CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

This chapter is divided into two main sections. The first is an overview of palaeontology, specific to this study. It covers terms, definitions and a general literature review, and concludes with a short motivation for this study. The second section deals with general chemistry related to processes in palaeontology and mineral oxide coatings.

1. PALAEONTOLOGY

1.1 Composition and chemistry of bone and tooth

All bone material was once living tissue before the onset of fossilization. It consisted of water (20%), organic (30 to 40%) and inorganic material (40 to 50%). The organic component is the fibrous collagen, whereas the main inorganic component is hydroxyapatite comprising calcium carbonate and calcium phosphate. The properties and synthesis of apatite has been extensively examined (Skinner, 2004). Apatite strongly sorbs metals (Gauglitz *et al*., 1992), has a high adsorption capacity for actinides and other heavy metals, low water solubility ($Ksp>10^{-40}$), and high stability under reducing and oxidising conditions. Synthetic production of apatite can be carried out through calcium and phosphate precipitation reactions or high temperature solid state processes (LeGeros, 1991), or obtained from apatite ores, or derived from animal bones by heat treatment (Joschek *et al*., 2000) or treatment with hydrogen peroxide (Erts *et al*., 1994). The heat treatment method produces apatite of a higher crystallinity.

Tooth material is composed of an inner dentine core and an outer enamel layer, which is the hardest material of the body (Plenderleith and Werner, 1971; Von Endt, 1984). The enamel has a chemical composition of approximately 95-98% inorganic material, with 90-92% of this consisting of a modified form of calcium phosphate, namely hydroxyapatite ($Ca_5(PO_4)_3OH$). Enamel also consists of 1% protein (enamelins and amelogenins, unique to enamel) and 4% of water. The tooth's bulk is comprised of dentin which also contains a high percentage (although lower than the enamel) of hydroxyapatite. The organic composition of dentin comprises approximately 90% collagen and 10% other proteins. There is also 5-10% by mass of water (Wesson, 1942; Skinner, 2004; Chng, *et al*., 2005).

1.2 Fossil bones and teeth, preservation through natural processes

Organisms vary from microscopic soft-bodied protists to large creatures that are constructed by an enormous variety of substances, ranging from soft tissues that rarely are conserved as fossils, to hard tissues such as bones and teeth, commonly represented in the fossil record. Post-mortem processes introduce change and their traces are often unpredictable (Johanson and Edgar, 1996). There is a range of probability of preservation. This range is directly influenced by the anatomy and structure of the organism. Approximately 98-99% of species known from fossils consisted of hard tissues (Lyman, 1994). The harder parts also vary in their resistance to physical and chemical destruction, thus the correlation between skeletons and their potential for fossilization is not clearly defined. Hard part materials are often characteristic of a particular group.

There are two methods by which hard parts can be produced (Lyman, 1994; Skinner, 2004).

1) The use of enzymes to catalyze normal inorganic reactions (e.g., calcite, silica).
2) Deposition of organic substances (e.g., cellulose, chitin).

The inorganic substances are more likely to be soluble, and therefore are most easily decomposed by inorganic or organic solutions, whereas organic substances are more likely to be insoluble, but most vulnerable to oxidation.

After burial, preservation of the hard tissues as fossils depends upon the chemical condition of the surrounding sediment, and this may or may not reflect the conditions in which the organisms used to live. Normally, preservation of organisms possessing organically structured hard body parts would be more likely in sediment with low oxygen levels, in which they are protected from oxidation (Zipkin, 1970; Lyman, 1994).

An organism's life habits and behavioural pattern may also affect its preservation. For example, rodents are small and have fragile bones, but their teeth are strong. For this reason rodent teeth are very common fossils. In addition, rodents outside of burrows can be preyed upon by owls and other animals, and the hard enamel of the teeth ensures their preservation in the predator's faeces.

There are many preservational processes that allow organisms to become fossilized, including unaltered (e.g. Siberian mammoths and insects in amber); mummification (e.g. Pleistocene sloths in caves); replacement of organic material by calcite, silica, or pyrite (e.g. bones and shells**),** carbonization**,** through preservation of carbon and loss of oxygen,

nitrogen, and hydrogen (e.g. graptolites, leaves, and Burgess Shale fossils); recrystallization of aragonite-calcite and calcite-calcite (e.g. shells and corals) and permineralization, when minerals are added to the original framework tissue (e.g., impregnation or petrifaction).

1.2.1 Biases in the fossil record

Anatomy

The anatomy of an organism plays a very important role in its preservation. As a result of this certain biases exist with respect to where and what types of fossils are collected in the field (Johanson and Edgar, 1996).

- Animals with hard parts are more likely to be preserved than those that have only soft bodies.
- Animals may have hard parts, but if they are fragile (or thin), they will not preserve as well as those that have more resistant structure.
- Certain hard parts may have a chemistry that allows then to dissolve easily, reducing their chances of preservation.
- Certain animals have an anatomy that makes fragmentation after death more likely.

- Vertebrates have bony skeletons, but the bones are held together by soft tissue (tendons and muscles). As a consequence of this, bones of these animals are often scattered by water currents, predators, scavengers, etc.
- Plants disintegrate during life and after death. Flowers, pollen/spores, leaves, and branches may be shed during life; stems and trunks may be broken away from roots after death, and as a result only parts of the plant become fossilized.
- Some animals moult their hard parts during life. Arthropods moult their skeletons as they grow. Therefore, many fossilized skeletons of animals such as crustaceans and trilobites may represent instances of this process of moult and not a dead individual.

Size

- Larger fossils are more visible and therefore, more likely to be found protruding from the rock.
- Large shells or bones are stronger, so less likely to be destroyed.
- On the contrary, large animals tend to be a great deal less in number than small ones, giving the reverse bias to the fossil record.

Habitat, environment

- **Physical geography of habitat:** Organisms living in terrestrial environments are less easily fossilized than those that live in the sea.
- **Transport history:** How, or the mechanism and the time taken for the bones to reach the burial site.
- **Resistance to physical damage.** Physical geography of depositional environment. Irrespective of where the organism lived, it is important where it is deposited after death. There is a bias that is related to the transport history of the remains of the animal from where it lived to where it was deposited. If the organism is dead and immediately buried, the chances of it fossilising increase (Koch, 1978; Lyman, 1994).

1.2.2 Geological processes after death

Biostratinomy

This term describes the processes that occur between the death of an organism and burial in the sediment. Generally, this includes the decomposition and scavenging of an organism's soft parts, and at least some amount of post-mortem transport. With regard to molluscs, the amount of shell breakage and the concentration of shells in layers may indicate the level of water energy and post-mortem transport (Lyman, 1994; Johanson Edgar, 1996).

Geological history and time both affect fossil preservation. Fossils, once formed in a rock, may be destroyed by a number of geological processes. Seeping water may dissolve them, or tectonic processes which could destroy them, or heat them intensely in metamorphism. Thus, only few fossils have been found after metamorphic processes. The older a fossil is, the more chance there is that it will be destroyed by geological processes, because the beds in which they are deposited have more probability to be exposed to metamorphism. A bias is thus expected in which more recent fossils would be more numerous, better preserved, and more diverse than older fossils. In general, this is true, but there are enough exceptions to this bias to assess the real abundance and diversity of life of the past (Lyman, 1994; Johanson and Edgar, 1996).

1.3 Taphonomy - palaeontology and archaeology

Although studied since the beginning of the century, research on vertebrate taphonomy intensified in the late eighties, when a number of workers started to focus on biostratinomic and diagenetic aspects of vertebrates (Holz and Barberena 1989, 1994; Holz and Schultz, 1998, Souto-Ribeiro and Holz, 1998). One of the main interests of taphonomy is the study of marks found on bone surfaces, for example carnivore and rodent tooth marks, insect mandible bore marks and hominid butchering marks. These play a vital role in reconstructing palaeoenvironmental conditions and identifying the agent(s) responsible for the modification and accumulation of fossil faunal assemblages. These taphonomic markers provide important information on the presence and activities of non-fossilized biomes in the habitat under study.

1.3.1 Summary of taphonomic indicators and their palaeo-environmental implications

According to Lyman (1994), the most important taphonomic signatures on bone surfaces are:

Abrasion

The wearing-down of bone as a result of contact with sediments is an indicator of environmental energy. Significant abrasion is most evident on skeletal material collected from beaches, or areas of strong currents or wave action. Wind also causes sand abrasion of bones in desert environments. In both, bones are entirely smoothed.

Articulation

Multi-element skeletons are soon disarticulated after death. Articulated skeletons therefore show rapid burial or a quick removal of the skeleton from the effects of energy in the original environment. A high degree of articulation can also be indicative of burials in protected environments, such as burrows.

Bioerosion

Bioerosion consists of destructive processes by organisms, such as boring and grazing. These processes remove information from the fossil, but leave identifiable traces made by organisms on the skeletons or surfaces. Therefore, trace fossils produced by bioerosion add information on the diversity of ancient assemblages.

Dissolution

Skeletal remains commonly are in equilibrium with surrounding waters, but changes in chemical conditions can cause skeletons to dissolve. Dissolution represents fluctuation in temperature, pH or pCO_2 in calcium carbonate skeletons. Siliceous skeletons also can dissolve because normal sea water is usually under-saturated with respect to silica.

