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THE SEQUESTRATION OF PHOSPHATE BY
IRON PHASES IN THE SEDIMENTS FROM
LAKE ROTORUA, NEW ZEALAND.

A thesis
submitted in partial fulfilment
of the requirements for the degree of

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ABSTRACT

A sequential extraction method was used to determine which dominant sedimentary mineral phase was involved in phosphorus retention in the sediments of Lake Rotorua and to verify the importance of iron phases in the role as a phosphorus sink. The observed influence of the experimental conditions upon the extent of phosphate adsorption to various iron phases shows a considerable quantity of phosphorus is present in the reducible phase and in the residual mineral phase. The phosphorus associated with iron(III) oxide phases was released into solution under reducing conditions when ferric iron oxide/oxyhydroxides, including amorphous and poorly crystalline Fe(III) phases, were solubilized. The residual primary and secondary mineral phases remained stable in the sediments until they were exposed to extremely acidic media analogous to strongly reducing conditions. Manganese is not involved in phosphorus retention to the same extent as iron. Aluminium phases present were released from surface complexes with relative ease and also from mineral structures under the prevailing conditions. The results show a strong agreement between aluminium and phosphorus suggesting it is associated with various aluminium phases to some extent. The sediments of Lake Rotorua are rich in organic-bound P which is released when organic material is oxidized under conditions analogous to anaerobic degradation. The degradation of refractory organic material represents a significant source of phosphorus for incorporation into diagenetic minerals forming in oxic and anoxic layers of the sediment.

Heavy liquid separation of the sediments concentrated the small quantities of dense minerals into a separate fraction and the presence of iron sulfides could be verified. Three density fractions obtained by this method separated the diatoms ($d < 2.6 \text{ g cm}^{-3}$), the silicates ($d > 2.6 < 3.7 \text{ g cm}^{-3}$) and the heavy minerals ($d > 3.7 \text{ g cm}^{-3}$) present in the sediment sample. In the heavy mineral phase spherulitic framboidal pyrite and rhombohedral siderite were observed by scanning electron microscopy (SEM).

Energy dispersive x-ray fluorescence (XRF) analysis of the framboidal pyrite detected significant fluorescence's for sulphur and iron. The elemental analysis of siderite characterised it as an iron-rich, non-sulfidic particle with no phosphorus fluorescence. Particles were also observed that had a variable morphology to the framboidal pyrite minerals but similar ratio of Fe to S in the XRF spectrum. It is likely they are other stable forms of iron sulfides or pyrites in various stages of diagenetic dissolution. Digestion of the three density fractions shows the heavy mineral phase is significantly enriched in sulfur and in iron confirming the presence of sulfides. The sulfide-forming trace metals are concentrating in the heavy mineral phase but a progressive enrichment of trace metals down core is not found in the results. Many of the trace elements show maximum concentrations in the Tarawera tephra.

There is a good agreement between iron and phosphorus in both treatments that implies iron phases are the predominant phosphorus fixers in the sediments of Lake Rotorua. However the identity of the phosphorus sink could not be confirmed by SEM or XRF analysis of the heavy minerals. The most likely explanations for the observed concentrations of iron and phosphorus and enrichment in the heavy mineral fraction are the persistence of the highly insoluble crystalline iron oxyhydroxides (goethite) in reducing sediments or the formation of the reduced iron mineral vivianite. Considering the density of vivianite it would have being taken into the heavy fraction by default which would account for the enrichment demonstrated by the solution analysis.

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CHAPTER ONE

INTRODUCTION



Lake Rotorua at sunset, North Island, New Zealand

1 INTRODUCTION

1.1 NUTRIENT LOADING

Excessive levels of the nutrients nitrogen (N) and phosphorus (P) are attributed to the increasing incidence of phytoplankton (algal) blooms and subsequent decline in water quality in a variety of lakes worldwide. These key nutrients are biologically significant for growth at a ratio of 16N:1P, subsequently nutrient levels in a system can be a growth-limiting factor. Relatively high levels of dissolved forms of N and P present in surface waters is causing nutrient enrichment (eutrophism) that results in excessive productivity of microscopic algae. Surface algal blooms develop within hours; the scum that forms is unsightly and problematic and can be a significant health issue for animals. Blooms of cyanobacteria algae are particularly troublesome due to their toxic nature. Cyanobacteria have several features that gives them a competitive advantage over other types of algae. The dominant species of cyanobacteria have bouyant properties, can fix atmospheric nitrogen and can store phosphorus. They can undergo prolific growth when nutrients (especially nitrogen) are limiting and when condtions are less favourable for other species (Oliver and Gant, 2000).

Water quality is rapidly declining in many lakes in New Zealand in a similar fashion to lakes in the northern hemisphere that have (also) been affected by intensive land use and by the geological aspects of the surrounding catchments. Many cenral North Island lakes located in the Taupo Volcnic Zone (TVZ) are showing signs of significant deterioration and reduction in trophic status. Of the fourteen lakes in the Rotorua District water quality classification ranges from oligotrophic (good) to eutrophic (very bad). Lakes Okareka and Tikitapu are still only showing early signs of decline while Lakes Rotorua, Rotoiti and Okaro are in seriously poor condition (EBoP, 2006). Subsequently the focus of remediation efforts are directed at nutrient reduction for many of the lakes in the Rotorua district.

Nutrient budgets are suggesting that nutrient loading of N and P is the result of agricultural land use, domestic and industrial sewage discharge practices and in some cases of the underlying geology in the catchments draining the lakes. As a result of direct and diffuse inputs from anthropogenic activities terrestrial and aquatic systems are unable to process the amount of burden they are receiving at the rate they are receiving it; soils, sediments and waterways are becoming contaminated (Hamilton, 2003). Pastoral land cover is significant in many catchments in the Rotorua district, but not all of them. Sewage effluent disposal is now treated to a higher standard before being discharged or diverted to other disposal systems. The characteristic pumice and ignimbrite substrate of the TVZ is known to be a significant source of phosphorus and silica and the (20) geothermal systems in the zone are responsible for the mobility of heavy metals (e.g. As, and Hg), as well as sulphur compounds. Collectively these factors influence the chemistry of the ground and surface waters in this region (Timperley, 1975). Inflow and outflow measurements have indicated that external loading has been relatively constant (over the period of past 40 years of monitoring) and that a large amount of phosphorus entering Lake Rotorua is being incorporated into the sediments (Rutherford et al., 1996).

Settling particles transport an array of contaminants to the bottom of lakes; the main biogenic and inorganic components of the particles are effective carrier phases that potentially contribute large amounts of material to the sediments. Natural sediments have the capacity to act as a sink and accumulate considerable amounts of reactive material i.e. trace and heavy metals, nutrients and mineral phases. The cycling of major elements is very active in the sediments and the dominant sedimentary processes can cause the regeneration of dissolved nutrient elements from the sediments (Sigg et al., 1987). Providing the sediments remain relatively undisturbed and providing bottom waters remain well oxygenated, ensuring there is an oxygen-rich surface layer, the material will remain buried and 'trapped'. If the oxic barrier layer is compressed or lost when bottom waters become void of oxygen (anoxic), or there are major disturbances, soluble components are likely to be regenerated from the sediments and returned to the water column (Scholkovitz, 1985). Sediment bound

phosphate associated with oxidized iron and manganese fractions are subject to remobilization under anoxic conditions. Ferric and manganic oxide/hydroxides are known to have highly reactive surfaces that bind large amounts of dissolved P but which is released during post-depositional dissolution and early diagenesis. The redox nature of iron and manganese has a strong influence on the mobility and distribution of phosphorus in freshwater sediments. Pore water elemental profiles confirm the reductive mobilization of Fe and Mn high in the sediment column and supports the notion that nutrient loading is being amplified by an internal supply of phosphorus (Shaw et al., 1990).

1.2 AIMS AND OBJECTIVES

The principal aim of this study is to gain an understanding of the significance of the sediments in supplying dissolved nutrients to Lake Rotorua. Internal loading of this nature is thought to be contributing to the organic enrichment that is fueling the increasing duration of algal blooms.

This project is intended to determine the roles played by various iron and manganese sedimentary phases in controlling the mobility of dissolved phosphorus in subsurface layers as well the permanent burial of P in deeper layers of the sediments of Lake Rotorua. Knowledge of this role is important for predicting the consequences of lake remediation strategies that involves disturbing or removing the top layers of the sediment column and thus exposing diagenetic material to an oxidising environment. Subsequent oxidative dissolution of sulphide minerals could result in a significant amount of trace metals being released into the water column (Cooper and Morse, 1998).

The primary objective of this study is to obtain detailed information about the (phosphorus) mobilization mechanisms that are operating in the sediments of Lake Rotorua. I intend to characterize the iron- and manganese-bound P, to determine the distribution of the Fe and Mn phases in the various reservoirs in order to elucidate the

chemical mechanisms of P release/retention by diagenetic iron and manganese oxyhydroxides. Based on reports about Fe-P-S systems, I also intend to investigate the importance of iron sulphide minerals in the retention of phosphorus to evaluate the role of dissolved sulfides in controlling pore water concentrations of ferrous iron and phosphorus.

1.2.1 MY FIRST APPROACH

Based on the assumption that the iron cycle (i.e. the ferrous wheel) is intimately involved in the mobilization of P iron is considered to be regulating the concentration of dissolved phosphorus in the porewaters confined in the upper layers of lake sediments.

Iron and manganese (and to a lesser extent aluminium) oxides/hydroxides are considered to be the primary constituents controlling P adsorption in many types of sediments, particularly non-calcareous. Iron and manganese are redox-sensitive elements subject to reductive dissolution under oxygen demanding conditions typically caused by organic loading. Coincidence of anoxia, lowering of the redox potential, mobilization of iron and release of reactive elements such as phosphate has led to a strong argument for associated cycling at the sediment-water interface of the sediments. The concept of redox cycling coupled to the cycling of trace metals and nutrients in sediments is reported by numerous authors and is a well established theory (Davison, 1993).

Exchange across the sediment-water interface promotes P recycling; as phosphate is released from oxidized carrier phases that are taken into subsurface anoxic zones it is rapidly re-adsorbed by the newly forming iron oxyhydroxides derived from the reduced iron diffusing up into the oxic layer of the sediments. Oxidation of reduced iron to Fe³⁺ in natural waters produces very insoluble ferric ions which precipitate as ferric oxyhydroxides or adsorb onto particulate surfaces. In any case they act as binders, particularly for multivalent oxy anions such as phosphate and arsenate and

effectively scavenge freshly released anions accumulating in the porewaters. Fe-P bound P is often the largest pool in the sediments; phosphate adsorption by manganese is of a similar nature to iron but is less far less significant unless when it is abundant.

The total sediment iron and manganese can be analytically separated to determine the fractional composition and the dominant phase that is binding P. The binding characteristics of the various iron and manganese phases can be investigated using chemical extraction methods. Selective separation of the different fractions can potentially be induced by water, acids, bases, salts, reducing and oxidizing and complexing agents. The solubilization of iron and manganese will be in response to changes in pH and redox conditions, ionic composition (CEC), and desorption from within the crystal structure of minerals (Tessier et al., 1979). It is expected that the results of sequential extraction will reveal the distribution of the various Fe and Mn phases in the sediments. Solution analysis is supposed to reveal elemental enrichment as a function of binding-capacity and associations of phosphorus and other trace elements with Fe and Mn and subsequently that the release is a function of the prevailing conditions as implied by the nature of the extraction reagents to be used.

1.2.2 MY SECOND APPROACH

Knowing that iron plays an important role in sediment phosphorus diagenesis enables the investigation to focus on the dynamics of their relationship. P is associated with diagenetic Ferric iron mineral phases such as ferrihydrite and goethite in oxic environments and is also incorporated into Ferrous iron mineral phases such as vivianite and pyrite in the reducing conditions of the deeper regions the sediments (Gachter, 2003). It has been established that sedimenting particulate material undergoes diagenetic transformations following its burial and that chemical properties are altered that favour the desorption and disassociation of phosphorus from the

carrier phases and that the remobilized P is then reabsorbed by intermediate and metastable mineral phases forming at depth (Shaw et al., 1990).

Pore water and sediment column profiles from related studies on Lake Rotorua have shown features that are common for the boundary between oxic and anoxic sediments; subsurface peaks of dissolved iron, sulphur and phosphorus presumably from reductive dissolution, and then a dropping out of solution with depth. There is also a concomitant increase in solid-phase supposed to be the result of conditions favouring precipitation of insoluble metal sulphides. The profiles are supported by Eh/pH measurements from the same studies that suggest sulphate reduction is occurring; with Fe(II) also disappearing with depth it is plausible that the iron mineral pyrite (ferrous sulphide) is forming. Pyrite formation does not account for dissolved phosphorus being removed from the pore water as pyrite immobilizes dissolved reduced iron preventing it from reabsorbing phosphorus.

Other ferrous minerals likely to be forming in the sediments could be playing a role in P retention, e.g. vivianite iron phosphate. The transformation of iron minerals deeper in the sediments could be involved in sequestering P in reducing conditions which would explain the depth profile. To evaluate if iron mineral formation is having any significant influence on the elemental concentrations of the pore water and to confirm the associations of P with iron minerals, the heavy minerals can be separated from lighter silicates and planktonic debris by density and analyzed to quantify how much P is concentrated in the heavy phase (Huerta-Diaz et al., 1993). A key point will be to identify if soluble P is being incorporated into ferrous iron minerals and to investigate if mineral formation is controlling the distribution of elements in the sediments. The different density phases can be analyzed to show any elemental enrichment in the heavier material that can be inferred as an indication of retention capacity of the minerals.

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CHAPTER TWO

LITERATURE REVIEW



Mokoia Island, Lake Rotorua

2 LITERATURE REVIEW

2.1 IRON AND MANGANESE

2.1.2 BEHAVIOUR OF IRON AND MANGANESE IN THE SEDIMENTS

Settling particulate iron (Fe) and manganese (Mn) hydrous oxides scavenge dissolved constituents from the water column and by doing so play a major role in transporting reactive trace elements and nutrients like phosphate to the sediments. The cycling nature of iron and manganese between solid and soluble phases influences the fate of the associated trace elements co-deposited on the sediments with the carrier phases. Numerous factors are responsible for the retention and release of trace element and nutrient species; exchange determinants are both physical parameters as well as compound-specific parameters (Sigg et al., 1987).

The dissolution of iron and manganese solid phases is in response to progressively declining oxygen concentrations, and specific Eh and pH conditions often encountered in the sediments. Peaked solution profiles of these elements are typically observed at depths in the sediment column corresponding to active redox cycling near the sediment-water interface (Stumm and Morgan, 1970). Solutes accumulating in the pore waters of the upper layers of oxic sediments can escape from the sediments and be mixed into the water column or be oxidatively precipitated into a newly-forming solid phase within the sediments. Reduced iron and manganese will be removed from solution in this manner and the sedimentary iron oxyhydroxides that form will be able to scavenge and re-adsorb dissolved anions liberated from the same processes (Davison, 1985).

Phosphate itself is not sensitive to the redox conditions but as a consequence of its associations sedimentary P will be recycled in this highly active region of the sediment before it is entrained into surface waters or incorporated in diagenetic mineral phases and finally buried deeper in the sediments (Carignan and Lean, 1991; Petersen et al., 1995).

2.1.3 Iron and Manganese cycling

The reductive dissolution and oxidative precipitation of iron and manganese in the sediments is characteristic behaviour of redox-sensitive elements. Due to the nature of these elements they are involved in cycling at an interface between oxic and anoxic zones and in mineral formation in both the water column and the sediments (Davison, 1985). Iron and manganese undergo chemical and biological reactions that involve electron transfers between a donor and an acceptor and which causes a change to their valence (oxidation) state, their phase and subsequently their form (Scholkovitz, 1985). The process is referred to as redox cycling as it involves the continual interchange between oxidation states. The conversions typically occur at a redox boundary and are induced spontaneously by thermodynamic or kinetic (abiotic) factors and/or mediated by microbes depending on the element. Sedimentary redox cycles are influenced by the settling flux of biological material and reactions are driven by oxygen depletion (Davison, 1985; Sigg et al., 1987). Oxidized compounds undergo reduction with increasing electron activity and are transformed into their alternative stable state as the oxidizing potential decreases. As a result of the transformations the elements may become more or less mobile. Reductive dissolution of iron and manganese results in the generation of 'free' charged metal ions which can form soluble complexes (with soluble anions), or remain as hydrated ions and hydrated hydroxo ions or which are sequestered into solid phase minerals (Wetzel, 2000).

2.1.4 The Ferrous Wheel

The redox cycle of iron is termed the 'ferrous wheel' due to the rotational nature of the Fe^{3+} - Fe^{2+} couple. The 'manganous wheel' involves the two dominate oxidation states Mn(IV) and Mn(II). In the case of iron and manganese the higher oxidation state is less mobile than the lower. Insoluble ferric and manganic oxide phases are reduced to form ionic divalent ferrous iron and manganous manganese that are generally highly mobile in the pore waters of the sediments. Iron mineral formation removes Fe(II) from the 'loop' and potentially interrupts the iron cycle; ferrous iron and reduced sulfur form amorphous

and highly insoluble crystalline FeS phases in strongly reducing sediments (Kawashima and Hori, 1985; Wetzel, 2000).

The redox behavior of iron and manganese are very similar and they can be observed following analogous patterns of distribution. The primary difference appears to be that the Mn^{4+} - Mn^{2+} couple has a higher redox potential than the Fe^{3+} - Fe^{2+} couple and Mn is reduced before Fe. Mn^{2+} is also precipitated at higher oxidation potential than Fe^{2+} and there is variable distribution of the two elements in the sediment column accordingly. The precipitation of manganese is more common in the water column, with greater distance from more reducing conditions (Brown et al., 2000; Kawashima and Hori, 1985). Reduction of Mn(IV) is reported to begin at DO concentrations of 2-3mg l⁻¹ but the reduction of Fe(III) does not begin until conditions are anoxic and Eh values begin to approach (Scholkovitz, 1985). Soluble manganese ions are observed to be present in appreciable amounts mainly in the upper sedimentary layers at concentrations of DO < 0.5mg l⁻¹ (Sigg et al., 1987). The oxidative-precipitation of soluble Mn(II) occurs after Fe(II) and in more oxygenated waters, and often with distance from the sediment-water interface where re-oxidized Fe(III) accumulate. Particulate Mn appears in the oxic zone where the upward and downward flux of the Mn couple maintains at equilibrium (Kawashima and Hori, 1985).

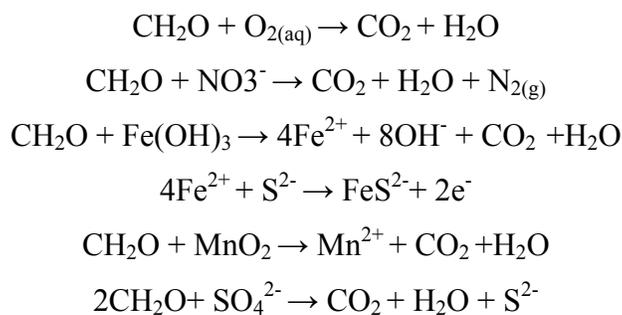
These locations are variable in relation to whether the bottom waters become anoxic which causes the redox front to be repositioned into the water column; because the oxic/anoxic boundary migrates out of the sediments the reduced species are mobile in the water column (Davison, 1985).

2.1.5 Aquatic Redox Cycling

In limnetic environments electron cycling generally occurs in the vicinity of a boundary between oxic and anoxic conditions which in sediments is often in close proximity to the sediment-water interface. The signature characteristic of a redox front is generally low pH (6.5 to 5) and Eh (redox potential) below +200 mV (Wetzel, 2000). Measurements of redox potential are an indication of the degree of oxygen demand in the sediments. In

well oxygenated systems Eh remains fairly high. Increasing oxygen demand is indicated when Eh values begin dropping below +450 mV. Values approaching +0 mV are an indication of persistent oxygen demand and a shift to reducing conditions (Maher and DeVries, 1994). Eh-pH diagrams illustrate the simultaneous influence of hydrogen ions (protons) and electrons on the equilibria of aqueous metals and give an indication of redox intensity. The boundaries represent upper and lower limits of stability and enable predictions to be made about the distribution and predominance of different phases under the prevailing conditions (Gill, 1989; Wetzel, 2000).

Redox cycling is associated with anaerobic respiration of organic carbon and is most pronounced in anoxic layers of organic-rich sediments. Anaerobic bacteria in the anoxic zone make use of what is chemically reactive (as per kinetics and thermodynamic stability). The microbes are catalysts of a succession of reactions that occur over a certain range of pH and Eh conditions where the reductant is thermodynamically unstable (Wetzel, 2000):



Ferric iron is used as an electron acceptor when oxygen and nitrate have been consumed by other chemical species as well as by microbes (Gunnars et al., 2002). The range of compounds occurring in the sediments that are able to chemically reduce iron and manganese oxides includes nitrate and sulfide, organic acids and organic ligands (consisting of hydroxyl and carboxyl groups and through ligand exchange reactions) and aromatic compounds (phenolic groups) (Davison, 1993). Chemical metal reduction of Fe and Mn oxides will depend on the reactivity of the compound being utilized as an

oxidant. Amorphous ferric iron species are more labile and readily reducible by both methods. In contrast crystalline Fe(III) oxides are not accessible for direct microbial reduction but are subject to sulfide-linked reductions (Roden and Edmonds, 1997).

2.2 AQUATIC PHOSPHORUS

2.2.3 PHOSPHORUS IN LAKES

Major inflows draining into a lake deliver considerable amounts of particulate matter that is derived from the terrestrial environment which can often constitute a significant source of phosphorus (P) to the lake system. Dissolved and particulate P can be supplied to a lake by rivers and streams, by overland flow and by leaching from the soil into groundwater systems and emerging with spring waters. Autochthonous material generated in the lake includes planktonic debris that can also contribute to the P pool and to the sedimentary stores of P (Holtan et al., 1988).

Phosphorus occurs as organic and inorganic compounds in natural systems. Organic P is highly reactive and is able to be released from solid material and utilized by aquatic macrophytes and algae in surface waters. Particulate bound P that is considered unavailable is generally associated with inorganic material and is typically the fraction that settles relatively rapidly to the sediments (Reddy et al., 1995).

Organically bound P compounds exist as dissolved organic substances and are associated with inorganic matter and are generally very labile. Exchangeable P is recycled and transferred between solid and soluble phases within the sediments, particularly at the sediment-water interface (Wetzel, 2000). The process of biomineralization releases much of the very labile organic-bound P as settling material sinks through the water column. If mineralization is incomplete P continues to be released from the seston decomposing in the hypolimnion and in the surficial sediments (Gachter and Mares, 1985).

Phosphorus is present primarily as the inorganic orthophosphate ion PO_4^{3-} . It is the only stable species in the field of stability of water and occurs in soluble and solid phases. The

distribution of soluble phosphate species is pH-dependant; the most common dissolved species (H_2PO_4^- and HPO_4^{2-}) predominant over the range of pH (4-10) corresponding to both acid and alkaline conditions (Holtan et al., 1988). Within the range of pH typical to natural waters the anionic species are capable of forming solid complexes with metallic cations present either on particle surfaces or as suspended flocs of metal precipitates. Inorganic phosphorus minerals can also be formed in the sediments due to soluble P reacting with precipitating metal cations transforming into crystalline phases. Some of these associations can be responsible for the diagenetic remobilization of phosphate and its cycling in the sediments or alternatively the formation of highly insoluble minerals permanently sequester P in marine and freshwater sediments (Mucci et al., 2000).

2.2.4 PHOSPHORUS BINDING

Phosphate is commonly bound by calcium, iron, aluminium and manganese compounds, and can be retained in the solid fraction of the various amorphous and crystalline forms of these elements. Orthophosphate is associated with organic ligands, humic substances, clay minerals, Fe-Mn oxyhydroxides and minerals, aluminium hydroxide compounds and calcium carbonate minerals. The mobility and distribution of P in the water column and in the sediments is typically a consequence of associations with carrier phases. Chemical precipitation of mineral phases can often serve to permanently remove dissolved phosphorus from a solution phase and promote its retention in the sediments (Wetzel, 2000).

Solid phase binding mechanisms include adsorption onto surface binding sites, coprecipitation with metal ions or incorporation into lattice structure of mineral precipitates. The phosphate poly oxyanion forms covalent bonds with particulate hydrated oxides (Gunnars et al., 2002). Ligand exchange occurs between OH^- groups on the surfaces of hyrous oxides and phosphate anions (HPO_4^{2-} , H_2PO_4^-) in solution. Lijklema (1980) discusses phosphate adsorption and considers this simple equilibrium equation a representation of the exchange process:

The fractional composition of the sediments defines which components contain the most substantial amounts of P and therefore represent the releaseable sediment P pool. The different fractions in solid phase are considered to consist of labile forms that are readily available for subsequent transformations. These forms are generally loosely bound and exchangeable and are generally included in the dissolved reactive phosphorus (DRP) fraction. They are readily desorbed and interact with pore water species. Refractory (non-reactive) forms of P are not easily exchangeable and are more likely to be associated with minerals and accumulate at depth (Pettersen et al., 1988).

Percent composition of labile and refractory P in the sediment column can change with depth as phosphate is removed from the labile pool when it either escapes to the water column or is sequestered for the formation of diagenetic iron minerals. Penn *et al.* (1995) reports sediment column profiles of sequential extraction of P showed the more labile component is represented in the upper layers of the sediments, and also that decay was fast ($k=4.8 \text{ year}^{-1}$) within the top centimeter and then slow ($k=0.1 \text{ year}^{-1}$) through the column down to depths of 30cm below which all the P was refractory. This behaviour is considered to be influenced by external P loadings.

2.2.6 FE-P SYSTEMS

Iron-bound P exists in oxic environments as a surface complex adsorbed onto ferric hydroxide Fe(OOH); orthophosphate ions are covalently bound to hydrated iron oxides as a surface complex (Fe(OH)₂-PO₄) (Kawashima and Hori, 1985). The adsorption of P onto the surface of Fe(OOH) involves the exchange of OH⁻ ions for phosphate ions. The chemical process is pH- and temperature- dependant, factors which will regulate the quantity of phosphate that is adsorbed. It is suggested two molecules of Fe(OOH) are involved with the adsorption of one P giving rise to a binuclear complex (Golterman, 1995). Precipitation of iron phosphate minerals incorporates pore water phosphate into an insoluble solid phase in non-sulfidic reducing sediments. Sedimentary P is transformed by diagenetic processes into the iron mineral precipitate vivianite (Fe₃(PO₄)₂) (Gunnars et al., 2002; Kawashima and Hori, 1985). The coupling of sulfate reduction and iron sulfide

formation controls the Fe:P ratios in bottom waters and affects the flux of P from the sediments. Sulfate enhanced P release is attributed to iron-sulfide mineral formation. Sulfur alters P cycling by disrupting the iron-phosphate system (Caraco et al., 1993).

2.3 AQUEOUS IRON AND MANGANESE

Iron and manganese are transition metals and exist in a number of oxidation states in the environment. Iron (III) and (II) and manganese (IV) and (II) oxidation states are the most significant in aquatic systems; the intermediate oxidation states of Mn are not typically thermodynamically stable in natural waters and not detectable to any large extent (Stumm and Morgan, 1981). Iron oxides are reported to have a large surface area and consequently are highly reactive. This feature is enhanced in the more finely dispersed particles and including particulate surface-bound oxides, but is less effective when oxides are incorporated into mineral structures (Sigg et al., 1987).

