Geology and Geochemistry of the Que River Shale, Western Tasmania

by

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A thesis submitted in partial fulfilment of the requirements for the degree of Bachelor of Science with Honours.

CENTRE FOR ORE DEPOSIT AND EXPLORATION STUDIES
A National Key Centre at the University of Tasmania

Geology Department, University of Tasmania, November 1994
Acknowledgements

Firstly I would like to thank Dr J.B. Gemmell and Dr R.R. Large for suggesting the project. I would also like to thank the Tasmanian Government for providing the opportunity for me to undertake my honours degree at CODES. I owe thanks to many of the staff and post graduate students of both CODES and the Geology Department for their assistance, in particular Dr P. McGoldrick, Dr J. McPhie, Dr A. Crawford, Dr R. Berry and Dr S Abbott. Special thanks to Dr D. Cooke for reading the thesis.

Thanks must also go to Aberfoyle Resources with out whom the project would not have been possible. In particular for the logistical support offered during the field work component of the project.

Finally I would like to thank my fellow honours students for their humor, advice and assistance during the year. Special thanks to A. Verbeeten for her friendship and assistance.
Abstract

The Que River Shale Formation overlies the Que-Hellyer Volcanics, which are the host sequence to the Hellyer and Que River massive sulphide deposits, western Tasmania.

The Que River Shale is a homogeneous unit of finely laminated, fine grained (<100μm) quartz, muscovite and calcite grains in a dirty brown chloritic matrix. The shale contains intercalated resedimented volcanioclastic sandstones at the top and base of the unit. Shale composition varies by less than 5 wt % with regards to major elements.

Deposition of the Que River Shale began after the formation of the Hellyer Massive sulfide deposit but contemporaneous with the mixed sequence. Shale deposition extended throughout the end of deposition of the Mount Charter group, synchronous with the Southwell Subgroup volcanism. However the eruption of Upper Basalts and Andesites and the influx of predominantly rhyolitic volcanioclastic mass-flows and turbidites associated with the Southwell Subgroup restricted the finely laminated shale mostly to a period of quiescence between the two styles of volcanism.

The depositional environment of the Que River Shale is interpreted to represent quiet, reducing bottom waters, due to a high proportion of complete agnostid trilobite specimens along with the presence of carbonaceous material and pyrite nodules. Geochemical techniques have been used to further define the basin as inhospitable (little or no oxygen present) to euxinic (free H₂S). While S-isotopes range from δ³⁴S +17 to +43 suggesting that the sediment may have been a closed system with respect to SO₄²⁻ and H₂S.

The Que River Shale has an andesitic provenance suggesting a local source for the shale. However, the Que River Shale cannot be derived directly from any one source, or combination of sources in the Mount Read Volcanics without significant modification. The only quantification that can be placed on the source rocks is that the Que River Shale must contain 20-25 % Hellyer Basalt, to obtain the high Cr values observed (up to 1.3 wt % Cr₂O₃). The Que River shale must have been well homogenised by sedimentary processes to account for its restricted range in chemical composition.

The Que River shale does not show an extensive alteration plume unlike the underlying basalts. Alteration in the suite therefore cannot be used as an exploration indicator. However, anomalous base metal values (up to 400 ppm Pb and 938 ppm Zn) are spatially association to the orebody and may be useful as vectors to mineralisation.
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CHAPTER 1
INTRODUCTION

1.1 INTRODUCTION

The Que River Shale Formation overlies the Que-Hellyer Volcanics, which are the host sequence to the Hellyer and Que River massive sulphide deposits. The definition of the Que River Shale is 'that unit of black and grey siltstone and shale with minor greywacke and tuff, conformably overlying the Que-Hellyer Volcanics and conformably overlain by felsic tuffs of the Southwell Subgroup in the area between the Murchison Highway and the Hellyer mine' (Corbett and Komyschan, 1989). Hellyer is the northern-most of a series of massive sulfide orebodies which lie within the Cambrian Mount Read Volcanics and is located approximately 90 kilometres south of Burnie, on the West Coast of Tasmania (Fig. 1). The principal aims of this study are:

(1) To describe the Que River Shale, detailing its contact relationships, lithofacies and sedimentology through detailed core logging.

(2) Characterise the environment of deposition of the Que River Shale using geochemical methods including Organic Carbon versus Sulfur, Degree of Pyritisation Index, and Sulfur Isotopes.

(3) Use the bulk elemental composition of the shale (determined by XRF) to:
A. Define the average and range of values for the Que River Shale.
B. Constrain the provenance of the Que River Shale.
C. Investigate whether the fuchsite-carbonate halo seen in the underlying basalts over the orebody can be detected in the Que River Shale using geochemical methods.

The project is designed to increase understanding of the sedimentology and relationship of units in the Cambrian Mount Read Volcanics, as part of on-going research in the area. In addition, this project will determine if the Que River Shale has any distinctive geochemical features which may be used to assist exploration for massive sulfide mineralisation. The study is concentrated on drill holes along a three kilometre east-west cross section with a one kilometre northward extension centred on the
FIGURE 1: Geology of the central part of the Dundas Trough from Mount Darwin to Moina, showing distribution of major lithologic associations of the Mount Read Volcanic Belt, associated Cambrian and Proterozoic sequences, and showing the location of volcanic-hosted massive sulfide and related deposits. Based on published maps of the Mount Read Volcanics Project and Geological Survey of Tasmania. From Corbett (1992).
Hellyer orebody (Figs. 2 and 3).

1.2 METHODS

Approximately six weeks of detailed diamond drill core logging was undertaken on holes MAC 10, MAC 11, MAC 15, MAC 19, MAC 31, HL 026, HL 040, HL 080, HL 246, HL 345, HL 469, BRD 1 and BRD 3 (Fig. 2). Logging was focused on the Que River Shale and its contact relationships with the underlying basalts and overlying Southwell Subgroup (Appendix 1). Geochemical sampling for XRF, organic carbon, degree of pyritisation index and sulfur isotopes was also carried out.

Logging was carried out on 1:200 scale log sheets which were redesigned from standard log sheets to account for the lack of visible grain size variation in the shale and to highlight features such as the stratigraphy, rock type, colour, presence of faulting, veining and mineralisation. As well as a graphical representation of the drill core.

Sampling for geochemical analysis was carried out at 10 m intervals being careful to avoid altered zones. Sampling for thin section work and pyrite samples for sulfur isotopes were selected in areas of interest. Fifty one samples covering the shale portions of the holes logged were the selected at regular intervals for XRF analysis, to represent spacial variation of the Que River Shale. The remaining samples were kept in reserve for more detailed work later on if required. Analytical techniques applied in this study are summarised in Appendix 2.

1.3 PREVIOUS WORK

Due to the status of Hellyer as a world class massive sulfide orebody much work has been carried out on various aspects of the deposit: geophysics and discovery (Sise and Jack, 1984; Skey, 1984; Eadie et al., 1985), geochronology (Perkins and Walsh, 1993; Perkins 1993) geology (McArthur, 1986, 1989; McArthur and Dronseika, 1990), deformation style and strain partitioning (Drown and Downs, 1990), metal zonation (McArthur, 1988; 1990), hydrothermal alteration (Jack, 1989, 1990), and geology of the alteration pipe and stringer zone (Gemmell et al., 1990; Gemmell and Large, 1992).

The study area has been mapped at 1:25000 scale as part of the Tasmanian Division of Mines and Mineral Resources, Mount Read Volcanics Project (Corbett and Komyshtan, 1989; Pemberton et al., 1991). The volcanology and sedimentology of the Hellyer host succession including the Que River Shale, has been described by Waters and Wallace, (1992). The most detailed work to date on the sedimentology of the Que River Shale has been carried out by Waters as part of his PhD study (Waters 1990; and PhD in progress). The palaeontology of the Que River Shale has been extensively studied by Jago (1973, 1977).
FIGURE 2: Plan view showing the distribution of logged drillholes and the distribution of Que River Shale outcrop. Also shown are Tailings Dam, Tailings Dam Fault and the Hellyer ore body.
FIGURE 3: Schematic east-west cross section looking north, showing the location of drill holes logged with respect to the geology of the Hellyer area. Adapted from Gemmell (1990).
CHAPTER 2
REGIONAL GEOLOGY

2.1 INTRODUCTION

Tasmania is divided into two distinct geological zones by the Tamar fracture system (Fig. 4). The eastern Tasmanian terrane consists of Ordovician-Devonian turbidite sequences (Mathinna Beds), with an unknown basement. The western Tasmanian terrane is more complex, consisting of blocks and inliers of Precambrian rocks, thick Cambrian sedimentary and volcanic sequences, and ultramafic-mafic complexes. The western terrane is overlain by Ordovician-Devonian siliciclastic and carbonate sequences. Both terranes were folded and intruded by granites during the Devonian Tabberrabberan Orogeny (Corbett, 1992).

2.2 THE MOUNT READ VOLCANICS

The Que River Shale crops out in the Mount Read Volcanics, an arcuate belt of predominantly Cambrian volcanic rocks exposed along the eastern margin of the Dundas Trough. The Dundas trough forms a 200 km long, 10-15 kilometres wide belt, extending from Elliott Bay in the south to the Dial Range in the north (Corbett, 1992; Fig. 4). The Mount Read Volcanics are bounded to the east by the Precambrian metamorphic basement terrane known as the Tyennan nucleus and are faulted or interfingered with sedimentary rocks of the Dundas Group to the west (Corbett, 1992). This belt is one of the most mineralised volcanic provinces of its kind, being host to numerous world class volcanic hosted massive sulfide deposits including Hellyer, Que River, Rosebery, Hercules and Mount Lyell (Large, 1992; Fig. 1).

The Mount Read Volcanics comprise four major lithostratigraphic units, the Central Volcanic Complex, the Western Volcano-Sedimentary sequences (Dundas Group, Mount Charter Group and Yolande River sequence), Eastern Quartz-Phyrnic Sequence, and the Tyndall Group (Corbett, 1992; Fig. 5). All four units contain rhyolitic to dacitic lavas, volcaniclastic rocks and minor accumulations of mafic volcanics (Corbett, 1992). Several major base metal deposits, including Rosebery, Hercules and Mount Lyell are hosted by the Central Volcanic Complex (Corbett, 1992). In the Hellyer area the main unit of interest is the western volcano-sedimentary sequence which consists solely of the Mount Charter Group.
FIGURE 4: Simplified geological map showing the distribution of major early Palaeozoic tectonic elements of western Tasmania. As well as the Mathinna Beds and Devonian granitoids of the eastern terrane. Most of the Ordovician and Siluro-Devonian cover rocks are not shown. From Corbett (1992), after Corbett and Turner (1989).

2.3 THE MOUNT CHARTER GROUP

The Mount Charter Group, consists of a volcano-sedimentary sequence lying stratigraphically between the Central Volcanic Complex below (Corbett, 1992) and the Owen Conglomerate above. The Mount Charter Group replaces the poorly defined “Dundas Group Correlates” used prior to 1992.
FIGURE 5: Distribution of the principal lithostratigraphic formations and major massive sulfide deposits in the Cambrian Mount Read Volcanics of western Tasmania. From McPhie and Allen, (1992)

(Corbett, 1992). Equivalents of the Mount Charter Group are exposed in the Pinnacles-Mount Block area and the Burn's Peak-Boco Road area (Fig. 1; Reid, 1990). The Mount Charter Group hosts the Hellyer and Que River ore deposits and has been divided into six units (Fig. 6; Corbett, 1992):

The **Black Harry Beds** are a sequence of interbedded marine shard-rich mudstone, tuffaceous sandstone, volcaniclastic mass-flow breccia, and green to black shale which overlies, or is faulted against, the Central Volcanic Complex. On the Murchison Highway this sequence is approximately 300 m thick although its base is poorly defined due to poor exposure and faulting. Tuffaceous rocks in the sequence are generally quartz and feldspar bearing. Sandstones commonly show turbidite characteristics and contain detritus of both volcanic and metamorphic provenance. The upper boundary of this unit is gradational with the Animal Creek Greywacke (Corbett, 1992).

The **Animal Creek Greywacke**, was defined by Pemberton et al. (1991) and comprises some 300 m of well-bedded grey micaceous to siliciclastic sandstone interbedded with grey-black siltstone and shale. Tuffaceous sandstone, shard-rich mudstone, and volcaniclastic breccia are minor components. Graded bedding and other features typical of turbidites are common. Sandstone detritus is predominantly of Precambrian basement derivation, but also includes chromite grains possibly sourced from ultramafic rocks (Corbett, 1992).
The Que-Hellyer Volcanics comprise a marine sequence of calc-alkaline, dominantly intermediate to mafic volcanics (andesites to basalts) and volcaniclastics (Corbett and Komysnhan, 1989; Waters and Wallace, 1992), with minor felsic (dacitic) volcanics and rare sedimentary units (Corbett, 1992). The sequence has a maximum stratigraphic thickness of approximately 1 km near the Que River mine but thins dramatically to the west. Extensions of this unit occur south of the Mount Charter Fault in the Sock Creek area (Fig. 1) and 10 km north-east of the Hellyer mine beneath Tertiary basalt cover. Four informal subunits have been recognised within the Que-Hellyer Volcanics by Komysnhan (1986a, b). These units correspond in broad terms to units recognised in the informal mine terminology:

1. The lower tuff and lava (50-200 m) comprises interbedded felsic-andesitic derived volcaniclastic rocks, tuffaceous sandstone, and siltstone, and minor felsic to andesitic and basaltic lavas (equivalent to the Lower Basalt of Waters and Wallace, 1992).

2. The lower andesites and basalts (300-600 m) correspond to the feldspar-phyric sequence (footwall andesites) and consist of breccia and coherent flows of andesite and basalt, with
minor volcaniclastic and sedimentary interbeds and minor dacitic units. The andesitic and basaltic lavas range from aphyric to plagioclase- clinopyroxene-phyric and are commonly vesicular.

3 The mixed sequence (mine sequence; 50-200 m) is characterised by flows and dome-like bodies of cream weathered feldspar-phyric dacite intercalated with polymict mass-flow breccias, thin andesite-basalt flows, and minor shale and sandstone. The massive sulfide deposits at Hellyer and Que River are hosted by this unit.

4 The upper (hanging-wall) basalts and andesites (100-200 m) include pillowed lava flows and pillow breccias of the Hellyer basalt (pillow lava sequence), which overlies the Hellyer orebody (equivalent to the Hellyer Basalt of Waters and Wallace, 1992).

