U–Pb dating of silicic lavas, sills and syneruptive resedimented volcaniclastic deposits of the Lower Devonian Crudine Group, Hill End Trough, New South Wales*

E. A. JAGODZINSKI AND L. P. BLACK

Australian Geological Survey Organisation, GPO Box 378, Canberra, ACT 2601, Australia.

The Hill End Trough of central-western New South Wales was an elongate deep marine basin that existed in the Lachlan Fold Belt from the early Late Silurian to late Early Devonian. It is represented by a regionally extensive, unfossiliferous sequence of interbedded turbidites and hemipelagites of substantially silicic volcanic derivation, which passes laterally into contemporaneous shallow-water sedimentary rocks. The Turondale and Merrions Formations of the Lower Devonian Crudine Group are two prominent volcanogenic formations in the predominantly sedimentary trough sequence. They contain a range of primary and resedimented volcanic facies suitable for U–Pb dating. These include widespread subaqueous silicic lavas and/or lava cryptodomes, and thick sequences of crystal-rich volcaniclastic sandstone emplaced by a succession of mass-flows that were generated by interaction between contemporaneous subaerial pyroclastic flows and the sea. Ion microprobe dating of the two volcanogenic formations by means of the commonly used SL 13 zircon standard yields ages ranging between 411.3 ± 5.1 and 404.8 ± 4.8 Ma. Normalising the data against a different zircon standard (QGNG) yields preferred slightly older mean ages that range between 413.4 ± 6.6 and 407.1 ± 6.9 Ma. These ages broadly approximate the Early Devonian age that has been historically associated with the Crudine Group. However, the biostratigraphically inferred late Lochkovian – early Emsian (mid-Early Devonian) age for the Merrions Formation is inconsistent with the current Australian Phanerozoic Timescale, which assigns an age of 410 Ma to the Silurian–Devonian boundary, and ages of 404.5 Ma and 395.5 Ma to the base and top of the Pragian, respectively. There is, however, good agreement if the new ages are compared with the most recently published revision of the Devonian time-scale. This suggests that the Early Devonian stage boundaries of the Australian Phanerozoic Timescale need to be revised downward. The new ages for the Merrions Formation could also provide a time point on this time-scale for the Pragian to early Emsian, for which no data are presently available.

Key words: Devonian, geochronology, Hill End Trough, Merrions Formation, New South Wales, Turondale Formation.

INTRODUCTION

From the Late Silurian to the late Early Devonian, the palaeogeography of the Lachlan Fold Belt of southeastern Australia consisted of localised deep marine basins or 'troughs', separated by shallow marine environments with locally emergent land areas (Cas 1983a; Powell 1984). The Hill End Trough of central-western New South Wales was flanked to the west and east by the shallow marine to emergent platforms of the Molong and Capertee Highs (Packham 1960, 1969). Dominant facies on the bounding highs were mafic to silicic volcanics, shallow marine to subaerial siliciclastics and volcaniclastics, and thick, shallow-water carbonate sequences (reefal and associated shoalwater limestones), flanked by derivative volcaniclastic, siliciclastic and carbonate debris-flow aprons (Pemberton *et al.* 1994). Beyond the southern apex of the trough, the Middle Silurian – Early Devonian Canberra Magmatic Province (Cas 1983a) contained similar shoal-water to emergent facies, dominated by silicic volcanics and volcaniclastics, mudstone and limestone (Crook *et al.* 1973; Cas & Jones 1979). Coeval sedimentation in the Hill End Trough was characterised by deep-water turbiditic sedimentation of alternating silicic volcanic, quartzose and lithic provenance. Unlike the rock associations of the adjacent highs, there is a marked absence of demonstrably authochthonous shoalwater limestones or any other indication of shallow-water deposition (Packham 1968; Cas & Jones 1979).

Because the transported clastic fill of the Hill End Trough contains few *in situ*, age-diagnostic faunal assemblages, direct biostratigraphic constraints on the age of the sequence are sparse and the constituent formations are poorly constrained. Dating of the Hill End Trough sequence has relied largely on lithological correlation with the fossiliferous sequences of the adjacent Molong and Capertee Highs, which are biostratigraphically well-constrained by conodont species. The principal aim of this paper is to

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*Table 3 [indicated by an asterisk (*) in the text and listed at the end of the paper] is a Supplementary Paper lodged with the National Library of Australia (Manuscript Section); copies may be obtained from the Business Manager, Geological Society of Australia.

Table 1 Modal analyses for samples analysed in this study.

Sample no.	Member	Rock type	Grid Ref.[a]	Geochemical classification	Framework constituents recalculated to 100%					Matrix/ groundmass
					qtz	plag.	Kspar	maf.	lithics	
Merrions Formation										
94843524	E	volcaniclastic	417376	andesite	3	93	0	4	0	48%
96843526	H	porphyry lava	418375	dacite	3	95	2	0	0	64%
94843523	D	volcaniclastic	422376	rhyolite	41	38	19	0	2	17%
94843525	D	volcaniclastic	532172	rhyolite	34	42	22	0	2	25%
94843522	P	volcaniclastic	424375	andesite	12	88	0	0	0	53%
Turondale Formation										
93844559B		porphyry sill	271386	dacite	11	89	0	0	0	59%
94843520		volcaniclastic	453383	dacite	40	60	0	0	0	37%

[a]Bathurst 1:250 000 scale map sheet SI/55-08.
Maf. denotes a mafic phase (pyroxene or amphibole) pseudomorphed by chlorite $\pm$ epidote. All samples contain accessory Fe–Ti oxides and zircon. The matrix/groundmass of all samples is recrystallised and composed of secondary metamorphic minerals (quartz, albite, chlorite, sericite, epidote, biotite and clinozoisite).

provide some numerical age control to the trough sequence by presenting U–Pb zircon ages for the Turondale and Merrions Formations, two widespread volcanogenic units in the Lower Devonian Crudine Group. Prior to this study, the only direct isotopic constraint for the sequence was an imprecise whole-rock Rb–Sr isochron age of 395 ± 32 Ma for the Merrions Formation (Cas *et al.* 1976).

Seven samples from the Turondale and Merrions Formations were selected for U–Pb dating by SHRIMP (Sensitive High Resolution Ion Microprobe), the locations and stratigraphic positions of which are presented in Figures 1 and 2 and Table 1. The selected samples include five syneruptive, crystal-rich volcaniclastic sandstones, one porphyritic lava in the Merrions Formation, and a porphyry of similar composition intruding the Turondale Formation. When the results are placed in the context of the limited fossil control available for the Early Devonian sequence, several problems become apparent with the existing Australian Phanerozoic Timescale (Young & Laurie 1996). The results are therefore also discussed in conjunction with a recently published alternative version of the Phanerozoic time scale (Tucker *et al.* 1998). In common with some other dating systems, Phanerozoic SHRIMP dating is critically dependent on the use of an appropriate standard. The new SHRIMP data are also discussed in terms of two different zircon standards, one of which yields significantly more consistency than the other.

