Iridium Anomaly in the Upper Devonian of the Canning Basin, Western Australia

Abstract. *A moderate iridium anomaly, about 20 times the local background, has been found in Upper Devonian rocks in the Canning Basin. It occurs at or near the Frasnian-Famennian boundary, which is known to be associated with a major mass-extinction event of global extent. The anomaly occurs in an extremely condensed limestone sequence laid down under quiet deepwater conditions. Its occurrence suggests a causal link with some form of meteoroid impact. Moreover, carbon isotope data indicate that a large reduction in biomass could have occurred at this level. However, the anomaly coincides with a stromatolite bed containing the fossil cyanobacterium* Frutexites; *iridium, platinum, iron, manganese, cobalt, arsenic, antimony, and cerium are preferentially concentrated in filaments of this organism, with concentrations ranging from two to five times that of the matrix. It is possible that* Frutexites *extracted these elements directly from seawater, without the need for their derivation from an extraterrestrial source.*

A major global extinction of shallow-water metazoans occurred at or near the end of the Frasnian Age of the Late Devonian (~365 million years ago), at a time when warm shallow seas covered much of the world's continental areas and organic reefs were widespread (*1*). The extinction was marked by the abrupt disappearance of most shallow-water taxa and a large decrease in biomass, including the great majority of reef-building stromatoporoids and corals and most brachiopods and fish. The succeeding early Famennian was characterized by markedly diminished faunas, and reef building ceased in most areas. The cause of this mass extinction has not been established; McLaren proposed that impact by a large extraterrestrial body could have been responsible, whereas others have suggested abrupt changes in temperature or sea level as the causative factors (*1, 2*).

Alvarez *et al.* (*3*) discovered that the horizon marking the major extinction at the Cretaceous-Tertiary (K/T) boundary is characterized by anomalously high concentrations of iridium and other platinum-group elements, and this observation has since been confirmed in many parts of the world in both marine and continental sequences. The iridium anomaly is regarded as strong evidence that the extinction is a consequence of the impact on Earth of a large asteroid or comet, the iridium being derived from the fallout material. Raup and Sepkoski have recently claimed that there is a 26-million-year periodicity in extinction events through the Mesozoic and Cenozoic, and it has been suggested that this is related to periodic showers of comets entering the solar system, each lasting up to a million years (*4*).

The extinction at or near the close of the Frasnian is one of the largest known, and it is consequently important to investigate whether this represents another impact-related biological crisis. Geochemical studies to test the hypothesis were recently carried out on samples collected across the Frasnian-Famennian boundary at three localities in New York and at the type locality in Belgium, but no iridium anomalies were found (*5*). It is possible that the absence of anomalies in these areas is due to local preservation factors. Therefore, we decided to test a locality in the Canning Basin of Western Australia where all conodont subzones of the late Frasnian and early Famennian are preserved in a strongly condensed sequence laid down under quiescent deepwater conditions. It was felt that these conditions might favor preservation of any fallout material.

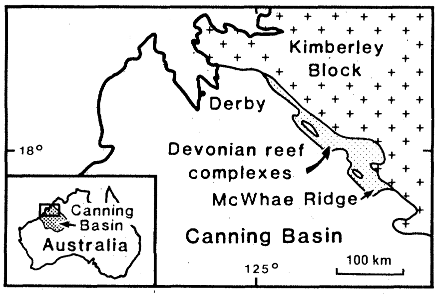

Fig. 1. Map of a part of northwestern Australia showing the outcrop belt of the Devonian reef complexes and the location of the McWhae Ridge section that was sampled for geochemical analysis.

The northern margin of the Canning Basin (Fig. 1) is marked by a well-exposed belt of Middle and Upper Devonian reef complexes, about 300 km long, adjoining Precambrian rocks of the Kimberley Block (*6*). These complexes of Givetian, Frasnian, and Famennian age consist of reef-fringed limestone platforms that formed close to sea level. They are flanked by steeply dipping marginal-slope limestones that interfinger with basin deposits laid down in water up to several hundred meters deep.

The Givetian and Frasnian reefal platforms in the Canning Basin were built by stromatoporoids, cyanobacteria (blue-green algae), and corals. The extinction event at or near the close of the Frasnian resulted in the disappearance of most stromatoporoids, all reef-building corals, and most brachiopods and other shallow-water organisms. Although reef growth continued strongly in the Canning Basin during the succeeding Famennian Age, the surviving reef builders were almost exclusively cyanobacteria. Conodonts in the basin and lower marginal-slope deposits allow precise correlation with zones and subzones of the standard European Upper Devonian. Diagnostic conodonts do not extend into the reefal platforms, whose dating is consequently less precise.

