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To link to this article: https://doi.org/10.1080/00288306.1988.10417768

Published online: 21 Dec 2011.

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An iridium-rich calcareous claystone (Cretaceous–Tertiary boundary) from Wharanui, Marlborough, New Zealand

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Abstract Abundances for iridium and 18 other elements were determined in samples from a Cretaceous–Tertiary (K-n boundary sequence near Wharanui, Marlborough Province, South Island, New Zealand. Physical correlation and biostratigraphic evidence pinpointed a 20 mm layer of calcified boundary clay containing highly anomalous concentrations of iridium (33 ng/g [ppb]) and other siderophiles such as nickel (497 µg/g [ppm]), chromium (140 µg/g), and cobalt (137 µg/g). Concentrations expressed on a decalcified (CaCO$_3$-free) basis to avoid false anomalies caused by redissolution of carbonates after deposition are: 62 ng/g, 929 µg/g, 262 µg/g, and 256 µg/g, respectively. The integrated iridium deposition is 132 ng/cm$^2$ after correction for background, and is almost exactly the same as the 134 ng/cm$^2$ recorded for the Flaxbourne River K-T boundary sequence which is virtually complete. This indicates the probable completeness of the Wharanui sequence, though thorough paleontological confirmation will

Keywords Cretaceous; Tertiary; boundary; Wharanui; iridium; siderophile elements; chalcophile elements

INTRODUCTION

Since the discovery by Alvarez et al. (1980) of an iridium anomaly in Cretaceous–Tertiary (K-T) boundary clays and shales at Gubbio (Italy), Stevns Klint in Denmark, and Woodside Creek in New Zealand, there has been widespread discussion concerning the theory that this iridium may have resulted from the impact of a large extraterrestrial body (or bodies) upon the Earth some 66 m.y. ago, an impact coincidental with the extinction of 70% of all living species. Since this initial discovery, iridium-rich boundary clays have been identified at over 75 sites worldwide (Alvarez 1986). In New Zealand, the Woodside Creek site has been extensively studied (Strong 1977; Brooks et al. 1984), and a further four iridium-rich boundary sites have been reported at Waipara (Strong 1984a; Brooks et al. 1986a), Chancet Rocks (Strong 1984b; Brooks et al. 1986a), Needles Point (Strong 1985; Brooks et al. 1986a), and Flaxbourne River (Strong et al. 1987). The latter is one of the most complete K-T boundary sequences yet recorded anywhere. The geochemistry of most of the New Zealand K-T sites has been reported by Brooks et al. (1986b).

Except for the Waipara site, the remaining four iridium-rich boundary sequences are located within an area of about 200 km$^2$, south of Ward (Fig. 1), a
village situated some 40 km south of Blenheim, Marlborough, South Island, New Zealand.

A new outcrop of the Cretaceous–Tertiary boundary within the above area was first reported to one of us (C.P.S.) by J. Morris of the University of Canterbury, Christchurch. He recognised a characteristic bed of black argillaceous limestone just above the K-T boundary, similar to the bed marking this boundary at Chancet Rocks some 15 km farther north (Fig. 1). This paper reports the geochemistry and preliminary biostratigraphy of this new boundary site.

SITE LOCATION GEOLOGY AND BIOSTRATIGRAPHY

The Wharanui K-T boundary sequence is exposed on the shore platform about 150 m south of the mouth of Woodside Creek (P30/997185)* and is accessible only at low tide. Access is best achieved by walking 1.5 km south of Wharanui Station along the beach.

Nine distinct lithic units (Table 1), dipping eastward at c. 88°, can be recognised within the sequence. The rocks are highly indurated. The lithified K-T boundary calcareous claystone contains 46% CaCO₃ compared with only 26% at the Flaxbourne River K-T site. The high induration explains the resistance of this sequence to marine weathering and erosion.

The lithological sequence at Wharanui is very similar to that at the Chancet Rocks site (Strong 1984b) with a characteristic black limestone, unique within the succession, marking the first appearance of Tertiary rocks. Correlation of lithological units is the main criterion for recognition of the boundary at this site. The rocks are extremely hard and nearly impossible to process for paleontological studies. Only meagre results have been obtained from samples collected to date. However, the upper Haumurian species Globigerinelloides volutus, Heterohelix globulosa, and Rugoglobigerina spp. have been identified from P30/f267 at the top of unit 5 (Table 1). P30/f266 from the boundary “clay” (unit 6) yielded only rare specimens of Quadrimorpha allomorphinoides. Total stratigraphic range of this species is from Haumurian to uppermost Dannevirke Series, but its unusual abundance is a characteristic of the boundary clay at Chancet Rocks.

