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Zircon U-Pb ages for the Early Cambrian time-scale

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Abstract: Single zircons from two Early Cambrian volcanic horizons have been analysed using the SHRIMP ion microprobe. Full details of the analytical procedures and data reduction are given. Zircons from tuff within the Lie de Vin Formation, near Tiout, Morocco, show little spread in U-Pb age and have a mean value of 521 ± 7 Ma (2σ). Those from a bentonite within unit 5 of the Meishucun section near Kunming, southern China, show relatively dispersed U-Pb ages, revealing the presence of both detrital or xenocrystic grains as well as areas within grains that have lost radiogenic Pb. The main population has a mean age of 525 ± 7 Ma, but a mean $^{207}Pb/^{206}Pb$ age of 539 ± 34 Ma which is a maximum estimate for the bentonite age. These results conflict with previous Rb-Sr whole rock ages of *c*. 580 Ma for overlying Cambrian shales at Meishucun, and *c*. 570 Ma for Atdabanian shales from the E. Yangtse Gorges area.

The Precambrian–Cambrian boundary interval is one of the most interesting, but also one of the most poorly understood, portions of geological time. In the early Cambrian, the few simple forms of the Ediacara fauna were succeeded by at least 34 new metazoan groups (Bengston *et al.* 1991). The need to explain this apparently explosive radiation has generated a variety of evolutionary and geobiological hypotheses concerning, for example, organism size (Nicol 1966), the development of collagen (Towe 1970), metazoan predators (Lowenstam 1980), biomineralization (Lowenstam & Margulis 1980), new niches (Sepkoski 1979) and global rifting (Bond *et al.* 1984).

Discrimination between many of these hypothesized events depends to some extent upon the rate at which they occurred. If the faunal changes occurred gradually over the order of 100 Ma, then they could be accounted for plausibly by normal rates of evolution and ordinary geological processes. On the other hand, a short time interval between the Ediacaran fauna and the Cambrian radiation event would require triggering mechanisms of a more fundamental nature. A proper radiometric calibration of the late Proterozoic and early Cambrian time-scale therefore becomes a critical factor in understanding the boundary events. Unfortunately, recent estimates for the base of the Cambrian range widely, from 530 Ma (Patchett *et al.* 1980; Odin *et al.* 1983) to 600 Ma (Ma *et al.* 1984).

Until recently, a major hindrance to radiometric calibration of the stratigraphic time scale has been the poor reliability of biostratigraphic correlation close to the Precambrian–Cambrian boundary, partly due to the restricted occurrence of endemic faunas, and partly due to the lack of a clear stratigraphic definition of what the boundary is. During the past 15 years, multidisciplinary work conducted with the encouragement of the Precambrian–Cambrian Working Group of the ICS has identified several stratigraphically continuous reference sections, and with the recognition of new faunal groups as well as the application of magnetic and carbon isotope stratigraphies, many of the correlation problems are being resolved (e.g. Bengston & Fletcher 1983; Cowie 1985; Magaritz *et al.* 1986; Kirschvink & Rozanov 1984; Latham & Riding 1990; Brasier *et al.* 1990). Formal agreement on the definition of the Precambrian–Cambrian boundary has not yet been reached. However, there is a large decrease in seawater $^{13}C/^{12}C$ ratio at the base of the Tommotian stage on the Siberian Platform (Magaritz *et al.* 1986), similar in character to that at the Permian–Triassic boundary (Baud *et al.* 1989), which marks a major turnover in the biosphere (Magaritz 1989). If radiometric dating of several reference sections confirms it to be a unique, globally synchronous event, this step in seawater $^{13}C/^{12}C$, wherever it can be recognized unambiguously, could become a standard against which intercontinental correlations are tested.

Many attempts to date the base of the Cambrian have dealt with indirect geological evidence, such as the ages of igneous rocks overlain by early Cambrian strata (e.g. the Ercall granophyre of Wales, Patchett *et al.* 1980; Cope & Gibbons 1987; and the basement volcanic rocks of Morocco, Odin *et al.* 1983). Dating authigenic glauconite and illite within Cambrian sediments is more direct, but in some cases these minerals contain an inherited component (e.g. Plumb *et al.* 1976), in others their determined ages are too young through loss of radiogenic isotopes (e.g. Morton & Long 1980), and in yet others they formed much later than deposition (e.g. Morton 1985).

In an extensive survey of Ordovician stratotypes, Ross *et al.* (1982) determined fission-track ages on zircons extracted from thin bentonites interbedded with the fossiliferous sequences, thereby emphasizing the availability and importance of such material for radiometric time-scale work. Tucker *et al.* (1990) continued this study by making more precise U-Pb age determinations on some of the same bentonite zircons by mass spectrometric isotope-dilution.

In this paper, we report ion microprobe U-Pb ages for single zircons extracted from two separate volcanic and bentonite units interbedded in fossiliferous strata of early Cambrian age (Fig. 1):

(1) a volcanic tuff from the uppermost portion of the Lie de Vin Formation in the Anti-Atlas Mountains of Morocco, which is correlated with the *Dokidocyathus lenaicus* zone of latest Tommotian age in Siberia (Latham & Riding 1990);
(2) a bentonite extracted from Bed 5 of the Meishucun section near Kunming in South China, from strata that palaeomagnetic, $^{13}C/^{12}C$ and faunal interpretations place

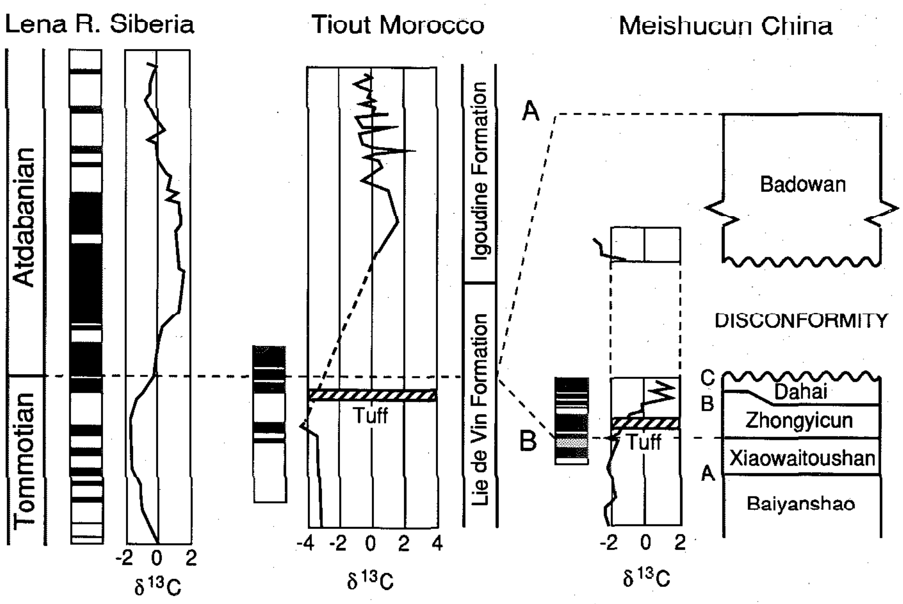

Fig. 1. Possible correlations between the section at Meishucun, China, and the Moroccan and Siberian sequences. A is based on palaeontology (Luo *et al.* 1984), B is based on $\delta^{13}C$ and palaeomagnetism (Kirschvink *et al.* 1991).

as either early Atdabanian or Tommotian. The present authors are divided on the issue.

The *maximum* ages for these Early Cambrian units are <530 Ma for the Tiout zircons and <570 Ma for the Meishucun, in agreement with the estimates of Odin *et al.* (1983). The same conclusion is reached in a companion paper on the U-Pb age of an Atdabanian tuff from South Australia (Cooper *et al.* this volume).

Geological background

Tiout section, Morocco

A thick sequence of platform carbonate rocks, of late Proterozoic to early Cambrian age, crops out along the Western Anti-Atlas Mountains of Morocco (Choubert 1952). In the central and eastern areas of the mountains, the sediments, deposited on a deformed Pan-African age basement containing late Proterozoic tilloids (Leblank 1981), form layer-cake exposures in which the only deformation is gentle Hercynian folding. The lack of a developed cleavage and absence of any thermomagnetic overprint (Kirschvink *et al.* 1991) testify to their extremely low metamorphic grade. About 100 km to the east of our collection site, zircon from volcanic rocks within the basement complex have been dated by the U-Pb method as 563 ± 20 Ma (Mifdal & Peucat 1985). The oldest sedimentary unit, the basal member of the Adoubou Formation (formerly the Série de Base), contains upper Riphean acritarchs (Choubert *et al.* 1979) as well as poorly-preserved imprints of an Ediacaran-type soft-bodied metazoan fauna (Houzay 1979). Following Geyer (1989), units above this include, in order, the limestone member of the Adoubou Formation (formerly the Calcaire Inférieur), the Lie de Vin Formation (formerly the Série Lie de Vin), the Igoudine Formation (formerly the Calcaire Supérieur), and the Amouslek Formation (formerly the Série Schisto-Calcaire). The middle horizons of the Igoudine Formation contain the first trilobites and archeocyathids, which mark the probable time-equivalents of the mid-Atdabanian stage of Siberia (Debrenne & Debrenne 1978; Sdzuy 1978). Newly discovered fossils from the Lie de Vin Formation at the Tiout locality in Morocco (Latham & Riding 1990) have refined the interpretation of the Tommotian-stage equivalents within this sequence. *Turthinia* group cyanobacterial fossils of early Tommotian age occur near the base of the Lie de Vin Formation whereas the late Tommotian fossils *Diplocraterion* and *Kordephyton* occur towards the top.

Magaritz *et al.* (1991) have demonstrated that the carbon isotope pattern in the limestone member of the Adoubon Formation strongly resembles that of the Vendian Yudoma formation from the Aldan River of Siberia, including the sharp drop in $\delta^{13}C$ which marks the base of the Tommotian Stage. Similarly, using both magnetostratigraphy and carbon isotopes at the Tiout section in Morocco, Kirschvink *et al.* (1991) have refined the position of the Tommotian–Atdabanian boundary, having identified Siberian Carbon Cycle IV as well as a characteristic switch in geomagnetic polarity bias which marks the late Tommotian (Kirschvink & Rozanov 1984).

