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

**A thesis presented in partial fulfillment of the requirements for the degree of  
Master of Science in Earth Sciences at Massey University**

**Andrew William Cook 1998**

## 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).*

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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 Yucatan 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.

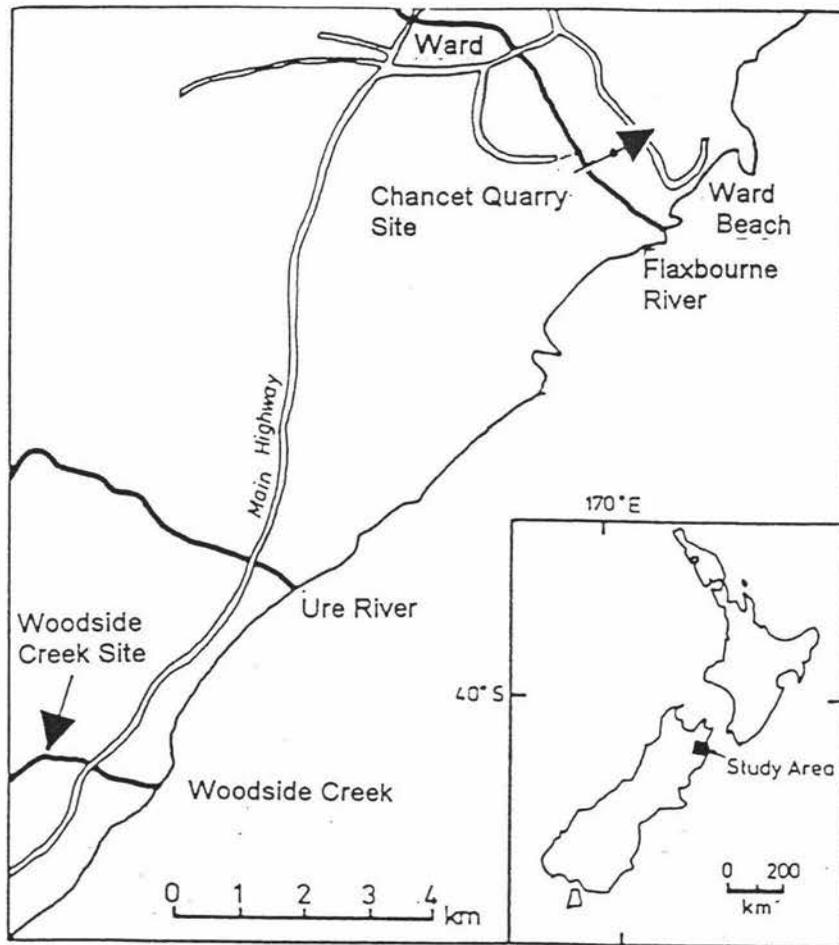


FIGURE 1.1 LOCATION MAP OF K/T BOUNDARY SITES, MARLBOROUGH, NEW ZEALAND

## 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).

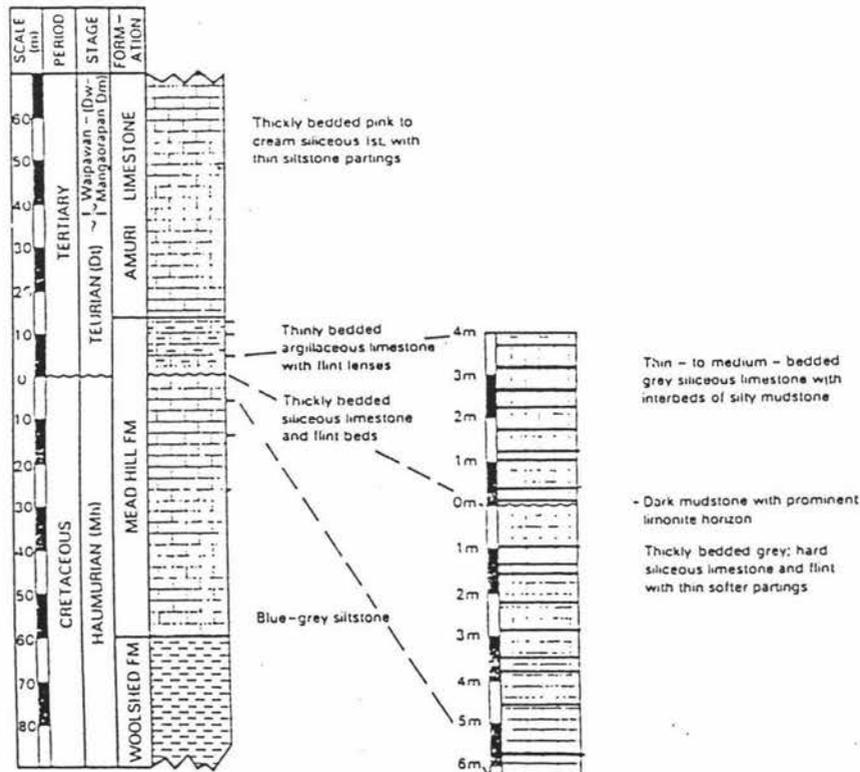


FIGURE 1.2 STRATIGRAPHIC COLUMN FOR WOODSIDE CREEK SITE K/T BOUNDARY (SOURCE STRONG 1977).

### 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.

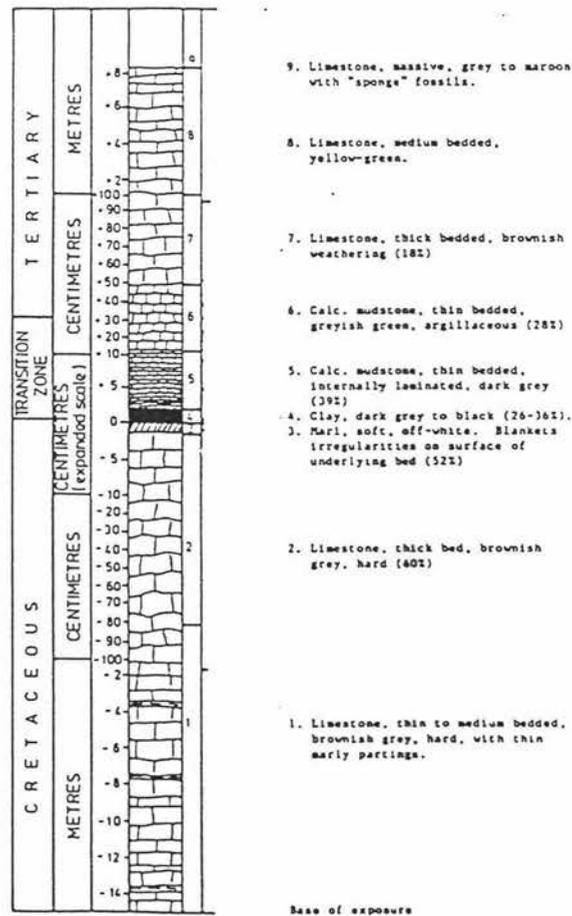


FIGURE 1.3 STRATIGRAPHIC COLOUMN FOR CHANCET QUARRY K/T BOUNDARY SITE (SOURCE STRONG *ET AL.* 1987)

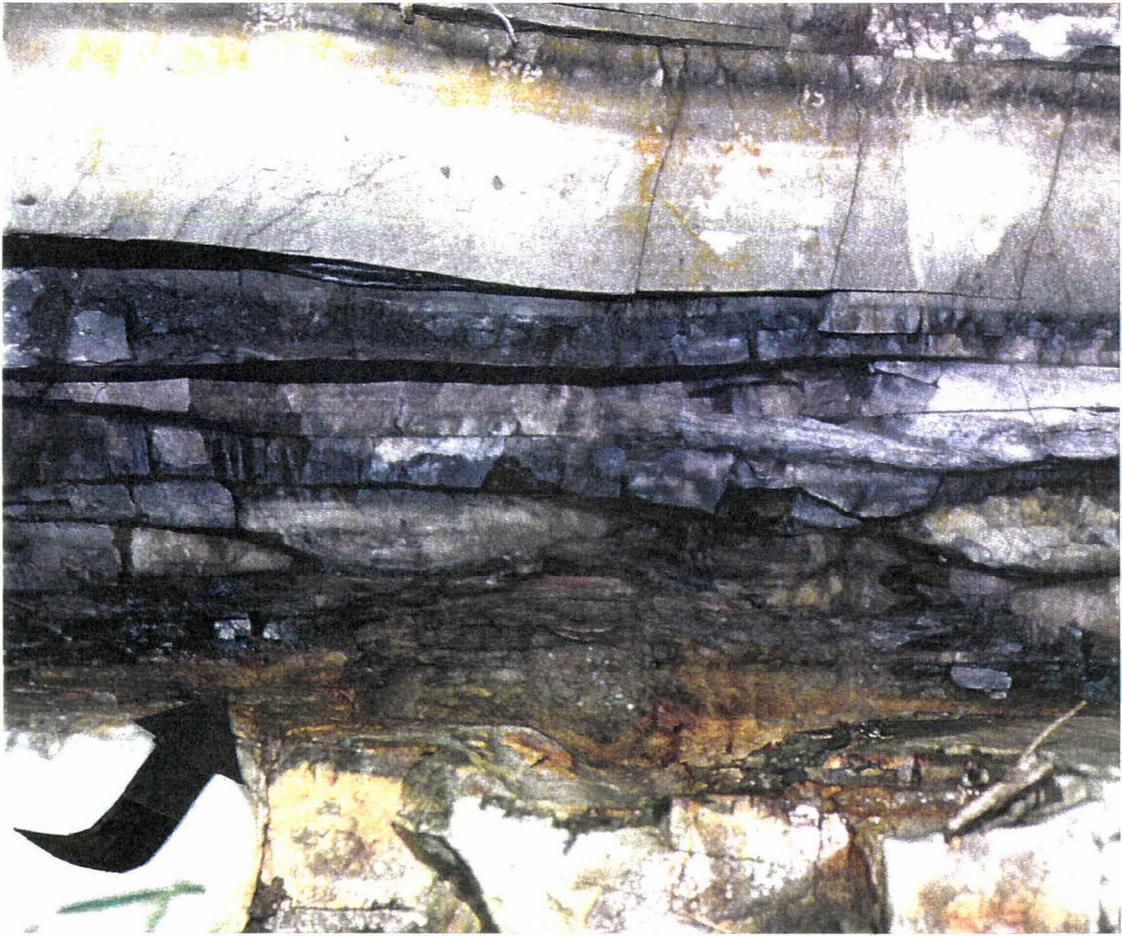


FIGURE 1.2A CLOSE UP OF WOODSIDE CREEK SITE. RUST COLOURED 1CM THICK BOUNDARY LAYER (ARROWED) IS RESTING ON THICK BEDDED CRETACEOUS LIMESTONE. THINNER ALTERNATE GREY/WHITE TERTIARY BEDS LIE ABOVE BOUNDARY LAYER.



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.

## 2.0 Platinum group elements in the K/T boundary layer

### 2.1 Iridium as an indicator of the ETC in K/T boundary sediments

#### 2.1.1 Introduction

Alvarez *et al.*(1980) first published chemical data which they interpreted as evidence for a major meteorite impact at the K/T boundary. They noted the abundance of iridium (a platinum group element) peaked at the palaeontological boundary. Alvarez was initially using iridium to measure the rate of limestone accumulation due to the constant flux of this metal from small meteorites that continually impact Earth. Iridium's usefulness as an indicator of the ETC of marine sediments is based on its following properties:

1. It is depleted in the Earth's crust by a factor of  $10^5$  relative to solar abundances, (Ganapathy, 1980). In absolute terms, this means that it is found in very low abundances in Earth's crust, less than 0.1 ng/g (Brooks, 1987) as compared with 500 ng/g in chondritic meteorites (Anders and Grevesse, 1989).
2. It can be determined at low abundance levels by Instrumental Neutron Activation Techniques (INAA) with a detection limit of 1 ng/g. Radiochemical Neutron Activation (RNAA) has an even lower detection limit of 10 pg/g (Brooks 1987).
3. Iridium is a refractory element which means that it is not lost due to volatilisation during heating of small meteorites as they enter Earth's atmosphere. This was confirmed by Ganapathy *et al* (1978) who found spherules of presumed cosmic origin in marine sediments with 535 ng/g Ir (comparable with a C1 chondrite value of 514 ng/g Ir). This allowed iridium to be used as an indicator of the flux of small meteorites impacting Earth (Kyte, 1988).

4. Iridium has a long residence time in oceans of about 10,000 years (Kyte *et al.* 1980) compared with the oceanic mixing time of 1,000 years (Kennett, 1982) allowing a constant accumulation rate of iridium in marine sediments (Kyte, 1988) at various sites around the world.

### 2.1.2 Chondritic abundance patterns for iridium

A compilation of iridium abundance data by Palme (1982) showed iridium abundances for K/T boundary sediments, impact melts, and upper mantle rocks all ranging from 1-100 ng/g, compared with typical marine sediment iridium abundances of less than 1 ng/g (Crocket *et al.* 1973). These abundances coincide with values for lunar impact rocks but are below values for Chondritic meteorites. The dilution effect is expected as a large meteorite impacting the Earth's crust with cosmic velocity could vaporise many times its own mass in target rocks (Melosh, 1982; O'Keefe and Ahrens, 1982).

Carbonaceous chondrite meteorites are the objects that have nonvolatile element abundances (relative to silicon) virtually identical to Solar abundances (Wasson, 1985; Anders and Grevesse, 1988). They represent the original abundance of elements thought to have existed in the Solar System prior to chemical fractionation of the elements. This is supported by the presence of determinable amounts of  $^{129}\text{Xe}$  in chondritic meteorites indicating they formed within 16 Myr of the Solar System formation (Wasson, 1985). Any material containing  $^{129}\text{Xe}$  must have been closed to prevent its loss within the decay half life of the parent isotope  $^{129}\text{I}$  of 16 Myr. The only known source of  $^{129}\text{I}$  is a supernova explosion thought to have just predated the formation of the Solar System (Fisher, 1987), thus carbonaceous chondrites containing  $^{129}\text{Xe}$  must have formed within 16 Myr of the Solar System age.

### 2.1.3 Quotient of ETC in K/T boundary layer

Earth has, due to its mass, been able to chemically differentiate itself into separate layers of which the crust is highly depleted in the siderophiles or elements with an affinity for iron (Mason, 1982). Chondritic meteorites are enriched in siderophile elements compared to the Earth's crust therefore an impacting chondritic meteorite leaves a siderophile-enriched abundance pattern on the Earth's surface. The ETC in the K/T boundary layer is at most 20% of total volume of the K/T boundary layer (Kyte, 1988). The K/T boundary can be assumed to comprise pure debris from the impact, comprising a mixture of the impacting meteorite and the target rock (Kyte, 1988). The element abundances in the K/T boundary layer reflects the nature of the impactor (Palme, 1982) and the composition of the target rock (Gilmour and Anders, 1989). Another factor that can influence the ETC in the boundary layer is the velocity of the impactor in that a higher velocity impact can result in a more dilute ETC signature (O'Keefe and Ahrens, 1982).

The impact of a chondritic meteorite should leave a chemical signature enriched in siderophile elements (Ganapathy, 1980; Palme, 1982) in proportion to chondritic abundances, e.g. the enrichment factor for iridium in the K/T boundary layer should be matched by an enrichment of gold in proportion to their abundances in chondritic meteorites. This assumes complete vaporisation and even dispersal of the impactor around the Earth's surface and that the target rocks are typical of the Earth's crustal composition. The following figure compares the chondritic siderophile abundances with the K/T boundary layer data taken from Stevns Klint, Denmark. This data is plotted against average crustal and standard basic igneous rock (Diabase) siderophile abundances.

The term 'abundance' is technically the atomic ratio of the element relative to a normalising element (Wasson, 1985) which is useful when the total amount of an element is unknown i.e. in solar, meteoric, and terrestrial measurements. Concentration is the term used in sample results where the total mass of the sample and the element can be determined.

