

**Immobile Element Geochemistry
of Altered Volcanics and Exhalites
at the Thalanga Deposit,
North Queensland**

by:

Walter Herrmann B.Sc.(Hons.)
c/- PO Box 873 Charters Towers QLD 4820

Submitted in fulfilment of the requirements
for the degree of M.Econ.Geol.
University of Tasmania

December, 1994.

ABSTRACT

Thalanga is a deformed and metamorphosed volcanic hosted massive sulphide deposit consisting of several thin, stratiform semi-connected lenses located at a sub-vertically dipping contact between rhyolite and dacite formations. Rocks composed of quartz-magnetite-barite and chlorite-tremolite-carbonate, which have previously been interpreted to be exhalites, exist in intimate stratabound association with sulphides, particularly in the western lenses. Rhyolites stratigraphically beneath the deposit are extensively hydrothermally altered with a stratabound stringer zone of intense silicification containing 4-20% pyrite in the immediate footwall of the sulphide lenses, grading outwards and downwards through progressively weaker zones of quartz-chlorite-sericite and quartz-sericite alteration.


Titanium, aluminium and zirconium remained chemically immobile during alteration, and subsequent metamorphism. These immobile elements permit identification of the volcanic precursors of altered rocks and quantitative estimation of the chemical changes due to alteration. Large gains of silica, iron, sulphur and loss of sodium are indicated for the zone of most intense footwall alteration.

Chlorite-tremolite-carbonate rocks associated with sulphides have immobile element contents and ratios identical to those of altered footwall rhyolites and their chemistry is consistent with a derivation from rhyolite involving large gains of calcium, magnesium, CO₂ and losses of silica and sodium. They are re-interpreted to be metamorphosed chlorite-carbonate alteration assemblages which probably formed in permeable rhyolitic volcanoclastics by hydrothermal fluid and sea water mixing at the upper and outer parts of a mineralising sub-marine hydrothermal system.

Magnetite-quartzites have very low immobile element contents and may be the only true exhalites at Thalanga, other than massive barite and base metal sulphide assemblages.

Declaration

This thesis contains no material which has been accepted for the award, to me, of any other higher degree or graduate diploma in any tertiary institution. To the best of my knowledge and belief this thesis contains no material previously published or written by another person except when due reference is made in the text of the thesis.



1 /12/94

Walter Herrmann

ACKNOWLEDGEMENTS

The Managers of Pancontinental Resources (Base Metals) Pty Ltd are acknowledged for providing the opportunity to study the Thalanga deposit and funding for chemical analyses and petrographic sections.

It is my pleasure to sincerely thank all the following people for their contributions to the work.

A great deal of knowledge and helpful, stimulating discussion was volunteered by Pancon geologists Andrew Blair, Haydn Hadlow, Anthea Hill, Mel Jones, Colin Kendall, Ian Levy, Rodney Sainty and Ian Warland.

Kim Burleigh, Krista Davies and Harold Webber cheerfully provided invaluable technical assistance in drillcore handling and sampling. Robin Voss expedited colour photocopying of photographic figures.

Ron Berry, Bruce Gemmell, Ross Large and Joe Stolz, of the University of Tasmania - Centre for Ore Deposit and Exploration Studies, are acknowledged for their guidance and interest in the project.

Not least, the encouragement and forbearance of Danielle, Alina and Eva Herrmann is greatly appreciated.

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2 INTRODUCTION

Metamorphic assemblages of carbonate, tremolite, actinolite, chlorite, epidote, barite, quartz and magnetite are spatially associated with stratabound volcanic hosted massive sulphide mineralisation at the Thalanga deposit in North Queensland. These interesting rocks have been traditionally termed "exhalites" following the original interpretation of Gregory et al. (1990) that they represent metamorphosed Ca-Mg carbonate and iron-silica chemical sediments which precipitated on the Late Cambrian sea floor from the same hydrothermal system responsible for massive base metal sulphide deposition; perhaps from the lower temperature and more oxidised hydrothermal fluids exhaled during early or waning stages of mineralisation.

This study is an attempt at discriminating the various assemblages previously grouped as "exhalites" and interpreting their modes of formation. The method is largely geochemical with a focus on immobile element geochemistry to identify the precursors and chemical changes of altered volcanic host rocks and their chemical relationships with so-called exhalites.

Wills (1985) and Gregory et al. (1990) observed that the "exhalites" associated with sulphide ores are composed of Mg, Ca, Ba and carbonate rich minerals and the most distal types are dominated by cherty quartz-magnetite assemblages.

Wills (op. cit.) used a threefold classification as follows:

carbonate-tremolite exhalite = low SiO₂, high Mg/Fe+Mg ratio;

shaley exhalite = moderate SiO₂, moderate Mg/Fe+Mg;

siliceous exhalite = high SiO₂, low Mg/Fe+Mg ratio.

He speculated that these chemical trends, particularly the Mg/Fe+Mg ratio, reflected proximal and distal settings and could be useful exploration vectors.

A detailed study by Duhig et al., (1992) of the distal siliceous types, found that they are composed essentially of silica and iron oxides with <0.5% alumina and that less metamorphosed equivalents from further east in the Mt Windsor Volcanics contain filamentous microbial fossils. These provide good evidence that the ironstones formed from crystallisation of silica-iron oxyhydroxide gels deposited in sea floor depressions by mixing of seawater and low temperature hydrothermal fluids in distal or waxing and waning-proximal settings, more or less as envisaged by Gregory et al. (1990). This type of siliceous ironstone is reasonably classified as exhalite - a term which carries a strong genetic connotation.

At Thalanga, however, the term "exhalite" has evolved into a large basket into which any odd rocks (i.e. anything not recognisably like the massive sulphides, meta-volcanic host rocks and younger intrusive dykes) have been uncritically placed. This misuse was mentioned by Wills (1985, p.37) who recognised that some rocks classed as exhalites were really rhyolitic "pyroclastics" that had been strongly replaced by "exhalite" type minerals in a form of primary Mg metasomatism. He nevertheless

applied the term exhalite extensively and not only in situations closely associated with stratiform sulphides.

Rivers (1985) in studying the footwall alteration system, interpreted cross-cutting, pipe like or sheet like zones of actinolite-carbonate-epidote+/-chlorite which previous workers had classed as exhalites but which she considered to represent pathways for primary CO₂ bearing hydrothermal-mineralising fluids, essentially perpendicular to stratigraphic layering in the footwall of the West and Central Thalanga orebodies.

The enigma was also noted by Stolz (1989, 1991) who found petrographic evidence for carbonate-actinolite alteration in footwall vitric rhyolites, suggested that the assemblage represented thermally metamorphosed carbonate-chlorite alteration and observed that the high Ca, Mg, CO₂ and lack of Na depletion in these rocks starkly contrasted with the chemistry of the more widespread quartz-sericite-chlorite style of footwall alteration. Stolz (1991, p.55) stated that many of the actinolite rich rocks which had previously been classified as exhalites were "clearly due to alteration processes" but had reservations about some other well banded carbonate-actinolite-barite and quartz-barite assemblages which he conceded might be genuine exhalites or mixtures of exhalites and volcanoclastic materials.

The close spatial association of carbonate-tremolite-chlorite assemblages with ore in some parts of the deposit, notably West Thalanga, has led to the presence of these minerals being used for identification of the favourable horizon. This is a fundamental concept of exploration for stratabound sulphide mineralisation. In view of the uncertainty of origin of the carbonate-tremolite-chlorite assemblages it is important, however, to discriminate between true exhalites which may be the lateral equivalents of stratiform sulphide ore and alteration assemblages which may fit into zoned hydrothermal alteration patterns and provide exploration vectors of a different kind.

3 GEOLOGY

3.1 Regional Setting

The Thalanga deposit lies near the western end of an E-W trending narrow belt of deformed Cambro-Ordovician marine sediments and volcanics known as the Mt Windsor Subprovince, (Berry et al., 1992; Gregory et al., 1990). The stratigraphic sequence is grossly conformable and has an exposed thickness of upto 10km, faces south and comprises (in ascending order) the following major formations:

- Puddler Ck Fmn. - up to 9000m of continent and volcanic derived, massive to laminated wackes and siltstones with minor basaltic-andesitic volcanics concentrated in the upper few hundred metres; the volcanics have geochemical signatures typical of intraplate volcanism (Stolz, 1994) and have been related to lithospheric thinning and incipient back-arc basin development.
- Mt Windsor Fmn. - a 400m to 5000m thick sequence of subaqueously deposited rhyolites dominated by passively extruded thick flows, domes and high level intrusives with subordinate volcanoclastics and mass flow breccias. Isotopic evidence (Stolz, op. cit.) suggests they were derived from melting of continental crust.
- Trooper Ck Fmn. - a 500-2000m thick sequence of highly variable basaltic andesitic, dacitic and rhyolitic volcanics, mass flow volcanoclastic breccias, volcanogenic siltstones and vitric ash units with minor calcareous metasediments and probably exhalative siliceous ironstones. Stolz (op. cit.) interpreted the volcanics to have been derived from melting of a variably subduction modified, sub-arc mantle wedge and erupted during back arc extension.
- Rollston Range Fmn. - Lower Ordovician fossiliferous sandstones and siltstones of volcanic provenance and uncertain thickness which conformably overlie the Trooper Ck Fmn.

The rocks have experienced at least one, possibly two, major deformation event(s) of which the most recognisable is termed D2 (after Berry et al., 1992). This deformation produced a large E-W trending upright fold (or folds?) and a near vertical, axial plane penetrative cleavage or foliation called S2. The greater part of the Mt Windsor Subprovince represents a single south facing limb of a large D2 antiform. D2 appears to have coincided with or followed the intrusion of the Mid-Late Ordovician? gneissic, early phases of the Ravenswood Granodiorite Complex and it produced relatively low pressure regional metamorphic assemblages ranging from prehnite grade in the east to upper greenschist andalusite-biotite grade in the west.

A locally developed ENE trending cleavage, S3, occurs in association with steep NE to ENE trending faults with south side up displacements which Berry et al., (1992) suggested were related to emplacement of unfoliated (post D2) granitoids of Siluro-Devonian age. Post kinematic granitoids produced local contact metamorphic aureoles up to cordierite grade which are most recognisable in the eastern areas where prograde contact metamorphism exceeded the grade of the earlier regional metamorphism.

3.2 Local Geology

The Thalanga massive sulphide deposit consists of several semi-connected, thin stratiform lenses of pyrite-sphalerite-galena-chalcopryrite lying conformably at the near vertically dipping contact of the Mt Windsor Formation (MWF) and the Trooper Creek Formation (TCF). The geological and structural features of the deposit have been described by Wills (1985), Berry (1989), Gregory et al. (1990), Hill (1991) and Berry et al. (1992). There is consensus that it is a synvolcanic, volcanic hosted massive sulphide deposit of the thin, extensive, layered sheet style as discussed by Large (1992).

In longitudinal projection (Figure 1) the sulphide lenses show a semi continuous, broad arcuate distribution, partly attributable to faulting, over a known strike extent of about 3000m. The maximum vertical dimension is about 400m and thickness ranges from <1m to about 25m with an average of about 5m.

The total mineral resource is estimated at 8.6Mt consisting of:

mined production to June 1994: 2.5Mt

in situ resources at June 1994: 6.1Mt @ 1.6%Cu, 3.0%Pb, 9.3%Zn, 77g/tAg and 0.4g/tAu.

The deposit is located at the foot of the eastern end of the Thalanga Range - a low strike ridge flanked to the north, east and south by an extensive peneplain which covers the basement with upto 100m of semi consolidated Tertiary alluvial sediments known as the Campaspe Beds. Surface exposure in the vicinity of the deposit is poor and most of the geological interpretation is based on observations from RAB/Percussion holes, diamond drill holes and mine development. Figure 2 shows the locations of significant drillholes mentioned in the text and Table 1; Figures 3 to 6 illustrate typical cross-sections of the deposit.

The following presents a brief description of the main geological units which are further subdivided and described in greater detail in the discussion of alteration geochemistry in Section 4 and in Appendix II.

Footwall Rhyolites

Rocks in the footwall consist of massive rhyolitic lavas with probably subordinate rhyolitic breccias and volcanoclastic units. In the vicinity of the ore deposit they are

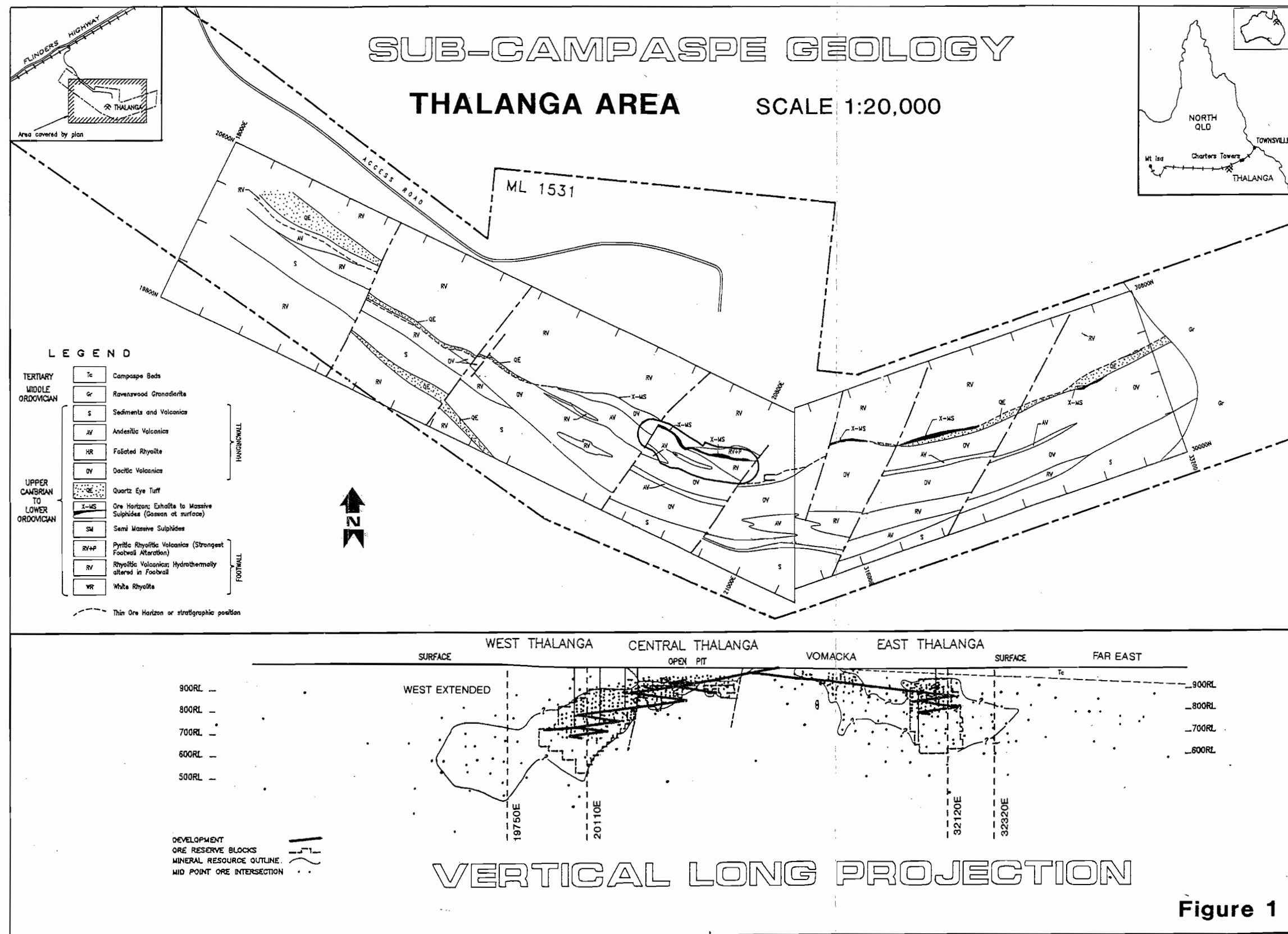
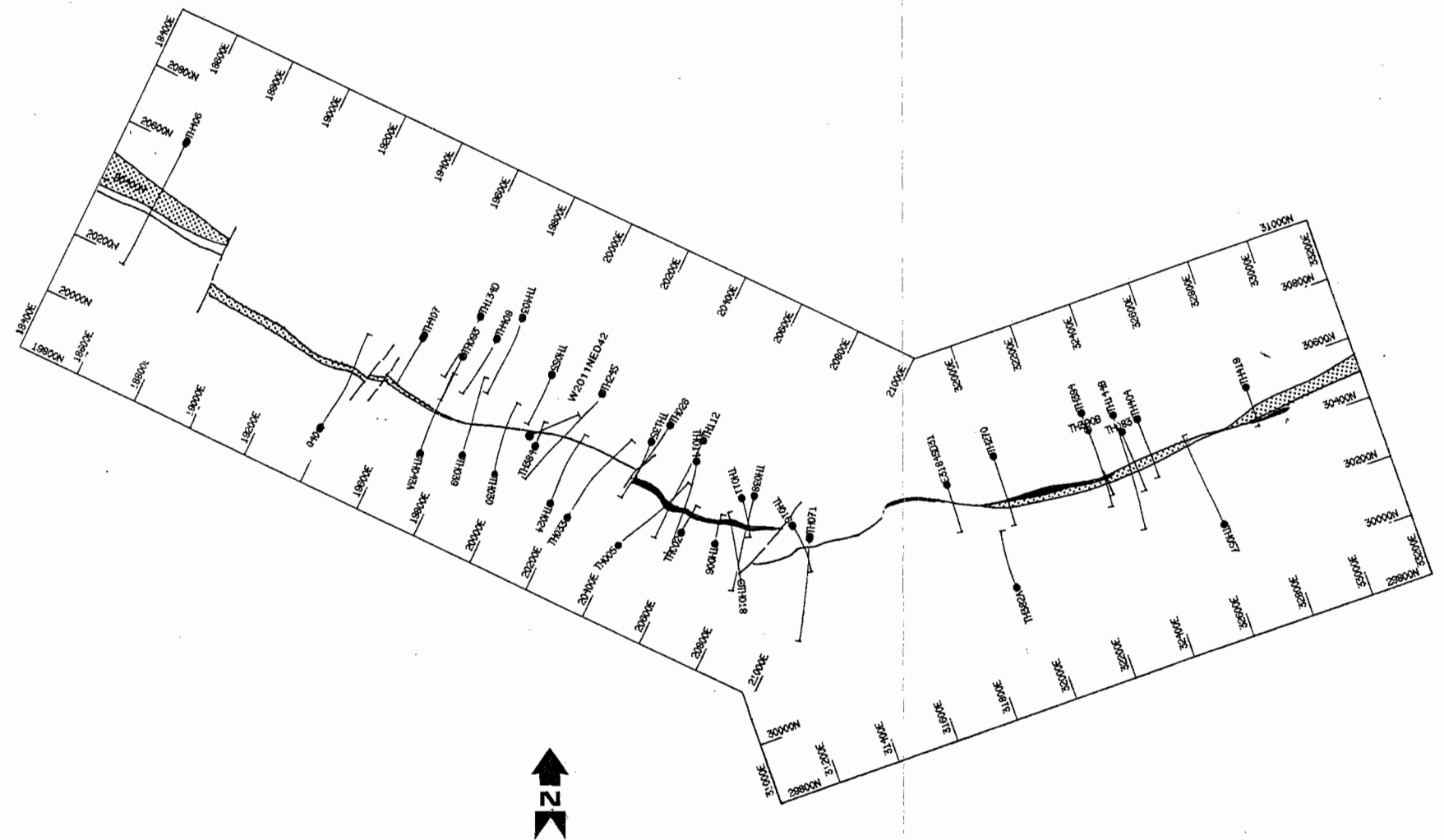


Figure 1

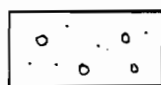


THALANGA MINE GRID and BOREHOLE LOCATION PLAN

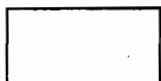
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Figure 2

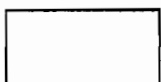
Geological Legend for Figures 3, 4, 5 & 6



Tc: Campaspe Beds, unlithified Tertiary terrestrial sediments.



Dol: dolerite dyke.



Dv: Dacite, mainly coherent.



HWF: Hangingwall Fragmental unit, sericitic siltstone with dacite clasts.



QFP: coherent quartz feldspar porphyry.



QEV: quartz crystal rich volcanoclastics and breccias



Rv: Footwall rhyolitic rocks with weak quartz-sericite alteration.



Rv: Footwall rhyolitic rocks with moderate quartz-chlorite-sericite alteration, 1-4% pyrite.



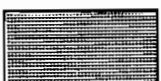
Rv: Footwall rhyolitic rocks with intense quartz-(sericite) alteration and 4-20% disseminated and veiny pyrite, minor chalcopyrite.



Massive sulphides.



wR: intensely silicified "white" rhyolite with <2% pyrite.



Chlorite-tremolite-carbonate rocks.

