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The Weathering of Platinum from Nuggets and Platinum Immobilisation by *Cupriavidus metallidurans*

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Graduate Program in Geology
A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science
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THE WEATHERING OF PLATINUM FROM NUGGETS AND P
IMMOBILISATION BY AVIDUS METALLIDURANS

(Spine title: WEATHERING AND IMMOBILISATION OF PLATINUM)

(Thesis format: Integrated Article)

by

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Graduate Program in ~~Deep Earth~~ Earth Sciences

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science

The School of Graduate and Postdoctoral Studies
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entitled:

The Weathering of Platinum from Nuggets and P
Immobilisation by *Cupriavidus metallidurans*

is accepted in partial fulfillment of the
requirements for the degree of
Master of Science

Date

Chair of the Thesis Examination Board

Abstract

Two studies were conducted to investigate the biogeochemistry of the first project. The first project was examined to evaluate mine precipitation processes occurring at the mine-grain interface. The precipitation pits demonstrated as well as acicular, iron oxide grain surface evidence that this interface is an important chemical weathering. Element mapping revealed that structure can be linked to morphological features on the grain surface. In the second soil bacterium was reacted with aqueous platinum and rapidly immobilised platinum. XANES/EXAFS analysis demonstrated that platinum coordinated to the bacteria and platinum from chloride to carboxyl functional groups. This was revealed able to precipitate colloidal platinum. Both of these studies demonstrate the importance of natural platinum compounds in natural systems.

Keywords: platinum, surficial weathering, Fifield Platinum Project, *Cupriavidus metallidurans*, secondary mineralisation

CoAuthorship Statement

Chapter 2, entitled Surface weathering of platinum grains, S.G Campbell, R. Gordon and E. Seitzman has been prepared as a manuscript for submission for publication. Campbell performed microscopy and analyses, drafted and prepared the figures provided technical support at Argonne National Laboratory platinum grains and Reith and Southam provided the funding and advised on all aspects of this study.

Chapter 3, titled Immobilisation of particulates by alliduran was authored by S.G. Campbell, L. Maclean, D. Brewster, F. has been prepared as a manuscript for publication. Campbell designed the experiments, microscopy and analysed the manuscript and prepared the tables and figures. Maclean provided synchrotron data, Brewster provided technical support at Argonne and Reith and Southam provided support this research and advised on all aspects of this study.

Acknowledgments

No man is an island a thesis one man. I have to admit, I
words& I hope I didn't miss anyone, but in case I did, that

There are many people who make a thesis come to fruition.
financial, motivational and emotional support make it possible
happen in every way possible. You're simply wonderful! My
been a great supporter especially my pal Tommy Campbell. Thank you
much. Dr. Southam, thank you for believing in me, a scientist
just two years ago. You have the uncanny knack for turning
way of inspiring things. And to you lablings & Jer, Jenine,
Bird, Andrea, Nahed, Alex and Jie, I wish you the best
friendship and support. I would be remiss if I didn't mention
Maclean, and our good friend, who provided instrumental support

There are many people who have made me the scientist
to Dr. Stephen Altaner. If I hadn't sat in his class a decade ago
a geologist. A special thank you to my family and friends
especially to my Grandpa Havlena who taught me to love the
me wonder as a boy. I owe my formal geology education to
Gordon Southam, Stephen Altaner, Duke Ferrel, Wally Mackenzie, and

¹Donne, J. in Meditation XVII.

Cam Tsujita and Burns Cheadle. You have all provided and nurtured my enthusiasm.

I would also like to thank my defence committee and Moser, Richard Gardinore, Robert S. Taylor, Nathan A. B. Zepf, and the beamline scientists at the Advanced Photon Source Laboratory have helped make this all happen.

I would like to thank a number of groups for funding my Ontario Graduate Scholarship and the Department of Earth Science

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List of Abbreviations

°C	Celsius
µg	Microgram
µL	Microlitre
µm	Micron or micrometre
µM	Micromolar
µXRD	Micro-X-ray Diffraction
aq	Aqueous
ATP	Adenosine triphosphate
CFU	Colony forming unit
DDI water	Distilled-deionised water
EDS	Energy dispersive spectroscopy
EMS	Electron Microscopy Sciences
eV	Electron volt
EXAFS	Extended X-ray Absorption Fine Structure
FEG	Field emission gun
hr	Hour
ICP-AES	Inductively coupled plasma emission spectroscopy
keV	Kiloelectron volt
km	Kilometre
L	Litre
M	Molarity
mg	Milligram

min	Minutes
mL	Millilitre
mm	Millimetre
mM	Millimolar
nm	Nanometre
g	Gram
PGE	Platinum group element
PGM	Platinum group mineral
pH	$-\log[H^+]$
ppb	Parts per billion
ppm	Parts per million
SEM	Scanning electron microscope
SRB	Sulphate-reducing bacteria
t	Time
TEM	Transmission electron microscope
XANES	X-ray Absorption Near Edge Structure
XAS	X-ray Absorption Spectroscopy

Chapter 1

Introduction

Platinum, one of the six platinum group elements (PGEs) along with rhodium, ruthenium, iridium, palladium, and rhenium, has become highly sought after because of its physical and chemical properties (Macdonald 1991, 1987; Nixson and Hammack 1991). Platinum is resistant to oxidation and corrosion and it is used in a wide range of chemical and industrial processes (Macdonald 1991). Platinum is also used in the treatment of cancer (Auerbach 2005). The price of this metal has increased over time because the supply is limited and the demand is increasing. Platinum is among the rarest elements in the lithosphere and its concentration is typically less than 1 ppb. To be mined profitably, platinum deposits require enrichment over background level concentrations (Mungall and Odette 2008). There has been an increase in platinum deposit exploration and research over the past few decades and it is expected that new discoveries will be made in the future. The genesis of many platinum deposits remains unclear (Maier 2005).

1.1 Platinum enrichment in the crust

Platinum group element (PGE) deposits are enriched by hydrothermal and magmatic processes (Macdonald 1991). Most of the world's platinum deposits are associated with ultramafic complexes (Nixson and Hammack 1991). The genesis of platinum deposits in ultramafic complexes is still unclear.

primary deposits that are inextricably tied to sulphur chemistry and the processes that transport platinum and other metals from the mantle to the crust (Macdonald 1987; Mungall 2005; Naldrett 2008).

Platinum is deposited when sulphur concentration exceeds the available platinum from the silicate melt (Macdonald 2005; Naldrett 2008). During a metallogenic event, the sulphur ascends from the mantle where it becomes trapped. Once sulphur saturation in the magma occurs and an immiscible sulphur phase accumulates at the bottom of the magma chamber, highly chalcophile platinum is incorporated into the sulphur phase (Macdonald 2005; Mungall and Naldrett 2008; Kretz 2008). Platinum sulphide is a common product of magmatic processes often forming platinum-bearing reefs within large mafic intrusions (Macdonald 2005). Although poorly understood, normal brines are a cause of redistribution (Mungall and Naldrett 2008).

Alluvial PGE placens were either dominantly zoned mafic-ultramafic "A-type" (and to a lesser extent "B-type") or primary magmatic intrusions that were formed by processes above the mantle (Macdonald 2005; Nixon and Hammarck 2005; Kretz et al. 2010). A-type complexes intrude into continental and oceanic crustal environments and are associated with continental and oceanic arcs (Hammarck; Tost et al. 2005).

1.2. Platinum placer deposit formation

An important source of platinum is the Bushveld Complex in South Africa (Bassett, 2005). There are several types of alluvial placers worldwide that are major sources of platinum (Merrill, 1969). Formation of an alluvial platinum placer begins with extractions of platinum from source rocks at the surface or near the surface. Keekstra et al. (2010) describes a process where minerals from primary magmatic deposits (or primary magmatic intrusions) are supergene and later diagenetic alteration of secondary mineralization experience chemical and physical weathering. Over time, the platinumiferous minerals and chemical elements from the source deposit are washed into streams where they are concentrated, deposited and transported by gravitational sorting. In some cases, platinum-bearing material is winnowed and lighter mineral fractions are preferentially eroded away. In primary magmatic intrusions, primary sources of placer platinum, other types of magmatic intrusions are also important. Platinum minerals have been documented in igneous rocks in several areas of South Africa, including the Bushveld Complex, the world's largest reserve of platinum (Merrill, 2005).

1.3 Platinum in supergene systems

In alluvial placers and other surficial weathering profiles, the conditions for platinum mobilization can be removed from exposed primary magmatic intrusions and secondary

enrichment (Bowers 1986; Bowers et al. 2001; Hanley 2005). Supergene enrichment and laterization are processes that occur in primary ore deposits containing subeconomic sulphides (Guilbert 1986). These regions only occur in tropical and semiarid climates where high temperatures and humidity promote chemical weathering. Groundwaters above the water table are able to leach a large volume of metal and redeposit them into smaller volumes of high grade material (Guilbert 1986).

Pyrite is the most common hypogene sulphide and its oxidation leads to enrichment that takes place in the supergene environment with metal sulphides (Guilbert 1986). When exposed to oxygen and iron/sulphur oxidising bacteria above the water table, pyrite forms ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) and ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) which in turn act as solvents for other sulphides, including copper, zinc, lead, and gold (Mason 1986; Guilbert 1986; Enders 2000). Ferric sulphate is reduced to ferrous sulphate during the oxidation of other metal sulphides. The oxidized metal ions will either be carried from the site of oxidation by meteoric waters or will precipitate (Anderson 1982; Enders 2000). Because of its similar chemical properties, it is reasonable to think that processes responsible for the gold are comparable for the dissolution of other metals. Iron is more easily oxidised and more soluble than gold, making it more favourable for gold dissolution. However, the solubility of gold is very low (Bowers 1986; Bowers et al. 2001; Reith 2007).

Acidified and oxidised waters descend and deposit that lack the target metal. An insoluble mixture of iron sulphates including jarosite ($K_3Fe_3(OH)_6(SO_4)_2$), iron oxyhydroxides such as goethite and hematite (Fe_2O_3) are also formed during the oxidation of iron in the leach heap, giving it the characteristic orange colour (Anderson 1982; Emswiler 2000; Sárnezet al 2008). As evidence of this oxidising process, iron oxyhydroxide coatings have been found on termite mounds (Augusthiusson et al 1986; Sárnezet al 2008).

Descending surface water oxidises metal below the water table where redox conditions favour reduction and precipitation. This process mediates deposition of the ores as it readily transfers its oxygen to other metals. These metals usually have a stronger affinity for sulphur than pyrite. Much metal sulphides are formed, however, they are not reduced in the reductive zone. The acidic water is neutralised when they come into contact with carbonates. This process is cyclical and ongoing. Fluctuations in the physical location of the ore redox interface in a leach heap can form and be of economic importance (Anderson, Emswiler 2000).

