Gold and palladium as indicators of an extraterrestrial component in the Cretaceous/Tertiary boundary layer at Woodside Creek and Chancet Quarry, Marlborough, New Zealand

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Abstract

It is widely believed that a large meteorite approximately 10 km in diameter impacted Earth at the termination of the Cretaceous Period with cosmic velocity, vaporising itself, along with a greater mass of the terrestrial target rocks into a cloud of hot rock vapour. The vapour cloud condensed into particles of sand to clay size at high altitude before returning to Earth to form a worldwide layer marking the Cretaceous/Tertiary boundary. Chemical evidence from this boundary layer suggests that the impactor was a chondritic meteorite, enriched in the platinum group elements compared to the Earth's crust. An enrichment of these elements above their background crustal abundances to approximately 0.1 of the chondritic abundance has been observed in a number of Cretaceous/Tertiary boundary layers worldwide.

Iridium is the platinum group element traditionally used as an indicator of the extraterrestrial component (ETC) in likely impact layers due to its rarity in the Earth's crust and low detection limits possible using neutron activation analysis methods. Neutron activation analysis is however expensive and requires specialist facilities, this thesis proposes that the elements gold and palladium can also be used to indicate the ETC in the Cretaceous/Tertiary boundary layer. Samples from two Cretaceous/Tertiary boundary sites, Woodside Creek and Chancet Quarry, were analysed for gold and palladium using graphite furnace atomic absorption spectrometry. A strong correlation was found between iridium, gold, and palladium abundances at these sites, with all showing enrichment at precisely the Cretaceous/Tertiary boundary in proportion to iridium, indicating a common origin for all three elements. Gold showed almost precisely the expected 0.1 of its chondritic abundance in the clay size fraction at both Woodside Creek and Chancet Quarry (15 ng/g). Palladium showed exactly 0.1 of its chondritic abundance at the Chancet Quarry boundary with 53 ng/g. Gold abundances on the boundary at Woodside Creek (55 ng/g) and Chancet Quarry (44 ng/g) showed excellent agreement with published values as did the palladium result for Woodside Creek (22 ng/g).

Acknowledgments.

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The co-operation of Margaret Parsons and Herby Thomson for access to the Woodside Creek and Chancet Quarry sites respectively is also gratefully acknowledged.

Finally I dedicate this thesis to my parents Bruce and Beverley Cook of Renwick, Marlborough. Since I can remember Dad has talked with me about astronomy and how it relates to life on Earth, so here is a small part of the answer!

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1.0 Introduction

1.1 The Cretaceous/Tertiary boundary and impact event theory

The Cretaceous/Tertiary (K/T) boundary at 65 Ma was the first major boundary to be recognised and formed part of the Paleozoic, Mesozoic, and Cenozoic divisions of Earth history proposed by Phillips in 1841 (Ryder, 1996). The connection between an extraterrestrial influence and divisions in Earth history was first noted by Harold Urey in 1973 when he suggested cometary impacts could have been responsible for some of the geological boundaries (Urey, 1973). Prior to this McLaren had proposed in 1970 a palaeontologic argument for mass extinction by meteorite impact in the late Devonian period (McLaren, 1970). The meteorite impact theory resurfaced when Napier and Clube (1979) mentioned a personal communication from the Alvarez group about an iridium abundance peak that jumped to twenty times the background level at the K/T boundary. Napier and Clube (1979) favoured an interstellar source for the impactor while Alvarez *et al.* (1980) and Davis *et al.* (1984) argued for a solar system source based on isotope quotients of platinum group elements.

Literature published on the origin of the K/T boundary layer has been reviewed by Glen (1994) with the vast majority of papers in support of an impact origin since the benchmark paper by Alvarez *et al.*(1980). Although the K/T boundary layer is characterised by mass extinctions (Ryder, 1996), this is not direct evidence of an impact event. Biological extinctions are temporal to the K/T boundary but of themselves do not prove an impact event occurred there. In this chapter I will outline some of the key evidence presented in support of the impact theory, particularly the chemical evidence obtained from platinum group element determinations of the boundary layer. I hope to show in this thesis that gold and palladium abundances correlate extremely well with iridium abundances (the traditional indicator of meteoritic material). Gold and palladium can be used to indicate meteoritic material at two established New Zealand K/T boundary sites, a result entirely consistent with the meteorite impact theory.