The Que River Shale is a distinctive unit of black, carbonaceous, pyritic shale and siltstone directly overlying the upper andesites and basalts in the Hellyer mine area (Corbett and Komyshan, 1989). The contact with the Hellyer basalt is interpenetrating and peperitic, and in places there is large-scale interdigitation of lava flows and shale (Corbett, 1992). The shale contains a trilobite-rich fossil fauna indicative of a middle Middle Cambrian age (Gee et al., 1970; Jago, 1979). The Que River Shale represents a major hiatus in local volcanism, marking a change from proximal andesitic-basaltic volcanism of the Que-Hellyer Volcanics to the distal felsic volcaniclastics which constitute the overlying Southwell Subgroup (Corbett, 1992).

The Southwell Subgroup corresponds to the Upper Rhyolitic Sequence of Hellyer mine terminology. The unit comprises quartz-feldspar-crystal-rich pumiceous mass-flow breccia and sandstone interbedded with greywacke, siltstone, shale, and minor felsic lava. Stratigraphic thicknesses exceed 1,000 m to the north of Hellyer. The lower part of the subgroup comprises graded mass-flow units up to 20 m thick, intercalated with similar thicknesses of bedded greywacke and siltstone. The basal mass-flow unit contains shale rafts up to several metres long and large clasts of quartz-phyric pumice. A mappable unit of well-bedded greywacke turbidites (Murrays Road Greywacke; Pemberton et al., 1991) occurs in the middle of the succession. Above this is an informally defined upper unit (400 m) of pumice-rich mass-flow breccia and sandstone with intercalated flow-banded felsic lava flows.

Mount Cripps Subgroup consist of a distinctive sequence of purple-weathering volcaniclastic conglomerate, sandstone, siltstone and minor crystal tuff and is in the order of 500-600 m thick. This unit has been mapped as a Tyndall Group correlates by Corbett and Komyshan, (1989) and Pemberton et al. (1991).

The Que-Hellyer Volcanics and overlying units are intruded by two types of Cambrian felsic intrusive rocks; (1) coarse grained quartz-feldspar porphyries and (2) finer grained spherulitic quartz. Dolerite bodies (possibly Devonian in age) also intrude the Mount Charter Group porphyries (Corbett
and Komysshan, 1989). Intrusions tend to be concentrated around sedimentary contacts, with the Cambrian intrusions occurring mostly within the Que River Shale (Burrett and Martin, 1989). The area has been regionally metamorphosed to prehnite-pumpellyite facies during the Devonian Tabberrabberan Orogeny (Waters, 1990).

2.4 QUE RIVER SHALE DISTRIBUTION

The Que River Shale crops out along the Murchison Highway from the Mount Charter fault northward to within 1.2 km of the Cradle Mountain Link Road intersection, and around the Hellyer mine site where it defines the anticline (Fig. 7). The Que-River Shale is also exposed in the mine canal, which diverts the Que River around the tailings dam (Fig. 2). The shale is not present south of the Hellyer mine at Que River. North of the Hellyer mine the shale plunges beneath Tertiary basalts and has been intersected in drillcore (MXRD 1) as far north as the Black Marsh Syncline (Fig. 7)

The Que River Shale has an average thickness of around 125 m in drill core (Appendix 1). It decreases to 5-10 m thick east of the Hellyer mine, and increases to nearly 200 m thick north of Hellyer mine, where it plunges beneath Tertiary basalts. The distribution of shale is complementary to the Que Hellyer Volcanics which thicken eastward being thickest where they abut the Henty Fault Zone.

2.5 STRUCTURE

The Que-Hellyer Volcanics terminate abruptly to the southwest against the northwest-trending Mount Charter Fault zone (Fig. 7), a possible splay from the Henty Fault which, longitudinally bisects the Mount Read Volcanic belt. Equivalents of the Que-Hellyer Volcanics do not occur southeast of the Mount Charter fault, indicating that this structure was active in the Cambrian, possibly as a basin margin fault (Burrett and Martin, 1989). The quartz-feldspar porphyry and quartz porphyry bodies that intrude the Que-Hellyer Volcanics increase in abundance near the Mount Charter Fault (Corbett and Komysshan, 1989).

The structure of the Que-Hellyer area is dominated by upright, shallowly plunging folds, that trend northeast-southwest and vary from open to isoclinal (Waters and Wallace, 1992). Fold wavelengths decrease from ≈2 km to 500 m approaching the Henty Fault zone. Cleavage associated with these folds is poorly developed west of the Murchison Highway, but is prominent and axial planar to the folds east of the highway (Corbett and Komysshan, 1989). At Hellyer the major mesoscopic structure consists of a broad anticline plunging between 20° and 30° NNE. The Hellyer volcanic-
hosted massive sulfide deposit is located within the hinge area of this anticline. The western limb of the anticline dips gently but the eastern limb steepens to vertical close to the Henty fault zone. The structural complexity of the area increases south of Hellyer with the development of tight parasitic folding on the synclinal structure at Que River (Large et al., 1988). Folding is interpreted as being part of the widespread regional deformation which occurred during the Middle Devonian (Waters and Wallace, 1992). A major north-south fault, the Jack Fault, transects the Hellyer ore body and the overlying sedimentary and volcanic units and has a measured horizontal displacement of 130 m, east block north and 30 m up (Gemmell and Large, 1992).

2.6 TECTONIC SETTING

A tectonic model for western Tasmania has been proposed by Crawford and Berry, (1992). This section presents a synthesis of this model.

In the Early Cambrian, a thinned passive continental margin formed by the attenuation and eventual rifting of Proterozoic continental crust (Fig. 8a). Rifting was followed by the commencement of eastward-directed intra-oceanic subduction to the east of the passive margin sometime before the Middle Cambrian, forming an oceanic arc (Crawford and Berry, 1992). Subduction of oceanic crust between the arc and the passive margin resulted in an arc-continent collision in the Middle Cambrian. During this time, one or more extensive sheets of forearc crust were overthrust onto thinned continental crust, forming allochthonous sheets of mafic-ultramafic composition (Fig. 8b; Crawford and Berry, 1992). Compression continued during the Mid Cambrian, causing a short-lived episode of westward-directed subduction beneath the newly-emplaced allochthon and passive margin basement (Crawford and Berry, 1992). The basal part of the Mount Read Volcanics (the Central Volcanic Complex) is interpreted to have been deposited during this phase (Fig. 8c).

In the Late Middle Cambrian, rebound back thrusting along the eastern side of the Central Volcanic Complex exhumed previously underthrust Proterozoic crystalline crust (the Tyennan Nucleus), and created a foreland basin half-graben known as the Dundas Trough along the western edge of the basement inlier (Fig. 8d). The Upper Mount Read Volcanics were deposited into the Dundas trough. The Upper Mount Read volcanics are interpreted to represent a post collisional sequence of volcanism generated by delayed partial melting of subduction-modified underthrust passive margin subcontinental mantle (Crawford and Berry, 1992). Deposition of the Mount Read Volcanics ended in the late Cambrian with the uplift and excavation of Tyennan region Proterozoic crystalline crust (Fig. 8e). This provided abundant
FIGURE 7: Subbasalt map of the Hellyer area. Adapted from Pemberton et al. (1991).
coarse siliciclastic detritus of the Owen conglomerate which flooded into and eventually filled the Dundas Trough.

2.7 HELLYER

Economic mineralisation at Hellyer consists of single, stratabound, massive orebody (Fig. 9). The deposit is unusually sulfide-rich, averaging 54% pyrite, 20% sphalerite, 8% galena, 2% arsenopyrite and 1% chalcopyrite with minor tetrahedrite. The remaining gangue (15%) is dominated by quartz, barite, calcite, chlorite, sericite and siderite (McArthur, 1989). A distinct metal zonation exists within the orebody, with a hanging-wall zone enriched in Zn, Pb, As, Ag, and Au, and a footwall zone enriched in Fe and Cu (McArthur, 1986). Economic mineralisation extends over 750 m north-south, and 200 m east-west, with a true thickness of up to 75 m. At its southern extremity, the sulfides are 90 m below the present day surface, while sulfides occur to depths of at least 500 m to the north (McArthur in Burrett and Martin, 1989). Beneath the deposit, an extensive well-defined alteration zone occurs in the footwall andesitic sub-parallel to the Jack Fault (Gemmell et al., 1990). Alteration is spatially zoned, with a central upper core of quartz-barite giving way to concentric shells of chlorite, chlorite-sericite, sericite and outer sericite-quartz alteration. Hanging wall alteration at Hellyer is dominated by extensive fuchsite and calcite extending approximately 100 m above the central portions of the orebody. Minor fracture-controlled barite, pyrite and iron-rich chlorite also occurs in the hangingwall (Jack, 1990).

The Hellyer massive sulfide deposit is an example of a Kuroko-style volcanic hosted massive sulfide (VHMS). Controlled by a deep fracture system (the Jack Fault; Fig. 9), metal rich hydrothermal solutions vented onto the seafloor, causing precipitation of the ore body in an adjacent structural trap (McArthur, 1989). The deposit was then preserved by the deposition of high energy hangingwall volcanioclastics and extrusion of the Hellyer basalt. Hydrothermal activity continued during deposition of the hanging wall sequence redistributing some metal to the hanging wall and causing fuchsite-carbonate alteration in the overlying pillow basalts (McArthur, 1989).
FIGURE 9: Schematic cross section of the Hellyer deposit showing the relationship of the Que River Shale to ore and presence of footwall and hangingwall alteration zones, Burrett and Martin (1989).
CHAPTER 3

THE QUE RIVER SHALE:
CONTACT RELATIONSHIPS AND LITHOFACIES
CHARACTERISATION

3.1 INTRODUCTION

The Que River Shale was originally described by Gee et al., (1970), as the ‘Que River Beds’ a sequence of “black siltstones with subordinate shales” exposed along the Murchison Highway north and south of the Que River bridge. Mapping by Komyshan in the late 1980’s further defined the unit and clarified its upper and lower boundaries allowing formal definition of the Que River Shale as a formation (Corbett and Komyshan, 1989). The Que River Shale was redefined by Corbett and Komyshan (1989) as a “distinctive unit of black, carbonaceous, pyritic shale and siltstone directly overlying the andesites and basalts in the Hellyer mine area”. Fossil evidence from carbonaceous shales adjacent to Que River indicate a late Middle Cambrian age for the Que River Shale (Gee et al., 1970).

The low grade prehnite-pumpellyite regional metamorphism and lack of penetrative fabrics has allowed detailed sedimentological and volcanological studies of the Mount Charter Group (Waters, 1990; Waters and Wallace, 1992), including the Que River Shale. Detailed examination of core has revealed that the Que River Shale is a remarkably homogeneous unit of fine grained, finely laminated black shale marked by volcaniclastic layers at the top and bottom of the unit.

In this chapter the contact relationships of the Que River Shale with the over and underlying units and the lithofacies characteristics and pyrite morphology are examined in detail. This was done in order to characterise the sedimentology of the Que River Shale. To determine the extent of deposition of the shale, the relationship of over and underlying shales to the Que River Shale and the effect of volcanism on the Que River Shale deposition. The overlying and underlying units are also described with particular attention being paid to the shale units they contain. A review of the paleontological and geochemical work done on the shales is given, and then used to estimate the sedimentation rate of the Que River Shale.
3.2 QUE-HELLYER VOLCANICS

The Que-Hellyer Volcanics directly underlie the Que River Shale, and have been subdivided into four units (Corbett, 1992; chapter 2). The lower two units of the Que-Hellyer Volcanics are interpreted to have been deposited rapidly as a succession of small volume eruptions and volcaniclastic flows (Waters and Wallace, 1992) and contain little or no shale.

The Mixed Sequence lies above the lower two units of the Que-Hellyer Volcanics, and is characterised by flows and dome-like bodies of feldspar phryic dacite intercalated with polymictic mass-flow breccias, thin andesite-basalt flows, and minor shale and sandstone. The Mixed Sequence hosts the massive sulfide orebodies of Que River and Hellyer. A thinly bedded to laminated shale facies occurs in the Mixed Sequence volcanics, above the Hellyer ore position. The shale facies consists of up to 8 m of light grey to black laminated shale with interbedded, fine to medium grained, quartz-rich sandstone. According to Waters and Wallace (1992), this facies is identical to the Que River Shale. Individual beds range up to a few cm in thickness, but most are less than 1 cm thick. The beds typically have sharp contacts, with little or no soft sediment deformation. Deposition of this facies is considered to have been by a combination of low-energy, small-scale turbidity currents and background hemipelagic sedimentation (Waters and Wallace, 1992).

The uppermost unit of the Que Hellyer Volcanics, known as the Upper Basalts and Andesites, consists of pillows and sheet flows of basaltic and minor andesitic lavas intercalated with shales (Waters and Wallace, 1992). Most of the shale in the Upper Basalts and Andesites occurs in the pillowed lavas, along with varying amounts of interpillow fine-grained hyaloclastite derived from the quenched margin of nearby pillows. Minor intercalations of shale and brecciated lava occur between individual sheet like-flows of massive basaltic lavas (Waters and Wallace, 1992). Individual basalt flows are interpreted to have been extrusive or shallow intrusives into wet sediments, due to the presence of peperites, hyaloclastites and chilled margins (Waters and Wallace, 1992). The sediment in contact with pillowed intrusions is usually locally indurated (baked) or altered, and contains numerous thin quartz and carbonate veins. Alteration has caused silica addition and loss of muscovite compared to the overlying shales (Table 1; sample 1), any pre-existing bedding is disturbed or destroyed by the emplacement of the lava. In contrast, sediment that occurs between pillows or at the top of pillow lava flows either settled from the water column or was washed into the interpillow space by currents, it is typically irregularly bedded (incontrast to the laminated Que River Shale above), but has simmilar compositions to the Que River Shales (Table 1; sample 2)

The basalts of the Upper Basalt and Andesite unit have a maximum thickness of 220 m just to the northeast of the Hellyer deposit. Thin abruptly to the northeast, and gradually to the southwest, suggesting a source for the basalts around the Hellyer orebody (Waters and Wallace, 1992). Laminated shales occur within the Upper Andesite and Basalt sequence distal to the basalt pile, where
The eruption of basalts had a much smaller influence on the sedimentation in the basin. For example, north of the Hellyer ore deposit in drill hole HL 469 (Fig. 2), finely laminated shales similar to the Que River Shale are abundant. The shales are also similar geochemically to the overlying Que River Shale Formation (Appendix 2), suggesting that this material is equivalent to the Que River Shale.