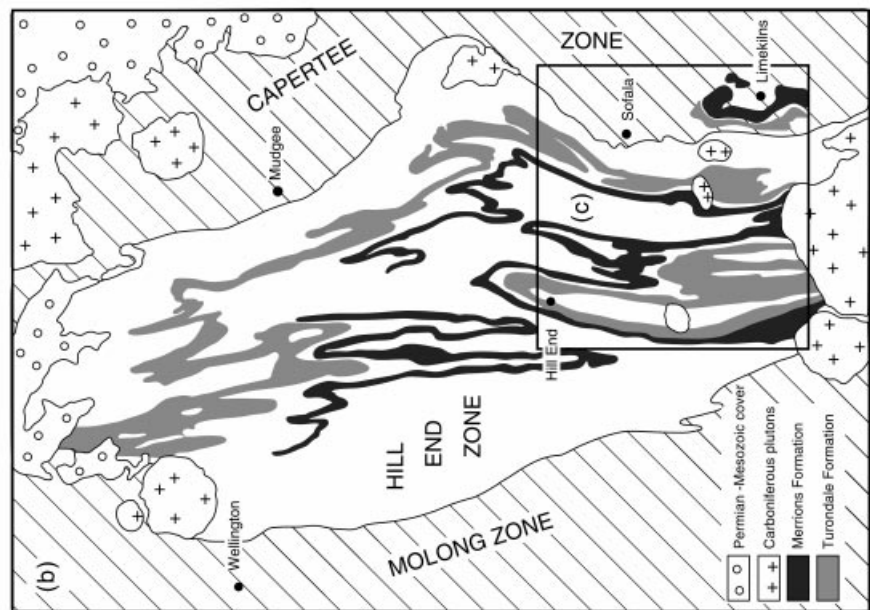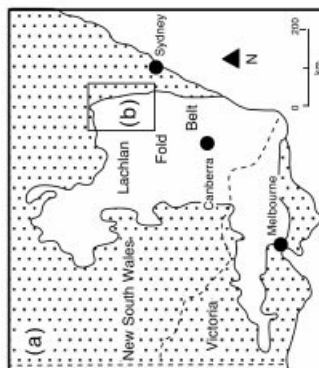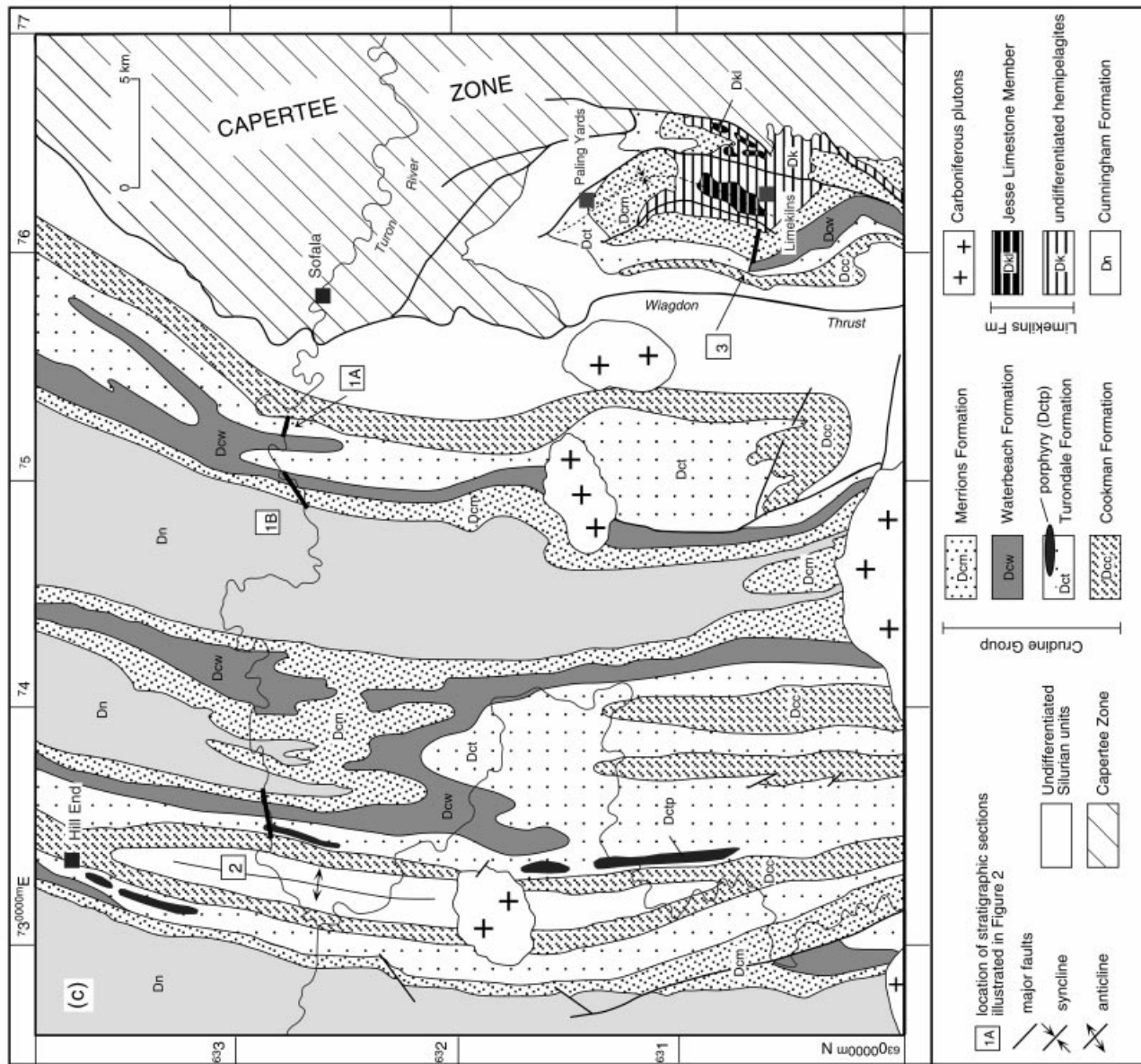## GEOLOGICAL SETTING

Regional stratigraphy

Sedimentation in the Hill End Trough commenced at the start of the Late Silurian and continued uninterrupted to the end of the Early Devonian, when it was terminated by uplift associated with the Middle Devonian Tabberabberan Orogeny (Glen & Watkins 1999; Packham 1999). The Chesleigh Group is the basal unit of the deep-water Hill End Trough sequence. It contains no age-diagnostic fossils, but it has been assigned a late Ludlow to late Pridoli (Late Silurian) age range on the basis of its stratigraphic position

(Pogson & Watkins 1998). Along the eastern margin of the Hill End Trough, the Chesleigh Group conformably overlies the Bells Creek Volcanics which in turn conformably overlies the Tanwarra Shale, both shallow-water constituents of the underlying Mumbil Shelf. Pickett *et al.* (1996) have established a late Wenlock to earliest Ludlow age (*lundgreni-testis* to *nilssoni* graptolite Zones) for the latter.

The Chesleigh Group is overlain by the Crudine Group, which comprises about 2.5 km of turbiditic sandstone (mainly of silicic volcanic provenance) and shale, with rare concordant lavas. In present usage (Pogson & Watkins 1999), the Crudine Group in the Hill End–Sofala–Limekilns region includes the Cookman Formation, Turondale Formation, Waterbeach Formation and Merrions Formation (formerly Merrions Tuff: Packham 1968), in ascending stratigraphic order (Figure 3).

The Cunningham Formation, conformably overlying the Merrions Formation, represents the final fill of the Hill End Trough. It comprises over 3 km of thinly bedded slate, siltstone, quartzo-feldspathic and lithic sandstone, and minor conglomerate. In the Limekilns district east of the Wiagdon Thrust (Figure 1), the Crudine Group is overlain by the Limekilns Formation (formerly Limekilns Group: Packham 1968), inferred to be laterally equivalent to the Cunningham Formation, and deposited in a proximal slope to base-of-slope setting marginal to the Capertee High. The Limekilns Formation comprises a comparatively thin shale sequence (about 200 m thick), in which condensed horizons enriched in shelly debris alternate with

Figure 1 (a) Location map showing the study area in the northeastern Lachlan Fold Belt of southeastern Australia. (b) Outcrop distribution of the Turondale and Merrions Formations in the Hill End Trough. The Silurian–Devonian palaeogeographic elements (Molong High, Hill End Trough and Capertee High) coincide approximately with structural zones defined by Scheibner (1993). (c) Simplified geological map of the Hill End–Sofala–Limekilns district (modified after Raymond *et al.* 1997) showing the geological setting of samples selected for U–Pb zircon analysis, and the location of the stratigraphic sections from which samples were obtained.

(a) Map of Australia showing states (Western Australia, Northern Territory, South Australia, Queensland, New South Wales, Victoria, Tasmania) with location of area (a).

(b) Map showing Sydney, Lachlan Fold Belt, New South Wales, Canberra, Victoria, Melbourne, with location of area (c).

(c) Geological map of the Capertee Zone and Hill End Zone region showing Sofala, Hill End, Paling Yards, Limekilns, Turon River, Wiagdon Thrust, with grid references and stratigraphic units.

Legend:
- Carboniferous plutons
- Jesse Limestone Member (Dkj) — Limekilns Fm
- undifferentiated hemipelagites (Dk) — Limekilns Fm
- Cunningham Formation (Dn)
- Merrions Formation (Dcm) — Crudine Group
- Waterbeach Formation (Dcw) — Crudine Group
- porphyry (Dctp) Turondale Formation (Dct) — Crudine Group
- Cookman Formation (Dcc) — Crudine Group
- [1A] location of stratigraphic sections illustrated in Figure 2
- major faults
- syncline
- anticline
- Undifferentiated Silurian units
- Capertee Zone

(b) legend:
- Permian–Mesozoic cover
- Carboniferous plutons
- Merrions Formation
- Turondale Formation

comparatively barren mudstone sequences, indicating a quiet, sub-storm wave-base environment characterised by slow hemipelagic deposition and sediment starvation over long periods (Colquhoun 1998). The sequence contains a fossiliferous limestone member (Jesse Limestone Member) containing allodapic limestones, mass-flow breccias with clasts of limestone and lesser silicic volcanics, isolated allochthonous limestone blocks and hemipelagic mudstone (Voorhoeve 1986; Wright & Chatterton 1988). The sequence at Limekilns is significant to the present study because it contains age-diagnostic fossils in a trough-margin succession that appears to conformably overlie the Crudine Group.

The Hill End Trough succession has been folded into broad, generally upright north–south-trending folds with axial-plane cleavage, and overthrust onto the Capertee High to the east along the Wiagdon Thrust (Glen & Watkins 1999; Packham 1999). The associated axial-plane cleavage is typically only developed in finer sediments regionally, and in

the coarser rocks in the axial region of the trough (Packham 1968). The sequence has been regionally metamorphosed to greenschist facies, which varies in intensity from biotite grade about the trough axis, to chlorite grade towards the margins (Smith 1969). Primary textures and structures are still well preserved in the lower chlorite grade rocks.