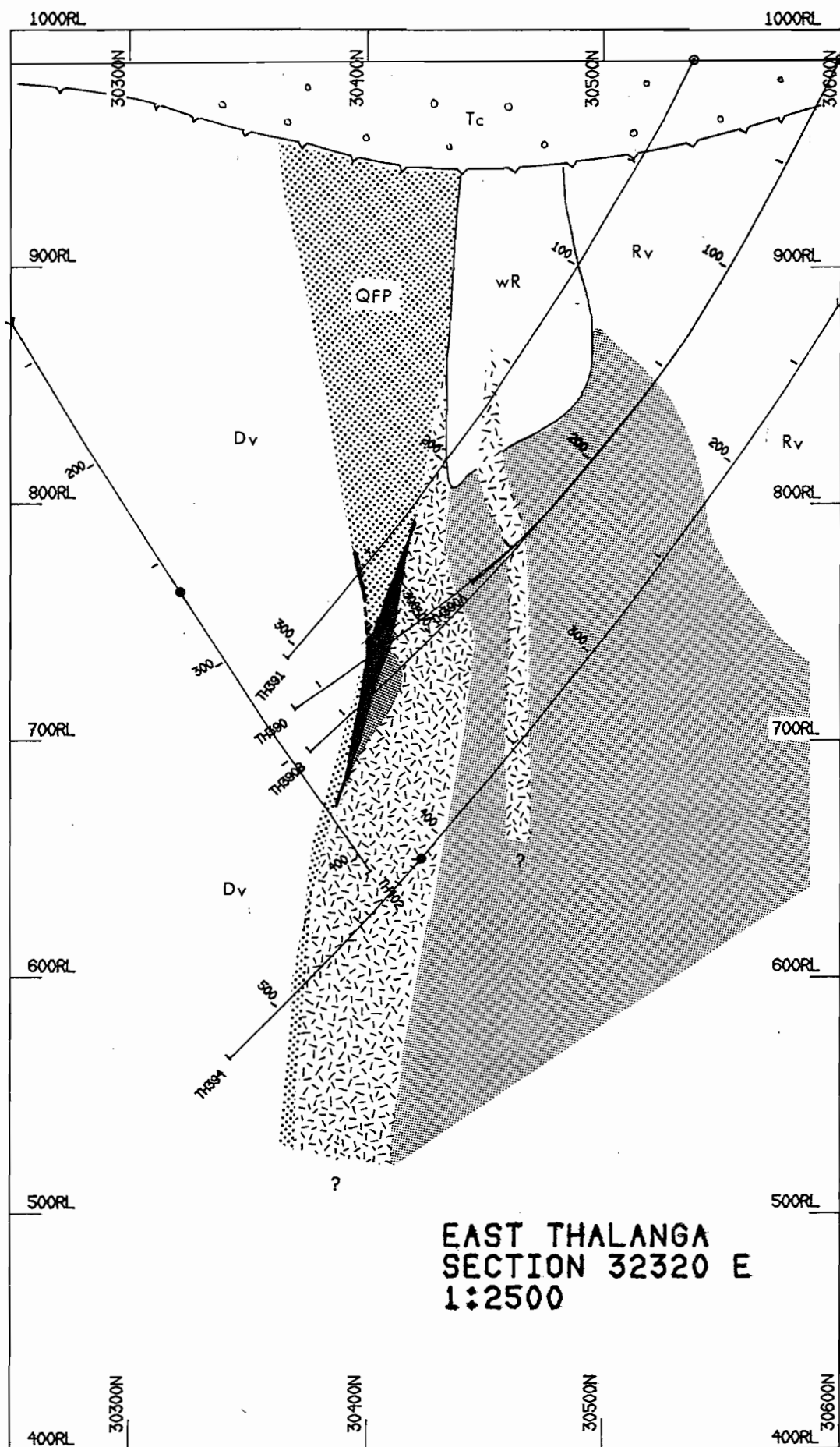


Figure 3. Geological cross section, East Thalanga 32320E

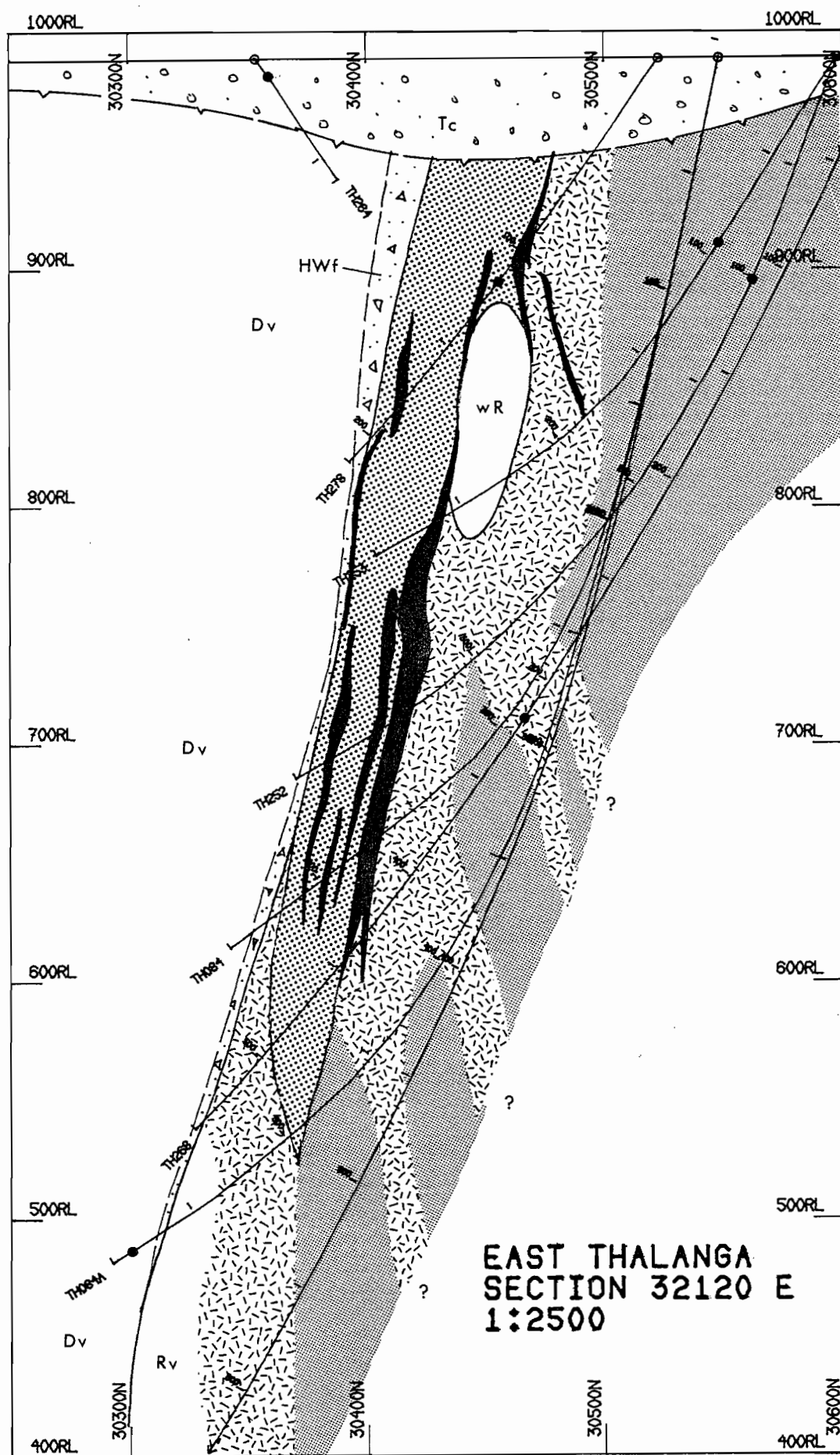


Figure 4. Geological cross section, East Thalanga 32120E

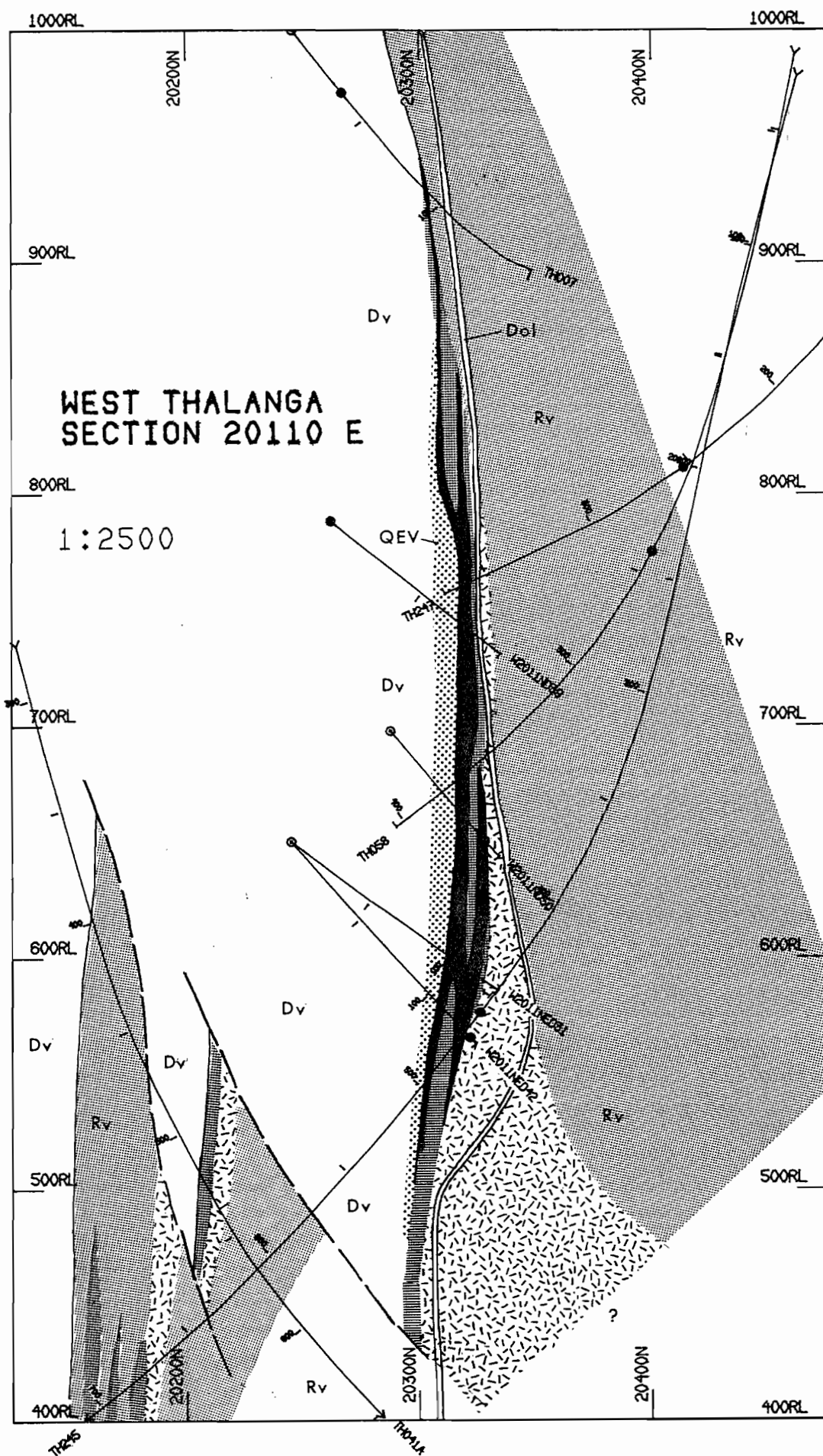


Figure 5. Geological cross section, West Thalanga 20110E

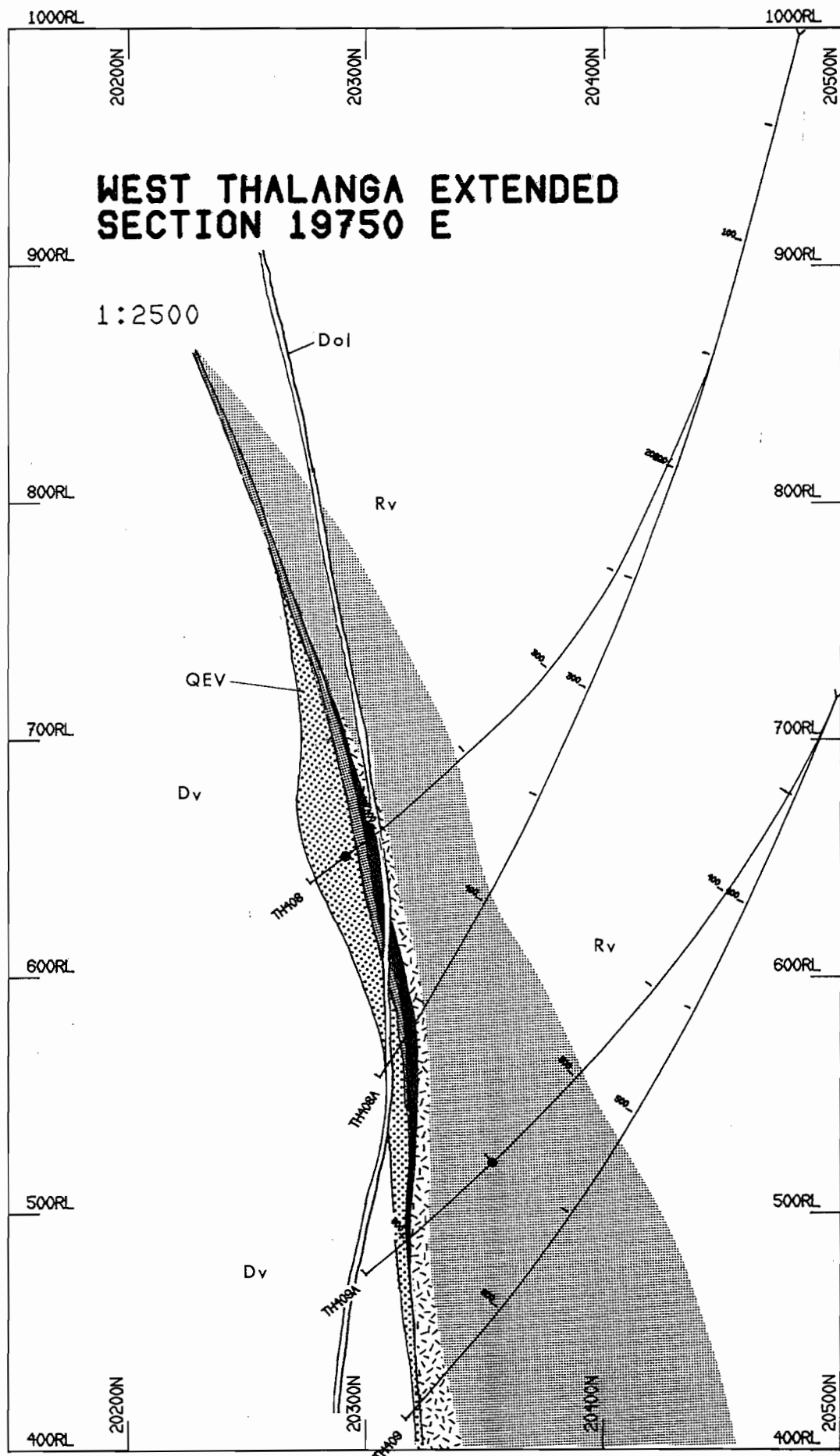


Figure 6. Geological cross section, West Thalanga 19750E

zonally altered to quartz, sericite, chlorite and phlogopite dominant assemblages with extensive minor disseminated sulphides (mainly pyrite) and pyrite-chalcopyrite stockworks in the most intense proximal zones. Alteration and subsequent metamorphism produced considerable textural modification and often the only convincing relict fabric is of sparse, small (<5%, <2mm) phenocrysts or crystals of quartz. Common angular-fragmental, wispy and mottled fabrics are interpreted to be largely due to devitrification and hydrothermal alteration effects in formerly coherent lavas as described by Stolz (1989) and Allen (1988). A systematic footwall stratigraphy, distribution of coherent and volcanoclastic units, or possible permeability control of the latter on hydrothermal alteration zones, has not yet been fully mapped out.

Favourable Horizon

Most of the sulphide lenses are associated with a group of distinctive crystal rich volcanoclastic mass flow sediments and felsic porphyries characterised by abundant, large bluish grey quartz crystals/phenocrysts. In West Thalanga a Ca-Mg rich suite of carbonate-actinolite/tremolite-chlorite rocks and quartz-magnetite-barite rocks termed "exhalites" are closely associated with ore. These collectively comprise the Thalanga favourable horizon, of a few metres to a few tens of metres thickness, which is sandwiched between the altered MWF rhyolites of the footwall and relatively unaltered TCF dacites and mafic volcanics in the hanging wall.

Rocks composed of carbonate-tremolite-chlorite (CTC) are virtually ubiquitous associates of ore in the West and West Extended lenses, of limited occurrence in Central and absent or minor in the Vomacka and East Thalanga lenses. They range from <1m to a maximum of about 20m in thickness and are co-extensive with ore but usually do not extend laterally and vertically more than about 150m beyond ore. Massive barite, with or without quartz-magnetite, of upto a few metres in thickness is common in the favourable horizon in the West Extended, updip fringes of West, parts of Vomacka and Far East lenses, but is largely absent from Central and East Thalanga lenses.

The coarse quartz phyric rocks, traditionally known as variations on "quartz-eye" tuff/porphyry/sandstone, have been described by Wills (1985) and Gregory et al. (1990). They partly overlie and partly host the sulphide lenses and associated Ca-Mg carbonate/silicate and barite where present, at West Extended, West and East Thalanga but are poorly developed at Central and Vomacka. Detailed observations by Sainty and Hill (in prep.) have enabled a twofold subdivision as follows.

- * Quartz eye volcanoclastics (QEV): massive to bedded, sometimes graded, volcanoclastic sandstones and polymictic breccias representing mass flow deposits of pyroclastically or hyaloclastically disaggregated volcanogenic detritus. Clasts of altered rhyolite, massive sulphide, barite and magnetite-quartzite occur in the polymictic breccias and indicate sedimentary reworking of previously formed massive sulphide mineralisation.

- * Quartz-feldspar porphyry (QFP): massive, coherent, coarse quartz and feldspar phyrlic porphyry probably formed as flow/dome complexes or cryptodomes partly intrusive into co-magmatic QEVs within the favourable horizon and also occurring as thick intrusive sills within the footwall and hanging wall sequences.

Within the favourable horizon the "quartz-eye" rocks extend laterally and vertically well beyond the limits of the sulphide lenses and have very variable thickness. QEV units range from <2m upto about 30m thick; QFP bodies are rarely <5m thick and range upto 50-150m thick in the areas up dip of the eastern parts of the East Thalanga and Far East sulphide lenses and along the Thalanga Range to the west of the deposit. Thick coherent QFP at the favourable horizon is negatively correlated with occurrence of ore. Alteration intensity in QEV and QFP is variable but generally much weaker than that of the footwall; the QFPs often contain fresh feldspar and may be essentially unfoliated. In some parts, notably the down dip fringes of the West Thalanga lens, strong footwall style quartz-sericite-pyrite alteration transgresses stratigraphically up into QEV and may mark foci where hydrothermal discharge continued after the broad unfocussed zone of the footwall had been partly capped off by deposition of QEV units.

Hangingwall Sequence

Over most of the deposit the hanging wall is defined by unmineralised and relatively unaltered feldspar phyrlic to aphyric dacite conformably overlying the QEV/QFP unit of the favourable horizon or in direct contact with massive sulphides. Dacite units show some variations in feldspar phenocryst content but are usually massive and interpretable as thick coherent flows.

In Central and West Thalanga, the hanging wall sequence includes one or more thick units of meta basalt and basaltic andesite which are essentially conformable, massive and appear to be sills or coherent flows. Narrow intervals of deformed mafic rocks of similar composition occur sporadically in the footwall and are interpreted to be feeder dykes to the hanging wall units. Following the traditional usage, these mafic rocks are collectively called "andesites" in this thesis.

Volcaniclastic sediments of mostly dacitic derivation are a minor component of the hanging wall sequence in the mine area but increase in proportion westward. In drill holes TH45 and TH406 (on Section 18600E, ~1km west of West Extended) the hanging wall is a southward fining and facing sequence of dacitic lithic mass flow breccias, sandstones and massive to laminated siltstones.

A distinctive volcaniclastic sandstone/breccia unit known as "Hangingwall Fragmental" (HWF) is widespread in the Vomacka to East Thalanga area as a layer up to 15m thick between the favourable horizon and the base of the dacite. It is characterised by coarse, matrix supported, clasts of white aphyric dacite and sparse fresh feldspar crystals (but a general absence of quartz crystals) in a foliated sericitic matrix. It is interpreted as an unsorted mass flow deposit of mixed dacitic and rhyolitic detritus, possibly from an exotic source and introduced in a single flow unit. Like the dacites

and andesites of the hanging wall, it is essentially devoid of pyrite and other sulphides and does not contain clasts of massive sulphides or other lithologies of the favourable horizon.

Alteration in the coherent dacites and andesites of the hangingwall sequence is generally weak or patchy with apparent fracture control of alteration assemblages including epidote, clinozoisite, chlorite, carbonate, quartz and hematite stained albite but without significant sulphide. This marked change, from widely distributed sulphides (mainly pyrite) in the footwall and favourable horizon, to an essential absence of sulphides in the hanging wall, is a striking feature of the Thalanga deposit. It suggests that the hanging wall sequence was not in place at the time of local massive sulphide deposition and that the contrasting alteration styles are due to different hydrothermal systems.

Mafic dykes

Two kinds of post tectonic (post D2) mafic dykes occur at Thalanga.

"Microdiorites" are medium to coarse grained holocrystalline rocks occurring as near vertical dykes upto a few metres in thickness, most abundant in the East Thalanga to Far East area. They contain primary hornblende and plagioclase with poikilitic to porphyritic textures and have sharp and often fine grained chilled margins with mainly north to north easterly trends which transect the stratigraphy and S2 foliation.

Microdiorite dykes lack the S2 schistosity of the enclosing volcanics and their textures and contact relationships convincingly indicate that they were intruded after massive sulphide deposition and ductile deformation. Wills (1985) considered them to be related, on mineralogical grounds, to post tectonic phases of the Ravenswood Granodiorite Batholith.

Microdiorite dykes commonly display fracture controlled to semi pervasive, green and pink epidote-actinolite-albite-carbonate alteration which is megascopically similar to that in the hangingwall dacite, (Figure 12).

The coincidence supports the interpretation that this style of alteration is post tectonic and unrelated to the footwall alteration and massive sulphide mineralisation. It is contrary to Stolz' (1991, p.62) observation that it forms a proximal zone confined to the hangingwall of the orebodies and the inference that it is synvolcanic alteration and a useful exploration vector.

Black, fine grained ophitic/amygdaloidal "Dolerite" occurs in one continuous dyke of about three metres thickness and associated minor dykelets which run semi parallel to stratigraphy within or in close proximity to the favourable horizon in West Thalanga and extending west along the Range. The main dyke cuts through the West Extended lens at an acute angle and, like the microdiorites, clearly post dates massive sulphide deposition and ductile deformation. The dolerite is thought to be younger than the microdiorites; Wills (1985) noted that the dolerite dyke cuts across a group of NNE trending brittle faults and quoted a K-Ar radiometric age of ~340 Ma for it.

4 SAMPLING, ANALYTICAL METHODS and LITHO-GEOCHEMICAL GROUPINGS

This investigation of host rock and favourable horizon geochemistry is based on major and trace element data from rocks analysed for Pancontinental Resources in 1994 and substantially augmented by data presented by Wills (1985) and Stolz (1989, 1991). Manipulation of these diverse analyses has produced a useful data set comprising of 220 volcanic/intrusive rocks and 71 favourable horizon lithologies including "exhalites" and massive sulphides. The analyses are listed in Table 1 of Appendix I with explanatory notes on methods of analyses and the nature of recalculations applied to bring them into compatible form.

The majority of analytical samples are of unoxidised, half sawn 50mm or 36mm diameter drill core segments, mostly of 0.3 to 1.0m length, from exploration diamond drill holes in the immediate vicinity of the Thalanga deposit. A few are rock chip samples from outcrops in the railway cutting ~5km west of the mine. The spatial relationships and mineralogical and textural observations are based on detailed megascopic core logging backed up by microscopic examination of a suite of 38 representative thin sections prepared for this study.

To facilitate geochemical comparisons of volcanic units and alteration types the 291 analyses have been subdivided into 28 litho-geochemical groupings into which the analyses in Table 1 (Appendix I) have been sorted. The separations are made on megascopically visible mineralogical/textural differences and, in the case of rhyolites, also on location, whether from footwall or apparent hangingwall settings. The litho-geochemical groups are numbered (not strictly sequentially) from 1 to 45, briefly listed here in Table 2 and described in greater detail in Appendix II.

Table 2 **Litho-geochemical Groups****Group No.** **Description****n=****RHYOLITES**

- | | | |
|---|----|---|
| 1 | 25 | Least altered-weakly altered footwall rhyolites, <1% pyrite. |
| 2 | 18 | Moderately Qtz-sericite-chlorite altered footwall rhyolites with mottled, foliated or pseudo-fiamme fabrics; 1-4% pyrite. |
| 4 | 13 | Intensely altered footwall rhyolites [QSeChlPy] commonly with pyrite stringers; >4% pyrite. |
| 5 | 19 | Siliceous White and Grey Rhyolites in footwall; low Na, high K; usually low pyrite. |
| 6 | 21 | Siliceous QFpR and Buff Rhyolite in hangingwall settings; >1% Na ₂ O, variable Na/K, low pyrite. |
| 7 | 20 | Foliated Buff and [Chl-Ser] altered Rhyolite in hangingwall settings; Si depleted?, low pyrite. |
| 9 | 11 | Railway cutting (outcrop) Rhyolites. |

DACITES, HWF, QFP-QEV and MAFICS

- | | | |
|----|----|--|
| 10 | 36 | Fresh looking Fs phyrlic or aphyric Dacites. |
| 12 | 10 | Pervasively altered Dacites. |
| 13 | 3 | Hangingwall Fragmental unit (HWF) - bulk rock. |
| 14 | 2 | Clasts from within HWF unit. |
| 15 | 9 | QFP or undifferentiated "Qtz eye" rocks. |
| 16 | 3 | QEV Breccias and volcanoclastic sediments. |
| 17 | 21 | Undifferentiated Mafic rocks; mainly hangingwall (TCF) meta-Andesites. |
| 18 | 8 | Microdiorite. |

QTZ-MAGNETITE-BARITE ROCKS

- | | | |
|----|---|---|
| 21 | 3 | Magnetite-quartzite. |
| 22 | 3 | Quartz dominant: Qtz-Ba, Qtz-Mt with relict rhyolitic fabrics (e.g. TH5, 158.0m). |
| 23 | 6 | Qtz-Ba-Mt-Chl-Act+/-Cb+/-Sulphides; in very variable proportions. |

ALTERITES (not in favourable horizon)

- | | | |
|----|---|--|
| 26 | 2 | Ac-Ep/Czo-Qtz+/-Cb alteration of rhyolite. |
|----|---|--|

CARBONATE-TREMOLITE-CHLORITE ASSEMBLAGES

- | | | |
|----|----|---|
| 31 | 5 | Chl-(Phl-Ser) schist (+/- pyrite, sulphides). |
| 32 | 2 | Chlorite > tremolite; <5% carbonate |
| 33 | 7 | Tremolite > chlorite; <5% carbonate |
| 34 | 6 | Tremolite + chlorite (variable); 5-50% carbonate |
| 35 | 10 | Carbonate >50% > tremolite + chlorite |
| 37 | 2 | Ep-Cb > Ac; mainly in QEV in mid-upper parts of favourable horizon. |

SULPHIDES

- | | | |
|----|----|---|
| 41 | 5 | Massive to semi massive Barite >> Sulphides +/- minor Cb. |
| 43 | 12 | Massive Sulphide, Sp+Gn > Py+Cp. |
| 45 | 8 | Massive pyrite, +/- minor Cp, Sp. |

28 groups.

291 analyses.

5 HOST ROCK ALTERATION AND GEOCHEMISTRY

The procedures outlined by Finlow-Bates and Stumpfl (1981) and expanded by MacLean and Kranidiotis (1987) and MacLean and Barrett (1993), have been used to examine the host volcanics for chemically immobile elements and mass changes associated with hydrothermal alteration as a basis for interpreting the chemistry and origin of chlorite-tremolite-carbonate assemblages and other possible exhalites.

5.1 Immobile Element Geochemistry

The major element data for most components (plotted as Harker diagrams in Figures 7a & 7b) shows a broad range of concentrations within, and overlap between, the felsic volcanic groups. The rhyolites and dacites, for instance, have the following ranges:

	SiO ₂ %	MgO%	Na ₂ O%	K ₂ O%
Rhyolites	56-86	0-10	0-6	1-9
Dacites	55-80	0.2-8	1.5-9	0.1-5.5

There is no relationship between Si and Mg or Na+K to indicate that these rocks represent part of a magmatic fractionation trend; the variations point to mobility of these elements during hydrothermal alteration or metamorphism.

However, an examination of the data suggests that Ti, Al, Zr and, to a lesser degree, Y and Nb have remained relatively immobile during alteration at Thalanga.

MacLean and Barrett (1993) recommended that element immobility be tested on variably altered and fresh samples from an identifiable volcanic unit which can be traced laterally through an alteration zone. In such a single precursor system, X-Y scatter plots of immobile element pairs will form highly correlated linear trends due to mass gains and losses of the mobile components in the altered parts. Ideally, the lines of regression pass through the origin of the plot which represents infinite mass gain; relative mass loss is represented by points which plot on the "alteration line" farther away from the origin than the unaltered precursor composition. Application of this test to alteration zones at a number of Canadian volcanic hosted massive sulphide deposits in greenstone belts (MacLean and Barrett, 1993; Barrett et al., 1993; MacLean and Kranidiotis, 1987; Skirrow and Franklin, 1994) has shown that Ti, Al and the high field strength elements (HFSE): Zr, Nb and (to a slightly lesser degree) Y, were essentially chemically immobile during hydrothermal alteration and greenschist facies metamorphism.

