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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

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for the degree of

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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