Turondale and Merrions Formations

The Crudine Group contains two volcanogenic units, the Turondale and Merrions Formations, which record the influx of large volumes of volcaniclastic debris sourced from active volcanic terranes on the surrounding highs. These volcanogenic units are separated by the Waterbeach Formation, a ~600 m-thick interval of ambient hemipelagic sediment comprising mainly shale and siltstone, which reflects an interval of volcanic quiescence in the source region (Packham 1968) (Figure 2). Subaqueous volcanic
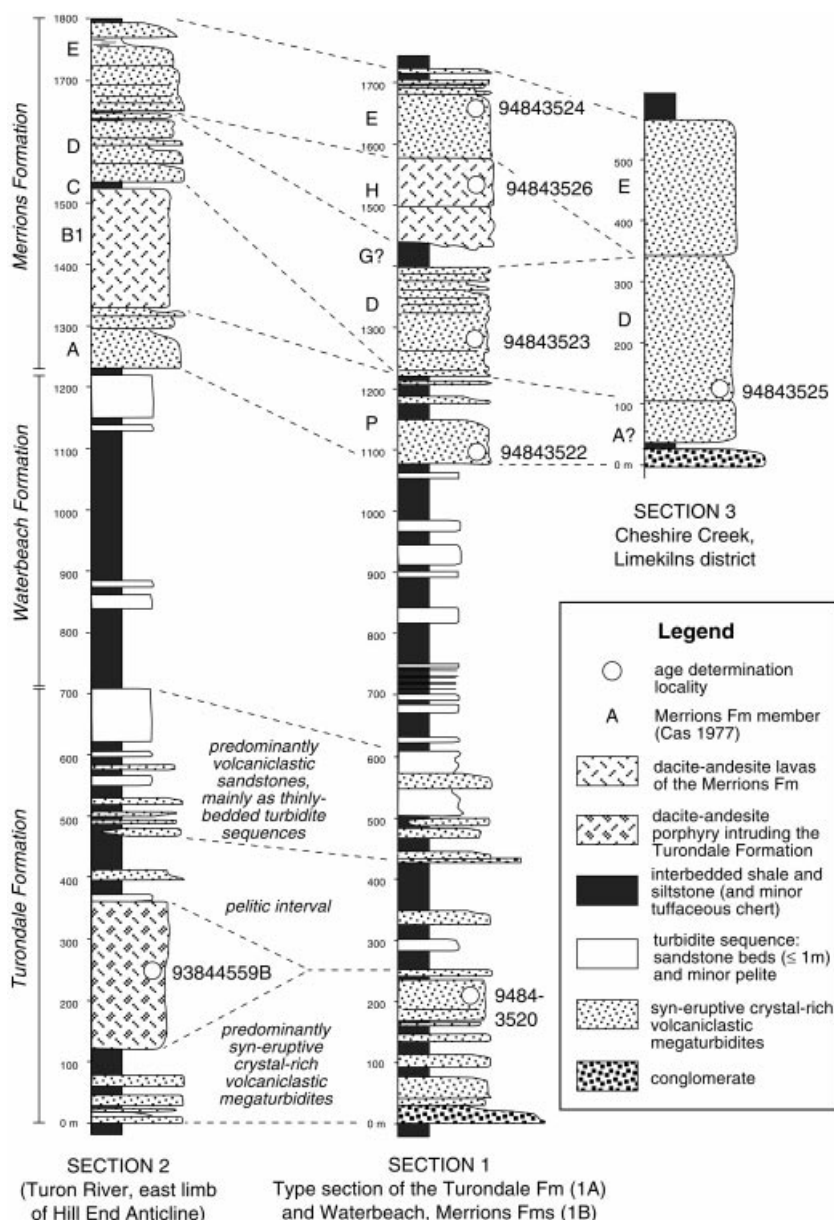

Figure 2 Measured stratigraphic sections showing the stratigraphic context of samples selected for U–Pb zircon analysis. See Figure 1 for locations. For the Merrions Formation, sections 1 and 2 are from Cas (1977), and section 3 from Voorhoeve (1986).

centres also contributed to the Crudine Group. Dacite porphyries occur as regionally extensive submarine lavas within the Merrions Formation and intrude the underlying Turondale Formation as sills.

The volcaniclastic component of the Merrions Formation and much of the Turondale Formation occurs as very thick (tens to hundreds of metres), massive, crystal-rich megaturbidites (Figure 2). The abundance of unabraded juvenile pyroclasts (crystals, crystal fragments and rarely preserved shards) in the volcaniclastic deposits indicates they have not been significantly reworked and were probably emplaced synchronously with or shortly following eruption. Cas (1983b) proposed that the deposits originated from subaerial explosive volcanic eruptions, producing pyroclastic flows which fed into the sea. Upon entering the sea, the hot pyroclastic flows ingested and interacted explosively with water, transforming into water-supported mass-flows that continued to travel underwater to their final setting, well below storm wave-base. Although their final emplacement was not by pyroclastic flows, the deposits are primary in the sense that they were deposited during the eruptive cycle. This style of deposit is becoming more widely recognised, and is categorised as a 'syneruptive volcaniclastic deposit', emphasising the genetic connection with active volcanism (McPhie *et al.* 1993).

Three conformable, coherent porphyry units are recognised in the clastic sequence of the Merrions Formation. Cas (1978) interpreted these units as subaqueous lava flows because: (i) they have a topographic influence on the sedimentation patterns of overlying units; and (ii) the upper margin of one unit is locally quench fragmented, and clasts are reworked into the overlying sediments, suggesting the porphyry was at least exposed during emplacement of the overlying sediment.

A dacite porphyry, of similar composition to the Merrions Formation lavas, outcrops within the Turondale Formation as discontinuous bodies around the nose of the Hill End Anticline (Figure 1). Unlike the porphyries of the Merrions Formation, which have features consistent with lava flows, those of the Turondale Formation are interpreted as post-sedimentation sills. The porphyry bodies are broadly discordant, occurring at several stratigraphic levels in the Turondale Formation, and their upper surfaces cross-cut the sedimentary sequence. There is also evidence of small-scale stoping near the upper margin of the porphyry, and thin apophyses of porphyry protrude into the overlying sediment.

SAMPLE SELECTION

Two samples were selected for analysis from the Turondale Formation. Sample 94843520 is a thick, crystal-rich volcaniclastic sandstone collected near the base of the type section, and sample 93844559B is from a dacite porphyry body intruding the base of the Turondale Formation on the eastern limb of the Hill End Anticline (Figure 2).

The Merrions Formation has a complex internal stratigraphy, which Cas (1977) subdivided into informal members (members A to P), distinguished by gross lithological type (i.e. lava, arenite, pelite) and composition. The volcaniclastic component of the Merrions Formation was sampled at three stratigraphic levels in the type section (Figure 2), in order to assess whether this unit was deposited over a significant interval of geological time. The samples represent arenite members P (sample 94843522), D (94843523) and E (94843524). P is only found in the type section but is correlated with the more widespread basal arenite member A elsewhere (Cas 1977). D and E have a tabular, sheet-like form, and are the most widespread members of the Merrions Formation, occurring in the middle and at the top of the formation, respectively. Member H lava near the top of the type section was also selected for analysis (96843526), in order to confirm the assumption that the resedimented volcaniclastic members were emplaced during the eruptive cycle and do not contain a significant component of reworked detritus, which would introduce inheritance into the zircon populations. The modal compositions of all samples selected for dating are presented in Table 1.

A fourth sample (94843525) was collected from a 600 m-thick volcaniclastic interval in the Limekilns district, east of the Wiagdon Thrust (Figure 1). This volcanogenic unit was originally mapped as the Winburn Tuff (Hawkins 1953; Packham 1968), and interpreted to overlie the Limekilns Formation (Figure 3). More recent mapping, however, has reinterpreted the sequence to lie on the inverted limb of an overturned syncline, placing the Winburn Tuff stratigraphically below the Limekilns Formation and overlying the Waterbeach Formation (Voorhoeve 1986; Pogson & Watkins 1998). It has consequently been assigned to the Merrions Formation, and the term 'Winburn Tuff' has been suppressed. The sample was collected near the base of the volcaniclastic succession, from a distinctive 200 m-thick interval which is rich in pink orthoclase (Figure 2). The sample contains 34% quartz, 22% K-feldspar and 42% plagioclase (Table 1). These framework constituents occur in similar abundance in sample 94843523, from Member D in the type section, and on this basis, these units are correlated. The sample site was selected because in this region there is fossil age control from units immediately above and below it, enabling the numerical ages obtained in this study to be tied to the regional biostratigraphy. The aim was also to test the structural and stratigraphic reinterpretation of the Limekilns sequence, by determining if the volcaniclastic unit is the same age as samples of the Merrions Formation collected from the type section. The Limekilns Formation ranges up to late Emsian in age (Wright & Chatterton 1988; Wright & Haas 1990). If the volcaniclastic 'Winburn Tuff' sequence overlies the Limekilns Formation as originally interpreted by Packham (1968), it will be significantly younger than the ages obtained for the type section of the Merrions Formation.

ISOTOPIC TECHNIQUES

The analyses were made on the SHRIMP I and SHRIMP II ion-microprobes at the Research School of Earth Sciences, Australian National University. Operation at a mass resolution in excess of 5000 at 1% peak height ensured there were no significant spectral interferences (Compston *et al.* 1984). Variable discrimination between U and Pb was referenced to a $^{206}Pb/^{238}U$ ratio of 0.0928 (equivalent to an age of 572 Ma) for interspersed analyses of the SL 13 zircon

Figure 3 Stratigraphy of Early Devonian and some Silurian sequences of the Hill End Trough and adjacent Molong and Capertee Highs, showing biostratigraphic stages, the standard international conodont and graptolite zonation for the Early Devonian and the shelly faunal zonation of Garratt and Wright (1988). The correlation of stratigraphic units between the trough and highs, and with Devonian biostratigraphic stages, is after Colquhoun (1995, 1998). Also shown is the previous stratigraphic scheme for the Limekilns district (Packham 1968), which was modified during the latest regional mapping program (Pogson & Watkins 1998).

standard, based on the power law relationship $^{206}Pb^+/U^+ = a(UO^+/U^+)^2$ (Claoué-Long *et al.* 1995). All of the analysed samples can be calibrated against this standard. A $^{206}Pb/^{238}U$ value of 0.33241 was used, where appropriate, for calibration against the 1850 Ma QGNG standard (Daly *et al.* 1998).

