Supplementary Data for manuscript - "*Dating low-grade metamorphic events by SHRIMP U-Pb analysis of monazite in shales*" by Rasmussen et al.

SAMPLE SELECTION AND PREPARATION

Polished thin-sections of shales collected from drill-core were prepared and examined by optical microscope and scanning electron microscope (SEM). After initial identification of monazite crystals, petrographic textures were used to establish the relative timing of monazite growth in each sample. Polished thin-sections containing the largest monazite crystals, with inclusion-free areas greater than 15 μm in diameter, were then selected for further analysis. Once identified, suitable crystals were cut out of polished thin sections and mounted in epoxy discs. The mounts were photographed in transmitted and reflected light, and by SEM back-scattered electron (BSE) imaging. High-contrast SEM-BSE examination was carried out on all monazite crystals to identify compositional zonation and possible multiple growth zones, and to locate possible detrital monazite cores that would give anomalously old ages during SHRIMP analysis.

SHRIMP MINERAL STANDARDS

Monazite U/Pb calibration standards were mounted on separate discs and re-used as necessary, though in all cases they were re-polished and gold-coated with the samples for each analytical session. The primary reference for monazite analyses on the Perth SHRIMP is MAD-1 (Kinny, 1997; Foster et al., 2000). Because supplies of MAD-1 are severely limited, most of the analyses reported here used "MPN", an in-house multi-grain Proterozoic monazite standard with U and Th contents similar to those of MAD-1. MPN has been calibrated against MAD-1 through multiple SHRIMP analyses. It has the limitations common to any multi-grain

standard, including variable U abundances. This is not a major disadvantage, since MAD-1 is not well calibrated for element abundances. On the other hand, the $^{207}Pb/^{206}Pb$ data for MPN provide an additional reproducibility check for the $^{207}Pb/^{206}Pb$ data for the samples.

SHRIMP PROCEDURES

Analytical procedures for xenotime have been reported elsewhere (Fletcher et al., 2000) and are not discussed here. The procedures used for monazite are similar to those described by Williams et al. (1996) and have been documented by Kinny (1997) and Foster et al. (2000).

The principal operating conditions used for these analyses were:

1. The primary ion beam spot was ~15 µm in diameter in all cases. This provides good sampling of the limited areas of solid monazite within the sample crystals.
2. The reduced spot size (from the ~25 µm typical for zircon analyses) conveniently limits the O_2^- primary ion current to a level that avoids generating excessively high ThO_2^+ secondary ion currents, which would damage the electron multiplier in the secondary ion collector. The primary beam currents used in this study ranged from ~0.8 nA to ~1.4 nA.
3. The retardation lens was activated for all analyses, to minimise spurious secondary ion counts caused by scattering of the very large ThO^+ ion beam. Excess counts at ^{204}Pb (<1 per second in all cases) were determined from the data for standards and corrections were applied to the data for samples on the assumption that the overcounts correlate with Th content (Kinny, 1997).

4. The data acquisition sequence was:

Nominal Mass	Species	Integration time (sec)
202	$LaPO_2$	2
203	$CePO_2$	2
204	^{204}Pb	10
204.1	Background	10
206	^{206}Pb	10
207	^{207}Pb	30
208	^{208}Pb	2 or 5
232	^{232}Th	2
254	^{238}UO	2
264	$^{232}ThO_2$	2
270	$^{238}UO_2$	2

Each analysis consisted of six cycles on the mass spectrum. In cases where the data were considered to be of good quality and only limited areas of good sample were available, an additional measurement (or measurements) was (were) made before the primary ion beam was moved to a new spot.