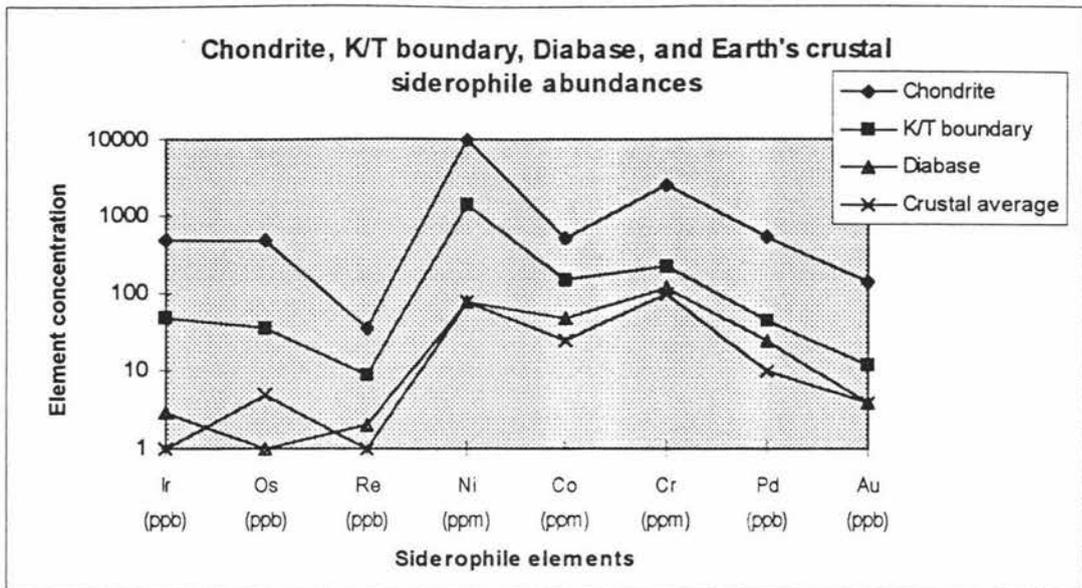


FIGURE 2.1 SIDEROPHILE ABUNDANCES IN CHONDRITE, K/T BOUNDARY, DIABASE, AND EARTH'S CRUST COMPARED<sup>1</sup>.

Figure 2.1 illustrates that the K/T boundary layer is enriched in siderophile element abundances above that of basic igneous and crustal rocks, and the enrichment follows the chondritic abundance pattern. The K/T boundary abundances are generally 0.1 of the chondritic abundances indicating that they represent a mixture of chondritic and crustal material.

#### 2.1.4 Chondritic abundances for other siderophiles

Ganapathy (1980) noted that plots of siderophile abundance patterns for Ir, Os, Au, Pt, Co, Ni, Pd, and Ru in the Stevns Klint K/T boundary sediments were almost all 0.1 of Chondritic abundances. This led him to suggest that these siderophiles could be used to indicate the ETC of sediments. Among these siderophiles only rhenium was enriched relative to carbonaceous chondrites and this can be explained by noting that rhenium is more abundant in the Earth's crust than are other platinum group elements. A significant contribution from the Earth's crust due to the impact process could therefore explain the high rhenium abundance (Kyte, 1988). The rhenium/osmium isotope system

<sup>1</sup> Sources for figure 2.1 Chondrite abundances (Anders and Grevesse, 1989), K/T boundary data from Stevns Klint, Denmark (Kyte *et al* 1985), diabase and crustal rock data from Mason and Moore (1982).

is discussed in a later section as it provides more evidence for an ETC in the K/T boundary sediments.

Evans *et al.* (1993) specifically choose platinum group elements to identify the impacting meteorite for the K/T boundary event. Their data for the Woodside Creek site gave a flat chondrite-normalised abundance pattern for the platinum group elements at just below 0.1 of chondritic abundance values, indicating a chondritic impactor for the K/T event.

### **2.1.5 Crustal abundances of the siderophiles**

Terrestrial sources of the platinum-group elements have different abundance quotients than have chondritic meteorites. This is due to the Earth's crust having been chemically fractionated, leaving it depleted in siderophile elements, especially the platinum group elements (Mason, 1982). K/T boundary abundance quotients of the siderophiles, especially when plotted against the refractory siderophiles like nickel and chromium (Palme, 1982; Gilmour and Anders, 1988) are markedly similar to chondritic abundance quotients for these elements. This is particularly so when the element abundances are integrated (determined at close intervals across the K/T boundary layer and the resulting mean abundance identified). Gold, palladium, platinum, and nickel integrated K/T boundary values correlate extremely well with iridium and chondrite normalised abundances (Kyte *et al.* 1985).

### **2.1.6 Problems with using iridium as an indicator**

Despite iridium's usefulness as an indicator for the ETC in K/T boundary sediments, there are problems with its use in this regard. These include the danger of using iridium as the only indicator of an ETC in the K/T boundary layer. This was highlighted by a late Devonian study in the Canning basin of Australia which showed that the stromatolite bacteria *Frutexites* could produce an iridium peak in the sedimentary record as a result of biological fractionation.(Orth, 1990).

Dissolution of the carbonate sediment, or long periods of non-carbonate deposition appeared to be a feature of the K/T boundary layer (Kyte, 1988; Kennett, 1982), and may give an anomalous high abundances of this element. This is true for any condensed sequence such as Woodside Creek, where time appears to be missing from the sedimentary record (Strong, 1977). The problem of non-carbonate deposition is traditionally overcome by presenting iridium abundances on a carbonate free basis (Brooks, 1987).

High iridium abundances alone do not therefore prove an impact origin for a specific deposit, just as the lack of an anomalously high iridium abundance does not discount an impact. The iridium abundance for eucrites and possibly certain iron meteorites is not high enough to leave an enrichment pattern on impact (Palme, 1982). Terrestrial processes can also effect the iridium abundance in sediments, depending on the source of those sediments, with upper mantle rocks having iridium abundances within a similar range as for the K/T boundary values (Palme, 1982; Sawlowicz, 1992).

The high cost of iridium determinations using INAA and RNAA techniques is a significant disadvantage with using iridium as an indicator for the ETC in sediments (Brooks, 1987). Other platinum group elements can be determined using different analytical techniques with sensitivities at least as good as INAA, making them equally useful indicators of an ETC in sediments.

Sources of mantle material such as basaltic volcanism and outcrops of mantle rocks at the surface e.g. ophiolites, may locally influence iridium values. Iridium values of 650 ng/g in Kilauea basalts have been reported and the weathering of ultramafic rocks that containing up to 3.8 ng/g iridium (Salowicz, 1992) may contribute to the iridium abundances in marine sediments.

## **2.2 Gold and palladium as indicators of an ETC at the K/T boundary**

### **2.2.1 Introduction**

Ganapathy (1980) was probably the first to use siderophile abundances, other than iridium, as indicators of the ETC at K/T boundary sites (refer section 2.1.4). This work was followed by that of Kyte *et al.* (1985) who observed that palladium showed the strongest correlation with iridium and carbonaceous chondrites in K/T boundary sediments from Caravaca, Spain. At Caravaca they observed that palladium and gold return to background levels only 10 cm above the boundary, with peak abundances higher than other platinum group elements. Siderophile abundances correlated well with chondritic siderophile abundances with the exception of iron, cobalt and rhenium. This result inferred that the siderophiles at this K/T boundary site were enriched in chondritic proportions (Kyte *et al.* 1985).

### **2.2.2 Integrated values for platinum group elements abundances**

Integrated values for gold and palladium in K/T boundary material at Caravaca, Spain and Stevns Klint, Denmark, were closer to their respective chondritic values than were the individual sample values (Kyte *et al.* 1985). This was attributed to reworking of the sediment after deposition and possible migration of elements through the sequence. The above authors noted that this reworking of sediments probably influenced the abundances more than differences in the oceanic residence times. Integrated abundance values would help solve the problem of the different oceanic residence times for gold and palladium. These integrated values are particularly useful when comparing sites that experienced different reduction and oxidation conditions at the time of deposition (Kyte *et al.* 1996).

### 2.2.3 Local conditions influence element abundances

Kyte *et al.* (1980) analysed the Stevns Klint and Deep Sea Drilling Project (DSDP) leg 62 hole 465A sites containing the K/T boundary and, like Ganapathy (1980) found siderophile enrichment with chondritic interelement quotients. They argued that reducing conditions prevailed at the K/T boundary for this site, this is supported by the presence of pyrite in the boundary layer (Kyte *et al.* 1980). Brooks *et al.* (1985) argued that reducing conditions existed in general after the K/T boundary event and used this to account for the formation of spheroids *in situ* with high chalcophile abundances.

In a later paper (Kyte *et al.* 1996) it was argued that most of the deep central Pacific sites were well oxygenated at 66 Ma and that reducing conditions existed only in localised areas. They suggest that chalcophile enrichment is more related to local chemical conditions than to possible target rocks, e.g. the oxygen minimum layer is today found between 150 and 1,000 metres depth (Kennett, 1982) therefore sediments deposited in this water depth are in a reducing environment. Gilmour and Anders (1989) believe that an enrichment of the chalcophile elements in the K/T boundary layer, especially arsenic, antimony and zinc, may reflect the target rock composition. They argue that arsenic, antimony and zinc are highly enriched in the K/T boundary sites of Woodside Creek and Chancet Quarry, at levels above that expected from either a purely meteoritic or oceanic source. A possible explanation for the chalcophile abundances being a combination of input from target rocks, plus the addition of land and marine biomass killed by the impact and subsequent environmental stress (Gilmour and Anders, 1989).

### 2.2.4 Oceanic residence times can affect element abundances

Localised reducing conditions would have affected the oceanic residence times for the siderophiles involved (Kyte *et al.* 1980; Kyte *et al.* 1996). This reinforces the need for a worldwide correlation of siderophile abundances at K/T boundary sites to reduce the effect of regional variations due to different reducing conditions at the time of deposition. Distinguishing the meteoritic from the terrestrial sources of the elements is

difficult (Kyte *et al.* 1980) as any process that affects the oceanic residence times of meteoritic elements would equally effect the residence times of the same terrestrial elements. The shorter oceanic residence time for iridium than for gold and nickel (Kyte *et al.* 1985) should lead to enhanced Ir/Au and Ir/Ni quotients, at least initially in the first deposits to settle out after the event.

Calculating the oceanic residence times for siderophiles can produce wide variations in estimates in the order of  $10^3$  (Kyte *et al.* 1980). This means that inferring local environmental conditions prevalent during the K/T boundary event, using possible changes to oceanic residence times is problematic i.e. there is a danger in attributing high element abundances to solely a reduced oceanic residence time for that particular element, without other collaborative evidence.

#### **2.2.5 Variation in interelement quotients expected at the K/T boundary**

Differences in interelement quotients across the K/T boundary layer could be expected for an single large ETC input over a short time span. A major meteorite impact would inject large amounts of siderophiles into the ocean over a short time scale of less than 200 yr (Smit and Hertogen, 1980) with some suggesting the K/T boundary layer was deposited within a year (Gilmour and Anders, 1989). This sudden massive input would create an initial deposit higher in the siderophiles with a shorter oceanic residence time. Observed variations in element quotients across the K/T boundary support the sudden influx of material from a meteorite impact (Kyte *et al.* 1996) and the integrated abundances show a chondritic signature (Kyte *et al.* 1985). Crocket *et al.* (1973) in a study of gold, palladium and iridium abundances, noted that these elements when normalised to palladium, showed a sharp dip in the iridium abundance of marine sediments and basic igneous rocks when plotted against a Carbonaceous chondrite. This suggests that a basaltic volcanic source, while able to supply the gold and palladium, could not have produced iridium in the required chondritic proportions.

### 2.2.6 Value of interelement quotients

Despite the possible localised effect of reducing conditions at K/T boundary sites, Ir/Au quotients for Stevns Klint K/T boundary site plot on the extra terrestrial quotient of 3.3 (Palme, 1982). This value groups it with those for terrestrial impact melt rocks and upper mantle rocks and distinguishes it from terrestrial crustal rocks which have a Ir/Au quotients of 0.2 (Palme, 1982).

Variations in the Ir/Au quotients within a site can be large with the most extreme variation exhibited by DSDP site 465A (Kyte *et al.* 1996) where the Ir/Au quotient changes by a factor of 65 across the boundary layer. The large variation being in part due to the difference in oceanic residence time between gold and iridium. The Ir/Pd quotient at site 465A is close to the chondritic value and follows the pattern observed by Kyte *et al.*(1985). This may be due to a combination of more-similar oceanic residence times for iridium and palladium and to the lower susceptibility of palladium compared with gold in leaching from sediments.

### 2.2.7 Problems regarding the use of gold and palladium as indicators

Remobilisation of palladium and gold can occur as chloride complexes (Crocket *et al.* 1973) and these two elements appear to be more mobile than iridium within sediments. Submarine volcanism can produce high gold values (Crocket *et al.* 1973) however the Ir/Au quotients can distinguish these deposits from meteoritic sources. Interelement abundances of siderophiles can in general show great variation, possibly due to mobility of elements during the process of sedimentary diagenesis (Kyte *et al.* 1996).

In a study of platinum group elements in an early Archean impact deposit from the lower Fig Tree Group, Barberton Greenstone Belt, South Africa, Kyte *et al.*(1992) discovered low Ir/Pt and Ir/Os quotients but high Ir/Pd and Ir/Au quotients. The extreme age of this formation would have provided time for leaching of platinum group elements, possibly indicating that gold and palladium are more prone to leaching than platinum and osmium. The high platinum, osmium abundances are not typical of

terrestrial volcanic processes as Archean basalts (komatiites) although rich in gold and palladium are poor in iridium and osmium. Arguing for an impact origin the explanation for the lower than expected gold abundances in the Fig Tree Group could be explained by hydrothermal alteration as gold is more easily removed by this process than are other platinum group elements (Kyte *et al.* 1992). Thus gold and palladium abundances alone do not provide proof of an impact in the geological record.

## 2.3 Isotopic quotients for rhenium and osmium in K/T boundary sites

### 2.3.1 Rhenium and osmium isotopes as ETC indicators in the K/T boundary

Another important piece of evidence for the proposed impact of a chondritic meteorite at the K/T boundary is given by the Re-Os isotope system. Rhenium is an element that accumulates in the Earth's crust due to magmatic fractionation of mantle rocks (Kyte, 1988). The radionuclide  $^{187}\text{Re}$  decays with a half life of  $4.6 \times 10^{10}$  yrs to produce  $^{187}\text{Os}$  in proportion to the quotient of  $^{187}\text{Re}/^{186}\text{Os}$  originally present in the system. This process alters the  $^{187}\text{Os}/^{186}\text{Os}$  quotient in the Earth's crust to create, over time, a different isotopic quotient of  $^{187}\text{Os}/^{186}\text{Os}$  from that found in chondritic meteorites and the Earth's mantle.

Chondritic meteorites and the Earth's mantle have a  $^{187}\text{Re}/^{186}\text{Os}$  quotient of 3.2 which gives a  $^{187}\text{Os}/^{186}\text{Os}$  value of about one. Osmium is depleted in the crust relative to rhenium giving a high  $^{187}\text{Re}/^{186}\text{Os}$  crustal quotient and, using a crustal age of  $2 \times 10^9$  yrs, a crustal  $^{187}\text{Os}/^{186}\text{Os}$  quotient of about ten i.e. ten times that of the mantle or chondritic  $^{187}\text{Os}/^{186}\text{Os}$  quotient (Luck and Turekian, 1983). The  $^{187}\text{Os}/^{186}\text{Os}$  quotients for K/T boundary sites are much closer to mantle and chondritic values, e.g. Stevns Klint K/T boundary site averaged at 1.65 (Luck and Turekian, 1983) and the Woodside Creek K/T boundary site gave a  $^{187}\text{Os}/^{186}\text{Os}$  quotient of 1.12 indicating a mantle or meteoritic source for this layer (Lichte, *et al.* 1986).