The precision of the Pb/U ratios of the unknowns has been augmented by the uncertainty of the calibration of the appropriate standard during each relevant session. Th/U ratios were derived from the linear relationship $^{232}ThO/^{238}U = (0.03446.UO^+/U^+ + 0.868).ThO^+/UO^+$. Radiogenic Pb compositions were determined by the subtraction of contemporaneous common Pb (Cumming & Richards 1975), there being no detectable Pb in the Au coating that was used. All reported ages for the Palaeozoic zircons have been derived from ^{207}Pb-corrected $^{206}Pb/^{238}U$ ratios (Compston *et al.* 1984). Precambrian ages obtained for xenocrystic zircon have been derived from ^{204}Pb-corrected $^{207}Pb/^{206}Pb$ ratios. All ages have been calculated from the U and Th decay constants recommended by Steiger and Jäger (1977). Except for the data in Table 3* (which reports 1σ errors), age uncertainties are given at the 95% (tσ) confidence level.

SL 13-CALIBRATED ISOTOPIC DATA

Initial assessment of the isotopic data is based on the SL 13 zircon standard, because all of the zircons were co-jointly analysed with it. However, as will be seen later, these data are not as consistent as those based on the QGNG standard.

Merrions Formation, type section

Zircons from the stratigraphically oldest sample (94843522, from member P) were included in three of the sample mounts, as an 'internal standard'. This permits an intercomparison of the relative ages of the samples on the same mount that is independent of the calibration assigned to the standard zircon (see below). It also provides an extra measure of quality control, through the comparison of ages derived for a single unit from different ion-microprobe mounts and using different instruments and instrumental conditions. An added advantage is that the intensive analyses should produce a more precise age for that reference sample (94843522).

All three volcaniclastic samples from the type section of the Merrions Formation contain morphologically

similar zircons, which were set separately in a single ion-microprobe mount. These clear zircons are mostly euhedral, though some terminations are slightly rounded, a feature that appears to be slightly more common in the uppermost sample (94843524). Although prismatic faces are dominated by 100 and 010 forms, more complex facets are locally present. Normal and steep pyramids are about equally common. Aspect ratios are mostly about 2:1, but range up to about 4:1 in the uppermost sample. Grain lengths (200 μm or less) are slightly smaller in the stratigraphically intermediate sample than the other two, which average about 250 μm. The prismatic zoning that is characteristic of igneous growth is ubiquitous (Figure 4a); sector zoning is neither as common nor as prominent. Silicate inclusions that are mostly rod-like, and rounded fluid inclusions are present in most grains. Although most grains have no obvious core they are still relatively common. Both relatively large, luminescent cores (relatively low in U) and generally smaller poorly luminescent cores (relatively high in U) are present.

In the first mount, 24 analyses of the jointly mounted SL 13 standard yield a 1.85% calibration for the session in which these samples were dated. The appropriate reference line is shown on Figure 5 a–c. This calibration yields an age of 404.8 ± 4.8 Ma (Figure 5a) for the volumetrically dominant, continuously zoned zircon in sample 94843524, from member E, near the top of the Merrions Formation. That age is derived from 18 of 20 analyses, which yield a χ^2 of 0.54. One of the outliers (analysis 208.1) represents a relatively rounded, *ca* 530 Ma xenocrystic grain with subdued zonation. It has distinctively low Th/U. No distinguishing morphological or chemical criteria could be found to explain the young age (*ca* 370 Ma) obtained for the other outlier, analysis 219.1, which presumably reflects a small component of recent radiogenic Pb loss.

All 20 ages obtained for sample 94843523, the intermediate-level representative (member D) of the Merrions Formation, are within error of each other (χ^2 is 0.92) and a weighted mean crystallisation age of 405.5 ± 4.6 Ma (Figure 5b).

The age distribution for sample 94843522, the lowermost representative (member P) of the Merrions Formation, is similarly simple. All 20 analyses conform to a single population (χ^2 is 0.89) with a mean age of 409.6 ± 4.6 Ma (Figure 5c) for the crystallisation of the vast majority of zircon in this rock.

The second mount to contain zircons from Merrions Formation sample 94843522, also includes zircons from member H lava (sample 96843526) near the top of the type section. A small calibration change occurred at about the mid-point of the analytical session, both calibrations being determined to 2.4% precision. All 35 analyses of sample 94843522 from this session define a single population (χ^2 is 0.70) with a mean age of 410.7 ± 5.0 Ma (Figure 5d).

The accompanying zircon grains from the lava (sample 96843526) are clear and euhedral. Simple prisms are more common than more complex forms; normal and steep pyramids are about equally common. The grains are relatively squat, with aspect ratios ranging from about 2:1 to 2.5:1. Average length is about 250 μm. Although silicate and fluid inclusions are common, they are heterogeneously distributed. Most grains have continuous prismatic zoning (Figure 4b). However, some also contain anhedral cores, most of which are small, rounded and poorly luminescent.

Thirty three of the 35 analyses of the lava represent a single population (χ^2 is 0.45) with an age of 406.2 ± 5.1 Ma (Figure 5e) for zircon crystallisation. The most obvious outlier is a rounded *ca* 1000 Ma core (131.1) with distinctively low Th/U. Although the deletion of this analysis alone yields a perfectly acceptable χ^2 of 0.55, the probability

Figure 4 Cathodoluminescence images of typical continuously zoned zircons. (a) Zircon from the volcaniclastic components of the Merrions Formation. These grains were taken from 94843524, the uppermost of the analysed samples. Note the small, poorly luminescent cores in some of the extensively zoned grains. (b) Zircon from the Merrions Formation lava (sample 96843526). (c) Zircon from the volcaniclastic component of the Turondale Formation (sample 94843520). (d) Zircon from the porphyry in the Turondale Formation (sample 943844559B).

(a) Merrions Fm (94843524) Member E — 404.8±4.8 — 1.85 % coefficient of variation — $\chi^2 = 0.54$ — 219.1

(b) Merrions Fm (94843523) Member D type section — 405.5±4.6 Ma — 1.85 % coefficient of variation — $\chi^2 = 0.92$

(c) Merrions Fm (94843522) Member P first mount — 409.6±4.6 Ma — 1.85 % coefficient of variation — $\chi^2 = 0.89$

(d) Merrions Fm (94843522) Member P second mount — 410.7±5.0 Ma — 2.4 % coefficient of variation — $\chi^2 = 0.70$

(e) Lava in Merrions Fm (96843526) Member H — 406.2±5.1 Ma — 2.4 % coefficient of variation — $\chi^2 = 0.45$ — 111.1

(f) Merrions Fm (94843522) Member P third mount — 408.0±4.3 Ma — 2.0 % coefficient of variation — $\chi^2 = 1.54$

(g) Merrions Fm (94843525) Member D (Limekilns) — 406.0±4.3 Ma — 2.0 % coefficient of variation — $\chi^2 = 1.01$ — 225.1

(h) Turondale Fm (94843520) volcaniclastic — 409.5±4.3 Ma — 2.0 % coefficient of variation — $\chi^2 = 0.74$

(i) Turondale Fm (93844559B) porphyry session 1 — 411.5±4.1 Ma — 1.8 % coefficient of variation — $\chi^2 = 0.87$

(j) Turondale Fm (93844559B) porphyry session 2 — 410.4±5.4 Ma — 2.2 % coefficient of variation — $\chi^2 = 0.44$

diagram (Figure 5e) identifies analysis 111.1 as another possible outlier. Its deletion is justified by cathodoluminescence evidence that it was produced by the inadvertent partial overlap of the ion-beam on a small, anhedral, poorly luminescent core.

