Fig. 2 $^{18}O/^{16}O$ ratios of the water in the different environmental compartments in Jülich. Solid lines characterize the common values, the light bars include extreme values. The flow of water through the local ecosystem is symbolized by the arrangement of the data from top to bottom and the arrows.

between the δ value of water from grapes and from wines could result from an isotope fractionation or an exchange during fermentation. Irrespective of that difference, the wine samples from the FRG have the nearly same δ value. This is in accordance with the fact that the δ values of groundwater (and precipitation) in all wine-growing regions are within the same range.

These results are supported by measurements of wine samples from an area of similar oxygen isotope ratios in the environment12: from the wine district near the American Great Lakes (New York State, Ohio, Michigan). As a result of the different local δ value of precipitation1, the wine samples from California have a higher $^{18}O/^{16}O$ ratio. Their δ value is comparable with results from countries of similar geographical location (Spain, Portugal).

The differences between the δ value of tap water and fruit juice should be large enough to detect the addition of water. Additionally, the geographically distribution of δ values should enable one to trace the region of origin of commercial wines.

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Ion microprobe identification of 4,100–4,200 Myr-old terrestrial zircons

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We report here the existence of detrital zircons from Western Australia which are far older than any known terrestrial rocks. They are from quartzites at Mt Narryer (Fig. 1), a locality which has created interest because of the nearby occurrence of 3,630±40 Myr orthogneisses1. The older zircons were discovered during reconnaissance U–Pb age determinations of zircon concentrates from Archaean metasandstones, using the ion microprobe SHRIMP2–7 at the Australian National University.

Fig. 1 Simplified geological map of the Mt Narryer region showing: ●, Location of dated gneiss with Sm–Nd model ages7 in Myr, +, Location of quartzite samples ('A', OSWA sample site 71923, 'B', OSWA sample sites 71921 and 71924).

The quartzites in which the zircons occur are part of a thick sequence of waterlain clastic metasedimentary rocks. The sequence includes metaconglomerates and quartzites with well preserved cross-bedding despite metamorphism at high amphibolite to granulite facies4. The more argillaceous beds are now biotite–cordierite–garnet–sillimanite–gneiss. The quartzite outcrop is surrounded by banded granitic gneiss (Fig. 1) which gives a Sm–Nd model age of 3,630±40 Myr (ref. 1). This gneiss is intruded by anorthogneiss which contains abundant inclusions of a meta-anorthosite–gabbro–ultramafic suite and gives a Sm–Nd model age of 3,510±50 Myr (ref. 1). The orthogneisses show a more complex deformation history than the quartzites, but the current primary contact relations between these rocks are obliterated by local zones of intense deformation. Samples of anorthogneiss define a Rb–Sr total-rock isochron of 3,350±43 Myr (ref. 1) which may date regional deformation and the amphibolite-to-granulite facies metamorphism of both orthogneisses and quartzites.

The present discovery would have been impossible without the use of SHRIMP. This instrument differs from other ion microprobes mainly in its high sensitivity when operating at high mass resolution, which is achieved by the combination of wide slits and a physically-large secondary mass analyser. Its first geological applications were made in 19805. For U–Pb age determinations5–7, it is operated at mass-resolution 6500 to separate all significant molecular interferences from the Pb, Th and U isotopes. In addition, methods8–10 have been devised for the accurate measurement of Pb/U and Th/U in zircons so that $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}Pb$ ages can be measured, as well as the $^{208}Pb/^{206}Pb$ age. The zircon concentrates were mounted in an epoxy resin disk and polished using diamond paste until the grains were sectioned approximately in half (Fig. 3). The spatial resolution for individual analyses...
was 25 μm and the depth of the spot was ~3 μm after a full analysis lasting ~45 min. The oldest zircons occur in sample 71932 (Fig. 1). The $^{207}$Pb/$^{206}$Pb model ages of two of these zircons are 4,110 Myr (Table 1); the other two are apparently older at 4,180 Myr. One of the former zircons was analysed at seven different places, one of which, 34–1, was detected as being slightly younger than the others relative to experimental precision. However, using the Concordia diagram (Fig. 2), all four grains may be interpreted as having the same age, ~4,150 Myr, and having suffered redistribution of radiogenic Pb during one or more later metamorphic periods; grains 31 and 12 either gained radiogenic Pb or lost U at the analysed spots, a process that is rare in zircons but documented using SHRIMP in unpublished analyses of other zircons. We favour this interpretation because the quartzite has clearly undergone high-grade metamorphism at least as early as 3,300 Myr. In addition, some very discordant zircons (Fig. 2) show evidence of Pb loss at an intermediate age, as well as the usual ‘recent’ Pb loss observed in nearly all zircons.

