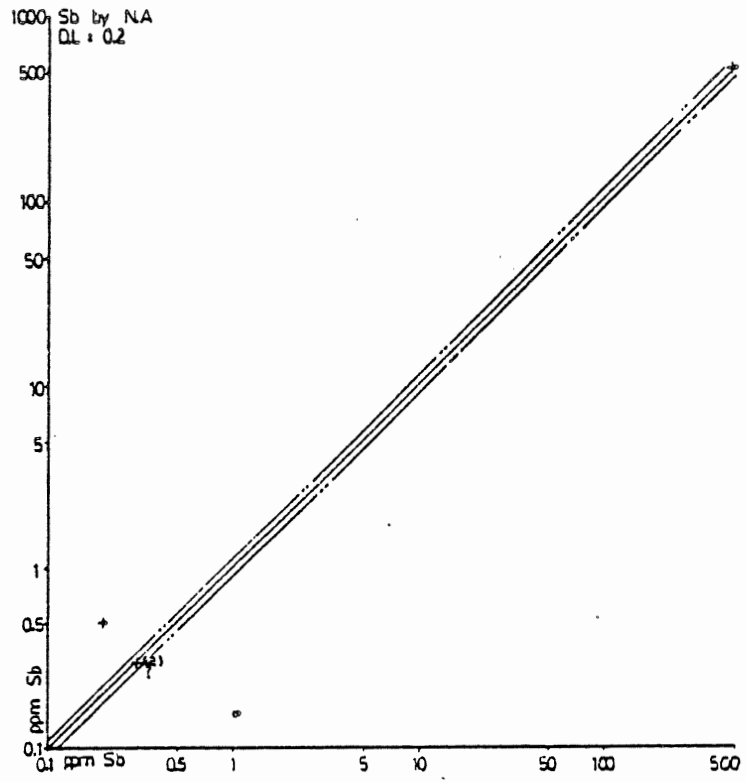
Figure III-2   Accuracy of whole rock analyses
                      using reference samples. Results of
                      analyses are plotted against
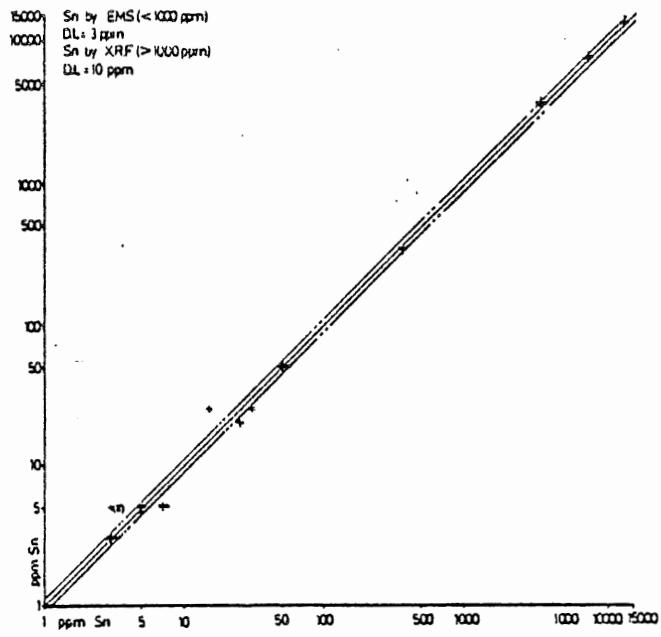   'usable' values. Precision limits
                      of ± 10% are marked.

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Fe₂O₃ by X.R.F
D.L = 0.01%

% Fe₂O₃

% Fe₂O₃

MnO by XRF
DL = 001%

% MnO

% MnO

Sr by X.R.F
D.L = 10 ppm

Zr by X.R.F
D.L = 10 ppm

Cr by X.R.F
D.L = 10 ppm

Rb by X.R.F
D.L = 10 ppm

MgO by XRF
D.L = 0.01%

% MgO (vertical axis)

% MgO (horizontal axis)

TiO₂ by X.R.F
D.L = 0.01%

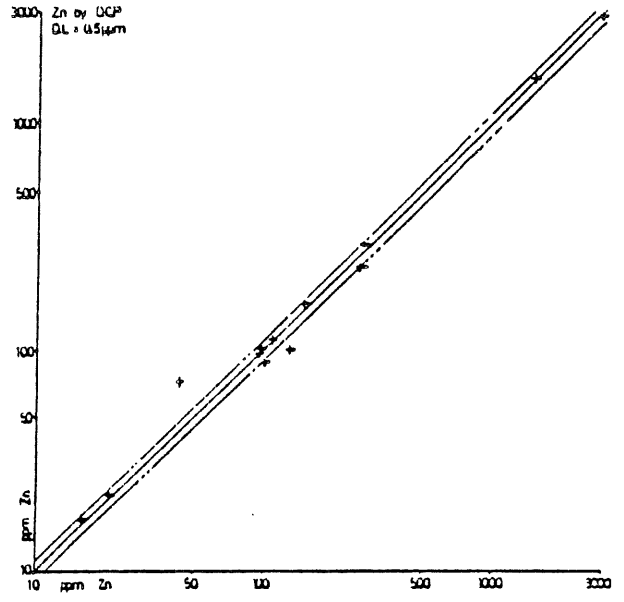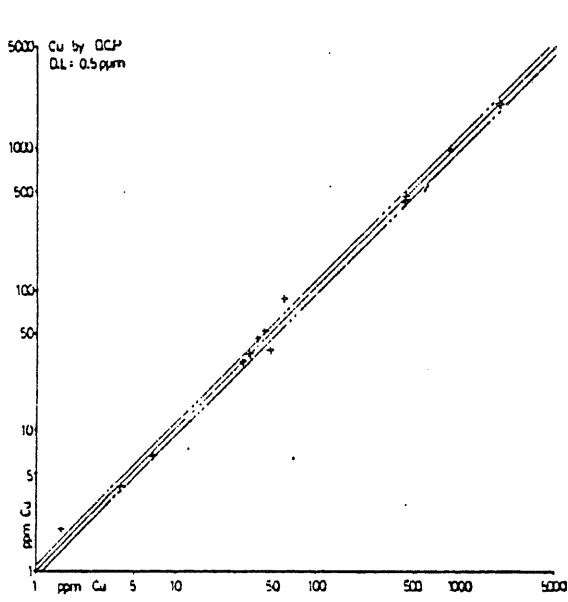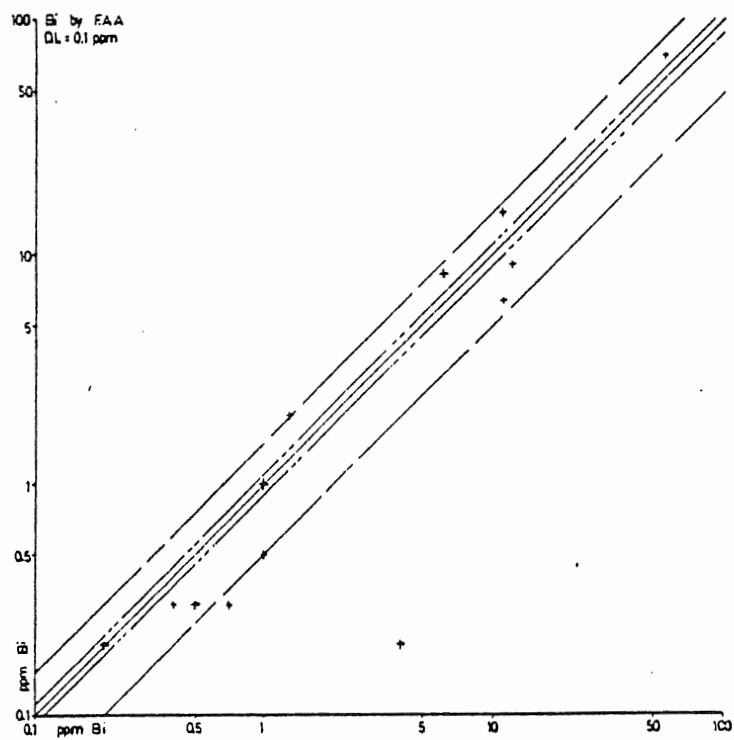% TiO₂ (vertical axis)

% TiO₂ (horizontal axis)
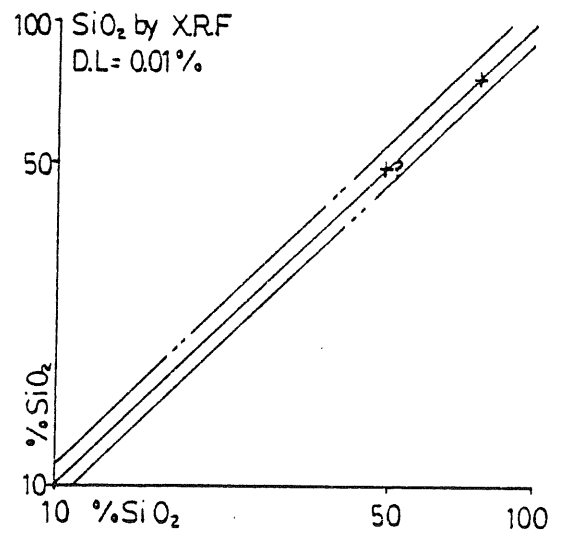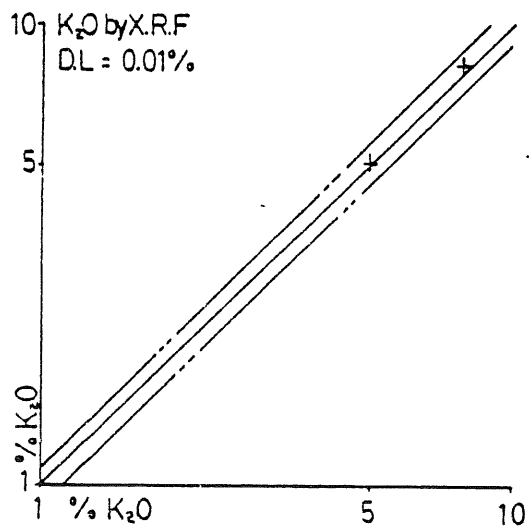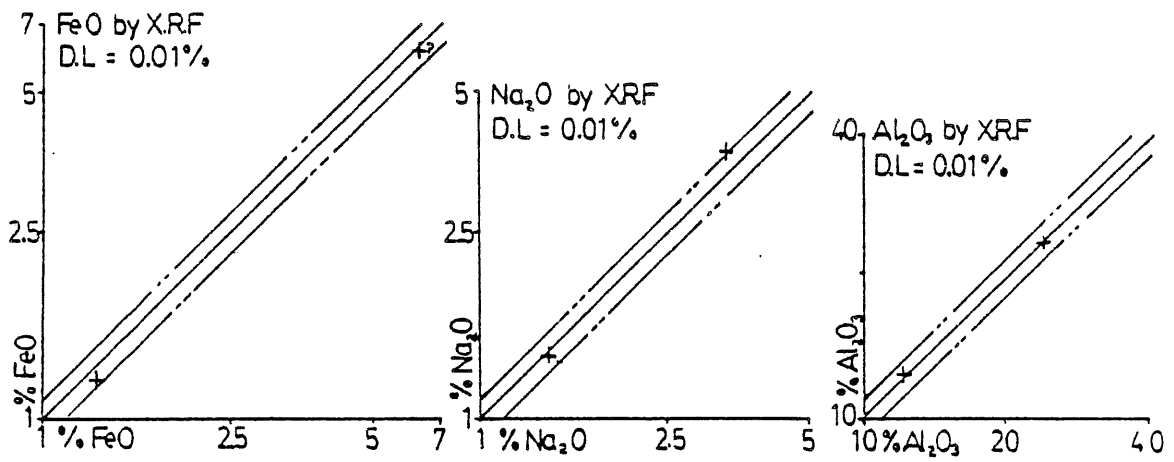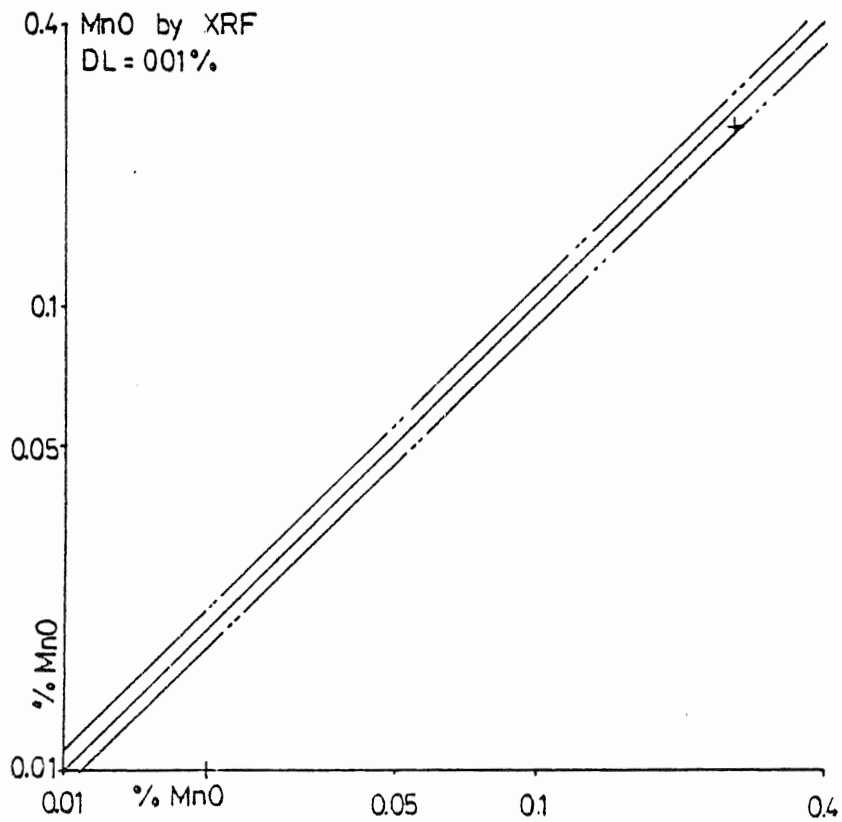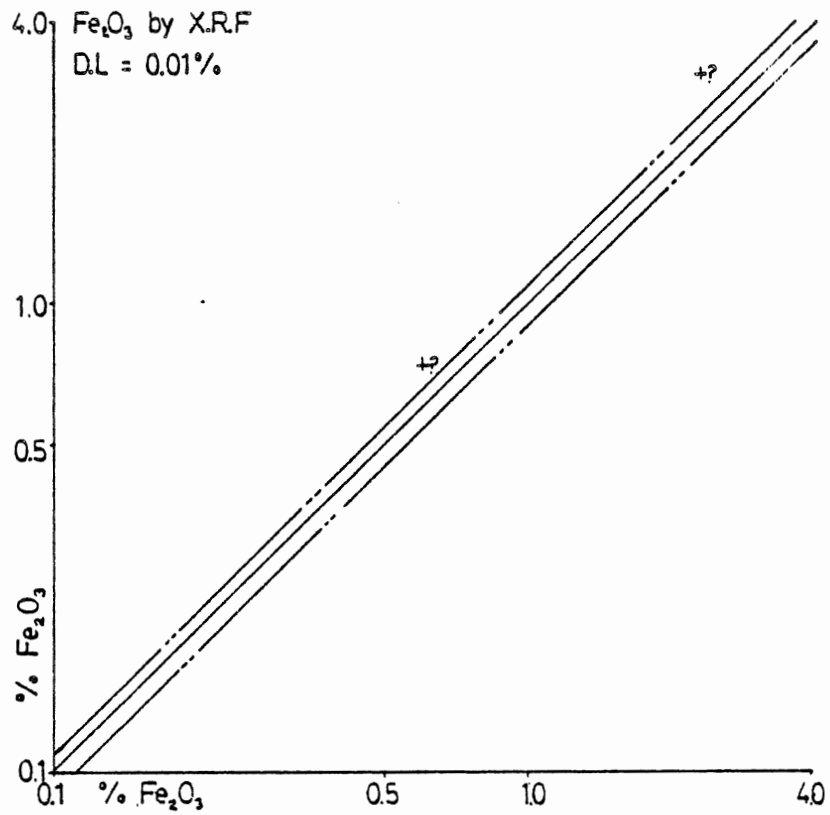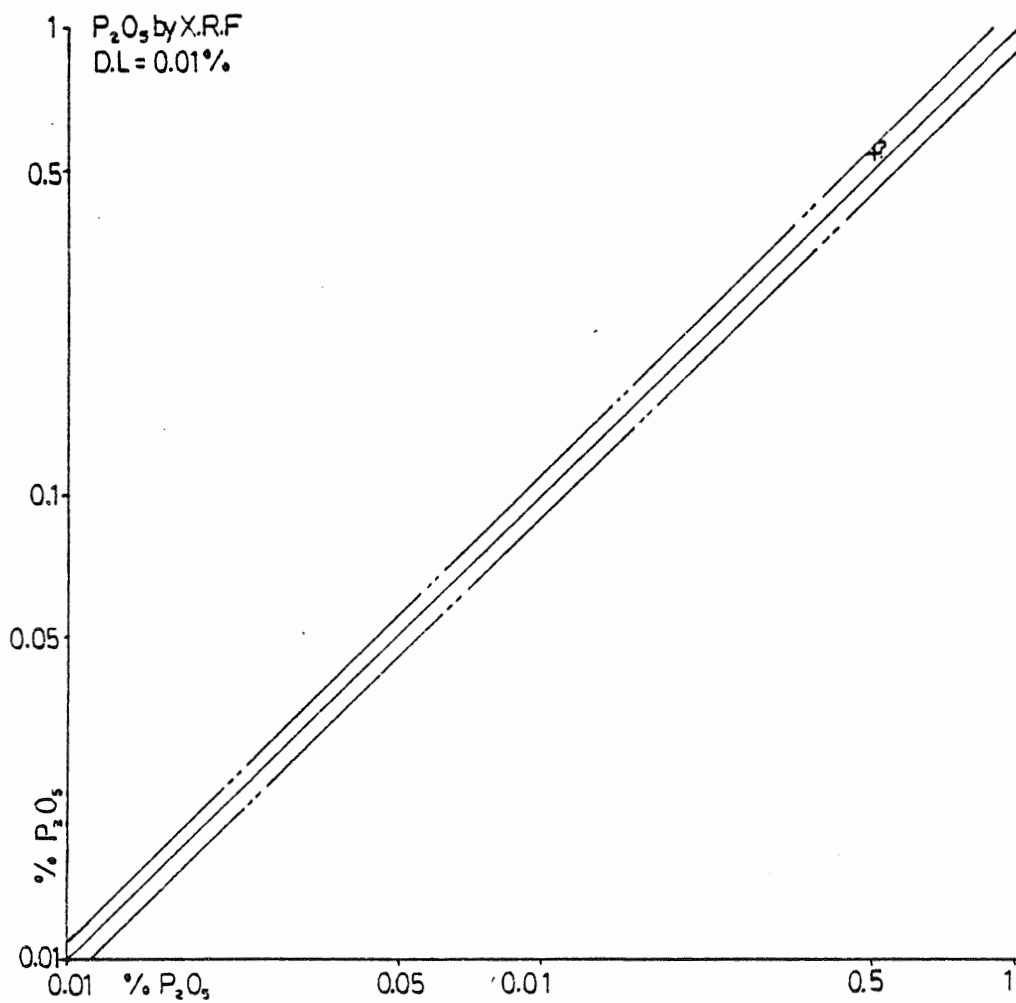
Figure III-3   Precision of trace element analyses
using duplicate samples. Duplicate
results are plotted against each
other. Precision limits of ± 10%
are marked. In the graphs of Bi
and Li, ± 25% limits are also
marked.

