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Gemstone Characteristics, North-East Barrington Plateau, NSW

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Abstract: Corundum and zircon concentrates from gravel deposits in two northern Barrington plateau prospects were studied for their features, to investigate potential gemstone sources within the catchment zone. The studies utilized field research, colour sorting, gemmological microscopy, EDAX and PIXE trace element analysis and zircon fission-track dating. The results showed statistical differences in corundum suites from different gravel horizons, which suggested different source areas. Anorthoclase and ilmenorutile were identified as inclusions in Barrington corundums for the first time. Zircon fission-track results showed that several episodes of volcanic eruptions were involved (66–4 Ma), reinforcing and adding to previous eruption ages. This suggests multiple corundum delivery both in space and time into drainage systems.

Keywords: Corundum, ruby, gravels, terraces, eruption, trace elements, mineral inclusions, zircon, gemstone sources.

INTRODUCTION

The Barrington volcanic plateau, 150 km north-northwest of Newcastle (Figure 1, page 117) is one of the many basalt lava fields in eastern Australia (Mason 1989, O’Reilly and Zhang 1995, Sutherland and Fanning 2001). The field is particularly noted for its association with gemstones (ruby, sapphire, zircon), brought up in multiple basaltic eruptions between 60 and 4 Ma and concentrated by erosion into adjacent alluvial deposits (Sutherland et al. 1998, Sutherland and Fanning 2001). The presence of gem quality ruby in the Barrington deposits (Webb 1997) has promoted investigations into the economic potential of the gem deposits by the Australian exploration and mining company Cluff Resources Pacific NL. Exploration and testing programs have been concentrated in the northeastern part of the province, particularly in the terraces and recent alluvial deposits of the upper Manning River at Gummi Flats. Plates 1 to 3 show examples of rubies and sapphire from the Gummi Flats deposits.

This study presents:

1. The first detailed comparison of corundums found in the Gummi Flats terraces, to assist in evaluating their origin and distance travelled from source regions.
2. Detailed fission-track dating on zircons concentrated from the northeastern Barrington field that helps to clarify the extent of gem bearing eruptive episodes in this area.

GEOLOGICAL SETTING

The general geology of the Barrington Plateau region, its economic deposits and literature are outlined in Gilligan et al. (1987) and Sutherland and Graham (2003). The general geology of the study area in the North-East Barrington Plateau is summarised below.

Basement geology consists of Late Devonian to Early Carboniferous mudstone and siltstone with minor interbedded conglomerate, lithic sandstone and limestone. Most of this material was deposited in a deep marine environment. The sheet-like deposits of greywacke within the mudstone were probably deposited by turbidity currents, while some of the conglomerates may have been deposited as submarine fans. A Permian hornblende-biotite granodiorite pluton and associated dykes intruded through the folded Devonian, Carboniferous and Early Permian sedimentary rocks at Gummi Flats. These sequences are capped mostly by Cenozoic basaltic flows.

This volcanic activity most likely extended from around 60 Ma to perhaps < 5 Ma. Alkali basaltic flows and tuffaceous and fragmented volcanics are common, and form the resistant plateau region. Underlying these massive basalt flows is a basaltic horizon containing highly altered basalt bombs. The sequence includes ankaramitic basalt that may mark an intrusive sheet.

This elevated basalt plateau has been subjected to radial drainage patterns over time, cutting into the basalts and underlying Palaeozoic sediments and granodiorites. Local stream and drainage patterns have accumulated clasts of these rocks as well as gem stones in many river flats and catchment areas. Changes in stream patterns and velocities have created river terraces in localised areas.

STUDY AREA

Two study sites were investigated in this study in the northern Barrington Plateau.

Gummi Flats Area

The main sampling sites for corundum and zircon included sections of older terraces and the present alluvial terrace deposits of the upper Manning River. These lie below the eastern edge of the basalt field both upstream and downstream of Backwater Creek junction (Figure 2, page 101). The deposits were excavated during bulk testing and sampling programs by Cluff Resources Pacific NL, during the period 2000–2003.

Suites of corundums were recovered from heavy mineral concentrates from four specific gravel horizons: The upper (A) and lower (B) horizons of the Upper Terrace deposit (Trench 11); the Middle Terrace deposit (C; Trench 4A) and Recent alluvial deposit (D; Trench 2A). The zircons were recovered from heavy mineral concentrates from the Upper Terrace deposit (Trench 11).

(A). Upper gravel horizon of the Upper Terrace (Section 18-A; Figure 3, page 102).

This grey gravel horizon ranges in thickness up to 0.5 m and overlies the lower gravel horizon for approximately 55 m strike-length in the test trench. It is moderately to well sorted and exhibits mostly rounded to sub-rounded lithic fragments with sizes from sub-mm up to 250 mm. There is an upward fining in the sequence, and a grey clay matrix makes up approximately 45% volume of this horizon. Lithic types include, igneous, metamorphic and meta-sedimentary rocks. Generally more granodiorite fragments are present than in the underlying gravel horizon.

(B). Lower gravel horizon of the Upper Terrace (Section 18-B; Figure 3).

This gravel contains rounded to sub-angular, igneous, metamorphic and meta-sedimentary lithic fragments, with sizes ranging from sub-mm to > 256 mm. The horizon is up to 2.6 m thick and has a reddish fine sandy clay matrix, with occasional sand and silt lenses up to 20 cm in length and 10 cm thick. There is indistinct upward fining, but generally the horizon is very poorly sorted. This horizon is overlain in part by the grey gravel horizon (Section 18-A), and a medium grey sand or a fine silty clay. Humus topsoil some 0.5 m thick caps the sequence. Weathered granodiorite forms the underlying basement.

(C). Middle Terrace horizon
(Section T4A; Figure 4, page 103).

The horizon consists of sub-rounded to sub-angular, igneous, metamorphic and meta-sedimentary rocks. Rock sizes vary from sub-mm to > 256 mm. An orange clay matrix, with sporadic black clay lenses up to 20 cm thick underlies a grey gravel in some places. Some fragments show heavy manganese staining. The horizon ranges up to 2.5 m thick, is poorly sorted but shows a slight fining upwards. Basement is weathered granodiorite, and large sporadic fresh granodiorite boulders appear at the base of the gravels. A fine sandy clay of varying colour overlies the gravel horizon, and is up to 2.7 m thick. Black organic topsoil cover is variable, but averages 0.5 m.

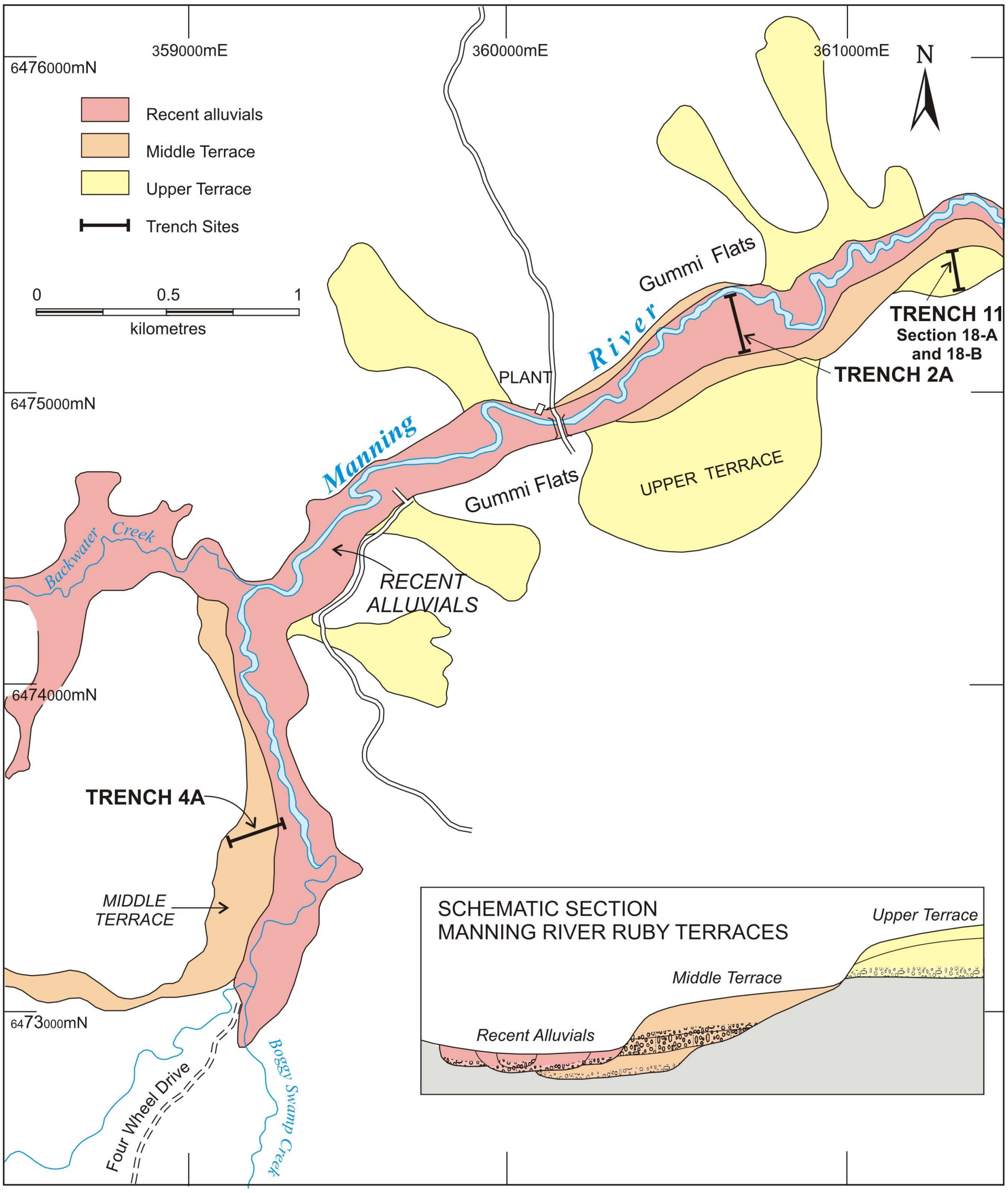

Figure 2. Sample site locations, Gummi Flats, Manning River deposits, with schematic section showing gem-bearing deposits (inset).

(D). Recent Alluvials
(Section T2A; Figure 5, page 103).
The gravel horizon here is composed of igneous, metamorphic and meta-sedimentary rocks, that are sub-angular to sub-rounded, with a colour gradation laterally from grey, black, grey-brown to light brown. Rocks range from sub-mm to > 256 mm, with most exhibiting sub-rounded to rounded shape. The horizon is up to 2.6 m thick. A sandy clay and clay overlies the horizon below a black humus topsoil. The basement is weathered granodiorite.

East Tomalla

East Tomalla is an alluvial site, within the basalt field itself (Figure 1, page 117). This site produced zircons from a ruby prospect, and is 3 km northwest of the Gummi Flats deposits (G. Jeffreys lease). The site at 1160 m asl lies at the head of a small tributary creek that drains a local basalt cap that rises to 1200 m asl. The drainage descends north into Tomalla Creek and the alluvial deposit consists of an upper 30 cm of coarse gravels with heavy minerals concentrated towards the base and overlies a 0.5 m layer of clay. The overlying basalt shows cracking and pitting which is typical of the weathering of nepheline-bearing lavas. It contains prominent megacrysts of spinel and sparse clinopyroxene (up to 5 cm), sporadic xenoliths of spinel-metaperidotite (up to 8 cm) and rare granulites (up to 6 cm). This basanite flow descends north to 1075 m asl, where it overlies ‘deep lead’ alluvial deposits. These contain fragments of metasediments, igneous rocks and waterworn boulders of silicified conglomerate up to a meter across from basement sources. Obvious fragments of typical Barrington basalts are not seen. Heavy mineral concentrates from the East Tomalla zircon site for fractions both above and below 2 mm size range are described in Appendix 1.

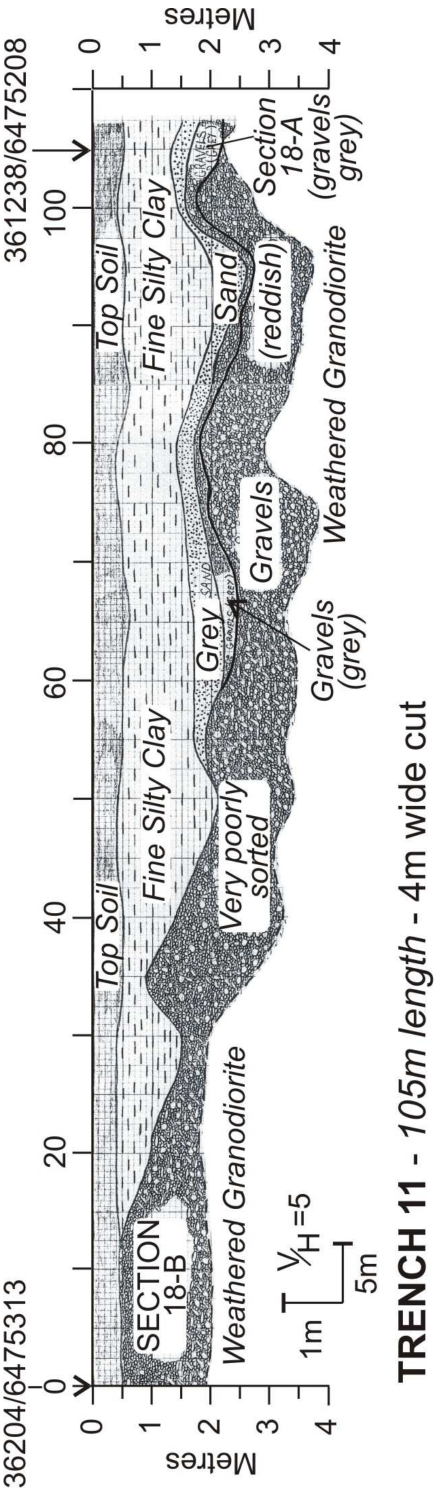

Figure 3. Cross-section, showing Section 18-A and 18-B in the Upper Terrace.

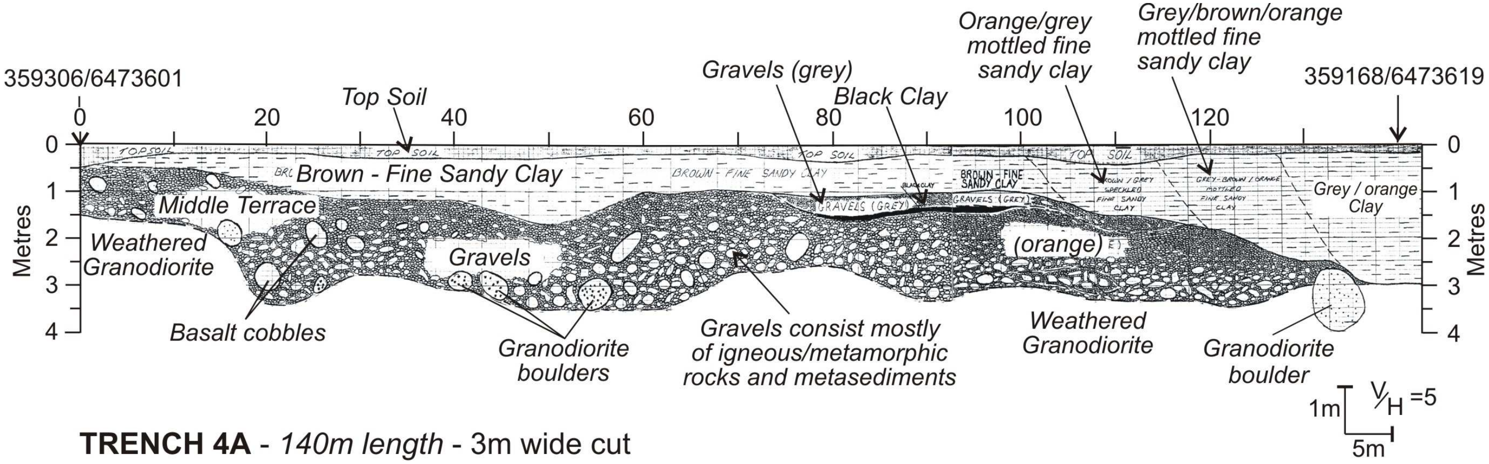

Figure 4. Cross-section, showing Section T4A in the Middle Terrace.

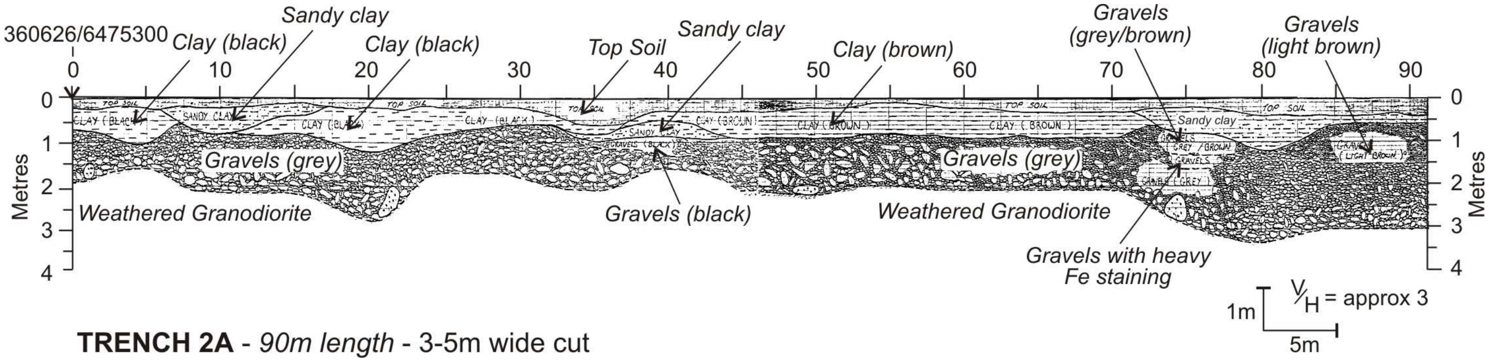

Figure 5. Cross-section, showing Section T2A in the Recent Alluvials.

METHODOLOGY

Corundum Suites

Representative suites of corundums were sampled from each of the corundum concentrates obtained from the four study horizons. The number of corundums studied from each suite was considered to represent statistical sets, based on earlier work using check monitoring of more extensive counting from one of the corundum suites. The statistical method used for this study, involved ‘carat weight (ct) / sample %’ analysis of corundums. The following sample weight to percentage ratios are as follows. 0–5 ct(100%), 6–10 ct(50%), 11–20 ct(30%), 21–30 ct(20%), 31–40 ct(10%), 41–60 ct(7%), 61–100 ct(5%). Note that when individual suites exceeded 100 ct, the percentage of stones analysed was calculated to conform to the above mentioned ct/% calculations, e.g. if sample weight was 200 ct then 3% of the sample would be analysed.

The selected corundums were viewed under a gemmological binocular microscope and the visible features noted, among a range of physical parameters. These parameters included: colour, magmatic corrosion (resorption), alluvial abrasion, fusion crusts, fracture surfaces, percussion marks, mineral inclusions, hydrothermal fluid lines and growth zoning. The mineralogy of surface crusts and exposed inclusions in the corundums were investigated using an EDAX system, linked to a JEOL JXA-8600 Superprobe, in the School of Science, Food and Horticulture, BRCI campus, North Parramatta, University of Western Sydney.

The examined corundums were divided into five separate colour groups and percentages of each feature noted within them are listed in Table 1, (Upper Terrace - upper and lower horizons) and Table 2, (Middle Terrace and Recent Alluvials). Colour ranges were further subdivided for each unit/suite into a Colour-Shade grouping, (e.g. very pale, pale, medium and dark). The percentages of features counted in each colour subdivision are presented as a series of histograms and represent a more detailed analysis of colour sorting and associated corundum features. (Figures 6 and 7, pages 118 to 120).

Previous work on Gummi alluvial corundums (Sutherland and Coenraads 1996; Sutherland et al. 1998) demonstrated that the Pink - Red Group and some Blue Group corundums have mineral inclusions such as sapphirine, trace element ratios with Cr / Ga > 1 and colour absorption patterns (decreasing absorption at 600–850 nm) that typify metamorphic origins. Some Blue, Green, Yellow and related Grey - Brown - Black corundums however, have different mineral inclusions (e.g. peonaste spinel), trace element ratios with Cr / Ga < 1 and colour absorption (sustained or increasing absorption between 600–850 nm) that characterise magmatic origins.

To supplement this work, further trace element determinations were made on Gummi corundums by Proton-induced X-Ray Emmission (PIXE) methods and are presented in Table 3. The analyses were made on the PIXE analytical facility at Guelph University, Canada, using a beam current between 1 to 3 nA, a charge accumulation above 0.5 μc and approximately 5 minutes analytical time per sample (M.I. Garland, University of Toronto, analyst). A mylar filter was used to eliminate the intense Al X-rays produced by the corundum, which eliminated some light element determinations (e.g. Mg).

The overlap in characteristics for the Blue Group Gummi corundums makes precise assignment of the origin of these stones uncertain in this colour group (Tables 1 and 2 on pages 106, 107; Figures 6 and 7). However specific features, such as colour growth zoning, may indicate a magmatic origin, while specific inclusions such as sapphirine may indicate a metamorphic origin.

Zircon Suites

Zircon grains up to 2 mm in size from each of the two study sites were grouped into colour subsets prior to submission to Geotrack International P.L., for mounting, etching and irradiation at the Lucas Heights NSW reactor. The resultant fission-track counting used a Zeiss

®AXIOplan microscope. Details of the analytical methods and statistical treatments used in the analyses are outlined in Green (1981, 1983), Galbraith (1981, 1988, 1990) and Hurford and Green (1982, 1983). The fission-track results are summarised in Tables 4 and 5 on page 111.

RESULTS

EDAX Analysis

Analysis identified the following mineral phases associated with the corundums in inclusions and alteration crusts. Mineral inclusions identified were Mg-rich to Fe-rich pleonaste to hercynite spinel, sapphirine, anorthoclase feldspar, ilmenorutile and a magnesium-iron aluminosilicate. The spinels and sapphirine were previously recorded from Barrington Tops corundums, but anorthoclase and ilmenorutile are new records as inclusions in these corundums. Differences in fusion crust mineralogy were also noted, with Mg and Fe-rich spinels being the most common, although aluminosilicates (mullite) were also present. Some specimens exhibited fusion crusts combining both Mg-rich and Fe-rich spinel, but usually on different sides of the stone.

Grouped Corundum Features

The main aspects of the features found in different corundum groups (Tables 1 and 2) are summarized for each sample horizon. Three main corundum groups are considered, a Ruby Group, with colours ranging from dark red to very pale pink, a Grey-Brown-Black Group (GBB), and a Blue-Green-Yellow Group (BGY).

Section 18-B, lower gravel horizon (Upper Terrace)

Ruby Group Over 80% of these corundums exhibit both magmatic resorption and heavy fracturing, while another 14% show either resorption or heavy fracturing. Nearly 2% have a surface fusion crust, 3.3% include percussion marks and 0.4% contain sapphirine inclusions.

Grey-Brown-Black Group (GBB) Nearly 85% combine resorption and heavy fracturing, while a further 10.7% show resorption, and only < 2% of stones show percussion marks.

Yellowish Group (BGY) Nearly 86% exist as resorbed and fractured stones. Stones showing only resorption make up 14.2%. Nearly 5% contain spinel inclusions.

Greenish Group (BGY) Nearly 95% show resorption and heavy fracturing, 5.4% show only heavy fracturing, whilst 5.2% show a combination of resorption and heavy fracturing, along with spinel inclusions.

Blue Group (BGY) Nearly 99% show both resorption and heavy fracturing, with 2.4% containing spinel inclusions and 1.2% showing percussion marks. Some 1.5% of stones show only fracturing.

Section 18-A, upper gravel horizon (Upper Terrace)

Ruby Group Here 52.6% show a combination of resorption and heavy fracturing, 1.9% show a fusion crust and 0.5% have percussion marks. Some 3.5% of stones contain spinel, sapphirine or ilmenite (optical identification) as inclusions.

Grey-Brown-Black Group (GBB) Only 7.4% of stones show either resorption or heavy fracturing, 2.8% contain spinel inclusions, while 0.3% have a fusion crust and 0.3% show percussion marks.

Yellowish Group (BGY) While 19.7% of stones show only resorption, nearly 78% of stones show a combination of resorption and heavy fracturing. About 4% have spinel inclusions, 1.3% show percussion marks and 2.6% of stones show only heavy fracturing of which 1.3% have a fusion crust.

Greenish Group (BGY) About 77% show resorption and heavy fracturing, 3.8% contain spinel inclusions and 1.9% show percussion marks. About 23% show resorption as the only feature.