Plots of immobile-incompatible* element pairs such as Zr-Y and Zr-Nb are useful for identifying rocks of magmatic affinity within a volcanic sample set: they produce linear magmatic enrichment (fractionation) trends which pass through the origin and which are co-incident with the alteration lines for each magmatic suite.

***FOOTNOTE:** Cox et al., (1979) defined an incompatible element as one which is largely excluded from the lattices of minerals crystallising in a magma and therefore becomes concentrated in (is fractionated into) the liquid. MacLean and Barrett, (1993) cautioned that in felsic calc-alkaline suites where K-feldspar may be a phenocryst phase, the HFSE may become semi-compatible.

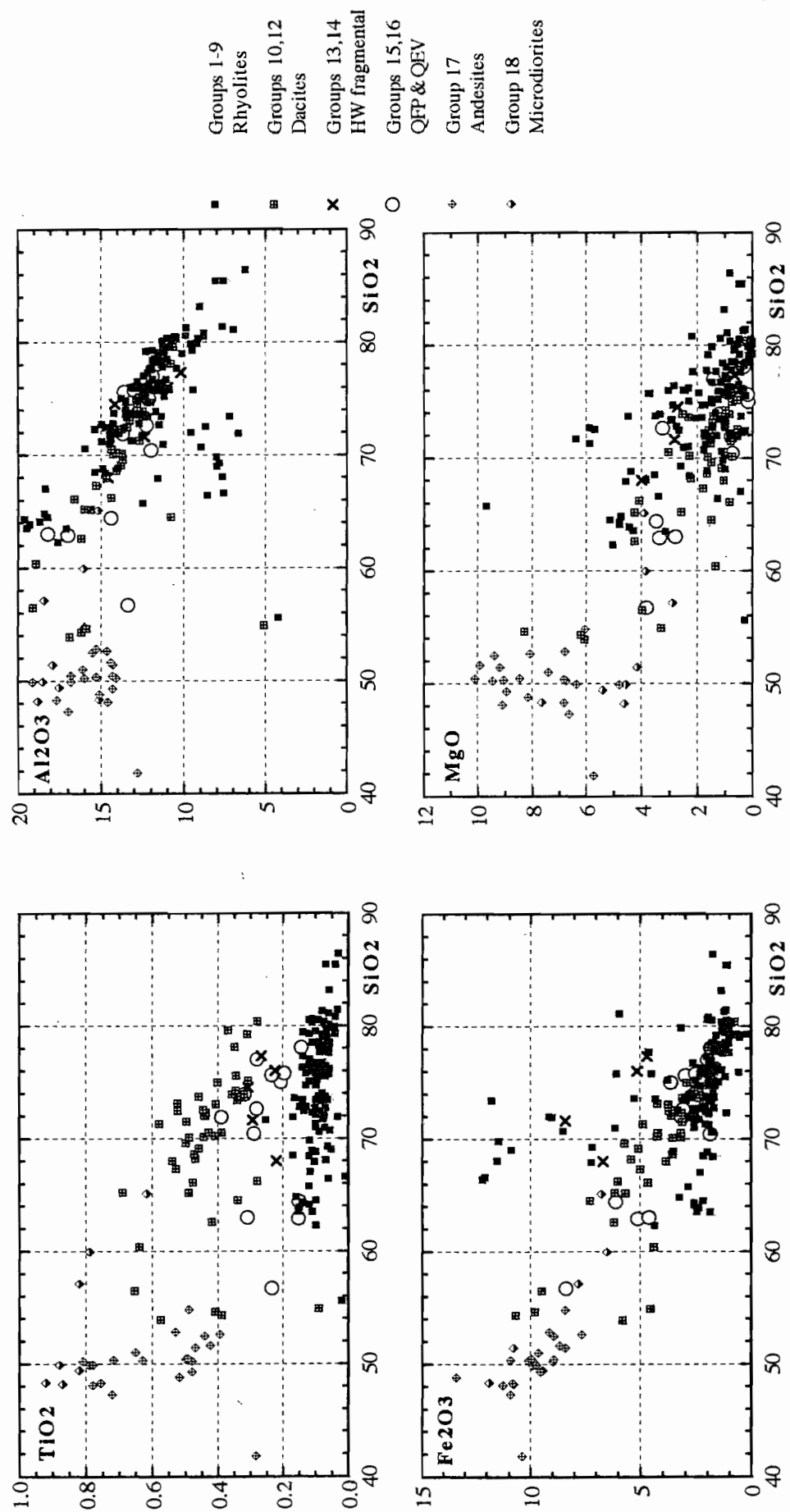


Figure 7a Harker diagrams of TiO₂, Al₂O₃, Fe₂O₃ and MgO for Thalanga volcanic rocks. All axes in wt%.

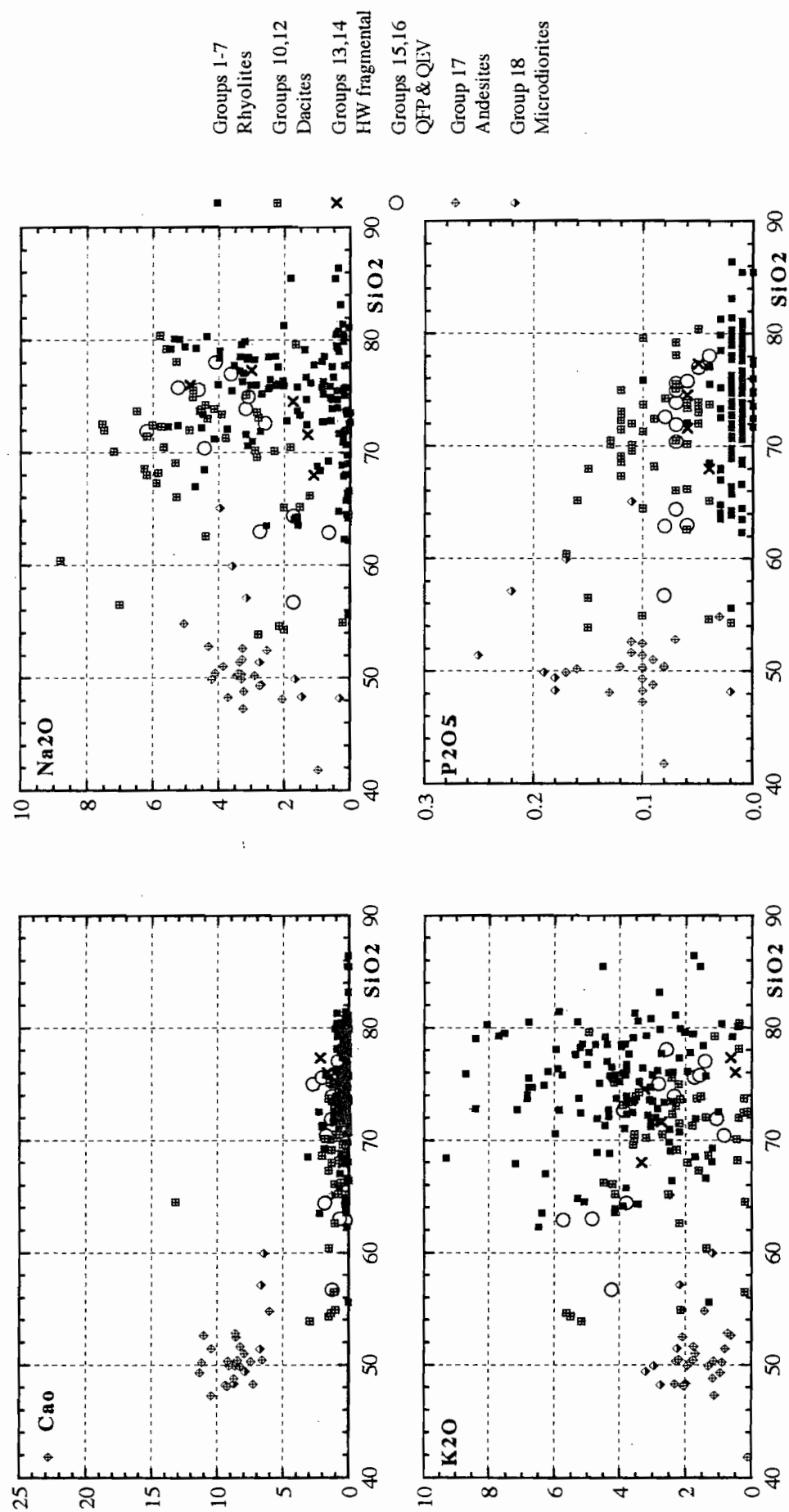


Figure 7b Harker diagrams of CaO, Na₂O, K₂O and P₂O₅ for Thalanga volcanic rocks. All axes in wt%.

Rocks from different magmatic fractionation series fall on separate fractionation/alteration lines and the element ratios may provide a discriminant of magmatic suites and tectonic setting (MacLean and Barrett, 1993).

Plots of immobile compatible-incompatible or compatible-compatible element pairs, on the other hand, form separate alteration lines for each chemically distinct rock unit and are therefore useful for discrimination and correlation of individual homogenous volcanic units within and through zones of alteration.

The plots of incompatible pairs Zr-Nb, Zr-Y and Y-Nb, illustrated in Figures 8a & b, show a fair amount of scatter but the linear fractionation/alteration trends referred to by MacLean and Barrett, (1993) are discernible.

The Trooper Creek Formation (TCF) series metabasalt to dacite forms crude linear arrays with calculated regression lines passing close to the origin and having correlation coefficients ranging from $r = 0.61$ (Y-Nb) to 0.83 (Zr-Y).

If it is accepted that these TCF volcanics from the Thalanga hangingwall stratigraphy do form a single magmatic differentiation series then the significantly lower r -value for Y-Nb compared to Zr-Y and Zr-Nb suggests that of these three, Zr was possibly least chemically mobile.

Two interesting asides, concerning magmatic affinities and origins, may be gleaned here from the immobile-incompatible plots. The range of Zr concentration of TCF dacites is similar to that of the rhyolites, most of which are from the Thalanga footwall and are without argument assigned to the Mt Windsor Formation (MWF). Although substantial overlaps and a few scattered outliers exist, the rhyolites in general have significantly higher values of Nb and Y than the dacites; i.e. they have higher Nb/Zr and Y/Zr ratios which can be taken as an indication that the two sets are not co-magmatic. This accords with the interpretation of Stolz, (1994) that the MWF and TCF have different partial melting sources; namely continental crustal and subduction modified mantle melting, respectively. Furthermore, there is no indication in these plots that the so-called Hangingwall Rhyolites (Groups 6 & 7) have any closer affinity to the TCF dacites than do the other rhyolites (Groups 1 to 5) which are undoubtedly from the footwall and MWF. This is consistent with, but not proof of, the interpretation that the Hangingwall Rhyolites of the Central and West Thalanga deposits are equivalent to less altered parts of the footwall rhyolites and have been structurally emplaced.

The plots of compatible-incompatible element pairs Zr-Ti, Nb-Ti, Y-Ti and Al-Zr, (shown in Figures 9a & b) display to varying degrees the radial alteration lines satisfying MacLean and Barrett's (1993) test for chemical immobility.

Each of the plots shows a relatively tight alteration line for the collective rhyolites and rather broader scatter, sometimes barely recognisable as linear alteration trends, for the dacites, metabasalts and other groups.

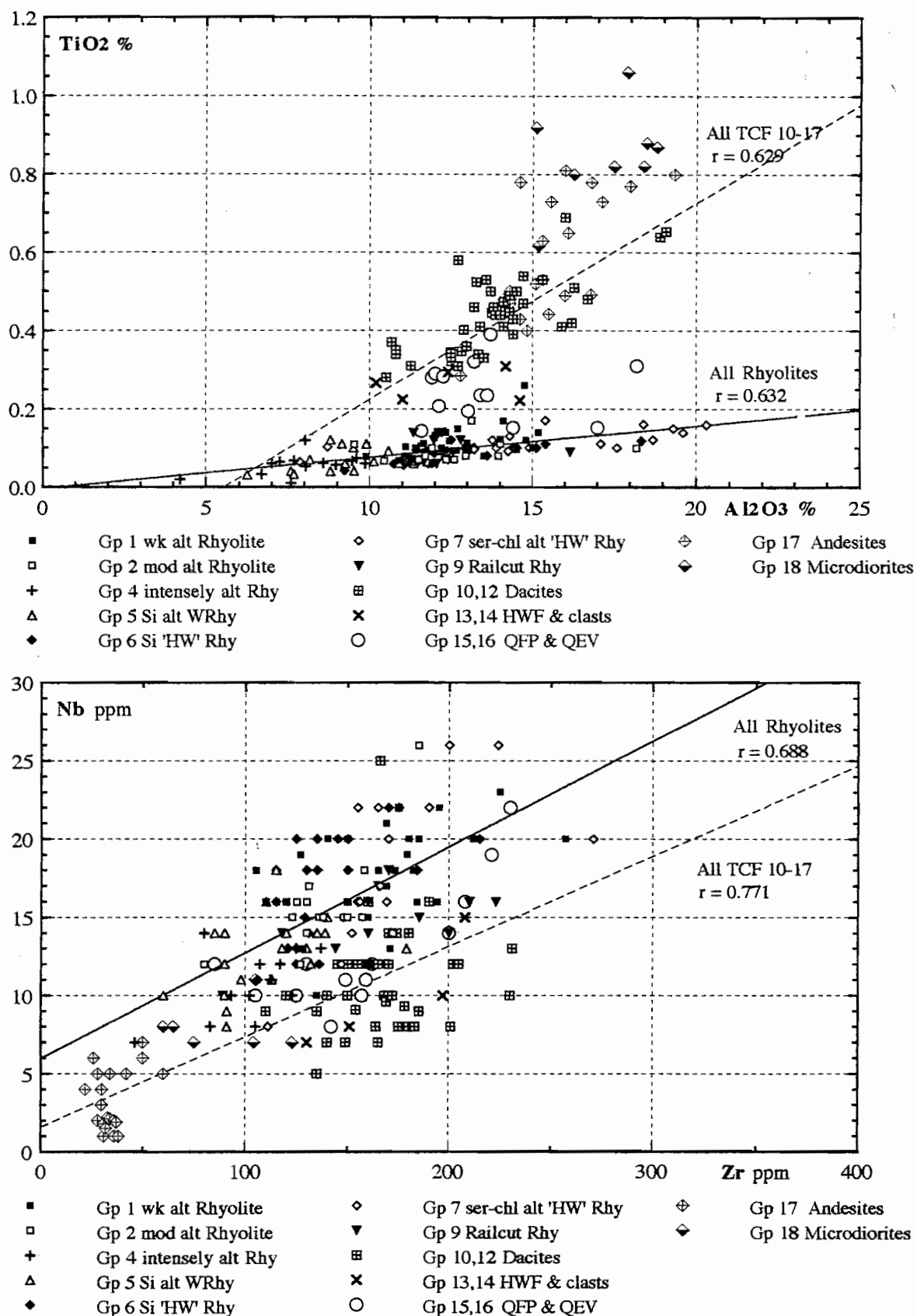


Figure 8a. TiO₂-Al₂O₃ and Zr-Nb scatterplots for Thalanga volcanics with linear regression lines and "r" values for rhyolites and Trooper Creek Formation rocks.

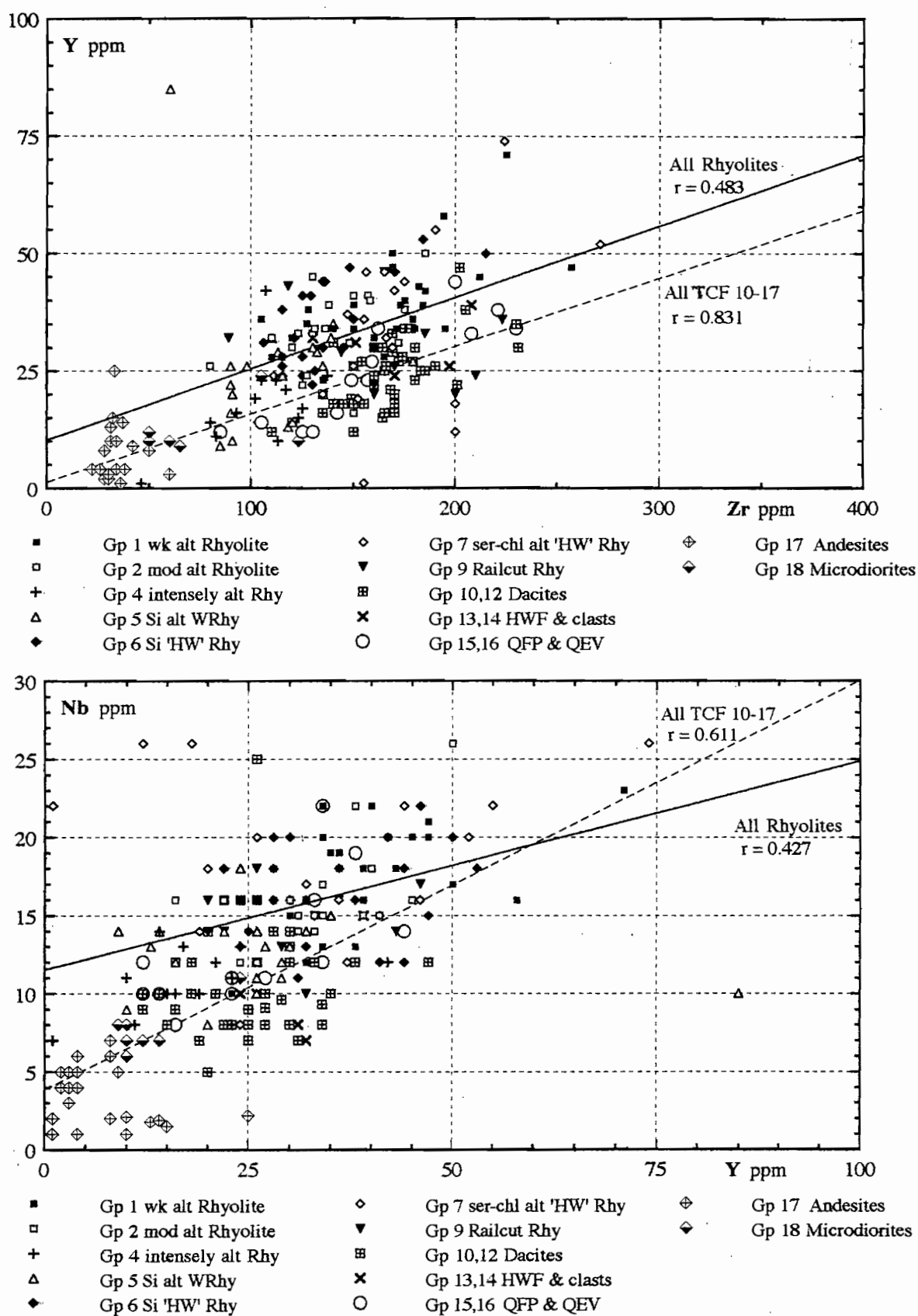


Figure 8b. Zr-Y and Y-Nb scatterplots for Thalanga volcanics showing linear regression lines and "r" values for rhyolites and Trooper Creek Formation rocks.

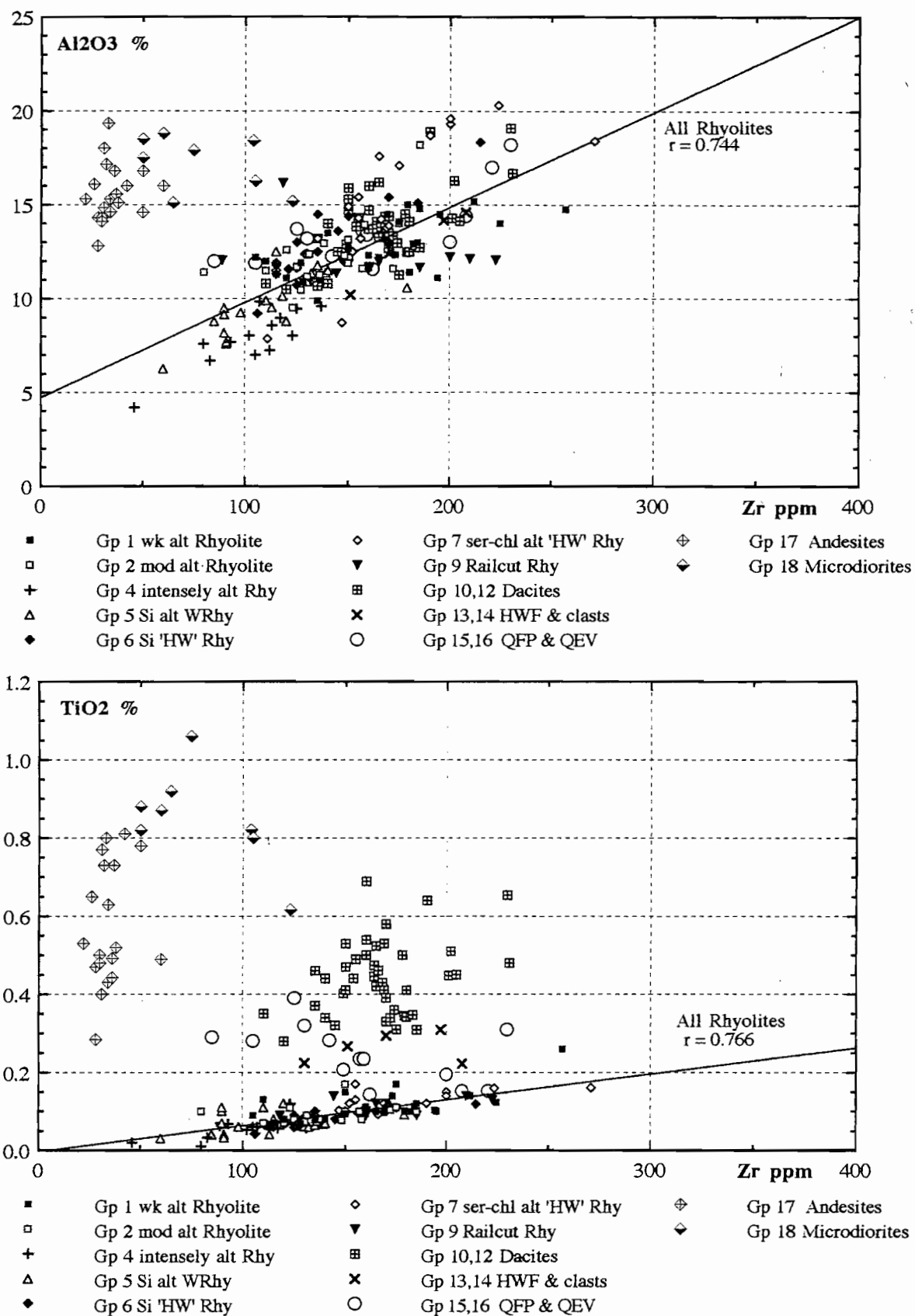


Figure 9a. Incompatible-compatible element plots Zr- TiO_2 and Zr- Al_2O_3 for Thalanga volcanics, showing linear regressions for all rhyolites combined.

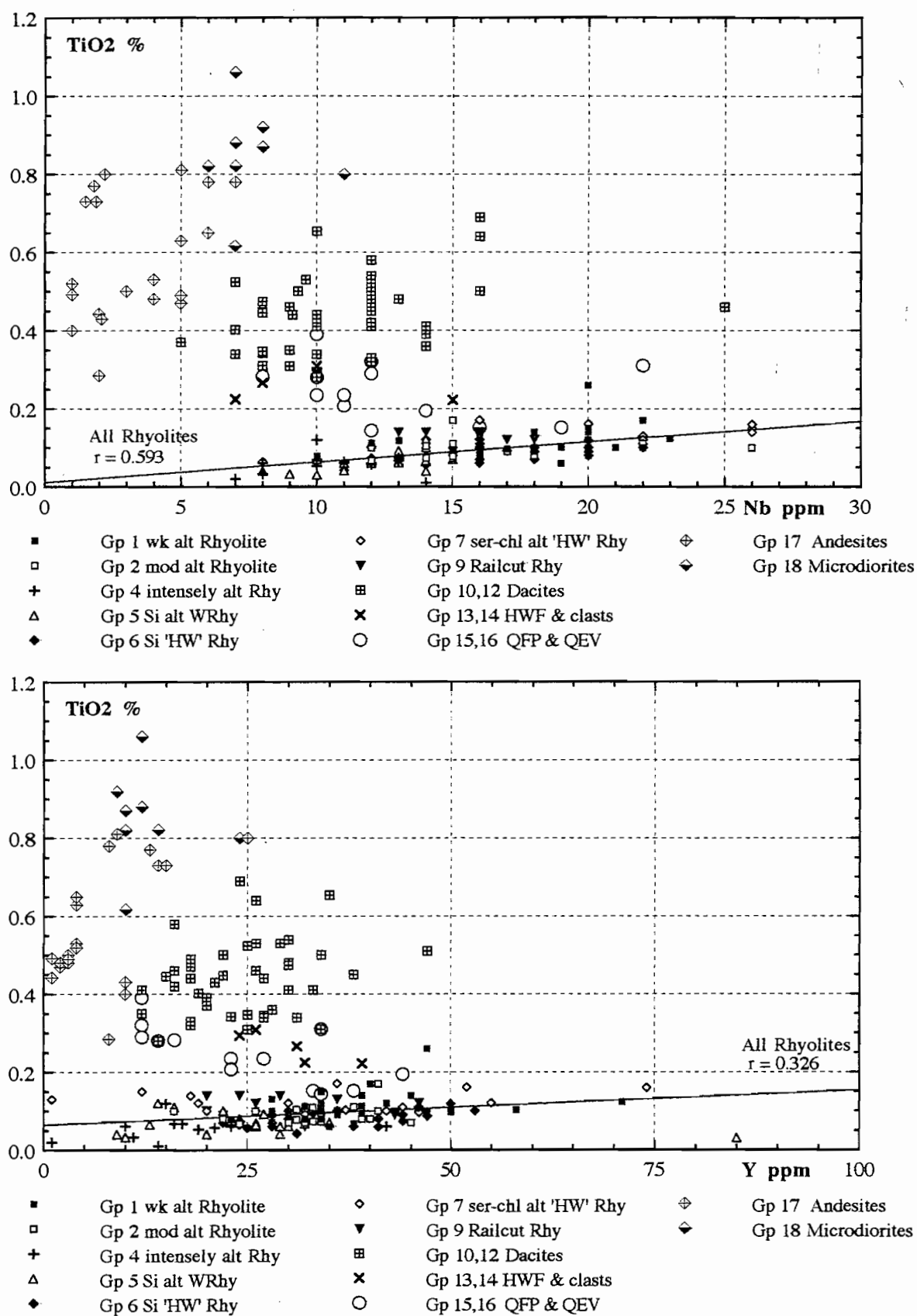


Figure 9b. Incompatible-compatible element plots Nb-TiO₂ and Y-TiO₂ for Thalanga volcanics, showing linear regressions for all rhyolites combined.