### 2.3.2 Limitations of osmium isotope data as K/T indicators

One limitation of the Re-Os isotope quotient study is its inability to distinguish between meteoritic and mantle sources (Sawlowicz, 1993; Kyte, 1988). Luck and Turekian (1983) point out that a problem with using the  $^{187}\text{Os}/^{186}\text{Os}$  quotient as an indicator for ETC in marine K/T boundary sites is that the oceans accumulate material derived from crustal, mantle and meteoritic sources.

To counter this problem they analysed manganese nodules for  $^{187}\text{Os}/^{186}\text{Os}$  quotients from a variety of sites on the ocean floor and were able to determine that crustal sources dominated the  $^{187}\text{Os}/^{186}\text{Os}$  quotients for these nodules with values between six and eight. The average  $^{187}\text{Os}/^{186}\text{Os}$  value for Stevns Klint K/T boundary layer was 1.65 and much closer to the chondritic meteorite value of about one. This implied that the Stevns Klint K/T boundary layer osmium abundance was dominated by a single large meteoritic ETC input and not by the steady accumulation of osmium from a combination of mantle, crustal and meteoritic sources.

## 3.0 The Impact Event

### 3.1 Source of the K/T meteorite

#### 3.1.1 Introduction

Abundant chemical evidence exists supporting the impact of a large meteorite at the K/T boundary; *inter alia* iridium peaks, chondritic platinum group element abundances, shocked quartz, and nickel-rich spinels. The origin of the K/T meteorite is not abundantly clear and it may be impossible to determine whether it was a cometary or asteroidal body, for example, comets can lose their volatile components, move into asteroid orbits and effectively become asteroids (Weissman, 1982). I use the term meteorite for the K/T impactor to cover both asteroid and cometary bodies that enter Earth's atmosphere. The previous chapter indicated that the K/T boundary impactor was a chondritic meteorite, thus implying that the source object was small enough to escape chemical fractionation processes that occurred in the planets. Asteroids and comets in general are small enough to have escaped this process and therefore provide an obvious source for the chondritic meteorites.

The total population of Earth crossing asteroids is currently estimated at around 1300, of which only 2% have been observed to date (Shoemaker, 1983). Although the life expectancy of Earth crossing asteroids is only about 30 million yrs, the Earth crossing Apollo asteroids are constantly resupplied from the asteroid belt. Napier and Clube (1979) maintain that the asteroid belt is itself resupplied by interstellar material collected as the Sun enters a region of high density (a spiral arm) that sweep through the galaxy's star population (Croswell, 1996).

### 3.1.2 The Asteroid Belt

Unlike the planets, asteroids are not constrained to orbit the Sun at a fixed distance, although most of them dwell somewhere between the orbits of Mars and Jupiter. Their orbits are generally elliptical and easily perturbed by Jupiter's gravity (Shoemaker, 1983) with two asteroids, 1566 Icarus and 1862 Apollo crossing Earth's orbit to approach the Sun to 0.19 and 0.65 AU respectively (Krisciunas and Yenne, 1989). An AU is an astronomical unit or the mean distance from Earth to the Sun, thus any asteroid that comes within 1 AU of the Sun must intersect Earth's orbit.

Last century it was discovered that the asteroid 433 Eros came within the orbit of Mars, and in 1931 and again 1975 it came within 0.15 AU of Earth (Krisciunas and Yenne, 1989). This asteroid, with a diameter of 20 km, has a 24% chance of colliding with Earth in the next 400 Ma (Wetherill and Shoemaker, 1982). Evidence from terrestrial and lunar cratering rates indicate that 10 km diameter bodies have struck the Earth approximately once per 50 Ma during the Phanerozoic (Shoemaker, 1983).

### 3.1.3 Comets as possible impactors

Comets may have played a significant role in creating impact features on Earth. Five hundred comets have been observed as Earth crossing over the centuries and comet impacts may account for 30% of recent large craters of 10 km and above on Earth (Shoemaker, 1983). Significantly more than  $10^{12}$  comets exist in the Oort Cloud which represents the outer regions of the solar system (Weissman, 1990). Here they are disturbed by passing stars with a frequency that means at least 7 comet showers have been set off by stellar encounters since 3800 Ma, although this does not imply a periodicity to match extinction patterns (Weissman, 1990).

Earth-crossing comets impact Earth with mean a velocity of  $56.6 \text{ km sec}^{-1}$  this is faster than asteroid impact velocities of  $25 \text{ km sec}^{-1}$  (Napier and Clube, 1979). The higher velocity cometary impact could result in larger impact craters and a more diluted ETC signature than for the slower asteroids as more energy is available to excavate and displace target rock (Weissman, 1990). The probability of a 10 km diameter comet impact with Earth is greater than one per 4,500 Ma, with such an impact producing a crater size between 120 and 200 km depending on its impact velocity (Weissman, 1990). thus the K/T boundary event may have been a large cometary impact.

### 3.1.4 Origin of the K/T boundary impactor

Napier and Clube (1979) argued that to explain the relatively constant impact cratering rate over the last 3,000 Ma an interstellar source had to be invoked. They proposed that planetesimals occur in abundance in the galaxy's spiral arms and that a 10 km diameter planetesimal could be expected to impact Earth each 58 Ma leaving a crater 200 km diameter. Smit and Hertogen (1980) argued for a Solar System source of the K/T boundary impactor based on  $^{184}\text{Os}/^{190}\text{Os}$  isotope quotient within 0.1 % of the Solar System value. Alvarez *et al.* (1980) noted that the isotope quotients of iridium and rhenium imply a Solar System source for the K/T boundary impactor rather than an interstellar source where the isotope quotients may be different due to the contributions of supernova different from the one thought to have immediately preceded Solar System formation.

Hills (1981) proposed that a star with one solar mass, approaching within 3000 AU of the Sun each 500 Ma, could trigger a shower of comets sending 10-200 of them to Earth over a 1 Ma period. He suggested that this random stellar encounter could provide a possible mechanism for the K/T impact. This contrasts with the approach taken by Davis *et al.* (1984) who argued that the periodic extinctions in the fossil record is due to a dim, as yet unseen, companion to our Sun. This dwarf star would orbit at 2.4 light years from the Sun and perturb the Oort cloud of comets, sending a shower of them

towards the inner planets on a regular basis. The bulk of chemical evidence suggests that the K/T impactor originated within our Solar System or at least near enough to it in order to have inherited material from the same supernova.

## **3.2 Mechanism of Impact**

### **3.2.1 Atmosphere and Ocean interaction with the K/T impactor**

The Earth's atmosphere and oceans are able to absorb significant energy from impacting objects, for example a cometary body of density  $1.0 \text{ g/cm}^3$  and a  $0.17 \text{ km}$  diameter impacting at  $72 \text{ km/sec}$  would completely lose its cosmic velocity to the atmosphere (O'Keefe and Ahrens, 1982). Oceanic impact of an asteroid with a density of  $2.9 \text{ g/cm}^3$  and velocity of  $25 \text{ km/sec}$  requires 15 times the asteroids diameter of seawater depth to lose its cosmic velocity (O'Keefe and Ahrens, 1982). Entry through the atmosphere can even cause the break up of solid silicate bodies up to  $1 \text{ km}$  in diameter depending on the angle of entry (Melosh, 1982). The K/T boundary impactor, assuming an oceanic impact at  $25 \text{ km/sec}$ , would in less than a second have created a  $1000 \text{ km}^3$  mixture of target rock and water at a pressure of  $4.4 \text{ Mb}$  (Melosh, 1982).

The resultant water and rock vapour plume, at over four thousand times atmospheric pressure, would be sent hundreds of kilometres into the atmosphere as it expanded and cooled. Theoretical models of this oceanic impact predict that the vapour cloud should condense into rock particles of fine sand of  $100 \text{ }\mu\text{m}$  size (Melosh, 1982). This fine sand condensate would be predominantly of meteoritic origin and thus carry the chemical signature of the impacting meteorite, therefore a high ETC in the fine sand size particle range in the K/T boundary would support an oceanic impact.

### **3.2.2 Solid Earth absorbs most impact energy**

Large impacting bodies lose most of their energy to the solid Earth, thus creating high pressures in the target rock and within themselves. The release of this pressure causes large amounts of the target rock and all of the impactor to melt, with calculations by O'Keefe and Ahrens (1982) indicating that for an asteroid body with impact velocity of 45 km/sec, the energy released is sufficient to melt ninety times the impactor's mass of target rock (depending on the density and impact velocity of the asteroid). This high impact energy accounts for the diluted ETC signature in the K/T boundary layer worldwide.

A land impact generates higher initial pressures and creates a different vapour cloud than an ocean impact, this difference could account for a range of particle sizes condensing from these vapour clouds (O'Keefe and Ahrens, 1982). The vapour phase would carry a higher proportion of the impactor than material ejected ballistically from the impact site which would have contained a higher proportion of the target rocks (Melosh, 1982). Included in this ballistic material was found shocked quartz grains, these grains resulted from the high pressures created in the target rock during the impact process. Their distribution was plotted by Bohor (1992) who discovered that their particle size decreased with increasing distance from the proposed impact site.

### **3.2.3 Significance of vapour phase process in K/T boundary sediments**

Studies of the impact process and resulting deposit of ejecta indicate that for the K/T boundary impact (assuming a 10 km diameter meteorite) two dominant particle-size fractions emerge. Sand size particles were the expected mode for the vapour phase ejecta deposits (Melosh, 1982) based on the argument that a large impactor produces a larger vapour cloud and more time for condensation to occur. O'Keefe and Ahrens (1982) calculate that the maximum particle size resulting from the vapour cloud

condensation is sand size and that a fraction (0.01) of the impactors mass is deposited 10 km into the atmosphere as particles of clay size. Assuming that the strongest ETC signal is in the vapour phase deposits you could expect to find the strongest ETC signal in the sand and clay particle sizes. Melosh (1982) also proposed that the impact vapour plume was the vehicle for distributing the shock melted glass spherules (tektites) over the Earth's surface. These spherules may be the precursor to the smectite clays which compose a high percentage of the K/T boundary layer (Kastner *et al.* 1984).

### **3.2.4 Sand and clay fractions have highest ETC in boundary layer**

The mechanism of impact suggests that the vapour deposit layer of the K/T boundary should have a high ETC. Gold and palladium had higher abundances in the sand and clay size fractions than in the silt size fraction at the Woodside Creek K/T boundary site (Evans *et al.* 1993). This result fits with the model predicted for the impact where the sand size fraction represents the condensate from the vapour cloud formed due to the impact. A small fraction (0.001) of the total mass ejected by the impact was predicted to have been in the clay size fraction, but this size fraction was predicted to have contained a higher ETC (0.01) than other size fractions (O'Keefe and Ahrens, 1982).

This concentration in the clay size fraction means that, although not the predominant particle size, it was predicted to have contained a higher proportion of the ETC than other size fractions. Gold and palladium determinations in the sand, silt and clay size fractions for Woodside Creek and Chancet Quarry would add to the global picture of how the platinum group elements were distributed through the particle size ranges during the impact event.

### **3.2.5 Re-entry of vapour cloud particles and global wildfires**

A Key process in the impact event was the atmospheric re-entry of debris carried by the vapour cloud resulting from the impact event. The total of ejected mass from this

impact process was  $5 \times 10^{15}$  kg giving a global spread of  $10 \text{ kg m}^{-2}$  (Melosh *et al.* 1990). The heat released by atmospheric re-entry of these particles is sufficient to melt them with temperatures up to  $1300^\circ\text{C}$  generated on the particle surface. It is this release of thermal energy into the atmosphere that may have produced the lethal heat stress to animals and ignited the global wildfires described in Wolbach *et al.* (1988). The total amount of energy released in this process at  $5 \times 10^8 \text{ J m}^{-2}$  is more than sufficient to ignite the global fires, although the time over which this energy release occurred is important regarding its effect on biota (Melosh *et al.* 1990).

According to Melosh *et al.* (1990) after removing the fraction lost to re-radiation and water absorption, only one third of this total energy reaches the surface. They claim this still gives a  $10 \text{ kW m}^{-2}$  radiation for a few hours after the impact, the equivalent of a domestic oven set to broil. This represents a significant heating effect on the surface considering the average Solar Constant is  $1.37 \text{ kW m}^{-2}$ , where the Solar Constant is the rate at which the Sun's energy is received at the Earth's surface per unit area. Spontaneous ignition requires  $29 \text{ kW m}^{-2}$  but if heated at  $12 \text{ kW m}^{-2}$  for 20 mins or longer then ignition of vegetation can occur (Melosh *et al.* 1990). It seems likely that this re-entry heat of particles was sufficient to ignite vegetation particularly if applied over tens of minutes.

### 3.3 Cosmic spherules and nickel-rich spinels

#### 3.3.1 Origin of spherules

Cosmic spherules have been regarded as the molten droplets resulting from atmospheric entry of interplanetary dust (Kyte, 1988). The accretion of meteoritic material to the Earth is dominated by two size fractions, with large meteorites up to 5 km diameter having a total influx of  $20 \text{ Gg a}^{-1}$  ( $\text{Gg a}^{-1}$  equals billion grams per year) which just exceeds the influx of cosmic spherules at  $16 \text{ Gg a}^{-1}$  (Kyte, 1988). The cosmic origin of spherules has been recognised since the HMS Challenger expedition of 1891 (Kyte,

1988) with analysis of spherules collected from marine sediments revealing close to a chondritic abundance pattern (Ganapathy, 1978). The small particles size of many spherules ( $< 50 \mu\text{m}$ ) means they may survive atmospheric entry without melting (Kyte, 1988) and larger particles up to  $400 \mu\text{m}$  may survive the passage with some melting but still essentially intact (Ganapathy, 1978).

The chemical composition of spherules will reflect their sources with two major groups of spherules, stony and iron spherules. Stony spherules are composed of olivine, magnetite, and glass with a chondritic composition, and iron spherules composed of iron and nickel oxides, these spherules may contain high platinum group element abundances in the form of metal nuggets (Kyte, 1988). Ganapathy (1978) points out that spherules represent a truer sample of interplanetary material than do meteorites because meteorites represent only the stronger material that survived atmospheric passage intact whereas the spherules small size protects them against atmospheric disintegration.

### 3.3.2 Terrestrial spheroids

Brooks *et al.* (1985) classified spheroids in the K/T boundary deposits at Woodside Creek as having a terrestrial origin. They argued that although the spheroids had typical K/T boundary siderophile abundances (roughly 0.1 chondritic abundances), they were enriched in chalcophile elements such as arsenic above the chondritic abundances of these elements. These spheroids had a mean diameter of  $300 \mu\text{m}$  and are proposed to have been formed *in situ* due to reducing conditions at the time of deposition (Brooks *et al.* 1985). The Woodside Creek K/T boundary deposits formed in relatively shallow water, (200-600m water depth according to Strong 1977) reducing conditions. Brooks *et al.* (1985) proposed that the high iridium content of these spheroids was not due to their having arrived with it as for the cosmic spherules, but rather having collected it during their formation on the sea floor as they observed that the iridium abundance in the spheroids was lower than that of the surrounding matrix.

### 3.3.3 Nickel-rich spinels at the K/T boundary

In the vicinity of the K/T boundary sites evidence for a meteorite impact is present as nickel-rich spinels (Bohor *et al.* 1986; Robin *et al.* 1991; Rocchia *et al.* 1996). The occurrence of these nickel-rich spinels at precisely the K/T boundary in association with other indicators of meteoritic input, such as high platinum group element abundances and shocked quartz, is highly significant. Rocchia *et al.* (1996) reported on the presence of nickel-rich spinels in the most complete section of the K/T boundary located at El Kef, Tunisia. At this site a distinct mineralogical change occurred at the palaeontological K/T boundary signaled by a thin rusty brown layer containing the iron rich mineral goethite. This goethite layer contained an iridium peak and the nickel-rich spinels implying a common origin.

