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DEVELOPMENT OF METHODS FOR THE  
DETERMINATION OF BISMUTH AND THALLIUM  
IN GEOLOGICAL MATERIALS  
AND THEIR SIGNIFICANCE FOR  
THE CRETACEOUS-TERTIARY  
BOUNDARY EVENT

A thesis presented in partial fulfilment  
for the degree of

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New Zealand

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## ABSTRACT

Solvent extraction methods have been developed for the determination of thallium and bismuth in rocks. The method for thallium is based on the extraction of the chlorocomplex into methylisobutyl ketone followed by removal of the interfering chloride ion as insoluble silver chloride. The method for bismuth is based on the extraction of a stable metal complex with ammonium pyrrolidine dithiocarbamate into methylisobutyl ketone. Both elements are analysed on a electrothermal graphite furnace atomic absorption spectrometer. Tests on the efficiencies of the methods showed a good precision and accuracy with limits of detection of 9.5 ng/ml (ppb) for thallium and 20 ng/ml (ppb) for bismuth. Recovery studies on synthetic samples showed recoveries of >99.9% for both elements.

A geochemical study was performed on a Cretaceous-Tertiary boundary site located near Flaxbourne River, Ward, New Zealand. Investigations were carried out to determine the enrichment of thallium and bismuth in the stratigraphic column. The results show a good correlation between the iridium and thallium content throughout the rock sequence, but the samples have very low bismuth contents. This is indicative of the different geochemical behavior of bismuth to other chalcophiles. These findings do not contradict the impact theory initially hypothesized by Alvarez et al. (1980), and instead suggest that bismuth's mobility and solubility are far greater than those of thallium and the other chalcophile elements enriched in the Flaxbourne River sequence. This results in the leaching of bismuth from the stratigraphic column by sea water after deposition.

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## I. GENERAL INTRODUCTION

Very early in the history of modern geology it became convenient to divide regional lithologic sequences into large stratigraphic units that could be distinguished from one another on the basis of fossil content (Raup and Stanley, 1978). There was a natural tendency for early workers to establish system boundaries at major floral and faunal breaks. Many of these boundaries seem especially well-placed, for some of the chosen breaks represent distinct evolutionary changes or extinctions that occurred during short time intervals on a worldwide scale. Explanations of these often dramatic changes in the fossil record have not been totally satisfactory, especially since a global scale and a short, limited time must be considered.

In their benchmark paper, Alvarez et al. (1980) suggested that the extinctions at the terminal Cretaceous were due to catastrophic events caused by the impact of a large (>10 km diameter) asteroid with the earth. This scenario developed from evidence of a significant iridium enrichment in the Cretaceous-Tertiary (K-T) boundary clay in three locations: Gubbio in Italy, Stevns Klint in Denmark, and Woodside Creek in New Zealand. The Alvarez group suggested that the anomalously high iridium concentrations arose from the presence of particulate remains of a large impacting bolide in the boundary sediment. Since then, iridium and other siderophile element anomalies have been found in over 90 K-T boundary sediments worldwide, including several sites in New Zealand (Kyte et al., 1980; Brooks et al., 1986).

Several extinction mechanisms have been suggested as side effects of the initial impact (Alvarez, 1986). These include:

1) Ignition of wildfires and the generation of nitric acid rains by the heat of the meteorite's entry and impact;

2) Meteoritic and terrestrial dust resulting from the impact being thrown into the atmosphere, blocking sunlight and suppressing photosynthesis, resulting in extreme cold and the destruction of food chains;

3) Ejected water vapor remaining in the atmosphere after the impact dust had settled, resulting in a greenhouse effect to follow the extreme cold.

Although some of the elements enriched in the K-T boundary clay are apparently meteoritic (Ir, Ni), others are clearly terrestrial (As, Sb). The latter group are noted to be mainly chalcophile, or sulphur-loving, elements (Strong et al., 1987). Absolute concentrations of all chalcophiles are much higher than would be provided directly from a mantle, crustal or meteoritic source; therefore, an enrichment process must be invoked at the boundary.

Anoxic conditions following the K-T boundary impact would readily cause scavenging of chalcophiles from the water column (Brooks et al., 1984; Kyte et al., 1980). Researchers have noted that chalcophiles can be similarly enriched in coal ash, caused by the low oxidation potential of the medium (Mason and Moore, 1982). Efficient sweep-out of the ejecta would be able to concentrate most of the dissolved chalcophiles into the thin clay boundary layer (Strong et al., 1987).

Thallium and bismuth were chosen as representative and as yet unstudied chalcophile elements regarding the K-T boundary event. All of the chalcophiles in Table 1 have been analysed by instrumental neutron activation analysis with the exceptions of thallium, bismuth, tellurium, cadmium, sulfur and lead for the Flaxbourne River K-T

H		Atmophile: <u>N</u>															<u>He</u>
Li	Be	Lithophile: <u>Na</u>										B	C	<u>N</u>	O	F	<u>Ne</u>
Na	Mg	Chalcophile: <u>Zn</u>										Al	Si	P	<u>S</u>	Cl	<u>A</u>
		Siderophile: <u>Fe</u>															
K	Ca	Sc	Ti	V	Cr	Mn	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>	<u>Zn</u>	<u>Ga</u>	<u>Ge</u>	<u>As</u>	<u>Se</u>	Br	<u>Kr</u>
Rb	Sr	Y	Y	Nb	<u>Mo</u>		<u>Ru</u>	<u>Rh</u>	<u>Pd</u>	<u>Ag</u>	<u>Cd</u>	<u>In</u>	<u>Sn</u>	<u>Sb</u>	<u>Te</u>	I	<u>Xe</u>
Cs	Ba	La-Lu	Hf	Ta	<u>W</u>	<u>Re</u>	<u>Os</u>	<u>Ir</u>	<u>Pt</u>	<u>Au</u>	<u>Hg</u>	<u>Tl</u>	<u>Pb</u>	<u>Bi</u>			
			Th		U												

TABLE 1: Geochemical classification of the elements in relation to the periodic system (Mason and Moore, 1982)

boundary samples (Strong et al., 1987; Orth, 1987, Appendix 1). Difficulties have been noted by previous investigators in the analysis of thallium by graphite furnace atomic absorption spectrometry in the presence of halide ions. Bismuth was chosen from the other five unanalysed chalcophiles to discover if it behaves like the other group VA metals (As, Sb) in the K-T boundary. Analysis of bismuth by hydride generation of bismuthine is possible (Thompson and Thomerson, 1974) but for this study, graphite furnace atomic absorption spectrometry was utilised.

The following project is divided into two main parts:

1) The development of solvent extraction methods to separate thallium and bismuth from rock matrices and their determination by graphite furnace atomic absorption spectrometry;

2) An application of the methods to determine thallium and bismuth levels for samples collected at a K-T boundary site at Flaxbourne River, New Zealand.

It is hoped that this work will provide new, rapid, inexpensive and sensitive methods for the determination of thallium and bismuth in geochemical materials and that a contribution can be made towards clarifying the series of events that destroyed 70% of life forms at the end of the Cretaceous period.

## II. DEVELOPMENT OF ANALYTICAL METHODS

## II.1. Introduction

Aspiration into a flame is the most convenient and reproducible means of obtaining atomic vapor in atomic absorption spectrometry (Christian, 1978). However, it is one of the least efficient in terms of converting all of the sample elements into atomic vapor and presenting this to the optical path. The overall efficiency of conversion and measurement of atoms presented has been estimated at as little as 0.1%. In addition, aspiration methods require several ml of solution for analysis.

Furnace atomizers have higher conversion efficiencies than flame atomizers. Absolute detection limits are typically 100-1000 improved over flame aspiration methods:

Production of atomic vapor:  $n = \text{number of analyte atoms} / \text{volume}$

$$n = \left( \frac{N B E F C}{Q \text{ ef}} \right) \cdot 0.001$$

N: Avogadro's number

B: atomization efficiency (1)

E: aspiration efficiency (0.1)

F: solution flow rate (0.05 cm<sup>3</sup>/s)

Q: unburned gas flow rate (100 cm<sup>3</sup>/s)

ef: flame expansion factor (10)

C: analyte concentration (0.0001 mol/l)

For flame,  $n = 3 \times 10^{11}$  atoms/cm<sup>3</sup>.

Production of atomic vapor in a non-flame situation:

$$n = (N B V_s C) / V$$

$V_s$ : volume of solution (1 mm<sup>3</sup>[1 ul])

$V$ : volume of gas phase (1 cm<sup>3</sup>)

For non-flame,  $n = 6 \times 10^{13}$  atoms/cm<sup>3</sup>.

A major difficulty with graphite furnace atomic absorption spectrometry (GF-AAS) is that interelement interferences are much more pronounced than in flames and precision is generally poorer (Christian, 1978). By introducing digested or liquid samples directly into the furnace, the problem lies in the accumulation of unvolatilized material, which decreases sensitivity, precision and furnace life. Separation or extraction methods must be utilized to overcome these disadvantages. This holds true even for all but the simplest of water samples.

Korkisch (1969) lists as possible separation methods for thallium: anion and cation exchange, co-precipitation, solvent extraction, paper and reverse phase partition chromatography. Bismuth can be extracted similarly. Solvent extraction is chosen for its ease and speed of operation, selectivity and simplicity.

## II.2. List of Reagents

The following reagents were used in the course of research and are AnalaR grade unless otherwise specified:

## Stock solutions:

thallium (100 µg/ml)

bismuth (1000 µg/ml)

arsenic (1000 µg/ml)

antimony (100 µg/ml)

gallium (100 µg/ml)

indium (1000 µg/ml)

germanium (100 µg/ml)

tin (100 µg/ml)

lead (100 µg/ml)

Ammonium pyrrolidone dithiocarbamate (APDC)

Concentrated hydrochloric acid

Concentrated nitric acid

70% perchloric acid

40% hydrofluoric acid

Methylisobutyl ketone (MIBK), technical grade

Distilled deionised water

Rock digest solution: Mix equal proportions concentrated nitric,  
perchloric (70%) and hydrofluoric (40%) acids

Silver nitrate

Crystal Violet

Brilliant Green

Xylene

Toluene

Hydrobromic acid

Bromine

Sodium nitrite

Sodium hexametaphosphate

Hydroxylamine hydrochloride

Sodium bromide

Disodium ethylene diamine tetra-acetic acid

### II.3. Atomic Absorption Spectrometry

#### II.3.1. Introduction

Free atoms cannot undergo rotational or vibrational translations as do molecules. Only electronic transitions can take place when energy is absorbed or emitted. The quantised nature of the transitions allow the observation of line spectra (Christian, 1978).

In order to make measurements in atomic absorption it is necessary to convert material to a population of ground state atoms and then pass resonance radiation of the element to be measured through that population. Spectrophotometric analysis is the determination of the concentration of a substance according to its absorption of a specific monochromatic radiation (Pinta, 1966). Ideally, the measuring device should "see" only the wavelength which is being absorbed as the presence of other radiation lowers the proportion of absorbed radiation. This results in decreased sensitivity (Price, 1979).

### II.3.2. Flame Spectrometry

In conventional flame spectrometry, a solution is aspirated into a flame and the compounds are thermally dissociated into atomic vapor. The flame burner is supplied with an optimised mixture of fuel and oxidant. Air/acetylene fuel-oxidant mixtures are used successfully for most elements which do not form highly refractory oxides (Price, 1979). Nitrous oxide/acetylene mixtures are used for cations whose dissociation energies for the metal-oxygen bond are greater than 5 electron volts. Both thallium and bismuth can be determined by flame atomic absorption with an air/acetylene mixture.

In flame atomic absorption spectrometry (flame-AAS) it is important that a matrix-matched blank is used as a reference when proceeding with analyses. In the case of methylisobutyl ketone (MIBK), up to three times enhancement of the signal occurs due to the efficient burning and atomization characteristics of many organic solvents (Viets, 1984).

### II.3.3. Flame-AAS Instrumentation

Flame-AAS was performed using an IL457 instrument with emission capability and digital display of absorption or concentration. Sampling was done manually. Air/acetylene fuel mixtures were used for all of the elements in the APDC section of this work with the exception of germanium when a nitrous oxide/acetylene mixture was used. Hollow cathode lamps were used as spectral line sources.

#### II.3.4. Graphite Furnace Spectrometry

The main difference between graphite furnace atomic absorption spectrometry (GF-AAS) and conventional flame atomic absorption spectrometry is the use of an electrothermal atomizer as the atomization source. The atomizer of the GBC 1000 graphite furnace consists of a pyrolytically coated furnace tube. Unlike some atomizers which involve fixed heating, the atomization process in the above instrument is divided into four stages:

- 1) initial temperature
- 2) final temperature
- 3) ramp time
- 4) hold time

The advantage of ramp heating over fixed heating allows the sample to be dried more reliably and prevents the possibility of losing analyte by spluttering in the ashing stage. Like all automated instruments, the GBC 1000 is equipped with a warning device that indicates the absence of inflow of cooling water and inert gas.

The general principle of atomization in a temperature programmed furnace has been discussed by Fuller (1977) and Price (1979). The graphite tube is held between two electrodes. When a voltage is applied to the electrodes, the temperature of the tube is raised and by varying the voltage across the electrodes, the temperature of the atomizer can be varied. The unit is sheathed in a stream of inert gas (usually oxygen-free nitrogen or argon) which prevents oxidation of the graphite atomizer and also removes vapor as it diffuses from the

furnace. The generation of a population of free atoms whose absorption is measured is achieved in three stages:

- 1) drying--solvent removal
- 2) ashing--organic matrix and reagent removal
- 3) atomization--atom production.

#### II.3.5. GF-AAS Instrumentation

Graphite furnace atomic absorption spectrometry was carried out by use of a GBC 1000 graphite furnace instrument coupled to a GBC 902 double-beam atomic absorption spectrometer with automatic background correction. Automatic sampling was performed by use of a PAL 1000 automatic sampler capable of delivering up to 10 ul of sample with the option of 10 multiple loadings. Readout was printed with an Epson LX 80 printer. Thallium and bismuth hollow cathode lamps were used as line sources.

#### II.3.6. Investigation of Parameters for GF-AAS

In each stage of the thermal program in GF-AAS, the temperature and the time are selected according to the nature of the sample matrix and analyte element to be determined. Therefore to obtain the best results of any analysis, the instrumental parameters must be optimized.

### II.3.6.a. Solubility of Phases and Acid Concentration

MIBK is generally immiscible in hydrochloric acid up to 9 M in strength. At 9 M, MIBK solubility increases radically (Figure 1). For this reason, only acid concentrations ranging from 0 to 6 M will be investigated.

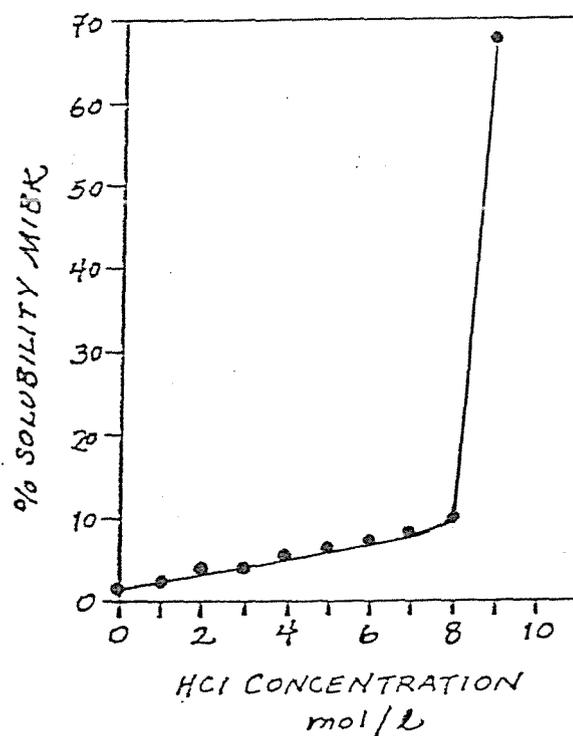


FIGURE 1: Solubility of MIBK in varying HCl concentrations

#### II.3.6.b. Lamp Current

The lamp currents must be chosen with consideration to the life of the lamp. In general, increased amperage will give a more stable and less noisy background, while lower currents will prolong the life of the lamp. The amperages recommended by the manufacturer are used as a compromise between these two considerations. Thallium was analysed at 10 amps; bismuth at 8 amps.