Rounding

Broken edges of skeletons become rounded owing to dissolution and/or abrasion of exposed surfaces. Processes that control edge rounding probably include a combination of dissolution, abrasion, and bioerosion. Rounding gives an estimate of time since breakage.

Encrustation

The growth of hard skeleton substrates by other organisms is a common occurrence. Besides indicating exposure of the skeleton above the sediment-water interface, encrustation can specify a particular environment. Different patterns of encrustation, as well as different biota, occur in different environments.

Fragmentation

Breakage of skeletons is usually an indication of high energy resulting from wave action or current energy. Fragmentation also can be caused by other organisms through either predation or scavenging, trampling or weathering.

Orientation

After death, skeletal remains are moved by the transporting medium and oriented relative to their hydrodynamic properties. Fossil skeletons in life positions indicate rapid burial, attachment to a firm substrate, or death of in-place fauna. Hard parts tend to orient their long-axis parallel to unidirectional flow in current-dominated areas and perpendicular to wave crests on wave-dominated bottoms. Similar orientation of the long axis of bones in accumulations of vertebrates is a good indication of the presence of unidirectional currents in the environment when the bones were buried.

Size

After death and if not rapidly buried, a skeleton behaves as a sedimentary particle and is moved and sorted with respect to the carrying capacity of the flow of currents, waves, or tides. Size can therefore be an effective indicator of flow capacity in a hydraulic or wind-driven system (Clarkson, 1986; Boardman *et al*., 1987; McRoberts, 1998)

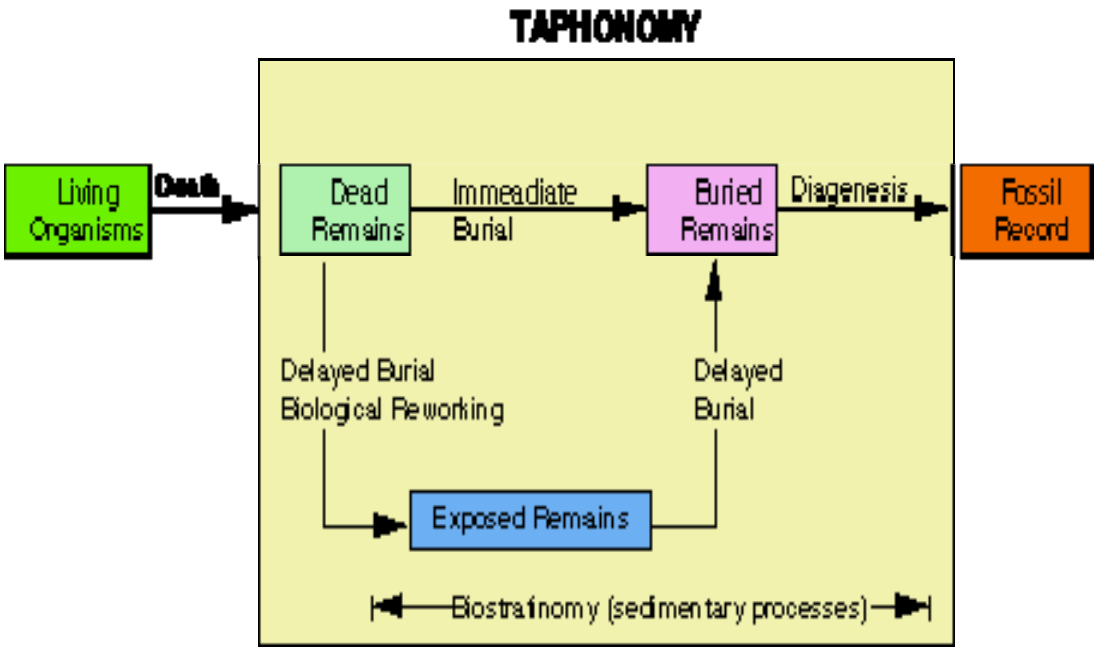

Figure 1.1 Flow chart showing the general process of fossilisation and the influence of immediate and delayed burial on taphonomy (McRoberts, 1998)

1.4 Bone diagenesis

The physical and/or chemical effects on organisms after burial are called diagenesis. This is the realm in which dissolution, replacement, or recrystallization of original material occurs, as well as the formation of moulds and casts (McRoberts, 1998). The bone alteration after burial and the degree of diagenesis is dependent on a wide variety of environmental factors. Furthermore the amount of alteration can vary from nil to total disappearance of the bone.

The interaction of calcite minerals present in bone with surrounding metals either found in solution or present in soils has been extensively covered. Morgan (1967) investigated the interaction of manganese in the +2 oxidation state with dissolved bicarbonate and carbonate ions and carbonate minerals. The Mn(II) species is of particular importance because this divalent ion forms strong ion pairs with the carbonate ions and coprecipitates with calcite. Wangersky and Joensuu (1964) and Robbins and Callender (1975) showed that under reducing conditions in sediments the Mn(II) cation forms an association with calcium carbonate. Pingatore (1978) further demonstrated that this association is partitioned into calcite during carbonate diagenesis (Franklin and Morse, 1983).

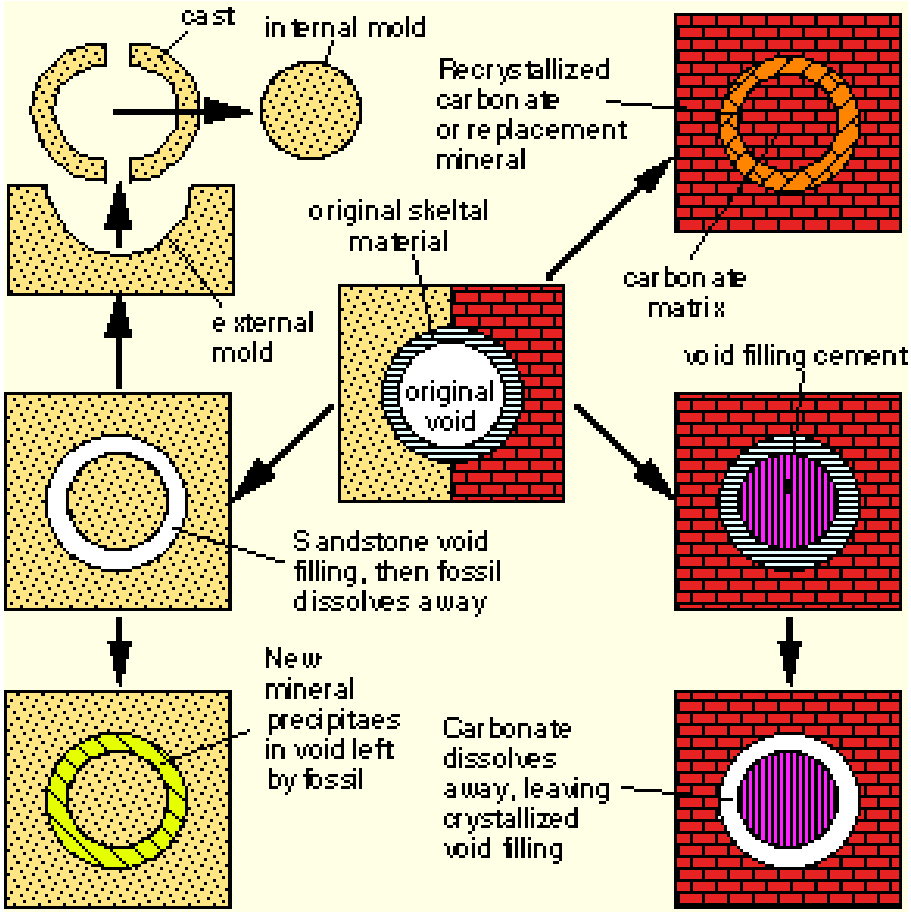

Figure 1.2 Different diagenetic processes leading to different preservation styles in skeletal materials (Modified from McRoberts, 1998)

The most common form of preservation involves chemical and/or physical alteration or replacement of original skeletal material. To accurately identify replacement and recrystallization, the original constituents of the organism's skeleton must be known. Replacement with various minerals occurs often by the occupation of the void after dissolution of original skeletal material. The replacement can also occur on a molecule by molecule basis. Common replacement minerals easily recognized include Silica (SiO_2) as shown in coral, and Pyrite (FeS_2).

The physical alteration of crystalline structure of skeletal material is known as recrystallization. This is a common in shells that were originally aragonite and/or calcite (both forms of calcium carbonate-$CaCO_3$).

During the decomposition of organic remains in sediments, volatile components such as oxygen, hydrogen and nitrogen are over a long period of time removed to the surrounding sediments often leaving behind a carbon film. This process known as carbonization, is also referred to as distillation. It occurs more frequently in oxygen deficient, organic-rich environments such as basinal black shales, and coal swamps. The carbon films often exhibit much details of plants and soft-body parts of animals not readily preserved, and can often be recognized by a dark gray or black film with a metallic sheen such as observed on fern-like fossil plants (Prothero, 1998).