Monninger (1979) noted the presence of several volcanic tuff units within the Lie de Vin Formation at the Tiout locality, although no attempt was made to date them at the time. We collected samples from one of the tuffs 730 m above the base of the Lie de Vin Formation at Tiout, and 20 m below the level with *Kordephyton* reported by Latham & Riding (1990). The carbon isotope and magnetic reversal patterns (Kirschvink *et al.* 1991) suggest that this horizon correlates best with the latest Tommotian *Dokidocyathus regularis–D. lenaicus* Zone boundary of the Lena River of Siberia.

The tuff is a typical acidic ash cemented with silica and mainly composed of plagioclase and quartz, with trace amounts of altered biotite, hornblende, magnetite and zircon. It is thin (several centimetres) and situated near the middle of a 1 m thick dolomite bed.

The zircons are a mixed population of generally stubby, colourless grains with a variety of crystal forms and structures. The grain size ranges from > 100 μm to < 30 μm diameter, with the majority of the smaller grains being irregular or embayed grains or grain fragments that are otherwise euhedral. The habit of the larger grains also varies, with few being perfectly euhedral crystals while the majority are stubby prisms with complex pyramidal terminations. Some grains are strongly rounded with obvious abrasion pitting. The grains of all sizes are generally internally structureless and of high clarity. Euhedral growth zoning is rare, with only about 10% of the grains showing either zoning or an obvious core-rim structure. Most of the grains contain a small number of inclusions, most of them crystalline.

Meishucun section, South China

The stratigraphy, lithology and palaeontology of the Sinian–Cambrian sequence at Meishucun, near Kunming in South China, have been described in detail by Luo *et al.* (1984). They recognized 18 lithological units within their upper Yuhucun and Qiongzhusi formations and proposed two reference points for the Sinian–Cambrian boundary ('China A', 80 cm above the base of Unit 1, and 'China B' at the base of Unit 7) on the basis of abundant and diverse shelly faunas at these horizons. As is typical of many early Cambrian faunas, the Meishucun fossils tend to be largely endemic forms, and belong to groups with long stratigraphic ranges, so that palaeontological correlations with other areas are somewhat uncertain. For example, Luo *et al.* (1984) and Brasier *et al.* (1990) interpret these assemblages as pre- or early Tommotian in age, whereas Rozanov (1984) prefers a correlation with the late Tommotian, at least for the China B horizon. The latter interpretation is in broad agreement with an analysis using the combined carbon isotope and magnetic reversal stratigraphies from Meishucun, which correlates the increase in the $\delta^{13}C$ values between the 'China A' and 'B' horizons with the base of Siberian Carbon Cycle IV, roughly at the Tommotian–Atdabanian boundary.

Ma *et al.* (1984) reported Rb-Sr whole-rock ages of 587 ± 17 Ma (2σ) for the overlying Badaowan Member (Meishucun units 9 to 12), and 588 ± 13 Ma for the Badaowan equivalent at Wangjiawan. These shale ages were regarded as maximum limits for deposition because of the known presence of detrital feldspar and kaolinite in the samples. Other relevant results are Rb-Sr and U-Pb isochrons for shales from the Shuijintuo Formation, which Luo *et al.* (1984) regarded as Atdabanian in age. All of the latter are closely grouped around a weighted mean value of 573 ± 7 Ma, interpreted by Ma *et al.* (1984) as recording the time of early diagenesis.

Recently, a thin clay horizon within unit 5 of the Meishucun section has been identified as a bentonite, on the evidence of euhedral quartz, sanidine, biotite, plagioclase, apatite and zircon preserved in tuff fragments and as crystal clasts. It also contains small zircons (<60 μm), as stubby colourless grains, of which the majority are sharply euhedral with simple pyramidal terminations. Less than 5% of the grains are strongly rounded and show remnants of fine surface pitting probably due to abrasion. The euhedral grains commonly show pronounced euhedral growth-zoning. About 70% consist of a zoned core (some very small) surrounded by a thick structureless mantle. In a number of cases, the boundary between core and mantle is rounded and/or discordant, suggesting an hiatus in the growth of the crystals. Needle-like and rounded inclusions are common, particularly in the structureless portions of the grains and structureless whole grains. In contrast, most of the rounded grains are inclusion-free.

Analytical methods

Following normal extraction procedures, zircons were mounted in epoxy, polished until sectioned in half, photographed, cleaned and gold-coated for maximum surface conductivity. Chips of the standard zircon SL13 were mounted near the sample grains in both mounts from the Meishucun section and one of the two from Tiout (Z902). Another fragment of SL13 in a movable plug was analysed successively in all mounts.

U-Th-Pb analyses were made using the SHRIMP I ion microprobe. Data for each spot were collected in sets of either four or five scans through the mass range of Zr_2O^+, Pb isotopes, $^{238}U^+$, ThO^+ and UO^+, at a mass resolution of 5500. The probe diameter was 25 μm and sensitivity ranged from 7 to 30 cps per ppm Pb. A Wien mass filter was installed prior to analysis of mounts Z902 and Z903, to minimize the introduction of OH^- or other impurities by the primary beam: mount Z837 was rerun using the Wien filter. Variable discrimination in $^{206}Pb^+/^{238}U^+$ ratio as the raw, directly counted ratio (denoted in this paper as Pb^+/U^+) was corrected using UO^+/U^+ as described below and previously (Compston *et al.* 1984; Williams & Claesson 1987). The reduced $^{206}Pb/^{238}U$ ratios were normalized to the value 0.0928 for the SL13 standard (equivalent to 572 Ma), based on replicate isotope dilution analyses of milligram-sized fragments by conventional U-Pb dating (Williams *et al. unpubl.*). Analyses of samples and standard were alternated for the closest control of Pb/U ratios.

$^{206}Pb/^{238}U$ ages. Data were processed first by stripping common Pb from the measured compositions, then determining the best-fit 'calibration curve' relating Pb^+/U^+ with UO^+/U^+ for the SL13 analyses in each session. The common ^{206}Pb in the zircons was usually less than 1% of the total ^{206}Pb, so that errors in $^{206}Pb/^{238}U$ due to common Pb corrections were insignificant. After forming the calibration curve for a particular analytical session, each standard analysis was processed as 'unknown' to obtain an empirical measure of the overall reproducibility. The latter was between 2 and 3% (coefficient of variation) and much exceeds ion counting statistics. The origin of this variability is not presently known, but it is primarily an instrumental effect rather than target-variability as it is found in replicate analyses of all zircons. It represents the limiting precision in that session for the unknown zircons and was added in quadrature to the error in $^{206}Pb/^{238}U$ for each analysis arising from its individual ion counting statistics.

Common Pb correction. The amounts of common Pb were estimated by two independent methods. The first was use of the observed $^{204}Pb/^{206}Pb$, which has the advantage of being more direct but is subject to large statistical fluctuations due to the very low contents of ^{204}Pb in clean zircons (*c.* 10 ppb). The second method involved use of the simultaneously measured $^{208}Pb/^{206}Pb$ and Th/U ratios. If U, Th and Pb have remained undisturbed in the analysed sites since crystallization, the radiogenic $^{208}Pb/^{206}Pb$ for each site will correlate exactly with its Th/U along a straight line of known slope through the origin ('^{208}Pb method', Compston *et al.* 1984). The full relationship is

$$\text{radiogenic } ^{208}Pb/^{206}Pb = {}^{232}Th/^{238}U[(e^{\lambda 232T}-1)/e^{\lambda 238T}-1)]$$

The value for the slope changes only very slowly with increasing age T and is well-determined even when T is poorly known. If the zircons contain detectable common Pb the *total* $^{208}Pb/^{206}Pb$ will lie above this correlation line; if they lie below it, we infer that Th/U has been altered at the analysed site and the method therefore is not applicable.

Age estimation by use of the total $^{207}Pb/^{206}Pb$ and $^{238}U/^{206}Pb$. In the usual procedure for common Pb correction, an individual amount of common Pb is separately determined for each analysis and subtracted from the total Pb to give its radiogenic Pb content. Each analysis thereby has an individual value for radiogenic $^{206}Pb/^{238}U$, for which the error must exceed that in the directly-measured $^{206}Pb/^{238}U$ because of error in the correction. For the ion probe, the main error in the latter arises from determination of the individual amounts of common Pb. For example, if the ^{204}Pb count-rate is 20 cpm, there will be an error of 25% in the determined amount of ^{204}Pb due to counting statistics, and hence the same error in the amount of common Pb if ^{204}Pb is used to estimate it. For the same level of common Pb, the corresponding error in ^{208}Pb for low Th-zircon would be $\geqslant 4\%$, so that the amount of common Pb would be determined more precisely.

There is an alternative to the above procedures for estimation of the mean radiogenic ^{206}Pb/^{238}U age. Instead of subtracting common Pb from each analysis according to its individual ^{204}Pb or ^{208}Pb contents, the regression of total ^{207}Pb/^{206}Pb against total ^{238}U/^{206}Pb for the collective data will give an estimate of the age without explicit correction for common Pb in each analysis. For cogenetic samples that have had no later Pb loss, the data will lie, within measurement error, on the mixing line between purely radiogenic Pb at one extreme, and common Pb at the other (Tera & Wasserburg 1972). For samples that have lost Pb at any later time, the data will be displaced to the right hand side of the mixing line and may be recognized as 'outliers' provided they are a minority. The younger intersection of the regression line with Concordia determines their age, and the intersection with the *y*-axis, the common ^{207}Pb/^{206}Pb ratio. In practice, the value for the latter cannot be determined with any accuracy because the contents and range of common Pb in the analysed areas are so small. We have therefore fitted the line through 0.90 ± 0.03 (σ) for common ^{207}Pb/^{206}Pb, using our observation that it is a blend of surface-Pb contamination on the polished mount, which has a 1.6 Ga model age, and indigenous common Pb within the zircon crystals whose model age we take as 550 Ma.