The oxidation of reduced iron to very insoluble Fe(III) occurs when Fe(II) comes into contact with oxygen and hydroxide ions and is converted into ferric oxide/hydroxides. Iron and manganese oxides are distributed as insoluble oxidized Fe(III) and Mn(V) in colloids, precipitates and mineral compounds (Davison et al., 1991). At neutral pH in oxic conditions metal oxidation is generally an autocatalytic chemical process e.g. Fe^{2+} is spontaneously oxidized, however Mn requires living microbes to catalyze the oxidation of Mn^{2+} ions (Kawashima and Hori, 1985). In both cases however it is likely that the rate of oxidation is influenced by microbes (Tipping et al., 1984).

In oxic waters iron commonly occurs as hydrated Fe(III) oxides (FeOOH). The most common and predominant solid species of iron that is stable in the pH range of 5-8 is ferric hydroxide $\text{Fe}(\text{OH})_3$ occurring in a variety of forms (Wetzel, 2000). Manganese (IV) exists in a solid state in oxic waters as manganese oxides (MnO_2) over a wide range of pH conditions but in alkaline conditions the hydrated oxides are relatively more abundant. Between pH 6-8 in anoxic waters the manganous ions (Mn^{2+}) are the dominant solution species present as hydrated aquo ions and are often abundant in a variety of

different types of waters (Davison, 1993). It has been reported that in the sediments of acid lakes ($\text{pH} < 5.5$) Mn oxides do not form even though the sediments are oxic (Heurta-Diaz, 1998). Manganese compounds are much more soluble than iron and Mn sulfide (MnS) is more soluble than other metallic sulfides and are significantly less abundant than FeS phases (Davison, 1993).

2.3.4 SORPTION BY IRON AND MANGANESE OXIDES

Particulate fractions of iron entering a lake have a tendency to sink rapidly from surface waters to the sediments, especially the Fe that is preferentially associated with large (charged) clay mineral particles. Smaller (uncharged) suspended particles are capable of reacting and forming flocs, coagulants and precipitates, which assists their sedimentation. Such transformations can alter the surface charge of the solid surface and enhance scavenging abilities. Colloidal particles of $\text{Fe}(\text{OH})_3$ carry a positive charge and so are highly reactive to dissolved anions they encounter as they settle through the water column (Sigg et al., 1987; Wetzel, 2000). Mn (IV) does not give up OH groups with hydroxide ions in solution as actively as iron (II) and is not engaged in competitive ligand exchange to the same extent (Stumm, 1991).

2.3.5 SEDIMENTARY IRON AND MANGANESE OXYHYDROXIDES

Diagenetic iron and manganese oxyhydroxides form in the uppermost sediment by sediment-derived $\text{Fe}(\text{II})$ and $\text{Mn}(\text{II})$ diffusing upwardly from the reducing layers. Mn oxyhydroxides form closer to the sediment-water interface than Fe oxyhydroxides due to the slower rate of chemical oxidation of Mn and particularly at pH below 6.0 (Davison, 1989). Accumulation and enrichment of the metal oxyhydroxides in oxic surficial sediments occurs when the chemocline is encroaching on the sediments and the water overlying the surface sediments is oxygenated thus the Fe-Mn oxyhydroxides are preserved (Fortin et al., 1993). The oxidation and hydrolysis of sediment-derived iron results in oxyhydroxides precipitated from pore water that can incorporate dissolved

phosphate during the process. However the fixation capacity of precipitating Fe (II) requires the Fe/P stoichiometry to be greater than two for the formation of iron-phosphate compounds (Gunnars et al., 2002).

Diagenetic metal oxide/hydroxide phases such as δMnO_2 and $\text{Fe}(\text{OH})_3$ that are formed eventually resettle toward the anoxic zone. Reductive dissolution liberates the Fe(II) and Mn(II) ions and their cycling at the interface continues, unless iron precipitates as highly insoluble reduced iron minerals. The formation of Mn (II) minerals does not remove Mn from cycling at the interface because even the least soluble Mn (II) mineral is highly soluble. However Mn incorporated into precipitating framboidal pyrite particles or carbonate minerals with high solubilities may serve as potential mechanisms of Mn removal (Perry and Pedersen, 1992). Sedimentary P is highly active in the upper sediment column and is redistributed many times over due to cycling of Fe and Mn at the interface. In the course of dissolution of metal oxides and the reformation of the metal oxyhydroxides P will 'switch sink' as it is released from one iron phase and re-adsorbed by another (Huerta-Diaz et al., 1993).

Authigenetic Fe- and Mn-oxyhydroxides are also formed with upwardly diffusing Fe(II) and Mn(II) supplied by the reducing waters in an anoxic hypolimnion. They form closer to the chemocline and precipitate above the sediments in the oxic water column when the two waters are mixed (Brown et al., 2000). Accumulation of authigenetic oxyhydroxide precipitates in the surficial sediments can occur depending on the depth of the chemocline but is usually minimal. The particulates are subject to gravitational sinking and are re-dissolved as they drop back into the reduced waters before they can reach the sediments (Brown et al., 2000). The Fe/Mn ratio is different in authigenic oxyhydroxides compared to those formed in the sediment column because of the different redox chemistry of Fe and Mn. This factor serves as a signal for the origins of the manganese. Lower levels of Mn are observed in oxic zones of upper sediments because Mn^{2+} is generally transported farther a field than Fe before it is oxidized and precipitates. The ratio of particles that precipitate in the water column will be lower and with greater

distance from mixing and therefore distinguishable from diagenetic oxyhydroxides (Fe-oxy-silicates) (Brown et al., 2000).

Iron and manganese oxyhydroxides are present in most natural sediments and occur in a variety of solid forms (amorphous and crystalline), each with different adsorptive properties (specific surface areas and site density) and variable affinity for trace elements and nutrients (Fortin et al., 1993). Newly forming Fe(III) oxyhydroxides are poorly crystalline phases and are highly reactive. The 'young' diagenetic phases can fix large amounts of dissolved species that are also diffusing along a concentration gradient into the oxic zone. (Belzile et al., 1989; Brown et al., 2000; Fortin et al., 1993).

The sorption of phosphorus to amorphous Fe(OH)₃ was reported to be far greater (~20-fold higher) than that of crystalline Fe(III) oxides (e.g. goethite and hematite) (RODEN). In trace metal sorption studies it has been reported that zinc (Zn) and nickel (Ni) are preferentially retained by Mn oxyhydroxides, and arsenic (As) and copper (Cu) are more often associated with Fe oxyhydroxides (Belzile and Tessier, 1989; Davison, 1989; Fortin et al., 1993; Petersen et al., 1995). The different trace element geochemistry of diagenetic Fe-Mn oxyhydroxides is related to changes in their supply to the sediments as well as variable physico-chemical conditions influencing their adsorption and also revealed a seasonal influence. The presence of a suspended floc layer can be a significant source of trace elements for precipitating oxyhydroxides but the settling floc also creates a high oxygen demand on the surface sediments that can enhance the reductive dissolution of the oxyhydroxides. The effects of seasonal deposition can be seen in the changes to the the oxygen status of bottom and/or pore waters. There is often a pronounced shift in redox intensity, the formation of iron sulfides (e.g. framboidal pyrite aggregates) in the top few centimeters and a reduction of trace elements available for oxyhydroxides forming in the oxic zones. Changes to the pH is a major factor that will influence the adsorption of dissolved trace elements and metals on oxyhydroxides (Douglas and Adendy 1998).

Trace metals are reported to bind to the functional groups of organic matter adsorbed on iron oxyhydroxides in conditions of decreasing pH, and in circumneutral conditions trace metals bind directly to surface hydroxyl groups of Fe and Mn oxyhydroxides. With regard to organic coatings on particles it is suggested that the reactivity of the functional group of the underlying Fe and Mn oxyhydroxides can be unaltered despite potential competition from organic matter on the surface of the particle. The hydroxyl groups of the oxyhydroxides are less favoured by alkaline earth metals calcium and magnesium that preferentially bind to organic coatings. It is suggested that this contrasting behaviour between alkaline earth and trace metals is to do with the types of surface complexes that are formed. Alkaline earth metals form outer-sphere surface complexes which are a function of charge, which can be imparted to an aquatic particle by organic coatings (Tessier et al., 1996).

2.3.6 FERRIC IRON MINERAL PHASES

In a series of phase transformations the first iron oxyhydroxide precipitate is the poorly crystalline ferrihydrite. It is metastable and serves as the precursor for more stable oxides such as goethite or hematite. The transformations are pH and temperature dependant, are influenced by the presence of foreign ions in solution and occur slowly over time. The more crystalline oxides result from different processes under variable conditions and give rise to structurally different solid phases. Goethite is one of the more stable crystalline forms of an iron oxyhydroxide it is thermodynamically stable and highly insoluble under natural pH values and can be of diagenetic origin. Its formation in the sediments is slow and considered to occur during the process of dissolution of other less crystalline oxyhydroxide particles rather than directly from Fe(II) oxidation (Fortin et al., 1993).

A wide range of ferric iron oxide minerals exist in the environment and during the process of transformation they serve as important absorbents of oxyanions such as arsenate and phosphate. The association of arsenate with ferrihydrite is thought to be similar to phosphate as a surface precipitate but is thought to be incorporated into the

crystalline structure of the more stable minerals as demonstrated by a lack of desorption from goethite phases (Pedersen et al., 2006).

Goethite has a net positive surface charge that readily mops up metal ion complexes from aqueous solutions. The surface of goethite is dominated by FeOOH surface species whose sorption capacity is influenced by pH (Tipping, 1981b). Phosphate adsorbs onto the surface of goethite by forming inner-sphere surface complexes. The process is suggested to occur in two steps over different time scales. The initial adsorption is very fast; dissolved phosphate binds with surface groups on goethite surface within milliseconds and precipitates as an iron-phosphate coating. The other stage of the process is thought to involve a much more time consuming method; the diffusive penetration of P into the pores of the crystal possible achieved by the migration of surface complexes (Luengo et al., 2006).

Phosphate adsorption on iron oxides/hydroxides can be reduced by high concentrations of aquatic humic substances. Humic acids are organic residues from the decomposition of plant material. They are adsorbed by iron oxides by ligand exchange mechanisms involving the participating anionic groups of humic molecules (Tipping 1981a). The surface of goethite (α FeOOH) has surface-coordinated H_2O - and OH^- -exchanging groups that are able to be replaced by carboxylic (COOH) and (to a lesser extent) phenolic groups of humic substances (Tipping 1981b).

2.3.7 SULFIDE SYSTEMS

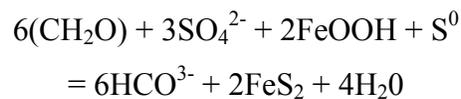
Certain aspects of the geochemistry of sulfur are different to those of iron and manganese which has a significant influence on their mobility and on the mobility of other metals and phosphate. The oxidized state of sulfur is soluble and the reduced state is solid (Wetzel, 2000). Reduced sulfur reacts with reduced aqueous Fe and Mn ions incorporating them into a solid phase in anoxic environments. Particulate sulfides

compete amongst themselves for iron and reduced sulfur during their formation as well as scavenge dissolved trace metals as they precipitate (Perry and Pedersen, 1992).

Sulfate (SO_4^{2-}) is the oxidized form of sulfur; sulfate reduction to sulfide (the insoluble form) occurs in anoxic and strongly reducing conditions ($\text{Eh} < 100\text{mV}$). The reduction of sulfate and formation of iron sulfides consumes H^+ ions during the process and generates alkaline conditions. If an adequate quantity of Fe^{2+} ions is present at the time of sulfate reduction, iron sulfide minerals are likely to precipitate e.g. *pyrite* (FeS_2). Eh/pH diagrams are useful to define the zone of iron sulfide precipitation and pyritization (Schindler, D. W., 1985).

Pyrite formation occurring in anoxic marine and freshwater sediments is extensive in Fe-rich layers of strongly reducing conditions where sulfate reduction to hydrogen sulfide (HS^-) coincides with the reduction of iron oxides. Evidence of the transformations from pore water data is often supported by observations of purple sulfate-reducing (chemosynthetic) bacteria (Wetzel, 2000).

Pyrite is produced from the oxidation of organic-C through sulfate reduction and Fe oxide/oxyhydroxide reduction according to reactions similar to the following:



High sulfate reduction rates generated by elevated concentrations of labile organic matter in the sediments supplies the pore waters with excess sulfide for pyrite precipitation (Perry and Pedersen, 1992).

2.3.8 REDUCED MINERAL PHASES

Fe(II) generated in reducing conditions can react with aqueous sulfur and precipitate as a highly insoluble iron sulfide mineral if both are present in appreciable quantities in the pore waters (Perry and Pedersen, 1992). The removal of soluble Fe^{2+} ions concomitantly with dissolved S is observed in many pore water profiles of metal concentrations. Coupled with alkalinity this is a reasonable indication of sulfate to sulfide reactions and subsequent iron mineral precipitation. P mobilized by iron reduction at the time of sulfate reduction can become surplus if ferrous iron is sequestered into insoluble complexes of sulfide (Kleeberg, 1997). Similarly the depletion of Mn^{2+} ions in reducing bottom waters (chemically analogous to anoxic sediment pore waters) was attributed to the formation of manganese sulfides, alabandite (MnS) (more common the hydrothermal deposits) and haurite (MnS_2). Both are considered relatively soluble MnS_2 being the least soluble Mn(II) precipitate; their formation via precipitation of soluble ions is considered a rare occurrence (Suess, 1967).

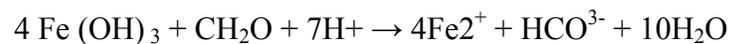
In marine and freshwater sediments bacterial reduction of amorphous or crystalline Fe(III) oxides facilitates the formation of crystalline Fe(II) containing phases such as magnetite (Fe_3O_4), siderite (FeCO_3), vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$), and iron sulfide (FeS). The reactions of ferric oxide reductions can produce large quantities of OH^- ions and the local Eh/pH conditions resulting from the mineralization of iron oxides can be favourable for the nucleation and formation of crystals. The type of Fe mineral precipitated is dependant on pH, concentration of Fe^{2+} ions and factors specific to controlling crystal growth. Siderite formation is favourable over magnetite in alkaline conditions as well as different bacteria involved in producing siderite particles with different morphology (e.g. globule, disk-like, rhombohedral and flakes) (Song and Muller, 1995).

Soluble trace metals released from the reductive dissolution of iron oxides/oxyhydroxides in the anoxic zones can be removed from sediment pore water through adsorption with a reduced iron phase such as iron monosulfide (FeS) and/or precipitated as discrete metal

sulfides (Hamilton-Taylor et al., 1996; Song and Muller, 1995). Precipitating framboidal pyrite which are highly reactive acquire dissolved trace metals and can incorporate them into the cuboidal lattice structure (Perry and Pedersen, 1992). Arsenic, cobalt, copper, nickel and (to a lesser extent) Mn have been found to associate with FeS phases particularly pyrite. Trace metals are cycled between the various iron sulfide phases as they are being transformed into pyrite. Trace metals are able to replace atoms to become incorporated into the crystal lattice of the iron sulfide. It is plausible that several processes, including adsorption or co-precipitation with metal sulfides, and complexation with reduced sulfur compounds could be controlling the distribution and concentrations of dissolved Fe, Mn and trace elements (Huerta-Diaz et al., 1998).

2.3.9 FE-S-P SYSTEMS

In reducing sediments iron-phosphate associations are greatest in non-sulfidic-Fe(II)-rich sediments where pore water iron is not being taken into pyrite formation. The reduced iron mineral vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$) serves to lock up P acting as a sink; the incorporation of phosphorus into the lattice structure is an efficient retention mechanism (Roden and Edmonds, 1997). The formation of vivianite traps P that has been mobilized at depths in anoxic sediment pore water. The formation of Fe(II) hydroxide ($\text{Fe}(\text{OH})_2$) by hydrolysis under alkaline conditions can also serve to adsorb P as a surface precipitate. Locally high pH can result from the hydroxide ions that are generated during Fe(III) reduction (Song and Muller, 1995):



In iron-poor sediments different abiotic mechanisms may operate that cause the dissolution of vivianite in order to supply reduced iron for pyrite formation and which causes P to be released from the mineral structure in the process:



Under similar low iron conditions a downward flux of reduced Fe(II) may be generated that pumps the metal ions from the upper sediment layers deeper down into the sulfate reduction zone during pyritization (Gachter, 2003).

2.4 NATURAL SEDIMENTS

Natural sediments are made up of two distinct domains; an upper oxic layer and anoxic layers beneath it. In organic-rich sediments the oxidized layer is usually only a few centimeters thick compared to a thin microzone that is often only millimeters in depth. The appearance of the two zones is clearly distinguishable. The oxic layer is a light brown colour, high in water content and organic material; the underlying anoxic layer generally grades into a black sediment of a lack of oxygen penetration and comparatively low water content and organic material (Blomqvist and Lundstedt, 1995). The zones have very different chemistries which affect the mobility of sedimentary phases and in some cases the oxidized layer is often reduced to only a few millimeters thick. The exchange of dissolved constituents across the boundary between the two regions is the result of transport within interstitial (pore) waters. Generally a relatively narrow band of the uppermost 5cm of the sediments is involved in exchange. The upward advective transport of porewaters during sediment compaction facilitates the movement of solutes from depth (Emerson, 1976).

Benthic fluxes of solutes across the sediment-water interface are calculated from Fick's first law using pore water profiles and the direction of the flux can be determined i.e. whether dissolved phases are being driven into or out of the sediment. Benthic fluxes in either direction are generally promoted due to an increase of algae biomass and subsequently an increased sedimentation rate and that is most commonly observed as a seasonal effect (Carignan and Lean, 1991). It is assumed that exchange across the sediment-water interface can primarily be due to molecular diffusion when there is little evidence of a more major role played by other factors such as wave or current induced resuspension or biological disturbances (Carignan and Lean, 1991; Emerson, 1976).

Bioturbation is considered improbable when overlying waters are anoxic and/or showing appreciable concentrations of hydrogen sulfide (Huerta-Diaz et al., 1998).

2.4.4 ZONATION IN THE SEDIMENTS

Depth-dependant concentration profiles of solid and dissolved phases show a characteristic sequence of zones in the sediments that relates to the various dominant carbon oxidation reaction pathways. The profiles show the reductive dissolution and oxidative precipitation of the different elements as indicated by concentration peaks and dips. They also serves as evidence for the likely exchange of trace elements between two phases based on their recognized geochemical behaviour (Canfield et al., 1993; Shaw et al., 1990). The location of the peaks is a good indication of the reactivity of organic-C and the depth that decomposition is occurring. Microbial degradation of biogenic material is often intense in the uppermost layer of the sediment at the sediment-water interface where labile organic-C is most abundant (Barbanti et al., 1995). Sediment pore water profiles compared with thermodynamic calculations can assist in identifying the zones of the redox reactions and of the dominant diagenetic processes occurring, the response of different elements as well as giving an indication of the layer of the sediment most actively involved in nutrient release (Carignan and Lean, 1991). Pore water profiles also reveal the subsequent mobilization of elements associated with different redox-sensitive metals and corresponding to certain zones more than others. Apparently arsenic is more often released and enriched in the iron reduction zone and similarly cobalt is typically released from manganese oxide phases in the manganese reduction zone (Petersen et al., 1995).

2.4.5 SEDIMENTARY PROCESSES

Surface sediments represent a very active region where particulate material is constantly being deposited and redistributed at a rate relative to its accumulation. Newly deposited organic material subject to biomineralization processes which can initiate the release of trace elements and nutrients (e.g. arsenic, cobalt and phosphate) causing a flux of the

associated contaminants into the dissolved phase. Many liberated species are rapidly re-adsorbed by sedimentary metal oxide phases forming in the oxic sediments and by other particles coated in reactive metal oxides (Petersen et al., 1995; Shaw et al., 1990).

Oxidized material is eventually buried deeper into anoxic zones where further transformations occur as a result of the conditions. The sedimentary process of reductive dissolution, acting on Fe and Mn oxides in the anoxic zones, results in soluble divalent ferrous and manganous ions concentrating in the pore waters of the subsurface sediment. The ions are highly mobile and can travel about in the sediments to reform as new solid phase compounds (Davison, 1985; Davison et al., 1991). The diffusive flux of reduced metal ions can be dichotomous; they can migrate to surface sediments, to be oxidized and precipitate as hydrous metal oxide phases or migrate to deeper regions of the anoxic layers where they are scavenged by other reduced species and are incorporated into highly insoluble mineral phases. The formation of mineral phases at depth is the result of a build up of metabolites and is an effective mechanism that will enhance the sediments 'sink' capacity (Davison, 1993; Scholkovitz, 1985).

Metal oxide precipitation in surficial sediments is an effective mechanism that can prevent reduced species escaping into the water column in which case they can become trapped in surface sediments. Saturation of oxidized manganese oxides serves as a capping mechanism that prevents excess Mn^{2+} being released from the sediments and which results in enriched subsurface layers. However, the forces driving the exchange across the sediment-water interface could be acting to supply other (i.e. deeper) regions of a lake with dissolved species; if the rate of oxidation is slower than the rate of diffusion the sediment-derived species can be transported away from their point of generation (Canfield et al., 1993).

Depth-dependant regeneration is likely to occur as deeper regions of a lake basin have the potential to receive more material than littoral sediments. The sediment-focusing effect also distributes particulate material of variable quality in which case can cause deeper

basins to accumulate significant amounts of labile and refractory material and thus sustain higher regeneration over a longer period of time as well as short term (Carignan and Lean, 1991).

2.4.6 DEOXYGENATION AND THE DEVELOPMENT OF REDUCING SEDIMENTS

The development of anoxic waters in the bottom of a lake is initially caused by a weakened mixing regime that would usually replenish oxygen levels to compensate oxygen demand. Water column anoxia in the hypolimnion is common over the summer months in many lakes but is not restricted to a seasonal effect in eutrophic lakes. A low level of oxygen compresses the sediment oxic layer reducing its cycling potential and its trapping capacity. Oxygen penetration is significantly reduced once levels drop below 0.2mg/L. If anoxia is prolonged and the microzone is eventually lost altogether surface sediments become void of oxygen and the oxic/anoxic boundary shifts into the hypolimnion (Wetzel, 2000). The onset of anoxia in the hypolimnion typically causes the pH to decrease due to the input of CO₂ from respiration and decomposition processes. These conditions influence the binding mechanisms of pH-dependant chemical processes and can initiate the release of nutrients and trace metals from sedimentary ferric and manganic oxide phases (Davison, 1993; Davison, 1981).

The sediments of productive lakes typically have a constant fresh supply of organic material and which serves to perpetuate oxygen deficiencies and redox cycling intensity. High sedimentation and accumulation rates mean the deposition of settling particles in the oxic layers is appreciable but is also brief as it is progressively buried beneath incoming material. The surface sediments can be rapidly depleted of Fe and Mn metal oxides and which translates to low pore water ferrous ions (Carignan and Lean, 1991). In contrast, as a consequence of low sedimentation rate decomposable material remains in contact with oxic conditions and aerobic bacteria for a longer period and to greater depths within the sediments. Aerobic metabolism is superior to anaerobic and the reactivity of the organic-C is

weak by the time it reaches anoxic zones and is often too low to drive sulfate reduction (Barbanti et al., 1995).

2.4.7 PHOSPHORUS-BINDING CAPACITY OF SEDIMENTS

Release of chemical species from the sediments is not simply a matter of the binding capacity being exceeded but more about the interplay between all of the important parameters that influence binding capacity. Settling material that includes surface reactive particulate clay, sand and silt can bind P directly and also indirectly. Metallic coatings on particle surfaces can enhance scavenging abilities (Mather & De Vries 1994); iron and manganese coatings on particles are common on oxidized freshwater sediments and can promote P-binding onto otherwise non-reactive material (Buckley, 1989). Iron, manganese, aluminium (Al) and calcium compounds and minerals have a strong tendency to bind P and often represent major components in sediments with significant retention capacity. Different fractions will contain more or less phosphorus as a result of the variable affinities of the dominant sediment types (Holten et al. 1988).

The binding capacity of the sediments is diminished by a suite of physico-chemical factors. Elevated pH interferes with ligand exchange mechanisms; hydroxide ions compete for sorption sites on metal oxides/hydroxides substituting weakly held phosphate anions (Golterman, 1995). Alkalinity can promote silica to an anionic form that can out compete phosphate (Koski-Vahala et al., 2001). Decreasing pH generally increases metal solubility and decreasing redox interferes with iron complexes stability; iron-bound P was observed to be released from iron complexes at $E_h < +200\text{mV}$ (Maher and DeVries, 1994). Organic content dictates the consumption of dissolved oxygen and drives redox conditions, and organic anions can block reactive sorption sites (Holtan et al., 1988).

Iron-rich and sulfidic sediments that often have a higher level of organic carbon are more responsive to the effects of anoxia; phosphate and trace metals can be

mobilized as a result (Pettersson et al., 1988). A low Fe/P ratio of sediments or settling material can mean there is less reactive iron to bind P in the surficial sediments and it can escape into the water column (Lehtoranta and Pitkanen, 2003). In reducing sediments with low iron content and in sulfur-rich sediments ferrous iron can be sequestered for the formation of pyrite and removed from the pool of Fe^{2+} available for oxidative conversion and precipitation that would readsorb benthic P (Holdren and Armstrong, 1980; Roden and Edmonds, 1997).

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CHAPTER THREE

MATERIALS AND METHODS

3 MATERIALS AND METHODS

3.1 SITE DESCRIPTION

3.1.1 ROTORUA LAKES REGION

The Rotorua District lakes are located in the central volcanic region of the North Island of New Zealand that is known as the Taupo Volcanic Zone (TVZ). They are situated in the Bay of Plenty region near the east coast of New Zealand. The TVZ covers an extensive area from Mount Ruapehu to White Island that is mantled with a plateau of welded ignimbrite (formed from a cooled pyroclastic flow of pumice and ash) and is New Zealand's most significant geothermal region. The volcanic activity in the zone is caused by subduction of the Pacific tectonic plate beneath the Indo-Australian tectonic plate (Cox, 1989).



Figure 3-1: Rotorua District lakes. Scale 1:250 000 (Scholes and Bloxham, 2005)

The localized nature of volcanism in the zone is strongly linked to the variety of landforms that have been produced in the region; the volcanic lakes are an idiosyncratic surface feature of underlying peculiarities (Lowe and Green, 1975). The fourteen volcanic lakes in the Rotorua district (Figure 3-1) are considered young on geological timescale; their episodic development is testimony to the numerous volcanic events occurring in New Zealand over thousands of years. The basaltic eruption of Mount Tarawera in 1886 was the last major eruption that occurred in the TVZ resulting in the formation of Lake Rotomahana (Cox, 1989; Healy, 1982).

3.1.2 SOILS AND HYDROLOGY

The soils and the hydrology of the region are distinctly different from other regions of the central north island particularly those that lie in calcium-dominated marine sediments. The aquatic chemistry of the lakes in the region is heavily influenced by the origins and types of soils in the local catchment and the occurrence of geothermal activity. Sulfate salts are derived from andesitic strata and geothermal steam and to a lesser extent from rhyolitic rock. High levels of sodium, potassium and silicate are attributed to a dominant rhyolite pumice strata and high levels of phosphorus to the underlying ignimbrite (Timperley, 1983). The silicate is abundant enough in most of the lakes to promote a rich diatom flora.