The correlation coefficients for calculated (least squares) linear regression lines of the combined rhyolites (Groups 1 to 9) range from $r = 0.766$ for Zr-Ti down to $r = 0.326$ for Y-Ti. This tends to support the earlier inference from incompatible pairs that Zr was less mobile than Nb and Y. On the shaky basis of rhyolite alteration line correlation coefficients alone, it would seem that Zr, Ti and Al have been less chemically mobile than Nb and Y although this could be partly due to the relatively low concentrations and consequent lower analytical precision of the latter two.

Even so, the "r" correlation values of rhyolite alteration lines for the Zr, Ti and Al combinations fall considerably short of the values anticipated by MacLean and Barrett (1993) of $r = 0.90-0.99$ for single precursor data sets. The Thalanga rhyolites, however, are not from a single precursor homogenous volcanic unit. This rhyolite data set includes samples from about 6.5km of strike length (from Thalanga railway cutting to East Thalanga) and about 300-400m of stratigraphic thickness and undoubtedly combines various lava and volcanoclastic units of the footwall stratigraphy which has not yet been unravelled due to the alteration overprint and lack of exposure. Given this, it is remarkable that the rhyolites fall on fairly tight alteration trends and suggests considerable magmatic uniformity in the footwall rocks whatever their lithofacies variation may be.

The broader scatter for lithotypes of the TCF suggests greater variations in magma compositions which may be attributable to fractionation. In general, the TCF volcanics, existing as they do in the hangingwall sequence, are less hydrothermally altered than the rhyolites of the footwall and, having suffered lesser mass gains and losses, are less radially strung out along their alteration lines. Two or more compositional groups can be inferred for the dacites from the immobile element data but the spatial distribution of these samples has not been examined to check if they do split into stratigraphically sensible units.

The nearest approach to testing for immobility in a single precursor system, which has been attempted in this study, involves pairs of adjacent altered and unaltered segments of core from TCF dacite and andesite in which hangingwall style epidote-quartz-(albite-carbonate) alteration is strong and pervasive but patchy on a several centimetres to metres scale and is confidently interpreted to occur within previously homogenous volcanic units.

The two pairs tested are:

Sample Nos: 60209 & 60210 from 279.0-279.9m and 280.1-280.3m in hole TH407; these are, respectively, epidote-albite-(actinolite-carbonate) pervasively altered and relatively unaltered metabasalt (Figure 10a) in a >30m thick unit stratigraphically overlying the favourable horizon updip of the West Thalanga Extended sulphide lens.

Sample Nos: 60224 & 60225 from 79.35-79.65m and 80.3-80.4m respectively, in drill hole W2007NED70; (depicted before sampling in Figure 10b). These



Figure 10a. Photograph of altered and unaltered "andesite" samples 60209 & 60210 from TH407 showing sharp boundary of pervasive epidote-albite-(carbonate-actinolite) alteration.



Figure 10b. Diamond drill core from W2007NED70 (before sawing of samples 60224 & 60225) showing strong, domainal, partly fracture controlled, epidote-quartz alteration in fresh dacite.

samples are from unaltered and pervasively epidote-quartz altered dacite, situated about 30m stratigraphically above the West Thalanga ore horizon at ~530RL on 20060E.

The two sample pairs are highlighted on X-Y plots for supposed immobile elements in Figures 11a & 11b. They fall close to radial alteration lines passing through the origin on the Zr-TiO₂, Zr-Al₂O₃ and (less consistently) Al₂O₃-TiO₂ plots and appear to satisfy the MacLean and Barrett (1993) test for chemical immobility. The altered samples always plot closer to the origin implying bulk mass gains and relative dilutions of the immobile elements by alteration. The plots with combinations of Nb and Y, on the other hand, show some very peculiar alteration lines connecting these sample pairs suggesting, as inferred above, that these elements have not been immobile or are subject to analytical/sampling errors due to the low concentrations, or both.

Consideration of the major element data for these sample pairs (Table 1, Appendix I) even without calculation of mass changes, points to major addition of Ca and CO₂ with consequent relative dilution of most other components as the main chemical changes associated with this type of hangingwall alteration.

It is quite different to the Ca, Na depletion and moderate to strong Si, Fe and S addition characteristic of the much larger scale of footwall alteration.

There are two lines of evidence to suggest that the hangingwall style of Ca metasomatism postdates the footwall alteration and massive sulphide mineralisation.

- 1 In the dacite it often occurs as selvages to veinlets which appear to cut across the main foliation (S2 of Berry et al., 1992) and the selvages sometimes have feathery outer margins suggesting that alteration has been controlled by fluids pervading outwards along the pre-existing cleavage; e.g. Figure 12a.
- 2 Megascopically similar, green and pink, vein associated to pervasive epidote-(albite-carbonate) alteration is common in microdiorite dykes which cut across and clearly postdate the footwall pyritic stringer alteration zone, massive sulphide lenses and S2 forming deformation event; e.g. Figure 12b.

The contrasting styles of footwall and hangingwall alteration are, therefore, not necessarily comparable in terms of fluid chemistry and mobility or immobility of elements.

Nevertheless, it seems reasonable to conclude that:

- * Precursor Zr, Ti and Al ratios remain well preserved despite strong hangingwall alteration involving substantial chemical, and virtually total mineralogical changes, and can be reliably used to infer the parent rock type in rocks otherwise altered beyond recognition.
- * Nb and Y behave erratically in the same kind of alteration system and are best excluded from rock classification and alteration mass balance calculation exercises.

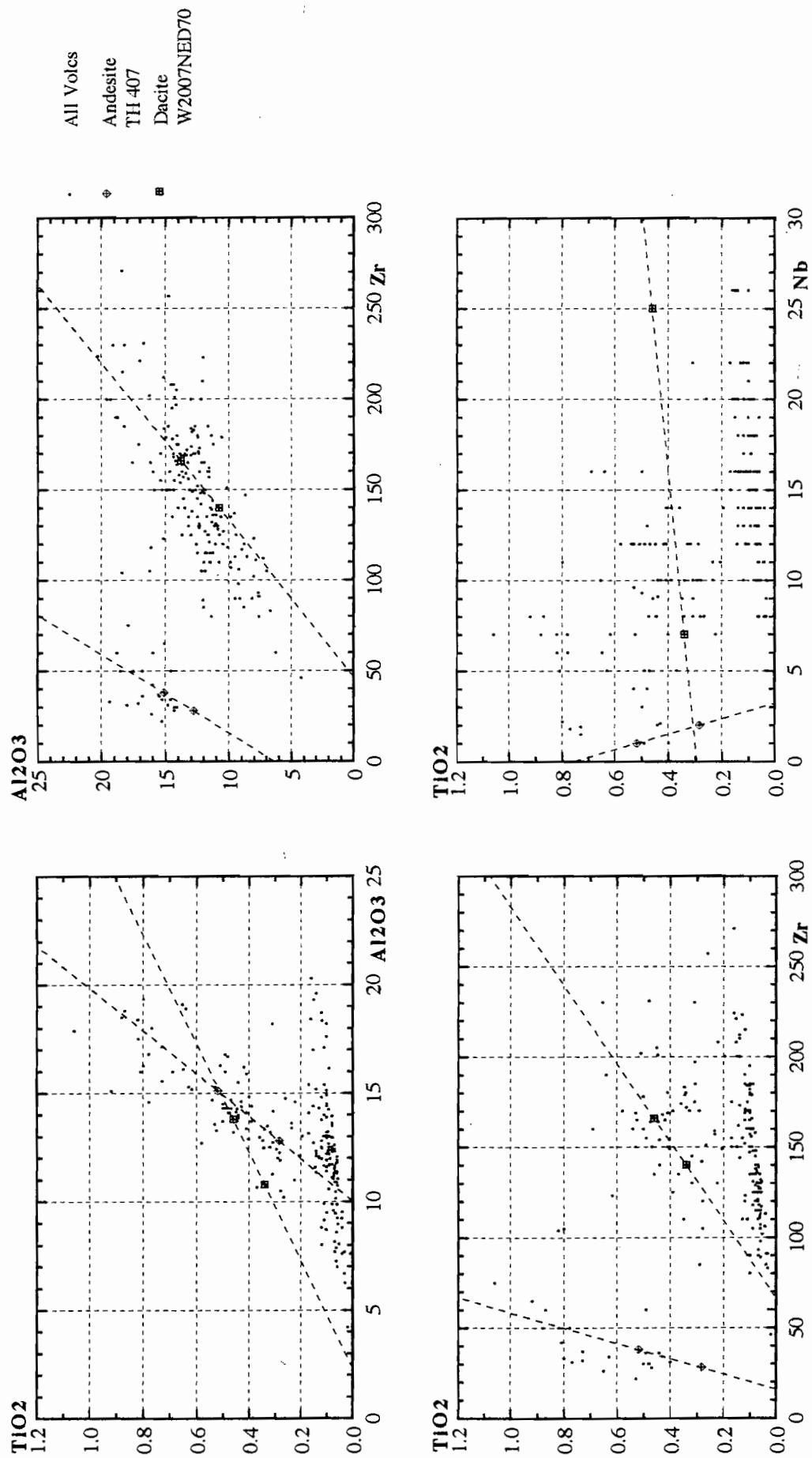


Figure 11a. "Immobile element" plots showing two sample pairs of altered/unaltered andesite and dacite. The regression lines joining the data points for each pair on plots combining Ti, Zr and Al are approximately radial and pass near the origin indicating relative immobility of these elements.

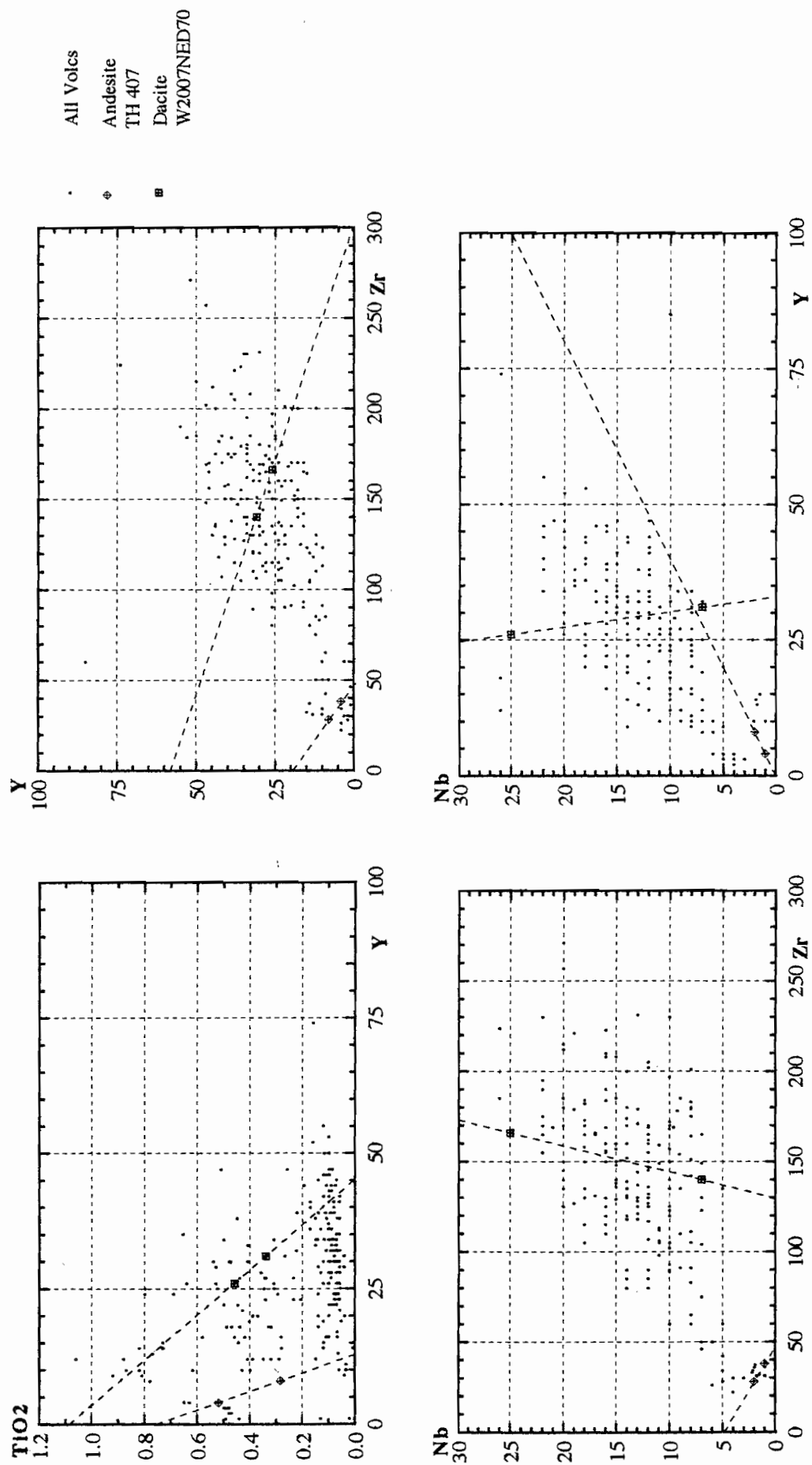


Figure 11b. "Immobile element" plots showing two sample pairs of altered/unaltered andesite and dacite. The regression lines joining the data points for each pair on plots involving Nb and Y are generally not radial and do not pass near the origin which suggests some mobility of these elements during alteration.



Figure 12a Sawn core specimens of porphyritic dacite showing vein epidote-albite alteration selvages with feathery margins suggesting alteration pervaded outwards along pre-existing weak S2 cleavage



Figure 12b Semi pervasive and vein selvage epidote-albite alteration similar to that in dacite (above) but here occurring in post D2 deformation microdiorite dyke. Also shows multiple phases of mafic magma injection with feldspar porphyritic type intruded by finer grained, more mafic phase.

Mention has been made of the difficulties of applying the single precursor test for immobility in the footwall alteration zones and the fair, but not excellent, correlation coefficients obtained for alteration lines regressed from the Thalanga wide rhyolite data set. However, it has been found that narrowing down the areal extent of a footwall rhyolitic sample set will obtain considerably higher correlations.

This is exemplified by the Zr-TiO₂ data from TH 406 which is an 804.7m deep hole drilled southwards under Thalanga Range, 2km along strike to the west of the mine (Figure 2). Every tenth metre of the core was sampled and analysed for Zr, Ti (and a number of other major elements including Na and K but full major element analyses, notably Si and Al, are not available). It yielded a population of 54 footwall rhyolitic rocks ranging from weakly altered to strong pyritic stringer zone alteration types (lithological Groups 1, 2, 4 & 5), 5 samples of coherent Quartz-Feldspar Porphyry (Group 15), 3 samples of associated foliated quartz-eye volcanoclastics (Group 16) and 21 samples from the stratigraphically overlying dacitic volcanoclastic and siltstone sequence.

The Zr-TiO₂ scatterplots in Figures 13a & b are notable for the significantly higher correlation coefficient of $r = 0.883$ for the combined footwall rhyolites (compared to $r = 0.766$ for the 127 rhyolites plotted on Figure 9a). The TH406 rhyolites do not necessarily represent a single precursor unit either; the samples are derived from a stratigraphic interval estimated at about 200m and a down dip extent of about 500m but their tight correlation and clear separation from the other lithotypes, despite significant quartz-sericite alteration, supports the conclusion that Zr and Ti have remained essentially immobile during footwall alteration and metamorphism.

There is nothing in the accumulated geochemical data to suggest otherwise and Ti/Zr ratios have been used with confidence for the classification of volcanic rocks and interpretation of magmatic affinities in the Thalanga area; (e.g. Stolz, 1991; Sainty and Hill, in prep.)

In general, footwall MWF rhyolites are easily discriminated by their low Ti/Zr and Ti/Al ratios and the tendency to fall close to consistent alteration lines on immobile compatible-incompatible plots. TCF dacites have greater scatter and are clearly separated from rhyolites on all plots having TiO₂ as one variable.

Rocks such as the quartz-feldspar porphyries (QFP), quartz-eye volcanoclastics (QEV) and the distinctive Hangingwall fragmental unit (HWF), which mainly occur in the favourable horizon between the MWF and TCF, have immobile element concentrations which partly overlap with the dacites and partly fill the gap between dacites and rhyolites. This is consistent with the interpretation that these may be hybrids originating by mixing of magmas, in the case of the porphyries, or mixing of detritus from separate volcanic sources in the case of volcanoclastics. The relationships are well illustrated by the Zr-TiO₂ plot for TH406 (Figure 13a) which shows the coherent QFPs (of which two samples are from a 10m thick, sill like unit enclosed by rhyolites in the footwall) plotting between the dacite and rhyolite fields. The quartz-

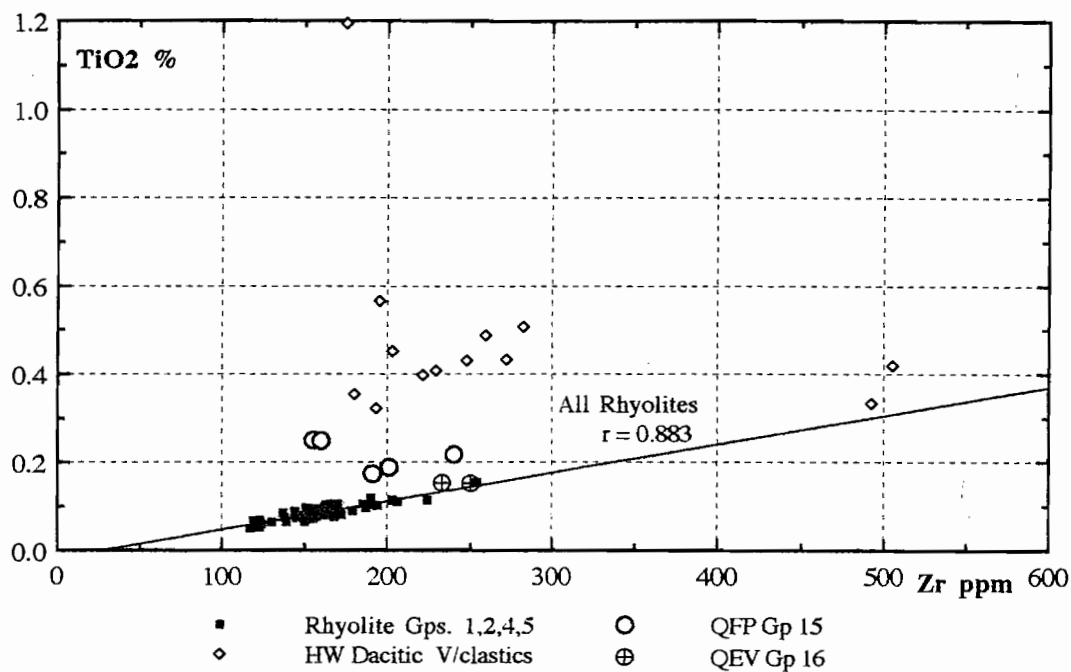


Figure 13a. Zr-TiO₂ plot for analyses from TH 406, Thalanga Range; showing linear regression and correlation factor "r" for all rhyolites combined.

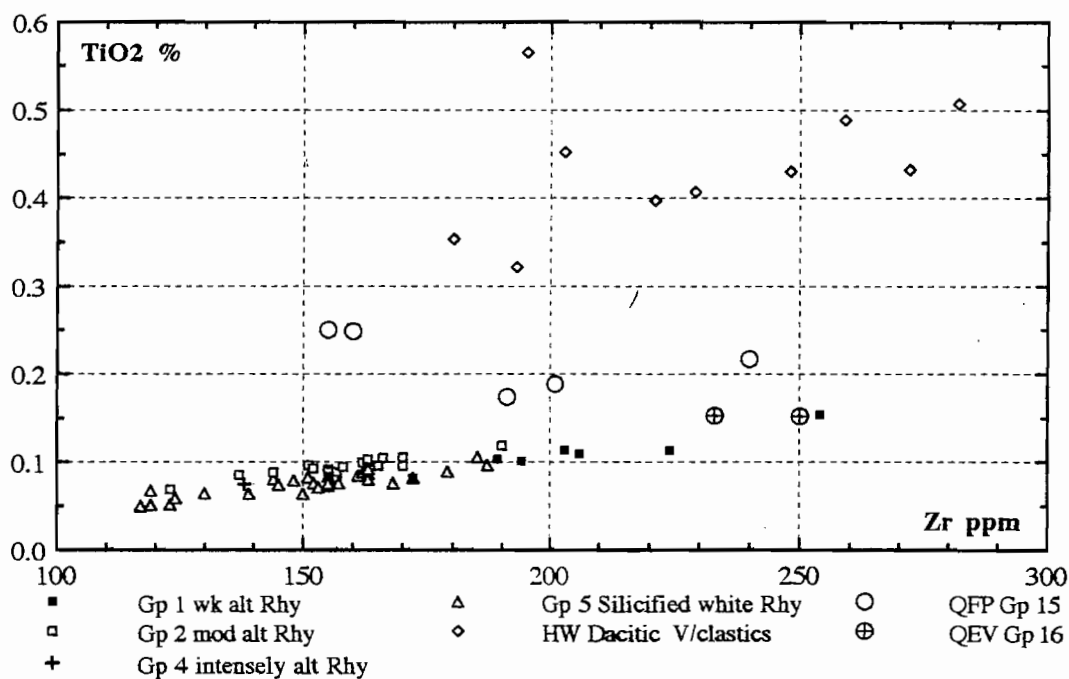


Figure 13b. Same data as Figure 13a with Rhyolites subdivided into litho-geochemical Groups and axes stretched for clarity.

eye bearing volcanoclastics between 644-678m, which apparently overlie coherent QFP, have Ti/Zr ratios similar to footwall rhyolite implying that the latter was the dominant source of volcanoclastic materials.

The volcanoclastic sediments further "up" in the hangingwall sequence mostly have the Ti/Zr signature of dacite. The exceptions include two samples of unusually high Zr content which approach the rhyolite alteration line (~500ppm Zr) and one of 1.2% TiO₂ content from near the end of the hole, which appears to reflect an input of mafic volcanoclastic materials near the top of the intersected sequence.

5.2 Mass changes in altered rhyolites

The immobile compatible-incompatible plots (Figures 9a,b) show systematic geochemical variations for the rhyolite groups. Despite substantial overlaps between groups, there are qualitative drifts, progressive along the alteration lines towards the origins of the plots, from the least altered to the most intensely altered footwall rhyolitic rocks (Groups: 1, 2 & 4) which imply significant mass gains associated with this type of alteration. Group 7 foliated rhyolites, on the other hand, plot with higher immobile element concentrations (away from the origins) relative to the Group 6 less altered rhyolites with which they are closely associated. This indicates relative mass loss associated with Group 7 type phyllosilicate alteration.

In single precursor systems, the relative mass changes can be quantified by calculations based on the dilution or concentration of a single immobile component "monitor" as outlined by Maclean and Barrett (1993). Alternatively, the Isocon method employed by Gemmell and Large (1992), after Grant (1986), provides a graphic means of estimating mass changes based on several immobile elements. Both methods rely on determination of an unaltered or least altered equivalent rock - the "precursor" of the altered rocks.

Such calculations are not straightforward for the Thalanga footwall alteration zones because of the difficulty in identifying a single precursor unit which can be traced from unaltered into altered zones. Nonetheless, the apparent primary geochemical uniformity of the footwall rocks (despite probable variation of volcanic facies) suggests that the mass change calculations may be employed in a general way to provide at least approximate indications of gains and losses of the mobile components.

Three possibilities for a rhyolite precursor composition are obvious:

- * Least altered footwall rhyolites in Group 1.
- * Freshest of Group 6 "hangingwall rhyolites" which are interpreted to be more or less equivalent to Group 1 representing structurally emplaced, weakly or unaltered, footwall rhyolite.
- * Group 9 railway cutting rhyolites which are from the footwall sequence several kilometres west of the Thalanga deposit and outside its alteration zone.

