

## CHAPTER 5

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## CHAPTER 5

### MINERALIZATION IN THE EMMAVILLE-TENTERFIELD REGION

#### INTRODUCTION

Since the discovery of cassiterite orebodies associated with the Mole Granite in 1853 by the Rev. W.B. Clarke, the Emmaville district has been, and still remains, a region of considerable economic importance. Alluvial cassiterite was discovered near Emmaville in the 1860's and by 1874 the Vegetable Creek alluvial deposits (immediately east of Emmaville) were in full production. The search for cassiterite and gold lead to the discovery of the Kingsgate (1877) and Glen Eden (1883) molybdenite deposits which were largely worked for bismuth and silver throughout the 1880's and 1890's. During this period of intense exploration, the three major polymetallic sulfide orebodies in the area were also discovered, including the Ottery Mine (1881), Collisons (formerly Webbs) Silver Mine (1884) and Webbs Consols Mine (1885).

By 1900 the use of Mo and W as additives in the production of hard, high-temperature steels had created a demand for these metals and by 1918 the Kingsgate and Torrington mining districts had become leading producers of molybdenite and wolframite respectively. The production of molybdenite, cassiterite and wolframite from the Emmaville region declined later in the twentieth century and mining activity has been largely restricted to small operations in the Mole Granite roof pendant until quite recent times. The Ottery (arsenic), Collisons and Webbs Consols (silver) Mines ceased production before 1965 and have not been subsequently re-opened. However, the current high metal prices have initiated a revival in exploration for cassiterite and molybdenite and the (Halls) Grampians Range "stockwork" cassiterite deposit is currently being re-assessed as a prospective open-cut mining operation.

#### EARLY LITERATURE

Much of the available information on the discovery, the tenor, mineral assemblages and nature of occurrence of cassiterite orebodies now largely mined out, is recorded in publications of the New South Wales Geological Survey, including

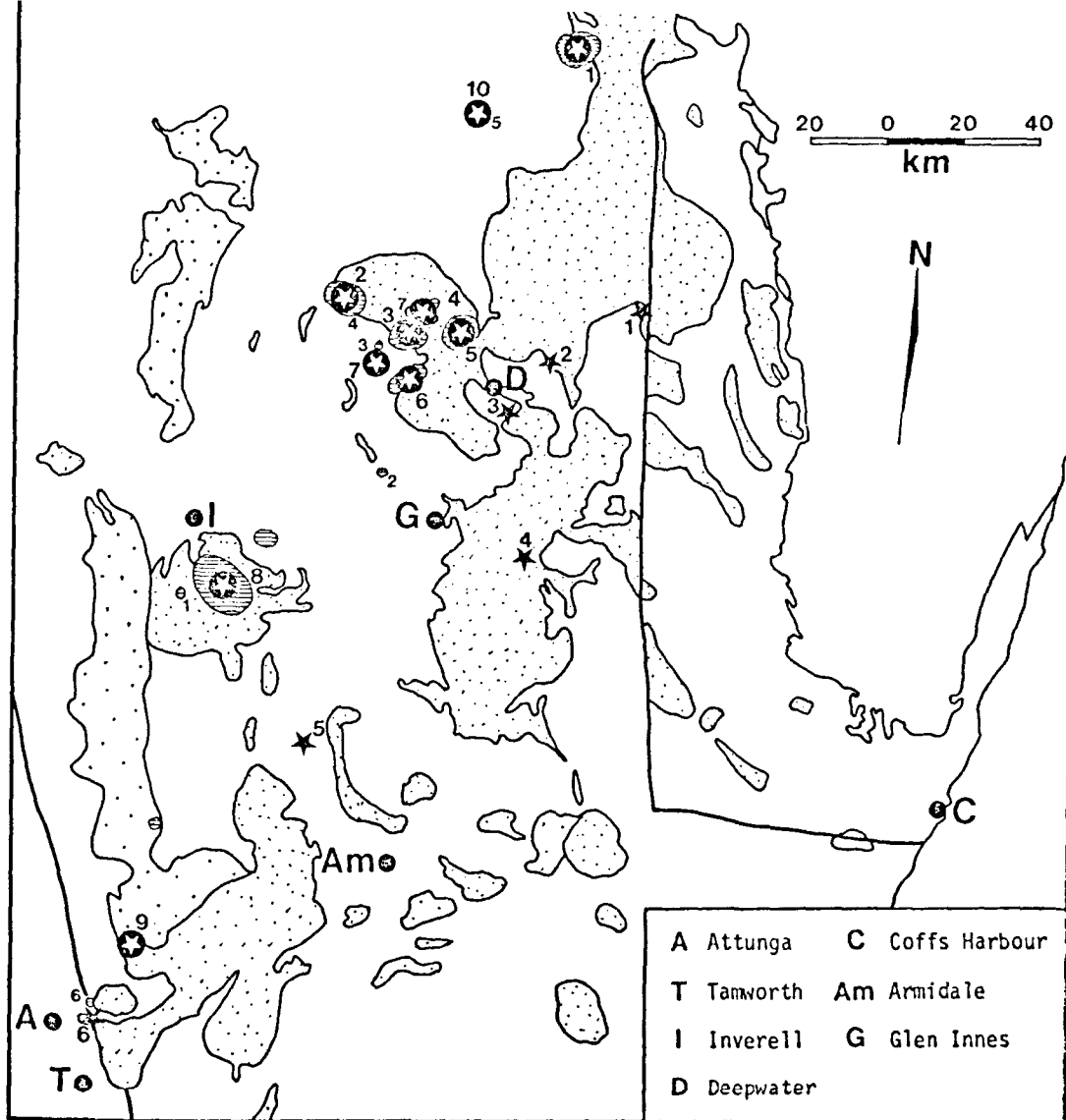


Figure 5.1 Principal Tin, Molybdenum and Base Metal Deposits in the New England Region

● Cassiterite Deposits

- 1 Stanthorpe tin field
- 2 The Gulf
- 3 Torrington tin lodes
- 4 McCowans and Butler lodes
- 5 Stannum
- 6 Ottery - Tent Hill
- 7 Grampians Range
- 8 Tingha tin field
- 9 Watsons Creek
- 10 Sundown Group

★ Molybdenum Deposits

- 1 Wunglebung mines
- 2 A.W. mine and 4 mile deposits
- 3 Allies mine
- 4 Kingsgate pipes
- 5 Boorolong
- 6 Attunga scheelite prospects

Base Metal Deposits

- 1 Conrad mine
- 2 Webbs Consols mine
- 3 Collisons Silver mine
- 4 The Gulf
- 5 Sundown group
- 6 Attunga copper mine

■ Permian and Triassic granitoids and the Dundee Rhyodacite

■ Bundarra and Hillgrove Plutonic Suite granitoids

Wilkinson (1883), Cox (1886), David (1887) and Carne (1911). Wilkinson (1884) and Andrews (1916) described the molybdenite deposits in the Kingsgate and neighbouring regions, and the Torrington wolframite deposits were first described by David (1887) and Carne (1912).

## CASSITERITE DEPOSITS

Major cassiterite deposits in northeastern New South Wales occur in three principal areas, namely the Stanthorpe tin field, Tingah tin field and the deposits in and surrounding the Mole Granite in the Emmaville region (Figure 5.1). The deposits in the Emmaville region have been economically the most important and the major orebody types are briefly described below.

### A. Alluvial Deposits

Alluvial cassiterite deposits may be categorized into 3 types according to age and form of occurrence. These are (i) recent stream alluvial deposits, (ii) ancient stream alluvial cassiterite concentrations, now exposed or shallowly buried (Quaternary), and (iii) deep leads - Tertiary stream alluvial cassiterite deposits which have been buried by up to 60m of poorly indurated sedimentary material and thin alkali olivine basalt flows.

The Quaternary cassiterite deposits, including the Vegetable Creek lead (near Emmaville), and those near Stannum and the Gulf, were the most important sources of alluvial cassiterite. Total production from at least 16 mines working the Vegetable Creek lead yielded 19,441 t. of cassiterite concentrates (Rasmus, 1968b). The Vegetable Creek deep lead is traceable west of Emmaville for 8 km (Weber, 1974) and has yielded 6,500 - 8,000 t. of concentrates. In 1976 alluvials with a grade of 1 - 2.7 kg/m<sup>3</sup> were mined but grades worked in the 1880's over much smaller areas were up to 100 kg/m<sup>3</sup> (David, 1887). Total production from all types of placer deposits associated with the Mole Granite has been estimated at 80,000 t. of cassiterite (Weber, 1974).

### B. Cassiterite Deposits in the Mole Granite

Cassiterite mineralization is largely confined to the dominant vertical joint set in the apical portions of the Mole Granite which trends 040° - 050°, but branching fractures trending 030° and 060° are also mineralized at some localities (Mulholland, 1943). Randomly oriented shearing and tension fractures may further

complicate the pattern of ore deposition. The cassiterite-bearing quartz-fluorite veins range in thickness from < 1cm to < 3m and mineralization tends to be more fully developed at the intersections of major joint planes (Lonergan, 1971) and in wider-spaced joints in relatively coarsely crystalline granite. In several of the larger veins mineralization persists to depths of at least 250m although ore grades diminish rapidly at the deeper levels (Weber, 1974).

Granite adjacent to mineralized veins is almost invariably silicified and chloritized, and coarsely crystalline quartz and chlorite line the walls of the veins. Cassiterite is localized at the inner margin of the quartz-chlorite vein lining, or occurs as disseminations in the hydrothermally altered country rock. Cassiterite deposits situated within 1 - 2km of the sedimentary Torrington (roof) Pendant contain significant concentrations of wolframite (Weber, 1974). These "bung" deposits are characteristically small and very rich and are generally located at major mineralized joint intersections. The ore and vein mineralogy of these deposits is very similar to the larger vein deposits situated further from the roof pendant and the mineral assemblages are summarized in Table 5.1.

### C. Cassiterite Deposits in Rocks Surrounding the Mole Granite

#### (i) Deposits associated with Acid Intrusives

The McDonalds lodes (location "c", Figure 5.2) and Taylors lodes (2km due west of the Ottery Mine) are prominent examples of cassiterite orebodies spatially associated with small porphyritic adamellites which have intruded the Early Permian sedimentary basement rocks. These adamellite porphyries predate intrusion of the Mole Granite (i.e. they are contact metamorphosed) and although field evidence is equivocal, the ore metals and most of the components of the gangue assemblage in the associated orebodies, are presumed to have been derived from the Mole Granite.

The McDonalds lodes consist of a number of narrow quartz- or tourmaline-rich veinlets largely within a porphyritic adamellite adjacent to a much larger metadolerite intrusion. Scheelite in addition to wolframite, cassiterite, bismuth, base-metal sulfides, fluorite, tourmaline, quartz and feldspars comprise the vein assemblage (David, 1887; Lonergan, 1971). The Taylors lodes lack scheelite but contain molybdenite and stannite in addition to the more common ore minerals (see Table 5.1). The Ottery Mine (Figure 5.2) which was worked for cassiterite in the nineteenth century resembles the McDonalds and Taylors lodes in that mineralization is largely confined to quartz veins within a small adamellite plug. However, because

Figure 5.2 Key to mines and major occurrences (numbered), and small prospects (letter symbol).

Cassiterite Deposits

- 1 Ottery Mine
- 2 Emmaville Stockworks
- 3 Emmaville Alluvials
- 4 Grampians Range
- 5 The Gulf
- 6 Torrington tin lodes
- a Binghi lodes
- b Butler lodes
- c McDonalds lodes

Wolframite Deposits

- 1 Fielders Hill and Bismuth Mine
- 2 Wolfram Hill and Heffernans lodes
- 3 Rockvale Mines
- a James Mine
- b McGowans lodes

Base Metal Deposits

- 1 Collisons Silver Mine
- 2 Webbs Consols Mine
- a Reids Copper Mine
- b Hellhole Adit
- c Mole (Castlerag) Silver Mine

Molybdenum Deposits

- 1 Wunglebung mines
- 2 Jondol
- 3 Birthday and A.W. mines
- 4 Bungulla Molybdenum prospect
- 5 Surprise Mine
- 6 Allies (and Manbundi) Mine
- a Parish Graham
- b Parish Ballandean
- c Parris Glen Lyon
- d Tenterfield Greek
- e Parish Bluff Land (A)
- f Parish Bluff Land (B)
- g Fearnside and Fletchers claim
- h Applebys claim
- i Deepwater greisen deposits
- j Coronation Mine
- k Edwards pipe
- l Bow Creek mines
- m Boundary Creek
- n Glen Elgin
- o Glen Eden
- p Bismuth Mine
- q Leis Molybdenum Mine

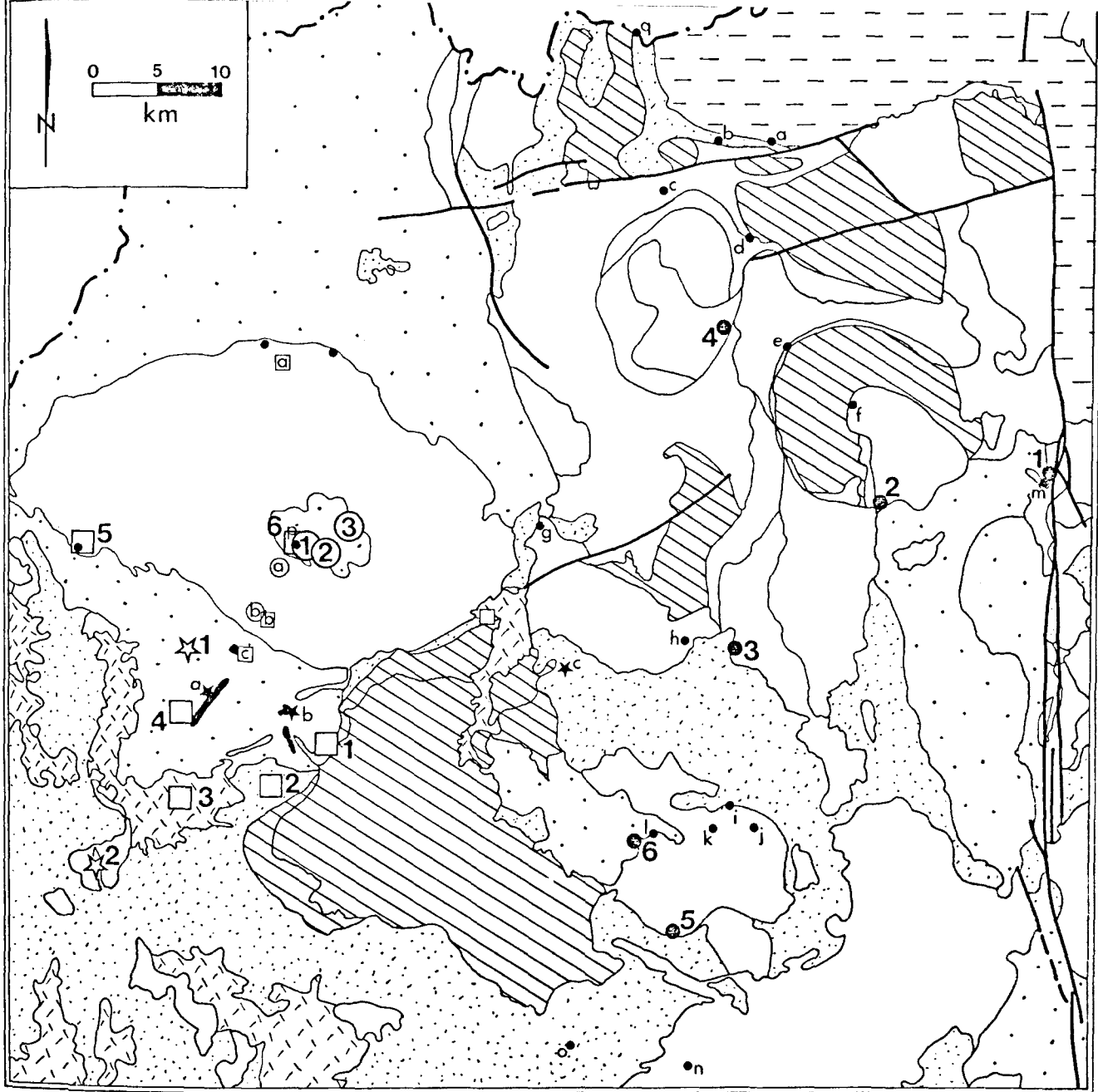
















Figure 5.2 Tin, Tungsten, Molybdenum and Base Metal deposits in the Emmaville-Tenterfield region.

-  Tertiary basaltic rocks
-  Triassic granitoids
-  Permian granitoids
-  Dundee Rhyodacite Suite
-  Emmaville Volcanics
-  Sedimentary basement rocks

Key to Mines and Prospects

-   Molybdenite
-   Cassiterite
-   Wolframite
-   Base metals

the Ottery Mine ore assemblage is dominated by arsenopyrite, this orebody has been grouped with the other polymetallic sulfide occurrences and will be described in a later section.

(ii) Stockwork Deposits      The (Halls) Grampians Range and the Vegetable Creek or Emmaville vein deposits (see Figure 5.2) have been classified as "stockwork" or "stockwork-like" deposits by Weber (1974) but mineralization is largely confined to pre-existing joints forming a network of narrow (2 - 20mm; Carne, 1911) veins of quartz, cassiterite, arsenopyrite, pyrite, purple fluorite and rarer tourmaline, chalcopyrite, sphalerite, molybdenite and galena in contact metamorphosed Early Permian siltstones (Weber, 1974). An estimated 15 - 20 million tonnes of sediments containing 0.2 wt% SnO<sub>2</sub> may be recoverable by open-pit mining methods. In the upper reaches of Vegetable Creek between Emmaville and Tent Hill, weathered rhyolites at the base of the Emmaville Volcanic sequence contain numerous closely spaced joints (oriented 050°) filled by quartz and cassiterite - Wynn (1968) and Rasmus (1968, 1968a) termed this deposit the Emmaville tin-bearing stockworks. Associated minerals include wolframite, pyrite, chalcopyrite (replaced by covellite and digenite; Wynn, 1968) and rare sphalerite (Weber, 1974).

Between the Ottery Mine and Tent Hill 3 km further south, the major joint set strikes in a northeasterly direction and a series of narrow, parallel cassiterite-bearing quartz veins occur within fine-grained basement sediments and a composite granite-adamellite intrusive southwest of the Ottery Mine. Mineralization in this region may be an extension of the Emmaville tin-bearing stockworks.

The source for the cassiterite and other granite-derived minerals in the "stockwork" deposits is unknown. At the Grampians Range orebody the sediments are locally thermally metamorphosed which suggests the presence of a granitic source at shallow depths beneath the deposit. The Emmaville "stockwork" mineralization may have been derived from the same, or a similar, shallowly buried granitic source. Future studies may show these proposed subsurface granitoids to be apophyses of the Mole Granite pluton, or independent intrusions of similar age to the Mole Granite.

### WOLFRAMITE DEPOSITS

Although wolframite has been mined from deposits in the Ruby Creek Adamellite (principally near Stanthorpe, north of the field area) the major



TABLE 5.1 WOLFRAMITE-BISMUTH, CASSITERITE AND MOLYBDENITE DEPOSITS:  
ORE AND GANGUE ASSEMBLAGES

WOLFRAMITE-BISMUTH (PEGMATITE) ASSOCIATION

(largely Mole Granite Roof Pendant)

Wolframite	(1)	
Bismuth	(2)	
Co, Ni, As, Fe Arsenides and Sulfarsenides	}	
Uraninite-Torbernite		
Pyrrhotite		
Pyrite		
Marcasite		
Chalcopyrite		
Cubanite		
Molybdenite		
Bismuthinite		(3)
Sphalerite		
Tetrahedrite	}	
Cosalite		
Joseite A+B		
Cassiterite		
Beryl		
Monazite		

PEGMATITE TYPES

- (1) Topaz-Quartz
- (2) Orthoclase-Quartz  
Biotite-Beryl
- (3) Quartz-Orthoclase  
Beryl-Tourmaline

CASSITERITE DEPOSITS

(a) Mole Granite

Cassiterite  
Rutile  
Magnetite  
Pyrite  
Arsenopyrite  
Pyrrhotite  
Stannite  
Chalcopyrite  
Sphalerite  
Galena  
Molybdenite  
Beryl  
Tourmaline  
Wolframite  
Bismuth  
Monazite  
Fluorite

(b) Other Deposits

Cassiterite  
Fluorite  
Tourmaline  
Sphalerite  
Molybdenite  
Wolframite  
Chalcopyrite  
Marcasite  
Pyrite  
Bismuth  
  
Galena  
Stannite

MOLYBDENITE DEPOSITS

Molybdenite-Jordisite  
Bismuth  
Bismuthinite  
Gold-Electrum  
Silver  
Pyrrhotite  
Pyrite  
Chalcopyrite  
Galena  
Sphalerite  
Valleriite  
Arsenopyrite  
Joseite A+B  
Cosalite  
Ikunolite  
Galenobismutite  
Pyrargyrite  
Gudmundite  
Cassiterite  
Wolframite (Ferberite)  
Cubanite  
Tetrahedrite  
Magnetite  
Beryl  
Fluorite  
Aikinite  
Stannite

References

Mulholland, 1943; Rayner, 1960;  
Lawrence and Markham, 1962, 1963;  
Wynn, 1968; Rasmus, 1968, 1968a;  
Weber, 1974; Jones, 1976.

wolframite deposits in New South Wales occur in the sedimentary roof pendant of the Mole Granite. Approximately 40 such deposits occur in the Torrington area (Rasmus, 1970).