1.1.1 Iridium abundance peak at the K/T boundary

Alvarez's research in the Umbrian Apennines of Northern Italy had shown that an abrupt change from the foraminiferal genus *Globotruncana* (upper Cretaceous) to *Globigerina eugubina* (lower Tertiary) occurred in limestone rocks of Jurassic to Oligocene age. Coincident with this foraminiferal change was an increase in the iridium abundance from the background of 0.3 ng/g to a peak of 9.1 ng/g precisely on the K/T boundary, followed by a decrease to pre-boundary abundances (Alvarez *et al.* 1980). These iridium levels were compared with those found at another established K/T boundary site at Stevns Klint in Denmark where the peak value for iridium was 29 ng/g on a whole-rock basis. This was more iridium than could have been removed from a column of seawater above the site over the expected time period, assuming typical iridium seawater abundances (Alvarez *et al.* 1980). They proposed a sudden input of a large amount of iridium from a cosmic source to account for the observed abundance at the K/T boundary.

1.2 Meteorite impact proposal

1.2.1 Supernova proposal rejected

Initially the Alvarez group proposed a supernova explosion to account for the excess iridium and other platinum group elements observed at the K/T boundary. Supernova are known to produce iridium and other elements heavier than iron in the 'r' process of nucleosynthesis (Mason and Moore, 1982). The Alvarez group later decided to drop the supernova proposal because no plutonium was detected in the K/T boundary sediments, an element expected to be present if a supernova had exploded nearby (Alvarez *et al.* 1980). They then proposed a large chondritic meteorite impact to account for the observed iridium peak. Chondritic meteorites are enriched in platinum group elements, compared with the Earth's crust (Mason and Moore, 1982) therefore an impacting chondritic meteorite should leave evidence of the impact as an enrichment of these elements in the geological record. Platinum group elements include Os, Ir, Pt, Ru, Rh, and Pd, with Au and Ag often added to the list to form the larger group of noble metals (Sienko and Plane, 1961).

1.2.2 Chondritic meteorite impact proposed for the K/T boundary

Ganapathy (1980) noted that if a high iridium content is found in the K/T boundary layer then you should expect to find high abundances of other siderophiles. This was supported by abundance patterns for Ir, Os, Au, Pt, Co, Ni, Pd, Ru, and Re in the Stevns Klint K/T boundary site which showed 0.1 of their chondritic abundances. The only exception to this trend was rhenium which is not depleted in the Earth's crust probably due to its fractionation in igneous rocks (Kyte, 1988). These siderophiles showed abundances in proportion to a chondrite meteorite which suggests that the Stevns Klint K/T boundary sediments were enriched in siderophiles in chondritic proportions (Ganapathy, 1980).

1.3 Supporting evidence for the meteorite impact at the K/T boundary

1.3.1 Physical

Visible evidence of impacts on Earth are rare due to the Earth's thick atmosphere and abundant liquid water shielding the surface from all but the larger impactors (Grieve, 1994). This helps to explain the vast difference in the apparent cratering rate between the Earth and the Moon with the Moon having recorded a virtual photographic record of impacts since 3800 Ma. Impact ejecta blankets the Lunar surface, in places between two and ten kilometres deep (Grieve, 1994). You would expect a higher number of impact craters on Earth than the Moon due to Earth's higher gravity, and this is most likely true but for our thick atmosphere and thinner hotter crust which actively recycles and erases impact craters (Grieve, 1994).

Ironically it was the Earth's active crust that helped identify the impact crater most likely excavated by the K/T boundary meteorite. Hildebrand *et al.* (1990), in a search for the crater, used gravity and magnetic data to isolate the Chicxulub structure in the Yučatan Peninsula, Mexico. The impact left a negative gravity anomaly in the crust, implying that the crater had filled with less dense sediment following the impact and crater excavation. A 200 km diameter crater dimension suggested that Chicxulub fitted the size criteria for the K/T boundary impactor. Subsequent drilling, which dated the buried impact melt sheet at 65 Ma, strongly supported Chicxulub as the impact crater of the K/T boundary meteorite (Hildebrand *et al.* 1990).

1.3.2 Mineralogical

Mineralogical evidence for an impact was also found at the Chicxulub site with shocked quartz and petrographic indications that an impact melt sheet and breccia layer were present (Hildebrand *et al.* 1990). Shocked quartz and the high pressure quartz polymorph stishovite were also discovered in marine and nonmarine K/T boundary sections worldwide, with the size of the shocked quartz particles decreasing away from the proposed impact crater (Bohor, 1990). Other supporting evidence for the Chicxulub site is that the target rocks included Anhydrite (Calcium Sulphate) which could explain added trauma to the Earth's biota as the impact may have sent 600 billion tonnes of sulphates into the atmosphere that later condensed into sulphuric acid (Grieve, 1994).