ANALYTICAL METHODS

The abundances of 18 elements (Al, As, B, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, and Zn) were determined at Massey University by use of plasma emission (ICP) spectrometry using an ARL 34000 instrument. Samples were decomposed by a 1:1 mixture of nitric and hydrofluoric acids, taken to dryness, and redissolved in 2M hydrochloric acid before instrumental quantification.

*Grid reference based on the 1:50 000 topographical map series NZMS 260.
†Geological Society of New Zealand Fossil Record File locality number.
Iridium concentrations were determined at Los Alamos using radiochemical neutron activation analysis (RNAA). This procedure involved decomposition of the samples with a 1:1:1 HF/HNO₃/HClO₄ mixture and separation of the iridium (plus added carrier) by ion-exchange chromatography. The limit of detection was about 0.001 ng/g (ppb).

The abundances of 19 elements in 5 samples from the Wharanui K-T sequence (Table 2) are expressed on a decalcified (CaCO₃-free) basis in order to avoid the appearance of false anomalies due to redissolution of carbonates after their original deposition.

**RESULTS**

A feature of the geochemical data is the enrichment of iridium and four other siderophiles (Fe, Ni, Co, and Cr) in the boundary sample (f267). The iridium content of 62 ng/g (ppb) is extremely high and compares with 70 ng/g at Woodside Creek (Brooks et al. 1984). It is much higher than values obtained at other K-T boundary sites in New Zealand such as 21 ng/g at Flaxbourne River (Strong et al. 1987), 4.6 ng/g at Chancet Rocks (Brooks et al. 1986a), 5.4 ng/g at Needles Point (Brooks et al. 1986a), and 0.49 ng/g at Waipara (Brooks et al. 1986a). The integrated iridium deposition (total nanograms in a section of sequence with a surface expression of 1 cm²) or surface density (after correction for background) at Wharanui is 132 ng/cm² for the −30 to +100 mm interval (i.e., where zero is taken as the top of the Cretaceous) and is almost identical to the 134 ng/cm² deposited at the Flaxbourne River site (Strong et al. 1987) for approximately the same interval. The latter sequence is believed to be one of the most complete so far recorded and compares with such classic K-T sequences as Caravaca, Spain (Smit & Hertogen 1980), and El Kef in Tunisia (Perch-Nielsen et al. 1982). Because of the similarity in the integrated iridium levels, it is reasonable to suppose that the Wharanui sequence may also be relatively complete, although the apparent difficulty of recovering identifiable microfossils may hinder paleontological confirmation.

In addition to iridium, the other siderophiles are considerably enriched in the boundary clay relative to the other lithological units. This is particularly evident for nickel (929 µg/g), chromium (262 µg/g), cobalt (256 µg/g), and iron (2.80%). The Wharanui K-T sequence also shows an enrichment of chalcophile elements in the boundary layer. High concentrations of arsenic, copper, molybdenum, and zinc are consistent with similar findings at other K-T boundary sites in New Zealand and elsewhere (Strong et al. 1987).
DISCUSSION

The Ni/Cr/Ir ratio (Table 2) in the boundary layer is quite close to that of meteorites and is very different from that of crustal or mantle rocks. This lends support to the Alvarez et al. (1980) theory of an asteroidal (or cometary) impact having occurred at the end of the Cretaceous. The countervailing view of Officer & Drake (1985) proposes a mantle source for anomalous iridium due to a hypothetical period of massive volcanic activity at this time. This theory is not supported by our data, not only because of the Ni/Cr/Ir ratios, but because the Deccan Traps, suggested as a source for iridium, could only have supplied about 6% of the iridium deposited worldwide (Strong et al. 1987).

If the concept of an asteroidal/cometary impact is accepted, the extraterrestrial component (ETC) in the Wharanui sequence can be determined as being 1.43%, assuming 4400 ng/g iridium in chondrites, an integrated iridium mass of 132 ng/cm², and a rock density of 2.5. This compares with values of 1.6% for Gubbio and 21% for Stevns Klint as determined by Kyte & Wasson (1982), and 0.6–2.5% for freshwater sites in the Raton Basin (Gilmore et al. 1984).