14. Aqueous geochemistry

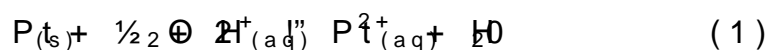
Platinum is mobile under supergene conditions (Brown 1984; 1986; Zaroc et al 2001). The platinum concentration in the leachate is 3 to 6 orders of magnitude less concentrated than in the heap leachate;

concentrations are dependent on a number of factors (Barnes 1997; Mungall and Naldrett 2008a, 2010; Kubrakov 2011). Surficial water flowing through areas with elevated elevations and/or their mine tailings, would presumably have more waters draining areas lacking platinum cementation. The solubility of platinum is also controlled by its solubility properties of an aqueous medium as well as platinum's ability to form complexes with ligands commonly found in its solution, transportation and sequestration (Barnes 1986; Coleman 2008; Kubrakov 2011). Furthermore, hydrodynamic characteristics will also influence the migration of dissolved platinum (Kubrakov 2011).

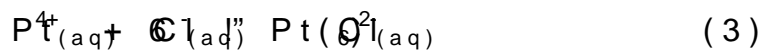
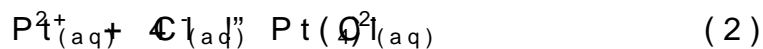
At standard surface water temperatures (25°C) and partial pressures as simple aqueous ions except at extremely high pressures, and must complex with other dissolved ligands to be stable (Wood 1988). Complexation is an important process by which platinum cations bind to one or more negatively charged anions or other complexing species, concentrations of simple metal ions in solution would remain too low to form economic deposits. Platinum complexed to anions in solution, however, can be concentrated to generate profitable grades of metal (Hanley 2005).

The literature lacks reliable experimental and stability data for platinum species and complexes in natural waters (Mumtaz and Wood 1988; Coleman 2008). The predicted oxidation state for platinum

Pt^{2+} as shown in Equation 1 (Hamley 2005). In very oxidizing conditions, platinum can exist as Pt^{4+} , but Pt^{2+} is the more common aqueous species. Experimental data relating to the thermodynamic stability systems related to this particular oxidant are given by Colborn et al. (2008). Platinum forms a wide range of covalent interactions with anions such as chloride, cyanide, amine, hydroxide, sulfide and thiolate (Mason and Wood 1990; Vlassopoulos 1990). Complexation, however, depends on platinum's preference for various ligands; it ultimately depends on the transporting fluids and the availability of ligands in the environment (Rose 1974).

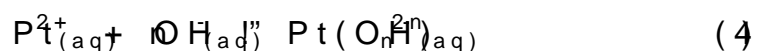


In oxidizing waters that are acidic, common chloride anions form stable complexes with Pt^{2+} (Mason and Rose 1974; Bowles 1986; Wood 1988). These reactions are given in Equations 2 and 3 (Hamley 2005). The aqueous Pt^{2+} compounds $PtCl_2$ and $PtCl_4$ are known to exist, but $PtCl_4^{2-}$ is the predominant anion at 25°C (Mason and Wood 2001).



In oxidizing environments with more basic (less acidic) conditions, complexation with the species PtO_2 (Colborn et al. 2008). Equation 4 shows a simplified hydration reaction (Woodward 1991) that occurs in water, especially in neutral and basic waters, and platinum

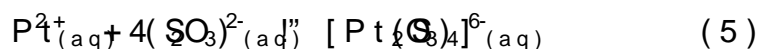
predominate in weakly acidic complexes when chloride is limiting (Mountain and Wood 1992; Azarova 2001). Aqueous hydroxide compounds, in Pt(OH)₂ and Pt(OH)₄, pH increases, predominance of these complexes is shifted to species (Mountain and Wood 1988; Wood 1991, 2001). Mixed hydroxyl complexes are considered to be unimportant for platinum mobility (Mountain and Wood 1992; Azarova 2001).



Depending on the concentration of other anions that Pt²⁺ cations, aqueous platinum carboxylic acids can mobilise platinum (Mountain and Wood 1990; Hanley 2005). Humic substances are components of normally found and water-soluble functional groups in humic acids abundant oxygenated and dissolved in neutral weakly acidic become negatively charged and react with platinum to form platinum organo complexes (Mountain and Wood 1990; Wood 1990; Kubratova 2011). Humic substances have been shown to increase the stability of Pt(OH)₂ (Mountain and Wood 1990; Hanley 2005). Despite the fact that they form stable complexes with platinum, they are not abundant in natural waters, their solubility with platinum is insufficient in waters by hydroxides (Mountain and Wood 1988; Azarova 2001).

Bisulphide would be expected to form a significant portion of platinum complexes in sulphidic environments, however platinum is not mobile when conditions are favourable for bisulphide formation (Mountain and Wood 1988; Azarova 2001). There are, however, metastable platinum bisulphide complexes that

form oxides and acid sulphate environments (Anthony and Williams 1994). Thiosulphate appears to be important during the weathering of sulphide ores as well as the formation of platinum sulphates in alluvial sediments containing the Bushveld complex and adjacent areas (Anthony and Williams 1994; Mellor 1995). Equation 5 depicts the reaction (Anthony and Williams 1994).



These aqueous platinum complexes are stable in acidic solutions but when the solution encounters an environment that favours chemical precipitation. Subsequent deposition of platinum (Wood 1990). Chemical transformation involves the formation of a metastable dissolved platinum perchlorate complex which is transformed to a platinum hydroxide precipitate in acidic, neutral, or basic lakes, rivers or ground water (Wood 1990). In a humic acid-rich aqueous system, an organic matter protected platinum complex is stable (Wood 1990; Wood 1992). If dissolved platinum is not stable, it may be chemically reduced to elemental platinum and precipitated (Wood 1986). It is worth noting that while a number of aqueous platinum complexes are possible, the kinetics of the reaction are generally slow, to occur unless catalysed (Wood 1990).

15. Formation of secondary platinum and platinum grains

Placer platinum is commonly associated with platinum grains. Archaean type complexes weathering profiles commonly occur as platinum (Bowles 1986; Cabot 1996; Todt et al. 2005). The grains are often in deposits where no nuggets of that size are in the matrix. PGE in host rocks are commonly < 5 but placer grains up to several (Bowles 1986; Mall 2005). This increase in platinum nugget size from the source to evidence that platinum nuggets grow during diagenesis (Cousins and Kinloch 1976; Bowles 1990, 1996; Cabot 1996) is thought that elemental and alloyed platinum nanoparticles grow through the continual accretion of platinum from metal alloy Bowles (1986; Cabot 2005). As iron is freely available in the lateritic zone, it could form alloys (Bowles 1986) but it is fair to speculate that copper and iron combined Fe alloys to form Pt-Fe-Cu grains in placers (Cabot et al. 1996). Primary high temperature magmatic and hydrothermal alteration, however, cannot be ruled out as a mechanism (Slanket et al. 1996; Cabot et al. 1996, Telmeier et al. 2005).

Mineralogical and petrologic studies of alloys have shown accretionary zones of platinum nuggets. Tarkenton (1976) noted the presence of platinum growth halos around proof that this process is well described by Bowles (1986) and is

overgrowth of PGE crystal faces on older, weathered grains (2011) find that iron hydroxides in supergene environments from the iron sulphides could preferentially scavenge inorganic PGE or adsorb them to their positively charged surfaces. Mixed platinum species could be transported as colloids in the sediments.

On the other hand, some platinum alloy grains show alteration suggesting that the nuggets are "shrinking" and undergo particular grains, the periphery has experienced selective platinum. In essence, all the platinum grains are becoming enriched as they are altered and weathered (2007, Tena (2008), et al (2008) describe highly irregular and fractured shapes of supergene platinum nuggets as a result of weathering profiles.

The alteration of platinum grains, is the subject of ongoing controversy (2008). Further characterisation of the precipitation processes occurring at the nugget solution interface needs to be undertaken geochemical cycling of platinumiferous material in surficial

1.6 Microbiology of platinum

Changing conditions within surficial weathering con- placers or supergene/laterite deposits are important factors

promote the abiotic dissolution and precipitation of complex minerals. The role the biosphere plays in platinum mobility in reactive systems with bacteria is largely unknown. However, recent work has been conducted to study this interaction. In any future work, it could be possible to study this interaction in relation to other metal-bacterial reaction systems.

Microbes survive in environments with high metal concentrations have the ability to either use these as a part of their metabolism or as sources of nutrition rather than as a toxic effect (Reithel et al 2009). Metal resistance is genetically encoded and involves detoxification mechanisms (Schwartz 1996; Reithel et al 2009). Metal ions must first be internalised. They passively if driven by a chemiosmotic gradient or the energy molecule adenosine triphosphate (ATP) is expended during transport. Once internalised, they are necessary for normal cell activity or compete with other physiological processes (Nies 1999). Metal resistance requires that the toxic metal ions are and/or expelled from the cell. This requires that the toxic metal ions are chemically reduced and/or complexed to other ligands at the cell surface. Commonly, these products are toxic to themselves so subsequently they may still be toxic. Efflux systems pump out ions at the expense of a cation/proton antiporter proteins within the cell envelope. This energy gradient that exists across the membrane and pumps in protons (Silver 1996; Nies 1999).

The ability to metabolise metallic compounds allows participate in a number of reactions in a number of ways to catalyze reactions (Singer and Stumm 1970; 2006) Acidithiobacillus, thiooxidans, oxidising and Acidithiobacillus ferriferus iron and sulphate have been shown to contribute to the formation of acid mine drainage by generating oxidising pyrite faster than the abiotic rate (Singer and Suzuki 1989; Neal 2006). Symbiotic, chemolithoautotrophic bacteria have contributed to the enrichment of copper in the Morenci Porphyry Copper Deposit. Calculations suggest kilograms of bacteria in a 10³ m² weathered rock with the potential to mobilise between 0.01 and 0.1 times the amount of copper as they are able to (Neal et al. 2006). Aerobic sulphate reducing bacteria in acid mine drainage sites produce sulphate as a by-product of their metabolism, forming metal sulphates (Donald and Fradette 2006). Neal et al. (2006) calculated that approximately 2% of all copper in the Morenci deposit is fixed by sulphate reduction. The enrichment of copper in the Morenci deposit is attributed to the enrichment of copper by inorganic processes.