The filling in of pore and/or moieties in shell or bone by secondary minerals in solution is known as permineralization. The tiny pore spaces in the fossil are filled and the original skeletal material is still retained. However, it is often common for other types of preservation (e.g. replacement) to occur during and/or after permineralization. Bone is especially vulnerable to permineralization because of its porous structure (Prothero, 1998).

One approach adopted by Lambert *et al*., (1984) for determining the effects of diagenesis-involved examination of elemental concentrations in bone as a function of depth from the surface of the bone. It has also been demonstrated that two different types

of contamination can occur: certain elements can replace components in the hydroxyapatite matrix while others (Mn, Se and Fe) move into voids in the bone as a result of depletion in organic material (Parker and Toots, 1970).

1.4.1 Limestone caves in South Africa

Dolomitic limestone is highly alkaline and is the sedimentary remains of an ancient seabed 2.6 billion years old. Dolomite ($CaMg(CO_3)_2$) outcrops composed of calcium carbonate (lime), magnesium and silica occur in the Cradle of Humankind, and look like elephant skin - grey, cracked and flat. At the time of formation, South Africa as we know it had not yet formed. The land was much smaller, limited to the Kaapvaal Craton, and a large percentage of it was covered by shallow sea water. Sea water is saturated with calcium carbonate ($CaCO_3$) due to weathering of rocks globally. At 2.6 billion years ago the atmosphere was saturated with CO_2. In the shallow sea blue-green algae, the earliest forms of life evolved. Algae depend on CO_2, water and sunlight to produce carbohydrates for energy and tissue manufacture (photosynthesis). The tissue takes the form of slimy mats. The algae take CO_2 from the water to produce carbohydrates and thus create an imbalance between the $CaCO_3$ and the CO_2 in the water. As a result, tiny calcium carbonate crystals form and sink to the bottom, where they stick onto the slime. The slime prevents the crystals from dissolving. In deep water thick slime mats form domes where as in shallow water the action of waves creates mushroom-shaped stromatolites (fossilised colonies of algae that once grew on the edge of the sea, and were created by layers of calcium carbonate as it was deposited on the algae as it grew to the sunlight)-(Clarke and Kuman, 2000).

1.4.2 Cave formation

Dolomite is very porous and composed mostly of calcium carbonate (lime), magnesium and silica. Below are the steps in the formation of dolomitic caves.

1. Underground caves form in dissolved dolomite below the water table.

2. The water table drops due to water erosion of the valley, and the cave becomes filled with air. Slightly acidic rain water filters through the dolomite from the surface, dissolving calcium carbonate and magnesium as it goes, and becoming highly alkaline lime water that finally drips into the cave from the roof.

Stalactites are limestone deposits hanging from the roof that form through the evaporation of lime-rich water. Stalagmites grow from the floor up. A bed of limestone on the floor is called travertine.

3. Joints in the roof open to the surface, admitting surface sediment which forms a talus cone below the shaft. The sediments contain animal bones, stones and plants. It could take 20 000 years for one deposit (member) to accumulate. Entrances become obstructed when the cave is full. Other shafts open and admit different deposits. The new deposits form other members, and record life from a different time period.

4. The sediments deposited become calcified by drip from the roof. The highly alkaline limestone solution also cements the sand and fossils together to form breccia.

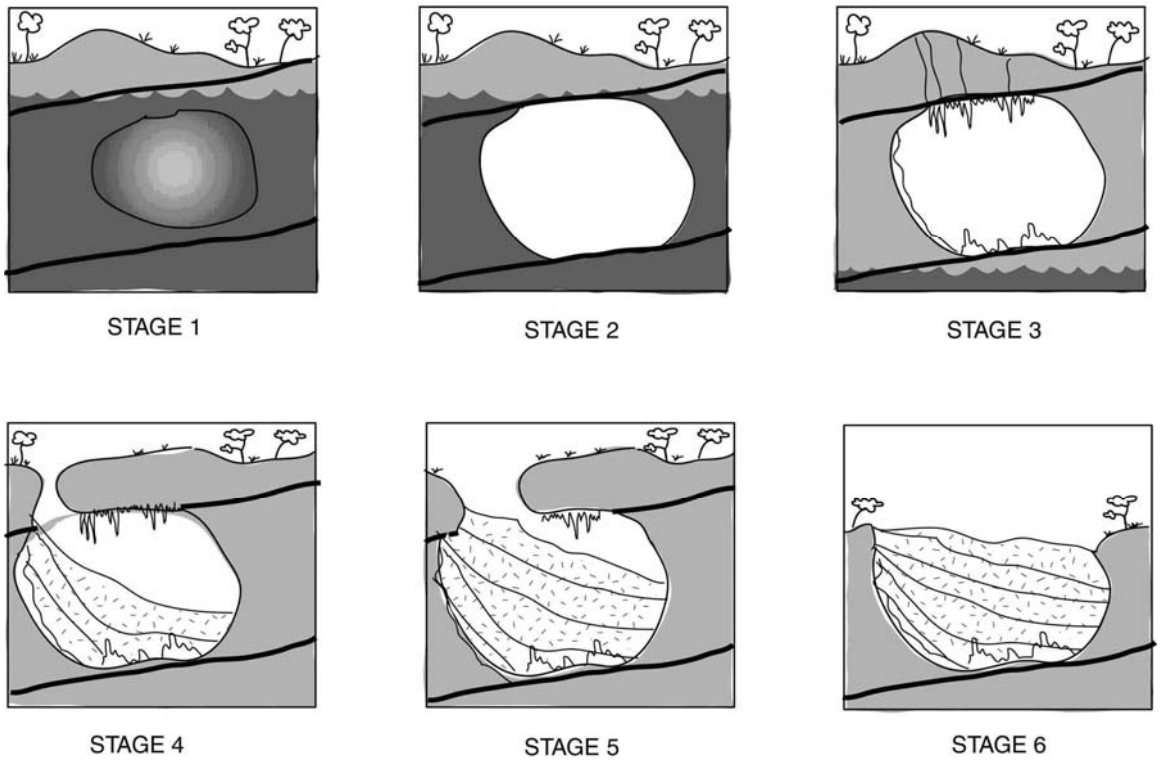

Figure 1.3 Stages in dolomitic cave formation (modified after Brain 1993).

All fossil assemblages in the Cradle of Humankind are dated less than 4 million years old as caves only opened then. This was an important time period in human evolution as early ancestors were only recorded here and in East Africa.

One of the main problems experienced by palaeontologists is the cleaning of excavated fossil specimens. This arises due to these fossils possessing coatings that are formed in cave contexts in the presence of water. Thick black manganese oxide coatings prevent the study of surface modifications, making it difficult to determine how fossil bones got to the burial cave site, for example, identifying hyena tooth marks versus cut marks indicative of human involvement.

Removal of these coatings is possible by mechanical abrasion; however, damage of the underlying fossil surface can occur, rendering the specimen useless for taphonomic and morphological studies. Acid techniques for removal are not good as they weaken and destroy calcium-based fossils, so the focus here has been to develop new non-invasive chemical techniques specifically for the removal of these fossil bone coatings.

II. CHEMISTRY

1.5 Methods for the cleaning and preparation of fossil specimens

Palaeontologists use various methods to remove matrix that surrounds a fossil, including chemical treatment, abrasive blasting, hand power tools, acid, or soap and water. The most common types of matrix are sand and mudstone. Ferecrete (solidified rock) and ironstone are harder matrixes that also occur.

A method that has been used by Tomoyuki *et al*., (2002) for manganese oxide dissolution by soil drying demonstrated how air drying treatment of soils increases water soluble sugars in soils, and those sugars then improve the dissolution of soil manganese oxides. Glucose was added to the manganese oxides to determine the effect of the reducing power of sugars on manganese dissolution. Glucose was found to dissolve manganese oxides, while the reducing sugars in water extracts proportionally decreased as the dissolution of manganese oxides proceeded (Tomoyuki *et al*., 2002).

In a study carried out to determine the origins of certain minerals such as manganese and iron in and on the surface of buried bones, fourteen ribs from graves were collected. One of the first steps in the sample preparation of these bones was to clean the outer surface of

the sample. This was done using light sample surface abrasion, followed by immersion in a solution of hydrogen peroxide and ethanol in an ultra-sonic cleaner. However the peroxide in this study was used to remove organic matrix (Edward *et al*., 1993).

A chemical method for the removal of hematite from fossil bones previously developed called 'Howie's Method' has been used. Thioglycolic acid is used to remove the hematic bone sample coatings. Thioglycollic acid does have a drawback in that a foul odour is produced by the acid and if the acid is not neutralized after treatment it can potentially damage the bone surface (Howie, 1974).

1.5.1 Dissolution chemistry and surface complexation of calcium carbonate minerals

There are six main stages involved when mineral dissolution occurs in the natural environment. They are: Adsorption of solutes; mass transport of dissolved reactants from bulk solution to a mineral surface; chemical reactions; interlattice transfer of reacting species; detachment of surface reactants; and mass transport into the bulk of the solution.

Evaporite and calcareous minerals are extremely soluble with fast dissolution kinetics. The same stoichiometric proportions are obtained in the solution as those found in the dissolving mineral (Stumm and Wollast, 1990).

The efficiency of carbonate and evaporate dissolution is reflected in the fact that according to Wollast and Mackenzie, (1983) approximately 17% and 38% of the total dissolved load in rivers worldwide is linked directly to these evaporates and carbonates, respectively.