The signature for geothermal steam is typically high levels of mercury; alternatively high levels of arsenic and chloride are an indication of the influence of geothermal fluids (Timperley, 1975; Timperley and Vigor-Brown, 1986). Cold springs in the TVZ are derived from rhyolitic aquifers; phosphorus release by rhyolitic substrate is due to reaction with acidic recharge water. Water from the cold springs of the TVZ contain concentrations of phosphorus of up to 0.3g/m³ which inserts directly into the hypolimnion of the lakes delivering a substantial load of to the sediments. The spring water has low concentrations of calcium and is undersaturated in terms of the precipitation of a discrete calcium-phosphate mineral phase (hydroxyapatite). The

phosphorus is not taken into a solid state and remains dissolved in the spring water (Timperley, 1983).

Overall the Rotorua lakes receive major ions from rainfall, geothermal fluids and steam, and spring water; many products originate from the easily erodable tephra-derived substrate in the catchments and some from evaporation from the sea (relative to proximity) (Timperley and Vigor-Brown, 1986). The characteristic elemental composition of the water in each lake is credited to local geology in the different catchments. The contribution of major ions from external sources is supplemented by contributions from the pumice aquifer (Timperley, 1983; Timperley, 1975).

3.1.3 LAKE ROTORUA

Lake Rotorua is the oldest lake in the region forming approximately 240,000 years ago (Esler, 2007) and originating from a rhyolitic volcano located in the Rotorua volcanic centre. The lake occupies a caldera basin that was formed when the roof of the magma chamber collapsed; it eventually filled with water to form Lake Rotorua. Mokoia Island rises out from the centre of the lake; it is one of the younger rhyolitic domes formed in the area (Healy, 1982).

The basin is underlain by the Mamaku ignimbrite plateaux and is scattered with pumice tephra (Cox, 1989). Data from tephra marker beds in the sediments serve to elucidate the history of its development. The modern lake sits 280.6 m above sea level (asl) but the lake levels have fluctuated on several occasions in the past and were once 120 m asl higher than the present level (Esler, 2007). Numerous springs feed into the lake supplying substantial amounts of water to the lake (Figure 3-2). The lake receives an extensive geothermal input from small inflows and emerging hot springs at the lakes edge (Healy, 1975; McColl, 1975). Lake Rotorua has only one surface outflow and lake water drains out through the Ohau Channel into Lake Rotoiti and out the Kaituna River (Rutherford et al., 1996).

The rhyolitic soils in Lake Rotorua catchment are derived from surface deposits of Rotomahana mud that resulted from the violent eruptions of Mount Tarawera and Lake Rotomahana and are chemically different from the basaltic soils derived from the Tarawera ash (McCull, 1975). Soils in the region are also derived from older deposits such as from the Taupo and the Kaharoa eruptions; the region has been receiving distal tephra from other volcanic centres for the past 26,000 years (Jones and Lowe, 2005).

3.1.4 MODERN LAKE ROTORUA

Lake Rotorua is a large, shallow, nearly circular, cold-water lake and has been eutrophic for more than thirty years. It has an area of 81km², a mean depth of 10.7 m and a maximum depth of 25 m. The lake is polymictic and thermal stratification is typically short term (hours to days); there are few prolonged calm periods occurring to allow significant stratification to develop (WHITE 1975). Lake Rotorua has been showing trends of increasing total nitrogen and total phosphorus over the past decade which correlates with increased incidence of algal surface blooms of cyanobacteria. The algae are toxic and the blooms are particularly troublesome when they become concentrated in bay areas by winds blowing across the lake (Scholes and Bloxham, 2005).

Lake Rotorua catchment is the largest of all the Rotorua lakes; it covers an area of 520 km² that is predominately pasture (51.8%). The remaining area is dominated by indigenous forest (25.1%), exotic forest (14.3%), and urban settlement (8.1%). Wetlands and buffer zones currently occupy a minimal 0.2% of the lake margin area. They function to intercept overland and subsurface flows, offering effective mechanisms to reduce both nitrogen and phosphorus imports. Constructed wetlands are being trialed as a viable remediation option to remove dissolved N and P before they enter lake (EBoP, 2006; Scholes and Bloxham, 2005).

Cold water streams feeding into Lake Rotorua (Figure 3-2) are delivering dissolved salts as well as water into the lake. Waingaehe stream drains to the lake through a large area of pasture land on pumice soils. Puarenga and Waiohewa streams deliver geothermal inputs to the lake. The majority of the P load and the greatest flow to Lake Rotorua is derived from Hamurana springs (22%) (McColl, 1975; Scholes and Bloxham, 2005). Rainfall is only a dilute source but geothermal activity is a considerable source of ammonium-nitrogen as well as numerous other dissolved salts (Bloxham, 2005; Timperley and Vigor-Brown, 1986). There is also measurable movement of subsurface water flow to the lake through the Whakarewarewa forest via the Waipa stream due to the free draining features of the tephra-derived soil (Lowe and Jones, 2007; Scholes and Bloxham, 2005). Urban effluents and aerial application of superphosphate fertilizer also contribute to the lakes nutrient budget (Fish, 1975).

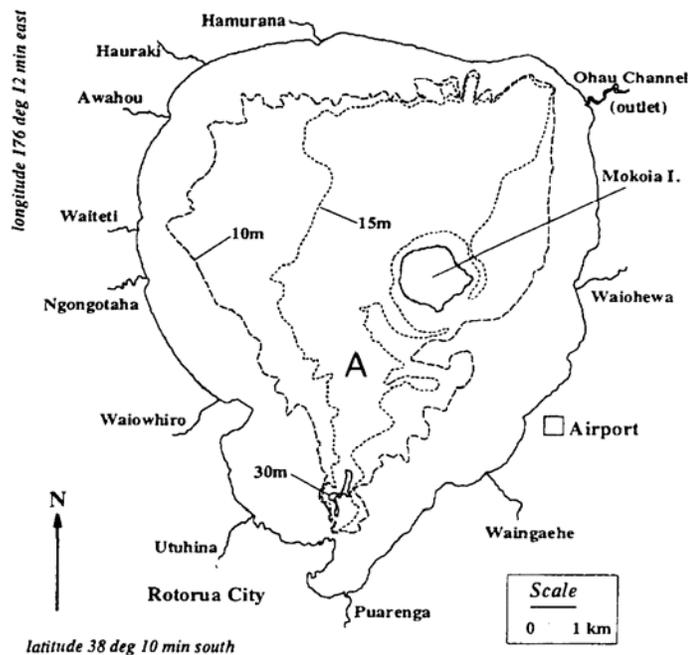


Figure 3-2: Location map showing the main inflows delivering water and dissolved salts to Lake Rotorua (Rutherford et al., 1996).

The area has a long history with the dairy industry; pastoral farming practices have intensified over the years with comparatively increasing usage of phosphorus containing feeds and fertilizers as well as synthetic nitrogen applications for improved productivity. This type of land use is considered to be having a serious impact on lake water quality. The Regional council has installed a regulation ('Rule 11') in the proposed Regional Water and Land Plan to put constraints on further farming intensification in an attempt to improve water quality. Other proactive measures are being taken by the council including chemical trials, diversion schemes, riparian protection and environmental programmes for landowners (Taylor, 2007).

3.1.5 LAKE ROTORUA SEDIMENTS

Sediment investigations of Lake Rotorua have found that the sediments are made up of two types of material. Coarse dense sediments primarily clastic erosion products and rhyolitic air fall components cover approximately 60% of the lake bottom in water depths of less than 10 m. Diatomaceous ooze dominates the remaining 40% of the lake bottom. Wave action focuses lighter material into deeper central regions of the lake. In these shallow regions the sediments are constantly reworked by wave action; low levels of P are an indication of little P retention or recycling (Pearson in prep, 2007).

The diatomaceous ooze is a soft and spongy, olive green 'soup' of organic debris, a large proportion of which consists mainly of the silica frustule remains of the eukaryotic algae (Pearson in prep, 2007) *Aulacoseira granulata* (diatom) (Cassie, 1996). The inorganic structure of the diatom is not degraded during the microbial oxidation of the organic material and remains relatively intact to various depths in the sediment column (Sheath and Wehr, 2003). The ooze accumulates at rates of up to 1cm/year containing up to 6% organic carbon (Pearson in prep, 2007). Another feature of the bottom sediments is a nephloid layer of unconsolidated material suspended above the surface sediments (Motion, in prep. 2007).

Oxidation of the organic material in the sediments reduces the level of carbon down to 2% to the point of anaerobic fermentation as indicated by the production of methane gas in the sediments. The amount of gas generated is a consequence of the large amount of organic matter in Lake Rotorua (Pearson in prep, 2007)

Methanogenesis occurring within the sediments is an indication of the strongly reducing environment. The gas voids observed in sediment cores (Pearson in prep, 2007) suggests the methane (CH_4) is being released into the gas phase and diffusing through the sediment column, and that carbon dioxide (CO_2) is being released into the aqueous phase and forming bicarbonate (HCO_3^-) in solution. This can be confirmed by stable isotope analysis (Motion, in prep. 2007).

3.2 SAMPLING METHODS

Surficial and deep bottom sediment samples were collected from Lake Rotorua during 2005 and 2006 as part of a wider research programme looking at aspects of water quality in the Rotorua lakes. Cores have been retrieved from various sites on Lake Rotorua over this period using either piston, box or gravity corers depending on depth and the type of sample required.

Deeper cores were expected to reveal diagenetic material and volcanic tephra (silt and pumice) containing heavy minerals derived from Tarawera eruption (June 10 1886). Rotomahana mud deposited on the lake floor from the 1886 Tarawera eruption is a consistent feature of almost all the cores retrieved and is characteristically a silty grey band with grain-size fragments of pumice. Soft sediment cores are collected in the gravity corer, a plexiglass tube collects a half metre core that contains the seston. The core often captures the thin oxidizing boundary layer that separates the oxic from the anoxic reduced sediments.

For this study samples were used from two cores collected during field trips as part of a third year paper in geochemistry at Waikato University (Hamilton, New Zealand). A composite core made by combining portions of box core samples from above the

Tarawera tephra (Carter, 2006) was used in a sequential extraction analysis method and samples from Core Ru79 were used in a density separation analysis method. Ru79 was collected at a site (38° S and 176° N) close to Mokoia Island. Sampling sites in this area of the lake were chosen as they are thought to be accumulation areas focusing sediment deposition. A 2.29 m core was obtained using a 3m piston corer. The core was split, described and photographed then sectioned into 20 cm sub-samples for storage until further processing in the laboratory. Pore water profiles obtained from this study showed the elements Fe, P and S were highly active throughout the sediment column suggesting a link between the iron and P cycling, an iron and sulfur which motivated this investigation about iron phases in the sediments of Lake Rotorua (Hurrell, 2005).

3.3 ANALYTICAL METHODS

3.3.1 SEQUENTIAL EXTRACTION

The sequential extraction method as described by Tessier (*et al.*, 1979) was performed on the composite core sample to determine the various solid-phase reservoirs of sedimentary Fe and Mn. This separation technique was developed for speciation of particulate trace metals incorporated in heterogeneous sediments. The application of this selective leaching approach is intended to reveal the conditions that Fe and Mn are likely to be mobilized into solution. Selective leaching schemes for metals are considered an effective method of evaluation for quantifying the various reservoirs. Dissolution is in accordance with the different chemical reactivity associated with each phase and is selective to the partitioning of metals into the specific sedimentary fractions (Ruttenberg, 1992). The most labile fraction is expected to be the first to dissolve through to the most refractory. The dissolution of elements in a particular sedimentary phase by sequential extraction is induced by water: competitive ions: weak acids: reducing and complexing agents: due to the oxidation of organic matter: and finally attack of the mineral structure (Table 3-1).

Ten representative 1-g sub-samples from a composite sample of Lake Rotorua sediments were used for the extraction treatment. Modifications to Tessier's method

was the inclusion of an initial extraction of a water soluble fraction, the carbonate extraction was omitted due to the non-calcareous nature of the sediments, and the final residue procedure was substituted for an aqua regia digestion. The samples were centrifuged at maximum rpm (4085) for 30 minutes using a Heraeus Swinging Bucket Rotor Multifuge 3 S, model 75006445. The residue was rinsed with 8ml deionized water to and spun for a further 30minutes to reclaim any soluble ions still in the pellet. The residue from the initial extraction was reused for each successive extraction treatment. The leachate (supernatant) from extraction treatments 1, 2, 3 & 6 was made up to 50ml in volumetric flasks and the leachate from extraction treatments 4 & 5 was made up to 20ml, also in volumetric flasks with deionized water in preparation for elemental analysis.

Table 3-1: Sequential chemical extraction treatments performed on sediments for the analysis of the partitioning of elements amongst various sedimentary phases

Treatment	Extractant	Geochemical Phase	Reaction mechanism
I	Distilled H ₂ O	<i>Water soluble</i>	<i>Hydration</i>
II	1M MgCl ₂ pH 7.0	<i>Exchangeable or loosely sorbed matter</i>	<i>Ion exchange by magnesium cations and chlorine anions</i>
III	0.01M CH ₃ COOH	<i>Coordinative surface complexes</i>	<i>Addition of protons by a weak acid; ligand exchange</i>
IV	20ml 0.04M NH ₂ OH.HCL in 25% (v/v) HOAc at 96±3 ⁰ C for 6hrs	<i>Reducible metal oxide phases Fe and Mn to ferrous and manganous forms*</i>	<i>Reduction of amorphous & crystalline oxyhydroxides</i>
V	H ₂ O ₂ /HNO ₃ (pH ~2) and subsequently NH ₄ OAc	<i>Oxidation of organic matter*</i>	<i>Organic-C digestion</i>
VI	Aqua regia (3:1 conc.HCL:conc HNO ₃)	<i>Highly resistant lattice-bound metals</i>	<i>Dissolution of 1⁰ & 2⁰ mineral phases</i>

* The liberated metals were kept in solution as oxides with the second agent (acetic acid) in steps VI and V as prescribed by the method.

3.3.2 DENSITY SEPARATION

Investigation of the sedimentary Sulfide phase was carried out on 12 sub-samples of Ru79 using a density separation method. The core had previously been sectioned at various intervals and oven dried. For the heavy liquid treatment one gram of sample from each interval was dissolved in 10ml of a solution of 30% sodiummetatungstate (density of 2.6 g cm^{-3}) in a 50ml centrifuge tube. The samples were centrifuged for 5 minutes at maximum rpm (4500). The liquid was decanted off through a vacuumed filtering device and the low density suspended solids were captured on the millipore filter paper. The liquid was collected in a 200ml plastic bottle to be recovered. The pellet of solid material was then washed through the filtering device and captured on filter paper. All of the solids collected were oven dried at 50°C for approx. 3 hours.

Descriptive analysis of the high density material from the pellet (using a 500 fold magnification) revealed a significant amount of diatomaceous debris was retained in solid phase. A heavier sodiummetatungstate solution (density $\geq 3.7 \text{ g cm}^{-3}$) was prepared and the separation treatment was performed on the dried solids from the pellet. The same separation procedure was carried out to separate the lighter material in the pellet from the heavier except the solids were dissolved in 5ml of the heavier metatungstate solution. The samples were placed in an ultrasonic bath to break up the material and aid the separation. The samples were spun as before, filtered through glass fibre filter papers (it was difficult to scrape the dried material from the millipore paper) and dried in the oven overnight. The two density separation treatments produced three sets of solid material, low density ($d < 2.6 \text{ g cm}^{-3}$), medium density ($2.6 < d < 3.7 \text{ g cm}^{-3}$) and high density ($d > 3.7 \text{ g cm}^{-3}$). A segment of the sub-samples of the high density material was cut from each piece of filter paper to be used for SEM detection. The dried samples were stored in labeled ziplock bags to prevent the loss of an already small sample size. The three sets of dried samples were prepared for solution analysis. Approximately 100mg of dry sample was transferred to 15ml centrifuge tubes treated with one tenth of a reversed aqua regia digest (3:1

conc. HNO₃ to conc. HCL) and left overnight. The samples were inserted into a specifically designed hot plate heated at 50⁰C and left for 180min. The samples were made up to the 5ml mark with 100ppm (mg/L)Rb solution, weighed, centrifuged at maximum rpm on a Heraeus Swinging Bucket Rotor Multifuge 3 S, model 75006445. Two ml of supernatant was decanted off each sample for solution analysis by the ICP-OES.

3.4 ANALYSIS

Elemental analysis was undertaken on the individual aqueous fractions from each step of the sequential fractionation. Solution concentrations of the elements in the leachate of the different phases were determined by inductively coupled plasma-Optical Emission Spectroscopy (ICP-OES). A one in five dilution was prepared for samples from treatments 1, 2, 3 and 6, and a one in ten dilution was prepared for treatments 4 and 5. Heavy mineral and trace metal concentrations for the three different densities samples obtained were determined by ICP-OES and sulfur was analyzed by inductively coupled plasma-Mass Spectroscopy (ICP-MS).

The solid phase samples with the highest density (greater than 3.7 g cm⁻³) were analyzed by electron excited x-ray fluorescence (XRF) and the morphological observations obtained from the images generated by the scanning electron microscope (SEM).

All glassware and centrifuge tubes were acid-cleaned; milli Q water was used for the preparation of all solutions. Blanks and standards were used; certified standards were used for ICP-OES and ICP-MS analysis for quality control.

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CHAPTER FOUR

RESULTS

4. RESULTS

4.1. SEQUENTIAL EXTRACTION

Sequential extraction is a technique designed to distinguish between sedimentary components that may be mobilized under different conditions. The sequence is designed so that the most reactive phases are removed first and the severity of the extractants increases with each successive step. The extraction reagents each target a certain fraction intending to liberate a particular phase into solution while the remaining phases resist the attack (Tessier et al., 1979). The metal partitioning scheme yields 'operationally defined' fractions that are commonly referred to by the geochemical phase the extracted metals are associated with (Sigg et al., 1987). The amount of an element extracted is a function of the different aspects of the scheme such as the reagent type and the extraction sequence therefore its application is typically infused with cautionary warnings of a tendency for erroneous results (La Force and Fendorf, 2000). Characterizing the sediments by its fractional composition is a popular scheme to determine the dominant iron, manganese and phosphorus phases; it is regularly used to identify the more labile sedimentary fractions most likely to be recycling P in the surficial sediments and the refractory fractions that are preventing P release (Penn et al., 1995). From the results conclusions can be drawn about the primary mechanisms of P release into the pore water of Lake Rotorua sediments.

4.1.1. TREATMENTS 1 - 6

The sequential extraction technique has successfully revealed the solid phase partitioning is occurring in the composite sediment sample. Concentrations of iron, manganese and phosphorus in each of the six treatments are variable and obviously relative to the selectivity of the extractant (Figure 4-1). In general higher concentrations of iron and phosphorus appeared with each successive dissolution. In contrast manganese concentrations reduced with each extraction procedure. Manganese is more reactive than iron and is clearly lost under less strenuous

conditions than iron. The vertical separation of Mn^{2+} and Fe^{2+} down the core is a common pattern of distribution in oxic sediments that are typically not as organic rich and oxygen depleted as anoxic sediments (Sorensen and Jorgensen, 1987).

There was minimal dissolution of phosphorus by the first three extractants however the following three extractants (IV, V and VI) were more effective at inducing phosphorus release. Phosphorus concentrations increase considerably with hydroxylamine leaching, peroxide oxidation, and aqua regia leaching, suggesting that a significant portion of the phosphorus in the sediments is bound to Fe/Mn oxides, organic matter and mineral phases.

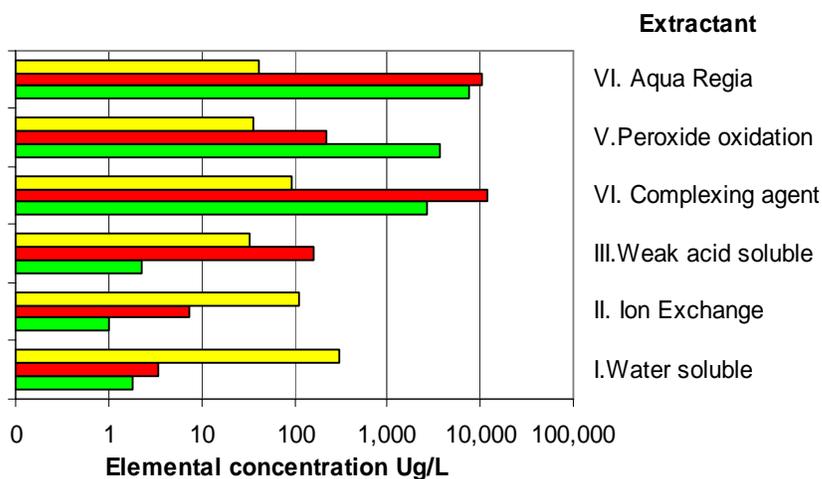


Figure 4-1: Solid phase concentration of phosphorus (green), iron (red), and manganese (yellow) derived from selective leaching experiments performed on a composite core sample from Lake Rotorua sediments as determined by ICP-OES analysis.

Phosphorus and iron release appeared to occur simultaneously; plotting one against the other shows a reasonable correlation between the results (Figure 4-2a). In contrast there was an inverse relationship between manganese and phosphorus (Figure 4-2b). This would suggest the phosphorus that is mobilised in the final three extractions is associated more with iron than with manganese.

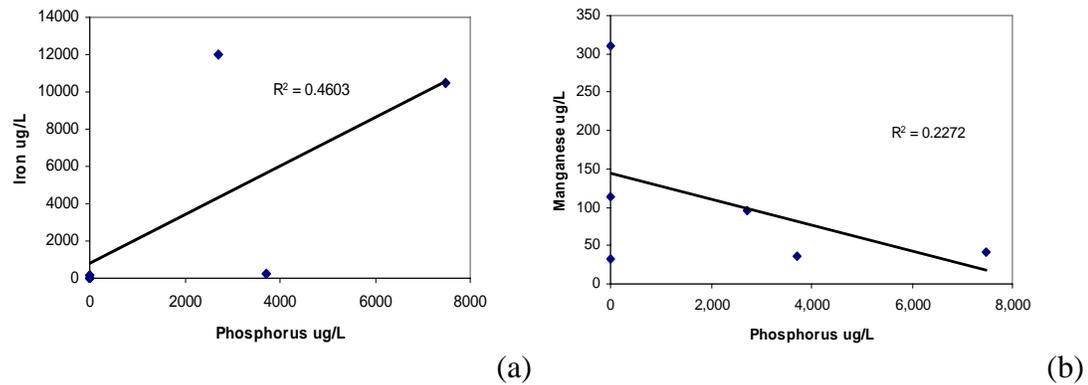


Figure 4-2: Solution concentrations of the solid phase (ug/L) derived from the sequential extraction scheme. Positive correlations are shown between iron and phosphorus (a); manganese versus phosphorus shows an inverse relationship (b).

Iron concentrations show a positive correlation to arsenic (Figure 4-3a) suggesting preferential associations between iron oxyhydroxides and arsenic (Belzile and Tessier, 1989). In contrast to iron there was no relationship between arsenic and manganese (Figure 4-3b) and therefore it can be assumed there was little association of these two elements in any of the phases.

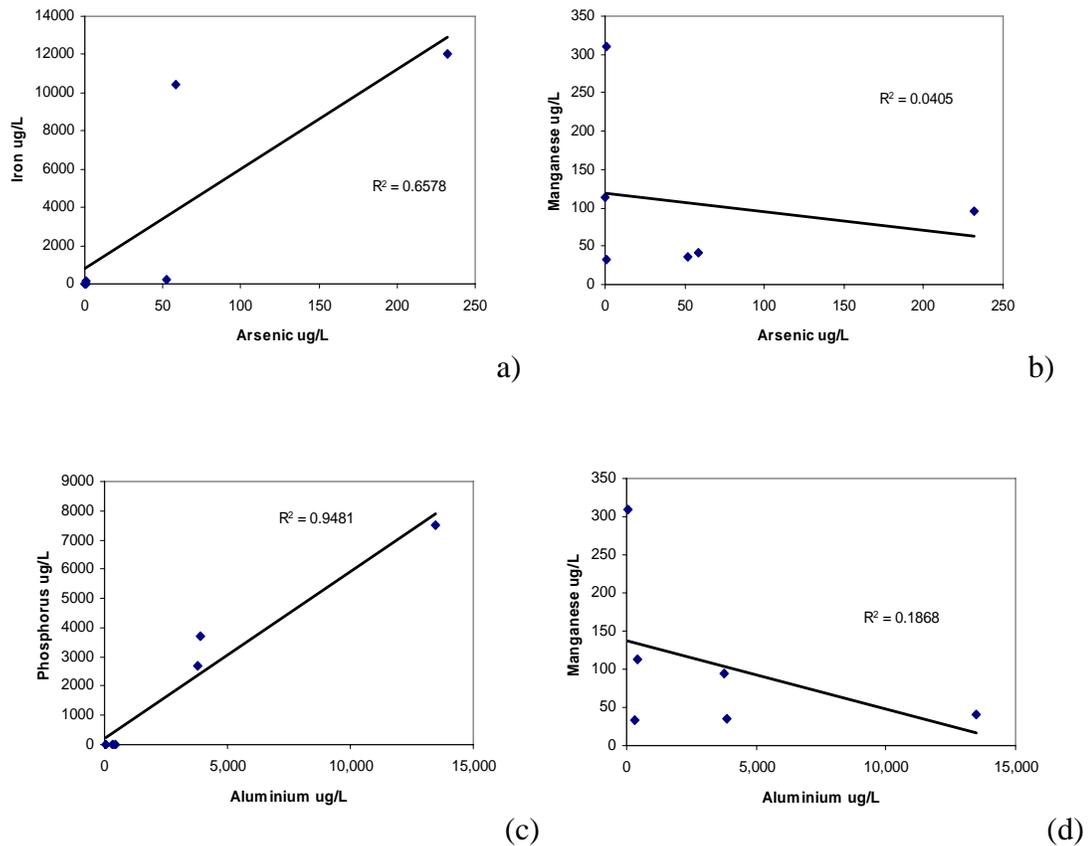


Figure 4-3: Solution analysis showing comparisons between concentrations of elements in the solids (ug/L) from sequential extraction: iron versus arsenic (a) and manganese versus arsenic (b); phosphorus versus aluminium (c) and manganese versus aluminium (d).

Aluminum was strongly correlated to phosphorus (Figure 4-3c) but its relationship with manganese was very weak (Figure 4-3d). Considering the similar levels of Al and Fe obtained from the six leaching treatments it could be supposed that Al is a P-bearing multiphase hosting Fe in sedimentary clays such as aluminosilicate (Ruttenberg, 1992).