Sn by EMS (<1000 ppm)
D.L = 3 ppm
Sn by XRF (>1000 ppm)
D.L = 10 ppm

ppm Sn

1 ppm Sn   5   10   50   100   500   1000   1000 10000 15000

W by NA
D.L = 1 ppm

ppm W

1 ppm W   5   10   50   100   500

Cu by DCP
D.L = 0.5 ppm

Zn by DCP
D.L = 0.5 ppm

Pb by DCP
D.L = 2 ppm

Sb by NA
DL = 0.2 ppm

ppm Sb

ppm Sb

Bi by FAA
DL = 0.1 ppm

ppm Bi

ppm Bi

311
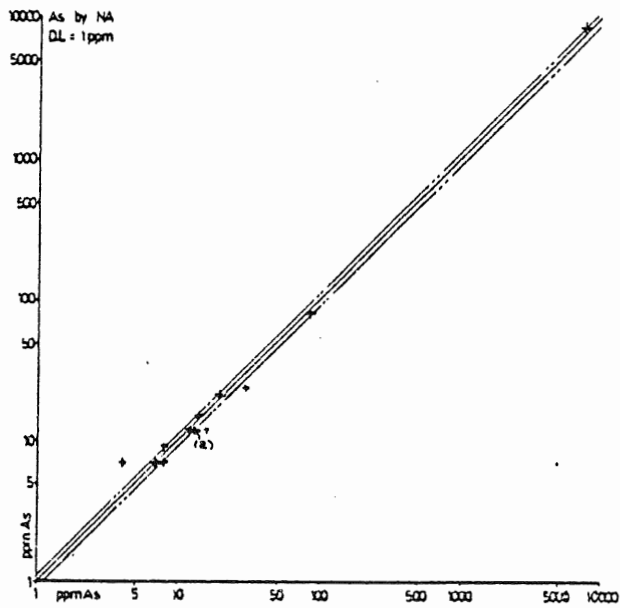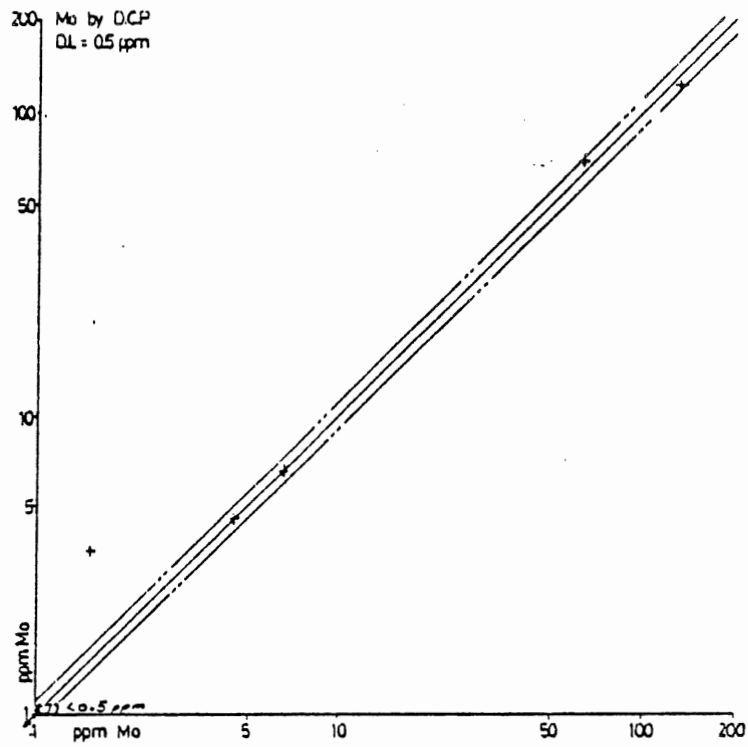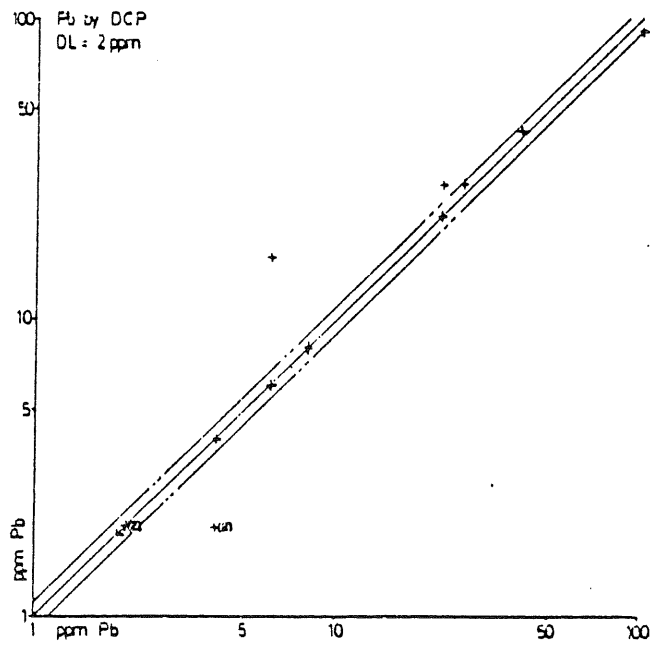
Figure III-4   Precision of whole rock analyses
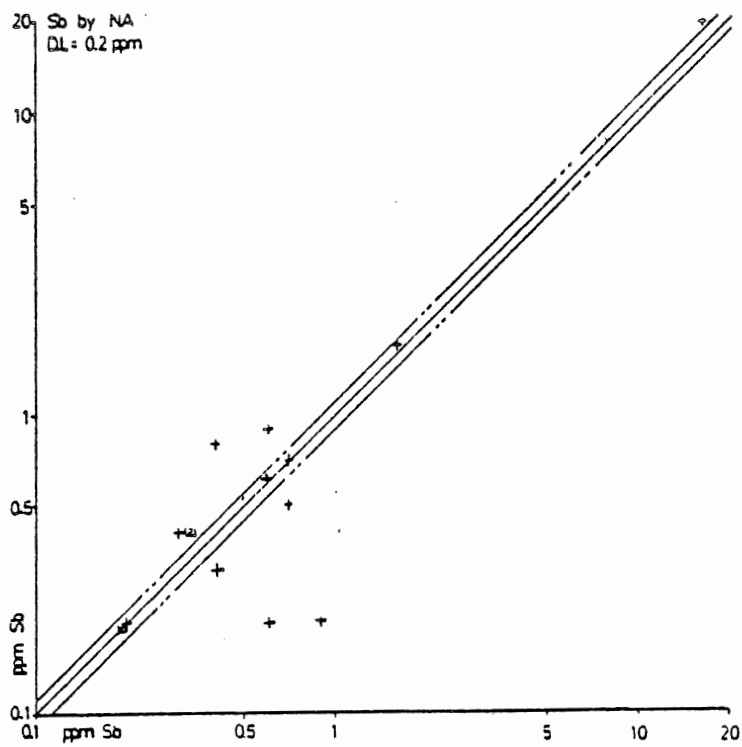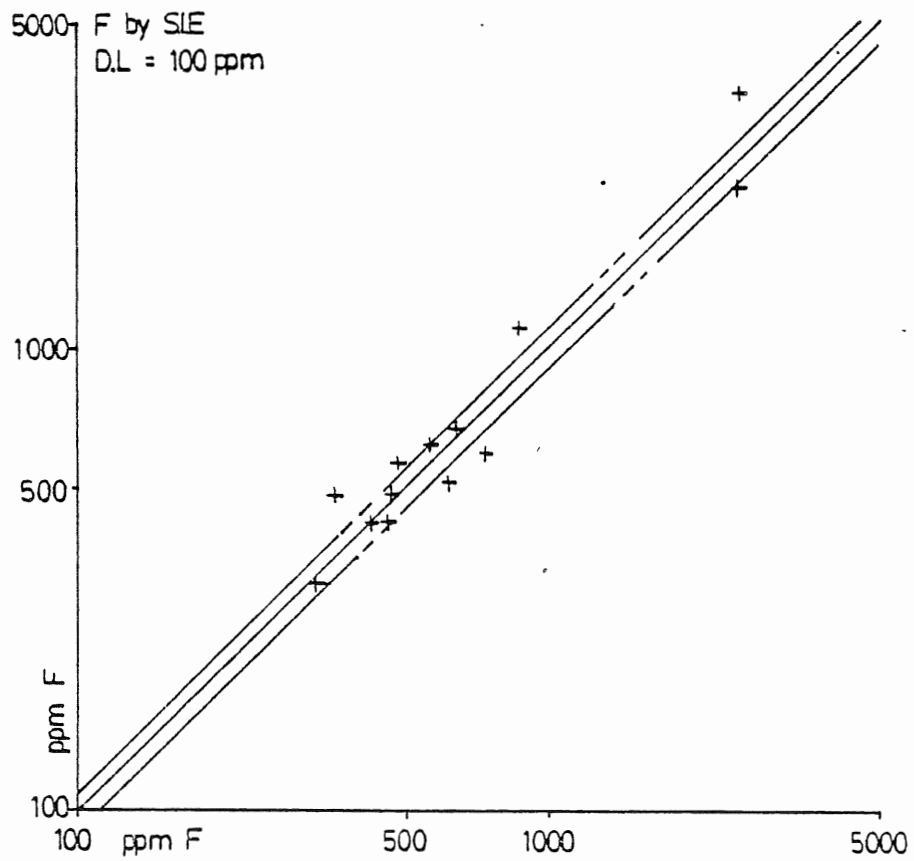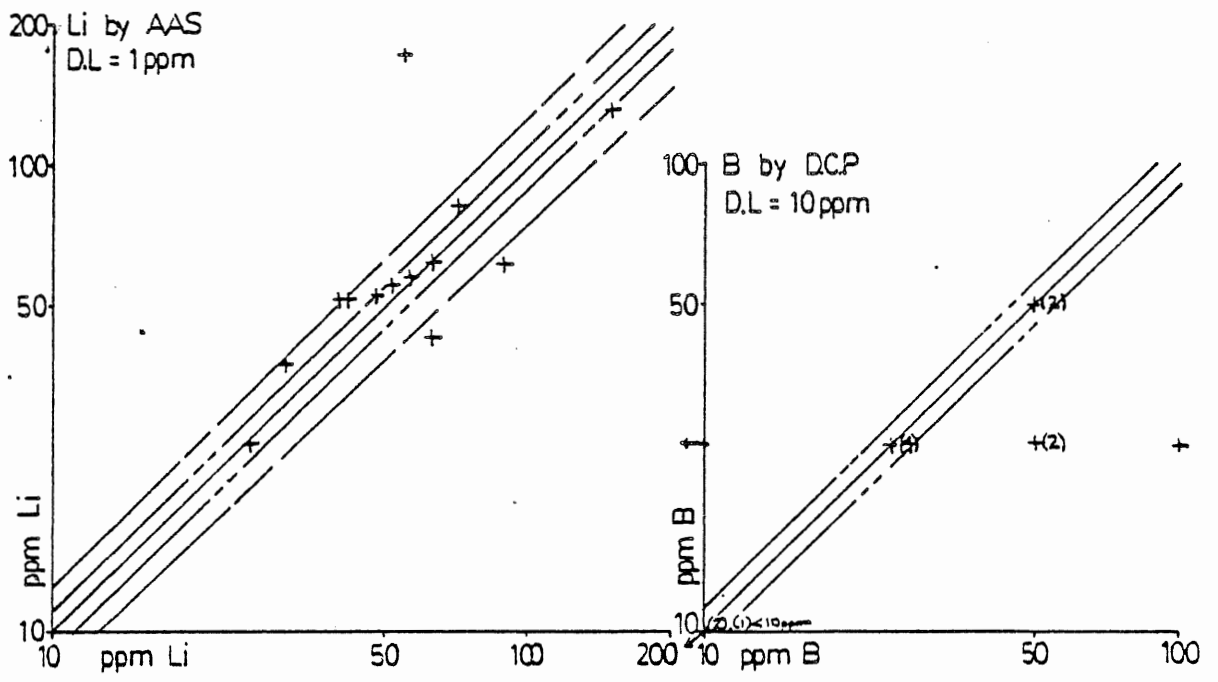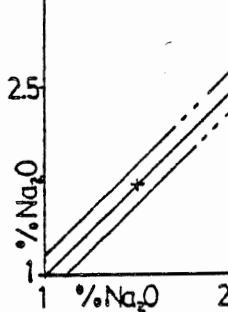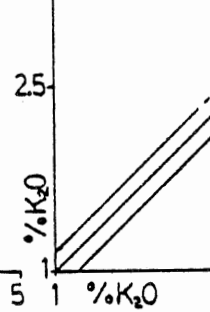   using duplicate samples. Duplicate
                      results are plotted against each
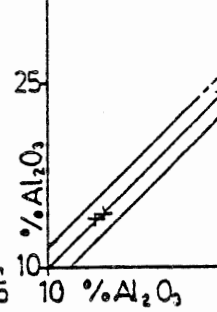   other. Precision limits of ± 10%
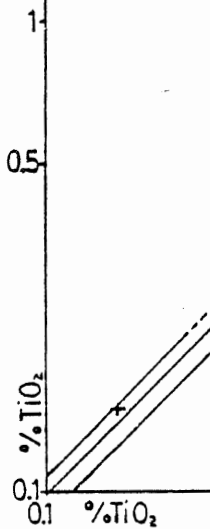   are marked.
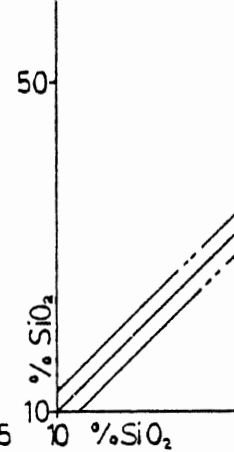
MnO by X.R.F
D.L = 0.01%