Nickel-rich spinels are formed when meteoritic material is melted and oxidised in passage through the Earth's atmosphere. Regularly found within cosmic spherules (Kyte *et al.* 1996), they are strongly associated with the K/T boundary layer (Bohor *et al.* 1986; Kyte, 1988). Characteristic features of these spinels are a high nickel (> 1.0 wt%) content and the high  $\text{Fe}^{3+}/\text{Fe}^{\text{tot}}$  ratio (> 70.0 atom%), the latter due to the high oxygen content in Earth's atmosphere (Robin *et al.* 1991). No known terrestrial process can form spinels with such high nickel contents and high  $\text{Fe}^{3+}/\text{Fe}^{\text{tot}}$  quotients (Rocchia *et al.* 1996). The nickel rich spinels therefore appear to indicate the vapour phase deposit of the K/T impact event, as the meteoritic rich vapour cloud condensed and re-entered the oxygen rich atmosphere (Bohor *et al.* 1986).

### 3.3.4 Spinel as vapour phase deposits

Rocchia *et al.* (1996) argue that the presence of nickel-rich spinels at precisely the K/T boundary and the underlying early sediments containing the cosmic spherules, indicates at least a two stage process for the impact event. Their in situ studies at

Mimbral (Mexico) and Brazos River (Texas), both shallow marine sites, and the deep water environments Beloc (Haiti) and Hole 536 (Gulf of Mexico) show exact correlation between the iridium abundance peak and nickel rich-spinels. This observation supports the earlier study of Robin *et al* (1991) who identified the same feature at the K/T boundary sites at El Kef (Tunisia) and Bohor *et al.* (1986) at Caravaca (Spain). Spherules were not restricted to the K/T boundary but rather spread across the sequence indicating they resulted from a process independent of the nickel rich spinel formation event. Kyte *et al* (1996) classifies two types of spherule, the larger type composed of target rock melt glass formed by ballistic processes resulting from the impact, and a smaller type that contains the nickel-rich spinel formed directly from the impact vapour cloud.

This interpretation is supported by Rocchia *et al.* (1996) who proposed the spherules represent the initial impact where significant amounts of molten/vaporised target rock were ejected on impact to solidify as spherules. This was followed by ricochet fragments of the bolide eventually landing, but only after some time in the oxidising conditions of Earth's atmosphere. This proposal appears to involve the Earth having a ring of debris from the initial impact that orbits at high altitude until it re-enters the atmosphere. The above interpretation differs from Bohor (1990) who proposed that the spherules represent the low-angle ejecta from the impact that arrived first at nearby sites, to be overlain by the spinels representing the vapour phase deposits of the same single impact event. Possibly both the single impact, vapour cloud condensation interpretation and the single impact followed by the gradual re-entry of material from a debris ring orbiting Earth, fit with evidence of cosmic spherules and nickel-rich spinels at the K/T boundary.

## 4.0 Methodology

### 4.1 Element determination methods

#### 4.1.1 Introduction.

Platinum group element analysis was, prior to the advent of instrumental neutron activation analysis (INAA) and graphite furnace atomic absorption spectrometry (GFAAS) mainly limited to  $\mu\text{g/g}$  (ppm) determinations (Potts, 1987). This level of sensitivity was not adequate for K/T boundary studies as typical crustal abundances of 0.01, 0.001, 0.01, and 0.004  $\mu\text{g/g}$  for palladium, iridium, platinum, and gold respectively have been reported (Mason, 1982).

The traditional tool for determinations of the platinum group elements at the K/T boundary has been INAA. This technique has been in use for element determinations in the  $\mu\text{g/g}$  to  $\text{ng/g}$  range since the 1960's (Potts, 1987). It was used for the iridium determinations in the Alvarez *et al.* (1980) paper proposing a meteoritic source for the observed iridium abundance anomaly at Gubbio, Italy.

#### 4.1.2 Instrumental neutron activation analysis

INAA requires that samples be homogeneous and ground to 0.075 mm size mesh before being irradiated in a flux of neutrons (Potts, 1987). This exposure to neutron bombardment creates isotopes of the elements which are then removed from the neutron source and allowed to decay. This process of nuclear decay emits specific packets of energy as gamma radiation which are characteristic of the elements in the sample. Certain elements can be measured with great precision by this method, iridium being a good example.

### 4.1.3 Radiochemical neutron activation analysis

A refinement of the INAA technique is radiochemical neutron activation analysis (RNAA) in which an already irradiated sample is chemically treated to further concentrate the desired element. This procedure is complex and involves handling radioactive samples, but results in exceptionally low levels of detection for specific elements i.e. pg/g for iridium (Brooks, 1987).

### 4.1.4 Graphite furnace atomic absorption spectrometry

Graphite furnace atomic absorption spectrometry (GFAAS) is a powerful analytical tool for element determinations at the ng/g level. Some of the platinum group elements such as platinum, gold, and palladium lend themselves well to GFAAS analysis at this level. Comparison of detection limits for these elements between GFAAS and neutron activation techniques (Potts, 1987) is as follows:

	INAA	GFAAS pub	GFAAS own
Au	0.3	1	0.5
Pd	15	1	1

TABLE 4.1  
TABLE OF DETECTION LIMITS IN NG/G: INAA AND GFAAS<sup>2</sup>

The above figure illustrates the potential of GFAAS determinations to at least match and, with palladium, exceed INAA detection limits for these two elements.

### 4.1.5 Determination limits

Results for the above detection limits are based on a 1 g sample extracted into 1 mL of MIBK (methyl isobutyl ketone) and using a visually identifiable peak of approximately 2 s above the background value. Potts (1987) recommends using the

<sup>2</sup> INAA and GFAAS pub are published INAA and GFAAS data values for gold and palladium taken from Potts (1987), except for GFAAS palladium data from Wilson *et al.* (1989). GFAAS own are this thesis results.

term 'limit of determination' as an average value that signifies the smallest value of quantitative measurement. This value sits at 6 s above the background mean (as opposed to the lower limit of detection which lies within 3 s of the background mean), but this is a rather conservative approach.

#### 4.1.6 Analysis theory

Emission spectrographs have been used since the early nineteenth century for qualitative determinations, as did Fraunhofer to determine the composition of the Sun in 1811, and in 1868 they were used to identify the element helium at the time undiscovered on earth (Fisher, 1987). Atomic absorption spectrometry (AAS) has been used since the early 1960's for quantitative element determinations. The principle of AAS is that the electrons of an atom absorb light at specific wavelengths. Each element, when in vapour form, produces a specific absorbance pattern as light is shone through it. The intensity of that specific absorbance pattern is dependent on the concentration of the element present.

Walsh in 1955 proposed that a continuous light source be replaced with an element specific line source. This had the great advantage of sending a specific frequency of light through the analyte that should be strongly absorbed by the element sought. This was achieved by using a hollow cathode lamp that was coated with the element to be analysed, meaning that the lamp would emit radiation that only the analyte would be able to absorb (Potts, 1987). The analyte is vaporised in a flame, through which light from the cathode lamp is shone and the amount of light absorption measured as the concentration of the analyte. This technique is known as flame atomic absorption spectrometry.

A refinement of this technique was proposed by L'vov in 1958 in which the flame was replaced by a graphite furnace. A small volume of analyte was injected into the

graphite tube and the tube heated through a series of steps up to the final atomisation temperature of the analyte. The key to high sensitivity with the graphite furnace is that during the atomisation stage the analyte is concentrated in the tube, thus allowing ample opportunity for absorption (Potts, 1987).

## **4.2 Sample analysis**

### **4.2.1 Sample pre-treatment.**

Samples were labeled to within one cm of their source in relation to the K/T boundary. Material from each sample was then dried and ground using a disk grinder before being sieved through a 0.5 mm plastic sieve.

### **4.2.2 Digestion**

For element determinations, approximately 1.0 g of sample was weighed out and the weight recorded to within 0.01 g. Initially this was then treated in a single digestion process that involved adding 10 mL of concentrated hydrochloric (HCl) followed by 3 mL of concentrated nitric acid (HNO<sub>3</sub>) and 5 mL of hydrofluoric acid (HF). This digestion was carried out in polypropylene beakers heated for 4-5 hrs. It was necessary to keep a close watch on the end point as the process had to go almost to dryness. This method was found to be slow and led to some samples being accidentally baked dry in the process.

### **4.2.3 Two stage digestion**

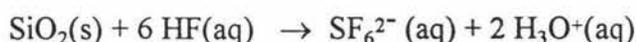
A new method of sample digestion was tried that involved adding to the 1 g sample, 5 mL of conc HNO<sub>3</sub> and 5 mL of conc HF. This mixture was taken to dryness in polypropylene beakers. The residue was taken up in 10 mL of aqua regia (1:4 mixture

of conc HCL and HNO<sub>3</sub>), decanted into glass beakers, and taken to almost dryness on a hot plate. This method not only improved the control of reaching exactly the point of dryness but also sped up the digestion time.

A crucial point in the digestion process was to ensure no excess HNO<sub>3</sub> remained in the aqueous solution as this can interfere with the later extraction process (either by oxidising the KI complexing agent or interfering with the absorption signal of the graphite furnace). The new method ensured that any residual HNO<sub>3</sub> is boiled off at the second stage of the digestion process by the addition of excess HCl as the solution nears dryness. This is possible because HNO<sub>3</sub> has a lower boiling point (83° C) than has HCl (110° C).

#### 4.2.4 Digestion theory

The choice of digestion acids accords with classical techniques for silicate rock analysis. It is widely accepted that hydrofluoric acid is required to attack silicate rock samples, usually combined with nitric acid although the actual proportions are debated (Potts, 1987). The key factor in using hydrofluoric acid is the solubility of the fluorosilicate ion (SF<sub>6</sub><sup>2-</sup>) in acidic solutions as the reaction proceeds (Atkins, 1989)



In the initial digestion the silicon is removed as volatile silicon tetrafluoride (SiF<sub>4</sub>). This stage is taken to dryness before the second step of aqua regia attack. Aqua regia is used to take up the residue of the first digestion. Nitric acid oxidises the gold metal to Au<sup>3+</sup> which then complexes with the chloride ions from hydrochloric acid to form soluble (AuCl<sub>4</sub>)<sup>-</sup>. This solution is heated over a hot plate until almost dry. When only one or two mL remain, more HCl is added to ensure that no HNO<sub>3</sub> remains. This almost dry residue is then taken up in 10 mL of 5M HCl and filtered to remove any insoluble residue.

#### 4.2.5 Extraction

As noted by Brooks and Lee (1987) the extraction process allows the analyte to be concentrated prior to determination. This lowers the limit of detection for each analysis by the ratio of the volume of, in this case, aqueous phase to organic phase. Previous work by Brooks and Naidu (1985) established that gold could be extracted as a chloro complex into methyl isobutyl ketone (MIBK). The relationship that controls the efficiency of extraction is:

$$E = 100 D / (D + V_a/V_o)$$

**E** = the extraction percentage of the analyte

**D** = the distribution co-efficient of the reaction

**V<sub>a</sub>** = the volume of the aqueous phase

**V<sub>o</sub>** = the volume of the organic phase

**D** was obtained by experimenting with various amounts of 100% KI solution added to 10 mL of the aqueous phase containing the analyte, and extracted with two mL of MIBK. The highest value of **D** obtained being 550 which was produced by adding 0.2 mL of a 100% KI solution, this was the amount used for the all extractions as it gave the high extraction coefficient for a small amount of KI added (refer figure 4.2 below).

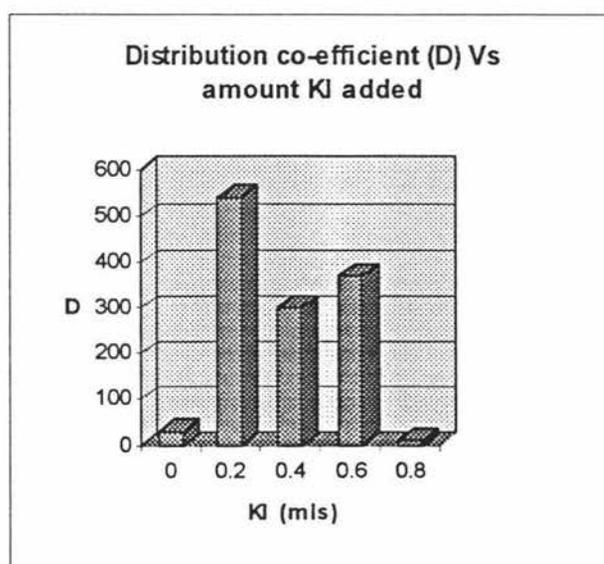


FIGURE 4.2 EXPERIMENTAL VALUES FOR D

#### 4.2.6 Furnace method development

To obtain the maximum sensitivity for determinations, various time/temperature combinations were trialed. The first stage of the firing was the drying stage in which the organic solvent was removed. Optimum time/temperature settings here were important in preventing spluttering of the sample out of the tube.

Trialing various ashing temperatures using standard solutions was important to ensure the best setting was achieved. This stage was the most difficult to arrive at the optimum, as too high a temperature results in loss of analyte and too low a temperature causes the risk of absorption by non-analyte elements in the atomisation stage. Potassium, used in the extraction process, was of particular concern as this appeared able to interfere with palladium determinations if the correct ashing temperature was not used.

The final stage of analysis was the atomisation phase where the analyte was vaporised in the tube at 2500° C and held for 2 or 3 seconds. This was the read stage of the firing in which light from the cathode tube passed through the volatilised analyte and the amount of absorbance measured. Settings for this stage are important, not for possible interference effects as in the ashing stage, but to give the best absorbance signal. In palladium determinations the concentration was measured as peak area under the absorbance signal, for gold determinations peak height was used. The table below gives the settings used for all gold and palladium determinations.

	Ash Temp	Ash hold	Atomisation Temp	Atomisation hold
Gold	400 °C	15 secs	2500 °C	2 secs
Palladium	900 °C	10 secs	2500 °C	3 secs

TABLE 4.2  
TABLE OF FURNACE SETTINGS FOR GOLD AND PALLADIUM

#### **4.2.7 Contamination Problems**

Assuming no inherent problems with sample inhomogeneity, the single greatest problem I encountered in analysing samples was contamination. This could be divided into the following areas:

##### **1. Contamination from reagents used**

The digestion acids (hydrochloric, nitric, and hydrofluoric acids) were separately analysed for gold and palladium as was the extraction reagent (MIBK). No source of contamination was identified in these reagents (with the exception of one bottle of MIBK which was not further used for analysis).

##### **2. Contamination between samples**

This was a real problem mainly in the extraction process where glassware was used for consecutive samples. For example, the separating funnel required careful washing and rinsing between each sample extract. Another way intersample contamination could occur was at the determination stage. The primary way was through accidental spillage of extracted samples, often caused by pressure build-up under the lid of the polypropylene sample extract vial. This was caused by the high vapour pressure of the MIBK solvent that could send the vial lid into the air.

##### **3. Standard-sample contamination**

Another route of contamination was present during the determination phase. It was noticed that there appeared to be a slight carry-over between a high standard and the first sample to follow it. The practical solution was to place a distilled water sample between the last standard and the first sample.

##### **4. Contamination from environmental sources.**

Gold and palladium are fortunately found in low levels in the environment with published values in the pg/g range for fresh water sources (Brooks, 1992)

making contamination from water used in the laboratory is unlikely. Despite this, a study undertaken in Berkeley in 1974 analysing atmospheric dust found 4 ng/g palladium, which in the pre-catalytic car exhaust days could be taken as background (Kothney, 1992).