Microorganisms are involved in the biogeochemical cycling of metals, such as gold, under natural conditions (Southam et al. 2009). The formation of gold in Australia, Alaska and the famous Witwatersrand in South Africa have been attributed to bacterial activity (see references). Bacteria are also involved in the enrichment of platinum in aqueous

platinum produced by bacterial platinum (II) precipitation in water
 reduced to crystalline elemental platinum (C2011)
 supports experimental evidence that precipitation is a common
 platinum nugget formation mechanism. Scanning electron
 microscopy (SEM) of small alluvial platinum grains has
 morphologies that resemble those of the first
 evidence of bacterioformation. The authors propose that
 growth started with bioreduction of platinum covered decay
 roots. As the nugget grew and microbial activity increased,
 microbial activity concentrated biogenic precipitation of
 platinum. Subsequent electrochemical accretion of elemental
 growing grain likely worked in conjunction with bioreduction
 and microbially mediated precipitation were not necessarily
 mechanisms complementary and both platinum formation in
 placer deposits.

1.7 Hypothesis and study objectives

In order to improve our understanding of the biogeochemical
 studies were conducted as part of this thesis. In a periglacial
 environment, signs of physical weathering should be identifiable
 surface of placer grains. Microorganisms have proven successful
 immobilising aquifer metals. They should be able to play a role in
 weathered placer material. For example, metal ions

negative precipitating, a bacterium found to be living on the grains obtained from auriferous soils in northern Queensland (the Hit or Miss Gold Mine and the Hit or Miss Gold Mine), was cultured on platinum chloride (Richey 2006; 2009)

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Chapter 2

Surficial weathering of platinum grains

2.1. Introduction

Platinum, of the six platinum group elements (PGEs), is resistance to oxidation and corrosion has made it an ideal and automobile catalytic converters; yet, platinum is not (Nixon and Hammack 1991). Platinum is mobile under some environments. It can be oxidised, dissolved, complexed with ligands, transported, precipitated and deposited (Fuchs and Azarova 2001; Hyslop 2005). Proper conditions for platinum recovery commonly occur in alluvial systems and environments (Barnes 1986; Azarova 2001; Freytsis 2005; Hanley 2005)

Alluvial platinum typically occurs as platinum alloys and are associated with Alaskan type primary magmatic intrusions (Barnes and Macdonald 1987; Nixon and Hammack 1991; Freytsis 2005; Koettlitz 2010). These are mafic/ultramafic complexes 10 km in diameter and are located in tectonic arc sutures (Nixon and Hammack 1991; Teluk 2001, 2005). When platinum bearing host rock weathered, platiniferous material is physically and chemically broken down and transported in fluvial systems. Alternatively, in some cases, platiniferous material is weathered in situ and eroded away, leaving a residue of PGEs (Koettlitz 2010).

Favourable chemical and biological conditions for metal weathering commonly prevail in arid tropics (Anderson 1971; Sillitoe 2005). Mobilisation can occur when the chemical processes of enrichment and the extract metal from source rock exposed at the surface. Pyrite (FeS_2) is a common mineral in supergene environments exposed to water and sulphur oxidising bacteria, it can be oxidised to sulphuric acid (H_2SO_4) and ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$), the latter of which mobilises metal sulphides including copper, silver and gold (Mann 1984; Enders 2000; Sillitoe 2005). Surficial waters dissolve metal and carry it with the water table where it is possible to find economic concentrations (Guilbert 1986).

The acidic and oxidising supergene waters that mobilise metal could presumably solubilise platinum because it is more soluble than gold (Bowling 2007; Bickel 2017). To date, however, mineralogical and petrologic analyses of platinum grains have not explained the alteration processes affecting them. Platinum grains commonly larger than the source rock they are believed to be derived from platinum grains and undergo secondary mineralisation (Coulson 1976; Stumpfl and Tarkian 1976; Bowring 1994; Sillitoe 2006). Conversely, other studies indicate that platinum is susceptible to dissolution and weathering in supergene environments (Coulson 2007; Tertilt 2008).

In order to fully understand the basic principles of sulfation in weathering environments, further characterization of the processes occurring at the weathering interface needs to be based on chemical evidence of these processes and should be identifiable and detectable using electron microscopy.

2.2. Material and Methods

Platinum nuggets by gravity separation from platinumiferous and auriferous soils near Fifield, New South Wales, Australia, were examined to characterise surface weathering products. Grains were immersed in 2% formaldehyde to chemically fix any biological

Description of Fifield, New South Wales, Australia

The Fifield Platinium (Figure 1) is an area of past and current exploration and excavation located 380 km WNW of Sydney, Australia (Johannes 1989; Alford 1995, Teluk 2001). Alluvial and platinum and gold may be genetically linked to a 500 Ma Devonian ultramafic pluton that intrudes Ordovician Cambrian metasedimentary rocks. An Ordovician paleosuture reopened as a result of crustal extension during the Orogeny in the Alaska/Ural dunitites and peridotites were emplaced (Johannes 1995; Teluk 2001; Gray and Florko 2004). Subsequent period of eluvial weathering and fluvial erosion have reworked platinumiferous material throughout the Cenozoic (Teluk 2001) thought to be primary, having been eroded directly from the primary source of mineralisation has not been found (Slansky 1991; Teluk 2001).

Scanning electron microscope

Platinum grains were dehydrated at 50%, 75%, and 100% ethanol series for 15 minutes at each step. Grains were using a Tousimis® VSB drier and placed onto 12 mm carbon (Electron Microscopy Sciences [EMS]). Samples were osmium coated 5 nm with a CFIG-80 osmium plasma coater. Osmium coating reduces sample charging. A LEO 1530 field emission scanning electron microscope (SEM) at the University of Western Ontario, Western Ontario Nanofabrication Facility (UNF) Zeiss 1540-SXM (SEM) at the University of Western Ontario, Nanofabrication Facility (UNF) SU 6600 Analytical SEM at the University of Western Ontario, Department of Electrical and Computer Engineering (ECE) platinum grains and resolution high resolution scanning electron microscope (HRSEM) representing the diversity of morphology and features of platinum grains in SEM, were selected for further analysis. An Instruments INCA sight energy dispersive spectrophotometer (EDS) on the Zeiss 1540-SXM Xmax Silicon Drift Detector EDS on the SEM was used for elemental identification.

X-ray emission spectroscopy (XES) and X-ray Absorption Near Edge Structure (XANES) spectroscopy data collection and analysis

Two platinum grains selected for further analysis were analyzed at the Pacific Northwest National Laboratory (PNNL) Sector-20 Insertion Device beamline at the Advanced Photon Source, Argonne National Laboratory, Argonne, IL. X-ray emission spectroscopy

conducted to map the element distribution of the grains. X-ray energy reference values from Kortright and Thompson (2001) for 20 elements present in the sample. X-ray Near Edge Structure (XANES) measurements were conducted to determine the oxidation state of iron. XANES energy measurements were collected from each spot and were compared to the inflection of an iron foil (Williams 2001). Beam energy was set to 10.0 keV so that the iron would not be excited.

Element maps and X-ray emission spectra were analysed using Instruments VIEW D Scan Plot v. 4 and Instruments VIEW D Scan Plot v. 3. XANES data was processed by Athena (Ravel and Newville 2005). The edge of the samples was compared to the reference foil. Sample edge energy shift of 0.7 eV (at the 7100 eV) indicated oxidised iron.

Micro-Ray Diffraction (μ XRD)

Micro-Ray diffraction (μ XRD) patterns were collected using the Bruker AXS D8 Discover microdiffractometer in the Debye-Scherrer mode at the University of Western Australia X-ray source. An omega scan was performed from 7.5 to 45 degrees, with a step size of 0.2 degrees and a beam size of 300 μ m. Data was collected using a GADDS (Grazing Incidence Diffraction) system associated with the Bruker D8 Discover using Bruker's DIFFRACT software. The sample was intact for analysis.

2.3. Results and discussion

Examination of the weathering texture around the periphery of the plagioclase grains generally in good agreement with that of the plagioclase grains in the Fife Islands (Fife, 1991), concluded that the plagioclase grains in the Fife Islands are primary (magmatic) in nature.

The overall morphology of the grains varies considerably. This heterogeneity suggests that the grains were subjected to differing degrees of chemical weathering. A number of fluvial and eolian features are visible on the Fife Islands throughout the Cenozoic era and the late Pleistocene and Holocene. This and previous work is indicative of those conditions (Telmer, 1991). The grains in Figure 2.1A and Figure 2.2A exhibit more rounding and higher sphericity, while the grain in Figure 2.1C is rounded but has low sphericity. Roundness projections dominated the grain in Figure 2.2A shows a sub-angular/rounded grain with low sphericity, a distinct crystal face or a plane of weakness. The grain in Figure 2.1C and Figure 2.2A indicate impressions of micro-crystals that have been removed from the grain.

Pitting, cavities and striations are common on the surface of the grains and demonstrate that the grain is an important site of mechanical and chemical weathering. These features are dissolution pits and cavities observed in the grains and are from the environment (Figures 2.1D and 2.3A). Long parallel scars on the grains may relate to