**Table 1 U–Pb analytical data for >4,100 Myr zircons from Mt Narryer quartzite, GSWA sample 71932**

<table>
<thead>
<tr>
<th>Grain—spot</th>
<th>$%f^*$</th>
<th>$^{206}$Pb/$^{238}$U</th>
<th>$^{207}$Pb/$^{235}$U</th>
<th>$^{206}$Pb/$^{206}$Pb age (Myr)</th>
<th>$^{206}$Pb/$^{206}$Pb</th>
<th>U (p.p.m.)</th>
<th>Th (p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12–2</td>
<td>0.025</td>
<td>0.989 ± 0.018</td>
<td>65.7 ± 1.4</td>
<td>0.4819 ± 0.019</td>
<td>4.190</td>
<td>0.1731 ± 0.011</td>
<td>275 ± 10</td>
</tr>
<tr>
<td>31–2</td>
<td>0.042</td>
<td>0.934 ± 0.023</td>
<td>61.6 ± 1.6</td>
<td>0.4782 ± 0.008</td>
<td>4.180</td>
<td>0.2829 ± 0.018</td>
<td>332 ± 9</td>
</tr>
<tr>
<td>34–1</td>
<td>0.023</td>
<td>0.870 ± 0.049</td>
<td>54.1 ± 3.4</td>
<td>0.4507 ± 0.031</td>
<td>4.090</td>
<td>0.0341 ± 0.012</td>
<td>399 ± 18</td>
</tr>
<tr>
<td>34–2</td>
<td>0.063</td>
<td>0.898 ± 0.027</td>
<td>56.8 ± 1.7</td>
<td>0.4581 ± 0.03</td>
<td>4.110</td>
<td>0.0389 ± 0.04</td>
<td>389 ± 12</td>
</tr>
<tr>
<td>34–3</td>
<td>0.053</td>
<td>0.799 ± 0.036</td>
<td>50.8 ± 1.5</td>
<td>0.4605 ± 0.038</td>
<td>4.120</td>
<td>0.0292 ± 0.04</td>
<td>538 ± 39</td>
</tr>
<tr>
<td>34–4</td>
<td>0.065</td>
<td>0.879 ± 0.033</td>
<td>55.5 ± 2.2</td>
<td>0.4574 ± 0.013</td>
<td>4.110</td>
<td>0.0280 ± 0.04</td>
<td>568 ± 14</td>
</tr>
<tr>
<td>34–5</td>
<td>0.172</td>
<td>0.879 ± 0.011</td>
<td>56.3 ± 2.5</td>
<td>0.4644 ± 0.014</td>
<td>4.130</td>
<td>0.0295 ± 0.07</td>
<td>461 ± 32</td>
</tr>
<tr>
<td>34–6</td>
<td>0.057</td>
<td>0.877 ± 0.044</td>
<td>55.8 ± 2.8</td>
<td>0.4614 ± 0.06</td>
<td>4.120</td>
<td>0.0263 ± 0.03</td>
<td>589 ± 12</td>
</tr>
<tr>
<td>34–7</td>
<td>0.094</td>
<td>0.810 ± 0.022</td>
<td>51.2 ± 1.8</td>
<td>0.4583 ± 0.014</td>
<td>4.110</td>
<td>0.0396 ± 0.06</td>
<td>459 ± 10</td>
</tr>
<tr>
<td>63–1</td>
<td>0.095</td>
<td>0.790 ± 0.043</td>
<td>51.3 ± 3.0</td>
<td>0.4703 ± 0.023</td>
<td>4.150</td>
<td>0.2039 ± 0.02</td>
<td>228 ± 8</td>
</tr>
<tr>
<td>63–2</td>
<td>0.385</td>
<td>0.809 ± 0.099</td>
<td>51.2 ± 6.7</td>
<td>0.4581 ± 0.06</td>
<td>4.110</td>
<td>0.1469 ± 0.02</td>
<td>564 ± 61</td>
</tr>
</tbody>
</table>

The uncertainty shown is ±1σ and refers to the last two digits; it may include real dispersion in the target during analysis, as well as experimental error.