The distributions across the different solid phases of all of the elements analyzed are shown in Figure 4-5. Variable trace element enrichment amongst the phases is apparent and the final three treatments have been responsible for liberating the greatest proportion of almost all the elements. A few of the heavy metals were only

distributed in the oxide and the residual phases. Zinc (Zn), chromium (Cr), strontium (Sr) and barium (Ba) were distributed across all the phases. Chromium results are complicated by serious isobaric interferences between argon and carbon. Both mass 52 and mass 53 are reported, but both are likely to be over estimates. Zinc was associated mostly with the oxide phase and the mineral phase which is fairly typical of its behaviour (Carroll et al., 2002). Gallium (Ga) and silver (Ag) were only present in the mineral phase and their concentrations were very low. Copper (Cu), and lead (Pb) were only released in treatments 4 and 6. Lead is reported to be associated with oxide phases (Carroll et al., 2002) and copper with sulfide phases (Otero et al., 2003). Davranche and Bollinger (2000) also found reductive dissolution of oxides released the heavy metals cadmium (Cd) and Pb into solution. In general the concentrations of the heavy metals were very low (Figure 4-4) but expressing them as proportions (Figure 4-5) of the total amount for each element demonstrates heavy metal partitioning across the different phases in the sediments.

The most substantial concentration peaks for Fe, P and As (Figure 4-4) occurred in treatments 4 and 6; phosphorus solubility dramatically increased under reducing conditions and in the oxidation treatment. Treatment 5 of the sequence was designed to extract organic-bound P and at the same time retain iron and manganese in the ferric and manganous phases. Concentrations of aluminium (Al) increased with each progressive step and like iron significant solubilization occurred in the final three treatments except that in contrast to the redox sensitive elements, Al continued to be mobilized during the oxidation treatment in step 5.

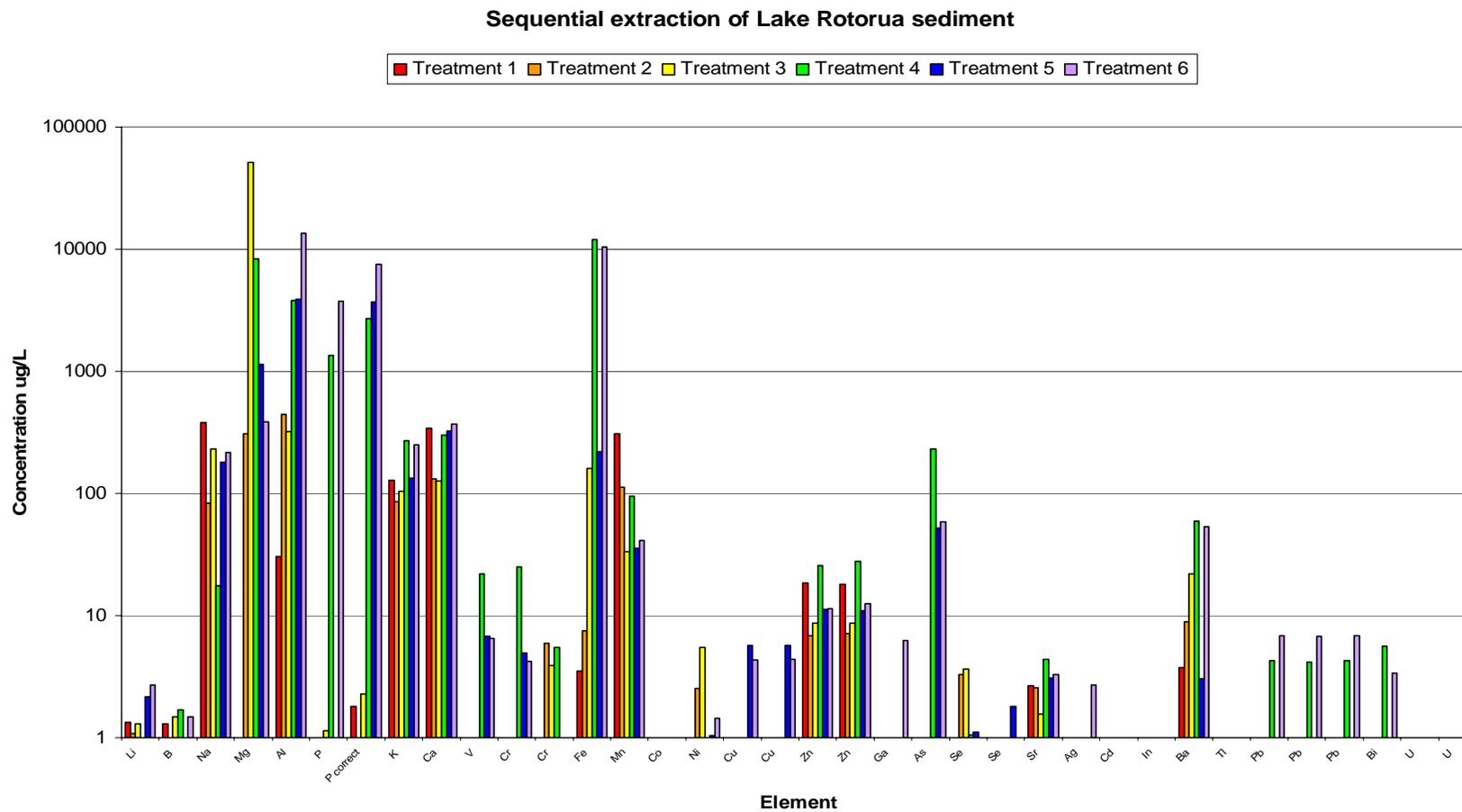


Figure 4-4 Concentrations of all the elements analyzed by ICP-OES from the composite core taken from the sediments of Lake Rotorua

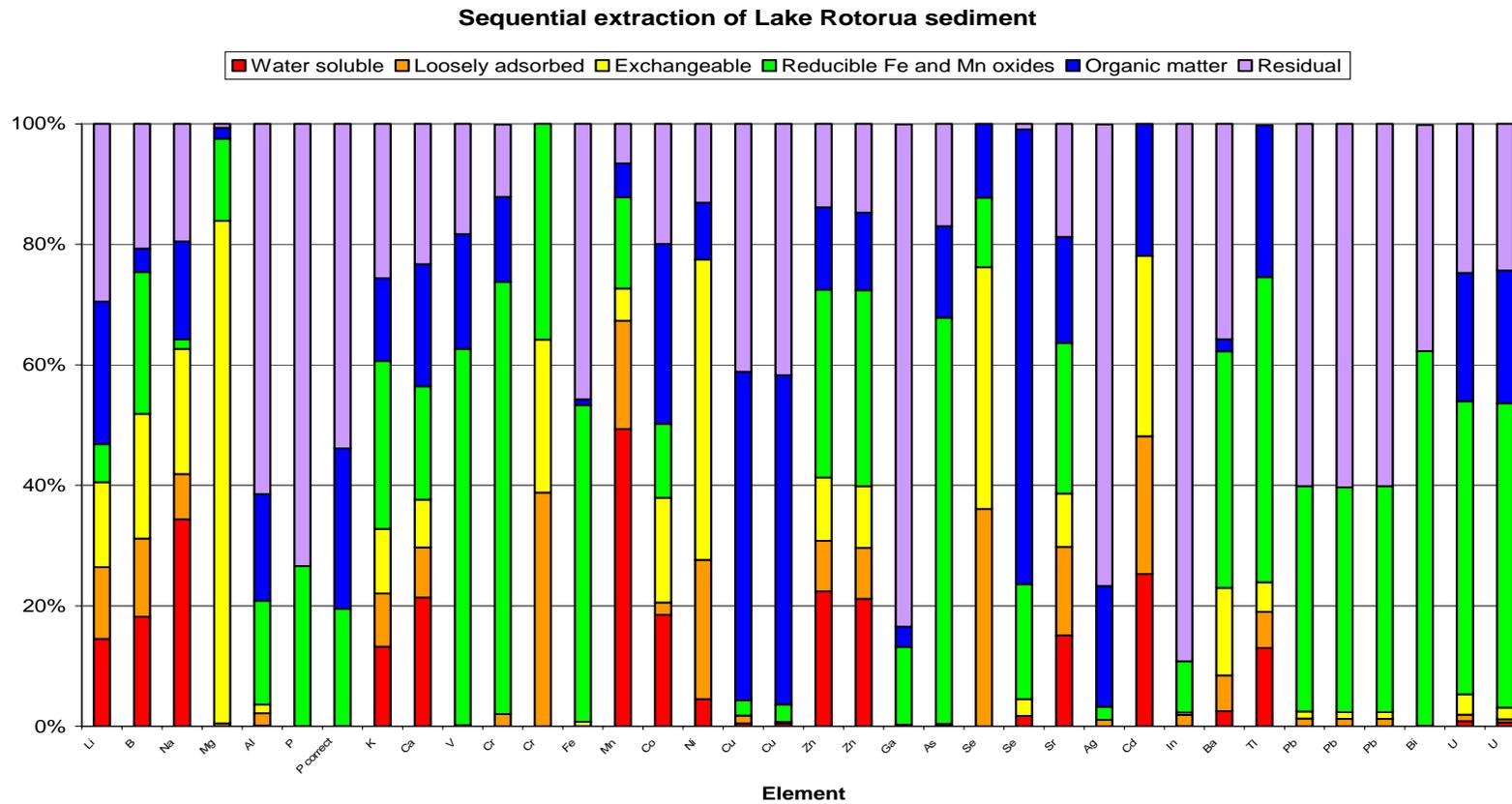


FIG. 4-5 The distribution of elements among six operationally defined geochemical phases in the sediments of Lake Rotorua, expressed as a percentage of the total in the sediments

The alkali and alkaline earth metals sodium (Na), potassium (K), and calcium (Ca) were distributed evenly across the phases; their concentrations were similar in all of the leachates. Magnesium (Mg) was readily removed by each extractant; the quantity of magnesium liberated in each step following step 2 however was likely to be an artifact of the reagent used in dissolution by ion exchange and therefore may be an overestimation (Figure 6).

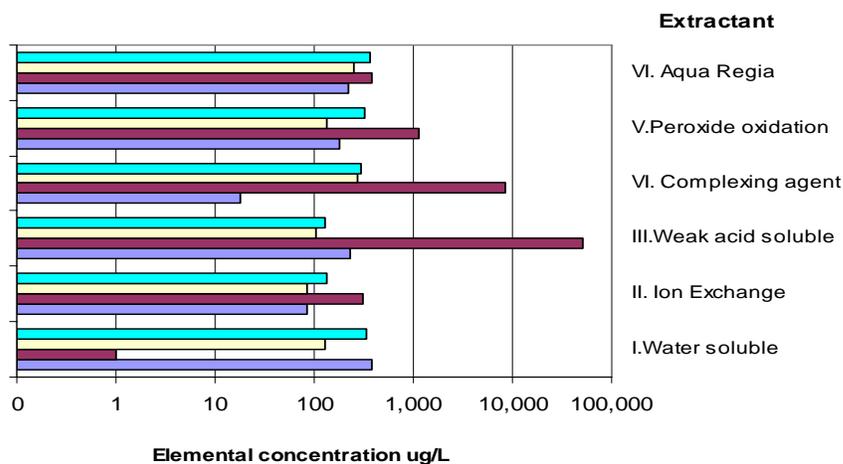


Figure 4-6: Concentrations of sodium (lavender), magnesium (plum), potassium (ivory) and calcium (turquoise) derived from selective leaching experiments performed on a composite core sample from Lake Rotorua as determined by ICP-OES analysis.

Phosphorus, iron, aluminium, arsenic and barium were all concentrated in the less reactive phases (Figure 4-7). The dissolution of primary and secondary mineral phases by concentrated nitric and hydrochloric acid in the final treatment generated significant levels of aqueous iron similar to reductive conditions and also the most substantial amount of dissolved P and Al. The reduction of iron oxide in step 4 extracted the easily reducible (amorphous) iron oxides/oxyhydroxides, ferric iron precipitates and metallic coatings (Poulton and Canfield, 2005); the remaining Fe phases were solubilized by strong acids in final treatment (step 6). The P concentrations obtained in the dissolution of the less reactive phases are significant and are a good indication that P was associated with the crystalline ferric oxyhydroxides, ferrous iron mineral phases and aluminium hydroxides (Penn et al., 1995) as suggested by the strong correlation between Al and P in Figure 4-3(c).

The levels of Fe-P in an aqueous phase at this stage could be due to the dissolution of a ferrous iron phosphate mineral such as vivianite which is often present in appreciable quantities in sulfide-poor sediments (Mucci et al., 2000) or at depths below the zone of sulfate reduction in the methanogenic zone (Anderson and Rippey, 1988). Arsenic release in the final three treatments was substantially greater than in previous the leaching procedures. The remobilization of arsenic into a dissolved phase is often found following the reductive dissolution of iron and manganese oxides, presumed to be As carrier phases. The reduced form of arsenic (arsenite) released to the porewaters coprecipitates with iron sulfide minerals and is also found distributed in the sulfide phase. As discussed above arsenic can take the place of phosphate and is taken up by aquatic plankton which would account for its release from the organic phase.

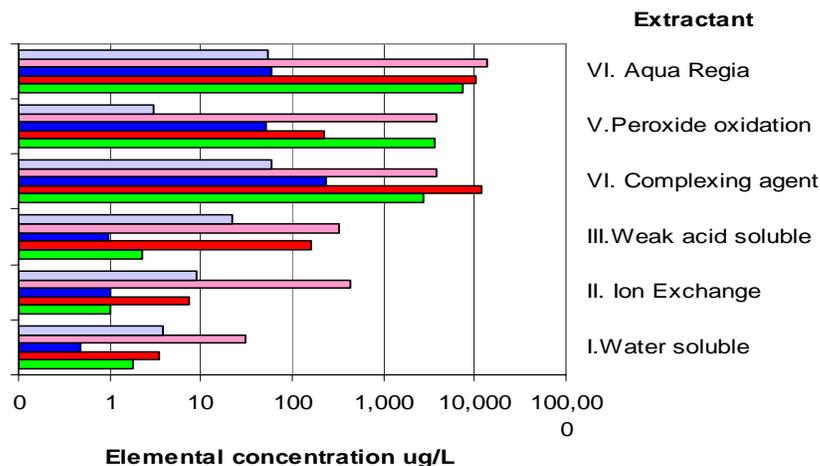


Figure 4-7: Concentrations of phosphorus (green), iron (red), arsenic (dark blue), aluminium (pink) and barium (light blue) shown are a function of the six different extraction leachates.

This particular scheme has not been developed to identify separate iron minerals, which would include determination of iron sulfide minerals. In any case it has identified the fact that less reactive phases are important phosphate sinks in the sediments and that iron is critically involved in this role.

Sequential extraction results are qualitative, and are only able to infer phase associations occurring between various elements in a broad sense but they do lend additional support to quantitative data. These results appear to give a reasonable indication of the likely release mechanisms that are having the greatest affect on the transport of trace elements and of nutrients such as phosphorus.

4.2. DENSITY SEPARATION

4.2.1. MINERAL IDENTIFICATION

Studies of the pore water chemistry (Motion, in prep. 2007) composition of the sediments and the results of sequential extraction above suggest that iron sulfides may form in the sediments. Heavy liquid separation of the sediments from core Ru79 allowed separation of minerals by density difference and produced three distinct fractions ($d < 2.6$, $2.6 < d < 3.7$, $d > 3.7$ g cm⁻³). The fraction of interest for this analysis was the heaviest fraction ($d > 3.7$ g cm⁻³) which was expected to contain iron sulfide minerals as well as other minerals that may be concentrating the elements S, Fe, Mn and P, thus removing them from solution. Pyrite is often an abundant iron sulfide mineral in reducing environments, serving as a sink for sediment-derived Fe(II). It has a density of 5 g cm⁻³ (Weast, 1988) and therefore would be present in the heavy fraction as one example for a dominant iron mineral phase.

Scanning electron microscopy (SEM) images of the heavy fraction showed a surprisingly high content of biogenic detritus at shallow depths (10 – 63 cm) in the core. The material largely consisted of whole and fragmented skeletal material from planktonic organisms and was dominated by diatoms. The images showed coarse volcanic tephra (mineral grains and glass shards), fragments of platy minerals (probably micas) and clusters of grains (Figure 4-8a). The energy dispersive X-ray fluorescence analysis (XRF) of the samples from the shallower depths consistently showed massive peaks of silica and in some cases calcium (Figure 4-8b) which suggests the nature of the debris was predominately siliceous.

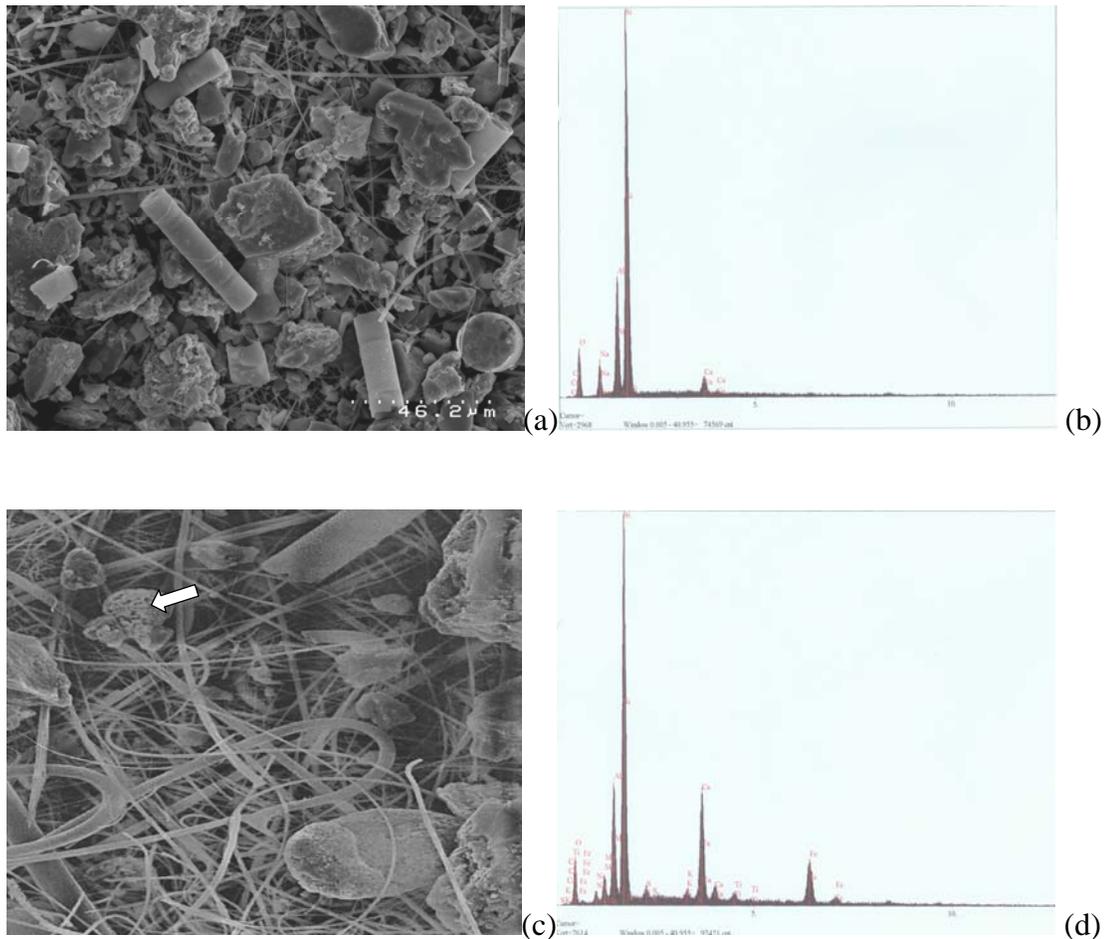


Figure 4-8: SEM images of heavy liquid separates from Ru79. At depth 20 – 40 cm solids contain primarily diatom debris and some volcanic tephra (a); (b) energy dispersive X-ray spectrum is not corresponding to any particular particle, it shows a massive silica peak, a small iron peak but no peaks for phosphorus or sulfur were detected; (c) material at depth 40 – 63 cm; (d) XRF shows same pattern despite the presence of framboidal pyrite as indicated by the arrow.

Inspection of the video imagery/photomicrographs of the samples revealed the presence of discrete mineral structures. Spherical clusters of cubic crystals were observed in the 40 – 63 cm sample (Figure 4-8c) but the XRF analysis of this sample (Figure 4-8d) covered the entire field of view and did not show significant sulfur. The clusters were mostly ball-like aggregates of individual cubes. The spherical particles became more recognizable and appeared to be more abundant down the core. These were able to be isolated for XRF analysis in almost all of the subsequent samples.

At a depth of 63 – 67 cm cuboidal particles are observed and the XRF spectrum corresponding to the particle in the SEM image (Figure 4-9a & b) showed significant peaks of sulfur and iron. This is a reliable indication that the clusters are iron sulfide minerals (probably framboidal pyrite); the Fe and S enrichment found in the framboids confirms that iron and sulfur are concentrated in this phase in the heavy fraction. There were no particles of this similar nature detected throughout the sample at 67 - 90 cm depth however the particles were apparent in the following sample. At a depth of 90 -110 cm the isolated particle is characteristic of framboidal pyrite and the spectrum shows significant peaks of sulfur and iron (Figure 4-9c & d).

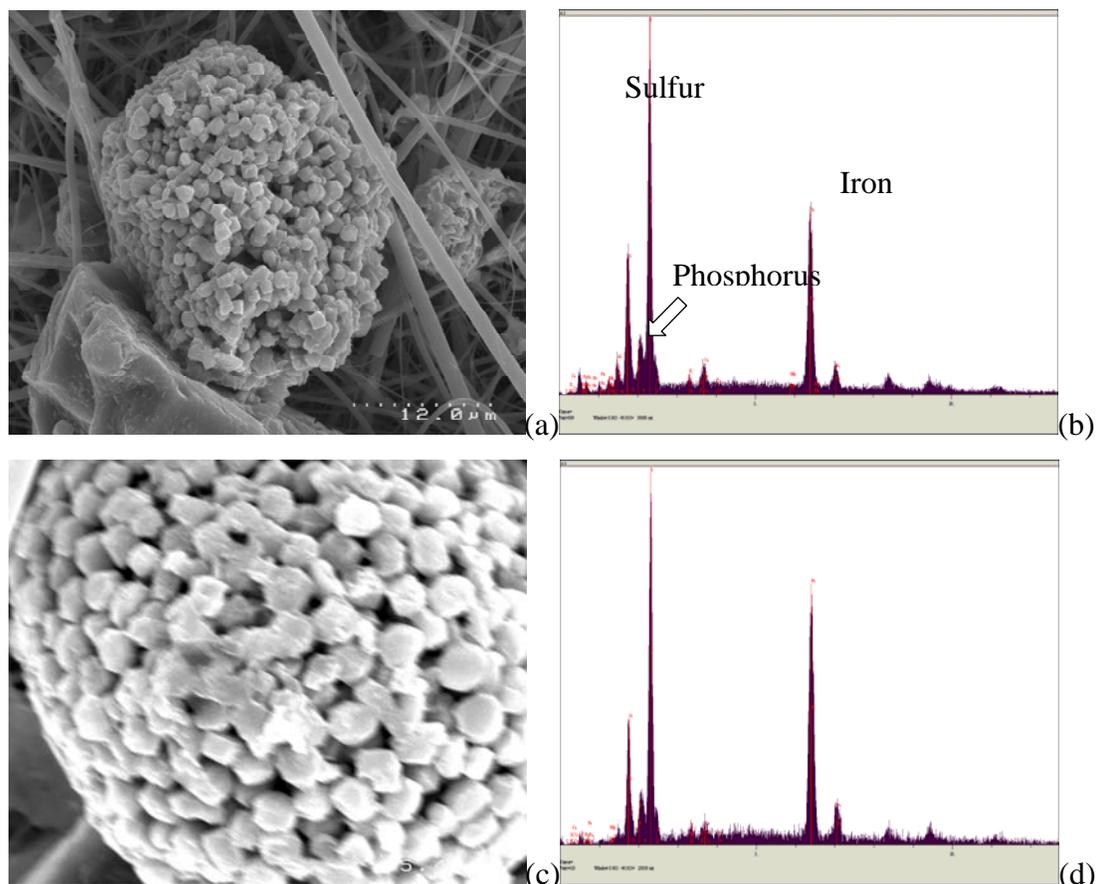


Figure 4-9: SEM images of (a) framboidal pyrite on glass fibre filter paper and (b) corresponding energy dispersive X-ray spectrum showing a strong peak of sulfur, an iron peak and a weak phosphorus peak (depth 63 - 67 cm); (c) pyrite on glass fibre filter paper at

depth 90 – 110 cm and (d) corresponding energy dispersive X-ray spectrum showing similar peaks of sulfur, iron and phosphorus.

The framboidal pyrite particles were present at 110 - 130 cm depth but the cluster of cubic crystals isolated showed slight structural variations to the previously identified pyrite. The XRF spectrum also showed a major silica peak and apparently less enrichment of iron and sulfur compared with the other framboids (Figure 4-10a & b). The SEM image in Figure 4-10(c) (depth 130 - 150 cm) is of a particle with seemingly different morphology and chemical composition to those previously observed. The particle is not cubic and the corresponding XRF spectrum (Figure 4-10d) shows a lone iron peak suggesting it is not an iron sulfide mineral.

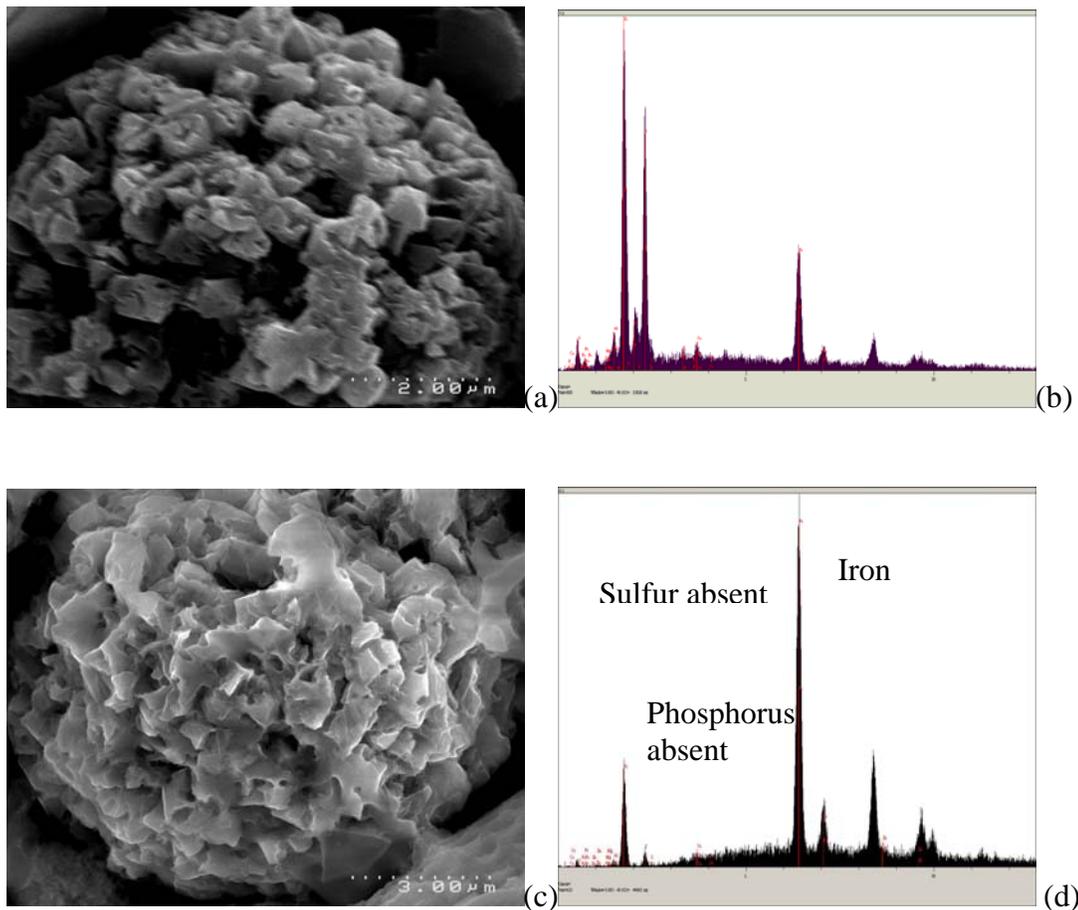


Figure 4-10: SEM image of particle that appears to be structurally different from the others (a) and (b) the corresponding energy dispersive X-ray spectrum showing silica peak as well as sulfur and iron peaks (depth 110 -130 cm); (c) Another particle isolated with variable morphology and (d) variable chemistry as shown by the corresponding energy dispersive X-

ray spectrum. There is no sulfur and no phosphorus but a massive iron peak (depth 130 -150 cm).