Blue Group (BGY) Nearly 74% have a combination of resorption and heavy fracturing and of these 0.5% are fusion crusted stones. Some 3.2% have percussion marks and 2% of these show heavy fracturing only. Another 24.8% of stones are resorbed, with only 0.6% having percussion marks.

	Corundum 'Ruby' Metamorphic	Corundum (GBB) Magmatic	Corundum 'Yellowish' (BGY) Magmatic	Corundum 'Greenish' (BGY) Magmatic	Corundum 'Blue' (BGY)
R	37.4	6.7	19.7	23.0	24.4
F	6.4	0.7	1.3		2.0
R-F	50.3	89.2	72.5	71.3	67.8
R-C	0.7				
F-C			1.3		
R-SpI	0.8	0.5			
F-SpI		0.5			
R-SapI	0.5				
F-SapI	1.6				
R-P					0.6
F-P					
R-F-C	1.2	0.3			0.5
R-F-SpI	0.4	1.8	3.9	3.8	1.7
R-F-SapI	0.1				
R-F-ILI	0.1				
R-F-P	0.5	0.3	1.3	1.9	3.2
R-C-SpI					
R-C-SapI					
F-SpI-P					
R-F-C-SpI					
R-F-C-SapI					
ZONED					11.1%
No. of stones analysed:	116	117	21	38	65

Section 18-A
Upper Terrace, Upper Horizon Gravels
Grouped percentages

	Corundum 'Ruby' Metamorphic	Corundum (GBB) Magmatic	Corundum 'Yellowish' (BGY) Magmatic	Corundum 'Greenish' (BGY) Magmatic	Corundum 'Blue' (BGY)
R	10.7	10.2	14.2	5.2	22.8
F	3.6	2.2		5.4	1.5
R-F	80.1	83.0	81.1	84.2	72.1
R-C					
F-C					
R-SpI				2.6	
F-SpI					
R-SapI					
F-SapI					
R-P					
F-P					
R-F-C	1.9				
R-F-SpI		2.8	4.7	2.6	2.4
R-F-SapI	0.4				
R-F-ILI					
R-F-P	3.3	1.8			1.2
R-C-SpI					
R-C-SapI					
F-SpI-P					
R-F-C-SpI					
R-F-C-SapI					
ZONED					2.6%
No. of stones analysed:	276	204	76	52	114

Section 18-B
Upper Terrace, Lower Horizon Gravels
Grouped percentages

Table 1. Grouped corundum percentages, from the Upper Terrace, Sections 18-A and 18-B. R Shows Resorption, F Heavily Fractured, C Fusion Crust, P Percussion Marks, SpI Spinel Inclusions, SapI Sapphirine Inclusions, Ili Ilmenite Inclusions

	Corundum 'Ruby' Metamorphic	Corundum (GBB) Magmatic	Corundum 'Yellowish' (BGY) Magmatic	Corundum 'Greenish' (BGY) Magmatic	Corundum 'Blue' (BGY)
R	7.8	7.1	30.8	7.7	12.2
F	8.7	1.8		15.5	
R-F	71.7	84.8	69.2	69.2	84.7
R-C					
F-C					
R-SpI	0.4				
F-SpI		0.8		7.6	
R-SapI					
F-SapI					
R-P					
F-P					
R-F-C	2.3	1.6			
R-F-SpI	3.1	1.6			
R-F-SapI	1.2				
R-F-ILI					
R-F-P	1.7	2.3			3.1
R-C-SpI	0.9				
R-C-SapI	0.7				
F-SpI-P					
R-F-C-SpI	0.8				
R-F-C-SapI	0.7				
ZONED				13.5%	
No. of stones analyzed:	105	105	13	13	76

Section T2A, Recent Alluvials, Grouped percentages

	Corundum 'Ruby' Metamorphic	Corundum (GBB) Magmatic	Corundum 'Yellowish' (BGY) Magmatic	Corundum 'Greenish' (BGY) Magmatic	Corundum 'Blue' (BGY)
R	14.4	23.1	10.0		23.6
F					1.9
R-F	28.1	69.4	60.0	78.6	64.5
R-C	12.2				
F-C					
R-SpI					
F-SpI			10.0		
R-SapI					
F-SapI					
R-P		2.5	10.0		
F-P					
R-F-C	28.1			7.2	2.3
R-F-SpI		2.5	10.0	14.2	4.0
R-F-SapI	5.1				
R-F-ILI					
R-F-P	3.5				1.8
R-C-SpI	2.5				
R-C-SapI					
F-SpI-P					1.9
R-F-C-SpI	3.1	2.5			
R-F-C-SapI	3.0				
ZONED					
No. of stones analyzed:	53	43	10	14	58

Section T4-A, Middle Terrace, Grouped percentages

Table 2. Grouped corundum percentages, from the Middle Terrace (Section T4A) and the Recent Alluvials (Section T2A). R Shows Resorption, F Heavily Fractured, C Fusion Crust, P Percussion Marks, SpI Spinel Inclusions, SapI Sapphirine Inclusions, Ili Ilmenite Inclusions

SECTION T4A (Middle Terrace)

Ruby Group Almost 71% of stones show resorption and heavy fracturing, 34.2% contain fusion crusts, while 8.1% contain sapphirine inclusions, 3.1% spinel inclusions and 3.5% show percussion marks. Some 14.4% show only resorption and 12.2% show resorption with fusion crusts.

Grey-Black-Brown Group (GBB) Nearly 75% of stones are resorbed and heavily fractured, with 5% containing spinel inclusions and 2.5% a fusion crust. Otherwise 23.1% are resorbed only and 2.5% are resorbed and show percussion marks.

Yellowish Group (BGY) Only 70% of stones are resorbed and heavily fractured with 10% of these containing spinel inclusions. Just 20% show resorption with 10% of these having percussion marks. Stones showing only heavy fracturing but containing spinel inclusions account for 10% of the suite.

Greenish Group (BGY) All stones show resorption and heavy fracturing, with 7.2% of these having a surface fusion crust and 14.2% spinel inclusions.

Blue Group (BGY) About 73% show resorption and heavy fracturing, with 2.3% having a fusion crust. Some 4% contain spinel inclusions and 1.8% show percussion marks, Just 23.6% of this suites stones show resorption only, nearly 2% show heavy fracturing only and just 1.9% show heavy fracturing, percussion marks and spinel inclusions.

SECTION T2A, Recent Alluvials

Ruby Group Nearly 82% of stones are resorbed and heavily fractured showing combinations of either spinel or sapphirine inclusions, fusion crusts and percussion marks. Only 9.8% show resorption as the main feature.

Grey-Brown-Black Group (GBB) Some 90.3% are resorbed and heavily fractured, while 3.2% contain spinel inclusions and fusion crusts and 2.3% show percussion marks. Only 1.8% are just fractured and 0.8% are fractured with spinel inclusions.

Yellowish Group (BGY) Around 69% of stones are resorbed and heavily fractured, with 30.8% showing resorption only.

Greenish Group (BGY) In this group 92.4% are resorbed or heavily fractured or a combination of both, while 7.6% are heavily fractured and contain spinel inclusions.

Blue Group (BGY) Nearly 85% show resorption and heavy fracturing, while 3.1% are resorbed, heavily fractured with percussion marks and 12.2% show resorption only. Some 13.5% of the group show growth zoning.

Colour-Shade Features

The main features in each colour shade group (Figures 6 and 7) are summarised for each shade.

RUBY GROUP

Very Pale The Middle Terrace (T4A) lacks very pale pinks. The other 3 terraces feature strong percentages of heavily fractured and resorbed stones. The Upper Terrace (Section 18-B), contains some small percentages ($< 2\%$) with sapphirine mineral inclusions.

Pale Resorption and heavy fracturing dominate as features throughout all four sections. The Recent Alluvials (Section T2A) and Middle Terrace (Section T4A) show the most variation between features and mineral inclusions.

Medium Section 18-B (Upper Terrace) shows stones with spinel inclusions and fusion crusts in $< 10\%$ of the suite. Middle terrace (T4A) gravels show up to 38% stones with fusion crusts and 9.5% spinel inclusions. Recent Alluvials (T2A) stones have spinel, sapphirine inclusions, plus fusion crusts in amounts $< 5\%$.

Dark Resorbed and heavily fractured stones feature heavily in the upper terrace horizons. The Recent Alluvials (T2A) and Upper Terrace gravel horizons contain stones with spinel and sapphirine inclusions plus fusion crusting in $<$ 10%. Middle Terrace gravels contain no stones with mineral inclusions. However fusion crusting is present in around 35% of the suite.

Grey-black-brown Group (GBB)

Very Pale Resorption and heavy fracturing dominate. Less than 10% of stones show spinel inclusions in both horizons of the Upper Terrace, plus approximately 2% show fusion crust and percussion marks.

Pale Over 80% of stones in the Upper Terrace horizons and Recent Alluvials (T2A) feature resorption and heavy fracturing, and < 5% with spinel inclusions were noted in each of the 3 horizons. The Middle Terrace (T4A) stones show higher (10%) spinel inclusions, fusion crusts and percussion marks in the resorbed and heavily fractured stones.

Medium All 4 horizons show high percentages of resorbed and heavily fractured stones; Only the Recent Alluvials contain stones with fusion crusts and spinel inclusions in < 5%.

Dark Resorbed and heavily fractured stones are predominant in all 4 horizons. Only the Recent Alluvials and Section 18-A feature stones with percussion marks.

Blue-greenish-yellowish Group (BGY)

Very Pale Resorbed and heavily fractured stones are only noted in Section 18-B and the Middle Terrace.

Pale Resorption and heavy fracturing dominate as coupled and single features in stones from both horizons of the Upper Terrace and Recent Alluvials (T2A), while < 10% fusion crusting, percussion marks and spinel inclusions are seen throughout all 4 suites.

Medium High percentages of resorbed and heavily fractured stones occur in all 4 suites. The Middle Terrace shows minor (approximately 6%) percussion marks.

Dark Only resorption and heavy fracturing is seen as single or combined features in Section 18-A stones. Section 18-B stones show > 10% percussion marks and the Middle Terrace (T4A) stones contain approximately 12% with fusion crusts and spinel inclusions.

Yellowish Resorbed and or heavily fractured stones feature heavily throughout the 4 suites, however small percentages (< 5%) of spinel inclusions, fusion crusts and percussion marks are present in the Upper Terrace gravel horizons. The Middle Terrace (T4A) shows approximately 10% assemblages of spinel inclusions and resorbed or heavily fractured stones with percussion marks.

Greenish Resorbed and heavily fractured stones are dominant features in all suites. Only the Middle Terrace has stones with > 10% spinel inclusions.

Apricot Group

Detailed examination showed that apricot coloured stones are actually light pink rubies, but the orange/apricot colouration is due to penetration by iron oxide minerals into numerous fractures and fissures within each stone.

Light Apricot Resorption and heavy fracturing dominate stones from Upper Terrace gravels (Section18-B) and contain < 10% sapphirine and spinel inclusions. Section T4A, (Middle Terrace) shows > 20% fusion crusting on stones. One stone showed pronounced surface resorption, with intersecting fluid inclusion trails.

Dark Apricot Less than 10% of stones have sapphirine and spinel inclusions in Section 18-B Upper Terrace, with approximately 10% fusion crusted stones present. Section 18-A Upper Terrace stones show 5% with fusion crusting. Stones from the Recent Alluvials (T2A) contain 10% spinel inclusions and 10% fusion crusting. The Middle Terrace (T4A) contains 30% resorbed, heavily fractured stones showing fusion crusts and nearly 30% resorbed, heavily fractured and fusion crusted stones with sapphirine inclusions.

Corundum Trace Element Contents

Among the chromophore elements, iron is the dominant trace element and ranges from about 2500 to 13,300 ppm. Titanium ranges from about 15 to 1200 ppm, and vanadium is relatively minor ranging from below detection to nearly 200 ppm. Gallium and chromium are the only other important trace elements in corundum trace element comparisons, with gallium ranging from below detection to nearly 300 ppm. The Cr/Ga ratios of the corundums fall into 3 main groups of element ratios and are summarised below.

Colour	Fe(ppm)	Ti(ppm)	Cr(ppm)	Ga(ppm)	V(ppm)	Ca(ppm)	Cr/Ga
Colourless	3027-3045±4	15.16±2	BD-6±1	19-20±1	BD	0-49±3	<0.02-0.34
Pale blue-green	5780-6160±6	212-245±2	BD	64-65±1	45-69±2	BD	<0.02
Light blue-green	9925_10065±8	51-62±2	BD	259-261±1	7-9±2	0-69±3	<0.02
Green-blue	6105-7610±6	62-183±2	BD	128-142±2	BD	BD	<0.02
Yellow-blue	12308-13325±9	481-1242±4	BD	109-110±2	24-31±4	BD	<0.02
Dark blue	8462-9536±8	75-361±3	BD	220-299±2	12-14±2	BD	<0.02
Pale lavender	5383-5607±6	175-193±2	180-195±2	29-30±1	53-59±2	0-12±3	6.13-6.63
Lavender	4990-5063±6	207-214±2	315-322±2	44-47±1	95-97±2	BD	7.07-718
Grey-lavender	5570-5607±6	84-89±2	355-363±2	23-25±1	27-29±2	BD	14.16-15.90
Violet	5660-5811±6	365-385±3	499-501±2	48-49±1	194-195±3	BD	10.26-10.48
Purple	3765-3827±5	42-46±2	165-480±2	22-25±1	12-14±2	BD	7.60-19.20
Light purple	5610-5660±6	292-326±2	490-500±2	45-46±1	154-162±2	BD	10.83-10.90
Browny pink	3720-3838±5	64-65±2	248-258±2	26-27±1	25-26±2	BD	9.07-9.90
Pink	2565-2607±4	30-41±2	688-730±2	29-37±1	15±2	BD	31.42-32.31
Purple pink	4416-4426±5	256-258±2	946-961±3	33-34±1	18±2	BD	27.63-27.65
Pink	2859-3104±4	29-37±2	688-730±2	22-23±1	15±2	BD	31.42-32.28
Bright pink	3074-3125±4	43-44±2	722-763±2	20-21±1	13-14±2	BD	36.66-37.59
Bright pink	2607-3190±4	30-41±2	907-957±3	15-18±1	16-17±2	BD	36.97-52.12
Bright pink	7542-7576±7	338-346±2	1444-1683±3	46-52±1	93-2	BD	27.80-36.41
Red	2986-3190±5	41-45±2	2191-2253±4	16-18±1	12-14±2	BD-22±3	122.40-138.38
Bright red	2529-2556±4	57-60±2	1575-1629±3	22-25±1	15-16±2	BD	63.52-74.71

Table 3. Trace element contents related to a range of colours in Gummi corundums, PIXE probe results, M. Garland, analyst, range of 2 analyses each corundum.

Grns	Ns	Ni	Na	$\rho\,$s(10^6)	$\rho\,$i(10^6)	U(ppm)	Age($\pm 1\sigma$)
Latest Cretaceous (1 grain)							
1	18	15	100	0.2860	0.2384	10.0	66.5±23.2
Eocene group 1 (av.) Yellow to Orange							
8	138	142	100	2.187	2.260	37-138 (Av. 93)	53.7±6.9
Eocene group 2 (av.) Yellow							
3	130	146	83	3.013	3.352	8-260 (Av. 140)	48.5±10.0
Eocene group 3 (av.) Red							
3	219	275	93	3.769	4.742	148-233 (Av. 200)	43.7±4.1
Oligocene group (av.) Orange to Red							
2	266	349	100	3.591	5.554	105-363 (Av. 234)	35.6±3.6
Pliocene group (av.) Red							
2	34	443	100	0.540	7.039	252-345 (Av. 298)	4.2±0.7

Table 4. Zircon fission-track results, Gummi Flats. $\rho_D = 1.257\text{–}1.284 \times 10^6\,\mathrm{cm}^{-2}$ ND = 1966. Ages calculated using a zeta of 87.7 ± 0.8 for U3 glass.
Analyst P.F. Green.

Grns	Ns	Ni	Na	$\rho\,$s(10^6)	$\rho\,$i(10^6)	U(ppm)	Age($\pm 1\sigma$)
Eocene group (av.)							
7	207	179	100	3.290	2.842	101-237 (Av. 153)	49.7±5.3
						Pooled age	50.2±2.2
Oligocene group (av.)							
6	177	207	100	2.805	3.477	57-417 (Av. 187)	36.8±4.2
						Pooled age	35.1±1.5
Early Miocene group (av.)							
2	136	243	200	1.743	2.958	48-317 (Av. 108)	23.5±2.7
						Pooled age	24.3±1.8
Late Miocene (?)							
1	59	277	300	0.313	1.467	79	9.2±1.3
Pliocene Group							
2	27	332	350	0.223	2.781	46-289 (Av. 168)	3.5±0.7
						Pooled age	3.5±0.5

Table 5. Zircon fission-track results, East Tomalla suite. $\rho_D = 9.906 \times 10^5\,\mathrm{cm}^{-2}$ ND = 1468. Ages calculated using a zeta of 87.7 ± 0.8 for U3 glass.
Analyst P.F. Green.

Low Cr/Ga Group (< 1)

Colourless, blue-green, yellow-blue and dark-blue. These characteristically have low Cr (up to 6 ppm) and high Ga (19 to 299 ppm) giving very low Cr/Ga ratios (< 0.02–0.34).

Mid Cr/Ga Group (6–20)

Lavender, grey lavender, violet, purple and browny pink. These have greater Cr contents (165 to 501 ppm) and relatively low Ga (22 to 49 ppm), giving Cr/Ga ratios of 6.13–19.20.

High Cr/Ga Group (> 20)

Pink, purple pink and red. These contain the highest Cr contents (688–2253 ppm) and relatively low Ga (15–52 ppm), giving Cr/Ga ratios of 27–138.

Zircon Fission-Track Results

Gummi Flats

Fission-track results have delineated 6 distinctive zircon groups based on uranium contents and age results.

Group 1. (Latest Cretaceous) Yellow colour. 1 grain (U 10.0 ppm) and age of 66.5 ± 23.2 Ma.
Group 2. (Early Eocene) Yellow and orange colours, 8 grains (av. U 93 ppm) and central age of 53.7 ± 6.9 Ma.
Group 3. (Mid Eocene) Yellow colour, 3 grains (av. U 140 ppm) and central age of 48.5 ± 10.0 Ma.
Group 4. (Late Eocene) Red colour, 3 grains (av. U 200 ppm) and central age of 43.7 ± 4.1 Ma.
Group 5. (Oligocene) Orange and red colours, 2 grains (av. U 234 ppm) and central age of 35.6 ± 3.6 Ma.
Group 6. (Pliocene) Red colours, 2 grains (av. U 298 ppm) and central age of 4.2 ± 0.7 Ma.

East Tomalla

Fission-track dating delineated five separate zircon groups. The colours and uranium contents do not vary greatly within the separate age groups.

Group 1. (Eocene) 7 grains (av. U 187 ppm) and central age of 49.7 ± 5.3 Ma.
Group 2. (Oligocene) 6 grains (av. U 187 ppm) and central age of 36.8 ± 4.2 Ma.
Group 3. (Early Miocene) 2 grains (av. U 108 ppm) and central age of 23.5 ± 2.7 Ma.
Group 4. (Late Miocene) 1 grain (U 79 ppm) and central age of 9.2 ±1.3 Ma.
Group 5. (Pliocene) 2 grains (av. U 168 ppm) and central age of 3.5 ± 0.7 Ma.

DISCUSSION

Depositional Relationships, Terraces and Corundums

Deposits from the three terraces, which yielded the corundum suites, show both differences and similarities. The lower gravel horizon of the Upper Terrace, Section 18-B, lacks obvious alluvial characteristics. The horizon is very poorly sorted in size and shape of its lithic fragments, and has a heavy clay matrix; it displays some characteristics of a mass debris flow (Cas and Wright, 1987). The two upper terrace gravel horizons occur intermittently over the Gummi Flats area. The upper gravel (Section 18-A) has a different colour and shows slight fining upwards. It contains more sub-rounded lithic fragments, so could possibly have some alluvialy derived component, or mark the end of a debris flow.

The Middle Terrace (Section T4A) displays a clearer fining upwards, compared to Section18-B. The Middle Terrace has a slightly larger percentage of rounded and sub-rounded stones, but sub-angular and sub-rounded lithic fragments still dominate. Overall it is poorly sorted.

The Recent Alluvial terrace (Section T2A) shows stronger alluvial characteristics than the Middle and Upper terraces. Upward fining sequences are present, lithic fragment sizes are smaller and there is a larger percentage of rounded and sub-rounded lithic fragments. The Recent Alluvial gravels are intermittently overlain by sandy-clays and clays, with sequence patterns more typical of alluvially derived deposits.

The features noted in each corundum suite help to indicate distances travelled from their sources. Heavy fracturing dominates corundums from Recent Alluvials and the lower gravel in the Upper Terrace (Section 18-B). Preservation of fusion crusts probably indicates a lesser distance travelled by corundums. The Middle Terrace has a greater percentage of such crusted stones. Larger average sizes, poorer gem quality and more prominent surface inclusions also suggest these stones have undergone less transportation. The corundum traits from the terraces suggest the following order of increasing transport effects: Middle Terrace, Section 18-A and Recent Alluvials, Section 18-B.

Overall, sapphirine, and Mg to Fe-rich spinels (pleonaste to hercynite) dominate as inclusions in the corundums. Rubies in all four gravel horizons contain sapphirine inclusions, indicating a metamorphic origin. The Middle Terrace rubies contained the largest percentage of sapphirine inclusions, over 8%, while Section 18-B and the Recent Alluvials contain some 2–2.5% and Section 18-B under 0.5%. These differences are most likely due to varied transport processes within the gravels, including distances from the sources.

Spinel inclusions are present in all colour groups from the terraces. The Middle Terrace shows the largest percentages of spinel inclusions, while both the Upper Terrace horizons contain similar spinel inclusion percentages and the Recent Alluvials the least. These results also complicate any linking of the upper horizon gravels (Section 18-A) to the other horizons as a continuous depositional sequence. It could mark a separately derived deposit.

The Middle Terrace shows higher percentages of stones with percussion marks, which may indicate more complex transport processes than straightforward alluvial transport. Percussion marks need not entirely indicate fluvial transportation, as they can occur during eruptive processes.

Magmatic Relationships

The great majority of corundums (50–95%) show magmatic resorption indicating a hot igneous source for their provenance. The most likely hosts are the basalts which elsewhere in eastern Australia are known to carry corundum as xenocrysts (Coenraads 1992), and the corundums show fusion crusts that indicate reaction temperatures around 1000°C (Sutherland and Coenraads 1996). The ruby group in particular shows more extensive resorption and indicates more than one stage of resorption has occurred, (up to 80% secondary resorption in some colour suites). This secondary resorption is seen on fractured surfaces, suggesting some fracturing took place during igneous explosion events, which exposed further surfaces to the corrosive attack.

This magmatic scenario is reinforced by the fusion crust mineralogy, where spinels (pleonaste to hercynite) dominate the main phases. Sapphirine appears mainly in fusion crusts in the ruby suites, but is rarely seen on blue, green and yellowish corundums. Two stones were analysed which showed a dominance of pleonaste on one side and hercynite on the other side of the same crust, indicating variation in crystallization of the spinels during magmatic reactions.

Colour-Shade Relationships

The colour-shade histograms clarify relationships within colour groups from each terrace. Section 18-B contains less features throughout its colour groups than the other sections. It also exhibits heavily fractured and resorbed stones. Fusion crusts along with sapphirine and spinel inclusions exist only in small percentages.

When looking at the ruby groups, colour does not control all the features present within these corundums. Section 18-B shows the biggest range of features to occur in the dark pink colours, whereas in Section 18-A the very pale pinks and dark pinks contain the most features, (including an ilmenite inclusion in a dark pink ruby). The Recent Alluvials show only resorption and heavy fracturing in very pale pinks, whereas other pink shades show more varied features. The Middle Terrace shows most variation in corundum features in the pale pink rubys. These ruby histograms clearly show the much higher percentages of fusion crusted stones in the Middle Terrace, with pale, medium and dark colour groups all containing over 30% of such stones.

The blue, greenish and yellowish coloured corundums lack sapphirine inclusions, suggesting their predominant non-metamorphic origin. Spinel inclusions are found in $< 10\%$ amounts throughout these corundums. Only greenish corundums from Section T4A (Middle Terrace) show $> 10\%$ spinel inclusions. Resorption and heavy fracturing dominate throughout the blue, greenish and yellowish colour suites, and none have $> 10\%$ fusion crusts. In comparison to the Middle Terrace rubies, which show $> 30\%$ fusion crusts in three colour shades the blue, greenish and yellowish corundums may have undergone greater erosive transport prior to their deposition with the rubies. This suggests separate origins (i.e. magmatic vs metamorphic), eruptive mechanisms and initial transportational processes were involved.