### **4.3 Mineral analysis**

#### **4.3.1 Methodology**

The method followed for sample separation into sand, silt and clay size fractions and their respective mineral analysis was that of Whitton and Churchman (1987). No significant problems were encountered in the mineral analysis, except the low amount of silt fraction recovered from Chancet Quarry at the K/T boundary layer meant gold and palladium determinations for this fraction were not possible. Mineral analysis was undertaken using X ray diffraction facilities with quantitative estimates of the mineral groups present broadly following the procedures set out in Whitton and Churchman (1987).

Samples for mineral analysis were selected from three K/T boundary sites with two at Woodside Creek (East and West of the stream) and one at Chancet Quarry. Samples were taken at 1-2 cm intervals across the K/T boundary at both sites and analysed for major mineral groups (refer results section).

Sand, silt, and clay size fractions across the K/T boundary at these sites were also determined for gold and palladium. The objective of this exercise was to identify which size fraction the gold and palladium were concentrated in and test the impact theory described in chapter three that predicted the highest ETC of the impact layer would be found in the sand and clay size fractions. These results could be correlated with similar

studies of the platinum group element abundances among sand, silt, and clay size fractions from other K/T boundary sites (Evans *et al.* 1994).

#### 4.4 PTC 1 Standard rock analysis

##### 4.4.1 Introduction

Palladium standard rock analysis was performed on the standard rock PTC 1. This was necessary to check the accuracy of the method used for element determinations. The following method developed for the determination of palladium in K/T boundary samples was used to determine palladium in the PTC 1 sample.

##### 4.4.2 Method

1. Weigh out 1 gm of the standard rock and record the weight precisely.
2. Dissolve the sample in 10 mLs of a 1:1 mixture of concentrated nitric and hydrofluoric acid. Take this mixture to dryness in a polypropylene beaker.
3. Take up in 10 mLs of a 1:4 mixture of concentrated nitric and hydrochloric acid. Any residual sulphur undissolved in this solution is oxidised by the addition of 1 mL of liquid bromine.
4. Take the solution almost to dryness on a hotplate then take up in 10 mL of 5 M hydrochloric acid. Filter to remove any remaining undissolved material and make up to 100 mL using 5 M hydrochloric acid.
5. Extract 10 mLs of this stock solution with 2 mL of methyl-isobutyl-ketone (MIBK). This removes the iron and gold from the aqueous solution.

6. Further dilute 1 mL of this extracted organic solution to 10 mLs with 5 M hydrochloric acid. Extract this solution with 1 mL of pre-equilibrated MIBK and determine for palladium by graphite furnace spectrometry.

#### 4.4.3 Results

Figure 4.2 plots results of the PTC 1 standard rock analysis for palladium concentrations. The accepted value for this standard rock is 12.7  $\mu\text{g/g}$  palladium. The range of results obtained from PTC 1 was less than 5 ppb indicating a high degree of reproducibility for the method used and the high accuracy (less than 6% error) indicates that the extraction process and analysis stage were efficient. Palladium standards used in the analysis stage were prepared in MIBK solutions to ensure they were in the same organic solution that the samples were extracted into.

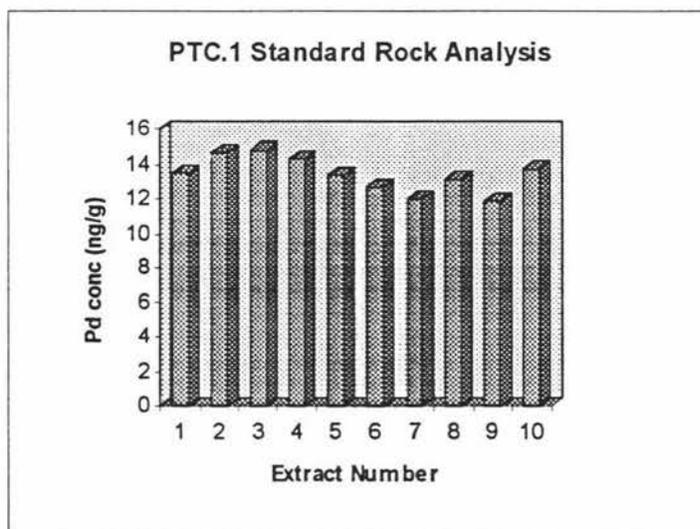


FIGURE 4.2 PALLADIUM DETERMINATION RESULTS FOR 10 EXTRACTS OF PTC.1<sup>3</sup>

<sup>3</sup> Palladium concentration plotted in ng/g as determined from diluted sample. Concentration in standard rock PTC1 obtained by multiplying this result by  $10^3$ .

#### 4.4.4 Analysis of results.

The mean palladium concentration was 13.4  $\mu\text{g/g}$  with a standard deviation of 1.0665. The difference between the sample mean and the published mean of the sample was 0.7 which is 5.2 % of 13.4. This gave a percentage error of 5.2 from the published value of 12.7  $\mu\text{g/g}$ . This percentage error is within the limits for published error values using standard rock element determinations. Evans *et al.*(1993) had a 7 % error on palladium determinations with K/T boundary samples using ICP-MS techniques.

## 5.0 Results

### 5.1 Iridium, gold, and palladium abundances across the K/T boundary.

Gold and palladium abundances are plotted against iridium to establish if a close relationship exists between their abundances across the K/T boundary and that of iridium. Gold and palladium abundances are given on a decalcified basis using carbonate data from Brooks *et al.*(1984) and Strong *et al.*(1987) for Woodside Creek and Chancet Quarry. Iridium data was supplied by Orth (pers comm to R. R. Brooks) and are also presented on a decalcified basis.

#### 5.1.1 Woodside Creek gold Vs iridium abundances

There appears to be a strong correlation between gold and iridium abundances in whole-rock determinations of Woodside Creek samples (figure 5.1 below). The  $r^2$  value for the regression trend line in figure 5.1 indicates a strong positive correlation between gold and iridium abundances. This result supports the argument for using gold as an indicator for the ETC component in K/T boundary samples at this site. Gold results for this site agree well with Lichte *et al.* (1986) who used INAA techniques for gold determinations. The Ir/Au quotient is about 2.2 for these samples which indicates an extraterrestrial source (Palme, 1982).

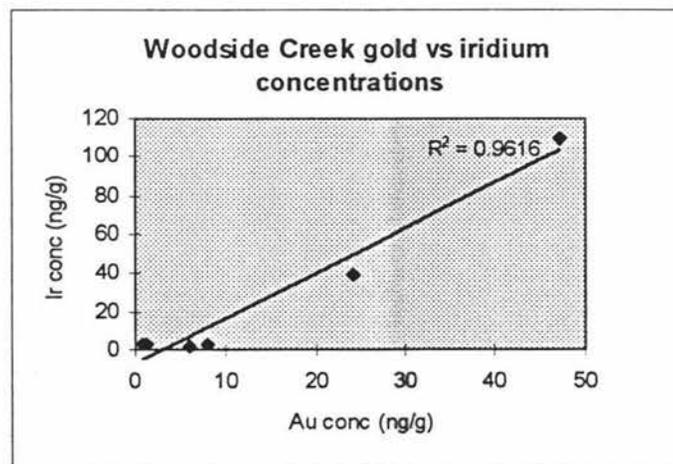


FIGURE 5.1 WOODSIDE CREEK IRIDIUM VS GOLD ABUNDANCES

Significantly, the integrated gold abundances across the K/T boundary give 15 ng/g which is 0.1 of the chondritic value of 140 ng/g (Anders and Grevesse, 1989). This is in good agreement with the expected abundances of the platinum group elements at the K/T boundary (Ganapathy, 1980) and demonstrates the value of using integrated abundances across the K/T boundary (Kyte *et al.* 1985).

### 5.1.2 Woodside Creek palladium Vs iridium abundances

The correlation between palladium and iridium abundances at Woodside Creek is close as shown in figure 5.2 (below). The Ir/Pd quotient (about 4.0) does not match a chondritic quotient of these elements, but does follow the trend for high Ir/Pd quotients in ancient impact derived deposits (Kyte, 1992). The  $r^2$  value for the regression trend line shown in figure 5.2 indicates a strong positive correlation between palladium and iridium. Integrated palladium values at this site are less than the expected 0.1 of the chondritic value.

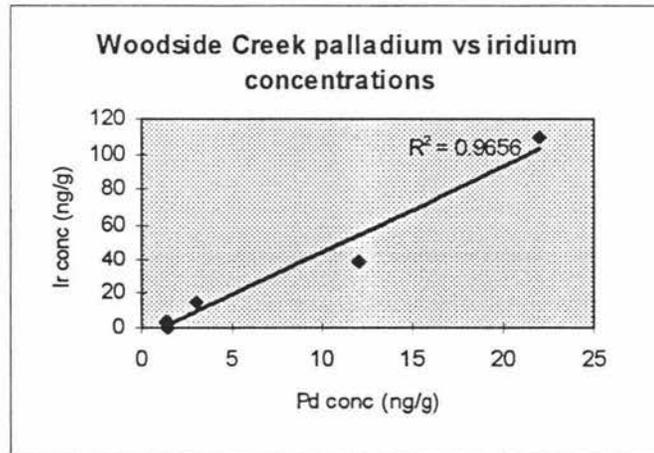


FIGURE 5.2 WOODSIDE CREEK IRIDIUM VS PALLADIUM ABUNDANCES

### 5.1.3 Chancet Quarry gold Vs iridium abundances

Chancet Quarry gold results show a strong positive correlation between gold and iridium abundances ( $r^2$  value of 0.9489). The Ir/Au quotient (0.3) appears to have a more terrestrial signature than that of Woodside Creek. Gold values across the boundary are almost exactly the expected 0.1 of chondritic gold abundance, i.e. a mean value of 18 ng/g observed instead of the predicted 15 ng/g.

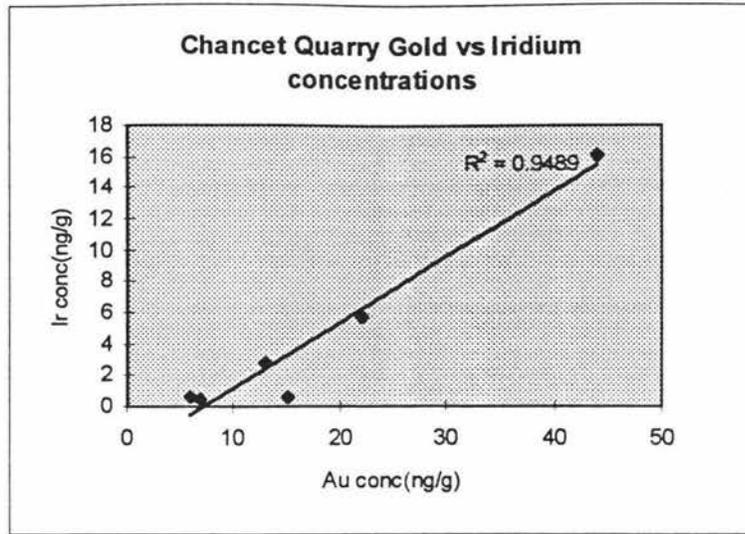


FIGURE 5.3 CHANCET QUARRY GOLD VS IRIDIUM ABUNDANCES

#### 5.1.4 Chancet Quarry palladium Vs iridium abundances

Chancet Quarry palladium results show a strong positive relationship between palladium and iridium (refer figure 5.4 below) with an  $r^2$  value of 0.9077. The Ir/Pd quotient at Chancet (0.3) is markedly different from the Woodside Creek Ir/Pd quotient (4.0). The integrated palladium abundance across the Chancet K/T boundary is 25 ng/g, this value agrees well with the K/T boundary palladium abundance at Gubbio (Ebihara and Miura, 1996).

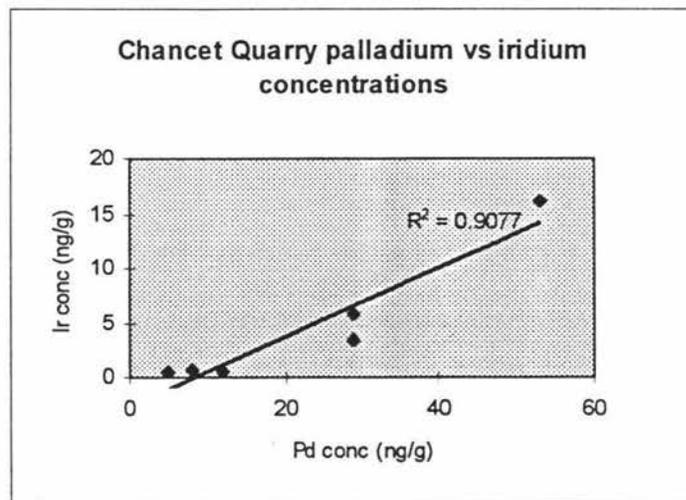


FIGURE 5.4 CHANCET QUARRY PALLADIUM VS IRIDIUM

Smaller Ir/Au and Ir/Pd quotients at Chancet Quarry than at Woodside Creek reflect a higher abundance of iridium at Woodside Creek than at Chancet Quarry. Gold and palladium abundances across the boundary at both Woodside Creek and Chancet

Quarry are similar, iridium is above the expected 0.1 of its chondritic abundance at the Woodside Creek boundary and below it at Chancet Quarry. Possibly more iridium determinations at these two sites could reduce the large variability in observed iridium abundances.

Dissolution of the limestone sediment at Woodside Creek, combined with the ability of gold and palladium to form chloride complexes in seawater (Crocket *et al.* 1973) may help to account for the higher Ir/Au and Ir/Pd quotients at Woodside Creek. This explanation is supported by an observed time gap in the foraminiferal record at Woodside Creek (Strong, 1977). Chancet Quarry, in contrast, represents the most complete foraminiferal record of the K/T boundary event identified to date in New Zealand (Strong *et al.* 1987). Iridium abundances at this site agree well with those from the K/T boundary site at DSDP Hole 465A of 10 ng/g (Kyte *et al.* 1996).

## 5.2 Whole-rock determinations

### 5.2.1 Woodside Creek gold abundances across the K/T boundary

Gold abundances rise from a background of less than 5 ng/g to a peak of 55 ng/g at the K/T boundary. This maximum value for gold agrees well with that of Lichte *et al.* (1986) who reported 59 ng/g for gold at the Woodside Creek K/T boundary. Comparison between these gold values and those of Orth show an excellent correlation ( $r^2 = 0.9907$ ).

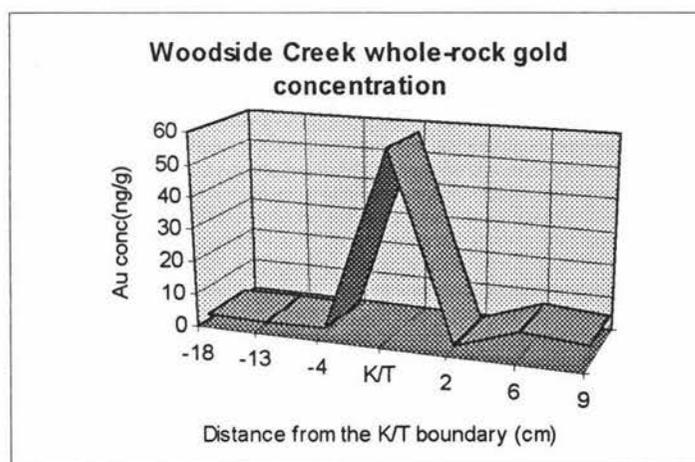


FIGURE 5.5 WOODSIDE CREEK WHOLE-ROCK GOLD ABUNDANCES

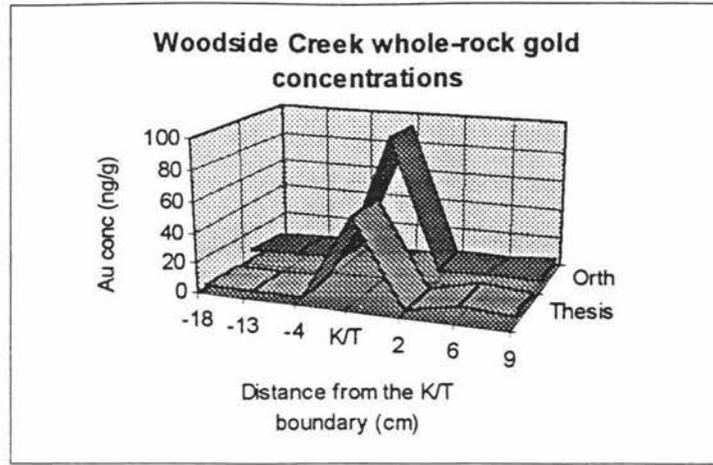


FIGURE 5.5A COMPARISON OF WOODSIDE CREEK WHOLE-ROCK GOLD ABUNDANCES

Woodside Creek whole-rock gold abundances in both this thesis and Orth's data peak on the K/T boundary implying the sudden input of material enriched in gold compared with the surrounding rocks.