A locality was selected for geochemical study in the Virgin Hills Formation on the west flank of McWhae Ridge, near the southeastern end of the outcrop belt (Fig. 1). At this locality the formation was laid down over a drowned spine of Frasnian reef (*7*). The section sampled is in lower marginal-slope facies, consisting of reddish limestones that were deposited in water depths that probably exceeded 100 m, about 25 km from the mainland shore. Conodonts have been used to date this section (*8*), most recently by Druce, and his zonation in relation to the analyzed section is shown in Fig. 2.

Samples were collected as a continuous channel in 1- to 2-cm intervals over 5.5 m of vertical section, from 1.5 m above to 4.0 m below a selected datum that coincides with the base of the Upper *Palmatolepis triangularis* Subzone; 95

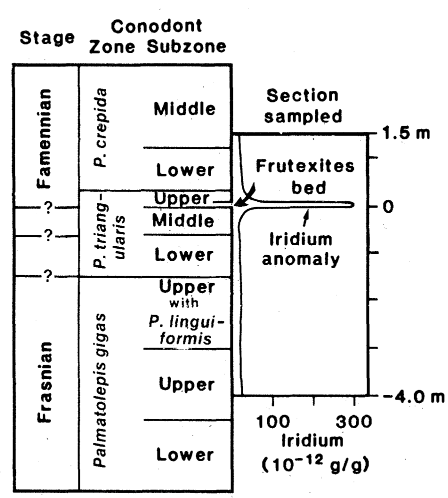

Fig. 2. Diagram showing the Frasnian and Famennian stages of the Upper Devonian and the relation of the iridium anomaly in the section sampled to the conodont zones and subzones.

samples were analyzed for iridium and other elements, and 52 for carbon and oxygen isotopes (Figs. 2 and 3). The datum horizon has been adopted by stratigraphers as the Frasnian-Famennian boundary in this area. However, it is only one possible position of the global Frasnian-Famennian boundary in relation to the conodont zonation, others being the base of the Middle *P. triangularis* Subzone and the base of the Lower *P. triangularis* Subzone (*1, 9*). The sampled section extended over the *P. triangularis* Zone and parts of the *P. crepida* and *P. gigas* zones.

Elemental abundances for some of the more significant elements are plotted in Fig. 3. A moderate iridium anomaly, about 20 times the local background and reaching a maximum of 300×10^{-12} g per gram (300 ppt) of whole rock (600×10^{-12} g/g on a carbonate-free basis), begins at the base of the Upper *P. triangularis* Subzone (Fig. 2). The integrated excess-iridium content (over background) is 7.5×10^{-9} g/cm^2, which can be compared with a range of 8×10^{-9} to 187×10^{-9} g/cm^2 and a global average of $\sim 50 \times 10^{-9}$ g/cm^2 at the K/T boundary. Anomalously high concentrations of platinum, vanadium, cobalt, nickel, copper, arsenic, antimony, rare earths (especially cerium), lead, and thorium coincide with the iridium anomaly. On the other hand, there are no increased concentrations of gold, alkali metals, alkaline-earth metals, aluminum, titanium, chromium, zinc, and selenium.