The iron-rich crystals in the particle could be diagenetic Fe oxyhydroxides such as goethite which is reported to have variable forms including a cubic morphology (Herbert, 1997). If it is goethite it can be speculated that it is actually dissolving at these depths; goethite is a ferric iron mineral and would not be expected to be forming in reducing sediments (Fortin et al., 1993). The particle cannot be a ferrous iron-phosphate mineral e.g. vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$), as it should also be enriched in P. Siderite (FeCO_3) is a Fe(II)-containing mineral and has a rhombohedral morphology and is a likely candidate for Figure 4-10(c). It does adsorb P but only weakly and so has been considered to be a source of dissolved P (Krom and Berner, 1980).

At depths of 130 -150 cm the crystals of the particles isolated (Figure 4-11a & c) were of a variable morphology; they had a less cubic form. Despite the differences the corresponding XRF spectrum for both particles was enriched in sulfur and iron and they are clearly iron sulfides but probably not pyrite (Figure 4-11b & d).

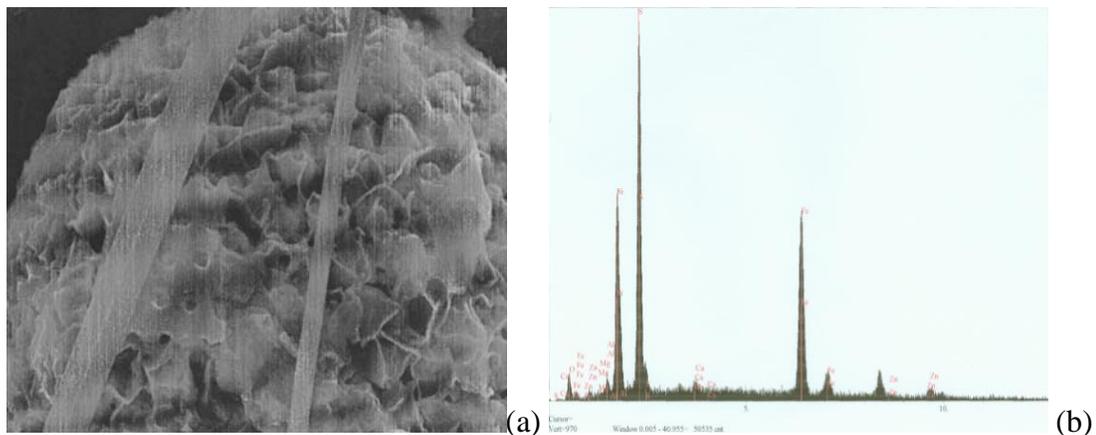


Figure 4-11: SEM images of a slightly dissimilar iron sulfide mineral (a) at depth 130 - 150 cm and (b) the energy dispersive X-ray spectrum corresponding to the image; (c) another spherical iron sulfide with a non-cubic crystals form and (d) corresponding energy dispersive X-ray spectrum; (e) non-spherical crystals lacking a framboidal form at 150 - 170 cm depth; (f) energy dispersive X-ray spectrum corresponding to the non-pyrite particle.

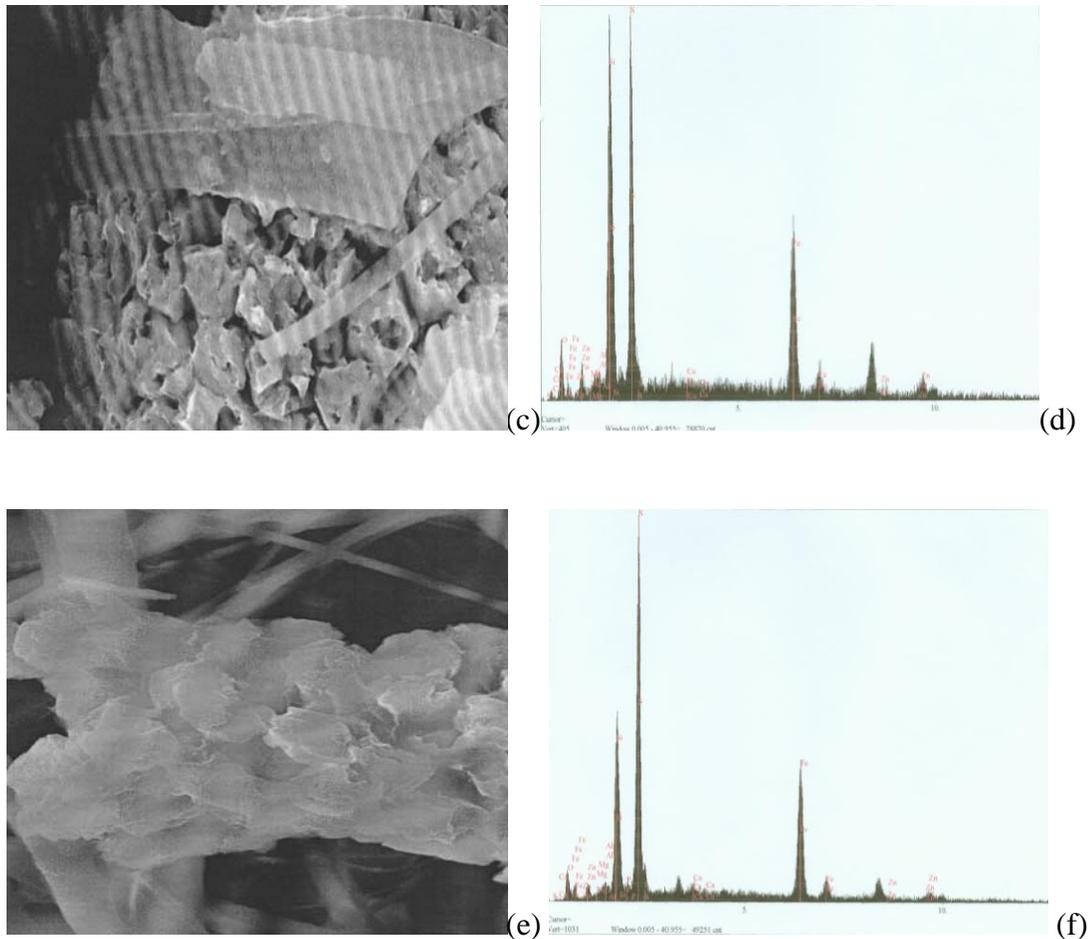


Figure 4-11: Continued

At 150 -170 cm depth a particle was observed that was non-spherical and appeared platy but the XRF analysis showed the sulfur and iron peaks consistent with pyrite (Figure 4-11e& f). The few morphological differences between the iron sulfide particles occurring in this section of the sediment column are suggesting that variations are a function of depth due to late diagenesis and the chemistry of the pore water during crystal formation. The particles with what appears to be clusters of hexagonal crystals (e.g. Figure 4-11e), and are likely to be iron monosulfides.

Further down the sediment core at depths of 170 - 190 cm (not shown) and 190 - 210 cm (Figure 4-12a-d) the framboidal pyrite particles were observed in the samples. In Figure 12(c) a relatively large framboidal pyrite was cemented to a cluster of diatomaceous debris. In the last section of the core at depths of 210 - 229 cm (Figure 4-12e-f) the framboidal pyrite, characterized by the sulfur and iron peaks in the XRF spectrum, was lodged inside the cylindrical frustule of *Aulacoseria granulata* (Cassie, 1996).

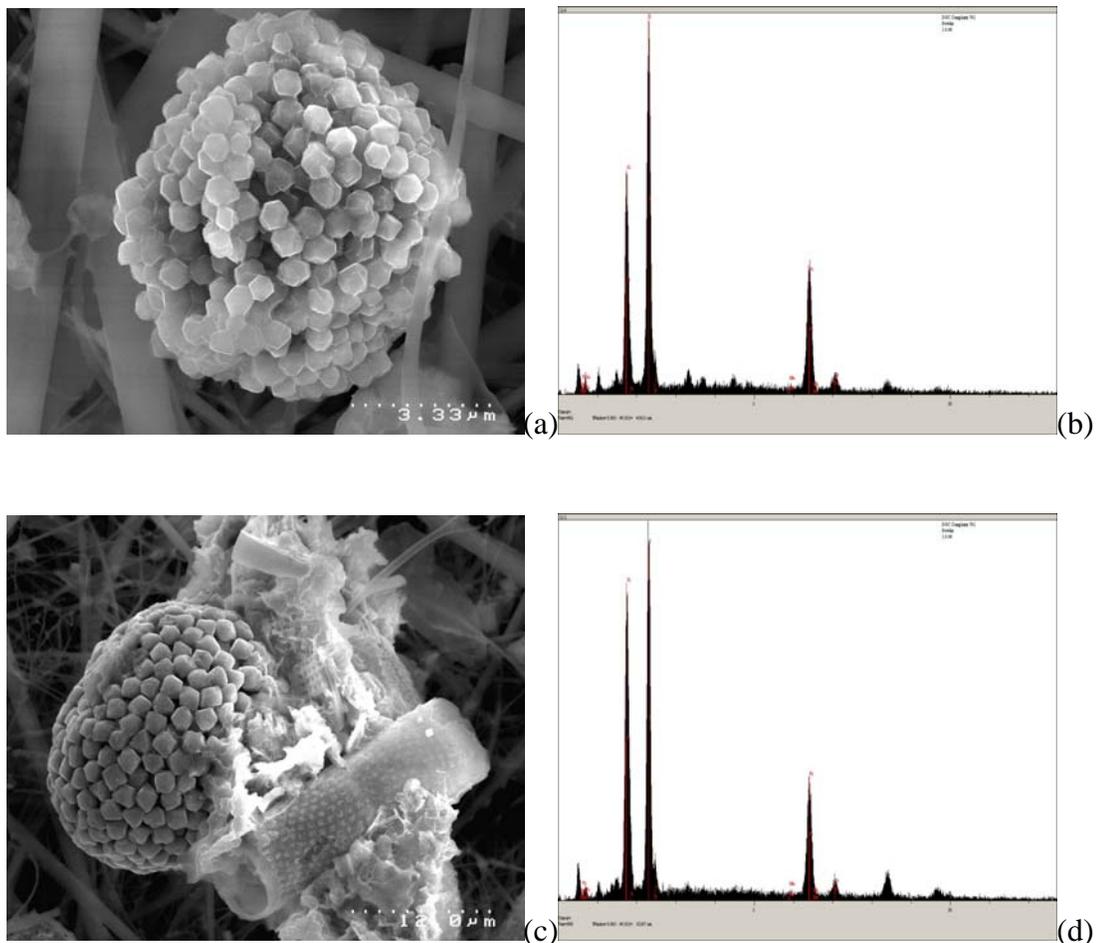


Figure 4-12: SEM images of (a) framboidal pyrite on glass filter paper at depth 190 - 210 cm and (b) corresponding energy dispersive X-ray spectrum; (c) Cuboidal pyrite cemented with tubular diatom at depth 190 - 210 cm and (d) corresponding energy dispersive X-ray spectrum; (e) framboidal pyrite infilling cylindrical frustule of *Aulacoseria granulata* (Cassie, 1996) (f) corresponding energy dispersive X-ray spectrum dominated by a silica peak (depth 210 - 229 cm).

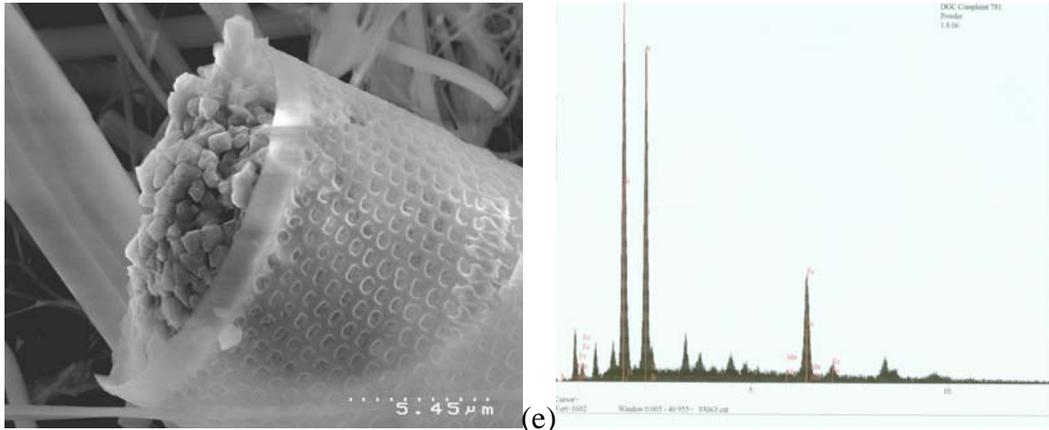


Figure 4-12 Continued.

Silica peaks appearing within the series of spectra are attributed to the siliceous planktonic debris and glass fibre filter paper. The weak aluminium peaks in the XRF spectra confirms that discrete aluminosilicate minerals have been concentrated in the medium density fraction as intended. The diatom frustules appear well-preserved and are still relatively abundant at these depths in the sediments.

In all of the spectra corresponding to the framboidal pyrite, phosphorus peaks are either very weak or absent thus the formation of pyrite does not in itself provide the sink for phosphorus.

4.2.2. TRACE METAL ANALYSIS OF DENSITY FRACTIONS

Comparison of the concentrations between different density fractions show that relative to the diatom fraction the heavy minerals are enriched in uranium, lead, arsenic, manganese, iron, potassium, sulfur, phosphorus, aluminium and magnesium. The diatom (low density) fraction is slightly more enriched than the silicates in arsenic, manganese, iron, calcium and aluminium; phosphorus enrichment in the diatom fraction is substantial. Uranium, lead and sulfur are enriched in the silicates rather than in the diatoms (Figure 4-13).

Sulfur is slightly more enriched in the heavy fraction than are lead, arsenic, iron and potassium and substantially more enriched than are phosphorus, aluminium and

manganese. The enrichment of iron, manganese and sulfur in the heavy mineral phase suggests the presence of sulfides. Sulfur is enriched in the heavy mineral fraction and the silicate fraction more than the diatom fraction. Some of the sulfur present in the low density fraction could be as elemental sulfur. The presence of sulfide minerals in the heavy phase may also account for much of the enrichment of other elements along with heavy minerals sourced from volcanic eruptions. Potassium and lead exhibit concentrations that correspond to levels originally found in tephritic feldspars and glasses. Thus the bulk of the heavy mineral enrichment is a consequence of the source minerals rather than diagenesis. Arsenic is sourced from geothermal fluids and tends to be incorporated into organisms in place of phosphorus. Within the sediments arsenic is most likely present as adsorbed or co precipitated trace elements, but can form sulfides (e.g. arsenopyrite).

The comparisons between the phases show that most of the phosphorus is incorporated into heavy mineral phases but that there still remains a substantial proportion associated with diatoms. The latter could be the result of phosphate ion adsorption by the diatom frustules (Stamatakis and Koukouzas, 2001).

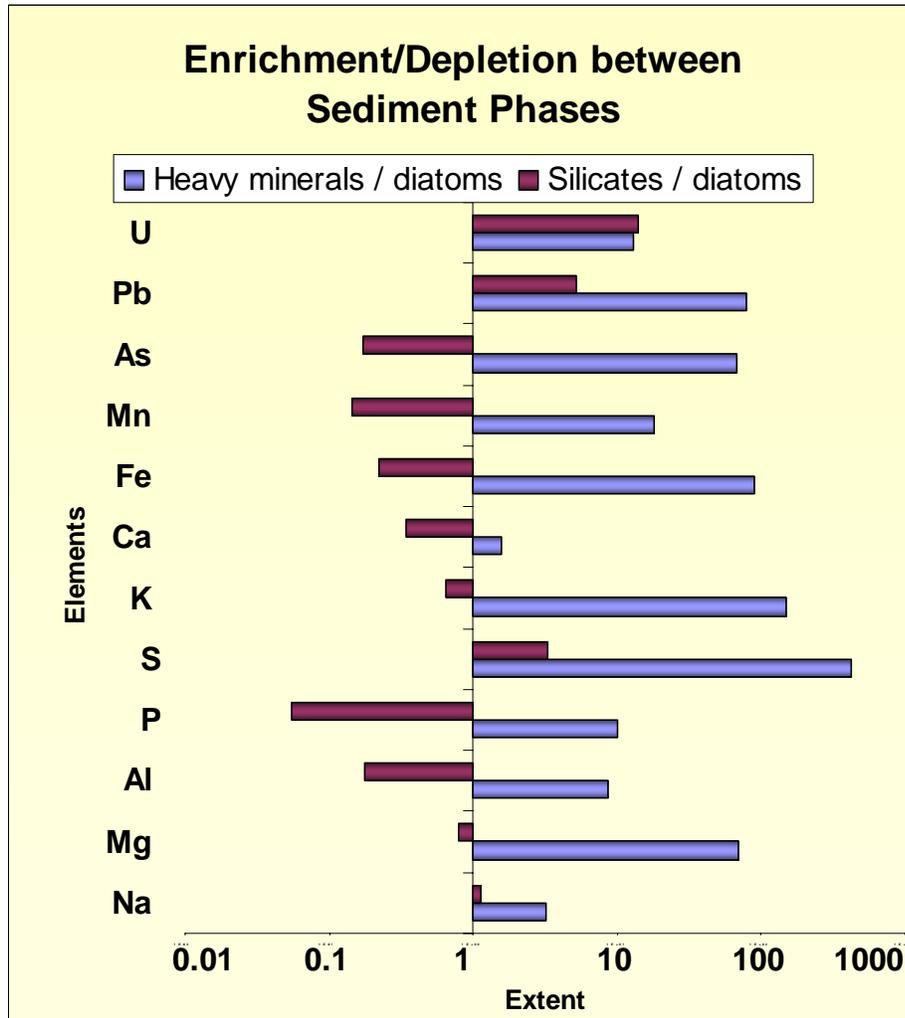


Figure 4-13: Comparison of the average concentrations for the elements of interest; heavy versus light fraction and medium versus light fraction. The bars on the logarithmic scale to the left of one represent enrichment in the diatom phase and subsequent depletion in the other phases. The bars to the right of one represent enrichment in the heavy mineral phase or the silicate phase and depletion in the diatom phase.

The concentrations of the elements Fe, Mn, P, S, As and K in the three different density fractions are plotted against depth (Figure 4-14a – f) and show a general enrichment in the heavy fraction but do not show clear signs of a progressive increase down the core. Sulfur and potassium in the high density phase are the exceptions to the general enrichment of these elements in the heavy mineral phase as the data show no consistent pattern down core. The only horizon that shows comparable enrichment in the low density phase is that containing the Tarawera tephra (June 10 1886).

Manganese concentrations are highest in the heavy fraction but they rapidly decline at depths below the tephra layer (~100 cm), which is likely related to its availability and subsequent depletion higher in the sediment column. Similarly phosphorus and arsenic concentrations are higher at depths greater than 100 cm. The highest P concentration (250mg/kg) was removed from the graph to bring the remaining data into range; it too is in the low density fraction and occurs at 65 cm depth. In the high density fraction P increases with increasing depth to approximately 85 cm then rapidly declines linearly from depths of 125 cm.

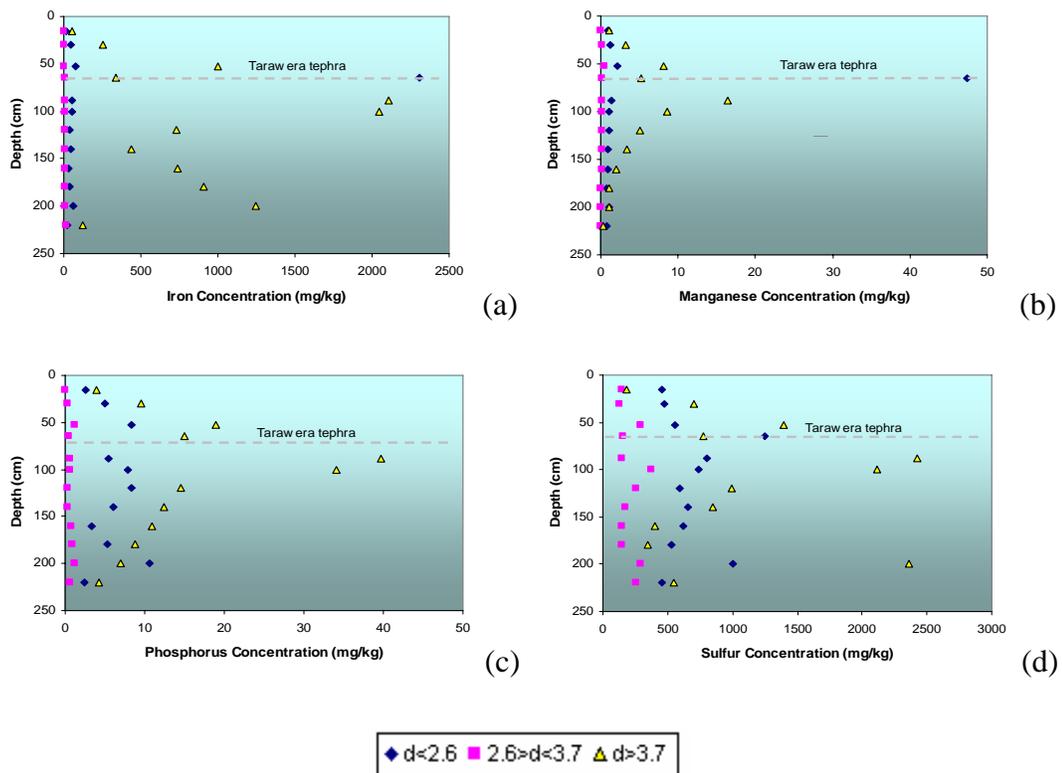


Figure 4-14: Solution analysis of the solids in core Ru79 from density separation method. Downcore concentrations of trace metals associated with the three density phases present in the solid. The dashed line represents the depth that the Tarawera tephra that is visible in the core.

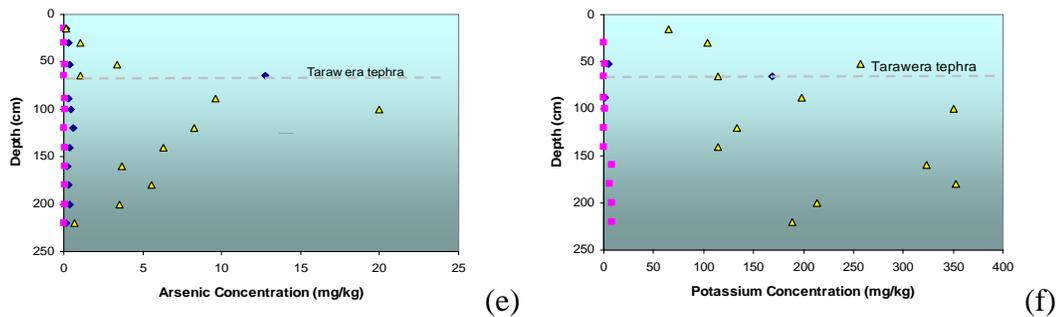


Figure 4-14: Continued.

The highest concentrations of iron are at similar depths (85 to 120 cm) however in contrast to phosphorus iron concentrations remain high to 220 cm. The coincidence of a phosphorus, manganese and iron maxima in the upper (100 cm) portion of the sediment column suggests associations in related mineral phases. Significant concentrations of sulfur occur in all three density fractions, possibly a result of its variable speciation and associations with particulates in each different phase (Perry and Pedersen, 1992). It too has a maximum at similar depths to iron suggesting that iron sulfide minerals have precipitated. Arsenic closely tracks the other elements showing similar behaviour with increasing depth. Although the concentration of potassium is relatively significant in the heavy fraction it does not appear to be responding to the same geochemical processes assumed to be operating in the anoxic sediment. It is likely that potassium is mainly present in detrital minerals.

In order to check if common mechanisms were responsible for the observed enrichments and depletions of elements between the phases the elements S, P, Al, As, Mn, Pb, K and Mg were plotted against Fe (Figure 14-5 a-h). With the exception of K (FIG. 14 h) there were significant correlations between the elements and iron in the heavy mineral phase. There is a striking agreement between iron and sulfur (Figure 15a); the strong correlation ($[Fe]=0.73[S]$, $R^2=0.7$) suggests approximately one quarter more sulfur than iron is present in the heavy fraction which is consistent with the ratio of Fe and S present in the form of pyrite (FeS_2). Figure 4-14(b-e) indicates that iron controls the concentration of phosphorus, arsenic and aluminium and to a

lesser extent Mn. The agreement between iron and phosphorus could indicate the presence of vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$). Aluminum and iron are expected to be in a (separate) mineral phase. Manganese and arsenic probably do not occur as discrete Mn or As compounds. They are more likely to be associated with an iron mineral in a solid solution (Carroll et al., 2002; Huerta-Diaz et al., 1993).