#### II.3.6.c. Atomization Temperatures

Atomization temperatures were investigated with an unvarying amount of sample. For thallium, the optimum atomization temperature ranged from 1400°C to 1500°C. The signal decreased on either side of this temperature peak (Figure 2a). 1500°C was chosen as this temperature was also recommended by the manufacturer of the GF-AAS spectrometer.

There was no real optimum atomization temperature for bismuth (Figure 2b). 1700°C was chosen under the guidance of the operator's manual and in consideration of prolonging the graphite furnace rod's life time.

#### II.3.6.d. Wavelength

The most sensitive line for thallium is 276.8 nm and is used in all thallium determinations in this report. The most sensitive line for bismuth is 223.1 nm. However this bismuth line is close to an iron

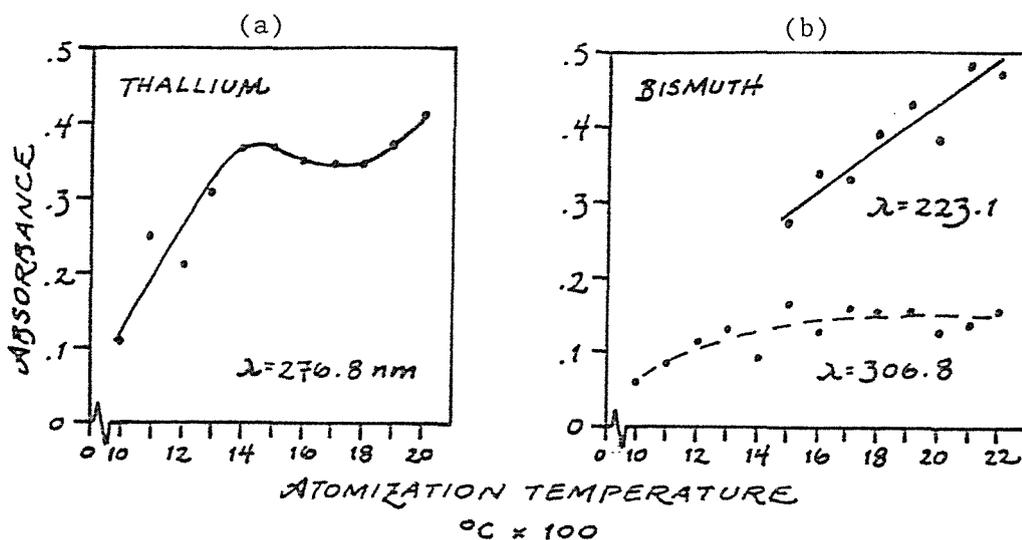


FIGURE 2: Determination of optimum atomization temperatures for:  
 a) thallium  
 b) bismuth

line, increasing the possibility of spectral interference as most geologic samples contain iron. The second choice for a bismuth line is 306.8 nm, which is used in all bismuth determinations in this report. Incidentally, the latter wavelength gives a slightly clearer optimal atomization temperature (Figure 2b).

#### II.3.6.e. Ramp Times

For the drying stage, the ramp time is chosen to be slow enough to not cause spluttering of the sample and the possible loss of analyte. A slow increase in drying temperature produces a more reproducible result, as does a longer hold time for both the drying and the ashing stages (Brooks and Lee, 1988).

For atomization, a ramp time of 1 s was chosen in order to generate a population of free atoms as quickly as possible. A 3 s hold time was chosen to remove all analyte atoms and to reduce memory effects (Sighinolfi, 1973).

The final furnace programs used for bismuth and thallium are presented in Tables 2 and 3 along with the temperature-time graphs of these programs (Figures 3 and 4).

STEP NUMBER	FINAL TEMP. (°C)	RAMP TIME (sec)	HOLD TIME (sec)	INERT GAS	AUX. GAS	READ ON	PEN DOWN
1	120	10.0	10.0	NO	NO	NO	NO
2	500	5.0	5.0	YES	NO	NO	NO
3	1700	1.0	3.0	YES	NO	YES	NO

SAMPLE VOLUME	3.0
NUMBER OF MULTIPLE INJECTIONS	1
NUMBER OF SAMPLE REPEATS	5
BLANK REPEAT RATE (zero on blank)	4
DRY STEPS FOR MULTIPLE INJECTIONS	1
INJECT ON STEP NUMBER	1

TABLE 2: Furnace sampler program for bismuth

STEP NUMBER	FINAL TEMP. (°C)	RAMP TIME (sec)	HOLD TIME (sec)	INERT GAS	AUX. GAS	READ ON	PEN DOWN
1	120	10.0	10.0	NO	NO	NO	NO
2	400	5.0	5.0	YES	NO	NO	NO
3	1500	1.0	3.0	YES	NO	YES	NO

SAMPLE VOLUME	3.0
NUMBER OF MULTIPLE INJECTIONS	1
NUMBER OF SAMPLE REPEATS	5
BLANK REPEAT RATE (zero on blank)	4
DRY STEPS FOR MULTIPLE INJECTIONS	1
INJECT ON STEP NUMBER	1

TABLE 3: Furnace sampler program for thallium

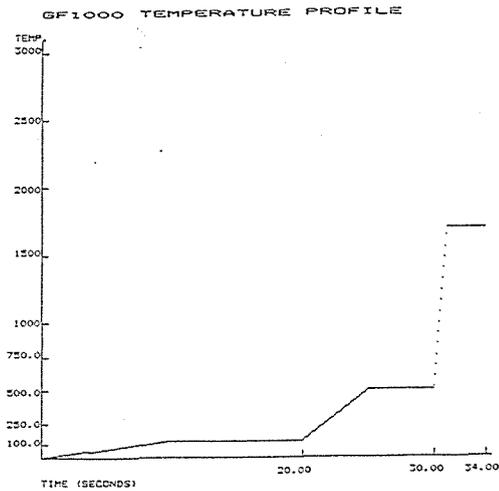


FIGURE 3: Temperature profile of sampler program for bismuth

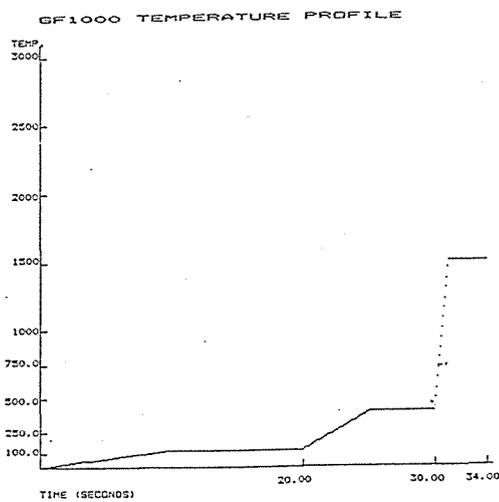


FIGURE 4: Temperature profile of sampler program for thallium

#### II.3.6.f. Background Correction

The GF-AAS instrument is capable of background correction using a deuterium lamp. This was utilized for bismuth analyses, but was found not to be beneficial for thallium. The GBC instrument often altered its baseline from  $<-0.100$  absorption units to  $>0.700$  units. This did

not occur in the absence of the deuterium background correction. The baseline doubles as did the limit of detection, but this is seen as acceptable in light of the alternative.

#### II.3.6.g. The Furnace Tube

The graphite tube's pyrrolitic coating should be clearly visible to the eye for optimum sensitivity for any element. When the coating wears off, the result is a wetting of the furnace by sample solutions especially by organic solvents including MIBK. This in turn results in lower sensitivity and precision and increases memory effect problems due to contamination (Sighinolfi, 1973).

#### II.3.6.h. The Sampling Vial

It was discovered that the sampling vials supplied by the GF-AAS manufacturer cannot be used when an organic solvent matrix is to be analysed. The bottom of the vials are glued rather than tooled, and MIBK readily dissolves this glue. To circumvent this problem, glass test tubes that fit into the sampling carousel were cut down to 25 mm in height and initially used in place of the plastic vials. However, this vial requires 2 ml of sample and the large exposed surface area allows rapid evaporation of MIBK.

The teflon plug developed by Brooks and Lee (1988) was considered but proved to be difficult to clean thoroughly and expensive to produce the number necessary to perform these analyses.

Another sampling vial was devised using the manufacturer's supplied plastic vials and cap and Durham sample tubes. This vial requires 0.25 to 0.50 ml of sample, will not disintegrate with use of solvents or acids, is easy to clean, and cheap to replace the Durham tubes. The main disadvantage of this vial is that the sampling arm on the PAL sampler does not come down on the center of the sampling surface. Instead, the probe tip descends off center. To accommodate this, holes were punched in the plastic caps with a #3 cork borer off-center and the probe tip was watched carefully to insure the Durham tube was in the correct position for sampling.

Though this procedure appears tedious, the sampler must be watched and attended no matter which sampling vial was used. MIBK has a low vapor pressure which causes significant evaporate out of the cut-down test tubes which in turn causes the sample to concentrate, causing faulty readings and decreasing reproducibility (Brooks and Lee, 1988). It is necessary to introduce the sample into the vials immediately before the automated sampling carousel positions the sample beneath the probe tip. This could result in timing error and is only a step away from injecting the sample into the graphite furnace manually with a syringe.

The different sampling vials and their advantages and disadvantages are summarized on Appendix 2.

#### II.3.6.i. Digestion of Rock Samples

A wet acid attack method is preferred as a convenient and less costly method of digestion of geologic samples than fusion in zirconium

crucibles. Brooks (1987) observed that the crucibles became easily contaminated, producing a distinct memory effect for osmium determinations after successive fusions.

Of the acid digest solutions available, aqua regia is rejected as it is used to dissolve elements from secondary weathering products such as soils and altered rocks, ie. loosely bound elements (Hubert and Chao, 1985). Hydrofluoric acid is a necessary component of a digestion solution to decompose silica minerals and other siliceous materials.

Sighinolfi (1973) uses a 30:1 mixture of HF:HClO<sub>4</sub> taken to dryness in a Teflon beaker placed in an aluminum vessel on a heating plate. Simon et al. (1977) uses a mixture of HF:HNO<sub>3</sub>:HClO<sub>4</sub> in unspecified proportions in covered Teflon beakers on a heating plate. The rock digest solution used in this report will be a 1:1:1 mixture of HF:HNO<sub>3</sub>:HClO<sub>4</sub> in Teflon beakers in a sandbath on a heating plate. It was found that the sandbath is necessary to remove the risk of burning or melting the Teflon.

Strong et al. (1987) digests the Flaxbourne River K-T rocks with a 1:1 mixture of HF:HNO<sub>3</sub> in polypropylene beakers. For the case study done on these rocks for bismuth and thallium content, the digest solution will be the 1:1:1=HF:HNO<sub>3</sub>:HClO<sub>4</sub> solution chosen in the previous paragraph.

## II.4. Solvent Extraction of Thallium and Bismuth

### II.4.1. Introduction

Solvent extraction occupies a very important position among separation methods in trace analysis because of its simplicity, rapidity, wide applicability and relatively small contamination hazard (Morrison and Freiser, 1957). The method is based on the distribution of a solute between two essentially immiscible phases. The solvent extraction methods proposed here involve the formation of a chlorocomplex of thallium in hydrochloric acid and the formation of a bismuth complex with APDC in hydrochloric acid. Both complexes are extracted into MIBK.

The extent of extraction is described in terms of the distribution coefficient ( $K_d$ ). It is important to determine the distribution of thallium and bismuth between hydrochloric acid and MIBK. This would enable calculation of the proportion of the metals extracted from the acid into the MIBK phase for any particular extraction.  $K_d$  is calculated as follows:

$$K_d = C_o/C_a$$

$C_o$  : concentration of analyte in organic phase

$C_a$  : concentration of analyte in aqueous phase.

For these extractions, the analytes are in the same chemical form in both phases, so  $K_d = D$ , the distribution ratio. The percentage of analyte extracted into the organic phase from the aqueous phase is given by the percent extraction (E):

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

$V_o$  : volume of the aqueous phase

$V_a$  : volume of the organic phase.

Large distribution ratios for the elements of interest are preferable. Hence the proper choices must be made of the extraction system, solvent, reagent concentration and the aqueous phase acidity.

#### II.4.2. Calibration Curves

All standards must be treated and prepared in the same way as the samples to eliminate the possibility of enhancement or suppression by contamination during sample preparation or from the elemental content in the reagents used. This also holds true for the preparation of a blank, which should be analysed at the same time as the samples and standards.

The following standards were prepared from the 1000  $\mu\text{g/ml}$  bismuth and the 100  $\mu\text{g/ml}$  thallium stock solutions: 0.01, 0.10, 0.50, 1.0  $\mu\text{g/ml}$  in 1 M nitric acid to insure that chloride ions were not present. Each standard was subjected to GF-AAS analysis and the results are presented in Figure 5 for bismuth and in Figure 6 for thallium.

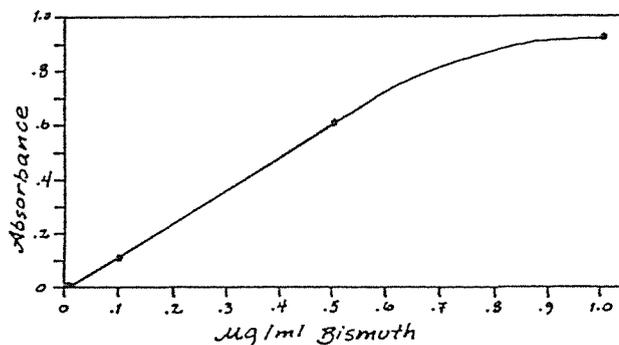


FIGURE 5: Calibration curve for bismuth

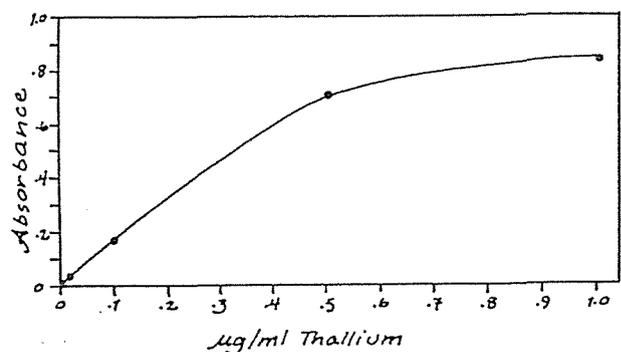


FIGURE 6: Calibration curve for thallium

### II.4.3. The Ammonium Pyrrolidine Dithiocarbamate System

#### II.4.3.a. Introduction

Because of their ionic nature, simple metal salts are usually more soluble in aqueous media than in organic solvents (Mulford, 1966). In order to extract a metal into an organic phase, it is first necessary to convert the metal ion to an uncharged species.

The analytical significance of ammonium pyrrolidine dithiocarbamate (APDC) as a ligand for metal complexes extractable into MIBK was first suggested by Malissa and Schoffmann (1955). Following this early report, other workers employed extraction of the APDC-metal complex into organic solvents for the determination of trace elements in brines and sea water (Brooks et al., 1967). However, there have been very few examples of the use of an APDC extraction system for samples other than natural waters.

Although extraction of metal-APDC complexes from aqueous solutions in the pH range of 2 to 14 has been considered standard procedure, it had not been appreciated previously that some APDC-metal complexes can be extracted from strongly acidic (ie. 1 to 6 M) solutions of hydrochloric and nitric acids. The significance of such an extraction lies in the obvious potential for extracting trace elements from solutions of silicate rocks which normally require acid concentrations at a strength of at least 2 M. As far as is known, this is the first study to show the stability of some metal-APDC complexes in strong mineral acids.

Addition of APDC is done in the aqueous phase, usually in 1% to 5%

solutions (Mulford, 1966). For some metals, this much APDC is unnecessary. Wilson (1987) showed that for palladium, 1 ml of a 0.05% solution per 5 ng of palladium was sufficient in pure solutions.