Calcium carbonate minerals

Carbonate minerals play an extensive part in the chemical control of aquatic environments such as in lakes, soils, hydrothermal systems and the ocean via precipitation, dissolution, and sorption reactions. These reactions are regulated by chemical processes occurring at the interface between the mineral lattice and the bulk solution (Morse, 1986; Van Cappellen, *et al*., 1993).

Adsorption and/or exchange of metals on carbonate mineral surfaces results in an initial rapid uptake of metals from solution. These metals are then incorporated with the formation of surface precipitates and/or solid solutions. Equilibrium adsorption onto carbonate minerals is difficult to measure compared to metal oxides because dissolution and growth occur faster, thus making pH regulation difficult (Wersin 1990; Stipp and Hochella, 1992; Brady *et al*., 1996).

It is also often very difficult to determine the surface charge of calcium carbonates due to rapid precipitation and dissolution kinetics (Van Cappellen *et al*., 1993).

1.5.2 Hematite

Hematite is a crystalline (hydr)oxide of α-Fe_2O_3 (Bigham *et al*., 2002) and deposits are commonly found on fossil specimens buried in iron rich soils. Research carried out by Gonzalez-gil *et al*., (2005) on the feasibility of using bacteria (*Shewanella oneidensis MR-1)* for the reduction of Fe(III) was conducted using natural hematite in an open system under dynamic flow conditions to determine how Fe(III) reduction occurs in the

environment. All previous studies on biological iron reduction have been conducted using soluble Fe(III) in closed systems (Liu *et al*., 2001a, 2002; Haas and Dichristina, 2002)

It was determined that the bacterial cells used in the reduction of the insoluble Fe(III) were accumulated on the hematite surface, and resulted in the release of soluble Fe(II) into the aqueous phase (Gonzalez-gil *et al*., 2005).

1.5.3 Calcite and other coatings

Calcites have been found to be important inorganic and biogenic components in modern marine sediments and Pleistocene rocks. They form part of a complex mineral network containing an approximate maximum of 30 % by mole fraction of magnesium carbonates. Characteristics which have been found to affect the thermodynamic and kinetic properties and reactivity of the different phases in aqueous solution include: carbonate positional disorder, chemical and micro structural heterogeneities and dislocations and plane defects (Tribble *et al*., 1995)

The formation of bacterial scum inside the pores of fossil bones has also been shown to influence mineral formation on fossil specimens (Seilacher *et al*., 1985). An extensive study on Brazilian concretions by Martill (1988) found that both high and low pH microenvironments within the body cavities of fish enabled precipitation of microcrystalline francolite inside the partially decomposed soft tissues. Francolite forms when diagenetic changes transform biogenetic bone tissue into crystalline carbonate fluorapatite (Elorza *et al*., 1999).

1.5.4 Manganese oxides

Most manganese oxide minerals are brown-black and typically occur as a complexed intermixed, fine-grained, poorly crystalline mass or coating (Post, 1999). Most manganese oxide nodules form around nuclei of carbonate mineral fragments, pumice shards, animal remains, and coral fragments to list only a few (Mero, 1977). Manganese oxides are most commonly found in soil horizons that are seasonally saturated with water during soil formation (Ross *et al*., 1976). Manganese oxide, hydroxide and hydrous oxides all have extremely complexed mineralogy. This is due to manganese's capability to exist in many oxidation states. In nature Mn(II) to Mn(IV) range is the limit of what has been observed (Bricker, 1965). Manganese is normally found in an intermediate valence of between 3+ and 4+ when present in soils as an oxide or hydrous oxide. In contrast to manganese oxides in natural deposits or synthesized materials, only a small proportion of mineral species have been identified in soils (Ross *et al*., 1976).

Identification of minerals in manganese oxides is not easy. Powder x-ray diffraction is diagnostic for well-crystallized, monophasic samples. One disadvantage is that the crystal structures, and therefore powder diffraction patterns are similar for most of the manganese oxide minerals (Post, 1999). Methods that have been used to study the atomic structures of manganese oxides include: IR spectroscopy, extended x-ray absorption fine-structure spectroscopy, and thermo gravimetric analysis (Pluth *et al*., 1997).

Manganese oxide coatings

Manganese oxides form a brownish-black coating and commonly form on fossils from decalcified cave breccia derived from the surrounding dolomite, which contains divalent iron and manganese substituting for magnesium in the lattice (Eriksson *et al*., 1975). These coatings commonly exist as an encrusted layer up to a millimetre thick and can also penetrate the bone. A hypothesis has been proposed as to how manganese oxide shales form in deep anoxic basins. It has been suggested by Calvert and Padersen (1996) that high accumulation rates of organic matter in sediments would promote anoxic conditions in the underlying sediment surface causing surface sediment to be enriched in manganese oxyhydrides. These oxyhydrides are supersaturated (with respect to manganese carbonates) and release diagenetic fluids that will precipitate calcium-manganese carbonates (Calvert *et al*., 1996). There have been numerous studies conducted on the nature of manganese oxides formed in the environment with the most extensive deposition of manganese oxides documented to occur in oceans as microconcretions, nodules, coatings and crusts (Crerar and Barnes, 1974). Burns *et al.* (1977) has done more detailed studies of the mineralogy of manganese oxide nodules, and found the dominant manganese oxide phases to be birnessite, todorokite and vernadite (Burns *et al*., 1977).

a) Manganese oxidation and oxide formation

The manganese oxide coating is derived from the surrounding dolomite, which contains divalent manganese as well as iron. In the natural environment, cycling of Fe and Mn occurs at oxic/anoxic interfaces where precipitation and dissolution occur simultaneously (Duckworth *et al*., 2004).

Most manganese oxides are formed by oxidative precipitation in nature. Iron and manganese are normally the most common metals to undergo this process. In general this precipitation is complex and occurs in a two step process (unbalanced for major species) involving various different mechanisms. In the first step (1.1) whereby a solid surface is generated, the reaction kinetics is relatively slow. The second step (1.2) however occurs much faster involving a surface catalyzed reaction (Evangelou, 1998).

Step 1: $Mn^{2+} + O_2 \leftrightarrow MnO_{xs}$ 1.1

Step 2: $MnO_{xs} + Mn^{2+} \leftrightarrow 2MnO_{2s}$ 1.2

When dissolution occurs these elements are oxidised, forming insoluble oxides.

Manganese is reduced on the collective surface when the soil contains moisture. It is then transported to the concretion interior and is oxidised and precipitated when O_2 diffuses to the concretions interior during soil drying (Ross *et al*., 1976).

Bacteria have also been found to oxidise Mn(II). In a study done by Stein and Nealson. bacteria were isolated from metallogenium minerals using a growth medium that isolates manganese oxidisers. The dominant types of bacterial isolates were Pseudomonas,

Comomonas, Cytophaga, Flexibacter, Arthrobacter, Corynebacterium, and Rhodococcus (Stein and Nealson, 1999).

b) Manganese reduction

Reductants dramatically accelerate iron and manganese oxide dissolution (Stone, 1987; Schmidt, 1999 Jun *et al*., 2003). Typical reductants are hydrogen sulphide, ascorbic acid and phenols. Most reductants form an inner sphere complex at the surface. When electron transfer occurs towards a manganese (III/IV) oxide, a surficial Mn(II) ion locked inside an oxide lattice is produced. Due to Mn(II) oxides being more soluble than the higher oxides, fast Mn(II) depolymerization occurs, followed by Mn(II) release into aqueous phase. Iron(III) oxides are reduced in the same way (Martin, 2003).

Due to the chemistry of manganese in nature being rather complex with respect to the different oxidation states, a wide variety of oxides and oxyhydroxides with various degrees of chemical stability can form (Bricker, 1965; Parc *et al*., 1989; Huang, 1991).

1.5.5 Iron oxides

a) Formation

Hydrous iron(III) oxides, FeO(OH), have different types of structures in chain arrangements (alpha, beta and gamma) and are often red-brown gels which are major constituents of soils (Cotton *et al*., 1988).

b) Dissolution

The hydrous oxides are soluble in acids and to a lesser degree bases. Iron(III) has the tendency to hydrolyze and even form complexes (Cotton *et al*., 1988).

1.6 Chemistry of manganese

When examining the chemistry of manganese and the differences of each oxidation state, the chemistry is complex due to manganese having five different oxidation states. The chemistry and in particular the speciation of this metal is complex compared to other transition metals like Cr and Fe (Majors, 2004; Ottaway *et al*., 1986). From the Frost diagram in fig.1.4 it is shown that the most common and most stable oxidation state of manganese is the divalent state (d^5) (Shriver *et al*., 1998).