The presence of nickel-rich spinels at the K/T boundary (Bohor *et al.* 1986; Bohor, 1990; Rocchia *et al.* 1996) coincided exactly with the palaeontologic boundary and the highest iridium abundance. These spinels were formed from the condensation of the vapour phase of material created by the impact of the K/T meteorite with the Earth. No known terrestrial process can account for the specific siderophile abundances and oxidation state of these spinels which, due to their non-mobility in the sedimentary environment, form an accurate record of the timing of the impact event (Rocchia *et al.* 1996).

1.3.3 Chemical

Chemical evidence for a meteorite impact at the K/T boundary had to wait the development of analytical techniques that could determine platinum group elements at the part per billion (ppb) level. Gold and palladium are well suited for this level of determination precision using graphite furnace atomic absorption spectrometry, a technique that does not require the expensive highly specialised equipment required for neutron activation analysis.

Abundant chemical evidence for the K/T boundary impact exists, characterised by an enrichment of siderophile elements in chondritic ratios (Ganapathy, 1980; Kyte *et al.* 1996; Kyte *et al.* 1980; Palme, 1982). Chondritic meteorites represent the solar abundance of non-volatile elements (Wasson 1985) as does the whole Earth, this differs from the Earth's crust which is generally depleted in the siderophile elements. Impacting chondritic bodies therefore leave a siderophile enriched deposit on the Earth's crust with the enrichment in proportion to the siderophile chondritic abundance (Ganapathy, 1980). Iridium abundances for the K/T boundary layer of between 1 and 100 ng/g Ir have the same range of values as known Earth and Lunar impact melts, although lower iridium values than chondritic meteorites (Palme, 1982). This strongly supports a chondritic source for the K/T boundary impactor based solely on iridium data with other siderophile abundances showing a chondritic pattern (Ganapathy, 1980; Palme, 1982).

This thesis shows that at the two New Zealand K/T boundary sites studied, Woodside Creek and Chancet Quarry (refer Fig 1.1 below), gold and palladium are enriched in the K/T boundary layer in proportion to their chondritic abundances. There are variations on this theme, with the closest chondritic signature in the sand and clay size fractions indicating that these sites received direct fallout from the impact event. Whole-rock gold and palladium abundances for both Woodside Creek and Chancet Quarry show the expected peak at the K/T boundary as consistent with the sudden input of material rich in these elements from the meteorite impact. Gold abundances at both sites are higher than the 0.1 of the chondritic abundance observed at Stevns Klint (Ganapathy, 1980) although palladium at Chancet Quarry shows the expected 0.1 of the chondritic value. At Woodside Creek and Chancet Quarry gold and palladium correlate very well with iridium indicating that these elements abundances can be used to signal the presence of an ETC in the K/T boundary layer.

1.4 The sites

Two previously identified and well described K/T boundary sites were chosen for this thesis, they were Woodside Creek and Chancet Quarry, both in the Marlborough province of New Zealand. Element abundances for gold had been carried out for Woodside Creek (Brooks *et al.* 1984) and Chancet Quarry (Strong *et al.* 1987) although no palladium results have been published for these sites. Woodside Creek is the original K/T boundary site and was sampled at two locations, Woodside Creek West is the original location, sampled by Brooks *et al.* (1984) and shown in Fig 1.2a. Woodside Creek East is the mirror image of the original location and is located directly across the stream from the original sampling location.