The third mount to include zircons from Merrions Formation sample 94843522 also contains zircons from volcaniclastic samples collected from the Merrions Formation in the Limekilns district (94843525) and from the type section of the Turondale Formation (94843520). Analyses of these were interspersed with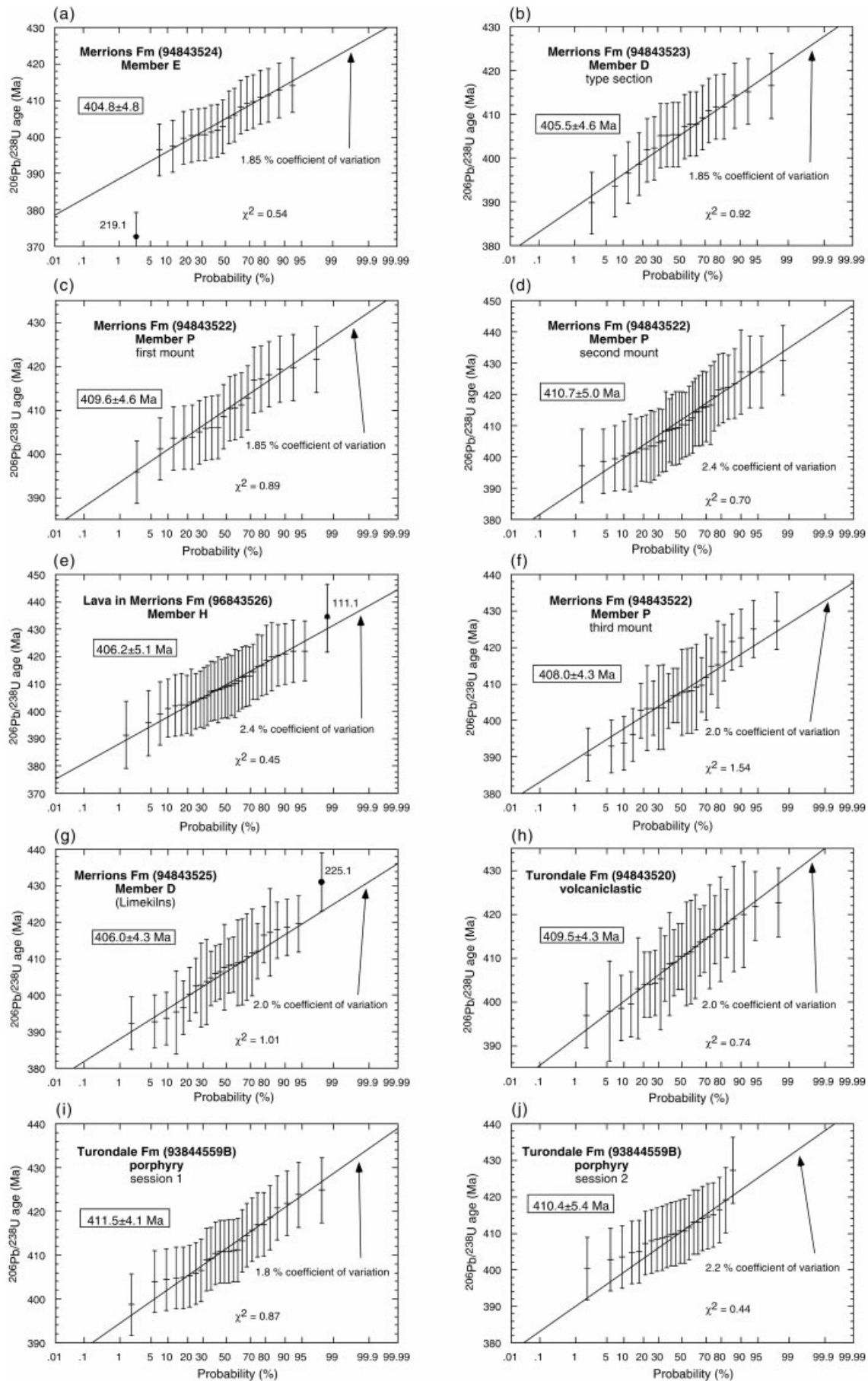 40 analyses of the SL 13 standard in two separate sessions on SHRIMP I. Near the end of the second of these sessions there was a change in the ionisation characteristics of the ion-microprobe, which required a referencing of the measured compositions of the unknown zircons to different values of $^{206}Pb/^{238}U$ and UO/U in the standard. Different calibrations were also found for the two analytical sessions. As each of the calibrations for the standard was determined to about 2.0%, this value has been used in the determination of the ages of the three concurrently analysed unknown zircon suites. The similar precision for each calibration allows the data for different sessions of each particular zircon suite to be presented on a single probability diagram (Figure 5f–h).

All 25 analyses of sample 94843522 on this mount (these are morphologically identical to previously described zircons from this rock) have indistinguishable $^{206}Pb/^{238}U$ (χ^2 is 1.54), which can be combined to yield a crystallisation age of 408.0 ± 4.3 Ma (Figure 5f).

Figure 5 Probability plots of individual zircon ages for each sample analysed. A normal distribution is represented by a straight line, the slope of which is proportional to the standard deviation. The plotted straight line defines the calibration of the interspersed analyses of the SL 13 standard, providing a reference for the variation expected from the sample analyses. (a) Sample 94843524, from near the top of the Merrions Formation. One xenocrystic grain, with an age of 530 Ma, plots above the range of this diagram. Analysis 219.1 also clearly represents an outlier from the main population, because it has lost some of its radiogenic Pb. (b) Sample 94843523, the intermediate-level sample from the Merrions Formation. All 20 ages are within error of each other. (c) Sample 94843522 (mount 1), the lowermost sample of the Merrions Formation. All 20 ages are within error of each other. (d) Sample 94843522 (mount 2), the lowermost sample of the Merrions Formation. All 35 ages are within error of each other. (e) Sample 96843526, a lava within the Merrions Formation. A *ca* 1000 Ma xenocrystic grain plots well above the range of this diagram. The oldest plotted grain (111.1) partially overlaps a small discordant core, and has therefore been discarded from mean age calculation. (f) Sample 94843522 (mount 3), the lowermost sample of the Merrions Formation. All 25 ages are within error of each other. (g) Sample 96843525, a volcaniclastic representative of the Merrions Formation in the Limekilns district. This diagram strongly suggests that analysis 225.1 is older than the other 25 analyses. (h) Sample 94843520, a volcaniclastic representative of the Turondale Formation. All 27 ages are within error of each other. (i) Sample 93843559B, a porphyry intrusion in the Turondale Formation (first analytical session). One *ca* 2500 Ma age lies well above the range of this diagram. (j) Sample 93843559B, a porphyry intrusion in the Turondale Formation (second analytical session). Three older values, which reflect inheritance, plot above the diagram.

Merrions Formation, Limekilns district

The analysed zircons from sample 94843525 are morphologically comparable with many of those studied in the preceding samples. They are clear and mostly euhedral. Local embayments presumably are indicative of growth late in the magmatic crystallisation of the source rock. 100 and 010 prisms and simple pyramids are dominant. Steep pyramids are also present, as are rare 001 prisms. Aspect ratios average about 2:1. Most grains contain fluid and rod-like silicate inclusions. Prismatic zonation is ubiquitous; sector zoning is much less common. Some grains contain discordant, anhedral cores. The largest of these are strongly luminescent and zoned; smaller varieties are poorly luminescent.

The appropriate 2.0% calibration for the standard has been applied to the analyses, as discussed above. Although the 26 analysed zircons from sample 94843525 fulfil one of the requirements of a simple population, with χ^2 being 1.34, the probability diagram (Figure 5g) suggests that the oldest of the analyses is an outlier. Its deletion yields a χ^2 of 1.01. Even though no independent criteria could be found to support this view, it is considered the more realistic of the two scenarios. This option yields a preferred crystallisation age of 406.0 ± 4.3 Ma for these zircons, though the alternative age of 407.0 ± 4.3 Ma is essentially the same.

Turondale Formation

Sample 94843520 is a volcaniclastic rock from the Turondale Formation, sampled near the base of the type section. The zircons in this rock have euhedral form that is dominated by simple prisms and pyramids, though steep pyramids are relatively common. Aspect ratios are relatively constant, at about 2:1. Fluid and rod-like silicate inclusions are present in most grains, which are characteristically clear. Cathodoluminscence (Figure 4c) shows that most of the grains consist of uninterrupted prismatic zones that would have formed during a single igneous event. Sector zoning is locally developed. Some grains also contain discordant cores, some of which have high luminosity and are zoned, and smaller, poorly luminescent varieties. Neither core type was selected for analysis.

This rock was analysed in the same two analytical sessions in which sample 94843525 of the Merrions Formation was dated, and has therefore also been assigned a calibration uncertainty of 2.0%. All 27 zircons from this Turondale Formation sample have mutually indistinguishable 206Pb/238U ages (χ^2 is 0.74), which combine to yield a mean crystallisation age of 409.5 ± 4.3 Ma (Figure 5h) for the vast majority of zircon in this rock.

Sample 93844559B was collected from the intrusive porphyry that cuts volcaniclastic rocks at the base of the Turondale Formation in the Hill End Anticline. The zircons in this rock are primarily euhedral, and are dominated by simple prismatic and pyramidal faces [according to Bossière *et al.* (1996) such forms are typical of high-temperature, relatively alkali-rich magmas]; however, steeper pyramids occur on some crystals (Figure 4d). The aspect ratio of the grains ranges from about 2:1 to 4:1. Fluid and silicate inclusions are common. Some grains have distinctly embayed margins. Cathodoluminscence identifies

the widespread occurrence of prismatic zonation and the presence of discordant, anhedral cores, some of which have been dated. Although the latter are clearly exotic, most of the zoned zircon in this rock is cogenetic.

Dating was accomplished in two separate analytical sessions, on different ion-microprobes. In the first session, utilising SHRIMP I, all 26 analyses of the SL 13 standard yield a 1.8% reproducibility. Except for a 2500 Ma core, the remaining 27 ^{206}Pb/^{238}U ages of the Turondale zircons are within error (χ^2 is 0.87) of a mean value of 411.5 ± 4.1 Ma (Figure 5i).

In the second session (on SHRIMP II), 22 analyses of the standard yield a 2.2% reproducibility. Twenty three of the Turondale porphyry ages are within error (χ^2 is 0.44) of a mean value of 410.4 ± 5.4 Ma (Figure 5j). The three exceptions, with ages of about 460 Ma, 580 Ma and 1450 Ma, all reflect the presence of inherited components.

Because the results of the two sessions are within error of each other, they can be combined to give a preferred age of 411.1 ± 3.2 Ma for the crystallisation of the porphyritic magma.

Significance of the isotopic ages

The ages obtained above for the lava from the Merrions Formation and the porphyry from the Turondale Formation can potentially be assigned to the crystallisation of those rocks. In other words, they have the ability to provide direct stratigraphic information. In contrast, all of the other dated rocks are secondary resedimented volcaniclastic deposits. Strictly, the ages derived for them will be only maximum values for their time of deposition. In practice, those ages are very likely to be indistinguishable from, and to provide reasonable estimates of depositional age, because those zircons would be expected to have been derived from newly created volcanic products.

Table 2 reveals that there is only a limited range in the ages derived above. Indeed, on the basis of the quoted errors, it is not possible to statistically discriminate between any of the ages. However, those precision limits incorporate a component to allow for the uncertainty of the calibration, so that the ages can be justifiably compared with samples dated during different analytical sessions. This extra component of uncertainty is not required for

ages that have been calibrated against a common set of standard analyses (i.e. jointly analysed samples) and are being compared with each other.