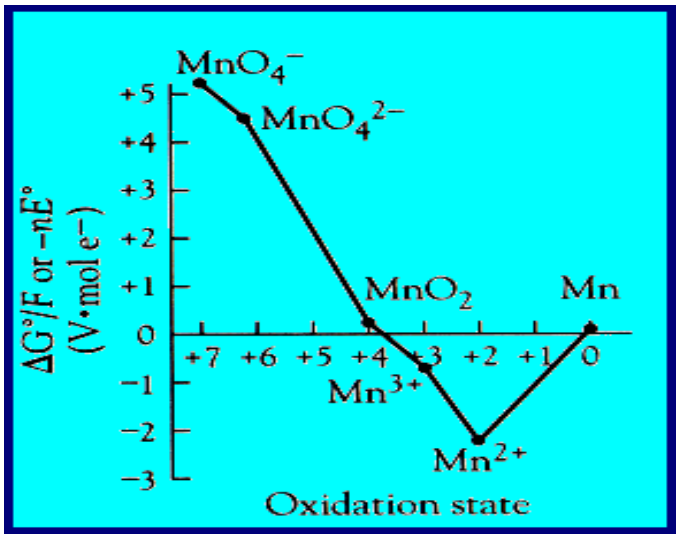

Figure 1.4 Frost diagram for manganese (Mackay *et al*., 1981)

Manganese metal is acquired from its oxides by reduction with aluminum. Typical ores of manganese are pyrolusite, MnO_2, and hausmannite, Mn_3O_4 (Liptrot, 1992). The main

use of pure manganese is in ferromanganese of steels (Cotton *et al*., 1988). Manganese in its elemental form is present in more than 100 common salts and mineral complexes that are abundant in rocks, soils and on lake floors and oceans. The most common form this trace element is found in is as manganese dioxide, carbonate or silicate. Manganese in its +2 and +4 oxidation states is the most significant in aquatic systems (Canadian council of resource and environment ministers march, 1987).

Looking at an element that has similar features on a physical and chemistry comparison to manganese, iron falls into that category. Iron has similar physical and chemical Properties to manganese. The significant difference between the two metals is that manganese is harder and more brittle, but less refractory (mp 1247°C). It is a fairly electropositive metal ion and dissolves with relative ease in dilute non-oxidizing acids. At room temperature it has a low reactivity towards non-metals, however at higher temperatures it reacts vigorously with a wide variety reactions. One good example of this would be when Mn^{2+} is placed in Cl_2(g) and burned; it reacts with the chlorine forming $MnCl_2$ (Cotton *et al*., 1988).

a) Manganese(II) complexes, d^5

When comparing the equilibrium constant for complex formation in aqueous solution of Mn^{2+} with constants for Fe^{2+}-Cu^{2+}, they are not high. The reason for this is due to Mn(II) being the largest of these ions and it has no ligand field stabilization energy in its complexes (except in the few of low spin). Manganese(II) complexes can have an extensive series of ligands, such as halide ligands ($MnCl^{+}$), (MnX_3^{-} octahedral) and

MnX_4^- tetrahedral). Oxygen ligands for example, acetylactonate $[Mn(acac)_2]_3$. Sulphur ligands, for example, dithiocarbomate (18-D-I). Nitrogen ligands, for example, $[Mn(NH_3)]^{2+}$ and $[Mn(en)_3]^{2+}$. Phosphine ligands with general stoichiometery $MnX_2(PR_3)$ and finally, carbon ligands, which include alkoxides and dialkyamides.

b) Binary compounds

These compounds can include manganese(II) oxide, which is a grey-green to dark green powder obtained by roasting the carbonate in H_2 or N_2, or through the action of steam on $MnCl_2$ at 600°C. The crystal structure is that of a rock salt type and the compound is insoluble in water. Another binary compound is manganese(II) hydroxide, that has an identical crystal structure to that of $Mg(OH)_2$. Other manganese binary compounds that exhibit a NaCl structure include, Manganese Sulphide, MnSe and MnTe (all strongly anti-ferromagnetic) (Cotton *et al*., 1988).

c) Divalent manganese and manganese(II) salts

The divalent oxidation state of manganese is the most common and stable oxidation state in which manganese can occur. This is shown in fig. 1.4.

A wide variety of salts are formed by Mn(II) with all common anions, of which contain $[Mn(H_2O)_6^{2+}$ crystallize from water as hydrates. The sulphate, $MnSO_4$, made on fuming down H_2SO_4 solutions, is relatively stable and may be used for Mn analysis, provided no other cations giving non-volatile sulphates are present.

d) Manganese(III), d^4

Binary compounds: Oxides are the most important of these compounds. The complete oxidation of Mn or MnO at high temperatures yields Mn_2O_3 which decomposes at 1000° yielding a black Mn_3O_4 compound (hausmannite) (Cotton *et al*., 1988). Manganese(III) exists in numerous mixed oxides including the alkali oxides such as $LiMnO_2$, $NaMnO_2$, and $K_6Mn_2O_6$.

Manganese(III) Complexes

Various anions ($C_2O_4^{2-}$, SO_4^{2-} and $EDTA^{4-}$) can form stable complexes in aqueous phase (Davies, 1969, Cotton *et al*., 1988).

e) Manganese(IV), d^3

Manganese dioxide is one of the most important compounds of the Mn(IV) oxidation state. It occurs in nonstoichiometric ratios and has a grey to black appearance. Pyrolusite is one of the ores in which it is found. There are several different methods of obtaining manganese dioxide, the main one being through the heating of $Mn(NO_3)_2{\cdot}6H_2O$ at 530^oC in air. Reduction of $KMnO_4$ in basic conditions produces the hydrated form of Mn(IV). Manganese in the IV valence state is found in numerous mixed oxides.

A number of acids do not dissolve manganese dioxide unless heat is added. When dissolution of the manganese(IV) occurs, it functions as an oxidizing agent (Cotton *et al*., 1988).

Complexes

Manganese(IV) complexes can be utilized for oxidation reactions involving one electron in aqueous solutions (Cotton *et al*., 1988). Manganese(IV) can exist in a number of similar complexes including polyhydroxo, Schiff bases and macro cyclic ligands. For example the polymer, $[Mn(IV)sal_2enO]_n$ that has Mn-O-Mn bridges (Cotton *et al*., 1988).

f) Manganese (V)

One example of a compound containing manganese in the (V) oxidation state is that of the oxyhalides, namely $MnOCl_3$. This compound is obtained by the reduction of $KMnO_4$ using sucrose and HSO_3Cl (Jasinsku *et al*., 1975).

Another class of manganese(V) compounds are the hypomanganates (MnO_4^{3-}). These are blue salts that are produced from the reduction of MnO_4^- or by disproportionation when concentrated KOH is reacted with MnO_2 (Cotton *et al*., 1988).

g) Manganese(VI)

Exists as MnO_4^{2-} manganate ion with an olive green appearance and is only stable in highly alkaline conditions. For any other pH conditions the MnO_4^{2-} disproportionates (Sulter *et al*., 1974, Cotton *et al*., 1988).

h) Manganese(VII)

One of the most well known and common compounds are permanganate salts. In solution the permanganate ion is relatively unstable with slow decomposition occurring. In acidic conditions this decomposition rate is increased remarkably. Light is known to be a

catalyst for permanganate disproportionation. One of the main uses of the permanganate ion is as an oxidant (Cotton *et al*., 1988)

1.7 Chemistry of iron

1.7.1 Iron(II), d^6

Fe(II) in the absence of complexing agents appears as a pale blue-green ion, $[Fe(H_2O)_6]^{2+}$

Although this is oxidized in acid solution, the oxidation is more favourable in basic solution. When Fe(II) is oxidized under basic to neutral conditions , the corresponding Fe(III) exists normally as a hydroxo complex. When Fe(II) to Fe(III) oxidation is carried out under neutral conditions, by molecular oxygen, a reaction between $FeOH^+$ and O_2H^- is thought to occur. Other ions that play a role in the oxidation of Fe(II) include NO_3^- and NO_2^- and occurs by the transient formation of a brown nitrosyl $[(FeNO(H_2O)_5]^{2+}$ with the overall reaction as follows (Cotton *et al*., 1988):

$$3Fe^{2+} + 4H^+ + NO_3^- \leftrightarrow 3Fe^{3+} + 2H_2O + NO \qquad 1.3$$

Fe(II) oxidation by addition of nitrate and nitrite to activated sludge has been studied to determine whether the process was biological or chemical (chemodenitrification). It was proved that the process (1.3) was mainly biological. Investigations in a full scale treatment plant suggested that the process most likely took place in the anoxic conditions

(Nielsen and Nielsen, 1998). Most iron(II) complexes are octahedral (Cotton *et al*., 1988).

1.7.2 Mixed iron and manganese oxides

Ferrites are an important class of mixed oxide materials with octahedral Fe(III) ions such as $M^{(II)}Fe_2O_4$. Ferrites are made by fusing Fe_2O_3 with carbonates or through other hydrothermal methods using $Fe(OH)_2$ or FeO(OH) suspensions in the presence of metal ions (Tamuara, 1985; Cotton *et al*., 1988).

In a study done by McKenzie (1975), six manganese nodules derived from soils and two ocean nodules were analyzed using electron microprobe techniques, and various inter-element relationships were determined. In half of the soils of the nodules manganese and iron were found to be inversely related, however the relationship was not close (r = -0.46) and of the two elements iron was determined to be more evenly distributed. Spots of high iron were found to contain 50-60% iron and much lower concentrations of manganese (below detection level- 0.8%), where as manganese spots contained 3-10% iron.