Bismuth and wolframite mineralization occurs as "veins and pods" of pegmatite (Weber, 1970) associated with small intrusions of topazite (silexite) within and near the periphery of the Torrington Pendant (see Lawrence and Markham, 1963, Figure 1). Total production from the two major deposits, the Fielders Hill and Bismuth mines, was of the order of 75,000 t. with an average head grade of <1.6%  $WO_3$  (Weber, 1970). The Fielders Hill orebody was described by Griffin and Weber (1972) as a "probable pipe-like body with accompanying sill" of silexite. The mineralized topazite (silexite) at the Bismuth mine is associated with beryl- and tourmaline-bearing pegmatite, and very coarse-grained biotite- and beryl-bearing pegmatite (Lawrence and Markham, 1963).

As shown in Table 5.1 the ore assemblage varies according to the mineralogy of the host; wolframite is concentrated in the topazite and co-exists with native bismuth in coarse-grained biotite pegmatite. Arsenides, molybdenite and uraninite occur in the surrounding more fine-grained biotite pegmatite and sulfides are largely restricted to pegmatite veinlets pervading the adjacent sedimentary country rocks. Ore deposition therefore appears to have been intimately associated with the evolution of the pegmatite complex and ore mineral zoning may partly reflect response to a temperature gradient, i.e. oxides were deposited at high temperatures near the core of the complex, and sulfides at the lower-temperature margins of the main pegmatite mass or in narrow pegmatite veinlets well distant from the core of the complex.

As already described, wolframite is also associated with cassiterite in quartz-fluorite vein or bung deposits situated within 1 - 2km of the margins of the Torrington Pendant. Deposits near the margins of the Mole Granite (e.g. McGowans lodes, see Figure 5.2) are generally small, low-grade wolframite orebodies of relatively little importance.

### MOLYBDENITE DEPOSITS

Of the six major molybdenum localities in the Tablelands Complex (see Figure 5.1) only those in the Mt. Jonblee Leucoadamellite (A.W., Birthday and Sunrise mines) and the Kingsgate Granite (Surprise and Allies mines east of the Dundee (Rhyodacite) mass, and the Kingsgate deposits ~ 20 km east of Glen Innes) have been of major importance.

All of these major molybdenite-bismuth orebodies are pipe deposits, situated near the margins of leucogranitoid plutons. The largest single pipe deposit in the New England region, the A.W. mine, has yielded 153 t. of molybdenite concentrates from approximately 3000 t. of ore (Weber et al., 1978). Jones (1976) described the Kingsgate pipes as "irregularly shaped cylindrical bodies of quartz, roughly circular to ovoid in cross section and varying in diameter from 0.5 to 20m, and at least 120m in length". The orientation of the pipes is highly variable and "branches, bulges" and bifurcations of the main stem are often characteristic (Jones, 1976).

Similar to many of the pipes near Kingsgate, the main pipe at the A.W. mine, Bolivia is concentrically zoned with very coarse (black) quartz crystals occupying vugs in the core, grading outwards into coarsely granular "granitoid quartz" and finally into hydrothermally altered and silicified leucogranitoid host rock (Andrews, 1916; Plimer, 1969; Hutchinson, 1970). Large crystals and aggregates of molybdenite, which constitute the bulk of the rich ore, form "collars" marking the contact between the pegmatitic quartz core and the "granitoid quartz" zone (Plimer, 1969; Jones, 1976). Disseminated molybdenite and bismuth, or clots of these minerals, also occur in the sericitized and silicified zone surrounding the pipes. Aplite dykes and, more rarely, pegmatite veins are associated with the pipes and constitute low-grade molybdenite deposits. The primary ore and gangue assemblages from a number of pipe deposits are listed in Table 5.1.

Orebodies such as the Glen Elgin and Deepwater greisen deposits (see Figure 5.2) contain significant concentrations of cassiterite and wolframite and comparatively small quantities of molybdenite. The ore minerals are disseminated throughout the sericitized and silicified margins of the Kingsgate Granite.

At the Glen Eden "stockwork" deposit south of Dundee (see Figure 5.2), mineralization is developed in strongly silicified ignimbritic rhyolites and volcanogenic sediments which mark the base of the Emmaville Volcanic pile (cf. Jones, 1976; Weber et al., 1978). The silicified zone is a locus for extensive development of narrow quartz veins which are also mineralized. The dominant ore minerals in the Glen Eden deposit include molybdenite, wolframite, cassiterite, bismuth, chalcopyrite, sphalerite, pyrite, pyrrhotite, arsenopyrite and ferrimolybdite (Smith, 1926; Williams, 1964). The presumed leucogranitoid source for the metals in this deposit is not exposed.

#### POLYMETALLIC SULFIDE OREBODIES

In a comprehensive study of the principal base metal deposits in the New England region, Herbert (1981) demonstrated that the minor element composition of

pyrite and sphalerite could be used to assign deposits within a three-fold general classification.

	<u>STEINMANN</u> <u>ASSOCIATION</u>		<u>FELSIC VOLCANIC</u> <u>ASSOCIATION</u>		<u>GRANITOID</u> <u>ASSOCIATION</u>	
<u>SPHALERITE</u>						
<u>wt %</u>		<u>Av.</u>		<u>Av.</u>		<u>Av.</u>
Fe	0.1-2.8	1.5	0-0.8	0.4	1.94-15.0	8.0
Cd	0.00-1.36	0.2	0.1-0.6	0.25	0.10-1.00	0.4
Mn	0.00-1.00	mostly none	0.00-0.1	mostly none	0.10-1.5	0.5
<u>PYRITE</u>						
<u>ug/g</u>		<u>Av.</u>		<u>Av.</u>		<u>Av.</u>
Ni	15-99	43	15-100	43	17-34	25
Co	98-2741	646	36-563	145	40-64	49
Mn	143-624	385	12-253	93	11-43	26

Average values obtained for polymetallic sulfide deposits in the Emmaville area support conclusions based on field evidence that the ore-bearing fluids of the major episode of mineralization were derived from a granitic source.

	<u>COLLISONS SILVER</u> <u>MINE</u>		<u>WEBBS CONSOLS</u> <u>MINE</u>		<u>OTTERY As-Sn</u> <u>MINE</u>	
<u>SPHALERITE</u>						
<u>Wt %</u>		<u>Av.</u>		<u>Av.</u>		<u>Av.</u>
Fe		10.33		8.45		12.27
Cd		0.71		0.43		0.46
Mn		0.26		0.95		0.26
<u>PYRITE</u>						
<u>ug/g</u>		<u>Av.</u>		<u>Av.</u>		<u>Av.</u>
Ni		no		19		no
Co		data		41		data
Mn		available		36		available

TABLE 5.2 POLYMETALLIC SULFIDE OREBODIES ASSOCIATED WITH GRANITIDS:  
ORE ASSEMBLAGES

<u>COLLISONS SILVER MINE</u>		<u>WEBBS CONSOLS MINE</u>	
MAJOR EPISODE OF MINERALIZATION		MAJOR EPISODE OF MINERALIZATION	
Sphalerite	M-m	Arsenopyrite	M
Galena	M-m	Sphalerite (Marmatite)	M
Chalcopyrite	M-m	Chalcopyrite	M-m
Stannite-Zincian Stannite	M-m	Stannite-Zincian Stannite	m-tr
Tennantite (Ag-free)	m	Pyrite	m-tr
Arsenopyrite	m	Pyrrhotite	tr
Pyrrhotite	m-tr	Cubanite	tr
Cubanite	tr		
Pyrite	tr		
SECOND EPISODE OF MINERALIZATION		SECOND EPISODE OF MINERALIZATION	
Freibergite	M-m	Galena	M-m
Tetrahedrite (Ag-bearing)	M-m	Freibergite	m-tr
Boulangerite	m	Stibnite	tr
Stibnite	m-tr	Bismuthinite	tr
Pyrrhotite	m-tr		
Bismuth-Bismuthinite	tr		
Stephanite	tr		
Antimony	tr		
ALTERATION OR REPLACEMENT ASSEMBLAGE		ALTERATION OR REPLACEMENT ASSEMBLAGE	
Marcasite	(Pyrite)	Marcasite	(Pyrite)
Goethite	(Pyrite)	Bornite	(Chalcopyrite)
Chalcocite	(Chalcopyrite)	Covellite	(Chalcopyrite)
Covellite	(Chalcopyrite)	Malachite	(Chalcopyrite)
Azurite-Malachite	(Chalcopyrite)		
Bournonite	(Chalcopyrite)		
Bornite	(Chalcopyrite)		
Cerrusite	(Galena)		
		<u>OTTERY MINE</u>	
		MAJOR EPISODE OF MINERALIZATION	
		Arsenopyrite	M
		Marcasite	M
		Sphalerite	m
		Pyrite	m-tr
		Stannite-Zincian Stannite	m-tr
		Cassiterite	m-tr
		Chalcopyrite	m-tr
		Pyrrhotite	m-tr
		Cubanite	tr
		SECOND EPISODE OF MINERALIZATION	
		Pyrrhotite	tr
		Bismuth-Bismuthinite	tr

Abbreviations

The abundance of each mineral in a given ore specimen may be:-  
M - major, m - minor, tr - trace.  
Minerals in brackets are those replaced.

Data Sources - Herbert (in prep),  
Godden (1976)

High Fe, Mn in sphalerite and generally low abundances of Co, Mn in pyrite are the best discriminators for deposits of granitoid association. Although the source largely determines the initial bulk chemistry of the mineralizing fluids, the minor element composition of sphalerite and pyrite in the ores is predominantly controlled by physicochemical conditions prevailing during deposition (Herbert, pers.comm.).

Sulphur isotope studies support the conclusions drawn from the mineral chemistries. The Ottery As-Sn mineralization ( $\delta^{34}\text{S}$  approx. zero) was deposited from primary magmatic fluids whereas the mineralizing fluids for Collisons Silver Mine ( $\delta^{34}\text{S}$  - 10% to -7.5%) and Webbs Consols Mine ( $\delta^{34}\text{S}$  - 8% to -10%) display evidence of minor crustal contamination (Herbert and Smith, 1978).

#### A. Orebodies Associated with Granitoids

The Collisons and Webbs Consols (silver) mines and the Ottery (arsenic-tin) mine are the most important (polygenetic) sulfide orebodies in the Emmaville-Tenterfield region. The ore assemblages in these deposits are listed in Table 5.2.

Collisons Silver Mine is a hydrothermal vein-type polymetallic sulfide orebody situated 3.5 km from the Mole Granite contact northwest of Emmaville. Mineralization occurs as irregular veins and joint fillings specifically within a 5m-thick sequence of vertically dipping very fine-grained sandstones and stilstones. The sediments in this sequence were mildly silicified, sericitized and bleached during the mineralizing episodes and are readily distinguished from the adjacent weakly contact metamorphosed units of the sedimentary basement.

Although the Collisons deposit was mined only for silver, large amounts of tin are present in the form of stannite which occurs as tiny exsolution blebs in sphalerite. The stannite, arsenopyrite and base-metal sulfides associated with quartz, fluorite, calcite and sericite (Godden, 1976) were deposited from granite-derived hydrothermal solutions during the first episode of mineralization. During a subsequent mineralizing episode, Sb, Bi, Ag sulfides and native metals were deposited in association with barite (Herbert, in prep.), quartz or chalcedonic silica, and (perhaps) sericite.

Estimated production from the Collisons Silver Mine is 50,000 t., including 30,500 t. mined before 1901 which yielded 2,030 t. of concentrates containing 3.43 kg/t Ag, 7% Pb, 4% Cu, 13% Zn, 9.5% As and 7.5% Sb (Weber, 1974).

Webbs Consols Mine, 12km west southwest of Emmaville (see mapsheet) is the largest of several polymetallic sulfide deposits in a northerly trending linear zone of

hydrothermally altered, porphyritic granite which has intruded the contact between a coarse-grained leucoadamellite and dominantly rhyolitic flow-banded lavas and welded tuffs forming the base of the Emmaville Volcanics sequence. The porphyritic granite is characterized by embayed quartz phenocrysts set in a quartz-feldspar matrix displaying a pronounced granophyric texture. Mineralization occurs in strongly chloritized and sericitized portions of the host, as disseminations and semi-spherical masses (< 4 cm) or elongate pods up to 1 m in length.

The Webbs Consols deposit assumes a pipe-like form, reputedly controlled by the intersection of fractures with a "northerly shear" (Walker, 1970). Lead and silver values decrease rapidly with depth, matched by a sympathetic increase in sphalerite (marmatite) (McManus and McClatchie, 1963). A somewhat similar but less well established vertical zonation was reported in the Collisons Silver Mine by McManus and Cormack (1962), with tetrahedrite decreasing in proportion to increases in the amount of sphalerite present. Lead, silver, antimony and bismuth mineralization in the Webbs Consols mine is considered by Herbert (in prep.) to post-date the major episode of mineralization which was presumably derived from a local granitic source.

Total production from the Webbs Consols mine has been estimated at 18,000 t. of ore with an average grade of 7.5 wt% Pb and 230 g/t Ag (Weber, 1974).

The Ottery Mine, 7km northeast of Tent Hill consists of two major, subparallel cassiterite lodes and a more westerly arsenopyrite lode, each of which occupies a quartz-rich fissure developed within the Ottery host porphyritic adamellite. The adamellite host rock has intruded the contact between silty sedimentary basement rocks and the Ottery Rhyolite, the adamellite-Rhyolite contact being characterized by intense sericitization and post-intrusive shearing with attendant development of quartz augen and disrupted quartz veining.

The arsenopyrite lode occurs in a steeply dipping major quartz vein which roughly parallels the western adamellite-sediment contact for 150m. Coarse-grained arsenopyrite totally dominates the ore assemblage, with subordinate co-precipitating and later sulfide phases occupying the interstices and filling microfractures in the brittle sulfide.

The major cassiterite lodes occupy steeply dipping sub-parallel fissures which strike in a northeasterly direction, cut across the central portion of the intrusion and parallel the adamellite-Rhyolite contact in the northeastern sector of the deposit. The intense sericite alteration in this northeastern sector can be attributed to greisenization of the adamellite-Rhyolite contact during the tin-mineralizing episode.

The porphyritic adamellite host rock typically contains trace amounts of all the sulfide and oxide phases represented in the arsenopyrite and cassiterite lodes.

The Ottery Mine commenced its life as a tin producer (1881 to 1905) and later (1920 to 1929, 1931 to 1936) was an important source of arsenic. Production from 1920 to 1936 totalled 109728 t of ore which yielded 2625 t of cassiterite and 1892 t of  $As_2O_3$  (Weber, 1974). The mine was partly redeveloped for extraction of cassiterite during World War II but no production figures are available.

The Ag, Sb, Bi mineralization accompanying deposits of granitoid association appears in no way related to the intrusion of granitic magmas and represents a much later episode of mineralization derived from a deep crustal source (Herbert, 1981).

#### B. Orebodies Spatially Associated with Meta-Dolerites

Reids Copper Mine, 6km northwest of Emmaville, is located 20m from the contact between a metamorphosed microgabbro and conglomeratic siltstones of the sedimentary basement sequence. The microgabbro, which grades locally into plagioclase- and clinopyroxene-rich cumulate facies, has a dyke- or elongate plug-like form and is displaced by a north-trending minor fault which has acted as a locus for copper mineralization.

The principal ore minerals chalcopyrite, bornite and covellite (ref. Table 5.3) are intimately associated with the other sulfides and occur as fine disseminations and network veinlets within the altered conglomerate host rock. Intense metasomatism of the host rock was associated with sulfide deposition and coarse-grained muscovite, quartz and recrystallized biotite comprise a large proportion of the gangue mineral assemblage.

A shallow shaft into the orebody revealed a network of fluorite-rich veins, and a leucocratic granitoid (not sampled) is exposed at the shaft bottom. This granitoid, possibly an apophyse of the Mole Granite which is exposed only 6km northeast of the mine, was probably the source of the mineralization and also caused the hornblende-facies thermal metamorphism of the microgabbro and surrounding sediments. The north-trending fault and the presumably steep-sided walls of the microgabbro may have influenced the emplacement of the granitoid and imposed a structural control on ore deposition.

Hellhole Adit is a small Cu, Pb, Zn prospect hosted by a small meta-dolerite plug situated 5km northeast of Emmaville. Mineralization occurs as coarse veins or, more rarely, disseminations in the brittle host rock. Although the sulfide assemblage



TABLE 5.3 POLYMETALLIC SULFIDE OREBODIES SPATIALLY  
ASSOCIATED WITH META-DOLERITES: ORE ASSEMBLAGES

REIDS COPPER MINE

Pyrite	M
Pyrrhotite	M-m
Chalcopyrite	M-m
Arsenopyrite	m
Sphalerite	m
Galena	m-tr
Tennantite	tr

HELLHOLE ADIT

Sphalerite	M-m
Galena	M-m
Pyrite	M-m
Chalcopyrite	M-m
Pyrrhotite	m-tr

REPLACEMENT MINERALS

Covellite (Chalcopyrite)  
Bornite (Chalcopyrite)

REPLACEMENT MINERALS

Marcasite (Pyrite)  
Goethite (Pyrrhotite)

Abbreviations

The abundance of each mineral in a given ore specimen may be:-

M - major  
m - minor  
tr - trace

Minerals in brackets are those replaced.

is comparatively simple (ref. Table 5.3) gangue minerals in the veins include pink calcite, ferroan dolomite, minor quartz and occasional grossular garnet.

Orebody formation is considered to have involved the interaction of acidic hydrothermal fluids with dolomitic facies of the sedimentary basement sequence, examples of which are known to outcrop north and west of the mine (c.f. Vickery, 1972). The metalliferous fluids were probably granitic in origin and related to intrusion of the Mole Granite. Ore mineral precursors in the hydrothermal fluid may have become unstable when the sedimentary carbonate layer was intersected, and deposition of sulfides in the fractured meta-dolerite host rock probably followed soon afterwards. Those sulfides which precipitated within the carbonate horizon at depth may also have been remobilized by circulating magmatic hydrothermal or mixed magmatic and meteoric fluids. Any leaching of primary sulfides from those portions of the sedimentary sequence affected by the hydrothermal solutions is not considered to have significantly affected the tenor or composition of the resultant ores.

It is notable that the orebodies spatially associated with basic intrusives display no evidence of superimposed Ag, Sb, Bi mineralization typical of the major polymetallic orebodies of granitoid association. Reids Copper Mine and Hellhole Adit are small deposits (no production data are available) and it is possible that the hydrothermal plumbing system linking the deposits to the source, was insufficiently extensive to later induce ingress of mineralizing solutions originating from deeper levels.

## DISCUSSION

Of the variety of major mineral deposits in the Emmaville region, those associated with the Mole Granite have been by far the most economically important. Compared with the majority of compositionally similar leucogranitoids in the region, the Mole Granite is exceptional in only two respects, namely its enormous size and the abundance of rare metals in economic concentrations. The Mole Granite is also the only major pluton spatially associated with economic polymetallic mineralization.

Regardless of the original abundances of ore trace metals in the Mole Granite magma, it is clear that fractionation processes in the melt were exceptionally efficient. For the production of large Sn, W or Mo orebodies Smith (1979) and Westra and Keith (1981) have emphasized the requirement of a large body of magma,

preferably located at a high level in the crust, in which large-scale, efficient convection and/or diffusion fractionation mechanisms can operate within a regime possessing substantial thermal and pressure gradients. Many of the (smaller) barren or weakly mineralized leucogranitoids associated with the Mole Granite contain similar background levels of Sn and other ore trace metals (e.g. Flinter et al., 1972) but none was able to duplicate the degree of fractionation and local concentration of these metals displayed by the Mole Granite. The volatile content of high-level magmas is a critical factor determining their capacity for generation of orebodies and this observation is the subject of a detailed discussion in chapter 6.