At present, the determination of Cambrian zircon ages using SHRIMP must be based primarily on their ^{206}Pb/^{238}U ratios, rather than the combination of radiogenic ^{206}Pb/^{238}U with radiogenic ^{207}Pb/^{206}Pb. The reason for this is the low precision of ^{207}Pb measurement achievable for zircons with average U contents and ages less than *c.* 1.0 Ga. The small amounts of radiogenic ^{207}Pb formed in such zircons give lower count rates than ^{206}Pb, by a factor of 20, and hence much larger statistical variations. In addition, the ^{207}Pb/^{206}Pb ratio becomes progressively a less sensitive measure of age for younger zircons. Thus ^{207}Pb/^{206}Pb ages by SHRIMP for individual Phanerozoic zircons are often too imprecise to be of value as an independent age estimate. Nevertheless, because of the importance of having an independent, second measure of age, we have assessed the ^{207}Pb/^{206}Pb ages in detail for both the standards and unknowns in each analytical session in order to arrive at a best estimate for the combined data set

Pb hydrides. Because it was not intended initially to use the measured ^{207}Pb/^{206}Pb ratios, special precautions against hydrides, such as very high vacuum at the sample (Long & Hinton 1984) and use of a mass filter in the primary beam, were not taken during work on mounts Z833, Z837/1 and Z902. On some occasions, the apparent radiogenic ^{207}Pb/^{206}Pb diminished with time as the source vacuum improved, which we attribute to a decreasing Pb-hydride contribution. We have assigned any significant elevation of the mean ^{207}Pb/^{206}Pb of the standard per session relative to 0.05913, the value required for the known age of 572 Ma of the standard, as due solely to the presence of ^{206}Pb^{1}H.

The fractional amount of PbH^{+}/Pb^{+}, denoted h, was calculated for each SL13 analysis from the measured ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios, denoted R^7_m and R^8_m, the 'true' radiogenic ratios R^7_* and R^8_*, and the common Pb ratios R^7_c and R^8_c, from the following mass-balance relationship:

$$R^7_m = R^7_* + S\,(R^8_m - R^8_*) + h + h\,R^7_m S$$

where S denotes the slope of the mixing-line between radiogenic and common Pb, $(R^7_* - R^7_c)/(R^8_* - R^8_c)$. R^7_* is taken as 0.05913 and R^8_* is calculated from the measured Th/U in the same SL13 site. Values of h in the standard were used to subtract hydride from the associated sample ratios: They ranged between 0.3% and zero.

Statistical treatment. The data were assessed both assuming a Gaussian error distribution for the final results and, following Rock *et al.* (1987), for *no* assumed error distribution. Rock *et al.* (1987) have emphasized that the arithmetic mean is more sensitive to the presence of outliers than any other estimator of central tendency, and therefore proposed the median as the simplest 'robust' estimator and 95% confidence limits of the median as the best measure of dispersion. Our results here confirm both the sensitivity of the mean to the inclusion of outliers and the comparitive 'robustness' of the median.

Because of their widely differing contents of radiogenic and common Pb, the precision achieved for ^{207}Pb/^{206}Pb varied between different grains, owing both to the range of total ^{207}Pb ions counted and to error-magnification accompanying the common Pb correction. Also, the machine sensitivity varied with operational factors, which further added to the range in ^{207}Pb/^{206}Pb precision. Consequently, we weighted the individual analyses inversely to their variances when combining them to form the mean. Similarly, we adjusted the median by taking the least precise ^{207}Pb/^{206}Pb value as a single observation (equivalent to unit weight), then repeating other entries by the ratio of the inverse of their variance relative to that of the least precise value, rounded to the nearest integer.

In contrast to ^{207}Pb/^{206}Pb, the precision of the ^{206}Pb/^{238}U ages is dominated by the empirical reproducibility for the standard zircon rather than by ion-counting statistics and common Pb correction, so that all observations have approximately the same weight.

Results: Tiout section

A total of 33 individual zircons from the Tiout section were analysed in two mounts Z833 and Z902, plus second areas within seven grains, concurrently with 44 analyses of the SL13 standard. Analytical results are listed in Tables 1 and 2.

Ratios for both the standard and Tiout zircons are plotted against UO^{+}/U^{+} in Fig. 2. Several points are obvious. First, none of the Tiout zircons have greater Pb^{+}/U^{+} than the standard for a given UO^{+}/U^{+}. Secondly, a few have Pb^{+}/U^{+} that is well below the average (34.1, 35.1), which signifies loss of Pb relative to U from these areas, while second areas analysed within the same grains have higher Pb^{+}/U^{+}. Thirdly, the bulk of the Tiout data define an array that is about 9% lower in Pb^{+}/U^{+} than the standard. The simple interpretation of Fig. 2 is that most of the Tiout zircons have lost none of their radiogenic Pb and that they are about 9% younger than the standard. This conclusion is independent of any more sophisticated processing of data.

^{206}Pb/^{238}U ages. The standard error for a single ^{206}Pb/^{238}U result was 3.2% during the analytical session with Z833, with one of the 27 SL13 analyses deleted as an outlier. The processed ^{206}Pb/^{238}U ages for the Z833 Tiout zircons have therefore been assessed on the basis that any variability greater than this must be due to loss of Pb relative to U. Grain 31.1, which differs in texture from the rest, gives concordant ^{206}Pb/^{238}U and ^{207}Pb/^{235}U ages at *c.* 130 Ma (Table 1), strongly suggesting that it is a genuinely younger zircon and possibly a mechanical contaminant picked up in the field or during mineral separation. Areas 34.1, 35.1 and 36.1 also lie significantly below the main group in a plot of ages versus U content (Fig. 3). Excluding these, the remaining 20 analyses agree within error to give a mean age of 520 ± 5 Ma (σ).

For Z902, the population standard error for the SL13 'chip' analyses was 2.5%. Assigning them the same individual precision, all 16 Tiout zircon analyses for mount Z902 agree within error in ^{206}Pb/^{238}U age at 522 ± 5 Ma (σ). No Pb loss or inheritance is detected, and the mean age is indistinguishable from that for Z833: the combined ^{206}Pb/^{238}U age for both mounts is 521 ± 7 Ma (2σ).

Table 1. *U-Th-Pb analyses of zircons from the Tiout tuff, mounts Z833 and Z902*

Grain area	U (ppm)	Th/U	206+/U+	UO/U	204 (ppb)	%*	206/238†	±	207/206†	±	Age 6/38	±	Age 7/6	±
Z902														
1.1	236	0.406	0.2381	7.273	2	0.22	0.0818	21	0.0589	15	507	12	563	55
2.1	313	0.603	0.2465	7.365	2	0.17	0.0826	21	0.0575	14	511	12	510	57
3.1	145	0.410	0.2404	7.171	1	0.22	0.0848	21	0.0582	18	525	13	536	71
4.1	235	0.312	0.2154	6.804	1	0.13	0.0844	21	0.0599	14	522	13	599	51
5.1	475	0.565	0.2186	6.831	0	0.00	0.0848	21	0.0585	12	525	13	550	44
6.1	368	0.587	0.2558	7.257	2	0.11	0.0882	22	0.0576	13	545	13	514	50
7.1	266	0.526	0.2111	6.754	4	0.40	0.0835	21	0.0566	16	517	13	476	63
8.1	337	0.390	0.2056	6.715	1	0.05	0.0824	21	0.0584	12	511	12	543	47
9.1	377	0.730	0.2163	6.785	0	0.02	0.0850	21	0.0587	15	526	13	555	57
10.1	216	0.270	0.1829	6.361	0	0.00	0.0817	21	0.0592	14	506	12	575	53
11.1	152	0.536	0.2104	6.589	0	0.07	0.0876	22	0.0581	21	541	13	534	82
12.1	119	0.386	0.2147	6.713	2	0.32	0.0859	22	0.0549	20	531	13	408	82
13.1	131	0.214	0.2128	6.814	2	0.35	0.0833	21	0.0624	16	516	13	689	56
14.1	447	0.639	0.2168	6.752	2	0.11	0.0860	22	0.0581	12	532	13	532	47
15.1	118	0.252	0.2016	6.614	2	0.48	0.0834	21	0.0595	19	516	13	584	70
16.1	359	0.565	0.2249	6.863	2	0.12	0.0864	22	0.0584	13	534	13	543	49
Z833														
21.1	303	0.448	0.2434	7.241	5	0.39	0.0842	23	0.0576	18	521	14	515	70
22.1	73	0.292	0.2560	7.354	5	1.56	0.0859	24	0.0551	34	532	14	415	144
23.1	221	0.308	0.2520	7.352	5	0.59	0.0847	23	0.0586	19	524	14	551	72
23.2	148	0.472	0.2131	6.924	4	0.76	0.0804	22	0.0609	31	498	13	634	113
24.1	610	0.853	0.2600	7.399	0	0.00	0.0863	23	0.0595	17	533	14	586	63
24.2	289	0.718	0.2208	7.058	5	0.43	0.0802	22	0.0574	25	498	13	505	98
25.1	414	0.660	0.2582	7.432	13	0.77	0.0850	23	0.0545	18	526	14	393	77
25.2	256	0.521	0.2281	7.063	3	0.27	0.0828	22	0.0603	21	513	13	615	76
26.1	288	0.529	0.2563	7.365	2	0.13	0.0858	23	0.0612	20	531	14	647	71
27.1	345	0.726	0.2573	7.414	6	0.46	0.0851	23	0.0650	22	526	14	775	72
28.1	114	0.252	0.2515	7.398	5	1.06	0.0835	23	0.0573	26	517	14	504	105
29.1	297	0.508	0.2554	7.641	5	0.46	0.0797	22	0.0561	20	494	13	457	79
29.2	318	0.591	0.2721	7.600	11	0.81	0.0858	23	0.0549	20	531	14	408	84
30.1	195	0.323	0.2757	7.576	7	0.88	0.0875	24	0.0570	20	540	14	492	80
31.1	373	0.381	0.0636	7.520	6	1.75	0.0205	6	0.0469	32	131	4	452	145
32.1	81	0.199	0.2452	7.344	4	1.26	0.0825	23	0.0563	31	511	14	466	127
33.1	195	0.349	0.2581	7.431	8	0.98	0.0850	23	0.0579	21	526	14	524	84
34.1	490	0.581	0.2080	7.671	121	7.40	0.0644	18	0.0518	67	402	11	274	273
34.2	350	0.462	0.2374	7.175	4	0.26	0.0836	23	0.0555	17	517	14	433	70
35.1	329	0.561	0.2298	7.502	20	1.70	0.0743	20	0.0549	22	462	12	408	93
35.2	351	0.670	0.2561	7.271	4	0.25	0.0879	24	0.0573	18	543	14	504	71
36.1	244	0.479	0.2194	7.180	3	0.32	0.0772	21	0.0584	24	479	13	543	93
36.2	235	0.416	0.2430	7.187	0	0.04	0.0853	26	0.0585	20	528	15	549	77
37.1	724	0.711	0.2254	7.042	13	0.47	0.0823	22	0.0571	14	510	13	497	57