% MnO

% MnO

MgO by X R F
D L = 0.01%

% MgO

% MgO

P₂O₅ by X.R.F
D.L = 0.01%
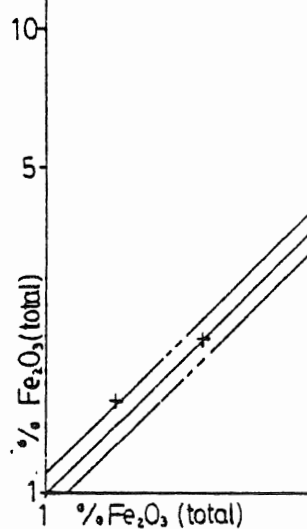
FeO by X.R.F
D.L = 0.01%
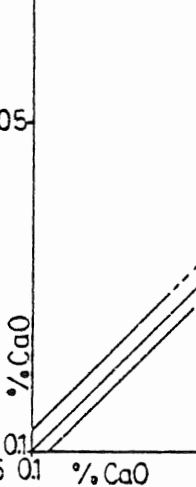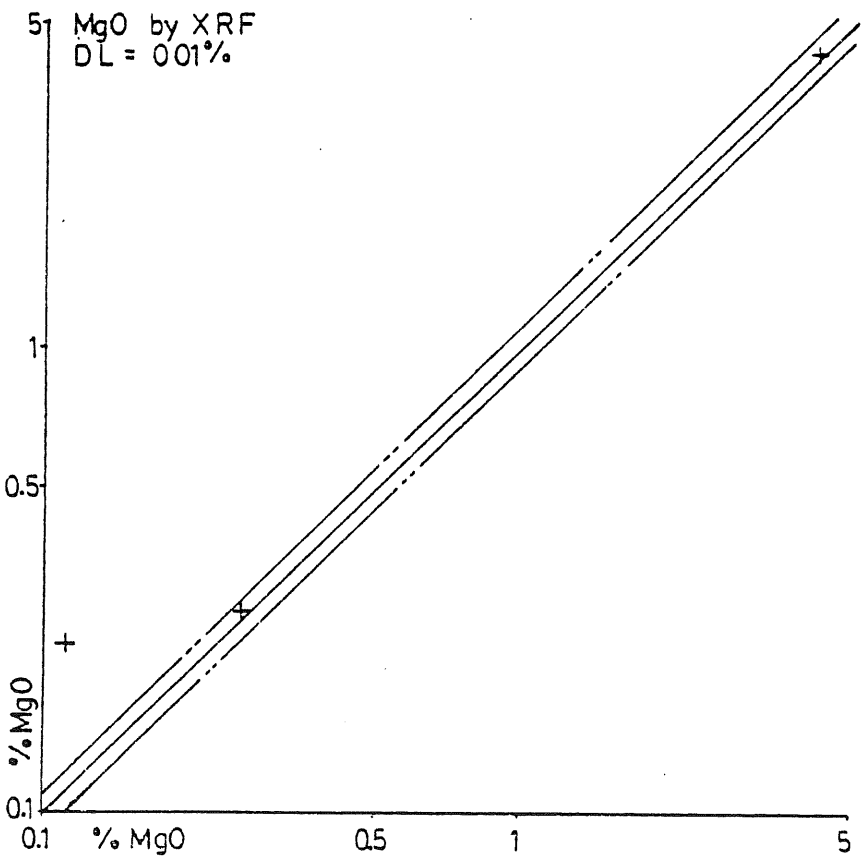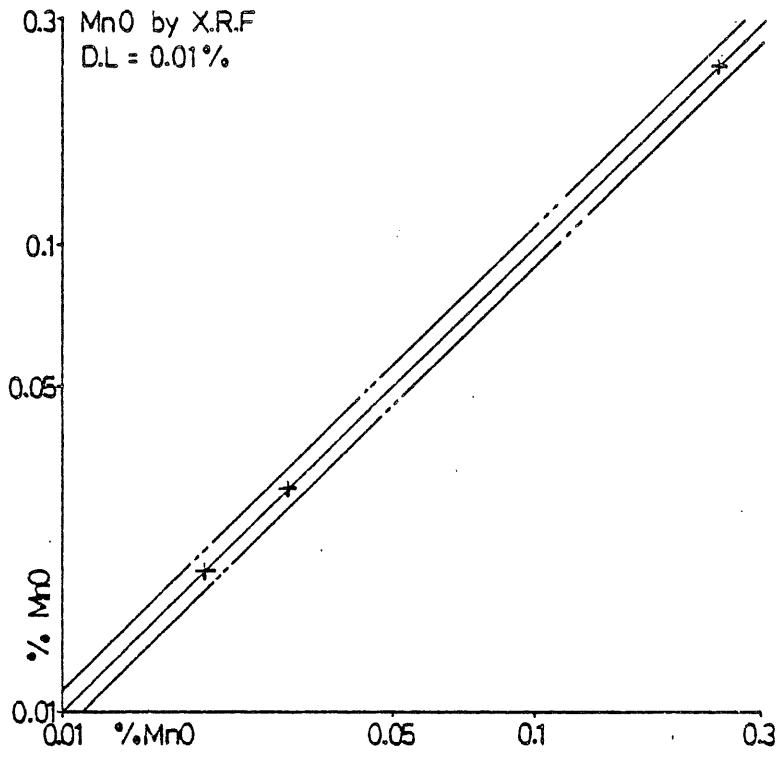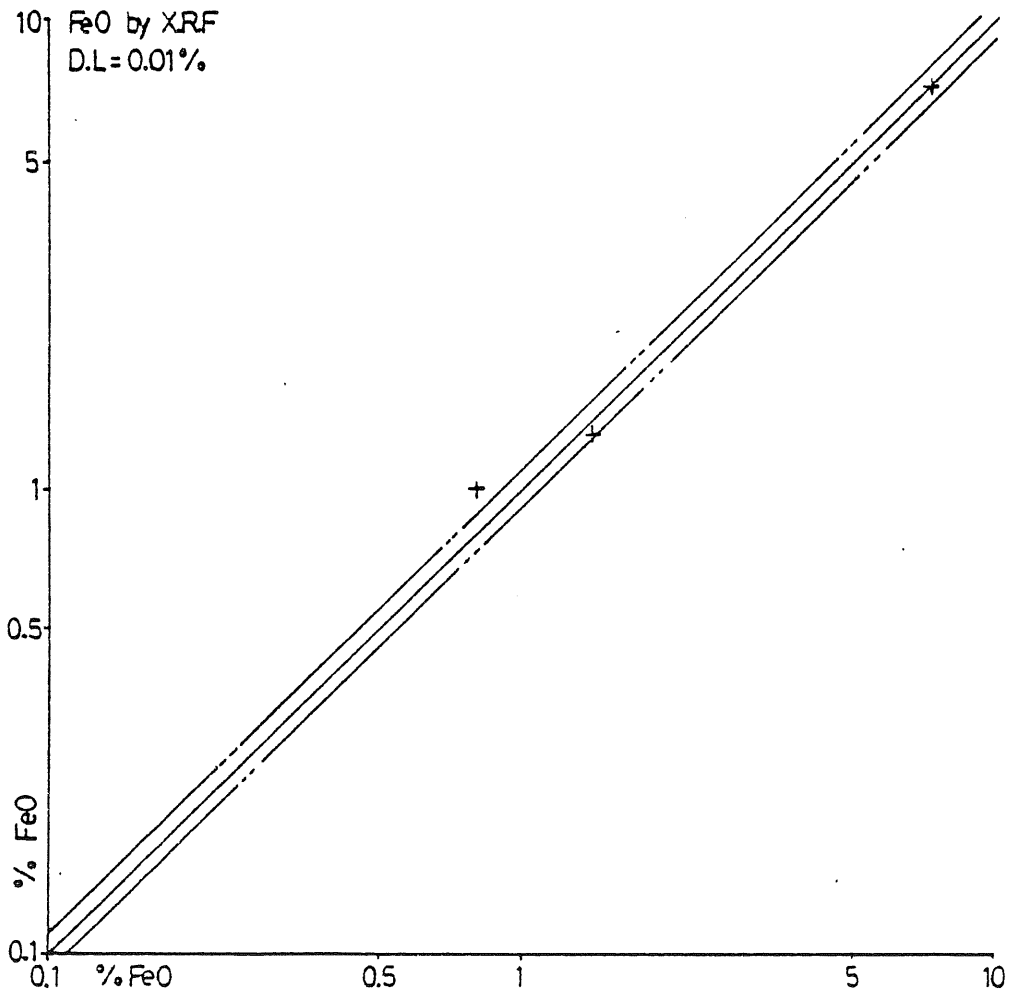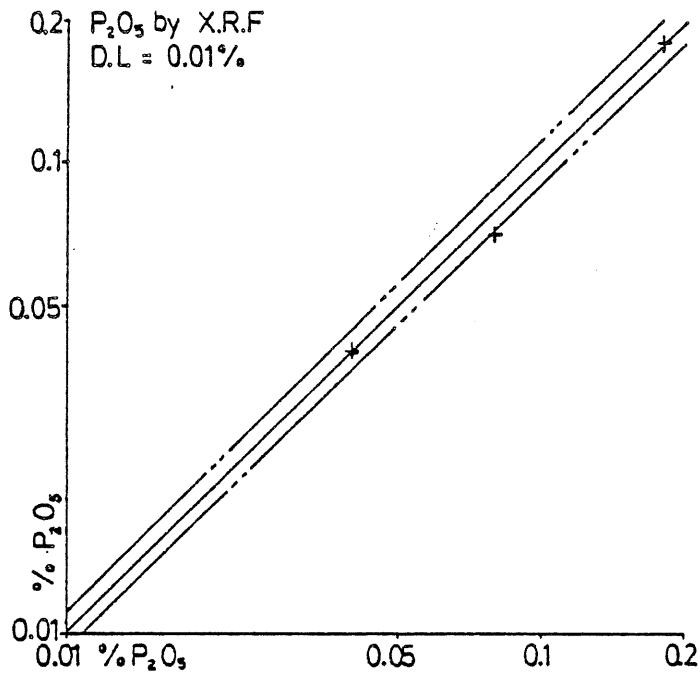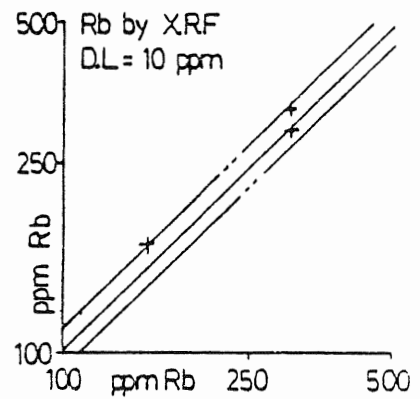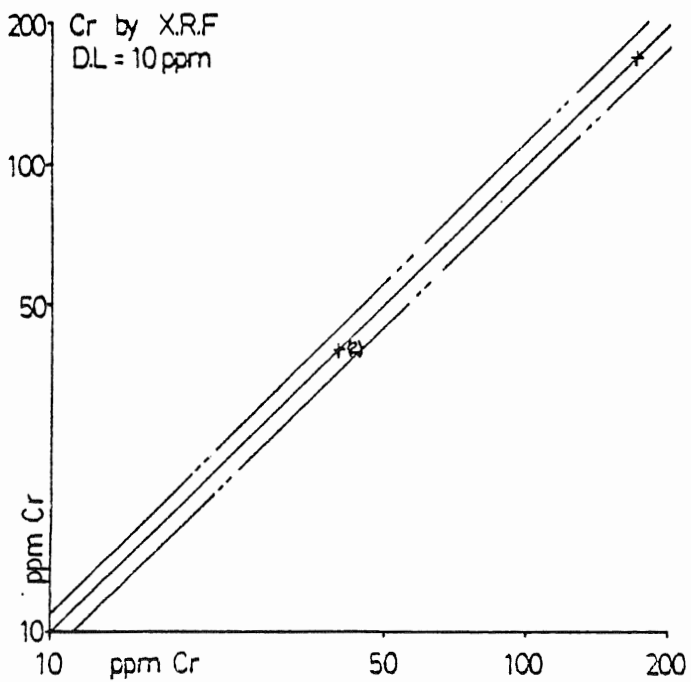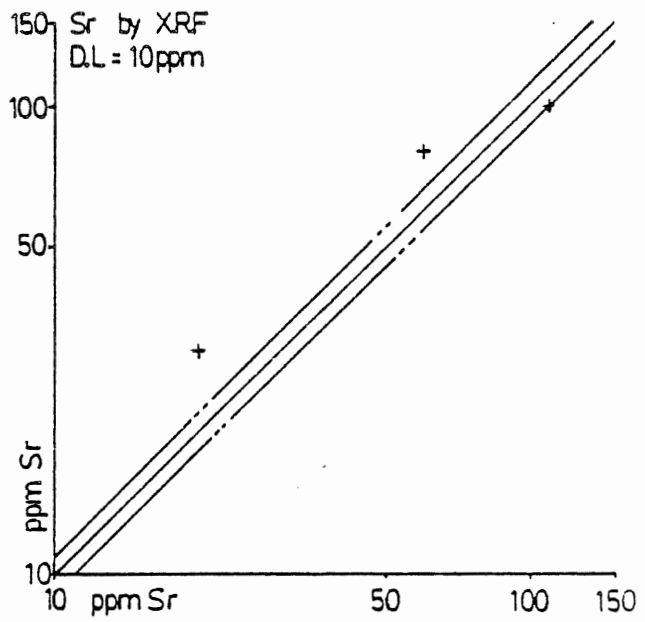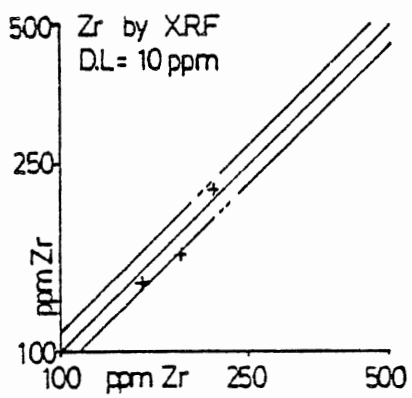
APPENDIX IV

PARTITIONING OF POLYMODAL DISTRIBUTIONS

This section summarizes the procedures used by Sinclair (1974) to choose background and threshold values from a set of geochemical data. It is an arbitrary method of segregating the data into background and anomalous groups by partitioning a cumulative probability plot. Other methods (e.g. Levinson,1974) established the mean (background) and standard deviation of a set of data, with the threshold arbitrarily chosen to correspond to the mean plus two standard deviations, i.e. the upper 2.25% of a normal population. This procedure is not recommended as it assumes that 2.25% of any sample population will be anomalous; also, the ranges of background and anomalous populations in a data set may overlap, so that the mean and standard deviation are actually obtained from the sum of two populations and thus would be of no use.

Sinclair's method uses lognormal probability paper, with a lognormal abscissa scale and an ordinate scale of cumulative frequency percent. A lognormal cumulative distribution of a single population will plot as a straight line; that of two populations will plot as a curve. The approximate proportions of each population is shown by a

change in curvature or slope, i.e., the inflection point. In
an example taken from Sinclair (Fig.IV-1), 20 percent of the
anomalous population A is combined with 80 percent of
background population B. The slope of the combined
populations changes at about the 20th cumulative frequency
percentile, forming an inflection point. The less
perceptible the change in slope, the greater degree of
overlap in the populations.

To separate multiple populations in a data set, a
cumulative frequency diagram must first be constructed. The
steps are similar to those used for creating histograms and
are presented here. An example using tungsten values in the
monzogranite will be shown later.

1. Determine range of log values.

   Range = log(Xmax) - log(Xmin)

2. Determine width of each class interval by dividing the
   range by the number of intervals desired. Construction
   of a histogram may aid in deciding on the number of
   intervals.

   Width = Range / # of intervals

3. List the ranges of each of the class intervals and their
   corresponding antilogs.

4. Record the number of samples in each interval and determine
   their percentages of the total.

5. Sum (cumulate) the percentages of samples in each class
   from the maximum to the minimum value and record the
   cumulative value for each class interval. This is done
   because of the poor precision of values in the lower ranges
   (due to poor sample preparation or analyses or both) and of
   the importance of the higher values in establishing the
   threshold. Cumulation from highest to lowest values will place

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the lowest (and therefore less desirable) class interval in the 100 percent cumulative range, which will not be plotted due to the nature of the graph paper(Lepeltier,1969).

6. Plot points at the antilog of the lower class limit of each class against the cumulative percentage for that interval. Draw a best fit line or lines through the points.

According to Koch and Link(1970) a small sample population(less than 100) gives a poor estimate of the metal content in a data set because the standard deviation is larger(giving a less precise confidence interval) than that of a population with more than 100 values. They have derived an arbitrary 'correction factor' to replace the cumulative frequency percentages by a 'plotting percentage' where,

Plotting Percentage =100 * [3(Cumulative Frequency)-1]/3n + 1

where n is the sample size.

This manipulation was accomplished in the course of population partitioning and an example is given with the usual cumulative frequency determination. It was found that there is not much difference between the two partition models. The background and threshold values changed slightly within the same order of magnitude, and so the plotting percentage formula was not used.

Figure IV-2 shows a graph for tungsten with both the cumulative and plotting percentage points. Note the existence of essentially two lines of different slopes. This implies the existence of two lognormal populations, a higher anomalous one and one of a lower background. Points

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Figure IV-1   Two idealized hypothetical populations
                     A and B are combined in the proportions
                     A/B = 20/80 to produce the dotted curve
                     with an inflection point at 20 cumulative
                     percent.
                     (Modified after Sinclair,1974)
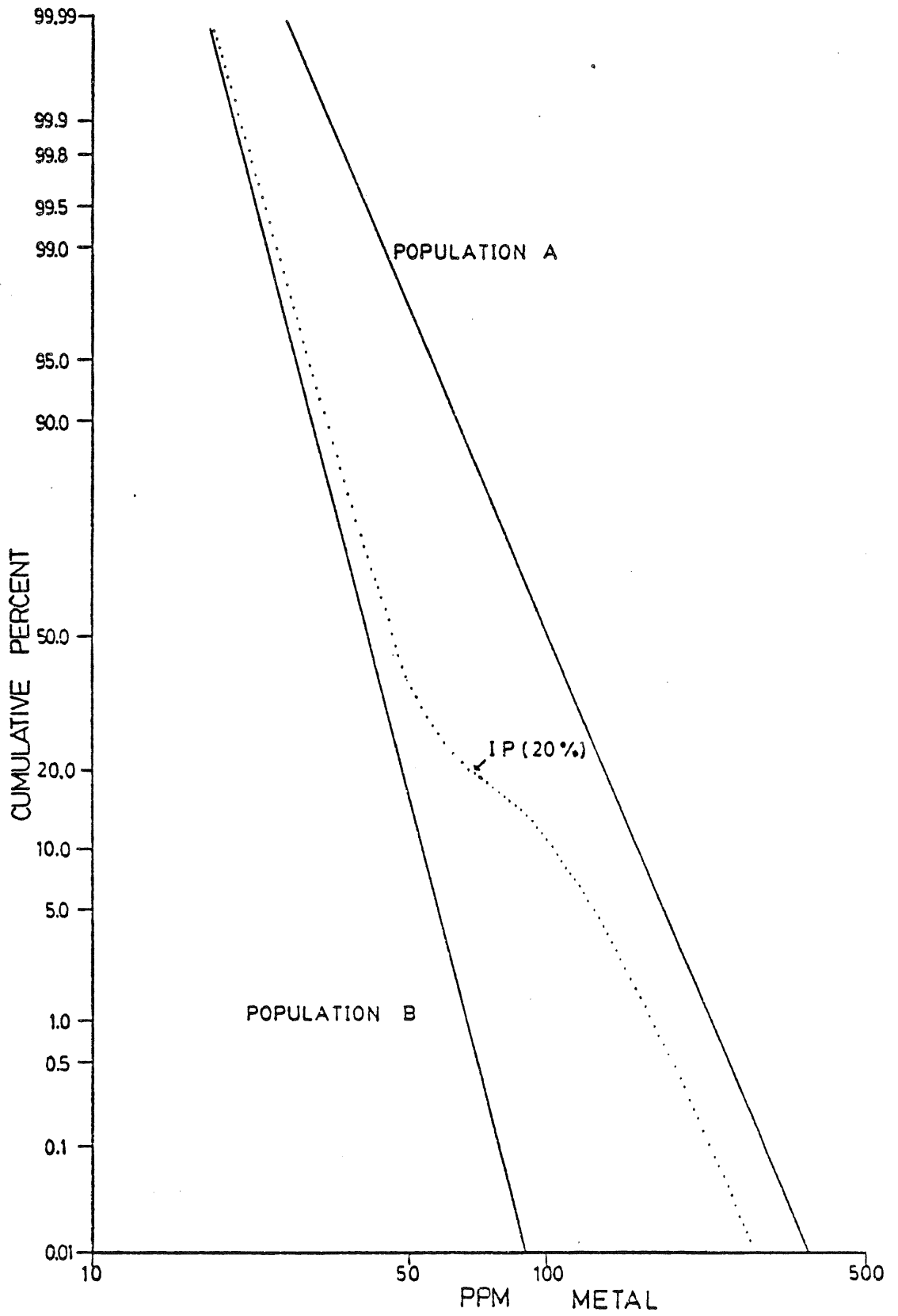
Figure IV-2   Cumulative frequency plot of 25 values
                   of tungsten in plutonic samples, using
                   both cumulative frequency and plotting
                   percentage formulae. Solid lines denote
                   cumulative frequency populations; dashed
                   lines denote plotting percentage popula-
                   tions. There is little difference between
                   the two methods.