In this study, three separate precursor compositions, designated Precursors: 1, 6 and 9 respectively, have been constructed by averaging the compositions of several more or less subjectively chosen samples from each of the likely groups. The main selection parameters included presence of relict feldspar, lack of Na depletion, Alteration Index <70 (Ishikawa et al., 1976), $\text{Na}_2\text{O}/\text{K}_2\text{O} \sim 1$ and moderate levels of Al_2O_3 and Zr. Table 3, in Appendix I, lists the three estimated possible precursor compositions, the samples from which they were derived and the mean compositions and standard deviations of the seven rhyolite groups.

The absolute and relative mass changes of all major components have been calculated by the MacLean and Barrett (1993) method, using Zr* as the immobile monitor element, and are shown graphically in Figures 14a & 14b.

The calculated absolute mass changes are presented in units of g/100g, (i.e. grams of a component added to or removed from an original precursor bulk mass of 100grams). The relative mass changes are presented as multiples of the amounts of components assumed to have been present in the unaltered precursor, (i.e. if an unaltered bulk mass of 100g of precursor contained, say, 60g of SiO_2 a relative mass change of 0.5 would indicate that an additional 30g of SiO_2 had been added to the bulk rock; a negative relative mass change factor indicates removal of a component).

The mass changes show similar patterns for all three model precursors in most major components except Al_2O_3 , suggesting that the estimates of the three precursor compositions are equally valid. Al_2O_3 shows small gains for all groups with respect to Precursors 1 and 9 and, contrarily, small losses with respect to Precursor 6. However, the approximate constancy of Al_2O_3 relative mass changes across all rhyolite groups supports the previous interpretation that it was essentially immobile during alteration and hence the problem is likely to lie in the choice of precursor compositions. A possible cause of the discrepancies could be plagioclase phenocryst fractionation. Plagioclase alumina contents range from 19.4wt% (albite) to 36.6wt% (anorthite) which are significantly higher than the average concentrations in the rhyolites and therefore variations in plagioclase phenocryst contents may account for the calculated alumina mass changes of about 2-4 g/100g.

Notwithstanding that, it is apparent that the main chemical changes in the progressive footwall alteration (Groups 1, 2 and 4) involve substantial additions of Si, Fe and S and depletion of Na, and that these changes are consistent for all precursors.

Footnote: The Maclean and Barrett (1993) method has been applied here with confidence in the immobility of Zr. It may be argued that the Isocon method has an advantage in that it is not solely dependent on the altered/unaltered ratio of a single immobile "monitor" element but takes for its mass change calculations the gradient of the line of best fit through a series of plotted points which ideally lie on a straight line passing through the origin if the points represent immobile elements, (Grant, 1986). In this study, however, it was found that the elements suspected of being immobile did not clearly plot on single lines and a degree of subjectivity was required to place the isocons despite Grant's (1986) assurance that they could readily be determined by inspection. It is considered that the tests for immobility outlined MacLean and Barrett (1993) are more useful in that they are able to simultaneously examine a large suite of geochemical data from alteration zones of varying intensity.

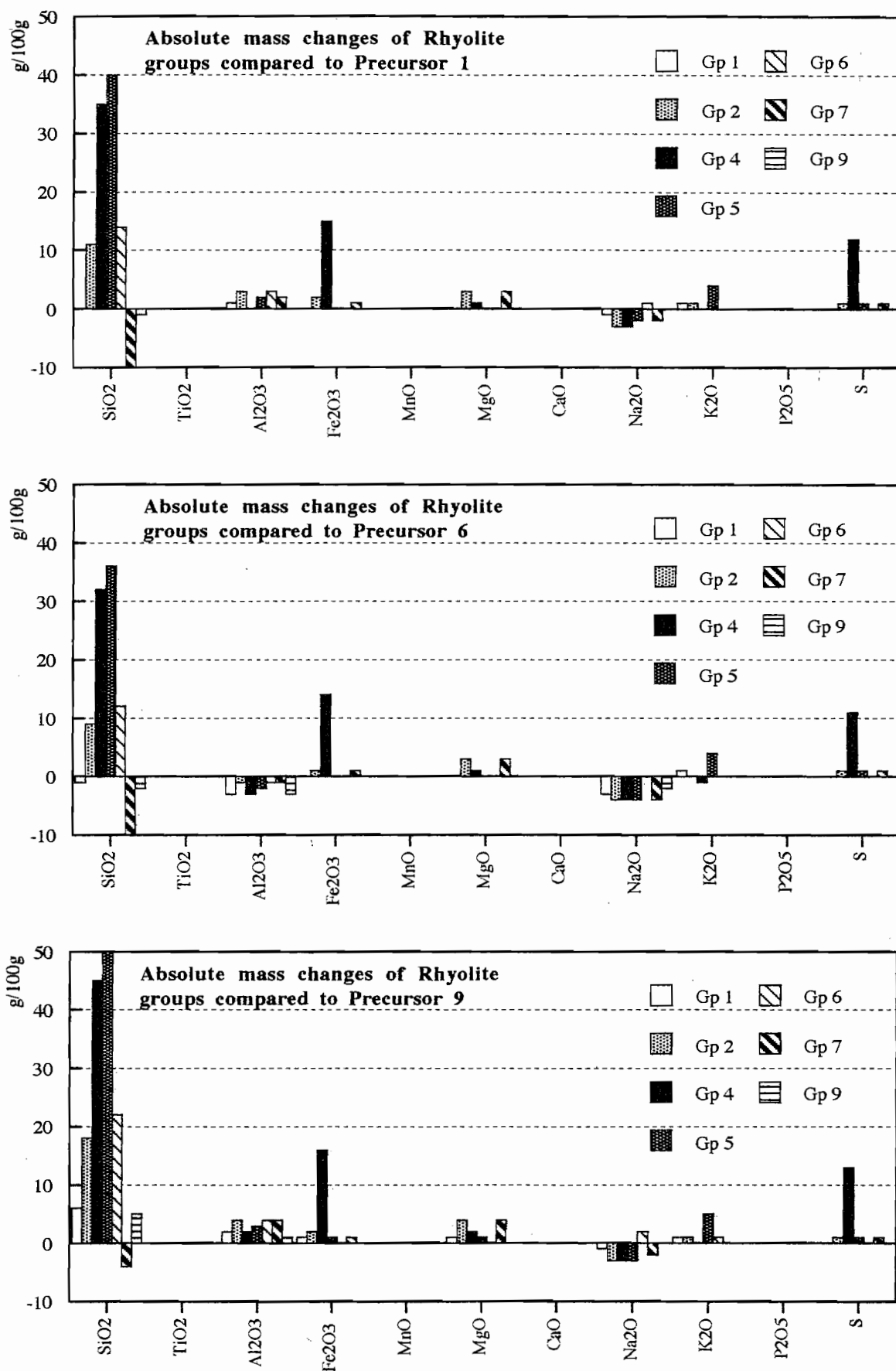


Figure 14a. Absolute mass changes of Rhyolite Groups 1 to 9 compared with "Precursors 1, 6, and 9". Mass change units are g/100g.

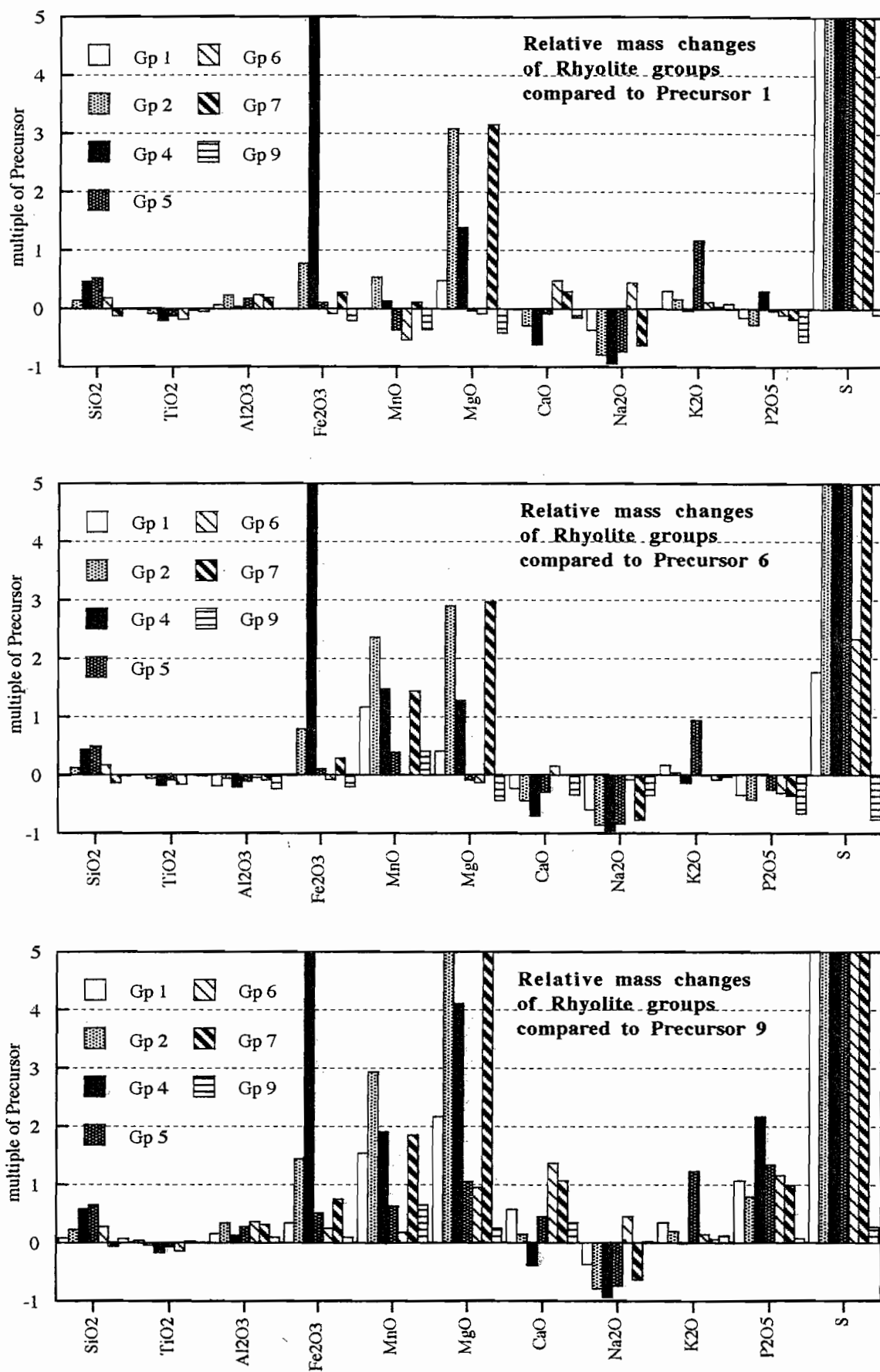


Figure 14b. Relative mass changes of major components for Rhyolite Groups 1 to 9 compared with "Precursors 1, 6, and 9".

Taking the Precursor 1 case as an example: SiO_2 , Fe_2O_3 and S combine to produce an absolute gain of 62g/100g for the average Group 4 intense pyritic stringer zone alteration. This implies a substantial volume increase which could be partly, but not entirely, accounted for by the stockwork of pyrite veins. Sodium depletion only slightly offsets this gain with a mass reduction of 3g/100g which in relative terms represents a virtually complete loss of this element reflected in feldspar destruction. It is notable that the Na loss is also essentially complete in the Group 2 zone of moderate alteration even though this has gained only about 17g/100g from SiO_2 , Fe_2O_3 , MgO and S.

The Group 5 rhyolites on average appear to have gained even more silica than Group 4 footwall stringer zone alteration (35 to 50 g/100g depending on choice of precursor composition), but negligible Fe and S (pyrite) and are alone in having gained significant K_2O (4 to 5 g/100g) which has remained essentially immobile in the other rhyolite groups. Group 5 rhyolites also appear to have undergone major Na depletion (~ 0.8 in relative terms) similar to Groups 2 and 4 which are recognised as parts of a zoned footwall hydrothermal alteration system. Although the Group 5 rocks including the "white rhyolites" of East Thalanga, do not unambiguously fall into this alteration zonation, and despite their apparent megascopic "freshness", coherence, sometimes sharp contact relationships and ellipsoidal forms which have led to previous speculations of their origin as small volcanic domes, the geochemical features are consistent with them being alteration products derived from massive silicification of fairly ordinary footwall rhyolites.

5.3 Synthesis

The data presented and discussed in this chapter has demonstrated several important aspects of the geochemistry of the Thalanga host rocks and hydrothermal alteration system which are fundamental to an examination of the "exhalites".

- * The elements Ti, Al and Zr have been chemically immobile despite strong hydrothermal alteration and subsequent metamorphism.
- * The immobile element ratios clearly discriminate between the major volcanic lithotypes and can be used to identify the precursors to otherwise unrecognisable, very altered volcanic rocks.
- * The immobile element concentrations and judiciously selected least altered precursor compositions can be used to estimate the mass gains and losses of chemical components which were mobile during alteration. Absolute mass gains of silica, iron and sulphur totalling ~ 60 g/100g, and complete removal of sodium, are indicated for the most intense zone of footwall alteration.

6 GEOCHEMISTRY of EXHALITES, PSUEDO-EXHALITES AND SULPHIDE ASSEMBLAGES

Rocks which have been previously classed as "exhalites" have a remarkable diversity of mineral assemblages and range of chemical compositions. Wills (1985, p.48) tabulated the following extremes (from 0.5m drill core samples) for some major components:

SiO ₂	6.6 - 91.9%
Al ₂ O ₃	0.41 - 15.6%
MgO	0.26 - 22.6%
FeS ₂	0.13 - 5.03%
CaCO ₃	0.2 - 73.2%
BaSO ₄	0.01 - 28.0%

On the basis of differences in SiO₂ content and Mg/Fe ratios, Wills (1985) identified three main groups which he termed siliceous, shaley and carbonate-tremolite exhalites. I regard that as an oversimplification in that the carbonate-tremolite category includes near monomineralic end members of those minerals with or without chlorite. Accordingly, in this study, these rocks have been further subdivided to reflect the proportions of chlorite-tremolite-carbonate and other important phases into a total of 13 mineralogical groups covering all rocks which have been previously interpreted as exhalites. These are (non-sequentially): Groups 21 to 45 in Table 1 of Appendix I.

The modes of occurrence and essential mineralogical and textural features of the groups are presented in Appendix II as a background to the following examination of their chemistry.

6.1 Immobile element geochemistry of exhalites, psuedo-exhalites and sulphides

It has been shown that Al, Ti and Zr remained chemically immobile in the footwall rhyolites despite significant mass changes of other components during alteration and metamorphism. In other words, the footwall rocks have chemically interacted with presumably great volumes of hydrothermal fluids which have not been able to dissolve and transport Al, Ti and Zr. It therefore follows that such fluids, when "exhaled" from seafloor hydrothermal vents, would not be carrying these elements and could not precipitate them into any chemical sediments - "exhalites" - which might be deposited from solution.

True exhalites may be expected to contain very low amounts of the immobile elements.

The immobile element data presented by Duhig et al. (1992) and graphically reproduced here in Figure 15, from siliceous ironstones which have been demonstrated

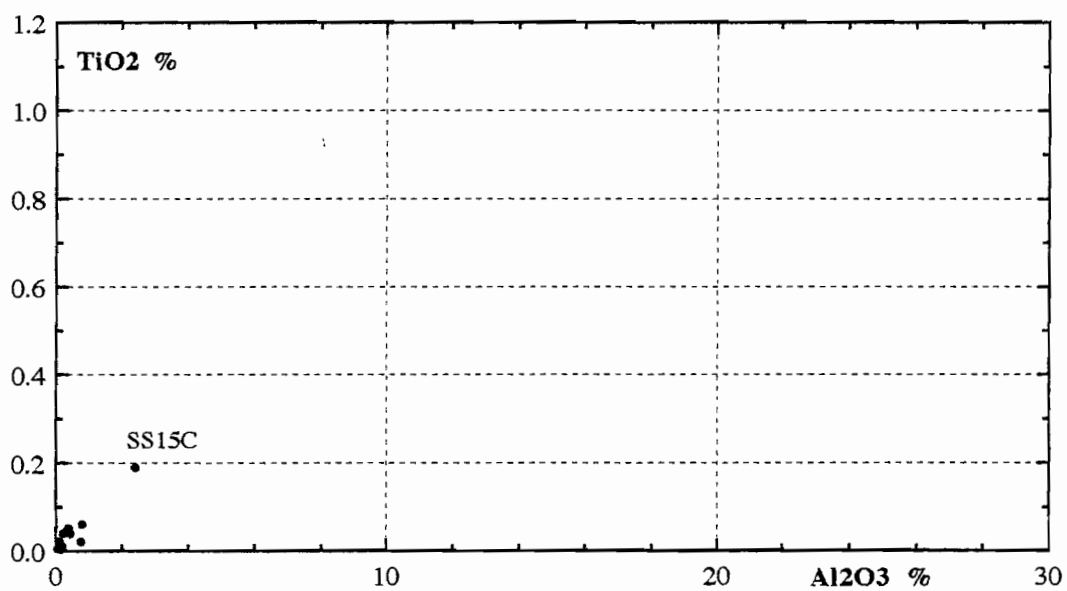
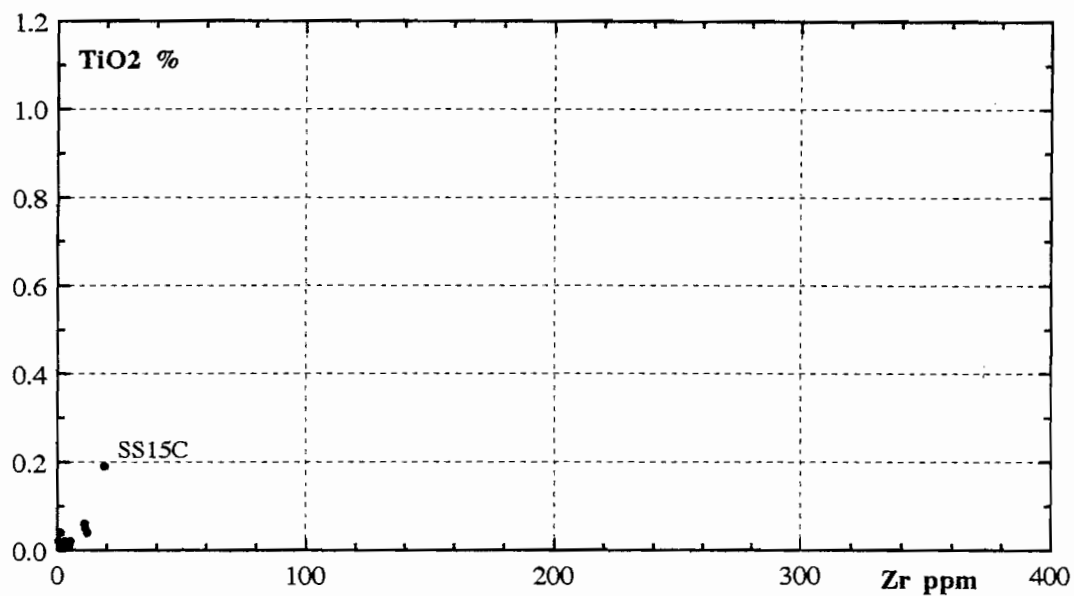


Figure 15. Zr-TiO₂ and Al₂O₃-TiO₂ plots of 13 quartz-hematite and quartz-magnetite exhalites analysed by Duhig et al., 1992. All except sample SS15C, have very low concentrations of the immobile elements. SS15C probably contains minor detrital volcanoclastic materials.

on relict textural grounds to be true exhalites, shows that this is the case. Most of their data points plot close to the origins of the immobile element graphs with $\leq 0.06\%$ TiO_2 , $\leq 0.8\%$ Al_2O_3 and ≤ 1 ppm Zr. The only exception is sample SS15C which, it may be supposed, contained some clastic material; probably from a mafic source judging by the anomalous TiO_2 .

Similar graphical treatment of immobile component data from the chlorite-tremolite-carbonate rocks and other so called exhalites and sulphide assemblages in Groups 21 to 45 (Figures 16 a & b) shows that only two samples fall within this low Ti-Zr-Al field. Both are magnetite quartzites (Group 21) which Duhig et al. (1992) recognised as metamorphically recrystallised equivalents of the silica-iron exhalites.

Most of the remaining data points form crude linear arrays which approximate to the rhyolite "alteration lines" discussed in the preceding sections. Furthermore, the data are systematically arranged with the most chloritic types (Groups 31 & 32) plotting furthest away from the origin and samples with greater tremolite and carbonate (Groups 33 to 35) plotting progressively nearer to the origin. This pattern imitates the mass losses and gains associated with alteration in the footwall rhyolite. In terms of immobile element geochemistry, these rocks are interpretable as altered rhyolites.

There are, however, a number of outliers and litho-geochemical groups which plot away from the "rhyolite alteration line" and there are plausible reasons, outlined below, for these deviations.

- * The base metal sulphide rich samples of Group 43 have surprisingly high Zr values and form a linear array which intersects the "rhyolite line" at about 80ppm Zr. On the other hand they have low TiO_2 and Al_2O_3 values, which would be expected in mainly exhalative sulphides, indicating a unique (for Thalanga) disassociation of Al and Zr. There is an imperfect but distinct correlation between high Pb and Zr values: sample 71068 contains 1.45% Pb and 67ppm Zr whilst at the other end of the spectrum sample 61473 contains 17.6% Pb and 477ppm Zr. It is notable that the massive pyrite samples of Group 45, which have even greater sulphur levels (up to 34%) but low lead, lie on the TiO_2 -Zr plot on a linear array which is very close to the "rhyolite line" and has an $r = 0.92$ correlation factor. There is a strong suspicion that the Zr values for Group 43 are spuriously high, caused by XRF "line overlap" of the Pb and Zr spectra as noted by Dunn (1994) and in Appendix Ic.
- * Some of the barium rich samples of Groups 23 and 41 have moderately high TiO_2 (to 0.11%) coupled with low Zr and Al_2O_3 values and may similarly be affected by Ba and Ti XRF "line overlap".
The origin of massive sulphides is not a major focus of this study and the problem has not been further pursued. However, it is clearly a caution that the use of standard XRF immobile element analyses may lead to misinterpretation of volcanic affinity in mineralised samples containing high levels of lead and barium.