Compared with many other large volcano-plutonic regimes, the Emmaville-Tenterfield region is notably devoid of mineralization specifically related to cauldrons (e.g. McKee, 1979; Smith, 1979; Smith and Bailey, 1968). However Smith (1979), Elston (1978), McKee (1979), Lipman et al. (1976) and many others have noted that significant (often polymetallic) mineralization is only associated with the resurgent phase(s) of caldera development, arguably because only those magmas involved in cauldron resurgence possess the high volatile concentrations essential to the processes of concentration and transport of the ore metals. "The main stage of eviscerating ash-flow tuff eruptions (associated with the actual formation of the caldera)\* was likely to have dispersed the metallic trace elements that tend to concentrate in the volatile-rich cupolas of magma chambers. It was not likely to have concentrated them into ore deposits." (Elston, 1978, p.111). A substantial period of time is required before the volatile-depleted magma remaining beneath the caldera is able to re-establish a volatile- and metal-rich cupola, in preparation for the initiation of caldera resurgence eruptions or a major episode of ore mineral deposition. Additions of fresh magma to the base of the chamber (Smith, 1979) may shorten the period between caldera formation and caldera resurgence.

As described in chapter 4, none of the proposed calderas in the Emmaville-Tenterfield region displays any evidence of resurgence, which may explain the absence of cauldron-related mineralization in the region.

Convincing arguments to explain the simultaneous occurrence of strongly mineralized and totally barren granitoids are themselves often difficult to formulate, but of equal importance for consideration are the problems posed by the mineralized granitoids : why are apparently similar granitoids hosts for specific Sn, Sn-W or Mo mineralization?

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\* Brackets are mine.

Juniper and Kleeman (1979) devised a number of triangular and rectangular plots involving all the felsic and mafic rock components in an attempt to classify Sn-bearing granitoids on the basis of major element chemistry. However these plots do not distinguish between Sn-bearing and barren leucogranitoids of similar  $\text{SiO}_2$  content, and were not intended to discriminate exclusively Sn, Sn-W or Mo types.

Several Japanese authors consider  $f\text{O}_2$  in the magma to be an important determinant in the speciation of ore minerals in leucogranitoids (e.g. Tsusue and Ishihara, 1975; Ishihara and Terashima, 1977; Sato, 1980). In molybdenum granitoids the opaque oxide is chiefly ilmenite (with minor hematite) reflecting high  $f\text{O}_2$  in the fractionating magma, whereas Sn-W granitoids contain mostly magnetite reflecting relatively lower  $f\text{O}_2$  in the magmas. Unfortunately, the opaque oxide mineralogy of the mineralized leucogranitoids at Tenterfield is no indication of the likely composition of associated ores as all contain titanomagnetite  $\pm$  exsolved or granular ilmenite.

Tsusue and Ishihara (1975) concluded that high oxygen fugacity is essential to the concentration of Mo in fractionating granitoids (c.f. Smith et al., 1980) but the concentration of Sn and W is controlled by oxygen, chlorine, fluorine and boron fugacities. Certainly fluorine may be less important in the transport and deposition of W and Sn species than it is in the magmatic fractionation of Mo (see Westra and Keith, 1980; chapter 6), but the concentration of F, Cl and other volatiles in magmatic hydrothermal solutions appears to be more dependant on the physical and subtle chemical conditions prevailing during fractionation than on the initial volatile content of the partial melts.

## CHAPTER 6

### GENESIS AND EVOLUTION OF THE MAGMAS

#### INTRODUCTION

#### **A. MAGMA GENESIS**

##### Some Aspects of Partial Melting

Mafic Xenoliths and Source Rock Composition  
Recognition of Restite Mafic Xenoliths

#### I. PETROGENESIS OF THE MAJOR GRANITOID LINEAGE

- (a) Leucogranitoids
- (b) Adamellites

Fractional Crystallization  
Partial Melting  
Origin of the Mafic Xenoliths

#### II. PETROGENESIS OF THE RHYODACITE-RHYOLITE SUITE

#### III. PETROGENESIS OF THE DUNDEE RHYODACITE SUITE

- (i) GENERATION OF THE MAGMA
- (ii) CRYSTALLIZATION OF THE MAGMA
- (iii) ERUPTION OF THE MAGMA
- (iv) WATER CONTENT OF THE DUNDEE RHYODACITE MAGMA

#### **B. MAGMA EVOLUTION**

##### Source of the Metals for the Mineralized Leucogranitoids

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#### ELEMENT PARTITIONING IN SILICIC ROCK MELTS

- (1) MELT STRUCTURE AND THE SPECIATION OF MELT COMPONENTS
- (2) COMPOSITIONAL ZONING IN MAGMAS

- (i) Evidence for the Existence of Zoned Magmas
- (ii) Origin of the Compositional Zoning

Thermogravitational Diffusion  
Gaseous Transfer  
Formation of Hydrothermal Solutions

##### Formation of Hydrothermal Solutions

- (a) Liquid-Liquid Systems
- (b) Liquid-Vapour Systems

#### (3) APPRAISAL OF MAGMA ZONING MECHANISMS

Thermogravitational Diffusion  
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#### (4) EVOLUTIONARY PROCESSES IN SILICIC CALC-ALKALINE MAGMAS : CONCLUSIONS

Metal Loss from Magmas in Open Systems

#### EVOLUTION OF SILICEOUS MAGMAS IN THE TENTERFIELD REGION

- (a) The Leucogranitoid-Rhyolite Association
- (b) The Mole Granite and Ruby Creek Adamellite
- (c) The Mole Granite Topazite
- (d) Adamellites and Leucoadamellites of the "Porphyries Group"

## CHAPTER 6

### GENESIS AND EVOLUTION OF THE MAGMAS

#### INTRODUCTION

This chapter consists of two major parts. The first is concerned with the generation and crystallization history of the parent magmas for each rock suite. In the second section, discussion will be centred on processes which may have operated during evolution of the magmas of the rhyolite-leucogranitoid association. A theoretical model is designed to predict the response of compatible and hydro-magmatophile (Wood et al., 1979) trace elements to P, T-controlled changes in melt structure and composition which take place as silicic magmas rise to upper crustal levels. Although it is chiefly concerned with processes which may ultimately result in orebody formation, the model also provides an alternative explanation for the observed trace element distribution in the rhyolitic volcanics, which represent slightly modified tapings of the evolving silicic magmas.

#### A. MAGMA GENESIS

In this chapter the available geochemical and petrographic data will be used in support of models describing the generation of magmas for each suite by partial melting of igneous source rocks. It has not been an important objective of this study to accurately determine the mineralogy and composition of the source rocks for the various lineages. In general, the data are considered insufficient to support a rigorous investigation of partial melting processes and parent rock composition, and this has not been attempted. Therefore, discussions of magma genesis are based only on simplistic models of partial melting as these are believed adequate for the purpose of this study.

In some cases the magmas for individual members of a suite appear to have been generated during progressive partial melting of a particular source rock. The following discussion is presented partly to justify the approach which has been adopted, and partly as a basis for discussions to follow.

#### Some Aspects of Partial Melting

White and Chappell (1977) and Winkler and Breitbart (1978) considered that

most granitoid magmas generated by partial melting of lower crustal source rocks consist of melt plus variable amounts of incorporated refractory residua. "Consanguinous" suites of granitoids may therefore form by the ". . . progressive separation of residual material and precipitates from a non-minimum melt" or separation of residua from a minimum melt (White and Chappell, 1977). Progressive equilibrium partial melting (Presnall and Bateman, 1973) of a particular source rock may thus generate low-temperature minimum melt-restite and a number of high temperature, non-minimum melt-restite magmas. To accurately estimate the composition and mineralogy of the source rock, and meaningfully investigate the partitioning behaviour of trace elements in magmas derived by partial melting, is not only important to discriminate between suites of minimum melt granitoids and non-minimum melt granitoids, but it is also necessary to determine the relative temperatures of the individual magmas (these would reflect the degree of melting of the source rock required to produce magmas of a given composition). Although the concept of progressive partial melting is well accepted, it should be noted that the maintenance of crystal-melt compositional equilibrium during partial melting is now being questioned (Johannes, 1980) and in all studies on granitoid genesis provision should be made for possible low-temperature metastable melting of selected refractory phases (e.g. plagioclase).

On a Harker diagram illustrating variation in components which largely do not enter a minimum melt (e.g. MgO, CaO or P<sub>2</sub>O<sub>5</sub>) granitoids belonging to a non-minimum melt magma suite ideally should define a linear trend with a shallower slope than the trend for the minimum-melt magmas generated by the same source rock (see White and Chappell, 1977, Figure 5). Unfortunately, the slopes of the lines defining the respective suites are often confusingly similar. The efficiency of incorporation of restite into a partial melt will also strongly influence the composition of the magmas (melt plus crystals) which leave the melting zone. The first magma to leave the melting zone may therefore in some circumstances be more 'basic' than subsequent higher temperature magmas containing lesser amounts of restite. Consequently a comparison of the whole rock compositions of a number of related granitoids may therefore not provide an indication of the temperatures of partial melting which correspond to the order of formation of the individual magmas, i.e. it may be difficult to assign individual granitoids their correct position in a progressive partial melting sequence.

Unfortunately, the composition and morphology of minerals in granitoids may also fail to provide the information required to distinguish relatively low-temperature non-minimum melt magmas with a significant restite component from

magmas generated by large amounts of partial melting of the same source rocks. This is largely because recognition of restite is frequently subject to interpretation.

Hornblende and Biotite: Experimental studies of the partial fusion of ferromagnesian-rich granitoids (e.g. Wyllie et al., 1975; Winkler, 1976; Wyllie, 1977) suggest that intermediate calc-alkaline source rocks which lack significant amounts of intergranular pore fluid commence melting at temperatures corresponding to the initial breakdown ("dehydration") of biotite. Non-minimum melting commences when one of the low-melting felsic components of the parent is exhausted (cf. Presnall, 1969). Both biotite and hornblende in the parent melt incongruently over a considerable temperature range (e.g. Wyllie, 1977; cf. Rutherford, 1969; Helz, 1973) so it appears reasonable to expect that moderate temperature non-minimum melt magmas may consist of restite ferromagnesians, and melt containing hornblende, biotite and felsic components (see Winkler and Breitbart, 1978).

Euhedral hornblendes may be assumed to be magmatic, but in granitoids containing both euhedral and subhedral hornblende of the same composition, or subhedral hornblende only, there exists the possibility that magmatic hornblende has mantled re-equilibrated restite amphibole. The hornblende in granitoids is typically unzoned so there is little to indicate the possible contribution of restite in rocks presumed to also contain magmatic hornblende. Similarly, the proportion of restite biotite in relatively silicic non-minimum melt granitoids may be impossible to determine.

Ferromagnesian phenocrysts containing apatite inclusions are supposed to be restite (White and Chappell, 1977). However, the presence or absence of apatite inclusions in hornblende and biotite is here not considered an adequate criterion for the recognition of restite because (a) the distribution of apatite in the source rock is not known and it may therefore be invalid to presuppose that apatite was restricted to the ferromagnesian phases, and (b) apatite suspended in a non-minimum melt or, possibly more rarely, crystallizing from the melt, may be included by hornblende or biotite crystallizing from that melt.

Plagioclase: Partial melting under conditions of high  $P_{H_2O}$  will induce melting of relatively calcic plagioclase and thus promote the stability of a highly calcic plagioclase residuum (e.g. Whitney, 1975; Winkler, 1976). However, in most instances the volatiles required to maintain partial melting at moderate temperatures are probably supplied by the breakdown of OH-bearing ferromagnesians



in the source (e.g. Wyllie, 1977). Because incongruent melting of these phases is progressive, any increase in the An contents of the residual plagioclase should reflect an increase in the temperature and (presumably) the degree of melting of the source rock. The composition of restite plagioclase in granitoids of a related suite, if indeed it can be identified, may therefore be a guide to the relative temperatures of the magmas.

As noted by White and Chappell (1977) plagioclase phenocrysts in many granitoids are complexly zoned and twinned, and may contain distinct, relatively calcic cores (commonly characterized by late-stage sericitization). Presnall and Bateman (1973) considered that these cores represent refractory residua that have been subsequently mantled by more sodic, magmatic plagioclase. The presumed restite cores of plagioclase phenocrysts in the I-type granitoids of the Moonbi district have been described by Chappell (1978) as having rounded margins, patchy and slightly anomalous extinction, and a "relatively" uniform composition. Although the above authors did not specifically describe zoning in "restite" plagioclase, weak to moderate compositional zoning is commonly observed in the resorbed cores of plagioclase phenocrysts in granitoids. It is here considered uncertain that zoning should be preserved after recrystallization under amphibolite (and perhaps ultimately) granulite facies conditions, followed by a high-temperature partial melting event (see Piwinski, 1968).

The relatively calcic cores of plagioclases in many granitoids suggest magmatic crystallization at pressures (and temperatures) considerably higher than those of the more strongly zoned rims (see Vance, 1965). Magmatic plagioclase in granitoids is invariably zoned to some degree, due primarily to the relatively low maximum temperatures of calc-alkaline magmas (e.g. Winkler and Breitbart, 1978), and because these magmas always contain significant amounts of H<sub>2</sub>O (see Vance, 1962, 1965; Fen, 1977; Johannes, 1978). Unzoned relatively Ca-rich core plagioclase may therefore be indicative of restite. Weakly zoned or patchy-zoned core plagioclase may be suggestive of restite, but may be very difficult to distinguish from high P-T magmatic plagioclase.

From the above discussion it must be concluded that the discrimination of restite and magmatic phenocrysts in granitoids may not be as straightforward as has been proposed by White and Chappell (1977). In many cases, the composition and morphology of mineral phases and the whole-rock composition of granitoids may not provide sufficient information for an estimation of the degree of partial melting of the source required to generate individual magmas of a granitoid suite. Xenoliths of refractory mafic residua persisting after partial melting may, however, provide useful information. This aspect of granitoid genesis is discussed the following

sections.

Mafic Xenoliths and Source Rock Composition      Restite xenoliths may be potentially useful indicators of original igneous parent rock composition in cogenetic granitoid series generated by partial melting. Such xenoliths may represent modified or unmodified residua originally in equilibrium with the melt component of the magmas at the site of generation. During the emplacement of magmas textural and compositional re-equilibrium of mineral phases in the xenoliths may be expected to occur (e.g. Chappell, 1978). Compositional re-equilibration may involve reaction between the xenolith and the enclosing melt, or reactions may be confined to the xenolith so that mineral components remain in equilibrium with the bulk chemistry of the xenolith as P and T decrease during emplacement of the magma. Only xenoliths which have not interacted with the adjacent melt may represent compositionally unmodified partial melting residua.

In an ideal system a good approximation of parent rock major element composition can be made using Harker variation diagrams (cf. White and Chappell, 1977; Chappell, 1978). For a given major element oxide, the parent must plot on the linear trend between the (unmodified) xenoliths and their host rocks, and the parent will be positioned on this trend somewhere between (a) the composition of the xenoliths representing source rock least depleted of low-temperature melting components (i.e. "mafic" xenoliths with the highest silica contents), and (b) the composition of the most mafic (lowest silica) granitoid of the suite (i.e. the granitoid presumed to have crystallized from the highest temperature non-minimum melt). In cases where there is adequate justification to invoke this simple approach, the accuracy of the estimation of parent rock composition may be limited only by the range of xenoliths and host rocks analysed.

An acceptable estimation of the composition of the source rock for the main Tenterfield granitoid suite cannot be made using the method outlined above. This is due primarily to the general paucity of xenoliths in the granitoids and the fact that none of the xenoliths sampled or analysed in this study can be considered to represent unmodified partial melting residua (see next section).

Recognition of Restite Mafic Xenoliths      White and Chappell (1977) have stated that "more than 99%" of all xenoliths in granitoid plutons "are pieces of relict source rock material". If this is indeed the case, it is somewhat surprising that the recognition of restite has eluded

geologists until recent times.

Xenoliths and mafic aggregates representing the residua of partial melting of igneous rocks in the middle-lower crust may be expected to display the following characteristics.

(a) Monomineralic or polymineralic mafic aggregates (microxenoliths) should display evidence of recrystallization (e.g. Chappell, 1978) with polygonal or pseudo-polygonal grain boundary relationships. Plagioclase adjacent to ferromagnesian minerals may be relatively poorly zoned or unzoned and be devoid of any evidence of interaction with the melt. Plagioclase partly exposed to the melt (i.e. at the perimeter of the aggregate) should be assymetrically resorbed due to local interaction with the melt and/or zoned due to subsequent crystallization of intensely zoned, more albitic plagioclase from the melt. If restite hornblende and biotite of the aggregates have been in contact with a non-minimum melt they may locally develop euhedral crystal faces.

(b) Mafic xenoliths representing the residua of a granulite-facies partial melting event may have originally contained calcic plagioclase, pyroxene(s)  $\pm$  quartz  $\pm$  K-feldspar  $\pm$  interstitial melt. In xenoliths lacking an interstitial melt, the observed low P-T (re-equilibrated) assemblage may be plagioclase lacking intensely zoned rims, hornblende, biotite, vestigial pyroxene(s) (as cores in the stable ferromagnesian),  $\pm$  quartz  $\pm$  K-feldspar, forming a distinctly metamorphic texture. In the presence of an interstitial melt the equilibrium assemblage may be the same as above but the plagioclase may display thin, possibly discontinuous rims of zoned "magmatic" plagioclase and the xenolith should have a less developed metamorphic texture.

Restite fragments which contained a considerable portion of interstitial melt at the time of incorporation into the magma (ideally all magmas generated by moderate to high temperature amphibolite-facies ultrametamorphism of intermediate source rocks should contain restite xenoliths of this type) may be subject to plastic deformation and marginal spalling. Such xenoliths might therefore be discoidal or semi-lenticular in shape, display an incipiently developed to well developed foliation, and have "ghosty" or ill-defined margins (see Chappell, 1978). "Magmatic" rims on the restite plagioclase phenocrysts (xenocrysts) may be narrower and perhaps more intensely zoned than those on the plagioclase phenocrysts (xenocrysts) in the host granitoid. Euhedral ferromagnesian phenocrysts may occur in the xenoliths but should be extremely rare (cf. Chappell, 1978).

Although the mafic aggregates and xenoliths in some I-type granitoids may display some or all of the features described above, xenoliths in the Tenterfield granitoids exhibit dominantly igneous textures. One of the more speculative points of the above description is the assumption that the refractory residua may be incorporated into the magmas not as solid fragments but in the form of a dense mush composed of discrete crystals, aggregates and interstitial melt. "The occasional well shaped mafic minerals", and the oscillatory and normally zoned rims which characterize the "mantled" plagioclase in supposedly typical restite mafic xenoliths in the Moonbi granitoids (Chappell, 1978) are indicative of crystallization from a melt and strongly suggest that the xenoliths contained a melt component. (Although Chappell failed to compare the width and compositions of the zoned rims of plagioclase in the xenoliths and the host rock, there is little doubt that such rims are of magmatic origin in both cases). Furthermore, "the observed gradations from massive xenoliths through those in various stages of disintegration, to patches of granitoid of relatively high colour index, or xenolith ghosts" (Chappell, 1978, p. 275) also strongly suggest that the "massive" xenoliths were incorporated as a crystalline mush.

Chappell (1978) considered the mafic xenoliths in the Moonbi I-type granitoids to be "in every sense equivalent" to the cordierite-bearing xenoliths in an S-type granitoid from the Berridale Batholith, Southeastern Australia. However, this analogy is a poor one. The metasedimentary xenoliths have a pronounced foliation which is absent from the I-type xenoliths. If Chappell's interpretation of the origin of the I-type xenoliths is correct (i.e. they are restite) the absence of a recognizable foliation suggests that magmatic convection or similar processes are not capable of stretching or of inducing a foliation in a mafic crystalline mush (cf. above). This is an important point which clearly warrants investigation.

From the above discussion, it is clear that many features of presumed restite mafic xenoliths are shared by xenoliths which may be interpreted as cognate or even accidental in origin. If restite mushes can indeed survive the rigors of assimilation in granitoid magmas, the following observations may be relevant.

Restite xenoliths are generally presumed to represent fragments which not only contain all the phases of the partial melting residua, but also reflect the original modal proportions of all the phases comprising the partial melting residua. However, depending on the efficiency of incorporation of individual restite components into the melt, some fractionation of the residual phases of partial melting is possible, resulting in the formation of mafic xenoliths which may not be representative of the entire restite assemblage. Furthermore, the volume of interstitial melt trapped

between the refractory phases will not only influence the "buoyancy" of the poorly aggregated residua, but may also determine the extent to which the resulting xenoliths re-equilibrate with the magma during emplacement to upper crustal levels. However, unfractionated restite, which above the melting zone experiences only limited interaction with the melt, may produce xenoliths truly representative of the partial melting residua, and these xenoliths should plot on the extensions of the geochemical trends delineating the various host rocks.\*

Because the majority of mafic xenoliths in a given granitoid or suite of granitoids may have initially been incorporated into the magmas as crystalline mushes, it may be impossible to determine the extent to which the xenoliths have been metasomatized. Xenoliths which represent the true composition of the refractory residue may therefore be not only rare, but in fact impossible to identify. Attempts to determine the composition of the source rock by employing the compositions of selected xenoliths and granitoids in a given suite (as described above) may therefore be invalid in some cases.