Ketones have been successfully used as the organic phases for the APDC system. MIBK has an extraction ratio of approximately 5 (Sprague and Slavin, 1964). Pre-equilibration of MIBK with acid prevents the MIBK from dissolving into the aqueous phase during the extraction of the metal ion (Boswell and Brooks, 1965). Methylamyl ketone has been used as the organic phase in the analysis of metals in urine (Willis, 1962) and some workers use a MIBK-10% Aliquat mixture to provide the necessary chloride to enhance the extraction (Viets, 1978; O'Leary and Viets, 1986).

APDC is not very stable once in solution and daily preparation is necessary (Brooks et al., 1967). Even with refrigeration, APDC solutions suffer a reduction in activity by one-half when stored overnight. Brooks et al. (1967) suggested that for the analysis of some metals the chelate complex is also unstable and the solution should be analysed within three hours. Wilson (1987) discovered the metal-APDC product to be unstable with time and that determination of the metal (in his case, palladium) should take place within two hours of forming the complex.

The type of reaction vessels used is unimportant, although Boswell and Brooks (1965) preferred to use polypropylene containers to reduce contamination and absorption effects of glass on some cations.

In most cases in this work, equal volumes of sample and MIBK were used in the extraction (ie.  $V_o/V_a = 1$ ). When very small amounts of the element of interest is present in the sample, enrichment is necessary. To achieve this, Willis (1962) used a larger sample volume. To acquire the same effect, the sample volume is kept constant in this work and

the amount of MIBK is varied as necessary.

For all preliminary analyses done in this report, 9 ml of acidified sample was mixed with 1 ml of 1% APDC solution and 10 ml of pre-equilibrated MIBK. This mixture was shaken for a minimum of 10 min. For the determination of the optimum amount of APDC necessary for the extraction of bismuth, all of the additions remained the same except that only 1 ml of MIBK was used. Under the conditions described, 1% APDC by weight is the optimum amount to use (Figure 7).

For the sake of interest and completeness, the extraction of

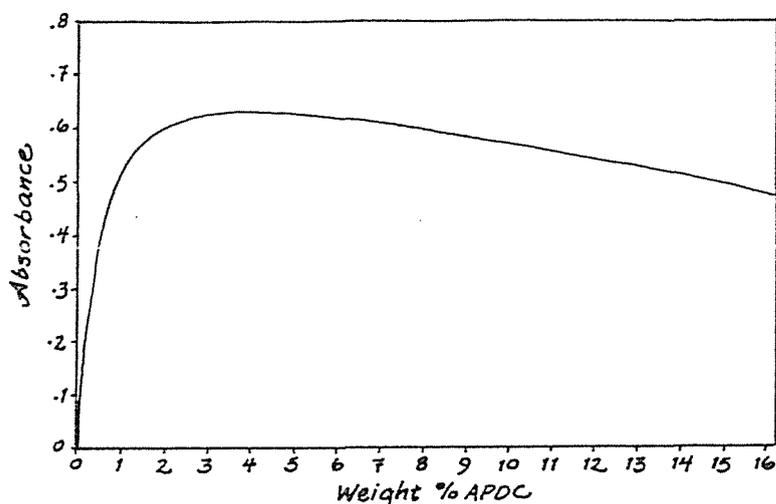


FIGURE 7: Effect of increasing amounts of APDC on bismuth extraction into MIBK .

metal-APDC complexes of nine elements into MIBK was studied from hydrochloric and nitric acid solutions in the range of 0.5 to 6 M. Experiments were also carried out on hydrochloric acid solutions without the addition of APDC because many elements form chlorocomplexes which are also extractable into MIBK (Boswell and Brooks, 1965). Comparison of the extractions would establish the degree to which chlorocomplexes rather than those with APDC were responsible for

extraction in specific cases.

#### II.4.3.b. Experimental

The extractability of metal-APDC complexes was determined by equilibrating equal volumes of organic and aqueous phases and determining the concentrations of the metal ions in the aqueous phases before and after equilibration. When extraction is not excessively great or small, it is possible to carry out these determinations by flame-AAS. When extractions are very great (or very small) so that the concentrations in the aqueous or organic phases were very low, determinations of metal concentrations were performed by GF-AAS.

From the ratio of absorbances in the two phases, values of the distribution coefficient ( $K_d$ ) were obtained and were related to the percentage extraction (E).

Extractions are carried out on 5 ml aliquots of three sets of solutions which are prepared as follows:

- 1) 0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 M hydrochloric acid;
- 2) Same as (1), but with the addition of 0.01 g APDC to each aliquot;
- 3) Nitric acid solutions of the same strengths as (1) and with the addition of 0.01 g APDC to each aliquot.

The original metal ion concentrations in the aqueous phases ranged from 10 to 100  $\mu\text{g/ml}$  (ppm) depending on the analytical sensitivity in flame-AAS of the metals concerned. The oxidation state of each metal was chosen to represent the most likely oxidation state expected to be found in a rock solution. This is in order to approximate to the conditions likely to be encountered in the course of silicate rock

analysis.

#### II.4.3.c. Results and Discussion

Figure 8 shows the percentage extraction into MIBK of 9 metals as a function of concentrations of mineral salts, with and without addition

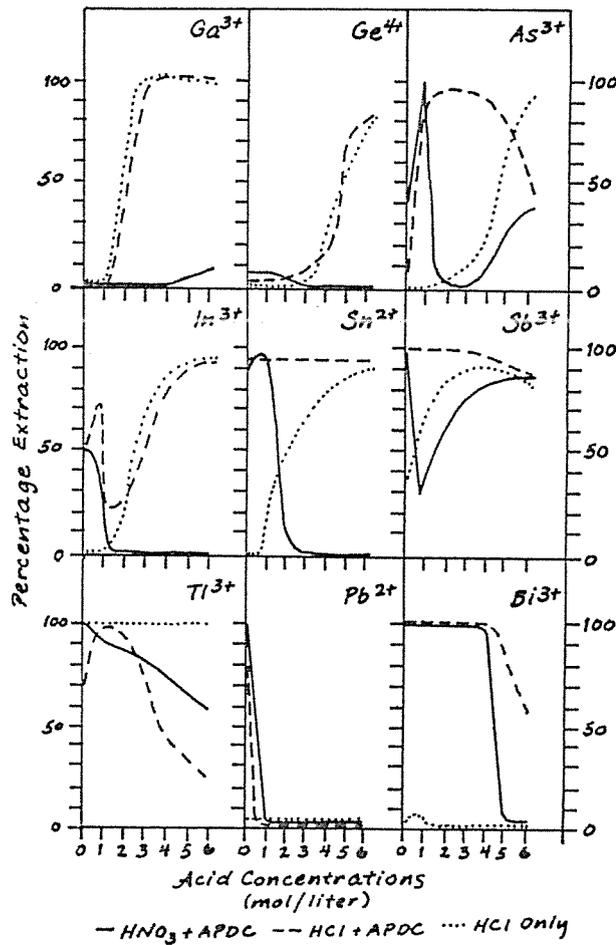


FIGURE 8: Extraction of 9 elements in different concentrations of acids with and without addition of APDC

of APDC. Table 4 gives values for  $K_d$  for the extraction of each ion

from 2 M solutions of nitric and hydrochloric acids with and without

TABLE 4: Distribution coefficients ( $K_d$ ) for extraction of selected chalcophile ions in 2 M acid with and without APDC

Ion	2M HCl	2M HCl + APDC	2M HNO <sub>3</sub> + APDC
Ga(III)	11.2	0.51	<0.01
Tl(III)	>10,000	2.70	5.70
Ge(IV)	<0.01	0.04	<0.01
In(III)	0.73	0.51	<0.01
Sn(II)	1.20	17.0	<0.01
Pb(II)	<0.01	<0.01	0.12
As(III)	0.06	53.0	0.01
Sb(III)	6.40	>10,000	1.50
Bi(III)	<0.01	1250	3500

APDC. Solutions of this strength were chosen because they represent the most likely acid concentrations in rock solutions prepared for trace analysis. Graphs showing the extraction of bismuth alone from the three solutions are presented with  $K_d$  values in Figure 9.

The curves in Figure 8 demonstrate that the extraction of metal ions may be divided into the following categories:

1) Ions whose extraction is not affected by the addition of APDC and are influenced solely by the formation of chlorocomplexes in hydrochloric acid solutions. These ions include gallium (III), germanium (IV), indium (III) and thallium (III). These extraction curves are the same as those of Goto and Kakita (1959). Only thallium and gallium lend themselves to quantitative extraction in the pH range investigated as the other elements require higher acid concentrations

for quantitative extraction.

2) Ions whose extractions are dependent on the presence of APDC and which have values of  $K_d$  sufficiently high in the pH range investigated to be advantageous of their separation and subsequent quantification. These elements include arsenic (III), antimony (III), and bismuth (III). It is clear that in general, the hydrochloric acid-APDC system is preferable to the nitric acid-APDC system. It may be that nitric acid has an oxidative effect on the APDC, particularly at higher acid concentrations.

3) Ions whose extraction is dependent on the presence of APDC but which have values of  $K_d$  too low to be of use for their separation and quantification. These ions are tin (II) and lead (II). These ions extract strongly under relatively neutral or weakly acidic conditions, but not under the strongly acidic solutions necessary to stabilize a rock digest.

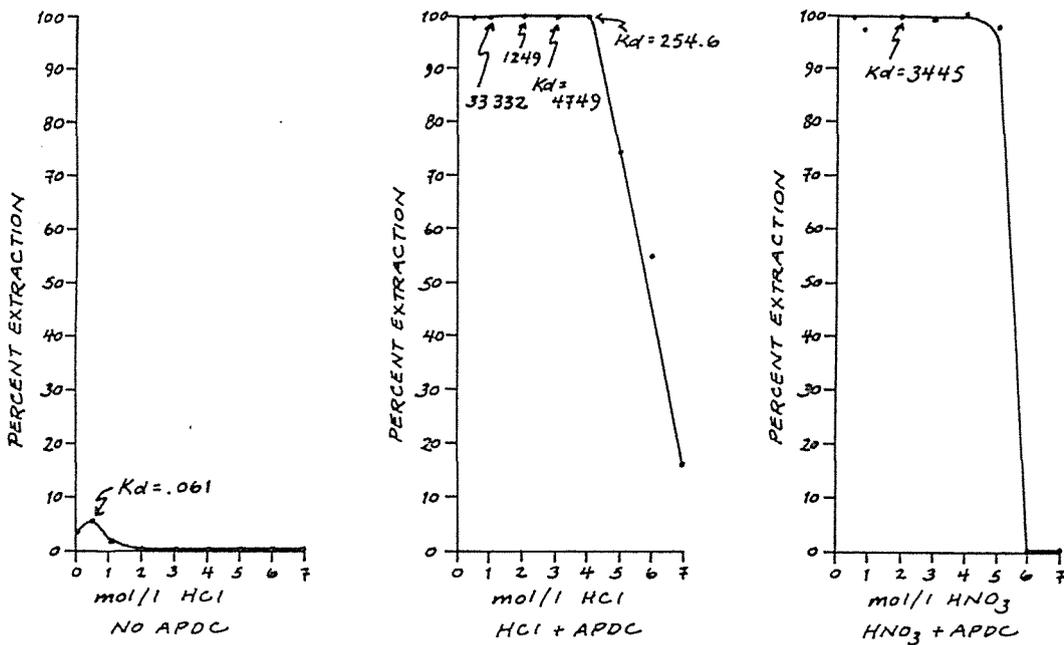


FIGURE 9: Extraction and  $K_d$  values for bismuth with and without APDC

#### II.4.3.d. Determination of Bismuth in a Standard Rock

The proposed procedure was tested with a reference rock with a recommended value for bismuth. GXR-1 is a jasperoid from the Drum Mountains, Juab County, Utah, USA and is distributed by the United States Geological Survey (Ficklin and Ward, 1976). The published values for GXR-1 are presented on Table 5 with their references.

TABLE 5: Published values for bismuth concentrations in GXR-1

Bi Concentration ( $\mu\text{g/g}$ )	Reference
1700	Ficklin and Ward, 1976
1725 $\pm$ 1.4%	Viets, 1978
1600	Viets <u>et al.</u> , 1984
1640 $\pm$ 3.4%	O'Leary and Viets, 1986

Iron was separated from bismuth in 2 M hydrochloric acid prior to addition of APDC, as bismuth does not extract significantly into MIBK without APDC (<1%, Figure 10) (Brooks et al., 1985).

Another method that could have been used is to add the APDC to the rock solution with MIBK and shake. Iron(III) forms an APDC complex that is unstable with time and will re-extract into the aqueous phase in under three hours (Brooks et al., 1967). Bismuth (and antimony, graphed for interest) forms an APDC complex that is unstable with time, but it is more stable than the iron complex (Figure 11). By allowing

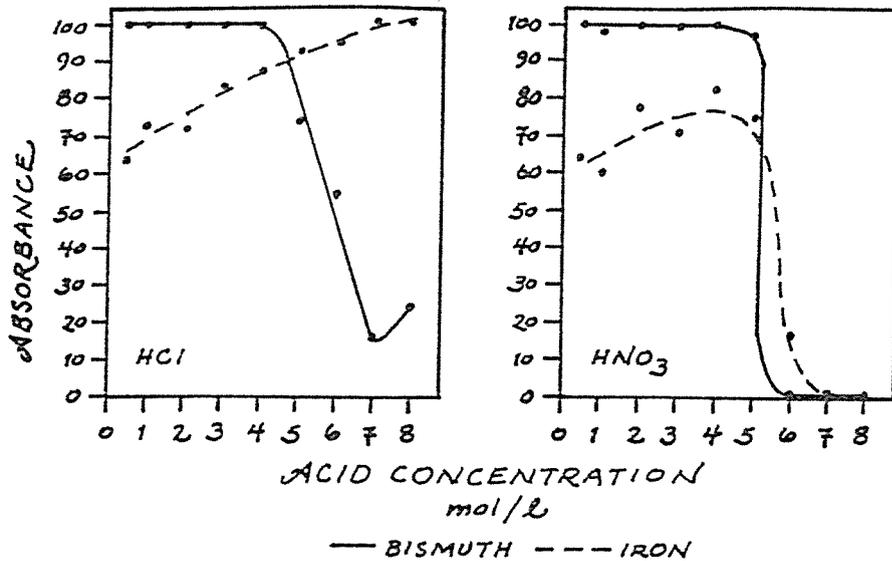


FIGURE 10: Bismuth and iron extractions in HCl and HNO<sub>3</sub> with APDC

the solution to stand for three hours, most of the iron would have re-extracted into the aqueous phase, but only a small amount of bismuth would have been lost from the organic phase.

The large amount of bismuth present in GXR-1 (1666.25 ug/g) required dilution of the sample in order to be able to analyse the rock using GF-AAS. The sample (0.1 g) was digested as described in the section II.3.6.i., the salts redissolved with 2 M HCl, and the solution cooled. The supernatant was then placed in a 100 ml volumetric flask and made up to mark with 1 M HNO to prevent hydrolysis and adsorption of bismuth on to the glass. When extracting, 10 ml MIBK, 1 ml 1% APDC and 1 ml of the diluted GXR-1 solution were shaken together and centrifuged to separate the phases. This results in a 10,000 times dilution

(approximately 0.1 to 0.2 ug/ml), which brought the bismuth concentration within the working range of the calibration curve plotted in Figure 5. By pipetting an aliquot of this diluted rock solution into the extraction system, this system has the added advantage of minimizing errors due to sample variability.