Apricot coloured corundums resemble the rubies, in having $> 10\%$ fusion crusted stones and sapphirine inclusions. As mentioned earlier the apricot colour results from iron penetrating through fractures and fissures, changing them from pale pink to apricot. Thus, these apricot coloured stones were most likely derived from the same source as the rubies. When compared to the blue, greenish and yellowish corundums, the rubies and apricot stones show a larger range of features. To elucidate the exact mechanisms that helped accumulate all these different coloured stones together will need further detailed investigation.

Inclusion Relationships

EDAX analysis identified anorthoclase, ilmenorutile and a magnesium, iron aluminosilicate in addition to previously recorded inclusions in Barrington Tops corundums. The ilmenorutile within a green corundum from the Recent Alluvials (section T2A), suggests a magmatic origin which agrees with other blue, greenish and yellowish corundums in this horizon. The magnesium, iron aluminosilicate appears in a corundum from the Middle Terrace (T4A) and anorthoclase was found included in a blue corundum from section 18-A.

The analysis suggest a range of spinel compositions from pleonaste to hercynite. Only $< 1\%$ of rubies analysed (section T4A) contained hercynite inclusions, which is more common in corundums of magmatic origins (Sutherland and Coenraads 1996).

Analyses indicate a clear link between the mineral inclusions and their host corundum origins, either as metamorphic (ruby and apricot corundums), or magmatic (some blue, greenish and yellowish) types. This correlates well with trace element Cr/Ga ratios in these corundums. For colourless, greens, yellow and blue corundums the Cr/Ga ratios are typical of magmatic origin (< 1), while lavender, violet, purple, brown pink, pink and red corundums show Cr/Ga ratios typical of metamorphic origin (> 1).

Zircon Relationships

The zircon fission-track analyses from the Gummi Flats and East Tomalla suites suggest several eruptive episodes were involved in their magmatic transport. Correlation between the two sites show at least three main age groups, at around 50 Ma, 35 Ma and 4 Ma, as consistent eruptive events. The East Tomalla suite also indicates possible eruption of zircon at around 23 Ma and 10 Ma. Some earlier eruptive episodes for zircon are possible from the Gummi Flats zircon data at around 66 Ma and 54 Ma, particularly as these zircons show substantially lower uranium contents (10–93) than in the other groups.

The new zircon age data from northern Barrington areas can be amalgamated with previous results for the general Barrington volcanic plateau (Sutherland and Fanning 2001). The new results not only indicate an extra eruptive episode at ~ 50 Ma, but also help to confirm some previously recorded eruptive episodes at both the older (over 65 Ma) and younger (3–5 Ma) ends of the eruptive history. The young eruptive-age zircons are now known at three sites in the Barrington plateau, each one showing distinctive U contents and colours. This suggests several geographically separate eruption sites were involved. The complex history of zircon-eruptive episodes would provide multiple opportunities for associated corundum release into the Barrington drainage systems.

CONCLUSIONS

1. The terrace deposits in the northern Barrington area, show some differences in corundum features within the separate horizons.
2. The ruby suite from the Upper Terrace (Section 18-B), generally lacks fusion crusts, inclusions and are heavily fractured. This suggests greater transport processes for these corundums. This contrasts with the deposit in which the corundums occur, as it shows mass deposit features with no prolonged transportation.
3. The Middle Terrace corundums, particularly the ruby suite show the most fusion crusts and inclusions, suggesting a more proximal origin.
4. The Recent Alluvial corundums show some features that characterise both the Upper and Middle Terrace horizons. This suggests it may contain some corundums derived from these horizons. These corundums, however, also show features that suggest sourcing from additional areas.
5. As the rubies generally show a difference in transport-derived features, it is possible that the other colour groups have undergone separate transportation before amalgamation with the rubies in each terrace.
6. Colour Shade histograms and EDAX analyses of corundum inclusions and fusion crusts emphasise the distinct differences between the ruby and other corundum groups.
7. The trace element data further distinguish the ruby suites from the other corundums, with Cr/Ga ratios indicating metamorphic origins for the ruby group and magmatic origins for most other corundums.
8. Zircons that accompany the corundums yield zircon fission-track ages that range between 66 Ma to ~ 4 Ma, and augment the previously known multiple eruptive history of the Barrington province.
9. Although the precise corundum sources remain to be located, the terrace study has narrowed down potential source targets, with the Middle Terrace indicating a possible nearby source.

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Six pages consisting of color figures and an Appendix for this article follow.

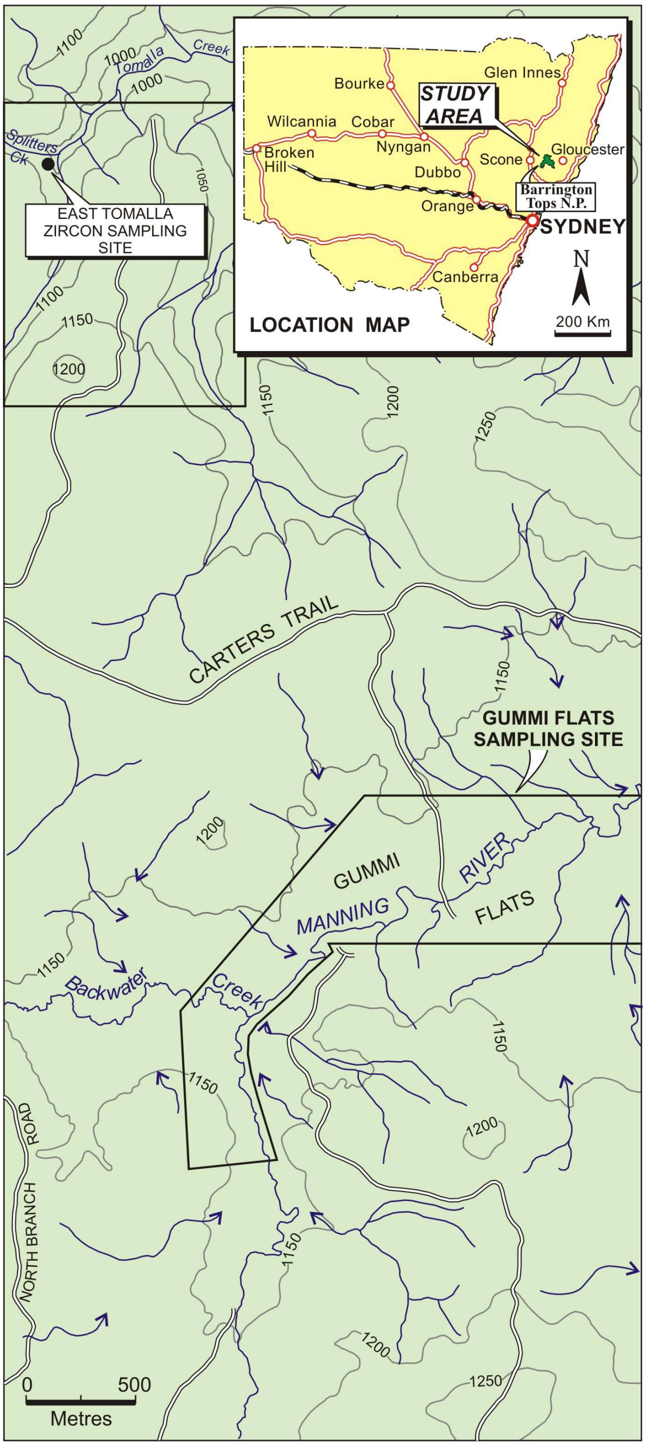


Figure 1. Locality map, study areas, showing Gummi Flats and East Tomalla sampling sites (boxes), general topography, drainage and access trails and location within New South Wales (inset).

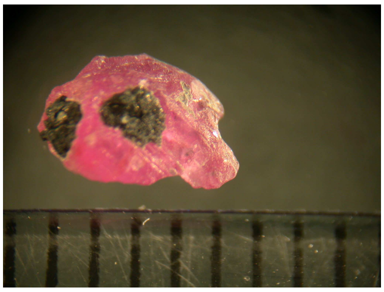


Plate 1. Resorbed ruby with preserved spinel fusion crust. (scale is in mm).

Plate 2. Resorbed ruby with sapphirine inclusion. (scale is in mm).

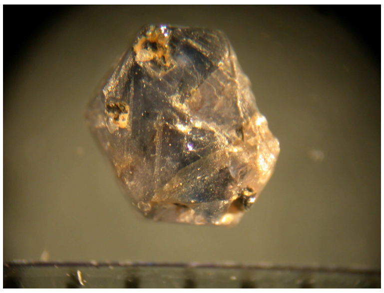


Plate 3. Pale to medium blue sapphire with several spinel inclusions. (scale is in mm).

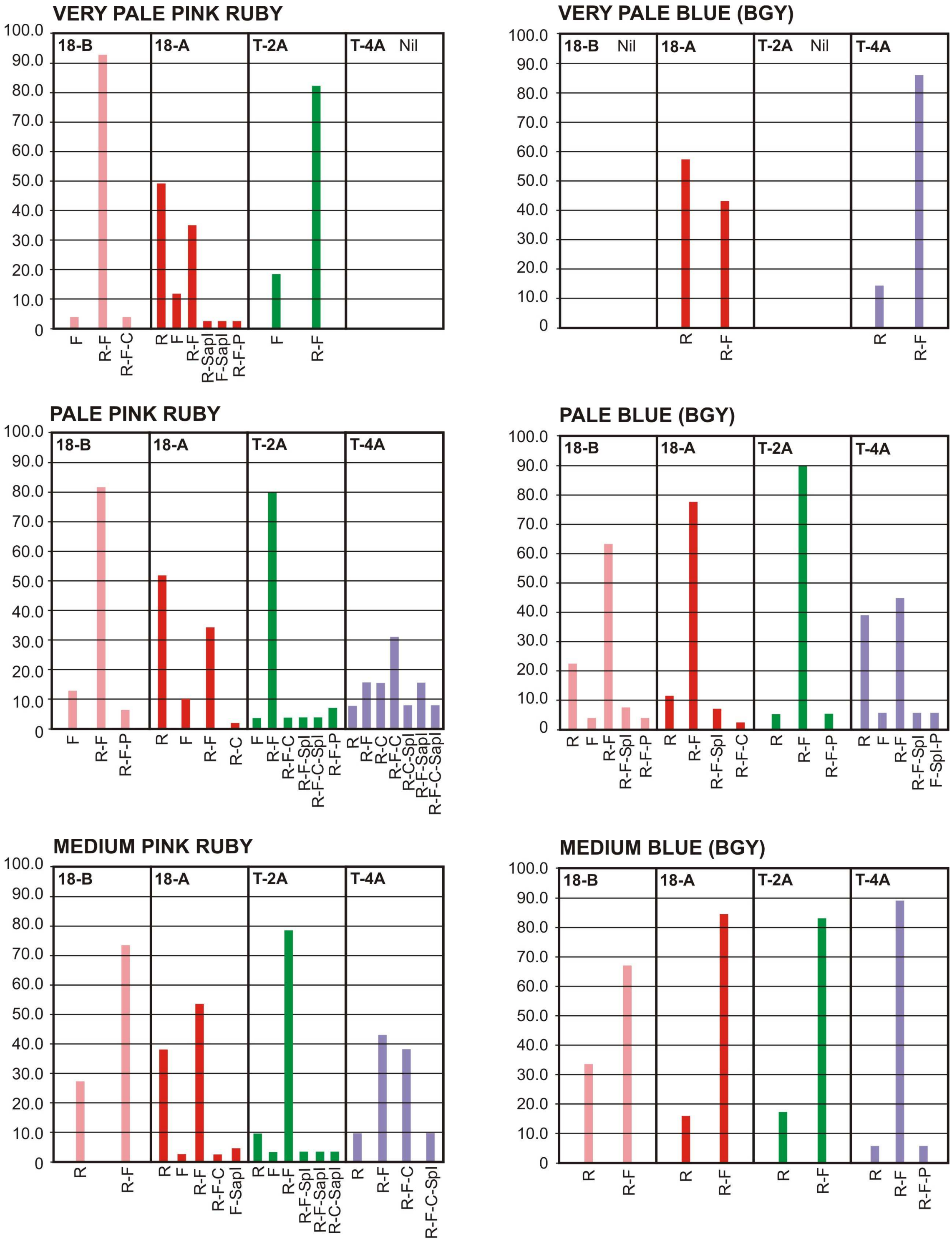
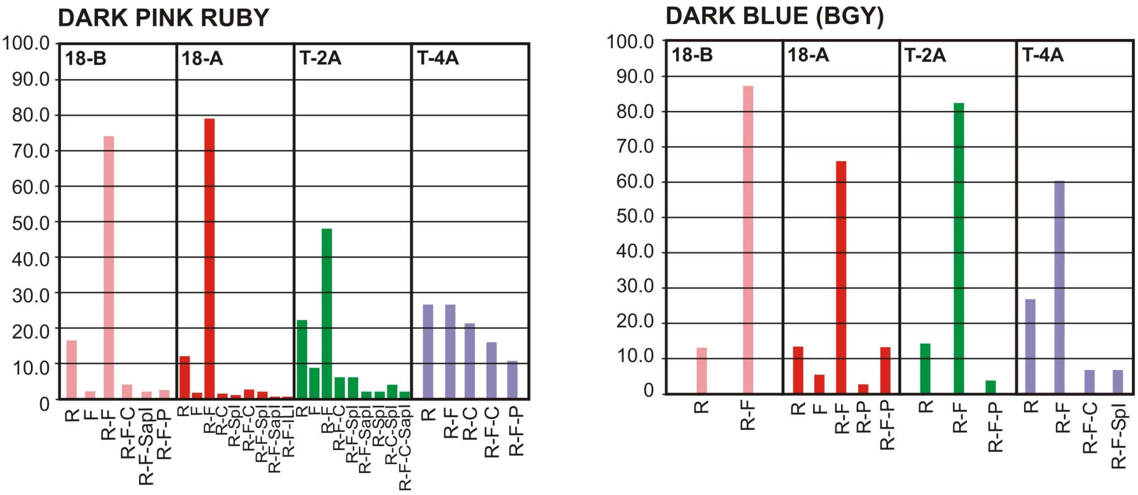


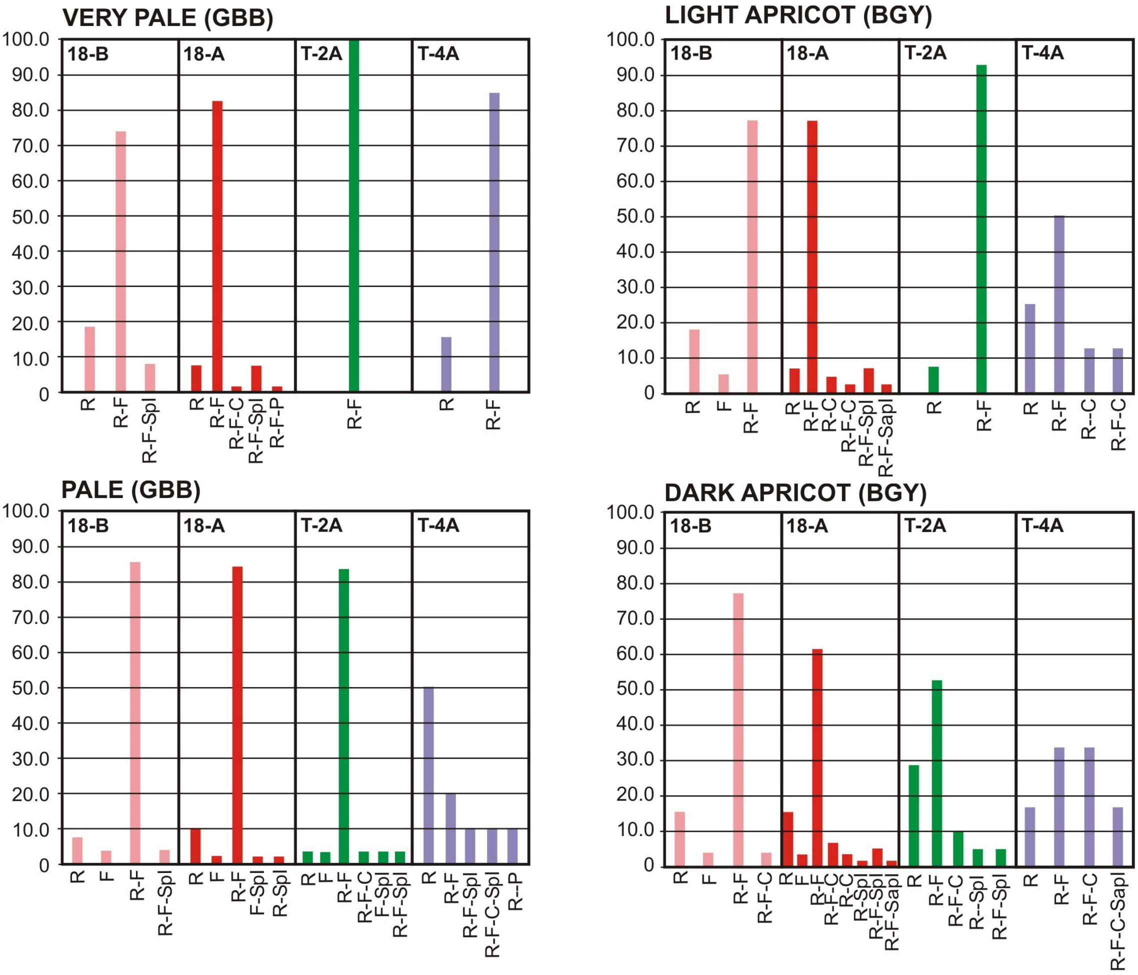
Figure 6. Colour-Shade histograms of Ruby, Blue Group corundums.



DARK PINK RUBY

DARK BLUE (BGY)

Figure 6 (continued). Colour-Shade histograms of Ruby, Blue Group corundums.



VERY PALE (GBB)

LIGHT APRICOT (BGY)

PALE (GBB)

DARK APRICOT (BGY)

Figure 7. Colour-Shade histograms of Grey-Brown-Black (GBB), Apricot, Greenish and Yellowish Group corundums.

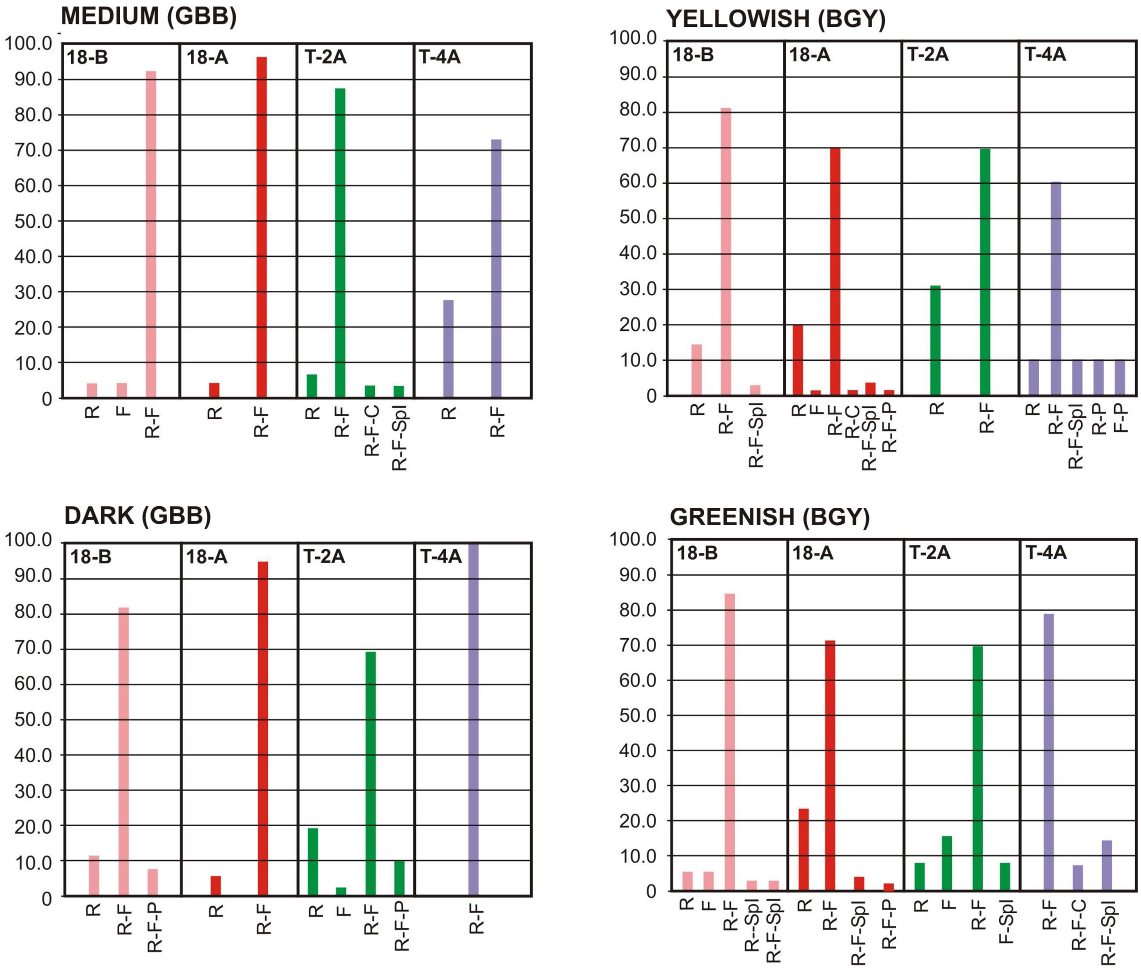


Figure 7 (continued). Colour-Shade histograms of Grey-Brown-Black (GBB), Apricot, Greenish and Yellowish Group corundums.

APPENDIX 1

Heavy Mineral Sample Description, East Tomalla
31° 49.88´S 151 ° 30.31´E 1200 m asl

> 2mm size fraction

Magnetic	Vol%	Description
	10	Weathered ferruginous fine-grained olivine basalt with spinel and clinopyroxene xenocrysts, and rare feldspar xenocrysts.
Non-magnetic	**Vol%**	**Description**
Spinels	65	Abundant (> 85 Vol % of sample) anhedral to subhedral, equant to subprismatic, magmatically corroded, etched and polished spinel xenocrysts (some with thin basalt rinds) up to 10 mm. Rare crystal faces present on some grains.
Glassy volcaniclastics	1	Uncommon dark brown to black, finely banded, scoriaceous, vesicular vitric tuff.
Other rock and mineral fragments	24	Moderately common muscovite aplite, muscovite granite, fine-stained quartz fragments, gibbsite and lateritic ironstone. Uncommon dark brown to black anhedral prismatic magmatically corroded and polished clinopyroxene xenocrysts and well rounded milky quartz grains. Rare massive monazite.

continued on next page…

< 2mm size fraction

Magnetic	Vol%	Description
	< 0.01 – 10	Well rounded spherical to ovoid fragments of weathered ferruginous olivine basalt and ironstone (> 1 mm) and well rounded, equant, spherical to ovoid highly pitted spinels, some with adhering basaltic crust (< 1 mm).
Non-magnetic	Vol%	Description
Spinels	50–90	Grey to black, angular to well rounded, equant to subprismatic, anhedral to subhedral, smooth to highly pitted, commonly partially resorbed and magmatically corroded grains with rare crystal faces.
Lherzolitic detritus	∼1–5	Olivine-common, olivine-green to yellow-green anhedral, equant to subprismatic, generally glassy angular grains with pronounced conchoidal fracture. Orthopyroxene-uncommon, brown-bronze glassy, partially to highly resorbed, finely etched and striated, anhedral to subhedral, short prismatic to prismatic, angular to subrounded grains.Clinopyroxene-uncommon, lime-green to emerald green (Cr-diopside), partially resorbed, finely etched and striated, subhedral subprismatic, angular to subrounded grains.
Rock and mineral fragments	9–40	Quartz, abundant and two distinct types: 1. Well-rounded spherical to ovoid opaque white and Fe-stained grains. 2. Angular to sorted, glassy colourless (some Fe-stained) equant to prismatic grains. Muscovite aplite - common as fine grained fragments. Ironstone and gibbsite - moderately common as well-rounded grains. Gorceixite-goyazite - uncommon yellow-brown resinous concentrically zoned rounded grains. Zircon - uncommon, generally as well rounded equant, anhedral to subhedral colourless to pink (rare yellow-brown) grains. Feldspar - rare, partially resorbed glassy colourless angular subprismatic grains. Corundum - extremely rare (6 grains), generally pale pink to pink-purple (very rare blue-green) highly resorbed grain fragments.

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Studies on Aragonite and its Occurrence in Caves, including New South Wales Caves

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Abstract: Aragonite is a minor secondary mineral in many limestone caves throughout the world and is probably the second-most common cave mineral after calcite. It occurs in the vadose zone of some caves in New South Wales. Aragonite is unstable in fresh water and usually reverts to calcite, but it is actively depositing in some NSW caves.