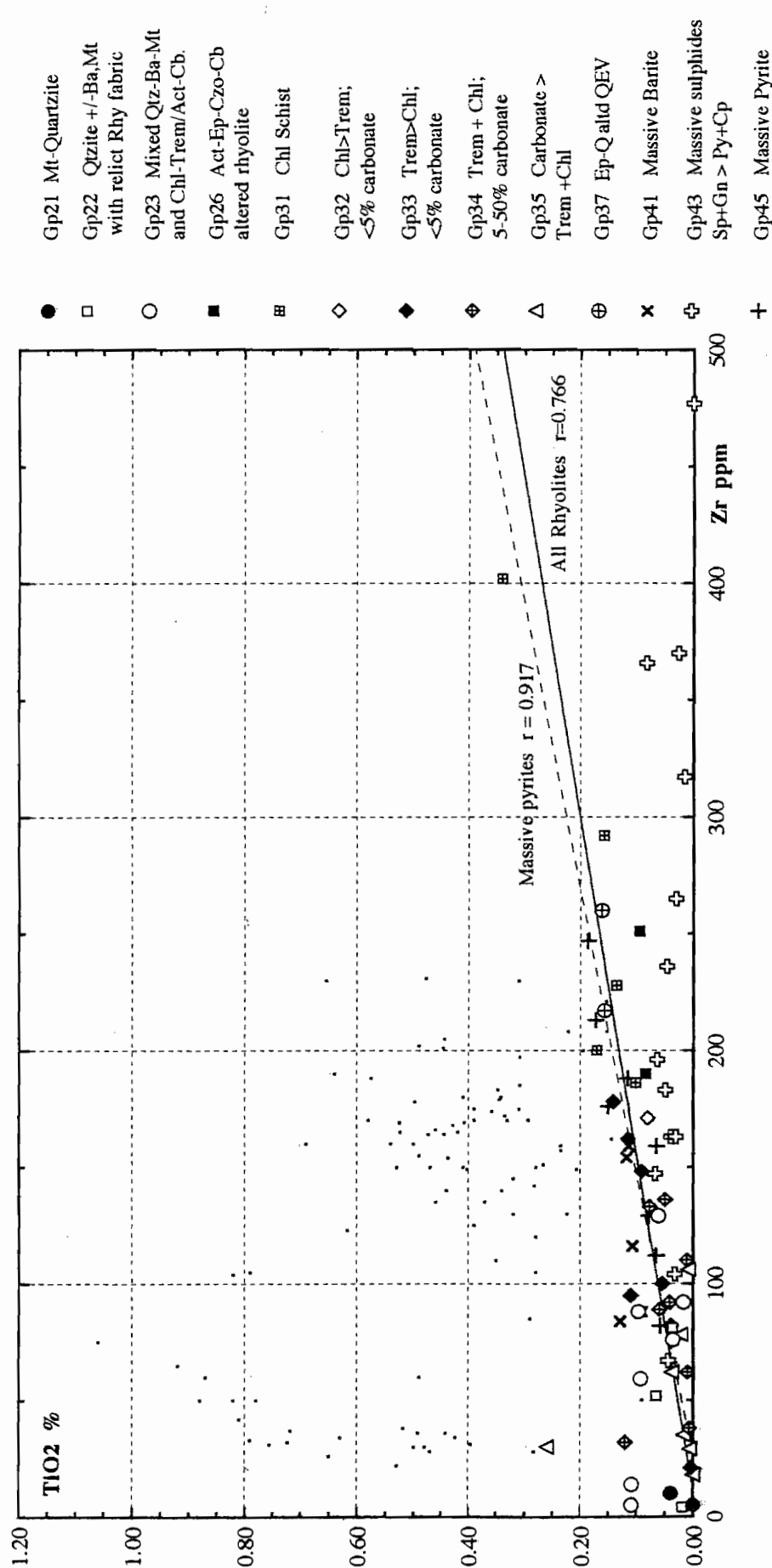
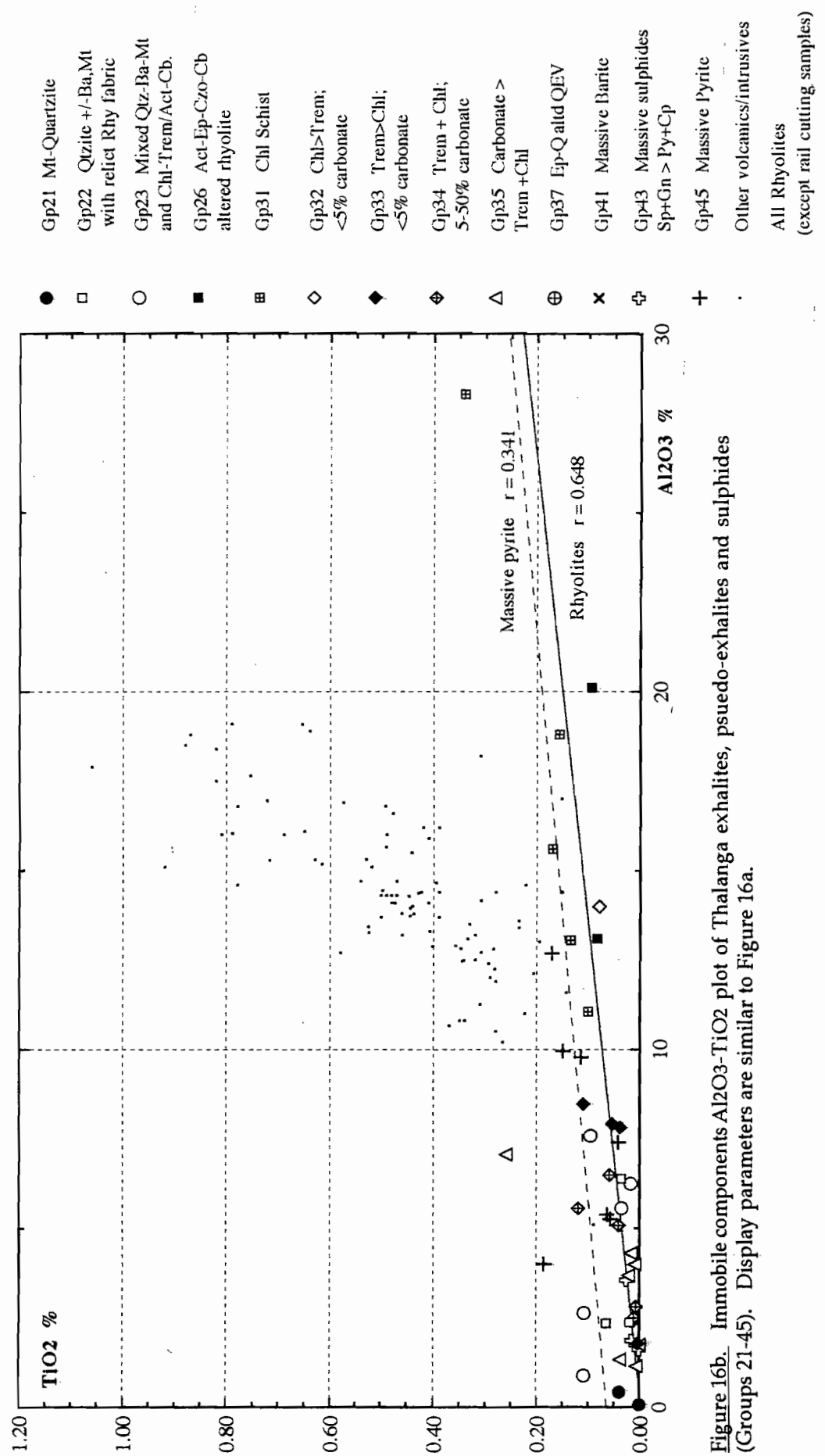


Figure 16a. Immobile component Zr-TiO₂ plot of Thalanga exhalites, psuedo-exhalites and sulphides (Groups 21-45). The rhyolite linear regression (as in Fig. 9a) is shown for comparison; all other Thalanga volcanics are shown as small dots, rhyolite dots are removed for clarity. The Gp 21 magnetite-quartzites have very low Zr-Ti concentrations; most other groups follow the rhyolite alteration trend. Note the linear regression for massive pyrites.



- * Wills' (1985) sample of "carbonate exhalite" from TH40, 260.8m; contains 0.26% TiO_2 and plots well away from the "rhyolite line". This is not surprising given its location amongst feldspar phyric dacite well up in the hanging wall stratigraphy at West Thalanga Extended; there are clear gradational alteration boundaries up and down core into dacite and sheared dacite and there are relict feldspar phenocrysts even in the relatively massive carbonate-epidote assemblage. The setting, relict texture and immobile element geochemistry support the interpretation that this is an altered volcanic rock - probably a dacite or andesitic dyke.
- * Another of Wills' (1985) samples which plots significantly off the "rhyolite line" is TH43A, 405.8m. It is an assemblage of chlorite-tremolite-carbonate (CTC) from the favourable horizon immediately below 2m of baritic massive sulphide and it contains some relict qtz crystals. Patchy to spotty chlorite-carbonate alteration occurs in the quartz-eye volcanoclastic unit immediately overlying the sulphide and it is interpreted that the analysed CTC from below the sulphide represents a more pervasively altered equivalent of the QEV above.

Apart from these significant outliers the remaining immobile element data points lie within the range of scatter of altered footwall rhyolites despite radically different modal and major element composition in most groups.

The samples from Group 26, and some from Group 23, retain modal quartz and relict rhyolitic or volcanoclastic fabrics and can be interpreted as examples of partial alteration, transitional to more complete chlorite-tremolite-carbonate assemblages of Groups 32, 33, 34 & 35 which generally do not contain quartz and relict volcanic fabrics.

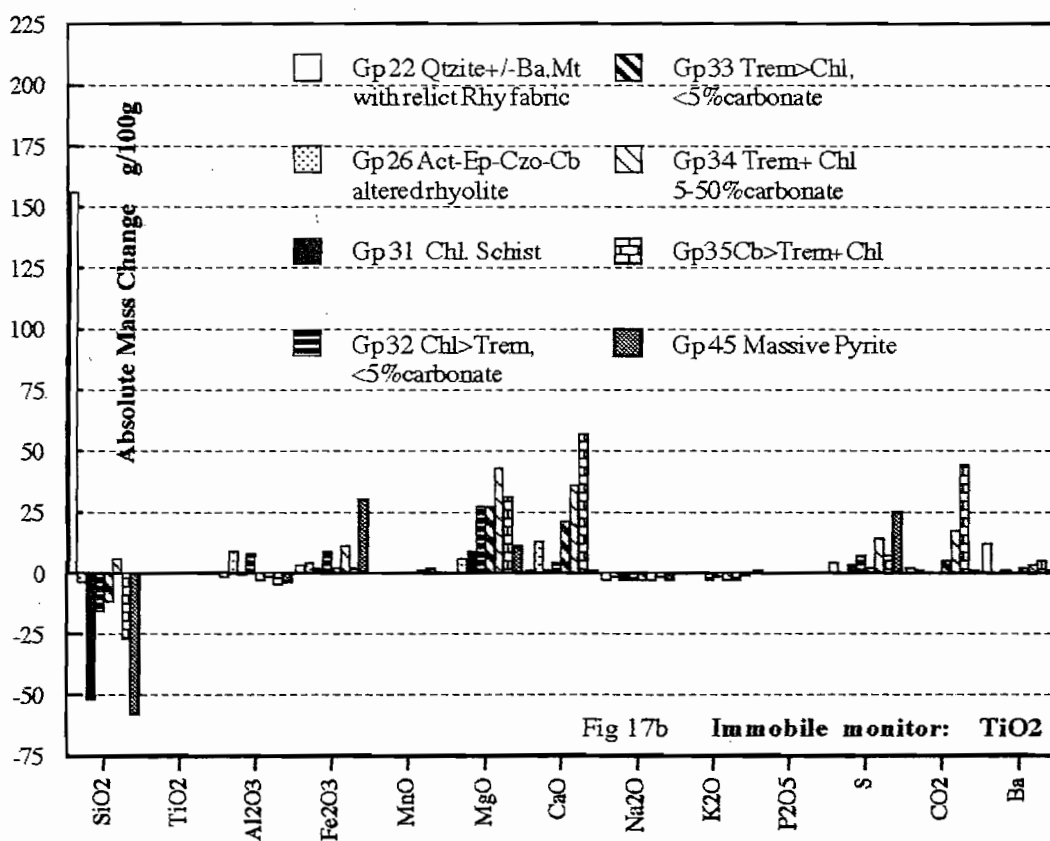
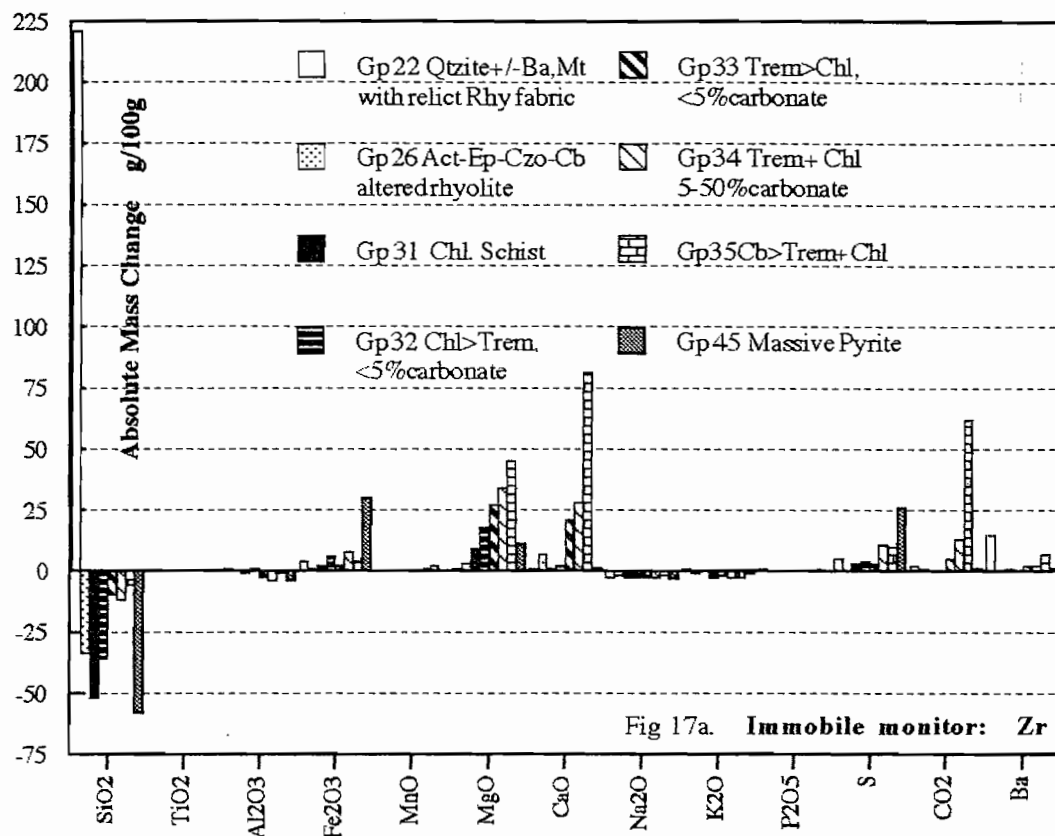
6.2 Mass Changes relative to a rhyolite precursor

In view of the immobile element trends, it is interesting to treat the so-called "exhalites" as altered rhyolites and estimate the major component mass changes using the procedure of MacLean and Barrett (1993) as has been done for the variously altered footwall rhyolites (ref: Section 5.2)

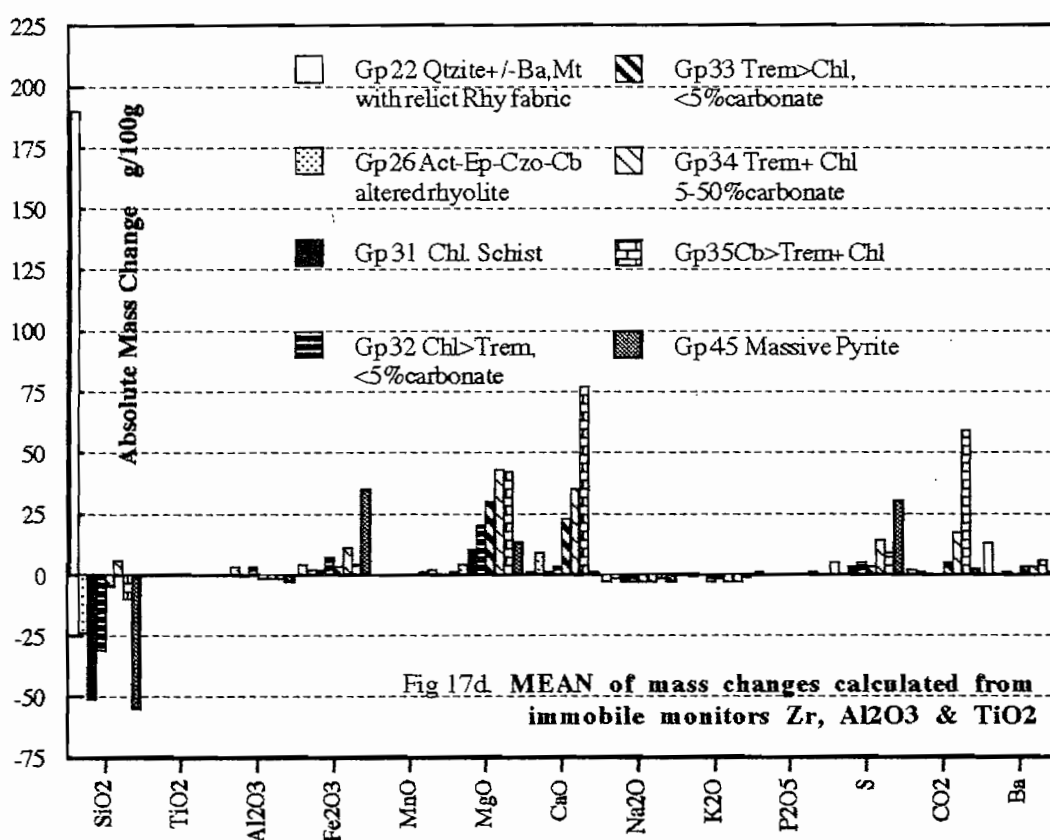
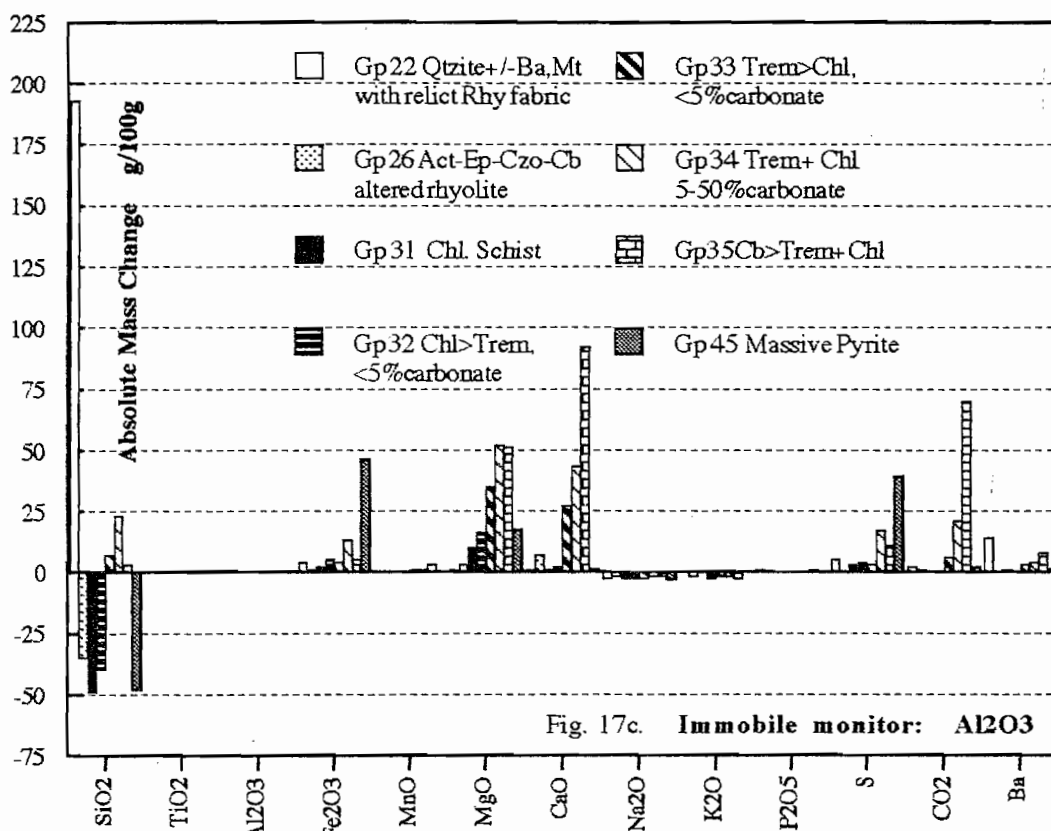
In calculating mass changes for rhyolites, Zr was used with confidence as the immobile monitor. The "exhalite" assemblages, however, sometimes carry anomalous Pb and Ba which, as noted above, are suspected of causing analytical errors in Zr and Ti respectively. To insure against this potential problem, mass changes have been separately calculated for three immobile monitors: Al_2O_3 , TiO_2 and Zr, as a check for consistency and these values then averaged to arrive at mean mass changes.

"Precursor 1" (fabricated from the least altered of footwall rhyolites) has been used as the precursor composition, as before.

The results of this approach are presented graphically in Figure 17a-d as absolute mass changes expressed in g/100g units.



Figures 17 a & b. Graphic representation of absolute mass changes of Thalanga psuedo-exhalites and massive pyrite relative to rhyolite composition "Precursor 1", calculated with Zr (a) and TiO2 (b) as immobile monitors.



Figures 17 c & d. Graphic representation of absolute mass changes of Thalanga psuedo-exhalites and massive pyrite relative to rhyolite composition "Precursor 1; calculated with (c) Al₂O₃ as immobile monitor and (d) Means of mass changes calculated with Zr, TiO₂ and Al₂O₃ immobile monitors.

It is apparent that although there are slight to significant differences in the quantities calculated with respect to the three different immobile monitors, the mass change patterns are similar for most litho-geochemical groups and major components. In general, the Al_2O_3 monitor tends to exaggerate the mass changes relative to those calculated by TiO_2 and Zr.

There is an anomaly in Groups 33, 34 & 35 for SiO_2 which is calculated as a mass gain according to Al_2O_3 , as a mass loss according to Zr and some each way according to TiO_2 .

However, the means of the three sets of calculated mass changes provide acceptable average values for discussion, and reduce the SiO_2 anomaly to insignificance. In the following paragraphs the calculated mass changes are simply referred to, for brevity, as "mass changes" but it must be kept in mind that these are hypothetical mass changes, based on an artificial precursor composition and, in some cases, with no evidence other than the linear immobile element trends to suggest that they were derived by alteration of rhyolite. The approach is partly experimental leading to a test of whether these assemblages could have been derived from alteration of rhyolite.

Group 22 Siliceous "exhalites"

The mass change for this group is dominated by a vast gain of almost 200g/100g SiO_2 overshadowing small gains of Fe, S and Ba and depletion of Na with other components essentially stable. This pattern is like a more extreme, silica dominated, form of strong footwall rhyolite alteration as represented by Groups 4 and 5 from pyritic stringer zones and the "white" rhyolites (which these rocks most resemble). Rocks of this class in TH5 were interpreted by Wills (1985) and Stolz (1991) as siliceous exhalites on the basis of the silica, barite and magnetite content. Close examination during this study has shown, however, that the barite and magnetite occurs largely in veins and there are sparse but distinct relict quartz phenocrysts which support the immobile element and mass change data in suggesting an origin by silicification of a rhyolitic precursor. An alternative which cannot be ruled out, is that these rocks formed by limited rhyolitic volcanoclastic input into siliceous exhalative sediment.

Group 26 The two samples in this group both have relict rhyolite fabrics and occur intra-footwall. The main chemical changes (relative to "Precursor 1") are moderate depletion of SiO_2 and slight gains in CaO and MgO to produce a net loss of about 8g/100g.

Groups 31 & 32 These are chlorite dominated assemblages with moderate to strong depletion of SiO_2 offset by moderate gains of MgO to produce a net mass loss of ~36g/100g in Group 31 and near parity in Group 32. CO_2 is insignificant and reflected in low carbonate contents. Wills, (1985) referred to rocks of this type as "shaley exhalite" and, as noted in Appendix I-a, some of his samples of that description have been recognised as altered dacite and placed with Group 12.

Groups 33, 34 and 35 These are chlorite-tremolite-carbonate (CTC) assemblages with low, moderate and high carbonate contents respectively. They are characterised by relatively minor mass changes in SiO₂ but strong enrichment in MgO, CaO and progressively increasing CO₂. They have net mass gains of around 60, 140 and 190g/100g respectively with a contribution from CO₂ of about 60g/100g in the carbonate rich Group 35.

Group 45 Massive Pyrite

These are not directly relevant to the hypothesis that CTCs are formed from altered rhyolite but are shown in Figures 17a-d to emphasise the difference in the pattern of mass changes. Massive pyrite has strong depletion in SiO₂ and strong enrichment in Fe₂O₃, MgO and S, relative to rhyolite, but no significant changes in CaO and CO₂. This suite of major mobile components shows that the massive pyrite lenses have a chemical affinity with the footwall style of alteration.

It is noteworthy that Na₂O is significantly depleted in all of the groups charted, with most groups reporting a loss of ~3g/100g Na₂O. In relative terms this represents virtually all of that component originally present in the parent rhyolite, ("Precursor 1" contains 3.17% Na₂O). Sodium depletion by feldspar destruction is the unifying characteristic of the footwall hydrothermal alteration system. The group with the least amount of sodium loss here is Group 26 which agrees with the interpretation that this style of intra rhyolite actinolite-clinzoisite alteration may be an incipient stage transitional to more pervasive and complete chlorite-tremolite-carbonate assemblages.

7 DISCUSSION and GENETIC INTERPRETATION

7.1 Magnetite quartzites (Group 21)

The data introduced above shows that magnetite quartzite samples, from the dacite and mixed volcanoclastic dominated hanging wall sequence at West Thalanga, have distinctive silica-iron rich compositions and low immobile element contents. Their composition is similar to siliceous ironstones from elsewhere in the Mt Windsor Subprovince which are less metamorphosed and have textures which Duhig et al. (1992) have convincingly shown to be of exhalative origin. The Thalanga magnetite quartzites are entirely recrystallised to a fine granuloblastic texture but the chemical similarity and absence of relict volcanic phenocrysts leaves little doubt that they also originated as exhalites.

Although the only two analyses available are from a single unit in TH40 there are other occurrences of mineralogically and texturally similar rocks within the favourable horizon at West Thalanga, Vomacka and, rarely, East Thalanga. They occur as thin bands, lenses and medium sized clasts within volcanoclastic sediments and breccias in the stratigraphically upper part of the favourable horizon, in apparently distal settings and often in association with barite. These observations are consistent with Duhig et al.'s (1992) interpretations of deposition from relatively cool fluids discharged by weak or waning hydrothermal systems, or from the cooled remnants of fluids which had already precipitated sulphides. The survival of clasts within volcanoclastic breccias suggests that the magnetite-quartzite protoliths were reasonably lithified soon after formation.

7.2 Siliceous psuedo-exhalites (Group 22)

Rocks in this category may be as siliceous as the magnetite quartzites and contain some magnetite and barite but they differ by containing higher levels of immobile elements including Al, Ti, Zr and Y, significant traces of Mg and K and relict quartz phenocrysts. These belie a purely exhalative origin and imply formation by gross silicification of a rhyolitic precursor or, at least, rhyolitic volcanoclastic input into otherwise nearly pure siliceous exhalite.

However, in the most sampled occurrence in TH5, the siliceous rock is quite massive, absolutely without relict stratification or compositional layering, the contacts tend to be gradational or sheared and the associated magnetite and barite is concentrated in brittle style veins rather than layers. The siliceous rock is not restricted to the favourable horizon but also occurs in patches for about 30m down the hole, in association with quartz-barite-minor sulphide veins and patchy actinolite-chlorite-carbonate alteration gradational into less altered quartz-feldspar phyric rhyolite. The overall impression is of domainal alteration with the relationships confused by structural complexity.

The structural set up is not well understood, but thought to be related to D3 brittle-ductile shearing, (Hill, 1991), where the favourable horizon is displaced 120m southwards, adjacent to the down dip termination of the Central Thalanga massive sulphide deposit.