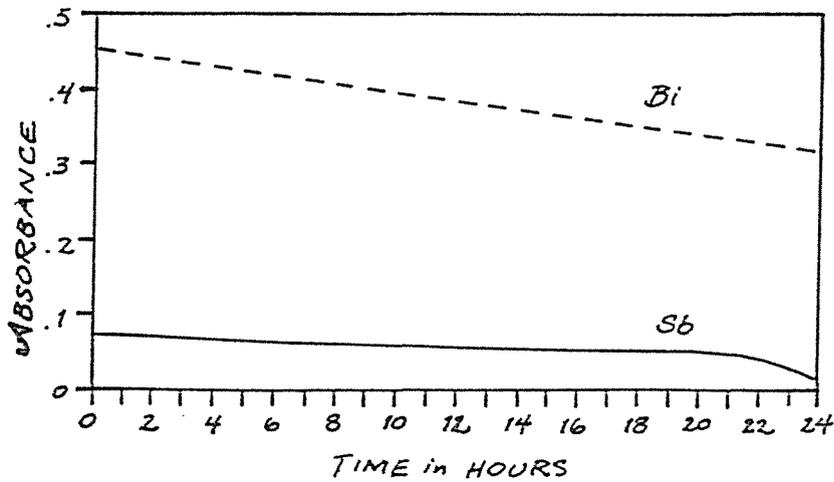


FIGURE 11: Stability with time of APDC complexes with bismuth and antimony

#### II.4.3.e. Limit of Detection, Precision and Accuracy

The limit of detection as defined by twice the signal to noise ratio was found to be 20 ng/ml for bismuth using GF-AAS in both the aqueous and organic phases.

The precision and accuracy of the proposed technique were measured by quintuplet determinations of the reference rock GXR-1 and are summarized in Table 6.

TABLE 6: Statistical information for the proposed method of extraction for bismuth

Limit of Detection (LOD).....	20 ng/g
Precision (RSD), n=6.....	1680.86 µg/g ± 5.99%
Deviation from recommended value (1666.25 µg/g)	
(relative error).....	0.88%

#### II.4.3.f. Recommended Procedure for the Determination of Bismuth in Rocks

1) Digest 0.5 g of finely powdered rock in a Teflon beaker with 10 ml of 1:1:1 mixture of concentrated nitric, 40% hydrofluoric and 70% perchloric acids. Heat over a sandbath on a hotplate till all fumes of perchloric acid have disappeared.

2) Add 10 ml 2 M hydrochloric acid and heat till the solution becomes relatively clear. Pour into glass centrifuge tube and cool.

3) To remove iron, add 5 ml MIBK pre-equilibrated with 2 M HCl and

shake for a minimum of 10 minutes. Centrifuge to separate phases and remove MIBK.

4) Add 1 ml 1% APDC and shake with 5 ml of the pre-equilibrated MIBK for 10 minutes.

5) Centrifuge to separate the two phases and separate the organic phase immediately with a Pasteur pipette. This serves to prevent the bismuth from returning to the aqueous phase as the APDC complex is unstable with time (Figure 11).

6) Analyse the organic phase by GF-AAS using the furnace program summarized in Table 2, section II.3.6.e.

#### II.4.4. The Determination of the Thallium Chlorocomplex

##### II.4.4.a. Introduction

Separation of thallium from the rock solution is necessary to avoid the complex matrix interferences common to the GF-AAS technique. The recurring problem in utilizing the chlorocomplex to separate thallium lies in the interference from the halide necessary for the extraction into the organic phase. Many writers have cited this to be the major problem in thallium analysis by GF-AAS. Their attempts to overcome the dilemma are summarized in Appendix 3.

L'vov (Slavin and Manning, 1980) proposed that at least part of the chloride interference is due to a gas phase phenomenon. The  $Tl(III)Cl_4^-$  complex has a boiling point of 40°C which is lower than the drying temperature of the furnace program. The volatility of this complex needs to be considered, and the cause of the interference removed.

An attempt has been made to find a different extraction method in which to avoid the interference by chloride. The fuming of the solution with sulfuric and nitric acids was found to be inappropriate, as the interest lies in directly testing the organic phase, which is one of the advantages of GF-AAS (Elson and Albuquerque, 1982). In addition, combination of an organic solvent with a concentrated acid is dangerous even when the mixture is cold due to the potential for explosions. Heating and fuming the mixture would present a greater probability of this.

Palladium conditioning of the furnace prior to addition of the

thallic chloride complex could not be used because platinum metal research is also occurring simultaneously with thallium research in this laboratory. The crustal abundance of palladium is low (0.01  $\mu\text{g/g}$ , Mason and Moore, 1982), and conditioning of the furnace requires a Pd:Tl ratio of 2000 to 4000 (Shan et al., 1984). This would heavily contaminate the furnace, the probe tip and the area around the machine, making the furnace conditioning method inappropriate for this laboratory.

#### II.4.4.b. Overcoming Chloride Interference

An initial attempt was made to extract thallium colorimetrically for analysis by GF-AAS. These attempts are summarized in Appendix 4, and in essence, they were not successful.

A comparison was made between the extraction and determination of Tl(I) and Tl(III) with and without APDC (Figure 12). It appears that the

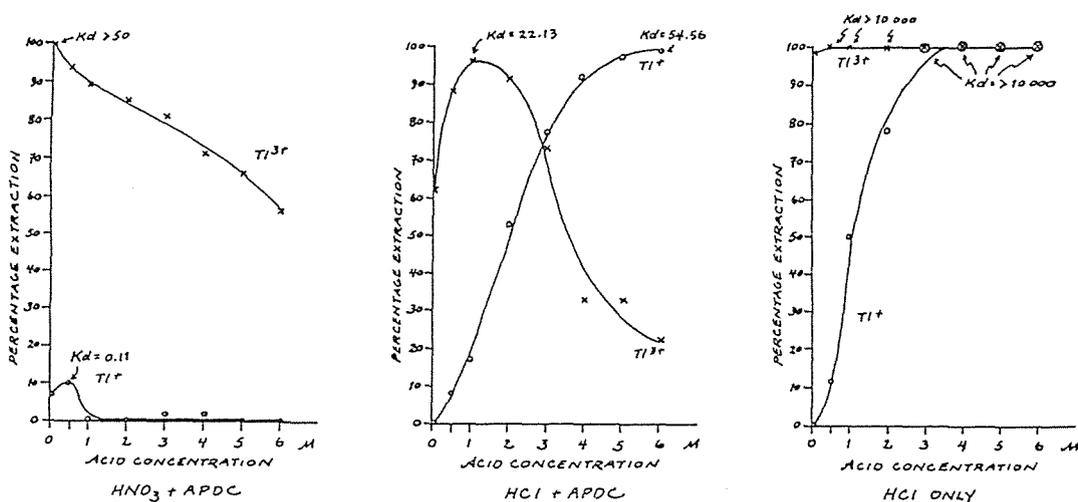


FIGURE 12: Extraction and maximum  $K_{d1}$  values for thallium (I) and (III) with and without APDC in HCl and HNO<sub>3</sub>

TABLE 7: The effect of different halide ions on the absorbance signals of 0.05 µg/ml thallium

	Cl	Br	I
aqueous	0.001	0.002	0.001
organic	0.000	0.000	0.000

bromine used to oxidise the thallium present in the solution to Tl(III) deteriorates the APDC compound, resulting in a decrease in  $K_d$  values at higher acidities in the presence of APDC. From these graphs, it can be seen that the halocomplex extracts best when no APDC is present. Hence only the halocomplex will be considered in the extraction of thallium.

Different halides were then tested to see if any of them would cause less of an interference than chloride. These results are summarized in Table 7. All of these halides interfere equally and form a volatile halide with the general formula  $TlX_4^-$ .

When determinations were run on the GF-AAS it was discovered that thallos chloride ( $TlCl$ ) can be analysed using GF-AAS, as can thallium (III) in the absence of chloride (Table 8). In either case, thallium sensitivity is adversely affected by the presence of a halide ion,

TABLE 8: Absorption signals for thallium (I) and (III) in the presence and absence of chloride ions

-----		
For 0.10 ug/ml thallium:		
	1M HNO <sub>3</sub>	1M HCl
-----		
Tl(I)	0.273	0.074
Tl(III)	0.245	0.003
-----		

though less so for Tl(I)Cl.

Thallium must be oxidised to Tl(III) before complete extraction will occur into MIBK (Figure 12) (Hall et al., 1987). To accomplish this a strong oxidising agent is necessary as Tl(III) reduces easily down to Tl(I) even in the presence of peroxide (Sidgwick, 1950). Bromine vapor was used to insure the complete oxidation and extraction of the species. The vapor has to be poured directly into the centrifuge tube to excess, i.e. till the smell of bromine was quite strong and the solution takes on an orange color.

Straight reduction of the thallium back to Tl(I) does not give a large signal (Table 8) in the presence of chloride.

To remove the interfering chloride, I considered the use of silver nitrate. Silver chloride is insoluble in the aqueous solutions used here and in MIBK and silver nitrate is readily available from most chemical stores and laboratories. A study was made to discover the best way to add the silver nitrate to the solution and in what amounts.

In general, silver nitrate must be in its aqueous form in order to react with chloride and precipitate as silver chloride.

Back-extraction of thallium is readily accomplished when the organic phase is removed after centrifuging and shaken with a silver nitrate/1 M nitric acid solution.

The optimal amount of silver was determined for the extraction of 0.05  $\mu\text{g/ml}$  thallium in MIBK (Figure 13). A minimum of 0.67 M silver nitrate is necessary for every 0.5 M chloride ion (as hydrochloric acid) in the original acidified rock solution.

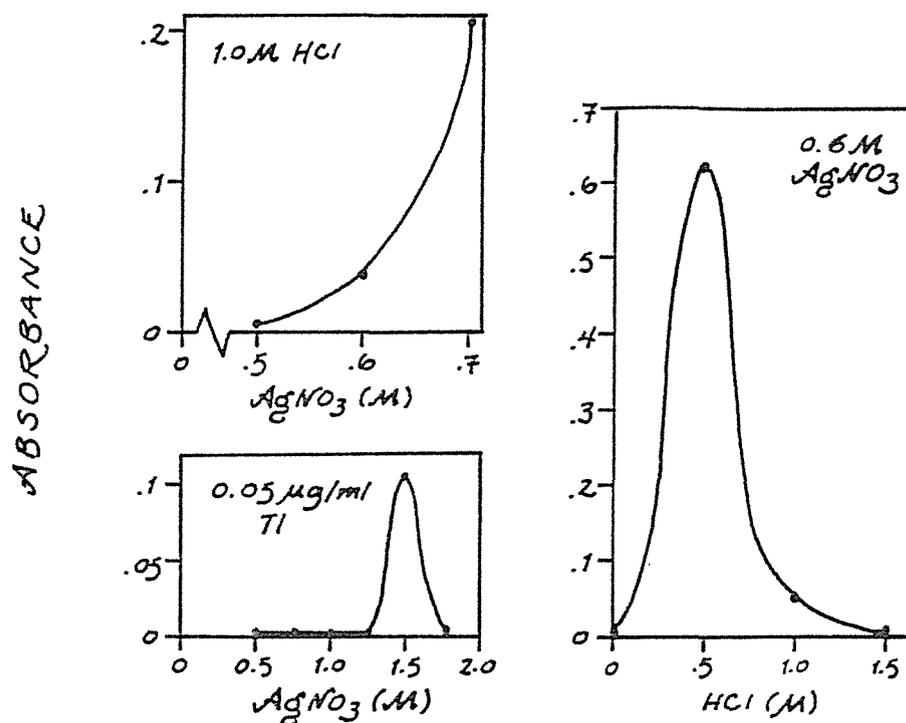


FIGURE 13: Determination of the optimum amount of  $\text{AgNO}_3$  to add to a known amount of thallium for  $\text{Tl}$  quantification by GF-AAS

Removal of the aqueous back-extraction phase proved to be a problem as it is located below the organic phase in the test tube. Separation using a Pasteur pipette sometimes results in contamination by the organic phase, resulting in lower readings when analysing on the GF-AAS. In addition, although the back extraction distribution coefficient of  $K_d = 332.3$  can be considered a good extraction ( $E=99.72\%$ ), the initial extraction of Tl(III) into MIBK is better with  $K_d > 10,000$  ( $E > 99.99\%$ ).

The evaporation rate of MIBK has always been a problem when preparing samples for automated injection into the GF-AAS (Brooks and Lee, 1988), but this apparent drawback can be used to advantage. A comparison was made between the evaporation rates of water and of MIBK (Figure 14). MIBK evaporates about twice as fast as water due to the former's

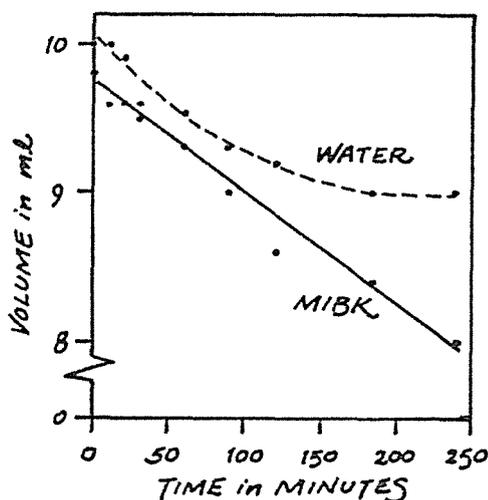


FIGURE 14: Evaporation rates of MIBK and water

relatively high vapor pressure. By evaporating off the MIBK phase after introducing it to the silver nitrate/1M nitric acid aqueous solution, all of the thallium can be guaranteed to be in the aqueous

phase and no interference will be present from the organic phase.

The quickest and easiest way to evaporate off the MIBK phase is to place the vial in a fume cupboard overnight. Positioning the vial just underneath the partially closed door gives a very efficient removal of the MIBK due to faster airflow.

MIBK will of course evaporate first as it is situated on top of the aqueous phase. To insure that none of the aqueous phase is lost, a 10 ml beaker or wide-mouthed vial can be weighed with the silver nitrate solution added to it before the addition of the organic phase. After the MIBK is evaporated, reweigh the vial assuming the the weight of chloride removed from the MIBK phase will be negligible and make up any difference in weight from the original reading with distilled water dropped from a Pasteur pipette. This is also a good way to check that all of the MIBK has evaporated off: if the reweighed value exceeds the preweighed value, all of the MIBK has not been removed and further evaporation is necessary.

The back extract solution needs to be filtered or centrifuged prior to analysis to separate the precipitated silver chloride. Analysis of the filtrate in the graphite furnace resulted in a white vapor emitted during the atomization stage. A trace of this peak was taken and it was discovered that two peaks were present (Figure 15). The  $<1$  s peak is thallium; the broad peak located at  $>1$  s is the result of a physical blockage of the spectral line. Sighinolfi (1973) notes that this sometimes occurs in GF-AAS work: "The source of these absorptions is undoubtedly smoke that may occur because thallium atomization takes place before the refractory matrix has been totally destroyed." These peaks may lead to analytical failure of the method. However, in this case the two peaks are well resolved and the matrix signal does not

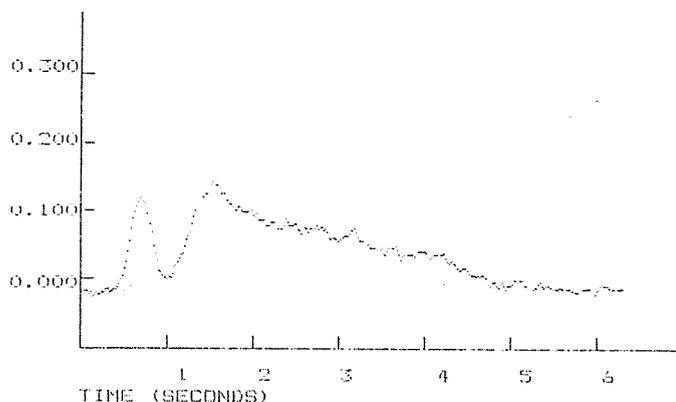


FIGURE 15: Plot of absorbances  
of thallium and  
"silver cloud" peaks

interfere with the thallium signal.

There was concern that the matrix signal (assumed to be unreacted silver ions) could overshadow the thallium signal if too much excess silver was added initially to the MIBK phase. Several atomization temperatures were tested and the results are shown on Figure 16. For maximum peak height with no matrix "cloud" interference of the signal, a 1500°C atomization temperature was chosen. The silver cloud interferes less with decreased atomization temperature (1400°C), but the size of the thallium peak decreases as well. To be absolutely certain that the peak observed was indeed thallium, a trace was taken on every fifth quantification of the sample, with each sample determined in quintuplicate.