ELEMENT: W
POPULATION SIZE : 25
LITHOLOGY : GRANITOID

+ "Cumulative Frequency %" Data Points

⊙ Partition Points establishing
    populations A & B

△ Check Points obtained by combining
    populations in ratio A/B = 32/68

✕ Data Points using plotting
    percentage formula
    (see text for discussion)

● Partition Points derived from
    plotting percentage formula

POPULATION A

IP(32%)
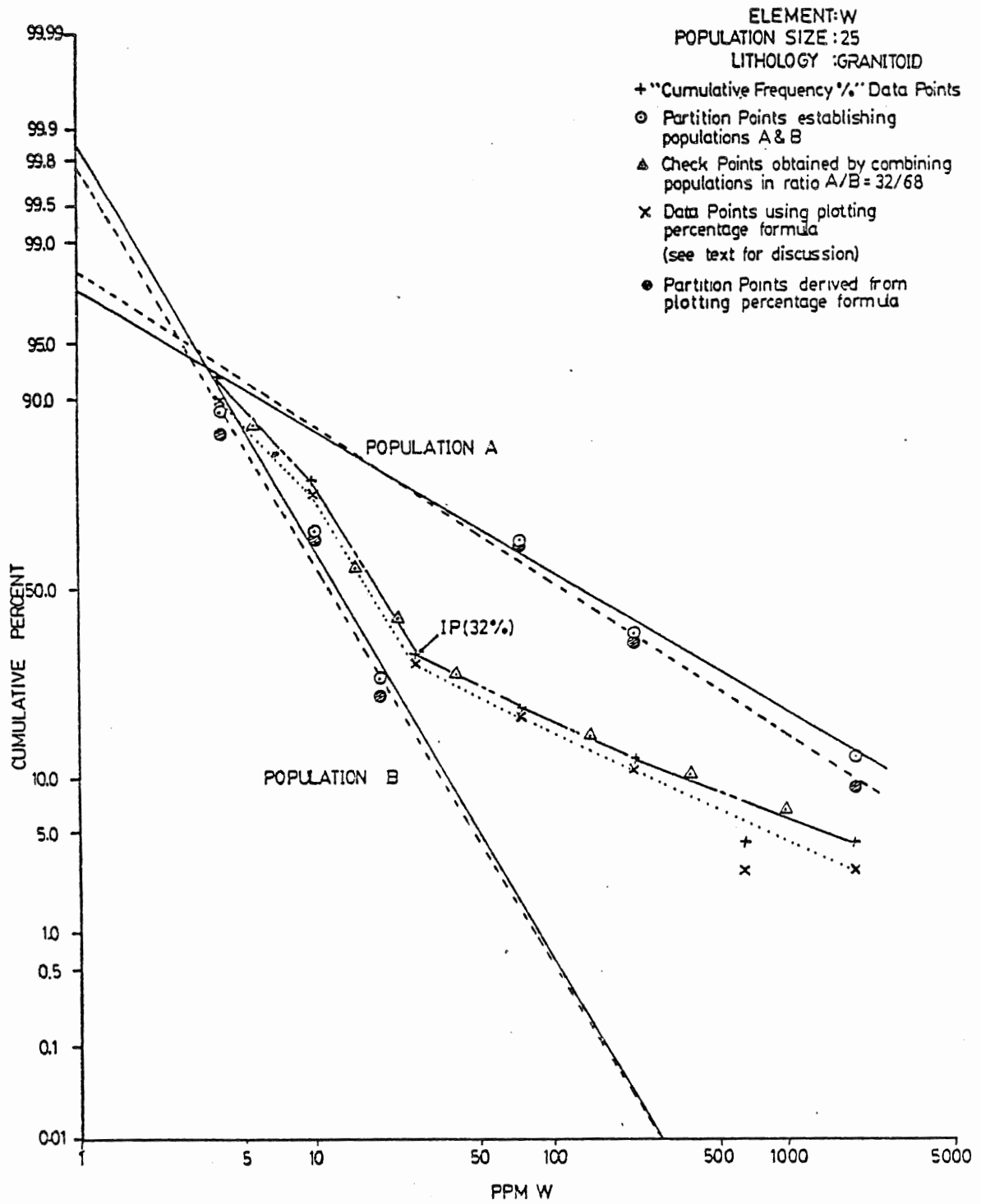
POPULATION B

representing class intervals accounting for 0 percent of the
total population (e.g. 662-1950 ppm interval) are plotted but
are not connected. The types of curves obtained in the study
range from straight lines (one population) to smooth curves
(more than one population) to ragged curves. Data points
were connected by straight lines instead of smooth curves to
facilitate drafting and this may account for some departure
from a smooth curve. Other reasons for such departures
include: incomplete sampling of the data set;
non-lognormality of the distributions (although most trace
elements have log-normal distributions (Levinson,1974)) or;
polymodality of data due to different bedrock types or change
in element concentration by secondary dispersion effects
(Parslow, 1974). Care was taken to ensure appropriate sample
collection (unweathered) and adequate preparation of core
before analysis, but errors can occur, resulting in poor
cumulative frequency plots.

The graph can now be partitioned into its constituent
populations. According to Sinclair (1974), the position of
the inflection point indicates the relative proportions of
the data set. If the populations are very different from
each other (background vs. anomalous), there is a
discernable change in slope of the curve, making the
inflection point readily apparent. Less disparate
populations or populations with a greater degree of overlap
have more subtle slope changes, complicating establishment of

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the inflection point. Parslow (1974) states visual

estimation of the inflection point position may result in

errors of ± 5-10 percent; he also states that because most

anomalous populations constitute a small portion of the total

data set (less than or equal to 10 percent), this estimation

may not compound any large error. It may be possible to

formulate an equation of each cumulative frequency curve and,

by using second derivatives obtain an accurate position of

the inflection point. For the purposes of expediency, this

was not done; instead, visual estimations were performed.

Uncertainties in the inflection point position occurred, and

so several different values were tried to obtain the 'best

fit'. On the tungsten curve, the point was estimated at 32

cumulative percent, corresponding to 27 ppm on the abscissa

scale.

Once the inflection point is obtained, each population

of the data set can be defined. Each data point plotted on

the graph represents a certain percentage of the total data,

but also represents a certain cumulative percentage of one of

the populations. For example, the last point plotted on the

tungsten curve at the 1951 ppm abscissa level represents 4

percent of the total data. It also corresponds to $(4/32 *$

$100) = 12.5$ cumulative percent of population A, so a point is

plotted at this ordinate level on the 1951 ppm level. This

formula is repeated until there are enough points to draw a

straight line, representing population A or until the points

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start to curve. This would indicate the influence of the other population(s). The lines are fitted by regression analysis. One of the problems encountered were too few data points to effectively partition the population. Where this happened, points from the cumulative curves were used and an approximate line was drawn.

The second population (B) is derived in the same way, although the complements of the cumulative frequency scale are used instead, e.g., 30 cumulative percent on the A scale is equivalent to 70 cumulative percent on the B scale.

Defining three or more populations is more complex and is described in Sinclair (1974).

To ensure the method is correct, the two populations are recombined using their defined proportions (e.g. 32 cumulative percent of A plus 68 cumulative percent of B) at various abscissa levels. If these 'check points' do not plot close to the original curve, the process should begin with a new inflection point or different proportions of each population.

The geometric mean of each partitioned population is chosen at the 50th cumulative percentile. The background corresponds to the mean of the lower population. Choosing a threshold is more difficult. If the populations did not overlap too much, there would be a significant change in

327

slope and the threshold could be chosen at that point. Usually this does not happen and thresholds are often chosen arbitrarily from various cumulative percentiles. Threshold values were chosen arbitrarily by Sinclair (1974) at the 97.5 (or 98; or 99) and the complementary 2.5 (or 2; or 1) cumulative percentiles of the partitioned populations A and B, respectively. This divides data into three groups at the corresponding ppm levels, so that for example, 99 percent of population A (and 1 percent of population B) is above a certain ppm value, and 99 percent of B (and 1 percent of A) is below a certain level. See Sinclair for further information.

The purpose of choosing the threshold is to effectively segregate the anomalous values from the normal background data set. Sinclair's method of choosing a threshold value from each population divides the data into three groups. The upper group contains most of the anomalous population; the middle group contains a mixture of anomalous and background values; the lower group contains most of the background values. In this way priorities can be attached to the data for subsequent work: top values demand top priority for follow-up investigation, whereas those of the middle group are of secondary importance.

It is important to compare the values in each group with rock types, sample locations and topography - do not simply

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look at the numbers. For example, those values in the middle
group which occur in the same location as those of the
anomalous group can be included in any follow-up
examination.

The following is an example of constructing a cumulative
frequency diagram using tungsten in monzogranite.

1. Range : <1 to 5400 ppm   Use 1 in the computations, so that,
                            Range = log 5400 - log 1
                                  = 3.73   Round to 3.75

2. Use 8 intervals; thus Interval Width = 3.75 / 8 = 0.47

Interval Range	Antilog of Range(ppm)	Count	% Total	Cumul. %
0-0.47	1-3	2	8	100
0.47-0.94	4-9	4	16	92
0.94-1.41	10-26	11	44	76
1.41-1.88	27-76	3	12	32
1.88-2.35	77-224	2	8	20
2.35-2.82	225-661	2	8	12
2.82-3.29	662-1950	0	0	4
3.29-3.76	1951-5754	1	4	4

		TOTAL 25		

[+]1 includes values <1 ppm

Cumul. Freq.	Plotting %
25	97.4
23	89.5
19	73.7
8	30.3
5	18.4
3	10.5
1	2.6
1	2.6

Partition the population :

3. Inflection Point(visually) = 32 cumulative % (equivalent
                                                to 27 ppm)

    Therefore, Population A consists of 32 % of the data set
              and, Population B consists of (100 - 32) = 68 %
              of the data set.

4. Partition Points of Population A

   i. at 1951 ppm level = 4 cumulative % = 4/32 * 100
                                          = 12.5 % of pop'n A

  ii. at 225 ppm level = 12 cumulative % = 12/32 * 100 = 37.5 %

 iii. at   77 ppm level = 20 cumulative % = 20/32 * 100 = 62.5 %

5. Partition Points of Population B

   i. at 19 ppm level = 50 cumulative %(A scale) = 50 cumul. %(B)
      = 50/68 * 100 = 73.5 % (on B scale) = 26.5 % (A scale)

  ii. at 10 ppm level = 76 cumulative %(A scale) = 24 cumul. %(B)
      = 24/68 * 100 = 35.3 % (B)

 iii. at 4 ppm level = 92 cumulative %(A scale) = 8 cumul. %(B)
      = 8/68 * 100 = 11.8 % (B)

        Plot partition points on graph; draw best fit lines
through the points. Recombine the two populations in the
proportions 32 percent A plus 68 percent B at various ppm
levels to see how well the partitioned populations correspond
to the original curve.

6. Check Point Calculations

   Recombined Populations at a particular ppm level
   = "Point of Mixture"(Pm)

   Pm = fAPA + fBPB

   where   fA = 32 % or 0.32
            PA = A's cumulative % at any ppm level

            fB = 68 % or 0.68
            PB = B's cumulative % at any ppm level

Thus:

    i. at   5.6 ppm level, Pm = 0.32(90.5) + 0.68(84) = 86.1 %

   ii. at   15   ppm level, Pm = 0.32(81.5) + 0.68(43) = 55.3 %

  iii. at   23   ppm level, Pm = 0.32(78)   + 0.68(24) = 41.3 %

   iv. at   40   ppm level, Pm = 0.32(69)   + 0.68(8.5) = 27.9 %

    v. at   150   ppm level, Pm = 0.32(48) + 0.68(0.175) =15.48 %

   vi. at   390   ppm level, Pm = 0.32(32)   + 0.68(0) = 10.24 %

  vii. at   1000   ppm level, Pm = 0.32(20)   + 0 = 6.4 %

        The check points appear to closely correspond the
original curve, so the partitioning is judged a success.

        The above steps were repeated for the plotting
percentage curve (not shown here) and similar populations
were obtained.

	Proportion	Proportion * N (# of samples)	Background (50th %-ile)
Population A	32 %	8	~ 135 ppm
Population B	68 %	17	12 ppm

7. Arbitrary Thresholds

   i. By eye on graph; at inflection point = 27 ppm
      Use as a 'lower threshold'

  ii. 99 cumulative % of population A = < 1 ppm
       1 cumulative % of population B = 90 ppm

 iii. 98 cumulative % of population A = < 1 ppm
       2 cumulative % of population B = 70 ppm

  iv. 2.5 cumulative % of population B = 65 ppm
      Use as an 'upper threshold'

	# samples in group
Group I <27 ppm	17
Group II >27 <65 ppm	3
Group III >65 ppm	5

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This appears to correspond well with the population partitioning. When compared back to the samples, those of groups II and III consist of 2 greisens and 6 'unmineralized'(with regard to tin) samples, containing rare to minor scheelite-bearing quartz veinlets. Tungsten does not appear associated with tin mineralization in greisens, but with other vein stages.

Figure IV-3   Cumulative frequency graphs of 11 elements in 3 lithologies(33 graphs)

ELEMENT: Sn
POPULATION SIZE: 23
LITHOLOGY : Metapelites

+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations A & B
▲ Check Points obtained by combining populations in ratio A/B = 42/58

POPULATION A

IP(42%)

POPULATION B

CUMULATIVE PERCENT

PPM Sn

ELEMENT: Sn
POPULATION SIZE : 51
LITHOLOGY : Metapsammites

+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations A & B
▲ Check Points obtained by combining populations in ratio A/B/C=16.75/46.25/37

ELEMENT: Sn
POPULATION SIZE : 25
LITHOLOGY : Granitoid

+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations A & B
▲ Check Points obtained by combining populations in ratio A/B/C = 25/37/38

POPULATION A

POPULATION B

POPULATION C

IP(62%)

IP(25%)

CUMULATIVE PERCENT

PPM   Sn

ELEMENT: W
POPULATION SIZE : 23
LITHOLOGY : Metapelites

+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing
   populations A & B
▲ Check Points obtained by combining
   populations in ratio ———

ELEMENT:W
POPULATION SIZE : 51
LITHOLOGY :Metapsammites

+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations A & B
▲ Check Points obtained by combining populations in ratio A/B = 17/83

POPULATION A

POPULATION B

IP(17%)

CUMULATIVE PERCENT

PPM W

ELEMENT: Mo
POPULATION SIZE : 23
LITHOLOGY : Metapelites
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing
  populations A & B
▲ Check Points obtained by combining
  populations in ratio A / B = 15.5 / 84.5

POPULATION A

POPULATION B

IP(15.5%)

CUMULATIVE PERCENT

PPM Mo

ELEMENT: Mo
POPULATION SIZE : 51
LITHOLOGY : Metapsammites

+ "Cumulative Frequency %" Data Points

⊙ Partition Points establishing
populations A & B

▲ Check Points obtained by combining
populations in ratio ⟋

ELEMENT: Mo
POPULATION SIZE: 25
LITHOLOGY : Granitoid
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations
△ Check Points obtained by combining populations in ratio A/B = 25/75

POPULATION A

POPULATION B

LP(25%)

CUMULATIVE PERCENT

PPM Mo

342

ELEMENT: As
POPULATION SIZE: 23
LITHOLOGY: Metapelites
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations
△ Check Points obtained by combining populations in ratio A/B/C = 25/40/35

POPULATION A

I.P (65%)

I.P (25%)

POPULATION B

POPULATION C

CUMULATIVE PERCENT

PPM As

343

ELEMENT: As
POPULATION SIZE: 51
LITHOLOGY : Metapsammites
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations
△ Check Points obtained by combining populations in ratio A/B = 13/87

POPULATION A

IP(13%)

POPULATION B

CUMULATIVE PERCENT

PPM As

ELEMENT: As
POPULATION SIZE: 25
LITHOLOGY : Granitoids
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations
△ Check Points obtained by combining populations in ratio A/B = 32/64

ELEMENT: Cu
POPULATION SIZE : 23
LITHOLOGY : Metapelites

+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations A & B
▲ Check Points obtained by combining populations in ratio A/B=50/50

POPULATION A

I.P (50%)

POPULATION B

CUMULATIVE PERCENT

PPM Cu

ELEMENT: Cu
POPULATION   SIZE : 51
LITHOLOGY : Metapsammites
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations
▲ Check Points obtained by combining populations in ratio A/B = 49/51

POPULATION A

POPULATION B

IP (49%)

CUMULATIVE PERCENT

PPM Cu

347

ELEMENT: Pb
POPULATION   SIZE : 23
LITHOLOGY : Metapelites
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations
▲ Check Points obtained by combining populations in ratio A/B = 51/49

CUMULATIVE PERCENT

POPULATION A

POPULATION B

IP(51%)

PPM Pb

349

ELEMENT: Pb
POPULATION   SIZE: 51
LITHOLOGY : Metapsommites

+ "Cumulative Frequency %" Data Points

⊙ Partition Points establishing
   populations

▲ Check Points obtained by combining
   populations in ratio A/B = 10/90

POPULATION A

P(10%)

POPULATION B

CUMULATIVE PERCENT

PPM Pb

350

ELEMENT: Pb
POPULATION SIZE : 25
LITHOLOGY : Granitoid

+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations A & B
▲ Check Points obtained by combining populations in ratio A/B = 25/75