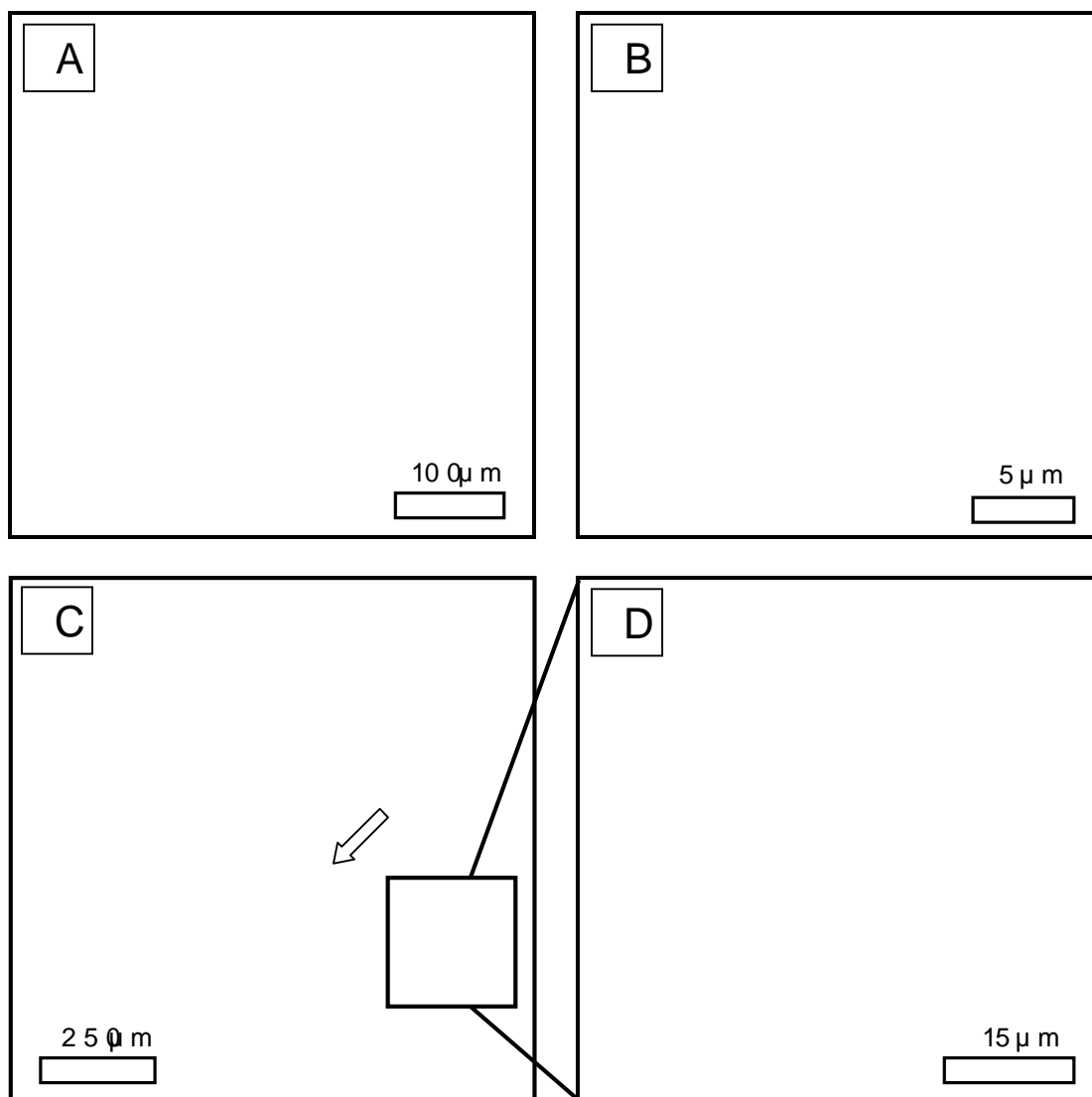


Figure 2.1. A: SEM micrograph of a scratched surface with clay and organics (darker regions). B: SEM micrograph of a deep crevice with secondary mineral grains. C: SEM micrograph of a deep crevice with secondary mineral grains. D: Higher magnification SEM micrograph of a region from within the relatively deep crevice with secondary mineral grains from

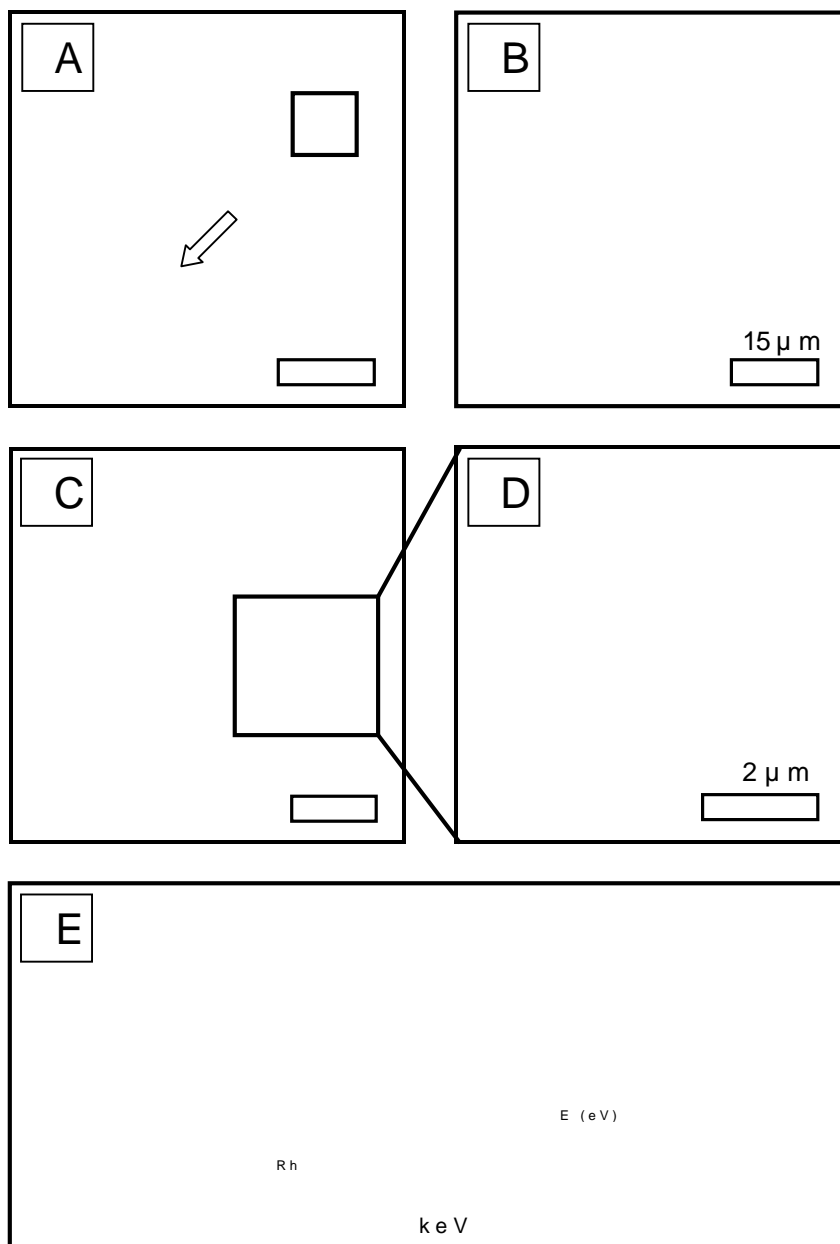


Figure 2. A: SEM micrograph of a heavily weathered platinum alloyed grain. Note the absence of deep oxides and cubic chromium grains. B: SEM micrograph of squared area in A. A acicular, iron oxides coats the grain surface. C: SEM micrograph of the acicular iron oxide coating on the grain surface. D: SEM micrograph of the acicular iron oxide coating on the grain surface. E: EDS spectrum of the acicular iron oxide coating on the grain surface. The inset is the EDS spectrum of oxidised platinum. The presence of oxidised platinum indicates this nugget was in an aerobic weathering environment.

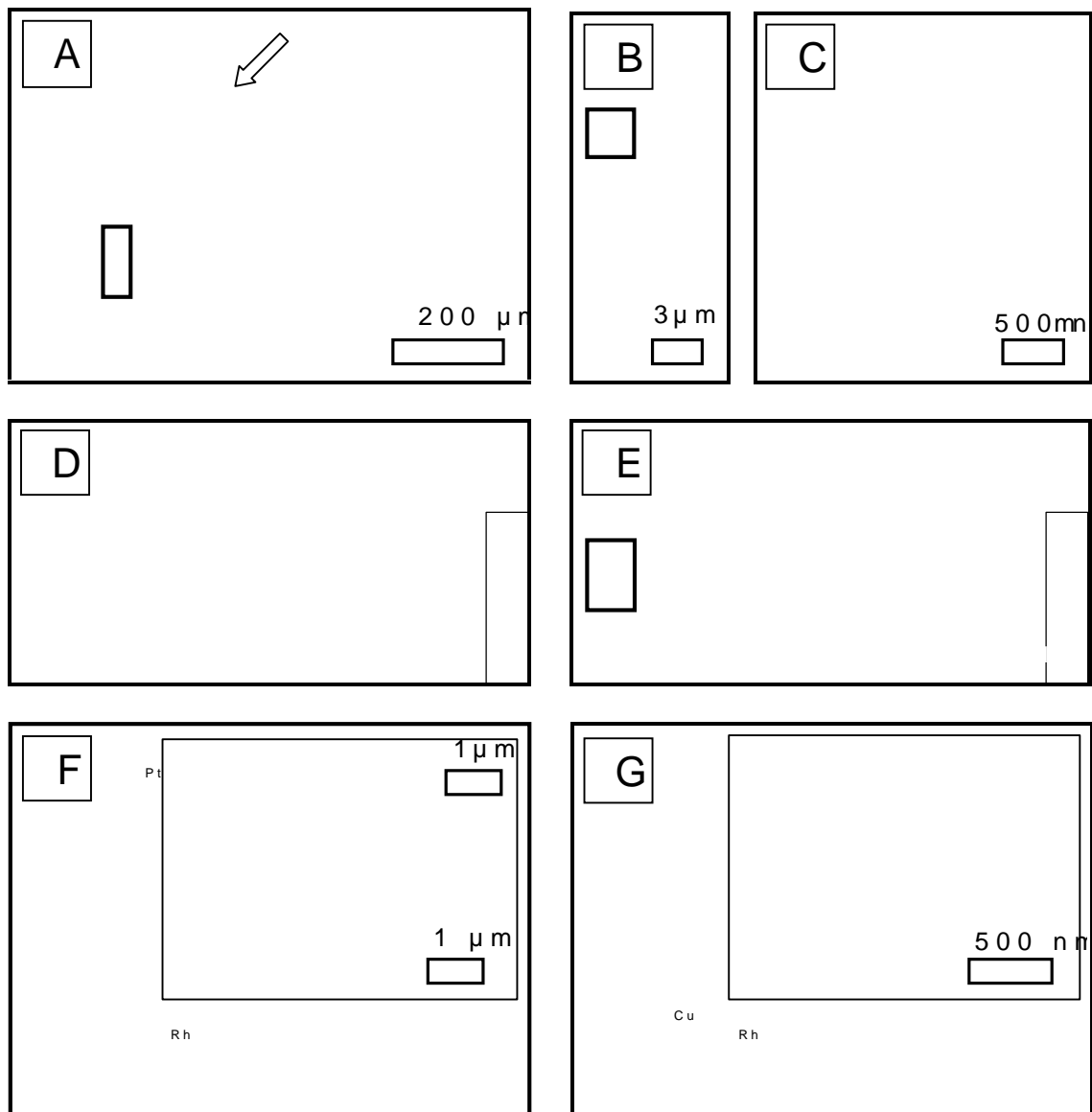


Figure 23. A: SEM micrograph of a weathered BSE Mn iron ore grain of area noted C. B: SEM micrograph of squared area in B. Note mineral. D and E: Iron and copper element map of grain in A, respectively, rectangular area in E, which shows a streak of copper-rich cubic mineral. F: SEM micrograph of cubic pits and E comparing the elemental composition of the bulk grain and the bulk nugget alloy (with trace Cu, Ni, and Rh). G and H show elevated Cu and EDS of the acicular, iron oxides. of Ce. Scale bars in D and E show relative element concentration upward from low concentration (black) to high concentration (white).

the preferential leaching of osmiridium solution of osmiridium isoferroplatinum, as observed by (Slyuzberg & Chou 1995) 50 nm sized cubic mineral embedded with surface of the grains. The cubic mineral protruding out from the surface of the platinum with similar holes in the surface (Figure 2.3) that they likely grew out from the grain boundaries to the environment. The presence of these inclusions in phase materials would be at greater distances than grains and may contribute to the development of larger grains from these grains.