3.3 QUE RIVER SHALE

3.3.1 Shale Component.

In drill core, the Que River Shale consists of mud, with minor intervals of fine to medium (rare coarse) sand near the base and top of the unit. The mud, which constitutes the main body of the shale, is black to very dark grey and commonly laminated. Three lithotypes (Plate 1) have been identified on the basis of their laminations:

Lithotype 1: Weakly laminated, dark fine grained chlorite-sericite-quartz and pyrite-rich mud with disseminated quartz, muscovite and calcite clasts (up to 50 μm). The laminations are defined by different proportions of quartz, muscovite and calcite in a dark chlorite-rich matrix, but the Quartz clasts are rarely concentrated into distinct layers. Occasionally the dark layers thicken to form elongate blebs (Plate 1A), almost devoid of quartz, muscovite and calcite. The laminations bend around the blebs suggesting that the blebs are primary rather than an alteration feature.

Lithotype 2: Strongly laminated shale with laminations defined by quartz-muscovite layers and dark chlorite-rich layers (Plate 1B). The grain size of quartz and muscovite in lithotype 2 laminations is coarser than in lithotype 1, with quartz clasts up to 100 μm and mica fragments up to 150 μm long. Quartz and muscovite grains are more abundant than in lithotype 1, and are concentrated in layers which appear to be microscours. This type of lamination may represent a slightly higher energy environment, with more detrital quartz and muscovite input than lithotype 1. Unlike lithotype 1, this sample contains no calcite, which may be a function of the energy of deposition.

Lithotype 3: Similar to lithotype 2, with prominent laminations. However, the laminations differ from lithotype 2 in that they are defined mainly by calcite with less quartz and muscovite (Plate 1C). The darker mud-rich layers are also calcite-enriched and contain fossils such as a 1.5 mm trilobite fragments and 150 μm sponge spicules (Plate 2).

The three lithotypes are end members, and tend to grade into each other, making it difficult to determine their distribution in drill core. The variation in mineralogy between the three lithotypes is summarised in Table 1. XRD analyses indicate that the major constituents of the Que River Shale are quartz, muscovite, chlorite and pyrite with minor albite, calcite and dolomite in some samples. The quartz grains in the Que River Shale are probably detrital in origin. In thin section, quartz grains
generally have straight extinction. Many of the grains have triangular to cuspate margins, although a few show signs of annealing (two or more domains with different extincting and sharp contact) and occasional undulose extinction. The predominance of straight extinction and cuspate margins suggests a volcanic source for quartz with a minor input of strained metamorphic quartz. The likely source of metamorphic quartz is the Tyennan Nucleus. Muscovite is not seen in volcanic deposits within the Mount Read Volcanics, suggesting a metamorphic (Tyennan Nucleus) source. However, the breakdown and weathering of volcanic glass and ash results in formation of clays which ultimately become muscovite and chlorite during metamorphism, which may explain the presence of muscovite and chlorite in the Que River Shale.

**TABLE 1: Approximate mineralogical composition (%) of Que River Shale Samples**
(Determined by XRD, appendix 2). LSF-Lower shale facies, Musc-Muscovite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Quartz</th>
<th>Musc</th>
<th>Chlorite</th>
<th>Pyrite</th>
<th>Albite</th>
<th>Calcite</th>
<th>Dolomite</th>
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<tbody>
<tr>
<td>1</td>
<td>LSF altered</td>
<td>83.3</td>
<td>2</td>
<td>4.9</td>
<td>4.9</td>
<td></td>
<td></td>
<td>4.9</td>
</tr>
<tr>
<td>2</td>
<td>LSF unaltered</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Lithotype 1</td>
<td>57.3</td>
<td>15.6</td>
<td>10.4</td>
<td>10.4</td>
<td>5.2</td>
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<td>4</td>
<td>Lithotype 2</td>
<td>60</td>
<td>30</td>
<td>5</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Lithotype 3</td>
<td>44.1</td>
<td>19.6</td>
<td>19.6</td>
<td>4.9</td>
<td>2</td>
<td></td>
<td>9.8</td>
</tr>
</tbody>
</table>

The Que River Shale has a well developed bedding-subparallel cleavage, which is crenulated in some thin sections (Waters, 1988). Quartz and calcite veins in the shale are wispy to straight and are generally <0.1 mm, rarer calcite-quartz veins up to 5 cm occur as well as massive veins 2-3 m wide. Vein orientations range from bedding-parallel to high angle (80°). Zones of shearing are common in the Que River Shale, which appears to have more susceptible to strain than the more competent basalts.
PLATE 1: Lithotypes. All photos 2.5x magnification. Scale bar 600 µm. See text for explanation.  
A. Lithotype 1: HL 246 118.3m,  
B. Lithotype 2: HL246 67.25m,  
C. Lithotype 3: MAC31 88.60m
PLATE 2: Fossils from the Que River Shale; A. Agnostid trilobite fragment
B Sponge Spicules.
Both from MAC 31, 88.60. Magnification 5x. Scale 300 μm.
3.3.2 Volcaniclastic Layers

Sand at the base of the Que River Shale is concentrated as layers of fine grained crystal-rich (quartz, feldspar) volcanic sandstones, with minor pumice clasts and fine sandy laminations. On all scales, the sand layers exhibit scour bases and graded tops, with the sandy laminations forming microscours, suggesting mass flow transport. The sandy laminations are up to 1 mm thick while the sandy beds vary from 5-10 cm up to approximately 2 m. Some sandstone layers contain pyrite in altered pumice clasts, and as disseminated cubes in the matrix. The influx of sand resulted in the disruption of laminations underlying the sandy layers to produce massive layer, or (when the disruption was less intense) soft sediment deformation, slump folds and microfaults. Occasionally the coarse sandy volcaniclastic layers show reverse grading at their base. These sandy layers are interpreted to represent volcaniclastic turbidites.

The top 20 m of the Que River Shale also contains layers of sandstone, mixed sandstone and shale and volcaniclastic layers. Like the lower sandy units, the upper units are pyrite-rich compared to the shales. However they differ from the lower sandy beds in that they occur only as discrete units of sandstone or polymict volcaniclastic with scoured bases and sharp to slightly graded tops. They do not occur as laminations. The upper sandstone layers are confined to a narrow interval (up to 20 m below the Southwell Subgroup/Que River Shale contact), while the lower sandstones extend up to 60 m above the Basalt/Que River Shale contact. The sandy layers represent an increase in the sediment supply to the basin from fine grained weathered detrital material to coarse resedimented volcaniclastics of the Southwell Subgroup (Corbett and Komyshev, 1989).

It is not possible to correlate individual sandstone layers between drill holes, although there does appear to be a higher concentration of volcaniclastic sandstone layers at the base of the Que River Shale over the Hellyer orebody (Appendix 1). As mentioned above, the shale thins eastward, and to the west, the contact with the basalt is faulted suggesting that the basal sandstone layers may have been faulted out. However, the basal sandstone layers are also absent in the north. This is probably due to faulting in HL 345 (Fig. 2). However, in HL 469 (Fig. 2) the basal contact appears conformable and no sandstone layers are present, suggesting that the source of sands may have been to the south. Samples such as a quartz, plagioclase crystal rich slightly pumiceous volcaniclastic sandstone (HL 246, 159 m; Appendix 1), is interpreted to be a volcaniclastic turbidite that contains transported and reworked detritus (rounded plagioclase crystals and fragments of pumice). This is unlikely to be a modified andesitic to basaltic volcanic deposit sourced from within the Que-Hellyer Basin as the local intrabasinal volcanism during the late Middle Cambrian was basaltic to andesitic in composition. A more likely source is that of basin margin volcanism or extrabasinal volcanism from an adjacent part
of the Mount Read Volcanic belt, possibly south or east. The volcaniclastic intervals were probably emplaced as mass flows into the basin, forming lensoidal sheets which appear continuous in core but are not extensive enough to be correlated across the drill holes logged.

In the Que River Shale we also see basaltic to andesitic volcanism which was interpreted by Corbett and Komynshan (1989) to be related to the Que Hellyer Volcanics as the very end of that system. In MAC 15 (Appendix 1) andesitic dykes at 32.5-33.5 m and 44.1-46.2 m have peperitic bases and sharp tops, probably indicating intrusion into wet sediments. The shale on top of the lower sheet is massive suggesting that the emplacement of the andesite either upset already bedded shales, destroying the laminations, or caused redeposition of shales to give massive rather than laminated shales. A basaltic dyke at 30 m above the Upper Basalt and Andesite Sequence/Que River Shale contact (HL 246, Appendix 1), indicates that basaltic volcanism also occurred well after deposition of the main Que-Hellyer volcanics.

3.3.3 Pyrite

3.3.3.1 Petrography

Pyrite occurs in the Que River Shale as fine grained disseminations, concentrations along bedding plane laminations and as pyrite nodules of various shapes. Pyrite euhedra (cubes) also occur in cross-cutting carbonate and quartz-carbonate veins.

Fine grained disseminated pyrite in the Que River Shale occurs as euhedral crystals around (20-50 μm) and less commonly as clusters of fine grained (5-10 μm), rounded pyrite grains which form frambooids similar in size to the euhedral crystals (Plate 3).

Nodular pyrite varies from well-defined ovoid to elongate concretions, to irregularly shaped nodules and aggregates of equidimensional pyrite grains with euhedral to subhedral margins that contain internal massive to radiating pyrite crystals. In thin section, the nodules can be divided into two groups. The first group consists of ovoid to elongate concretions comprised of aggregates of fine grained (20μm) pyrite euhedra (Plate 4) that are concentrated along bedding laminations. Laminations pass through and wrap around the concretions. The second form of pyrite nodules comprise irregular aggregates of radiating-massive subhedral pyrite (Plate 5). In thin section, the nodules can be seen to have nucleated around frambooids of pyrite. Between the radiating massive pyrite, rounded pyrite nodules with rectangular to oval silicate centres and elongate pyrite nodules occur (Plate 6). These irregular aggregates are often rimmed by quartz fibres, and show fracturing with minor chalcopyrite occurring along fractures (Plates 6 & 7).
Rare macroscopic styles of pyrite in the Que River Shale include bedding parallel-laminated pyrite, and vein related pyrite. Bedding-parallel laminated pyrite is fine grained and has a sharp base and graded top. Vein pyrite occurs as distinct, well defined, striated cubes in quartz-carbonate veins and on fracture planes.

**Summary:** Four types of pyrite have been identified in the Que River Shale:
1. Fine grained disseminated pyrite.
2. Concretionary nodules.
3. Irregular aggregates of massive subhedral pyrite grains.
4. Vein pyrite.

### 3.3.3.2 Pyrite Interpretation

The fine grained pyrite disseminated throughout the Que River Shale probably represent syngenetic pyrite, although the framboids may be either syngenetic or early diagenetic.

The concretionary nodules are transected by laminations (Plate 4B) and have laminations wrapping around their ends (Plate 4A). These textures suggest that the concretions formed during diagenesis incorporating the sedimentary layers. Later in their history, differential compaction caused a warping of the laminations outside the nodule around the ends of the nodule, while the laminations inside the nodules were preserved.

The irregular aggregates are also transected by the laminations (Plate 7A) and show wrapping of the laminations around the nodules (Plate 7B). However, the laminations cannot be seen within these nodules. This indicates that the irregular aggregates are also diagenetic but may have had a longer formation history. This is supported by the fact that they show nucleation around framboids which would not be preserved if these nodules had undergone recrystallisation, as has previously been interpreted by mine geologists at Hellyer. The elongate pyrite crystals and rounded clasts with oval centres (Plate 6B), have been interpreted to represent the replacement of phyllosilicate minerals and microorganisms respectively which supports the protracted pyrite crystallisation of this nodule type.

The fracturing, quartz fibres (Fig. 6A & 7A) and minor chalcopyrite development on some nodules is probably related to deformation during the Tabberrabberan Orogeny.
PLATE 3

A. Pyrite framboid in shale matrix (MAC 31, 99.1m)
B. Pyrite framboids and euhedral crystals disseminated in shale (HL 345, 223.90m)
Both slides taken 40x magnification. Scale: A. 40 μm. B. 50 μm.
PLATE 4

Concretionary nodule made up of fine (20 μm) pyrite euhedra (HL 345, 223.90m).
A. The end of a concretionary nodule showing pyrite halo and the wrapping of laminations around the nodule.
B. The centre of a concretionary nodule, showing laminations transecting the nodule, parallel to bedding.
Both slides 2.5x magnification. Scale: 600 μm.
Irregular aggregate nodule, (etched), showing radiating-massive subhedral texture and central frambooidal pyrite.
Both slides from MAC 31, 99.1m. A. 2.5x magnification. Scale: 600 μm.
B. 10x magnification Scale: 150 μm.

PLATE 5
PLATE 6

A. Irregular aggregate nodule, (unetched), showing quartz fibres and fractured margin. B. Enlargement of A. showing the elongate pyrite nodules (E) and rounded clasts (R). Both slides from MAC 31, 99.1m. A 2.5x magnification. Scale: 600 µm. B. 20x magnification. Scale: 75 µm.
PLATE 7

A Irregular aggregate nodule showing transecting laminations and quartz fibres. HL 469B, 655.35m. Magnification 2.5x, Scale: 600 μm.

B. Irregular aggregate clasts showing transecting laminations and warping of laminations around the clast due to differential compaction. MAC 31, 99.1m. Magnification 2.5x, Scale: 600 μm.
3.3.4 Fossils

The Que River Shale contains a fossil fauna which includes hydroids, dendroids, agnostid trilobites, inarticulate brachiopods, various sponge spicules, one bradoriid specimen and a possible aglaspid specimen (Jago, 1977). Sponge spicules and an agnostid trilobite fragment were found in core; (Plate 2). The agnostid trilobites indicate a late Middle Cambrian age (Undillan or middle to late Menevian age; Jago 1973). Agnostid trilobites are considered to have been pelagic inhabitants of oceanic environments, where most non-agnostid trilobites were benthic inhabitants of neritic environments (Robinson 1972). At the Que River locality the trilobite fauna is limited entirely to agnostids, and is unusual in that it contains a large proportion of complete agnostid specimens. This high proportion of complete specimens, together with the presence of carbonaceous material and pyrite nodules, probably implies quiet, reduced bottom conditions. The lack of any polymerid trilobite fragments indicates that polymerids were rare or absent in the seas above the depositional area of the Que River Beds. Jago (1973) suggests that the seafloor may have been unsuitable for polymerid trilobites, but suitable for sponges and inarticulate brachiopods. This may have been due to the sea floor being too deep for the existence of polymerid trilobites. Jago (1973) interpreted the Que River fossil assemblage to represent a shelf margin-open sea setting, rather than a restricted environment.

3.3.5 Age and duration of sedimentation

Biostratigraphically the age of the Mount Read Volcanics (Fig. 10) is well controlled with all fossiliferous sedimentary units (Que River Shale and Tyndall Group) indicating a late Middle Cambrian age (Perkins and Walshe, 1993).