The high concentrations of chalcophile elements indicate that conditions were strongly anoxic at the end of the Cretaceous since the chalcophile elements readily form insoluble sulphides under such conditions. A similar pattern was also observed by Strong et al. (1987) at the Flaxbourne River boundary sequence.

The discovery of an iridium-rich K-T boundary “clay” layer at Wharanui raises to six the total number of such sites in New Zealand so far discovered. To date, none has been found in North Island, despite the presence of a boundary sequence (with the lowermost Danian missing) at Te Uri (Brooks et al. 1986b). The Wharanui site seems to have greater geological and geochemical affinities with those at Chancet Rocks and Flaxbourne River, rather than with the nearby Woodside Creek sequence.

Table 2 Elemental abundances (CaCO₃ free) in rock samples from the Wharanui Cretaceous-Tertiary boundary sequence. Column headings in parentheses give the location in millimetres of the sample in the stratigraphic sequence (zero is the top of the Cretaceous).

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>f267* (30 to 0)</th>
<th>f266 (0 to +10)</th>
<th>f268 (+20 to +100)</th>
<th>f269 (+1100)</th>
<th>f270 (+1300)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃ (%)</td>
<td>89.4</td>
<td>46.5</td>
<td>45.0</td>
<td>53.0</td>
<td>51.3</td>
</tr>
<tr>
<td>Al (%)</td>
<td>2.75</td>
<td>3.27</td>
<td>1.13</td>
<td>2.23</td>
<td>2.03</td>
</tr>
<tr>
<td>As (±g/g)</td>
<td>&lt;10</td>
<td>50</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>B (%)</td>
<td>3.88</td>
<td>0.58</td>
<td>0.34</td>
<td>0.59</td>
<td>0.57</td>
</tr>
<tr>
<td>Co (±g/g)</td>
<td>52</td>
<td>256</td>
<td>13</td>
<td>13</td>
<td>4</td>
</tr>
<tr>
<td>Cr (±g/g)</td>
<td>35</td>
<td>262</td>
<td>11</td>
<td>11</td>
<td>25</td>
</tr>
<tr>
<td>Cu (±g/g)</td>
<td>&lt;10</td>
<td>121</td>
<td>25</td>
<td>21</td>
<td>47</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>1.63</td>
<td>2.80</td>
<td>0.36</td>
<td>0.66</td>
<td>0.66</td>
</tr>
<tr>
<td>K (%)</td>
<td>1.28</td>
<td>1.03</td>
<td>0.30</td>
<td>0.65</td>
<td>0.63</td>
</tr>
<tr>
<td>Mg (%)</td>
<td>1.16</td>
<td>0.83</td>
<td>0.12</td>
<td>0.49</td>
<td>0.39</td>
</tr>
<tr>
<td>Mn (%)</td>
<td>0.99</td>
<td>0.11</td>
<td>0.06</td>
<td>0.11</td>
<td>0.08</td>
</tr>
<tr>
<td>Mo (±g/g)</td>
<td>&lt;10</td>
<td>39</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Na (%)</td>
<td>4.52</td>
<td>1.18</td>
<td>0.68</td>
<td>1.20</td>
<td>1.12</td>
</tr>
<tr>
<td>Ni (±g/g)</td>
<td>215</td>
<td>929</td>
<td>38</td>
<td>25</td>
<td>12</td>
</tr>
<tr>
<td>P (±g/g)</td>
<td>3200</td>
<td>676</td>
<td>222</td>
<td>526</td>
<td>572</td>
</tr>
<tr>
<td>Pb (±g/g)</td>
<td>&lt;10</td>
<td>37</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Sr (±g/g)</td>
<td>3820</td>
<td>439</td>
<td>444</td>
<td>632</td>
<td>641</td>
</tr>
<tr>
<td>Zn (±g/g)</td>
<td>&lt;100</td>
<td>935</td>
<td>691</td>
<td>479</td>
<td>164</td>
</tr>
<tr>
<td>Ir (±g/g)</td>
<td>5.1</td>
<td>62</td>
<td>4.2</td>
<td>–</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Ni/Cr/Ir in f266 = 15 000/4250/1
in chondrites = 33 000/5714/1
in Earth’s crust = 750 000/1 000 000/1
in Earth’s mantle (dunite DTS-1—data from Gilmore et al. 1984) = 5 301 000/2 391 000/1

*Geological Society of New Zealand Fossil Record File locality number for NZMS 260 map P30.
REFERENCES