* Percentage of total ^{206}Pb which is common Pb
† Radiogenic Pb
Uncertainties 1σ

Excluding the one obvious outlier (31.1), the median of 39 ^{206}Pb/^{238}U ages for Z902 and Z833 combined is 522 Ma, with the distribution peaked and negatively skewed because of the presence of several areas that have lost Pb. (The mean age for the same group is 516 Ma.) The skewness decreases when 34.1, 35.1 and 36.1 are deleted, giving 524 +2/ −7 Ma for the median (95% limits), indistinguishable from the mean.

^{207}Pb/^{206}Pb ages. Hydrides in the Z833 analyses were low and constant at 0.11 ± 0.03%, presumably because the mount was pumped overnight prior to analysis and run over two successive days. Statistical analysis of the whole data-set detected only two 'outliers' in radiogenic ^{207}Pb/^{206}Pb ratios, both lower than the mean: grain 31.1 is the suspected contaminant described already, and 34.1 has the largest common Pb correction. The mean ^{207}Pb/^{206}Pb age is 517 ± 33 Ma (2σ). The second mount Z902 was loaded and run in a single day; Pb hydride decreases from *c.* 0.3% to 0.1% over the session. All 16 grains have the same ^{207}Pb/^{206}Pb age to within error at 514 ± 30 Ma (2σ), in good agreement with the result for Z833. The pooled mean for the two mounts is 515 ± 21 Ma. With the two outliers deleted, the median ^{207}Pb/^{206}Pb age is 531 + 17/−27 Ma, with the distribution showing positive skewness. The latter vanishes when 27.1 is also deleted, but the median is only very slightly reduced. Making allowance for the unequal analytical precisions, the median increases slightly to 536 + 13/−25 Ma.

The combined ^{207}Pb/^{235}U and ^{206}Pb/^{238}U results are illustrated on the conventional Concordia diagram Fig. 4.

Table 2. *Analyses of the zircon standard SL13 run concurrently with analyses of zircons from the Tiout tuff mounts Z833 and Z902*

Analysis	U (ppm)	Th/U	206+/U+	UO/U	204 (ppb)	%*	206/238†	±	207/206†	±	Age 6/38	±	Age 7/6	±
Z902														
181	223	0.089	0.272	7.484	5	0.49	0.0909	3	0.0584	11	561	2	543	43
1	240	0.087	0.221	6.632	6	0.47	0.0931	2	0.0613	12	574	1	650	41
182	214	0.087	0.265	7.459	4	0.42	0.0892	2	0.0597	11	551	1	591	41
2	236	0.089	0.226	6.795	4	0.36	0.0909	2	0.0604	12	561	1	619	42
183	225	0.087	0.252	7.152	2	0.19	0.0918	2	0.0601	11	566	1	608	40
3	270	0.091	0.203	6.226	2	0.15	0.0970	2	0.0598	11	597	1	596	41
184	218	0.089	0.259	7.181	4	0.39	0.0938	3	0.0602	11	578	2	612	40
4	238	0.088	0.223	6.540	4	0.32	0.0966	3	0.0598	11	595	2	597	42
185	233	0.089	0.241	7.024	3	0.25	0.0908	2	0.0615	11	560	1	657	39
5	249	0.090	0.213	6.357	4	0.33	0.0977	2	0.0613	11	601	1	649	40
186	233	0.090	0.232	6.892	3	0.26	0.0908	2	0.0622	11	560	1	682	38
6	283	0.091	0.186	5.955	4	0.24	0.0975	2	0.0583	11	600	1	542	42
187	227	0.088	0.256	7.156	2	0.19	0.0931	2	0.0602	10	574	1	612	38
7	277	0.092	0.189	6.054	3	0.22	0.0957	2	0.0618	11	589	1	666	40
188	232	0.090	0.225	6.738	6	0.53	0.0922	2	0.0585	12	568	1	549	44
8	255	0.091	0.211	6.405	2	0.18	0.0954	2	0.0579	11	587	1	527	41
189	237	0.088	0.228	6.858	4	0.35	0.0900	2	0.0590	11	556	1	567	42
Z833														
297	228	0.086	0.292	7.542	14	1.19	0.0934	3	0.0589	14	576	2	565	54
298	223	0.087	0.305	7.651	13	1.17	0.0948	4	0.0600	15	584	2	604	54
299	229	0.086	0.287	7.614	10	0.90	0.0902	3	0.0591	14	557	2	571	54
300	235	0.087	0.306	7.435	10	0.74	0.1006	4	0.0595	14	618	2	584	51
301	241	0.085	0.262	7.250	7	0.60	0.0903	3	0.0589	15	558	2	562	56
302	237	0.088	0.299	7.546	21	1.67	0.0955	4	0.0595	15	588	2	586	57
303	225	0.085	0.304	7.664	16	1.39	0.0942	4	0.0616	15	580	2	661	55
304	221	0.087	0.296	7.654	42	3.68	0.0921	4	0.0609	18	568	2	634	60
305	222	0.088	0.277	7.515	15	1.41	0.0892	3	0.0603	17	551	2	616	60
306	239	0.088	0.307	7.650	19	1.57	0.0957	4	0.0612	15	589	2	646	55
307	254	0.088	0.274	7.334	12	0.95	0.0925	3	0.0609	15	570	2	636	53
308	265	0.088	0.287	7.287	16	1.11	0.0980	4	0.0552	14	603	2	419	59
309	223	0.088	0.321	7.761	11	0.90	0.0972	4	0.0591	14	598	2	569	53
310	239	0.087	0.291	7.380	11	0.85	0.0971	4	0.0587	14	598	2	555	53
311	237	0.087	0.300	7.565	10	0.82	0.0954	4	0.0601	14	587	2	606	52
312	246	0.088	0.259	7.160	9	0.76	0.0914	3	0.0607	15	564	2	628	55
313	217	0.086	0.288	7.637	9	0.88	0.0900	4	0.0629	16	555	2	703	54
314	242	0.086	0.278	7.414	10	0.81	0.0919	3	0.0598	14	567	2	596	53
314.1	232	0.087	0.289	7.637	3	0.28	0.0903	3	0.0579	12	557	2	527	47
315	257	0.086	0.284	7.446	2	0.13	0.0930	3	0.0616	12	573	2	661	41
316	259	0.086	0.276	7.367	5	0.42	0.0923	3	0.0601	13	569	2	606	46
317	260	0.088	0.246	7.150	4	0.31	0.0871	3	0.0595	14	538	2	587	50
318	211	0.086	0.301	7.950	13	1.34	0.0872	3	0.0600	16	539	2	603	59
319	249	0.089	0.270	7.153	9	0.69	0.0956	3	0.0624	14	588	2	689	49
320	223	0.086	0.318	7.747	14	1.24	0.0966	4	0.0609	14	595	2	636	49
321	282	0.088	0.255	7.086	6	0.45	0.0920	3	0.0607	12	567	2	629	45
322	262	0.089	0.246	7.033	4	0.32	0.0900	3	0.0603	13	556	2	614	47

* Percentage of total ^{206}Pb which is common Pb
† Radiogenic Pb
Uncertainties 1σ

Results: Meishucun section

$^{206}Pb/^{238}U$ ages. A total of 72 standard and 68 sample analyses were made in four sessions using two different mounts, Z837 and Z903 (Table 3). Z837 was later repolished as Z837/2, cleaned by immersion in dilute HCl, recoated with gold, and those grains with the highest U content were rerun with cryogenic pumping for the best measurement of ^{207}Pb/^{206}Pb.

Five grains (18, 19, 40, 47, and 49, Table 3) are obviously detrital in origin, from both their rounded shapes and their mid-Proterozoic or Archaean ages. Four others (3, 6, 51, and 52) have euhedral shapes but give late Precambrian ages and are clearly older than the main population. The presence of older euhedral xenocrysts in the Meishucun bentonite means that multigrain samples might be contaminated by unnoticed older grains, and if so, could give composite ages that exceeded the magmatic age. Excluding these nine xenocrysts, the measured $^{206}Pb^{+}/^{238}U^{+}$ values for the remaining Meishucun zircons were less than those of the concurrent standard analyses at the same UO^{+}/U^{+}, confirming that their primary

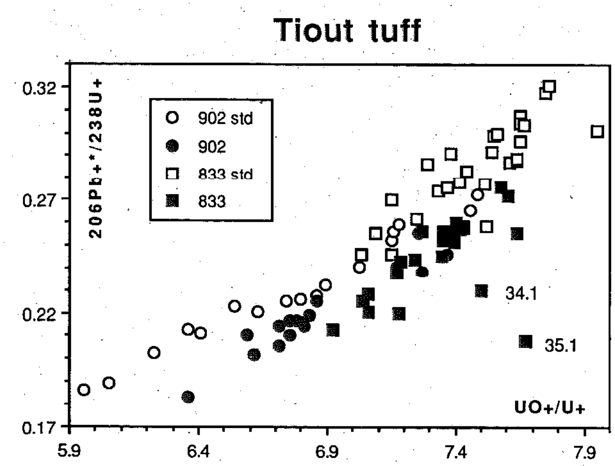

Fig. 2. Comparison of raw ion probe data for standard zircon SL13 and Moroccan tuff zircons. The correlation of collected $^{206}Pb^+/^{238}U^+$ with UO^+/U^+ is due to variable discrimination in the ion probe. Analyses 34.1 and 35.1 are low in $^{206}Pb^+/^{238}U^+$ because of Pb loss. The remainder reflect an age difference of *c.* 9%.