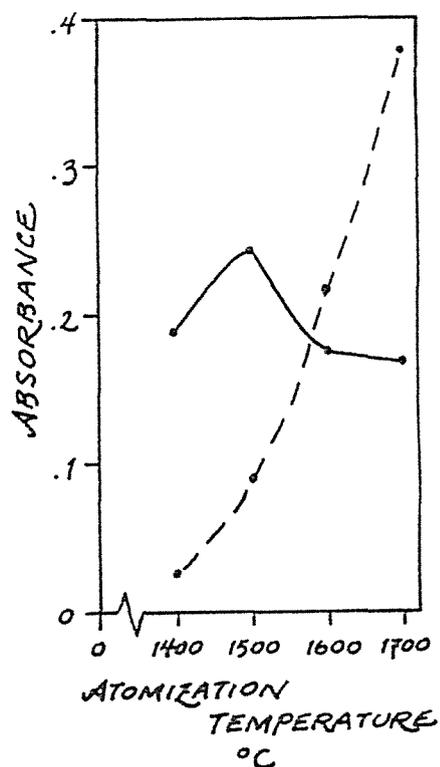


FIGURE 16: Effect of varying atomization temperatures on the relative absorbances of thallium and silver

#### II.4.4.c. Determination of Thallium in Reference Rocks

The accuracy of the proposed method was checked with reference materials that have recommended values for thallium. GNO-1 and CHRT are in-house control samples produced by the Geological Survey of Canada and have been analysed by Hall *et al.* (1987). GNO-1 is a composite outcrop containing 1.50  $\mu\text{g/g}$  thallium and 5.7  $\mu\text{g/g}$  gallium. CHRT is a carbonaceous chert containing 1.91  $\mu\text{g/g}$  thallium and 13.5

µg/g gallium.

Iron (III) is co-extracted with thallium (III) and then back-extracted into 0.1M hydrochloric acid. This method of separating iron from the sample is used by Hall et al. (1987) over other methods because of the need to oxidise thallium in order for extraction to take place. Ascorbic acid reduces Fe(III) to Fe(II) which does not extract significantly into MIBK (Sukhoveeva et al., 1979). Unfortunately, it also reduces Tl(III) to Tl(I) which also does not extract significantly at 2M hydrochloric acid concentration into MIBK (Figure 12). Brooks et al. (1985) first extracted Fe(III) in 6 M HCl into MIBK in the absence of other reagents.  $K_d > 3000$  in this case, and the elements of interest in their study extracted <1% at this acidity. Unfortunately, this cannot be used for thallium, as Tl(I) and Tl(III) both extract quite well (>90%) in the presence of a chloride at 6M (Figure 12). For these reasons, the method of Hall et al. (1987) is used here.

#### II.4.4.d. Limit of Detection, Precision and Accuracy

The limit of detection as defined by twice the signal to noise ratio was found to be 9.5 ng/ml for thallium using GF-AAS and the parameters described.

The precision and accuracy of the proposed technique as measured by quintuplicate analyses of 6 replicates of the reference rocks GNO-1 and CHRT are summarized in Table 9.

Results for CHRT do not show a good accuracy, but the precision is better than for GNO-1. Keeping in mind that these rocks are not standards but control samples that have not undergone the rigorous

TABLE 9: Statistical information for the proposed method of extraction for thallium

Limit of Detection (LOD).....	9.5 ng/g
Precision (RSD), n=6	
CHRT.....	2.02 µg/g ± 8.86%
GNO-1.....	1.92 µg/g ± 4.72%
Deviation from recommended values	
(relative error)	
CHRT (1.905 µg/g).....	6.04%
GNO-1 (1.50 µg/g).....	28.00%

testing required for standards, the fairly large deviation for CHRT from the result obtained by Hall et al. (1987) may not be significant.

II.4.4.e. Recommended Procedure for the Determination of Thallium from Rocks

1) Digest 0.5 g of finely powdered rock in a teflon beaker with 10 ml of 1:1:1 mixture of concentrated nitric, 40% hydrofluoric and 70% perchloric acids.

2) Heat in a sandbath till all fumes of perchloric acid have disappeared.

3) Add 10 ml 2 M hydrochloric acid and heat till the solution becomes relatively clear.

4) After cooling, brominate each sample with bromine vapor to excess. Shake with 5 ml pre-equilibrated MIBK for 1 minute. Centrifuge to

separate the phases.

5) Remove organic phase and shake with 5 ml 0.1 M hydrochloric acid. Centrifuge to separate the phases.

6) Pipette out 3 ml of the MIBK phase and place in a 10 ml vial or beaker which has been previously weighed with 3 ml 1 M silver nitrate in 1 M nitric acid.

7) Place in a fume cupboard overnight till the MIBK phase evaporates. Reweigh the vial and make up any difference in weight with distilled water. Centrifuge or filter to remove the silver chloride precipitate.

8) Determine thallium using GF-AAS using the program outlined in Table 3, Section II.3.6.e.

9) As a cautionary measure, take a trace of the peak height every fifth reading to check that there is no interference of the thallium signal by the "silver cloud."

#### II.4.5. Summary of Techniques

The techniques use an oxidising acid mixture to dissolve thallium and bismuth in rocks followed by extraction of the chlorocomplex  $Tl(III)Cl_4^-$  or the chelate complex  $Bi(III)\cdot APDC$  into MIBK. Quantification of thallium and bismuth in the organic phase is accomplished using electrothermal atomization of a graphite furnace coupled with atomic absorption spectrometry.

### III. FLAXBOURNE RIVER K-T BOUNDARY: A CASE STUDY

### III.1. Introduction

When Alvarez et al. (1980) reported the presence of anomalous iridium concentrations in Cretaceous-Tertiary (K-T) boundary clays at three diversely located sites worldwide, they postulated that these high levels had resulted from the impact of a large (>10 km diameter) chondritic asteroid with the earth, causing mass extinction of some 70% of all life forms on earth. Their hypothesis was initially based on iridium anomalies found in Gubbio in Italy, Stevns Klint in Denmark and Woodside Creek in New Zealand.

Since the initial paper by Alvarez et al. (1980), iridium anomalies have been found at more than 90 K-T boundary sites worldwide (Alvarez, 1986), though only a few of these have been studied in detail. Reported here is a biostratigraphic and geochemical study of a recently discovered K-T boundary site in New Zealand along the Flaxbourne River Valley, Marlborough Province. This site has 3 special features that make it particularly interesting:

- 1) It is one of only six K-T sites on land in the Southern Hemisphere. These are all located in New Zealand with the exception of one in Antarctica. These sites are separated by some 10,000 to 11,000 km from the next nearest sites in Japan and North America, and so are important for establishing worldwide trends. For example, Bohor and Izett (1986) found a steady decrease in the abundance and size of shocked, impact-derived quartz grains along a line running southeastwards from New Mexico to New Zealand. Maximum grain sizes declined from 0.58 to 0.11 mm along this same bearing.

2) The site is relatively unweathered and comparatively free of small-scale tectonic effects such as shearing. Many other such sites have been affected by weathering, oxidation and disturbance by vegetation and plant roots (Woodside Creek) or by pervasive tectonism (Needles Point and Chancet Rocks) (Brooks et al., 1986).

3) Most importantly, the sequence shows an exceptionally complete stratigraphic and biostratigraphic succession. Smit and Romein (1985) proposed a standard K-T boundary sequence of lithologic and paleontological units based on their analyses of a dozen of the most complete known boundary sequences, both onshore and in oceanic DSDP drillholes (Table 10). All units of this standard sequence can be clearly recognized at the Flaxbourne River site (Strong et al., 1987).

Standard K-T boundary sequence (SMIT and ROMEIN, 1985)			Flaxbourne River equivalent (for lithology see Fig. 2)	
Unit	Lithology	Biostratigraphy	Unit	Biostratigraphy
1	Uppermost Maastrichtian carbonates	<i>Abathomphalus mayaroensis</i> zone (M <sub>3</sub> ) Lge. K planktic forams	1-3	<i>A. mayaroensis</i> and lge. Cretaceous planktics
2	Extra-terrestrial component rich layer		lower 4	Lge. <i>Allomorpha</i> cretacea
3	Boundary clay	<i>Guenbelitria</i> cretacea zone P <sub>0</sub> Tiny K planktic "survivors"	upper 4 & 5 and most of 6	<i>G. cretacea</i> and tiny K holdover planktic forams
4	Lowermost Danian carbonate	<i>Globigerina eugubina</i> zone Pl <sub>a</sub> & Pl <sub>b</sub> Tiny lowermost Danian planktics	upper 6	<i>Globigerina</i> cf. <i>G. frings</i>
5	Lower Paleogene Carbonate	<i>Globorotalia pseudobulloides</i> zone Pl <sub>c</sub> , etc. Burgeoning planktic fauna	7 & 8	<i>Globoconusa daubjergensis</i>

Table 10: Standard K-T boundary event units and their equivalents at Flaxbourne River (Smit and Romein, 1985; Strong et al., 1987)

### III.2. Site Location

The Flaxbourne River K-T boundary site is in the NZMS Quadrangle P29 (1:50,000) about 4 km southeast of the settlement of Ward in the Marlborough Province, South Island, New Zealand. The locality lies near the mouth of the Flaxbourne River within a belt of moderately to complexly deformed Upper Cretaceous and Paleogene limestone which are approximately parallel to the coast for 20 km from the Ure River to Cape Campbell (Lensen, 1962). Other K-T boundary localities within this belt are shown in Figure 17.

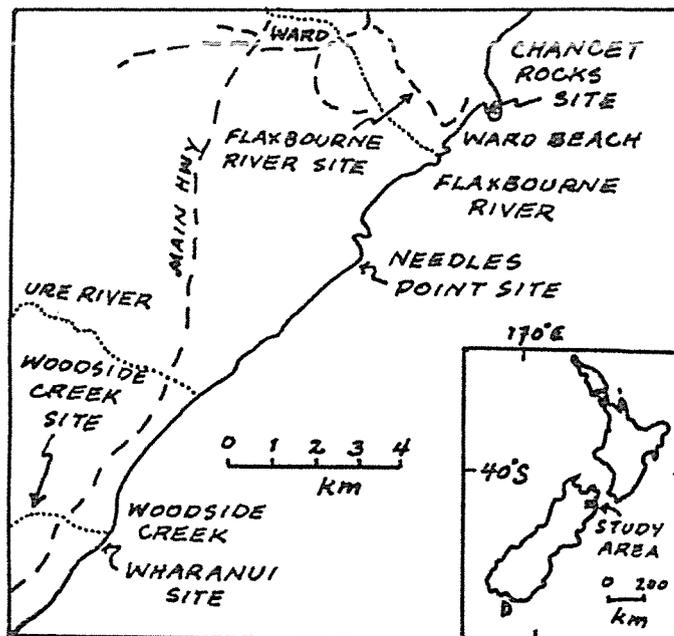


FIGURE 17: Flaxbourne River and other K-T boundary site locations (Strong *et al.*, 1987)

### III.3. Lithology

Lithologically, the Flaxbourne River K-T boundary sequence is similar to the nearby Chancet Rocks site (Strong, 1984; Brooks, 1986). The essential difference between the sites is that at Chancet Rocks, the lowest few cm of the boundary interval, including the boundary clay, is usually missing owing to marine erosion of the relatively soft boundary unit and the infilling of the resultant cleft with sediment.

A columnar section of the Flaxbourne River sequence is shown in Figure 18. The calcium carbonate contents are shown in parentheses after the rock descriptions. Nine lithologic units were defined within or adjacent to the interval samples (Strong *et al.*, 1987):

1) The interval -100 cm to -14 m (unit 1) consists of a thin to medium bedded brownish grey limestone with thin, marly partings.

2) Unit 1 is overlain by 100 cm of thickly bedded massive brownish grey limestone without marly partings (unit 2). As the thickest bed in the succession, it is an excellent marker for the Uppermost Cretaceous throughout the whole region, including Woodside Creek (Strong, 1977).

3) Unit 3 is a 2-5 cm layer of soft off-white marl with very irregular thickness. The contact with unit 2 undulates, as unit 3 tends to mask and fill irregularities on the surface of unit 2. This unit is not well represented at Chancet Rocks.

4) The boundary clay (unit 4) is defined on the basis of the sharp lithologic and biostratigraphic changes that occur at what is defined as zero on the scale of the stratigraphic column. The contact with unit 3 is planar and very sharp, and is marked by an abrupt color

change from off-white to dark grey. The average thickness is 20 mm. The lower half of the clay, consisting of finely divided material, merges into the upper part of the unit which is interspersed with small limestone lenses. The basal contact shows no evidence of erosion. Instead, it appears to represent continuous sedimentation during a sudden drastic change in oceanic conditions which altered accumulation rates of various sedimentary components. A major decrease in carbonate deposition was one such change.

5) Unit 5 consists of an 8 cm layer of laminated dark grey limestone, technically a calcareous mudstone. A similar dark limestone also occurs at Chancet Rocks where it is comparable in thickness.

6) The dark limestone of unit 5 is overlain by a 40 cm layer of thinly bedded grey-green calcareous mudstone (unit 6).

7) Unit 6 is overlain by a thickly bedded brownish weathered limestone (unit 7).

8) Unit 8 consists of an 8 m layer of medium bedded yellow-green limestone that overlies unit 7.

9) The uppermost recorded unit consists of massive a grey limestone with "sponge" fossils (unit 9).

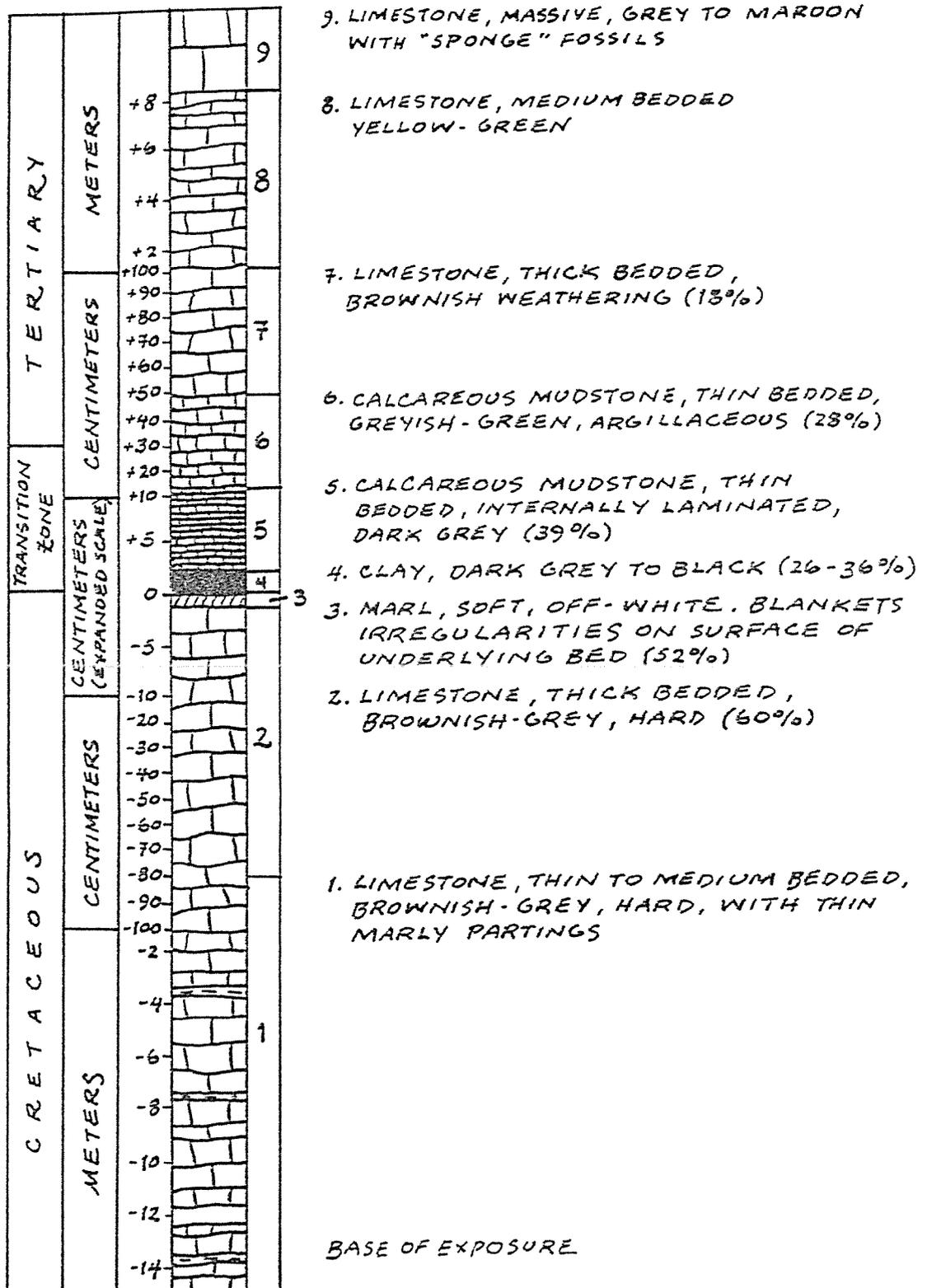


FIGURE 18: Lithologic section of the Flaxbourne River K-T boundary sequence (Strong et al., 1987)

#### III.4. Biostratigraphy

A preliminary foraminiferal study was undertaken by Strong et al. (1987) to confirm the position of the K-T boundary and to survey the general stratigraphic succession. The zero point on the scale not only indicates a position of sharp lithologic and biostratigraphic change, but also marks the lower boundary of the abrupt rise in the iridium content. This zero point lies between lithologic units 3 and 4.