DATA REDUCTION

Data files were processed using Krill, a software package prepared by P. Kinny. This uses a $\ln(Pb^+/UO_2^+)$ vs UO^+/UO_2^+ trend for Pb/U calibration and Pb^+/Th^+ vs ThO_2^+/Th^+ for Pb/Th calibration. The former is considered to be quite robust, but we find that the latter is inappropriate for the samples in this study. The reasons for this are unclear, but may include a Th-abundance effect on Th^+ secondary ionisation efficiency, comparable to that observed for U^+ in xenotime (Fletcher et al., 2000). These effects are not a significant problem in cases

(e.g., Foster et al., 2000), where samples were of similar composition to the MAD-1 standard. In this study only $^{207}Pb/^{206}Pb$ is used for chronology, so minor defects in Pb/U and Pb/Th do not affect the interpretations.

We do not record ThO^+ because, at the primary ion current necessary to obtain good U-Pb data for these samples, ThO^+ from the standards is well beyond the safe working range of the electron multiplier in the secondary ion collector. Using a $^{208}Pb^+/^{206}Pb^+$ versus UO^+/ThO^+ calibration (Willams et al., 1996) is not an option. Because a reliable Pb/Th calibration is not yet available, Pb/Th data are not reported in this study, but it is notable that none of the data sets display scatter in $^{208}Pb/^{232}Th$, which would suggest open system behaviour. Work is continuing to identify a more robust Pb/Th calibration.

U/Pb CONCORDANCE

The duality of the U-Pb decay scheme is an important attribute for its use in geochronology, providing an internal assessment of closed-system behaviour. This is done on the basis of concordance, the agreement between the $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ data (but expressed here in terms of the agreement between $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ dates). For monazite data there are several factors which require consideration because of their possible effects on measures of concordance:

1. U-abundance (matrix trace-element) effects.

It is known that U can affect the efficiency of secondary ion generation in a way that causes perturbations in recorded Pb^+/UO^+. This has been documented for another phosphate mineral, xenotime (Fletcher et al., 2000), as well as for zircon (Williams and Hergt, 2000). In this study, the U contents of neither the standards nor the samples are high enough to cause significant problems.

2. Th-abundance (matrix trace-element) effects on Pb/U.

Similar matrix effects can be anticipated when Th (or other trace elements) differs widely between the standards and samples. However, in the case of xenotime (Fletcher et al., 2000) it was noted that although U had a strong effect on Pb^+/U^+, similar Th abundances had no detectable effects on Pb^+/U^+. This also appears to be true for monazite. Despite Th contents of >5% in the standards and a >5:1 difference between the standards and samples, the Pb/U data for all except one monazite sample are tightly clustered and highly concordant. The one exceptional case (Table 1) is attributed to the poorer crystal quality of the sample (see below).

3. Incomplete primary beam coverage.

Having the sample crystal incompletely filling the primary beam spot is known to cause variations in recorded Pb^+/U^+ (Fletcher et al., 2000). This is usually an edge-of-crystal effect, and there might be some component of this in the data for xenotime A-1 (Table 2), a small, irregular grain that was not clearly visible on the video monitor, for which the spot placement was chosen by simultaneously maximising Y_2O^+ and minimising $^{204}Pb^+$. Edge effects are not relevant for the monazite data. For the data in Table 1 and for xenotime A-1 (and to a lesser extent xenotime A-2) a greater problem is likely to be mineral inclusions within the analysis area. These samples have few, if any, areas of sufficient area which are completely free of visible inclusions. These gaps in the monazite surface are expected to have a similar, but unquantified effect on Pb^+/U^+. In addition, elements emitted from the inclusions might have local effects on ion production from the monazite comparable to trace elements in the monazite.

An additional concern is possible contamination of the monazite U–Pb data by contributions from the inclusions. However, the inclusions are generally <1% of the analysed areas and SEM-EDS analysis indicates that the inclusions all have low U contents, so there is no significant U contamination. Analyses with high common Pb, which might come from inclusions, have not been used in determining the ages.

It is considered that the apparent discordance of some data in the main block of Table 1 and xenotime A-1 in Table 2 is largely due to instrumental effects on recorded Pb^+/U^+, though the possibility of the samples being discordant cannot be discounted. The $^{207}Pb/^{206}Pb$ data are not considered to have been significantly affected, either by the instrumental U/Pb fractionation or by any minor loss of radiogenic Pb from samples.