In another study it was found that in concretions, iron and manganese tend to occur in regions of primarily iron or primarily manganese, with minimal intermixing occurring (Ross *et al*., 1976; Palumbo *et al*., 2001).

Most studies carried out in order to determine the phase nature of iron and manganese oxides in natural environments have been difficult and often yielded poor inconclusive results. This is due to the low crystallinety of many soil clay components. Chukhrov and Gorshkov (1981) illustrated this, and showed that using a combination of techniques (X-ray diffraction (XRD), transmission electron microscopy (TEM) and microprobe analysis (MPA)) allows complete and unambiguous identification of the iron and manganese

oxides, and determination of structural and chemical features. Chukhrov and Gorshkov concluded the following main points from their study:

a) The type of oxide minerals of iron and manganese formed is significantly influenced by the soil conditions.
b) Manganese oxidizing micro-organisms can cause rapid precipitation of vernadite, but altering soil conditions can cause abiogenic formation of hausmannite, todorokite or birnessite.
c) The formation of iron oxides in soils could also be due to biogenic or abiogenic processes. However, the activity of iron oxidizing bacteria could depend on the presence of organic material.
d) Iron and manganese coexistence can be brought about through repeated change in the soil environment (pH and Eh).

In an investigation by Young and Harvey (1992) in which pore-water chemistry and pore-water profiles of total dissolved Mn and Fe were obtained to determine the contribution of diagenesis to concentrations of particulate Mn and Fe recovered from the sediment-water interface.

1.8 Redox catalysis on a hydrous surface

There are two main types of reactions that can be identified when a metal ion is absorbed onto an aqueous mineral surface: Inner-sphere and outer-sphere coordination. The majority of transition metal ions are involved in strong inner-sphere complex formation at

the oxide-water interface. It is also important to note that the absorption occurs against the electrostatic potential of a positively charged double layer (Wehrli *et al*., 1989).

1.9 Methods of manganese oxide and iron oxide characterization in synthetic and environmental samples

It is often very difficult to perform a successful complete characterization of environmental manganese oxides. All the manganese oxides that are found in nature are mostly impure and have a low crystallinety. Impurities in these oxides also cause a decrease in the stability of the oxide resulting in the boundaries/limits between stability field regions of different species being more broadly defined compared to the ideal system (Hem, 1978).

In soils with limited internal drainage, manganese and iron often forms concretions. Concretions are mixtures of soil materials fixed together by cementing agents, in this case iron and manganese oxides (Radden and Porter, 1962; Zhang and Karathanais, 1997). For this reason, shown by Rhoton *et al*., (1993), most cretionary material is characterized by higher concentrations of iron and manganese oxides as compared to the surrounding soil matrix.

The ratio of iron to manganese found in most concretions also varies considerably according to Schwertmann and Fanning (1976). Concretion size, colour and drainage capacity of the surrounding soil are correlated with concretion manganese concentration. Darker coloured, larger concretions have a greater content of manganese (Phillippe *et al*., 1972; Zhang and Karathanasis, 1997). In terms of the characterization of these manganese and iron mineralogy, chemistry and oxide components many studies have

been performed. For example, using XRD, Gallaher *et al*. (1973b) and Schwertmann and Fanning (1976) determined goethite to be the only iron oxide mineral found in most concretions. Tokashiki *et al*. (1986) has shown that manganese oxides of a fine grained nature can also be found in concretions using XRD. However, the characteristic peaks were diffuse as a result of the oxides poor crystallinety and low concentration.

Scanning electron microscopy (SEM) studies by Zhang and Karathanasis (1997) showed that concretion matrix, regardless of its density, has many cavities and large micro pore structure that plasmic iron and manganese in solution can diffuse and precipitate.

Hayes *et al*. (1987) demonstrated using EXAFS in synchrotron X-ray spectroscopy that the type of surface reaction (i.e. inner-sphere or outer-sphere surface catalyzed reactions) can provide important information regarding the type of thermodynamic interaction between surface ligands and absorbed metals. This can be useful in determining the range of possible kinetic effects (Hayes *et al*., 1987; Wehrli *et al*., 1989).

1.10 Dissolution methods of manganese and iron oxides

Potential dissolution pathways

Proton-promoted dissolution

$$Mn_3O_4 + 8H^+ \leftrightarrow Mn^{2+} + 2Mn^{3+} + 4H_2O \qquad 1.4$$

Incongruent dissolution

$$Mn_3O_4 + 2H^+ \leftrightarrow Mn^{2+} + 2\gamma\text{–}MnOOH \qquad 1.5$$

$$Mn_3O_4 + 2H^+ \leftrightarrow Mn^{2+} + Mn_2O_3 + H_2O \qquad 1.6$$

Disproportionation

$$Mn_3O_4 + 4H^+ \leftrightarrow 2Mn^{2+} + MnO_2 + 2H_2O \qquad 1.7$$

Reductive dissolution

$$Mn_3O_4 + 8H^+ + 2e^- \leftrightarrow 3Mn^{2+} + 4H_2O \qquad 1.8$$

Ligand-promoted dissolution

$$Mn_3O_4 + 2H^+ + 2H_4DFO\text{-}B^+ \leftrightarrow Mn^{2+} + 2Mn(III)HDFO\text{-}B^+ + 4H_2O \qquad 1.9$$

$$Mn_3O_4 + 3H_4DFO\text{-}B^+ \leftrightarrow Mn(II)HDFO\text{-}B + 2Mn(III)HDFO\text{-}B^+ + 4H_2O + H^+ \qquad 1.10$$

($H_4DFO\text{-}B^+$ = desferrioxamine B complex)

1.10.1 Hydrogen peroxide as a reducing agent

Under certain conditions, hydrogen peroxide not only acts as an oxidizing agent, but also as a reducing agent. This can be observed for manganese oxides when placed into a solution of hydrogen peroxide at sufficiently acidic conditions.

$$MnO_{2(s)} + 2H^+ + H_2O_2 \leftrightarrow Mn^{2+} + O_{2(gas)} + 2H_2O \qquad 1.11$$

Reductive dissolution of MnOOHs is represented by the following equation:

$$MnOOH_{(s)} + 1/2H_2O_2 + 2H^+ \leftrightarrow Mn^{2+}\ 1/2O_{2(gas)} + 2H_2O \qquad 1.12$$

Both above reactions can be quantified through the determination of Mn^{2+} concentration or O_2 gas evolution both with respect to time.

The mechanism of the reactions (1.11 and 1.12) is not completely clear and the reductive dissolution is fairly complex. There are more than one elementary steps involved which includes the formation of a Mn-oxide-H_2O_2 complex, surface electron transfer, and dissolution (Huang, 1991; Evangelou, 1998).

1.10.2 Reductive dissolution of manganese dioxide by complexing agents and ligands

Increased dissolution rates have been observed for ligands that bind as inner-sphere complexes to the surface groups of iron and manganese oxides (Zinder *et al*., 1986; Furrer *et al*., 1986; Stone, 1997; Stum, 1997). This dissolution rate increase is proportional to the ligand surface concentration and the ligand-binding strength.

This relationship is because strong electron donation by the oxygen-ligand to a surficial metal atom removes electron density in the bonds between the metal atom and the oxygen atoms of the mineral lattice, thus causing weakening of the bond and lowering the energy barrier for the dissolution of the metal atom (Martin, 2003).

Manganese and iron cations bind far more strongly to oxygen than nitrogen-containing ligands. The ligands that have proved effective for promoting dissolution have two or more functional groups capable of chelation to form inner-sphere bidentate binuclear complexes (Martin, 2003).

Manganese(III, IV) oxide dissolution

Reductive:

$$MnOOH + e^- + 3H^+ \leftrightarrow Mn(II)(aq) + 2H_2O \qquad 1.13$$

$$MnO_2 + 2e^- + 4H^+ \leftrightarrow Mn(II)(aq) + 2H_2O \qquad 1.14$$

Examples: e^-(donor) = ascorbate, hydroquinone, dithionite, H_2S and pyrogallol. (Martin, 1991).

a) Cyanide complexation chemistry with manganese ions

Manganese(IV) is a strong Lewis acid and in aqueous solutions is only soluble in the form of coordination compounds (Yamaguchi, *et al*., 1985). In aqueous solutions, the relatively few Mn(IV) known complexes have a strong tendency to hydrolyze in neutral as well as acidic media (Cooper *et al*., 1977; Magers *et al*., 1978; Cotton, *et al*., 1980).

Cyanide has a preference for joining two transition metals in a linear bridging geometry (Heinrich *et al*., 2001).

Thiocyanogen is obtained by oxidation of aqueous SCN^- with MnO_2 (Cotton *et al*., 1988).

Some examples of CN ligands known to exist and to have strong interactions with manganese include: $[Mn(CN)_6]^{4-}$, $[Mn(CN)_5NO]^{3-}$, and $[Mn(CNR)_6]^{2+}$ (Cotton *et al*., 1988).

b) Cyanate

A linear cyanate ion OCN^- is obtained by mild oxidation of aqueous CN^-. This free acid, $K=1.2*10^{-4}$, decomposes in solution to NH_3, H_2O and CO_2. The evidence for the

existence of $(OCN)_2$ is not evident. However covalent compounds such as $P(NCO)_3$ and some metal complexes are known (Cotton *et al*., 1988).