From all of the data presented above, it is possible to demonstrate the existence of only one likely age difference, even without the precision limits of the mean ages being augmented by uncertainty related to the calibration of the standard. That age difference applies to the session in which the three samples of the Merrions Formation itself were analysed. Without the augmented uncertainties, the ages (with 1σ precision) for the three samples are 409.6 ± 1.6. Ma (lower), 405.5 ± 1.6 Ma (intermediate) and 404.5 ± 1.7 Ma (upper). The difference between the ages for the upper and lower parts generates a Student's t value of 2.18, which is significant for 36 degrees of freedom (n–2) at slightly more than the 95% confidence level (for which t is 2.03). It is therefore probable that the apparent age differences are real, and that the zircon ages from the lower part of the Merrions Formation are older (by about 5 million years) than those derived from the youngest dated unit.

REGIONAL BIOSTRATIGRAPHY

Fossils are generally rare in the Crudine Group in the Hill End Trough and are confined to those in transported limestone blocks and rare non-age diagnostic plant stems (Packham 1968). Bischoff and Fergusson (1982) described conodonts ranging in age from late Wenlock to middle Lochovian (early *delta* Zone) in allochthonous limestone blocks within a limestone–mudstone breccia facies at Palmers Oakey. This unit correlates with undifferentiated lower Crudine Group (Turondale and Waterbeach Formations: Raymond *et al*. 1997; Glen & Watkins 1999), so the conodont fauna provides a maximum age for the overlying Merrions Formation. Age-diagnostic fossils have also been found in the Crudine Group and the overlying Limekilns Formation in the Limekilns district, east of the Wiagdon Thrust. Fossils occur in three units in the Limekilns sequence: (i) in sedimentary rocks underlying the Merrions Formation; (ii) at the base of the Limekilns Formation; and (iii) throughout the Jesse Limestone Member.

Table 2 Summary of U–Pb zircon ages obtained in this study.

Location	Member	Sample no.	Rock type	IP mount	Age (Ma) calibrated to SL 13	Age (Ma) calibrated to QGNG	No. of analyses
Merrions Formation							
Type section (upper)	E	94843524	volcaniclastic	1	404.8 ± 4.8	407.1 ± 6.9	18
Type section	H	96843526	porphyry lava	2	406.2 ± 5.1	408.0 ± 5.3	33
Type section (intermediate)	D	94843523	volcaniclastic	1	405.5 ± 4.6	407.8 ± 6.6	20
Limekilns (section 3)	D	94843525	volcaniclastic	3	406.0 ± 4.3	409.9 ± 6.6	25
Type section (lower)	P	94843522	volcaniclastic	3	408.0 ± 4.3	–	25
Type section (lower)	P	94843522	volcaniclastic	1	409.6 ± 4.6	–	20
Type section (lower)	P	94843522	volcaniclastic	2	410.7 ± 5.0	411.9 ± 5.0	35
Turondale Formation							
Section 2		93844559B	porphyry sill	4	411.1 ± 3.2	–	49
Type section		94843520	volcaniclastic	3	409.5 ± 4.3	413.4 ± 6.6	27

(1) Wright (*in* Packham 1969) recorded a transported brachiopod fauna in fine-grained volcanogenic sediments below the base of the Merrions Formation at Paling Yards, about 8 km north of Limekilns (Figure 1). Garratt and Wright (1988) correlated the fauna with their 'late' Lochkovian *australis* assemblage zone (Figure 3). Unfortunately, the exact stratigraphic position of the faunal assemblage in the Crudine Group is uncertain. Packham (1969) initially described the fauna as located near the top of the (undifferentiated) Crudine Group, which originally comprised only the Turondale and Waterbeach Formations (Figure 3). Subsequent publications have assumed from this description, that the fauna lay at the top of the Waterbeach Formation (Strusz 1972; Garratt & Wright 1988). However, based on the most recent mapping of the area (Raymond *et al.* 1997), the Turondale Formation is immediately overlain by the Merrions Formation at Paling Yards (Figure 1). Interpreting the nature of the contact between the two formations is hampered by poor outcrop and structural complexity. If the Waterbeach Formation has been removed by faulting or erosion, the brachiopod fauna would lie at the top of the Turondale Formation. The possibility exists, however, that the Waterbeach Formation is present in condensed form, but could not be distinguished from fine-grained sedimentary rocks of the upper Turondale Formation (J. J. Watkins pers. comm. 1998), in which case the fauna may also lie at any stratigraphic level within the Waterbeach Formation. Regardless of its precise stratigraphic position, the faunal assemblage constrains the upper limit of the Turondale Formation and the lower limit of the Merrions Formation to the 'late' Lochkovian.

(2) Fossils are scattered at different levels in the basal unit of the Limekilns Formation (formerly the 'Rosedale Shale' of Packham 1968), which conformably overlies the Merrions Formation. The basal shales yield a mostly pelagic fauna, comprising graptolites, tentaculitids, hyolithids and conulariids, and plant fragments (Wright & Haas 1990). Benthic faunas comprising mostly brachiopods with some corals, rare bivalves and trilobites, are also present. The occurrence of the tentaculitid (dacryocanarid) *Nowakia acuaria*, a well-known Pragian index fossil (Wright & Haas 1990), indicates a Pragian to early Emsian age for the base of the Limekilns Formation (Lütke 1979).

(3) The Jesse Limestone Member contains mass-flow breccias representing slump-transported platform carbonate material that was redeposited in fans on the flank of the Capertee High. The unit is well constrained to the Emsian. Conodonts from the matrix of the breccias are of the late Emsian *serotinus* Zone (Mawson *et al.* 1990; Mawson & Talent 1992). The conodont data from the Jesse Limestone Member do not conflict with the faunal data from the base of the Limekilns Formation. However, they suggest that the Limekilns Formation encompasses a considerable time period (Figure 3). The assignment of the Jesse Limestone Member to the late Emsian (*serotinus* Zone) implies that the underlying 200 m condensed shale sequence could possibly span the Pragian, and all of the Emsian *dehiscens, perbonus and inversus* conodont zones. Alternatively, as the sequence contains no trace of early Emsian faunas, a hiatus during this period may be inferred.

According to the biostratigraphic constraints described above, the allowable biostratigraphic range of the Merrions Formation spans from the middle Lochkovian to the early Emsian (i.e. late *delta* to *dehiscens* conodont Zones) (Figure 6). The *australis* zone brachiopod fauna constrains the upper limit of the Turondale Formation to the top of the Lochkovian *pesavis* Zone. Graptolites in the Tanwarra Shale, assigned a late Wenlock to earliest Ludlow age, provide the only fossil control for the base of the Turondale Formation. However, Colquhoun (1998), suggested that the Turondale Formation is probably equivalent to the lower Kandos Group on the adjacent Capertee High, which would imply that the unit is of Lochkovian age.

DISCUSSION

Consequences of the SL 13-calibrated dataset

Figure 6a shows that the ages obtained for the Turondale and Merrions Formations are broadly consistent with the historical assignment of the Crudine Group to the Early Devonian (Packham 1968). The samples selected for analysis span almost the entire group, excluding only the basal, non-volcanic Cookman Formation. The envelope of analytical errors encompassing the derived ages straddles the Silurian–Devonian boundary at 410 Ma as defined on both the Australian Phanerozoic Timescale (Young & Laurie 1996) and the IUGS 1989 Global Stratigraphic Chart (Cowie & Bassett 1989). Within this envelope of analytical uncertainty, Early Devonian Lochkovian ages were consistently reproduced, spanning a limited range of about 6 million years (411.1–404.8 Ma).

It is not possible to statistically discriminate between ages obtained for the Turondale and Merrions Formations. The age of 409.5 ± 4.3 Ma for sample 94843520 from the base of the Turondale Formation lies within the range of ages derived for sample 94843522 at the base of the Merrions Formation (408.0 ± 4.3, 409.6 ± 4.6 and 410.7 ± 5.0 Ma). However, about 900 m of predominantly hemipelagic sediment, representing over half of the Turondale Formation and the entire Waterbeach Formation, was deposited in the intervening period. If only data obtained from the same sample mount are compared, the mean for the bases of the Turondale and Merrions Formations are 409.5 Ma and 408.0 Ma, respectively. Although statistically indistinguishable, these ages are nevertheless in the correct sense, and when considered with the analytical uncertainties, would allow up to several millions of years for the deposition of the Waterbeach Formation and remainder of the Turondale Formation.

Figure 6a identifies a conflict between the isotopic data and the biochronological framework provided by the Limekilns sequence. Fossil control from contiguous units indicates a mostly Pragian age for the Merrions Formation. In contrast, isotopic ages derived for the Merrions Formation consistently yield Lochkovian, not Pragian, ages (as defined above). The stratigraphically oldest sample of the Merrions Formation yielded ages ranging between 410.7 ± 5.0 and 408.0 ± 4.3 Ma, placing the base of the Merrions Formation close to the base of the Lochkovian (410 Ma) on the current Australian Phanerozoic Timescale

(Young & Laurie 1996). This discrepancy between the existing biochronological constraints and the new isotopic data suggests that the numerical calibration of the Silurian–Devonian boundary requires some revision.