4. Variable secondary ion ratios over time.

It is well known that secondary ion ratios for differing molecular species vary with time, probably due to a combination of effects including local sample charging and varying pit geometry. This has been shown to cause significant changes in Pb^+/U^+ ratios recorded from xenotime when second measurements are made on a single location in a sample, using small, highly focussed primary ion beam (Fletcher et al., 2000). In the present case, using a larger primary beam and Kohler focussing, the effect is small; the average change between first and second measurements for the data presented below is <1.5% and probably not statistically significant. However, element concentration and element ratio data are not tabulated for second (and subsequent) measurements except where second measurements were also made on the standard, allowing direct calibration of the second measurement data.

5. Standards on separate mounts.

Having the samples and standards on separate mounts in the SHRIMP ion source is a potential source of error in the Pb^+/U^+ calibration, though our experience with the Perth SHRIMP suggests that effects >1% are extremely rare when the two mounts are cleaned and gold-coated simultaneously under conditions that give uniform coats. There is an additional possible factor in the different surface texture of the polished thin section compared to the grain-in-epoxy surface. The concordance of the data for the more solid monazite crystals (Tables 3 to 5) suggest that there is no significant mount-to-mount effect in these data.

DATA

For the data tables below:

- Analysis locations are given as Xn-mq, where X = fragment of thin section, n = grain within fragment, m = location in grain, and q = measurement on location;
- All data are corrected for common Pb contamination, based on measured ^{204}Pb and the isotopic composition of Broken Hill galena. 4f206 (%) is the percentage of ^{206}Pb calculated to be common Pb;
- Uncertainties are 1σ, based on counting statistics and expanded to allow for non-linearity in data profiles, and apply to the last digits quoted;
- conc. (%) is concordance, as 100•{t[^{206}Pb/^{238}U]/t[^{207}Pb/^{206}Pb]};
- U and Th contents assume MAD = 1000 ppm U and 7% Th. The accuracy of absolute values is limited by variability in the standards, but internal comparisons are valid for each data set; and
- Element abundances and ratios are reported for first measurements only, except for sample RG102 (Table 5), where second measurements were also made on the standard.

TABLE 1. SHRIMP U-Pb DATA FOR MONAZITE FROM THE HORNBLENDE HORNFELS ZONE OF THE WILDMAN SILTSTONE (UWA MOUNT A-23)

grain-spot	U (ppm)	Th (ppm)	Th/U	4f206 (%)	$^{207}Pb^*/^{206}Pb^*$	$^{208}Pb^*/^{206}Pb^*$	$^{206}Pb^*/^{238}U$	$^{207}Pb^*/^{235}U$	conc. (%)	$^{207}Pb/^{206}Pb$ age (Ma)
A1-1a	225	3461	15.4	1.018	0.1107 ± 12	4.475 ± 22	0.3068	4.682	95	1810 ± 20
A1-2a	163	5063	31.1	0.753	0.1124 ± 19	8.104 ± 40	0.3116	4.830	95	1839 ± 31
B1-2a	99	4479	45.3	0.284	0.1111 ± 16	10.957 ± 95	0.3121	4.781	96	1817 ± 26
B1-2b				1.388	0.1116 ± 21	7.576 ± 49				1825 ± 34
B1-4a	311	7555	24.3	1.799	0.1103 ± 16	5.348 ± 43	0.2645	4.025	84	1805 ± 26
B1-5a	182	3484	19.2	0.367	0.1112 ± 12	5.243 ± 36	0.2995	4.590	93	1818 ± 20
B1-5b				0.507	0.1136 ± 13	3.272 ± 20				1859 ± 21
B1-5c				0.239	0.1131 ± 10	2.267 ± 14				1849 ± 16
B1-5d				0.065	0.1131 ± 8	1.588 ± 12				1850 ± 13
B1-6a	192	5633	29.3	1.780	0.1130 ± 22	8.604 ± 61	0.2679	4.172	83	1848 ± 34
B1-7a	350	490	1.4	0.491	0.1134 ± 8	0.375 ± 4.3	0.3003	4.695	91	1854 ± 13
High common Pb										
A1-2b				3.221	0.1064 ± 29	9.204 ± 51				1739 ± 50
B1-1a	323	9106	28.2	2.224	0.1085 ± 17	10.309 ± 42	0.2335	3.491	76	1774 ± 29
B1-2c				5.294	0.1178 ± 41	4.919 ± 46				1924 ± 63
B1-3a	76	2678	35.4	4.202	0.1022 ± 43	9.761 ±100	0.2756	3.886	94	1665 ± 78