Cretaceous samples contain a typical New Zealand latest Cretaceous bathyal fauna with very abundant large planktonics and sparse benthics. Transition zone samples are characterised by a fauna of diminutive Cretaceous planktonic and benthic specimens. Except for their tiny size, practically all of them appear identical to Late Cretaceous species that have been recorded from underlying strata at Flaxbourne River or from elsewhere in New Zealand. The decrease in specimen size is the most striking feature at and above the iridium anomaly, below which many species of forams are two to three times the size of the same species found above the boundary. Only the benthic Allomorpha cretacea, rare below the anomaly but common above it, reaches about the same size.

Other contrasts between the pre- and post-anomaly faunas are the appearance of new benthic taxa, an increase in the abundance of benthics from < 1% to an estimated 10% and an overall decrease in foraminiferal abundance.

The question arises as to whether the post-anomaly Guembelitra cretacea zone (the boundary clay) was somehow reworked from older

underlying strata. A number of factors suggest that this is not the case:

- 1) appearance of taxa not recorded below the boundary clay;
- 2) absence of other taxa which are abundant below the boundary;
- 3) drastic decrease in size for most species;
- 4) changes in relative abundance of planktonic taxa;
- 5) increase in proportion of benthic foraminifera;
- 6) lack of sedimentological evidence for bioturbation or other

reworking. The contact between the boundary clay and the underlying marl shows no signs of erosion and the sediment containing fauna Guembelitria cretacea is finely laminated.

Reference to the existence of "Cretaceous survivors" recognizes that taxa above the boundary are not just reworked sediments (Hsu et al., 1982).

Because of New Zealand's late Cretaceous paleolatitude of approximately 60°S (Windly, 1984; Condie, 1982) tropical/subtropical globotruncanids never formed a major part of Flaxbourne River's foraminiferal assemblage. Thus in New Zealand the same taxa persisted in general but with diminished size and abundance rather than disappearing altogether.

### III.5. Geochemistry

Chromium, cobalt, nickel and iridium are depleted in the earth's crust relative to chondritic meteorites (Strong et al., 1987). All four elements show a double peak at the boundary (-2 to -1 cm and 0 to +1 cm), split by a notch at -1 to 0 cm. This seems due to the slight brecciation of the boundary layer which contains limestone lenses of up to cm size. Apart from this brecciation, there is no evidence for other forms of disturbance such as bioturbation or burrowing. Of these four elements, iridium shows the largest enrichment at the boundary and has the largest meteoritic component. The integrated iridium mass for the Flaxbourne River sequence is estimated at  $134 \text{ ng/cm}^2$  after integration in the interval -2 to +6 cm and subtracting background. This calculation assumes a density of 2.5 and 2.7 for Cretaceous and Tertiary rock respectively with backgrounds of 0.08 and 0.17 ng/g. The integrated iridium value for Woodside Creek approaches  $187 \text{ ng/cm}^2$  (Brooks et al., 1984) and  $197 \text{ ng/cm}^2$  for Caravaca, Spain (Smit and Hertogen, 1980). About 85% of the total iridium at Flaxbourne River was deposited within the interval of -2 to +6 cm (Strong et al., 1987). The section below this contains 4.6% of the total iridium with an integrated value of  $7.3 \text{ ng/cm}^2$  of iridium.

Kyte et al. (1985) suggest that only the basal layer of the boundary clay should be used to estimate the primary fallout of impact particles as the iridium in higher layers may come mainly from secondary lateral transport. They note that only six sites worldwide have iridium fluences over  $120 \text{ ng/cm}^2$  and although some of the iridium may indeed be

derived from lateral transport and settling of other sedimentary material into a topographic low (as the site may well have been), Strong et al. (1987) suspect that the iridium fluence is actually somewhat higher than estimated by Kyte et al. (1985).

Chromium, cobalt and nickel have higher background abundances and although they peak at the boundary, it is not clear that the entire excess is meteoritic as other non-meteoritic elements also peak at the boundary. Nickel also shows a secondary peak in the +9 to +13 cm interval, conceivably due to diffusion or secondary mineralization.

The chalcophile elements arsenic, antimony and gallium resemble the siderophiles by being enriched in the boundary, but then reverting more or less back to their previous levels. Indium does not show any enrichment or depletion at any point along the column. It was decided to investigate the enrichments of thallium and bismuth. These chalcophiles are clearly terrestrial, but from unknown sources. Strong et al. (1987) suggest that though oceanic abundances of the above elements would be a sufficient source for the chalcophile elements present in the Flaxbourne River K-T boundary clay, the rocks of the impact site are most likely the source for these chalcophile elements.

### III.6. Sampling Method

Twenty-six rock samples were collected in the interval of -60 to +72 cm relative to the dark grey-black clay considered to be the K-T boundary. Sampling was continuous between -17 and +39 cm.

The samples were air-dried and ground individually in a tungsten carbide concentric ring grinder to -100 mesh size. Ground and whole samples are stored in zip-lock polyethylene bags separately and carefully labelled.

### III.7. Results

The samples to be analyzed were chosen to correspond with enrichments in iridium. It was assumed that where iridium enrichment occurs, a corresponding enrichment in thallium and bismuth could also be expected.

The finely ground rocks were digested and redissolved and the thallium and bismuth extracted as described in sections II.4.3.f. and II.4.4.d. The results are tabulated on Table 11 and graphed in Figure 19 with the other elements of interest for this study. The samples were checked by hydride generation-AAS (HG-AAS) to confirm the low levels of bismuth determined by GF-AAS. These results are also presented in Table 11.

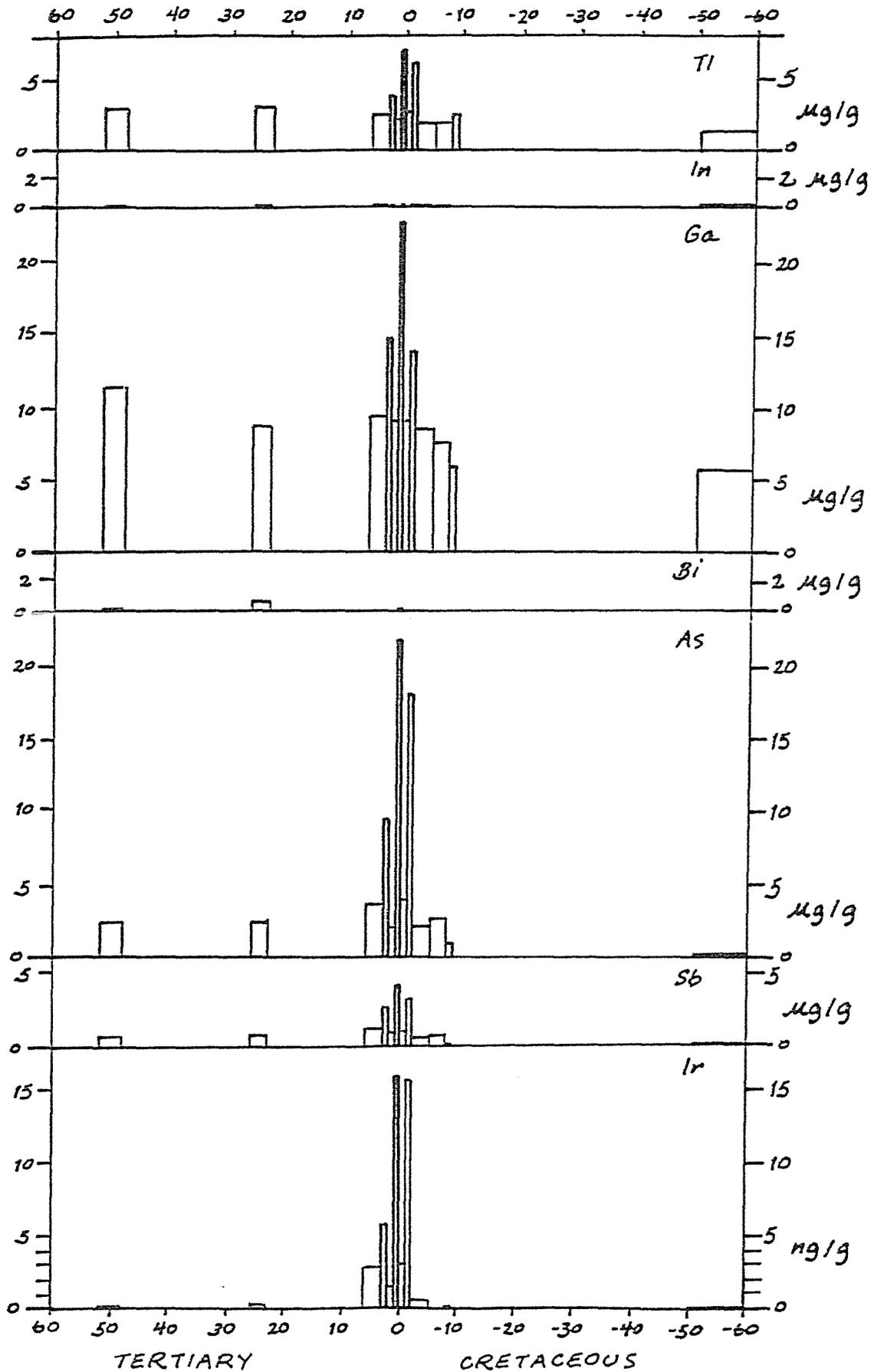


FIGURE 19: Results of thallium and bismuth determinations by GF-AAS in Flaxbourne River K-T boundary samples with iridium, arsenic, antimony, gallium and indium

TABLE 11: GF-AAS determinations of thallium and Bismuth for selected intervals in the Flaxbourne River K-T boundary sequence

Interval (cm)	Tl( $\mu\text{g/g}$ )	Bi( $\text{ng/g}$ )	Bi (HG-AAS)
+48 to +52	2.88	<20	0.23 $\mu\text{g/g}$
+23 to +26	2.96	"	1.00 $\mu\text{g/g}$
+3 to +6	2.56	"	<4 $\text{ng/g}$
+2 to +3	4.01	"	"
+1 to +2	2.28	"	"
0 to +1	7.22	"	"
-1 to 0	2.81	"	"
-2 to -1	6.17	"	"
-5 to -2	1.97	"	"
-8 to -5	1.92	"	"
-9 to -8	2.73	"	"
-60 to -50	1.52	"	"

The result is a highly significant correlation between thallium and iridium (Appendix 5) with their values plotted against each other in Figure 20.

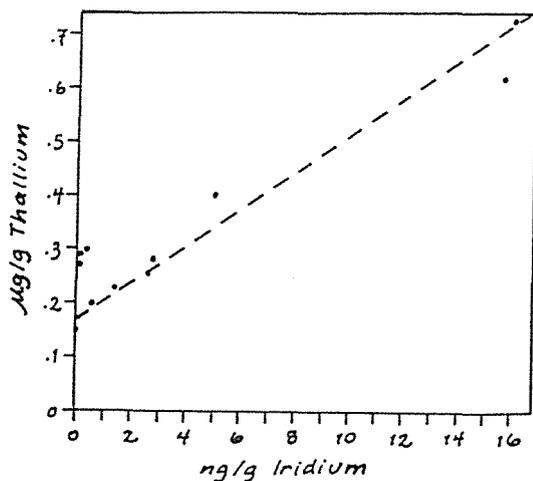


FIGURE 20: Correlation of thallium vs iridium abundances in the Flaxbourne River K-T boundary samples

### III.8. Discussion

Figures 19, 20 and 21 suggest that thallium correlates approximately with iridium, the meteoritic element that originally lead to the development of the impact hypothesis (Alvarez et al., 1980). Thallium, like arsenic and antimony is only a negligible meteoritic component (Appendix 7) and yet enriched in the Flaxbourne River K-T boundary site relative to average crustal abundance by 5 to 50 times (crustal abundance Tl: 0.13 to 1.3  $\mu\text{g/g}$ , Mason and Moore, 1982). This is the same order of magnitude of enrichment for arsenic and antimony in other K-T boundary sites (Gilmour and Anders, 1988).

Bismuth is not detectable in the Flaxbourne River site. The abundances of bismuth are summarized on Appendix 7. Though not plentiful, a similar enrichment to arsenic and antimony could have been expected as bismuth's chemical behavior parallels those of antimony and arsenic (Angino, 1972) and like thallium, bismuth is a chalcophile element. Accumulation and enrichment of chalcophile elements in the K-T boundary can be explained in terms of oxidation potentials. The anoxic conditions following the impact would cause scavenging of chalcophiles from the water column (Brooks et al., 1984). Efficient sweep-out by the ejecta would be able to concentrate most of these dissolved chalcophiles (Strong et al., 1987). In addition, Goldschmidt (1954) observed that chalcophile elements are remarkably concentrated in coal ash due to the material's low oxidation potential. This includes bismuth, which is enriched 100 times in that medium (Table 12). Instead, a bismuth depletion seems to have occurred at the

TABLE 12: Enrichment of selected chalcophile elements in coal ash (Mason and Moore, 1982, after Goldschmidt, 1954)

Element	Coal Ash ( $\mu\text{g/g}$ )	Lithosphere ( $\mu\text{g/g}$ )	Enrichment Factor
Ga	500	1.5	330
In	*	0.1	enriched
Tl	---	0.5	---
As	500	2.0	250
Sb	*	0.2	enriched
Bi	20	0.2	100

\* Mentioned in Goldschmidt (1954), but no value given  
 --- Not determined

Flaxbourne River site all throughout the rock column (Table 11). The small amount of bismuth at +23 to +26 cm is most likely due to contamination of the sample when analysed by hydride generation-AAS.

Possible sources of the chalcophile elements observed in the Flaxbourne River site and in other K-T boundary rocks include the bolide, the ocean, volcanic sources and the impact ejecta debris. The bolide itself is rejected as a source as it's chalcophile content is too low (Gilmour and Anders, 1988). The ocean is deficient in terms of mass balance and is unlikely to give the very good correlations that exist between meteoritic iridium and the chalcophile elements, including thallium (Strong *et al.*, 1987). Volcanic sources can also be rejected as the high iridium anomalies observed in K-T boundary clays do not characterize volcanic products, and no satisfactory deposition

mode is available that could account for the element's widespread distribution (Alvarez, 1986). This leaves the impact ejecta as the sole remaining possibility.

Chalcophile elements are clearly terrestrial (Strong et al., 1987) which strengthens support for the idea that the impact ejecta was their source. The next step is to identify a rock type that would be regionally distributed and be enriched in all of the chalcophiles except for bismuth and indium.