The numerical age of 410 Ma presently used for the Silurian–Devonian boundary on the Australian Phanerozoic Timescale is deduced indirectly from measured ages at widely separated stratigraphic levels,

which lack precise biostratigraphic control. The age is presently based on isotopic dating of Late Silurian – Early Devonian volcanic sequences in the Yass district, New South Wales (Young 1995). Owen and Wyborn (1979) produced a Rb/Sr age of 406 ± 5 Ma from the Boggy Plain Granite, inferred on similar geochemical characteristics to be comagmatic with the Mountain Creek Volcanics, which underlie fossiliferous limestones of late Pragian *pireneae*
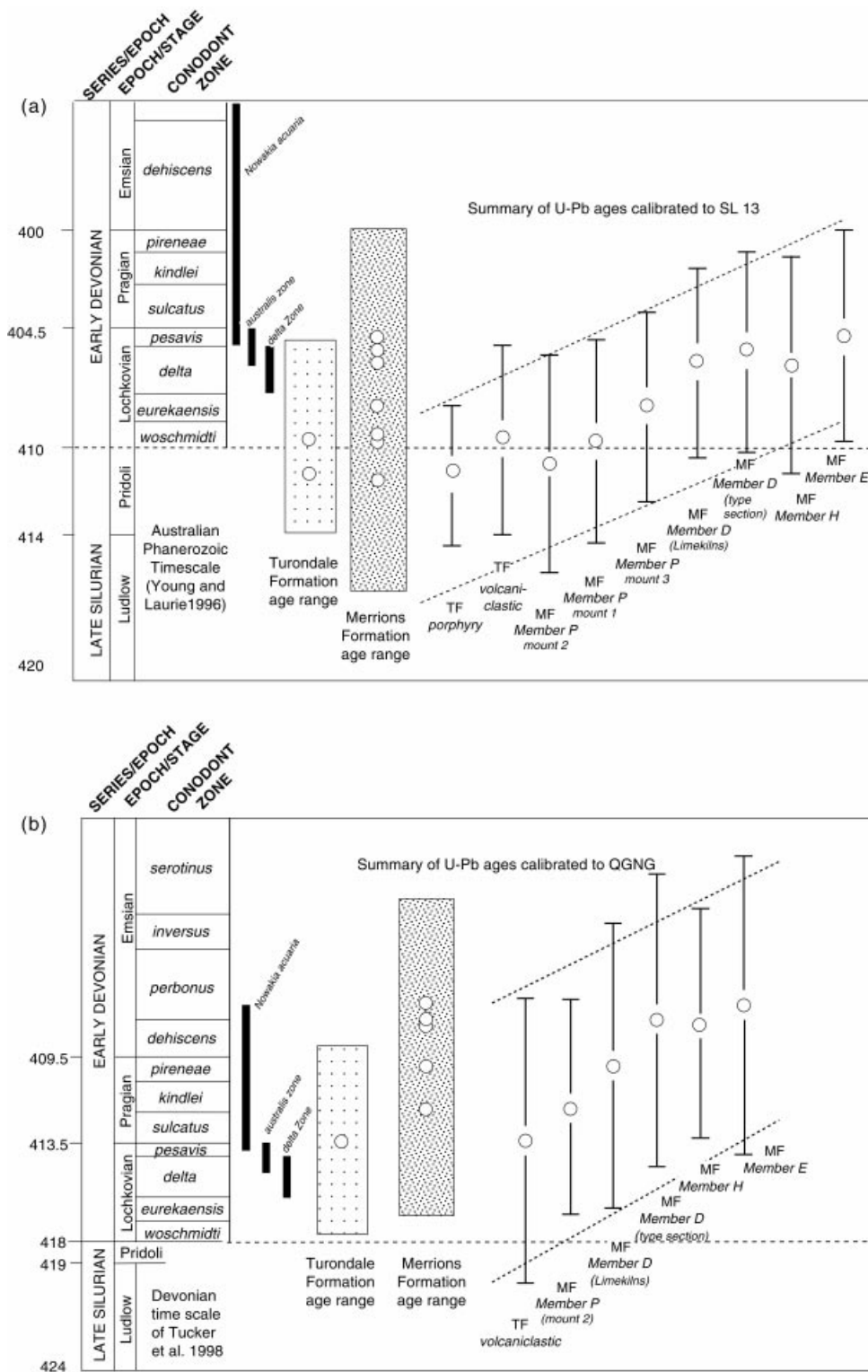

Figure 6 Graphic presentation of the (a) SL 13-calibrated data plotted against the Australian Phanerozoic Timescale; and (b) QGNG-calibrated data plotted against the recently published time-scale of Tucker *et al.* (1998). Faunal zones constraining the allowable biostratigraphic range of the samples, as discussed in the text, are also illustrated.

age. Earliest Devonian strata of the Bowning Group, containing the conodont *Icriodus woschmidti* underlie and are separated from the volcanics by an unconformity representing the Early Devonian Bowning event of southeastern Australia. Owen and Wyborn (1979) estimated that the unconformity represents a break in sedimentation of about 4 million years, in order to accommodate the entire Ludlovian of the underlying Yass Basin sequence above the biostratigraphically constrained earliest Ludlow date of 421 ± 2 Ma for the Laidlaw Volcanics (Wyborn *et al.* 1982). On this basis, they estimated a numerical age of 410 Ma for the Silurian–Devonian Boundary, interpolating from the oldest 406 Ma age for the granites that intrude the Mountain Creek Volcanics.

This estimated age of the Silurian–Devonian boundary is incompatible with the isotopic ages presented above for the Crudine Group. In addition, the results for the Merrions Formation suggest that the base of the *delta* Zone in the middle Lochkovian is no younger than about 410 Ma. These inconsistencies necessitate a reassessment of the core assumptions reached above.

A preferred interpretation

It is clear from the preceding discussion that the ages obtained in this study are inconsistent with those assigned by Young and Laurie (1996) to the appropriate part of the Australian Phanerozoic Timescale, an issue that was also identified by Young (1997), largely on the basis of the new data presented above. This inconsistency could be a consequence of either or both of two issues, namely: (i) whether or not the chronological ties to the time-scale are correct; and (ii) whether the new data accurately depicts the crystallisation ages of the dated rocks. The evidence presented below suggests that both issues are relevant.

DATA ASSESSMENT BASED ON CALIBRATION TO THE QGNG STANDARD

There is a lack of consensus on which isotopic ages are best used as benchmarks in the derivation of the Phanerozoic time-scale, and this has led to widely differing estimates of the age and duration of its component Periods (Harland *et al.* 1982, 1990; Fordham 1992; Gradstein & Ogg 1996; Tucker *et al.* 1998). Although this divergence of opinion has arisen from a variety of factors, it primarily results from different assessments of the most appropriate isotopic ages to use for numerically constraining key biostratigraphic horizons. Each isotopic dating scheme has its own strengths and weaknesses, and it requires judicious assessment of all available data (acquired from a variety of sources over the past several decades) to assemble a meaningful time-scale. It is not only the relative robustness of the different chronometers that is important. Other considerations include achieving a balance between accuracy and precision, and even assessing the effects of uncertainty in the decay constants of the relevant radioactive isotopes. Naturally, due to advances in technology and knowledge, recently acquired ages are generally more reliable.

Over recent years, U–Pb zircon geochronology has played a pivotal role in numerically constraining geological time, and it has therefore been extensively used in the definition of the different time-scales. The most recently published, authoritative division of Devonian time is that of Tucker *et al.* (1998), which is based not only on previously obtained data, but on six new and precise isotope dilution U–Pb zircon ages. Although the Tucker *et al.* (1998) time-scale will almost certainly require adjustment as more information becomes available, it currently represents a benchmark with which the ages produced in this study should be compared.

Another vital issue that must be addressed before meaningful comparisons can be made with an established time-scale is whether the ages in question can be justifiably compared with each other. As an example, the change in the recommended decay constants of some parent isotopes (Steiger & Jäger 1977) would lead, if uncorrected, to non-agreement between genuinely concordant ages that were published before and after that time. The current data are susceptible to a different effect of this type, namely the choice of the particular SHRIMP standard that was used for age calculation.

Ages derived from ^{207}Pb are unsuitable for the ion-microprobe dating of Phanerozoic zircon, because that isotope and its parent ^{235}U were so depleted by then that they are not capable of being measured with sufficient precision. Consequently, the ^{207}Pb/^{206}Pb dating technique, which is extensively used for Precambrian dating, is replaced by the ^{206}Pb/^{238}U technique for the dating of Phanerozoic rocks by ion microprobe. However, unlike the Pb isotopes, which are not significantly fractionated during the SHRIMP sputtering process, there is a dramatic change in Pb/U in the secondary ion beam compared with that in the target zircon. This is compensated for by comparing the relative proportion of those ions in the zircon being dated with that in a zircon (known as the standard) of independently determined age. Until now, at least most SHRIMP ages that have been used as tie points for the time–scale (Claoué-Long *et al.* 1991, 1995; Compston & Williams 1992; Compston *et al.* 1992; Roberts *et al.* 1996) have been calibrated against a late Neoproterozoic zircon (SL 13) from Sri Lanka that yields an isotope dilution age of 572 Ma. In common with those studies, all of the analyses reported above have also been calibrated against SL 13. Several years ago the near exhaustion of SL 13 led to the introduction of two new zircon standards in the Australian National University SHRIMP laboratory. Fortunately, one of these, a 1850 Ma zircon known as QGNG was used as a backup standard for the last batch of analyses performed in this study.

Recent comparative studies (Black *et al.* 1997; Black in press) have revealed a small, but often significant inconsistency between SHRIMP analyses of those two standards, even though their ages have been independently documented by isotope dilution U–Pb zircon studies. Those studies indicate that, on average, SL 13-derived SHRIMP U–Pb ages are approximately 1.5% younger than those derived from QGNG. A difference of similar magnitude (1–2%) and sense has also been reported by Tucker and McKerrow (1995) between SL 13-calibrated SHRIMP ages and isotope dilution zircon ages. These observations indicate that it is inappropriate to compare SL 13-derived ages with the most recently reported Devonian time-scale (Tucker *et al.* 1998), and that QGNG-derived SHRIMP ages would be much better suited for that task.