Calibrated against MPN; Pb/U scatter for MPN was 1.88% (1σ; n = 8).

TABLE 2. SHRIMP U-Pb DATA FOR XENOTIME FROM THE HORNBLENDE HORNFELS ZONE OF THE WILDMAN SILTSTONE (UWA MOUNT A-23)

grain-spot	U (ppm)	Th (ppm)	4f206 (%)	$^{207}Pb^*/^{206}Pb^*$	$^{208}Pb^*/^{206}Pb^*$	$^{206}Pb^*/^{238}U$	$^{207}Pb^*/^{235}U$	$^{208}Pb^*/^{232}Th$	conc. (%)	$^{207}Pb/^{206}Pb$ age (Ma)
A1-1a	2127	2863	0.385	0.1107 ± 5	0.3637 ± 17	0.2208	3.370	0.0597	71	1811 ± 8
A1-1b			0.559	0.1100 ± 10	0.3509 ± 44					1800 ± 16
A1-1c			0.265	0.1121 ± 5	0.3651 ± 17					1834 ± 9
A1-1d			0.154	0.1114 ± 4	0.4030 ± 20					1822 ± 7
A2-1a	1105	1034	0.029	0.1116 ± 4	0.3012 ± 16	0.3008	4.627	0.0968	93	1825 ± 6
A2-1b			0.058	0.1117 ± 5	0.3259 ± 24					1827 ± 8
A2-1c			0.042	0.1113 ± 4	0.3558 ± 20					1821 ± 7
A2-1d			0.063	0.1121 ± 5	0.3492 ± 21					1834 ± 7

Pb/U scatter for xtc was 2.2% (1σ; n = 4).

TABLE 3. SHRIMP U-Pb DATA FOR MONAZITE FROM THE ALBITE-EPIDOTE HORNFELS ZONE OF THE WILDMAN SILTSTONE (UWA MOUNT A-24)

grain-spot	U (ppm)	Th (ppm)	Th/U	4f206 (%)	$^{207}Pb^*/^{206}Pb^*$	$^{208}Pb^*/^{206}Pb^*$	$^{206}Pb^*/^{238}U$	$^{207}Pb^*/^{235}U$	conc. (%)	$^{207}Pb/^{206}Pb$ age (Ma)
A2-1a	119	738	6.2	0.080	0.1122 ± 12	1.627 ± 14	0.3255	5.035	99	1835 ± 20
A2-1b				0.637	0.1080 ± 19	2.405 ± 20				1767 ± 32
A2-2a	148	252	1.7	0.177	0.1116 ± 17	0.433 ± 7	0.3253	5.007	99	1826 ± 28
A2-2b				0.068	0.1126 ± 15	0.653 ± 8				1842 ± 23
A2-3a	216	507	2.3	0.119	0.1114 ± 10	0.585 ± 6	0.3244	4.982	99	1822 ± 17
A2-3b				0.076	0.1121 ± 14	0.886 ± 11				1833 ± 22
A2-4a	299	287	1.0	0.000	0.1119 ± 7	0.246 ± 3	0.3281	5.065	100	1831 ± 11
A2-4b				0.148	0.1110 ± 10	0.348 ± 5				1817 ± 16
A2-5a	121	2130	17.6	0.432	0.1109 ± 16	4.564 ± 34	0.3222	4.926	99	1814 ± 27
A2-5b				0.141	0.1103 ± 17	4.739 ± 32				1804 ± 28
B1-1a	129	722	5.6	0.140	0.1091 ± 11	1.464 ± 16	0.3297	4.960	103	1785 ± 18
B1-1b				0.062	0.1102 ± 12	1.706 ± 14				1803 ± 20
B2-1a	244	1457	6.0	0.094	0.1123 ± 8	1.492 ± 9	0.3261	5.049	99	1837 ± 12
B3-1a	195	1039	5.3	0.198	0.1122 ± 15	1.375 ± 13	0.3212	4.970	98	1836 ± 23
B3-2a	347	333	1.0	0.025	0.1125 ± 10	0.250 ± 3	0.3345	5.189	101	1840 ± 16
High common Pb										
A1-1a	129	2288	17.8	4.305	0.1106 ± 35	4.107 ± 31	0.3304	5.039	102	1810 ± 58
A2-6a	110	2389	21.8	9.281	0.1235 ± 64	5.410 ± 58	0.3369	5.736	93	2007 ± 92
B2-2a	114	1138	10.0	7.510	0.1106 ± 59	2.384 ± 32	0.3261	4.972	101	1809 ± 96