No fossils have been reported from sedimentary units underlying the Que River Shale. There is little doubt, however, that the Que River Shale is interbedded with the Mount Read Volcanics, even though the Mount Read Volcanics is partly comprised of intrusive units (Perkins and Walshe, 1993). The Mount Read Volcanics must therefore, at least in part, be upper Middle Cambrian (Gee et al., 1969).

Isotopic U-Pb and $^{40}$Ar/$^{39}$Ar dating of the Mount Read Volcanics yields a concordant age of $502.6 \pm 3.5$ Ma (Perkins and Walshe, 1993). No resolvable age differences have been obtained between units of the Mount Read Volcanics, with the possible exception of the Comstock Tuff (Tyndall Group) in the upper part of the volcanic sequence, or the Mount Black Dacite (Central Volcanic Complex). These units have weighted mean $^{206}$Pb/$^{238}$U ages of $494.4 \pm 3.8$ Ma and $494.9 \pm 4.3$ Ma, respectively, and may be slightly younger than the rest of the Mount Read Volcanics (Perkins and Walshe, 1993). The consistent ages imply that the Mount Read Volcanics were deposited rapidly, in a period of no more than a few million years. Relatively rapid emplacement of the succession is supported by the consistent ages of the faunal species.
3.3.6 Sedimentation Rate

Estimates of sedimentation rate and comparison with a modern analogue, have been made to quantify the deposition rate of the Que River Shale which until now has been thought to be relatively fast. It is reasonable to assume that deposition of the Que River Shale in the Que-Hellyer Basin was a protracted event, whereas the volcanics were erupted essentially instantaneously. The duration of Que River Shale deposition may therefore be assumed to be anywhere between 0.5 and 3 Ma based on the work of Perkins and Walshe (1992). Sedimentation rates for the Que River Shale have been calculated assuming an average thickness of 125 m for the Que River Shale giving compacted thicknesses.

For comparison with modern basins the uncompacted thickness was calculated using the method of Ruby and Hubbert, (1960; Appendix 1). This gave a compaction factor of 30% for the Que River Shale and uncompacted thickness 162.5 m which was used to calculate the uncompacted sedimentation rate. Table 2 lists estimates of the compacted and uncompacted thicknesses for the Que River Shale.

<table>
<thead>
<tr>
<th>Time of Deposition</th>
<th>Sedimentation rate (compacted)</th>
<th>Sedimentation rate (uncompacted)</th>
</tr>
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<tr>
<td>3 Ma</td>
<td>4.16 cm/kyr</td>
<td>5.4 cm/kyr</td>
</tr>
<tr>
<td>2 Ma</td>
<td>6.25 cm/kyr</td>
<td>8.125 cm/kyr</td>
</tr>
<tr>
<td>1 Ma</td>
<td>12.5 cm/kyr</td>
<td>16.25 cm/kyr</td>
</tr>
<tr>
<td>0.5 Ma</td>
<td>25 cm/kyr</td>
<td>32.5 cm/kyr</td>
</tr>
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</table>

A modern basin analogy for the Que-Hellyer basin is that of the Sumisu Rift in the Izu-Bonin Arc, Japan. The Sumisu rift (Fig. 11) is a 120 km long 30-50 km wide, early syn-rift stage assymetric back-arc basin bounded by normal faults, that is flanked to the east by volcanoes. ODP sites 790 and 791 were drilled on the western margin of the inner-rift graben. Both sites contained vesicular basalt (Fig. 12), interpreted as a syn-rift deep submarine eruption (Gill et al., 1990; Taylor et al., 1990). This was underlain in the inner arc basin (791) by tuffs interpreted as a sequence of island arc pyroclastic flows. Nannofossil-rich clay and claystones overlie the volcanics, and are in overlain by a thick sequence of puniceous and vitric gravels, sands and silts sourced from the basin margin volcanics (Taylor et al., 1991).

FIGURE 12: Stratigraphy of ODP leg 790, and similarity to Que-Hellyer sequence.
The sequence of deposition in the Sumisu rift is similar to the section of the Que-Hellyer basin (Fig. 12) considered during this study. Sedimentation rates in the Sumisu rift (not corrected for compaction) range from 90 mm/kyr to 4 m/kyr. Table 2 shows that the sedimentation rates for the Que River Shale are normal to low in the context of Sumisu rift basin. Thus the popular belief that the Que River Shale was deposited unusually rapidly is a misconception for shales in active volcanic arcs.

3.4 SOUTHWELL SUBGROUP

The Southwell Subgroup marks a return to active, pumice-rich, quartz-phyric felsic volcanism. The subgroup contains abundant mass-flow breccias and tuffaceous rocks intercalated with turbidite-type greywacke and siltstones (Pemberton et al., 1991). The Southwell Subgroup has been subdivided into seven sub-units by Corbett and Komyshan (1989): (1) lower tuff; (2) greywacke and siltstone; (3) felsic tuff; (4) greywacke and siltstone; (5) interbedded tuff, greywacke and siltstone; (6) greywacke and siltstone; (7) upper pumice-rich tuff and minor lava.

The lower tuff overlies the Que River Shale and is around 300 m thick on the Hellyer Haulage Road. Graded, pumice-bearing, quartz-feldspar-phyric crystal-vitric volcaniclastic beds up to 10 m thick that are separated by thin (< 0.2 m) intervals of black shale and siltstone, are typical of this sequence. Intervals up to 10 m thick of siltstone and greywacke also occur, as well as units up to 20 m thick of bedded crystal-vitric volcaniclastic rocks (Corbett and Komyshan, 1989).

The base of the lower tuff is exposed on a section of the Hellyer Haulage Road and in several drill holes (HL 026, HL 040, HL 246 and HL 469). It is represented by a graded lithic volcaniclastic bed that has an irregular erosional contact with the underlying Que River Shale. Flame structures of shale penetrate the basal volcaniclastic bed and in places (although not seen in core), and clasts of black shale up to 0.5 m long are prominent in the lower 3 m of the bed along the Haulage Road. The pumice clasts along the Haulage Road show reverse grading in the lower 2 m of the bed, increasing from 0.1 m long near the base to 1-2 m in length ~2 m above the base (Corbett and Komyshan, 1989). Reverse grading at the base of the beds is also seen in drill core. The pumice clasts contain large quartz and feldspar crystals in a sericitic groundmass, and are similar in composition to equidimensional, angular lithic clasts of cream to pink quartz-feldspar porphyry which occur in the lower part of the bed. Large quartz and feldspar grains are prominent in the matrix of the lower tuff. Lithic clasts, pumice clasts and quartz crystals become progressively less prominent in the upper part of the bed, where there is gradation through crystal-vitric volcaniclastic sandstone to fine grained, well-bedded vitric volcaniclastic sandstone and finally to grey-black siltstone (Corbett and Komyshan, 1989).
The presence of an erosional base and shale intraclasts, together with the overall grading of the unit, indicate that the lower tuff bed was deposited by a bottom-hugging mass-flow. The abundance of juvenile pumice clasts suggests that the flow was initiated by a pyroclastic eruption. Many other mass-flow beds of similar type and composition occur within the unit, indicating that similar eruptive events occurred repeatedly (Corbett and Komiysh, 1989). The deposition of the Que River Shale therefore probably did not cease, but was instead interrupted by the influx of mass flow breccias and tuffaceous turbidites, both of which have a mud matrix indicating that mixing with pelagic muds probably took place during transportation. This interpretation is supported by the presence of mud clasts in the tuff, the erosional base of the unit and the presence of shales between the volcanic units. Thus the Southwell Subgroup was deposited as a series of mass flow breccias and turbidites with background Que River Shale deposition.

3.5 SUMMARY

Black mudstone identical in lithofacies and composition to the Que River Shale began accumulating after the mineralising event which formed the Hellyer massive sulfide orebody and contemporaneous with the Mixed Sequence units. However, due to the eruption of the basalts and andesites of the Upper Basaltic and Andesitic sequence, the typical finely laminated nature of the Que River Shale was not preserved, except in parts of the basin which are distal to the erupting basalts. Thus, it was not until after the majority of the basaltic and andesitic volcanism ceased that deposition of the finely laminated shale which characterises the Que River Shale Formation began. Deposition of the Que River Shale was interrupted after a period of quiescence by the influx of mass flow breccias and volcaniclastic turbidites from an extrabasinal source. This transition from Que River Shale Formation to the Southwell Subgroup deposition occurred slowly at first with the emplacement of volcaniclastic layers in the top 20 m of the Que River Shale Formation. However the Que River Shale sediment was eventually swamped by the mass flow breccias and volcaniclastic turbidites allowing shales to accumulate only between the mass flows.

Three shale lithofacies associations have been identified and are represented on Figure 13.

(a) Lower massive to thickly bedded shale facies which is intercalated with fine to medium grained, quartz rich sandstones of the Mixed Sequence, and then andesites and basalts of the Upper Basaltic to Andesitic Sequence, with distal (away from the Hellyer orebody) laminated shales. The base of this facies occurs within the Mixed Sequence, above the Hellyer Ore deposit, while its top is at the contact between the Upper Basalts and Andesites and the Que River Shale Formation.
(b) The second shale facies is characterised laminated shale, with minor intercalated volcanioclastic sandstone. This facies lies above the Upper Andesites and Basalts, and is the Que River Shale formation as defined by Corbett and Komyshans (1989).

(c) The third shale facies, is also laminated but occurs as distinct but volumetrically minor intercalations between volcanioclastic mass-flows and turbidites of the Southwell Subgroup.

The depositional environment of the Que River Shale is interpreted to represent quiet, reducing bottom waters, due to the high proportion of complete agnostid trilobite specimens, along with the presence of carbonaceous material and pyrite nodules (Jago, 1973). This interpretation is very broad and limited by the known fossil assemblages. To further constrain the environment of deposition, geochemical methods will be applied in the next chapter. The morphology of pyrite clasts has been described and four types on pyrite identified, the interpretation will be reviewed in the light of geochemical and S-isotopic data.
Southwell Subgroup
very thick, massive to graded
pumice breccia; flow banded
ryolite; volcanic lithic breccia
and conglomerate; black
pyritic and grey micaceous
mudstone

Que River shale
black mudstone

Hellyer Basalt
massive and pillow basalt,
hyaloclastite breccia, peperite;
black mudstone

Mixed Sequence
dacite, polymict volcanic
breccia, volcanic sandstone
Feldspar-phyric sequence

KEY

Shale
Angular polymict clast
Rhyolite

Sandstone
Relic pumice
Basalt

Angular, juvenile lava
Fumice
Dacite

Mud intraclast
Andesite

FIGURE 13: Representative graphic log of the Hellyer stratigraphy, from the top of
the Feldspar-phyric sequence to the Base of the Southwell Subgroup. (Adapted from
McPhie et al., 1993)
CHAPTER 4

GEOCHEMISTRY OF THE QUE RIVER SHALE:
IMPLICATIONS FOR THE DEPOSITIONAL
ENVIRONMENT

4.1 INTRODUCTION

The environment of deposition of black shale can be constrained by palaeoecological methods, e.g. combining sedimentological criteria (degree of bioturbation) with observations on the mode of life and feeding strategies of benthic organisms (e.g. bivalves). However, the Que River Shale only has a limited fauna, including sessile hydroids, dendroids, sponges, and pelagic agnostid trilobites. The only burrowing inhabitants were the inarticulate brachiopods. The lack of bioturbation and impoverished fauna make it difficult to use the conventional environmental indicators to accurately determine the depositional environment of the Que River Shale.

In this chapter, chemical and isotopic parameters are used to further constrain the environment of deposition of the Que River Shale. The geochemical methods chosen are the ‘Degree of Pyritisation’ (Berner, 1970), the ratio of organic carbon to sulfide sulfur (Leventhal, 1983) and conventional sulfur isotope analyses of pyrite.

Twenty samples were chosen for Degree of Pyritisation and organic carbon to sulfide sulfur measurements. They consist of 15 samples of the Que River Shale Formation, 3 shales from the Southwell Subgroup and 2 shale from the Lower Shale Facies. None of the samples analysed contain pyrite nodules. However, all samples contain the fine grained (<20-50μm) frambooids and euhehedral crystals of pyrite found disseminated throughout the shale. This disseminated pyrite constitutes 5-10% of the shales composition (determined by XRD, Table 1). Samples for sulfur isotope analysis were picked for their sulfur clasts and the pyrite drilled out (Appendix 2).

4.2 DEGREE OF PYRITISATION INDEX

4.2.1 Preliminary Discussion

Degree of Pyritisation (DOP) was defined by Berner (1970) as a measure of the fraction of the reactive iron (HCl-soluble) in the sediment transformed to pyrite during diagenesis.
The OOP index (Fig. 14) was initially calibrated as a paleoenvironmental indicator of bottom water oxygenation for Devonian and younger rocks (Raiswell et al., 1988) but was extended to early Palaeozoic rocks by Raiswell and Al-Biatty (1989). Raiswell et al. (1987) found that aerobic sediments, i.e., those deposited in fully oxygenated bottom waters, will have a DOP \(< 0.42\) and can thus clearly be separated from restricted samples (those deposited in waters with low oxygen concentrations), which have DOP between 0.46 and 0.80. However the restricted samples have some...
overlap with the inhospitable bottom conditions (where little or no oxygen is present and H2S may be continually or intermittently present), which produce DOP values between 0.55 and 0.93.

### 4.2.2 Results

The method for DOP calculation is summarised in Appendix 2. HCl extractable Fe was determined by the method of Berner (1970) as modified by Raiswell et al. (1987). Fe contained within pyrite was determined via back calculation from sulfur values determined by XRF (Appendix 2). The results are shown in Table 3 and Fig. 14.