The other analysed example, from hole E3184SD31, contains ~2% relict quartz phenocrysts in a fine matrix of granuloblastic quartz with subordinate flaky muscovite which has strong preferred orientation anastomosing around 0.2-0.5mm ovoid bodies in a texture which could be inherited from perlitic fractures, (England, 1994). It is, without doubt, a silicified and metamorphosed rhyolite. Magnetite at ~2vol% occurs as fine euhedra disseminated amongst the granuloblastic quartz matrix and in fine quartz veins with minor barite and galena. The veins are internally recrystallised, irregular, may be folded and boudinaged, and are certainly of an early, pre-metamorphic, generation.

It is conceded that the requirement for an SiO₂ mass gain by alteration in coherent rhyolites of the order of 100-200g/100g is a daunting one, but this is merely about twice the net mass gain confidently interpreted for the most intensely quartz-pyrite-(sericite) altered footwall rhyolite. The possible relicts of perlitic fracturing suggest a mechanism for allowing silicifying fluids to thoroughly pervade the rocks and considerable SiO₂ may have been added as open vein fillings. The large volume increases implied by such large SiO₂ gains may be possible if the alteration occurred at, or at shallow depths below, the sea floor, unconstrained by great lithostatic loads - a setting which is consistent with the location of the occurrences at, or not far below, the favourable horizon and the association with iron oxides and barite which infer relatively cool, oxidised fluids. It is inferred that shallow sub-seafloor alteration may have occurred by reaction with fluids similar to those which precipitated the silica-hematite precursors of magnetite-quartzites above the sea-floor.

7.3 Chlorite-tremolite-carbonate assemblages (Groups 26 & 31-35)

These groups are collectively considered here because they all contain Mg and/or Ca bearing phases such as chlorite, tremolite, actinolite, clinozoisite, dolomite and calcite. Some of the unifying factors and distinctions are:

Groups 31 to 35 occur in close association with each other in the favourable horizon and also intra-footwall rhyolite (e.g. Section 20110E, Figure 5) but apparently not more than about 40m stratigraphically below the favourable horizon. They appear to form a modal mineral continuum from chlorite dominant without carbonate, through chlorite-tremolite mixtures with low carbonate, to carbonate dominated assemblages with variable chlorite-tremolite. Some examples of the chloritic types in Groups 31 and 32 contain sparse relict quartz crystals resembling phenocrysts but the carbonate-tremolite rich types are dominated by metamorphic and veiny fabrics without relict volcanic features.

Group 26 includes incipiently altered rhyolites, with unambiguous relict volcanic textures, which occur quite widely in the footwall in lateral? zones which have not undergone strong quartz-sericite, Ca-Na depleting, alteration.

Section 6.2 presented hypothetical mass changes, relative to a rhyolitic precursor composition, which suggested that the Group 31 and 32 chloritic assemblages could be produced from a rhyolite by relatively modest chemical changes mainly involving loss of Si, Na and gain of Mg. This pattern of chemical change is similar to that in Group 26 (but lacks the slight Ca gain) and, most significantly, involves a net mass loss which produced enrichment of the immobile components.

Mass loss is significant because it eliminates Wills' (1985) "shaley exhalite" concept of sedimentary mixing of exhalative and volcanoclastic materials as a mode of formation. As postulated above, true exhalites should have very low immobile element concentrations; addition of volcanoclastic detritus could increase the concentrations up toward the level of the source magma - but not beyond. To achieve that would require an unlikely chemical or sedimentary "winnowing" process to enrich the immobile elements above magmatic concentrations and then add them - in exactly the same ratios as in the footwall rhyolites - to the immobile poor exhalite.

These chlorite dominated assemblages have immobile element ratios very close to those of rhyolites and could only have been formed from rhyolitic precursors by alteration which resulted in a net mass loss. This conclusion is consistent with their modes of occurrence.

For instance: in TH245 (Figure 5 and Figure 18) the zone of tremolite-carbonate in the interval 672.5-675.9m is flanked at both contacts by narrow zones of Group 31 type chlorite schist which grade up and down core into quartz-sericite-(chlorite) altered rhyolite containing patches of (perhaps incipient) actinolite-clinozoisite-carbonate alteration similar to that of Group 26.

Similar chlorite dominated rocks, with or without relict quartz phenocrysts and sometimes significant pyrite, commonly occur in narrow zones at the contact between quartz-sericite altered footwall rhyolite and massive pyrite or massive base metal sulphides as in drill holes W2011NED42 (Figure 5 and Figure 19) and TH390B (Figure 3). In short, they often mark the boundary between "normal" quartz-sericite altered footwall rhyolite and tremolite-carbonate or massive sulphide assemblages and are best interpreted as altered rhyolite.

The loss of SiO₂ implied for this alteration (ref: Section 6.2) could be of either hydrothermal or metamorphic origin. If, as discussed below, the tremolite-carbonate rocks were formed by metamorphic reaction of dolomite, quartz and water to produce tremolite, calcite and CO₂ then a local excess of dolomite may have caused scavenging of SiO₂ from surrounding rhyolite and formed narrow alteration fronts of silica depletion.

Figure 18.

**TH245
670-680m
Graphic Log**

DEPTH (m)

670

671

**SAMPLE
NUMBER**

672

54359

Rhyolitic volcaniclastic breccia/sst; moderate-strong qtz-ser alteration with ~5% Py.

54360

54361

Chlorite schist, minor Tremolite, sphalerite.

673

54362

Massive carbonate with marbly bands and patches of Tremolite. Minor Ba, dissem Sp, Py, Gn.

674

54363

Massive Trem>Chl with ~30% carbonate. Sulphides <1%.

675

54364

54365

Massive Tremolite, minor chlorite, <10% Cb; local minor barite, diopside. Sulphides 1-3%.

676

54366

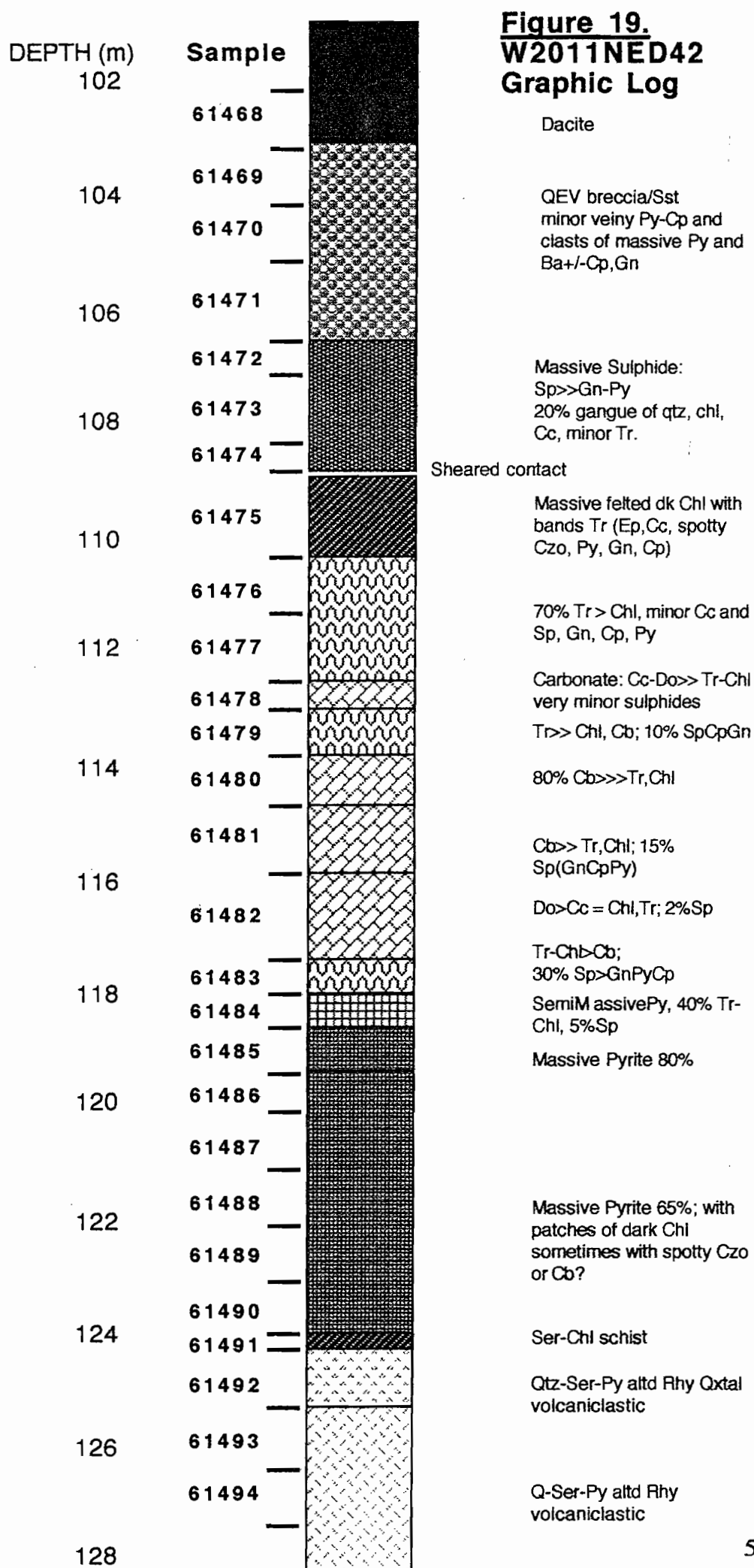
54367

Fine grained felted massive chlorite with subordinate Trem-Czo; minor barite, sphalerite.

677

678

Siliceous quartz phyric Rhyolite; scattered "cloudy" patches of incipient Act-Qtz-Czo-Cb alteration with traces of Ba, Gn, Py.

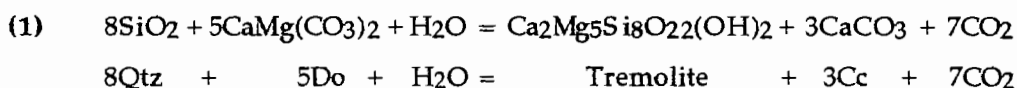


The origin of tremolite-carbonate rich assemblages is not so neatly constrained. These have immobile element ratios suggesting rhyolitic parentage but in view of the significant net mass gains due to addition of Mg, Ca and CO₂, it is not clear whether the relationship was by alteration of a rhyolitic precursor or by volcanoclastic input into carbonate exhalite. Certainly, there are near monomineralic end members of carbonate and tremolite with minor chlorite, and all gradations between, which could indicate fluctuations in exhalative vs. volcanoclastic deposition.

There is no convincing small scale compositional banding to suggest bedding but then, such features are not likely to be well preserved in these extensively recrystallised rocks where the grain size of tremolite often exceeds 20mm. As noted in Appendix II carbonate, dominantly calcite, appears to stand late in the (metamorphic) paragenetic sequence. It occurs as veins and ragged sparry patches which clearly cut across, replace and corrode other phases including tremolite, chlorite and sulphides. This form might suggest a late stage, post metamorphic introduction of calcite - it is, co-incidentally, the dominant phase in tensional veins within dolerite dykes and in association with brittle faults which are younger than deformation and metamorphism.

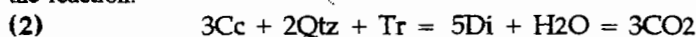
Chlorite and tremolite, on the other hand, are probably metamorphic phases; the typically random orientation of tremolite suggests that it crystallised after the peak of deformational strain. Wills (1985) and Gregory et al. (1990) appear to have regarded tremolite/actinolite in these rocks as "primary" exhalative phases but this would have required temperatures in excess of ~300°C which are unlikely in the hydrothermal fluid - sea water mixing model they envisaged.

An alternative origin, postulated by Rivers (1985) and Stolz (1991), involves metamorphic reaction of quartz and dolomite to produce tremolite and calcite as in the simple reaction:



According to the xCO₂ vs. Temperature phase diagrams presented by Rivers (1985) and kindly supplied by Berry (pers. comm.) this reaction would proceed at about 350-450°C at 2kb pressure and low to moderate activities of CO₂. These physical conditions are consistent with the grade of regional metamorphism estimated by Wills (1985) and Berry (1991).

Footnote: It is noteworthy that modal quartz is generally not present in the chlorite-tremolite-carbonate assemblages which implies that dolomite was in excess or neatly balanced to consume all quartz in the reaction stated. The only known exception to this observation is in Sample No. 54365 which contains a patch of coarse skarn-like diopside-quartz-barite. The diopside implies a higher temperature, some 50-70°C higher than the formation of tremolite at moderate xCO₂, and the local availability of excess SiO₂ to allow the reaction:



to proceed. Elsewhere the shortage of SiO₂ may have maintained the stability of tremolite even at the higher temperature range.

The question then arises: would quartz-dolomite-(chlorite) precursor assemblages have the appropriate balance of components to produce the assemblages now observed?

The chemical feasibility of this process has been investigated by devising a simple normative calculation after the style of the well known CIPW Norm (explained by Cox et al., 1979) using the minimal normative components of quartz, chlorite, dolomite for the precursor and chlorite, tremolite, dolomite, calcite for the metamorphic product. This normative system has been informally called the "QCT Norm" - (an acronym for quartz-carbonate-tremolite).

Some fundamental assumptions of the QCT Norm calculations are:

- * That Al_2O_3 , which has been shown to be immobile in this system, resides in chlorite before and after metamorphism and that the main changes involve quartz+dolomite transforming to tremolite+calcite+ CO_2 ; any excess Mg would be expressed as dolomite in the metamorphic assemblage.
- * The chlorite is an Mg rich clinocllore with an assumed composition of $(\text{Mg}_8\text{Fe}_2\text{Al}_2)(\text{Si}_6\text{Al}_2)\text{O}_{20}(\text{OH})_{16}$. This is not entirely arbitrary, the composition is a rounded average composition of seven micro-analyses of Mg rich chlorites from the footwall, presented by Rivers (1985).
- * Other phases used in the normative calculation have simple end member compositions.

Dolomite	$(\text{CaMg})(\text{CO}_3)_2$
Calcite	CaCO_3
Tremolite	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
Quartz	SiO_2
- * The molecular weight of water in the hydrous phases is ignored, it being assumed that the metamorphic system was not dry.

The procedure followed and the results of the QCT Norm calculations for mean compositions of the various litho-geochemical groups are presented in Appendix III. The concept being tested is that if the metamorphic system was isochemical, or closed, (except for volatile components H_2O and CO_2) the present bulk compositions of chlorite-tremolite-carbonate assemblages ought to be re-calculable into pre-metamorphic normative quartz-dolomite-chlorite assemblages and the major components ought to balance out. If they do not balance, then the postulated precursor assemblage is inappropriate or there have been significant mass changes during metamorphism; (i.e. the metamorphic system was not closed). It is a way of testing if quartz-dolomite-chlorite (altered rhyolite) assemblages could be direct pre-metamorphic precursors of the assemblages now observed.

The Groups 33, 34 & 35, rather surprisingly, pass the test with only minor imbalances in chemical components.

The average of Group 34 compositions ($n=5$), for instance, has near perfect component balances for SiO_2 , $\text{FeO}+\text{MnO}$, MgO and CaO and a deficit of CO_2

equivalent to ~18wt%. The CO₂ deficit, in molecular proportions, is almost exactly in the ratio 7:8 (CO₂:Qtz) as predicted by reaction (1), and is geologically sensible in that CO₂, being volatile, would be lost from the system during metamorphism.

Similarly, the average composition of Group 35 carbonate rich assemblages balances well in the QCT Norms, shows original calcite with dolomite in the precursor assemblage, residual dolomite in the metamorphic assemblage and a CO₂ deficit of ~10wt%. This also is geologically interpretable as indicating an excess of dolomite (i.e. insufficient quartz in the system to consume all precursor dolomite) and a lesser loss of volatile CO₂ reflecting the lesser production of metamorphic calcite.

Group 33, representing tremolite rich - carbonate poor assemblages, behaves slightly differently in the QCT Norm. It shows a slight deficiency in MgO equivalent to ~3wt%, (i.e. there is not quite enough MgO to balance the SiO₂ remaining, after an allocation to chlorite, to make pure tremolite) which suggests that the Al-Si proportion in the chosen chlorite composition may be inappropriate for this assemblage or that other silicate phases are present.

The MgO imbalances are even more pronounced in Groups 31 & 32 chlorite rich assemblages, which have very little or no carbonate, and support the implication that the assumed chlorite composition may be inappropriate. A more aluminous chlorite, say: $\sim(\text{Mg}_4\text{Fe}_3\text{Al}_5)\text{Si}_6\text{Al}_2\text{O}_{20}(\text{OH})_{16}$ may be nearer the mark. The problem does not arise in the carbonate rich Groups 34 & 35 probably because of the relative unimportance of chlorite in those assemblages.

Nevertheless, the QCT Normative relationships suggest that quartz-chlorite-dolomite-(calcite) in various proportions does constitute a chemically and geologically reasonable pre-metamorphic assemblage for the existing chlorite-tremolite-carbonate rocks. Furthermore, the QCT Norms of the weighted average of all Group 32, 33, 34 & 35 compositions, are nearly balanced. It suggests that, although there may have been internal small scale mass transfers, the overall metamorphic system was closed with respect to non-volatile components and the present assemblages could have been derived from metamorphism of a quartz-chlorite-dolomite-(calcite) precursor. There is no requirement for invoking significant syn or post metamorphic calcite input, despite what might be inferred from the replacive textural relationships of calcite and other phases.

7.4 Chlorite-carbonate alteration in other deposits and comparisons with Thalanga

Chlorite-carbonate alteration assemblages are known in association with several western Tasmanian VHMS deposits, including Hellyer (Gemmell and Large, 1992), Que River (Offler and Whitford, 1992), Rosebery (Lees et al., 1990) and South Hercules, (Khin Zaw and Large, 1992). Other mainland deposits with documented carbonate alteration include Mt Chalmers in central Queensland (Hunns et al., 1994) and the Mons Cupri, Teutonic Bore, Gossan Hill and Scuddles deposits in Western Australia, (Barley, 1992).

In the Western Australian examples the chlorite and carbonate are iron rich types occurring in the footwall zones proximal to massive sulphides, sometimes associated with stockwork mineralisation "in poorly developed, or laterally extensive, feeder zones", (Barley, 1992). These seem unlike the Thalanga style where chlorite-tremolite-carbonate rocks are mainly stratiform in the favourable horizon and the footwall feeder systems are distinctly siliceous.

A geological cross section of Mt Chalmers presented by Hunns et al. (1994, Figure 3) shows a stratiform zone of "massive dolomite alteration" underlying and laterally equivalent to a massive sulphide lens and immediately overlying a zone of footwall stringer pyrite-chalcopyrite mineralisation.

At Hellyer, chlorite-carbonate alteration appears to be restricted to small zones immediately below massive sulphides at the margin of a siliceous alteration pipe under the deposit; (Figure 6 of Gemmell and Large, 1992). The carbonate is reportedly mostly dolomite occurring as small crystals and rounded nodular forms in massive chlorite. Analyses given by Gemmell and Large, (1992, Table 1) show that the chlorite-carbonate zone contains the immobile components Ti, Al and Zr in concentrations very close to those of the adjacent unaltered footwall andesite. This supports the interpretation that the assemblage is an alteration product of andesite involving a loss of Si and Na balanced by gains of Fe, Mg, Ca and CO₂ with minimal net mass change.

Chlorite and carbonate of varying compositions are sporadically distributed in the Que River alteration system. Offler and Whitford, (1992) attributed this heterogeneity to successive influxes of variable hydrothermal fluids and mixing with seawater with the latter as the main source of magnesium. They identified both hydrothermal and metamorphic chlorites.

Lees et al. (1990) referred to carbonate alteration at the Rosebery deposit in a "loosely defined halo of variously textured carbonate rocks" surrounding the orebodies and confined to the host rock unit. They suggested that the spatial association indicated a relationship to ore formation and postulated several modes of carbonate origin

including feldspar alteration and sub-sea floor precipitation from depleted hydrothermal fluids. Recent studies by Orth and Hill, (1994) have recognised relict volcanic textures indicating that carbonate alteration nucleated on pumice clasts and feldspar crystals and that it formed by replacement in the uncompacted shallow substrate of the sea floor - not by exhalative deposition.

Khin Zaw and Large (1992) described carbonate alteration at South Hercules overlying and laterally interfingering with a stratabound, zoned sulphide deposit. The sulphide facies is dominated by disseminated and veiny, low grade, Pb-Zn mineralisation in a silica-sericite altered volcanoclastic sediment package about 20m thick which is underlain by felsic pumiceous volcanics and overlain by a shale-siltstone-quartz phytic volcanoclastic sequence. Thin stratiform lenses of semi-massive sphalerite-galena-pyrite occur toward the base of the sulphide facies and lenses of massive pyrite-barite-quartz occur at the top. Massive carbonate and cherty carbonate alteration zones occur around, laterally interfingering with, and overlying the upper part of the sulphide facies, (Figure 32). The cherty carbonates are fine grained, intergrown with cryptocrystalline silica, and appear to be spatially related to, perhaps lateral equivalents of, the massive pyrite-barite lenses. Carbonate-chlorite lenses with a distinctive blebby texture occur near the top of the carbonate facies and within the overlying hanging wall siltstones. No whole-rock chemical data is available but the carbonates are reported to be consistently Mn rich (kutnahorite and rhodochrosite) with minor Fe and Mg.

The deposit and alteration zones were interpreted to have formed by sub-seafloor replacement from relatively low temperature, moderately acidic hydrothermal fluids which cooled and increased to near neutral pH by mixing with sea water in the permeable volcanoclastic substrate. Khin Zaw and Large (1992) considered that local "variations in permeability controlled the shape and outline of the mineralised zone with the ore fluids mixing both vertically and laterally along the permeable horizon. Sulphide facies mineralisation was formed in the central (high temperature) zone of mixing followed by the carbonate facies in the cooler, lateral and stratigraphically higher zones." The genetic model is illustrated in Figure 33. Khin Zaw and Large (1992) were unable to define the depth at which mineralisation and alteration occurred below the sea floor but noted that the presence of carbonate-chlorite alteration lenses in the hanging wall sediments could indicate a sediment cover of at least 10-20m at the time of mineralisation.

A detailed study of the "Area of Active Venting" (AAV) in the Middle Valley of the northern Juan de Fuca Ridge, by Goodfellow et al. (1993), has revealed a vertically and laterally zoned alteration system in Holocene, hemipelagic and turbiditic sea floor sediments. It consists of an upwardly convex inner zone, about 200x400m in area, of Mg smectite-chlorite-silica-barite-pyrite-gypsum alteration enriched in Mg, S, Ba and depleted in Ca and CO₂ relative to unaltered sediments. An outer zone, up to 200m wide, consists of Mg smectite-carbonate-barite-minor pyrite which is enriched in Ca,

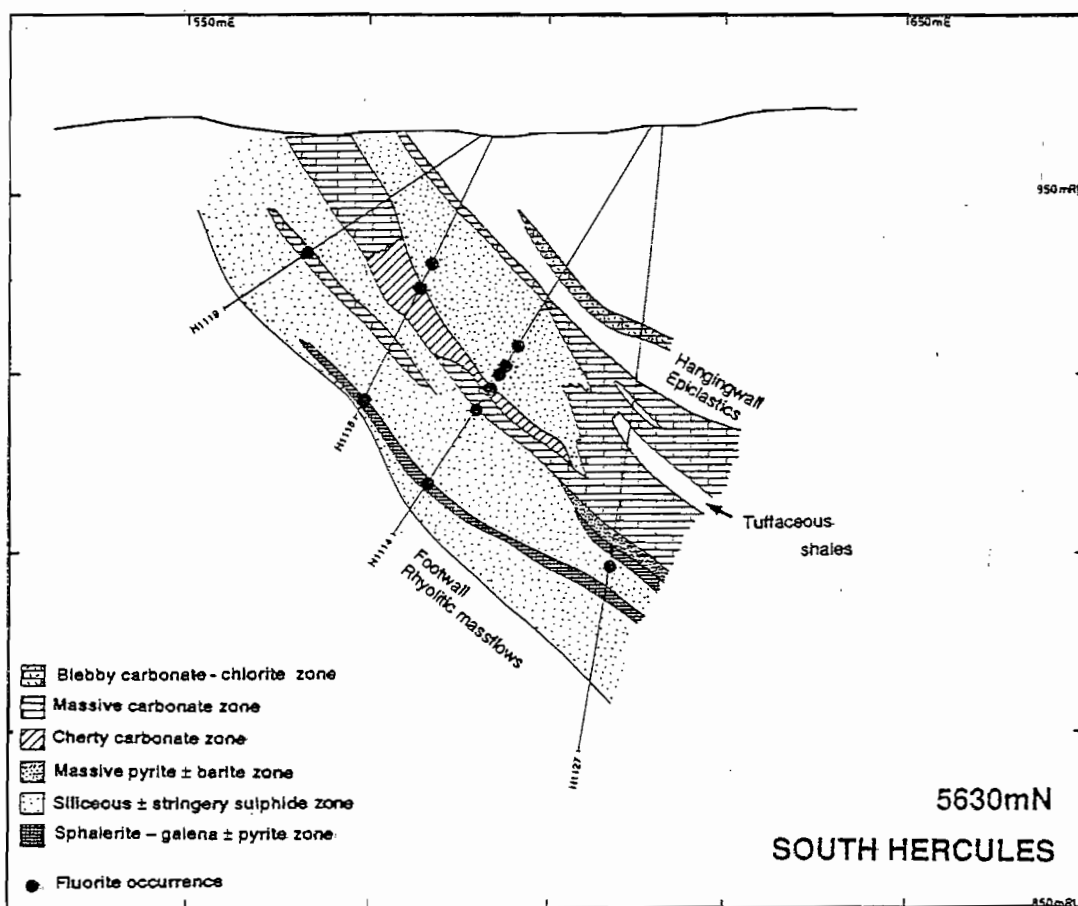


Figure 32. Geological cross section of South Hercules deposit showing distribution of sulphide and carbonate alteration zones, (from Khin Zaw and Large, 1992)

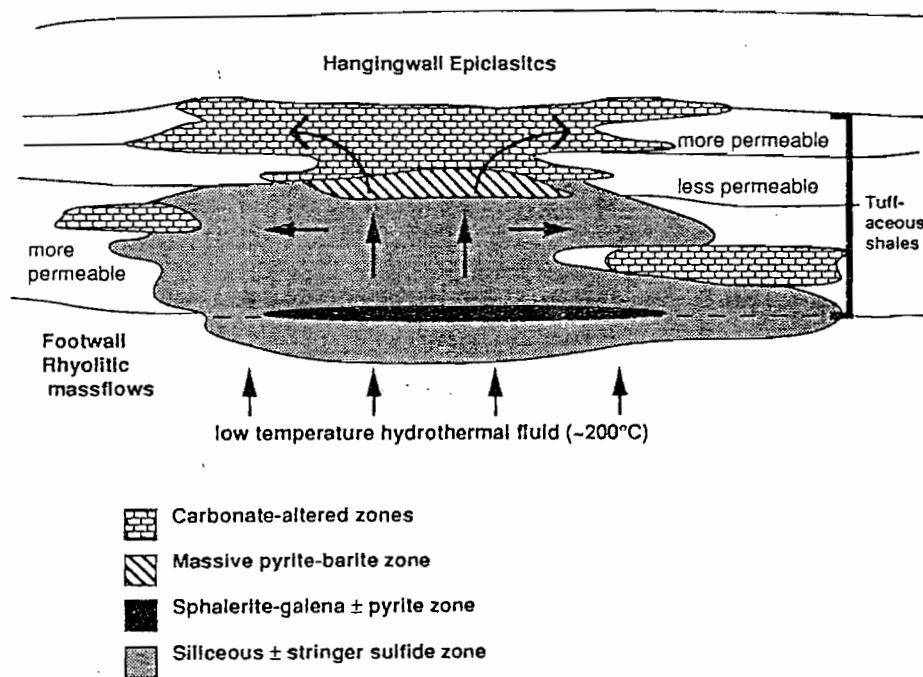


Figure 33. Schematic section illustrating a model for formation of the South Hercules deposit, (from Khin Zaw and Large, 1992). Carbonate alteration occurred in permeable volcanoclastic units by mixing and cooling reactions of hydrothermal fluids and sea water in the upper and outer parts of the system.