Calibrated against MPN; Pb/U scatter for MPN was 1.23% (1σ; n = 11).

TABLE 4. SHRIMP U-Pb DATA FOR MONAZITE FROM SAMPLE RG92 OF THE ROY HILL SHALE (UWA MOUNT A-10)

grain-spot	U (ppm)	Th (ppm)	Th/U	4f206 (%)	$^{207}Pb^*/^{206}Pb^*$	$^{208}Pb^*/^{206}Pb^*$	$^{206}Pb^*/^{238}U$	$^{207}Pb^*/^{235}U$	conc. (%)	$^{207}Pb/^{206}Pb$ age (Ma)
C1-1 a	154	983	6.38	0.268	0.1379 ± 11	1.587 ± 11	0.4048	7.699	100	2202 ± 14
C1-2 a	234	443	1.89	0.499	0.1354 ± 11	0.461 ± 5	0.3940	7.354	99	2169 ± 14
C1-3 a	306	1724	5.64	0.067	0.1363 ± 7	1.415 ± 7	0.4116	7.738	102	2181 ± 8
C1-4 a	642	415	0.65	0.032	0.1377 ± 4	0.160 ± 2	0.4152	7.882	102	2198 ± 6
C1-5 a	376	2431	6.46	0.013	0.1372 ± 5	1.576 ± 7	0.4209	7.960	103	2192 ± 7
C1-6 a	418	949	2.27	0.019	0.1378 ± 6	0.586 ± 4	0.4189	7.957	103	2200 ± 7
C1-7 a	234	1010	4.31	0.178	0.1356 ± 9	1.052 ± 7	0.4141	7.741	103	2172 ± 11
C1-8 a	391	635	1.62	0.000	0.1385 ± 5	0.400 ± 3	0.4120	7.867	101	2208 ± 7
C1-9 a	481	1626	3.38	0.048	0.1382 ± 5	0.858 ± 4	0.4193	7.991	102	2205 ± 6
C1-10 a	242	646	2.67	0.000	0.1374 ± 7	0.670 ± 6	0.3906	7.399	97	2195 ± 9
C1-11 a	162	677	4.18	0.026	0.1378 ± 9	1.048 ± 8	0.3938	7.480	97	2199 ± 11
C1-12 a	148	586	3.96	0.075	0.1375 ± 10	0.971 ± 9	0.3990	7.563	99	2195 ± 12
C1-13 a	168	562	3.34	0.040	0.1364 ± 9	0.821 ± 7	0.3950	7.428	98	2182 ± 11
C1-14 a	233	1662	7.13	0.069	0.1368 ± 8	1.707 ± 10	0.3947	7.445	98	2187 ± 10
C1-15 a	147	927	6.29	0.124	0.1353 ± 10	1.502 ± 10	0.4029	7.516	101	2168 ± 13
C1-16 a	139	839	6.02	0.000	0.1384 ± 9	1.433 ± 10	0.3937	7.514	97	2207 ± 11
C1-17 a	170	1204	7.10	0.066	0.1372 ± 8	1.618 ± 10	0.3958	7.490	98	2193 ± 11
C1-18 a	144	1082	7.50	0.078	0.1373 ± 9	1.787 ± 12	0.3941	7.461	98	2194 ± 12
C1-19 a	424	1277	3.01	0.019	0.1383 ± 5	0.705 ± 4	0.4032	7.689	99	2206 ± 6