A review of the cave aragonite problem showed that chemical inhibitors to calcite deposition assist in the precipitation of calcium carbonate as aragonite instead of calcite. Chemical inhibitors physically block the positions on the calcite crystal lattice which otherwise would develop into a larger crystal. Often an inhibitor for calcite has no effect on the aragonite crystal lattice, thus favouring aragonite depositition.

Several factors are associated with the deposition of aragonite instead of calcite speleothems in NSW caves. They included the presence of ferroan dolomite, calcite-inhibitors (in particular ions of magnesium, manganese, phosphate, sulfate and heavy metals), and both air movement and humidity.

Keywords: aragonite, cave minerals, calcite, New South Wales

INTRODUCTION

Aragonite is a polymorph of calcium carbonate, $CaCO_3$. It was named after the province of Aragon, Spain, where it occurs as pseudo-hexagonal twins. Calcite is the more common polymorph.

Aragonite belongs to the orthorhombic crystal system while calcite has been variously placed in the rhombohedral (Hurlbut 1970), hexagonal, trigonal (Berry, Mason & Dietrich 1983) or triclinic (Glazer 1987) crystal systems. Another polymorph of $CaCO_3$ in caves is vaterite, which belongs to the hexagonal crystal system and is less dense than calcite. It has been recorded from cave moonmilk, carbide dumps and in the shells of living gastropods.It is not stable in the vadose environment and commonly reverts to calcite via aragonite. Other polymorphs include the high temperature and pressure Calcite-IV and Calcite-V which are not stable in near-surface environments (Carlson 1983).

Aragonite often forms with a characteristic acicular habit known as "church steeples" (Figure 1). It has one cleavage plane $\{010\}$ (across the "steeples") while calcite has a perfect cleavage plane $\{10\bar{1}1\}$ producing angles of 75° and 105°. Aragonite twins on $\{110\}$, producing pseudo-hexagonal columnar crystals, whereas calcite readily twins on the cleavage plane. Compared with calcite, aragonite is harder (3.5 to 4 cf. 3), denser (specific gravity 2.930 cf. 2.711) and more brittle (Berry et al. 1983).

Aragonite is often produced in the growth of marine organisms, particularly in shells. When the organism dies, proteins in the shell decay exposing the aragonite. In time, aragonite reverts to calcite in the near surface environment in the presence of fresh water. The deposition of aragonite is also a the product of chemical influence, or high pressure on calcite. It also occurs in secondary deposits in caves (Siegel 1965, Ford & Cullingford 1976) and igneous rocks.

It is probably the second most common cave mineral after calcite Hill & Forti (1997). This reflects the discovery of extensive aragonite deposits in caves such as Lechuguilla Cave (Carlsbad Caves National Park, U.S.A.).

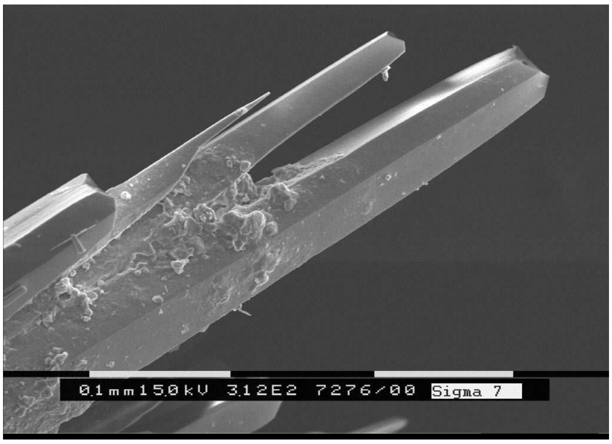

Figure 1. Aragonite from Sigma Cave, Wombeyan. SEM image by Jill Rowling and Dr Ian Kaplin.

Aragonite is typically white or colourless. It has also been recorded as blue, green, brown, yellow or orange depending on which trace metals are dissolved in the aragonite lattice. In the cave environment, aragonite tends to be either white or coloured by metal impurities such as copper, whereas calcite deposits are frequently coloured by organic (humic and fulvic) acids. The brown colouration of cave calcite was often incorectly attributed to iron oxy-hydroxide staining (Hill & Forti 1997). Kaolinite is frequently coloured by iron oxy-hydroxides and in some cases it is clay which coats speleothems.

THE CAVE ARAGONITE PROBLEM

Aragonite is being actively deposited in the vadose zones of many limestone caves around the world (Hill & Forti 1997). Similarly, aragonite is also deposited in the phreatic zones of thermal and hydrothermal caves (Dublyansky 2000). Curl (1962) recognised that these occurrences are thermodynamically unstable in fresh water and readily revert to calcite. So, why does aragonite exist at all in caves? What allows aragonite to deposit in caves without reverting to calcite?

Curl suggested that aragonite forms and persists in caves because calcite is prevented from forming, a concept arising from Saylor in 1928 who suggested that various substances inhibited the crystallisation of calcite and thereby allowed the precipitation of aragonite.

Hill & Forti (1997) noted that since Curl’s theoretical work, more experimental work was available on aragonite deposition in both cave and non-cave environments, so there was some consensus on determining the factors that cause aragonite to occur in caves. Hill and Forti discussed the following factors: magnesium, strontium, pH, supersaturation and rate of precipitation, temperature, pressure, speleothem surfaces and carbon dioxide content. These aspects will be discussed below.

Aragonite is also reported from the caves of NSW which have a vastly different geological history to those of Europe and North America. This article will investigate the presence of aragonite in cave deposits from both the international and local aspect.

PREVIOUS STUDIES ON ARAGONITE

Introduction to Studies

Shaw (1992) discussed cave aragonite in a historical context. The earliest reference he found was by Dr Charles S. Dolley in 1887 describing aragonite spicules depositing in a hollow on a helictite in Luray Cavern (U.S.A.). Shaw also included earlier references to flos ferri speleothems by John Hill in 1748 and sketches by Patrin in 1803.

Most work on carbonate diagenesis has focused on the marine environment, where aragonite is relevant to marine sediment diagenesis. Work on carbonate chemistry is also vital to industry, for example the curing of concrete for structural stability.

Descriptions of research on the chemistry of aragonite were summarised in Bathurst (1974) and Morse (1983). They referred to the experiments on solutions of calcium carbonate using varying amounts of chemical inhibitors such as magnesium ions. Bathurst noted that the solution needed to be supersaturated with respect to both calcite and aragonite in order for aragonite to deposit, and discussed the chemistry of aragonite precipitation in the marine setting, in lime muds, beachrock and mollusc shells.

Tucker & Wright (1990) discussed aragonite chemistry with more accent on diagenesis of marine carbonates. Tucker (1991) defined low magnesium calcite as containing less than 4 mole% $MgCO_3$, while high magnesium calcites commonly ranged between 11 and 19 mole% $MgCO_3$. Walter (1985) compared the relative solubilities of several carbonate minerals and found that the theoretical dissolution rates of the minerals varied with pH. For a given pH, high Mg-calcite dissolved fastest, then low Mg-calcite, then aragonite and then calcite which was the slowest. For a given dissolution rate, high Mg-calcite dissolves at a higher pH than does low Mg-calcite, aragonite or calcite.

Morse reviewed the kinetics in dissolution of calcite, and noted that both precipitation and dissolution of calcite are hindered by the presence of chemical inhibitors. If these chemical inhibitors are available in the drip water of a cave, and the water is also supersaturated with respect to calcium carbonate, then aragonite deposits in preference to calcite.

Calcite-inhibitors work by blocking crystal growth points on the calcite lattice, which are frequently at edges or around dislocations (Mercer 1990). This concept is shown in Figure 2.

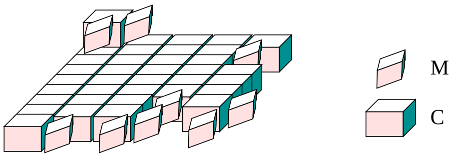

Figure 2. Schematic of a developing crystal, with a sheet of unit cells such as calcite (C) whose growth points are being blocked by an inhibitor such as a magnesium compound (M). Based on ideas in Morse (1983) and Mercer (1990).

Morse noted that inhibitors for calcite generally did not effect the aragonite crystal structure and may form solid solutions in the aragonite crystal. Both precipitation and dissolution of calcite are affected by inhibitors, including:

- magnesium
- heavy metals and rare earths (Cu, Sc, Pb, La, Y, Cd, Au, Zn, Ge, Mn, Ni, Ba, Co)
- sulfate, phosphate

Some organic compounds such as humic acids may inhibit precipitation of aragonite, while other organic materials apparently inhibit both calcite and aragonite precipitation. This may result from substances coating the mineral rather than any chemical kinetic effect.

For the cave environment, the review and discussion of cave aragonite by Hill & Forti (1997) is considered the main current reference.

For either aragonite or calcite to deposit, there needs to be bicarbonate ion, HCO_3^- in solution, a means of allowing carbon dioxide to outgas or be otherwise leave the reaction, and the solution needs to be supersaturated with respect to calcium carbonate. In caves, these conditions usually deposit calcite as the most stable polymorph of calcium carbonate.

Figure 3 illustrates the portion of the calcium carbonate phase diagram for the temperature and pressure ranges typical for caves in a meteoric environment. This is well within the stability region for calcite. For meteoric caves, the temperature of the cave is approximately that of the average annual temperature for the area.

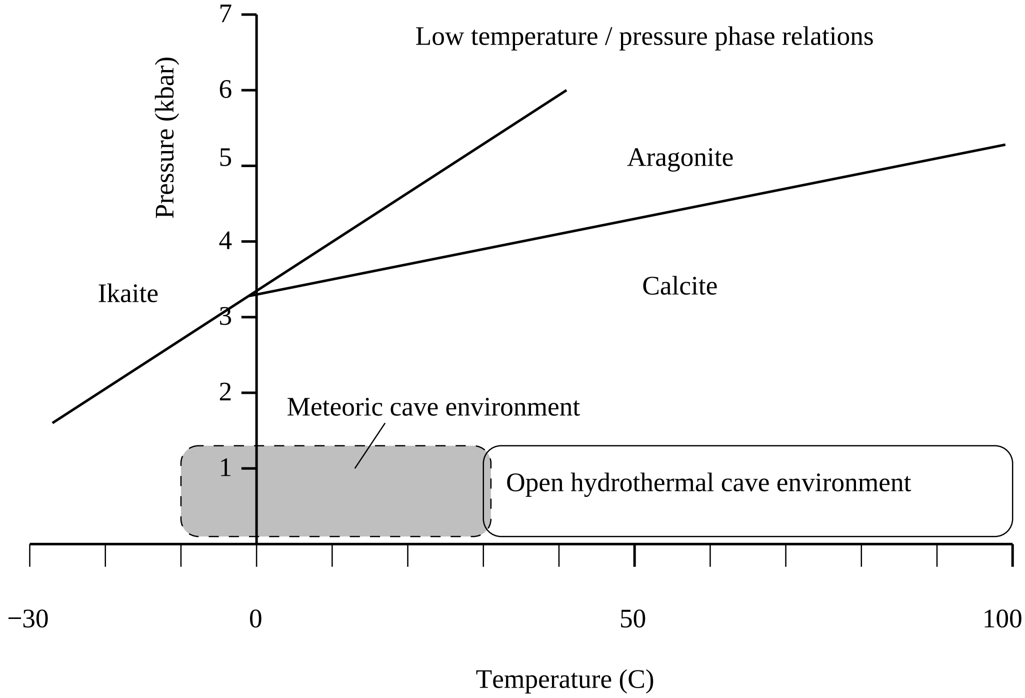

Figure 3. Stability Diagram for $CaCO_3$ at low temperatures and pressures shows that calcite is the expected polymorph in caves at atmospheric pressure. Based on Carlson (1983)

Included in this diagram are the typical ranges of temperatures for caves in a hydrothermal environment which are open to the atmosphere. In a closed environment, however, a water-filled cavity can experience much higher ranges of temperature and pressure.

Although Hill and Forti stated that temperature is not a factor in the precipitation of aragonite in caves, it is interesting to note the family of carbonate minerals which deposit at ambient pressures and low temperatures. The Pressure - Temperature (P-T) diagram of Carlson (1983) was extended by Tucker & Wright (1990) to include temperatures below 0°C and the hydrated calcium carbonates. At at sub-zero temperatures ikaite is stable (albeit at high pressure). Ikaite is $CaCO_3{\cdot}6H_2O$ which forms calcite pseudomorphs after ikaite as the temperature is increased above zero. Another hydrated mineral, monohydrocalcite $CaCO_3{\cdot}H_2O$, is also unstable at the earth's surface and reverts to calcite. Monohydrocalcite occurs in some types of moonmilk and as hydrated spheroids in pools in cold caves and sometimes accompanies aragonite. Aragonite is apparently unstable at sub-zero temperatures, but at much higher temperatures and pressures is sufficiently stable to designate the P-T of formation of particular rocks such as blueschists at around 4 to 6 kbar (Turner 1981, Essene 1983). The high magnesium content of serpentinites was noted by Essene to alter the P-T stability at which aragonite will form, but these P-T conditions are way above that found in meteoric caves. For a given pressure, as temperature is increased, aragonite will generally convert to calcite. Similarly, for a given temperature, as pressure is increased, calcite will convert to aragonite.

In the marine environment, there are a number of factors that govern which polymorph of calcium carbonate is deposited. They include whether or not the deposition is related to the life processes of marine organisms and the chemistry of the water.

Palaeodeposits, Paramorphs and Marine Cave Cements

The aragonite crystal structure is sometimes preserved in sediments, even after conversion to calcite.

Kendall & Tucker (1973) described a crystal fabric in limestones which resembled pseudomorphs of calcite after a "an acicular carbonate", potentially aragonite. The main arguments as to the precursor being an acicular carbonate included subcrystals diverging from the substrate, convergent optical axes, and curved twin lamellae.

Samples of marine aragonite in a reef in Belize (British Honduras) (Ginsburg & James 1976) came from cavities and small caves within the barrier reef, at depths between 65 m and 120 m. The aragonite formed "mamelons": hemispherical aggregates of aragonite deposited on the ceilings of the voids in the reef bedrock. Some were deposited on the floors or filled the whole cavity. The limestone bedrock and the aragonite were both dated as Holocene (samples ranged from 7000 to 13000 years). The substrates to the aragonite included high Mg calcite, aragonitic coral or aragonitic algal plates. The development of needle crystals was influenced by the substrate, for example, oriented aragonite substrate grains produced larger mamelons than did unoriented grains. The strontium in the crystals was similar in relative concentrations to that of Sr/Ca in sea water. Carbon and oxygen isotope ratios were consistent with that of marine limestones. The authors concluded that the mamelons formed shortly after the deposition of the limestone.

A piece of flowstone from Carlsbad Caverns, New Mexico (U.S.A.) contained crystals of calcite which had once been aragonite (Folk & Assereto 1976). The original aragonite fabric such as feathery or squared terminations were preserved. Small needle crystals were considered to be remaining aragonite. Unusually long length-slow calcite crystals were attributed to previous aragonite or vaterite. Length-fast calcite crystals were the most common type of calcite crystal development, with crystal elongation in the direction of the calcite optical axis (the c axis), and length-slow calcite crystals are elongated in the optically slower direction. They commonly exhibit undulatory optical extinction.

Assereto & Folk (1979) described the various aragonite, calcite and dolomite cements in metre-sized cavities in marine shoreline tepee structures from the Triassic Calcare Rosso limestone of the Southern Alps of northern Italy. Although the original aragonite was now calcite, all of the original fabric was preserved. The original depositional environment was described as near-marine semi-arid. The original aragonite formed in the tops of the cavities as hemispherical crystal aggregates approximately 10 cm long, with aragonite flowstones deposited in the sides and bottoms. Aragonite hemispheres had been deposited on the bottoms of the cavities. Dolomite was deposited in small cavities within the original carbonate tepees. The aragonite became converted to calcite after the Mg/Ca ratios of water percolating through the deposit became less than about 2:1.

Mazzullo (1980) examined samples from the Capitan Limestone deposit, Guadalupe Mountains, New Mexico (U.S.A.) and found fan-shaped crystal aggregates in a replacement calcite fabric. The crystal terminations were squared, as is aragonite, but no curved twin lamellae could be found. Some fabrics had no uniform crystal optical extinction. Some inclusions followed the original aragonite crystal outlines.

Temperature

Cser & Fejérdy (1962) analysed samples from hydrothermal caves near Budapest but very few of their subaerial samples contained any aragonite. Dublyansky (2000) discussed the speleogenesis of hydrothermal caves of the Buda Hills in Hungary, and noted that thermal springs in the area had temperatures up to 65°C. Aragonite was detected in the water coming out of nearby hot springs (subaqueous deposition), but converted to calcite on exposure.

In various aqueous solutions prepared from calcite or aragonite, calcite was the only precipitate in a variety of temperature regimes

(Siegel & Reams 1966). When carbon dioxide was bubbled through a solution prepared from artificially produced calcites and aragonites, there was a tendency to produce aragonite at higher temperatures e.g. above 65°C. This could explain the temporary aragonite precipitation in the hydrothermal springs near Budapest. With solutions made from dolomite, Siegel and Reams found the precipitates were 90% magnesian calcite. More aragonite was precipitated at temperatures above 50°C. Carbon dioxide exposure in this case did not affect the outcome.

Previously, an increase in temperature was thought to aid the formation of aragonite, but this became disputed (Morse 1983). Later research shows that the long-term stability for aragonite at high temperatures is only achieved at high pressures. The stability diagram for aragonite (Figure 3) suggests that for the meteoric cave environment, temperature should not normally be a factor. Temperature was not considered a factor by Hill & Forti (1997), but they noted that more aragonite appears in cold caves than in tropical ones, which is the inverse of that suggested by previous researchers. Nearly all minerals listed in Hill and Forti were recorded from the vadose zone of caves.

Aragonite will convert back to calcite at high temperatures (e.g. over 100°C) and pressures around 3 kbar (conditions unlike meteoric caves).

Leel-Ossy (1997) examined cave minerals in the Jozsefhegy hydrothermal cave near Budapest, Hungary, that included aragonite with gypsum. However the aragonite and gypsum considerably post-dated both the caves and the hydrothermal activity which formed them.

Association with Magnesium

The relationship between aragonite and magnesium has been described by Curl (1962) as being the strongest chemical influence in preventing calcite from depositing and allowing aragonite to deposit. Morse (1983) also listed magnesium as one of the calcite crystal poisoners.

Eibengrotte is a cave in the Fränkische Schweiz (Germany) which is developed in massive dolostone. Fischbeck & Müller (1971) found a number of minerals precipitating as surface coatings and as cave coral, including monohydrocalcite, hydromagnesite, nesquehonite, dolomite, aragonite and calcite. Both primary (from weathering of bedrock) and secondary dolomite was being deposited. The precipitation of aragonite was ascribed to the high magnesium content present in the cave seepage water. Monohydrocalcite was ascribed to an aerosol mode of formation after comparison with an industrial aerosol system.

Thrailkill (1971) sampled drip water and speleothems from various sites in Carlsbad Caverns and found that the "moonmilk" deposits were aragonite, hydromagnesite, huntite or dolomite and hydromagnesite. The dripping water was considerably undersaturated with respect to hydromagnesite, but saturated with respect to calcite, aragonite, huntite and dolomite. Hydromagnesite only occurred where slow seepage allowed evaporation to take place. Dolomite and huntite are said to be formed by alteration from one of the other carbonates.

Aragonite appears in minerals of the Frauenmauer - Langstein cave system in Austria (Seemann 1985). It forms in small amounts as hard, small fine spikes, coralloids, frostwork and crusts. These caves also had hydromagnesite and sulfate minerals. As the Mg content is increased, protodolomite and then dolomite can be produced (rather than aragonite, huntite and hydromagnesite).

A summary of Austrian cave minerals (Seemann 1987) shows aragonite occurs in many Austrian caves although not abundantly. It associates with magnesium minerals as flowstone (often interlayered with calcite), in moonmilk growths, cave coral and anthodite type helictites. Aragonite is deposited when the Mg/Ca ratio is 3:1 to 5:1.

The relationship between aragonite and magnesium compounds such as hydromagnesite has been described by others e.g. Hill (1987). Magnesium is a key component to aragonite deposition in many caves. Hill & Forti (1997) noted that on increasing magnesium in a mixed solution of magnesium and calcium carbonate, the following mineral sequence is deposited: calcite, high magnesium calcite, aragonite, huntite and hydromagnesite, magnesite. The presence of magnesium ions disrupts the calcite crystal lattice but not that of aragonite, suggesting that crystal poisoning by magnesium ions only affects the calcite crystal lattice, leaving aragonite to deposit freely given appropriate conditions of supersaturation.

Urbani (1997) listed several Venezuelan caves as having aragonite. One occurrence was associated with sepiolite (a hydrated magnesium silicate) and another was associated with dolomite. Urbani suggested that the aragonite crystallisation was promoted by a high concentration of strontium.

Frisia, Borsato, Fairchild & Longinelli (1997) examined stalagmites and drip points in Clamouse cave (France). Aragonite speleothems were being precipitated only where there was dolomitic bedrock, and only when the drip rate was very low. The authors suggested that magnesium inhibited the growth of calcite, either by crystal poisoning or by "difficulties in rapid dehydration of the Mg^{2+} ion". Clamouse cave water was not particularly high in dissolved Mg compared with other sites, so that the structure of the nucleation sites may play a greater role. Frisia, Borsato, Fairchild & Selmo (2001) examined both aragonite and calcite speleothems in Clamouse cave. Calcite speleothems had transformed from aragonite precursors over about 100 years. They suggested speleothem aragonite is a palaeo-aridity indicator.

Niggeman, Habermann, Oelze & Richter (1997) examined coralloids deposited in windy areas of several caves in Germany and Austria. More aragonite was deposited in the areas where the bedrock contained dolomite, either primary dolomite or from hydrothermal alteration of bedrock. They recorded the following data regarding the Mg/Ca ratio as mole % and the polymorph deposited: At Site 1 with Mg/Ca < 0.5: calcite; At Sites 2, 3 and 4 with Mg/Ca increasingly > 2: calcite + aragonite, with Mg/Ca 3–23 at site 4. Site 4 (Grauner Walls) included Mg calcite, aragonite, monohydrocalcite, nesquehonite and hydromagnesite.

Bohemia Cave in the Mount Owen Karst Area of the South Island of New Zealand was discovered in 1990 by members of the Czech speleological club Alberice. A large cavity and its mineralogy was briefly summarised in Tásler (1998). The cavity, called "Dream of Alberice Cavers", measures approximately 80 m wide by 650 m long which is a large cavern by world standards. Most of the ceiling, walls and floor of this cavern were covered with various aragonite speleothems together with hydromagnesite "snow". The overlying bedrock was dolomitic Ordovician units of the Mount Arthur Group whereas the underlying rock to most of the cavern was phyllite. Deposits of limonitised pyrrhotite were found near the junction area. About 90% of the speleothems are aragonite, and other minerals include calcite, hydromagnesite, dolomite, opal, Fe- and Mn- hydroxides, gypsum and sepiolite. The contact area between the two bedrocks was exceptionally rich in aragonite. Aragonite speleothems include stalactites, flowstone (including some yellow and yellow-red flowstone), stalagmites, soda straws, flos ferri (as thin intertwined branching forms), "winding needles", helictites, crystal coatings, linear needles, anthodites, "ball of threads", needle clusters. The needles and helictites were often hollow, with some solid needles. The different speleothem types were often clustered together and sometimes with hydromagnesite coatings on the tips. Grass shaped aragonite crystals as ultra thin needles were found in the insides of some hollow speleothems such as straws.

In several caves near Waitomo, New Zealand, aragonite occurs with hydromagnesite or other magnesium-based mineral. Overlying pyroclastic deposits influence mineralogy and cave water chemistry at Waitimo Caves (P. Maynard, pers. comm.).

In France, several caves have outstanding aragonite deposits, usually associated with metamorphosed dolostone. Some deposits are associated with gypsum and sulfur, and some with hydromagnesite (Cabrol, Gill & Gunn 2001).

Strontium

Tucker & Wright (1990) found that strontium substitutes for calcium in both lattice and non-lattice sites for both calcite and aragonite. This complicates the chemistry. Strontium ions are a common trace constituent of seawater. However strontium often deposits as strontium sulfate and it may be the sulfate component which is the calcite-inhibitor.

Strontium carbonate (strontianite) is rarer in meteoric caves than strontium sulfate (celestite) (Hill & Forti 1997), but can occur with aragonite and sometimes with high or low Mg calcite. Strontium is often considered a factor in the precipitation of aragonite, but Hill and Forti noted strontium readily substitutes for calcium without disrupting the aragonite crystal lattice.