Gilmour and Anders (1988) note that some continental igneous rocks approximate the required antimony levels, with the rock apparently derived from some depth as a silica-rich fractionation product of a more mafic magma. Though these rocks are depleted relative to the arsenic concentration requirements, Gilmour and Anders hypothesize that the target rock must actually come from the lower crust, which could provide the necessary arsenic and antimony.

De Paolo et al. (1983) and De Paolo and Kyte (1984) measured the  $^{87}/^{86}$  Sr ratios of HCl residues from DSDP 465A and at Caravaca. They concluded that the terrestrial rock source was an oceanic crust with a significant > 3 km depth component. This is not inconsistent with Gilmour and Ander's (1988) continental source rock from some depth, or a mixed source (Hawkesworth et al., 1979, 1982).

The mineralogy of an element, although a general guide, may not be altogether indicative of its geochemical character. For example, although all thallium minerals are sulfides, the greater part of the thallium in the earth's crust is contained in potassium minerals where Tl(I) (ionic radius 0.147 nm) proxies for K(I) (ionic radius 0.133 nm) in potash and plagioclase feldspars (Mason and Moore, 1982) where thallium concentrations can often exceed 100 ug/g (Goldschmidt, 1954).

Thallium is concentrated along with rubidium during the late stages of magmatic crystallization (Carapella, 1972).

Bismuth, which occurs in nature as Bi(III), becomes enriched in late magmatic differentiations (Angino, 1972). It tends to be concentrated in granitic magmas and is common in granitic pegmatites. Bismuth is widely distributed in hydrothermal mineral deposits where it is often associated with gold and is most commonly present in galena. It is enriched to a minor degree in sedimentary iron ores, but weathered residual sediments are essentially devoid of bismuth (Angino, 1972). This last statement seems to indicate that bismuth is leached easily from sedimentary rocks. This is a significant observation, as bismuth appears to be present in measurable quantities in all of the igneous rock types that thallium would be present in (Appendix 7). Bismuth tends to be concentrated in the late magmatic differentiation fraction and follows the sulfur enrichments. Thallium has the same tendency; however, as noted, it can proxy as Tl(I) for K(I) and be removed from the magma in a potassium-silicate mineral. Bi(III) does not enter silicate lattices by substituting for another element. To become part of a rock, it would be present in bismuth-rich nodules. These bismuth blebs would be among the last to crystallize out of a magma melt (Best, 1982).

Because the bismuth is not "fixed" in a crystal lattice as thallium is, it can be easily lost upon weathering of the rock. Potassium feldspars tend to be chemically inert, though they are susceptible to physical weathering processes (Selley, 1982). This would preserve the thallium and keep it from being lost from the lattice. Angino (1972) notes that bismuth compounds do not exhibit acidic tendencies and thus are insoluble in alkalis but dissolve easily in acids. The simple

formation of carbonic acid in rain and seawater is enough to dissolve the bismuth compounds. This helps to explain the absence of bismuth anywhere along the marine-deposited Flaxbourne River site. Even if bismuth was present in the source rock, it would be leached out of the boundary clay in time.

This may also be true of indium, which also shows no enrichment along the Flaxbourne River sequence. Like bismuth, indium does not proxy for another element in a silicate lattice and would be in the final magmatic differentiation product. Bismuth and indium are enriched in seawater relative to gallium and thallium, which both show definite enrichments that approximate the iridium content all along the K-T boundary sequence (Appendix 7). Arsenic and antimony both show very large enrichments in the K-T boundary sequence and the amount of these two elements present in seawater or in meteorites is not enough to account for the immense enrichment (Strong *et al.*, 1987).

### III.9. Conclusion

The following hypothesis does not contradict the possible scenario for chalcophile enrichment in the K-T boundary put forward by Gilmour and Anders (1988). They suggest that a single impact occurred on continental crust, possibly in the vicinity of a destructive plate margin, deriving material from the lower crust. This would result in a mixed continental-type source that could account for the high arsenic, antimony, gallium and thallium abundances observed in the Flaxbourne River K-T boundary site.

Following the impact, ejecta had settled to form a sludge deposit

that would later become the boundary clay. The anoxic conditions following the impact caused the chalcophiles in seawater to accumulate in the particulate ejecta layer once they had been dissolved. Bismuth and indium would not have been scavenged possibly as a result of their high solubilities in acidic seawater, or they could have been leached later after deposition.

This scenario could account for the depletion of bismuth and indium along the K-T boundary sequence at Flaxbourne River despite their apparent abundance in possible target rocks and in the ocean.

## SUMMARY AND GENERAL CONCLUSIONS

The analytical section of this thesis showed that with careful selection of the instrumental parameters, low concentrations of thallium and bismuth could be determined in rocks using the graphite furnace atomization technique. The limits of detection obtained here were 20 ng/ml (ppb) for bismuth and 9.5 ng/ml for thallium.

Thallium and bismuth in rocks were dissolved using a mixture of fuming nitric, hydrofluoric and perchloric acids over a sandbath. Thallium was extracted as a chlorocomplex into MIBK and bismuth as a chelate complex in HCl with APDC, also into MIBK. Bismuth could be analysed directly from the organic phase in this form on the graphite furnace but thallium requires removal of the chloride (or any halide) ion using silver(I) to form insoluble silver chloride. This back-extract could be placed directly into the furnace.

Using the above techniques, thallium and bismuth were determined from reference rocks and from the Flaxbourne River K-T boundary sequence. The study revealed a strong correlation between meteoritic iridium and chalcophilic thallium, but no detection was possible of bismuth, even when the samples were analysed by hydride generation atomic absorption spectrometry as a check. This is indicative of the differing geochemistry of bismuth and thallium, leading to insight as to the fate of bismuth after the impact.

The main achievements of this work are as follows:

- 1) Development of a method for the determination of thallium using GF-AAS;
- 2) Development of a method for the determination of bismuth from  $>2$  M acid concentrations using APDC and subsequent quantification by GF-AAS;
- 3) Demonstration of the close correlation of thallium with iridium in the K-T boundary and of the different geochemical behavior of bismuth (and possibly indium) from arsenic, antimony and other chalcophiles;
- 4) Proposal of an additional factor in the terminal Cretaceous impact scenario, where bismuth, and perhaps indium, are not enriched in the Flaxbourne River and possibly other K-T boundary sites because of their high solubility in seawater.

Further work on the study of chalcophiles should be carried out with the following aims:

- 1) To further substantiate bismuth and thallium behavior relative to iridium in other K-T boundary sequences;
- 2) To further test the reliability of the proposed methods of extraction in other materials, such as plant and animal tissue;
- 3) To determine the remaining untested chalcophiles (cadmium, lead, tellurium and sulfur) in the Flaxbourne River and other K-T boundary sequences to confirm the proposed scenario.

## REFERENCES

## REFERENCES

- Alvarez, L.W., W. Alvarez, F. Asaro, H.V. Michel, 1980, Extraterrestrial cause for the Cretaceous-Tertiary extinction. Science, 208: 1095-1108.
- Alvarez, W., 1986, Toward a theory of impact crisis. Eos, 67, 35: 649-658.
- Angino, E.E., 1972, Bismuth: Element and Geochemistry in The Encyclopedia of Geochemistry and Environmental Sciences, Vol. IVA, R.W. Fairbridge, editor. Van Nostrand Reinhold, New York.
- Ariel, M. and D. Bach, 1963, The determination of thallium in urine. Analyst, 88: 30-35.
- Barker, D.S., 1983, Igneous Rocks, Prentice-Hall, Englewood Cliffs.
- Best, M.G., 1982, Igneous and Metamorphic Petrology, Freeman, New York.
- Bohor, B.F. and G.A. Izett, 1986, Worldwide size distribution of shocked quartz at the K-T boundary: evidence for a North American impact site. Lunar and Planetary Science, 17: 68-69.

Boswell, C.R. and R.R. Brooks, 1965, The application of discontinuous, countercurrent, liquid-liquid extraction to the study of the distribution of metal ions between hydrochloric acid and methylisobutyl ketone. Mikrochimika Acta, 5/6: 815-821.

Brooks, R.R., 1987, Analytical chemistry and dinosaurs. Canadian Journal of Chemistry, 65: 1033-1041.

Brooks, R.R., B.J. Presley, I.R. Kaplan, 1967, APDC-MIBK extraction system for the determination of trace elements in saline waters by atomic absorption spectrometry. Talanta, 14:809-816.

Brooks, R.R., R.D. Reeves, X.H. Yang, D.E. Ryan, J. Holzbecher, J. Collen, V.E. Neall, J. Lee, 1984, Elemental anomalies at the Cretaceous-Tertiary boundary, Woodside Creek, New Zealand. Science, 226: 539-542.

Brooks, R.R., A. Siriwardena, J. Lee, 1985, A plasma emission method for determining elemental constituents of geological materials with a high iron content. Chemical Geology, 53:31-35.

Brooks, R.R., C.P. Strong, J. Lee, C.J. Orth, J.S. Gilmour, D.E. Ryan, J. Holzbecher, 1986, Stratigraphic occurrences of iridium anomalies at four Cretaceous-Tertiary boundary sites in New Zealand. Geology, 14: 727-729.

- Brooks, R.R. and B.S. Lee, 1988, The determination of platinum and palladium in rocks and soils by electrothermal atomic absorption spectrometry of extracts of their iodo complexes. Analytica Chimica Acta, 204: 333-337.
- Brooks, R.R., M. Hoashi, S.M. Wilson, R.Q. Zhang, 1988, Extraction into methyl isobutyl ketone of metal complexes with ammonium pyrrolidine dithiocarbamate formed in strongly acidic media. Analytica Chimica Acta, in press.
- Carapella, S.C., 1972, Thallium: Element and Geochemistry, in The Encyclopedia of Geochemistry and Environmental Sciences, volume IVA, R.W. Fairbridge, editor. Van Nostrand Reinhold, New York.
- Christian, G.D., 1978, Flame spectroscopy in Instrumental Analysis, H.H. Bauer, G.D. Christian, J.E. O'Reilly, editors. Allyn and Bacon, Boston.
- Condie, K.C., 1982, Plate Tectonics and Crustal Evolution, 2nd edition. Pergamon, New York.
- De Paolo, D.J., K.T. Kyte, B.D. Marshall, J.R. O'Neill, J. Smit, 1983, Rb-Sr, Sm-Nd, K-Ca, O and H isotopic study of Cretaceous-Tertiary boundary sediments, Caravaca, Spain: evidence for and oceanic impact site. Earth and Planetary Science Letters, 64: 356-373.

- De Paolo, D.J., and F.T. Kyte, 1984, Isotopic and chemical characteristics of Cretaceous-Tertiary boundary sediments from DSDP site 465A, Lunar and Planetary Science, 15: 220-221.
- Elson, C.M. and C.A.R. Albuquerque, 1982, Determination of thallium in geological materials by extraction and electrothermal atomic absorption spectrometry Analytica Chimica Acta, 134:393-396.
- Ficklin, W.H. and F.N. Ward, 1976, Flameless atomic absorption determination of bismuth in soils and rocks. Journal of Research: USGS, 4, 2: 217-220.
- Fuller, C.W., 1976, The effect of acids on the determination of thallium by atomic absorption spectrometry with a graphite furnace. Analytica Chimica Acta, 81: 199-202.
- Fuller, C.W., 1977, Electrothermal Atomization for Atomic Absorption Spectrometry, The Chemical Society, London.
- Gawali, S.B. and V.M. Shinde, 1976, Separation of gallium(III), indium(III) and thallium(III) by solvent extraction with 4-methyl-2-pentanone. Analytical Chemistry, 48, 1: 62-64.
- Gilmour, I. and E. Anders, 1988, Trace element evidence for a single impact at the Cretaceous-Tertiary boundary. Geochimica et Cosmochimica Acta, submitted manuscript.

- Goldschmidt, V.M., 1954, Geochemistry, Clarendon Press, Oxford.
- Goto, H. and Y. Kakita, 1959, Studies on the extraction and determination of metal salts with methyl isobutyl ketone. I-- extraction from acid solution. Scientific Reports of the Research Institute of Tohoku University, Ser. A, 11: 1-20.
- Green, J., 1972, Elements: Planetary abundances and distribution. in The Encyclopedia of Geochemistry and Environmental Sciences, volume IVA, R.W. Fairbridge, editor. Van Nostrand Reinhold, New York.
- Hall, G.E.M., K.N. de Silva, J.C. Pelchat, J.E. Vaive, 1987, Advances in analytical methods based on atomic absorption spectrometry in the geochemistry laboratories of the Geological Survey of Canada. Current Research, Part A, Geological Survey of Canada, Paper 87-A, pp.477-484.
- Hawkesworth, C.J., M.J. Norry, J.C. Roddick, P.E. Baker, P.W. Francis, R.S. Thorpe, 1979,  $^{143}\text{Nd}/^{144}\text{Nd}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$  and incompatible trace element variations in calc-alkaline andesites and plateau lavas from South America. Earth and Planetary Science Letters, 42: 45-57.

- Hawkesworth, C.J., M. Hammill, A.R. Gledhill, P. Van Calsteren, G. Rogers, 1982, Isotope and trace element evidence for late-stage intracrustal melting in the High Andes. Earth and Planetary Science Letters, 42: 45-57.
- Hsu, K.J., Q. He, J.A. McKenzie, H. Weissert, K. Perch-Nielsen, J. Oberhansli, K. Kelts, J. LaBreque, L. Tauxe, U. Krahanbuhl, S.F. Percival, R. Wright, A.M. Karpoff, N. Petersen, P. Tucker, R.Z. Poore, A.M. Gombos, K. Pisciotto, M.F. Carmen Jr., E. Schreiber, 1982, Mass mortality and its environmental and evolutionary consequences. Science, 216: 249-256.
- Hubert, A.E. and T.T. Chao, 1985, Determination of gold, indium, tellurium and thallium in the same sample digest of geological materials by atomic absorption spectrometry and two-step solvent extraction. Talanta, 32, 7: 568-570.
- Korkisch, J., 1969, Modern Methods for the Separation of Rarer Metal Ions, Pergamon Press, Oxford.
- Kothny, E.L., 1969, Trace determination of mercury, thallium and gold with crystal violet. Analyst, 94:198-203.
- Kyte, F.T., Z.M. Zhou, J.T. Wasson, 1980, Siderophile-enriched sediments from the Cretaceous-Tertiary boundary. Nature, 288: 651-656.
- Kyte, F.T., J. Smit, J.T. Wasson, 1985, Siderophile inter-element variations in the Cretaceous-Tertiary boundary sediments from Caravaca, Spain, Earth and Planetary Science Letters, 73:183-195.

Lensen, G.J., 1962, Sheet 16 Kaikoura, Geological Maps of New Zealand 1:250,000, DSIR, Wellington.

Liem, I., G. Kaiser, M. Sager, G. Tola, 1984, The determination of thallium in rocks and biological materials at ng/g levels by differential-pulse anodic stripping voltammetry and electrothermal atomic absorption spectrometry. Analytica Chimica Acta, 158: 179-197.

Malissa, H. and J. Schoffmann, 1955, Uber die Verwendung von substituierten Dithiocarbamaten in der Mikroanalyse, III. Mikrochimika Acta, 1: 187-202.

Manning, D.C., W. Slavin, S. Myers, 1979, Sampling at constant temperature in graphite furnace atomic absorption spectrometry. Analytical Chemistry, 51, 14: 2375-2378.

Mason, B. and C.B. Moore, 1982, Principles of Geochemistry, 4th edition, Wiley, New York.

Morrison, G.H. and H. Freiser, 1957, Solvent Extraction in Analytical Chemistry, Wiley, New York.

Mulford, C.E., 1966, Solvent extraction techniques for atomic absorption spectrometry. Atomic Absorption Newsletter, 5, 4: 88-90.

O'Leary, R.M. and J.G. Viets, 1986, Determination of antimony, arsenic, bismuth, cadmium, copper, lead, molybdenum, silver and zinc in geologic materials by atomic absorption spectrometry using a hydrochloric acid-hydrogen peroxide digestion. Atomic Spectroscopy, 7, 1: 4-8.