Range of coatings at the periphery of the grains determined to be iron oxides. SEM, EDX, and iron oxides were primarily within the clay patches and directly affixed to the surface (Figure 2.3). The morphology of the iron oxides was slightly different suggesting a variety of insoluble iron oxides. Various hydration states of these placers include hematite, goethite and other iron oxides and found on platinum nuggets (Ottemann and Augustinus 1991; al 2008). EDX and XANES spectra (Figure 2.2) confirmed that Fe³⁺ existed in an oxidised form and was likely bound to oxygen at approximately 13 eV up from the reference standard Fe³⁺ (Day et al 2007). The oxidation of iron promotes the formation of acid through the reaction which could contribute to platinum solubilisation (Quirke et al 1986; the precipitation of acicular, iron oxides immediately on

produced a local acidic interface that could have controlled dissolution and the release of additional immobile elements (see below) (Guilbert 1986).

The placer grains were determined to be all to be 2.35 (Fig. 2.35) with less than 1% of copper in the grain. As was performed on the grain in Fig. 2.35A in order to determine the element concentrations, however, a bulk nugget was sampled and analyzed (Fig. 2.35) which is consistent with Slansky et al. (1990) and Albert et al. (1996) trace amounts of nickel and rhodium were also detected. Pelletier et al. (1991) as being the most common mineral in the Fife mapping of the grain 2.35A was also found. The EDS map in Fig. 2.35B and the Cu map 2.35C clearly resemble those shown in the SE micrograph. Element mapping of the grain shows that a link is linked to morphological features on grains. The Cu map, in copper highs (squared area) that correspond to the area in Fig. 2.35B and 2.35C. These cubic minerals have a higher copper bulk grain 2.35D and their exposure at the nugget surface is more resistant than the bulk grain as noted by EDS. It was found in small quantities using synchrotron radiation but not found by EDS but not detected using synchrotron energy. these elements cannot be determined through the 2D and 3 dimensional nature of the sample surface and electron spectroscopy and detection. Nickel and copper, however, are known to be

iron in reducing environments (Merrill et al. 2005). Levels of iron have been detected in Fifield placer gravels (Sillitoe 1991). Trace amounts of the earth element, cerium, were found to be associated with iron and reported by Anand (1995) as being present in size comparable to the iron.

Platinum sulphide minerals were not observed in these grains, consistent with prior studies (Sillitoe 1991). This is likely because the primary PGMs were replaced during post-metamorphism and have been weathered at the surface conditions (Johan et al. 1989; Andrew & Frey 2005; Sillitoe 2005). Hydrothermal alteration of primary platinum minerals may explain why platinum hosted in the Fifield is so rare (1000 micron sized grains) while a large number of grains are present there (Johan et al. 1989; Sillitoe 1991; Teluk 2001). This has been attributed to the dissolution and precipitation of platinum in alluvial and clastic regimes by several groups and Kinloch (1991) and Bowles (1986) and (Bowles). However, the structural and chemical of these grains does not support the growth of platinum during diagenesis (Sillitoe 1991). Only when the hard rock source of platinum is found will the diagenesis be better understood. For this study and similar studies clearly show signs of chemical alteration at the nugget interface. The grains are dissolving from the weathering products are being mobilized where they can participate in a variety of abiotic, and probably biotic

these reactions is key to improving our ability to recover and track its movement in nature, leading to more precise metal.

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Chapter 3

Immobilisation of ^{238}Pu by metal-precipitating microorganisms

3.1 Introduction

Microorganisms are able to thrive in a variety of extreme conditions, including strongly acidic environments (Reith 2009). Some tolerant bacteria in these environments have evolved a niche existence by using metal compounds as sources of nutrition and energy. Alternatively, some bacteria invoke genetically encoded detoxification mechanisms to reduce metal concentrations. These mechanisms include precipitation, efflux or a combination thereof (Silver 1999, 2009).

The biogeochemical cycling of metals and the formation of metal deposits can be attributed to microbial activity (Cloud, Mossman and Dyer 1985; Southam and Jidgen 1996). Recent evidence from studies has shown that bacteria are able to precipitate gold from acidic solutions (Southam and Beveridge 1994, 2009; Lengke 2006c, d; Lengke and Southam 2007). The morphology of the precipitates so closely resemble the gold found in place in the South Africa's Witwatersrand basin that a biogenic origin is now suspected (Wilson 1984; Mossman 1993; Southam 1985;

and Beveridge 1994; Reith 2006, 7). The similar geochemical behaviour of platinum and gold suggests that a comparable cycle for platinum exists.

Platinum, one of the six platinum group elements, is a trace element (Nixon 1987; Nixon and Hammack 1991). Its concentration in the Earth's crust can reach economic concentrations in primary and secondary deposits (Naldrett 2008; Kozlov 2010). Under surficial weathering conditions, platinum is mobile as Pt^{4+} . It commonly forms complexes with chlorides and thiosulphates, but amorphous platinum oxide colloids occur (Mountain and Wood 1981, 1990; Wood 1990; Anthony and Williams 1994; Atza 2001; Hanley 2005; 2006). Aqueous platinum is transported in the surficial environment until precipitation or chemical precipitation. Subsequent deposition of platinumiferous material may occur (Bowles 1986; Wood 1990). It is assumed that biotic, bacterially mediated platinum immobilisation contributes to the formation of platinum placer deposits (Reith

Lenglet al (2006) demonstrated that cyanobacteria are able to precipitate aqueous Pt^{4+} species in a stepwise reaction that first produces extracellular spherical platinum(II) hydroxide. The amorphous platinum(II) colloids experienced further diagenesis to produce crystalline platinum(II) hydroxide. These experiments were independently supported by the discovery of platinumiferous alluvial platinum nuggets and platinumiferous platinum-crusted bacteria. Microbes attached to decaying organic matter (e.g. plant root) precipitated platinum from solution onto their

thought that continued bioreduction and electrochemical accumulation of platinumiferous nanoparticles likely contributed to the formation of gold grains (Cairns et al. 2011).

Further investigation is still needed to understand the biogeochemistry of platinum biomineralisation. For this work, biogeochemically diverse, proven ability to immobilise gold should be reacted with various bacterial characteristics in response to platinum to determine whether biogeochemical cycles exist. This study will employ a diverse set of metal-reducing bacteria, from the genera *Mycobacterium*, *Rhodospirillum rubrum*, *Ralstonia eutropha*, *Rhodospirillum rubrum* aerobic, gram negative, facultative anaerobic, and *Shewanella oneidensis*, for being resistant to toxic effluents of metals such as Cu, Pb, Zn, Cd, Ag and Hg (Mergelyan et al. 1985, 2003; Raut et al. 2006, 2007 and O'Driscoll et al. 2007). Resistance is primarily attributed to efflux proteins in the cell envelope and cation reduction mechanisms in the cytoplasm (Mergelyan et al. 2005; Raut et al. 2007). This bacterium was found on the surface of gold grains from auriferous soils in northern Australia (1986, 2009). It is a cultured bacterium and reacted it with gold ions and it partially precipitated gold within 48 hours. This is the first time that gold suggests that a multidisciplinary study of its biogeochemistry with species found in natural systems produce comparable reactivity with platinum.

3.2. Materials and methods

Cupriavidus metallidurans

Cupriavidus metallidurans ATCC 49619[®] (ATCC) acquired from the American Type Culture Collection in Manassas, Virginia. ATCC prescribed medium containing 5 g/L d-b-glycerol (ingredients[®] of Nutrient Broth [Difco Laboratories; Detroit, MI, USA]). Before experimentation, the culture was transferred (~10⁸ stationary/early death phase) to 13 x 100 mm borosilicate glass tubes (capped with plastic push caps to reduce evaporation and contamination) and grown to early stationary phase to maximise the amount of metabolically active biomass. The tubes were incubated at room temperature (21 ± 1 °C) in the dark.

After incubation, separate batches of 50 mL were transferred to 50 mL centrifuge tubes and thoroughly vortexed (VWR Vortex Mixer) to ensure a consistent suspension. For the platinum bioassay, 1 mL of the bacterial suspension was transferred to microcentrifuge tubes and centrifuged for 5 min using a VWR Galaxy 16 microcentrifuge. After centrifugation, the supernatant was discarded and the bacterial suspension filtered through a 0.22 µm filter. The filtered supernatant was then thoroughly vortexed to resuspend any remaining cells. After centrifugation, the bacterial suspension was discarded and the supernatant was discarded. The bacterial pellets were then resuspended in 5 mL of sterile water. The number of bacteria in the suspension was determined by the direct count method.

using a Heussler Counting Chamber (a phase contrast light microscope) and a Fluorescent Z1 microscope).

C. metallic and aqueous platinum experiments

The bacterial experiments were conducted to examine the immobilisation of platinum ions from a solution of platinum (II) chloride (PtCl₂ Prem[®], 99.99+ % [metal basis], Alfa Aesar, 4% min. Ward Hill, Massachusetts USA) in distilled water (Purified[®], 99.99+ % [metal basis], Pt 57%[®] min. Alfa Aesar) so were in a DDI at 16.2 MΩ obtained from a Millipore system.