## I. PETROGENESIS OF THE MAJOR GRANITOID LINEAGE

In Chapter 3 evidence was presented to suggest that all the major adamellite plutons, together with a number of smaller bodies of adamellite, comprise a single petrogenetic suite. Major element and selected trace element data also suggest that the mineralized and barren highly silicic granitoids of both the first and second intrusive episodes not only may have been derived from a common source, but may also be related to the adamellites of the main lineage.

### (a) Leucogranitoids

Leucoadamellite magmas which are generated by small degrees of partial melting of igneous parent rocks and are emplaced to similar levels in the upper crust, may be predicted to have very similar major element chemistries. Because only the low-melting felsic components of the parent may be involved in the partial melting process to produce highly silicic magmas, chemically similar magmas may be generated from deeply buried volcanic or deep crustal intrusive parent rocks spanning a considerable range in composition, i.e. intermediate to acid, but the

\* Xenoliths which contain a representative sample of the restite assemblage, but have also incorporated some of the melt from the host magma will also plot on the geochemical trends delineating the host rocks.

degree of partial melting may vary from source to source. Any conclusion on the nature of the source rocks of spatially associated leucogranitoids which are based entirely on major element similarities of the rocks, may therefore be subject to error. The following discussion of the possible origins of the leucogranitoid magmas is thus based largely on trace element data, which are regarded as more sensitive indicators of parent rock composition and magmatic processes.

The available trace element data confirm that the unmineralized leucogranitoids and adamellites in the area may, in fact, be genetically related (i.e. on trace element variation diagrams the rocks generate linear, well defined trends). However, genetic considerations based on the incompatible trace element data for the mineralized leucogranitoids are much more equivocal. The Mole Granite, Ruby Creek Adamellite, and the group of unmineralized leucogranitoids display widely differing levels of abundance in a number of incompatible trace elements including Li, Rb, U, Th, Cs and F (see Chapter 3). As all of these rocks have similar mineralogies, the observed ranges in trace element abundances clearly cannot be attributed to fractional crystallization of separate magmas with diverse phenocryst assemblages. (Fractional crystallization is virtually never 100% effective, especially at the scale required to produce the volumes of acid granitoids observed in the area). Furthermore, the available isotopic data (see Chapter 3), and the absence of recognizable xenocrystic material in these leucogranitoids, precludes assimilated country rocks as possible sources of incompatible elements for the enriched, mineralized leucogranitoids.

The barren leucogranitoids do not represent the eroded remnants of compositionally zoned plutons (Ludington et al., 1979) whose apical portions were mineralized (Wright and Mutschler, 1979), as several are only partly unroofed (e.g. the Nonnington and Billyrimba Leucoadamellites) and the enclosing country rocks are typically devoid of "granite"-derived polymetallic sulfide mineralization (Chapter 5).

If it is assumed the leucogranitoids represent magmas derived by limited partial melting (possibly modified only by very small amounts of crystal fractionation), it may be argued that the differences in the concentration of incompatible trace elements in the barren and mineralized leucogranitoids must largely reflect original parent rock composition, or differing degrees of partial melting of the same source rock.

Incompatible elements are concentrated in the late-crystallizing phases of igneous rocks, and certain incompatible elements (e.g. Rb) will therefore be concentrated in the first melts to form during ultrametamorphism as some of these

late-crystallizing phases in the parent enter the minimum melts. Furthermore, as many of the larger incompatible elements (e.g. U, REE) may be localized along grain boundaries and structural defects in the low-temperature phases in the parent (see Roaldset, 1975; Tieh *et al.*, 1980), these elements may be released by only small degrees of partial melting. Further melting should release only those trace elements that are wholly bound in the lattices of the low-temperature melting phases. As the LIL\* element-rich Mole Granite and Ruby Creek Adamellite are the youngest leucogranitoids of the first and second intrusive episodes respectively, from the above discussion it may be argued that the magmas for these leucogranitoids were not derived from the same source rock that had earlier generated the relatively LIL element-depleted barren leucogranitoids.

From the above discussion it may be concluded that the difference in LIL element concentration in the mineralized and barren leucogranitoids cannot be attributed to fractional crystallization, wall rock contamination, magma zonation or derivation of the magmas from the same source rock. These conclusions are based on the commonly accepted assumption that the leucogranitoids necessarily represent magmas that have not been affected by large-scale open-system fractionation processes. Provided this assumption is correct, the available data strongly suggest that although they may be closely related both spatially and temporally, the mineralized plutons and the group of unmineralized leucogranitoids crystallized from magmas derived from different parent rocks, or initially identical source rocks that have undergone a second, higher temperature, partial melting episode (Collins *et al.*, in prep.). In the second part of this chapter the behaviour of incompatible elements in magmas subject to open-system fractionation processes is investigated and the geochemistry of the leucogranitoids is interpreted accordingly.

(b) Adamellites

As already suggested the Shannonvale Granodiorite, and many of the small masses of quartz monzonite and hornblende adamellite from the broad belt of "undifferentiated granitoids and porphyries" west of Mount Mackenzie appear related to the large adamellite plutons of the main intrusive lineage (see Chapter 3).

Fractional Crystallization:                      Although there is a crude inverse correlation between silica content and the modal abundance of hornblende in granitoids of the main lineage, mineral chemistries and

\* Large Ion Lithophile element(s).

whole-rock geochemical data suggest the more leucocratic adamellites were not derived from the more basic members of the suite by simple fractional crystallization processes. Using mg as an indicator of ferromagnesian composition, only the ferromagnesian in the leucoadamellites and highly siliceous adamellites display compositional variations that can be correlated with whole-rock chemistry (Figure 3.20B). No uniform variation in the modal proportions of hornblende and biotite, or regular decrease of mg in these ferromagnesian is noted in the more mafic adamellites, granodiorite and quartz monzonites, which suggests mafic mineral chemistries were not controlled by the composition of successive liquids as would be the case if fractional crystallization was important in the development of the petrogenetic lineage.

Partial Melting. The linear major element and trace element trends are consistent with a partial melting origin for the granitoids of the main lineage, with whole-rock compositions being largely controlled by the amount of mafic restite incorporated in the relatively acid liquids generated by partial melting of the igneous source (cf. White and Chappell, 1977; Winkler and Breitbart, 1978). However, petrographic data suggest the whole-rock chemistries of these granitoids were not governed by processes inherent in the simplest models of melt-restite mixing. Progressive equilibrium partial melting of a presumed originally homogeneous parent may have generated successively more mafic liquids which incorporated correspondingly more mafic refractory residua.

The difficulties in the interpretation of the products of progressive partial melting have been discussed. However, in terms of a simple partial melting model (e.g. White and Chappell, 1977), the more leucocratic adamellites (e.g. the Mackenzie Adamellite) may represent magmas generated by relatively small amounts of partial melting of the igneous parent. Hornblende in the Mackenzie Adamellite is relatively iron-rich and may have crystallized directly from a non-minimum melt. The virtual absence of plagioclase phenocrysts containing distinctly calcic cores also suggests the magma was formed by limited partial melting.

Increased amounts of melting of the parent may have produced progressively more mafic melts which were able to transport substantial amounts of restite from the melting zone (e.g. White and Chappell, 1977). Magmatic hornblende and biotite in the hornblende adamellites may therefore be accompanied by a considerable quantity of re-equilibrated restite ferromagnesian. Many of the plagioclase phenocrysts contain sericitized cores of very weakly zoned or unzoned calcic plagioclase (ref. Chapter 2) which may be refractory residua that have been mantled



by relatively sodic magmatic plagioclase.

The quartz monzonites which contain zoned plagioclase with uniform, highly calcic cores, and abundant euhedral and subhedral hornblende and biotite, may have crystallized from the highest temperature partial melts of the presumably intermediate parent rock. Whether the quartz monzonites were the last magmas of the lineage to be emplaced in the upper crust is, however, impossible to determine from field relations.

Although in this case it appears that fractional crystallization was not an important process, gravitational settling of mafic restite from intermediate magmas may have contributed towards the formation of the more leucocratic adamellites of the lineage.

Compared with all other hornblende-bearing adamellites in the area, the Bungulla Porphyritic Adamellite is distinguished by magmatic actinolitic hornblende and sphene, and large K-feldspar phenocrysts (ref. Chapter 3). It is also depleted in Ba. However, excluding Ba, the geochemistry of the Bungulla Porphyritic Adamellite is compatible with the other granitoids of the major lineage, suggesting a cogenetic relationship. The cause of the Ba depletion is unknown. A Ba-poor I-type magma may have been generated by very small degrees of partial melting involving phases which included only the late-stage (low-Ba) K-feldspar of the parent. Alternatively a Ba-bearing biotite in the source rock would be required to remain in the melting zone as an immobile restite phase. However, the presence of magmatic (euhedral) hornblende in the Bungulla Porphyritic Adamellite, and possible restite pyroxene in some of its microgranodioritic xenoliths, suggest generation of the magma involved considerable non-minimum melting of the parent. If the low-Ba content of the Adamellite is not a reflection of the partial melting process, then Ba depletion must have been effected by some subsequent magmatic process(es). The distinctive mineralogy and texture of the Bungulla Porphyritic Adamellite indicates that the magma crystallized under somewhat different conditions to those prevailing in other adamellite magmas of the lineage (ref. Chapter 3), but no plausible explanation for the Ba depletion can be offered at this stage. However, with the exception of Ba, trace and major element geochemical data suggest that the Bungulla Porphyritic Adamellite, together with other adamellites in the Tenterfield region, are in fact part of the New England Batholith s.s. as defined by Korsch, 1977.

Origin of the Mafic Xenoliths: The tonalitic xenoliths (X445A\* and X426 A and B in hornblende adamellites west of Mount Mackenzie) are not only compatible with the trace and major element granitoid lineage, but also contain calcic plagioclase similar to that forming the cores of discrete plagioclase phenocrysts in their host rocks. X426A contains a more magnesian hornblende than its relatively silicic host rock (see Figure 3.20B), which suggests that this xenolith did not fully re-equilibrate with the surrounding magma. Although the data are not conclusive, it may be argued that the chemical and mineralogical features of the tonalitic xenoliths suggest they represent residua from the melting zone.

However, equally plausible is the suggestion that the tonalitic xenoliths are (cognate) cumulates formed early in the crystallization history of the host (non-minimum melt) magmas. The ferromagnesian phases in the xenoliths are frequently euhedral and subhedral and exhibit little evidence of subsolidus re-equilibration suggestive of a "restite origin". As already discussed, although incorporated fragments of mafic refractory residua from the melting zone may have originally contained a significant amount of interstitial non-minimum melt, it is considered unlikely that xenoliths of this type should contain (a) numerous hornblende and biotite euhedra and plagioclase phenocrysts with wide, strongly zoned rims, and (b) display well developed igneous textures. The textural characteristics of the tonalitic xenoliths therefore argue more strongly for a cumulate origin, and the available chemical data are not inconsistent with this hypothesis.

In contrast to the tonalite xenoliths, the quartz diorite (X433A) and microgranodiorite (X370A) xenoliths contain anomalous concentrations of several trace elements (e.g. see Figure 3.10) and plot away from the granitoid trend on a number of standard Harker diagrams (Figure 3.2). Although these xenoliths may contain some re-equilibrated restite components they exhibit several characteristics difficult to reconcile in terms of a purely restite origin.

The quartz diorite xenolith lacks K-feldspar (see Table 3 in Chapter 2) and the relatively high  $K_2O$ , Rb, Ba and Zn contents can be attributed to the abundance of biotite. Compared with the tonalitic types, the quartz diorite xenolith contains relatively little hornblende and unusually sodic plagioclase, resulting in low CaO and

\* The host rock for this xenolith is a seriate-textured hornblende-adamellite (446A) from the porphyries group of granitoids. A possible relationship between these granitoids and those of the main lineage is discussed on p.155.

Sr contents (see Figures 3.2 and 3.10 respectively). Few plagioclases contain calcic cores and, when present, such cores are very small and are mantled by a thick rim of more sodic magmatic plagioclase. The compositions of hornblende and biotite in the xenolith and its host rock (433A) are virtually identical (see Figure 3.20), which suggests the ferromagnesian in the xenolith may be in equilibrium with the bulk chemistry of the host. Although the major element composition of the ferromagnesian and the presence of relatively LIL element-rich biotite (ref. Table 3.2) suggest the xenolith may have been metasomatized by the enclosing melt and underwent chemical re-equilibration before crystallization was complete, the absence of K-feldspar in the xenolith apparently militates against this possibility. The available data suggest the xenolith may be a moderately low-pressure cumulate which formed prior to the crystallization of K-feldspar in the parent magma, or is accidental in origin and represents lower crustal country rock some distance above the melting zone.

The porphyritic microgranodiorite xenolith from the Bungulla Porphyritic Adamellite contains abundant hornblende, some of which has recognizable pyroxene cores which may be relict. Although magnesio-hornblende is dominant, significant amounts of actinolitic hornblende are present largely as a replacement of the pyroxene. Compared to the actinolitic hornblendes of the host, the hornblende separated from the xenolith contains more V and Y (see Table 3.2). This may partly reflect originally high V and Y values in the pyroxene of the xenolith that were inherited by the deuteritic hornblende. Hornblende in the xenolith also contains increased amounts of Ce and Nd which may be attributed to high  $D_{\text{mineral}}^{\text{light REE}}$  during crystallization of the deuteritic hornblende. In this case the abundance of REE in hornblende is apparently not influenced by accessory mineral inclusions as these are absent.

The mineral trace element data also confirm that the microgranodiorite xenolith interacted with the host magma. Plagioclase in the xenolith and host have virtually identical Sr, and very similar Ba contents (Table 3.2). Similarly the K-feldspar in the xenolith (megacryst plus groundmass K-feldspar) and host rock have identical concentrations of Sr. The composite K-feldspar separated from the xenolith is slightly enriched in Ba and Rb relative to the K-feldspars separated from the host, but this probably reflects the modal proportions of megacryst and groundmass K-feldspar in the xenolith, which differ from those in the host. (Shaw (1964) analysed individual separates of megacryst and groundmass K-feldspar from xenoliths and the Bungulla Porphyritic Adamellite host rock, and confirmed that Rb concentrations in the two types of K-feldspar differed significantly).

This metasomatism by the host magma also affected the whole-rock chemistry of the xenolith. Relative to the tonalitic xenoliths already discussed, which largely have not interacted with their host magmas, the microgranodiorite xenolith is depleted in Sr, enriched in Rb (Figure 3.10) and has high  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  (Figure 3.2). Clearly, the xenolith does not represent pristine restite from the melting zone and its use in genetic considerations is therefore limited. However, the presence of relict (possible restite) pyroxene in the xenolith may suggest the Bungulla Porphyritic Adamellite magma was generated during moderately high-temperature, granulite facies ultrametamorphism.

## II. PETROGENESIS OF THE RHYODACITE-RHYOLITE SUITE

In Chapter 3 it was shown that the unmineralized acid granitoids of the main intrusive lineage and the rhyodacites and rhyolites comprising an acid volcanic suite, have very similar major element abundances. A possible comagmatic relationship between the two suites is also supported by data for a number of relatively compatible trace elements and the light REE Ce and Nd. Field studies suggest members of the acid volcanic suite were derived from high-level siliceous magmas which, following the eruptive episode, continued to rise and ultimately crystallized to form the barren plutons of the main intrusive lineage (ref. Chapter 4). Any geochemical dissimilarities between the volcanics and their comagmatic granitoid equivalents should therefore reflect either small degrees of fractional crystallization accomplished during the protracted residence of the magmas in the upper crust following the eruptive episode, or open system fractionation processes which may have operated during the eruptions.

As noted in Chapter 3, the volcanics appear to contain more Pb, Ba and less Li and Rb than comparable granitoids with the same phenocryst mineralogy and virtually identical major element compositions. The concentrations of these trace elements in the volcanics apparently cannot be explained by conventional fractional crystallization processes. In fact, it appears difficult to justify the proposed comagmatic relationships of the siliceous volcanics and granitoids without recourse to open system fractionation processes. Open system processes are indicated because the abundances of only the relatively incompatible trace elements (see above) may be considered "anomalous". These, and other aspects of magma fractionation, will be discussed in a later section of this chapter.

### III. PETROGENESIS OF THE DUNDEE RHYODACITE SUITE

Generation of the Dundee Rhyodacite Suite magma has been attributed to partial melting of igneous material in the lower crust (Flood, 1971; Flood et al., 1977) and to "mixing of, and limited reaction between, nearly solid biotite-diorite and a low-melting silicic alkalic liquid" (Wilkinson, et al., 1964, p.481). These authors considered the mafic aggregates in the Dundee Rhyodacite to be critical in genetic interpretations and the hypotheses advanced to explain the formation of these aggregates will now be discussed.

Wilkinson et al. (1964) considered the aggregates and fragmented phenocrysts to be products of disaggregation of a biotite-diorite. However, there is no evidence to suggest that the proposed mechanisms whereby fragmentation and mixing of the diorite could have been accomplished were in fact operative. Biotite is not a primary component of the mafic aggregates and the morphology and composition of pyroxenes in the aggregates differ from the discrete euhedral and fractured pyroxene phenocrysts in the host (see Chapters 2 and 3). The discrete euhedral hornblende, pyroxene, plagioclase and biotite are not components of a disaggregated diorite and their morphology suggests they crystallized directly from the melt. Furthermore Flood et al. (1977) argued that the texture of the aggregates does not resemble that of a typical diorite. It may therefore be concluded that hybridism was not an important process in the formation of the Dundee Rhyodacite magma.

Of the several hypotheses of origin of the mafic aggregates discussed by Flood et al. (1977) only two were considered to provide reasonable explanations of the texture and bulk composition of the aggregates. These were that the aggregates may represent disrupted high pressure-temperature cumulates, or samples of refractory material (restite) carried up from the melting zone.

Several features of the aggregates are inconsistent with a restite origin.

(a) Magnesio-hornblende occurs as a primary constituent of many aggregates (Shaw, 1964; Wilkinson et al., 1964). Although this hornblende has the same composition as the phenocrysts in the host (cf. Garcia and Jacobson, 1979), textural relations indicate that it crystallized with the pyroxene and plagioclase of the aggregates. Admittedly some compositional re-equilibration may have occurred. However aggregates containing the most Mg- and Al-rich pyroxenes lack primary amphibole and it may be assumed that the constituent phases of these aggregates crystallized before hornblende became a stable liquidus phase (cf. Flood et al., 1977).

(b) Plagioclase of the aggregates has the same composition as phenocrysts in the host. According to the restite hypothesis of Flood et al. (1977), the core regions of both aggregate and phenocryst plagioclase are refractory residuals from the melting zone. However thermometric calculations in this study suggest that magma temperatures exceeded 850°C, and the mafic mineralogy of the Dundee Rhyodacite, coupled with its high K<sub>2</sub>O content, suggest the magma was produced by a considerable amount of melting at low P<sub>H<sub>2</sub>O</sub> during granulite facies ultrametamorphism (cf. Whitney, 1975; Winkler, 1976). A large proportion of the K<sub>2</sub>O and some of the mafic components of the melt were probably derived by the breakdown of biotite in the parent rock at high temperatures (see p.103). Although the contribution of plagioclase components to the melt was probably small under the conditions prevailing during the final stage of melting (e.g. Winkler et al., 1975), the restite plagioclase in equilibrium with highly magnesian pyroxene should be significantly more calcic than An<sub>53</sub> (av. An<sub>44</sub>). Only the highly calcic plagioclase (An<sub>81</sub>) of the porphyritic xenoliths may therefore qualify as restite (see Chapter 3).

(c) Titanomagnetite and pyroxene of the aggregates were coprecipitating phases. The titanomagnetite present as inclusions in ferromagnesian phenocrysts in the host apparently crystallized at an earlier stage. As  $D_{Mt}^{Fe} \gg D_{Px}^{Fe}$ , pyroxenes of the aggregates have higher mg (and slightly higher Al contents), than pyroxenes which post-dated the crystallization of titanomagnetite. Therefore, although at least two generations of pyroxene crystallization are indicated, significant changes in pressure and temperature required by the restite model may not have been as important as paragenesis in determining pyroxene compositions.

Pyroxenes of the aggregates are zoned from relatively magnesian cores to rims which closely approach the composition of the magmatic phenocrysts (clinopyroxene mg = 83 to 66; orthopyroxene mg = 80 to 59). According to the restite hypothesis advocated by Flood et al. (1977), this zoning is an inherent feature reflecting original zoning in the pyroxenes of the source rock that somehow managed to survive the granulite facies partial melting event! Furthermore, the restite hypothesis requires that the parent contained (primary) zoned pyroxenes and precludes the possibility that refractory pyroxene was generated by the breakdown of original hydroxylated ferromagnesian during prograde metamorphism.