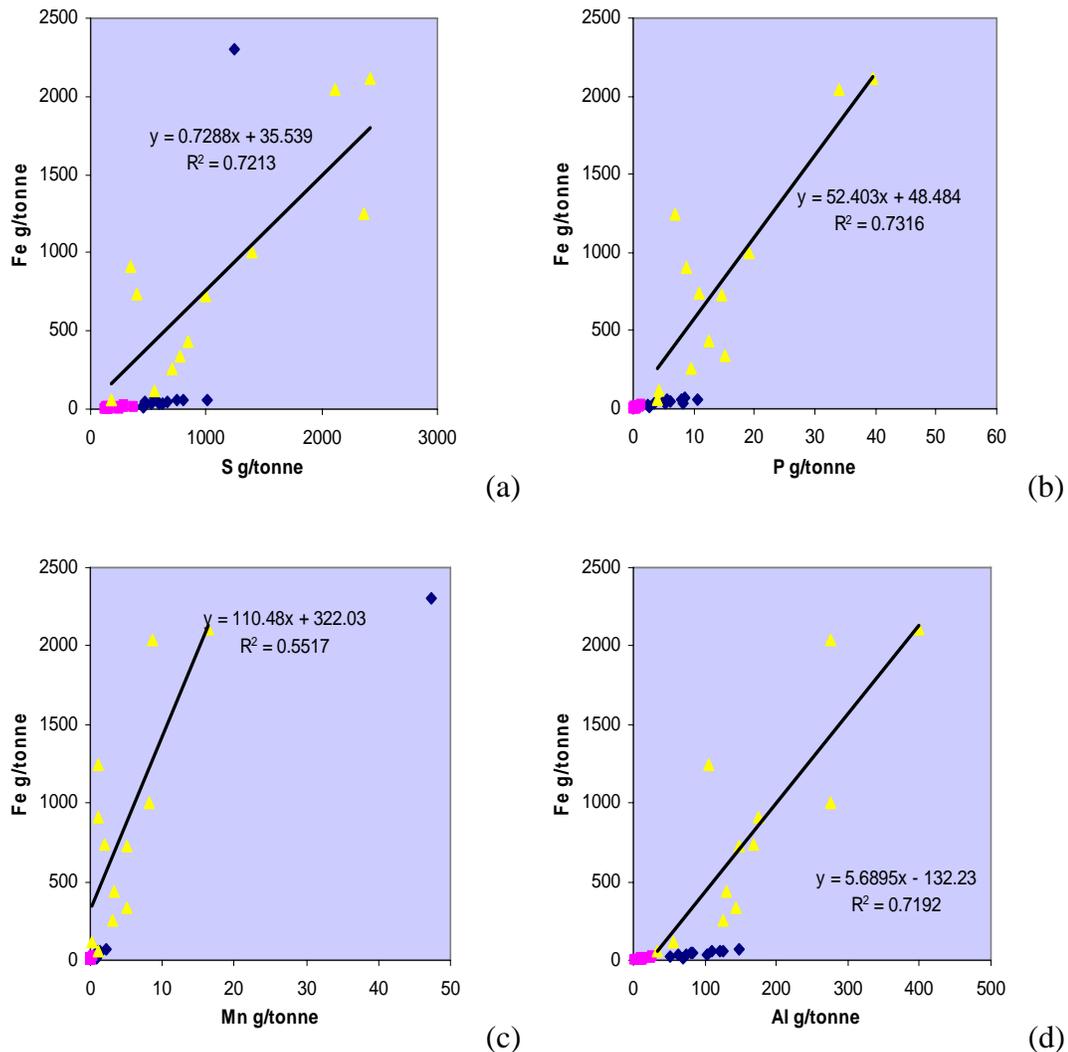


Figure 4-15: Solution analysis of the solid phase from density separation of Ru79 to identify relationships with iron. Correlating concentrations of iron (Fe) versus selected trace elements (a –h) within the three density fractions in the sediment of Lake Rotorua. Sulfur (S); phosphorus (P); manganese (Mn); aluminium (Al); arsenic (As); lead (Pb); magnesium (Mg); potassium (K).

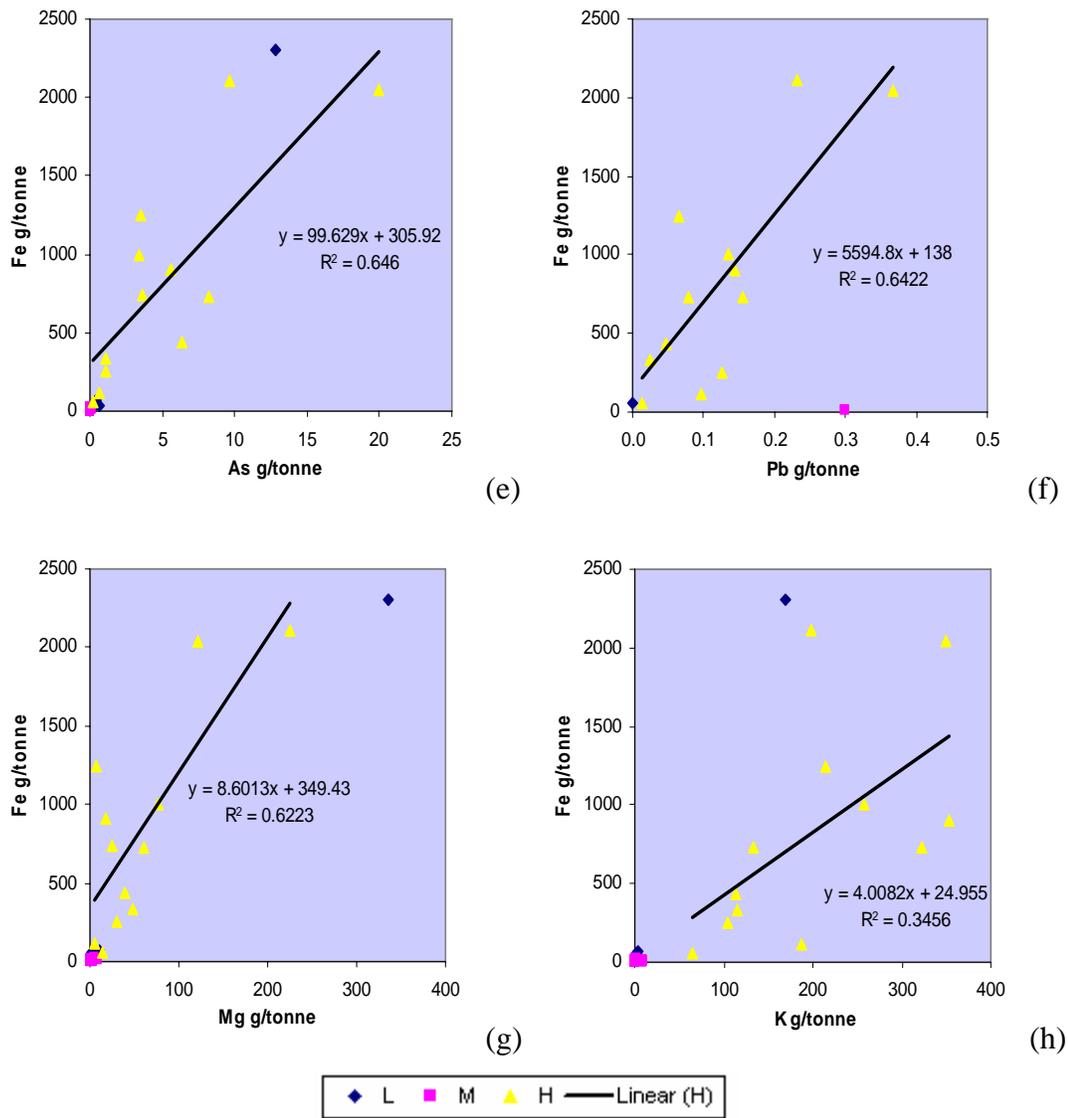


Figure 4-15 Continued.

Lead and iron (Figure 4-15f) and magnesium and iron (Figure 4-15g) show a correlation but on inspection the magnesium result may be the result of fortuitous composition of a small number of samples. The lead concentrations are very low and the correlation likely results from solid solution in coprecipitates.

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CHAPTER FIVE

DISCUSSION

5 DISCUSSION

5.1 SEQUENTIAL EXTRACTION

5.1.1 INTRODUCTION

This discussion is about the observed influence of the experimental conditions upon the extent of phosphate adsorption to various iron phases. A sequential extraction method was used to determine which dominant sedimentary mineral phase was involved in phosphorus retention in the sediments of Lake Rotorua.

The method was designed to gain insight into trace metal speciation and partitioning of elements amongst different geochemical phases. The desired sediment components are solubilized during each successive extraction and are found in the various leachates along with trace elements associated with them. The major sedimentary phases responsible for P mobility can be identified by this method of selective dissolution. The major operationally defined forms for Fe were: - reducible oxide and residual, for P: - residual, reducible oxide, and organic matter. Some of the species are clearly only associated with the less resistant phases. Aluminium was mainly present in residual, organic matter and reducible oxide fractions. Arsenic was only present in the same fractions but with variable distribution. Lead, copper and bismuth are present in very low concentrations and are liberated only in the reducible and mineral fraction of this scheme indicating heavy metal associations primarily with metal oxides and mineral phases. The alkali and alkaline earth metals are distributed across all of the phases. The solubility of these metals does not suggest they are being influenced by the same processes that are governing the release of iron or manganese. Alkaline earth cations (e.g. Ca and Mg) typically form outer-sphere complexes with Fe and Mn oxyhydroxides that are charge dependant and surface bound and so are highly reactive. Their adsorption to particles is often dominated by binding with organic coatings rather than directly with hydroxide groups, at least in circumneutral lakes (Koski-Vahala and Hartikainen, 2001; Tessier et al., 1996). It is possible then that their concentrations are due more to the effects of the treatments on the natural organic coatings ubiquitous to all aquatic particles. Treatments one and two resulted

in minimal dissolution in most cases; there is little solubilization of transition metals in either the water soluble phase or the exchangeable phase. It would be surprising to find significant water soluble ions in contact with lake water, or significant ion exchange capacity in sediment largely devoid of clay minerals. Treatments two, three and four deal with different types of surface reactivity; the extractants have caused the dissolution of elements that are affected by ion exchange, by the addition of protons, and by redox conditions. Mobilization is either a direct effect or a consequence of associations between metals and their carrier phases. Such is the case for lead, as it is only weakly affected by pH and redox its solubilization is due to links with reactive iron oxides (Davranche and Bollinger, 2000). Treatment five has attacked the oxidizable organic material in the sediment that remains undiminished after treatment with the previous extractants. Since iron and manganese mobilization is retarded in this step the focus of the discussion is directed at the organic phosphorus fraction. The extractant in treatment six releases some of the remaining elements which are held in lattice positions within the crystal structure of silicate minerals, resistant sulfides and refractory organic material (Tessier et al., 1979). Those which occur in refractory mineral phases represent the least extractable into an aqueous phase and most unreactive pool and require a more aggressive treatment to dissolve them. A more refined treatment would also distinguish between the various pools of iron (Fortin et al., 1993) including between a precipitate and a metallic coating and the various forms of iron present in the mineral phases (Poulton and Canfield, 2005). Considering iron and phosphorus are progressively dissolved through the treatments but manganese is largely released before the fourth treatment, the agreement between iron and phosphorus is a reasonable indication of the dominant iron phases serving as a sink of and the primary mechanisms involved in the retention of phosphorus. It is apparent that manganese is not playing as significant a role as iron as a phosphorus sink. This is likely to be related primarily to their differential redox chemistries (Anderson and Rippey, 1988) and the minor abundance of manganese oxides at depth compared to iron.

5.1.2 TRACE METAL MOBILIZATION

Trace metal contamination is a significant water quality issue and sediments can accumulate metallic pollutants derived from both natural and anthropogenic activities. Most metallic elements occur only as minor traces (with the exception of highly enriched sediments) (Davranche and Bollinger, 2000) but many are toxic to biological organisms. The associations they have with other geochemical phases put them at risk of being remobilized from the sediments and accessible to aquatic biota (Mucci et al., 2000). Trace element enrichment across the different phases is variable and aqueous levels are low, generally less than 10ppb. Selective dissolution data has produced a reasonable indication of phase associations and preferential metal adsorption. The data from these results shows a strong correlation between arsenic and iron, between aluminium and phosphorus and a weaker correlation between arsenic and manganese. Amorphous iron and aluminium hydroxides are reported to have a strong affinity for arsenic in natural systems but that adsorption is subject to arsenic speciation (Pierce and Moore, 1982). Lead and vanadium appear to be associated mostly with reducible oxides and reactive mineral phases whereas zinc and barium have been solubilized by all the extractants. Preferential sorption of lead to iron oxyhydroxides is common; Pb has a strong affinity for iron and is generally only mobilized when iron phases are completely dissolved (Davranche and Bollinger, 2000; Koski-Vahala and Hartikainen, 2001; Sigg et al., 1987). The distribution of lead and zinc in the residue phase is likely to be due to the associations of these trace metals with sulfide minerals (Brown et al., 2000). Aluminium has a similar distribution pattern to iron; its dissolution is significant in each step in particular the final three most abrasive treatments. The strong correlation between Al and phosphorus reflects the role of aluminium oxide as an important phosphate sorption component of the sediments. There is significant interplay between sedimentary iron and aluminium with regard to phosphorus retention and the two can be found exchanging their PO_4^{3-} ligands in anoxic conditions; the release of Fe and Al-bound P

occurs with the elevation of pH that typically accompanies anoxia (Koski-Vahala and Hartikainen, 2001).

Arsenic solubility is induced under reductive conditions and the remaining is released to a much lesser extent by oxidation of organic matter and by mineral dissolution but is not affected by the preceding treatments. Similar patterns have been described in the literature (Mucci et al., 2000; Pedersen et al., 2006). Mobilization of the heavy metal cations seems most apparent under reductive conditions indicating desorption from iron and manganese oxyhydroxides. The increased solubility at this point indicates associations with the amorphous and crystalline iron oxyhydroxides occurring as hydroxide coatings (adsorbing surfaces) on particles (Poulton and Raiswell, 2000). Metals that are mobilized in anoxic sediments will remain in an aqueous phase due to the destruction of their carrier oxide phase unless they are re-adsorbed onto another solid phase like clay or organic matter (Davranche and Bollinger, 2000). Transition metals (Mn, Cu, Ni, Co, Cr, Zn) are frequently being reported to associate with oxyhydroxides and with mineral phases in freshwater systems (Poulton and Raiswell, 2000) and marine systems (Jacobs and Emerson, 1985).

5.1.2 FRACTIONATION FE-MN-P

Fraction 1. Water soluble.

The very low level of Fe and P in the water soluble fraction is expected as sediments have been continuously exposed to water. Rehydration of the dried sample did yield significant amounts of manganese (relative to its overall concentration). This could be the result of chemical changes caused by dehydration. The water soluble P fraction is very labile and in a natural system it has generally been extracted before it reaches the sediments. Phosphorus carried to the sediments is expected to consist largely of biogenic P (Ruttenberg, 1992) or adsorbed onto sinking particulates. Mn present in sediments as a hydrated form was broken down when it was dehydrated and the product solubilized when rehydrated.

Fraction 2. Exchangeable.

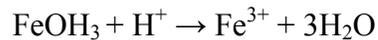
Overall the leachate has had little effect on a large proportion of the elements present in the Lake Rotorua sediments (figure 4.5). The magnesium ions have been effective in replacing some of the metals present on the surface of and loosely adsorbed to the various solids phases. The displacement by chloride anions for any loosely adsorbed hydroxyl ions of the surface of iron (oxy)hydroxide compounds was minimal (less than 10ug/L). In contrast to Fe the extractant has caused significant Mn dissolution (Figure 4.4). Phosphorus remains immobilized; PO₄ ions are not being displaced by Cl⁻ anions nor is Magnesium phosphate MgPO₄⁻ complex formation occurring as part of the reaction in this treatment (Ruttenberg, 1992). The cation exchange capacity (CEC) of solid material is governed by charge related reactions that are largely controlled by pH and ionic strength. Sediments and soils that have high clay content are actively exchanging anions and cations in adsorption/desorption reactions in the manner induced by this treatment. The paucity of clay minerals is likely to make ion exchange an insignificant feature of Lake Rotorua sediments.

Fraction 3. Weak acid/ligand exchange dissolution.

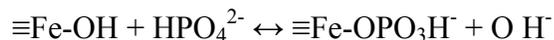
The weak acid wash effectively dispersed larger amounts of iron and aluminium into solution than the preceding treatments. Ligand exchange induced dissolution of iron and aluminium in this phase has been relatively effective. Only a minimal amount of phosphorus has been solubilized as a result of solubilization of host phases representing the labile inorganic P adsorbed on iron oxyhydroxides (Krom and Berner, 1981) and aluminium hydroxides (Lijklema, 1980) . The release of Mn in this treatment is very minimal as the previous two extractants removed a large proportion of the total Mn in the sediments.

Organic ligands are produced by bacteria (and aquatic plants) and are constituents of organic coatings/material on all nature of aquatic particles. They give solids a negatively charged surface to which metal cations are indirectly adsorbed. In this manner metal cations can act as carrier phases for a range of other dissolved ions and compounds. This is an effective mechanism for transferring material to the sediments and also for the remobilization of reactive material upon burial in anoxic sediments.

Sorbed metal cations are caused to be released by the addition of other cations and by protons, which destabilize organic complexes. The ligands themselves can cause the solubilization of Fe(III) especially when they are in excess (Luther et al., 1992). A ferric hydroxide cluster gains a positive charge to its surface by the addition of weak acids and Fe(II) ions go into solution as a result. During the process the central Fe(III) ion at a solid surface will exchange its structural OH groups:



The exchange of ligands and a high degree of protonation enhances the detachment of cationic surface groups that go into solution. Dissolution can be inhibited by phosphate ligands or by other cations such as aluminium blocking available binding sites and altering surface reactivity (Stumm and Sulzberger, 1991):



With the exception of freshwater systems influenced by acid mine drainage low pH values (<5) are uncommon in lakes and dissolution of this nature may not be a significant mechanism of P release (Koski-Vahala and Hartikainen, 2001). This same conclusion is suggested from the results of this treatment; P is not released to any large extent by the solubilization of either Fe or Al.

Fraction 4. Reducible Fe and Mn oxides.

In this treatment the extractant causes reductive dissolution of highly reactive Fe-Mn oxides (Shaw et al., 1990), amorphous oxyhydroxides (Brown et al., 2000) and poorly crystalline phases such as the easily reducible ferrihydrite and lepidocrocite. The more crystalline (and more resistant) iron phases such as goethite and hematite remain unaffected; they are generally selectively dissolved by a sodium dithionite solution extraction (Poulton and Canfield, 2005). Dissolution is induced by a transfer of electrons (the oxide serving as the donor species), a change in oxidation state and the generation of free ions into solution causing the release of other compounds associated the various metal oxide phases (Davranche and Bollinger, 2000). If the reductant is also a chelating agent it replaces the waters around the central Fe with other ligands, the molecule gets bigger which alters the charge distribution and facilitates Fe dissolution (Stumm and Sulzberger, 1991).

The concentrations of iron, phosphorus and aluminium increased considerably under reductive conditions. Most of the manganese has already been extracted. The small proportion of the remaining manganese (Figure 4.5) released is likely to be crystalline Mn (hydr)oxides and any Mn associated with crystalline Fe in the system (La Force and Fendorf, 2000). The chemical reduction of Fe and Mn oxides/oxyhydroxides results in the dissolution of their divalent ferrous and manganous forms. As a consequence of their removal from a solid phase Fe- and Mn-bound P is released (Shaw et al., 1990). Levels of aluminium are higher than in previous treatments, but only about 20% of the total aluminium is released. Predominantly it is Fe-bound aluminium being released; the extractant may have also had a slight affect on the aluminium components of silicate minerals and aluminium hydroxides (Tessier et al., 1979). Approximately half of the total iron is removed by the hydroxylamine-hydrochloride-acetic acid extraction, indicating that crystalline Fe oxides are abundant.

Arsenic is also a redox sensitive element and substantial concentrations of its reduced (and soluble) form, arsenite (As^{III}), is due to reductive dissolution of surface bound arsenate (As^{V}) compounds by the extractant. Arsenate incorporated into the structure of more crystalline iron oxides (goethite) will not be easily desorbed by this process (Pedersen et al., 2006). The reduction of arsenate is not dependent on the reduction of its Fe or Mn oxide host. Reductive dissolution of As^{V} can occur prior to the Fe-Mn oxide/oxyhydroxide carrier phases, as illustrated by a subsurface concentration maxima in pore water profiles at a higher position in the sediment column (Mucci et al., 2000). Although arsenic forms complexes with both Fe and Mn oxides in most cases it has been shown that the Fe-bound arsenic will be the larger fraction of the extractable particulate arsenic. In the pH range that the iron oxyhydroxide carries a negative charge the poorly crystalline Mn oxyhydroxides carries a positive charge and so iron is more favourable for As^{V} adsorption especially when it is diffusing up through oxic sediments encountering precipitating diagenetic iron oxyhydroxide (Belzile and Tessier, 1989; Mucci et al., 2000).

Fraction 5. Oxidizable organic matter.

The organic carbon content of the sediments has remained relatively stable until this point. The digestion of the biogenic material by acidified hydrogen peroxide is expected to release various forms of autochthonous-derived organic P including phosphosaccharides, nucleic acids, phospholipids and polyphosphates (Penn et al., 1995). The biogenic component of sediments includes a significant amount of microbial biomass that fixes P (Gachter and Mares, 1985) and which is released by oxidation. The Lake Rotorua catchment is not greatly affected by erosion and so the particulate organic material present is more typically from in-lake productivity. The freshly deposited material (seston) contains both labile and refractory organic fractions (Penn et al., 1995). and the organic P component is predominately derived from plankton (Krom and Berner, 1981). Seston is expected to contain high levels of soluble reactive phosphorus that is released under anoxic conditions either as the material settles through an anoxic hypolimnion or once it is buried into anoxic layers

(Gachter and Mares, 1985). Attack of the more resistant organic material by the extractant is analogous to anaerobic decomposition of the residual organic fraction in a natural system. A larger percentage of the total P in the sediments is released by the oxidation extraction than in the preceding treatments (Figure 4.5) and the concentration of P in this case is quite substantial (Figure 4.4). Although the labile P has been consumed or taken up by Fe compounds either by the time the seston reaches the sediments or in the initial stages of its burial, there is a larger portion of P associated with the organic fraction in the sediments that is potentially available for recycling under such conditions (Penn et al., 1995). As much as 30% of the total P in the seston (Figure 4.5) has been released by the oxidation extraction; 10% more than the Fe and Mn oxide phases but still less than release in the mineral phase. In the Lake Rotorua sediments the process of degradation of organic material plays a significant role in the release of dissolved phosphate to the pore waters. Phosphate diagenesis of this nature occurs below the zone of bioturbation and oxygen penetration and below the redox boundary in the anoxic zones where sulfate reduction and methanogenesis are occurring often at depths of about 5-10cm (Krom and Berner, 1981). The sulfidic zone in Lake Rotorua sediments is reported to be confined to the top one centimetre in the sediment column (Motion, in prep. 2007).

Precautions are recommended for this step in the scheme to ensure Fe and Mn remain in ferric and manganic solid phases; preventing Fe and Mn being oxidized reduces the potential for P to be readsorbed and for release be underestimated (La Force and Fendorf, 2000).

Fraction 6. Residual.

The concentrations of P and Fe obtained from this treatment (figure 4.5) would suggest the reagent has exposed the crystalline structure of Fe oxyhydroxides, caused the release of lattice bound Fe and the associated P (Belzile et al., 1989), and solubilized iron sulfide phases (Huerta-Diaz et al., 1993). Sulfides are expected to form because Lake Rotorua receives geothermal discharges including acid sulfate

waters. In Lake Rotorua sediments, the residual phase contained most of the P suggesting that once the P has entered this phase it is not likely to be remobilized readily. The proportion of the total iron that was extracted is also significant (Figure 4.5) indicating the iron mineral phases are relatively abundant and so could be the dominant P fixers. In the sediments of Lake Rotorua iron, copper, arsenic, lead, bismuth, aluminium and silver are distributed in the mineral phase as components of sulfides and crystalline Fe oxyhydroxides phases. Gallium concentrated in the mineral phases will be associated with the silicates as will some of the aluminium.

The presence or dominance of Fe oxide phases at depth in reducing layers of anoxic sediments was not generally expected to be significant however Fe(III) oxides have been found below the sediment surface to depths of 30 – 35 cm in marine sediments (Canfield, 1989) and similarly in the top 25cm in the sediments of a saltmarsh (Kostka and Luther, 1995). Wersin *et al.* (1991) also expected the reduced iron minerals (e.g. siderite, vivianite and iron sulfides) to be the abundant phases in anoxic freshwater sediments but instead found amorphous and crystalline Fe(III) oxides were present throughout the depths of sampling at some of their sampling sites. They suggested the slow rate of transformation of oxide phases in reducing sediments is responsible for them persisting in anoxic marine environments. Goethite is a highly resistant iron oxyhydroxide but is reactive to the hydrogen sulfide (H₂S) generated by sulphate reduction. At depths within and below the sulfidic zone it will be in the process of undergoing diagenetic dissolution serving as an oxidant and a source of aqueous iron for pyrite formation (Canfield, 1989).

The observed concentration of sulfide forming trace metals in the residual phase (figure. 4.4) such as iron, copper, silver, indium and lead suggests a similar behaviour to marine sediments. Arsenic is commonly found associated with iron sulfide minerals as well as with crystalline iron oxyhydroxides (Canfield, 1989; Jacobs and Emerson, 1985) and with the pyrite phase in marine sediments. Huerta-Diaz *et al.* (1998) reported 50% of the total arsenic in samples from reducing freshwater

sediments was sulfidized and suggested it was associated with acid volatile sulfides (AVS). The authors considered iron sulfides serve as temporary sinks incorporating downward diffusing arsenite either by simple adsorption, coprecipitation, or in solid solution formation. Microprobe analysis of a framboidal pyrite reported concentrations of As 800 -1000 ppm but overall results demonstrated that AVS is more likely the As sink (Mucci et al., 2000).

Approximately 50% of the total P in the sediment has been solubilized in this treatment (figure 4.5) suggesting there is a major P sink in the mineral phase. Pore water P has the potential to be adsorbed as surface species on diagenetic iron oxyhydroxides or precipitate out of solution as a discrete mineral. Phosphorus can also become structurally incorporated into diagenetic minerals during recrystallization of amorphous phases to minerals such as goethite (Luengo et al., 2006). Reduced iron minerals such as siderite are not efficient adsorbents of P (Curtis et al., 1986) as it the case in both marine and freshwater systems for iron sulfides (Krom and Berner, 1980). The reduced iron mineral vivianite more typically dominates freshwater lake sediments as the major reservoir for P. Nriagu and Dell (1974) reported encountering an abundance of vivianite nodules serving as a P sink in recent lake sediments.

5.2 DENSITY SEPARATION

Phase separation by density shows that the representative core (Ru79) of the sediments of Lake Rotorua consists of a low and a medium density fraction of siliceous skeletal debris (diatoms) and aluminium silicates respectively, and a high density fraction that contains iron sulfide minerals including framboidal pyrite. There are other iron minerals present of a slightly different physical and chemical nature, the identity of which have been more difficult to determine by SEM imagery without undertaking a detailed chemical and mineralogical analysis. The analytical XRF analysis for the isolated particles show weak fluorescence's for both manganese and phosphorus and may mean it is not possible to demonstrate conclusively by this

technique alone that these elements are associated with the mineral phases in the heavy fraction.

It was my intention to identify iron sulfide minerals using scanning electron microscopy to elucidate their presence and or role in Lake Rotorua sediments. Once identified only the cubical mineral particles were isolated for analysis and subsequently only the elements of interest (Fe, Mn, S and P) were selected for detection by XRF. The presence of other mineral phases was not investigated by this technique as the focus was on the diagenesis of iron-rich minerals. Due to the low abundance of calcium and magnesium in Rotorua waters the occurrence of carbonate minerals as a principal species was not thought to be significant; if it was expected to be important it would have needed to be investigated by other methods.

5.2.1 Mineral identification

Individual micron sized spherulitic particles were detected in the heavy fraction of the particulate material at depths particularly beyond 40 cm. In samples from the shallower 10 - 40 cm depth the particles were not as visually distinguishable amongst the abundance of fragmented debris and were not isolated for XRF analysis. It has since been noticed in the SEM images that the particles are indeed present at these depths (Figure 8c).