1.10.3 Organic ligands

In soils it has been determined that manganese solubility and thus toxicity is dependent on a number of factors such as: the soil's manganese concentration, pH and the availability of electrons (Adams, 1981; Sparrow and Uren, 1987; Hue *et al*., 2001). The latter is an indirect link to the amount and type of organic molecules present in the surrounding soils.

In an electron rich (reducing conditions) soil environment, manganese(II) can be released into the soil, even under alkaline pH conditions (Hue, 1988). It has been shown that organic compounds containing two functional groups that can bind to the metal oxide surface are better electron donors as opposed to ligands that form a monodentate surface complex (Darwent and Lepre, 1986; Wehrli *et al*., 1989).

Hydroquinone reduction of manganese dioxide

One of the main reasons for the formation of humic substances in soils is as a result of the oxidative polymerization of polyphenols (Scheffer and Ulrich, 1960; Felbeck, 1965; Huang, 1991). This polymerization causes a darkening of the polyphenols (Scheffer *et al*., 1959; Scheffer and Ulrich, 1960).

Manganese(IV) oxide has been determined to be the most effective for the abiotic oxidation of hydroquinone solutions of pH ranging from 4 to 8. When no oxides are present in the hydroquinone solution, the dark coloration only occurs when the initial pH of the solution is greater than or equal to 7.0. The addition of manganese oxide drastically increases the magnitude of oxidation in the manganese oxide systems. This accelerated oxidation can be attributed to a number of processes such as: manganese oxides Lewis acid behaviour that accepts electrons from hydroquinone, leading to its oxidative polymerization; the acceleration of oxidative polymerization pushed/driven by an increase in the pH that is also caused by the reduction of manganese oxide. In the absence of manganese oxide, hydroquinone forms a colourless solution.

The rate of radical formation on manganese dioxide at high pH (i.e. pH value of 9.0) was studied by Ono *et al*. (1977). It was suggested that the mechanism incorporated the removal of protons from hydroquinone prior to the process of electron transfer. The reduction of Mn oxide by hydroquinone was suggested to be a first order reaction (relative to oxide loading) by Stone and Morgan (1984a) and that the reaction has to occur on the oxide surface. This implies that phenols form a surface complex before electron transfer occurs.

McBride (1989a, b) investigated the factors that affect the oxidation of dihydroxybenzene and the degree of Mn^{2+} that is solubilized. Kung and McBride (1988) studied the kinetics of the oxidation of hydroquinone by hausmannite at pH 6. From the release or production of Mn^{2+} together with the decrease in hydroquinone from solution showed electron

transfer to be occurring from hydroquinone to the oxide. This proves that the manganese surface is reduced from the electrons drawn from the hydroquinone thus releasing Mn^{2+} into solution.

Browning caused by the high intensity absorption of conjugated chromophoric groups and upward shifts in the ultraviolet-visible spectral baselines shows that higher hydroquinone concentrations increase the amount of polymerization through probably the coupling of free radicals, as its been shown that the presence of these free radicals is correlated to the concentration of hydroquinone (Huang, 1991).

It has been shown that the addition of manganese oxides greatly increased the darkening over the pH range of 4.0 to 7.8. The amount and rate of darkening varies with the manganese oxide and the pH of the system. The oxidative polymerization of hydroquinone in the manganese oxide systems is greatly increased when conditions are brought to neutral rather than acidic pH values (Huang, 1991)

Weast (1978) showed that the reduction of manganese dioxide requires greater amounts of H^+ than that produced by the oxidation of diphenols $C_6H_4(OH)_2$ as indicated by the following reactions:

$$MnO_2 + 4H^+ + 2e^- \leftrightarrow Mn^{2+} + 2H_2O \quad E^o = +1.208\ V \qquad 1.15$$

$$C_6H_4(OH)_2 \leftrightarrow C_6H_4O_2 + 2H^+ + 2e^- \quad E^o = -0.6992\ V \qquad 1.16$$

The above overall redox reaction (from 1.15 and 1.16) E^o value of +0.509V shows that this oxidation process by manganese dioxides is thermodynamically favoured.

It was determined by Schnitzer (1982) that the rate determining step of the oxidative polymerization reaction in the formation of these humic compounds, to be the formation

of a semiquinone radical incorporating a one-electron transfer reaction. A fraction of the naturally unstable semiquinones will be stabilized, by coupling with each other to form stable humic acid polymers. As the coupling of radicals requires no activation energy, the semiquinone coupling is kinetically favoured over the formation of quinones during the reduction of manganese oxides (Chang and Allan, 1971).

The extent of darkening that occurs as a result of this surface polymerization among different manganese oxide systems varies. For example the darkening is more intense in systems containing birnessite and cryptomelane than in the presence of pyrolusite at the initial stages of the reaction. As the reaction proceeds towards the later stages, the opposite is true (Huang, 1991).

Birnessite and cryptomelane are short range ordered manganese oxides both having much greater specific surface areas than pyrolusite and cryptomelane (Oscarson *et al*., 1983; Huang, 1991).

The amount of manganese dioxide in the pyrolusite is much higher than the birnessite and cryptomelane oxides. This is the reason for higher concentrations of dissolved manganese and the greater extent of darkening in the former at a pH = 4 (Huang, 1991). Therefore the compounds responsible for darkening are most likely adsorbed in greater quantities by shorter range ordered manganese oxides such as cryptomelane and birnessite than pyrolusite which is a longer-range ordered oxide (Huang, 1991).

Many other organic compounds have been studied and determined to favour the reductive dissolution process of manganese oxides. These include: Salicyclic acid, pyruvic acid, and oxalic acids (Stone and Morgan, 1984a, b).The oxidative decomposition of maltate

(Jaurequi and Reisenauer, 1982) and glutamate (Traina and Doner, 1985) have also resulted in the reductive dissolution of manganese oxides (Huang, 1991).

Monophenolic compounds, especially those containing electron-donating substituent groups on the aromatic rings have also been determined to reduce manganese oxides (Lehmann *et al*., 1987; Stone, 1987; Huang, 1991).

1.10.4 Dissolution of metal oxides mediated by heterogeneous charge transfer

a) Dissolution using oxidation of reducing sugars

The kinetics of the oxidation of D-glucose by manganese(III) has been investigated by Bakore *et al*., (1965) and manganese(III) is determined to act as a one electron transfer oxidant (Gupta and Begum, 1999).

b) Siderophore ligands (DFO-B) for dissolution of hausmannite and manganese

Organic ligands known as siderophores with a very high affinity for Fe(III) have been shown to dissolve iron(III)-bearing minerals, thereby increasing the bioavailability of iron. A similar effect may occur for an application for the dissolution of manganese, since recent studies have shown that siderophores are capable of forming stable Mn(III) complexes in aqueous environments and that they can promote the dissolution of Mn(III)-bearing minerals such as manganite (γ-MnOOH) (Pena *et al*., 2004).

Desferrioxamine B (DFO-B), is a common trihydroxamate siderophore, produced by bacteria and fungi, which could play a role in the reduction of soluble Mn(III) to Mn^{2+}. The mixed-valence Mn(II, III) oxide mineral, hausmannite with the formula Mn_3O_4, is a proposed intermediate in the oxidation of Mn^{2+} to thermodynamically stable MnO_2 (Pena *et al*., 2004). In studies, dissolution was measured as a function of pH at 25°C.

Pena *et al*., (2004) determined that in the absence of the ligand, the highest concentration of total Mn in solution was observed at pH ≈ 5. A sudden decrease was observed in the extent of dissolution at pH > 5, however, no appreciable dissolution occurred at pH > 8. In the presence of DFO-B, ligand-promoted dissolution dominated at pH > 8, with more than 90 % of the ligand complexed within 1 hour after addition. Below pH ≈ 8, a combination of reductive, ligand-promoted, and proton-promoted dissolution was observed. Pena *et al*. (2004) showed that complex mechanisms are involved in the DFOB-promoted dissolution of hausmannite, with several possible simultaneous dissolution pathways.

The study showed how hausmannite dissolves, both in the absence and in the presence of a strong complexing ligand, such as DFO-B, which greatly enhances dissolution at pH 5,7 and 9 (Pena *et al*., 2004).

Faster kinetics for hausmannite dissolution compared to those for goethite, indicates that there may be competition between Fe(III) and Mn(III) towards DFO-B.

Duckworth and Sposito (2005) investigated the interaction of desferrioxamine B (DFOB), a common tri-hydroxamate siderophore, with manganese. They determined stability constants for both Mn(II) and Mn(III) complexes with DFOB, and found that desferrioxamine B stabilizes Mn(III) for the pH range 7.0-11.3, forming a $Mn(III)HDFOB^+$ complex. The $Mn(III)HDFOB^+$ complex may be formed by DFOB-promoted dissolution of solid Mn-oxides. At pH > 6.5, the dissolution of manganite (MnOOH) in the presence of DFOB is predominantly a non-reductive ligand-promoted reaction, whose rate (RL) is proportional to the adsorbed surface concentration of DFOB. At pH < 6.5, Mn^{2+} is the dominant species resulting from manganite dissolution, thus implicating a reductive dissolution pathway (RR). A change either in the chemical speciation of the surface or in the thermodynamic driving force within the system. is a reason for the change in dissolution mechanism from ligand-promoted to reductive (Duckworth and Sposito, 2005).