The available mineral chemistry and textural data argue more strongly in favour of a cumulate origin for the mafic aggregates. The presence of primary hornblende in some aggregates, zoned pyroxenes and the relatively sodic composition of the constituent plagioclase are features not readily explained by the restite

hypothesis. The following account is therefore presented as the favoured model of generation and crystallization of the Dundee Rhyodacite magma, incorporating evidence in support of a cumulate origin for the mafic aggregates.

i) GENERATION OF THE MAGMA

Petrographic evidence confirms that the vast majority of mafic phases and plagioclase in the Dundee Rhyodacite crystallized directly from the melt. As there is no evidence of significant fractionation of these crystalline phases, the composition of the initial liquid may therefore have approximated the average composition of the Dundee Rhyodacite. The final stages of melting of the igneous parent material occurred at temperatures in excess of 850°C and at unknown, but presumably moderate pressures in the lower crust; e.g. 8 - 10 kb (Flood et al., 1977).

Assuming that the melt was capable of transporting refractory phases representative of the entire restite assemblage, a reasonable approximation of the original parent composition might be made (e.g. White and Chappell, 1977). However indications of likely original parent rock composition will largely be determined by the choice of aggregate and phenocryst material that is considered to be restite. From the discussion already presented, clearly this choice is limited and unequivocal restite in the Dundee Rhyodacite may be extremely rare.

If it is assumed that zoned pyroxenes represent refractory residua, an intermediate to basic volcanic or relatively basic intrusive parent rock is indicated, both of which are unacceptable alternatives. No large volumes of volcanic rocks of appropriate age and composition are known, or are predicted to exist at deep levels in the northern part of the Tablelands Complex (cf. Chappel, 1978). A relatively basic parent would yield a siliceous calc-alkaline liquid after only a small degree of melting, necessitating enormous volumes of parent rock to produce the Dundee Rhyodacite magma. A parent approximating granodiorite in composition may be a more acceptable alternative.

It is envisaged that the Dundee Rhyodacite magma was generated by progressive partial melting of a relatively ferromagnesian-rich granodiorite, with this parent melting initially under amphibolite facies conditions and ultimately under conditions of granulite facies ultrametamorphism.

Melting of the felsic components in the granodiorite probably commenced at relatively low temperatures, and continued at increasingly higher temperatures as the resulting liquid rapidly became depleted in H<sub>2</sub>O (Winkler, 1976). The breakdown

of hornblende and biotite in the parent during prograde metamorphism provided some of the felsic components, the  $H_2O$  and other volatiles required to sustain melting at moderate temperatures. Final melting of the resulting granulite-facies mineral assemblage was accomplished under relatively dry, high-temperature conditions whereupon the melt migrated upwards with a clean separation from the highly refractory residuum. Only calcic plagioclase, perhaps the least dense of any residual phases, survived the journey to upper crustal levels. The paucity of restite suggests almost total melting of the parent, or almost complete separation of melt and restite due perhaps to protracted residence of the melt in the lower crust prior to slow intrusion and crystallization.

At all stages of partial melting, the contribution of An component to the melt was probably largely determined by the T,  $P_{H_2O}^{melt}$  and the An/An+Ab ratio of the residual solid phases. The relatively calcic composition of the Dundee Rhyodacite suggests that appreciable melting occurred at moderately high T and  $P_{H_2O}$ , possibly during dehydration of biotite (and amphibole) in the parent (e.g. Winkler, 1976), thereby promoting the stability of highly calcic plagioclase in the residuum. Subsequent high-temperature melting under relatively anhydrous granulite facies conditions would have involved the consumption of K-feldspar and other phases derived from the breakdown of biotite, but under these conditions appreciably lesser amounts of plagioclase components are required to maintain equilibrium melting (Whitney, 1975). Nevertheless, such high-temperature conditions would further promote the stability of only highly calcic plagioclase (cf. Flood et al., 1977).

## ii) CRYSTALLIZATION OF THE MAGMA

At lower crustal levels and under conditions of  $P_{H_2O} \ll P_{total}$ , crystallization of the magma probably commenced with the co-precipitation of pyroxene, titanomagnetite and sodic labradorite. The glomeroporphyritic clusters so formed represent the first generation of mafic aggregates now recognized in the Dundee Rhyodacite. Although it is possible that the first generation pyroxene and titanomagnetite crystallized only in the form of glomeroporphyritic aggregates containing plagioclase, the apparent absence of discrete euhedra of highly magnesian pyroxene is noteworthy. Because of their relatively high density, any discrete phenocrysts of magnesian pyroxene or pyroxene-titanomagnetite clots must have settled to the lower levels of the magma chamber as these phases have not been recognized in the Dundee Rhyodacite. However, euhedral or fractured phenocrysts of highly magnesian pyroxene may yet be found in the Tent Hill Volcanics as these volcanics possibly represent products of deeper tapings of the magma chamber (see



Chapter 3).

The crystallization of titanomagnetite ceased prior to the appearance of magnesio-hornblende as a stable liquidus phase. At this stage calcic andesine, relatively less-magnesian clinopyroxene ( $mg = 68 - 70$ ) and orthopyroxene coexisting with early crystallizing hornblende, formed a second generation of glomeroporphyritic aggregates and discrete euhedra.\* The non-adiabatic rise of the magma from the melting zone to the stage of hornblende crystallization is reflected in the delicate asymmetrical zoning in those pyroxenes of the first generation of aggregates that subsequently were partly exposed to the melt.

The bulk of the clinopyroxene ( $mg = 64.5$ ) and much of the orthopyroxene in the Dundee Rhyodacite and Tent Hill Volcanics crystallized at approximately  $850^{\circ}\text{C}$  (see above). At this temperature undercooling of the melt was sufficient to ensure a large number of nucleation sites and rapid crystal growth, resulting in the crystallization of discrete, weakly zoned (or unzoned) pyroxene euhedra. Hornblende continued to crystallize, forming euhedral phenocrysts and discontinuous rims around the relatively magnesian pyroxenes of the aggregates. The crystallization of quartz with  $\beta$ -type morphology probably commenced at temperatures above  $800^{\circ}\text{C}$  when the melt was still more basic than average adamellite composition (cf. Whitney, 1975). Biotite joined hornblende on the liquidus at a later stage, in response to both a decrease in temperature and an increase in a  $\text{H}_2\text{O}^{\text{melt}}$  caused by continued non-adiabatic rise of the magma. The melt was thus severely depleted in ferromagnesian components prior to final emplacement in the upper crust.

At low confining pressures quartz was partly resorbed due to contraction of the stability field of (plagioclase + quartz + liquid), and K-feldspar began to crystallize. The magma was vented through fractures in the roof zone after only a very small amount of K-feldspar had crystallized. The silicic groundmass of the volcanic products (representing the composition of the late-stage liquid) is therefore highly potassic (Wilkinson et al., 1964, Table 6).

### iii) ERUPTION OF THE MAGMA

No hydrous alteration of the (low-magnesium) pyroxene phenocrysts is evident in the Dundee Rhyodacite. Such alteration would suggest that the melt had attained

\* Fractured euhedra of second generation clinopyroxene have been analysed. They may be distinguished from the more common phenocrysts by the presence of hornblende alteration. Analyses of these pyroxenes appear with the other analyses of pyroxenes in aggregates, in Table 3.1.

levels of water saturation ( $P_{H_2O} \geq P_{total}$ ), the alteration resulting from the fluxing of volatiles through the magma. Disruption of the roof zone eventually leading to eruption of the magma, was therefore probably not the result of hydrofracturing caused by the hydraulic action of confined volatiles initially released during resurgent boiling (see Burnham, 1979). Metasomatic alteration caused by volatile fluxing and the abundant crystallization of K-feldspar, at least in the apical parts of the magma chamber, would be a natural consequence of episodic or continuous hydrofracturing and these products are not observed. Disruption of the brittle roof zone or the reactivation of pre-existing fractures dating to the first volcanic episode may therefore have been accomplished by doming as the magma attained isostatic equilibrium in the upper crust (cf. Oftedahl, 1978; Taylor, 1976).\*

The dramatic reduction of lithostatic pressure induced rapid boiling and the magma, charged with volatiles, was fluidized and expelled from the chamber (cf. Harris *et al.*, 1970). The style of eruption (*i.e.* relatively passive) was probably governed as much by vent geometry as by the water content of the late-stage magma.

#### iv) WATER CONTENT OF THE DUNDEE RHYODACITE MAGMA

Burnham (1979a) has shown that for a wide range of magma compositions a minimum of 3 wt% H<sub>2</sub>O is required to precipitate magmatic hornblende. This value will be reduced if other volatile components such as F and Cl are present in significant amounts (Holloway, 1979). In the Dundee Rhyodacite, hornblende was a liquidus phase after perhaps only 25% of the magma had crystallized, which suggests the initial melt may have contained at least 2 wt% H<sub>2</sub>O. A parent rock with an anhydrous granulite facies mineral assemblage is unlikely to generate a melt with 2 wt% H<sub>2</sub>O even after only 15% melting had occurred. (Viscosity calculations have shown that this is probably the minimum amount of melting required to enable separation of an acid melt from the residuum (Compston and Chappell, 1979)). Water for the Dundee Rhyodacite magma was therefore probably derived largely from the breakdown of hornblende and biotite in the parent rock during prograde metamorphism.

\* According to Burnham (1979) doming may in this case be attributed to the "telluric pressure or overpressure" which is a component of the internal pressure of the magma. The magnitude of this overpressure and the tensile strength of the roof and wall rocks at high crustal levels may largely determine the occurrence and extent of doming.

The composition of plagioclase in the Dundee Rhyodacite also suggests high water contents. Although the An/An+Ab ratio of the magma was quite high and the most calcic plagioclase may have crystallized at temperatures above 850°C, experimental studies by Johannes (1978) (cf. Holloway and Burnham, 1972 and Helz, 1976) showed that high water contents also promote the crystallization of more calcic plagioclase.

At the time of eruption almost 50% of the Dundee Rhyodacite magma had crystallized and the melt may have contained 4 wt% H<sub>2</sub>O. This agrees well with the water content of ignimbrites derived from calculations of flow rates and viscosity by Rutherford and Heming (1978). That retrograde boiling of the magma had probably not commenced prior to eruption suggests that the chamber was tapped through a considerable thickness of overburden, or that internal pressures were rather high.

## B. MAGMA EVOLUTION

Large volumes of comagmatic volcanic and subvolcanic rocks are typical of major volcano-plutonic associations (Ustiyev, 1970). By analogy, it has been proposed that the rhyolitic Emmaville Volcanics and the leucogranitoids in the Tenterfield region are comagmatic. However, it has been emphasised that the mineralized leucogranitoids, rhyolites and the barren leucogranitoids each possess distinctive incompatible trace element abundances, although in most other respects their geochemistries are very similar. Using mainly major element and compatible trace element data, Chappell (1978) delineated four distinct granitoid suites in the Moonbi district of New South Wales, proposing that each suite was derived by partial melting of a different source rock. Because the chemistries of siliceous members of the volcano-plutonic association in the Tenterfield area differ only in their abundances of selected incompatible trace elements there would be difficulties in proposing that they represent magmas generated from different source rocks. However the variable abundances of the incompatible trace elements present a problem warranting detailed discussion.

Derivation of the magmas from a common source rock and the existence of a comagmatic relationship between the rhyolites and the barren leucogranitoids may be valid, but this proposal demands that the incompatible trace element anomalies are the result of different magmatic processes operating within discrete bodies of originally identical magma. The following discussion is an attempt to provide such an explanation. If correct, the model should be applicable to other volcano-plutonic associations and may reveal hitherto unrecognized magmatic relationships between spatially associated unmineralized and ore-bearing leucogranitoids (cf. Hesp and Varlamoff, 1977).

### (a) Source of the Metals for the Mineralized Leucogranitoids

i. Metals from the Parent Rock: It may be assumed that the geochemical characteristics of magmas generated by partial melting are inherited from the ultrametamorphosed parent. For magmas which give rise to ore-bearing granitoids there is rarely a need to invoke a separate source for the ore metals because the processes leading to ore formation involve the concentration of trace amounts of the metals from large volumes of magma. For example, porphyry copper deposits, once thought to be generated from abnormally copper-rich magmas derived by melting of metalliferous sediments and

basaltic rocks (Sillitoe, 1972), are now considered to represent the mineralized apical portions of high-level plutons which crystallized from typical calc-alkaline magmas, usually of intermediate composition (Burnham, 1979).

The major and trace element chemistries of the leucogranitoids including the Mole Granite and Ruby Creek Adamellite, suggest their magmas were generated by very limited partial melting of the igneous parent.\* The leucogranitoids are especially depleted in Ba (see Figure 3.13) which may indicate that only the low-temperature (low Ba) K-feldspar of the parent was removed with the other minimum-melting components (cf. Wells, 1979) or that Ba in the parent was largely located in (refractory) biotite. If so, a corollary would be the proposal that the small amounts of biotite in the leucogranitoids must be restite. A problem immediately presents itself: if only the felsic components of the parent were involved in melting, how were the Sn and other ore metals and incompatible elements introduced into the melt?

Biotite, hornblende, sphene and a number of other accessory minerals in granitoids may contain significant amounts of Sn - i.e. several hundreds of  $\mu\text{g/g}$  (e.g. Flinter, 1971). Studies on the stability of sphene in basic rocks undergoing partial melting (Hellman and Green, 1979) suggest that sphene may not have been stable under the conditions of ultrametamorphism which generated the leucogranitoid magmas. The temperature stability of sphene at low  $P_{\text{CO}_2}$  (Hunt and Kerrick, 1977) supports this conclusion. Sphene may therefore be a potential source of Sn but, unfortunately, it is difficult to prove that this mineral was present in the source rock. Biotite and hornblende in the source rock may therefore be regarded as the most likely donors of Sn to the leucogranitoid magmas. Because only very small amounts of these phases were probably involved in melting, it is proposed that Sn and a number of other trace elements may have entered the melt during solid-state re-equilibration of the ferromagnesian, i.e. the relatively incompatible elements may have been rejected as the lattices of the ferromagnesian changed to a more ordered structure during ultrametamorphism. The ionic charge, ionic radius and preferred co-ordination number of a given element may determine its mobility and partitioning

\* Thomson (1976) and O'Neil et al. (1977) considered the Ruby Creek Adamellite possesses some S-type characteristics. However, of the several samples analysed by Thomson (1976), only one contains >1 wt% mesonormative corundum, and other S-type characteristics are lacking. Rare muscovite in the Ruby Creek Adamellite is considered to suggest only very high  $a_{\text{H}_2\text{O}}$

during the final stages of crystallization and, although it is more common in S-type granitoids (Chappell and White, 1974), muscovite can occur in highly siliceous I-types (Chappell, 1979).

behaviour during structural re-organisation of the mineral. For example, Sn (Mo) and to a lesser extent Ba should be more readily removed from biotite than the trace alkali metals. Trace amounts of base metals and Mo present as sulfide inclusions in the ferromagnesian may also have been rejected and entered the melt. Although the release of intragranular incompatible elements during high grade metamorphism and partial melting remains speculative, the mobility of intergranular complex species of B and U is now recognized (Ahmed and Wilson, 1981; Tieh et al., 1980). Future studies may expand this list to include Sn, Mo, W and other LIL elements, especially in rocks lacking primary accessory minerals rich in these elements.

Because it is an extremely lithophile element in siliceous rocks and magmas (Mason, 1966) any Sn in the parent not originally bound in the lattices of silicate phases or along crystal and grain boundaries, was probably largely present as discrete grains of refractory cassiterite. Although it has been suggested that Sn may be mobilized from certain cassiterite-bearing assemblages subjected to high grade metamorphism and anatexis (Plimer, 1980), cassiterite was probably not an important primary source of Sn for the Tenterfield Leucogranitoid magmas. The source rock for the low-temperature magmas was of initially intermediate composition for it later generated the higher temperature hornblende- and biotite-bearing non-minimum melts of the same petrogenetic suite. The parent was therefore likely to be virtually devoid of primary cassiterite as this mineral is generally restricted to only the most siliceous of granitoids.

The minor element composition of the parent rock may also militate against the dissociation of any existing cassiterite during partial melting. The Sn-bearing initial melts studied by Plimer (1980) were probably B-rich due to the contemporaneous breakdown of tourmaline in the source rocks, and recent studies (e.g. Pichevant, 1981; Charoy, 1981) have verified that B, usually in association with other melt-modifying ions such as F, induces structural changes in siliceous melts to favour accommodation of LIL elements including Sn. It therefore appears that for cassiterite to be an important source of Sn in siliceous partial melts, the parent rock should also contain tourmaline or other low melting minerals capable of supplying significant amounts of melt-modifying ions like B and F. It is considered unlikely that the intermediate source rock for the Tenterfield leucogranitoids fulfilled these mineralogical and chemical requirements.

Furthermore, the chemical stability of cassiterite virtually guarantees that any Sn not in the ferromagnesian or other leachable forms was probably resistant to attack by cognate (mildly acidic) fluids fluxing through the parent rock during the partial melting event (cf. Wodzicki, 1971). However it is also possible that portions

of the parent rock were metasomatized by halogen-rich fluids derived from a deep source (see below). In this case effective leaching of Sn and other elements from altered biotite and hornblende seems highly probable (cf. Hesp and Varlamoff, 1977).

Prior to partial melting the REE in the source rock were probably distributed amongst a number of silicate phases. Of the ferromagnesian, hornblende is the more likely to fractionate REE (Nagasawa and Schnetzler, 1971; Hanson, 1978). However, the high REE content and the relatively unfractionated light and heavy REE patterns of the mineralized plutons suggest refractory hornblende exerted little influence on the partitioning of REE into the initial partial melts. Roaldset (1975) has shown that appreciable amounts of REE are readily leached from magmatic biotite phenocrysts by rinsing in EDTA, which indicates that REE occupy exchangeable surface cation sites in addition to interlayer cation sites. During metamorphism REE not bound in silicate lattices are mobilized (cf. Chapter 3) and REE may be concentrated by surface absorption onto biotite (Roaldset, 1975). The strong partitioning of REE into initial partial melts (e.g. Koljonen and Rosenberg, 1974; Price and Taylor, 1977) may therefore be partly attributed to desorption of REE from biotite. Absorption of REE onto hornblende is probably less effective than onto biotite (Roaldset, 1975) but removal of REE from hornblende (and biotite) may also involve the rejection of cations from the ferromagnesian lattices during prograde metamorphism as discussed earlier.

REE are probably less readily mobilized from REE-rich refractory phases such as apatite and zircon.\* However it appears that both heavy and light REE strongly partitioned into the initial (leucogranitoid) melts (cf. McCarthy and Kable, 1978; Bendor, 1979), suggesting the parent either lacked heavy REE-rich refractory residuals (McCarthy and Kable, loc.cit.), or REE partitioning into the melts was enhanced by the presence of an accompanying fluid phase (e.g. Shaw, 1978).

The mineralized Mole Granite and Ruby Creek Adamellite have some, but significantly not all, of the mineralogical and geochemical characteristics of A-type granites as defined by Collins et al. (in prep.). Compared to spatially associated barren I-type granitoids of similar SiO<sub>2</sub> content, the mineralized granitoids are anomalously enriched in the trace alkali metals, U and Th but possess only marginally higher abundances of Ce and Y. That these rocks have generally higher overall REE

\* A recent study suggests some varieties of zircon may, however, be unstable at moderately high temperatures (Sommerauer, 1979). Dissociation of zircon during partial melting may proceed until the melt is saturated with Zr (approx. 60  $\mu$ g/g) (Watson, 1979). REE are presumably also released into the melt as zircon in the parent breaks down.

values remains unknown as no REE data are available for the unmineralized leucogranitoids. There is a considerable overlap in the abundances of other trace, minor and major element components.

Collins et al. (in prep.) propose high temperature, second generation partial melting of an already depleted granulite source rock to produce relatively anhydrous, F- and incompatible element-rich A-type magmas which are typically devoid of restite phases. "Up to 80% of the large highly charged cations . . ." in the melt are considered by these authors to be contributed by melting of accessory phases in the source rock, with minor contributions from the breakdown of mafic silicates.

It is considered doubtful that the Mole Granite and Ruby Creek Adamellite can be properly designated "A-type" granites. The distinctive F and incompatible element abundances of A-types are considered primary features by Collins et al. and the possibility of convection- or diffusion-enhanced enrichment of the magmas at levels above the zone of melting (Whitney, 1975a; Smith, 1979) has been dismissed because the A-type granitoids studied by them were apparently emplaced at relatively deep levels in the crust. The anomalous concentrations of selected trace elements in the Mole Granite and Ruby Creek Adamellite are here considered to be due to localized enrichment processes operating at high crustal levels in magmas generated by only small degrees of partial melting of an undepleted source rock.

ii. Extraneous Sources for the Metals: To explain the geochemistry of the Moonbi granitoids, Chappell (1978) concluded that the lower crust under the Moonbi area is heterogeneous and proposed the existence of four distinct source rocks. However, in cases where anomalous concentrations of trace elements in mantle-derived magmas cannot be explained by (a) unusual amounts of partial melting of a particular parent rock followed by crystal fractionation (e.g. Lopez-Escobar et al., 1977), (b) unusual parent rock mineralogies (e.g. Mertzman, Jr., 1977), (c) open-system fractionation (e.g. Ulmer and Drory, 1974; Stern, 1979), or (d) assimilation (e.g. Kay et al., 1978), most authors invoke partial melting of parent rocks conveniently enriched or depleted in the relevant trace and major elements (e.g. Helmke and Haskin, 1974; Beswick and Carmichael, 1978; Frey et al., 1978; Smith et al., 1981).