The particles observed exhibited a spheroidal form and were clearly aggregates of individual crystals as opposed to concretions adhered to the particle surface (Suess, 1967; Wilkin and Barnes, 1997). The partial elemental XRF analysis of these types of particles showed similar patterns detecting significant sulfur and iron implying that they are major components of the particles. These features are consistent with the characteristics of framboidal pyrite reported by Otero *et al.* (2003).

5.2.1.1 Pyrite

Pyrite (FeS_2) is a highly insoluble iron sulfide mineral. It is often a dominant crystalline phase common to water ways contaminated with sulfur-rich acid-mine

drainage (Lintnerova et al., 1999; Paktunc and Dave, 2002), to marine environments including those influenced by hydrothermal vents and to reducing environments in freshwater systems (Huerta-Diaz et al., 1993). The diagenetic formation of pyrite is generally governed by both iron and sulfate reduction occurring at a redox front between oxygen-rich and sulfide-rich conditions in the upper layers of sediments (Paktunc and Dave, 2002). The process is heavily influenced by the levels of organic carbon in the sediments, the abundance of reactive iron in the suboxic layers and the kinetics of mineral development. Under variable conditions different morphs of pyrite are likely to form (Passier et al., 1997). The formation of pyrite can be rapid and either a direct reaction between ferrous iron and sulfide species or as a succession of precursor transformations of less stable iron-sulfide compounds reacting with elemental sulfur (S^0) in a slow conversion to the end product which is often of a variable morphology depending on the pathway (Perry and Pedersen, 1992). Pyrite formation has been reported to also occur in the methanogenic zone providing the pore waters contain some hydrogen sulfide (H_2S) (Riedinger et al., 2005). Euhedral pyrite is reported by Roberts and Weaver (2005) to occur when concentrations of reactive iron are low and the rate of sulphate reduction is declining. The authors suggest this morph of pyrite precipitates directly from the pore waters without its iron sulfide precursor (greigite). Euhedral pyrite forms in the methanogenic zone and in some cases iron sulfide crystals will form simultaneously with the reduced iron carbonate mineral siderite that typically forms in this zone (Roberts and Weaver, 2005). Anaerobic oxidation of methane (AOM) can also exhaust the supply of interstitial sulfate and subsequently pyritization in the sediments will be arrested if sulphate is not replenished from the overlying water. Sulfate reduction driven by (AOM) releases HS^- leads to the diagenetic alteration of primary minerals and the formation of secondary minerals (Riedinger et al., 2005).

5.2.1.2 FRAMBOIDAL PYRITE

Framboidal pyrite is a secondary iron sulfide mineral and a common form of pyrite that occurs as spherical clusters of crystals. The genesis of this distinctive

morphology versus individual pyrite crystals is controlled by the chemistry of the porewaters, in particular the degree of supersaturation relative to the concentration of Fe(II) and sulfide. (Paktunc and Dave, 2002) Framboidal pyrite forms in the presence of abundant reactive iron during early diagenesis when sulphate reduction is rapid. The formation of framboids is thought to result primarily from the self assemblage of pyrite crystals that have formed from precursor iron-sulfide minerals (e.g. iron monosulfides (FeS) and greigite (Fe₃S₄)) (Paktunc and Dave, 2002; Wilkin and Barnes, 1997). The transformation of individual pyrite crystals into framboid structures in a tailings basin can result in irregular aggregates, densely packed spherical aggregates and polyframboids. The transformations are considered to be related to the magnetic properties of the minerals (Wilkin and Barnes, 1997). The morphology of the framboidal pyrite reported by Wilkin and Barnes (1997) resembles the pyrite particles that are observed in the solids of Lake Rotorua sediments.

The manganese sulfide mineral alabandite (MnS) has a density of 3.99 g cm⁻³ (Weast, 1988), it has a cubic morphology and crystals are reported to occur individually or in clusters. Alabandite forms in marine environments particularly in hydrothermally-influenced basins; the mineral crystals have a very similar appearance to the pyrite crystals observed in this study (Perry and Pedersen, 1992; Suess, 1967). In general the manganese concentration in Lake Rotorua sediments is about two orders of magnitude lower than iron. At such low concentrations the chances of observing discrete MnS minerals by random SEM imagery must be very low. There was also no major fluorescence for manganese in the analysis of the cubic particles to suggest they were MnS. Any Mn occurring in the heavy minerals of the sediments would more likely have been taken into the iron and sulfur mineral phase during the process of diagenetic transformations and will only be a minor component. This argument would support Mn depletion with depth that has been reported by (Motion, in prep. 2007) from pore water analysis in a subsequent study on Lake Rotorua sediments.

5.2.1.3 IRON-RICH

The most likely candidates for the non-sulfidic iron minerals with a similar morphology to the one observed are the crystalline Fe(III)-containing phase goethite (αFeOOH) and the Fe(II)-containing carbonate phase siderite (FeCO_3). Both minerals are formed diagenetically in subsurface environments although in different zones (Glasauer et al., 2003; Mortimer et al., 1997; Roh et al., 2003). Goethite has a density of $3.2 - 4.3 \text{ g cm}^{-3}$ (Weast, 1988) it is likely to be present in the heavy mineral fraction ($d > 3.7 \text{ g cm}^{-3}$) in the sediments of Lake Rotorua. It could even be a dominant iron mineral phase which could explain the enrichment of iron in the solid phase profiles. Goethite is repeatedly being reported to bind P during its formation which means it plays a role as a P sink in oxic sediments but which also means it may be a significant P source in anoxic sediments (Fortin et al., 1993). Siderite has a weak affinity for phosphate and will not generally take up interstitial phosphorus that has been released by reductive dissolution of iron oxide phases (Krom and Berner, 1980). It has a density of 3.96 g cm^{-3} (Weast, 1988) and a rhombohedral form occurs naturally in anoxic environments (Mortimer et al., 1997) so is expected also expected to be in the heavy mineral fraction.

5.2.1.4 Goethite

Goethite is a highly insoluble crystalline ferric iron mineral that is ubiquitous in a variety of aquatic and terrestrial oxic environments and has a strong affinity for phosphorus. It is the end-product of a suite of transformations of amorphous and poorly crystalline hydrous Fe(III) oxides. The recrystallization of iron oxides to goethite is more favourable when low concentrations of pore water P have an inhibitory effect on the formation of other P-fixing iron minerals thus leaving Fe(III) ions available for goethite (Glasauer et al., 2003). Goethite crystals have a variety of morphologies (platy, tubular, cubic and acicular) that is commonly reported in soil studies. Although there was some resemblance between cubic goethite and the particles in the SEM images, closer inspection revealed a more rhombohedral nature of the crystals in the image suggesting they were not goethite.

The presence of goethite in the sediments of Lake Rotorua can not be ruled out solely on the basis of a lack of visual evidence, as the occurrence of iron oxyhydroxide phases in the sulfidic zone or deeper still in the methanogenic zone is recognized in other studies (Canfield, 1989; Perry and Pedersen, 1992; Wersin et al., 1991). Transformations of iron oxides phases in these zones occur at a slow rate which could account for them being present in anoxic sediments. The rate of transformation is slower with greater distance from the sediment-water interface and is also related to the age and degree of crystallinity of the mineral (Wersin et al., 1991). The Reductive dissolution of well crystallized iron oxides in anoxic sediments occurs when they become less thermodynamically stable as they encounter the prevailing Eh-pH conditions (Karlin and Levi, 1983). The persistence of goethite at depth is due to its low solubility and selective reactivity to dissolved sulfide species. Goethite resistance to dissolution is greater than other less crystalline iron oxide phases which are more reactive and tend to be exhausted in the initial stages of pyrite formation. Goethite reactivity is preferential to hydrogen sulfide (H₂S) and can remain largely unaffected by reactions with other pore water sulfide species forming precursor pyrite crystals (iron sulfides) (Canfield, 1989; Perry and Pedersen, 1992).

5.2.1.5 SIDERITE

Siderite is a Fe(II)-containing iron carbonate mineral that is abundant in iron-rich and sulfide-poor reducing sediments, in both marine and freshwater environments (Postma, 1981). Siderite typically precipitates in alkaline conditions from supersaturated pore waters; it forms below the sulfidic zone where bacterial reduction of sulfate has generated favourable conditions for carbonate mineral precipitation. Siderite precipitation is promoted by methanogenesis which liberates iron and bicarbonate ions in the process of iron oxide reduction occurring in the methanogenic zone (Mortimer et al., 1997; Paktunc and Dave, 2002). In sulfidic-rich sediments siderite formation is often limited by pyrite formation as it is reactive to dissolved sulfide (Roberts and Weaver, 2005; Roh et al., 2003) in which cases it serves as a precursor for iron sulfides that are eventually transformed into pyrite (Paktunc and

Dave, 2002). In Lake Rotorua sediments the depth of the sulphate reduction zone is reported to be restricted to the top 1cm and much occurs above the sediment column (Motion, in prep. 2007) and means that siderite formation occurs high in the sediment column throughout the depth of the methanogenic zone.

Roh *et al.*(2003) reported the formation of single rhombohedral crystals and also of siderite globules and flakes of siderite crystals and that the different morphs were formed by different bacteria. Apart from the microbial assemblage the other important parameters influencing the morphology of siderite were the concentrations of aqueous carbonate and the concentrations of appropriate electron donors in reducing sediments (Roh *et al.*, 2003). Lim *et al.*(2004) describes the sequential growth of spherulitic siderite aggregates. Siderite crystallites featured centre-margin variations that they found was related to characteristic zones in the sediments. Manganese was concentrated in the centre and iron on the outer layers of the crystallite as a function of depth and the subsequent availability of the metals. They also suggest a reduction in Fe incorporated into siderite when it becomes depleted at which stage Mn is then taken up into the structure.

5.2.1.6 VIVIANITE

Iron-phosphate minerals were not observed in the high density ($>3.7\text{g cm}^{-3}$) fraction of the Lake Rotorua diatomaceous ooze. The dominant ferrous-phosphate mineral vivianite has a density of $2.58\text{ (g cm}^{-3}\text{)}$ (Weast, 1988) so is more likely to be found in the medium density fraction. The medium density ($2.6 > d < 3.7\text{g cm}^{-3}$) and low density fractions ($d < 2.6\text{ g cm}^{-3}$) were too voluminous to allow observation of the small quantities that are likely to be present. Vivianite and precipitations of Fe(II)PO_4 compounds are reported by Roden and Edmonds (1997) to be the dominant solid phases responsible for significant PO_4^{3-} immobilization in reducing sediments. Vivianite is considered the most stable Fe(II) orthophosphate solid that forms in sedimentary environments and the dominant mineral responsible for phosphorus immobilization particularly when it is not competing with calcium for the available

phosphorus (Glasauer et al., 2003; Nriagu, 1972) or with siderite for the ferrous iron (Postma, 1981). Vivianite forms under similar conditions to siderite with the exception of high levels of internally derived phosphate and low calcium content and with organic matter as the reducing agent as opposed to H₂S (Stamatakis and Koukoulzas, 2001). It does not form in sulfidic sediments of lakes as pyrite formation limits the amount of available Fe (Emerson, 1976; Roden and Edmonds, 1997) or when the formation of siderite has a similar competitive advantage (Emerson and Widmer, 1978).

Vivianite precipitates below the sediment-water interface from pore water fluids saturated with reduced iron and in alkaline conditions (pH 6.9), with a low redox potential ($E_h \leq 0$) and in the absence of sulfide ions (Nriagu and Dell, 1974). Such conditions are generated below the zone of sulfate reduction activity where methanogenic microbial reactions produce bicarbonate ions that cause an increase of alkalinity that is favourable for vivianite precipitation (Curtis et al., 1986; Paktunc and Dave, 2002; Stamatakis and Koukoulzas, 2001). The strongly supersaturated porewaters are considered to be the result of the slow kinetics of vivianite mineral precipitation (Postma, 1981). It is proposed that the formation of vivianite could be promoted over the formation of reduced sulfide minerals if the reduction sequence bypasses Fe and S and proceeds to methanogenesis. This is potentially possible during the decomposition of refractory organic material (Anderson and Rippey, 1988).

5.2.1.7 IRON SULFIDE

The crystal morphology in the unknown spherulitic solid particles (Figures 4.11 a & c,) is different to that of the other crystals observed. They appear to have more a hexagonal form as opposed to cubic. The solid particle in figure 4.11(e) has an appearance unlike any of the other particles. Aging could be a reasonable explanation for the variable shapes of the crystal in these images; they could be at various stages of development. Diagenetic dissolution of less stable mineral phases is a dominant

process that accounts for some of the variations in mineral morphology (Riedinger et al., 2005). The XRF analysis for the solid particles in figure 4.11 (b, d & f) shows a similar ratio of Fe to S to the other spectrums for pyrite. Variable forms of pyrite reported to be present in the methanogenic zone. The iron sulfide pyrrhotite has as platy morphology and greigite occurs as cubo-octahedra; both have similar X-ray energy dispersive spectra (not XRF). Greigite (Fe_3S_4) would be expected to be present under conditions of low concentrations of pore water sulphate when pyrite formation is arrested and subsequently greigite can accumulate (Roberts and Weaver, 2005).

5.2.1.8 THE DOMINANT MINERAL

Sulfate reduction and methanogenesis are two of the dominant processes that influence iron sulfide mineral formation as well as the formation of other reduced iron minerals below the sulfidic zone and subsequently have a significant influence on what minerals are being utilized as oxidants and source species in the process (Mortimer et al., 1997; Paktunc and Dave, 2002).

The results raise some questions about the identity of the dominant mineral acting as the phosphorus sink in the sediments of Lake Rotorua. Despite P occurring in some of the spectra corresponding to pyrite particles, pyrite does not generally play a significant role in P immobilization (Emerson, 1976), and unless it is the dominant mineral phase pyrite may not be present in significant enough abundance to remove large quantities of P from solution.

There was significant dissolution of phosphorus in the residual phase of the sequential extraction, the solution analysis of the three density fractions showed the highest concentrations of iron and phosphorus was in the heavy mineral fraction and the x/y plots showed there was a strong agreement between iron and phosphorus in the heavy fraction. It seems apparent then that the mineral phase that is concentrating phosphorus in the heavy fraction can be only be inferred from these results. Faced with similar disparities Emerson and Widmer (1978) came to the conclusion that

crystalline iron phosphate (Fe(III)PO_4^{3-}) minerals often found in anoxic lake sediments were in fact not being distinguished by X-ray diffraction due to a lack of crystallinity of recent mineral formation. Wersin *et al.* (1991) also found discrepancies between XRF and microscopic analysis and thermodynamic predictions. They could not confirm the presence of iron phosphate or iron carbonate mineral phases suggesting they too may have been below the limits of sensitivity of the XRF analysis. They did successfully identify non-crystalline Fe(III) oxide phases during the course of their investigation and came to the conclusion that amorphous Fe(III) oxides were present in reducing sediments because iron transformations are extremely slow.

Although phosphorus-rich solid particles were not identified by SEM and XRF in the sediments of Lake Rotorua they do support to the sequential extraction results. Collectively the results indicate that the phosphorus is localized in solid iron phases rather than homogeneously distributed in the sediments and that the iron phases which include crystalline iron minerals, are those that have a strong affinity for phosphorus and fix significant quantities of porewater phosphorus during diagenesis.

5.2.2. DENSITY FRACTION ENRICHMENT AND TRACE METAL ASSOCIATIONS

Solution analysis of the three fractions in the solid phase has revealed a substantial enrichment of sulfur, a reasonable enrichment of iron, arsenic and lead and a moderate enrichment of manganese, phosphorus, aluminium and uranium in the heavy minerals compared to the diatoms. This pattern of preferential phase association is similar to the results in treatment 6 (residual phase) of the sequential extraction. The inclusion of sulphur in the solution analysis has provided additional evidence for the presence of reduced sulphur species in the heavy minerals. The enrichment of the sulfide forming trace metals lead and arsenic in the heavy mineral fraction is in line with the sequential extraction results for the residual phase.

Depth profiles indicate an abundance of iron and sulfur in the heavy minerals which suggests a predominance of iron sulfides in the heavy density fraction. Although the down core analysis does show the highest concentrations for all the elements are in the heavy mineral phase it does not show enrichment as a function of depth in every case. The profile for manganese shows very low concentrations in the low and medium density fractions, but there is evidence of its enrichment in the heavy mineral phase. Manganese oxides (MnO_2) are used as oxidants high in the sediment column and are typically consumed within the top few centimeters. The subsurface maxima in the heavy fraction would be due to Mn substitution of Fe in more resistant phases rather than the formation of discrete manganese minerals such as rhodochrosite (MnS). The slow kinetics of mineral formation in freshwater sediments does not favour the precipitation of MnS (Wersin et al., 1991) which would explain why they are not being distinguished in any of the heavy mineral analyses. Motion (in prep) has shown that rhodochrosite is not thermodynamically favoured.

Because of scatter in the results for iron, sulfur and potassium it is not possible to discern if there is a systematic trend with depth. It is that likely iron and sulfur are being redistributed between their various forms within the sediment column as they go through diagenetic dissolution/precipitation processes. A progressive enrichment of phosphorus is occurring at depths above the Tarawera tephra that is a fair indication of its release in the upper layers and subsequent incorporation with precipitating iron phases. The profile for arsenic is similar suggesting it is either being affected by the same processes or is in the same phase as phosphorus. Both profiles also show a progressive decrease in concentration following the Tarawera tephra although the host phases (Fe and S) are still abundant. Figure 4.14 shows a concentration pulse at the depth corresponding to the Tarawera Tephra in all the profiles. The eruption was a significant source of material derived from basaltic scoria, rhyolite clasts and/or Rotomahana mud initially deposited into Lake Rotorua sediments at the time of the event (Jones and Lowe, 2005). Elsewhere in the sediment column the metals occur in considerably smaller (trace) amounts. The substitution of

Al(III) for Fe(III) in the lattice structure of an iron mineral is often seen in the simultaneous release of both elements down the core suggesting the same processes govern the development of both profiles (Wersin et al., 1991) In this case it is suggested by the agreement between aluminium and iron in the x/y plots. Similarly the strong agreement between iron and the other elements (except K) in the x/y plots indicate they are associated with iron minerals in the heavy mineral fraction.

5.2.1.9 METHOD CONCLUSIONS

Based on the visual information and the X-ray analysis it seems apparent that iron-sulfide minerals are present as framboidal pyrite in the largely organic ooze but it remains to be determined conclusively if pyrite is a dominant crystalline phase. The XRF analysis detecting significant sulfur fluorescence's confirms they are not precipitations of the Fe(II)-containing minerals vivianite or siderite. The XRF spectrum corresponding to the iron-rich particle isolated in the sample lacks a P peak that would otherwise suggest the presence of an iron-phosphate mineral phase in the heavy fraction of the sediments. Due to time restrictions it was not possibly to demonstrate conclusively the preferential occurrence of phosphatic material in the iron-rich particle by other techniques and so the presence of an iron-phosphate mineral as a dominant phase can not be confirmed solely by SEM observations and corresponding spectra.

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CHAPTER SIX

CONCLUSION

6 CONCLUSION

In the environment iron often plays a role in binding phosphates in the sediments of lakes. Phosphate is a biologically significant nutrient that is linked to the development of problematic toxic algal blooms that are affecting water quality. Iron is a redox sensitive element and is highly responsive to changes in pH and Eh. Conditions within the sediment column that affects iron phases ultimately control the phosphate exchange processes between sediments and overlying waters. The release of iron-bound phosphorus in the reducing sediments is a consequence of diagenetic transformations that are occurring in response to variable chemical conditions.

The adsorption capacity of the sediments and its ability to retain phosphorus may become diminished by seasonal variations in the thickness of the oxidized microzone that is related to the extent of organic loading and can result in the exchange of dissolved phosphate between sediment pore waters and the overlying waters. Soluble compounds that diffuse into the anoxic bottom waters can be mixed into surface waters recharging them with dissolved phosphate. This process of regeneration of nutrients from the sediments is responsible for increasing the concentrations of phosphorus that are available to fuel algal blooms.

6.1 SEQUENTIAL FRACTIONATION

Understanding the distribution of phosphate amongst the various iron phases in the sediment is paramount to appreciating the prevailing conditions under which it is mostly to be liberated into a solution. The results from the sequential extraction scheme have demonstrated how the major sedimentary components in the sediments of Lake Rotorua respond to a range of conditions analogous to a natural system.

Sedimentary manganese oxide phases are dissolved readily under the least aggressive conditions. Manganese is present in more resistant fractions only as minor components of various mineral phases. Exchangeable and acid soluble manganese and aluminium species that are displaced by magnesium and by protons at the solid surface do not have any phosphorus associated with them, neither are they present in

the same phase. Aluminium is generally abundant in various sedimentary phases, and aluminium hydroxides have an affinity for orthophosphate similar to ferric iron; it is often involved in phosphorus retention either directly and indirectly at different stages of mineral diagenesis. Phosphorus is primarily associated with iron oxide phases and other iron mineral phases which play a dominant role in its cycling and in its sequestration in the reducing sediments.

Iron oxides, oxyhydroxides and crystalline mineral phases are abundant in the sediments; their dissolution is attributed with more aggressive conditions. Ion exchange reactions are not an effective mechanism for desorption of reactive iron in sediments with low clay content. In contrast the more reactive Fe(III) phases are quite sensitive to acidity; even a weak acid is sufficient to destabilize surface bound metal ion complexes. Iron (hydr)oxides associated with particulate material as surface coordinated complexes are caused to dissolve by the addition of protons to the media. The same desorption effect can occur by mechanisms that involve organic compounds with acidic functional groups. There are minimal quantities of phosphorus bound to the iron species that are affected by protonation.

The reducible iron and manganese oxide phases contained in the sediments are converted to their divalent forms when they serve as oxidants in the absence of more thermodynamically favourable species (oxygen and nitrate). A considerable quantity of phosphorus is associated with reducible iron oxide phases and is released into solution during reductive dissolution of iron in anoxic sediments. Crystalline oxide phases (e.g. goethite) are resistant to mildly reducing conditions and require stronger reductants (e.g. sulfides) and lower (more negative) redox potentials to cause them to be solubilized.

The sediments of Lake Rotorua are rich in organic-bound P which is released when organic material is oxidized under conditions analogous to anaerobic degradation. The amount of organic-bound P released is substantial; the degradation of refractory organic material represents a significant source of phosphorus for incorporation into

diagenetic minerals forming in oxic and anoxic layers of the sediment. The largest proportion of the total phosphorus in the sediments is present in the mineral phase.

Sedimentary pore waters are precipitating iron mineral phases that are forming due to the abundance of and also at the expense of reactive iron phases, including the less reactive crystalline minerals. Iron diagenesis in these sediments is extensive; iron is being cycled between ferric and ferrous phases with significant amounts going into amorphous and crystalline mineral phases. The proportion of total iron released from the mineral fraction is only slightly less the proportion of total iron released from the reducible fraction indicating these fractions contain the dominant iron phases in the sediments. The sulfide forming trace metals, arsenic, copper and lead, are mostly in the reduced and mineral phase which suggests an iron carrier phase in both cases.

The phosphorus associated with Fe(III) oxide/oxyhydroxides is released when the various forms of iron in the host phases are buried deeper into anoxic sediments. In reducing layers the redox potential is lower, the oxides are less stable and subsequently ferric iron is transformed to ferrous iron, liberating the orthophosphate ion during the process. The phosphorus dissolves in the pore waters and is not only more mobile but is more reactive in a soluble form than when it was associated with the ferric iron phase. Dissolved phosphorus can migrate back up into the oxic layers of the sediment column and be reintroduced into the water column thus serving as a source of reactive phosphorus. The reducing sediments serve as a sink for phosphorus when instead the liberated Fe(III)-bound P is taken into a mineral phase and cannot diffuse up into the oxic zone to be recycled at the sediment water interface.

Iron solubilization, and the subsequent release of phosphorous is most effective under reducing conditions. The progressive lowering of the redox potential in anoxic sediments can cause the solubilization of the more resistant iron phases. Conditions induced by excessive organic loading that promote this type of reaction will be responsible for the remobilization of substantial quantities of phosphorus from phases that otherwise serve as a highly efficient sink.

6.2 DENSITY SEPARATION

In order to determine whether the sediments in Lake Rotorua are serving as a sink or as a source of phosphorus it is essential to be more familiar with various aspects of the phosphorus-binding nature of the sediments. This will enable us to better understand the degree of influence the sediments are having on algal productivity. Retrieving and sampling sediment cores gives us a snap shot of what dominant processes are operating in this system and how particular components are behaving. The information improves our understanding about the stability of the sediment system. Such knowledge can then be applied to predict the effects of a major disturbance such as dredging.

The results from the heavy mineral separation method have demonstrated the dominance of iron and sulfur in the heavy minerals, the importance of iron as a reactant for sulfide and the role of an iron mineral phase as a sink for phosphorus in the sediments of Lake Rotorua.

The heavy fraction of the sediments contains abundant iron mineral phases that have taken up dissolved phosphorus during the process of diagenesis. The iron phases are present to the depths of sampling, approximately 225 cm below the oxic zone of the sediments, but Fe(III) and Fe (II) phases cannot distinguished.

The conditions in the reducing sediments are favourable for the precipitation of pyrite and for framboidal pyrite formation. The framboids are detected at almost all depths whereas different iron sulfide minerals are only first detected at around 130 cm depth in the sediment column. Framboidal pyrite may not be a dominant mineral phase and the abundance of non- framboidal pyrites are not known. Framboidal pyrite is not the dominant P-bearing mineral phase.

Manganese is not present in the heavy fraction as a discrete mineral phase and plays a minor role as component of other more abundant minerals. Levels of Mn are low in the heavy fraction and there is minimal correlation between concentrations of iron

and manganese to imply they are in the same mineral phase. It is not involved in the incorporation of P to any large extent.

Sulphur is enriched in the heavy fraction of the sediments and is taking reduced iron into solid phase during the formation of iron sulphide minerals. The observed enrichment of sulfur and iron in the heavy fraction and good agreement between these elements indicate they are in the same mineral phase. The presence of framboidal pyrite confirms this association.

Apart from iron sulfide minerals iron-rich particles are present in the sediments that are of variable morphology and in various stages of development. The most likely candidate is siderite. Their identification could be confirmed by speciation calculations that would indicate if precipitation was thermodynamically favourable and therefore occurring in the reducing sediments of Lake Rotorua.

Particles are present in the heavy fraction that concentrate iron and sulfur but do not have the framboidal morphology. They are likely to be iron monosulfides or alternatively are other forms of pyrite present in the methanogenic zone. The particles have similar XRF spectra to pyrite but variable crystal morphology to framboidal pyrite. The iron sulfide greigite (Fe_3S_4) is involved in pyrite formation. It has a different morphology and it forms in the methanogenic zone.

Non-sulfide iron-rich minerals are first detected at a depth of 130 cm. The density of siderite is in the range of the heavy fraction. Siderite is an iron-rich mineral with a rhombohedral morphology similar to the particles in the images confirming its presence in the heavy fraction. Vivianite has a density of 2.58 gm cm^{-3} and is not present in the heavy fraction by its own devices but may have been taken into the heavy fraction indirectly and which would account for the observed iron and phosphorus enrichment. There is a good agreement between iron and phosphorus that could indicate the presence of mineral vivianite. The crystalline iron oxide mineral goethite could be present to these depths. Goethite has a density just within the range

of the heavy fraction. It is likely to be dissolving and it would be releasing the phosphorus it fixed in the oxic zones.