Association with Clastics and Clay

Craig, Horton & Reams (1984) suggested that aragonite is nucleated by clastics in caves, after studying speleothems from caves in Missouri (U.S.A.) but were only able to produce vaterite in an experiment mimicking current cave conditions.

In the aragonite caves of France, the aragonite is often associated with clays (Cabrol et al. 2001), exclusively in the clayey areas (David Gill, pers. comm. in 2001). However, clays are common minerals in caves, often as the substrate for a number of calcite speleothems such as flowstone and stalagmites.

Association with Vaterite

Hill & Forti (1997) noted that vaterite occurs in caves associated with moonmilk and sediments, and is found with hydromagnesite, baylissite, calcite, aragonite and monohydrocalcite. Vaterite can form when calcium carbonate is precipitated under conditions of high CO_2 degassing, but reverts to aragonite and calcite over time.

Possible Association with Carbide Dumps

Carbide (calcium carbide) is used as a lighting source for caves in many parts of the world. Dripping water on calcium carbide produces acetylene gas which is controlled and ignited to provide a bright flame. The solid waste is mostly calcium hydroxide with minor arsenic, and is occasionally dumped in caves. Cavers have noticed an unusual heligmite known as "carbidimites" associated with disused carbide dumps (Hill & Forti 1997). These form by the reaction between the spent calcium carbide dump with cave seepage water. Carbidimites have an inverted horn shape, and a tendency to change shape over months compared with other speleothems (decades). Sarigu (1999) included photographs of carbidimites from a cave in Italy and discussed their formation. Sarigu suggested that they form by the carbonation of calcium hydroxide with CO_2 to calcium carbonate and water, further carbonation to calcium bicarbonate and also the direct carbonation of calcium hydroxide to calcium bicarbonate. The photographs and text note that the crystals deposited in the tubes as feathery shapes, more like aragonite or possibly vaterite rather than calcite. Hill and Forti claim that most carbidimites are calcite but some are vaterite.

Influence by Sulfates

In caves containing gypsum (hydrated calcium sulfate), both calcite and aragonite can occur, e.g. Great Onyx Cave, Kentucky, U.S.A. (Siegel 1965). Morse (1983) lists the sulfate ion as a calcite crystal inhibitor.

Carlsbad Caverns in the Guadalupe Mountains, Carlsbad National Park, U.S.A., contain extensive deposits of aragonite associated with gypsum and sulfur (Thrailkill 1971, Hill 1987). Thrailkill noticed that where there was gypsum, there was very little calcite. According to Hill, the caves were formed in several stages. A late stage involved H_2S seeping though joints from nearby oil well brines. The reaction between H_2S and water formed sulfuric acid which corroded the porous limestone to form gypsum and large caves. The origin of this H_2S is apparently bacterial. The caves were probably not formed at high temperatures (the present cave temperatures are about 20°C).

According to Hill, aragonite in Carlsbad Caverns occurred as rims, stalactites, hollow stalagmites, moonmilk, frostwork, anthodites, flowstone, beaded helictites. Secondary sulfate in Carlsbad Caverns was less than carbonates, despite the large gypsum blocks present. The sulfate speleothems apparently had a sulfur isotope signature closer to that of the overlying pyritic beds rather than that of the gypsum blocks.

Hill listed speleothems and minerals that were deposited near lakes in Carlsbad Caverns. In the pools were calcite "cave clouds" (a mammillary coating). Closest to the pools were rounded cave popcorn (mostly aragonite). Further up were shrub-shapes of aragonite frostwork and further up again were corroded speleothems.

Lechuguilla Cave in Carlsbad National Park was well illustrated in Speleo Projects (1998) and has a similar sulfuric acid speleogenesis to Carlsbad Caverns. Both subaerial and subaqueous gypsum and aragonite speleothems occur, but not together (or not photographed together). Possibly in these caves, aragonite and gypsum speleothems have a different origin. Lechuguilla cave has subaqueous speleothems such as selenite needles, calcite pool crystal and subaqueous calcite helictites, but lacks aragonite in pool deposits. Calcite speleothems are less common in Lechuguilla Cave compared to other caves (Speleo Projects 1998).

Other outstanding caves which contain aragonite associated with gypsum include Cupp-Coutunn Cave (Turkmenistan) and Alum Cave (Vulcano Island, Sicily - Italy) (Hill & Forti 1997).

Cser & Fejérdy (1962) described aragonite precipitating in hot springs in hydrothermal caves in Hungary as well as subaerial deposits. Leel-Ossy (1997) mentioned that aragonite was a relatively young (subaerial) deposit in the in the Jozsefhegy Hydrothermal Cave (Hungary). Other reported minerals included calcite and gypsum.

Wall crusts in Humpleu cave in Romania (Ghergari, Onac & Fratila 1997) included gypsum, calcite, aragonite and a variety of sulfate minerals, apparently the breakdown products of bat guano. Some of the calcite was a paramorph after aragonite.

In Flower Cave, in the Puketiti district near Waitomo, New Zealand, cavers have reported aragonite deposits associated with large gypsum extrusions and crusts. The gypsum extrusions are typically 200 mm long. Pool crystal deposits there have been described as aragonite, but require confirmation. Photographs with cavers suggest crystal sizes of around 20 to 30 mm long in aggregates and a hydrothermal influence on cave development has been suggested.

Influence by Humidity

Siegel & Reams (1966) cited the work of Pobéguin in 1955 and 1957 which suggested that aragonite precipitation is enhanced by high rates of evaporation. Aragonite is 16% more soluble than calcite, so to precipitate aragonite the solution must already be saturated with respect to calcite. To get aragonite to precipitate first needs an increased rate of precipitation, too fast for calcite precipitation. Siegel and Reams suggest that a rapid rate of evaporation can result in the solubility product of aragonite to be exceeded, allowing both calcite and aragonite to form.

Hill & Forti (1997) described a "popcorn line" in Carlsbad Caverns as being due to a humidity effect. Cave Popcorn is a speleothem form of either calcite or aragonite, and probably forms by air moving over the speleothem surface, promoting mineral precipitation by evaporation of water at the outer surfaces. Some caves have a pronounced flow of cold dry air into the cave during winter, which may be more significant to the development of this speleothem than is the loss of CO_2. Aragonite frostwork and coralloids are similar speleothem forms, with frostwork being formed at times of high humidity and coralloids formed when the humidity is lower and the rate of precipitation higher, producing a smaller crystal size.

On the other hand, Cilek, Bosak, Melka, Zak, Langrova & Osborne (1998) argued that the high humidity in the Ochtiná Aragonite Cave helped aragonite to deposit in the cave. The humidity was kept constant by the buffering effect of saturated ochres. The ochres contained 47% to 56% water by weight, and this significantly influenced the cave's climate, which could aid the precipitation of large aragonite speleothems. However most caves have a high humidity buffered by clays and sediments. It is more likely that the constant high humidity controls the crystal size and growth rate of the deposited calcium carbonate rather than the polymorph.

Supersaturation and Rate of Deposition

Only minute amounts of foreign material is required to alter the form deposited (both crystal shape and polymorph) (Curl 1962), while a high rate of deposition favours aragonite a little more than calcite (Siegel & Reams 1966). Theoretical growth rates of stalagmites with both stagnant and flowing water were calculated by Dreybrodt (1981). The limits to precipitation in the case of stagnant films was the ability for the film to outgas CO_2, which did not occur for running water.

Supersaturation and rate of deposition are factors in the precipitation of aragonite Hill & Forti (1997). Unlike Siegel & Reams, Hill & Forti considered very low rates of deposition favour aragonite over calcite, while very high rates of deposition favour vaterite which may convert to aragonite. At other rates, calcite is the favoured polymorph. They noted that supersaturation can be achieved in dry caves with a high loss of CO_2 or a high evaporation rate, which could lead to increased percentage of magnesium in the remaining solution.

Supersaturation is necessary for the precipitation of either calcite or aragonite, and can be achieved either by physical means (e.g. evaporation) or chemical means. By allowing CO_2 to escape, or by application of the common ion effect, the solution may become supersaturated with respect to either calcite or aragonite (or vaterite). For example, the addition of calcium sulfate to a supersaturated solution of calcium carbonate will cause the less soluble substance (calcium carbonate) to deposit.

Fast deposition commonly occurs near cave entrances where evaporation is highest, yet the material deposited is primarily calcite. Aragonite has been found near cave entrances associated with monohydrocalcite (Hill & Forti 1997). Aragonite also occurs in areas with slow deposition rates, e.g. Ochtiná Aragonite Cave (Bosák, Bella, Cílek, Ford, Hercman, Kadlec, Osborne & Pruner 2002) in which three generations of aragonite deposition were identified. The oldest generation detected (U/Th dating) was 138000 years old.

In Clamouse Cave (France), Frisia et al. (1997) found that the drip rate controlled aragonite or calcite precipitation. Aragonite formed only under the slow drips in areas with dolomitic bedrock, which allowed more takeup of magnesium from the bedrock, and reduced the rate of outgassing of CO_2.

Carbon Dioxide

Carbon dioxide content is also a factor in the precipitation of aragonite in caves, based on the work of Cabrol in 1978 and Courdry and Cabrol in 1982 in which a stratification line was noted in some caves in France (Hill & Forti 1997). Above this line was only calcite whereas below the line, aragonite was deposited. This was ascribed to a lowering of the supersaturation of the seepage water to favour the deposition of aragonite.

Pressure

Pressure was also a possible factor in the precipitation of aragonite in caves (B. Rogers, pers. comm. in Hill & Forti (1997)). Aragonite was described from an active fault in a cave. Calcite will readily convert to aragonite at high pressures. This situation is unlikely for most cave environments.

Speleothem Surfaces

Speleothem surfaces may also assist the deposition of aragonite, where aragonite was formed over corrosion surfaces, or over older aragonite speleothems. However, it can be difficult to distinguish between calcite and aragonite and one researcher found one fifth of a supposedly aragonite collection was in fact calcite (Hill & Forti 1997).

Speleothem surfaces and substrates aid the precipitation of most speleothems. Seed crystals start crystal growth, so calcite accumulates on an existing calcite substrate following the pre-existing crystal boundaries, while aragonite may be similarly precipitated from solutions already supersaturated with respect to aragonite. Some substances, if present on the surface of a speleothem, inhibit the precipitation of either polymorph. Tucker & Wright (1990) noted that in the marine situation, oöids are frequently inhibited in development because of a coating of organic material. Grains of quartz and clays were observed to be nucleation sites for aragonite in some Missouri (U.S.A.) speleothems (Craig et al. 1984). In an attempt to produce aragonite, they made solutions of calcium carbonate and added various concentrations of clay in suspension. The clays comprised illite, kaolinite and chlorite (no carbonates or quartz). The resulting precipitate was vaterite and calcite, not aragonite, with the ratio of vaterite to calcite increasing in proportion to the clay present. Above 80 mg/l clay concentration, only vaterite was produced.

Associations with Biological Activity

In the marine environment, aragonite often forms due to biological activity, e.g. the influence of proteins in sea shells (Tucker & Wright 1990). The variety of carbonates precipitated in response to biological processes are calcite, Mg-calcite, aragonite, vaterite, monohydrocalcite, dolomite and amorphous carbonate.

"Moonmilk" is a white pasty material found in many meteoric caves. Northup, Reyenback & Pace (1997) described evidence for microorganisms in meteoric cave moonmilk comprised of calcium carbonate as calcite or aragonite. Such microorganisms are not present in moonmilk composed of magnesium minerals.

Stable Isotope Studies

Cilek & Smejkal (1986) sectioned calcite-aragonite stalactites from the Starý hrad cave (Low Tatras) and from two Bohemian Karst caves. They analysed the stable C and O isotopes of the calcite and aragonite. The values for δ^{13}C were mostly negative for calcite and positive for aragonite. In general, the values for δ^{13}C and δ^{18}O for aragonite were greater than those for calcite. Generally, an enrichment in the heavier isotope can indicate a higher rate of evaporation. It is also temperature dependent. Cilek and Smejkal interpreted the difference as a change in the way the two minerals had been precipitated. Formation of the calcite was based on the outgassing of CO_2 (the normal karst process) with minimal evaporation whereas the aragonite mainly formed by very slow evaporation, so slow that biogenic effects are suppressed.

However, in Gillieson (1996), such biological processes apparently enrich the calcite or aragonite with heavier oxygen isotopes. This process is also temperature dependent, with higher temperatures leading to heavier oxygen isotopes in precipitates.

Where the C and O isotopes are correlated (as in these samples), both authors favoured an evaporative condition. In Clamouse Cave (France), Frisia et al. (1997) similarly found isotope ratios that suggested that the aragonite deposits were formed under more evaporative conditions. They found this interpretation difficult because all their aragonite samples were collected in areas of no wind, constant temperature and very high (∼99%) humidity. Instead, they suggested another mechanism concentrated the heavier isotopes in the aragonite samples, a chemical kinetic effect caused by the slow outgassing of CO_2.

Niggeman et al. (1997) compared the stable isotopes of calcite and aragonite coralloids. The aragonite samples tended to have higher concentrations of these heavier isotopes. They attributed this to prior concentration of the isotopes in the solutions from which the carbonates were precipitated, because all samples came from draughty areas with similar climatic conditions.

Cilek et al. (1998) also measured C and O isotopes in Ochtiná Aragonite Cave which has very little air movement and very high humidity. The isotope ratios for the aragonite were similar to those for calcite speleothems from the well-ventilated Starý hrad Cave. They concluded that the aragonite was deposited as a result of slow CO_2 outgassing.

Association with Phosphates

In describing the mineralogy of Kartchner Caverns, Arizona (U.S.A.), Hill (1999) mentioned some deposits of aragonite. Magnesium plays little part in its deposition as the limestones are particularly pure. Kartchner Caverns has large deposits of phosphatic minerals derived from bat guano, as well as a large quantity of iron oxides, silicates and unusual clays including rectorite. Sulphates were associated with the bat guano. Cave mineralisation may have had a partially hydrothermal origin. The aragonite deposits were located at the ends of passages where one would expect the humidity to be high.

Humpleu cave in Romania also has aragonite with bat guano phosphates. However Ghergari et al. (1997) considered the phosphate to be more recent than the aragonite, with phosphate on the lower parts of the passage and aragonite in the upper parts. Gypsum, aragonite and ochres were also present.

Association with Ochres and Gossans

A photograph in Speleo Projects (1998) showed a cluster of aragonite popcorn and frostwork with a red, black and orange ochreous substrate, contrasting with the corroded and porous white bedrock.

In Slovakia, extensive aragonite deposits in show caves are associated with "ochres" containing Fe, Mn and Mg (Cilek et al. 1998, Bosák et al. 2002). Aragonite occurred as three forms: the oldest material was kidney-shaped and recrystallised; the intermediate aragonite speleothems form long needles and helictites; the youngest as small fan-shapes (frostwork) and helictites. Aragonite also occurred as flowstone. Ochtiná Aragonite Cave also has deposits of goethite and limonite, with the goethite of a particularly small crystal size. The ochres have high water content, 47% to 56%, which may buffer the humidity in the cave, keeping it at a constant high level. The two main factors in the deposition of aragonite in the cave were the presence of Fe and Mn in solutions, and the high humidity. Interspersed with the ochres were black manganese oxides including asbolane and birnessite. Some of these manganese minerals were ascribed to microorganism activity. Hydromagnesite was found in small quantities associated with the ochres.

Iron was not one of the elements listed by Morse (1983) which could cause aragonite to precipitate. It is more likely that it precipitates under the influence of other materials present such as manganese, apatite or La-Nd-bearing phosphates. Commonly, cave sediments contain of layers of clastics and calcite. The clastics usually include a component of iron oxy-hydroxides. The calcite layers usually contain no iron oxy-hydroxide (although they may be stained brown by humic acids) and aragonite is rarely present in such sediments. Where aragonite occurs with iron-rich sediments, the sediments are often hard yet porous, and these physical qualities may assist ions (e.g. magnesium or sulfate) to influence the form of precipitating calcium carbonate by keeping the humidity high, acting as a sturdy substrate and allowing slow movement of ions in solution.

Flos Ferri

On page 206 of Hurlbut (1970) is a photograph of tangled aragonite helictites (*"flos ferri"* from Styria (Steiermark, Austria):

> "*When aragonite in coral-like aggregates is found on the walls of iron mines it is called "Flos Ferri," meaning* iron flower. *This specimen*

> (depicted) *is from Styria, Austria, which is famous for this variety of aragonite.*"

Most of this material has now been mined away (Stephan Kempe, pers. comm., August 1997). Rowling saw large specimens of flos ferri aragonite in the private museum at the Glacier Gardens at Lucerne (Switzerland) in 1997. Here, it is known as *Eisernblut* (iron blood) although it is white. The tangled masses of helictites have a radius of curvature of around 5 to 10 mm. Other museums also hold this material, such as the Natural History museum at Lucerne and the Australian Museum collection, cat. no. D19158.

Although Hurlbut (1970) did not specify which iron mineral was associated with flos ferri, he did say:

> *"the Austrian deposit at Erzberg in Styria is the only concentration of siderite of sufficient size and purity to be considered a major source of iron. Here a folded limestone has been replaced by massive siderite through the agency of iron-bearing waters to form a deposit of many tens of million tons."*

Eisenerz is now a show-mine and is no longer worked (Austrian tourist bureau).

According to Shaw (1992), the term *flos ferri* was first used by John Hill in 1748 for a twisted form of helictite found in mines and in some Mendip (UK) caves. Shaw included two sketches by Patrin (1803) depicting "flos-ferri" which resembled the flos ferri samples mentioned earlier. Shaw described flos ferri as a particularly slender variety of helictite which is made of aragonite and often found in iron mines. In contrast, Hill & Forti (1997) described flos ferri as a variety of anthodite which resembles a sea urchin (Hill & Forti 1997), and defined it as a quill-like variety of anthodite. These differences in terminology appear to be localised to particular countries and show caves.

This article follows the definition of flos ferri as used by Patrin, Shaw and Hurlbut. Flos ferri occurs at Jenolan Caves (Figure 4).

Figure 4. Part of The Arabesque, behind wire netting at Cerberus Cave, Jenolan Caves, featuring flos ferri. Speleothem is about 20 cm high.

Blue Speleothems

The copper ion can form a solid solution in the aragonite crystal structure (Morse 1983). Blue aragonite speleothems occur in conjunction with deposits of heavy metals (e.g. copper) e.g. the Blue Cave, France, (Hill & Forti 1997). Not all blue speleothems are aragonite, but can include minerals such as allophane and some clays, and some calcite speleothems are described as "blue". The colour is not diagnostic tool as to whether the speleothem is calcite or aragonite.

Blue "Larium stone" from a mine near Larium, Greece has been traded amongst mineral collectors. Material I have seen is aragonite with copper carbonate present as discrete centres rather than being dissolved in the aragonite. A photograph of this material held by collectors and advertised on the Internet shows a light blue stone with light and dark banding characteristic of a sedimentary deposit. Smithsonite was also mined near Larium. Zn is one of the calcite-inhibitors listed by Morse (1983).

HISTORICAL PERSPECTIVES OF ARAGONITE IN NSW CAVES

C.S. Wilkinson, NSW Government Geologist, visited the "Belubula Caves" (Walli Caves – see Figure 5) near Licking Hole Creek, which is a tributary of Liscombe Pools Creek, between Orange, Canowindra and Mandurama about 1870 shortly after their discovery by road contractors (Wilkinson 1892). This article was reproduced posthumously by the Department of Mines from an original publication in the Sydney *Town and Country Journal*, Sept. 9, 1876, p. 419. Concerning aragonite in "The Long Cave," Wilkinson said:

> *Another small cavern, rather difficult to get into, has a mound of white stalagmite with a tracery-marked surface, meeting which, and hanging in the centre are two stalactites covered with translucent spikes curving in all directions. These singular stalactites are seen in some of the other caverns; also groups of long radiating crystals of aragonite.*

There was very little further reference to NSW cave aragonite until Frank (1974) described the Deep Hole (cave) at Walli. The lack of scientific interest in the subject in NSW in the interim is perplexing, given the amount of research on cave aragonite in other countries during that period. Historical aspects of cave science in NSW from 1830 to 1987 were discussed by Osborne (1991).

Dunlop (1977) described the show caves at Jenolan. In 1903 the Skeleton Cave (now Cerberus Cave, a branch of the southern show caves) was discovered, although other reports suggest an earlier date (Middleton 1991). It has a speleothem group known as the Arabesque: a combination of (apparently aragonite) stalactites, stalagmites and helictites (Figures 4 and 6). Also in 1903 the River Cave was discovered. This is also a branch of the southern show caves and has speleothems known as "Furze Bushes" which are very similar to the Arabesque. They are now known to be aragonite (Ross Pogson pers. comm.).

Frank (1974) described the development of Walli caves based on work done in 1968 and 1969. This is the first published reference to the use of XRD to analyse aragonite from a NSW cave. Concerning aragonite in Deep Hole (Deep Cave), Frank said:

> *X-ray diffraction of some speleothems on the wall at 105036, Figure 5, showed them to be aragonite.*

Welch (1976) published a catalogue of caves at Jenolan, north of the show caves. Glass, Hennings and Wards Mistake caves were said to contain "aragonite". A photograph showed an acicular mineral in Hennings Cave. Dunkley & Anderson (1978) included a photograph of "aragonite" near Upper Oolite Cavern, Mammoth Cave, Jenolan. Near the Pisa Chamber, there were "*a number of mud tunnels . . . one containing a unique cluster of aragonite crystals*". Webb & Brush (1978) analysed aragonite from Wyanbene Cave near Braidwood, southern NSW. The samples were found loose on the ground underneath anthodites near Frustration Lake. XRD analysis identified both aragonite and calcite. SEM photographs showed the general habit of the anthodite fragments.

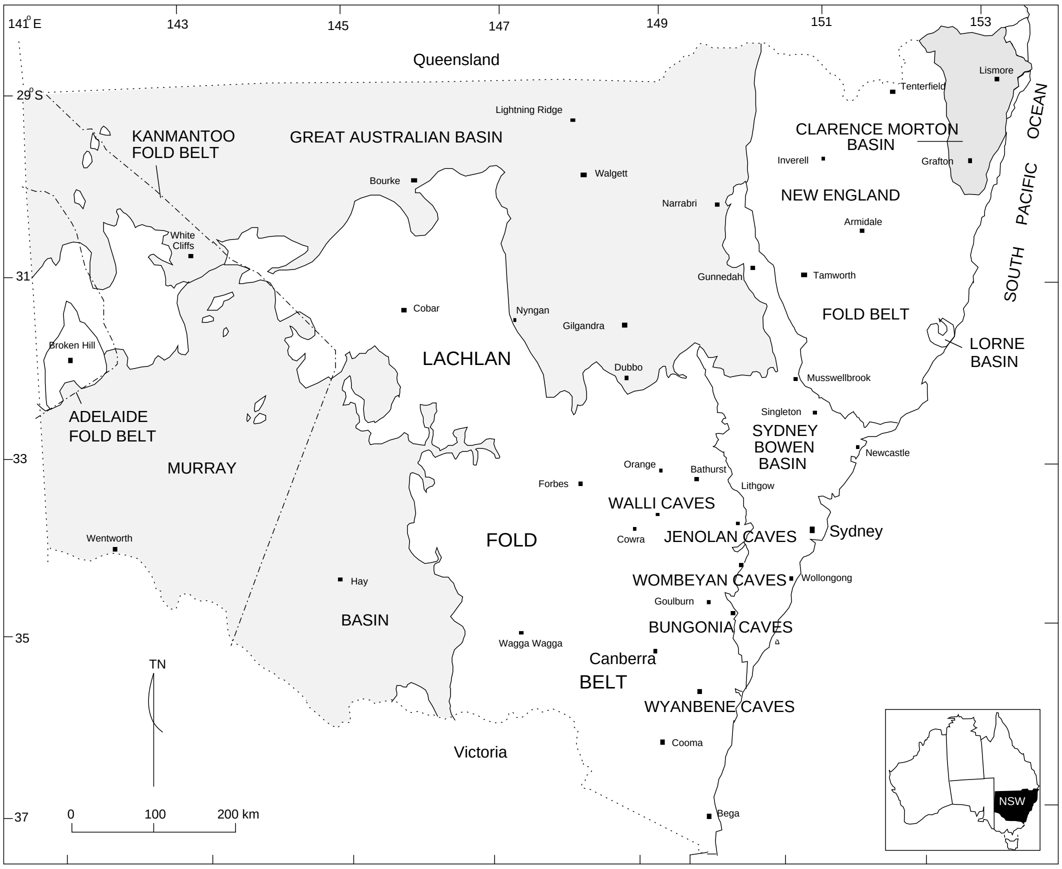

Figure 5. Map of NSW showing location of caves mentioned, with major tectonic features. Tectonic overlay re-drawn from NSW Department of Mineral Resources; Australian map from Geosciences Australia.