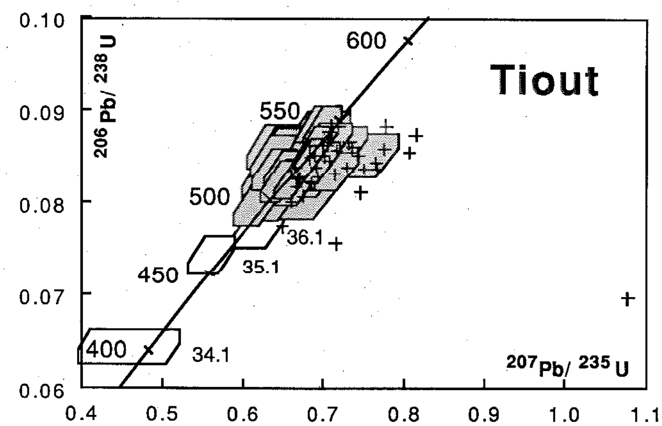

Fig. 4. Wetherill Concordia diagram for zircons from the Moroccan tuff, showing points uncorrected for common Pb (crosses) to the right hand side of the corrected radiogenic points (error boxes). The latter are concordant to within error. Unshaded points have lost Pb relative to U.

age must be younger than the standard. The mean $^{206}Pb/^{238}U$ age for the combined standards is 571 ± 3 Ma (2σ), with coefficient of variation 2.2% per analysis. The median for the same data is 574 +2/−5 Ma.

Relative to this, the $^{206}Pb/^{238}U$ ages of the Meishucun zircons were noticeably variable, indicative of Pb loss (Fig. 5) and in this respect they contrast with the bulk of the Tiout grains. Some areas within grains that show very young $^{206}Pb/^{238}U$ ages (e.g. 17.1, 36, 41.2, 43.2, 48 and 53) have obviously lost radiogenic Pb; others (e.g. 12.2, 14, 22, 23, 37.2 and 54) are indicated as 'young' outliers relative to the main population by use of the Grubb's T-test (Lister 1982). The remaining 41 analyses give a mean age of 525 ± 7 Ma (2σ), although the observed scatter is slightly more than expected from the estimated analytical errors. The actual distribution of the data is shown in Fig. 6, relative to ordered Gaussian distributions that would be expected from two different values for the experimental error. No truncation of data from the older edge of the distribution is warranted, but a reasonable approximation to a Gaussian distribution having error < 3% is obtained when the seven youngest ages are deleted.

Using non-parametric statistics, the most conservative estimate of the age is 518 +8/−28 Ma, given by the median of all analyses except for the nine obvious xenocrysts. Deletion of the slightly older grain (6.1) emphasizes the negative skewness of the distribution as expected for variable Pb loss. Successive deletion of the lowest ages results in a symmetrical distribution of 44 analyses around a median value of 522 +8/−31 Ma (95% limits), which agrees well within its greater uncertainty with the 525 ± 7 Ma result.

$^{207}Pb/^{206}Pb$ ages, '204- corrected'. For Z837/1, hydrides were high at *c.* 0.3%, but only 0.08% for Z837/2 and undetectable for Z903. Common Pb also was high for mount Z837/1 (Fig. 7) relative to Z903 and to the recleaned mount Z837/2. The values

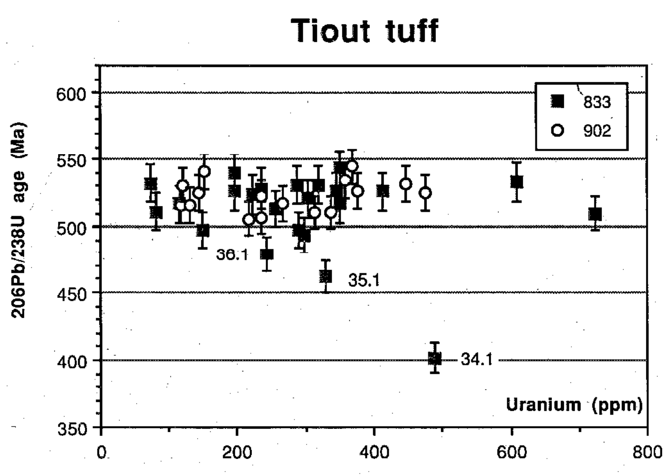

Fig. 3. Moroccan $^{206}Pb/^{238}U$ zircon ages *v.* U contents. The great bulk of the data group at 521 ± 7 Ma, with grains 34, 35 and 36 'younger' due to Pb loss. The correlation of Pb loss with U content is not significant.

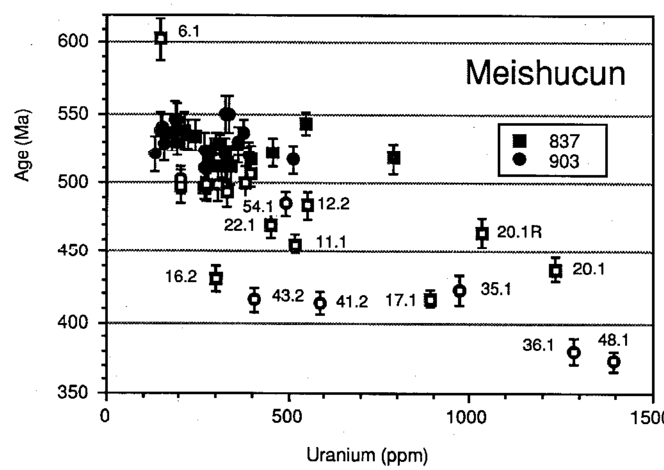

Fig. 5. $^{206}Pb/^{238}U$ ages for zircon from the Meishucun bentonite. Zircon sites that have lost Pb are shown as open symbols, and the older 6.1 is interpreted as a xenocryst. The mean for the remainder is 525 ± 7 Ma and median, 522 +8/−31 Ma.

Table 3. *U Th Pb analyses of zircons from the Meishucun bentonite, mounts Z837 and Z903*