**TABLE 3: Sample number, Hole number and DOP values for selected Que River Shale samples. See Appendix 2 for position samples in drill core.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hole No.</th>
<th>% Reactive Fe</th>
<th>wt% Fe in Pyrite</th>
<th>DOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>HL246</td>
<td>1.2</td>
<td>3.57</td>
<td>0.75</td>
</tr>
<tr>
<td>27</td>
<td>HL469(SSG)</td>
<td>1.89</td>
<td>2.17</td>
<td>0.53</td>
</tr>
<tr>
<td>31</td>
<td>HL469(SSG)</td>
<td>1.8</td>
<td>12.38</td>
<td>0.87</td>
</tr>
<tr>
<td>58</td>
<td>HL469</td>
<td>1.59</td>
<td>4.5</td>
<td>0.74</td>
</tr>
<tr>
<td>63</td>
<td>HL469</td>
<td>1.28</td>
<td>7.59</td>
<td>0.86</td>
</tr>
<tr>
<td>100</td>
<td>HL469</td>
<td>1.37</td>
<td>8.32</td>
<td>0.86</td>
</tr>
<tr>
<td>119</td>
<td>HL469</td>
<td>1.05</td>
<td>4.98</td>
<td>0.83</td>
</tr>
<tr>
<td>131</td>
<td>HL469</td>
<td>3.01</td>
<td>2.69</td>
<td>0.47</td>
</tr>
<tr>
<td>133</td>
<td>MAC15</td>
<td>1.64</td>
<td>7.07</td>
<td>0.81</td>
</tr>
<tr>
<td>138</td>
<td>MAC15</td>
<td>1.64</td>
<td>10.53</td>
<td>0.86</td>
</tr>
<tr>
<td>141</td>
<td>MAC10</td>
<td>2.48</td>
<td>2.13</td>
<td>0.46</td>
</tr>
<tr>
<td>144</td>
<td>MAC10</td>
<td>1.53</td>
<td>4.94</td>
<td>0.76</td>
</tr>
<tr>
<td>150</td>
<td>MAC10</td>
<td>2.06</td>
<td>1.64</td>
<td>0.44</td>
</tr>
<tr>
<td>158</td>
<td>MAC11(SSG)</td>
<td>3.35</td>
<td>3.41</td>
<td>0.5</td>
</tr>
<tr>
<td>241</td>
<td>HL026</td>
<td>1.11</td>
<td>6.67</td>
<td>0.86</td>
</tr>
<tr>
<td>245</td>
<td>HL026</td>
<td>1.56</td>
<td>5.06</td>
<td>0.78</td>
</tr>
<tr>
<td>249</td>
<td>HL026</td>
<td>0.42</td>
<td>3.05</td>
<td>0.88</td>
</tr>
<tr>
<td>253</td>
<td>HL040</td>
<td>1.26</td>
<td>7.51</td>
<td>0.86</td>
</tr>
<tr>
<td>259</td>
<td>HL040</td>
<td>1.16</td>
<td>4.98</td>
<td>0.81</td>
</tr>
<tr>
<td>263</td>
<td>HL040</td>
<td>0.49</td>
<td>3.09</td>
<td>0.86</td>
</tr>
</tbody>
</table>
Figure 14 illustrates the results of DOP calculations on the Que River Shale. The Que River Shale exhibits two distinct populations. Population 1 occurs in the inhospitable field of Raiswell et al. (1987) with values between 0.739 and 0.878. All samples from this population with one exception occur in the Que River Shale Formation of Corbett and Komysshan (1989). The exception is a shale unit from the Southwell subgroup 45 m above the Que River Shale/Southwell Subgroup contact. The second population occurs in the restricted class of Raiswell et al (1987) and is composed of two samples from the Southwell Subgroup, two samples from the Que River Shale Formation (near the Tailings Dam Fault, Fig. 2) and a sample from the base of the Lower Shale Facies.

4.2.3 Interpretation

The high DOP values for Population 1 are interpreted to represent deposition in an inhospitable basin with little or no free oxygen present at the time of Que River Shale deposition. This interpretation is consistent with the lack of bottom-dwelling fauna, and the pyritic nature of the shales.

Population 2 lies in the restricted category, and is less easily explained. The variation in basin oxygenation which created population 2 may be explained by the influx of oxygen-rich waters with mass flow deposits in the Southwell Subgroup. It is interesting that the Southwell Subgroup samples...
that plot in the restricted category lie stratigraphically above the sample that plots in the inhospitable range (Fig 2.1, Appendix 2), indicating that the basin was still inhospitable during the deposition of the Southwell Subgroup. The basin probably became more hospitable during the deposition of at least the early part of the Southwell Subgroup with turbulent mass flows oxygenating the stagnant bottom waters. The sample from the base of the Lower Shale Facies that plots in the restricted field lies in an area surrounded by volcaniclastic mass flows which may have had a similar influence to the oxygenated mass flows of the Southwell Subgroup (lowering sulfate reduction in the water column and thus decreasing pyrite formation). Alternatively this sample may have been affected by alteration, as it lies just above a sheared zone. The samples from the Que River Shale Formation may also be affected by alteration as they lie near the Tailings Dam Fault.

4.3 ORGANIC CARBON TO SULFIDE SULFUR

4.3.1 Preliminary Discussion

If organic carbon is plotted against sulfide sulfur for modern environments, three patterns emerge (Fig. 15). Normal marine environments give a straight-line correlation passing through the origin, reflecting that the amount of sulfur converted from sulfate to sulfide by bacteria is controlled by the amount of organic carbon they have to use as a food source (Fig. 15). In freshwater environments (where sulfate is sparse), the amount of sulfate is rate limiting, and a distribution of points close to the organic carbon axis, that passes through the origin is seen (Fig. 15). Under euxinic conditions, bacterial sulfate reduction occurs in the sediments and in the water column due to the presence of free H2S. This results a poor correlation between organic carbon and sulfide sulphur, generally with a positive intercept on the Y axis, and with high sulfide sulfur content at low organic carbon.

4.3.2 Results

Organic carbon was determined by the ‘ashing’ method of Krom and Berner (1982). Carbon (total) and sulfur analyses were performed on the Karlo Erber Elemental Analyser (Appendix 2). The results are summarised in Table 4 and on Figure 16a.
TABLE 4: Weight percentage of organic carbon and sulfide sulfur obtained from selected samples from the Que River Shale.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Hole No.</th>
<th>%Corg</th>
<th>%S</th>
<th>C/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>HL246</td>
<td>0.495</td>
<td>1.06</td>
<td>0.47</td>
</tr>
<tr>
<td>27</td>
<td>HL469(SSG)</td>
<td>0.099</td>
<td>0.44</td>
<td>0.23</td>
</tr>
<tr>
<td>31</td>
<td>HL469(SSG)</td>
<td>0.306</td>
<td>2.96</td>
<td>0.10</td>
</tr>
<tr>
<td>58</td>
<td>HL469</td>
<td>0.336</td>
<td>0.96</td>
<td>0.35</td>
</tr>
<tr>
<td>63</td>
<td>HL469</td>
<td>0.415</td>
<td>1.57</td>
<td>0.26</td>
</tr>
<tr>
<td>100</td>
<td>HL469</td>
<td>0.464</td>
<td>1.86</td>
<td>0.25</td>
</tr>
<tr>
<td>119</td>
<td>HL469</td>
<td>0.346</td>
<td>1</td>
<td>0.35</td>
</tr>
<tr>
<td>131</td>
<td>HL469</td>
<td>0.236</td>
<td>0.58</td>
<td>0.41</td>
</tr>
<tr>
<td>133</td>
<td>MAC15</td>
<td>1.013</td>
<td>1.72</td>
<td>0.59</td>
</tr>
<tr>
<td>138</td>
<td>MAC15</td>
<td>0.66</td>
<td>2.42</td>
<td>0.27</td>
</tr>
<tr>
<td>141</td>
<td>MAC10</td>
<td>0.0109</td>
<td>0.51</td>
<td>0.02</td>
</tr>
<tr>
<td>144</td>
<td>MAC10</td>
<td>0.287</td>
<td>1.16</td>
<td>0.25</td>
</tr>
<tr>
<td>150</td>
<td>MAC10</td>
<td>0.109</td>
<td>0.14</td>
<td>0.78</td>
</tr>
<tr>
<td>158</td>
<td>MAC11(SSG)</td>
<td>0.129</td>
<td>0.83</td>
<td>0.16</td>
</tr>
<tr>
<td>241</td>
<td>HL026</td>
<td>0.533</td>
<td>0.92</td>
<td>0.58</td>
</tr>
<tr>
<td>245</td>
<td>HL026</td>
<td>0.601</td>
<td>1.24</td>
<td>0.48</td>
</tr>
<tr>
<td>249</td>
<td>HL026</td>
<td>0.138</td>
<td>0.49</td>
<td>0.28</td>
</tr>
<tr>
<td>253</td>
<td>HL040</td>
<td>0.806</td>
<td>1.76</td>
<td>0.46</td>
</tr>
<tr>
<td>259</td>
<td>HL040</td>
<td>0.72</td>
<td>0.99</td>
<td>0.73</td>
</tr>
<tr>
<td>263</td>
<td>HL040</td>
<td>0.178</td>
<td>0.52</td>
<td>0.34</td>
</tr>
</tbody>
</table>
FIGURE 15: Plot of organic carbon against sulfide sulfur showing the relationship between freshwater, normal marine and euxinic environments, (from Shultz, 1991). Fields show the scatter of point within individual environments, (from Leventhal, 1983; and Raiswell and Al-Biatty, 1989).

FIGURE 16a: Scatter plot of weight percent organic carbon versus sulfide sulfur for selected samples of the Que River Shale.
FIGURE 16b: Scatter plot of weight percentage organic carbon versus sulfide sulfur for population 1 (as defined in Fig. 14).

FIGURE 16c: Scatter plot of weight percentage organic carbon versus sulfide sulfur for population 2 (as defined in Fig. 14).
Based on the OOP calculations, the samples have been divided into two populations, population 1 (Fig. 16b) and Population 2 (Fig. 16c). The first population is widely scattered (%Corg 0.138 to 1.105 and %S 0.49 to 3.59) with a poor correlation between organic carbon and sulfur, that corresponds to the inhospitable field of Raiswell and Berner (1987), suggesting a euxinic environment of deposition. The second population has lower, more restricted range of organic carbon content (<0.25) and sulfur content (<0.9), making its environment of deposition harder to determine. Based on the positive slope and the distribution of points (Fig. 16c) population 2 is assumed to have formed under normal marine to slightly euxinic conditions. The second population corresponds to the restricted category of Raiswell and Berner (1986).

4.3.3 Discussion

The variations between the normal marine and euxinic C-S plots are a function of pyrite formation in the two environments. In normal marine environments, H2S is only produced by bacterial sulfate reduction below the sediment-water interface. As a result, for most normal marine sediments that contain adequate detrital iron, the principal limiting factor for pyrite formation is the amount of buried organic matter. All pyrite is formed diagenetically, and a good correlation between pyrite content and residual organic matter content is found.

In euxinic environments, H2S occurs in the water column as well as below the sediment water interface. Consequently, pyrite can be formed from detrital iron minerals prior to burial (syngentic pyrite), either in the water column or at the sediment-water interface. In euxinic environments, organic carbon is not needed for pyrite formation, leading to the common association of high pyrite sulfur and low organic carbon. The limiting factor for pyrite formation under these conditions is the amount of reactive detrital iron available.

4.4 DOP VERSUS ORGANIC CARBON RELATIONSHIP

Plots of DOP against organic carbon have been successfully used to determine the environment of deposition of shale (Raiswell and Berner, 1985). In normal marine environments a strong positive correlation is noted between DOP and Organic Carbon (Fig. 17a) due to the relationship of organic carbon and diagenetic pyrite formation.

In euxinic environments bacterial reduction of organic carbon is not required, which leads to constant DOP values independent of organic carbon (Fig. 17b), limited only by the availability of detrital iron.
FIGURE 17: Plot of DOP against organic carbon for (A) diagenetic pyrite formation in normal marine environments (B) syngenetic pyrite formation in euxinic environments. (From Raiswell and Berner, 1985).
FIGURE 18: Plot of organic carbon against DOP for 15 samples of the Que River Shale Formation (squares), 3 shales from the Southwell Subgroup (diamonds) and 2 shale from the Lower Shale Facies (circles). Data is split into two populations as determined by DOP index.

Figure 18 shows that the two populations plot in distinct fields. The flat linear trends suggest syngenetic origins for the in each population, although the restricted range of values for population 2 makes this less convincing.

Summary: Population 1 is interpreted to represent inhospitable conditions (Fig. 14), that based on the spread of data Figure 16b, were euxinic and resulted in syngenetic pyrite formation. Population 2 is interpreted to represent restricted conditions (deposited in water with little or no oxygen present), and from Figure 16c a normal marine to slightly euxinic environment for pyrite deposition is interpreted. The narrow range %S (<0.6) and %C (<0.3) for population 2 make it difficult to establish if pyrite formation was purely syngenetic or if there was a component of diagenetic pyrite (Fig. 17). Because sulfur and organic carbon concentrations are low, both would impose limiting behaviour on pyrite formation. Note: Interpretations presented here apply only to the fine grained (20-50 μm) framboids and euhedral crystals of pyrite found disseminated throughout the shale.
4.5 SULFUR ISOTOPES

4.5.1 Previous Work

Sulfur isotope studies in the Hellyer-Que River area began with the work of Solomon et al., (1969). In more recent times, work has concentrated on isotopic variations in the alteration zones (Jack, 1989), the stringer system and alteration zone (McGoldrick, 1988; Jack, 1989; Gemmell and Large, 1992 McGoldrick and Large, 1992), the massive sulfide orebody (Gemmell and Large, 1992) and the barite and siliceous caps (Sharpe, 1991) at Hellyer. These studies which are summarised in Figure 19 (after Gemmell and Large, 1992), found that the $\delta^{34}$S of the ore forming fluids was between 4 and 9 permil with values of sulfides in the orebody between 7 to 8 permil. At both Hellyer and Que River an increasingly heavy $\delta^{34}$S values out from the centre of the stringer zone to values between 10 and 40 permil is observed and is interpreted to reflect an increased seawater sulfate component. The sulfur source for the Hellyer massive sulfide ore is therefore interpreted to be a mixture of evolved seawater sulfate, rock sulfate leached from the underlying Que-Hellyer Volcanics and possibly a component from deeper upwelling fluids (McGoldrick, 1988; Gemmell and Large, 1992; McGoldrick and Large, 1992).

![Figure 19: Summary of sulfur isotope values determined from the Hellyer massive sulfide deposit and surrounding host rocks from Gemmell and Large, (1992).](image-url)

4.5.2 Methodology and Results

Eighteen pyrite samples, 15 from the Que River Shale and 3 from the lower Shale Facies were selected for sulfur isotope analyses with out regard to their genesis. The sulfur analyses were performed by conventional methods in the Central Science Laboratory at the University of Tasmania.
The results are summarised in Table 5 and Figure 20 (distribution plotted on Fig. 2.2 Appendix 2).