POPULATION A

CUMULATIVE PERCENT

I.P.
(25%)

POPULATION B

PPM Pb

ELEMENT: Zn
POPULATION SIZE : 23
LITHOLOGY : Metapelites
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations
△ Check Points obtained by combining populations in ratio A/B = 22/78

POPULATION A

POPULATION B

I.P (22%)

CUMULATIVE PERCENT

PPM Zn

352

ELEMENT: Zn
POPULATION   SIZE : 51
LITHOLOGY : Metapsammites

+ "Cumulative Frequency %" Data Points

⊙ Partition Points establishing
populations

△ Check Points obtained by combining
populations in ratio A/B = 12/88

POPULATION A

IP (12%)

POPULATION B

CUMULATIVE PERCENT

PPM Zn

353

ELEMENT: Zn
POPULATION SIZE : 25
LITHOLOGY : Granitoid

+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations A & B
▲ Check Points obtained by combining populations in ratio n/a

ELEMENT: Sb
POPULATION SIZE: 23
LITHOLOGY: Metapelites
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing
populations
△ Check Points obtained by combining
populations in ratio A/B = 22/78

POPULATION A

POPULATION B

I.P (22%)

CUMULATIVE PERCENT

PPM Sb

355

ELEMENT: Sb
POPULATION   SIZE : 49
LITHOLOGY : Metapsammites
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing
  populations
△ Check Points obtained by combining
  populations in ratio A/B = 13/87

POPULATION A

IP(13%)

POPULATION B

CUMULATIVE PERCENT

PPM Sb

358

ELEMENT: Sb
POPULATION SIZE : 25
LITHOLOGY : Granitoid
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations
△ Check Points obtained by combining populations in ratio A/B = 28/72

POPULATION A

I.P (28%)

POPULATION B

CUMULATIVE PERCENT

PPM Sb

357

ELEMENT: Bi
POPULATION   SIZE : 23
LITHOLOGY : Metapelites
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations
▲ Check Points obtained by combining populations in ratio A/B : 46/54

POPULATION A

POPULATION B

I.P(46%)

358

CUMULATIVE PERCENT

PPM Bi

ELEMENT: Bi
POPULATION SIZE: 51
LITHOLOGY : Metapsammites
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations
△ Check Points obtained by combining populations in ratio n/a

359

ELEMENT: Bi
POPULATION SIZE : 25
LITHOLOGY : Granitoid
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations
△ Check Points obtained by combining populations in ratio   n/a

360

ELEMENT: Li
POPULATION SIZE : 23
LITHOLOGY : Metapelite

+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing
  populations A & B
▲ Check Points obtained by combining
  populations in ratio A/B = 50/50

ELEMENT: Li
POPULATION SIZE : 51
LITHOLOGY : Metapsammite

+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations A & B
▲ Check Points obtained by combining populations in ratio n/a

ELEMENT: F
POPULATION SIZE: 23
LITHOLOGY : Metapelite

+ "Cumulative Frequency %" Data Points

⊙ Partition Points establishing
  populations A & B

▲ Check Points obtained by combining
  populations in ratio n/a

CUMULATIVE PERCENT

PPM F

ELEMENT: F
POPULATION SIZE: 51
LITHOLOGY : Metapsammites

+ "Cumulative Frequency %" Data Points

⊙ Partition Points establishing
populations A & B

▲ Check Points obtained by combining
populations in ratio A/B = 18/82

POPULATION A

POPULATION B

I.P
(18%)

ELEMENT: F
POPULATION SIZE : 25
LITHOLOGY : Granitoid
+ "Cumulative Frequency %" Data Points
⊙ Partition Points establishing populations
△ Check Points obtained by combining populations in ratio A/B = 16/84

POPULATION A

POPULATION B

I.P.(16%)
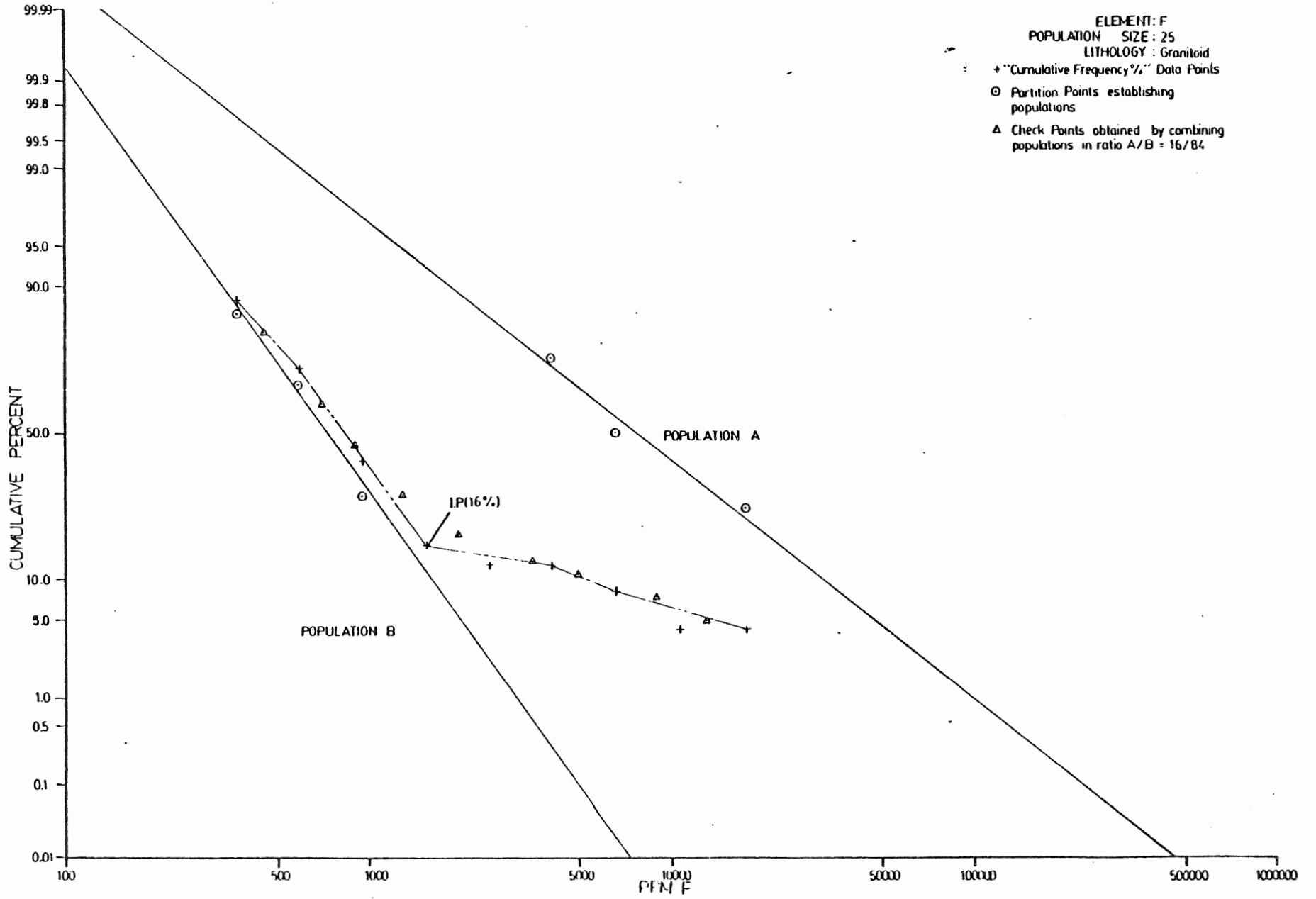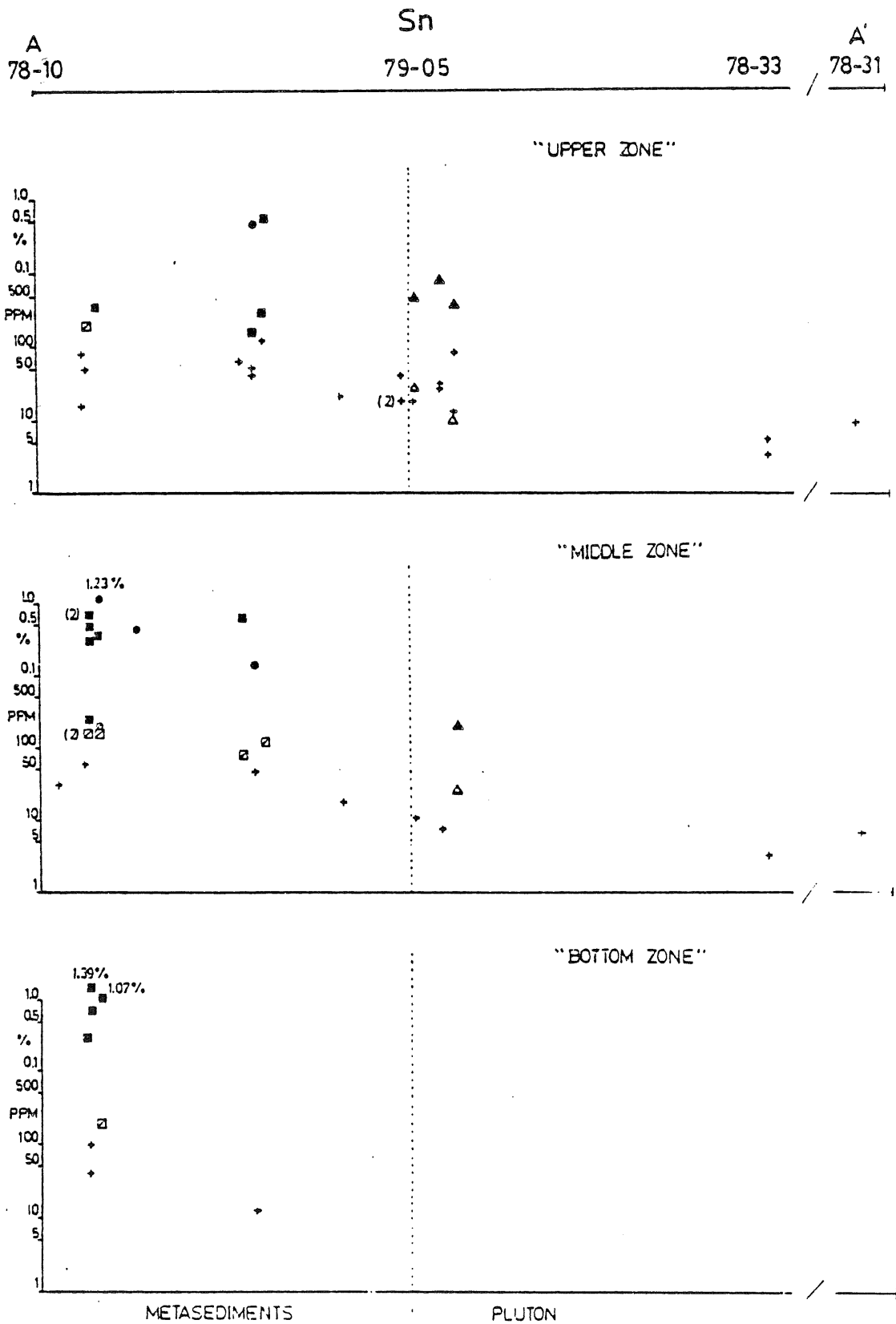
CUMULATIVE PERCENT
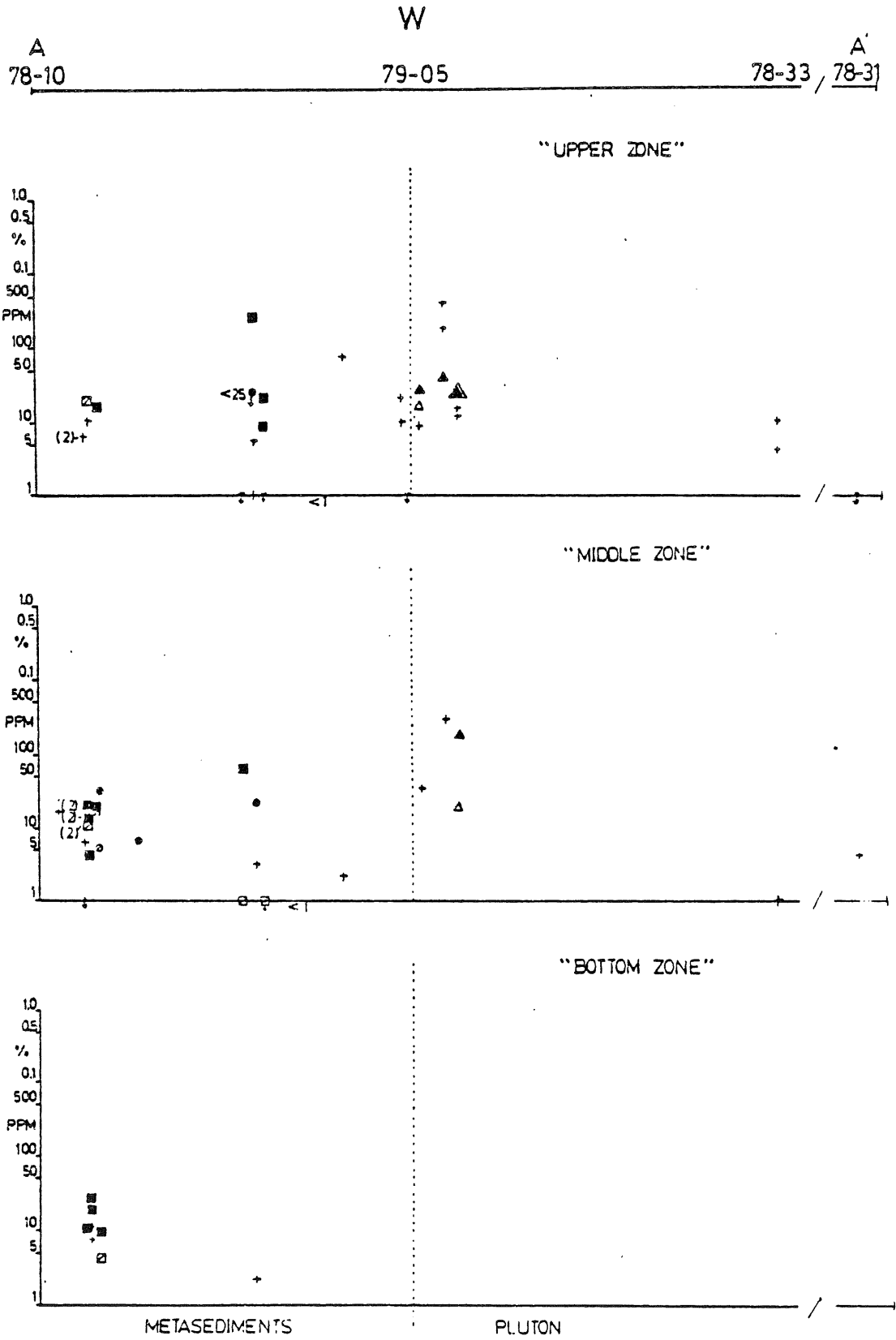
PPM F