Washed metallic samples were suspended in 1 mL aqueous platinum solutions (from stock solutions of 0.5 μM [0.1 μg/mL], 5 μg/mL, 500 μM [100 μg/mL], 500 μM [100 μg/mL] final Pt concentrations) at room temperature, (2 days, 2 weeks and 4 weeks). Experiments were maintained in the dark because when exposed to light (LED) the microcentrifuge tubes containing bacterial platinum mixture were only removed from darkness during longer exposure times. Reactions were performed in

Following exposure, reaction tubes were centrifuged and the supernatant was removed for chemical analysis. Remaining bacterial pellets were suspended in filtered DD water to remove any aqueous platinum and then centrifuged. Excess water was decanted and the suspended culture was

filtered sterilised DDI water in preparation for whole mount
microscopy examination of bacterial viability that were
thi-sectioned - were suspended in 2% glutaraldehyde rather than v

C. metallidurans P^{2+} chloride P^{4+} chloride kill curves

The effect of P^{2+} chloride P^{4+} chloride on bacterial viability was
determined by the spread plate method. Resuspended bacteria were
in 1 mL of water and used serial dilution in filtered sterilised DDI water.
Each dilution was plated in duplicate on plates to heat contain
(in g) of peptone, 5; beef extract, 3; agar, 15 (Difco Laboratories
for 4 days room temperature) under anaerobic conditions.
Colony forming units (CFU) were counted on the air New Brunswick C
Colony Counter digital counter and probe.

Chemical analyses

Platinum concentrations were measured over the course of the study
using a Perkin Elmer Optima DV System Inductively Coupled Plasma
Emission Spectroscopy (ICP-AES) instrument. Accuracy of platinum
was 5%, with detection limit of 0.05 $\mu\text{g/L}$ (0.05 $\mu\text{g/L}$ in 1 mL). Samples were
diluted as necessary with filtered DDI water (Table 3.1). Platinum
calibration curves were prepared using P^{2+} and P^{4+} stock solutions used in the
laboratory Cd metallidurans aqueous experiments. These calibration
standards were diluted by the same factor as the corresponding

(Table 1) The pH of the stock solutions was measured using a Basic pH meter. The electrodes were calibrated in buffer solutions after exposure to bacteria was cut in order to avoid ColorpHast bleeding Indicator strips.

Transmission electron microscopy (TEM)

Unstained whole sample mounts and thin sections (prepared by reaction with the Pt shadowing technique) were examined using a Phillips 10C transmission electron microscope (TEM) operated at 100 kV (thin sections). The whole mounts were prepared by floating on a copper grid on a drop of Formvar on a copper grid for several minutes to allow the bacteria to adhere to the grid by gentle dipping into distilled water. The grids were completely air dry prior to microscopy.

Samples for transmission electron microscopy were fixed overnight in 2% paraformaldehyde (EMS; Hatfield, Pennsylvania USA). Fixed cultures were centrifuged at 14,000 X g for 1 min. The supernatant was discarded and the pellet was embedded in 2% (weight/volume) lead citrate as a contrast agent using a 25%, 50%, 75% and 3 X 100% acetone series (including 100% acetone). The acetone was slowly replaced with an EMS epoxy resin (Epon 812) and the samples were incubated in a 50%:50% [v/v], 25%:75% [v/v] and 100%:0% [v/v] acetone:epoxy resin series). Epoxy resin embedded a 2.5:2

Table 3D Dilution factors for P^{2+} and P^{4+} supernatants and standards. Dilution factors were required because submitted samples concentrations exceeded a concentration of $100 \mu\text{g/mL}$ (i.e., the linear portion of the standard curve).

Initial concentration of platinum	Dilution factor for ICP-ES
5000 M or 1000 $\mu\text{g/mL}$	100x
500 M or 100 $\mu\text{g/mL}$	10x
50 M or 10 $\mu\text{g/mL}$	10x
5 M or 1 $\mu\text{g/mL}$	10x

812, DDSA (Dodeceny Succinic Anhydride) and NMA (NMA) Samples were incubated overnight in 100% epoxy resin and with fresh epoxy resin containing the (2,4,6-tribromotri(dimethylaminoethyl)phosphate) ratios by volume were 2.5:2:1:0 were cured in a 60°C oven (Blue M Electric Company Back Gravity Conveyor) until hard. Embedded samples were ultrathin using Reichert Ultratome microtome with a "Diatome" diamond knife to a thickness of 70 nm and collected on copper carbon grids.

X-ray Absorption Spectroscopy (XAS)

XAS energy measurements the bacterial reaction conditions XANES (X-ray Absorption Near Edge Structure) and EXAFS (X-ray Absorption Fine Structure) conducted at the Coors Scientific West Science and Technology Center (BM-20) beamline at the Advanced Photon Source National Laboratory, Argonne, Illinois, USA. The oxidation state of platinum can be determined by XANES while information regarding local coordination of platinum is provided by EXAFS data. Data state and coordination of platinum will shed light on how aquaplatinum bacterial cell (2006). XAS energy measurements were collected from each sample and were calibrated to the iron L_{2,3} edge (11564 eV) (Iams 2001).

Prior to any XAS measurements, the samples were reacted following previously described procedures. For XAS, replicate reactions were harvested by centrifugation and resuspended in water in order to concentrate the sample for detection. The cell suspensions were then placed in a standard fluid cell with a kapton film window. Whatman® 42 Ashless Filter Papers. XAS measurements on the conducted in fluorescence mode.

Reference compounds were needed to determine the platinum in these reactions. Standard reference compounds for the most likely oxidation states and coordination geometries expected in the reactions were measured. XAS spectra for model compounds including (IV-chloride)₄(PtCl₆)₂, platinum(IV) chloride (PtCl₄), platinum(II) chloride (PtCl₂), platinum(II) nitrate ((NH₄)₂Pt(NO₃)₆) were measured in aqueous solutions (up to 65 mM) prepared from solid compounds. XAS spectra for platinum(IV) dihydrate (PtCl₂(OH)₂), platinum(II) diamminedichloride (PtCl₂(NH₃)₂), platinum(II) foil (Pt) were measured in solid form. The standards were prepared in teflon fluid cells with kapton film windows. The samples were concentrated by ultrafiltration through 13 mm membrane filters. Compounds were commercially available from Alfa Aesar and Sigma-Aldrich.

exception of platinum (Pt) which was synthesized in the laboratory from an equal molar solution of platinum(IV) chloride (PtCl_4) with aqueous sodium sulphide (Na_2S) (J.T. Baker Phillipsburg, New Jersey USA) product (PtS) precipitated by the difference spectrum of platinum foil was simultaneously collected during measurement. The incident energy from the beam did not affect the standards or samples.

XAS data analysis

ATHENA analysis software was used (Raymond Newville et al. 2005) to process XAS data. Energy scans from samples and standards were aligned to the standard platinum foil reference energy. Multiple scans were collected and were averaged to produce a single spectrum representing the oxidation and complexation state. XANES spectra were analyzed by comparing the energy position of the platinum edge in the samples to the energy position from the standards. Linear combination fitting was mathematically identified which standard(s) aligned with the immobilized platinum. Energy position alignment corresponded to the immobilized platinum. EXAFS data analysis was performed in ARTEMIS, a XAS analysis software program complemented by IFEFFIT (Newville et al. 2005). Mathematical derivatives of post edge energy were used to bound platinum in the bacterial samples were fitted to post

platinum in the Pt standard, normalized to a platinum concentration of 1000 ppm, as indicated in the figure. The binding partners of the immobilized platinum (Pt) are

3.3 Results

Laboratory based metallic and aqueous platinum experiments

The addition of K_2PtCl_6 to filtered, DDI water promoted hydrolysis of K_2PtCl_6 as indicated by a drop in the pH of the overall K_2PtCl_6 solutions was 5000g/mL; pH 5.0) (100g/mL; pH 5.2) 50M (10g/mL; pH 5.2) (1g/mL; pH 5.4) pH of the solution after reaction with bacteria did not change significantly from the pH of the solution. The addition of K_2PtCl_6 to washed bacterial pellets immediately turned the white pellet yellow at all exposure times. Similar to the washed bacterial pellets, the white pellet were much fainter or not identifiable at lower concentrations provided macroscopic evidence was binding to the cells.

Table 3.2 and Table 3.3 were prepared by comparing CFU count to the unreacted count for the appropriate exposure to a standard CFU count. To allow comparison between exposure times and treatments. The experiments demonstrated that upon exposure of bacteria to K_2PtCl_6 solutions, bacterial growth was inhibited. Platinum toxicity was directly proportional to concentration and solutions being slightly less toxic than at given particle concentration.

Table 3T2. Toxicity study of *C. whittellii* in response to P^{2+} aqueous solutions. Increased exposure time and increased concentration resulted in fewer viable cells, as indicated by a decrease in CFU/mL.

P^{2+} concentration	CFU/mL after 1 min exposure	CFU/mL after 1 hr exposure	CFU/mL after 1 day exposure
0 μ M or 0 μ g/mL	5.0×10^8	5.0×10^8	5.0×10^8
0.5 μ M or 0.1 μ g/mL	4.9×10^8	2.7×10^8	4.6×10^8
5 μ M or 1 μ g/mL	3.7×10^8	3.2×10^8	4.3×10^6
50 μ M or 10 μ g/mL	4.1×10^8	1.3×10^7	2.1×10^3
500 μ M or 100 μ g/mL	9.9×10^6	0	0
5000 μ M or 1000 μ g/mL	0	0	0

Table 3T3. Toxicity study of *C. whittellii* in response to P^{4+} aqueous solutions. Increased exposure time and increased concentration resulted in fewer viable cells, as indicated by a decrease in CFU/mL.

P^{4+} concentration	CFU/mL after 1 min exposure	CFU/mL after 1 hr exposure	CFU/mL after 1 day exposure
0 μ M or 0 μ g/mL	5.0×10^8	5.0×10^8	5.0×10^8
0.5 μ M or 0.1 μ g/mL	4.5×10^8	3.2×10^8	3.3×10^8
5 μ M or 1 μ g/mL	4.9×10^8	2.5×10^8	7.6×10^7
50 μ M or 10 μ g/mL	1.1×10^8	6.4×10^6	4.8×10^3
500 μ M or 100 μ g/mL	6.6×10^2	0	0
5000 μ M or 1000 μ g/mL	0	0	0

The amount of soluble platinum remaining in solution after these results were determined from a concentration of 1 mg dry weight of metallic platinum averaged to determine the amount immobilized. The mass of metallic platinum was calculated using the mass of Escherichia coli (12.95 × 10¹⁰ dry weight per cell), a spherical bacterium approximately ~23% larger than the wild type (Murray et al. 1990). Volume estimates were based on diameter and measurements of bacteria shown in the electron micrographs (Figures 3.1, 3.2, 3.3, 3.6). As rod shaped bacteria are bounded by two half spheres, the volume can be calculated (Bankston 1988).

$$V = \frac{4}{3} (\frac{\pi}{6}) r^3 \quad (1)$$

ICP-AES results are shown in Tables 3.4 and 3.5. Immediately upon exposure to platinum. As exposure time increased and concentration, the amount immobilized also increased; however, at these longer exposure times, the amount immobilized did not increase. The effective concentration of platinum is based on cell volume and should not exceed the T = 0 solution concentration in all reaction systems. The maximum concentration was not reached at any exposure time. At 5000 μM solutions

Table 3 Immobilisation of *C. diphtheriae* in response to P^{4+} solutions. Measurements are concentrations within the bacteria and $\frac{1}{4}$ g Pt immobilised per mg dry weight of bacteria. It is noted that increased exposure time resulted in increased immobilisation.