TABLE 5: Sulfur isotope samples and results for selected pyrite samples from the Que River Shale and * from Lower Shale Facies.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>HOLE No.</th>
<th>DEPTH (m)</th>
<th>PYRITE TYPE</th>
<th>δ³⁴S</th>
</tr>
</thead>
<tbody>
<tr>
<td>25A</td>
<td>HL246</td>
<td>183.1</td>
<td>nodule</td>
<td>36.2</td>
</tr>
<tr>
<td>65</td>
<td>HL469B</td>
<td>655.35</td>
<td>nodule</td>
<td>23.3</td>
</tr>
<tr>
<td>68</td>
<td>HL469C</td>
<td>1069.4*</td>
<td>nodule</td>
<td>34.0</td>
</tr>
<tr>
<td>80</td>
<td>BRD1</td>
<td>221.3</td>
<td>nodule</td>
<td>33.3</td>
</tr>
<tr>
<td>81</td>
<td>BRD1</td>
<td>226.4</td>
<td>nodule</td>
<td>35.4</td>
</tr>
<tr>
<td>118A</td>
<td>HL469C</td>
<td>1024*</td>
<td>nodule</td>
<td>40.9</td>
</tr>
<tr>
<td>154</td>
<td>MAC10</td>
<td>449*</td>
<td>nodule</td>
<td>7.5</td>
</tr>
<tr>
<td>161</td>
<td>MAC11</td>
<td>243.5</td>
<td>nodule</td>
<td>17.0</td>
</tr>
<tr>
<td>162</td>
<td>MAC11</td>
<td>244.8</td>
<td>nodule</td>
<td>22.8</td>
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<tr>
<td>183</td>
<td>MAC31</td>
<td>98.4</td>
<td>nodule</td>
<td>42.9</td>
</tr>
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<td>184</td>
<td>MAC31</td>
<td>99.1</td>
<td>nodule</td>
<td>43.0</td>
</tr>
<tr>
<td>221</td>
<td>HL345</td>
<td>87.25</td>
<td>nodule</td>
<td>25.9</td>
</tr>
<tr>
<td>228</td>
<td>HL345</td>
<td>214.6</td>
<td>laminated</td>
<td>22.2</td>
</tr>
<tr>
<td>229</td>
<td>HL345</td>
<td>223.9</td>
<td>nodule</td>
<td>23.8</td>
</tr>
<tr>
<td>231</td>
<td>HL345</td>
<td>144.8</td>
<td>vein</td>
<td>22.9</td>
</tr>
<tr>
<td>233</td>
<td>HL345</td>
<td>232.9</td>
<td>mixed</td>
<td>-7.7</td>
</tr>
<tr>
<td>239</td>
<td>HL026</td>
<td>31.9</td>
<td>laminated</td>
<td>41.3</td>
</tr>
<tr>
<td>249</td>
<td>HL026</td>
<td>156.9</td>
<td>nodule</td>
<td>40.7</td>
</tr>
</tbody>
</table>
Most of the samples have $\delta^{34}\text{S}$ values 17.0 to 43.0 permil, with an average $\delta^{34}\text{S}$ of 31.7 permil. These values come from a variety of pyrite forms. There are two exceptions to this range, the lowest value (-7.7 permil) comes from a sample at the contact with the basalt (Fig. 20), and consists of pyrite concretions and disseminated pyrite. The other sample below the main range of values (+7.5) comes from a shale unit in the footwall andesites and basalts, and consists of a concretion of fine grained pyrite in a silty bed, with a halo of fine pyrite.

### 4.5.3 Interpretation

The lowest $\delta^{34}\text{S}$ value of -7.7 permil lies at the shale basalt contact and is consistent with the value of $\delta^{34}\text{S}$ -7.9 permil obtained by Jack (1989) for pyrite in basalt at shale contact. Jack (1989) also found $\delta^{34}\text{S}$ values averaging -13.7 with a range of -9.6 to -16.3 for interpillow hangingwall basalts underlying the Que River Shale. The source of sulfur in this pyrite is most likely to be seawater, with the negative values being consistent with open system bacterial sulfate reduction (Ohmoto and Rye, 1979). Jack (1989) postulated that heat and nutrients from the underlying basalts enhanced bacterial activity in the sediments in and around the basalts, causing fractionations of 40-50 permil from the +30 permil value of $\text{SO}_4^{2-}$ obtained for Cambrian seawater (Claypool et al., 1980). The observation that pyrite is the only sulfide to develop in the interpillow areas suggests that base metal rich hydrothermal fluids did not contribute to mineral deposition in the interpillow areas (Jack, 1989).

Two samples ($\delta^{34}\text{S}$ 40.9) and ($\delta^{34}\text{S}$ 34) both come from the Lower Shale Facies of chapter 3 and show that where Que River Shale deposition occurred distal to basalt deposition, its signature was
similar to that of the overlying Que River Shale and not controlled by the enhanced bacterial reduction fed by the nutrients from the basalt pile as is seen in samples from the basalt pile.

The sample of vein pyrite analysed has a $\delta^{34}S$ of 22.9 suggesting that this was probably sourced from the Que River Shale by leaching of sulfur, carbonate and quartz from the shale and depositing these minerals along fracture planes.

The interpretation of sulfur isotopes in the major group can be divided into two groups. The lower half of the group ($\delta^{34}S$ 17.0-30 permil) is consistent with a sample of Que River Shale with $\delta^{34}S$ 15.7 from Jack (1989) and can be explained by bacterial reduction of sulfate from Cambrian seawater. However the increase in $\delta^{34}S$ values of 35.0-43.0 permil are harder to explain. Thin section work has revealed evidence of two generations of pyrite within the nodules used for sulfur isotope analysis. Concretionary samples tend to have lower $\delta^{34}S$ value (17-30) and are interpreted to have formed during early diagenesis by bacterial sulfate reduction of seawater in sediment pore water before compaction. During diagenesis a second pyrite formation occurred forming aggregates of equidimensional massive pyrite grains with euhedral to subhedral margins. These samples tend to have higher $\delta^{34}S$ values suggesting that the sediment may have become a closed system during diagenesis allowing the light sulfur to be used up during the deposition of the disseminated sulfides and concretions and leaving heavy sulfur to form the latter aggregates.

Ohmoto and Rye (1979) suggested that if a system was closed to $SO_4^{2-}$ and $H_2S$ then the light sulfur isotopes would preferentially be used up by pyrite deposition early on, creating a progressively heavy reservoir of sulfur and causing the latter formed sulfides to be enriched in heavy sulfur (Fig. 21). A likely scenario for the Que River Shale is that of seawater sulfate with an average $\delta^{34}S$ of +30 permil. In an open system pyrite formation would draw on the light sulfur preferentially creating $\delta^{34}S$ values of +10 to -20 as is seen in the basalt pile. However if the system became closed to $SO_4^{2-}$ and $H_2S$, as is likely in a sediment pile with the only fluid movement being dewatering, then the $\delta^{34}S$ values would increase as the light sulfur was progressively used up. During early diagenesis the pyrite $\delta^{34}S$ would average 17 to 30 permil while later formed pyrite would have $\delta^{34}S$ of 30 to 40 permil.

An alternative model for formation of the heavy sulfur is an evaporite replacement model. Sulfate evaporites forming from concentration of surface water of the present day are enriched 1-2 permil in $\delta^{34}S$ relative to dissolved sulfate (Claypool et al, 1979). If the heavy pyrite nodules in the Que River Shale formed by the replacement of evaporitic minerals in the shale then an increase in $\delta^{34}S$ values would be expected. There is no direct evidence of evaporitic minerals in the Que River Shale although one sample from XRD analysis showed 5% dolomite. A shift of 1-2 permil for sulfate in evaporitic minerals assumed by Ohmoto and Rye (1979) may explain the values of 35-40 permil observed if the system were closed to $SO_4^{2-}$ and $H_2S$. 

53
Figure 21: Isotopic relationship between coexisting sulfate and sulfide as a function of \( \frac{\sum \text{SO}_4^{2-}}{\sum \text{H}_2\text{S}} \).

4.6 SUMMARY

During the deposition of the Upper Basalts and Andesites of the Que Helleyer Volcanics periods the Que-Hellyer basin was normal marine to restricted indicating that oxygen contents of the water column were often low. The volcanic pile was an open system with seawater circulation supplying light seawater sulfate for pyrite deposition.

During the quiescent phase in which the Que River Shale was deposited the Que-Hellyer basin became inhospitable (little or no free oxygen present) to euxinic (free \( \text{H}_2\text{S} \) present). Pyrite was deposited syngenetically from the euxinic water column forming framboids and euhedral pyrite crystals. Diagenetic pyrite also occurred initially forming concretions of fine grained pyrite and latter aggregates of equidimensional massive grains with euhedral to subhedral grain boundaries. These aggregates tend to have higher \( \delta^{34}\text{S} \) values than the concretions suggesting the sediment pile was a closed system with respect to \( \text{SO}_4^{2-} \) and \( \text{H}_2\text{S} \). The Que-Hellyer basin reverted to a normal marine to
restricted environment after the deposition of the Que River Shale with the influx of the Southwell Subgroup volcanic mass flow units.
CHAPTER 5
WHOLE ROCK GEOCHEMISTRY
PROVENANCE
AND
DISTRIBUTION OF ELEMENTS

5.1 INTRODUCTION

Whole rock geochemical analyses were performed on 51 samples of shale for a suite of 28 elements. The samples consist of 37 from the Que River Shale Formation, 9 unaltered samples from the Lower Shale Facies, and 5 from shale units in the Southwell Subgroup.

The aims of the whole rock analyses were to:
1) Characterise the Que River Shale in terms of its elemental composition
2) Suggest a provenance for the Que River Shale
3) Investigate the spatial distribution of elements throughout the Que River Shale.
4) Investigate if the hangingwall fuchsite carbonate halo recognised in the Hellyer basalt extends in to the Que River Shale Formation.

Major and trace elements were analysed by XRF spectrometry in the Geology Department at the University of Tasmania, using an automated Philips PW 1480 X-Ray spectrometer. Analytical methods are described in Appendix 2.

5.2 CHARACTERISATION OF THE QUE RIVER SHALE

5.2.1 Average Composition

The average composition of the Que River Shale Formation, the Lower Shale Facies and shales in the Southwell Subgroup are presented in Table 6. The mode for the analyses of the Que River Shale Formation is given as an indication of the central tendency of the values obtained as the mean is sensitive to extreme values, and may not indicate the central tendency in a distribution.
TABLE 6: Summary of the range of major element compositions for the Que River Shale Formation, and for comparison, the mean analyses for the Lower Shale Facies and Southwell Subgroup shales are presented. All shale analyses are presented in Appendix 2.

<table>
<thead>
<tr>
<th>Element</th>
<th>Que River Shale Formation</th>
<th>Lower shale Facies</th>
<th>Southwell Subgroup</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>66.06</td>
<td>66.14</td>
<td>64.52</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.56</td>
<td>0.6</td>
<td>0.69</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>11.99</td>
<td>12.22</td>
<td>12.5</td>
</tr>
<tr>
<td>FeO⁺</td>
<td>5.16</td>
<td>5.13</td>
<td>6.03</td>
</tr>
<tr>
<td>MnO</td>
<td>0.05</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>MgO</td>
<td>2.43</td>
<td>2.53</td>
<td>2.7</td>
</tr>
<tr>
<td>CaO</td>
<td>2.03</td>
<td>1.95</td>
<td>3.14</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.3</td>
<td>0.2</td>
<td>0.56</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.86</td>
<td>2.78</td>
<td>2.92</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.13</td>
<td>0.12</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Table 6 shows that the Que River Shale is compositionally consistent with little variation between the mean and mode values. The maximum and minimum values show less than 5% variation in the values for major elements, indicating that the unit is homogeneous. Mean values for the Lower Shale Facies and the shale units within the Southwell Subgroup are similar to the mean for the Que River Shale Formation, and occur within the range of Que River Shale analyses, indicating that these units had a similar source and post-depositional history to the Que River Shale Formation.

5.2.2 Covariance

To determine if there are correlations or variations between the major elements analyses, the covariances for the Que River Shale analyses were calculated. A centred log-ratio covariance matrix (Aitchison, 1986) was used to circumvent the effect of constant closure in the data. The principle consequence of closure being a negative bias induced between SiO₂ and all other major elements, by the abundance of SiO₂ in the Que River Shale (Rollinson, 1993). The statistical analysis shows that there is little variation between the elements (Table 3 Appendix 2), with a weak correlation between K-Al-Ti-Si-Fe, and minor variations of CaO and Na₂O.

The correlation between K, Al, Ti, Si and Fe is typical of clastic sequences. The variations of CaO and Na₂O are probably related to alteration (calcite veining and slight albitization). Overall the
results indicate the Que River Shale is compositionally consistent, the minerals being homogenised by sedimentary processes during deposition, producing little stratigraphic variation.

### 5.2.3 Frequency Distribution

To characterise the concentration variability and distribution of elements in the Que River Shale, the frequency distribution (Fig. 23) for each oxide and element analysed (except thallium, selenium, and cadmium which are generally below the detection limit) were determined. Frequency distributions are plotted against the midpoints of distribution range used to determine the distribution, using the method of Quinnby-Hunt et al., (1989). The frequency distributions (Fig. 23) show that the majority of the oxides and elements are unimodal, with the exception of CaO, Na2O, P2O5, Pb, Zn and Ni, which have complex frequency distributions.

Unimodality of elements suggests a well-defined depositional environment with respect to that element (Quinby-Hunt and Wilde, 1991). The most likely environmental interpretation is that the source composition is the major factor affecting the composition of the shale, and that all shales have been affected by depositional, diagenetic and post-diagenetic processes in a similar manner. Complex frequency distributions indicate that elements vary independently of the basic detrital shale component in the depositional environment (Quinby-Hunt and Wilde, 1991). Variations in element concentrations may be associated with redox conditions, biological activity (P2O5), presence of organic matter, or volcanic component (Pb, Zn). Na is highly mobile and multimodality of Na2O (Fig. 23) is probably related at least in part to processes occurring during the weathering of the source rocks to produce the Que River Shale. CaO variation is probably related to post-diagenetic quartz-carbonate veining rather than fractionation of CaO during weathering and transport of the shale components. The multimodality of Pb, Zn and Ni in shales worldwide is commonly associated with pronounced multimodality in other elements such as V, Mn, Fe, As, Se, Mo, Sb, Ba, and U (Quinby-Hunt and Wilde, 1991). This multimodality is induced by variations in redox condition, biological activity or the presence of organic matter. However, in the Que River Shale these elements are unimodal suggesting an alternate cause for the multimodal elements (this will be investigated in later sections.).
<table>
<thead>
<tr>
<th>Abundance in PPM</th>
<th>Percent Frequency</th>
<th>Percent Frequency</th>
<th>Percent Frequency</th>
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<tr>
<td></td>
<td>2</td>
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</tbody>
</table>

**FIGURE 23:** Frequency distributions - Continued
FIGURE 23: Frequency distribution - Continued
FIGURE 23: Frequency Distribution - Continued
5.3 PROVENANCE

5.3.1 Introduction

Igneous petrologists commonly use chemical variation diagrams to ascertain the tectonic environments of magmatism. Immature sediments derived from such igneous rocks would potentially have the same signature and could be used in provenance studies (Rollinson, 1993). The degree to which individual elements are affected by erosion, redeposition, diagenesis and, low-grade metamorphism will control the applicability of sediment geochemistry to provenance studies (Quinby-Hunt and Wilde, 1991).