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APPENDIX V

VARIATION OF TRACE ELEMENTS IN TWO CROSS-SECTIONS

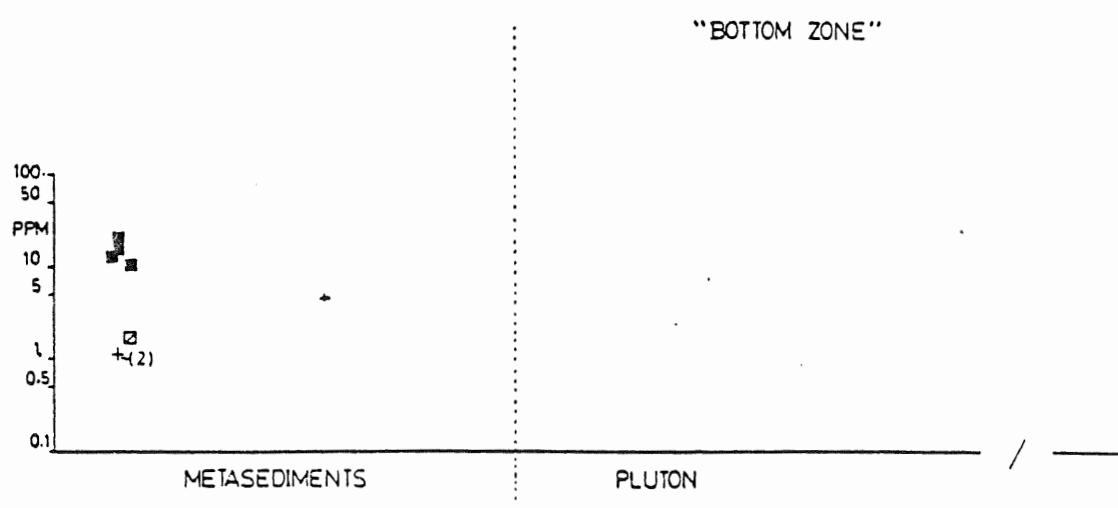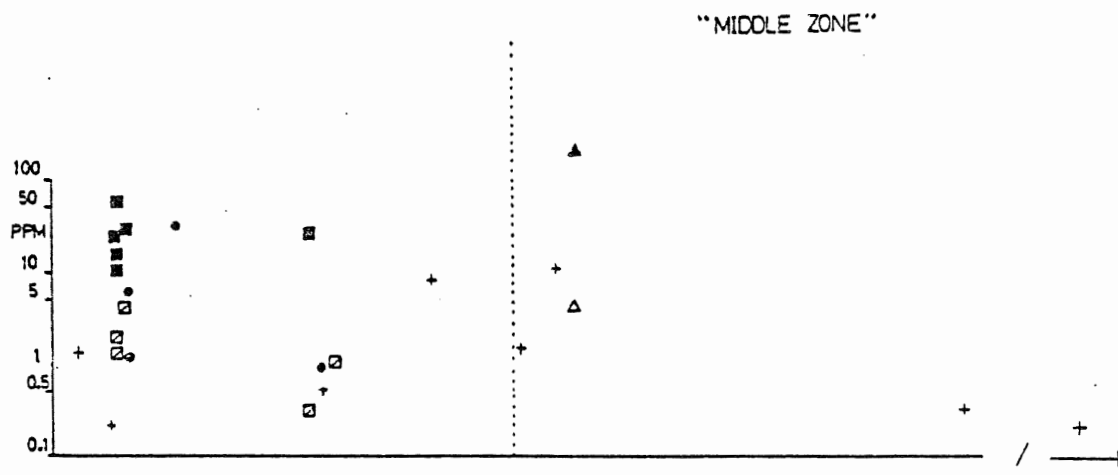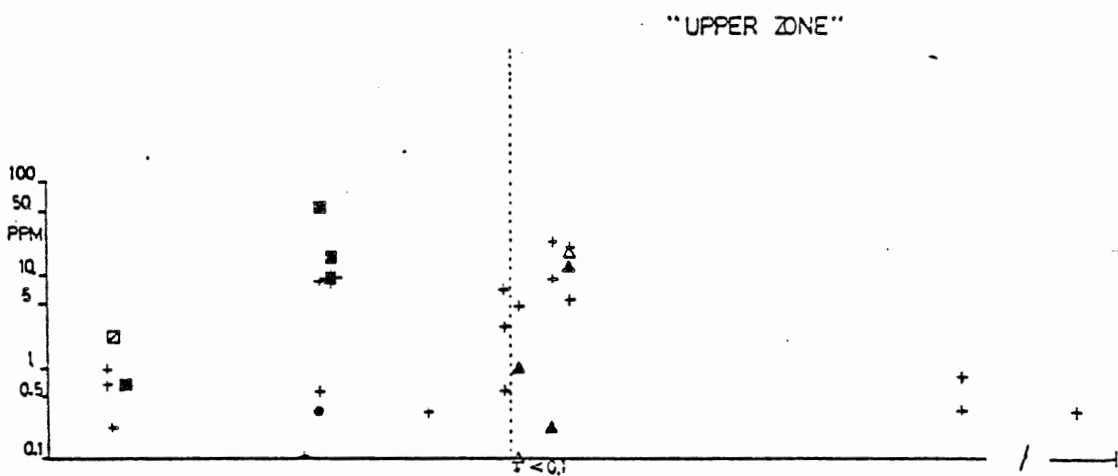Figure V-1   Variation of selected trace elements
                    in two cross-sections, A-A' and B-B'.
                    See Fig. 5.1 for location of cross-
                    section lines. There are slight
                    increases in trace element content of
                    barren samples toward the pluton, but
                    these appear due to thin veinlets
                    containing those elements. There does
                    not appear to be any variation in trace
                    element content with depth, either in
                    barren samples or mineralized 'patches'.
                    However, there is an apparent variation
                    of some elements(Sn, Zn) in metasediment
                    veins with depth and distance from
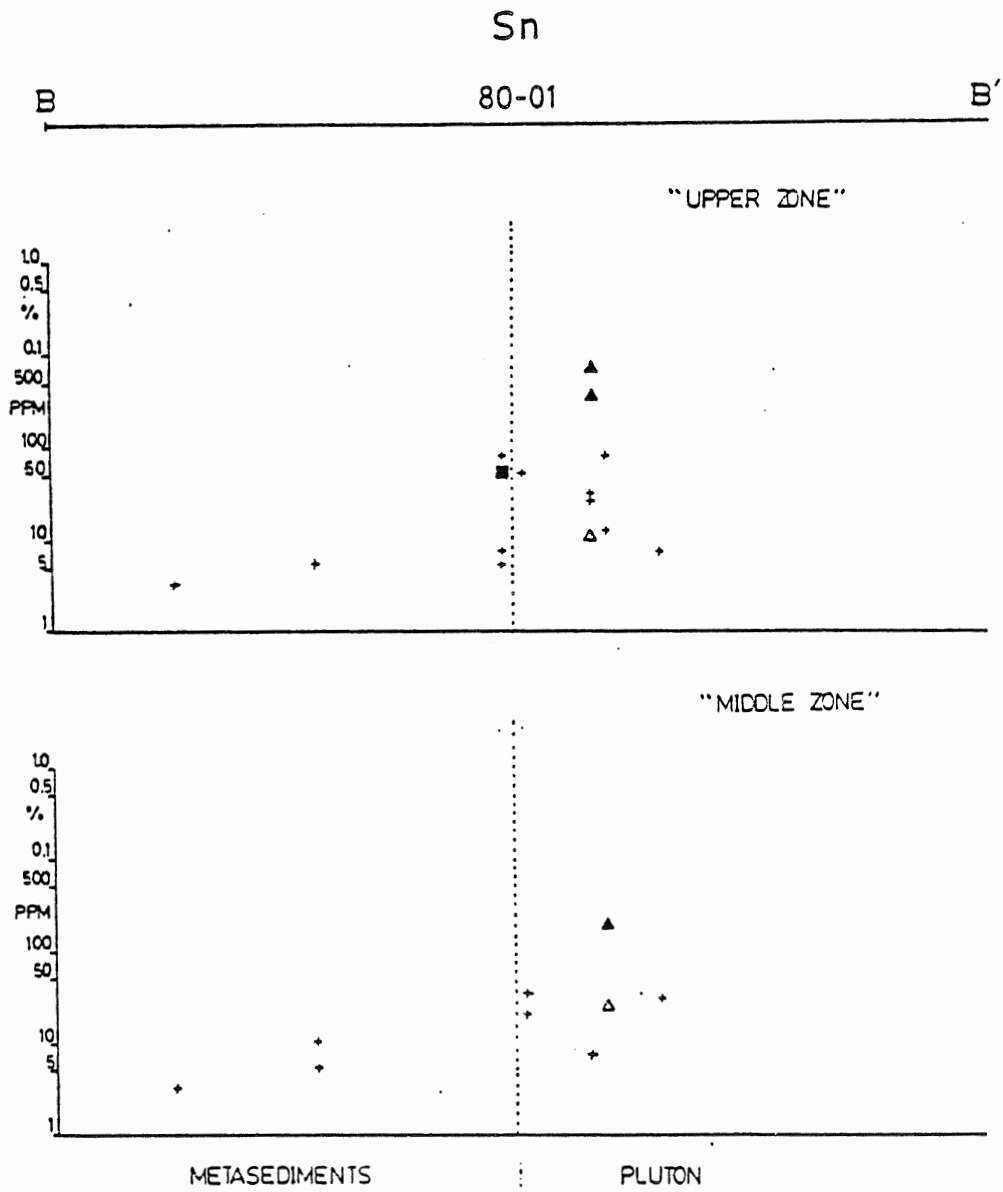   pluton(cross-section A-A').

    +   barren or unmineralized

    ▨   stratiform mineralized 'patch'

    ☒   adjacent mineralized 'patch'(cm to
         m distant)

    ●   vein in metasediments

    ⊘   sample adjacent vein

    ▲   greisen vein or alteration

    △   adjacent greisen

    ↓   below indicated detection limit(note:
         one vein has a high [As], complicating
         W analysis, so that W's detection
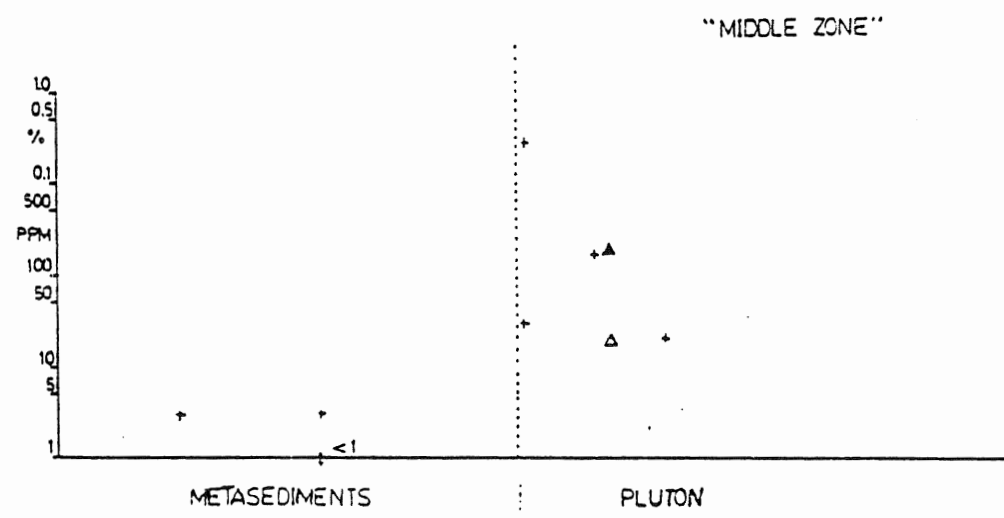   limit is raised to 25 ppm; on section
         A-A')

368

Sn

"UPPER ZONE"

"MIDDLE ZONE"

"BOTTOM ZONE"

METASEDIMENTS   PLUTON

W

A
78-10   79-05   78-33 / 78-31

"UPPER ZONE"

1.0
0.5
%
0.1
500
PPM
100
50

<25

10

(2)+

<1

"MIDDLE ZONE"

1.0
0.5
%
0.1
500
PPM
100
50

(2)+
(2)+

10
5

<1

"BOTTOM ZONE"

1.0
0.5
%
0.1
500
PPM
100
50

10
5

1

METASEDIMENTS   PLUTON

Cu

A
78-10

79-05

78-33 / 78-31
A'

"UPPER ZONE"

"MIDDLE ZONE"

"BOTTOM ZONE"

METASEDIMENTS

PLUTON

As

A
78-10

79-05

78-33 / 78-31

A'

"UPPER ZONE"

"MIDDLE ZONE"

"BOTTOM ZONE"

METASEDIMENTS · PLUTON

Zn

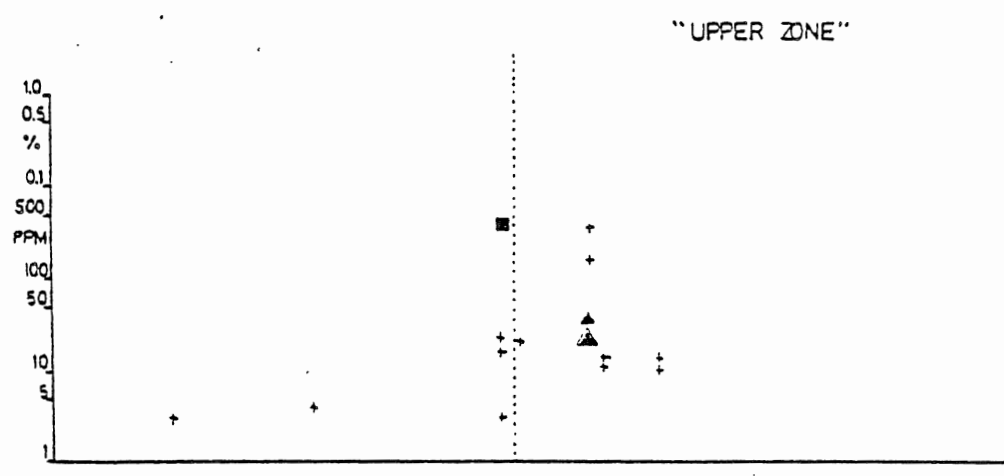A   A'
78-10   79-05   78-33 / 78-31

"UPPER ZONE"

"MIDDLE ZONE"

"BOTTOM ZONE"

METASEDIMENTS   PLUTON

373

A   Bi   A'

78-10   79-05   78-33 / 78-31

"UPPER ZONE"

"MIDDLE ZONE"

"BOTTOM ZONE"

METASEDIMENTS   PLUTON

Li

A   A'
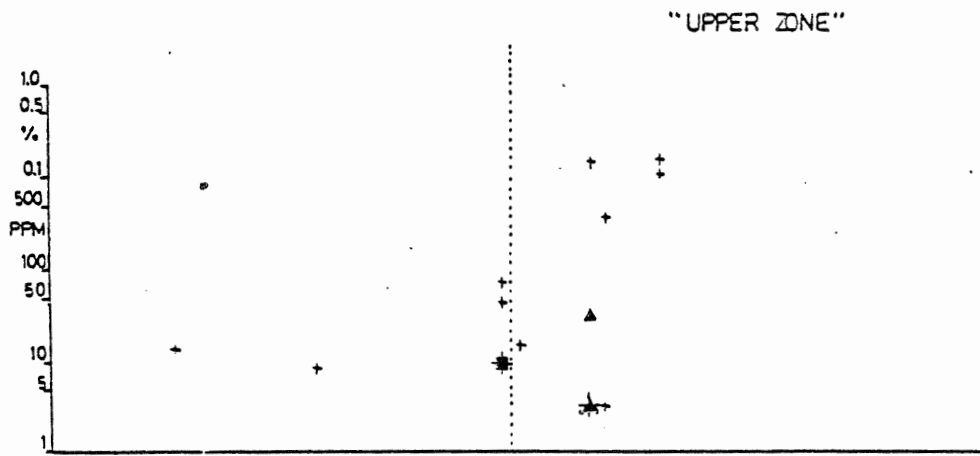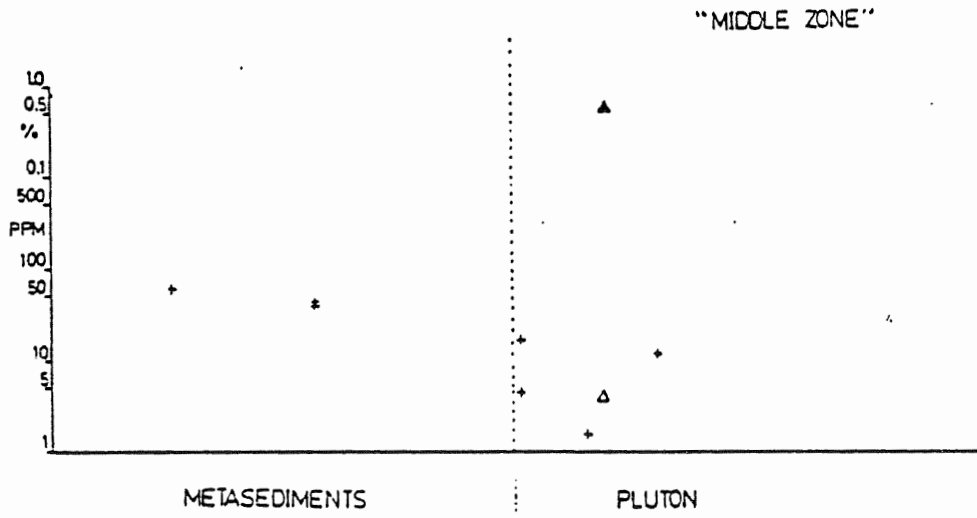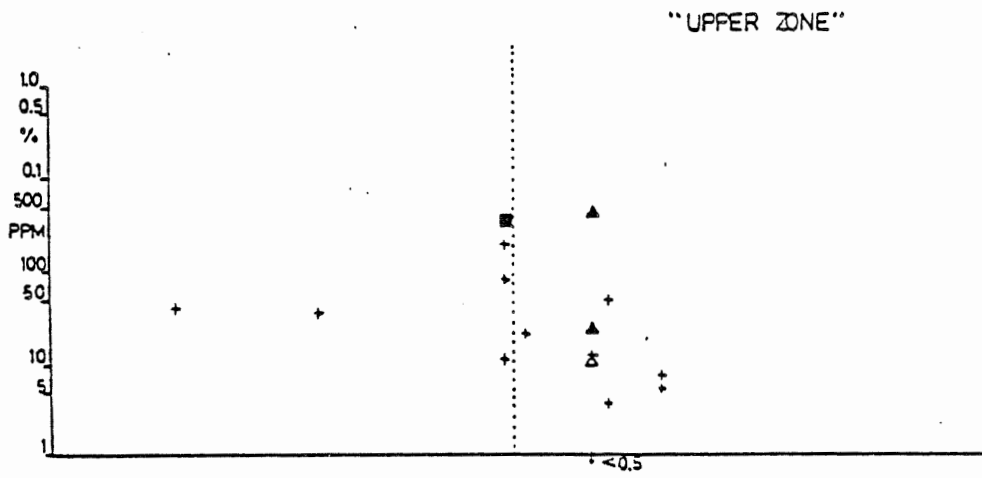78-10   79-05   78-33 , 78-31

"UPPER ZONE"

"MIDDLE ZONE"

"BOTTOM ZONE"

METASEDIMENTS   PLUTON

375

F

A
78-10 · 79-05 · 78-33 / A' 78-31

"UPPER ZONE"

"MIDDLE ZONE"

"BOTTOM ZONE"

METASEDIMENTS · PLUTON

Sn

"UPPER ZONE"

"MIDDLE ZONE"

METASEDIMENTS   PLUTON

W
80-01

"UPPER ZONE"

"MIDDLE ZONE"

METASEDIMENTS | PLUTON

As

B   80-01   B'

"UPPER ZONE"

"MIDDLE ZONE"

METASEDIMENTS   PLUTON

Cu
80-01

B — "UPPER ZONE" — B'

"MIDDLE ZONE"

METASEDIMENTS | PLUTON

Zn

B   80-01   B´

"UPPER ZONE"

"MIDDLE ZONE"

METASEDIMENTS   PLUTON

Bi

B   80-01   B'

"UPPER ZONE"

100
50
PPM
10
5

1
0.5

0.1

"MIDDLE ZONE"

100
50
PPM
10
5

1
0.5

0.1

METASEDIMENTS   PLUTON

Li
80-01

F

(2.8%)   "UPPER ZONE"