Grain area	U (ppm)	Th/U	206+/U+	UO/U	204 (ppb)	%*	206/238†	±	207/206	±	Age 6/38	±	Age 7/6	±
Z837														
1.1	381	0.647	0.3289	8.573	35	2.06	0.0807	21	0.0539	47	500	12	367	211
1.2	395	0.635	0.1667	5.839	5	0.27	0.0835	17	0.0563	22	517	10	463	91
2.1	275	0.518	0.3299	8.596	19	1.54	0.0805	21	0.0478	49	499	12	93	224
3.1	257	0.822	0.4644	8.564	20	1.25	0.1142	30	0.0597	39	697	17	592	148
4.1	203	0.683	0.3018	8.216	9	1.02	0.0802	21	0.0535	54	497	12	349	246
5.1	328	0.595	0.3353	8.531	2	0.16	0.0830	21	0.0586	36	514	13	554	141
5.2	323	0.609	0.1836	6.094	2	0.11	0.0843	17	0.0589	17	522	10	562	65
6.1	146	0.344	0.4102	8.694	4	0.56	0.0980	26	0.0748	51	603	15	1063	144
7.1	338	0.616	0.3438	8.666	6	0.37	0.0827	21	0.0564	27	512	13	470	111
7.2	242	0.646	0.2080	6.407	4	0.40	0.0864	18	0.0578	22	534	11	523	84
8.1	175	0.625	0.3534	8.567	1	0.18	0.0868	22	0.0646	42	537	13	762	142
9.1	277	0.622	0.3434	8.660	4	0.36	0.0827	21	0.0580	33	512	13	529	130
10.1	211	0.576	0.3245	8.179	5	0.48	0.0870	22	0.0592	43	538	13	573	168
11.1	519	0.432	0.2986	8.722	27	1.28	0.0733	12	0.0582	35	456	7	538	139
11.2	194	0.518	0.2345	6.837	1	0.16	0.0857	18	0.0590	42	530	11	569	162
12.1	301	0.406	0.3050	8.124	20	1.41	0.0856	14	0.0530	45	529	8	331	205
12.2	550	0.412	0.1874	6.401	7	0.29	0.0780	16	0.0584	12	484	10	544	45
13.1	549	0.392	0.3229	8.256	29	1.10	0.0879	14	0.0526	28	543	8	310	127
13.2	457	0.428	0.2303	6.833	4	0.19	0.0843	17	0.0580	11	522	10	529	43
14.1	268	0.475	0.2943	8.264	5	0.39	0.0800	13	0.0601	36	496	8	607	135
15.1	309	0.611	0.2925	7.965	2	0.16	0.0852	14	0.0589	36	527	8	565	141
15.2	281	0.669	0.1766	5.998	2	0.16	0.0838	18	0.0583	42	518	10	540	166
16.1	313	0.550	0.2702	7.767	32	2.29	0.0826	14	0.0498	55	512	8	185	241
16.2	300	0.535	0.1048	5.120	19	1.68	0.0692	15	0.0499	57	431	9	192	246
17.1	890	0.451	0.2477	8.301	19	0.59	0.0668	10	0.0548	18	417	6	405	76
17.2	791	0.609	0.1883	6.195	6	0.16	0.0836	18	0.0565	51	518	11	473	216
18.1	323	0.354	1.2299	8.223	21	0.35	0.3374	54	0.1133	12	1874	26	1854	20
19.1	49	0.170	0.9164	5.504	2	0.16	0.5184	125	0.2165	32	2692	53	2955	24
20.1	1234	0.405	0.1309	5.647	5	0.11	0.0702	14	0.0571	9	438	9	497	34
20.1R	1035	0.389	0.1466	5.785	7	0.16	0.0748	16	0.0566	51	465	10	477	215
21.1	397	0.773	0.1529	5.653	3	0.16	0.0818	17	0.0585	52	507	10	549	206
22.1	453	0.552	0.1629	6.062	3	0.16	0.0756	16	0.0572	14	470	9	501	56
23.1	328	0.711	0.1705	6.047	2	0.16	0.0795	17	0.0586	42	493	10	552	164
Z903														
31.1	269	0.483	0.1947	6.361	2	0.16	0.0844	22	0.0560	42	523	13	453	174
31.2	268	0.464	0.1534	5.753	8	0.66	0.0825	16	0.0564	32	511	10	468	132
32.1	186	0.662	0.2128	6.503	2	0.27	0.0884	22	0.0568	23	546	13	483	91
32.2	153	0.618	0.1755	5.955	0	0.04	0.0872	17	0.0644	15	539	10	754	49
33.1	146	0.397	0.2019	6.379	1	0.09	0.0871	22	0.0579	26	538	13	524	102
33.2	134	0.509	0.1646	5.862	−7	−1.17	0.0841	21	0.0709	158	521	13	955	538
33.3	151	0.514	0.1657	5.720	7	0.93	0.0874	17	0.0526	35	540	10	313	157
34.1	362	0.826	0.2200	6.738	8	0.47	0.0852	21	0.0561	16	527	13	456	65
34.2	377	0.777	0.1685	5.780	8	0.48	0.0867	17	0.0568	18	536	10	484	70
35.1	973	0.320	0.1823	6.880	7	0.21	0.0677	17	0.0581	8	423	10	532	31
36.1	1286	0.467	0.1482	6.550	20	0.48	0.0607	15	0.0585	10	380	9	550	38
37.1	195	0.456	0.2247	6.688	8	0.87	0.0883	22	0.0525	27	545	13	306	122
37.2	274	0.585	0.1601	5.865	9	0.73	0.0801	16	0.0588	27	497	9	558	105
38.1	306	0.716	0.2054	6.694	2	0.16	0.0805	20	0.0588	42	499	12	559	162
39.1	158	0.489	0.2136	6.621	3	0.46	0.0856	22	0.0544	28	529	13	389	118
40.1	245	0.437	1.2342	6.266	1	0.02	0.5517	140	0.2111	8	2832	58	2914	6
41.1	335	0.588	0.2287	6.726	4	0.27	0.0889	22	0.0560	14	549	13	452	56
41.2	588	0.782	0.1428	6.372	24	1.13	0.0663	13	0.0492	24	414	8	157	112
42.1	323	0.562	0.2285	6.716	6	0.36	0.0890	22	0.0558	16	550	13	443	63
42.2	391	0.559	0.1660	6.081	11	0.60	0.0840	16	0.0543	18	520	10	382	76
43.1	323	0.484	0.2248	6.658	8	0.53	0.0891	22	0.0582	18	550	13	539	69
43.2	404	0.501	0.1413	6.269	11	0.73	0.0667	13	0.0577	23	416	8	517	90
44.1	325	0.513	0.2224	6.871	3	0.23	0.0828	21	0.0578	15	513	12	521	57
44.2	691	0.531	0.1133	4.240	−10	−0.23	0.1244	25	0.0623	59	756	14	685	216
45.1	362	0.573	0.1609	5.863	−3	−0.16	0.0857	17	0.0584	42	530	10	544	167
46.1	225	0.671	0.1554	5.720	8	0.75	0.0865	17	0.0493	31	535	10	162	141
47.1	356	0.291	0.6122	6.279	5	0.09	0.2804	54	0.1126	8	1593	27	1842	13

Table 3 *continued*

Grain area	U (ppm)	Th/U	206+/U+	UO/U	204 (ppb)	%*	206/238†	±	207/206†	±	Age 6/38	±	Age 7/6	±
48.1	1392	0.650	0.1264	6.176	11	0.25	0.0595	11	0.0565	9	373	7	474	37
49.1	175	1.736	0.7139	5.782	−2	−0.05	0.3820	77	0.1279	16	2085	36	2069	23
50.1	204	0.605	0.1547	5.816	13	1.41	0.0810	16	0.0491	44	502	10	152	195
51.1	430	0.887	0.2108	5.870	10	0.42	0.1068	20	0.0632	15	654	12	715	51
52.1	406	0.895	0.2598	6.000	8	0.31	0.1257	24	0.0665	14	763	14	821	44
53.1	1810	1.160	0.1361	6.923	25	0.52	0.0494	9	0.0576	11	311	6	516	42
54.1	492	0.744	0.1593	5.942	12	0.57	0.0781	15	0.0571	18	485	9	495	73
55.1	511	0.466	0.1662	5.861	−4	−0.17	0.0835	17	0.0585	54	517	10	547	217

* Percentage of total ^{206}Pb which is common Pb
† Radiogenic Pb
Uncertainties 1σ

found for radiogenic ^{207}Pb/^{206}Pb depend in this instance upon the method used to estimate the amounts of common Pb. The ^{204}Pb method indicated slightly more on the average, with lower ^{207}Pb/^{206}Pb ages as a consequence. The weighted mean ^{207}Pb/^{206}Pb age by this method was 503 ± 24 Ma (2σ), with all magmatic analyses in agreement to within error. However, this is not a reliable result because the distribution of the data is not Gaussian; instead, it is peaked and negatively skewed, indicating the presence of systematic effects and/or outliers. The reason for the skew is error in the common Pb correction. The Tera–Wasserburg diagram (Fig. 8) shows that all magmatic analyses prior to common Pb correction plot either on Concordia or above it: none lie in the 'forbidden' area below Concordia. However, several results do fall below Concordia after correction for common Pb, which is obviously due to an overestimation of ^{204}Pb in those grains, and these correspond to the low ^{207}Pb/^{206}Pb tail in the population. Furthermore, the low ratios nearly all belong to the first two analytical sessions with Z837/1 and Z837/2 when, owing to abnormally low brightness in the ion probe primary source, the machine sensitivity was low by a factor of four compared with the third session (Z837/3)

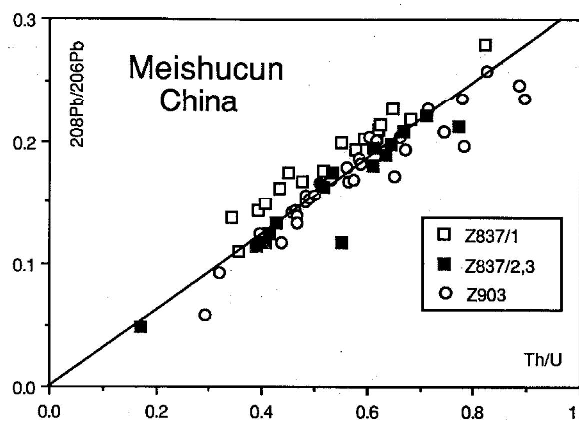

Fig. 7. Measured ^{208}Pb/^{206}Pb *v.* ^{232}Th/^{238}U for the Meishucun bentonite zircons, showing the enhanced surface-related common Pb in mount Z837/1, and several prominent instances of later change in Th/U. The undisturbed radiogenic Pb should plot exactly along the isochron shown.

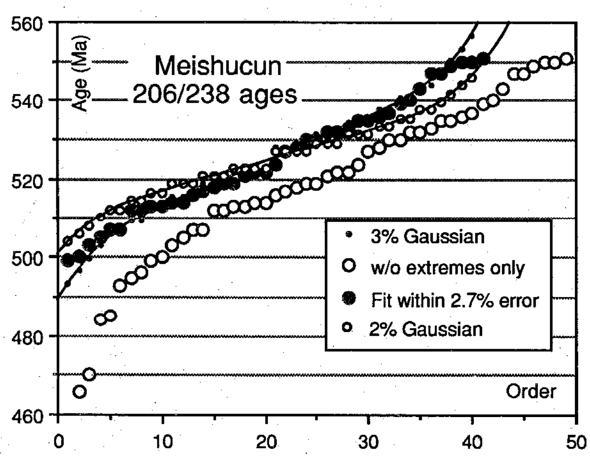

Fig. 6. ^{206}Pb/^{238}U ages of selected zircons from the Meishucun bentonite plotted in ascending order and compared to the distributions expected for modelled Gaussian distributions with standard errors of 2 and 3 percent respectively. The data set is shown both rejecting only extreme values, and rejecting all outliers.

and Z903. This resulted in larger errors for ^{204}Pb and ^{207}Pb due to the smaller number of ions counted. In addition, the Z837/1 and Z837/2 sessions were affected by higher proportions of surface-related common Pb (Fig. 7), as the practice of pre-analysis surface clean-up by rastering the probe was not then routine.

Because of their unequal quality we have screened the ^{207}Pb/^{206}Pb data in several ways, such as deleting all the Z837/1 and Z837/2 results, selecting more precise subsets, and selecting analyses having the lowest common Pb corrections. A statistical assessment of these and other combinations of the ^{207}Pb/^{206}Pb data is listed in Table 4. The medians for the different groupings are systematically greater than the weighted means, evidently due to the skewed ^{207}Pb/^{206}Pb distribution. For the reasons given by Rock *et al.* (1987), we prefer to use the median as the best estimator for ^{207}Pb/^{206}Pb age, and of the groups in Table 4, we prefer group #4 at 522 +8/−31 Ma as the most conservative and apparently the most precise. In any case, both the means and medians for all groups except the unweighted values of the first agree with the preferred ^{206}Pb/^{238}U age of 525 ± 7 Ma, so that the ^{207}Pb/^{206}Pb results are consistent with concordancy in most of the ages.