### 5.2.2 Woodside Creek palladium abundances across the K/T boundary

Palladium abundances at Woodside Creek rise from the background level of less than 1 ng/g to a peak over 20 ng/g (figure 5.6). This is comparable with palladium values for the K/T site at Gubbio which ranged from 9 to 25 ng/g (Ebihara and Miura, 1996). This trend also agrees well with palladium values across a Proterozoic impact ejecta horizon in Australia where the palladium abundance rises from a background of 1 ng/g to a peak of 10 ng/g at the impact horizon (Wallace *et al.* 1990).

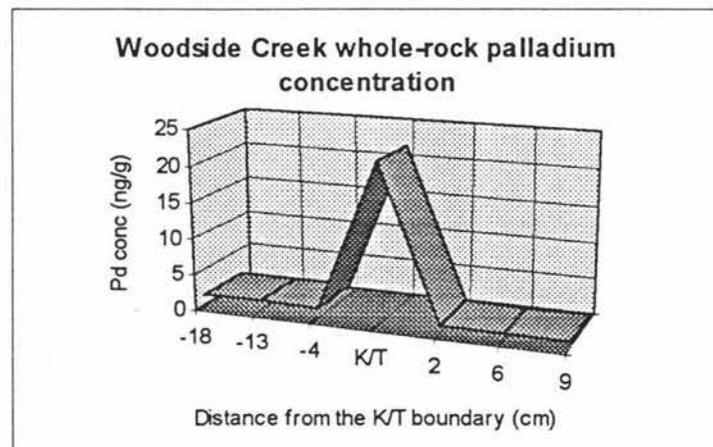


FIGURE 5.6 WOODSIDE CREEK WHOLE-ROCK PALLADIUM ABUNDANCE

Palladium whole-rock abundances at Woodside Creek, like gold, show a peak at the K/T boundary indicating the sudden input of material enriched in palladium. This observation fits well with an enrichment in the boundary layer from a chondritic meteorite source.

### 5.2.3 Chancet Quarry gold abundances across the K/T boundary

Gold abundances at the Chancet Quarry site are higher than at Woodside Creek (refer section 5.1), and demonstrate the same abundance pattern of a large peak at the K/T boundary (figure 5.7). Comparison of these gold values with those of Orth shows excellent correlation ( $r^2 = 0.9706$ ). The peak gold abundance (44 ng/g) shows good agreement with that found at Woodside Creek (55 ng/g) and agrees well with the mean gold abundance in the K/T boundary layer for Woodside creek reported in Brooks *et al.* (1984) of 42 ng/g. Excellent agreement also exists with that of Kyte *et al.* (1985) who determined a gold abundance value of 43 ng/g in the basal layer of the K/T boundary at Caravaca, Spain.

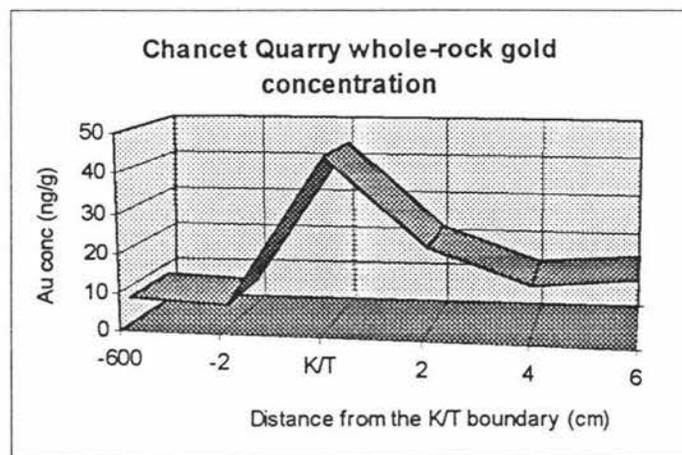


FIGURE 5.7 CHANCET QUARRY WHOLE-ROCK GOLD ABUNDANCES

Gold abundances across the K/T boundary at Chancet Quarry show excellent agreement to that of Orth, with both peak gold values precisely on the K/T boundary and within 7 % of each other (refer fig 5.7A below).

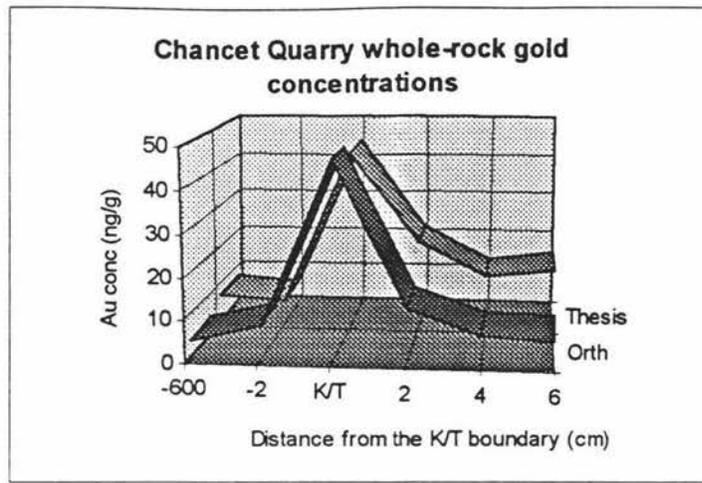


FIGURE 5.7A COMPARISON OF CHANCET QUARRY WHOLE-ROCK GOLD ABUNDANCES

#### 5.2.4 Chancet Quarry palladium abundances across the K/T boundary

Palladium abundances at Chancet Quarry demonstrate a peak of 53 ng/g at the K/T boundary (figure 5.8) which is close to the value of 46 ng/g determined for the K/T boundary at Stevns Klint (Kyte *et al.* 1985). The palladium concentration declines gradually from the K/T boundary peak over 8 cm to the background level of less than 10 ng/g, this may represent reworking of the initial deposit by sea floor currents or bioturbation. The peak palladium value of 53 ng/g is exactly on the expected 0.1 of the chondritic abundance (Ganapathy, 1980).

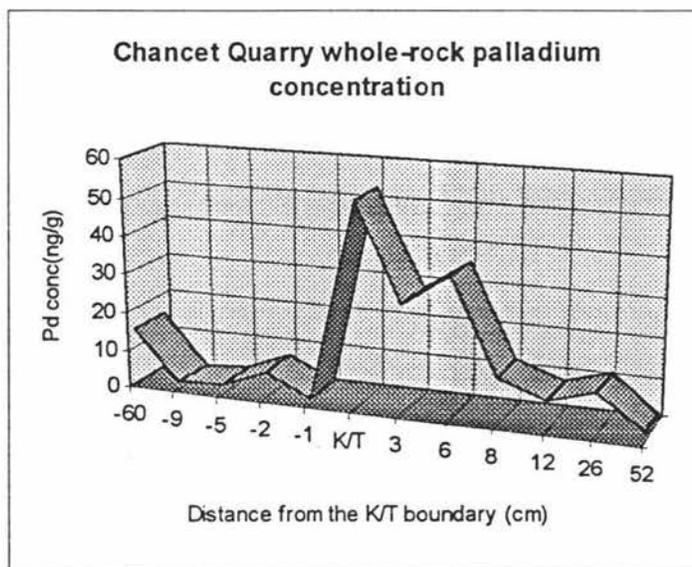


FIGURE 5.8 CHANCET QUARRY WHOLE-ROCK PALLADIUM ABUNDANCE

### 5.3 Particle size fraction gold and palladium determinations

#### 5.3.1 Woodside Creek West gold abundances

Gold abundances for the sand fraction peak at the K/T boundary for this, the original K/T boundary site, at over 500 ng/g (fig 5.9 a). This possibly indicates the site collected the high ETC sand fraction particles due to reworking of the initial deposit. The sand fraction at this site certainly represents material deposited from the re-entry of the vapour phase of the K/T impact event. I suspect sand fraction contains the nickel-rich spinels characteristic of re-entry material at K/T boundary sites world-wide. Silt and clay size fractions (fig 5.9 b, 5.9 c) are closer to the expected values of gold with the clay fraction exactly on the 0.1 of chondritic gold abundance (15 ng/g).

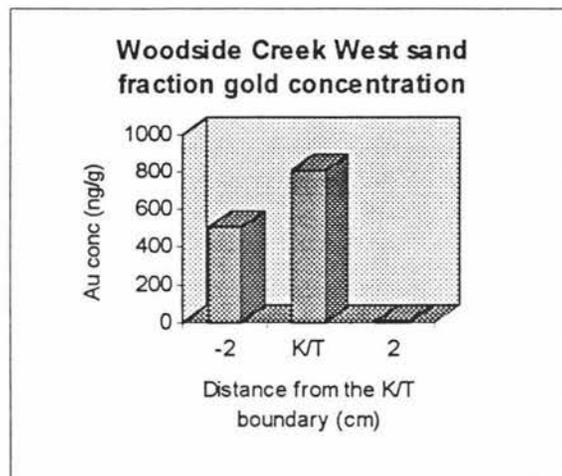


FIGURE 5.9 (A) WOODSIDE WEST GOLD SAND FRACTION

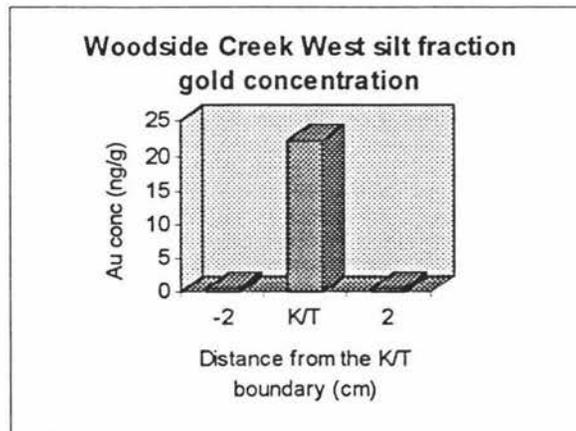


FIGURE 5.9 (B) WOODSIDE WEST GOLD SILT FRACTION

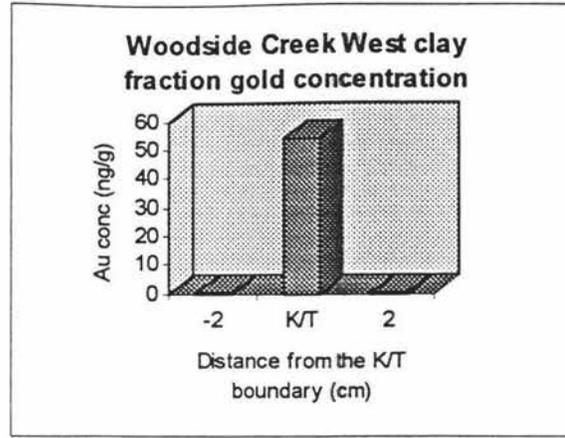


FIGURE 5.9 (C) WOODSIDE WEST GOLD CLAY FRACTION

### 5.3.2 Woodside Creek West palladium abundances

Palladium trends the same as gold abundances with a preference for the sand and clay size fractions. The sand fraction palladium abundance peak of 30 ng/g at the K/T boundary (fig 5.10a) is less than the expected 0.1 of the chondritic abundance (56 ng/g) and less than the value for these fractions in Evans *et al.* (1993) but within the same order of magnitude. The silt fraction abundance peak (8 ng/g) agrees very well with Evans *et al.* (1993) integrated silt value of 12 ng/g.

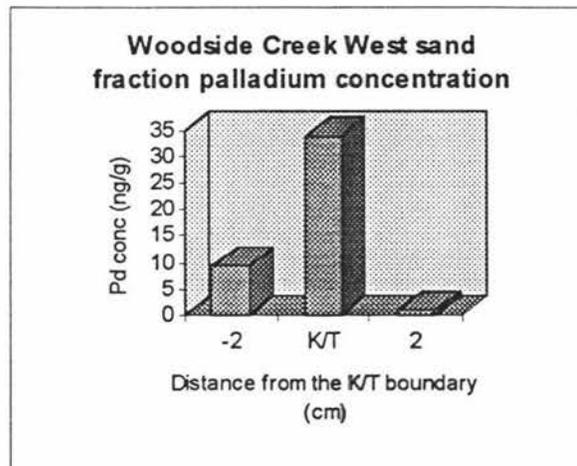


FIGURE 5.10 (A) WOODSIDE WEST PALLADIUM SAND FRACTION

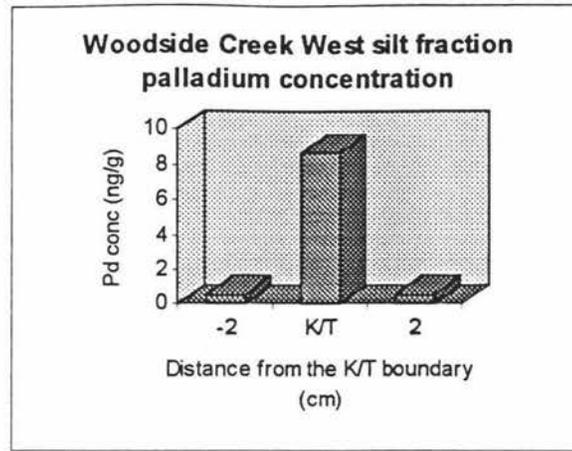


FIGURE 5.10 (B) WOODSIDE WEST PALLADIUM SILT FRACTION

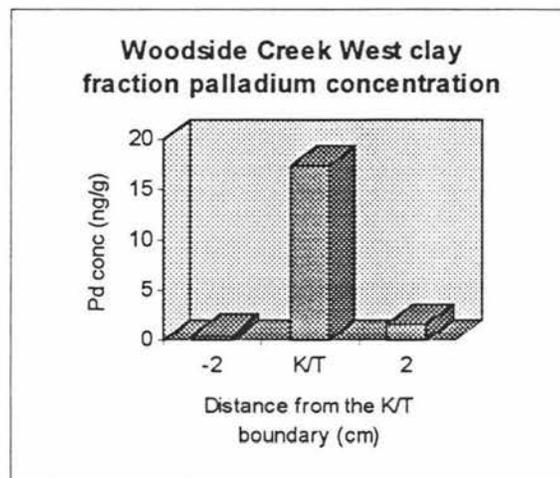


FIGURE 5.10 (C) WOODSIDE WEST PALLADIUM CLAY FRACTION

### 5.3.3 Woodside Creek East gold abundances

Gold abundances in the sand fraction for this site peak at the K/T boundary with 280 ng/g indicating a concentration of the ETC in this fraction (fig 5.11 a). The clay fraction gold abundance of 15 ng/g (fig 5.11 b) was exactly the expected abundance for gold from the vapour phase of 15 ng/g or 0.1 of the chondritic gold abundance. This indicates that this site received direct fallout from the vapour phase of the K/T impact (Ganapathy, 1980; Melosh, 1982).