Osborne (1978) reported calcite which may have inverted from aragonite, from Cliefden Caves, central NSW. He also described blue aragonite speleothems in the Australian Museum minerals collection, specimens D36380 and D23544 from Boonderoo Cave. A thin section (cat. No. USGD 54322) of the base of the small blue stalactite (specimen D36380) showed an inner sparry calcite layer coated with a blue aragonite layer, determined by XRD. The aragonite layer had radially oriented acicular crystals. The same radial structure was noted on the broken tip of the stalactite in Boonderoo Cave. The blue stalactites in both Boonderoo Cave and Murder Cave were developed at two different junctions of limestone members. Using revised stratigraphic nomenclature (Webby & Packham 1982), the one in Murder Cave is developed at the junction of two sub-units (upper and lower) of the Belubula Limestone, and the one in Boonderoo Cave is at the junction of the Belubula Limestone and Vandon Limestone.

Dyson, Ellis & James (1982) included a photograph of fine spiky “aragonite” helictite clusters on the walls of Shawl Cave, Wombeyan. Ralston (1989) recalled the discovery in 1964 of the Barralong Cave, Jenolan (southern show caves), saying on page 57: “*Hidden in its own little crevice is a Christmas Tree of aragonite.*”

Osborne (1990), Osborne (1993) examined palaeokarst deposits in the show caves at Jenolan and mentioned aragonite deposits (helictites) were hosted on a substrate of laminated dolomitic internal sediments and palaeokarst deposits. Many of these sediments, found in River Cave, Mud Tunnels, Cerberus Cave, Imperial Cave, Jubilee Cave and Ribbon Cave, were unconformable with the Jenolan Caves Limestone and most had been dedolomitised.

Figure 6. The Arabesque, Cerberus Cave, Jenolan Caves. Speleothem is about 30 cm high and features flos ferri, ribbed stalactites and beaded helictites.

Osborne (1994) noted that in eastern Australia, the longest cave systems, and the ones with most extensive deposits of aragonite and gypsum occur near areas of Permo-Triassic basinal sediments, e.g. at Jenolan Caves (NSW), Exit Cave at Ida Bay and caves at Mole Creek in Tasmania. Osborne suggested that dolomite in the palaeokarst produced aragonite speleothems instead of calcite ones at Jenolan, such as the Furze Bush, possibly the Arabesque, and the helictites in Ribbon Cave. He suggested that pyrite and dolomite were emplaced in buried palaeokarst deposits at low temperatures by basinal fluids from above. In both the Western edge of the Sydney Basin, and in Tasmania, this resulted in the association of Permian caprocks with large, well-decorated caves containing gypsum and aragonite speleothems.

Rowling (1995) described geological and mineralogical features of Wyanbene Cave, referring to rock chip analyses of Richardson, Byrnes & Degeling (1981). "Aragonite" anthodites and flos ferri were associated with "an oxide or weathered ore body".

Osborne (1996) described how weathering of sulfides deposited in palaeokarst can lead to ochreous deposits associated with gypsum and red calcite speleothems, as in Wyanbene Cave, Jenolan Caves and caves in Tasmania. Aragonite occurred with gypsum in a number of places in eastern Australia and where caves are associated with ore bodies. These bodies act as aquicludes: they prevent water from penetrating the rock during initial speleogenesis. Later, as pyrite in the ore bodies is oxidised, it assists in breakdown of bedrock, exposing palaeokarst and aids speleothem development. Thus, large, well-decorated caves are often associated with ore bodies.

Bauer & Bauer (1998) reported "aragonite" at Bungonia in the Coffin Chamber of the B-4-5 Extension (cave). "Ribbon helictites" from Jubilee Cave, Jenolan Caves, were described as "aragonite", but Rowling (1998*a*) showed them to be calcite.

Vizjak (1998*b*) described the discovery in 1997 of aragonite in a part of Mammoth Cave, Jenolan called "The World of Mud". The area lies near "a shale bed":

> *There lay the "Aragonite Snowfields" - a large, magnificent patch of white powdery formation covered in aragonite crystals as large as pencils.* (Further up, they found) *... several basketball sized clusters of aragonite crystals adorning the walls.*

Breezes were noted in this area, although no cave entrances are known nearby. Vizjak (1998*a*) described more "aragonite" speleothems in the area:

> *... at the "Mini Vortex" the aragonite clusters on the roof are spectacular, with crystals as big as chopsticks and there is an amazing white*

> *cross of calcite (or something) on the ceiling. ... Beyond the “Southern Cross”, Turfa entered “Pure Dilemma”. This small chamber is ... full of white crystal growths that are all over the walls.*

Photographs of “The World of Mud” presented by Mark Bonwick (pers. comm.) showed that it contains extensive deposits of “aragonite” as anthodites and wall coatings. Some blue and green “aragonite” was present.

Rowling (1998*b*) described the discovery of Aragonite Canyon in Sigma Cave, Wombeyan with Sydney University Speleological Society. Although the surveyors did not discover this part of the cave, they were the first to document it. Members of Sydney University Speleological Society, I. Cooper, P. Maynard and others have reported (pers. comm.) on “aragonite” in Wiburds Lake Cave during a re-survey of the cave in 1999. Rowling (1999) described speleothems in the Chevalier Extension of Glass Cave, Jenolan. Some of the “aragonite” was associated with a white moonmilk-like material.

Osborne (1999) mentioned Ribbon Cave (Jenolan) aragonite speleothems associated with magnesium rich minerals: huntite, dolomite and ferroan dolomite. Dolomitic palaeokarst was the most likely source of magnesium. Sulfates were also deposited. Weathering of pyrite was the most likely source of the sulfate. The cave is wet and there is little evaporation. Aragonite was shown as spirals and spikes in the feature known as the “Lyrebirds Nest” (Figure 7). Osborne suggested that pyrite was hydrothermally emplaced in palaeokarst sediments and its oxidation has formed sulfate and aragonite speleothems. The pyrite was emplaced between mid Permian and Late Cretaceous to Early Tertiary, or related to hydrothermal activity during opening of the Tasman Sea (Late Cretaceous). Osborne (2000) noted that aragonite in eastern Australian caves was mainly associated with dolomitic and pyritic palaeokarst and also with igneous dykes and other intrusions.

A photograph of anthodites in Fife Cave, Church Creek, N.S.W. (Pryke 2000) showed a helictite cluster resembling flos ferri. On the same page is a photograph by David Connard of aragonite anthodites in Genghis Khan Cave, Mole Creek, Tasmania.

Figure 7. Aragonite helictites (small, twisting bunches) and other speleothems at the Lyre Birds Nest, Ribbon Cave, Jenolan Caves. Area depicted is about 1 m high.

Osborne, Pogson & Colchester (2002) examined the white pasty substance found with aragonite at “The Lyrebirds Nest” (Ribbon Cave, Jenolan). It was huntite. Aragonite occurs in Ribbon Cave as spherulites about 2 cm diameter, embedded in gossan. Locally, these are called “stars”, and they also occur near the pool in the Orient Cave in a dark ochreous deposit (R.A. Osborne, pers. comm.). Pogson, Osborne and Colchester used XRD to analyse the aragonite from Ribbon Cave, the Furze Bush and small deposits in River Cave (R.A. Osborne, pers. comm.).

Turner (2002) analysed samples of blue and white speleothems from Cliefden Caves. One 40 mg sample from the blue aragonite stalactite in Boonderoo Cave, collected by the Orange Speleological Society in 1995 contained copper, barium, strontium, iron, zinc, magnesium, lead, nickel and uranium. Very small samples of blue speleothems and white speleothems from Taplow Maze cave were analysed. The blue speleothems contained copper, chromium and minor nickel at higher levels than in the white speleothem. Turner suggested copper caused the blue colour, but did not determine whether the Taplow Maze blue material was aragonite or calcite.

Aragonite (XRD analysis) is the main constituent of boiler scale on heating elements in electric kettles at Jenolan Caves supplied by water from the Jenolan underground river (R.A. Osborne, pers. comm.). A small quantity of calcite was present.

ARAGONITE IN OTHER AUSTRALIAN CAVES

The caves of Tasmania are well-known for their displays of aragonite, yet there was little scientific work done on their mineralogy in the 19th century. Most people visiting the caves did so out of curiosity and not research. Generally cavers and tourists are not mineralogists and do not have the resources to analyse minerals.

One problem with reporting minerals from caves is an ethical one. Over-collecting is a world-wide problem coupled with the lack of protection for the caves' contents in many places. This has meant that discoverers of unusual cave minerals have often had to keep their discoveries secret.

Pisoliths from a mine at Bendigo, Victoria were found to contain aragonite and possibly $MgCO_3$ associated with siderite (Baker & Frostick 1947).

In South Australia, aragonite occurs in caves associated with dolostone (Grant Gartrell, pers. comm.). Quarrying at Sellicks Hill Quarry uncovered a cave in September 1991. Photographs of the mined cave showed anthodites, popcorn, coralloids, and coatings of (apparently) dolomite and hydromagnesite. The cave has been closed by the quarry since 9th November 1991 and was the subject of a Parliamentary enquiry (Environment, Resources and Development Committee, Parliament of South Australia 1995).

Rowling (1993) sketched and described "aragonite" anthodites and helictites observed in Genghis Khan and Kubla Khan caves at Mole Creek, Tasmania.

Rowling (2003) examined subaqueous helictites found by cave divers from lakes in Mullamullang cave, Nullarbor Plain, Western Australia. Minerals in one helictite, determined by XRD, were calcite, magnesian calcite, aragonite, hydromagnesite, gypsum, celestite and halite. A subaqueous helictite from another lake in the cave contained calcite, magnesian calcite, aragonite, hydromagnesite, gypsum, huntite, cristobalite and halite.

RECENT STUDIES ON CAVE ARAGONITE IN NSW

Rowling (2004) examined aragonite in NSW caves, including Jenolan, Wombeyan and Walli. Aragonite in some NSW caves appeared to be associated with high evaporation rates allowing calcite, aragonite and vaterite to deposit, e.g. in cave sediments in areas with low humidity in Wollondilly Cave, Wombeyan. Several factors influence the deposition of aragonite instead of calcite speleothems in NSW caves, such as presence of ferroan dolomite, calcite-inhibitors (in particular ions of magnesium, manganese, phosphate, sulfate and heavy metals), and both air movement and humidity.

Several reported aragonite deposits were examined to confirm whether the material is aragonite. Substrates to the deposits were examined, as was the nature of the bedrock. The work concentrated on Contact Cave and Wiburds Lake Cave at Jenolan; Sigma Cave, Wollondilly Cave and Cow Pit at Wombeyan and Piano Cave and Deep Hole (Cave) at Walli. The study sites were all within Palaeozoic rocks in the Lachlan Fold Belt. Two sites, Jenolan and Wombeyan, are close to the western edge of the Sydney Basin. The third site, Walli, is close to a warm spring. The physical, climatic, chemical and mineralogical influences on calcium carbonate deposition in the caves were investigated.

Contact Cave lies near the eastern boundary of the Late Silurian Jenolan Caves Limestone, in steeply bedded and partially dolomitised limestone close to its eastern boundary with the Jenolan volcanics. Aragonite in Contact Cave is precipitated on the ceiling as anthodites, helictites and coatings. The substrate for the aragonite is porous, altered, dolomitised limestone which is wedged apart by aragonite crystals. Aragonite deposition was associated with a concentration of calcite-inhibiting ions, mainly magnesium, manganese and to a lesser extent, phosphates. Aragonite, dolomite and rhodochrosite are being actively deposited where these minerals are present. Calcite forms where minerals lack magnesium ions. The inhibitors appeared to be mobilised by fresh water entering the cave as seepage along the steep bedding and jointing. During winter, cold dry air pooling in the lower part of the cave may concentrate minerals by evaporation and is most likely associated with the "popcorn line" seen in the cave.

Wiburds Lake Cave lies near the western boundary of the Jenolan Caves Limestone, close to its faulted western boundary with Ordovician cherts. Aragonite here is associated with weathered pyritic dolomitised limestone, an altered, dolomitised mafic dyke in a fault shear zone, and also with bat guano minerals. Aragonite speleothems include a spathite, cavity fills, vughs, surface coatings and anthodites. Calcite occurs in small quantities at the aragonite sites. Calcite-inhibitors associated with aragonite include ions of magnesium, manganese and sulfate. Phosphate is significant in some areas. Low humidity is significant in two areas.

Other sites briefly examined at Jenolan included Glass Cave, Mammoth Cave, Spider Cave and the show caves. Aragonite in Glass Cave may be associated with weathering of dolomitised limestone (resulting in anthodites) and with bat guano (resulting in small cryptic forms). Aragonite in the show caves, and possibly in Mammoth and Spider Cave is associated with weathering of pyritic dolomitised limestone.

Wombeyan Caves are developed in saccharoidal marble, in metamorphosed Silurian Wombeyan Caves Limestone. Three sites were examined at Wombeyan Caves: Sigma Cave, Wollondilly Cave and Cow Pit (a steep sided doline with a dark zone). Sigma Cave is close to the south east boundary of the Wombeyan marble, close to its unconformable boundary with effusive hypersthene porphyry and intrusive gabbro, and contains some unmarmorised limestone. Aragonite occurs mainly in a canyon at the southern end of the cave and in some other sites. In Sigma Cave, aragonite deposition involves minerals containing calcite-inhibitors, as well as some air movement in the cave. Calcite-inhibitors at Sigma Cave include ions of magnesium, manganese, sulfate and phosphate (possibly bat origin), partly from bedrock veins and partly from breakdown of minerals in sediments sourced from mafic igneous rocks. Substrates to aragonite speleothems include corroded speleothem, bedrock, ochres, mud and clastics. There is air movement at times in the canyon, it has higher levels of CO_2 than other parts of the cave and humidity is high. Air movement may assist in the rapid exchange of CO_2 at speleothem surfaces.

Wollondilly Cave, in the eastern part of the Wombeyan marble, has anthodites and helictites in an inaccessible area of the cave. Paramorphs of calcite after aragonite occurred at Jacobs Ladder and the Pantheon. Aragonite at Star Chamber is associated with huntite and hydromagnesite. In The Loft, speleothem corrosion is characteristic of bat guano deposits. Aragonite, vaterite and calcite were detected in surface coatings in this area. Air movement between the two entrances of this cave has a drying effect which may serve to concentrate minerals by evaporation in some areas. The presence of vaterite and aragonite in fluffy coatings suggests vaterite inverting to aragonite. Calcite-inhibitors in the sediments included ions of phosphate, sulphate, magnesium and manganese. Cave sediment includes material sourced from detrital mafic rocks.

Cow Pit is located near Wollondilly Cave, and cave W43 is located near the northern boundary of the Wombeyan marble. At Cow Pit, paramorphs of calcite after aragonite occur in the walls as spheroids with minor huntite. Aragonite is a minor mineral in white wall coatings and in red phosphatic sediments with minor hydromagnesite and huntite. At cave W43, aragonite and paramorphs were detected in a coralloid speleothem. Dolomite in the bedrock may be a source of magnesium-rich minerals here.

Walli Caves are developed in the massive Belubula Limestone of the Ordovician Cliefden Caves Limestone Subgroup (Barrajin Group). Here, the limestone is steeply bedded, contains chert nodules with dolomite inclusions, and has gypsum and barite in veins. In Piano Cave and Deep Hole (Deep Cave), gypsum occurs both as a surface coating and as fine selenite needles on chert nodules in areas with low humidity. Aragonite at Walli caves was associated with vein minerals and coatings containing calcite-inhibitors and, in some areas, low humidity. Calcite-inhibitors include sulfate (mostly as gypsum), magnesium, manganese and barium.

Other caves which contain aragonite were not major study sites, but sufficient information was available for a preliminary assessment as to why they may contain aragonite. These caves include Flying Fortress Cave and the B4-5 Extension at Bungonia near Goulburn, and Wyanbene Cave south of Braidwood. Aragonite deposition at Bungonia has some similarities with that at Jenolan in that dolomitisation of the bedrock has occurred, and the bedding or jointing is steep allowing seepage of water into the cave, with possible oxidation of pyrite. Aragonite is also associated with a mafic dyke. Wyanbene Cave features some bedrock dolomitisation, and low grade ore bodies which include several known calcite-inhibitors and aragonite occurs with both features. Brief notes were made of aragonite-like speleothems at Colong Caves (between Jenolan and Wombeyan), a cave at Jaunter (west of Jenolan) and at Wellington (240 km NW of Sydney).

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APPENDIX: GLOSSARY OF TERMS

Some terms used in speleology may be unfamiliar to the general scientist. Most speleothem terms used here are those defined by Hill & Forti (1997) and are recognised internationally. Other terms are used in Australian caving.

anthodite: Speleothem, usually made of aragonite, with an acicular and often branching appearance. Usually, anthodites develop from the cave's ceiling. Anthodites often have a solid core of aragonite, and may have huntite or hydromagnesite deposited near the ends of their branches. Anthodites vary in size from a few millimetres to about a metre.

cave: A natural cavity in rock that a person can enter. Some show caves are subdivided into convenient sections, each called a "cave", although this terminology is not encouraged. Thus, all the Jenolan show caves could be called one "cave" as they are all interconnected via underground passages, including the Grand Arch.

chamber: A cavity that a person can stand in, varies from about 4 m diameter to about 20 m diameter.

coral, cave: Speleothem characterised by hemispherical to globular appearance. Cave coral is often calcite, deposited on surfaces where there is some air movement. Deposition is mostly by capillary movement across the surface, with the main deposit occurring at the outside edge of the speleothem. Sizes usually vary from a few millimetres to a couple of centimetres diameter.

coralloid: Speleothem resembling coral but not sufficiently analysed to determine its make-up. Examples occur near the entrance areas of caves where there is a mixture of deposits and deposition mechanisms at work, resulting in speleothems with a mixture of characteristics and mineral content. The term is also used for the transition forms taken by some aragonite speleothems which alternate between anthodite-like and coral-like depending on the growth conditions.

flowstone: A deposit of (usually) calcite as a surface coating on any substrate in a cave so that the mass resembles melted wax. The overall shape is controlled by gravity and the surface tension of water. Surface textures range from completely smooth to deeply pocketed depending on carbonate concentration, flow rate and other factors. Flowstone is usually built up from thin layers of calcite, caused by seepage or dripping water containing HCO_3 outgassing CO_2 into the cave to precipitate $CaCO_3$. Depending on the source of water, flowstone can grade into stalagmites and where flowstone builds up over steep drops, furled shapes can resemble draperies.

flos ferri: Helictite characterised by slender tightly twisted forms, usually aragonite. Three different usages of this term include its first usage in 1748 by John Hill for a twisting variety of speleothem from mines and some Mendip (UK) caves (Shaw 1992). Hurlbut (1970) used a similar definition for aragonite in iron ore mines in Austria. Hill & Forti (1997) define flos ferri as a quill-like variety of anthodite, and define the earlier usage as "an ancient word for aragonite and for frostwork and helictites growing in the cavities of iron deposits". Herein, flos ferri means the tightly twisted form of aragonite helictite associated with iron ores.

furze bush Combination helictite, stalagmite and anthodite characterised by a vertical carbonate deposit (stalagmite/tite or column), usually of aragonite, together with finely twisting (usually aragonite) helictites. The helictites' diameter is typically about 1 to 5 mm and their radius of curvature ranges from about 10 mm to 100 mm. The name was given by Jenolan Caves guides for the fancied resemblance to a fir tree, and a name was needed in the show caves.

helictite: Speleothem with a fine capillary tube surrounded by usually either calcite or aragonite. Helictites are often wormlike, with typical diameter of a few millimetres and typical length of a few centimetres. Development is usually outwards from a wall. Beaded helictites have alternating deposits of calcite and aragonite giving the speleothem a pipe-cleaner appearance. Ribbon helictites are flattened calcite helictites.

heligmite: Helictite that develops from the floor of a cave, like small stalagmites, but they retain a fine capillary tube and develop by mineral-rich water flowing gradually through the capillary and onto the surface of the heligmite where it can outgas CO_2.

moonmilk: Speleothem with a pasty appearance, with a texture like cottage cheese when rubbed in the fingers. This material has a high water content. Most moonmilk is made of needle-fibre calcite, some contain hydromagnesite and other minerals. Moonmilk may be biogenic. True moonmilk has to be at least 90% calcite (Fischer 1988).

oolite: A loose spherical concretion, often pea-sized but can be larger. Usually found in pools or underground creeks where calcite or aragonite is precipitating. Oolites are rarely cube shaped. Outside of speleology, the conventional term for similar concretions is "pisolites". Oöids are smaller concretions (of any material) with a diameter of 0.2 to 0.5 mm.

passage: Part of a cave which is much longer than it is wide, like a corridor and generally of walk-through dimensions. In Australian speleology, a passage with reduced width is a "rift", and one with reduced height is a "crawlway" or a "flattener" depending on the way a person moved through it.

popcorn: A speleothem which vaguely resembles the snack, popcorn. Similar to "coralloid". A "popcorn line" is a horizontal deposit of popcorn in a cave passage which marks a humidity change or layer. Hydromagnesite and huntite may occur with aragonite.

spathite: A stalactite of aragonite with a wider central tube than the conventional calcite stalactite. This is caused by the flaring of the aragonite crystal compared to calcite. Sometimes a spathite comprises a series of aragonite "petals" overlapping each other to form a wide (2 or 3 cm) tube.

speleothem: Secondary mineral deposit in a cave. May be subaerial or subaqueous. They are classified according to mineral and shape, for example, a calcite stalactite. Commonly calcite, but can be other carbonates, sulfates, phosphates, oxy-hydroxides, etc. Most carbonate speleothems are formed by bicarbonate-rich water outgassing CO_2.

stalactite: Speleothem, usually of calcite, deposited on the ceiling of a cave. Characterised by general conical shape and usually a central hollow tube of calcite with the C-axis pointing downwards. This is surrounded by layers of calcite with the C-axis pointing at 90° to the surface.

stalactite, straw: Also known as "soda straws", these are central hollow tubes of stalactites without surrounding deposits. They usually occur where bicarbonate-rich water comes from a single point or crack, rather than running across the ceiling. Diameters are typically 4 or 5 mm and lengths vary from a few cm to metres.

stalagmite: Deposit on the floor of a cave under a drip point, resulting in a pile of carbonate (usually calcite) that is often higher than it is wide. Often roughly cylindrical symmetry, they vary from a flat disc about 4 cm diameter to massive deposits that are tens of metres high. The calcite C-axis is always directed at 90° to the stalagmite surface.

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Thesis Abstract: Immunological Markers for Monitoring the Health of the Tiger Prawn Peneaus monodon

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Abstract of a thesis submitted for the Degree of Master of Science,
James Cook University, Townsville, Queensland, 2003

Prawn aquaculture is a widespread and economically important industry. However, in recent years the industry has been seriously affected by disease. Combating these disease problems through understanding the immune system and monitoring the health of cultured prawns is essential to the sustainability of the industry. This study aimed to investigate immunological markers in the cultured tiger prawn, *Penaues monodon.* The health condition of prawns is believed to be reflected by the blood cell (haemocyte) population. As such, the primary goal of this study was to produce monoclonal antibodies to haemocytes of *P. monodon* to provide a tool for studying and marking the penaeid immune system. Haemocytes were collected into anti-coagulant from healthy adult *P. monodon* via periopod bleeds and prepared as an immunogen of haemocyte lysate. Monoclonal antibodies were produced in balb/c white mice. A panel of six anti-prawn haemocyte monoclonal antibodies was produced, in which three antibody types were identified. Antibody typing was based on immunocytochemistry and immunoblotting. Type one monoclonal antibodies were found to bind to approximately 90% of the cell population, and bound to haemocyte and haemolymph proteins. Type two antibodies were found to be specific to approximately 20% of the population and cells demonstrating characteristics of the large and small granular haemocytes. The third antibody type was found to bind to approximately 80% of the cell population, but the binding pattern of this antibody was unique, staining the nuclear membrane of each cell type. Further immunochemical characterisation of the antibodies was conducted. The cross-reactivity of the antibodies to haemocytes and prawn tissue *in situ* was investigated. This study aimed to determine immunological links between cell and tissue types. Haemocytes were found to be selectively stained within connective tissue, muscle and gill, and no cross reactivity with these non-haemocyte tissues was found with any of the six monoclonal antibodies. However, some apparently non-freely circulating haemocytes were immunostained with five of the six monoclonal antibodies. Fixed cells, of what appeared to be of a phagocytic nature, were immunostained. Fixed cells were evident in many tissue areas, including the ovary, gill and connective tissue. However, the highest density of immunoreactive fixed cells was found in the heart. These immunostained cells also appeared phagocytic, being large, highly vaculolated cells. An enzyme-linked immunosorbent assay (ELISA) was developed with each of the three antibody types to determine if differences between healthy and diseased cultured *P. monodon* could be detected. Two experiments using ELISA were conducted. First, healthy *P. monodon* were inoculated with virus, and ELISA conducted on haemolymph samples of animals three weeks post-inoculation. Significant differences between inoculated and healthy control stock were found with two of the three antibody types. A second experiment, comparing a healthy control stock and a diseased stock from a north Queensland prawn farm was also conducted. Each of the three antibody types was used in ELISA to determine if differences between the diseased stock sampled on two consecutive weeks and the healthy stock could be detected. The diseased farm stock was found to yield significantly different results to the healthy control at the second week of sampling with each of the three antibody types. In conclusion, this study has indicated the potential of anti-prawn haemocyte monoclonal antibodies to provide a means of marking and tracking im-

munological changes, a method for studying cellular process, haemocytic and cellular disease processes, and finally to further the understanding of the crustacean immune system. This study also proposes haemocyte-specific monoclonal antibodies in ELISA as a novel technique for monitoring haemocyte changes in cultured penaeids. The results from this study demonstrated the potential of the technique, the further development of which has the potential to provide the industry with a mechanism for monitoring cultured penaeids and other crustaceans.