1.0
0.5
%
0.1
500
PPM
100
50
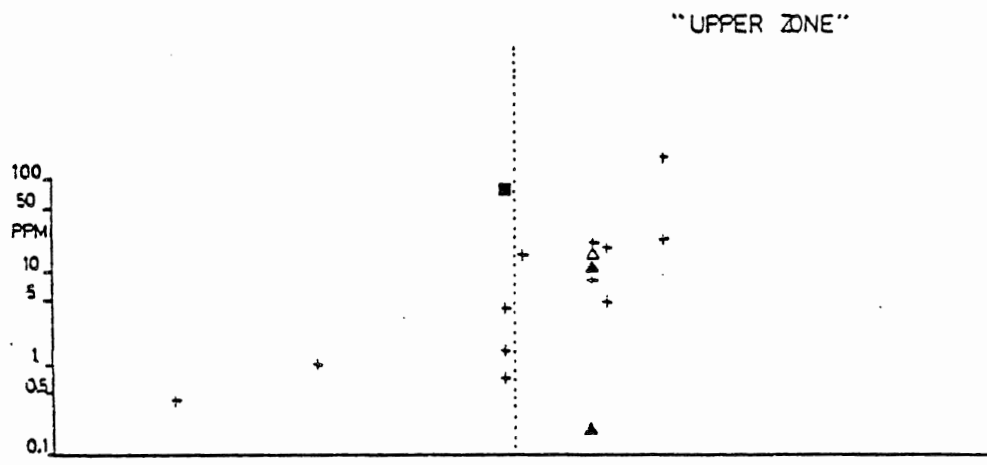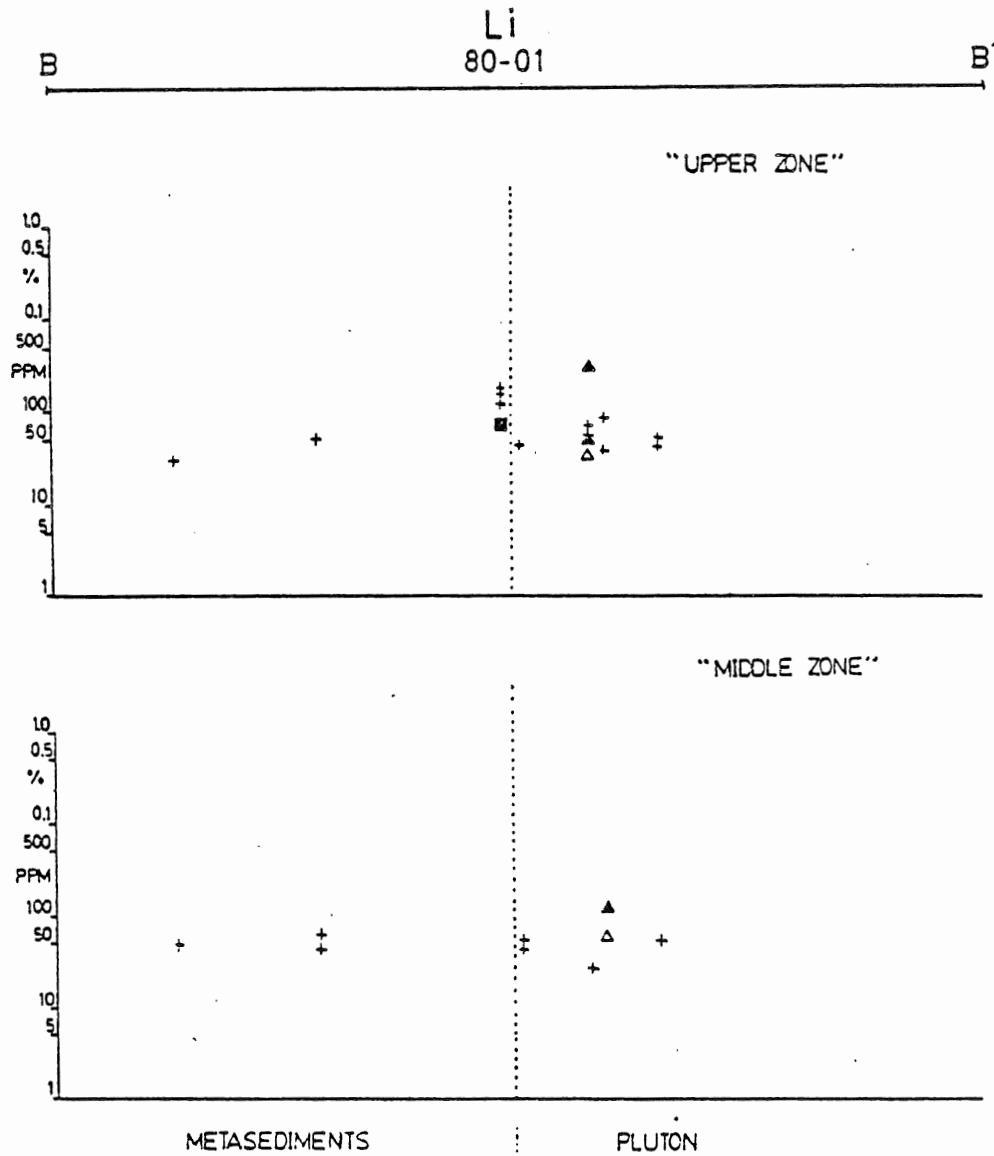
10
5

1

"MIDDLE ZONE"

1.0
0.5
%
0.1
500
PPM
100
50

10
5

1

METASEDIMENTS   PLUTON
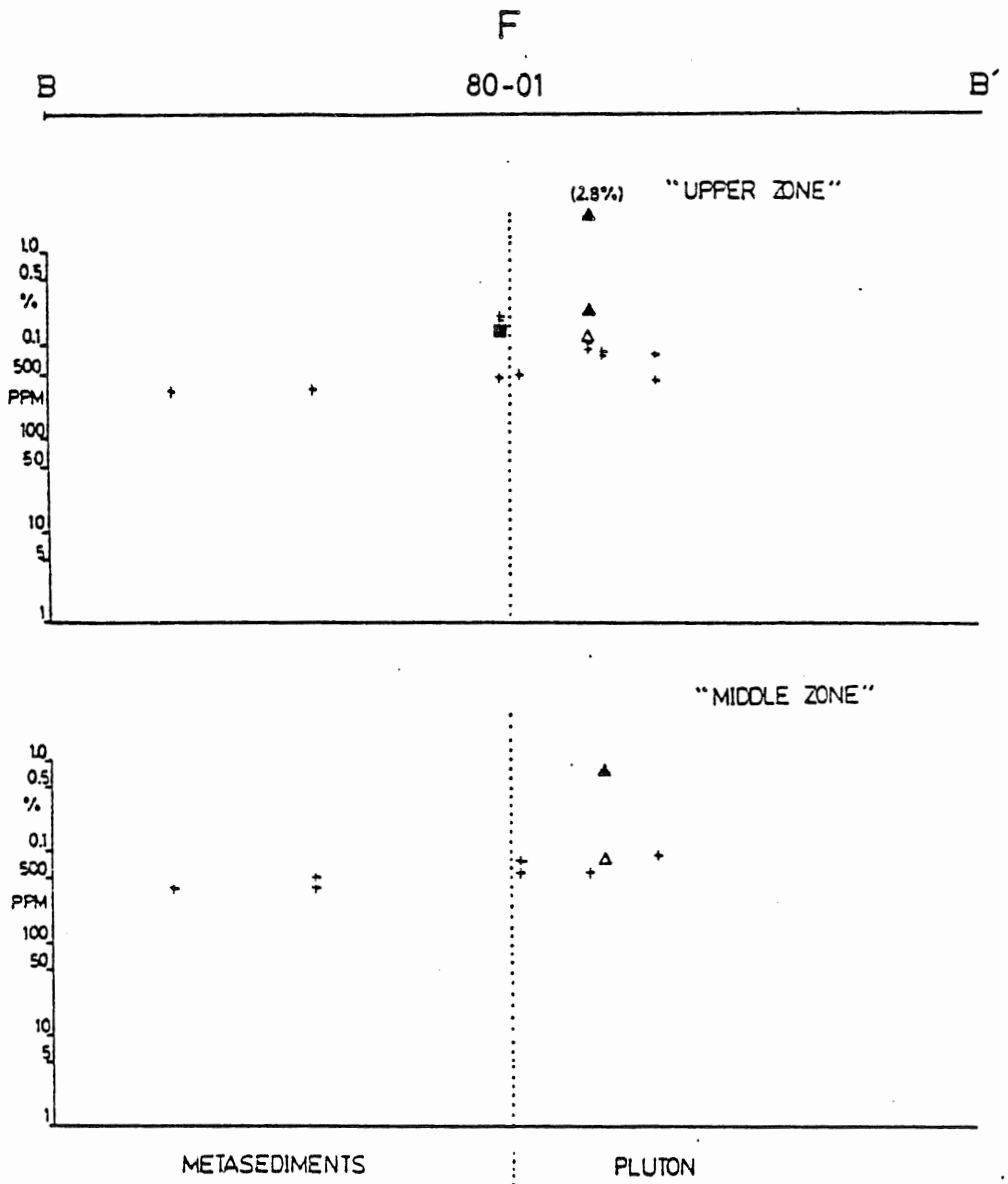
SELECTED BIBLIOGRAPHY

Abbey, S., 1980, Studies in "standard samples" for use in the general analysis of silicate rocks and minerals. Part 6: 1979 edition of "usable" values: Géol. Surv. Can. Paper 80-14, 30 p.

Bailey, J.C., 1977, Fluorine in granitic rocks and melts: a review: Chem. Geol., vol. 19, p. 1-42.

Barnes, H.L., 1979, Solubilities of ore minerals: in H.L. Barnes, ed. Geochemistry of Hydrothermal Ore Deposits, 2nd edition: J. Wiley and Sons, New York, p. 404-460.

Barr, S.M., 1982, Geochemistry of granitoid plutons of Cape Breton Island, Nova Scotia: in Y.T. Maurice, ed. Uranium in granites: Geol. Surv. Can. Paper 81-23, p. 55-59.

Baumann, L., 1970, Tin deposits of the Erzgebirge: Trans. Inst. Min. Metall. B79, p. 68-75.

_____ and Tischendorf, G., 1978, The metallogeny of tin in the Erzgebirge: in M. Stemprok, ed. Metallization Associated with Acid Magmatism(MAWAM): Czechoslovak Geol. Surv., vol. 3, p. 17-28.

Berry, L.G. and Mason, B., 1959, Mineralogy: Concepts, Descriptions, Determinations: W.H. Freeman and Company, San Francisco, 630 p.

Bischoff, J.L., Radtke, A.S. and Rosenbauer, R.J., 1981, Hydrothermal alteration of graywacke by brine and seawater: roles of alteration and chloride complexing on metal solubilization at $200°$ and $350°C$: Econ. Geol., vol. 77, p. 659-676.

Blatt, H. and Sutherland, B., 1969, Intrastratal solution and non-opaque heavy minerals in shale: Jour. Sed. Petrol., vol. 39, p. 591-600.

_____, Middleton, G. and Murray, R., 1980, Origin of Sedimentary Rocks: Prentice-Hall Inc., New Jersey, 728 p.

Boissavy-Vinau, M. and Roger, G., 1980, The TiO2 /Ta ratio as an indicator of the degree of differentiation of tin granites: Mineralium Deposita, vol. 15, p. 231-236.

Bromley, A.V., 1975, Tin mineralization of western Europe: is it related to crustal subduction?: Trans. Inst. Min. Metall. B 84, p. 28-29.

Burnham, C.W., 1979, Magmas and hydrothermal fluids: in H.L. Barnes, ed. Geochemistry of Hydrothermal Ore Deposits, J. Wiley and Sons, New York, p. 71-136.

_____ and Ohmoto, H., 1980, Late-stage processes of felsic magmatism: Mining Geology Special Issue, no. 8, p. 1-11.

Cant, J.W., Fisher, D.F., Wilson, B.H., Dickie, G.B. and Sarkar, P.K., 1978, Report of exploration in Yarmouth County, Nova Scotia, May 1976 to April 1978: Shell Canada Resources Limited, internal report, 54 p.

_____, 1979, Report on an induced polarization survey and diamond drilling program, Plymouth area, Yarmouth project: Shell Canada Resources Limited, internal report, 13 p.

Carmichael, I.S.E., Turner, F.J., and Verhoogen, J., 1974, Igneous Petrology: McGraw-Hill, New York, 739 p.

Cathles, L.M., 1981, Fluid flow and genesis of hydrothermal ore deposits: Econ. Geol. 75th Ann. Vol., p. 424-457.

Charoy, B. and Weisbrod, M., 1974, Interactions between rocks and solutions in mineralized greisens from St. Renan(Brittany, France): in M. Stemprok, ed. Metallization Associated with Acid Magmatism (MAWAM): Czechoslovak Geol. Surv., vol. 1, p. 254-261.

Chatterjee, A.K., 1980, Polymetallic tin mineralization related to acid magmatism, southwestern Nova Scotia: in K.A. McMillan, ed. Nova Scotia Dept. of Mines and Energy, Mineral Resources Division, Report of Activities 80-1, p. 59-65.

_____ and Muecke, G.K., 1982, Geochemistry and distribution of uranium and thorium in the granitoid rocks of the South Mountain batholith, Nova Scotia: some genetic and exploration implications: in Y.T. Maurice, ed. Uranium in Granites, Geol. Surv. Can. Paper 81-23, p. 11-17.

Clarke, D.B., Barr, S.M. and Donohoe, H.V., 1980, Granitoid and other plutonic rocks of Nova Scotia: in Proceedings, "The Caledonides in the USA", IGCP Project 27, p. 107-116.

_____ and Halliday, A.N., 1980, Strontium isotope geology of the South Mountain batholith, Nova Scotia: Geochim. et Cosmochim. Acta, vol. 44, p. 1045-1058.

Collins, P.L.F., 1981, The geology and genesis of the Cleveland tin deposit, Western Tasmania: fluid inclusion and stable isotope studies: Econ. Geol. vol. 76, p. 365-392.

Craig, J.R. and Vaughan, D.J., 1981, Ore Microscopy and Ore Petrography: J. Wiley and Sons, New York, 406 p.

Craw, D., 1981, Oxidation and microprobe-induced potassium mobility in iron-bearing phyllosilicates from the Otago schists, New Zealand: Lithos, vol. 14, p. 49-57.

Cullen, J.D., 1983, Metamorphic petrology and geochemistry of the Goldenville Formation metasediments, Yarmouth, Nova Scotia: Unpub. M. Sc. thesis Dalhousie University, 206 p.

Deer, W.A., Howie, R.A. and Zussman, J., 1974, An introduction to the rock-forming minerals: Longman Group Ltd., London, 528 p.

Dick, L.A. and Hodgson, C.J., 1982, The MacTung W-Cu(Zn) contact metasomatic and related deposits of the northeastern Canadian Cordillera: Econ. Geol., vol. 77, p. 845-867.

Dobson, D.C., 1982, Geology and alteration of the Lost River tin-tungsten-fluorine deposits, Alaska: Econ. Geol., vol. 77, p. 1033-1052.

Duursma, E.K. and Hoede, C., 1976, Principles of diffusion in sedimentary systems: in K.H. Wolf, ed. Handbook of Strata-bound and Stratiform Ore Deposits, vol. 2, Geochemical Studies: Elsevier Scientific Pub. Co., p. 29-51.

Edmond, J.M., 1982, The chemistry of the ridge crest hot springs: Marine Tech. Soc. Jour., vol. 16, p. 23-25.

Einaudi, M.T., Meinert, L.D. and Newberry, R.J., 1981, Skarn deposits: Econ. Geol. 75th Ann. Vol., p. 317-391.

El Sharkawi, M.A.H. and Dearman, W.R., 1966, Tin-bearing skarns from the north-west border of the Dartmoor granite, Devonshire, England: Econ. Geol., vol. 61, p. 362-369.

Gamble, R.P., 1982, An experimental study of sulfidation

reactions involving andradite and hedenbergite: Econ.
Geol., vol. 77, p. 784-797.

Garnett, R.H.T., 1966, Distribution of cassiterite in vein
tin deposits: Trans. Inst. Min. Metall. B 75, p. 245-273.

Germann, K., 1973, Deposition of manganese and iron
carbonates and silicates in Liassic marls of the Northern
Limestone Alps(Kalkalpen): in C. Amstutz and A.J.
Bernard, eds. Ores in Sediments, IUGS, series A, no. 3,
Springer-Verlag, p. 129-138.

Ghisler, M., Jensen, Aa., Stendal, H. and Urban, H., 1980,
Stratabound scheelite, arsenopyrite and copper sulphide
mineralization in the Late Precambrian sedimentary
succession of the East Greenland Caledonides: Geol. Surv.
Ireland Special Paper No. 5, p. 19-24.

Goncharov, G.N. and Filatov, S.K., 1972, The typical
structural features of cassiterite from Sherlovaya Gora:
Geochem. Int., vol. 1971, p. 268-275.

Graf, J.L., Jr. and Skinner, B.J., 1970, Strength and
deformation of pyrite and pyrrhotite: Econ. Geol., vol.
65, p. 206-215.

Grigoryan, S.V., 1974, Primary geochemical halos in
prospecting and exploration of hydrothermal deposits:
Int. Geol. Rev., vol. 16, p. 12-25.

Groves, D.I. and McCarthy, T.S., 1978, Fractional
crystallization and the origin of tin deposits in
granitoids: Mineralium Deposita, vol. 13, p. 11-26.

Hanor, J.S., 1979, The sedimentary genesis of hydrothermal
fluids: in H.L. Barnes, ed. Geochemistry of Hydrothermal
Ore Deposits, 2nd edition, J. Wiley and Sons, New York,
p. 137-172.

Harris, I.M. and Schenk, P.E., 1975, The Meguma Group: in
I.M. Harris, ed. Ancient Sediments of Nova Scotia:
Society of Economic Paleontologists and Mineralogists
(Eastern Section) Guidebook, 1975 Field Trip: Maritime
Sediments, p. 17-38.

Helgeson, H.C., 1964, Complexing and Hydrothermal Ore
Deposition: Pergamon Press, New York, 128 p.

Holland, H.D., 1972, Granites, solutions, and base metal
deposits: Econ. Geol., vol. 67, p. 281-301.

Hosking, K.F.G., 1979, Tin distribution patterns: Bull.

Geol. Soc. Malaysia, no. 11, p. 1-70.

Hutchinson, R.W., 1979, Evidence of exhalative origin for
    Tasmanian tin deposits: CIM Bull., vol. 72, p. 90-104.

_____, 1980, "Evidence of exhalative origin for
    Tasmanian tin deposits" - author's reply: CIM Bull., vol.
    73, p. 167-168.