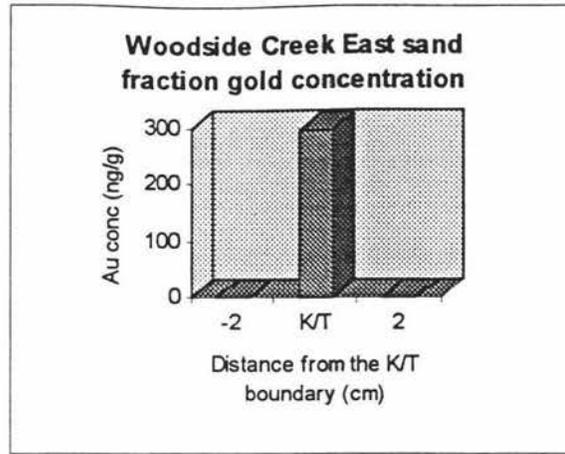


FIGURE 5.11 (A) WOODSIDE EAST GOLD SAND FRACTION

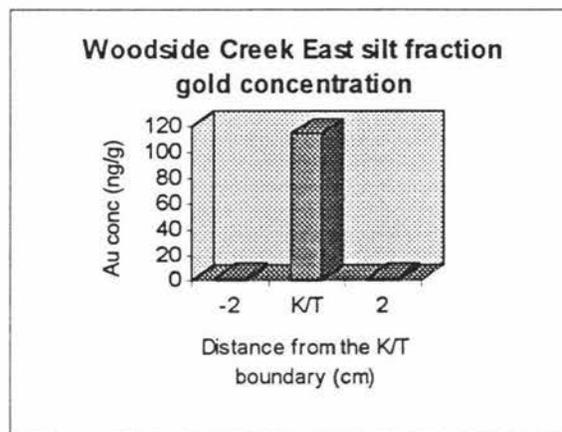


FIGURE 5.11 (B) WOODSIDE EAST GOLD SILT FRACTION

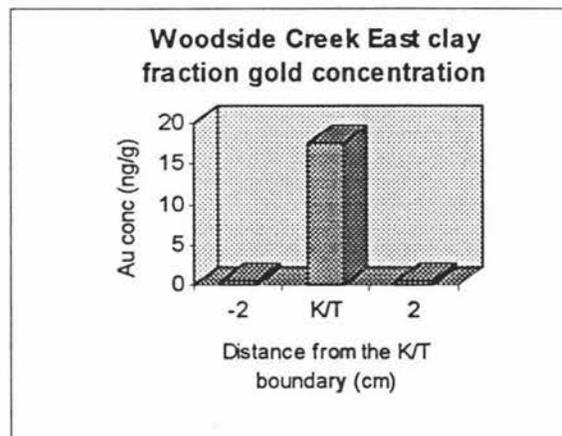


FIGURE 5.11 (C) WOODSIDE EAST GOLD CLAY FRACTION

### 5.3.4 Woodside Creek East palladium abundances

Palladium abundances at this site (figs 5.12a, b, c) peak at the K/T boundary but at significantly lower levels than palladium at the West site, with the exception of the clay fraction, which peaked on the boundary with 28 ng/g. This result supports the trend for both Woodside Creek sites to show the expected 0.1 chondritic gold abundance levels or above, yet less than 0.1 chondritic palladium abundance levels.

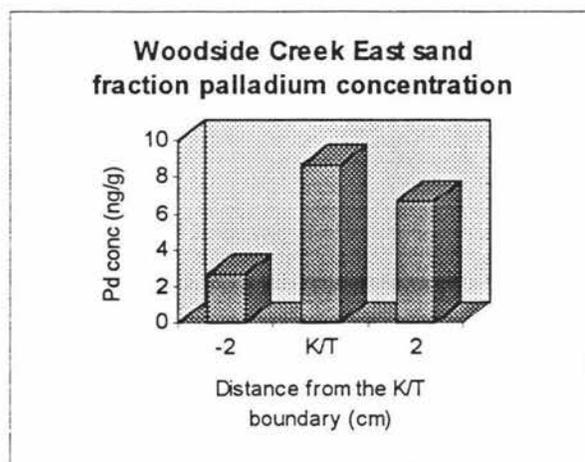


FIGURE 5.12 (A) WOODSIDE EAST PALLADIUM SAND FRACTION

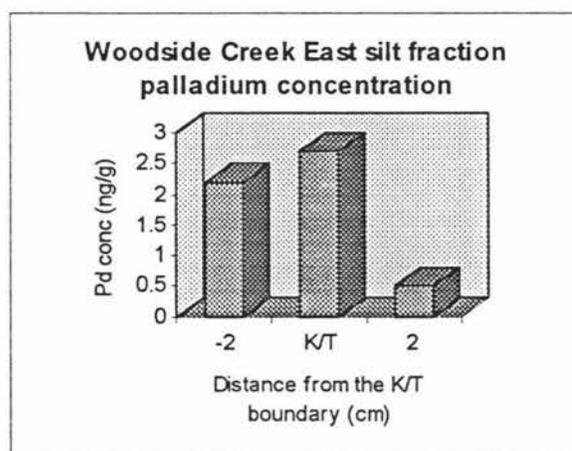


FIGURE 5.12 (B) WOODSIDE EAST PALLADIUM SILT FRACTION

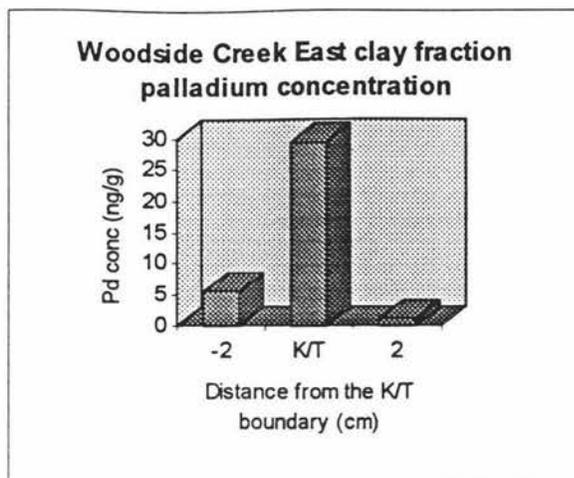


FIGURE 5.12 (C) WOODSIDE EAST PALLADIUM CLAY FRACTION

### 5.3.5 Chancet Quarry gold abundances

Gold abundances for this site peak at the K/T boundary with 2 ng/g for the sand fraction (fig 5.13a) and 12 ng/g in the clay fraction (fig 5.13b). The clay fraction gold abundance is in good accordance with the expected 0.1 chondritic pattern for gold at the K/T boundary.

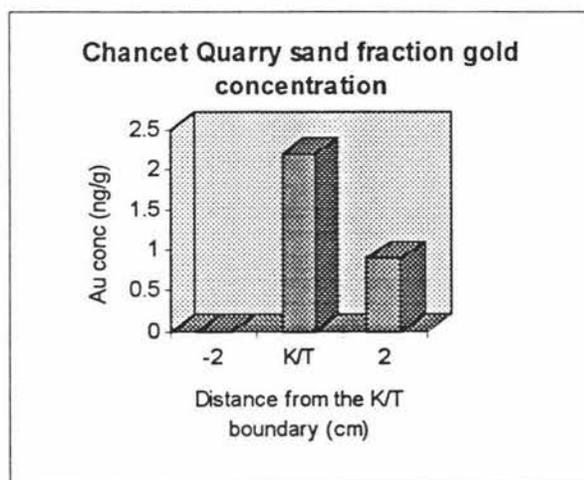


FIGURE 5.13 (A) CHANCET GOLD SAND FRACTION

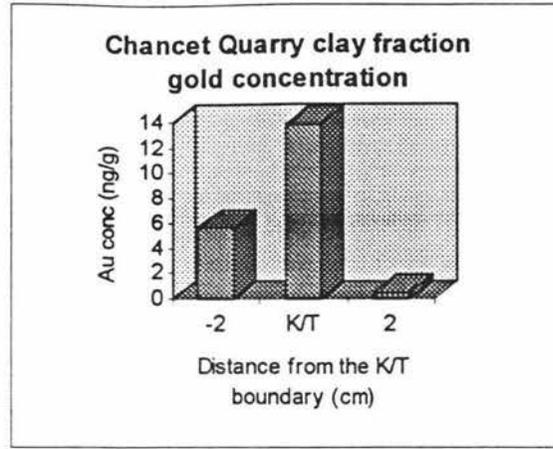


FIGURE 5.13 (B) CHANCET GOLD CLAY FRACTION

### 5.3.6 Chancet Quarry palladium abundances

Palladium abundances at Chancet Quarry (figs 5.14 a, b) peak at the K/T boundary and follow the Woodside Creek pattern of lower than expected levels for the vapour phase deposits. The distribution of palladium across the K/T boundary for this site indicates that the sand fraction suffered reworking (fig 5.14a) possibly due to sea floor currents which may have played a significant role in platinum group element distribution at marine K/T boundary sites (Kyte *et al.* 1985).

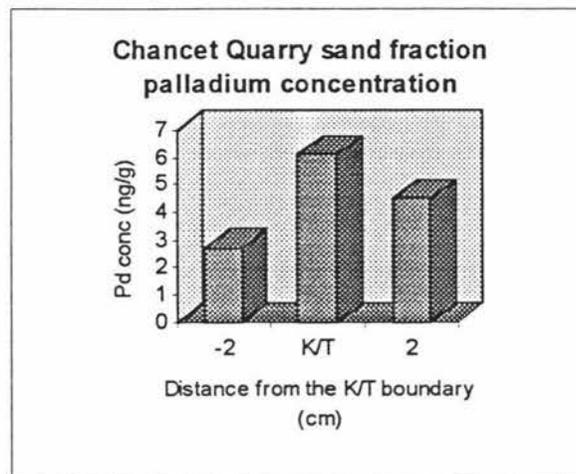


FIGURE 5.14 (A) CHANCET PALLADIUM SAND FRACTION

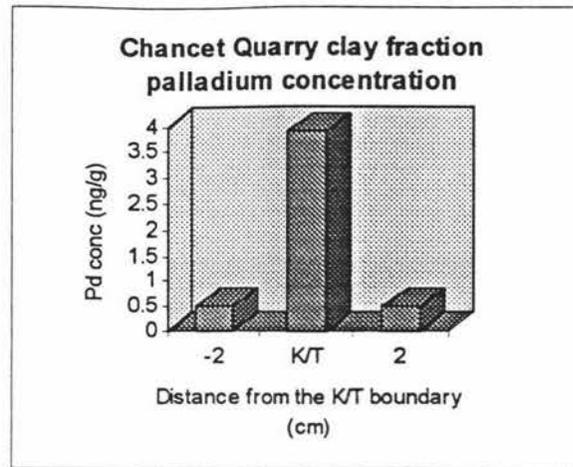


FIGURE 5.14 (B) CHANCET PALLADIUM CLAY FRACTION

## 5.4 Mineralogical analysis results

### 5.4.1 Woodside Creek West mineralogy

Sand, silt and clay size fractions for this site show significant changes at the K/T boundary. The sand fraction results (fig 5.15a) reveal a drop in the quartz component and the appearance of goethite and baryte at the K/T boundary. Goethite was also isolated at the El Kef K/T boundary site in Tunisia (Rocchia *et al.* 1996), its presence could be explained by the input of excess siderophile elements expected in the debris of a chondritic impact. Silt and clay fractions reveal an increase in smectite minerals that could have formed from the weathering of impact debris (Orth *et al.* 1990) although other terrestrial processes could also account for the changes in mineralogy observed. Shocked quartz has been identified at this site (Bohor, 1990) and gold and palladium abundance peaks on the K/T boundary supports the impact explanation for the observed change in mineralogy.

Brooks *et al.* (1986) commented that Woodside Creek was highly silicified and that this could have caused the finer clay particles to aggregate into coarser sand size fractions (Evans *et al.* 1993). In favour of this theory is the observed high palladium and gold abundances in the coarse sand size fractions at this site, against is the observed increase in smectite composition at the K/T boundary (fig 5.15a ) which if silicified should appear in the coarse sand fraction.

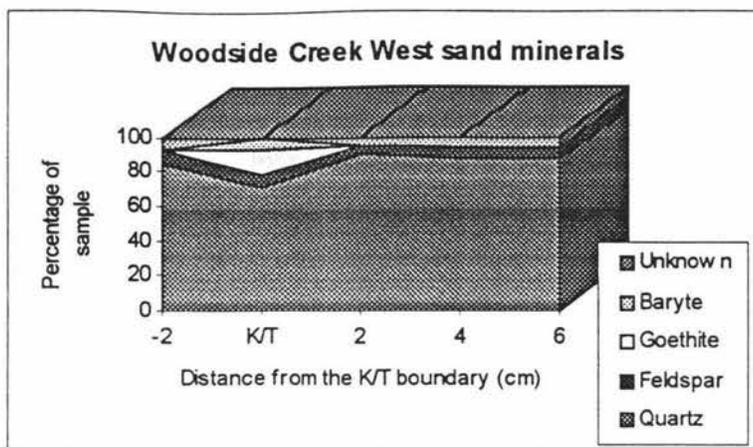


FIGURE 5.15 (A) WOODSIDE WEST SAND MINERALS

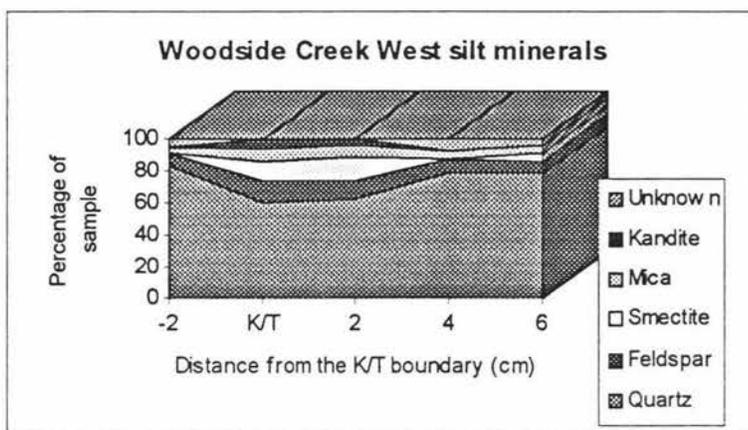


FIGURE 5.15 (B) WOODSIDE WEST SILT MINERALS

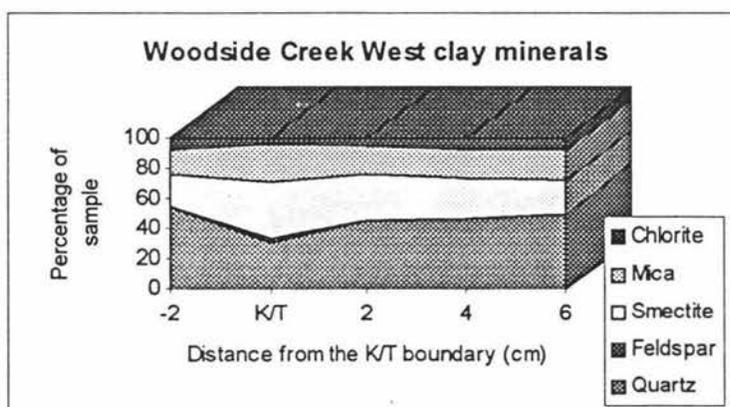


FIGURE 5.15 (C) WOODSIDE WEST CLAY MINERALS

### 5.4.2 Woodside Creek East mineralogy

This site reveals a sharp decrease in the quartz component at the K/T boundary particularly in the clay fraction (fig 5.16c) where the quartz component drops from 100% to less than 40%. The high smectite content of the clay fraction is in good agreement with that observed at the Stevns Klint K/T boundary site in Denmark where it is attributed to the alteration of impact spherules (Kastner, 1984). The silt fraction (fig 5.16 b) quartz component also decreases at the K/T boundary and recovers gradually above it to almost pre-boundary levels.