* Mean value of initial $^{206}$Pb/total $^{206}$Pb for 21 data cycles, based on the observed $^{204}$Pb and assuming mean terrestrial Pb at 4,100 Myr.
of regional metamorphism inferred from Rb–Sr analyses of the nearby orthogneisses. We therefore view both the 3,100 and 3,300 Myr zircons as having grown during later metamorphism, and infer that the sedimentation is earlier than 3,300 Myr. If the older zircons are regarded as detrital, a maximum limit to the age of sedimentation is set by the 3,500-Myr group. None of the zircons show the small-scale surface weathering that is characteristic of mechanical abrasion. Most of the crystals are rounded, but this is probably a metamorphic effect. Textural study and further ion microprobe analyses of zircons in situ in the quartzite will be necessary to confirm these interpretations.

The veracity of the ion microprobe for measurement of 207pb/206pb and Pb/U is demonstrated by our cited results for the Isua acid volcanics (Fig. 2), which show identical ages and the same small range of Pb loss as the new results of Baasgaard et al., who used mass-spectrometric isotopic dilution on multi-grain samples. Table 1 shows that the measured Th/U in the various zircon grains is highly correlated with the radiogenic 207pb/206pb, demonstrating both the accuracy of the ion microprobe determinations of Th/U and the presence of large differences in Th/U both between and within single grains. However, there are also second-order effects in the Th–Pb systematics which indicate later redistribution of radiogenic Pb and/or Th. These effects, together with 208pb/232Th ages, will be discussed in more detail elsewhere.

The present results demonstrate the former existence of Archaean rocks at least as old as 4,100 Myr in the vicinity of Mt Narrey. It is possible that intact remnants of these rocks may yet be found.

The suitability of Mt Narrey quartzites for this study was suggested by A. F. Trendall and D. Gee; their invitation to visit Western Australia and their participation in field work is gratefully acknowledged. I.R.W. and J.S.M. publish with the permission of the director of the Geological Survey of Western Australia. D.O.F., T.R.I. and P.D.K. hold scholarships from the Commonwealth Fellowship and Scholarship Plan, The Australian National University, and the John Conrad Jaeger bequest, respectively.

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Inter-layered clay
stacks in Jurassic shales

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As the average shale contains ~60% clay minerals, an understanding of the physical and chemical characteristics of these minerals is central to the question of burial diagenetic reactions and hydrocarbon generation. Much existing evidence concerning burial diagenesis relies on X-ray diffraction (XRD) data, particularly of the clay-size (<2 µm) fraction of shales. Here we use scanning electron microscopy (SEM) in the backscattered electron (BSE) mode, together with energy-dispersive X-ray microanalysis (EDXA), to show that Lower Jurassic shales from the North Sea Basin contain large numbers of clay mineral stacks up to 150 µm in size. By studying polished shale sections with BSE and EDXA, the size, shape orientation, textural relationships and internal compositional variations of the clays can be observed in situ. We present here preliminary evidence which suggests that the clay stacks studied are authigenic, and may have formed at shallow burial depths during early diagenesis.

Clay minerals in shales have been studied for many years using XRD and, more recently, transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). XRD is highly important for identifying and quantifying the structural types of clay minerals present, but this technique provides little information about crystal size, shape, textural relationships or chemical composition. Consequently the morphological and textural properties of clays in shales have been relatively neglected. As XRD is conventionally carried out on the <2-µm fraction after the rock has been disaggregated by ultrasonic or other methods, this procedure may overlook clay minerals which are present as silt or sand-size grains. Attempts to explain the mineral transformations which occur during diagenesis have commonly ignored the possibility that clay minerals might increase significantly in size.

TEM and STEM can provide useful information about the size, shape and textural relationships of small crystals in mudrocks, but the area of specimen which can be examined is extremely small and an overall impression of the rock microfabric is difficult to obtain. It is often difficult to relate TEM observations to those made at higher magnifications with the optical microscope. SEM examination of polished mudrock sections using backscattered electrons provides a means of bridging the gap between optical microscopy and TEM. The emission of backscattered electrons from a polished surface is strongly dependent on the average atomic number of the target, such that different minerals may display contrasting grey levels in the BSE SEM images. This technique has three principal advantages compared with optical microscopy: (1) higher resolution; (2) subtle variations in chemical composition can be detected with BSE which would be missed with the optical microscope; and (3) the nature of the chemical variations can be determined directly using an X-ray analyser attachment on the SEM.

We have recently examined several polished sections of Lower Jurassic (Lias) shales from the Yorkshire coast and

![Fig. 1 BSE micrograph of a polished section of Lias shale showing clay mineral stacks orientated sub-parallel to bedding. Several types of clay are present including chlorite (C), illite-smectite (I–S) and kaolinite (K). The finer-grained matrix is also a mixture of these minerals. Also visible in this picture are quartz (Q), albite (A), and zoned carbonate crystals (D).](image-url)