Phosphorus is localized in solid iron phases rather than randomly distributed in the sediments of Lake Rotorua. The dominant iron phases that fix pore water P during reductive dissolution/precipitation processes include crystalline iron minerals. Vivianite is the most likely candidate but as goethite is often found in reducing sediments it is likely to be present in the heavy minerals. Goethite could be a dominant iron mineral phase in shallower depths of the sediments which would explain the enrichment of iron in the solid phase profiles. The presence of siderite is confirmed but its abundance is unknown and it does not have a strong affinity for phosphorus so could not be the dominant P-fixing iron phase in the heavy mineral fraction.

In a concurrent study, Motion (in prep 2007) has determined the sulfidic zone of the sediments of Lake Rotorua is restricted to the top 1cm and so there is a strong possibility of vivianite and siderite formation occurring high in the sediment column. Furthermore positive saturation indices obtained by Motion (in prep 2007) support the precipitation of these minerals despite them not being detected in the heavy minerals. The results are inconclusive as to whether the crystalline iron oxide mineral goethite is present at depth in the sediment column and to whether it is contributing to a proportion of the phosphorus that is present in the mineral phase of the sediments. This type of distinction would require more extensive analysis.

APPENDIX ONE

SEQUENTIAL EXTRACTION ANALYSIS DATA

Sequential Extraction Data

Analyte	Water Sol.		Loosely Sor.		Weak acid		Reducible		Org. material		Residual	
	1.00	STDEV	2.00	STDEV	3.00	STDEV	4.00	STDEV	5.00	STDEV	6.00	STDEV
Li	1.33	0.13	1.08	1.72	1.29	2.52	0.58	1.07	2.16	0.49	2.70	1.38
B	1.31	0.20	0.93	1.12	1.48	2.39	1.69	0.97	0.28	0.18	1.48	2.40
Na	382.26	26.13	83.53	186.94	231.14	318.15	17.63	68.10	180.60	72.47	217.28	130.60
Mg	0.00	17.91	309.26	728.25	51092.60	2514.78	8347.38	3857.03	1142.54	420.40	384.96	200.68
Al	30.51	1.98	443.09	85.51	322.23	41.62	3775.17	500.52	3879.96	242.19	13466.21	6221.05
P	0.90	0.25	0.00	1.04	1.14	0.29	1356.12	192.85	0.00	125.22	3744.98	1205.66
P correct	1.80	0.49	0.00	2.07	2.28	0.58	2712.23	385.71	3701.11	250.44	7489.97	2411.32
K	128.60	15.82	85.74	55.44	104.23	86.01	270.90	66.58	133.56	50.73	249.02	142.08
Ca	341.74	71.85	132.28	149.09	127.26	58.94	299.51	49.31	323.93	21.00	371.77	162.46
V	0.01	0.01	0.06	0.21	0.00	0.23	22.05	2.32	6.72	0.58	6.47	2.08
Cr	0.00	0.02	0.71	0.30	0.00	0.76	25.08	2.02	4.93	0.95	4.19	2.22
Cr	0.00	0.49	5.93	3.46	3.88	0.62	5.47	0.79	-0.39	0.85	0.00	16.34
Fe	3.49	0.84	7.50	15.19	160.24	38.64	12019.98	1607.31	218.67	47.10	10450.90	4845.99
Mn	309.98	23.31	113.20	19.93	33.36	6.99	94.90	12.82	35.51	2.48	41.30	16.33
Co	0.47	0.03	0.05	0.48	0.44	0.82	0.31	0.15	0.76	0.06	0.51	0.19
Ni	0.50	0.25	2.54	6.14	5.47	13.31	-0.76	2.38	1.04	0.51	1.44	1.52
Cu	0.05	0.01	0.14	0.28	0.00	0.21	0.26	0.20	5.71	1.11	4.31	1.47
Cu	0.05	0.01	0.03	0.30	0.00	0.21	0.30	0.21	5.73	1.06	4.37	1.43

Sequential Extraction Data

Analyte	Water Sol.		Loosely Sor.		Weak acid		Reducible		Org. material		Residual	
	1.00	STDEV	2.00	STDEV	3.00	STDEV	4.00	STDEV	5.00	STDEV	6.00	STDEV
Zn	18.42	1.48	6.88	1.37	8.62	9.66	25.56	5.50	11.26	5.12	11.38	6.00
Zn	17.96	1.45	7.16	1.25	8.70	9.24	27.63	5.56	10.93	5.05	12.49	5.92
Ga	0.02	0.00	0.00	0.01	-0.01	0.00	0.96	0.13	0.25	0.04	6.23	2.23
As	0.47	0.28	0.00	0.18	0.95	0.20	231.93	36.53	52.26	4.24	58.48	19.43
Se	0.00	0.14	3.28	2.35	3.65	0.69	1.05	0.31	1.11	0.22	0.00	8.72
Se	0.04	0.02	0.00	0.07	0.07	0.05	0.46	0.07	1.80	0.19	0.02	0.18
Sr	2.65	0.52	2.57	1.26	1.56	0.70	4.39	0.87	3.09	0.25	3.29	0.91
Ag	0.00	0.00	0.04	0.01	0.00	0.01	0.08	0.08	0.71	0.25	2.71	0.93
Cd	0.09	0.03	0.09	0.12	0.11	0.14	-0.08	0.24	0.08	0.07	0.00	0.24
In	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	-0.12	0.00	0.17	0.06
Ba	3.77	0.21	8.92	4.13	21.84	4.99	58.95	13.60	3.05	2.15	53.67	12.65
Tl	0.10	0.01	0.05	0.02	0.04	0.01	0.39	0.08	0.20	0.02	0.00	0.03
Pb	0.00	0.03	0.15	0.22	0.13	0.27	4.25	0.55	-0.43	0.12	6.82	1.51
Pb	0.00	0.03	0.14	0.22	0.12	0.26	4.19	0.54	-0.45	0.12	6.77	1.51
Pb	0.00	0.03	0.14	0.22	0.13	0.27	4.27	0.55	-0.44	0.12	6.85	1.53
Bi	0.00	0.00	0.01	0.00	0.00	0.00	5.59	11.14	-0.06	0.15	3.38	6.05
U	0.02	0.01	0.02	0.02	0.07	0.02	0.95	0.23	0.42	0.07	0.48	0.15
U	0.01	0.00	0.00	0.00	0.02	0.00	0.46	0.09	0.20	0.02	0.22	0.04

APPENDIX TWO

DENSITY TREATMENT ANALYSIS DATA

Density Separation Data

d<2.6		Li 7	B 10	Na 23	Mg 24	Al 27	P 31	S	K 39
15	1 T1	-0.00465	-0.79469	3294.501	2.020756	68.6873	2.329841	452.7546	-3.10965
30	2 T1	0.001411	-0.732	3796.097	3.986594	80.62983	4.756879	476.1932	-1.19665
52.5	3 T1	0.038505	-0.79364	4232.261	10.75912	148.2814	8.135723	554.8102	4.367527
65	4 T1	2.00095	-0.44367	596.1674	335.815	3526.987	250.0121	1249.076	169.1158
88.5	5 T1	0.036283	-0.76475	5584.03	6.843366	125.3037	5.217851	800.7573	1.12896
100	6 T1	0.01635	-0.7739	4848.293	3.929541	109.0575	7.711927	741.589	-1.03299
120	7 T1	0.006399	-0.79692	3699.993	3.258559	104.1413	8.044562	595.2445	-1.94455
140	8 T1	0.007854	-0.83367	4646.813	2.628428	84.03398	5.876177	660.7052	-2.58932
160	9 T1	-0.00502	-0.78397	4025.506	1.449867	63.73439	3.107528	618.0077	-3.52171
180	10 T1	-0.00761	-0.78848	3683.985	1.171458	73.44297	5.03301	528.3403	-3.74311
200	Blank	0.008861	-0.8057	3937.952	1.8521	121.7526	10.30816	1006.046	-3.40106
220	1 T2	-0.00859	-0.80565	3565.028	0.881108	51.87129	2.189373	454.9551	-4.19906
	mean	0.008162	-0.78849	4119.496	3.525536	93.72149	5.701003	626.3094	2.449761

d<3.7

15	2 T2	-0.01689	0.362021	2455.173	0.103408	2.940599	-0.19063	148.2422	-1.811
30	3 T2	-0.01891	1.732098	3077.499	0.827061	12.46444	0.149438	127.4362	0.055857
52.5	4 T2	-0.00543	1.866488	3102.8	7.814749	35.82741	1.394651	292.2219	2.113059
65	5 T2	-0.01243	1.734058	2737.106	2.318061	16.59859	0.472609	155.8052	0.583069
88.5	6 T2	-0.01603	1.548297	2697.648	3.590231	15.3564	0.595925	143.2864	0.179085
100	7 T2	-0.01175	2.681619	3199.424	3.165583	18.68349	0.558336	369.3065	0.935322
120	8 T2	-0.0164	1.909175	2607.36	12.70042	13.25444	0.187084	254.0306	-0.16497
140	9 T2	-0.02067	1.768968	2519.356	0.516146	5.868421	0.10426	171.6272	-0.66981
160	10 T2	-0.00942	6.170499	7384.254	1.232897	14.84553	0.055844	145.6037	11.17289
180	blank	-0.01066	5.938501	7645.428	0.321945	16.74878	0.230568	141.8056	8.211659
200	1 T3	-0.0015	9.525626	8663.68	0.386489	33.35809	0.542857	290.9281	11.39921
220	2 T3	-0.00822	9.44425	7954.971	0.196407	11.62953	-0.16188	251.7701	10.61911
	mean	-0.01235	3.904322	4664.327	2.805031	16.45247	0.315132	212.3871	8.020856

d.>3.7		Li 7	B 10	Na 23	Mg 24	Al 27	P 31	S	K 39
15	3 T3	0.030677	59.56105	1027.792	20.61155	47.16087	4.359943	181.825	91.73607
30	4 T3	0.301629	343.2801	10710.16	125.524	531.0912	30.34514	702.9983	440.3915
52.5	5 T3	0.711044	708.7923	15536.44	331.6837	1185.297	71.78284	1395.701	1105.312
65	6 T3	0.625471	486.1193	14365.15	290.4815	874.3177	76.03991	774.7824	696.3373
88.5	7 T3	1.018587	567.725	14036.61	1120.623	1980.425	185.1221	2117.494	985.8761
120	9 T3	0.364887	421.4226	12565.72	286.8088	701.5117		997.1385	631.2407
140	10 T3	0.31493	423.5385	14191.06	202.0329	679.068	57.48343	848.6525	590.5568
160	blank	0.327226	1169.005	15625.14	130.7324	867.4206	51.379	400.6032	1672.691
180	1 T4	0.428979	1604.618	16725.74	120.0539	1131.866	43.68774	343.3509	2293.407
200	2 T4	0.166866	857.4104	14585.37	43.44039	584.019	40.29891	2364.795	1192.118
220	3 T4	0.153897	844.7837	16452.92	33.45889	387.5378	25.04788	546.8126	1317.974
	mean	0.381872	700.0137	13145.7	241.497	809.5398	56.61189	989.9371	1036.329

d<2.6		Ca 43	V 51	Cr 52	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 63	Cu 65
15	1 T1	-2.13979	0.069858	-0.13146	-0.39257	14.59395	0.870254	-0.01842	-0.09226	0.060502	0.037232
30	2 T1	0.080265	0.133169	-0.13199	-0.33463	42.38199	1.263897	-0.01361	-0.08409	0.008878	-0.01024
52.5	3 T1	1.475037	0.195053	-0.09857	-0.30006	73.77574	2.104102	-0.00659	-0.07428	0.021706	0.004708
65	4 T1	132.5142	3.840545	0.280848	0.555838	2305.213	47.3564	0.479625	0.34969	0.922302	0.928491
88.5	5 T1	1.233267	0.058052	-0.08254	1.874361	56.41534	1.385506	-0.01116	-0.05682	0.026262	0.004196
100	6 T1	-1.23779	0.106945	-0.12433	0.368749	54.5685	1.05611	-0.01368	-0.07755	0.013436	-0.00958
120	7 T1	-1.88749	0.15132	-0.14054	-0.32761	38.18939	1.043845	-0.01357	-0.08882	0.008997	-0.00919
140	8 T1	-2.12365	0.07843	-0.14543	0.370407	44.81321	0.903978	-0.01827	-0.08351	0.004541	-0.01881
160	9 T1	-1.11685	0.090828	-0.14016	-0.06281	32.77874	0.872094	-0.01705	-0.0858	0.000483	-0.02077
180	10 T1	-2.34509	0.119117	-0.14392	-0.32838	38.248	0.71514	-0.01763	-0.09044	0	-0.01996
200	Blank	-1.85643	0.160153	-0.14183	-0.15482	57.92543	1.001847	-0.01697	-0.08942	0.010724	-0.00911
220	1 T2	-2.7854	0.068264	-0.15154	-0.34436	24.59909	0.727779	-0.01941	-0.09284	-0.0057	-0.02539
	mean	1.630097	0.111926	0.021791	0.48948	43.48085	1.085868	0.003876	0.008743	0.013621	0.018007

d<3.7		Ca 43	V 51	Cr 52	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 63	Cu 65
15	2 T2	-2.98868	0.00026	-0.11078	-0.35052	-2.44998	0.017266	-0.01645	-0.07174	-0.01053	-0.02456
30	3 T2	-2.82838	0.010549	-0.10491	-0.4014	2.107686	0.112248	-0.02042	-0.08089	-0.00899	-0.02445
52.5	4 T2	2.788809	0.041805	-0.09303	-0.32668	24.50728	0.513597	-0.0153	-0.07231	-0.00875	-0.02167
65	5 T2	-2.04405	0.012306	-0.07193	-0.32141	4.579894	0.215702	-0.01702	-0.05118	-0.00586	-0.01922
88.5	6 T2	-2.31408	0.015798	-0.12442	-0.41838	7.056179	0.254205	-0.01827	-0.08509	-0.01375	-0.02549
100	7 T2	-1.66585	0.014149	-0.1092	-0.0141	13.21468	0.164934	-0.01855	-0.07356	-0.01097	-0.0239
120	8 T2	-1.615	0.013257	-0.11936	-0.38059	9.823559	0.245056	-0.01308	-0.07397	-0.00804	-0.01896
140	9 T2	-3.73731	0.002529	-0.14705	-0.45633	0.009483	0.105038	-0.02086	-0.08116	-0.01469	-0.02519
160	10 T2	-1.20325	0.018785	0.109823	-0.11877	12.57118	0.111175	0.002144	-0.01053	0.02326	-0.00475
180	blank	-2.2405	0.020939	-0.08207	-0.21059	13.34503	0.064215	-0.00024	-0.05548	0.01925	-0.00878
200	1 T3	-1.83072	0.024025	0.619292	1.135171	20.61474	0.093829	-0.00064	-0.04305	0.025433	-0.00213
220	2 T3	-1.30523	0.015472	-0.06618	0.372568	4.158587	0.051721	-0.00141	-0.05672	0.010698	-0.01583
	mean	1.063166	0.016143	0.131284	0.349669	9.541675	0.157571	0.007813	0.027954	0.000265	0.007208

d.>3.7		Ca 43	V 51	Cr 52	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 63	Cu 65
15	3 T3	16.85179	0.118799	1.012586	0.992676	79.77229	1.462217	0.032542	0.641152	0.658897	0.706176
30	4 T3	138.1826	2.326783	1.452595	2.990464	1075.555	13.45197	0.211481	1.917464	1.852655	2.053416
52.5	5 T3	367.5876	2.426365	3.741604	38.55735	4299.715	34.97914	0.551011	4.158935	3.31517	3.763166
65	6 T3	192.3438	1.848763	1.120168	3.579456	2041.452	31.28923	0.468543	2.457794	1.429541	1.850258
88.5	7 T3	448.7269	5.446694	3.333505	26.89316	10504.79	81.48698	1.812641	2.991442	5.119249	5.67649
120	9 T3	169.0751	2.266292	2.051921	9.154109	3465.703		0.567286	2.525704	2.427641	2.825026
140	10 T3	142.6956	1.705033	1.654644	11.81619	2257.861	17.59012	0.394923	2.054606	5.860854	6.175785
160	blank	302.285	2.683862	4.65328	37.98431	3806.547	10.07736	0.442362	5.157451	3.530409	4.473911
180	1 T4	408.8574	0.836174	6.038385	34.60572	5886.993	7.073968	0.318383	4.947504	4.686933	5.941194
200	2 T4	194.0913	0.453397	2.879938	17.65059	6961.816	6.296373	0.149581	3.013564	3.984845	4.738734
220	3 T4	214.3934	-0.07695	2.625412	4.262402	838.4043	1.644318	0.173134	3.72193	2.738087	3.38757
	mean	243.0597	1.818645	3.096387	18.9467	3917.716	19.34027	0.482234	3.204975	3.417474	3.999147

d<2.6		Zn 66	Zn 68	Ga 71	As 75	Se 77	Se 82	Sr 88	Ag 109	Cd 111
15	1 T1	0.055033	0.051098	0.011467	0.115967	-0.08766	-0.01089	-0.01012	-0.01521	-0.00528
30	2 T1	-0.1328	-0.11309	0.017027	0.306584	-0.06164	-0.01343	-0.00027	-0.01393	-0.00606
52.5	3 T1	-0.07483	-0.05139	0.031419	0.404031	-0.04837	-0.00907	0.018286	-0.01432	-0.0052
65	4 T1	5.637426	6.468017	0.814668	12.79471	0.315813	0.089301	1.963529	0.172412	0.05977
88.5	5 T1	-0.12405	-0.08501	0.031791	0.298259	1.077622	-0.01377	0.01945	-0.0035	0.009823
100	6 T1	-0.1926	-0.16296	0.02623	0.47846	0.081752	-0.01576	0.000198	-0.00998	-0.00035
120	7 T1	-0.17793	-0.1493	0.028388	0.605137	-0.05798	-0.01169	0.004234	-0.01453	-0.00746
140	8 T1	-0.13896	-0.11855	0.021531	0.40679	0.128277	-0.01491	-0.00737	-0.01223	-0.00128
160	9 T1	-0.21103	-0.19431	0.014059	0.194073	-0.0272	-0.01406	-0.00541	-0.01285	-0.0042
180	10 T1	-0.23325	-0.21024	0.016954	0.314045	-0.06486	-0.01526	-0.00116	-0.01337	-0.00528
200	Blank	-0.19464	-0.15059	0.026432	0.350412	-0.01309	-0.01405	0.016363	-0.00926	-0.00428
220	1 T2	-0.24467	-0.23192	0.011876	0.121514	-0.06802	-0.01366	-0.01004	-0.01463	-0.00565
	mean	0.093207	0.103249	0.021561	0.326843	0.078075	-0.01332	0.002195	-0.01217	-0.0032

d<3.7		Zn 66	Zn 68	Ga 71	As 75	Se 77	Se 82	Sr 88	Ag 109	Cd 111
15	2 T2	1.326258	1.365515	0.002009	0.002679	-0.07055	-0.01098	0.019163	-0.01604	-0.00681
30	3 T2	3.152632	3.20528	0.004667	0.033009	-0.08444	-0.01663	0.050996	-0.01954	-0.00744
52.5	4 T2	2.464234	2.493749	0.007715	0.060151	-0.07993	-0.0157	0.05284	-0.01696	-0.00592
65	5 T2	2.37518	2.389523	0.004498	0.013749	-0.07605	-0.01519	0.036834	-0.01731	-0.00628
88.5	6 T2	2.781482	2.919	0.005965	0.052425	-0.09022	-0.01612	0.05154	-0.01901	-0.00732
100	7 T2	2.232483	2.180241	0.005124	0.061675	-0.04	-0.0132	0.029477	-0.01433	-0.002
120	8 T2	2.773771	2.848101	0.004898	0.033615	-0.07963	-0.012	0.047591	-0.01852	-0.00679
140	9 T2	3.120264	3.232888	0.004231	0.06419	-0.09074	-0.01415	0.060251	-0.02057	-0.00856
160	10 T2	12.86378	12.96092	0.002704	0.102085	-0.04377	-0.00573	0.292504	-0.00918	0.002377
180	blank	10.91459	10.93095	0.002412	0.113282	0.012592	-0.01404	0.23105	-0.01312	0.004825
200	1 T3	12.39637	12.15789	0.008084	0.086336	0.21618	-0.01422	0.217043	-0.00967	0.025251
220	2 T3	11.89286	11.62113	0.001194	0.017461	0.110117	-0.01481	0.192605	-0.01229	0.004421
	mean	6.237611	6.224332	0.004455	0.056992	-0.02185	-0.01342	0.113187	-0.01538	-0.00072

d.3.7		Zn 66	Zn 68	Ga 71	As 75	Se 77	Se 82	Sr 88	Ag 109	Cd 111
15	3 T3	91.99039	95.65077	0.024181	0.243613	-0.01486	-0.00674	2.655136	0.055941	0.092031
30	4 T3	545.314	557.6774	0.226587	4.412359	1.150478	-0.0385	15.25249	0.673427	0.748469
52.5	5 T3	1207.442	1149.285	0.50693	14.57592	13.9492	0.13368	30.33387	1.246243	2.036824
65	6 T3	821.7304	843.7728	0.394562	6.555113	0.672549	-0.09192	23.3113	0.447619	1.195643
88.5	7 T3	937.1085	968.8993	0.854865	47.87185	10.11278	0.149689	28.34093	2.286851	2.212007
120	9 T3	707.3619	731.8498	0.367168	39.1621	3.182501	0.031358	20.24269	1.368327	1.680762
140	10 T3	728.1102	748.1984	0.325008	32.76536	5.10943	-0.00756	19.02494	0.934713	1.510406
160	blank	1900.699	1829.361	0.403579	18.97913	14.28222	0.148464	46.60369	3.598884	3.242571
180	1 T4	2551.557	2471.044	0.454115	36.3275	11.58328	0.261409	62.60918	2.742283	4.175007
200	2 T4	1483.093	1440.496	0.260604	19.72877	6.424681	0.185481	39.53266	1.375483	4.783941
220	3 T4	1538.318	1592.404	0.152065	4.485003	0.442454	-0.13283	39.4279	1.129495	2.222348
	mean	1169.344	1158.719	0.35751	21.85516	6.622217	0.072446	30.40235	1.541165	2.270437

d<2.6		In 115	Ba 137	Tl 205	Pb 206	Pb 207	Pb 208	Bi 209	U 238
15	1 T1	0.000144	-0.01439	0.086267	-0.00581	-0.00576	-0.00489	0.005374	0.001631
30	2 T1	9.11E-05	0.011974	0.075257	-0.00842	-0.00906	-0.00756	0.003506	0.001912
52.5	3 T1	0.000149	0.082362	0.058328	-0.01165	-0.01224	-0.011	0.002924	0.003172
65	4 T1	0.005056	26.54301	0.010915	1.334502	1.287489	1.336345	0.055092	0.129084
88.5	5 T1	0.000148	0.130963	0.017919	0.00079	0.003801	-0.00064	0.005085	0.00311
100	6 T1	9.88E-05	0.081604	0.05493	-0.01388	-0.01314	-0.01339	0.003408	0.002371
120	7 T1	9.62E-05	0.013905	0.066735	-0.01684	-0.01771	-0.01597	0.002213	0.002261
140	8 T1	5.34E-05	0.011594	0.049313	-0.0148	-0.01389	-0.01475	0.003152	0.001977
160	9 T1	9.66E-05	-0.03865	0.064546	-0.01638	-0.01623	-0.01609	0.002464	0.001498
180	10 T1	9.69E-05	0.014532	0.068205	-0.01603	-0.01628	-0.01526	0.001986	0.001889
200	Blank	0.000101	0.313307	0.054123	-0.01611	-0.01621	-0.01571	0.002316	0.003121
220	1 T2	4.83E-05	-0.0644	0.062664	-0.01777	-0.01835	-0.01695	0.001738	0.001062
	mean	0.000102	0.049345	0.059844	0.007555	-0.01228	-0.01202	0.003106	0.002182

d<3.7		In 115	Ba 137	Tl 205	Pb 206	Pb 207	Pb 208	Bi 209	U 238
15	2 T2	7.44E-05	1.268916	0.0675	-0.01414	-0.01481	-0.0134	0.001377	3.72E-05
30	3 T2	9.72E-05	2.608161	0.052746	-0.01945	-0.02017	-0.01857	0.001507	0.000194
52.5	4 T2	8.97E-05	2.370261	0.046112	-0.0166	-0.01687	-0.01601	0.001615	0.000628
65	5 T2	8.49E-05	2.146408	0.046722	-0.01706	-0.01761	-0.01634	0.0014	0.000297
88.5	6 T2	9.32E-05	2.472382	0.041195	-0.01789	-0.01883	-0.01715	0.001398	0.00028
100	7 T2	9.07E-05	2.22559	0.031064	-0.01737	-0.01601	-0.01764	0.002585	0.000408
120	8 T2	0.000135	2.448632	0.035682	-0.01901	-0.01982	-0.01811	0.001258	0.000225
140	9 T2	9.73E-05	2.82465	0.035353	-0.01974	-0.02052	-0.01887	0.001751	0.000146
160	10 T2	0.000373	7.563329	0.07062	-0.01706	-0.01785	-0.01664	-0.00023	0.000233
180	blank	0.000289	6.208003	0.061031	-0.0205	-0.02075	-0.01993	-0.00034	0.000289
200	1 T3	0.000182	6.693671	0.052728	0.387761	0.387307	0.37995	0.00059	0.000636
220	2 T3	0.000265	6.489214	0.057247	-0.01883	-0.01667	-0.0191	0.000309	0.000177
	mean	0.000162	3.924801	0.050116	0.038833	0.018638	0.018594	0.001075	0.000296

d.>3.7		In 115	Ba 137	Tl 205	Pb 206	Pb 207	Pb 208	Bi 209	U 238
15	3 T3	0.003549	147.9837	-0.0015	0.01979	0.017865	0.019609	-0.00078	0.001323
30	4 T3	0.021928	742.8396	-0.01218	0.538936	0.540886	0.532114	0.018517	0.013644
52.5	5 T3	0.044081	1549.972	-0.01342	0.582155	0.566343	0.563948	0.055101	0.028748
65	6 T3	0.038111	1225.386	-0.00673	0.149455	0.119564	0.150203	0.000747	0.029144
88.5	7 T3	0.036838	1438.707	0.004093	1.15015	1.120329	1.121499	0.066074	0.057888
120	9 T3	0.033068	1074.206	-0.00171	0.370019	0.351774	0.358616	0.025086	0.025086
140	10 T3	0.032123	1022.103	-0.0063	0.246276	0.234938	0.245016	0.13416	0.022675
160	blank	0.08726	2854.192	0.026663	0.807764	0.800493	0.792009	0.065445	0.038782
180	1 T4	0.098028	3992.555	0.103893	0.940906	0.869688	0.930851	0.104731	0.051109
200	2 T4	0.063157	2278.085	0.079777	0.361654	0.367637	0.357665	0.031911	0.023933
220	3 T4	0.078781	2394.57	-0.01374	0.676964	0.694369	0.665972	0.03023	0.016489
	mean	0.049881	1749.521	0.016557	0.589461	0.556432	0.55873	0.053047	0.027968