1.10.5 Oxidation of chromium(III) to chromium(VI) and the simultaneous reduction of manganese dioxide

Chemistry of chromium

Chromium can exist in a number of different oxidation states, ranging from –2 to +6 in the natural environment. The most stable and generally important states are Cr(III) and Cr(II) under surficial conditions. Some of the main oxides of chromium are: Cr_2O_3, CrO_2 and CrO_3 (Cotton *et al*., 1988; Fendorf *et al*., 1992).

a) Chromium(III)

Chromium(III) is considered to be less of a problem in terms of mobility and toxicity than the more toxic chromium(VI) (Fendorf *et al*., 1992). The main feature of Cr(III) complexes in aqueous solutions is that they are relatively kinetically inert. This is the main reason why there is an abundant number of these complexes that can persist for long periods in solution under thermodynamically unstable conditions (Cotton *et al*., 1988).

b) Chromium(VI)

This is the most toxic form in which chromium can exist (Fendorf *et al*., 1992). Chromium in this oxidation state is highly mobile in soil and aqueous environments. The reduction of Cr(VI) levels in the environment can be achieved by remediation and reactions with electron donors such as organic, sulfide and Fe(II) compounds. Manganese oxides and molecular oxygen are the most common natural oxidizing agents (Eary *et al*., 1987).

Oxidation of Cr(III) by MnO_2

It is well known that Mn(III) and Mn(IV) oxides are relatively strong oxidants and facilitate electron transfer reactions on a heterogeneous level. These electron transfer reactions have been studied for a wide variety of sorbates ranging from organic electron

donors such as phenols, humic substances and quinones, to metals in a polyvalent state i.e. Cr(III), U(IV), Fe(II) and even Co(II) (Stone, 1987).

It is believed that the exact mechanism by which electron transfer occurs between the sorbates and surface of the manganese dioxide concerns both an inner and outer sphere mechanism (Brown *et al*., 1999).

Oxidation of organic ligands can occur through adsorption by inner sphere complexation (Stumm, *et al*., 1992, Brown *et al*., 1999).

Metals such as Cr(III), Pu(III), and Co(III) are all shown to be oxidized by manganese oxides. Thus effecting/having an effect on their solubility, mobility and even toxicity (Haung, 1991). Thus manganese oxides can initiate the oxidation of Cr(III) to Cr(VI) because they and their oxyhydroxide counterparts form part of a reactive series of compounds found in the environment (Amacher, 1982; Haung, 1991). This subsequent oxidation process can thus convert a normally immobile inert chromium species into its more toxic form (Amacher, 1982). A similar case study has been shown for Pu(III) oxidation to Pu(VI) (Amacher, 1982).

a) Oxidation/reduction process Cr(III) MnO_2 interaction

Regarding the oxidation of Cr(III) to Cr(VI) by manganese oxides, many aspects of the reaction kinetics and other important conditions (experimental and environmental) have been investigated, such as general characterization of oxidation process (Johnson *et al*.,

1991; Fendorf, 1992), Kinetics (Eary *et al*., 1987) and other general aspects of catalysis and theoretical considerations (Selim, *et al*., 1996; Apte *et al*., 2005; Apte *et al*., 2006).

Proposed reaction

The overall reaction as proposed by Amacher and Baker (1982) produces Cr(VI) in the form of $HCrO_4^-$ species:

$$Cr^{3+} + 1.5\ MnO_2 + H_2O \leftrightarrow HCrO_4^- + 1.5\ Mn^{2+} + H^+ \qquad 1.17$$

Garrels and Christ's (1965) thermodynamic data shows that the forward reaction is not thermodynamically favoured under standard conditions i.e. $G^o = 2.48$ KJ mol^{-1}(Fendorf, 1992).

b) Chromium species distribution for the oxidation reaction

A typical distribution of chromium species as a function of time has also been determined for a set of selected standard conditions. These conditions (adopted by Johnson *et al*., 1991) include: $I = 0.01$, pH = 4.5, MnOOH = 0.92 $m^2\ L^{-1}$ (0.34 mM) and Cr(III)

concentration of 0.5 μM. The kinetics of the reaction was also reported to be fast (minutes for reaction to reach completion).

Factors affecting oxidation process and kinetics

The rate of oxidation by manganese dioxide on Cr(III) appears to be faster than for oxidation implementing/using oxygen. This was recognised by comparing the rate constants established in different environments. A rate constant of 1.34 $M^{-1}s^{-1}$ was found for a second order reaction of Cr(III) with MnO_x (Schroeder and Lee, 1975), while van Der Weij-den and Reith (1982), found the rate constant for MnO_2 in fresh and seawater to be 0.0063 $M^{-1}s^{-1}$) (Johnson, 1991).

The main reason for determining rate constants for the Cr(III) oxidation by environmental compounds such as manganese dioxide is to establish the rates and extent of the reaction in soils. This is important due to the potentially toxic products formed. Hem and Lind (1983), and later Murry *et al*. (1985) determined that one of the main forms of MnO_x is manganite, an important form of manganese oxide found in natural water systems (Johnson, 1991).

Many investigations have been done on the above effects of the oxidation process and kinetics with respect to characterization of the manganese dioxide phase (Eary and Rai, 1987).

Johnson *et al*. (1991) performed a study on the oxidation rate of Cr(III) with manganite. Factors such as manganite concentration, Cr(III) concentration, pH, temperature, ionic

strength and presence of other species, for example organic ligands, were investigated with respect to rate of oxidation of Cr(III).

a) pH

It has been suggested that a probable rate limiting factor in the oxidation of Cr(III) by manganese dioxide (B) is due to the slow de-sorption of anionic Cr(VI) in acidic conditions. Precipitation of $Cr(OH)_3$ in neutral-to-alkaline solutions could also be a contributing factor causing slow de-sorption at the surface of the oxide (Apte *et al*., 2006).

Fendorf *et al*. (1992) investigated the effect pH had on the rate of Cr(VI) formation. It was also hypothesized that an increased amount of anionic Cr(VI) would be expected to bind at lower pH values. However, as pH increased there was a faster decrease in the amount of Cr from the solution (Fendorf *et al*., 1992). Eary and Rai (1987) also did studies on the effects of pH. For a Cr(III) concentration of 9.6E-5 mol L^{-1} the rate of Cr(VI) formation was measured for solutions with pH between 3.0 and 4.7. There appeared to be only a minimal increase in the rate of Cr(III) oxidation, and higher pH values did not show a marked increase in the rate (Eary *et al*., 1987).

In a study performed using a stirred-flow cell, the rate of oxidation was investigated at pH=3 and pH=5 (Fendorf *et al*., 1992). The main significance of using a stirred-flow cell is that it allows for the fast mixing of reactants, which minimizes transport effects at the reacting surface (Sparks *et al.,* 1989). The rates for the reaction at pH=3 were slower than the rate of oxidation at pH=5 which was too fast to be accurately interpreted. At pH=3 the

rate of oxidation was however maintained for longer times as compared with those rates for pH=5. The rapid oxidation observed for pH=5 was found to be independent of the Cr(III) concentration. Once the rapid initial oxidation took place, higher Cr(III) concentrations caused a greater decrease in the oxidation rate (Fendorf *et al*., 1992).

b) Chromium(III) concentration

In general it has been determined that the dependence/relationship between of the kinetics for the Cr(III) concentrations is not that straightforward or linear. For high Cr(III) concentration there is a drop in the reaction rate, whereas for low concentrations of the metal the rate has been determined to exhibit a 1st order dependence. One possible reason for the above relationship has been suggested to be as a result of either Cr(III) or Cr(VI) inhibiting the reaction (Johnson *et al*., 1991).

c) Surface sites and electrophoretic mobility

The surface on which the oxidation of Cr(III) occurs plays a vital role in the kinetics of the oxidation/reduction reaction. Furthermore, it has been deduced that aqueous Cr(III) oxidation occurs via a direct interaction with the B-MnO_2 surface (Eary *et al*., 1987; Apte *et al*., 2006). Different oxides have been found to contain different surface sites based on the environmental conditions and how the oxides were formed.

There have been numerous electrophoretic mobility studies undertaken, many of which have focused on and shown that charge reversal is a common phenomena on oxide surfaces (Healy *et al*., 1968; Loganathan, 1971; James *et al*., 1972; Murray, 1974).

This surface charge is an important factor that is related to Cr(III) oxidation. An increase in pH and ionic strength cause an increase in the negative oxide surface charge. It has been demonstrated that in the presence of enough Cr(III) this surface charge can reverse to become positive. As the pH increased, this charge was also shown to increase (Fendorf *et al*., 1992).

d) Ionic strength effects

Fendorf *et al*. (1992) found that changing the ionic strength of the solution by changing the concentration of $NaNO_3$ had an effect on the oxidation process. Although it was found that an increase in the pH resulted in limiting the oxidation of Cr(III), higher ionic strengths assisted oxidation. Furthermore, increasing the ionic strength also causes an increase in the negative surface charge value (Fendorf *et al*., 1992).