An important distinction between studies which attempt to model compositional inhomogeneities in the lower crust (e.g. Chappell, 1978) and those in the upper mantle (e.g. Frey et al., 1978) is that crustal inhomogeneities are presumed to reflect variations in rock type, whereas inhomogeneities in the upper mantle are frequently considered to reflect only subtle variations in the trace or major element



content of a single source rock and are regarded as secondary in origin. Selected trace and major element enrichment of the upper mantle is supposed to accompany metasomatism resulting from the fluxing of fluids derived from subducted oceanic material (e.g. Nicholls and Whitford, 1976; Anderson et al., 1978; Johnson et al., 1978), or some other (unspecified) mantle source (e.g. Bailey, 1970; Michell and Bell, 1976; Sigvaldason and Oskarsson, 1976; Mysen and Holloway, 1977; Shimizu and Allegre, 1978; Wood et al., 1979; Spera, 1980; Lloyd and Bailey, 1975; Bailey, 1978; Taylor et al., 1980; Kyle, 1980; Kushev and Mironov, 1980).

Only rarely has the metasomatism of an originally homogeneous source rock been proposed to explain the chemical characteristics of crustal-derived granitoids (cf. Collerson and Fryer, 1978; Wells, 1979; Weaver, 1980). However, localized metasomatism of the parent rock underlying the Tenterfield area may explain why, in a region dominated by barren leucogranitoids, only the Mole Granite and Ruby Creek Adamellite are significantly mineralized. This hypothesis has the following advantages:

- (a) only magmas derived by partial melting of the metasomatized portion of the parent may be enriched in ore metals and other incompatible elements, and
- (b) provided the original mineralogy of the parent remains largely unchanged, these magmas should possess major and incompatible trace element contents virtually identical to those generated by partial melting of unmetasomatized portions of the parent.

The metasomatising fluids may represent the volatiles expelled from lower crustal rocks during prograde metamorphism to granulite facies (Drury, 1973; Sheraton et al., 1973; Collerson and Fryer, 1978; Wells, 1979). Si, Sr, La and Na (Wells, 1979) and K, Pb, Cs, Th, U, Y, heavy REE, CO<sub>2</sub> and the halogens may be transported in these fluids (Collerson and Fryer, 1978). Fluids of subcrustal origin may contain Ba (Ruth and Meijer, 1979), light REE and other incompatible elements (e.g. Mysen, 1979).

The presence of CO<sub>2</sub> and halogens in these predominantly aqueous metasomatising fluids is also important for the transport of Sn, W, and Mo. Experimental investigations and studies of mineralized greisens suggest W may complex with Cl and carbonate (e.g. Higgins, 1980; Reyf and Bazheyev, 1977), form

molecular polytungstates and  $(\text{WO}_4)^{2-}$  species and occur as complex hexachlorides at magmatic temperatures (Foster *et al.*, 1978); Mo may be transported in the vapour phase as hydroxide and oxymolybdate species (*see* Westra & Keith, 1981) and possibly as  $\text{H MoO}_4^-$ ,  $\text{H}_2\text{MoO}_4$ ,  $\text{MoO}_3\text{F}^-$ , thiomolybdate and halide complexes which are sensitive to high temperatures (Smith *et al.*, 1980; Arutyunyan, 1969; Khitorov *et al.*, 1967; *c.f.* Samarkin and Samarkina, 1978), and Sn may be transported as  $((\text{Na}), (\text{K}))_2 (\text{Sn}(\text{OH})_x\text{F}_{6-x})$ , tin oxy or hydroxy complexes,  $\text{Sn}(\text{I}, (\text{Cl}), (\text{F}))_4$  or  $\text{Na}_2\text{SnO}_3$ , depending on the pH, temperature and the activity of potential ligands in the fluids (Barsukov, 1957; Hesp and Rigby, 1972; Sushevskaya and Ryzhenko, 1977; Grushkin and Verdernikov, 1978; Eadington and Giblin, 1979; Groves and McCarthy, 1978). In this case the ultimate source of these metals is unknown.

In conclusion, it appears that the Sn and other incompatible elements concentrated in the mineralized plutons may have originated from a number of sources. These are:

- (a) the same parent rock which generated the barren leucogranitoids,
- (b) locally metasomatized portions of this parent rock, or
- (c) a parent rock entirely different to that which generated the barren leucogranitoids.

Alternatives (b) and (c) must be regarded as somewhat facile and convenient explanations for the geochemical differences between the mineralized and unmineralized leucogranitoids. Alternative (a) will be discussed at length in the following pages.

#### ELEMENT PARTITIONING IN SILICIC ROCK MELTS

The following discussion details the likely behaviour of some trace and major elements at various stages during the emplacement of leucogranitoid magmas. The theoretical discussion to be presented was researched prior to the publication of Hildreth's (1979) thermogravitational diffusion model and, although similar in most respects, emphasis is here placed more on events leading to orebody formation (*cf.* Wright and Mutschler, 1979) and includes speculation on the possible importance of removal of metals from the magmas in the form of fugitive volatile species, aspects mentioned but not fully developed by Hildreth.

(1) MELT STRUCTURE AND THE SPECIATION OF MELT COMPONENTS

Early investigations on the structural characteristics and ionicity of aluminosilicate glasses (Orlova, 1962; Hess, 1971) and melts (Toop and Samis, 1962, 1962a; Masson, 1966; Urnes, 1966) established that naturally occurring aluminosilicate melts probably consist of polymers and much smaller ionic species. Although it is now known that glasses are not structurally identical to melts (Weyl and Marboe, 1959; Boon, 1971; Boon and Fyfe, 1972), these early studies provided the framework for the semi-quantitative description of melt structures in terms of a quasi-crystalline model. "A premise underlying the . . . model . . . is that the short-range order of the crystalline state of a given phase (mineral) is largely preserved to temperatures well above its liquidus, hence the principal change on melting is the loss of long-range order." Thus, ". . . (1) the structural units in the melt of given composition tend to mimic those of the crystalline phases that appear upon cooling, and (2) electrical neutrality is preserved on a local, structural-unit scale" (Burnham, 1979a). Confirmation of the general applicability of the quasi-crystalline melt model is that it has formed the basis for numerous theoretical and experimental investigations of the mixing properties and solubility of volatiles in melts (e.g. Burnham and Davis, 1974; Burnham, 1975, 1975a, 1975b, 1977, 1979a, 1979b; Nelson and Carmichael, 1979).

Because, in general, melts mimic the structures of rock-forming minerals, the methodology of investigation of the co-ordination geometry of trace and major cations in melts is now largely by analogy with known crystalline systems. In rock and mineral melts the temperature, pressure and concentration-dependent co-ordination of elements such as Al, Fe and Mg is therefore now understood (Waff, 1977; Fujii and Kushiro, 1977; Mysen and Virgo, 1978; Leeman, 1978; Velde and Kushiro, 1978; Mysen and Kushiro, 1979; Burnham, 1979a), but of far greater importance to this study are the consequences of volatile solubility on the structure of rock melts.

Investigations of all the major volatile species in melts have confirmed that volatile solubility is dependent on the pressure, temperature and composition of the melt, and that at high pressures all such volatiles dissolve by breaking bridging oxygen bonds (usually Si-O-Si, Al-O-Si) thereby depolymerizing the melt in proportion to the amount of volatiles dissolved (e.g. halogens - Buerger, 1948; Whitney, et al., 1976; Fuge, 1977; CO<sub>2</sub> - Wyllie and Tuttle, 1959; Kadik et al., 1972; Mysen, 1976; Egglar and Rosenhauer, 1978; Swanson, 1979; H<sub>2</sub>S - Burnham,

1975, 1979a;  $H_2O$  - Burnham and Jahns, 1962; Hamilton *et al.*, 1964; Burnham, 1975). Dissolved volatiles therefore have the important effect of transforming the melt to a structure less closely approximated by compositionally "analogous" crystalline systems. Trace element crystal-liquid and liquid-liquid partitioning is strongly dependent on the melt structure (*e.g.* Fraser, 1975; Watson, 1976, 1977; Irving, 1978; Ryerson and Hess, 1978) and studies which model partitioning only on the composition of co-existing crystal-liquid pairs (*e.g.* Jensen, 1973; Matsui *et al.*, 1977; Philippotts, 1978; Banno and Yamasaki, 1979), while yielding useful results, offer no indication of the likely co-ordination of the trace elements in volatile-rich magmas.

In highly silicic, calc-alkaline melts, any increase in the degree of polymerization (induced by, for example, a decrease in temperature, pressure or the solubility of volatiles) is synonymous with an increase in the tetrahedral co-ordination of the liquid. At low pressures  $Al^{3+}$  and  $Si^{4+}$  are the essential tetrahedral network-forming cations and Na and K are essential for the formation of alkali feldspars which, together with quartz, comprise the cotectic assemblage which crystallizes upon cooling of the melt. Only trace elements that are compatible with a tetrahedrally co-ordinated liquid, or those able to substitute for Na, or K (*e.g.* Rb) will therefore partition strongly into a dry aluminosilicate melt at low pressures (*cf.* Watson, 1977); *i.e.* ". . . increased polymerization decreases the stability of high field-strength (charge/radius) cations in silicate melts. Since bridging oxygens cannot participate in the co-ordination polyhedra of such cations, strongly polymerized rhyolitic liquids provide relatively few suitable sites for highly charged species unable to co-polymerize with the aluminosilicate network. Poor anionic screening and the endothermic effect of high charge-density metallic cations on Si-O bond angles and lengths (Ryerson and Hess, 1978) would thus favour the migration of such cations into less polymerized parts of the magma chamber" (Hildreth, 1979, p.70). Metals such as Nb, Sb, Mo, Ta, U, W and Th which may migrate to the roof of a magma chamber are given as examples by Hildreth (1979), but others would include Li, Cs, B, Be, Tl, Sn, Zr, Hf, REE, Pb (and possibly Ba and Sr) when the ionic radii of the metals are also considered.

The observed close association of the above-listed metals with the volatile components of the magma is predictable for two reasons. (a) These highly incompatible elements will partition strongly into melts depolymerized by dissolved volatiles, and (b) theoretically, many of the metals are able to form complexes with some of the major volatiles. The influence of complexation on trace element partitioning is now becoming more fully appreciated and is frequently invoked in

cases where the quasi-crystalline melt model fails to predict partitioning behaviour (e.g. Margaritz and Hoffmann, 1978; Mysen 1979a; Virgo et al., 1979). It should be noted that the existence of metal complexes in melts has not yet been verified by direct measurement, and much speculation on the composition and stability of magmatic metal complexes has been based on analogy with the chemistry of metals in aqueous solutions (e.g. Beus, 1958; Kosterin, 1959; Ganeyev, 1962; Balashov and Krigman, 1975).

It is considered that complexation in volatile-bearing melts is favoured because it may enable metal ions to achieve appropriate co-ordination geometries in otherwise unfavourably co-ordinated melt polymers. By forming stable complexes the partitioning of trace elements may become independent of melt composition (cf. Ryerson and Hess, 1978) and the mobility of these elements is potentially increased. The identity of the ligands in a given metal complex, which is determined by the electronic structure of the metal ion and/or the availability of ligand species, may control the stability of the complex and hence its capacity to migrate in response to a pressure or temperature gradient in the melt. Physical separation of isoelectronic cations (e.g.  $Zr^{4+}$ ,  $Hf^{4+}$ ) or the lanthanides may therefore be possible (e.g. Zr, Hf - Buma et al., 1971; Kable and Fesq, 1976; REE - Schilling and Winchester, 1967; Balashov and Krigman, 1976; Flynn and Burnham, 1978). Migration and fractionation of trace elements is important in the development of compositional zoning in magmas and confirms that complexation may play a major role in magma evolution (ref. Appendix 4).

## (2) COMPOSITIONAL ZONING IN MAGMAS

### (i) Evidence for the Existence of Zoned Magmas:

The detailed study of the rhyolitic ash-fall and ignimbritic outflow sheets of the Bishop Tuff by Hildreth (1979) is probably the most convincing evidence for the existence of compositionally zoned acid calc-alkaline magmas yet presented.

Hildreth (1979) noted that the first volcanic products from the Bishop Tuff magma chamber were significantly enriched in W, Mo, Nb, Sb, Ta, U and heavy REE relative to later eruptives of the same volcanic cycle. Employing the supposition "that the earliest parts of the erupted sequence (were) derived from the upper part of the chamber and that successive products (came) from deeper levels" (Cox et al., 1979, p. 272), Hildreth (1979) concluded that the Bishop Tuff magma chamber was

compositionally zoned, with the upper portion being enriched in a number of selected incompatible trace elements and major elements.

Fractionation of Sr and Ba as extreme as that determined by Hildreth (1979) has been documented from subalkaline rhyolite flows at Mono Co., California by Noble et al. (1972). A list of references referring to other examples of silicic calc-alkaline volcanics derived from zoned magma chambers is given in Chapter 4. Notable recent additions to this list are Birch (1978), Harley (1979), Crecraft et al. (1979), Mahood (1979) and several listed by Mutschler et al. (1981) and Smith (1979). Smith and MacDonald (1979) believe all large, high-level acid calc-alkaline magmas may be compositionally zoned and Hildreth and Spera (1974) predicted such zoning should be preserved in some high-level silicic granitoids. Some have now been documented (e.g. Ludington et al., 1979; Miller and Mittlefehldt, 1979; cf. Litvinovskiy et al., 1980). The mineralization associated with the Mole Granite and Ruby Creek Adamellite may have developed from zoned magmas (cf. Wright and Mutschler, 1979). The rhyolitic Emmaville Volcanics may also have been derived from zoned magma chambers, but poor outcrop and pervasive alteration of the most silicic rhyolites have nullified attempts towards a detailed chemical study to prove this hypothesis.

Compositional zoning produced by processes other than fractional crystallization may not be restricted to silicic calc-alkaline magmas. The dacitic to rhyodacitic differentiates of stratovolcano-building andesitic magmas (Hopson, 1971; Smith, 1979 in Hildreth, 1979; cf. Sakuyama and Kushiro, 1979), may be examples. Furthermore, extreme fractionation of alkalis and incompatible elements in comagmatic alkaline, and peralkaline volcanics is well documented (Sahama, 1974; Kogarko et al., 1974; Rittman, 1974; Bailey and MacDonald, 1975; Tanguy, 1978).

(ii) Origin of the Compositional Zoning:

Brief descriptions of proposed mechanisms of magma zonation are presented below. An appraisal of these mechanisms is the subject of a subsequent discussion. The salient features of each mechanism are then selectively incorporated into a working model which may have application to the Tenterfield region.

Thermogravitational Diffusion:                      The diffusion model described in detail by Hildreth (1979) represents the first attempt to explain the mechanisms for development of compositional zoning in

silicic calc-alkaline magma chambers in terms of a comprehensive and experimentally verifiable model.

"The thermogravitational convection-diffusion model proposed by Shaw, Smith and Hildreth (1976) is designed to explain repeated establishment of associated thermal, compositional, volatile, and isotopic gradients in large silicic magma chambers, within time constraints empirically related to system volumes and to the known eruptive periodicities of zoned systems. The model permits diffusional influx of water, and perhaps some minor components from outside the magma chamber, but its main emphasis is on the combined effects of convective circulation and internal diffusion to develop chemical gradients within the thermal and gravitational field of the magma chamber itself." (Hildreth, 1979, p.67).

Briefly, the model is dependent on 3 fundamental premises.

- (a) Volatile concentration gradients can become established in volatile-undersaturated magmas, i.e. roofward migration and concentration of volatiles can occur in the absence of a discrete vapour phase (cf. Kennedy, 1955; Shaw, 1974).
- (b) Once volatile concentration gradients (and hence density gradients) are established, their permanency is not affected by potentially destructive large-scale convective circulation. Volatile concentration gradients may therefore be viewed as manifestations of equilibrium in magma systems possessing a permanent vertical temperature gradient.
- (c) Volatile concentration gradients are accompanied by metal concentration gradients.

Temperature is considered to be the most important parameter controlling the formation of metal concentration gradients in the magma. After a long absence, the Soret effect has therefore been re-introduced as a viable magmatic process (cf. Bowen, 1928) and assumes an important role in the thermogravitational diffusion model. In the model the Soret effect is assumed to be enhanced by convective circulation (e.g. Tyrrell, 1961; Rice, 1981), and, rather than disrupting the temperature and concentration gradients, convection is restricted to, and assists in maintaining, the zoned upper portion of the magma chamber.

**Gaseous Transfer:** In magmas the migration of metals by simple diffusion is considered too slow to be of any real importance as a fractionating control (e.g. Bowen, 1928; Shaw, 1974). However, the transfer of metals as species dissolved in bubbles of vapour streaming towards the apical regions of magma chambers, has long been a popular mechanism of magma fractionation (e.g. Daly, 1910; Fenner, 1926). Metalliferous sublimates encrusting the walls of fumeroles (White and Waring, 1963; Naughton et al., 1976) indicate that volatile transfer of metals does occur, but the importance of this process in the formation of compositional zoning in magmas has not been quantitatively assessed. Nevertheless, volatile transfer has been invoked to explain Na and incompatible trace element enrichment in alkaline volcanic rocks (e.g. Locardi and Mittempergher, 1967; Rittman, 1974; Kogarko, 1974; Sahama, 1974; cf. Tanguy, 1978; Taylor et al., 1980), andesitic magmas (Sakuyama and Kushiro, 1979) and mid ocean ridge basalts (Moore, 1979), and incompatible trace element fractionation and enrichment in silicic peralkaline lavas (e.g. Bailey and MacDonald, 1975). Burnham (1967) and Holloway (1976, 1979) consider gaseous transfer of metals to be potentially important in intermediate to acid calc-alkaline magmas.

For gaseous transfer to be effective, the magma must be saturated with respect to one or a number of volatiles. Because the common volatile components of magmas have different solubilities at a given P, T and melt composition (e.g. Willie, 1979; Burnham, 1979a), and the stability of metal complexes may be strongly dependent on the nature of the ligand species (i.e. the volatile) (e.g. Mitchell and Brunfelt, 1975; Balashov and Krigman, 1975; Ishihara and Terashima, 1977), there exists enormous potential for fractionation and selective mobility of cations as magmas pass into different P-T regimes during their emplacement in the crust.

#### Formation of Hydrothermal Solutions:

(a) **Liquid-liquid Systems:** In a preliminary study of water solubility in agpaite rock melts, Kogarko et al. (1977)

demonstrated that silicic melts may undergo a pressure- and composition-dependent gradual transition to a hydrothermal solution. Therefore, above a characteristic critical pressure  $P_0$ , agpaite melts display continuous solubility in water. For a given initial water content, the ratio (magma components)/ $H_2O$  increases with increasing pressure above  $P_0$ . Below  $P_0$  the water-saturated silicate melt is in equilibrium with an aqueous vapour phase.  $P_0$  is critically dependent on melt composition and decreases concomitantly with an increase in the agpaite index of



the melt.

Because melt structure strongly influences volatile solubility and element partitioning, whole-rock major element ratios are frequently used as indicators of the degree of polymerization in silicate melts (e.g. Watson, 1977; Feiss, 1978; Hildreth, 1979; Mason and Feiss, 1979). In low pressure leucogranite melts (essentially albite, K-feldspar and quartz components) the degree of polymerization may be calculated using  $O/(Si+Al)$  (Hildreth, 1979) or a more general ratio incorporating oxygen and all the potential network-forming and network-modifying cations (Anfilogov et al., 1978). Similarly, the atomic ratio  $(Na + K)/(Al)$  is particularly instructive as it provides a measure of "peralkalinity" or "peraluminosity" in silicate melts, i.e. the amount of alkalis or Al in excess of that required to satisfy the requirements of the alkali feldspars. Anfilogov et al. (1978) showed that normal (subaluminous) calc-alkaline magmas evolve towards compositions which, at low pressure, represent perfect tetrahedral polymerization (i.e.  $(Na + K)/(Al) = 1$ ). This implies that agpaitic or peraluminous magma chemistries cannot be generated by fractionation involving crystal-liquid equilibria; these chemistries are inherited, not developed (e.g. Carmichael, 1967; Kovalenko, 1977).