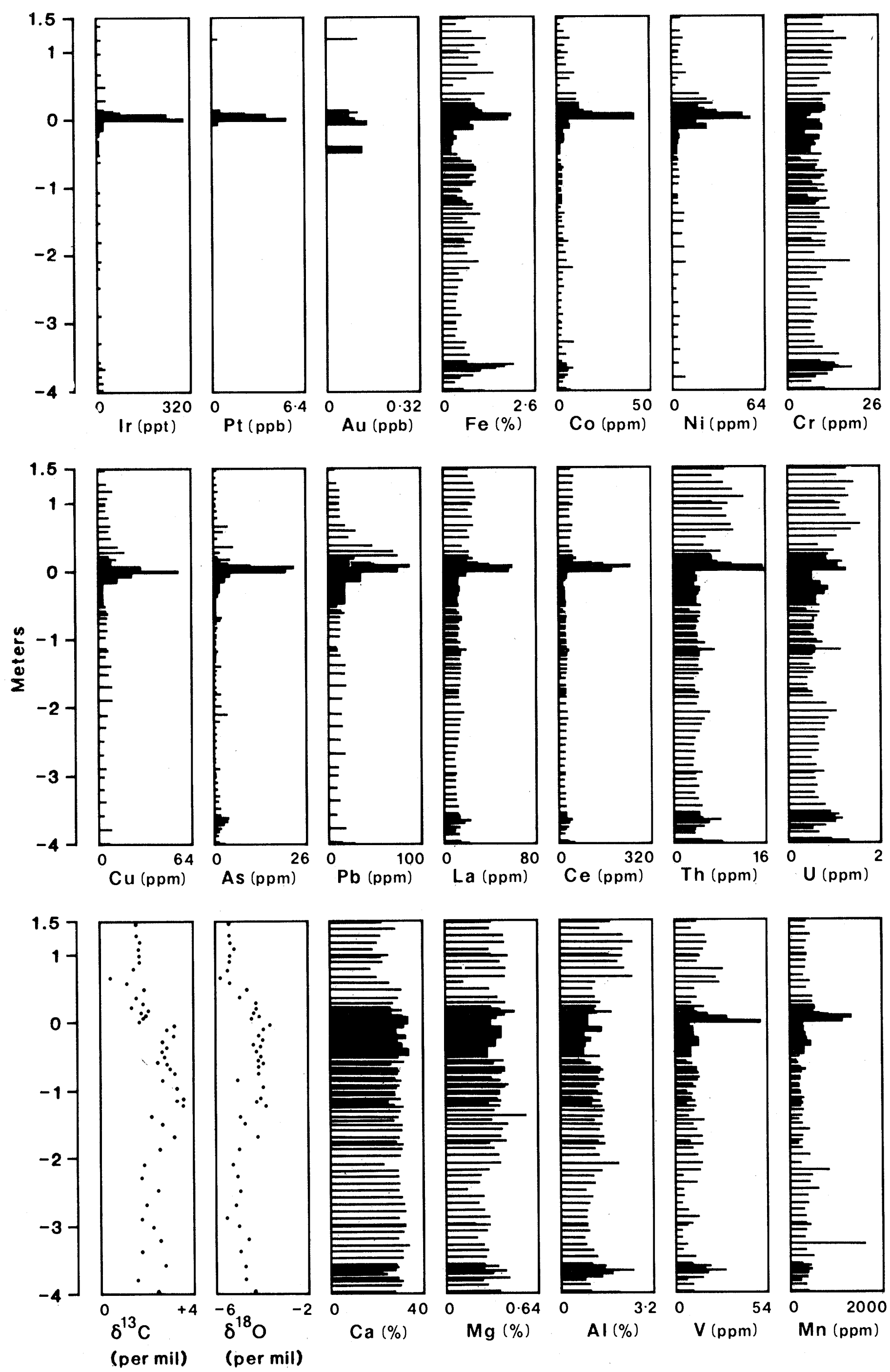

Fig. 3. Elemental abundances for some significant elements, and isotope ratios for carbon and oxygen. Columns represent the sampled portion of the McWhae Ridge section of the Upper Devonian Virgin Hills Formation, Canning Basin, Western Australia.

The anomaly and the lower part of the Upper *P. triangularis* Subzone coincide with a prominent stromatolite bed, about 12 cm thick. Values for iridium and associated anomalous elements are nearly constant through this interval. The bed is characterized by closely spaced microstromatolites of the iron cyanobacterium *Frutexites* (*7, 10*). The microstromatolites are bundles of filaments covered by micritic envelopes, which branch upward and average about 1 mm in diameter and 2 to 4 mm in height. The filaments are partly filled with iron oxide in the form of hematite and goethite, with smaller amounts of pyrolusite (manganese oxide). Iridium and other elements are also concentrated in *Frutexites* filaments, as will be discussed later.

The *Frutexites* bed is recognized at the same stratigraphic horizon at a number of other localities near McWhae Ridge, and whole-rock analyses of samples collected 4 km southwest and 1 km north of the ridge gave iridium concentrations of 330×10^{-12} and 255×10^{-12} g/g, respectively.

Noncarbonate material in the *Frutexites* bed occurs mainly in the interareas between microstromatolite columns. It consists of silt and very fine sand particles of quartz, potash feldspar, plagioclase, and zircon. This material is believed to have been derived as windborne dust from the nearby landmass of Precambrian rocks. No spheroidal or sanidine particles have been observed.

The section at McWhae Ridge is extremely condensed. If we assume an average timespan for an Upper Devonian conodont subzone of about 500,000 years, the period represented by the sampled section (5.5 m thick) is about 3 million years and the average rate of sedimentation is only 1.8 mm per 1000 years. The upper *P. triangularis* Subzone, which includes the iridium anomaly, appears to be the most condensed; if it is of average duration, the rate of sedimentation would average a minuscule 0.6 mm per 1000 years. Of course, sedimentation would not have been continuous throughout each subzone; individual bedding planes may represent significant intervals of nondeposition. However, as all conodont subzones of the latest Frasnian and earliest Famennian are present in the section, any such intervals must have been less than the duration of a subzone.