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Thesis Abstract: ISCOMs and Related Colloidal Particles Prepared by the Lipid Film Hydration Method for Antigen Delivery

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Abstract of a thesis submitted for the Degree of Doctor of Philosophy,
University of Otago, New Zealand, 2004

Purposes: The aims of this thesis were to physicochemically investigate the formation of ISCOM matrices and other types of colloidal particles formed in aqueous dispersion as a function of different mass ratios of Quil A, cholesterol and phospholipid (phosphatidylcholine (PC) or phosphatidylethanolamine (PE)) prepared by the hydration method and to investigate the delivery of subunit vaccines to antigen presenting cells using these colloids.

Methods: The hydration method, recently developed for the preparation of ISCOMs or ISCOM matrices, was used to produce these colloids and other related structures. Factors such as effects of buffer salts, equilibration time and type of phospholipid on the formation of ISCOM matrices and other colloidal particles prepared were investigated. The standard dialysis method for the preparation of ISCOMs was also used for comparison to prepare various colloidal particles. Colloidal particles were characterized by negative staining transmission electron microscopy (TEM). Polarized light microscopy (PLM) was used to identify samples containing cholesterol crystals. Incorporation of a model antigen (modified ovalbumin) into various colloidal particles was investigated by fluorescence spectroscopy following analytical sucrose density gradient ultracentrifugation. Physical properties of solid Quil A-cholesterol-phospholipid formulations (as powder mixtures or compressed to pellets) with or without model antigen were characterized by X-ray powder diffractometry (XRPD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and PLM. Release of model antigen from compressed pellets was investigated *in vitro*. Flow cytometric analysis (FACS) was used to investigate the *in vitro* delivery of antigen incorporated into various colloidal structures to murine bone-marrow derived dendritic cells (BMDC).

Results: Pseudo-ternary diagrams revealed that depending on the mass ratio of Quil A, cholesterol and phospholipid, various colloidal particles including ISCOM matrices, liposomes, lipidic/layered structures, ring-like micelles, and worm-like micelles could be identified in the different regions of the diagrams. In the presence of these predominant colloids, helices and lamellae (hexagonal patterns of ring-like micelles) structures were also formed as minor structures. Buffer salts and equilibration time were important factors for the formation of ISCOM matrices and liposomes. The type of phospholipid affected the morphology of ISCOM matrices and lamellae. ISCOM matrices were predominantly found near the phospholipid apex of the pseudo-ternary diagram following sample preparation by the hydration method. On the other hand, samples prepared by the dialysis method produced ISCOM matrices that were predominantly found near the Quil A apex of the pseudo-ternary diagram. No ISCOM matrices could be formed in any binary mixtures prepared by the hydration method in contrast to the dialysis method. Worm-like micelles could only be formed if samples were prepared by the hydration method. An incorporation study demonstrated that the various colloidal particles formed as a result of hydrating phospholipid/cholesterol lipid films with different amounts of Quil A are capable of incorporating antigen, provided it is amphipathic. Freeze-dried lipid powder mixtures were found to contain a lower degree of crystalline cholesterol compared to physically mixed powders. Consequently, physically mixed powders (with or without model antigen) and pellets prepared from the same powders did not spontaneously form ISCOM matrices and related colloidal structures upon hydration as expected from the pseudo-ternary diagram. Release of antigen incorporated into ISCOM particles was relatively slower from the pellets made using freeze-dried powders in contrast to pellets prepared from the physically mixed powders. Using ISCOMs, liposomes and ring-like micelles, it was demonstrated that the model antigen incorporated into these particles could be delivered to dendritic cells leading to activation and proliferation of transgenic T cells.

Conclusions: Depending on the mass ratio of Quil A, cholesterol and phospholipid, ISCOM matrices and other types of colloidal structures such as liposomes, lipidic/layered structures, ring-like micelles, lamellae (hexagonal array of ring-like micelles) and worm-like micelles prepared by the hydration method could be identified in the different regions of pseudo-ternary diagram. All the colloids containing Quil A were capable of incorporating an antigen, provided it is amphipathic. Delivery of antigen to DC and immunestimulatory effects of various colloidal particles could be demonstrated.

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Thesis Abstract: The Wellington Region Community Prostate Study

MARION GRAY

Abstract of a thesis submitted for the Degree of Doctor of Philosophy,
University of Otago, New Zealand, 2004

There is a paucity of New Zealand research into prostate disease, yet both benign prostatic hyperplasia and prostate cancer are substantial and increasing public health problems. The maj or aim of the Wellington Region Community Prostate Study (WRCPS) was to define prostate disease in New Zealand and highlight differences between New Zealand's three major ethnic groups; New Zealand European, Maori and Pacific Islands people.

Between January 2000 and February 2002 inclusive, 1 425 eligible subjects were recruited into the WRCPS. Blood samples were taken and questionnaires administered. The WRCPS used immediately available markers of prostate disease; lower urinary tract symptoms and serum Prostate Specific Antigen (PSA) levels, to answer clinical and epidemiological questions in a community-based sample of New Zealand males.

Findings indicated that prostatic diseases are more prevalent than is shown by health statistics, especially for Maori and Pacific Islands men.

The WRCPS addressed clinical prostate disease issues, with respect to enhancing the use of PSA as a diagnostic tool. Findings showed that the ratio of free PSA to total PSA (%fPSA; used to increase the sensitivity and specificity of total PSA as diagnostic test for prostate cancer) was significantly higher in Pacific Islands than New Zealand European men, both groups without symptomatic prostate disease ($p < 0.001$). Therefore, indicative PSA reference ranges were produced for the three New Zealand ethnic groups.

In addition, demographic and clinical factors (such as use of non-steroidal anti-inflammatory drugs) appear to have a significant effect on levels of PSA and its various molecular derivatives. Finally, PSA levels measured in the laboratory using the Abbott instrument were found to be significantly lower than those measured on the Roche instrument, by an average of 11%.

Enhancing clinical diagnoses is a particularly important step towards the reduction of the internationally high prostate cancer mortality rates faced by New Zealand men. In simple terms, the more accurate the diagnostic tools the more chance clinicians have of curing prostate cancers.

The other major findings elucidated New Zealand-specific and ethnic-specific prostate disease risk factors. In summary, exposure to prostate cancer risk factors was found to differ between ethnic groups, and it would appear from the perspective of ageing, endocrine and environmental factors (such as sexual activity, relationship status, diet, occupation and literacy), that Maori and Pacific Islands men are at increased risk of developing prostate cancer, as well as more rapid disease progression and mortality.

In conclusion; firstly, men's health should be a priority issue for research and health promotion; especially regarding prostatic diseases. Secondly, issues of health inequality faced by Maori and Pacific Islands groups generally, exacerbated by under-reporting in ethnic health statistics, also apply to prostate health. Thus, findings emphasise the importance of actively addressing the prostate health care needs of Maori and Pacific Islands groups, through the formulation of culturally appropriate health policy.

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Thesis Abstract: The Philosophy of Praxis

A Study of Radical Planning – Past and Future Directions

KERRY JAMES GRUNDY

Abstract of a thesis submitted for the Degree of Doctor of Philosophy,
University of Otago, New Zealand, 2004

This thesis is concerned with the theory and practice of planning in Western capitalist societies. Specifically, it examines the tradition of radical planning within the context of conventional planning theory. Its objectives are to evaluate the historical influence of radical planning thought on conventional planning theory and practice, and secondly to assess the relevance of radical planning to contemporary (and future) capitalist societies.

This is accomplished firstly through an analysis of the history of radical planning thought, particularly the theories of a small number of influential planning theorists from the turn of the nineteenth century up until the present. The contemporary relevance of radical planning is examined by critically evaluating Friedmann's theory of transformative planning and by offering an alternative theory based upon a Marxist critique of capitalism and Gramscian transition theory. The normative theory is presented as practice in the form of a critique of the resource management legislation in New Zealand undertaken by the author in the course of his Ph.D. studies. In this way theory is linked to practice and the dialectic between theory and practice made explicit.

The thesis evaluates three propositions:

1. That radical planning thought, although often obscured, possesses a rich history and has had a profound and lasting influence on modem planning theory and practice.
2. That radical planning theory has a positive role to play in contemporary (and future) planning aimed at the transformation of the capitalist mode of production.
3. That this theory can be applied to a practice of radical planning that can contribute to a progressive challenge to the dominant capitalist hegemony.

It is concluded that all three propositions can be answered in the affirmative. Radical planning thought does possess a fertile history and has had a significant influence on modem planning theory and practice since its inception at the close of the nineteenth century. Although its existence has gone largely unacknowledged by orthodox planning its presence indicates that historically there has always been resistance to the exploitation of capitalist class society and a search for a better, more sustainable mode of production.

Secondly, radical planning theory can have a positive role in contemporary and future planning. There is a legitimate rationale, founded upon a Marxist critique of capitalism, for adopting a radical approach to planning (a theory *for* planning). In addition, Gramscian transition theory provides a strong conceptual basis for a theory *of* radical planning, a methodology of radical planning practice. Lastly, this theory can be applied to a practice of radical planning that may contribute to a progressive challenge to capitalist hegemony. Whether this challenge escalates into fundamental socio-economic change remains to be seen. Radical planners can, however, continue the tradition of earlier proponents of radical change and search for alternatives to the exploitation of human and non-human nature inherent to the capitalist mode of production.

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Thesis Abstract: In Vivo Studies of the Mechanisms of Angiogenesis

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Abstract of a thesis submitted for the Degree of Doctor of Philosophy,
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Angiogenesis is seen in many pathological circumstances (e.g. diabetic retinopathy, cardiovascular diseases, rheumatoid arthritis, psoriasis, etc.). Understanding how blood vessels form has become a dominant principal, yet challenging, objective of medical research over the last decade. Development of therapies aimed at inhibiting the growth of new blood vessels is among the most intensively studied approaches in the treatment of cancer. Recently a number of inhibitors of angiogenesis have been discovered and some of them are in clinical trials for treatment of cancer.

Cartilage has been proposed as a possible source of anti-angiogenic material. A number of studies has shown that shark cartilage (SC) exhibits anti-angiogenic activity. This study has shown for the first time that oral consumption of SC inhibits angiogenesis in both the rat mesenteric window model and the rat foetal kidney transplantation model. It indicates that the active principle(s) of SC could survive the digestive system in order to be transported to the asite. SC from different processors is examined. Different fractions of SC are also examined. The active components of SC have not been identified. Several lines of evidence have suggested that they are more likely lipids. The mechanisms involved in these anti-angiogenic properties of cartilage extracts are not understood in detail. Several mechanisms of inhibiting angiogenesis by SC have been suggested by this project. VEGF is the essential growth factor for angiogenesis and is sufficient for the formation of new blood vessels if over-expressed *in vivo*. It is the only mitogen known to act specifically on endothelial cells. This study demonstrated for the first time that oral consumption of SC decreased the transcript level of VEGF in both rat grafted kidneys and adult rat tissues. It has been reported that elevated glutathione (GSH) levels are involved in angiogenesis. This study showed that SC decreased both GSH production and γ-glutamyl cysteine synthetase (γ-GCS), the rate-limiting enzyme in the GSH pathway. Mast cells (MC) have been noted to be involved in pathological or physiological examples of angiogenesis. It was demonstrated that SC inhibited MCs degranulation in the rat mesenteric window model and histamine release in an *in vitro* model. MCs have been reported to express and produce VEGF, which is found within secretory granules, and many other angiogenic agents like heparin, FGF2, IL-8 and proteases. SC could therefore inhibit the production of these angiogenic agents from MCs by inhibition of MC degranulation.

In conclusion, SC is reported to inhibit angiogenesis in both *in vitro* and *in vivo* models. The active component in SC is more likely a lipid, which is able to pass through and be absorbed by the gastro-intestinal tract. Several mechanisms of inhibiting angiogenesis by SC have been suggested in this project, which support the hypothesis that SC acts as a scavenger for reactive oxygen species.

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Thesis Abstract: Oral Health Disparities among Pacific and New Zealand Children

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Abstract of a thesis submitted for the Degree of Doctor of Philosophy,
University of Otago, New Zealand, 2004

The investigations described in this thesis involve studies of children anecdotally described as being dentally disadvantaged, whether by virtue of their ethnic status or their location. The findings do not always support that anecdotal evidence, and, as such, are valuable contributions to the limited dental health information available for these groups.

The dental experience of children living in the Pacific is recognised as having deteriorated in the last two decades. All prior oral health investigations in this area have been cross-sectional in design, lacking the suitable time-ordering which would enable caries risk factors to be identified. In this study of Fijian children, a longitudinal approach was used, and it was found that frequency of snack consumption and not having visited a dentist were predictors of future caries experience. Snack consumption and dental check-ups are fundamentally the responsibility of care-givers, indicating the important role these people have in influencing child dental health in Fiji. It may be beneficial for Fijian health policy makers to consider this when organising oral health promotion and education initiatives.

There has been much change in the ethnic make-up of the New Zealand population in recent times. The proportion of Pacific people in the population is now considerable, and continues to increase. Pacific people in New Zealand are recognised as having poor general health (and dental health) and difficulties in accessing health care services. In analyses of dental data from the National Child Nutrition Survey, Pacific children were found to be more likely than their non-Pacific counterparts to have not visited a dentist, to have not received a filling, or to have had had a tooth extracted because of decay. The dental health needs of this group will probably increase in future, making them a considerable burden on an already stretched dental health service. It seems that providing incentives to encourage School Dental Service enrolment of Pacific children, increasing the number of Pacific personnel in dental training, and creating a more culturally sensitive dental profession may improve the accessibility of dental services to this group, which, in turn, may encourage improved oral health.

Validity is an important aspect of items used in self-report health studies, and it refers to the extent to which items measure what they purport to measure. The National Child Nutrition Survey was a study of 5-14-year-old children's nutrition in New Zealand, and included a number of self-report dental items. In order to give the dental findings greater meaning, a validation study was conducted to determine whether child self-report measures were a valid indicator of clinical oral health. The dental items appeared to be clinically valid, and showed a high level of concordance between child and care-giver. The findings suggest that using self-report measures may be valuable in future dental epidemiological investigations of children where resource constraints preclude clinical examinations or caregiver involvement.

There is a paucity of oral health information on children living in remote communities in New Zealand. Evidence from other countries, however, suggests that living remotely is associated with lower access to dental services, and poor oral health. Children residing in the Chatham Islands (the most remote area of New Zealand) were found to have comparable oral health status to their counterparts in an urban New Zealand setting. This was most likely due to Chatham Islands children taking part in regular School Dental Service visits, and hav-

ing similar access to cariogenic food and beverage products as urban children. This trend may change, however, as the dental therapist is no longer a resident of the Chatham Islands, and is therefore unable to treat children’s dental needs as they arise on a day-to-day basis.

The findings presented in the thesis may be useful for dental policy-makers in the Pacific and New Zealand, who both face increasing constraints for health resources. It is hoped the findings also enable more effective distribution of oral health resources, and encourage initiatives that promote appropriate training of dental health personnel.

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Thesis Abstract: The Human Ligamentum Ncuhae and Related Ligaments

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Abstract of a thesis submitted for the Degree of Doctor of Philosophy,
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The aim of this study was to clarify the anatomy of the human ligamentum nuchae and to determine if nerve endings terminated within its connective tissue structure. Gross anatomical investigation and the microscopic study of plastinated epoxy-resin slices were carried out in preference to a histological study. The combined results indicate that, as with the supraspinous and interspinous ligaments of the thoracolumbar spine, the muscle aponeuroses make the major contribution to the dense connective tissue structure of the human ligamentum nuchae. The study of serial epoxy-resin slices reveals regional differences within the connective tissue fiber orientation which are directly attributable to the arrangement of muscle attachments along its length. In terms of its nerve supply a qualitative investigation has shown that small nerve endings may be found in close proximity to blood vessels in the connective tissue of the human ligamentum nuchae at least as early as nineteen weeks of fetal development. Quantitatively, the preliminary evidence from a small area of ligamentum nuchae sampled in a human fetus indicates that the nerve endings may not be uniformly distributed throughout the ligamentum nuchae during development. Using the brush-tailed possum (*Trichosurus vulpecula*) as an experimental model for the human cervical spine, an acetylcholinesterase nerve staining method was adapted and trialed for thick epoxy-resin slices. This latter approach proved to be less effective than immunocytochemistry in identifying nerves within the connective tissue of the ligamentum nuchae. Functionally, the regional differences in the connective tissue organization of the ligamentum nuchae along the length of the cervical spine and the well-defined attachments onto the C6 and C7 spinous processes suggest that the LN is designed to support the posterior elements within the lower cervical spine. In this light, it is argued that the role of the ligamentum nuchae may best be considered within the context of the human head and neck musculature rather than a diminished form of the animal ligamentous structure. However, whether or not the subtle differences in the distribution of nerve fibers within the fetal ligamentum nuchae is reflective of regional differences within the connective tissue of the adult structure is yet to be determined.

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Thesis Abstract: The Microstructures and Stability of Emulsions

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Emulsions are utilised in a wide range of biological and commercial environments. In their simplest form they are a dispersion of one liquid in another in the presence of emulsifiers. One of the simplest types of emulsifier is a surfactant. Surfactants are molecules which consist of two very different regions. One part is polar (head group) and the other is non-polar (tail group). The polar part associates with the more polar phase of the emulsion (water), while the non-polar part interacts with the less polar phase (oil). An input of energy is necessary to form the kinetically stablised emulsions. In this thesis, triton X-100 was used as the surfactant and three systems were studied: toluene/tritonX-100/water, octane/triton X-100 and tetradecane/triton X-100/water. Six techniques were used to probe the microstructures of the stabilised emulsions: PGSE-NMR, rheology, freeze-fracture transmission electron microscopy, creaming rate, conductivity and laser diffraction particle sizing.

Stable emulsions in the ternary toluene/triton X-100/water system can be prepared for a surfactant to oil weight ratio of 1:5. Emulsions are formed on continuum between 0.5 and 14 wt% triton X-100. For all triton X-100 wt% an oil-in-water emulsion is formed. At high triton X-100 concentrations a closed-cell fluid foam is stabilised. In addition, a bicontinuous emulsion can be stabilised for several hours for a triton X-100 composition of 6 wt%. This phase coexists with an oil-in-water emulsion. The bicontinuous phase is formed only when the input energy is minimised, for higher input energy no stable bicontinuous emulsion could be prepared. Moreover, the bicontinuous emulsion is extremely sensitive to external stimuli.

Coalescence and rupture of the oil droplets in the dispersed droplet emulsions occurs on a time scale faster than the PGSE NMR experiments (~200 ms) in toluene system. Microstructure tortuosity in addition to obstruction and/or hydration effects dominate the system at high oil content. The stability of the closed-cell foam emulsions is significantly greater than the droplet oil-in-water emulsions.

The series of oil-in-water emulsions, formed in the toluene/triton X-100/water system were further investigated by varying the energy input during the formulation process. Emulsion microstructure could generally be altered, for a single emulsion composition, by changing the amount of energy supplied during emulsification. The response of each of the different microstructures formed at a single chemical composition on application of a controlled shear; was also examined.

For high-oil content droplet phases, emulsion microstructure is markedly altered on increasing energy input. However, all high-oil content droplet microstructures respond identically to the application of a controlled external stress. This indicates that the systems collapse under shear and yield a single common microstructure. Hence, the strength of the interfacial domain of these emulsions, controlled primarily by the triton X-100, is extremely weak. In contrast, low-oil fraction droplet phases maintained the integrity of their microstructure before and after application of a controlled shear when low formulation energies were used during initial processing. However, at higher formulation energies, microstructures again collapsed as evidenced from a single shear response. The bicontinuous emulsion microstructure is extremely sensitive to energy input and cannot be realised at high-input energy. The microstructure of the closed-cell foam emulsion is almost completely independent of formulation energy and remains stable upon subsequent application of shear.

On changing the oil from toluene to either octane or tetradecane it was observed that no stable emulsions could be prepared for formulation energies below approximately 2600 J and additionally stable emulsions could only be formed for triton X-100 concentrations between 8 and 12 wt%. As for the toluene system, water is always the continuous phase. The oil domains in these two systems do not undergo the rapid and constant coalescence and rupture that occurs in the toluene system. Instead they collide, interact and then separate. In the octane system both unrestricted and restricted diffusion of the oil droplets occurred. Using this information a characteristic spacing between the droplets of 0.2 to 0.4 μm was measured. In the tetradecane system, the droplets undergo restricted diffusion only for the measurement times used.

The stability of the emulsions prepared with octane and tetradecane was signigicantly enhanced and this was seen to increase as the chain length of the oil was increased. Ostwald ripening is found to occur in all three systems.

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Thesis Abstract: Sippenhaft in the Third Reich: analysing the 'spectre' of family liability punishment against opposition in Nazi Germany 1933–1945

ROBERT LOEFFEL

Abstract of a thesis submitted for the Degree of Doctor of Philosophy,
University of New South Wales, Australia, 2004

This thesis examined the phenomenon of *Sippenhaft*, the punishing of family members for the crime of a relative. This assessment was restricted to investigating the incidence of *Sippenhaft* against those considered by the Nazis to be 'German' (*Reichsdeutsche*) or 'of German blood' (*Volksdeutsche*) The infliction of punishment regardless of the innocence or guilt of the individual determines that, practically applied, this policy must be considered a device of terror. Specifically, instances of *Sippenhaft* against civil Germany within the military and against particular resistance groups were investigated.

It was against the external Soviet sponsored 'National Committee for a Free Germany' (NKFD) and 'League of German Officers' (BDO) resistance groups and in particular after the assassination attempt on Hitler on 20 July 1944 that *Sippenhaft* came closest to becoming a practical reality. Assessing the manifestation of *Sippenhaft* involved assessing the dissemination of orders and directives from above as well as how these were, or were not, put into practice. It also relied on establishing an understanding of how *Sippenhaft* was practically applied against families. This involved contacting numerous family members connected to various German Resistance groups, both within the 20 July coup attempt and the NKFD and BDO resistance groups, to determine if they were placed under arrest in accordance with family liability. Their stories of arrest and imprisonment reveal how this terror became a reality. These individuals ranged from siblings, wives and parents to young children. Many of these children were arrested and housed in a specially created *Sippenhaft* 'children's home'.

As a result, this thesis is focused to a degree

in the period following 20 July 1944, when the practical application of *Sippenhaft* was mostly achieved and adds further to the awareness of the radicalisation of the Third Reich in the closing stages of the war. The investigation into this period after 20 July revealed that while many of the families connected to the German Resistance were punished, within the military in general, despite the widespread and open threat, *Sippenhaft* was not practically applied. Similarly, threats made against the German public were seldom followed up with actual arrests. In other words, within these two domains in Nazi Germany, *Sippenhaft* was never practically applied with any regularity. Consequently, this thesis offers a deeper comprehension of the potency of fear over practice, as a means of social coercion and how this was practically achieved. Rather than being used as an unconstrained device of terror, *Sippenhaft* was largely restricted in its extent and capacity. How effectively these fears were created and sustained are the main focus of this thesis.

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Thesis Abstract: Mast Cells and Microflora in the Possum cul-de-sac

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Abstract of a thesis submitted for the Degree of Doctor of Philosophy,
University of Otago, New Zealand, 2004

Keywords: possum, reproduction, mast cells, cul-de-sac, stereology

Mast cells are a common feature of the vaginal cul-de-sac of female brushtail possums. In the reproductive organs of other mammals empirical studies have found that mast cell numbers change at different stages of the reproductive cycle. The reason for the presence of mast cells in the cul-de-sac is unknown but may reflect microbial presence as mast cells are typically associated with biological responses to parasitic and/or bacterial invasion in gut and pulmonary tissues. Alternatively, it may indicate a role for mast cells in marsupial reproduction.