Lavas of the Mount Read Volcanics are dominated by rhyolites and dacites, with locally abundant andesites and basalts (McPhie and Allen, 1992). In the study area, the Que River Shale is underlain by the footwall andesites and hangingwall basalts of the Que-Hellyer Volcanics and overlain by the predominantly rhyolitic Southwell Subgroup (Fig. 6).

Crawford et al. (1992) identified two broad magma associations in the Mount Read Volcanics: (1) A calc-alkaline association defined by a progressive decrease in FeO and TiO₂ and Ti/Zr with increasing fractionation, (i.e. increasing SiO₂ content or FeO/MgO ratio); (2) A tholeiitic association which shows a broad general increase in FeO and TiO₂ with fractionation. When the Que River Shale samples were plotted on TiO₂ versus SiO₂ and FeO versus SiO₂ diagrams (Fig. 24A, B) they show a decrease in TiO₂ and FeO with increasing SiO₂, suggesting a calc-alkaline volcanic provenance.
Crawford et al. (1992) has further subdivided the calc-alkaline association into three suites using a $P_{2}O_{5}/TiO_{2}$ versus $SiO_{2}$ diagram (Fig. 25). The Que River Shale samples clearly plots in the suite I field of figure 25.

FIGURE 25: $P_{2}O_{5}/TiO_{2}$ versus $SiO_{2}$ for Que River Shale samples, also showing the fields of Crawford et al. (1992) for suites 1-5.
It is clear from figure 25 that the Que River Shale is primarily sourced from suite I calc-alkaline volcanics of the Mount Read Volcanics. To determine the exact provenance of the Que River Shale, whole rock geochemical analyses were plotted against suite I andesites and rhyolites of Crawford et al. (1992). The suite I analyses were divided into two groups.

- **Group I** consisting of: Central Volcanic Complex andesitic to rhyolitic lavas from north of the Henty fault
- Felsic lavas from the Central Volcanic Complex south of the Henty Fault
- Andesites from the Henty Fault Wedge
- Lavas from the Que-Hellyer footwall sequence and Quartz-Feldspar Porphyries from the Yolande River Sequence.

The second group is dominantly dacites and rhyolites, and includes:
- Granitoids of the Eastern Quartz-Phyric Sequence
- Tyndall Group dacites and rhyolites and
- Rhyolites of the Southwell Subgroup.

### 5.3.3 Major Elements

Harker variation diagrams of major elements indicate that the Que River Shale lies within the range for andesites to rhyolites of suite I and follows the fractionation trends of andesites towards rhyolites (Figs. 26, 27, 28 and 29).

CaO variations (Fig. 26) may be explained by Ca mobility in sedimentary environments and/or the presence of fine carbonate veins in the Que River Shale. These veins were generally too fine to be removed by hand picking during sample preparation (Appendix 2).

The Que River Shale consists predominantly of quartz, muscovite, chlorite and pyrite (Table 1). Andesitic volcanics are predominantly plagioclase, pyroxene, hornblende and oxide minerals with minor olivine or quartz in the form of phenocrysts, glass and ash (Gill, 1981). The correlation between K₂O, FeO and MgO (Fig. 27A, B, C) in the andesites and the shale can be accounted for by glass (K₂O) being converted to muscovite (sericite) during alteration, and ash (FeO and MgO) being altered to chlorite preserving these potentially mobile elements in the sediment.

TiO₂ and P₂O₅ (Fig. 28A, B) are generally considered to be immobile in aqueous fluids (Rollinson, 1993), so they should show the same distribution in the sediment as the source rocks. Two anomalously high values of P₂O₅ (Fig 28B) may be explained by the presence of phosphatic concretions in sediment which were undetected during sampling.

Al₂O₃ and Na₂O (Fig. 29A, B) show significant depletions with respect to the andesites and basalts of suite I. The low concentrations of Al₂O₃ and Na₂O can be explained mineralogically. Plagioclase comprises 3-20 modal percent of andesites and contains Al₂O₃ and Na₂O (Crawford pers.
If albite was removed from the sediment during weathering then Al₂O₃ and Na₂O would be lost. This is supported by the low albite content of the Que River Shale (0-5%).

![Harker variation diagram CaO versus SiO₂](image)

**FIGURE 26:** Harker variation diagram CaO versus SiO₂. Symbols: Squares suite: 1B andesites to rhyolites; Diamonds: suite 1B dacites to rhyolites; Triangles: Que River Shale Formation.
FIGURE 27: Harker variation diagram for K$_2$O, FeO and MgO. Symbols as for Fig. 26.
FIGURE 28: Harker variation diagrams for TiO$_2$ and P$_2$O$_5$. Symbols as for Fig. 26.
FIGURE 29: Harker variation diagrams for Al₂O₃ and Na₂O. Symbols as for Fig. 26.
5.3.4 Trace Elements

Trace elements such as Sc, Zr and Y are commonly considered immobile and should not be affected significantly by sedimentary processes (Quinby-Hunt and Wilde, 1991). They are therefore potentially reliable for determining the provenance of sediments. Sc from the Que River Shale Formation mimics the fractionation trend of the andesites (Fig. 30A) supporting the interpretation of an andesitic to dacitic regime. However, Y and Zr show depletion similar to that of Al₂O₃ suggesting they may have been mobilised during sedimentation and therefore are not reliable provenance indicators for the Que River Shale.
FIGURE 30: Variation diagrams for Sc, Zr and Y from the Que River Shale. Symbols as for Fig. 26.
Variation diagrams for the trace elements Cr, V and Ni (Fig 31 A, B, C) show that these three elements all appear to be enriched in the Que River Shale compared to the andesites, dacites and rhyolites of suite 1 (Crawford et al., 1992). The high Cr contents found in the Que River Shale may be derived from clinopyroxene-rich ankaramitic basalts (with up to 1.3% Cr$_2$O$_3$ in the clinopyroxene) such as the Hellyer Basalt (Crawford et al., 1992).

Enrichment of V in shales can occur either via complexing with organic matter which is then incorporated into the sediment, or by reduction of V(IV) to V(III) in euxinic waters. Under natural conditions, only H$_2$S is known to reduce V(IV) to V(III), an oxidation state that favours incorporation of vanadium into clay minerals (Breit et al. 1988). Because the Que River Shale is interpreted to be euxinic (chapter 4), there is potential for either method of V enrichment to occur.

Ni is enriched in some metalliferous black shales, together with V, Cu, Cd, Mn, Zn, and As (Conveney and Nansheng, 1991). In some cases, enrichment may be due to organic activity or organic carbon in the sediments, but in economically mineable metalliferous black shales (eg. China; Conveney and Nansheng, 1991) the transition metals are interpreted to be sourced from submarine hot springs or heated fluids which leached metals from basement sources and exhaled them into the water column (Pasava 1991). Euxinic bottom waters then caused efficient trapping of metals by reduction and preservation of organic matter and associated metals. Considering the geology of the Hellyer area, with the known presence of massive sulfide ores interpreted to be derived by exhalation of hydrothermal fluids on to the sea floor, it is not unreasonable to assume the Ni enrichments in the Que River Shale may be related to hydrothermal fluids in the basin.
FIGURE 31: Variation diagrams for selected trace elements from the Que River Shale showing enrichment in Que River Shale Samples. Symbols as for Fig. 26.
5.3.5 Principal Component Analysis

To fingerprint the source rocks for the Que River Shale, a principal component analysis was performed using average values for 7 units from the Northern Mount Read Volcanics (Rollinson, 1993). The average compositions of the Northern Central Volcanic Complex, Que Footwall Sequence, Eastern Quartz-phyric Sequence and Tyndall Group were taken from Crawford et al. (1992). The Southwell Subgroup and Hellyer Basalt compositions were obtained from Jack, (1989). Que River Shale analyses from the current study were used also in this analysis.

The principle component analysis suggests that the Que River Shale cannot be derived directly from any single source, or from a combination of these sources without significant modification. The only quantification that can be placed on source rocks is that the Que River Shale must be at least 20-25% derived from the Hellyer Basalt to obtain the high Cr values observed (up to 1.3wt% Cr$_2$O$_3$). The Que River Shale is therefore most likely to be derived from a combination of local volcanic and volcanioclastic sources, including 20-25% Hellyer Basalt. The resulting sediment has been efficiently homogenised during transport to give a compositionally consistent unit.

5.4 DISTRIBUTION OF ELEMENTS

5.4.1 Introduction

In order to determine the spatial variation of elements within the Que River Shale, a cluster analysis was performed on the bulk elemental data. Clustering was performed using the SYSTAT software package on IBM-compatible personal computer. Both the average linkage and Wards minimum variance method were applied to cluster samples with similar elemental composition. Cluster analyses produce recurring, empirical groups which are defined regardless of assemblage type, mode of accumulation or sedimentary environment (Scott, 1974).

5.4.2 Results

Using only major elements, a cluster analysis identified two groups (Fig. 32). Group 1 having a lower average SiO$_2$ content, and higher average CaO, FeO and TiO$_2$ content than group 2. Spatially group 1 occurs towards the top of the Que River Shale Formation (HL 026, HL345, HL469 and MAC 15; Fig. 33), and is underlain by and intercalated with Group 2. Group 2 constitutes the main body of the shale and using both major and trace element data can be broken down into four subgroups.

Subgroups 1 and 2 are closely related, both showing high SiO$_2$ and Ba, and low Fe and Ca compared with other group 2 shales. Subgroups 1 and 2 are distinguished in that subgroup 1 shows a greater enrichment in SiO$_2$ and Ba than subgroup 2. Subgroup 1 occurs at the base of holes directly
overlying the Hellyer orebody (HL 026 and HL 040) and approximately 1.23 km west of the orebody adjacent to the Tailings Dam Fault. While Subgroup 2 lies at the top of the Que River Shale Formation in a hole at the northern tip of the orebody (HL 040) and in a hole 1 km north of the orebody (HL 469; Fig. 33).

Subgroup 3 exhibits average values for all oxides and elements. Subgroup 3 is widely distributed and represents the main body of the Que River Shale.

Subgroup 4 is characterised by enriched metal values of up to 400 ppm Pb and 938 ppm Zn, and also shows enrichment in Fe, Ni, V, As and Sb. This metalliferous shale shows a spatial association to the Hellyer orebody occurring above the orebody one third of the way up the Que River Shale Formation (from shale basalt contact, HL026 and HL040), and at the base of the Que River Shale in a hole 1.8 km west of the Hellyer orebody (MAC 15).

5.4.3 Interpretation

The primary difference between group 1 and 2 is the enrichment of CaO and depletion in SiO₂ in group 1. Considering lithological data from chapter 3, these groupings probably represent primary sedimentological differences in the shale. Group 1 being more CaO rich, analogous to lithotype 3. While group 2 is analogous to lithotype 2. The higher average FeO and TiO₂ in group 1 is probably a factor of the inverse relation between SiO₂ and other elements (Fenton, 1987).

Subgroups 1 and 2 are compared with subgroup 3 which has average values for all elements. Subgroups 1 and 2 exhibit higher SiO₂ and Ba and lower Fe and Ca values. These values may represent a primary sedimentological difference between the three groups. However, the presence of Ba and their spatial distribution (Fig. 33) suggest that these samples may be the product of alteration. The distribution of subgroup 1 suggests it may be related to hydrothermal fluids over the orebody and associated with the fault. Subgroup 2 may also be related to fluid flow along faults. Subgroup 3 is interpreted to represent the normal unaltered shale.

Subgroup 4 with its enriched metal values is the most distinctive of the groups. There are two possible explanations for these metal enrichment; (1) Late carbonate veining, (2) Exhalative metal enrichment in the water column. Anomalous Pb and Zn values of up to 5200 ppm Zn and 1150 ppm Pb (Aberfoyle company report) have been recorded in the Que River Shale overlying the Hellyer ore position and are associated with late carbonate veins containing sphalerite and minor galena. The localities where anomalous Pb and Zn values have been recorded in this study did not contain visible sphalerite or galena in drill core. However, fine quartz-carbonate veining was present, which could have contained trace amounts of sphalerite and galena. Alternatively, metals may have been introduced into the shales syngenetically via exhalation of metals into the water column within the basin. Euxinic conditions would have provided ideal conditions for the trapping of these metals (Maynard, 1991).
FIGURE 32: Dendrogram showing the grouping of Que River Shale Formation. Numbers as in Table 7, Appendix 2.

Group 1: CaO enriched
Group 2: subgroup 1 Altered Shale
subgroup 2 Normal Shale
subgroup 3 Metal-rich Shale
FIGURE 33: Distribution of element groupings from Figure 23 on Schematic cross section of Hellyer area with top of the Que River Shale as datum

Group 1
Group 2-subgroup 1

2
3
4

Scale:
Horizontal: 0 500 1000
Vertical: 0 50 100
5.4.2 Zinc Ratio

The zinc ratio: \[ \frac{100 \text{ Zn}}{\text{Zn} + \text{Pb}} \]

has been applied to the Mount Read Volcanics which contain four major Zn-Pb-Cu-Ag-Au volcanogenic massive sulfide deposits and are a prospective area for further discoveries (Huston and Large, 1987). However, exploration for volcanogenic massive sulfide deposits is complicated by the presence of at least five other styles of Pb-Zn mineralisation:

1. Stockwork Cu-Fe or Pb-Zn veins associated with Cambrian porphyries.
2. Pb-Zn-Ag veins related to Devonian granites.
3. Pb-Zn-Ag fissure lodes.
4. Polymetallic sulfides along faults or associated with quartz-tourmaline veins related to Devonian granites, and
5. Ordovician Irish-style(?) Pb-Zn-Ag deposits.

The zinc ratio has proved useful in distinguishing among these styles. The volcanogenic massive sulfide deposits of the Mount Read Volcanic Belt having a restricted range of mean values (60-77) and low standard deviations (less than 15). Whereas other mineralisation styles have broader but lower ranges of mean values (39-61) and higher standard deviations (greater than 26; Large and Huston, 1986).

Twenty samples of Que River Shale Formation (Zn > 0.1%) plotted on a zinc ratio histogram (Fig. 34) give an average value of 73.20 with a standard deviation of 8.1 and a range between 61.14 and 86.25. The Que River Shale Formation plots in the range for Cambrian massive sulfides, suggesting that metals in the Que River Shale Formation are sourced from a massive sulfide source either by erosion or by the exhalation of hydrothermal fluids into the basin.
FIGURE 34 Zinc Ratio histogram for 20 samples from the Que River Shale all with Zn > 0.1%.