Because of the strongly condensed nature of the section containing the iridium anomaly, the question arises of whether it could have resulted from steady rates of iridium accumulation magnified by extremely slow rates of associated sedimentation. However, this explanation seems unlikely, as the iridium concentration in the anomaly is about 20 times the background, compared with a factor of only 3 for the relative sedimentation rates. The decreased rate of sedimentation in the zone that includes the anomaly could reflect a decline in organic productivity associated with the Frasnian-Famennian mass extinction, although there is not the associated decrease in carbonate content that might be expected. However, carbon isotope analyses appear to support the suggested decline in productivity. There is a drop in overall $\delta^{13}C$ values of about 1.5 per mil extending from the base of the anomaly to the top of the section (Fig. 3); this finding suggests a decrease in biomass (*11*) for at least 1 million years. The values of $\delta^{18}O$ in calcite also decrease sharply above the anomaly, a possible indication of an increase in water temperature.

It is clear that the results of this study are equivocal with respect to the basic question of whether the Frasnian-Famennian mass extinction was associated with the impact on Earth of a large extraterrestrial body. On the face of it, the iridium anomaly could plausibly be linked to such an impact; however, the Canning Basin data do not point with any high degree of assurance to this explanation. The siderophile atom ratios, notably Co/Ir (160,000), Ni/Ir (245,000), Pt/Ir (14), Ni/Co (1.5), Au/Ir ($\leq$0.2), and possibly Os/Ir ($\leq$0.4), are not compatible overall with either chondritic or iron meteoroids. Furthermore, analyses of material extracted with a microdrill show that iridium and platinum are concentrated by a factor of 2 in microstromatolites of the fossil cyanobacterium *Frutexites*, and iron, manganese, cobalt, arsenic, antimony, and cerium also increase, by a factor of 5. We cannot say whether biological mechanisms were the sole cause of the anomaly, or whether the organisms were only able to accumulate these elements to such a degree because of abnormally high concentrations of the elements in seawater at that time. In addition, it is not known whether the concentrating mechanism was biochemical, mechanical, or even diagenetic.

One fact is clear—a significant geochemical anomaly is present at or near the Frasnian-Famennian boundary in the Canning Basin, associated with a mass-extinction event of global extent. The association of the anomaly with the extinction may be purely coincidental, but it seems more likely that there is some genetic relation between them, involving either the impact of a large extraterrestrial body or an unidentified terrestrial process. The occurrence of this iridium anomaly at or near a mass-extinction horizon is clearly important in the search for geochemical signatures of global extinctions and the continuing debate on their origins.

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12. We thank C. Kerans and N. F. Hurley for assisting in sample collecting; C. Kerans for providing petrological information; C. Kerans, A. E. Cockbain, A. F. Trendall, and E. M. Shoemaker for advice; the Los Alamos National Laboratory reactor group for performing the neutron irradiations and for deriving some of the elemental data with their automated system; P. Q. Oliver and L. M. Quintana for performing some of the radiochemical separations; and J. Vaive and D. Walker for determining nickel, copper, and lead and conducting mineral identifications. Publication 12-84 of the Ottawa-Carleton Centre for Geoscience Studies.

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A New Basis for Recognizing the Paleocene/Eocene Boundary in Western Interior North America

Abstract. *Fossil pollen grains from Paleocene-Eocene rocks of the Bighorn Basin of Wyoming allow important sequences of terrestrial vertebrate fossils to be correlated with standard marine microfossil zonations. The Paleocene/Eocene boundary as based on pollen evidence falls within the Wasatchian land mammal age, much higher than the boundary used by some fossil mammal workers. This discrepancy partly results from multiple definitions of the Paleocene/Eocene boundary but may also indicate faulty mammal-based correlations to the type Sparnacian of France.*

Fossils from Paleocene and Eocene strata of the contiguous Bighorn and Clarks Fork basins of Wyoming provide one of the longest, most complete, and best studied records of terrestrial life in the world (*1–3*). The relatively high stratigraphic completeness of the strata (*4*) and the dense spacing of fossiliferous horizons (*5, 6*) have made these sequences an important testing ground for theories on evolutionary rate and mode (*7, 8*) and on intra- and intercontinental dispersal (*9, 10*). As a result, there is strong incentive to develop reliable correlations between these strata and rocks of similar age in other regions, particularly with deep-sea marine sequences and the type sections of stages in the Paleocene and Eocene of Europe. Previous correlations have been based largely on mammalian fossils, and particularly on similarities between European and North American species of the primate genus *Plesiadapis* (*11–13*). Stratigraphically important fossil pollen found in lower Tertiary rocks of the Bighorn Basin provides a means of correlating these continental sequences to standard ma-