P^{4+} concentration	Immobilisation after 1 min exposure (mM; $\frac{1}{4}$ g/n)	Immobilisation after 1 h exposure (mM; $\frac{1}{4}$ g/n)	Immobilisation after 1 day exposure (mM; $\frac{1}{4}$ g/n)
5 μ M or 1 μ g/L	1.80; 0.4	1.60; 0.4	153; 5
50 μ M or 10 μ g/L	51; 13	44; 11	67; 16
500 μ M or 100 μ g/L	120; 28	120; 29	410; 100
5000 μ M or 1000 μ g/L	850; 210	800; 200	850; 210

Table 3 Immobilisation of *C. diphtheriae* in response to P^{4+} solutions. Measurements are concentration within the bacteria and $\frac{1}{4}$ g Pt immobilised per mg dry weight of bacteria. It is noted that increased exposure time resulted in increased immobilisation.

P^{4+} concentration	Immobilisation after 1 min exposure (mM; $\frac{1}{4}$ g/mg)	Immobilisation after 1 h exposure (mM; $\frac{1}{4}$ g/n)	Immobilisation after 1 day exposure (mM; $\frac{1}{4}$ g/n)
5 μ M or 1 μ g/L	1.60; 0.4	2.60; 0.6	9.62; 4
50 μ M or 10 μ g/L	112; 7	133; 2	409; 8
500 μ M or 100 μ g/L	45; 11	160; 40	210; 51
5000 μ M or 1000 μ g/L	310; 75	350; 84	870; 210

TEM

TEM micrographs of metallic particles exposed to platinum solution presented in Figures 3.2 to 3.6. Micrographs of the control are shown in Figure 3.1. Note that the cytoplasmic contents are visible in Figure 3.1A. Further details of the cell are lacking in Figure 3.1B. The cell envelope is visible as a white halo. The staining was applied to these bacteria; therefore, any differences in the following micrographs are attributed to aqueous platinum.

Figure 3.2A demonstrates that bacterial staining occurred after exposure to $500 \mu\text{M Pt}^{2+}$. However, not all bacteria were stained. Generally, longer exposure times resulted in a greater number of platinum nanoparticles. Figure 3.2B shows that bacteria produced platinum colloids at a rate of 10^4 particles per cell per day. Figure 3.2C shows that platinum nanoparticles were not observed at short exposure times. Figure 3.3A shows that bacteria do not bind platinum from a $5000 \mu\text{M Pt}^{2+}$ solution. The majority of cells were stained within the first exposure time point. All bacteria were observed to be completely stained after 24 hours. Platinum formation was observed after exposure times of 1, 2, and 3 hours. Figure 3.3C shows a partially lysed bacterium with platinum nanoparticles associated with the cell envelope. The delay in response to platinum toxicity and/or the pH in this case is not clear. TEM micrographs of bacteria exposed to $500 \mu\text{M Pt}^{2+}$ are shown in Figure 3.4. Platinum nanoparticles were observed along the periphery of the cell wall, within the cytoplasm, and in vesicles. The metallic particles associated with the cell envelope are visible in

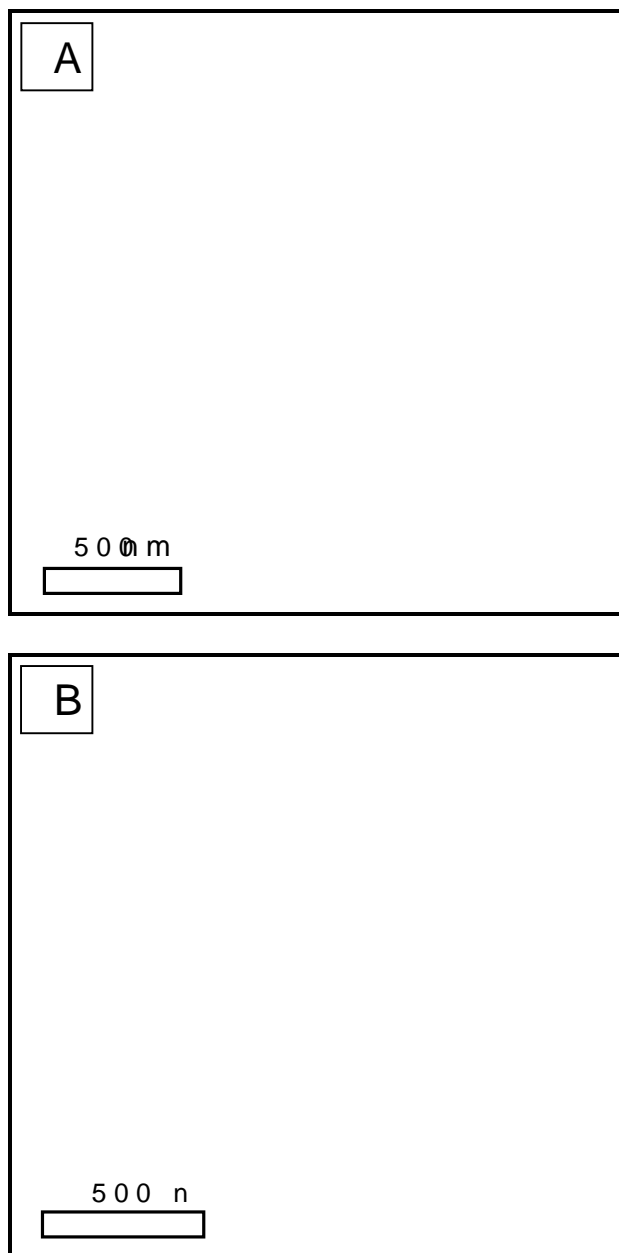


Figure 3A1 Whole TEM micrograph of *A. umbraticum* bacterium. Phosphate bodies within the cell are clearly visible. Generally electron transparent, thin section TEM micrograph of unreacted metalloid. Note the internal detail of cell is lacking as no contrast agent was applied.

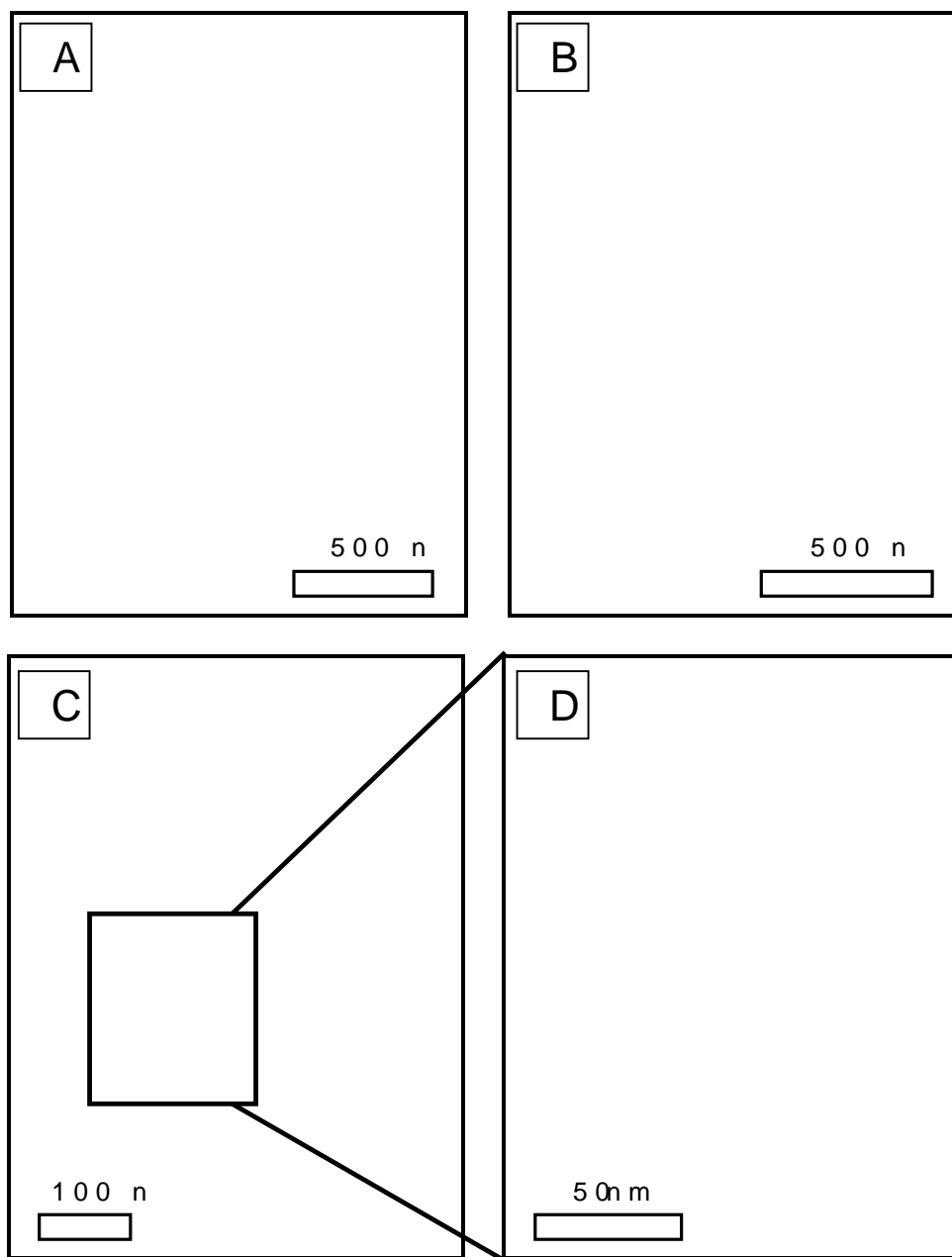


Figure 3. Whole mount TEM micrographs of cells treated with $500 \mu\text{M}$ ($100 \mu\text{g/mL}$) for A: 1 min & C: 1 day. Micrograph of squared area C. At 1 day, all cells were strained (s produced nanoparticles).