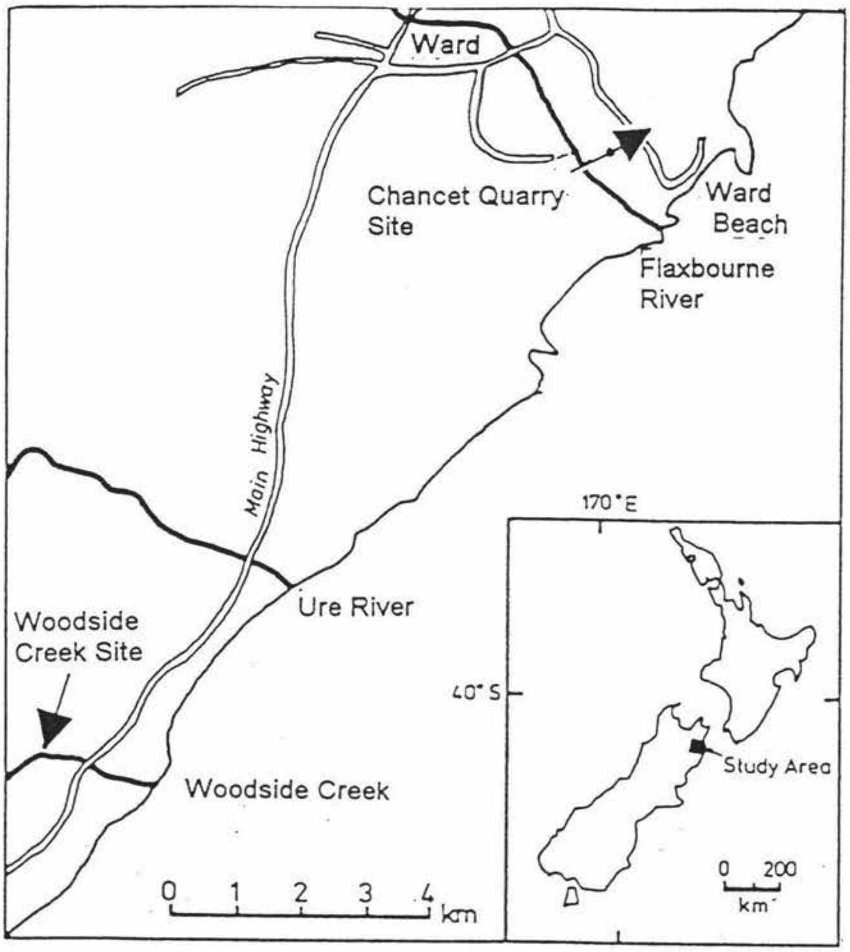

FIGURE 1.1 LOCATION MAP OF K/T BOUNDARY SITES, MARLBOROUGH, NEW ZEALAND

1.4 Woodside Creek

This site is located at the base of a steep ravine adjacent to the stream bed in Woodside Creek, Marlborough (refer figure 1.1). The K/T boundary was first described by Strong (1977) who defined the boundary palaeontologically and placed it within the Mead Hill Formation (refer figure 1.2). It was characterised by the disappearance of planktonic but not benthic foraminifer in a likely water depth of between 200 and 600 metres at the time of deposition. The geochemistry of this site showed an iridium anomaly of 28 ng/g (Alvarez *et al.* 1982) and Brooks *et al.* (1984) reported a mean iridium abundance across the boundary layer of 70 ng/g. Significantly, Brooks *et al.* (1984) found a Ir/Au quotient of 2.1 which is indicative of a meteoritic source for the boundary layer at this site as terrestrial rocks typically have a Ir/Au quotient of 0.2 (Palme, 1982).

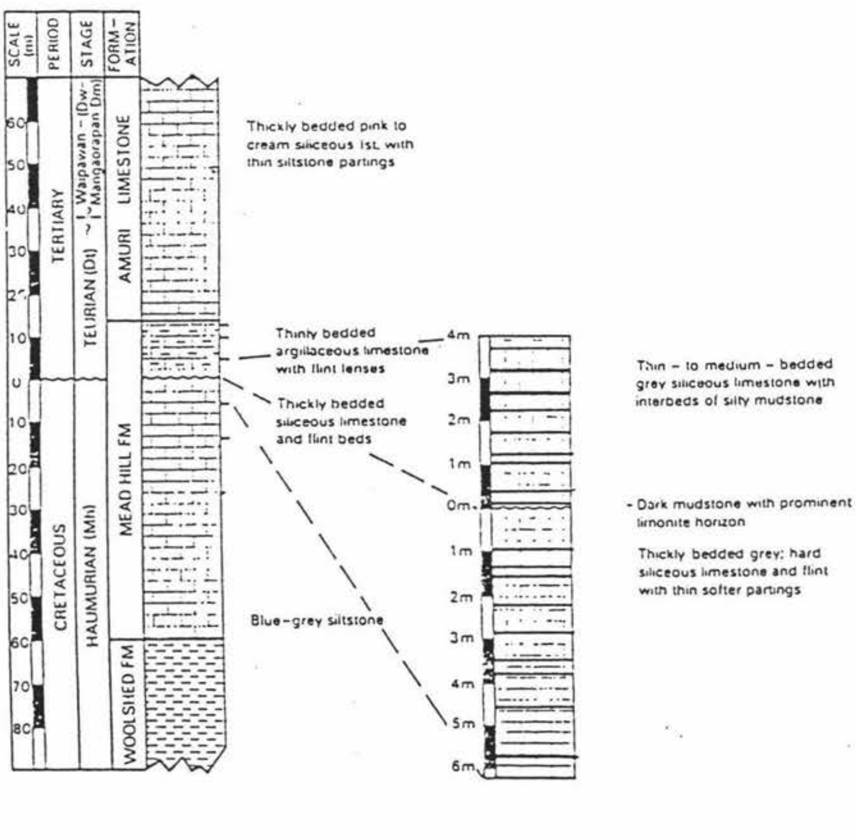

FIGURE 1.2 STRATIGRAPHIC COLUMN FOR WOODSIDE CREEK SITE K/T BOUNDARY (SOURCE STRONG 1977).