If the offset between SHRIMP U–Pb ages derived from the two standards was constant, the SL 13-derived data could be adjusted upwards by that fixed percentage to convert to QGNG-referenced ages. Unfortunately, the accumulated comparisons of Black *et al.* (1997) and Black (in press) indicate that the offset is variable, ranging from about 0% to 3%. It is therefore believed that an upward adjustment of all SL 13-derived ages by 1.5% would be an unreliable means of making the newly acquired data congruent with QGNG-calibrated data. An alternative (yet imperfect) approach is used for that purpose.

As stated above, the QGNG standard was in use by the time of the last dating session (labelled as the second mount in Table 3* and text), when both it and SL 13 were jointly analysed. The two unknowns analysed at that time, volcaniclastic sample 94843522 from the base of the Merrions type section, and sample 96843526 (lava from the same section) can therefore be directly calibrated against QGNG. This exercise yields slightly (but not significantly) older mean ages than those calibrated against SL 13, of 411.9 ± 5.0 Ma and 408.0 ± 5.3 Ma, respectively. As described above, sample 94843522 was also set in two of the other mounts, where it served as an 'internal standard'. It is therefore possible to adjust all ages on each of those mounts by the amount that the sample 94843522 age is different from 411.9 Ma, which indirectly normalises those ages to the QGNG standard. That procedure yields the ages listed in

Table 2, which are linked to an age of 411.9 ± 5.0 Ma for the base of the Merrions Formation. The ages determined for the 'internal standard' have an uncertainty of their own, which is combined in quadrature with that determined for the unknowns for the QGNG cross-calibrated results. It is not possible to derive a QGNG-based age for sample 93844559B, because it was analysed before QGNG was trialed as a standard and before sample 94843522 had been collected.

TIME-SCALE CALIBRATIONS

According to the biostratigraphic (and lithostratigraphic) constraints described earlier, the volcaniclastic sample from the Turondale Formation is of Lochkovian age, and the allowable biostratigraphic range of the Merrions Formation spans from the middle Lochkovian to the early Emsian (i.e. late *delta* to *dehiscens* conodont Zones) (Figure 6). The QGNG-based ages would therefore indicate that 413.4 ± 6.6 Ma (Turondale volcaniclastic) should be a Lochkovian age, and the 407.1 ± 6.9 Ma for the top of the Merrions Formation should provide a tie point close to the Pragian–Emsian boundary. These ages are well within error of the Tucker *et al.* (1998) estimates of 413.5 Ma and 409.5 Ma for the base and top of the Pragian, respectively (Figure 6b). There is therefore no discrepancy between the ages obtained in this study when based on the QGNG
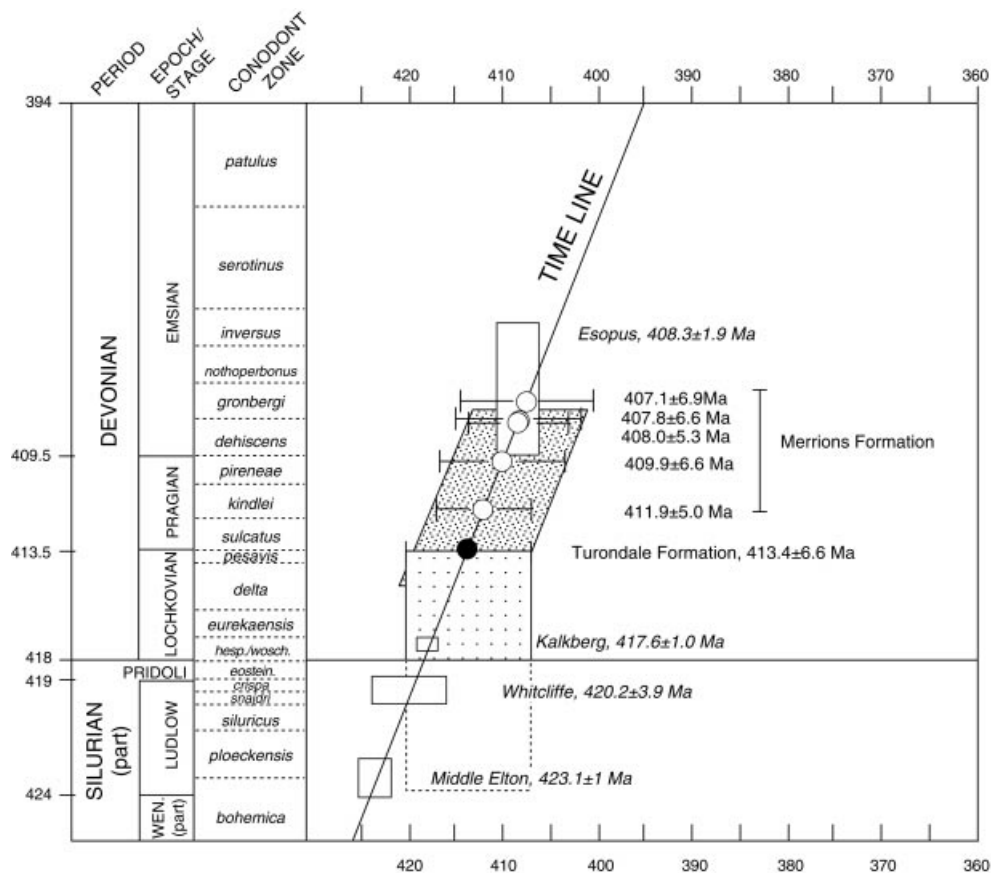

Figure 7 Time-scale for the Late Silurian and Early Devonian, showing pre-existing tie-points in italics (from Tucker *et al.* 1998) with the ages from this paper plotted for comparison. Each tie point on the time line has an assigned uncertainty represented by a rectangle, defined by the precision of the isotopic age (2σ error) on the horizontal axis, and the sample's allowable biostratigraphic range on the vertical axis. The possible biostratigraphic range of the Turondale Formation is denoted by dashed lines. Lithostratigraphic constraints based on calibrations with units on the Capertee High (after Colquhoun 1998) further confine the likely age range of the Turondale Formation (denoted by wide stipple). The duration of Lochkovian conodont zones follows Fordham (1992). All other conodont zone calibrations follow Tucker *et al.* (1998).

standard and the most recently published Devonian time-scale. Indeed, the estimates of Lochkovian time derived above might make a useful addition to that time-scale, which currently has no tie points between early Lochkovian and early Emsian times (Figure 7).

CONCLUSIONS

(1) U–Pb zircon ages were obtained for two samples of the Turondale Formation and five of the Merrions Formation. The samples from the Turondale Formation include a volcaniclastic sandstone at the base of the unit and a porphyry sill intruding the basal volcaniclastic sequence. The Merrions Formation was sampled at four stratigraphic levels of the type section. From base to top, the samples represent basal arenite member P, arenite member D, which occupies an intermediate stratigraphic position within the formation, a dacitic lava (member H) and upper arenite member E (Cas 1977). When the ages are recalibrated against zircon standard QGNG, an age of 413.4 ± 6.6 Ma is obtained for the base of the Turondale Formation, and ages ranging between 411.9 ± 5.0 Ma and 407.1 ± 6.9 Ma are obtained for the Merrions Formation.

(2) A sample was also collected at Limekilns, from a unit originally mapped as the Winburn Tuff, interpreted to overlie the Limekilns Formation. The derived age of 409.9 ± 6.6 Ma confirms more recent mapping, which recognised that the unit underlies the Limekilns Formation and forms part of the Merrions Formation (Voorhoeve 1986; Pogson & Watkins 1998). The age of the unit is within the range of ages quoted above for the type sequence of the Merrions Formation and well within error of member D (407.8 ± 6.8 Ma), which is compositionally similar to the analysed sample.

(3) The Limekilns sample is significant because there is fossil age control from units above and below the Merrions Formation in this area, enabling the numerical ages presented in this paper to be tied to the regional bio-stratigraphy. Based on these biostratigraphic constraints, the Turondale Formation is confined to the Lochkovian stage (approximately *delta* Zone, based on data from Bischoff & Fergusson 1982, and Garratt & Wright 1988), and the allowable biostratigraphic range of the Merrions Formation spans from the late Lochkovian to the early Emsian (late *delta* to *dehiscens* conodont Zones).

(4) The choice of SHRIMP standard used for age calibration can have a significant effect on isotopic data. Data normalised against the commonly used SL 13 zircon standard yield ages that are younger, and variably offset by 0–3%, from ages derived from QGNG (Black in press), and from isotope dilution zircon ages (Tucker & McKerrow 1995). These observations indicate that QGNG-derived SHRIMP ages are better suited than SL 13 for the task of numerical time-scale calibration.

(5) The new isotopic data presented in this paper support a revision of the Australian Phanerozoic Timescale, suggesting that the numerical calibration of the Silurian–Devonian Period boundary, and the Lochkovian–Pragian and Pragian–Emsian Stage boundaries require downward adjustment. The new ages are well within error of the division of Devonian time proposed by Tucker *et al.*

(1998), which places the Silurian–Devonian boundary at 418 Ma, and estimates ages of 413.5 Ma and 409.5 Ma for the base and top of the Pragian, respectively. The estimates of late Lochkovian time and the age of the Pragian–Emsian boundary derived from this study might make a useful addition to that time-scale, which currently has no tie points between early Lochkovian and early Emsian times.

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SUPPLEMENTARY PAPER

Table 3   U–Th–Pb isotopic compositions of the analysed zircons.