One explanation for the sudden change in mineralogy at the K/T boundary is that the impactor (presumably a chondritic meteorite, refer chapter two) was most likely comprised 90% of the minerals olivine and pyroxene (McSween, 1987). These minerals provided the basic ingredients for the iron-rich aluminosilicate impact spherules observed at the K/T boundary (Alvarez, 1986). Vaporised target rock (Melosh, 1982; O'Keefe and Ahrens, 1982) however, would have provided the bulk of the material from which these spherules condensed.

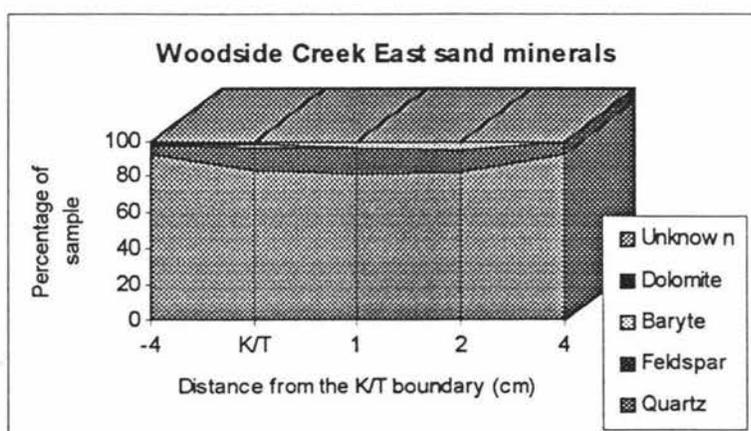


FIGURE 5.16 (A) WOODSIDE EAST SAND MINERALS

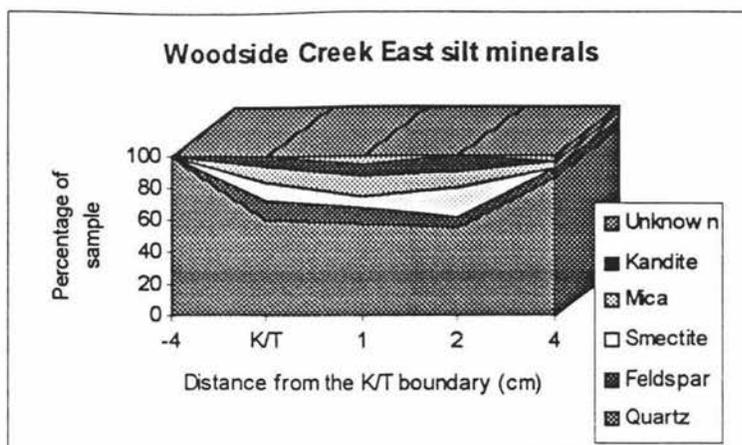


FIGURE 5.16 (B) WOODSIDE EAST SILT MINERALS

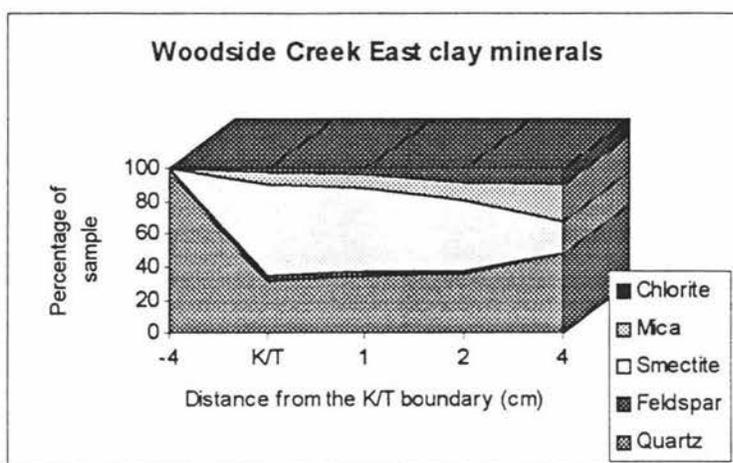


FIGURE 5.16 (C) WOODSIDE EAST CLAY MINERALS

### 5.4.3 Chancet Quarry

The mineralogical trend at this site reflects the alternating bands of hard siliceous sediment interlaid with calcareous mudstone (Strong *et al.* 1987). These alternating siliceous and calcareous mudstone bands dominate the mineralogy of the site making the K/T boundary clay difficult to distinguish from other thin calcareous mudstone layers. The presence of chlorite at this site but not at the Woodside Creek sites may indicate a greater burial depth (Kastner, 1984) of the K/T boundary layer here. As for the Woodside Creek sites, the highest clay component of the sequence coincides with the K/T boundary layer (fig 5.17 c). This can be explained by the addition of the impact debris that, over time, altered to smectite minerals that now compose the bulk of the boundary layer.

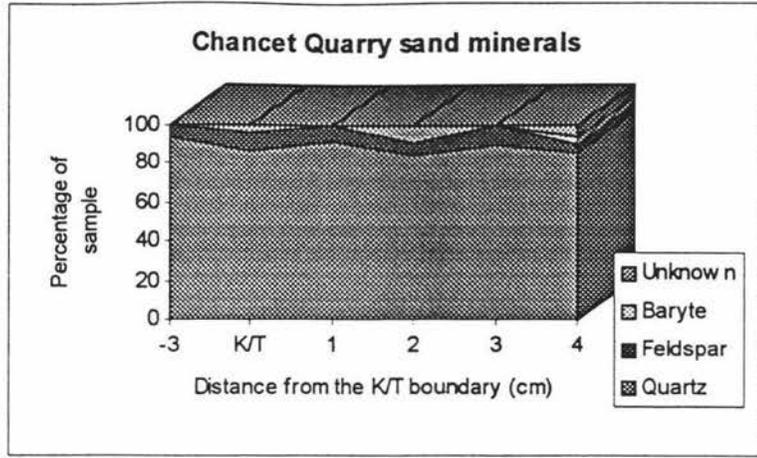


FIGURE 5.17(A) CHANCET SAND MINERALS

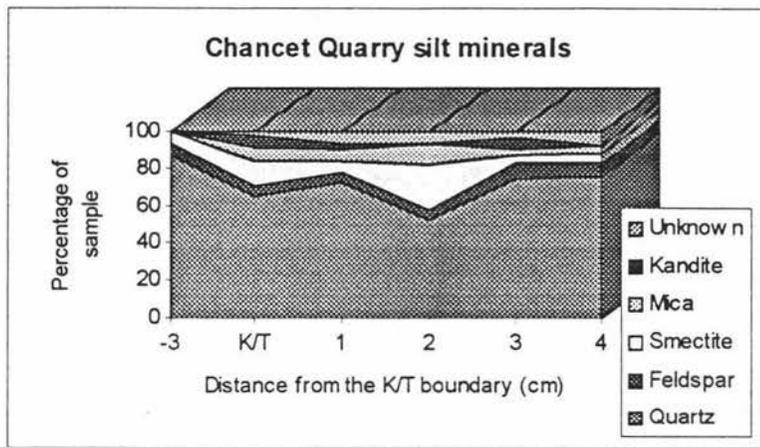


FIGURE 5.17(B) CHANCET SILT MINERALS

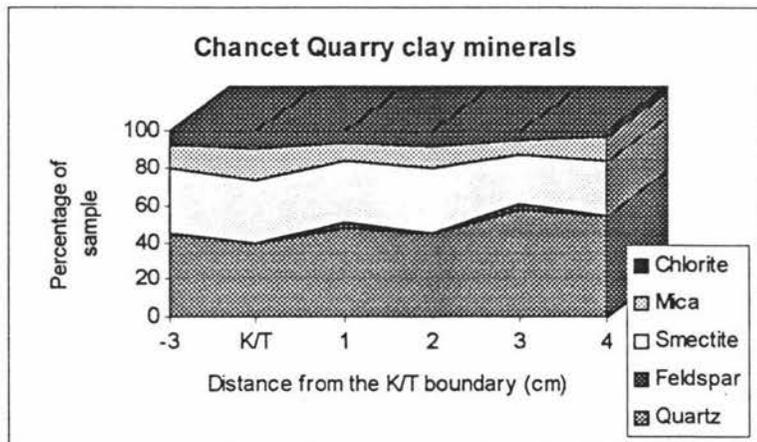


FIGURE 5.17(C) CHANCET CLAY MINERALS

## 6.0 Conclusion

### 6.1 Gold and palladium as indicators of the K/T boundary event

Models of the K/T boundary impact event, based on a 10 km diameter meteorite having impacted the Earth with cosmic velocity, predict that the entire meteorite would have been vaporised along with a much greater amount of target rock (O'Keefe and Aherns, 1982). Material from this impact would have been distributed worldwide as the resulting vapour cloud condensed into predominantly sand size particles, although the clay size fraction was also predicted to have a high proportion of meteoritic material (Melosh, 1982; O'Keefe and Ahrens, 1982). Deposits from this vapour cloud carried with it the meteoritic signature, enriched in platinum group elements, back to Earth to form the distinctive K/T boundary layer. A study of platinum group element abundances in this K/T boundary layer at Stevns Klint, Denmark revealed a trend for 0.1 of their chondritic abundances (Ganapathy, 1980).

This thesis presented results that support the impact theory for the origin of a gold and palladium enrichment in the K/T boundary layer. Gold and palladium both correlate extremely well with iridium for Woodside Creek and Chancet Quarry and their whole-rock abundances demonstrate clear peaks precisely on the K/T boundary. These abundance peaks agree well with data from other K/T boundary locations around the world (Ebihara and Muira, 1996; KYTE *et al.* 1996; Ganapathy, 1980).

The following sections summarise the gold and palladium results with gold at Woodside Creek having an integrated whole-rock abundance across the K/T boundary of 0.1 the chondritic value. The Woodside Creek East location shows exactly 0.1 of the chondritic gold abundance in the clay fraction, indicating this site received direct fallout from the impact event. Palladium whole-rock abundances across the K/T boundary at Woodside Creek are less than the expected 0.1 of the chondritic value, but approximate it in the clay and sand fraction abundances.

Chancet Quarry results show a trend for the palladium whole-rock abundances having 0.1 of the chondritic value on the boundary, and gold showing this abundance value only if taken as an average across the boundary. Despite the differences in which gold and palladium are distributed between the two sites, results from this thesis indicate that gold and palladium can reliably be used as indicators of an ETC in the K/T boundary layer.

### 6.1.1 Woodside Creek gold summary

The iridium/gold quotient plots for Woodside Creek (fig 5.1) lie in the meteoritic value of 2.2 indicating an extraterrestrial source for these elements (Palme, 1982). Integrated whole rock gold abundances across the K/T boundary at this site give 0.1 of the chondritic abundance value (15 ng/g), while the peak value of 55 ng/g at the boundary agrees well with that given in Lichte *et al.* (1986) of 59 ng/g.

Woodside Creek East site gave 0.1 of chondritic gold abundances in the clay fraction (fig 5.11 c) as expected for the K/T boundary impact (Ganapathy, 1980; Melosh, 1982). Sand fraction gold abundances at both West and East sites were two to three times the chondritic value (figs 5.9a, 5.11a), these abundances represent above the chondritic abundance of gold, possibly indicating some mechanism concentrated gold in the vapour phase of the impact process.

### 6.1.2 Woodside Creek palladium summary

Whole-rock palladium results at Woodside Creek correlated well with iridium (fig 5.2), although the lower than expected iridium abundances meant the Ir/Au and Ir/Pd quotients were below the meteoritic interelement quotient. Palladium abundances at this site agreed well with results obtained for palladium at the K/T boundary site in Gubbio, Italy (Ebihara and Muira, 1996). Palladium peaked at the K/T boundary with 22 ng/g, an increase

of ten times over the background level of 1 ng/g, before dropping back to pre-boundary levels (fig 5.6).

Size fraction results show the palladium more concentrated in the sand and clay than in the silt fraction for both East and West sites (figs 5.10a, 5.10c, 5.12a, 5.12c). This supports the impact model which predicts a higher ETC in the sand and clay fractions. Palladium abundances in the size fraction results for these sites, unlike gold, are slightly below the expected 0.1 of the chondritic value.

### 6.1.3 Chancet Quarry gold summary

Although gold correlates well with iridium at this site, the Ir/Au quotient is lower than expected for a meteoritic source (fig 5.3). A whole-rock abundance peak of 44 ng/g at the boundary (fig 5.7b) shows good agreement with the Woodside Creek results (55 ng/g) and the 42 ng/g result reported for Chancet Quarry in Brooks *et al.* (1984). The result for this site also shows excellent correlation with the value of 43 ng/g obtained at K/T boundary layer at Caravaca, Spain (Kyte *et al.* 1985). Clay fraction gold results of 14 ng/g (fig 5.13b) were in excellent agreement with the expected 15 ng/g (0.1 of the chondritic gold value) indicating that this site received direct fallout from the vapour phase of the K/T impact.

### 6.1.4 Chancet Quarry palladium summary

Palladium abundances at this site were within the range of those reported at the Gubbio K/T site in Italy (Ebihara and Miura, 1996). Correlation with iridium was highly significant even though the Ir/Pd quotient was lower than expected. Whole-rock palladium abundances peaked on the boundary with 53 ng/g, assuming that the boundary layer is composed wholly of impact derived material (Kyte *et al.* 1996), this value fits precisely with the expected 0.1 chondritic abundance value (Ganapathy, 1980).

Sand and clay size fraction results for palladium at this site peaked at the K/T boundary but were well below the expected 0.1 of chondritic values (figs 5.14a, 5.14b). This continues the trend observed for the palladium abundances in the size fractions to be less than 0.1 of the chondritic abundance at both Woodside Creek West and Woodside Creek East.

## 6.2 Mineralogical trends

Goethite was identified on the K/T boundary at the Woodside Creek West site, as it was for the K/T boundary at El Kef in Tunisia (Rocchia *et al.* 1996). This alone does not imply a meteoritic component but it does coincide with a significant drop in the quartz and increase in the smectite component of these sediments. The increase in the smectite component at the K/T boundary has been attributed to the alteration of impact spherules from the K/T boundary meteorite (Kastner, 1984). The drop in the quartz component at the K/T boundary may also reflect the lack of quartz in the impacting meteorite, this is consistent with a chondritic composition. The Woodside Creek East site showed a greater decrease in the quartz and increase in the smectite component at the K/T boundary although goethite was not identified here.

Chancet Quarry showed a variable mineralogy across the K/T boundary with the only noticeable change being in the clay fraction. This fraction revealed the highest mica/smectite and lowest quartz component at the K/T boundary (fig 5.17c). Mineralogical trends alone do not prove an impact occurred at the K/T boundary, but used in conjunction with other evidence such as platinum group element abundances, they do support the impact theory.

## 6.3 Analytical results

Gold and palladium determinations down to the 1 ppb level were possible on K/T boundary samples using solvent extraction and GFAAS techniques. The accuracy of the determinations were within six percent as measured against the standard rock PTC 1.

GFAAS techniques proved to be well suited for this type of work and easily able to match INAA results for gold and palladium determinations across the K/T boundary.

#### 6.4 Future Work

Gold and palladium abundances are useful indicators of an ETC at the K/T boundary at Woodside Creek and Chancet Quarry, but to date little work has been undertaken at these sites on isolating the nickel rich spinels characteristic of the K/T boundary layer (Rocchia *et al.* 1996). These spinels should mark the exact K/T boundary layer in that their size and chemical stability would have prevented them from migrating away from the boundary layer (Rocchia *et al.* 1996). As essentially condensates of the impact melt (Bohor *et al.* 1986; Bohor, 1990) they should show high platinum group element abundances and if sampled precisely represent the initial deposit of the K/T boundary layer. As they are chemically very stable spinels should not be affected by possible leaching, as platinum group elements may have been at other K/T boundary sites (Ebihara and Miura 1996). Platinum group element determinations of spinels at Woodside Creek and Chancet Quarry K/T boundary sites would also provide more abundance data, this may bring the Ir/Au and Ir/Pd quotients between the two sites into closer agreement.

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