Table 4. *Statistical assessment of* $^{207}Pb/^{206}Pb$ *ages for Meishucun zircons*

Group	*n*	Weighted mean (Ma)	Median
(a) Common-Pb corrected using ^{204}Pb			
1	42	476	511
2	42	503 ± 24	518 + 8/ −28
3	32	503 ± 24	526 +12/ −40
4	26	501 ± 24	522 + 8/ −31
5	18	509 ± 26	529 +12/ −45
6	32	515 ± 23	526 +17/ −44
7	17	521 ± 34	532 +22/ −31
(b) Common-Pb corrected using ^{208}Pb and Th/U			
8	30	531 ± 32	532 ± 35
9	28	544 ± 25	536 ± 36

Uncertainties shown are 95% confidence limits.
Groups: 1, all except for xenocrysts, unweighted; 2, as above, weighted inversely as the variance of each analysis; 3, ratio with $\sigma \geqslant 0.0045$ excluded, median unweighted; 4, low sensitivity Z837 analyses excluded, weighted; 5, ratios with $\sigma \geqslant 0.0028$ excluded, weighted; 6, ratios having common ^{206}Pb $\geqslant$ 0.60%, excluded; 7, ratios having common ^{206}Pb $\geqslant$ 0.25%, excluded; 8, ratios having significant 'negative' common Pb deleted; 9, as above, but deleting two lowest ratios.

$^{207}Pb/^{206}Pb$ ages, '208- corrected'. Figure 7 shows clearly that Th/U for areas 21.1 and 22.1 is strongly displaced to the right hand side of the isochron, signifying a later increase in Th/U and invalidating use of the ^{208}Pb method for these particular areas. Inspection of the '208-corrected' data (not tabulated here) shows that six other analyses (1.2, 12.2, 17.2, 20.1, 20.1 repeat, 35.1, 36.1, 42.1) have significant 'negative' common Pb and thus also lie to the right hand side. Excluding these, and also 17.1, for which the corrected ^{207}Pb/^{206}Pb at 0.0443 is impossibly low, Table 4 shows good agreement at 531 ± 35 Ma between the weighted mean and the median of the 30 remaining analyses. If the data from mounts Z837/1 and Z837/2 are included, the mean and median ^{207}Pb/^{206}Pb ages become 539 ± 34 Ma from 43 analyses. The large uncertainty easily embraces the ^{206}Pb/^{238}U age. A maximum age for the Meishucun bentonite is given by the older limit to the mean ^{207}Pb/^{206}Pb age at 573 Ma.

The '208-corrected' mean and median are slightly greater than any of the '204-corrected' groups. This might indicate that some of the 30 accepted analyses, in addition to the eight rejected, have suffered increases in Th/U so that the ^{208}Pb method is underestimating their true contents of common Pb. If so, the maximum age given by the '208-corrected' ^{207}Pb/^{206}Pb age will be too great.

Regression of total $^{207}Pb/^{206}Pb$ v. $^{238}U/^{206}Pb$. This procedure treats the majority of the Meishucun zircons as belonging to a concordant magmatic population and views the analytical data as lying on a mixing line whose end-members are common Pb at zero ^{238}U/^{206}Pb and radiogenic Pb on the Concordia curve. As in conventional U-Pb dating, we must assume a value for the common ^{207}Pb/^{206}Pb, taken here as 0.90 ± 0.03 (σ). The regression first seeks to identify outliers that are either too young because of post-crystallization Pb loss, or too old because they are detrital grains or xenocrysts in the original tuff. It then defines the mixing-line and finds the Concordia intersection.

Figure 8 indicates that the nine analyses having ^{238}U/^{206}Pb greater than 13.0, equivalent to ages of 480 Ma and younger, must have lost radiogenic Pb. Deleting these, the regression MSWD becomes 2.79 while analyses 12.2, 14.1, 23.1 37.2 and 54.1 are indicated statistically as other probable Pb-loss outliers. Regression of the remaining 41 analyses gives 1.64 for MSWD, and a Concordia intersection age of 526 ± 7 (2σ), which is the same as the mean ^{206}Pb/^{238}U age.

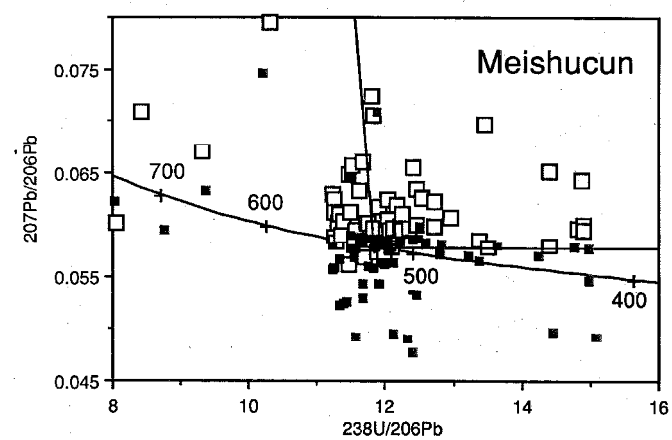

Fig. 8. Tera-Wasserburg concordia diagram for the Meishucun zircon data, showing data with and without common Pb correction (closed and open symbols respectively). The points that lie significantly below the horizontal line representing a ^{207}Pb/^{206}Pb age of 525 Ma reflect overcorrection for common Pb due to sampling errors in ^{204}Pb measurement.

Discussion

The numerical age of the Early Cambrian

Cowie & Harland (1989) and Harland *et al.* (1989) comprehensively reviewed the isotopic ages of rocks relevant to the Cambrian–Precambrian boundary and the biostratigraphical controls on those rocks. They were unconvinced by the arguments for placing the boundary as young as 540 Ma (Odin *et al.* 1983) because they considered the stratigraphical evidence to be equivocal. Nor did they accept the extreme 600 Ma estimate based on Rb-Sr shale isochrons (Ma *et al.* 1984) because of possible distortion of the latter if significant fractions of detrital clay minerals were present. They therefore adopted 570 Ma for the Cambrian–Precambrian boundary as an interim value. It was intended mainly for damage-control, and to be replaced in the future when the present contradictions might be understood and when more conclusive isotopic and stratigraphical data could be expected. We consider that the new zircon U-Pb results from Early Cambrian volcanic rocks, described here and in Cooper *et al.* (this volume), conclusively show that the younger of the above extremes is closest to the truth.

Both the $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ ages for zircons from the Meishucun bentonite are substantially younger than imprecise Rb-Sr whole-rock ages at 580 to 590 Ma for shales from the Badaowan Member within the Meishucun Formation, which disconformably overlies the bentonite at Meishucun (Luo *et al.* 1984; Ma *et al.* 1984). Because detrital mica and feldspar were present in their samples, Ma *et al.* regarded the Badaowan shale ages strictly as *older limits* to the age of deposition so that they do not in fact conflict with the zircon age. On the other hand, the latter is also much younger than well-defined Rb-Sr and U-Pb whole-rock isochrons at 573 ± 7 Ma and 568 ± 12 Ma for shales from the Shuijintuo Formation, some 1000 km distant in the E. Yangtze Gorges area, and a Rb-Sr isochron of 569 ± 12 Ma for shales from its biostratigraphic equivalent in Guizhou Province, the Niutitang Formation (Ma *et al.* 1984). The trilobite-bearing Shuijintuo Formation is placed stratigraphically as *later* in the Early Cambrian than the Meishucun Formation. Because the Shuijintuo and Niutitang results were interpreted by Ma *et al.* (1984) as diagenetic ages, a serious conflict therefore exists with the Meishucun zircon ages. One or other of the two isotopic age determinations must be incorrect if the biostratigraphic correlations between the Meishucun and E. Yangtze Gorge areas are conclusive.

The conflict would be diminished if we could accept that *all* the zircons had lost radiogenic Pb at some unknown later time, despite their well-defined age grouping close to 525 Ma, and that the SHRIMP measurements of $^{207}Pb/^{206}Pb$ age are too imprecise to be useable. We could then suspend judgement on the bentonite age until selected zircons had been analysed successfully by thermal-ionization mass-spectrometry to obtain more accurate $^{207}Pb/^{206}Pb$ ages. However, like the Shuijintuo Formation, the tuffs from the Lie de Vin Formation are also Atdabanian in age, and the fact that the great majority of their zircons have $^{206}Pb/^{238}U$ ages within error at 521 ± 7 Ma seems to us to exclude the possibility of Pb loss. Either the zircons have lost a constant 9% of their radiogenic Pb, or the Shuijintuo shales give spuriously old Rb-Sr isochrons. The pattern resulting from Pb loss as observed on the 20 μm sampling scale of the ion probe, both here and in all other cases examined, is characterized by *variability*. For example, the Meishucun $^{206}Pb/^{238}U$ ages show variability overall in addition to the older group, and the few Tiout zircons that do show Pb loss relative to the others have different $^{206}Pb/^{238}U$ ages when analysed at different sites (e.g. 34.1, 34.2 and 36.1, 36.2 in Table 1). We are therefore very reluctant to accept that nearly all of the Tiout zircons might have undergone nearly constant Pb loss. Instead, we consider that 521 ± 7 Ma is their original magmatic age, and therefore that the Shuijintuo shale age of 573 ± 7 Ma is too great.

Finally, we point out that the 525 ± 7 Ma zircon result is consistent with two recent zircon ages from elsewhere that set a reliable older limit for the Early Cambrian, whereas the 573 Ma shale interpretation is not. They are 565 ± 3 Ma for volcanic rocks within the Mistaken Point Formation, Newfoundland, which contains an Ediacara-type fauna (Benus 1988), and 563 ± 3 Ma for the Ercall Granophyre (Tucker *et al.* 1990), whose structural relationship with the Atdabanian Wrekin Quartzite has at last been demonstrated as unconformable (Cope & Gibbons, 1987). These ages demand that the earliest Cambrian must be younger than *c.* 560 Ma, so that 573 ± 7 Ma for the early Cambrian Shuijintuo Formation cannot be a correct interpretation.

Reinterpretation of previous shale Rb-Sr isochrons

If 525 ± 7 Ma is accepted for the age of deposition of the Meishucun Formation, the question arises as to how in detail the interpretations of the Badaowan Member and Shuijintuo Formation shale 'isochrons' were in error. Table 5 gives the regression results for the published shale isochron data of Luo *et al.* (1984) and Ma *et al.* (1984).