1.4.2 Chancet Quarry

This site (previously referred to as Flaxbourne River) contains the most complete biostratigraphic sequence across the K/T boundary so far discovered in New Zealand (Strong *et al.* 1987). The Cretaceous contains abundant planktonic foraminifer, some of which survive into the Tertiary, but at reduced numbers and with decreased average size of individuals (Strong *et al.* 1987). The geochemistry of the site reveals a sharp drop in the calcium carbonate level from 62 % in the Cretaceous to 26 % in the boundary layer (refer figure 1.3). The layer itself contains Ni/Ir and Cr/Ir quotients with the same value as C1 Carbonaceous chondrites, implying a meteoritic source for the boundary layer (Strong *et al.* 1987). Gold and palladium abundances for this site are not reported in Strong *et al.* (1987) but these elements being siderophiles should be enriched in proportion to iridium in the boundary layer.

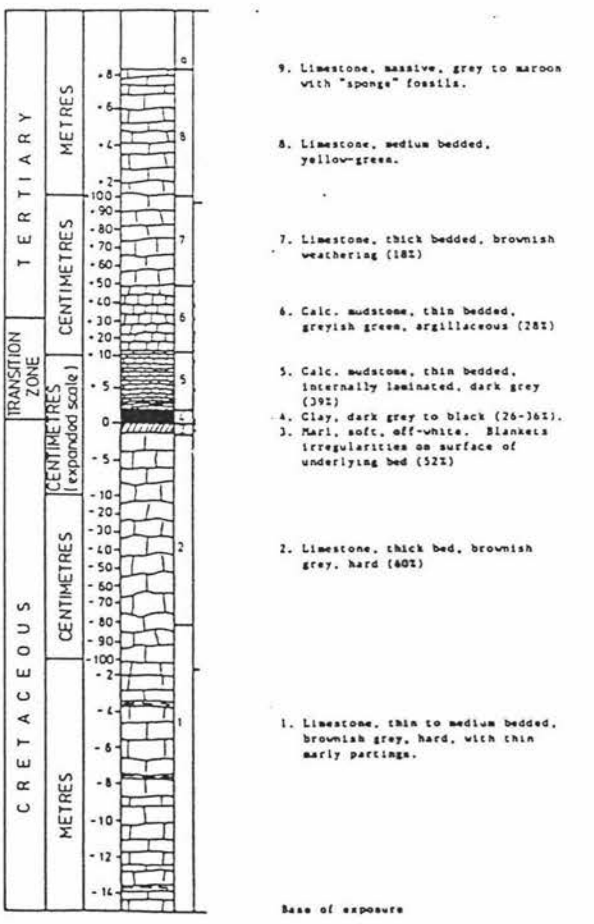

FIGURE 1.3 STRATIGRAPHIC COLOUMN FOR CHANCET QUARRY K/T BOUNDARY SITE (SOURCE STRONG *ET AL.* 1987)

FIGURE 1.2A CLOSE UP OF WOODSIDE CREEK SITE. RUST COLOURED 1CM THICK BOUNDARY LAYER (ARROWED) IS RESTING ON THICK BEDDED CRETACEOUS LIMESTONE. THINNER ALTERNATE GREY/WHITE TERTIARY BEDS LIE ABOVE BOUNDARY LAYER.

FIGURE 1.3A CLOSE UP OF CHANCET QUARRY SITE. K/T BOUNDARY LAYER IS 1CM THICK AND CHARCOAL COLOURED (ARROWED) RESTING ON CRETACEOUS MARL AND LIMESTONE. THIN BEDDED TERTIARY SEDIMENTS LIE ABOVE BOUNDARY LAYER.

1.5 Objectives of Thesis

The primary objectives of this thesis are outlined below:

- To refine analytical techniques for the determination of gold and palladium at the ng/g level in K/T boundary layer samples from Woodside Creek and Chancet Quarry using graphite furnace atomic absorption spectrometry.
- To compare these gold and palladium abundance results with iridium values obtained for these two sites and assess their usefulness as indicators of the presence of an ETC in the K/T boundary layer material.
- To mineralogically examine samples taken at intervals across the K/T boundary and identify any mineralogical changes across the boundary possibly caused due to the impact event
- To determine gold and palladium abundances in the separate sand, silt, and clay size fractions across the K/T boundary and compare with the particle size distribution predicted by the impact theory.