5.5 VECTORS TO MINERALISATION

In the Upper Andesites and Basalts, directly overlying the Hellyer orebody a 'plume'-shaped zone of light green fuchsite-calcite alteration occurs. This plume extends up to the boundary between the Upper Basalts and Andesites and the Que River Shale, and is interpreted to represent hangingwall alteration related to the Hellyer massive sulfide orebody. The hangingwall alteration is interpreted to have formed during and after the deposition of the basalts of the Upper Andesites and Basalts (Large, 1992). Minor sericite, chlorite, barite and pyrite enrichment occurs within the plume, with an irregular zone of albite alteration around the margins (Large, 1992). The zone is characterised by enrichment in CaO, K2O and Ba and depletion of Fe2O3, MgO and SiO2 (Jack, 1989). Similar element variations should be observed in the Que River Shale if it had been affected by the same fluids. However, the characteristic bright green fuchsite alteration would not be seen, as it is a product of the breakdown of primary chromium rich pyroxenes in the basalts (Jack, 1989).

As can be seen from the distribution of groups in Figure 33, there is a small geochemical alteration zone at the base of the Que River Shale Formation, directly overlying the orebody. This zone is marked by enrichment in Ba and SiO2 and slight depletion in FeO and MgO. It appears likely that the hydrothermal system responsible for hangingwall alteration ended soon after basalt eruption, and did not extend far into the shale. The alteration in the shale is not extensive enough to be used as a vector for massive sulfide exploration.
5.6 SUMMARY

The Que River Shale is a chemically homogeneous unit with less than 5 percent variation in the values for major elements. Means for the lower Shale Facies and the shale units within the Southwell Subgroup are similar to that of the Que River Shale and fall within the range of values for the Que River Shale, indicating that the shales have similar sources and post-depositional histories.

Most elements in the Que River Shale have unimodal frequency distributions, indicating that the sediment source was the major controlling factor for sediment composition, rather than depositional, diagenetic or post-diagenetic processes. Harker variation diagrams of immobile elements such as TiO$_2$ and P$_2$O$_5$ (Fig. 28) indicate that the Que River Shale is derived primarily from an andesitic source in the Que-Hellyer basin. The conversion of glass and ash to muscovite and chlorite, and chemical weathering of albite have resulted in Al$_2$O$_3$ and Na$_2$O depletions in the shale.

Clustering of elements using the SYSTAT program revealed two main divisions related to primary sedimentological processes (Fig. 32): Group 1 is a CaO enriched shale which shows depletions in SiO$_2$ and higher average FeO and TiO$_2$ than group 2. Group 2 can be divided into normal shale (subgroup 3), altered shale (subgroups 1 and 2), and metal-rich shale (subgroup 4). Thus although the Que River Shale is a geochemically extremely consistent unit, statistical analysis can define primary groupings which relate to differences in sedimentology within the basin and alteration occurring diagenetically to post-diagenetically.
6.0 INTRODUCTION

In this chapter a synthesis of the past and present work on the Que River Shale will firstly be given to summarise the characteristics of the Que River Shale. This is followed by a discussion which includes a brief synthesis of the tectonic environment and basin evolution as determined by previous authors. Also discussed, from the current study, are the deposition of the Que River Shale, its depositional environment, and provenance. Included in these discussions are the major findings of this thesis. Finally the significance of the Que River Shale for exploration is assessed.

6.1 SUMMARY

The Que River Shale is characterised by a predominance of mud-rich siltstones and shales which exhibit a characteristically finely laminated nature. Intercalated with the mudstones are minor layers of volcaniclastic sandstones. The type area is around the Hellyer Mine site (41º24'S, 140º43'E) in north-western Tasmania (Fig. 1). The Que River Shale Formation crops out along the Murchison Highway, from the Mount Charter fault northward to 1.2 kmS of the Cradle Mountain Link Road, and eastward to the Hellyer Mine site (Figs. 7). It is also exposed in the mine canal which diverts the Que River around the Hellyer Tailings Dam (Fig. 2). The unit thins east of Hellyer, and is not recognised to the south of the mine. The shale extends northward, where it plunges beneath Tertiary basalts. It has been identified as far north as the Black Marsh syncline, where it is exposed in drill hole MXRD 1 (Fig. 7). The unit average thickness is 125 m in drill core, but the shale thins dramatically to the east of the Hellyer orebody, where it is to be 5-10 m thick. The thickness of the unit west of the orebody appears reasonably consistent, however erosion has removed the upper parts of the sequence, making this impossible to test. North of the Hellyer orebody, the unit thickens slightly to around 200 m.
The Que River Shale occurs in the Mount Read Volcanic Belt. It is part of the Mount Charter Group, occurring between two volcanic units. The underlying Que-Hellyer Andesitic to Basaltic volcanics are subaqueous and locally derived. The overlying Southwell Subgroup is predominantly rhyolitic and is interpreted to have been deposited by bottom-hugging mass flows from an extra basinal source. The age of the Que River Shale Formation as determined by fossil evidence is Late Middle Cambrian (Undillan stage; Jago, 1973). The Mount Read Volcanics yield U-Pb and $^{40}$Ar/$^{39}$Ar age of 502.6 ± 3.5 Ma, with no resolvable difference for individual units (Perkins and Walshe, 1993).

The mineralogy of the Que River Shale, as determined by XRD, is quartz (45-60%), muscovite (15-30%), chlorite (5-20%) and pyrite (5-10%); with minor albite, calcite and dolomite (Table 1). The Que River Shale is characterised by a fine grained dark brown to black matrix of chlorite and sericite that hosts detrital quartz and muscovite grains up to 100 µm across and pyrite grains up to 20 µm. The quartz grains typically have straight extinction and cuspat e margins, indicating a volcanic source for the detritus. Quartz and muscovite grains are concentrated in bands that define laminations. The Que River Shale Formation has a well defined bedding parallel cleavage defined by aligned muscovite grains. Pyrite also occurs as digenetic nodules up to cm scale. Four generations of pyrite occur in the Que River Shale:

1. Syngenetic fine grained (<20 µm) disseminated euhedral crystals and fram boids
2. Early d i genetic nodules made up of concretions of fine (20 µm) crystals of pyrite concentrated along bedding planes. The nodules range from oval to elongate shapes.
3. Digenetic aggregates of massive to radiating pyrite grains with euhedral to subhedral margins.
4. Pyrite euhedra in late-stage quartz-carbonate veins

The Que River Shale contains a late Middle Cambrian fauna including hydroids, dendroids, agnostid trilobites, inarticulate brachiopods and various sponge spicules in reasonable abundance with one bradoriid specimen and a possible aglaspid specimen (Jago, 1973). The shale shows little evidence of bioturbation.

The principle component of the Que River Shale is shale, which can be divided into three lithotypes:

**Lithotype 1**: Weakly laminated, fine grained (<50 µm) alternating quartz, muscovite and chlorite-rich layers.

**Lithotype 2**: Strongly laminated, course grained (up to 100 µm) shale with laminations defined by concentrations of quartz and muscovite in a fine-grained chlorite matrix.

**Lithotype 3**: Similar to lithotype 2 in that it is strongly laminated and coarser grained than Lithotype 1, but different in that the laminations are defined by calcite with less quartz and muscovite than lithotype 2.
Volcaniclastics are a minor component of the Que River Shale, and are intercalated in the top 20 m and bottom 60 m of shale. The basal volcaniclastic layers consist of fine grained crystal rich (quartz feldspar) volcanic sandstones up to 2 m thick with the occasional pumice clast to fine sandy laminations (up to 1 mm). While the upper volcanic layers contain sandstone, mixed sandstone and shale and volcaniclastic layers and occur only as distinct beds.

The Organic Carbon content of the Que River Shale is typically 0.34 wt % but can be up to 1%, while the carbonate carbon averages 0.8 wt % giving a total carbon content of around 1.12 wt %. The sulfide sulfur averages 1.1 wt % and gives a Degree of Pyritisation index with a range of 0.74 to 0.88 putting the Que River Shale in the inhospitable field of Raiswell et al. (1987).

6.2 DISCUSSION

6.2.1 Tectonic History and Basin Evolution

Deposition of the Mount Read Volcanics began in the middle Cambrian during an episode of short lived, westward-directed subduction (Fig. 8), causing deposition of the basal Central Volcanic Complex (Crawford and Berry, 1992). In the late Middle Cambrian, rebound back-thrusting along the eastern side of the Central Volcanic Complex exhumed Proterozoic crystalline crust, which now forms the Tyennan Nucleus. This thrusting also created a foreland basin half-graben known as the Dundas Trough, where the Upper Mount Read Volcanics and the Que River Shale were deposited (Crawford and Berry, 1992). This basin is interpreted to be marine throughout its existence, and was dominated by volcanism and volcaniclastic sediments (Corbett and Komysshan, 1989). Deposition of the Que River Shale began in the Hellyer area during a break in volcanism after the formation of the Hellyer massive sulfide orebody. The Que River Shale Formation, with its characteristic finely laminated nature, accumulated after basaltic-andesitic volcanism ceased, forming ~125 m thick blanket of sediment in the Hellyer area, over a period of up to 3 Ma (Perkins and Walshe, 1993).

Deposition of the Que River Shale Formation ended with the influx of quartz-feldspar phric mass flows associated with the Southwell Subgroup. However, shale deposition did not completely cease, with shale layers accumulating between the mass flow units. Sedimentation in the Dundas Trough eventually ceased in the Late Cambrian, when renewed uplift and excavation of Tyennan Nucleus provided abundant coarse siliciclastic detritus that formed the overlying Owen Conglomerate (Fig. 8).
6.2.2 Deposition

The Que River Shale was deposited within the predominantly volcanic Mount Charter Group in the Dundas Trough. Deposition of the shale began after the emplacement of the Hellyer orebody, during a short break in volcanism represented by the mixed sequence. The first shales appearing as thinly bedded to laminated shales interbedded with fine to medium grained, quartz-rich sandstone. Deposition of shale continued through the eruption of Upper Andesites and Basalts, with shale intercalated between individual lavas flows. The shale is unlaminated, but may be bedded where it occurs in between flows. Distal laminated shales occur in this stratigraphic position away from the Hellyer orebody. The basalts were both extrusive and shallow intrusives into wet shale, based in the presence of peperites, hyaloclastites and chilled margins, indicating that basalt and shale deposition were synchronous (Waters and Wallace, 1992). This shale is classed as the Lower Shale Facies.

Eruption of the Upper Andesites and Basalts was followed by a period of quiescence, during which the Que River Shale Formation, with its characteristically laminated nature and minor intercalated volcanioclastics was deposited. Deposition of shale continued until a resurgence of volcanism characterised by predominantly myolitic, bottom-hugging mass flow units that swamped the basin. Shale deposition continued during the deposition of the Southwell Subgroup, forming minor shale units between the mass flow units that were in some cases incorporated into the mass flow units. This shale is considered as part of the Southwell Subgroup sequence, and is not distinguished as a separate facies.

6.2.3 Depositional Environment

The environment of deposition of the Que River Shale has been interpreted from DOP calculations to be inhospitable, indicating that there was little or no oxygen present in the Que-Hellyer basin at the time of Que River Shale deposition. This is consistent with the lack of bottom dwelling fauna and pyritic nature of the shale. C/S plots further define the environment as euxinic, and indicate that free H$_2$S was present in the basin, which allowed the formation of fine grained syngenetic pyrite in the water column.

Diagenetic pyrite in the Que River Shale, initially formed concretions of fine grained pyrite. Later formed pyrite aggregates consist of irregular aggregates of radiating-massive subhedral grains. The pyrite nodules give $\delta^{34}$S isotope ranging from +17 permil (early diagenetic pyrites) up to +34 permil for latter pyrite, suggesting that the basin, at least below the sediment water interface, was a closed system with respect to SO$_4^{2-}$ and H$_2$S, allowing the enrichment of $\delta^{34}$S isotopes.
6.2.4 Provenance

The Que River Shale is compositionally homogeneous, with less than 5% variation in major element contents. A weak correlation between K, Al, Ti, Si, and Fe reflects the clastic nature of the sequence. Variations in CaO and Na2O content are probably related to late calcite and albite alteration.

Overall, the Que River Shale was sourced primarily from andesitic volcanics and the analyses plot on a fractionation trend of andesites to rhyolites. However, provenance studies reveal that the Que River Shale cannot be obtained directly from units within the Que-Hellyer basin or surrounding Mount Read Volcanics without significant syn or post-depositional modification, suggesting a mixed source that has been well homogenised by sedimentary processes during deposition. The only constraint on the source region is that it must contain 20-25% Hellyer basalt to account for high Cr values in the Que River Shale (up to 1.3 wt% Cr2O3).

6.3 SIGNIFICANCE OF QUE RIVER SHALE FORMATION FOR EXPLORATION

The Que River Shale is a distinctive unit of finely laminated black shale which can be used to correlate sequences from other areas (e.g. the Pinnacles region; Reid 1990) with the Que-Hellyer area.

Stratigraphic markers in the Que River Shale Formation are mostly absent. The only distinctive features are the accumulations of volcaniclastic layers intercalated with the shale in the top 20 m and basal 60 m of shale, giving an indication that contacts are being approached.

Geochemically, the Que River Shale has a remarkably consistent composition that varies by up to 5% with respect to major elements. There is a small alteration zone (subgroup 1; Fig. 33) at the base of the Que River Shale Formation, marked by enrichment in SiO2 and slight depletion in FeO and MgO. This zone directly overlies the fuchsite-carbonate hangingwall plume in the Hellyer Basalt that is related to the hydrothermal system which formed the Hellyer ore deposit. The restricted extent and minor chemical variations of the hangingwall halo in the Que River Shale Formation prevent this unit from being of any use for exploration.

The Que River Shale deposition was a protracted event occurring for up to 3 Ma, whereas the volcanics were erupted essentially instantaneously. The likelihood of the hydrothermal system affecting significant portions of the shale would require, the shale to have been deposited prior to or synchronous with the Hydrothermal system. The Que River Shale is interpreted to have begun deposition after the emplacement of the Hellyer orebody (Waters and Wallace, 1992) and contemporaneously with the mixed sequence units, and continued until the deposition of the Owen Conglomerate. Thus any alteration in the Que River Shale related to the hydrothermal system would be expected to be associated with volcanism, which occurs only in lower shale facies where the shales are
intercalated with the Upper Basalts and Andesites which represent the hangingwall sequence. This pattern is seen and suggests that alteration halos of other ore deposits in overlying shales would also be minimal, and easily missed during exploration.

However anomalous metal values in the Que River Shale (subgroup 4) which show a spatial association with the Hellyer orebody (Fig. 33) and maybe useful as vectors to mineralisation. The shale compositions determined during this study provide the background data against which base metal values for the Que River Shale and its correlates can be compared in order to identify anomalous values in core grinds.