CO₂ and Ba. Elevated levels of most chalcophile elements occur in both zones, probably as sulphides.

It is interpreted that the alteration minerals are forming in the near sea floor substrate (<10m depth) from an evolving hydrothermal fluid as it moves upward and outward from a central conduit. In the inner zone, biogenic carbonates are dissolved by high temperature hydrothermal fluids (120-270°C) and Mg smectites deposited due to combination of hydrothermal silica with Mg from the down welling sea water. Carbonate concretions are deposited at the transition between the zones, and in the outer zone, at temperatures below ~100°C by laterally migrating evolved fluids. Isotopic evidence indicates that a major part of the carbon in the carbonate is derived by bacterial oxidation of hydrothermal methane. Goodfellow et al. (1993) interpret that lateral flow of the evolving hydrothermal fluids along sandy layers is promoted by poor cross-stratal permeability, in the outer zone, during episodic "throttling" of fracture permeability in the upflow zone by mineral precipitation.

Turner et al. (1993) suggest that areas of diffuse venting of hydrothermal fluids in the AAV may "eventually create impermeable crusts, restrict discharge, and pond hydrothermal fluids below an impermeable cap. Rupture of these caps may result in discharge at discrete centres, prerequisite for the initiation of chimney growth and mound development."

Similarly, a recent interpretation of present day sea floor hydrothermal activity at the Valu Fa Ridge in the Lau Basin, by Fouquet et al. (1994), proposed that formation of an impermeable crust (of Fe-Mn oxides in that case) occurs at an early stage by diffuse low temperature venting in highly permeable volcanoclastics which permit mixing of hydrothermal fluids and sea water. Sea water mixing is reduced by progressive sealing of the sea floor surface and the resulting higher temperature subsurface fluid circulation causes intense alteration and Cu-Fe sulphide precipitation in horizontal layers beneath the crust (Figure 34). Continued tectonic activity may create fault controlled permeability leading to focussed discharge and formation of sulphide mounds on the sea floor.

This brief review of a number of ancient and modern deposits shows that carbonate and carbonate-chlorite (or Mg-smectite) assemblages are not unusual in VHMS alteration systems. Several of the occurrences have such assemblages restricted to thin stratiform zones and the authors cited invariably refer to them as hydrothermal alteration products. This supports the assertion, made in Section 7.3, that quartz-carbonate-chlorite (or Mg-smectite) assemblages, produced by hydrothermal alteration of rhyolitic rocks, are feasible precursors to the chlorite-tremolite-carbonate metamorphic assemblages associated with mineralisation at Thalanga. On the other hand, there is little evidence apart from their thin stratiform distribution, that they are exhalative sediments.

South Hercules and the AAV carbonate bearing alteration zones appear to be analogous to West Thalanga in terms of their broad lateral extent and thin stratabound

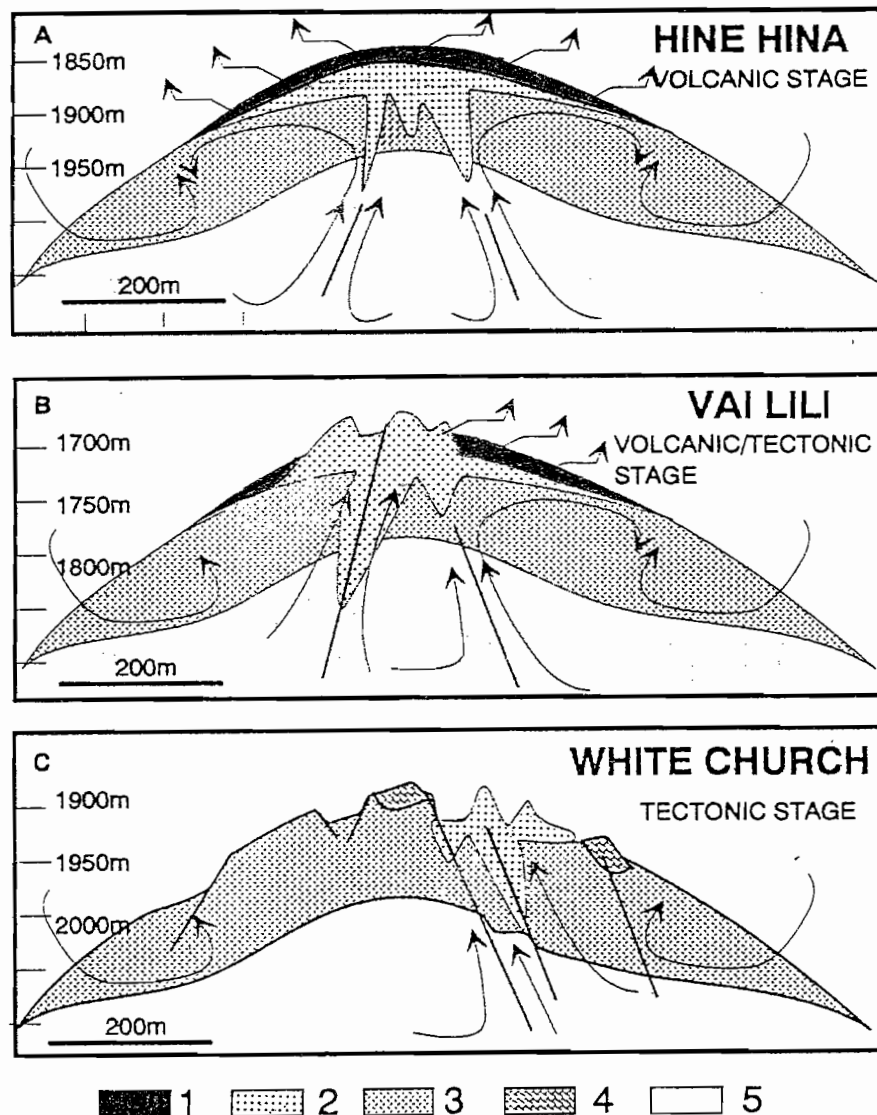


Figure 34. Schematic cross sections of the three hydrothermal deposits on Valu Fa Ridge, Lau Basin; (from Fouquet et al., 1993). Hine Hina (top) represents an early stage of activity in which diffuse discharge of low temperature hydrothermal fluids mixing with sea water in the upper zones of permeable volcaniclastics causes precipitation of an Fe-Mn crust. Sea water mixing is reduced as the crust develops and seals the sea floor; this forces lateral flow of higher temperature fluids to produce a stratiform zone of intense alteration and deposition of Fe-Cu sulphides in horizontal layers beneath the crust. Tectonic activity may create fault controlled permeability leading to focussed fluid discharge, development of stockworks along the faults and formation of sulphide mounds and chimneys on the sea floor; e.g. Vai Lili (centre).
Lithological reference: 1= Fe-Mn crust and sulphide impregnation in volcaniclastics; 2= massive sulphides; 3= brecciated andesite; 4= pillow lavas; 5= massive andesite.

character.

Possibly significant differences are:

- * the extremely low aspect ratio of the West Thalanga chlorite-tremolite-carbonate zone which has a thickness range of 0.5-20m, up to 350m dip extent and ~800m strike extent compared with 20-40m thickness and ~300m strike extent at South Hercules,
- * the high Mn contents of carbonates at South Hercules which may be a district scale feature since similar compositions occur at Rosebery,
- * the prominence of volcanoclastics and fine grained sediments in the host sequences at South Hercules and AAV contrasting with apparently coherent (?) felsic lava dominated sequences at Thalanga.

South Hercules and the AAV alteration zones have both been interpreted to have formed by sub-sea floor replacement of permeable sediments in the mixing zones of upwelling relatively low temperature hydrothermal fluids and sea water. In both cases there is lateral and vertical alteration mineral zonation, considered to have been strongly influenced by local permeability contrasts, with carbonate deposited in the outer and upper, cooler, parts of the hydrothermal system.

The presence of a cap rock, either of impermeable shaley sediment or a hydrothermal mineral crust formed by diffuse sea floor venting, seems to be an important factor in forcing hydrothermal fluids to migrate laterally in the sea floor substrate.

At Thalanga, the extensive, more or less stratiform, zone of footwall quartz-sericite-(chlorite-pyrite) alteration suggests lateral hydrothermal flow, at least in the upper parts of the footwall. The strongest pyritic footwall alteration at West Thalanga is partly confined within a crudely bedded unit of silty-sandy-quartz crystal rich rhyolitic volcanoclastics and forms a conformable zone, no where much greater than about 25m thick and thinning up dip, in the immediate footwall of the favourable horizon (Figures 5 & 6). At Central and East Thalanga this style of alteration is more intense, characterised by stringer pyrite and minor chalcopyrite mineralisation and it forms broadly stratiform zones upto 50m thick which also suggest some type of layered permeability contrast. The rocks in adjacent less altered parts of the footwall appear to be largely coherent rhyolites although the obscuring effect of alteration is undeniably strong and some of the footwall rocks have a relict or pseudo? fragmental fabric and may have originated as hyaloclastite breccias with presumably high permeability.

Sea floor capping presents a possible explanation for development of extensive stratiform high temperature alteration zones in the substrate and may also partly control the mixing/cooling reactions thought to be responsible for carbonate-chlorite alteration. A sudden rupture of the cap by tectonic disturbance, leading to discrete venting of ponded hydrothermal fluid, could promote entrainment of cold sea water from the lateral fringes of the capped area and deposition of Mg-silicates and carbonates at retreating mixing fronts below the cap. Alternatively, a cap of limited permeability, as for instance in clastic sediments, could act as a diffuser creating broad areas of diffuse

venting and developing a patchwork of small overlapping hydrothermal upflow and sea water recharge zones with Mg-silicates and carbonate alteration minerals deposited at waxing and waning mixing fronts eventually leading to massive chemical modification of the substrate. In an areally extensive permeable substrate, progressive sealing of the surface by carbonate and chlorite alteration could lead to lateral hydrothermal flow and incremental growth around the fringes of the alteration cap and, as the cap spread outwards, development of the lower stratiform sulphide and silica-pyrite alteration zones.

At Thalanga the "quartz-eye volcanoclastic" (QEV) unit(s) in the upper part of the favourable horizon may have acted as cap rocks but this concept, standing alone, has difficulty explaining why chlorite-tremolite-carbonate rocks are ubiquitous in West Thalanga and fairly minor in East Thalanga when QEV exists at both. Generally, the QEV is thickest over the East Thalanga ore body, thickening up dip where it is intruded by co-magmatic quartz-feldspar porphyry (QFP) sills but thinning sharply to east and west along strike off the fringes of the deposit (compare Figures 3, 4 & 5). It may be argued that the thicker zones of QEV were more effective cap rocks, inhibiting influx of sea water thereby excluding the source of Mg, maintaining the system at high temperature and suppressing production of Mg carbonates and silicates. If so, chlorite-tremolite-carbonate zones would be expected around the fringes of the deposit, where the QEV thins out, but that is not borne out by observations. Replacement mineralisation exists within the QEV at East Thalanga in the form of stratabound and disseminated "hanging wall lenses" (mine terminology), and some, particularly in the stratigraphically upper parts, is associated with patchy chlorite-tremolite/actinolite-carbonate alteration. This contrasts with West Thalanga where most sulphide mineralisation and chlorite-tremolite-carbonate rocks lie stratigraphically below the QEV unit. There is evidence in the occasional massive sulphide clasts within QEV, to suggest that QEV was emplaced by mass flows which covered a largely preformed sheet or low mound of massive sulphide. Accordingly, the QEV hosted sulphides and associated minor chlorite-tremolite-carbonate alteration, at East Thalanga may represent late stage mineralisation from hydrothermal circulation which persisted after QEV mass flows covered the main, footwall, sulphide lens.

The hanging wall dacite is not considered a likely cap rock; it also is ubiquitous over the orebodies as thick coherent flow(s?) of rather uniform composition and character and, as noted previously, its emplacement probably post dated alteration and sulphide mineralisation and perhaps was a factor in "shutting down" the hydrothermal system.

The difference between West and Central to East Thalanga may have been controlled by the temperature and flow rates of hydrothermal fluids. Central and East Thalanga are regarded, on the basis of their more extensive zones of intense quartz-(sericite)-pyrite footwall alteration and centres of elevated copper grades, as areas of high temperature and high fluid flux promoted by high permeability in presumably intensely fractured or brecciated but formerly coherent and glassy rhyolitic lavas. The rapid, diffuse discharge of high temperature fluids from multiple vents may have produced

overlapping mounds and hydrothermal crusts and allowed no opportunity for sea water influx thus inhibiting the cooling-mixing reactions which form carbonate alteration.

West Thalanga, in contrast, is interpreted as an area of lower temperature hydrothermal discharge (analogous to the AAV and South Hercules), draped with a veneer of bedded rhyolitic volcanoclastics which partly controlled lateral migration of upwelling fluids and provided a permeable unconsolidated surface sediment permitting gradual diffuse seepage of hydrothermal fluids and mixing with continually replenished pore space sea water. Carbonate precipitation and Mg-chlorite or smectite alteration of rhyolitic volcanoclastic material occurred in the zone of mixing and cooling in the few metres of sediment immediately below, and perhaps right up to, the sea floor and sulphides were progressively deposited in the deeper, higher temperature zones of the vertically condensed thermo-chemical system. Lateral propagation of the system, caused by progressive sealing of the surface layers, produced the thin but extensive, stratiform sulphide and alteration zones.

This model, schematically presented in Figure 35, accounts for the thin, extensive stratiform and stratabound distribution of the West Thalanga chlorite-tremolite-carbonate rocks, their intimate association with sulphides and it also accommodates the following features of the deposit.

- * The zone of pyritic quartz-sericite footwall alteration is relatively thin, weak and not fully co-extensive with the chlorite-tremolite-carbonate and sulphide lens. It thickens and intensifies down dip reaching an (apparent) maximum below 600RL on Section 20110E (Figure 5) where it is more siliceous, contains blebby disseminated sphalerite in addition to pyrite and may represent a low temperature feeder zone. By contrast, pyritic footwall stringers in East Thalanga contain minor chalcopyrite, but seldom sphalerite, indicating higher temperature.
- * Most of the QEV is relatively unaltered and unmineralised except for pervasive quartz-epidote-actinolite-chlorite and footwall style quartz-sericite alteration which is localised stratigraphically above the inferred feeder system, at the down dip fringe of the ore body. This may reflect a focus of upwelling fluids which persisted during the waning stages of hydrothermal activity after mass flow emplacement of the QEV.
- * Semi massive barite and magnetite-quartzite exist in the upper part of the favourable horizon and are best developed in the distal up dip and western parts of the ore body consistent with expected low temperature hydrothermal activity and fluid-sea water mixing.
- * Massive sulphide and particularly massive pyrite lenses tend to be concentrated toward the footwall of the chlorite-tremolite-carbonate zone. Some massive pyrite lenses seem to be enclosed by chlorite-tremolite-carbonate rocks but they are partly enveloped by shear zones and may be fault emplaced slices.
- * Six narrow intervals of chlorite-tremolite-carbonate alteration separated by zones of less altered rhyolite and rhyolitic volcanoclastics occur in drill hole TH245 where the

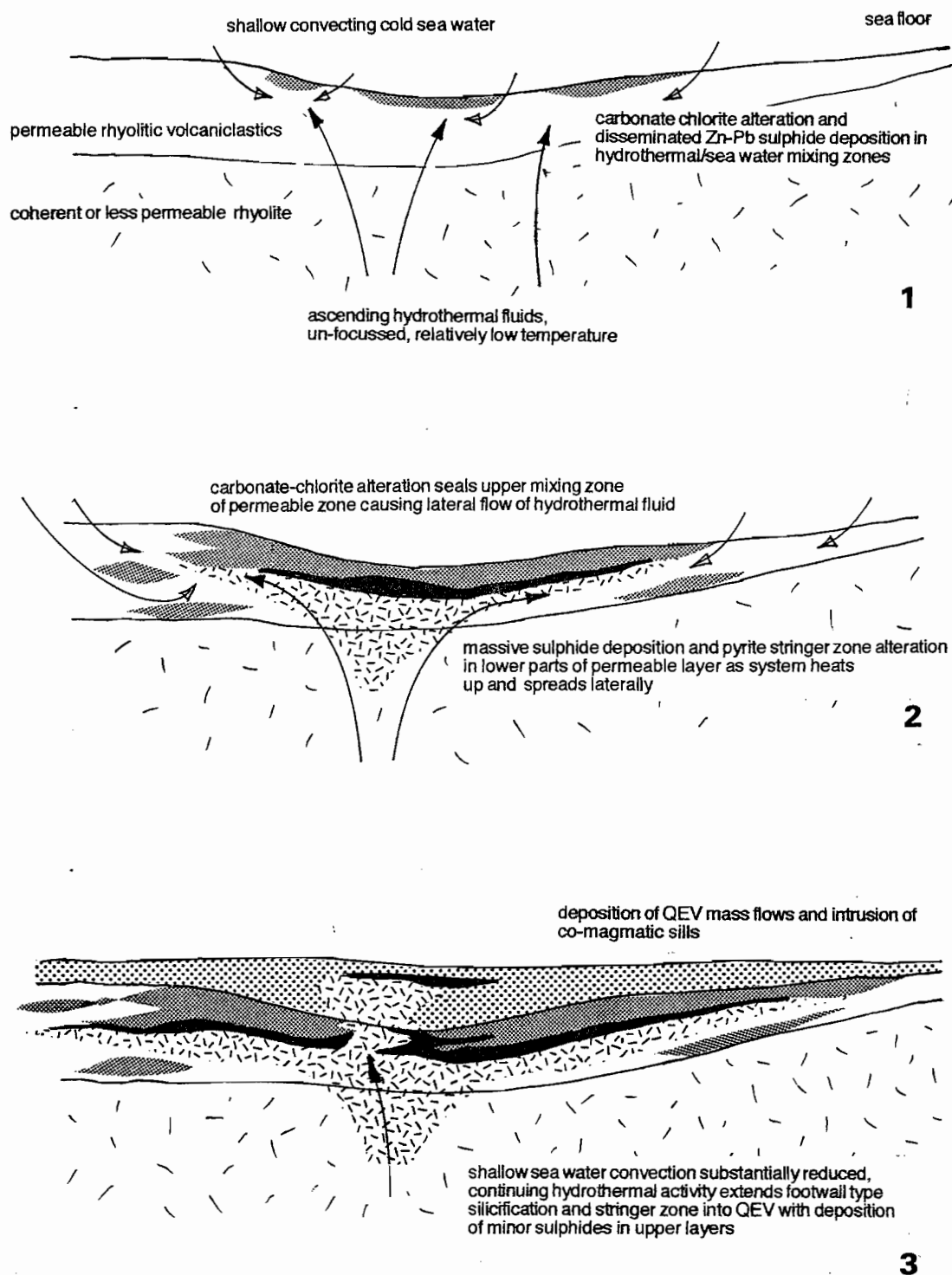


Figure 35.

Sequential schematic cross sections illustrating genetic model for West Thalanga type sulphide deposit and associated thin, laterally extensive chlorite-carbonate and siliceous-pyritic stringer alteration zones.

favourable horizon is offset southwards about 150m down dip of the ore lens, (Figures 5, 18). These alteration lenses or bands are not specifically at the favourable horizon but are within the footwall rocks upto about 40m stratigraphically below the favourable horizon. They may represent zones of lateral hydrothermal and sea water mixing around the outer margin of the system similar to the lateral interfingering of carbonate facies and sulphide facies reported at South Hercules (Khin Zaw and Large, 1992).

8 CONCLUSIONS

Titanium, aluminium and zirconium remained chemically immobile in Thalanga volcanic rocks during episodes of hydrothermal alteration and subsequent upper greenschist facies metamorphism.

Immobile elements can be used to identify the volcanic parentage of rocks otherwise altered beyond recognition and to estimate the mass changes of mobile chemical components. The most intense alteration, of rhyolites in the footwall of the massive sulphide deposit, involved complete loss of sodium and major absolute mass gains of silica, iron and sulphur, which together added about 60g/100g to the rocks.

Alteration mass gains of this order indicate interaction with great volumes of hydrothermal fluids. It is evident, by the preservation of primary Ti/Al and Ti/Zr ratios and the systematic variations in their concentrations relative to alteration intensity, that Ti, Al and Zr were not dissolved and transported by the fluids which altered the footwall rocks. It follows that any exhalative deposits precipitated from these fluids would have very low concentrations of the immobile elements.

The majority of rock types formerly interpreted as exhalites have immobile element concentrations and ratios remarkably similar to the range of altered footwall rhyolites.

It is consistent with their immobile element geochemistry and textural-mineralogical gradations, to interpret the chlorite-tremolite/actinolite-carbonate-etc. assemblages of Groups 26 and 31-35, as altered rhyolitic rocks. The chlorite rich types in Groups 31 and 32 could have formed by alteration dominated by loss of Si and gain of Mg - effectively by progressive chloritisation of aluminous phases in the rhyolite. Tremolite-carbonate dominated assemblages of Groups 33, 34 and 35 could have formed by metamorphism of carbonate-quartz-chlorite precursors derived from

rhyolite by hydrothermal additions of (progressively increasing) Mg, Ca and CO₂.

Comparable chlorite-carbonate assemblages are known, though perhaps not well documented, in the wall rock alteration systems of a number of (less metamorphosed) Palaeozoic and Holocene volcanic hosted massive sulphide deposits. They appear to be developed in relatively cool, or the cooler parts of, submarine hydrothermal systems; in the mixing zones of sea water and upwelling hydrothermal fluids, not far below the sea floor.

It is inferred that West Thalanga, in contrast to Central and East Thalanga, was formed in a cool, low intensity hydrothermal system, thereby accounting for the distribution of chlorite-tremolite-carbonate (meta) alteration assemblages. The thin stratiform character of the chlorite-tremolite-carbonate and quartz-sericite-pyrite alteration zones, and associated sulphide lenses, may be attributable to diffuse hydrothermal discharge through a permeable volcanoclastic sea floor substrate and lateral hydrothermal flow promoted by progressive sealing of the surface layer.

Thalanga magnetite-quartzites (Group 21) contain very low concentrations of immobile elements, have a simple mineralogy and major component chemistry similar to less metamorphosed exhalative quartz-hematite ironstones from elsewhere in the Mt Windsor Sub-Province and are reasonably interpreted to be thermally metamorphosed equivalents. Magnetite-quartzite exists at several stratigraphic horizons in the Thalanga area, forms but a minor component of the main mineralised horizon, and is the only rock type (possibly excluding massive sulphides and barite) which is unequivocally of exhalative origin.

Very siliceous rocks (Group 22) which share some chemical and mineralogical similarity with magnetite-quartzites and silicified rhyolite may have formed by sedimentary contribution of minor rhyolitic volcanoclastic material into silica-iron exhalites. A tentative alternative is that they originated by massive silicification of high porosity rhyolitic rocks by sub sea floor reaction with cool hydrothermal fluids similar to those which precipitated the exhalative silica-ironstones at surface.