Data collected in two sessions: session 1, spots 1–14; MAD as Std; session 2, spots 15–19; MPN as intermediate Std. Pb/U scatter for MAD was 1.00% (1σ; n = 4); for MPN 0.96% (1σ; n = 5).

TABLE 5. SHRIMP U-Pb DATA FOR MONAZITE FROM SAMPLE RG102 OF THE ROY HILL SHALE (UWA MOUNT A-20)

grain-spot	U (ppm)	Th (ppm)	Th/U	4f206 (%)	$^{207}Pb^*/^{206}Pb^*$	$^{208}Pb^*/^{206}Pb^*$	$^{206}Pb^*/^{238}U$	$^{207}Pb^*/^{235}U$	conc. (%)	$^{207}Pb/^{206}Pb$ age (Ma)
B1-1a	169	1372	8.1	0.240	0.1363 ± 12	1.924 ± 14	0.4064	7.639	101	2181 ± 15
B1-1b	172	1141	6.6	0.279	0.1384 ± 14	1.646 ± 14	0.3928	7.498	97	2208 ± 18
B1-1c				0.326	0.1357 ± 14	1.400 ± 13				2172 ± 18
B1-2a	114	2807	24.7	0.213	0.1362 ± 14	5.874 ± 39	0.4103	7.703	102	2179 ± 18
B1-2b	113	2175	19.3	0.263	0.1362 ± 15	4.539 ± 35	0.4089	7.682	101	2180 ± 19
B1-3a	129	1832	14.2	0.000	0.1358 ± 11	3.143 ± 22	0.4171	7.809	103	2174 ± 14
B1-3b	135	1679	12.4	0.000	0.1356 ± 11	2.863 ± 21	0.4053	7.576	101	2172 ± 14
B1-4a	204	1782	8.7	0.146	0.1372 ± 12	2.011 ± 16	0.3737	7.070	93	2192 ± 16
B1-5a	189	191	1.0	0.000	0.1364 ± 9	0.235 ± 4	0.4107	7.725	102	2182 ± 12
B1-5b	174	153	0.9	0.071	0.1346 ± 14	0.203 ± 5	0.3889	7.216	98	2158 ± 18
B1-6a	171	739	4.3	0.000	0.1373 ± 10	1.018 ± 9	0.3989	7.552	99	2193 ± 12
B1-6b	164	861	5.3	0.000	0.1383 ± 10	1.257 ± 12	0.3921	7.479	97	2207 ± 13
B1-7a	190	2153	11.3	0.123	0.1367 ± 11	2.638 ± 17	0.4074	7.680	101	2186 ± 14
B1-7b	191	2169	11.3	0.169	0.1361 ± 11	2.710 ± 17	0.4021	7.548	100	2179 ± 15
B1-8a	143	2187	15.3	0.102	0.1378 ± 13	3.529 ± 23	0.4047	7.689	100	2200 ± 17
B1-8b	146	2565	17.6	0.016	0.1381 ± 11	4.204 ± 27	0.4001	7.621	98	2204 ± 14
B1-9a	95	1018	10.8	0.118	0.1365 ± 16	2.411 ± 22	0.4076	7.674	101	2184 ± 21
B1-10a	72	1787	24.7	1.007	0.1400 ± 29	6.051 ± 52	0.3699	7.141	91	2227 ± 36

Pb/U scatter for MAD was 1.44% (1σ; n = 5; first measurements) and 1.27% (1σ; n = 4; second measurements).

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