This study will attempt to address the significance of mast cells in the cul-de-sac of the brushtail possum with the hypothesis: '*That mast cells in the vaginal cul-de-sac of the brushtail possum undergo numerical, spatial and morphological changes during different reproductive states.*' This investigation will assess whether the changes are due to microbial invasion or reproductive processes.

Cul-de-sac tissues were collected aseptically for microbiological, stereological and TEM analyses, from female adult possums (n = 6/group) that were lactationally anoestrous or in the follicular or luteal phases of the oestrous cycle, where oestrous cyclicity was induced by the removal of pouch young and reproductive status confirmed by laparoscopy. A similar analysis was undertaken on untreated seasonally anoestrous animals and those treated with subcutaneous implants of oestradiol 17β (n = 6/group) as well as juvenile animals (n = 5). Microbial populations were quantified and bacteria identified by media-culture and gram staining. The fractionator and optical disector stereological methods were used to quantify mast cell populations in both the epithelial and connective tissue components of the cul-de-sac.

Microflora were present at very low levels ($< 5 \times 10^5$ organisms g^{-1}) in the culs-des-sacs from all reproductive groups and were undetectable in 15/41 animals. The total number of mast cells present was significantly greater in adult than in juvenile animals. Amongst adult groups, mast cell numbers were greater in follicular and luteal phase animals than in oestradiol-treated animals. Changes in total mast cell number amongst adult animals were not reflected in changes to the number of epithelial mast cells. Mast cell populations displayed two aspects of anisotropy irrespective of reproductive status, where (i) cells were predominantly located in the epithelial tissue and/or in that region of connective tissue adjacent to the basement membrane and (ii) cells often appeared as aggregations of three or more cells per disector volume.

Mast cell density was significantly lower in those animals exposed to endogenous and exogenous oestradiol than in lactationally and seasonally anoestrous animals. This may be attributed to increases in total cul-de-sac volume. Electron microscope studies showed that the volume fraction (V_v) of granules in mast cells was greater in lactationally and seasonally anoestrous animals than in luteal phase animals.

In conclusion, the density of mast cells in the cul-de-sac of the female brushtail possum shows changes after exposure to oestradiol. This was not related to microbial invasion, but may be due to changes in tissue volume, or to some unidentified stimulus.

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Thesis Abstract: Investigation of a Decision-support Framework for the Sustainable Development of the South American Quarrying Industry: An Application of the Quadruple Bottom Line

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Abstract of a thesis submitted for the Degree Doctor of Philosophy,
University of New South Wales, New South Wales, 2004

This research examines the connection between the implementation of strategies addressing the environmental, social, economic and governance aspects of mining (what the author recognises as the quadruple bottom line of sustainable development) and the sustainability of the South American quarrying industry.

The project included the analysis of the quarrying industry of the capital cities of Colombia, Chile and Ecuador, as representative case studies of South America. Fieldwork in these cities involved interviewing stakeholders, visiting quarries, observing behaviour, and testing knowledge and understanding about sustainable quarry development. The information gathered was then combined with the information provided by national mining registers to identify the issues that inhibit the sustainability of quarrying in Colombia, Chile and Ecuador.

In parallel to the fieldwork, an analysis was conducted of specific environmental, social, economic and governance aspects of the minerals industries of various countries. These countries included Canada, the United States, Panama, Dominican Republic, Cuba, Brazil, Spain, England, South Africa, Australia, China and the Philippines. This investigation confirmed the connection between the implementation of strategies addressing the quadruple bottom line of sustainable development and the sustainability of the minerals industry.

A combination of three qualitative analysis methods namely, successive approximation, illustrative method and ideal types method, has been used in the development of specific sustainable development strategies for the South American quarrying industry. These strategies are presented as the 'decision-support framework for the sustainable development of the quarrying industry of South America'. This framework focuses on the implementation of strategies dealing with the quadruple bottom line of sustainable development. The key areas addressed in these strategies are: a regulatory framework for quarrying, special considerations for the small-scale and artisanal quarrying industry; environmental strategies for larger quarrying companies; the role of the quarrying industry's stakeholders; and additional environmental recommendations.

The research undertaken for this thesis was able to fill significant knowledge gaps about the unsustainable character of the South American quarrying industry. It was found that the key sustainability issues faced by the South American quarrying industry are: the marginal and undercapitalised character of this industry; the weaknesses of the regulatory framework for quarrying, the environmental and social impacts of quarrying operations; and the effects of quarrying in urban areas. Corruption and armed conflict were also found to be important limitations of the industry. It was confirmed that the South American quarrying industry is not based on a framework that reflects the consideration of the quadruple bottom line of sustainable development.

The thesis concluded that the quarrying industry of South America is not ready to achieve its sustainable development and to contribute to the sustainability of other economic activities of these countries. Further research, particularly in relation to small-scale and artisanal quarrying operations; implementation of cleaner production and eco-efficiency in quarrying; recycling and reuse of quarry resources; and quarry development in urban areas is recommended.

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Thesis Abstract: Near Infrared Spectroscopy of Aromatic Molecules

TIMOTHY WILLIAM ROBINSON

Abstract of a thesis submitted for the Degree of Doctor of Philosophy,
University of Otago, New Zealand, 2004

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in interstellar space, and are currently the best candidates for the carriers of the so-called unidentified infrared emission bands observed from many astronomical sources. Despite extensive investigation of the infrared spectral properties of PAHs, both from experimental study and quantum chemical calculations, a definitive assignment of the emission bands to specific PAHs has remained elusive.

Near-infrared spectroscopy is a technique that is very sensitive to subtle effects of molecular structure such as small differences in CH bond lengths. Near-infrared spectra are dominated by vibrational overtone transitions that correspond to localized CH-, NH-, or OH-stretching oscillators in the molecule. We have suggested that an analysis of the near-infrared spectroscopy of PAHs could provide better resolution and aid the identification of specific PAHs in interstellar and terrestrial environments.

We have calculated the fundamental and overtone CH-stretching spectra of small PAH molecules in their neutral, cationic, and anionic states. The calculations use an anharmonic oscillator local mode model with local mode parameters and dipole moment functions determined from *ab initio* and density functional calculations. The PAH cations are characterized by blue-shifted CH-stretching transitions which show dramatically decreased fundamental intensity compared to the neutral molecules. The anions are characterized by red-shifted frequencies and an enhancement of fundamental intensity. In contrast to the fundamental region, the overtone intensities are predicted to be remarkably similar for the neutral and charged species. The larger than expected overtone intensities for the cations should provide new impetus for experimental studies and perhaps provide a means for the first observation of CH-stretching transitions in PAH cations.

The low vapour pressures of PAHs makes experimental vapour-phase studies difficult. We calculated the vibrational spectra of the aromatic molecules phenol, aniline, and aminophenol, and measured the vibrational spectrum of phenol to 17 000 cm^{-1} with the use of conventional and laser photoacoustic spectroscopies. The calculated frequencies and intensities are compared to our experimental vapour-phase spectra of phenol, and spectra of the molecules under jet-cooled conditions obtained from Prof. M. Fujii's laboratory. We find that our simple local mode model can provide spectroscopically accurate absolute and relative vibrational intensities, and performs equally well for OH, NH, and CH oscillators.

The recent observation of low-lying electronic transitions in PAH cations has demonstrated that electronic transitions need to be considered to complement our work on vibrational overtone excitation. We have tested the ability of current theoretical methods to calculate electronic transitions accurately. The results from these studies showed that the multireference configuration interaction method can provide quantitatively accurate excitation energies and oscillator strengths, whereas the configuration-singles and time-dependent density functional methods do not provide consistently accurate predictions.

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Thesis Abstract: Powerfully Affected by the Foreign Tongue

Language in the Works of Emine Sevgi Özdamar

KATHERINE MARGARET ROY

Abstract of a thesis submitted for the Degree Master of Arts,
University of Otago, New Zealand

Born in Turkey and living and writing in Germany, Emine Sevgi Özdamar is an author who writes between the two cultures. This thesis examines the language of her works — the novels *Das Leben ist eine Karawanserei hat zwei Türen aus einer kam ich rein aus der anderen ging ich raus* and *Die Brücke vom Goldenen Horn*, the collections of *Erzählungen, Mutterzunge* and *Der Hof im Spiegel*, and the play 'Keloglan in Alamania'. It analyses the contribution of this language to the creation of a 'new' identity, the voicing of a hybrid German-Turkishness.

The thesis, divided into three chapters, begins with an introduction of the background against which Özdamar is writing, and includes a discussion of the appropriateness of the application of Deleuze and Guattari's theory of 'minor literature' and post-colonial literary theory for a reading of Özdamar's work. In Chapter One, Özdamar's first novel, *Karawanserei*, is then made the focus of a discussion of the linguistic techniques employed to construct difference, 're-place' German and restore the balance between centre and the perceived 'fringe'. Chapter Two examines the second novel, *Brücke*, written in what is initially perceived as a more 'standard' German. Here the focus shifts to the language of narrative itself, in particular its role in structuring the novel, and the result of a Deleuzian-style 'affect' on the reader: how it communicates the narrator herself and her environment to the reader. This chapter begins with an assessment of the initial reception of this work, concluding that it defies the German genre-categorisation many of the reviewers sought to apply. The third section of the thesis focuses on the author's own journey to hybridity through language, beginning with her discussion of the loss of her mother tongue ('Mutterzunge') and her attempt to regain it by going back to the Turkish language's Arabic roots ('Großvaterzunge'). This going back sparks a leap forward and we encounter several hybrid texts (such as 'Karriere einer Putzfrau' and 'Keloglan in Alamania'). The collection *Der Hof im Spiegel* highlights the division of Germany itself, provides a new take on the centre fringe relationship, and details the fact that the Turks are now staying ('Die neuen Friedhöfe in Deutschland').

It is this Turkish minority in Germany for whom Özdamar provides a voice, creating a new style of German-language literature in extending its boundaries and expressing an 'interior'. Özdamar's work resists marginalisation, demanding thoughtful reading. Narrative structure, idiom and syntax are all other than the norm of standard German, and the resultant narrative style re-writes the language of the centre. Through language, a new becoming-identity is conveyed.

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Thesis Abstract: Unintended Effects of Ethnically Targeted Advertising

ERNEST CYRIL DE RUN

Abstract of a thesis submitted for the Degree of Doctor of Philosophy,
University of Otago, New Zealand, 2004

Although advertising has been a major area of study in marketing, research investigating the unintended effects of targeted advertising beyond social and moral issues has been limited. This thesis contributes to the current body of knowledge by examining the unintended effects of ethnically targeted advertising on ethnic groups that are not targeted, but who are still likely to see the advertising. The thesis also develops a holistic model for measuring the effects of targeted advertising using four variables: emotions, attitude to the advertisement, attitude to the company and behavioural intentions. The conceptual basis of the model is accommodation theory, which allows for different levels of targeting based on the language mix used in advertisements (e.g. ranging from advertisements that are solely in the targeted group language to advertisements with a mixture of languages to advertisements that are solely in the non-targeted group's language). The model was tested on three different ethnic groups in Malaysia.

Five key propositions were tested during the research: 1. That targeted advertisements will elicit negative unintended reactions from ethnic groups that are not targeted (P_1); 2. That there will be a direct relationship between the strength of reactions and the degree of language accommodation (i.e. those not targeted will have stronger negative reactions to advertisements that accommodate the targeted ethnic group) (P_2); 3. That 'novel' advertisements with unexpected combinations of language and cultural cues, will elicit more negative reactions from those not targeted rather than 'standard' advertisements with more commonly used combinations of language and cultural cues (P_3); 4. That there will be significant differences within ethnic groups in their reactions to targeted advertisements (P_4); 5. That there will be significant differences between ethnic groups in their reactions to targeted advertisements (P_5).

A factorial design was used to analyse the data collected by a survey. The factorial design consisted of five different advertisement types (by language), three different ethnicities, ethnic identification strength and measures of social distance. The dependent variables used were attitude towards the company, corporate credibility, corporate image, rapport, attitude towards the advertisement, affective response towards the advertisement, attitude towards the product, attitude towards the brand, purchase intention, word of mouth, overall emotions, alienation, anger, feeling targeted and perceived threat.

Test for P_1 supported the proposition of negative responses by non-targeted ethnic groups, albeit that a lot of these were affective responses. The findings also suggested that ethnic dominance and the social and cultural context might have mediated the level of negative response. Test for P_2 showed that the strength of negative reactions was not necessarily directly linked to the level of language accommodation. Test for P_3 showed that 'novel' advertisements created stronger negative reactions among non-targeted ethnic groups than 'standard' advertisements. Test for P_4 showed that within-group effects were minimal. The interactions posited for P_5 did not occur.

The theoretical implications of this thesis include support for a 'holistic' approach to targeted advertising. In other words, instead of the previous view that looked at targeting as the end product, the thesis suggests that there are more factors to consider after targeting is implemented. The thesis also develops a model for

assessing the unintended reactions of those not targeted. The findings indicate that there are limits to Accommodation Theory, Distinctiveness Theory and the concept of cultural schema. This research also has managerial implications and identifies actions that can be taken to reduce the negative reactions of non-targeted ethnic groups to ethnically targeted advertising and towards the company itself.

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Thesis Abstract: Improving the Immunogenicity of Influenza Subunit Antigens through the use of Antigen Delivery Systems and other Immune Modulators

JEREMY ROBERT WALES

Abstract of a thesis submitted for the Degree of Doctor of Philosophy,
University of Otago, New Zealand, 2004

Subunit antigen vaccines, based on one or more epitopes, offer advantages over whole organism vaccines in terms of safety and purity. However, these vaccines are often less immunogenic. To increase their immunogenicity, specific signalling molecules and particulate delivery systems have come under scrutiny. This study investigated methods to improve the immune response to two Influenza haemagglutinin-derived subunit antigens, consisting of a T and B cell epitope (TB), or three T cell epitopes (TTT).

Through recombinant technologies, Interleukin-2 (IL-2) was fused to these subunit antigens. *In vitro*, the fusion of IL-2 to antigen was shown to increase the activation of an antigen specific T cell hybridoma induced by the subunit antigens. The use of IL-2Rβ antibody to block the receptor subunit on macrophages reduced the activity of the subunit IL-2 fusion protein, but not the subunit antigen alone. These results, amongst others, suggest that the adjuvancy exerted by IL-2 in our *in vitro* system was due, at least in part, to an IL-2Rβ mediated uptake mechanism rather than its T cell growth factor activity.

Encapsulation of the subunit antigens in liposomes also increased their antigenicity, although the response to subunit antigen IL-2 fusion proteins was not improved when encapsulated. This may be due to high doses of antigen being delivered to antigen presenting cells, through liposomal encapsulation, negating any affect that the IL-2Rβ uptake pathway may be able to confer.

In vivo, splenocytes from mice vaccinated with antigen-IL-2 fusion proteins in liposomes produced significantly higher levels of IFN-γ than splenocytes from mice immunised with antigen alone either delivered in solution or in liposomes, or antigen-IL2 delivered in solution. TB-IL2 delivered in liposomes was also able to induce significant levels of IgG1 reactive to the Influenza virus ($p < 0.05$). This work suggests that fusing antigen to IL-2 and delivering this within a particulate system enhances the immune response to a peptide antigen. However, the combination of these systems was unable to induce a sufficient immune response to comprehensively protect animals against influenza.

Therefore, other immune stimulators were examined. NF-κB inducing kinase (NIK) is

an intracellular signalling molecule involved in the signalling pathway upstream of NF-κB. Plasmid-based delivery on its own is not considered to be an effective adjuvant, as it is inefficient at penetrating the cell/nuclear membrane. A potential DNA delivery system is polyethylenimine (PEI), which is a cationic polymer that is able to bind DNA and actively traffic plasmids to cell nuclei.

The pNIKG1:PEI complex was able to increase T cell activation *in vitro* induced by preactivated macrophages presenting Influenza viral peptides. In vivo, pNIKG1:PEI complexes were shown to increase specific lymphocyte proliferation and IFN-γ production ($p < 0.05$) when used as an adjuvant with TB-IL2 delivered in liposomes. However, the addition of pNIKG1:PEI was not able to sufficiently improve the immune response to comprehensively protect animals against influenza.

These results contribute to our knowledge of the use of signalling molecules and particulate delivery. Through a better understanding of these systems, safe and effective vaccines may be developed from subunit antigens in the future.

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(Manuscript received 23.11.2004)

Thesis Abstract: Effects of Environmental Enrichment on Fundamental Cognitive Processes in Rats and Humans

ELIZABETH ANN WOODCOCK

Abstract of a thesis submitted for the Degree Doctor of Philosophy,
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This thesis examined whether it is possible to enhance core elements of the information processing system with specific forms of environmental stimulation. The first series of experiments demonstrated that a preweaning environmental enrichment procedure that provided 60 minutes of daily multisensory stimulation accelerated the development of long-term contextual memory and enhanced inhibitory processing in young rats. That is, whilst stimulated and nonstimulated rats exhibited long-term memory of a context at 26 days of age, only stimulated rats showed this ability at 18 days of age. In addition, stimulated rats showed a faster rate of extinction of long-term contextual memory at 21 days of age, which was taken as evidence of enhanced inhibitory learning (i.e., context - no US) in these rats.

Subsequent experiments with adult rats demonstrated that a combination of preweaning multisensory stimulation and postweaning rearing in an enriched environment improved the (1) specificity of long-term contextual memory, (2) speed of contextual information processing, and (3) availability of attentional resources. More specifically, enriched-reared rats demonstrated superior ability to discriminate between two similar contexts in comparison to standard-reared rats. In addition, enriched-reared rats showed superior memory of a context when there was limited time available to form a memory of that context. This finding was taken to indicate that rats that receive environmental enrichment are able to process contextual information more rapidly. Finally, standard-, but not enriched- reared rats showed less conditioning to a discrete stimulus when it was presented in combination with a stronger stimulus during training compared to when it was presented by itself. The finding that enriched-reared rats did not show this overshadowing effect suggests that these rats have greater availability of attentional

resources to divide between two stimuli that are competing for attention.

The experiments with rats were followed by two experiments with children that investigated the effects of a computerised cognitive training procedure on information-processing speed. These experiments demonstrated that 30-minutes per weekday of training in rapid decision-making for three to five weeks improved children's performance on two tests of processing speed (i.e., a choice reaction time and odd-man-out task). In addition, the speeded training improved children's ability to sustain their attention and inhibit impulsive responses on a continuous performance test (Test of Variables of Attention). The cognitive training procedure had no effect on children's performance on a measure of fluid intelligence (Raven's Standard Progressive Matrices).

The results of the experiments reported in this thesis suggest that a number of fundamental cognitive processes can be modified by environmental conditions that place increasing demands on the information-processing system. A neurobiological model, focusing on myelin, axon diameter, and the glutamatergic, glucocorticoid, noradrenergic, and cholinergic systems, was proposed in order to explain the observed effects of environmental stimulation on cognition in children and rats.

The rationale for attempting to enhance fundamental cognitive processes was that improving these processes should ultimately improve general intellectual functioning. With respect to this aim, the correlational data from the present experiments with children revealed promising trends towards greater improvements in the tests of fundamental cognitive processes in those children in the training group with *slower* processing speed at the start of the intervention. This finding suggests that cognitive training may be even more effective at enhancing processing speed and other fundamental cognitive processes in children with intellectual impairments, who reportedly have slower processing speed than normal children. However, the extent to which training-related improvements in fundamental cognitive processes generalise to improvements in *general* cognitive functioning is unclear. That is, there is insufficient evidence that processing speed and other fundamental cognitive processes are causally related to intelligence. It is therefore essential that future cognitive training research is mindful of related developments within the intelligence and information processing literature.

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Biographical Memoir

FREDERICK CHARLES LOUGHNAN

1923 – 2004

Frederick Charles (Fred) Loughnan, who passed away on June 19, 2004, was one of the earliest and most highly respected academic staff members in Geology at the University of New South Wales.

Fred was born in Sydney in 1923, and after an initial career in banking and service with the Australian Army in Bougainville, graduated with First Class Honours in Geology from Sydney University in 1950. He had also gained a sound training in chemistry as part of his degree program, and this was to prove invaluable in his later teaching and research activities.

As a student Fred was supported by a cadetship from the NSW Department of Mines, and after graduation joined the staff of the Geological Survey of New South Wales. In 1953 he accepted an appointment as Lecturer in Geology at what was then the New South Wales University of Technology but shortly (in 1956) became the University of New South Wales. Thirty years later, in 1983, he retired from the University as Associate Professor in Applied Geology, with a national and international reputation for a diverse range of research activities in sedimentary petrology, especially rock weathering and clay mineralogy.

Fred's interest in clay minerals began early in his academic career, and in 1957, shortly after joining the staff at UNSW, he was awarded a Fulbright Scholarship to work with the well-known clay mineralogist Professor Ralph Grim at the University of Illinois. However, with a baby due he declined the offer (allowing his second daughter to be born in Australia) and pursued a research program at UNSW that led in 1959 to the award of his PhD degree. A monograph based on his thesis, published by the University in 1960, went on to become a standard reference source for people seeking information on the commercial clay deposits of New South Wales.

Fred was promoted to Senior Lecturer in 1960, and to Associate Professor in 1967. His administrative skills were also highly regarded, and he was called upon a number of times to take over the role of Head of the (then) School of Applied Geology. Taking the opportunity to try out a previously considered career in architecture, he was also instrumental in designing the facilities to accommodate Geology in the new Applied Science Building, into which the School moved in 1969. In addition, he spent several periods of sabbatical leave in the USA, including a year at the University of Illinois in 1959–60 (finally taking up the Fulbright award), at Universities in Ohio and Oklahoma in 1967–68, and Florida in 1977, strengthening his research at the international level.

During his 30-year career, Fred published two books and over 60 scientific papers. In 1974 he was awarded a DSc degree for his research on the composition and properties of sedimentary rocks: the first and, to date, the only DSc in Geology awarded by the University of New South Wales.

Fred was the quintessential scientist, continually asking and seeking to answer those fundamental but important questions: 'what is it made of?', 'how did it get there?' and 'what might it be useful for?' There was always something new that drew his attention, and his boundless enthusiasm, his great thoroughness and his deep insight made working in his laboratory an interesting and pleasurable experience. His papers cover an alphabet of materials, from analcite to zebra rock, and include notes on new, unusual and often significant occurrences of minerals such as buddingtonite (ammonium feldspar) in Queensland oil shales, cookeite in the Pambula pyrophyllite, dickite in the Hawkesbury Sandstone, and dawsonite in the Greta Coal Measures and other units of the Sydney Basin. His most memorable contributions, however, were a wide-ranging series of papers on kaolinite clayrocks, also known as tonsteins and flint clays, in several different coal-bearing and coal-barren successions throughout eastern New South Wales. Others include a small but remarkably useful book on Chemical Weathering of the Silicate Minerals, published by Elsevier in 1969, and a contribution on kaolin genesis and synthesis in another Elsevier volume, published in 1982.

Fred's contribution over those 30 years embodied excellence in the three essential aspects of activity at any good university: teaching, research and scholarship. Many of his students themselves went on to become Professors and Associate Professors, senior members of Geological Surveys, and other well-respected members of the geological profession. When he retired from the University in 1983 the School established the FC Loughnan Prizes, one for First Year Geology and one for Third Year Geology, the award of which still continues to recognise and encourage new generations of students along the geological path.

Fred was one of the leaders in introducing new technologies to Australian geology, and in using them to learn more about the common things, such as clays and other sedimentary minerals, that we all too often take for granted. He was also keenly aware of the need for research on topics related to industrial applications, and his advice was sought for consultancy work on different aspects of applied mineralogy.

Professor Loughnan had two separate periods of membership in the Royal Society of NSW. The first, from 1949 to 1958, saw several addresses to the Section of Geology, and also publication of papers on the geology of the Stroud-Gloucester Trough (1954), clay minerals in the Hawkesbury Sandstone (1956) and the mineralogy of commercial dyke clays in the Sydney district (1957). The second, from 1979 until his acceptance as a retired member in 1994, saw publication of papers on the geology of the Merriwa-Binnaway-Balimore area (1978), magnesian calcite at Lake Illawarra (1979) and the Permian palaeoclimate of the Sydney Basin (1991). In between was a paper on the occurrence of aluminophosphate minerals in rocks of the Sydney Basin (1970). He also acted as a referee for many manuscripts submitted to the Society's Journal. It is perhaps fitting that the first and last scientific papers in his long and productive career were both published in the Journal and Proceedings of the Royal Society of New South Wales.

Fred is survived by Margaret (Peg), his wife for 52 years, by daughters Kerry and Karen, and by their respective families. We salute his achievements, and thank him sincerely for his contributions to the geological community as a teacher, researcher, advisor and friend.

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