However, according to Tuttle and Bowen (1958), Luth and Tuttle (1969) and Kogarko et al. (1977), siliceous melts with only a small degree of "peralkalinity" (i.e.  $(Na + K)/(Al) \geq 1$ ) may display continuous solubility in water above a characteristic critical pressure ( $P_o$ ). The gradual transition from saturated melt to hydrothermal solution may therefore be possible in hydrous, mildly "peralkaline" granitic magmas during their emplacement in the upper crust (cf. Taylor et al., 1980). In large magma chambers this transition may lead to trace (and major) element compositional zonation. The development of zoning may proceed through the following stages:-

(a) At a certain level in the crust the initially homogeneous, water-undersaturated magma becomes saturated. Saturation of the melt may be induced by the crystallization of anhydrous or relatively anhydrous phases, or simply by a reduction in lithostatic pressure. In any event, the prevailing pressure will determine the level at which the magma attains saturation.

(b) In a vertically extensive magma chamber a pressure gradient will exist and, initially, only the apical portion may be saturated. If at this stage  $P_{load} > P_o$ , this apical portion of the magma body is transformed into a hydrothermal solution. The composition (and density) of this solution depends on the prevailing pressure.

The system now consists of two magmatic components: magma located above a certain isopiestic level (call it  $P_1$ ) is oversaturated and now represents a hydrothermal solution, and the underlying magma, where  $P_{load} > P_1$ , remains undersaturated. A compositional and density gradient has been produced in the originally homogeneous magma.

(c) In response to the newly established compositional gradient, mobile trace elements in the volatile-undersaturated magma immediately underlying the isopiestic level  $P_1$  will migrate upwards into the less polymerized hydrothermal solution. Convective circulation in the main body of undersaturated magma will ensure that melt at the interface is continuously replenished (cf. Whitney, 1975a). Significant concentrations of incompatible trace elements may therefore be extracted from large volumes of volatile-undersaturated magma.

(d) The volume of volatile-undersaturated melt continuously decreases, and the volume of hydrothermal solution proportionally increases as more magma passes through isopiestic level  $P_1$  during its ascent through the crust. The distillation of trace elements from the undersaturated magma will remain significant provided convective circulation outstrips the rate of ascent of the magma through  $P_1$ .

(e) Eventually, all the magma passes through  $P_1$  and is transformed into a hydrothermal solution, destroying the original zonation of the system. However, compositional and density zonation is preserved in the hydrothermal solution, although the distribution of trace elements may not resemble that initially produced in stage (c). Solution at the top of the chamber will be more water-rich than the basal portion and may therefore be enriched in metal complexes stable in essentially aqueous solutions at moderate pressures. Convective distillation of elements may again operate; the permanency of the compositional zonation is maintained by the pressure gradient which, in turn, controls the density gradient in the system.

The above account is highly idealized and in practise may never proceed to completion. Following the initial stage of formation of the hydrothermal solution, further ascent of the magma may be impossible. In this case trace element enrichment of the apical regions of the magma system may continue to a late stage when sufficient heat and vapour have been lost to the wall rocks to enable the magma to polymerize and finally crystallize. Unfortunately, this is again an oversimplification because the agpaitic order of crystallization (Kogarko et al., 1977)

ensures that the remaining liquid becomes increasingly alkaline, thus promoting regeneration of the hydrothermal solution in those parts of the chamber where  $P_{load}$  is less than (the composition-dependent)  $P_1$ .

A somewhat different progression of events is envisaged in the case where water-saturation is attained in an originally homogeneous magma straddling the  $P_0$  isopiestic level. On slow cooling, all magma at a pressure  $> P_0$  will progressively change into a hydrothermal solution and events will proceed in the manner already outlined. However, magma above the  $P_0$  isopiestic level is expected to crystallize in a manner analogous to non-apatitic melts, with separation of an aqueous vapour phase accompanying second boiling (resurgent boiling). The possible production of compositional zonation in a melt undergoing second boiling is discussed in the following section.

The spectrum of possibilities for development of compositional zoning is presented in a large magma chamber which attains water saturation straddling both  $P_0$  and  $P_1$  isopiestic levels. The range between  $P_0$  and  $P_1$  may not be large for mildly "peralkaline" magmas and in environments where heat loss is gradual, trace element fractionation may be significant.

Leucocratic magmas in large, high level chambers are those most likely to evolve into mineralized hydrothermal solutions. The development of complimentary alkali, trace element enriched — mildly depleted silicic 2-liquid systems may have contributed to the formation of Mo-bearing alkali-calcic magmas from high-K calc-alkaline precursors, and to the formation of peralkaline hydrothermal solutions, as described by Westra and Keith (1981). The same processes may have assisted in the evolution of siliceous peralkaline compositions from alkaline intermediate magmas (e.g. Vennum, 1980). Some of the principals fundamental to the discussion of 2-liquid systems have also been applied by Mutschler *et al.* (1981) in their model of the evolution of granite molybdenum systems. This model is essentially that envisaged for the mineralized granitoids near Tenterfield (see later in this chapter).

Discussion so far has been restricted to intrusive systems. However, implicit in the discussion is the possibility that compositional zoning achieved in a magma resident in the crust may be registered in the volcanic products of that magma chamber (Smith 1979). The initial volatile content and stage of crystallization of the magma, and the duration of intervals between successive tappings of the large chamber, will largely control the successful re-establishment of compositional zoning.

(b) Liquid-vapour Systems: Closed system crystallization models with particular application to the development of porphyry copper deposits have been proposed to account for trace element fractionation and concentration in the apical regions of high-level, intermediate calc-alkaline magmas (Burnham, 1967, 1979; Whitney, 1975a, 1977). The models by both authors are similar and describe the controlling influence of P, T and melt composition on the formation of an aqueous vapour phase by resurgent boiling in a high-level magma.

Partial crystallization of the magma may be initiated by a decrease in T or P, and is accompanied by the evolution of a predominantly aqueous vapour phase. Resurgent boiling is therefore initiated in magma near the walls and apex of the chamber and a "boiling front" proceeds both inwards and downwards with time as the magma crystallizes. Detailed experimental studies support Whitney's (1975a) description of changes in the composition of the stable liquidus phases at various stages in the cooling history of the magma. Similarly, the composition of the major melt components dissolved in the vapour may change in response to shifts in equilibrium in the co-existing melt (e.g. Tuttle and Bowen, 1958; Luth and Tuttle, 1964, 1969). The trace element composition of the vapour is also expected to change with time and Burnham (1979) has shown that the Cl content of the vapour is usually sufficient to account for the transportation of Na, K, Fe, H and the mineralizing base metals as stable chloride complexes (also see Kilinc and Burnham, 1972; Holland, 1972; Naughton et al., 1976; Cunningham, 1978; Whitney, et al., 1979).

As already described, distillation of trace elements from undersaturated magma into the vapour phase may occur across the "boiling front", enhanced by convective circulation in the main body of undersaturated magma. In addition to T and P, the composition of the volatile species originally dissolved in the melt may determine the positions of liquidus boundary surfaces, causing changes in the order of crystallization of phases from the melt, and the relative solubilities of the volatiles will determine the anionic composition (and hence the trace element composition) of the vapour phase at a given P and T (e.g. Wyllie and Tuttle, 1960, 1961; Burnham, 1967, 1979; Holland, 1972; Gustafson, 1979).

It is considered that these theoretical mechanisms leading to the development of porphyry copper deposits may have application to more silicic high-level magmas, as the melt systems used to model resurgent boiling phenomena have generally been of granitic composition.

(3) APPRAISAL OF MAGMA ZONING MECHANISMS

Thermogravitational Diffusion: The thermogravitational diffusion model may be regarded as potentially the most viable, but nevertheless the most theoretical, of the four mechanisms of magma zonation outlined above. For the reasons given by Hildreth (1979) much work is still required before a quantitative appraisal of the Soret effect in magma systems can be made. However there appears little doubt that once volatile gradients are established in magma chambers, fractionation of trace elements may occur. However, the mechanism(s) of fractionation remains poorly understood.

Perhaps the most controversial premise of the thermogravitational diffusion model is the development of a volatile concentration gradient in (presumably) an originally homogeneous, volatile-undersaturated magma. To support this premise, Hildreth (1979) quoted studies by Kennedy (1955) and Shaw (1974). Kennedy (1955) argued that in a magma " . . . the partial pressure of water increases rapidly with depth, and there would be a strong tendency for water to diffuse upward. . . . In effect, higher confining pressure increases the partial pressure of the water by trying to squeeze it out of the melt, a consequence of the large partial molar volume of water in the melt." Studies of the changes in the specific volume of hydrous albite melts with varying P, T and water content (Burnham and Davis, 1971), completely contradict Kennedy's conclusion. Because the dissolution of water in granitic melts is analogous to that in molten albite (Burnham, 1975), conclusions drawn from the Ab-H<sub>2</sub>O system are relevant to granitic magmas and indicate that the apical regions of large magma chambers cannot be enriched in water by the process favoured by Kennedy (1955).

Similarly, qualitative data on the convection-enhanced diffusion of water and other components in volatile-undersaturated magmas subject to permanent thermal gradients (Shaw, 1974), may be incorrectly applied by Hildreth (1979). Shaw provided two contrasting models for the establishment of density and concentration gradients in magmas influenced by a temperature gradient, including

- (a) density gradients controlled by thermal expansion of melt across a convection boundary layer;
- (b) density gradients controlled by compositional changes in the melt across a convection boundary layer.

In both cases a concentration gradient was maintained to simplify the models, and it was concluded that diffusion of components across the convection boundary layer occurred at geologically realistic rates and could produce density (and compositional) zonation in large magma chambers. However, the thermogravitational diffusion model requires that volatile concentration and density gradients be established in initially homogeneous, volatile-undersaturated magmas subjected to a thermal gradient. Although convection will no doubt operate under these conditions, it is considered uncertain that, in response to the temperature gradient, the diffusivity of water through the melt will be significant in the absence of a concentration gradient.

Most of Shaw's (1974) diffusion data was obtained from experimentally determined rates of hydration of obsidian - i.e. in the presence of a concentration gradient. Furthermore, some of the water was "dissolved" molecularly, in contrast to the dissociation mechanism of water dissolution in silicate melts (Burnham, 1975). In undersaturated magmas, dissolved water is largely bonded to polymer species (as hydroxyl groups) and the amount of molecular water present may be assumed insignificant. In the absence of a volatile concentration gradient, migration of "water" towards the cooler apical regions of the magma chamber may therefore be too slow to be of geological importance (e.g. Burnham, 1967).\*

However, once volatile concentration gradients have been established in water-undersaturated magmas (mechanisms unknown?), the study by Shaw (1974) suggests such gradients will be maintained and enhanced by convective circulation (see footnote, this page). Trace element concentration gradients may then be produced by virtue of the Soret effect which, it will be argued, may be a viable process only in volatile-rich melts.

Other Mechanisms: In contrast to the thermogravitational diffusion model, the gaseous transfer and hydrothermal solution mechanisms for magma zonation involve transportation of metals in volatile-saturated magmas, and pressure assumes a major role in determining the advent of compositional zoning. In static magma chambers linked to volcanic conduits, the alkali and incompatible

\* Arzi (1979) has suggested the rate of diffusion of water in granitic melts is much more dependent on T than the concentration of dissolved water. These conclusions were based on melting data in systems possessing a water concentration gradient. At 760°C, approximately the average temperature of the Bishop Tuff magma (Hildreth, 1979), the diffusion coefficient of water in granitic melts may only be of the order of  $10^{-9}$  cm<sup>2</sup>/sec (Arzi, 1979) which is the value quoted by Shaw (1974) for water diffusivity in essentially dry granite magmas.

element-enriched apical portion (the "pyromagma") overlies a larger volume of essentially pristine, or mildly volatile- and trace element-depleted "hypomagma" (Rittman, 1974). In these systems the compositional zonation has been considered to be the result of "pneumatolytic differentiation" in the magma chamber (Kogarko et al., 1974).

Although the "pyromagma" concept is generally used to describe zoning in open magma systems associated with periodic or cyclic alkaline volcanism, the process responsible for the transportation of trace elements is considered similar to that operating in closed magma chambers undergoing resurgent boiling. In both systems the transporting medium is a dense vapour and only those metal complexes stable in an unpolymerized fluid may undergo fractionation. Trace element differentiation by gaseous transfer may therefore be highly selective and involve fewer trace elements compared to the potentially more efficient processes inherent in the thermogravitational diffusion and "peralkaline" hydrothermal solution models in which trace element fractionation is achieved in a more polymerized environment. However, because the rate of trace element transfer may be directly related to the volatile content of the magma, diffusion of metals through a hydrothermal solution may be more rapid than in a volatile-undersaturated magma (ref. Appendix 4). The convection-enhanced Soret effect modelled by Hildreth (1979) is therefore probably sensitive to melt major element composition and volatile concentration, and both of these parameters may strongly influence the variety of metals transported.

In the discussion on the formation of hydrothermal solutions, the atomic ratio  $(Na + K)/Al$  was used in preference to the commonly accepted ratio  $(Na_2O + K_2O)/Al_2O_3$  (mol. prop.) as an indicator of "peralkalinity" and polymer co-ordination in siliceous melts at low temperatures. However it is important to recognize that Ca, in addition to Na and K, is involved in tetrahedral network formation in subaluminous siliceous melts at low to moderate pressures, and the atomic ratio  $(Na + K)/(Al - 2Ca)$  may therefore be a more useful indicator of peralkalinity in high-level leucogranitic magmas.\* This ratio was calculated for the "early" and "late" eruptives of the Bishop Tuff, considered to represent (respectively) the compositions of the upper and lower portions of the compositionally zoned parent magma (Hildreth, 1979). The values 1.01 (upper) and 1.02 (lower) were obtained suggesting that, on a volatile-free basis, the Bishop Tuff magma was saturated with respect to

\* Implicit in these calculations is the assumption that all of the plagioclase is magmatic in origin. The absence of unequivocal relict plagioclase is a feature of all the leucogranitoids studied (ref. chapter 2).

K-feldspar and albitic plagioclase components. Similar calculations for some leucogranitoids from the Tenterfield region yielded the following maximum values:

1.00	Mole Granite	0.96	Clive Adamellite
0.98	Ruby Creek Adamellite	0.97	Bolivia Range Leucoadamellite
1.01	Nonnington Leucoadamellite		

These results suggest that the Tenterfield leucogranitoid and Bishop Tuff magmas (and, by implication, many other evolved calc-alkaline magmas in high-level environments (e.g. the rhyolitic magmas in Mono Co.; Noble et al., 1972)) may have compositions which approach those of melts capable of continuous solubility with H<sub>2</sub>O at suitable pressures. On this subject the comments of Tuttle and Bowen (1958) are considered particularly relevant. ". . . continuous gradation from magma to hydrothermal solution will obtain in hydrous liquids if the alkali to alumina ratio is such that crystallization results in concentration of alkali silicates in the residual liquids. This restriction may not apply to a complex system such as a granite magma in which many volatiles in addition to water are concentrated. Such a system concentrating lithia, carbon dioxide, sulfur, chlorine, fluorine, and many other materials may exhibit a continuous gradation even when alumina is present in excess of that amount required to combine with the alkalies to form feldspar." (also see Luth and Tuttle, 1969).

It may therefore be argued that the siliceous magmas of the Tenterfield leucogranitoids, which may have contained little or no "excess" Al, were potentially capable of generating concentrated hydrothermal solutions at some stage of their intrusive and cooling history.

(4) EVOLUTIONARY PROCESSES IN SILICIC CALC-ALKALINE MAGMAS:  
CONCLUSIONS

Up to this point discussion on the chemical evolution of siliceous magmas has been largely restricted to closed all-liquid systems. This limited approach is justified because there is abundant evidence that the distribution of trace elements in many high-level granitic magmas (i.e. the vertical compositional zoning) cannot be explained by any known crystal-liquid partitioning phenomena. Using the Bishop Tuff magma as an example, Hildreth (1979) has presented convincing evidence to demonstrate that the inferred levels of trace element abundance were produced by processes operating in a closed magma chamber and were not inherited from the magma source or by contamination from contact rocks.



It is considered that the four magma zoning mechanisms already outlined may operate to some extent in all high-level, siliceous calc-alkaline magmas containing appreciable amounts of volatiles. In magmas which remain closed throughout their cooling history, the roofward migration of incompatible elements may lead to economic concentrations of rare metals. In most cases these metals are probably transported as soluble complexes in a fluid phase generated by resurgent boiling of the crystallizing melt. However, in some circumstances the magma may initially be transformed into a concentrated hydrothermal solution which represents an ideal environment for the fractionation of trace and major elements by the thermogravitational diffusion process. Selective trace element transfer is efficient because in a hydrothermal solution the fluid phase is continuous and this melt polymer-fluid system closely approximates the environments created artificially for the industrial application of the thermogravitation convection-diffusion process (Tyrrell, 1961). If, however, thermogravitational diffusion can operate in volatile-undersaturated magmas (Shaw et al., 1976), some roofward migration and concentration of metals may occur prior to the operation of other processes.

The mechanical energy ( $P\Delta V$ ) released from a crystallizing magma undergoing resurgent boiling may be sufficient to induce brittle failure in the overlying roof rocks and thereby initiate a volcanic eruption (Burnham, 1975, 1979a). Not uncommonly the first products of the eruption may be more enriched in certain incompatible elements than subsequent flows of the same volcanic episode (e.g. Pitcher, 1974). The amount of volatiles lost in the initial eruptions, the stage of crystallization of the magma and the rate at which the latent heat of crystallization of magmatic minerals is lost to the wall rocks (Burnham, 1979a; cf. Harris et al., 1970; Harris, 1977; Marsh and Kantha, 1978; Holloway, 1979) are some of the factors determining the possible re-establishment of compositional zoning in the remaining magma.

The same factors pertain to magmas undersaturated with respect to volatiles prior to eruption. The dramatic reduction in pressure would induce crystallization and resurgent (and first) boiling, thereby depleting the magma in volatile components. The great advantage of the thermogravitational diffusion process as envisaged by Shaw et al. (1976) is that the time required to re-establish compositional zoning in the magma will be reduced if diffusion is effective at low volatile concentrations. Because the other processes operate only in volatile-saturated magmas, more time is required to recreate conditions conducive to trace element fractionation.

### Metal Loss from Magmas in Open Systems:

Magmas which give rise to volcanic products may be subject to an open-system fractionation process involving loss of trace and other elements via a fugitive gaseous phase. This process may significantly modify the trace element composition of a magma which had previously evolved in a closed system. The possible loss of trace elements from magmas linked to volcanic conduits is considered to be of particular relevance to this study for it may be one of a number of contributory factors controlling orebody occurrence in those leucogranitoids associated with proposed comagmatic volcanics.

The removal of metals and associated gaseous volatile components from magmas is probably the most economically important of all magmatic processes. Shallow submarine "volcanic-fumarolic activity" (Hutchinson, 1973) is considered to sometimes result in the formation of stratabound base-metal sulfide "volcanogenic" or "exhalative sedimentary" orebodies (Matsukuma and Horikoshi, 1970). The relative proportions of the first period transition metals and Pb in the orebodies varies according to the composition of the associated volcanic rocks (e.g. Stanton, 1972), confirming that a relationship exists between the composition of the magma and the nature and abundance of metals lost as volatile species. Stratiform Sn and W orebodies are generally associated with mafic volcanic rocks (Plimer, 1980). Studies of juvenile gaseous exhalations from fresh basalt and related lavas (e.g. Smirnov, 1978) provide direct evidence that the gaseous removal of metals from magmas is a real and potentially important fractionation process. It is therefore curious that this particular mechanism of fractionation is rarely considered in petrogenetic studies of volcanic rocks (cf. Stanton, 1967, 1978).

The loss of B, Be, Sn, W and Mo associated with fugitive halogen-rich aqueous vapours may be a possible explanation for the absence of primary ores of these elements in volcanic rocks (cf. Foshag and Fries, 1942). Similarly, many of the incompatible and other elements commonly employed as sensitive petrogenetic indicators may also display evidence of depletion from magmas evolving in an open system (cf. Taylor et al., 1968; Smith & Zielinski, 1979). Elements closely associated with magmatic volatile species over a wide range of P and T are considered the most likely to be components of the gaseous phase which escapes during the eruption of a magma. A list of these elements may include Li, Rb, Cs, Sn, Ta, Nb, Na, K, REE, Fe, Mn, U and Th (Locardi and Mitterpergher, 1967; Schilling and Winchester, 1967; Bostrom, 1967; Bell and Doyle, 1971; Anderson and Gotfried, 1971; Holland, 1972; Holloway, 1976; Kable and Fesq, 1976; Takenouchi and Imai,

1976; Ishihara and Terashima, 1977; Flynn and Burnham, 1978). In some rare circumstances even the relatively compatible transition elements Ni, Cr and V may form complexes mobile in aqueous magmatic and, perhaps, gaseous environments (e.g. Ringwood, 1955; Lawrence and Markham, 1963; Bostrom, 1967).