_____, 1982, Geologic setting and genesis of
    cassiterite-sulphide mineralization at Renison Bell,
    Tasmania - a discussion: Econ. Geol., vol. 77,
    p. 199-202.

Ishihara, S., Sawata, H., Arpornsuwan, S., Busaracome, P.
    and Bungbrakearti, N., 1979, The magnetite-series and
    ilmenite-series granitoids and their bearing on tin
    mineralization, particularly of the Malay Peninsula
    region: Bull. Geol. Soc. Malaysia, no. 11, p. 103-110.

_____, 1981, The granitoid series and mineralization:
    Econ. Geol. 75th Ann. Vol. p. 458-484.

Jackson, N.L., 1979, Geology of the Cornubian tin field "a
    review": Bull. Geol. Soc. Malaysia, no. 11, p. 209-237.

_____, Halliday, A.N., Sheppard, S.M.F. and
    Mitchell, J.G., 1979, Isotopic and fluid inclusion
    evidence bearing on the polyphase metallogenic evolution
    of the St. Just District, Cornwall[abs.]: Problems of
    Mineralization Associated with Acid Magmatism; Mineral
    Studies Group Meeting, p. 4-5.

Jeffery, P.G. and Hutchison, D., 1981, Chemical Methods of
    Rock Analysis, 3rd edition: Pergamon Press, New York,
    379 p.

Jenner, K.A., 1982, A study of sulphide mineralization in
    the Meguma Group sediments Gold Brook, Colchester County,
    Nova Scotia: Unpub. B.Sc. thesis, Dalhousie University,
    60 p.

Kelly, W.C. and Rye, R.O., 1979, Geologic, fluid inclusion,
    and stable isotope studies of the tin-tungsten deposits
    of Panasquiera, Portugal: Econ. Geol., vol. 74, p. 1721-
    1822.

Koch, G.S.,Jr. and Link, R.F., 1970, Statistical Analysis of
    Geological Data, vol. I: J. Wiley and Sons, New York,
    375 p.

Kodama, H., Longworth, G. and Townsend, M.G., 1982, A

Mossbauer investigation of some chlorites and their oxidation products: Can. Min., vol. 20, p. 585-592.

Krauskopf, K.B., 1979, Introduction to Geochemistry, 2nd edition: McGraw-Hill, New York, 617 p.

Kretschmar, U. and Scott, S.D., 1976, Phase relations involving arsenopyrite in the system Fe-As-S and their application: Can. Mineral., vol. 14, p. 364-386.

Kullerud, G. and Yoder, H.S.,Jr., 1965, Sulfide-silicate reactions and their bearing on ore formation under magmatic, postmagmatic and metamorphic conditions: Symposium, Problems of Postmagmatic Ore Deposition, vol. II, Czechoslovak Geol. Surv., p. 327-331.

Lane, T.E., 1975, Stratigraphy of the White Rock Formation: in I.M. Harris, ed. Ancient Sediments of Nova Scotia: Society of Economic Paleontologists and Mineralogists (Eastern Section) Guidebook 1975 Field Trip: Maritime Sediments, p. 43-62.

Lebedev, L.M., 1967, Metacolloids in Endogenic Deposits: Plenum Press, 298 p.

Lehmann, B. and Schneider, H.-J., 1981, Strata-bound tin deposits: in K.H. Wolf, ed. Handbook of Strata-bound and Stratiform Ore Deposits, vol. 9, Regional Studies and Specific Deposits: Elsevier Scientific Pub. Co., p. 743-771.

_____, 1982, Metallogeny of tin: magmatic differentiation versus geochemical heritage: Econ. Geol., vol. 77, p. 50-59.

Lepeltier, C., 1969, Simplified statistical trends of geochemical data: Econ. Geol., vol. 64, p. 538-550.

Levinson, A.A., 1974, Introduction to Exploration Geochemistry: Applied Pub. Ltd., Illinois, 614 p.

Long, D.T. and Angino, E.E., 1982, The mobilization of selected trace metals from shales by aqueous solutions: effects of temperature and ionic strength: Econ. Geol., vol. 77, p. 646-652.

Love, L.G., 1969, Sulphides of metals in recent sediments: in C.H. James, ed. Proceedings, Sedimentary Ores Ancient and Modern, 15th Inter-University Geological Congress, 1967, Spec. Pub. No. 1, Dept. of Geology, University of Leicester, England, p. 31-60.

Lufkin, J.L., 1977, Chemistry and mineralogy of wood-tin, Black Range, New Mexico: Am. Min., vol. 62, p. 100-106.

Marsh, B.D., 1982, On the mechanics of igneous diapirism, stoping, and zone melting: Am. Jour. Sci., vol. 282, p. 808-855.

Mason, R., 1978, Petrology of the Metamorphic Rocks: George Allen and Unwin, London, 254 p.

Maucher, A. and Rehwald,G., 1961, Card Index of Ore Microphotographs: Verlag, W. Germany, 3 vol.(published continuously).

McKenzie, C.B. and Clarke, D.B., 1975, Petrology of the South Mountain Batholith, Nova Scotia: Can. Jour. Earth Sci., vol. 12, p. 1209-1218.

Mercer, W., 1976, Minor elements in metal deposits in sedimentary rocks - a review: in K.H. Wolf, ed. Handbook of Strata-bound and Stratiform Ore Deposits, vol. 2, Geochemical Studies: Elsevier Scientific Pub. Co., p. 1-27.

Meyers, A.T., Havens, R.G., Connor, J.J., Conklin, N.M. and Rose, H.J.,Jr., 1976, Glass reference standards for the trace element analysis of geological materials - compilation of interlaboratory data: Geol. Surv. Prof. Paper 1013, 29 p.

Michard, A., 1976, Elements de geologie Marocaine: Editions du Service Geologique du Maroc: Notes et Memoires du Service Geologique, no. 252, 408 p.

Mitchell, A.H.G., 1979, Rift-, subduction- and collision-related tin belts: Bull. Geol. Malaysia, no. 11, p. 81-102.

Miyahisa, M., 1968, Lattice constants of cassiterites: Mineralogical Abstracts, vol. 19, p. 141.

Mookerjee, A. 1981, Ores and metamorphism: temporal and genetic relationships: in K.H. Wolf, ed. Handbook of Strata-bound and Stratiform Ore Deposits, vol. 4, Tectonics and Metamorphism: Elsevier Pub. Co., p. 203-260.

Moore, F. and Howie, R.A., 1979, Geochemistry of some Cornubian cassiterites: Mineralium Deposita, vol. 14, p. 103-107.

Morganti, J.M., 1981, Ore deposit models - 4. Sedimentary-

type stratiform ore deposits: some models and a new classification: Geoscience Canada, vol. 8, p. 65-75.

Mulligan, R., 1975, Geology of Canadian tin occurrences: Geol. Surv. Can., Econ. Geol. Rept. no. 28, 155 p.

Nekrasov, I. Ya., 1971, Features of tin mineralization in carbonate rocks, as in Eastern Siberia: Int. Geol. Rev., vol. 13, p. 1532-1542.

Newhouse, W.H. and Buerger, M.J., 1928, Observations on wood-tin nodules: Econ. Geol., vol. 23, p. 185-192.

Nicolini, P., 1970, Gitologie des Concentrations Minerales Stratiformes: Gauthier-Villars, Paris, 792 p.

Pan, Y. and Ypma, P.J.M., 1974, Heating and recrystallization of wood-tin - an indication of low temperature genesis of cassiterite and wood-tin veins in volcanics (abs.): Geol. Soc. Am. Abstracts with Program, vol. 6, p. 62-63.

Parslow, G.R., 1974, Determination of background and threshold in exploration geochemistry: Jour. Geochem. Explor., vol. 3, p. 319-336.

Patterson, D.J., Ohmoto, H. and Solomon, M., 1981, Geologic setting and genesis of cassiterite-sulphide mineralization at Renison Bell, Tasmania: Econ. Geol., vol. 76, p. 393-438.

_____, 1982, Geologic setting and genesis of cassiterite-sulphide mineralization at Renison Bell, Tasmania - a reply: Econ. Geol., vol. 77, p. 203-206.

Pettijohn, F.J., 1975, Sedimentary Rocks, 3rd edition: Harper and Row, New York, 628 p.

Plant, J., Brown, G.C., Simpson, P.R. and Smith, R.T., 1980, Signatures of metalliferous granites in the Scottish Caledonides: Trans. Instn. Min. Metall. B 89, p. 198-210.

Plimer, I.R., 1980, Exhalative Sn and W deposits associated with mafic volcanism as a precursor to Sn and W deposits associated with granites: Mineralium Deposita, vol. 15, p. 275-289.

Ramdohr, P., 1980, The Ore Minerals and their Intergrowths, 2nd edition: Pergamon Press, England, 1205 p.

Reynolds, P.H., Kublick, E.E. and Muecke, G.K., 1973, Potassium-argon dating of slates from the Meguma Group,

Nova Scotia: Can. Jour. Earth Sci., vol. 10, p. 1059-1067.

_____ and Muecke, G.K., 1978, Age studies on slate: applicability of the Ar/ Ar stepwise outgassing method: Earth Planet. Sci. Lett., vol. 40, p. 111-118.

_____, Zentilli, M. and Muecke, G.K., 1981, K-Ar and $^{40}Ar/^{39}Ar$ geochronology of granitoid rocks from southern Nova Scotia: its bearing on the geological evolution of the Meguma Zone of the Appalachians: Can. Jour. Earth Sci., vol. 18, p. 386-394.

Richardson, J.M.G., Spooner, E.T.C. and McAuslan, D.A., 1982, The East Kemptville tin deposit, Nova Scotia: an example of a large tonnage, low grade, greisen-hosted deposit in the endocontact zone of a granite batholith: Current Research, Part B, Geol. Surv. Can. Paper 82-1B, p. 27-32.

Rickard, D.T., 1969a, The microbiological formation of iron sulphides: in I. Hessland, ed. Stockholm Contributions in Geology, Univ. of Stockholm, vol. 20, p. 49-66.

_____, 1969b, The chemistry of iron sulphide formation at low temperatures: in I. Hessland, ed. Stockholm Contributions in Geology, Univ. of Stockholm, vol. 20, p. 67-95.

Rittenhouse, G., 1943, Transportation and deposition of heavy minerals: Bull. Geol. Soc. Am., vol. 54, p. 1725-1780.

Roedder, E., 1968, The noncolloidal origin of "colloform" textures in sphalerite ores: Econ. Geol., vol. 63, p. 451-471.

Rose, A.W. and Burt, D.M., 1979, Hydrothermal alteration: in H.L. Barnes, ed. Geochemistry of Hydrotheraml Ore Deposits, 2nd edition: J. Wiley and Sons, New York, p. 173-235.

Sarkar, P.K., 1978, Petrology and geochemistry of the White Rock metavolcanic suite, Yarmouth, Nova Scotia: Unpub. Ph.D. thesis, Dalhousie University, 350 p.

_____, 1980, Assessment report, Plymouth, Yarmouth County, Nova Scotia: Shell Canada Resources Limited, internal report, 32 p.

Saxby, J.D., 1976, The significance of organic matter in ore genesis: in K.H. Wolf, ed. Handbook of Strata-bound and

Stratiform Ore Deposits, vol. 2, Geochemical Studies:
Elsevier Scientific Pub. Co., p. 111-133.

Schenk, P.E., 1975, A regional synthesis: in I.M. Harris,
    ed. Ancient Sediments of Nova Scotia: Society of Economic
    Paleontologists and Mineralogists(Eastern Section)
    Guidebook 1975 Field Trip: Maritime Sediments, p. 9-16.

_____ and Lane, T.E., 1982, Excursion 5B: Pre-Acadian
    sedimentary rocks of the Meguma Zone, Nova Scotia - a
    passive continental margin juxtaposed against a volcanic
    arc: International Association of Sedimentologists Field
    Excursion Guidebook, 85 p.

Schuiling, R.D., 1967, Tin belts on the continents around
    the Atlantic Ocean: Econ. Geol., vol. 62, p. 540-550.

Shcherba, G.N., 1970, Greisens: Int. Geol. Rev., vol. 12,
    p. 114-150, 239-255.

Shneider, Yu. A., 1937, Morphological and genetic scheme of
    the habits of cassiterite: Chemical Abstracts, vol. 31,
    p. 5723.

Sinclair, A.J., 1974, Selection of threshold values in
    geochemical data using probability graphs: Jour. Geochem.
    Explor., vol. 3, p. 129-149.

Sinclair, P.E., 1978, An application of Pleistocene geology
    to mineral exploration in southwestern Nova Scotia:
    Unpub. B.Sc. thesis, Dalhousie University, 109 p.

Smith, F.G., 1947, Transport and deposition of the
    non-sulphide vein materials. Part II. Cassiterite: Econ.
    Geol., vol. 42, p. 251-264.

Solomon, M., 1980, "Evidence of exhalative origin for
    Tasmanian tin deposits" - a discussion: CIM Bull.,
    vol. 73, p. 166-167.

Spry, A., 1969, Metamorphic Textures: Pergamon Press,
    England, 350 p.

Stanton, R.L., 1972a, Ore Petrology: McGraw-Hill, New York,
    713 p.

_____, 1972b, Sulphides in sediments: in R.W.
    Fairbridge, ed. The Encyclopedia of Geochemistry and
    Environmental Sciences: Van Nostrand and Reinhold Co.,
    New York, p. 1134-1140.

Steele, T.W., Wilson, A., Goudvis, R.G., Ellis, P.J. and

Radford, A.J., 1978, Analysis of the NIMROC reference
    samples for minor and trace elements: Nat. Inst. Metall.,
    Rept. no. 1945, 25 p.

Stemprok, M., 1969, Geochemical association of tin: in W.
    Fox, ed. A Second Technical Conference on Tin, Bankok,
    vol. 1, p. 159-176.

_____, 1980, Tin and tungsten deposits of the west-
    central European Variscides: in J.D. Ridge, ed.
    Proceedings of the Fifth Quadrennial IAGOD Symposium,
    vol. I, p. 495-512.

Stendal, H., 1982, Geochemistry and genesis of arsenopyrite
    mineralization in Late Precambrian sediments in central
    East Greenland: Trans. Inst. Min. Metall. B 91, p. 187-
    191.

Streckeisen, A.L., 1976, To each plutonic rock its proper
    name: Earth Sci. Rev., vol. 12, p. 1-33.

Strong, D.F., 1980, Granitoid rocks and associated mineral
    deposits of eastern Canada and western Europe: in D.W.
    Strangway, ed. The Continental Crust and its Mineral
    Deposits: Geol. Assoc. Can. Special Paper 20, p. 741-
    769.

Sutherland, D.G., 1982, The transport and sorting of
    diamonds by fluvial and marine processes: Econ. Geol.,
    vol. 77, p. 1613-1620.

Takahashi, M., Aramaki, S. and Ishihara, S., 1980, Magnetite-
    series/ilmenite-series vs. I-type/S-type granitoids:
    Mining Geology Special Issue, no. 8, p. 13-28.

Tauson, L.V., 1974, The geochemical types of granitoids and
    their potential ore capacity: in M. Stemprok, ed.
    Metallization Associated with Acid Magmatism(MAWAM):
    Czechoslovak Geol. Surv., vol. 1, p. 221-227.

Taylor, F.C., 1967, Reconnaissance geology of Shellburne
    map-area, Queens, Shelburne and Yarmouth Counties, Nova
    Scotia: Geol. Surv. Can. Memoir 349, 83 p.

Taylor, R.G., 1979a, Geology of Tin Deposits: Elsevier
    Scientific Pub. Co., New York, 543 p.

_____, 1979b, Some observations upon the tin deposits
    of Australia: Bull. Geol. Surv. Malaysia, no. 11,
    p. 181-207.

Terry, R.D. and Chilinger, G.V., 1955, Summary of

"Concerning some additional aids in studying sedimentary formations" by M.S. Shvetsov: Jour. Sed. Petrog., vol. 25, p. 229-234.

Tischendorf, G., 1973, The metallogenic basis of tin exploration in the Erzgebirge: Trans. Inst. Min. Metall., B 82, p. 9-23.

_____, Schust, F. and Lange, H., 1978, Relation between granites and tin deposits in the Erzgebirge, GDR: in M. Stemprok, ed. Metallization Associated with Acid Magmatism(MAWAM): Czechoslovak Geol. Surv., vol. 3, p. 123-137.

Travis, R.B., 1955, Classification of Rocks: Quarterly of the Colorado School of Mines, vol. 50, 98 p.

Turekian, K.K. and Wedepohl, K.H., 1961, Distribution of the elements in some major units of the Earth's crust: Bull. Geol. Soc. Am., vol. 72, p. 175-192.

Valliant, R.I. and Barnett, R.L., 1982, Manganiferous garnet underlying the Bousquet gold orebody, Quebec: metamorphosed manganese sediments as a guide to gold ore: Can. Jour. Earth Sci., vol. 19, 993-1010.

Vaughan, D.J., 1976, Sedimentary geochemistry and mineralogy of the sulphides of lead, zinc, copper and iron and their occurrence in sedimentary ore deposits: in K.H. Wolf, ed. Handbook of Strata-bound and Stratiform Ore Deposits, vol. 2, Geochemical Studies: Elsevier Scientific Pub. Co., p. 317-363.

Wastnerack, J., Kuhne, R.K and Schulze, H., 1974, Late magmatic and high- to medium-temperature postmagmatic metasomatism in Saxonian Erzgebirge(GDR): in M. Stemprok, ed. Metallization Associated with Acid Magmatism(MAWAM): Czechoslovak Geol. Surv., vol. 1, p. 228-231.

White, D.E., 1981, Active geothermal systems and hydrothermal ore deposits: Econ. Geol. 75th Ann. Vol., p. 392-423.

Whitehead, R.E., 1973, Environment of stratiform sulphide deposition; variation in Mn:Fe ratio in host rocks at Heath Steele Mine, New Brunswick, Canada: Mineralium Deposita, vol. 8, p. 148-160.

Yeates, A.N., Wyatt, B.W. and Tucker, D.H., 1982, Application of gamma-ray spectrometry to prospecting for tin and tungsten granites, particularly within the Lachlan Fold Belt, New South Wales: Econ. Geol., vol. 77, p. 1725-1738.