Orth, C.J., 1987, INAA data for Flaxbourne River K-T boundary, unpublished.

Pinta, M., 1966, Detection and Determination of Trace Elements. Ann Arbor Science, London.

Price, W.J., 1979, Spectrochemical Analysis by Atomic Absorption. Heyden, London.

Raup, D.M. and S.M. Stanley, 1978, Principles of Paleontology, 2nd edition, Freeman, San Francisco.

Shan, X.Q., Z.M. Ni, L. Zhang, 1984, Application of matrix-modification in determination of thallium in waste water by graphite furnace atomic absorption spectrometry. Talanta, 31, 2:150-152.

Sidgwick, N.V., 1950, The Chemical Elements and Their Compounds. Clarendon Press, Oxford.

Sighinolfi, G.P., 1973, Determination of thallium in geochemical reference samples by flameless atomic absorption spectroscopy. Atomic Absorption Newsletter, 12, 6:136-138.

Simon, F.O., E.Y. Campbell, P.J. Aruscavage, 1977, Thallium contents of 16 USGS standard rocks, Journal of Research of the USGS, 5, 5: 579-581.

Slavin, W. and D.C. Manning, 1980, The L'vov Platform for furnace atomic absorption analysis analysis. Spectrochimica Acta, 35B: 701-714.

Smit, J. and J. Hertogen, 1980, An extraterrestrial event at the Cretaceous-Tertiary boundary. Nature, 285:198-200.

Smit, J. and A.J.T. Romein, 1985, A sequence of events across the Cretaceous-Tertiary boundary. Earth and Planetary Science Letters. 74: 155-170.

Sprague, S. and W. Slavin, 1964, Determination of very small amount of copper and lead in potassium chloride by organic extraction and atomic absorption spectroscopy. Analytical Chemistry, 34: 614-617.

Stanton, R.E. and A.J. McDonald, 1962, The spectrophotometric determination of antimony with brilliant green. Analyst, 87: 299-301.

Strong, C.P., R.R. Brooks, S.M. Wilson, R.D. Reeves, C.J. Orth, X.Y. Mao, L.R. Quintana, E. Anders, 1987, A new Cretaceous-Tertiary boundary site at Flaxbourne River, New Zealand: Biostratigraphy and geochemistry. Geochimica et Cosmochimica Acta, 51:2769-2777.

Sukhovееva, L.N., B.Y. Spivakov, A.V. Karyakin, Y.A. Zolotov, 1979, Atomic absorption determination of gallium by means of a flame and graphite furnace. Zhurnal Analiticheskoi Khimii, 34: 693-702.

Thompson, K.C. and D.R. Thomerson, 1974, Atomic-absorption studies on the determination of antimony, arsenic, bismuth, germanium, lead, selenium, tellurium, and tin by utilising the generation of covalent hydrides. Analyst, 99: 595-601.

Viets, J.G., 1978, Determination of silver, bismuth, cadmium, copper, lead and zinc in geologic materials by atomic absorption spectrometry with tricaprylmethylammonium chloride. Analytical Chemistry, 50, 8: 1097-1011.

Viets, J.G., J.R. Clark, W.L. Campbell, 1984, A rapid partial leach and organic separation for the sensitive determination of Ag, Bi, Cd, Cu, Mo, Pb, Sb and Zn in surface geologic materials by flame atomic absorption. Journal of Geochemical Exploration, 20: 355-366.

Voskresenskaya, N.T., N.F. Pchelintseva, T.I. Tsekhonya, 1981, Extraction atomic absorption determination of thallium in sedimentary rocks. Zhurnal Analiticheskoi Khimii, 36, 4: 667-671.

Willis, J.B., 1962, Determination of lead and other heavy metals in urine by atomic absorption spectroscopy. Analytical Chemistry, 34, 6: 614-617.

Wilson, S.M., 1987, personal communication of unpublished data.

Windly, B.F., 1984, The Evolving Continents, 2nd edition, Pergamon,  
New York.

## APPENDIX

APPENDIX 1: Concentration of chalcophile elements in the  
 Flaxbourne River K-T boundary sequence  
 determined by INAA (Orth, 1987) and GF-AAS  
 (this work).  
 All values are in µg/g on a calcified basis  
 unless otherwise specified

Interval (cm)	Fe	Cu	Ag	Zn	Cd	Hg
+70 to +72	9330	<170	<3.3	27	--	<0.52
+48 to +52	9480	<340	<5.1	66	--	<0.92
+36 to +39	13200	<260	<6.1	64	--	<4.7
+33 to +36	12510	<240	<3.6	88	--	<0.57
+28 to +33	10340	<210	<3.6	77	--	<0.56
+26 to +28	9850	<330	<5.2	87	--	<0.93
+23 to +26	11230	<220	<5.0	87	--	<3.7
+21 to +23	11810	<230	<3.0	93	--	<0.49
+21 to +15	10630	<210	<3.5	84	--	<0.55
+13 to +15	13110	<410	<6.7	110	--	<1.2
+12 to +13	12800	<220	<5.4	124	--	<3.9
+9 to +12	12600	<350	<5.5	183	--	<0.85
+8 to +9	7590	<220	<3.3	143	--	<0.52
+6 to +8	8400	<380	<4.8	215	--	<0.86
+3 to +6	8930	<290	<5.5	171	--	<4.1
+2 to +3	11280	<320	<5.1	248	--	<0.79
+1 to +2	7390	<240	<3.9	236	--	<0.61
0 to +1	17200	<410	<8.7	541	--	<1.5
-1 to 0	5130	<310	<5.5	124	--	<4.2
-2 to -1	9220	<350	<5.2	213	--	<0.81
-5 to -2	3380	<350	<3.0	86	--	<0.49
-8 to -5	3360	<480	<3.7	69	--	<0.71
-9 to -8	2060	<310	<2.7	35	--	<2.2
-17 to -9	2500	<340	<1.8	34	--	<0.32
-22 to -17	2470	<260	<2.4	<8.3	--	<0.51
-60 to -50	2430	<430	<2.3	39	--	<1.9

--- Not determined

## APPENDIX 1 (Continued)

Interval (cm)	Ga	In	Tl	As	Sb	Bi (ng/g)
+70 to +72	<8.10	<0.12	--	1.45	0.430	--
+48 to +52	11.6	<0.28	(2.88)	2.49	0.71	(<0.02)
+36 to +39	<11	<0.16	--	4.37	1.00	--
+33 to +36	<11	<0.16	--	4.04	0.81	--
+28 to +33	11.4	<0.14	--	2.95	0.72	--
+26 to +28	<9.8	<0.26	--	2.26	0.67	--
+23 to +26	<8.9	<0.14	(2.96)	2.60	0.752	(<0.02)
+21 to +23	10.0	<0.15	--	3.0	0.76	--
+15 to +21	8.9	<0.14	--	2.83	0.94	--
+13 to +15	<12	<0.34	--	4.26	1.32	--
+12 to +13	13.6	<0.13	--	6.55	1.83	--
+9 to +12	<16	<0.23	--	5.01	1.65	--
+8 to +9	<7.8	<0.15	--	3.18	0.99	--
+6 to +8	<9.1	<0.30	--	3.48	1.10	--
+3 to +6	<9.6	<0.18	(2.56)	3.70	1.11	(<0.02)
+2 to +3	<15	<0.20	(4.01)	9.6	2.52	(<0.02)
+1 to +2	<9.3	<0.16	(2.28)	2.17	0.89	(<0.02)
0 to +1	23.2	<0.33	(7.22)	22.1	4.09	(<0.02)
-1 to 0	<9.3	<0.20	(2.81)	4.06	0.963	(<0.02)
-2 to -1	<14	<0.22	(6.17)	18.3	3.19	(<0.02)
-5 to -2	<8.7	<0.24	(1.97)	2.19	0.66	(<0.02)
-8 to -5	<7.8	<0.38	--	2.77	0.751	--
-9 to -8	<6.1	<0.19	(2.73)	0.99	0.329	--
-17 to -9	<7.6	<0.22	--	<0.99	<0.18	--
-22 to -17	<6.4	<0.17	--	0.90	0.555	--
-60 to -50	<5.7	<0.34	(1.52)	0.45	0.204	(<0.02)

( ) Determined by GF-AAS      --- Not determined

## APPENDIX 1 (Continued)

Interval (cm)	Pb	S	Se	Te	Ir (ng/g)
+70 to +72	--	--	<2.9	--	0.17
+48 to +52	--	--	<6.3	--	0.17
+36 to +39	--	--	<5.4	--	--
+33 to +36	--	--	<3.3	--	--
+28 to +33	--	--	<3.1	--	--
+26 to +28	--	--	<6.4	--	--
+23 to +26	--	--	<4.4	--	0.28
+21 to +23	--	--	<2.8	--	--
+15 to +21	--	--	<3.0	--	--
+13 to +15	--	--	<7.9	--	--
+12 to +15	--	--	<4.5	--	--
+9 to +12	--	--	<4.9	--	0.79
+8 to +9	--	--	<2.8	--	--
+6 to +8	--	--	<5.8	--	0.61
+3 to +6	--	--	<4.8	--	2.8
+2 to +3	--	--	<4.4	--	5.8
+1 to +2	--	--	<3.3	--	1.4
0 to +1	--	--	<9.9	--	16.1
-1 to 0	--	--	<4.9	--	3.0
-2 to -1	--	--	<4.6	--	15.7
-5 to -2	--	--	<2.7	--	0.64
-8 to -5	--	--	<4.9	--	--
-9 to -8	--	--	<2.7	--	0.21
-17 to -9	--	--	<1.9	--	--
-22 to -17	--	--	<3.6	--	--
-60 to -50	--	--	<2.4	--	0.084

--- Not determined

APPENDIX 2: Description of sampling vials considered for use  
with MIBK

Description	Advantages	Disadvantages
Manufacturer's supplied plastic sampling vial with bottom glued in	Cheap	Glue and plastic readily dissolve when used with MIBK
Cut-down glass test tube	Cheap Inert to MIBK No positioning beneath probe tip	Large mouth allows quick evaporation of MIBK; must introduce sample when the probe tip is ready to sample 2 ml sample needed
Teflon plug (Brooks and Lee, 1988)	Inert to nearly all solvents and strong acids Will not allow MIBK to evaporate quickly 0.25 ml sample required	Positioning beneath probe tip necessary Expensive to produce Difficult to clean thoroughly
Plastic vial + cap + Durham tube	Cheap Inert to solvents Will not allow quick evaporation of sample 0.5 ml sample volume	Positioning beneath probe tip necessary

APPENDIX 3: Summary of attempts in the literature to overcome the interference of halide ions in GF-AAS determination of thallium

Reference	LOD(ng/g)	Method
Sighinolfi (1973)	50	Extract bromocomplex into isopropyl ether No note of bromide interference using GF-AAS
Fuller (1976)		Fume halocomplex with 1% sulfuric or nitric acids--this will decompose the complex to the stable oxide during ashing stage
Simon et al. (1977)	5 (inferred)	Extract iodocomplex into amyl acetate Increase atomization temperature to increase reproducibility and to decrease LOD
Manning et al. (1979)		Dry sample on tungsten wire coil and introduce into a hot furnace Decreased atomization temperature results in increased absorption signal due to longer residence time in the furnace
Slavin & Manning (1980)		Use L'vov platform, or add Li or H to bind with halide in vapor phase
Voskresenskaya et al. (1981)	7 (inferred)	Extract with brilliant green into toluene and fume TlCl with sulfuric acid
Elson & Albuquerque (1982)	40	Presumes bromide add across double bond of enol form of ketone and uses only fresh HBr to overcome this interference
Shan et al. (1984)	8	Palladium conditioning of graphite furnace: 2-4 ug Pd/1 ng Tl
Liem et al. (1984)		Fume bromocomplex with nitric acid
Hall et al. (1987)		Palladium as matrix modifier Add Pd to MIBK phase, not to furnace

APPENDIX 4: Summary of procedures and results of colorimetric extraction of thallium (determinations by GF-AAS)

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Brilliant Green (Stanton and MacDonald, 1963; Ariel and Bach, 1963; Voskresenskaya et al., 1981)

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In a separatory funnel, mix:

1 ml 10 ppm Tl(I) solution  
14 ml concentrated hydrochloric acid  
0.5 ml sodium nitrite  
25 ml sodium hexametaphosphate  
5 ml Brilliant Green, aqueous  
5 ml toluene or xylene

Separate and filter toluene layer

Need > 3 extractions to get >90% Tl in organic phase

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Crystal Violet (Kothny, 1969)

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In a separatory funnel, mix:

1 ml 1 ppm Tl(I) solution  
1 ml 5% sodium bromide  
10 drops 10% hydroxylammonium chloride  
2 ml 5% disodium EDTA  
5 ml 0.1% Crystal Violet in digol  
5 ml toluene

Separate and filter toluene layer

First extraction -- 63.3% extraction

Need > 3 extractions to get > 90% Tl into organic phase

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APPENDIX 5: T1 vs. Ir Pearson Product Moment correlation calculation for 11 intervals of the Flaxbourne River K-T boundary sequence

Interval	$x_i$	$y_i$	$x_i^2$	$y_i^2$	$x_i y_i$
+48 to +52	2.88	0.17	8.294	0.029	0.490
+23 to +26	2.96	0.28	8.762	0.078	0.829
+3 to +6	2.56	2.8	6.554	7.84	7.17
+2 to +3	4.01	5.8	16.08	33.6	23.3
+1 to +2	2.28	1.4	5.198	1.96	3.19
0 to +1	7.22	16.1	52.13	259	116
-1 to 0	2.81	3.0	7.896	9.00	8.43
-2 to -1	6.17	15.7	38.07	246	96.9
-5 to -2	1.97	0.64	3.881	0.410	1.26
-9 to -8	2.73	0.21	7.453	0.044	0.573
-60 to -50	1.52	0.084	2.310	0.007	0.128
$\Sigma =$	37.12	46.184	156.63	558.68	258.44
n = 11, r = 0.959    S**					

$$r = \frac{\Sigma x_i y_i - \frac{\Sigma x_i \Sigma y_i}{n}}{\sqrt{\left[ \Sigma x_i - n \right] \left[ \Sigma y_i - n \right]}}$$

APPENDIX 6: Significance of correlation values

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Value for r	Significance and Symbol
> 0.951	Very highly significant (S**)
0.874 - 0.951	Highly significant (S*)
0.753 - 0.951	Significant (S)
0.669 - 0.753	Possibly Significant (PS)
< 0.669	Not Significant (NS)

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APPENDIX 7: Abundance of selected chalcophiles in 13 geospheres  
in ppm ( $\mu\text{g/g}$  or  $\mu\text{g/ml}$ ), after Green (1972)

Geosphere	Ga	In	Tl	As	Sb	Bi
Igneous Rocks						
Ultramafic	1.5	0.01	0.06	1	0.1	---
Basaltic	17	0.22	0.21	2	0.2	0.007
High-Ca Granite	17	0.01	0.72	1.9	0.2	---
Low-Ca Granite	17	0.26	2.3	1.5	0.2	0.01
Syenite	30	0.01	1.4	1.4	0.1	---
Sedimentary						
Shale	19	0.10	1.4	13	1.5	---
Sandstone	12	0.01	0.82	1	0.01	---
Carbonate	4	0.01	0.01	1	0.2	---
Ocean						
Carbonate	13	0.01	0.16	1	0.15	---
Clay	20	0.08	0.8	13	1.0	---
Seawater	$3 \times 10^{-5}$	$<0.02$	$<1 \times 10^{-5}$	$3 \times 10^{-3}$	$5 \times 10^{-1}$	$2 \times 10^{-5}$
Extraterrestrial						
Chondrite	5.5	$8.6 \times 10^{-4}$	$9.2 \times 10^{-4}$	2.3	$8.6 \times 10^{-2}$	$2 \times 10^{-3}$
Solar	$9 \times 10^{-4}$	$7.3 \times 10^{-5}$	---	$2.1 \times 10^{-4}$	$6.9 \times 10^{-6}$	---

--- Not determined