We have sought to clarify this by calculating for each sample the $^{87}Sr/^{86}Sr$ ratio, at the time of deposition, taken as 525 Ma. Fig. 9 shows the results for 25 whole-rock and acid residue analyses of the Badaowan Member. The scatter in the depositional $^{87}Sr/^{86}Sr$ values emphasizes that none of the original 'isochrons' were well-fitted relative to analytical error. This is also evident from the high values for MSWD in the original isochron regressions, the smallest of which is 6.8 for the Ma *et al.* (1984) samples from the Meishucun area, after deleting one analysis as a possible outlier. Such scatter shows that unwanted geological processes have been operative, such as variable inheritence of detrital minerals or redistribution of Rb and Sr after deposition. Furthermore, the scatter remains

Table 5. *Regression parameters for Cambrian shale 'isochrons'*

Data set	*n*	$^{87}Rb/^{86}Sr$ range	MSWD	Age	±2σ	Initial $^{87}Sr/^{86}Sr$	±2σ
Badaowan Member, Meishucun section							
Table 6, Luo *et al.*	11	1.0–8.2	34.9	571	32	0.7115	0.0026
Table 18, Ma *et al.*	13	0.05–7.1	6.8	595	18	0.7074	0.0014
Table 17, Ma *et al.*	12	0.07–6.7	13.0	587	12	0.7073	0.0008
Shuijintuo Formation							
Table 14, Ma *et al.*	17	0.01–9.4	8.5	573	7	0.7090	0.0002
Table 13, Ma *et al.*	12	0.16–9.3	14.1	572	14	0.7088	0.0008

Ages and errors were assessed using the Model 3 solution of McIntyre *et al.* (1966), assuming 1-sigma errors of 0.5% on $^{87}Rb/^{86}Sr$ and 0.00005 on $^{87}Sr/^{86}Sr$.

even if the depositional age of the shales is taken as 580 Ma. We have *modelled* one of several interpretations permitted by the concept of variable inheritance in the shales. Diagenetic illite that formed at 525 Ma in a chemical environment buffered by seawater carbonate will lie along a horizontal line from 0.7089 (as measured for early Cambrian carbonates by Zhang & Compston, *unpubl.*), to some high value for $^{87}Rb/^{86}Sr$ as shown in Fig. 9. The average detrital component is shown as low in $^{87}Rb/^{86}Sr$ but high in $^{87}Sr/^{86}Sr$, reflecting an arbitrarily chosen mean age of 2.0 Ga for its provenance. The measured shales can be modelled as variable mixtures of diagenetic illite, seawater carbonate and 2.0 Ga detritus, with the constraint that the compositions of all the samples must lie within the area in Fig. 9 bounded by the assumed end-members.

The present-day Rb-Sr data for 41 whole-rock, acid leachate and residue samples from the Shuijintuo Formation in Fig. 10 show an apparently excellent definition of an isochron, but the range in depositional $^{87}Sr/^{86}Sr$ ratios calculated for 525 Ma, as well as the high MSWD, shows more realistically the extent of initial variability in $^{87}Sr/^{86}Sr$. Some of the high $^{87}Sr/^{86}Sr$ values at low $^{87}Rb/^{86}Sr$ in Fig. 10 were discarded from the original regressions as 'outliers', but they can be regarded equally well as revealing a genuine variability in the initial $^{87}Sr/^{86}Sr$. Many of the Shuijintuo Formation samples are rich in carbonate, and there is no doubt that most of the observed dispersion in $^{87}Rb/^{86}Sr$ reflects their variable contents of Sr-rich carbonate. On the other hand, nearly all of the Rb in the samples is located in clay minerals considered to be diagenetic in origin (Ma *et al.* 1984). Despite the presence of carbonate, the lack of a well-defined alignment of depositional $^{87}Sr/^{86}Sr$ ratios in Fig. 10 indicates that the Sr fixed in the clay minerals did *not* all equilibrate with carbonate Sr. The highest values for depositional $^{87}Sr/^{86}Sr$ occur in the most illite-rich samples, those which have the highest $^{87}Rb/^{86}Sr$ and which therefore control the slope of the original 573 ± 7 Ma isochron. We infer that these samples must contain significant proportions of illites that are detrital in origin and significantly older, rather than being wholly diagenetic. The inferred presence of such detrital illite is proposed as the fundamental reason why the Shuijintuo Formation isochrons were in error.

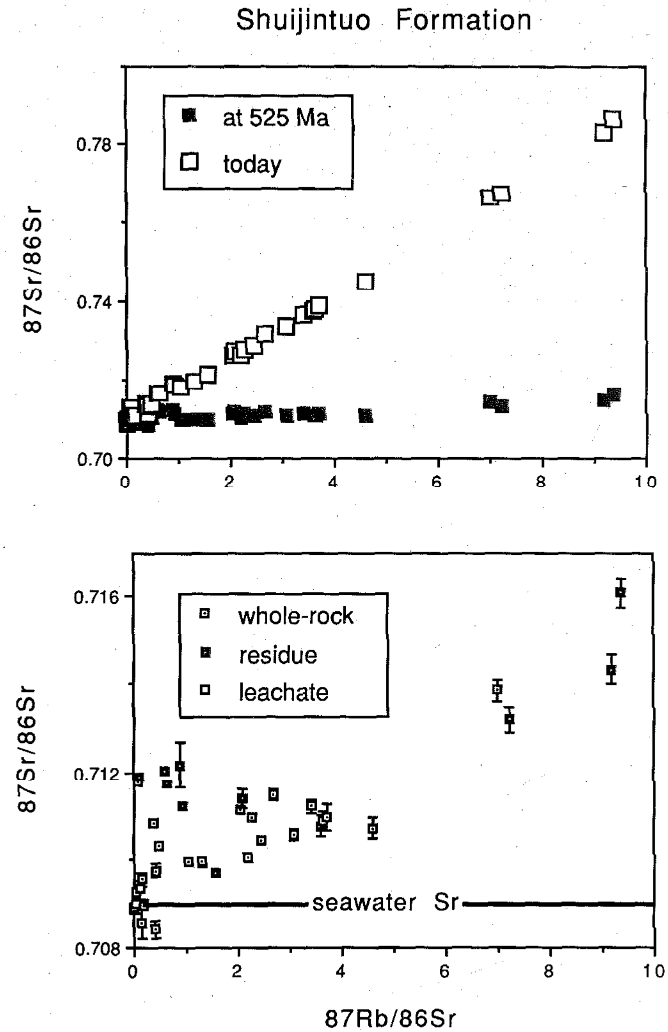

Fig. 10. The present-day and initial $^{87}Sr/^{86}Sr$ calculated for deposition at 525 Ma for whole-rock, acid-leach and residue samples for shales from the Shuijintuo Formation.

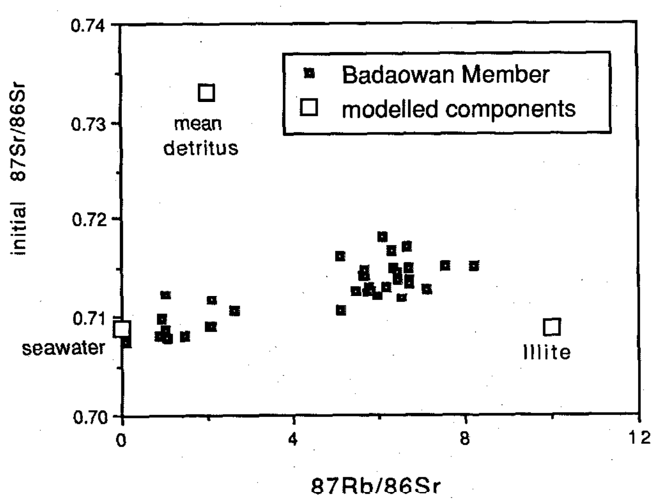

Fig. 9. The initial $^{87}Sr/^{86}Sr$ of whole-rock samples of Badaowan shales (Luo *et al.* 1984; Ma *et al.* 1984) calculated for deposition at 525 Ma. Diagenetic illite of this age buffered by contemporary seawater Sr would lie on a horizontal line on this diagram.

Because only whole-rock data are available, no such analysis as the above can be made of the U-Pb shale data that give the 568 ± 12 Ma age (Ma *et al.* 1984). However, on the assumption that the high U-enrichment of the shales is associated with their high contents of organic carbon, we can infer only that U-fixation in the latter occurred partially before deposition, rather than being wholly a diagenetic process.

Conclusions

(1) Deposition of an early Cambrian tuff within the Lie de Vin Formation at Tiout, Morocco, took place at 521 ± 7 Ma, the mean value for a selected group of $^{206}Pb/^{238}U$ ages within single zircons determined using the SHRIMP ion microprobe. This agrees with SHRIMP ages for Atdabanian volcanics from South Australia (Cooper *et al.* this volume).

(2) An age of 525 ± 7 Ma has been deduced similarly for an early Cambrian bentonite from Meishucun, China. However, Pb loss from the Meishucun zircons is much more pronounced and all zircons in the 525 Ma group might have lost a roughly constant fraction. An older limit for the original age is 539 ± 34 Ma, from their mean radiogenic $^{207}Pb/^{206}Pb$.

(3) It has not been possible to demonstrate with precision that the zircon ages are concordant, owing to limitations in $^{207}Pb/^{206}Pb$ measurement, for Phanerozoic zircons using SHRIMP. The Meishucun zircons are too small to permit conventional analysis of selected single grains to test the 525 Ma interpretation.

(4) On the basis that biostratigraphic correlations between widely separated Cambrian exposures in south China are correct, the above require that whole-rock Rb-Sr and U-Pb ages at *c.* 573 Ma for shales from the Shuijintuo Formation must be too old, presumably owing to the presence of detrital illite and detrital U-bearing mineral phases.

(5) The younger ages indicated here for the early Cambrian support the views of Odin *et al.* (1983) based on isotopic results from less conclusive geological situations in France, Morocco and Israel.

This work is a contribution to IGCP project no. 29 on the Precambrian–Cambrian Boundary, and is dedicated to the memory of the late Richard L. Armstrong.

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