The rate of degassing of volatiles in a high-level magma generally has a strong bearing on the style of the ensuing eruption and hence on the nature of the resulting dominant volcanic rock type - e.g. ash-fall tuff, ignimbrite, or relatively viscous lava (see discussion in Chapter 4). It is suggested that incompatible element composition may also vary subtly with volcanic rock type. For example, volatile metal loss from particulate glass and pumice comprising ash-fall tuffs may be rapid and effective. Similarly, because the vesiculation of a magma at the commencement of an ash-flow eruption involves rapid degassing, ignimbrites may also be somewhat depleted in pneumatophile trace elements. (Cation exchange reactions between vapour and semi-quenched melt may occur, but will be influenced by the quantity of air incorporated into the fluidized magma during emplacement of the ash-flow). Various deuteric alteration processes accompanying the welding and compaction of freshly deposited ash-flows (see Chapter 3) may further modify the trace element composition of ignimbrites so that they bear little resemblance to original magma compositions. Calc-alkaline magmas which erupt as lavas are generally relatively volatile-poor. Compared to ash-fall and ash-flow tuffs, lavas may therefore approximate more closely the composition of the magma immediately prior to a relatively passive eruption.

The possibility that many volcanic rocks may not be truly representative of original magma compositions has important implications. If loss of pneumatophile elements from siliceous magmas can occur as suggested, the degree of fractionation of these elements in a compositionally zoned magma chamber may in fact be greater than that suggested by the composition of the volcanic products from the chamber (cf. Hildreth, 1979; Crecraft et al., 1979). Although the major element composition of the volcanics may closely approximate that of the original magma (cf. Stanton, 1978), incompatible element concentrations and ratios may differ significantly.

In the following discussion, the concept of metal volatile loss will be integrated into a speculative model for the evolution of the Tenterfield leucogranitoid magmas. Although the available incompatible element data suggest some volatile metal loss has occurred, it has not been possible to determine the effects of this process quantitatively.

## EVOLUTION OF SILICEOUS MAGMAS IN THE TENTERFIELD REGION

In this section the proposed comagmatic relationship between the barren leucogranitoids in the Tenterfield region and the rhyolitic Emmaville Volcanics will be discussed. The magmatic processes which resulted in the formation of cassiterite deposits in the Mole Granite and Ruby Creek Adamellite will also be briefly described and it will be argued that these leucogranitoids, and the barren acid plutons, crystallized from very similar magmas derived from the same source rock. The incompatible and major element irregularities of the "porphyry group" of adamellites, and the origin of the Mole Granite topazite will also be discussed.

### (a) The Leucogranitoid-Rhyolite Association

(i) The leucogranitoid magmas are considered to have been generated by relatively small degrees of partial melting of an essentially homogeneous acid-intermediate igneous source rock in the middle to lower crust. Melting is assumed to have occurred under amphibolite facies, water-undersaturated conditions. Hornblende and biotite in the parent may have yielded small but significant amounts of incompatible trace elements to the melts but were largely not involved in melting.

(ii) Once sufficient melt had accumulated, these volatile-undersaturated magmas moved from the zone of partial melting and were emplaced at shallow levels (perhaps 3 - 4 km beneath the Permian land surface). Arcuate fractures developed in the country rocks over the larger magma chambers and these fractures eventually developed into volcanic conduits.

(iii) Eruption of magma from the upper levels of the chambers resulted in the formation of a number of rhyolitic ash-flows (i.e. the Emmaville Volcanics). Cauldron subsidence may have accompanied or post-dated the volcanic activity. The levels of volatile saturation in the magmas prior to the eruptions cannot be estimated and it is therefore uncertain that volcanism was initiated by resurgent boiling in the magma chamber. However, the low modal abundances of K-feldspar, quartz, biotite and Na-rich plagioclase phenocrysts in the highly siliceous rhyolites suggest the magmas were dominantly liquid prior to the commencement of volcanism. Because these weathered and poorly outcropping volcanics are unsuitable for analysis it was not possible to determine whether the magmas were compositionally zoned with respect to incompatible trace elements. However the trace element compositions of the unmineralized leucogranitoids suggests that if

zoning was present, it may have been restricted to the magma in the roof of the chamber which erupted to form the highly siliceous rhyolites.

SiO<sub>2</sub> contents of the analysed rhyolitic ignimbrites fall within the range 70 - 74 wt%. The most siliceous rhyolite analysed (73.8 wt% SiO<sub>2</sub>) has a trace and major chemistry virtually identical to that of leucogranitoids with equivalent silica contents. However, the porphyritic high-K rhyolites ( ~ 70 - 72 wt% SiO<sub>2</sub>) have relatively high Ba and are marginally enriched in Pb (cf. Figures 3.11 and 3.12) which may be attributed to moderately high concentrations of these elements in the K-feldspar phenocrysts (e.g. Oftedahl, 1967; Taylor, 1966; Dostal *et al.*, 1979) and in the glassy groundmass. The studies by Hildreth (1979), Noble *et al.* (1972) and Crecraft (*pers. comm.*) suggest Ba is not a pneumatophile element in siliceous melts. Similarly, at low to moderate volatile concentrations Pb may also favour the siliceous melt, theoretically due to its ability to occupy co-ordination sites in the melt polymers normally filled by K.

Compared to granitoids with equivalent silica contents, the high-K rhyolites may be slightly depleted in Rb and Li (cf. Figures 3.9 and 3.10). Although Li is commonly concentrated in biotite, and Rb in K-feldspar, these metals generally partition more strongly into the melt (Taylor, 1966). It therefore appears possible that small amounts of Li and Rb were removed from the liquid either during or after the eruption of the rhyolites. As already suggested, some Li and Rb may be associated with halogen anions in the melt and may therefore be transported as stable complexes in the fugitive gaseous phase during a volcanic eruption. Although large volumes of magma in a chamber may be only marginally depleted in pneumatophile elements as a result of this process, it may be presumed that degassing would be more effective in the upper portions of the chamber where comminution of the magma accompanied vigorous boiling. The small additional depletion of Rb and Li in the rhyolitic ignimbrites appears consistent with this hypothesis.\*

(iv) The magmas which remained in the chambers after the volcanic episode were probably depleted in volatiles and had progressed to a more advanced stage of crystallization. However, the magmas continued to rise and, following the second extrusive episode, were finally emplaced within or immediately

\* Loss of Li and Rb may also accompany devitrification of volcanic glasses as discussed in Chapter 3. However, in addition to removal by groundwater leaching, Zielinski *et al.* (1977) consider trace alkali metals may also be lost as high-temperature volatile halides.

below the Permian volcanic pile. During cooling, trace element concentration and fractionation processes were not able to operate due to the paucity of volatiles remaining in the melt and the resulting leucogranitoids are therefore devoid of significant mineralization - i.e. although it has been suggested that some loss of incompatible elements may have occurred during the volcanic episode, in terms of the overall incompatible trace element composition of the magma remaining in the chamber, such loss was probably very minor. The depletion of anionic volatile components is considered to have been far more significant. Loss of volatile components was apparently so significant that the development of trace element enriched residual solutions, even at near solidus temperatures, was minimal. This is illustrated by the paucity of associated Mo, Sn, W and base-metal showings, and the rare occurrence of miarolitic cavities in these leucogranitoids.

(b) The Mole Granite and Ruby Creek Adamellite

(i) In spite of their difference in age, the Mole Granite (  $\sim 236$  Ma) and Ruby Creek Adamellite (  $\sim 222$  Ma) are considered to have crystallized from magmas derived from the same source rock that generated all the leucogranitoid magmas represented in the Tenterfield region. However, unlike their barren counterparts, the Mole Granite and Ruby Creek Adamellite magmas were apparently not associated with Permian (or Triassic) volcanism.

(ii) The magmas were emplaced to approximately the same crustal levels as the barren leucogranitoids. The pegmatites, quartz-fluorite-cassiterite masses and hydrothermal base-metal sulfide deposits associated with the Mole Granite and Ruby Creek Adamellite suggest their magmas were highly enriched in volatiles, at least in the upper portions of the chambers. Therefore, the principal difference between the mineralized and barren leucogranitoids may be that the former crystallized from relatively volatile-rich magmas.

(iii) The Mole Granite and Ruby Creek Adamellite have been only partly unroofed, so it has not been possible to establish the existence (or absence) of large-scale vertical compositional zoning in these plutons. Although the average concentrations of Rb, Li, U, Th and other incompatible elements are relatively high (see table on p. 55), the distribution of these elements, at least in the exposed portions of the plutons, is irregular and appears to have been largely controlled by local variations in P, T and volatile concentration as the magmas crystallized. However, it should be noted that the concentrations of incompatible elements in the Mole Granite, although variable, are consistently higher than those in

comparable barren leucogranitoids. If, as has been suggested, all the highly siliceous magmas in the region initially had very similar trace element contents, it may therefore be argued that the local anomalous concentrations of F, Be, B, Sn and other incompatible elements now observed in the Mole Granite are an overprinting of a larger-scale mild incompatible element enrichment reflecting a primary magma zonation. The near-peralkaline composition of the Mole Granite  $((Na + K)/(Al - 2Ca) = 1.00)$ , coupled with an indicated "high" volatile content, suggest the development of compositional zoning in the upper portion of the Mole Granite magma may have been possible.\*

(iv) Because they were emplaced to very high crystal levels, the Mole Granite and Ruby Creek Adamellite magmas were probably volatile-undersaturated during the entire period of their emplacement (e.g. Cann, 1970; Harris *et al.*, 1970). During slow cooling the crystallization of anhydrous felsic phases would have caused an increase in the concentration of volatiles in the remaining melt. According to Smith *et al.* (1976) and Hildreth (1979) the development of compositional zonation in the upper parts of the magma chambers may be expected to have commenced prior to volatile saturation of the melts. As discussed above, evidence is lacking to establish that this indeed occurred. However, it is clear that transportation of various incompatible elements was effective once volatile saturation levels in the melts were attained.

The leaching of pneumatophile elements from large volumes of magma, and the concentration of these elements at the roof of the chambers was probably largely a consequence of resurgent boiling. Bailey<sup>#</sup> (1977) has suggested that granite melts crystallizing in the upper crust are unlikely to grade into a hydrothermal solution. This may be largely due to constraints imposed by pressure rather than melt composition, for it has already been suggested that many calc-alkaline granite magmas may approach a peralkaline composition. In the absence of metals such as B, Li and Be which increase volatile solubility in melts and decrease solidus

\* In fact, firm support for this hypothesis is lacking. Because the magmas of the unmineralized plutons may have lost small amounts of pneumatophile elements during the volcanic episode, the incompatible trace element content of these plutons may not be a useful standard for comparison with the Mole Granite magma, which probably evolved in a closed system. The levels of incompatible trace element abundance in some Mole Granite samples are only marginally higher than those in the barren leucogranitoids (see Figure 3.13 for Rb and Li). (For the Ruby Creek Adamellite there exists a considerable overlap). Although these small differences are probably real, it is considered possible that the "deficiency" in the barren leucogranitoids dates to the minor loss of volatile metal species from the magmas during the volcanic episode.

temperatures (Whitney et al., 1976; Glyuk and Trufanova, 1977; Kovalenko et al., 1977; Pichavant, 1981; Manning, 1981), high concentrations of volatiles such as HF in the melt are required to initiate development of a hydrothermal solution at low pressure (see Glyuk and Anfilogov, 1974, Figure 1).

Although the Mole Granite has a high average Li content and tourmaline and beryl occur in some pegmatites associated with this pluton (see Chapter 5), it is considered unlikely that B, Li and Be were present in sufficient concentrations to significantly increase fluorine solubility in large volumes of magma. However, there is evidence to suggest that during the latter stages of crystallization of the Mole Granite, HF concentrations in the melt were exceedingly high and that hydrothermal solutions rich in melt components may have formed locally. This will be discussed in the following section in association with the formation of the Mole topazite.

Due to the close association of fluorine with Na and K and its ability to bond directly with Si (Bailey<sup>#</sup>, 1977), fluorine is concentrated in late-stage granitic liquids. Therefore, during the initial stages of resurgent boiling of the Mole Granite and Ruby Creek Adamellite melts, selected incompatible elements may have been transported in relatively Cl-rich aqueous vapours which later became enriched in F. The fractionation of trace elements in dense hydrothermal solutions may therefore have occurred late in the crystallization history of the magmas, culminating in the precipitation of cassiterite, wolframite and other ore minerals from fluorine-rich aqueous fluids which formed by the late disintegration of the hydrothermal solutions. The quartz associated with the high-temperature cassiterite-fluorite ores filling joints in the early-crystallized roof zones of the Mole Granite and Ruby Creek Adamellite may also have crystallized directly from these low pressure, predominantly aqueous fluids (e.g. Tuttle and Bowen, 1958).

The evolution of Sn-mineralizing magmas in the Tenterfield region is considered to closely resemble the genesis of granite molybdenum systems as described by Mutschler et al. (1981) and Westra and Keith (1981). The development of granite molybdenum systems (Mutschler et al., loc. cit.) may be summarised as follows:

1) Batholithic stage

Once emplaced to a high level in the crust a typically potassic granitoid evolves an alkali- and incompatible element-enriched, relatively depolymerized zone in the apical region of the chamber. This compositional zonation is supposedly effected by the operation of large-scale, convection-enhanced thermogravitational diffusion



(Hildreth, 1979).

2) High-level magmatic stage

Failure of the roof rocks above the volatile-charged magma zone in some instances permits the growth of a cylindrical conduit extending 2 - 3 km above the original magma chamber and to within 1 - 3 km of the surface. Thermal gradients within this cylindrical plug initiate a second cycle of thermogravitational diffusion, thus producing an even greater upward concentration of volatiles, alkalis and incompatible trace elements. This second cycle enrichment of ore metals is a requirement of the model because thermogravitational diffusion in a single magma chamber of "batholithic" proportions is considered by Westra and Keith (1981) to be unlikely to produce the trace element enrichment necessary for ore deposition.

As cooling and crystallization in the cylindrical plug proceed, localized resurgent boiling is initiated and a vapour-saturated, supercritical hydrothermal fluid separates from the magma and accumulates at the top of the cupola (Whitney, 1975a; Groves and McCarthy, 1978; McCarthy and Groves, 1979). This hydrothermal phase is extremely alkali metal enriched and contains very high concentrations of incompatible elements and ore metals in the form of high-temperature complexes. An orebody is formed in and immediately surrounding the cupola region by the crystallization of ore minerals directly from the hydrothermal solution, and from the vapour resulting from boiling of this hydrothermal fluid.

3) Hydrothermal stage (magmatic fluid-dominated substage).

High fluid pressures in the hydrothermal phase induce brittle failure (hydrofracturing) in the chilled granitic lining and surrounding country rocks of the cupola, thereby increasing the volume of rock subjected to attack by highly corrosive fluids and vapours (greisenization). Hydrofracturing causes pressure quenching of the hydrothermal fluid which, in turn, accelerates the deposition of ore minerals through a) promotion of supersaturation of ore mineral components and b) "instantaneous" instability of some metal complexes, promoted by the rapid changes in the composition of the fluids engaged in greisenization, i.e. chemical transfer between the hydrothermal phase and fractured wall rocks causes depletion of some components of the fluids critical to the stability of many metal complexes (cf. Burt, 1981).

4) Hydrothermal stage (meteoric water-dominated substage)

"With time, increased permeability in the upper part of the system and cooling and cessation of convection in the underlying magma column cause collapse of the magmatic water-dominated plume and influx of meteoric water into the ore shell and zone of potassic alteration . . ." (Mutschler et al., 1981, p. 891). There is, however, no evidence to suggest that ore deposition in the Tenterfield leucogranitoids was significantly influenced by circulation of meteoric waters : the metals and other components of the ores are magmatic in origin.

5) Late magmatic stage

The final residual fluids associated with the last stages of crystallization of the source magma may invade fractures and cooling joints in the overlying mineralized zones, forming greisen veins.

(c) The Mole Granite Topazite

Fluid inclusion studies by Eadington and Nashar (1978) suggest the Mole Granite topazite (essentially quartz and 18 - 27% topaz) crystallized from a fluorine-rich hydrothermal phase at 570 - 620°C. This hydrothermal solution probably formed during the final stages of crystallization of the Mole Granite magma. Eadington and Nashar (1978) consider the quartz-topaz fluid developed during resurgent boiling of the leucogranite magma, with alkalis being removed as volatile species dissolved in a Cl-rich vapour. The high fluorine content of the remaining melt ( $\sim 3.4$  wt% F at 1 kb and 670°C; Glyuk and Anfilogov, 1974 and presumably  $\gg 3.4$  wt% F at the pressures prevailing during the crystallization of the Mole Granite magma - i.e.  $< 1$  kb) promoted the stability of quartz (see Wyllie and Tuttle, 1961) and topaz at the expense of biotite, orthoclase and albite components (Glyuk and Anfilogov, 1974).

Although the partitioning of alkalis into a Cl-rich vapour (e.g. Wyllie and Tuttle, 1964) may have significantly contributed towards the formation of the topazite melt (Eadington and Nashar, 1978), experimental studies on the granite-H<sub>2</sub>O-HF system at 1 kb by Kovalenko (1977) suggest the breakdown of alkali feldspar components occurs (in the absence of Cl) when the granitic melt becomes saturated in fluorine (3 - 3.5 wt% F). The high average abundance of F in the Mole Granite (0.3 wt%; Eadington and Nashar, 1978) and the common occurrence of fluorite as an accessory phase suggests concentrations of 3 - 3.5 wt% F in the residual melts at the top of the chamber may have been readily attained.

Glyuk and Anfilogov (1974) showed that at 1 kb a quartz topaz assemblage may crystallize from a melt containing  $\sim 3.4 - 6.8$  wt% F. Solidus temperatures increase with increasing F content in the melt ( $F > 1.5 - 2.0$  wt%; Glyuk and Anfilogov, 1974; Kovalenko, 1977), so the topazites may in fact have crystallized during the cooling and degassing of a more F-rich, high-temperature melt or hydrothermal solution, i.e. the F content of residual liquids formed during the crystallization of the Mole Granite magma may have actually exceeded the amount required to promote the stability of topaz. Unfortunately, this hypothesis appears impossible to verify because quartz may be the only relict mineral of a higher-temperature, higher-F magmatic history (see Glyuk and Anfilogov, 1974, Figure 1).

In summary, quartz-topaz rocks may crystallize from F-rich hydrothermal solutions produced during resurgent boiling of an evolved leucogranitoid magma (Eadington and Nashar, 1978), or they may crystallize from halogen-rich vapours formed by the boiling of these hydrothermal solutions (Burt, 1981). Cl, unlike F is not registered in the products of greisenization but the activity of HCl in hydrothermal solutions and vapours may be significant. However, the chemical activity of HF in these vapours is so high, and KF so low, that pre-existing feldspar may be directly replaced by topaz and quartz (see examples quoted in Burt, 1981).

(d) Adamellites and Leucoadamellites of the "Porphyries Group".

Experimental studies of hydrous granitic melts (e.g. Tuttle and Bowen, 1958; Luth and Tuttle, 1969) have shown that at low to moderate pressures, quartz and lesser amounts of K-feldspar are soluble in the aqueous phase co-existing with the melt. Jahns (1955) and Jahns and Burnham (1969) suggested that separation of a K-feldspar-rich fluid phase from a volatile-saturated granitic melt can lead to felsic mineral zoning in pegmatites at high crustal levels (also see Manning, 1981). It is therefore suggested that minor loss of a K-feldspar component-rich phase may partly account for the observed low abundance of K-feldspar in the seriate-textured and porphyritic adamellites and leucoadamellites in the Tenterfield region.

These seriate textured and porphyritic, high-level granitoids occur as small bodies which closely resemble the pipe-like form of the "intrusive rhyolites" east of Deepwater and near the Webbs Consols Mine. The granitoids and the "intrusive rhyolites" may have also experienced a similar cooling history. The fine-grained equigranular textures of the "intrusive rhyolites" resemble those of aplites and may therefore have been produced by pressure-quenching of the hydrous melt (see Fenn, 1977). To account for the absence of local metasomatism or metamorphism in the

country rocks enclosing the "intrusive rhyolites", the quench textures, relatively high  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratios (i.e.  $> 1$ ; see Chapter 3), and the effective removal of volatile components, it is suggested that these pipe-like bodies of leucoadamellite may represent quenched melts filling volcanic conduits.

The seriate-textured adamellites may also fill ancient volcanic conduits. This hypothesis appears to be supported by the available geochemical data. The adamellites are relatively depleted in K and Rb, but are not depleted in Ba or Pb which are generally closely associated with K in evolving siliceous magmas (e.g. Taylor, 1966). That Ba and Pb are not depleted is consistent with the observations by Hildreth (1979) that these elements apparently do not partition strongly into volatile-saturated environments. Ba and Pb may therefore remain with Na and other components of the melt during vigorous magma degassing, whereas silica, K-feldspar components and the trace alkali metals which partition more strongly into the vapour phase during resurgent boiling at low to moderate pressures may to some extent be lost during a volcanic eruption.

If the texture and slightly "anomalous" chemistries of the "porphyries group" and "intrusive rhyolites" are partly due to the processes outlined above, it may then be argued that these rocks may in fact be related to granitoids of the main intrusive suite.