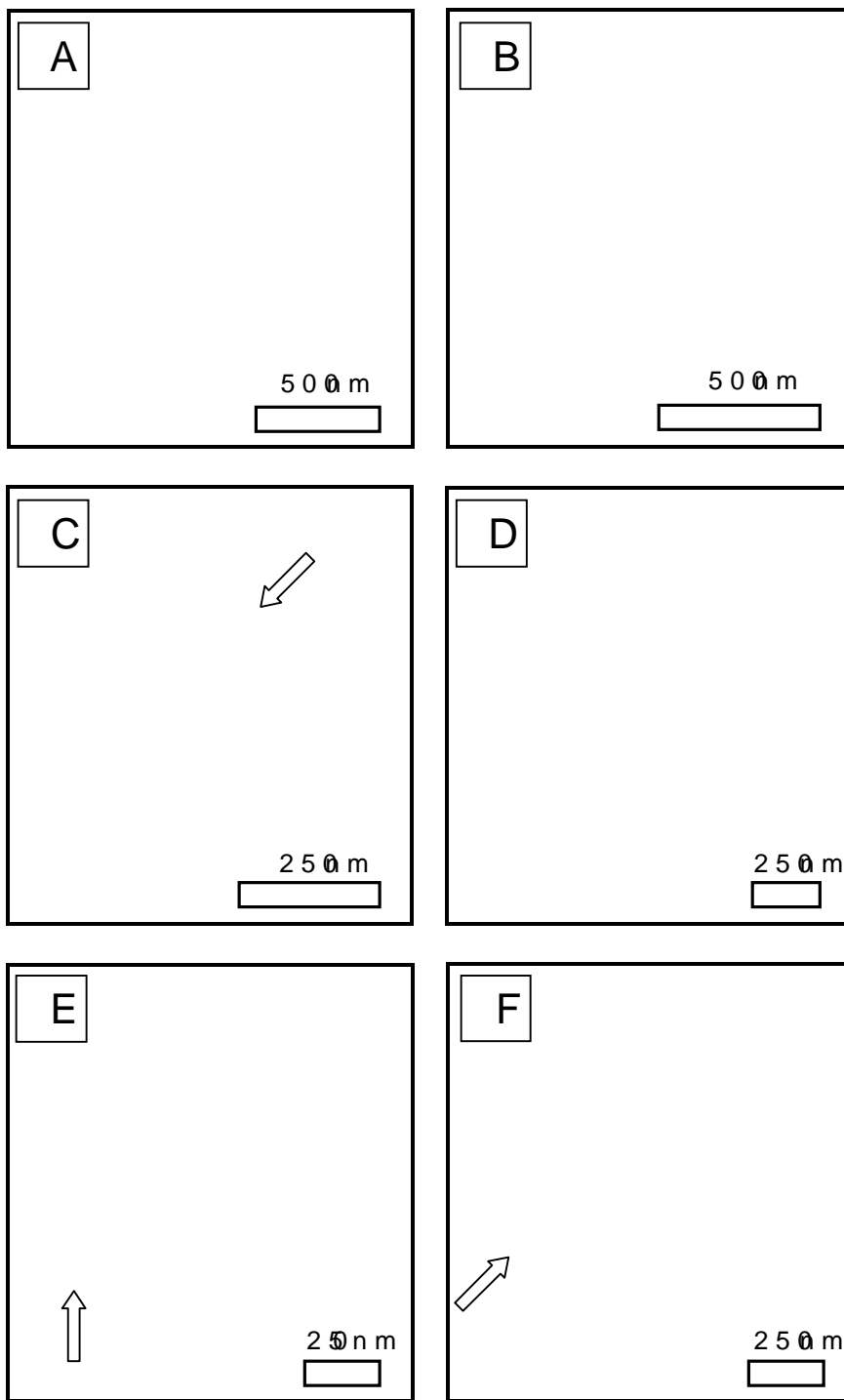


Figure 3. Whole mount TEM micrographs of cells exposed to $5000 \mu\text{M}$ PtCl_6^{2-} (1000 $\mu\text{g Pt}^{2+}/\text{L}$) for: A: 1 min. Binding of Pt is minimal as cell re electron param. B & C: 1 h; D; E and F: 1 day. At longer incubation times cell staining is apparent in all cells. Some cells show nan indicated by arrows.

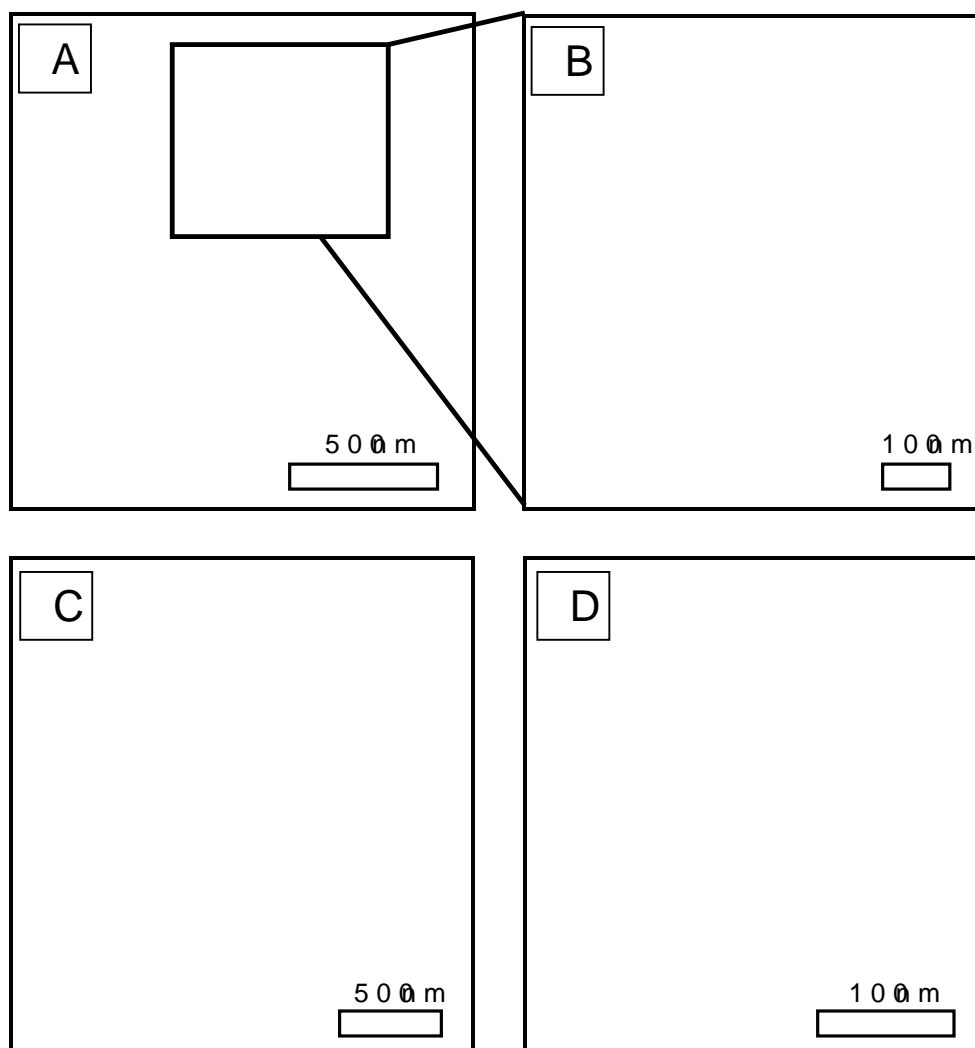


Figure 3.14 Thin section TEM micrographs prepared to 5000 $\mu\text{M Pt}^{2+}$ for 1 h. A: Nanoparticle Pt along cell envelope of square area note. C: Micrograph of immobilised Pt along cell envelope. D: Nanoparticle Pt immobilisation along the membrane of every vesicle.

to keep toxic material away from the cell (Liang et al., 2006).

As indicated by the micrographs in Figure 3.5, the cells responded to Pt much like it did to Pt. The cells appeared to be immediately inactivated (Figure 3.5A). Longer exposures produced a darker stain and precipitated the bacterial cells. Nanoparticles were observed to precipitate with the cells (Figures 3.6A and B). Cell lysis was observed at 5.0 μM Pt. Cytoplasmic material bound platinum. As a result, in 5.0 μM Pt²⁺ solutions, cell lysis could have been caused by the low pH of the solution, or a combination of both.

It was noted that cells adhered to each other upon solution. Perhaps a result of neutralization of anionic charge groups on the cell envelope by platinum, allowing hydrophobicity to dominate. This response could protect some of the cell's interior by shielding them from the platinum complex. Immediate platinum binding to all cells was observed.

XAS Spectra

XAS spectra in Figure 3.7 show the speciation and binding of platinum immobilized by bacteria. Figure 3.7 is the XANES spectrum with 5000 μM (1000 μM Pt) Pt. The peak edge binding energy is slightly less than that indicating that electrons are more tightly bound in the more oxidized platinum species. There

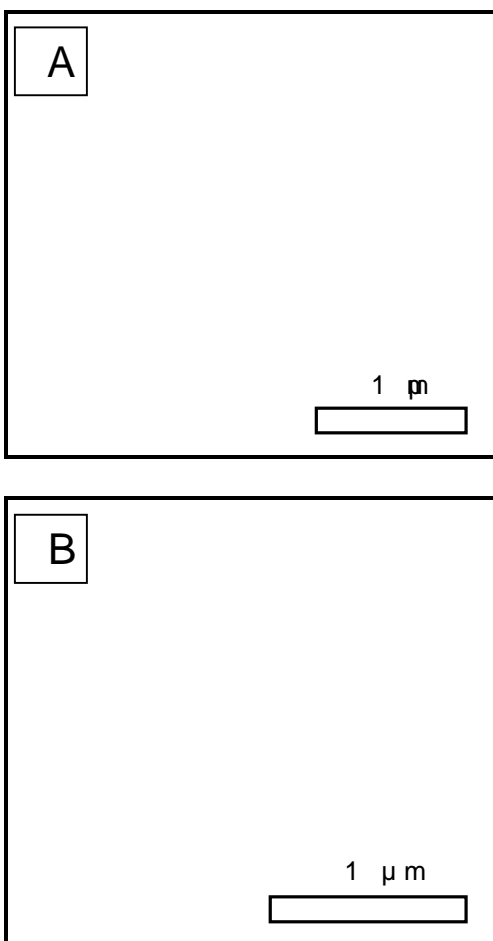


Figure 3.5. Whole mount TEM of *C. formosensis* cells incubated with 500 μM Pb^{2+} (100 $\mu\text{g}/\text{ml}$) for A: 1 min; B: 1 day. As incubation time increase metalloid formation became more pronounced. Colloidal platinum was not observed.

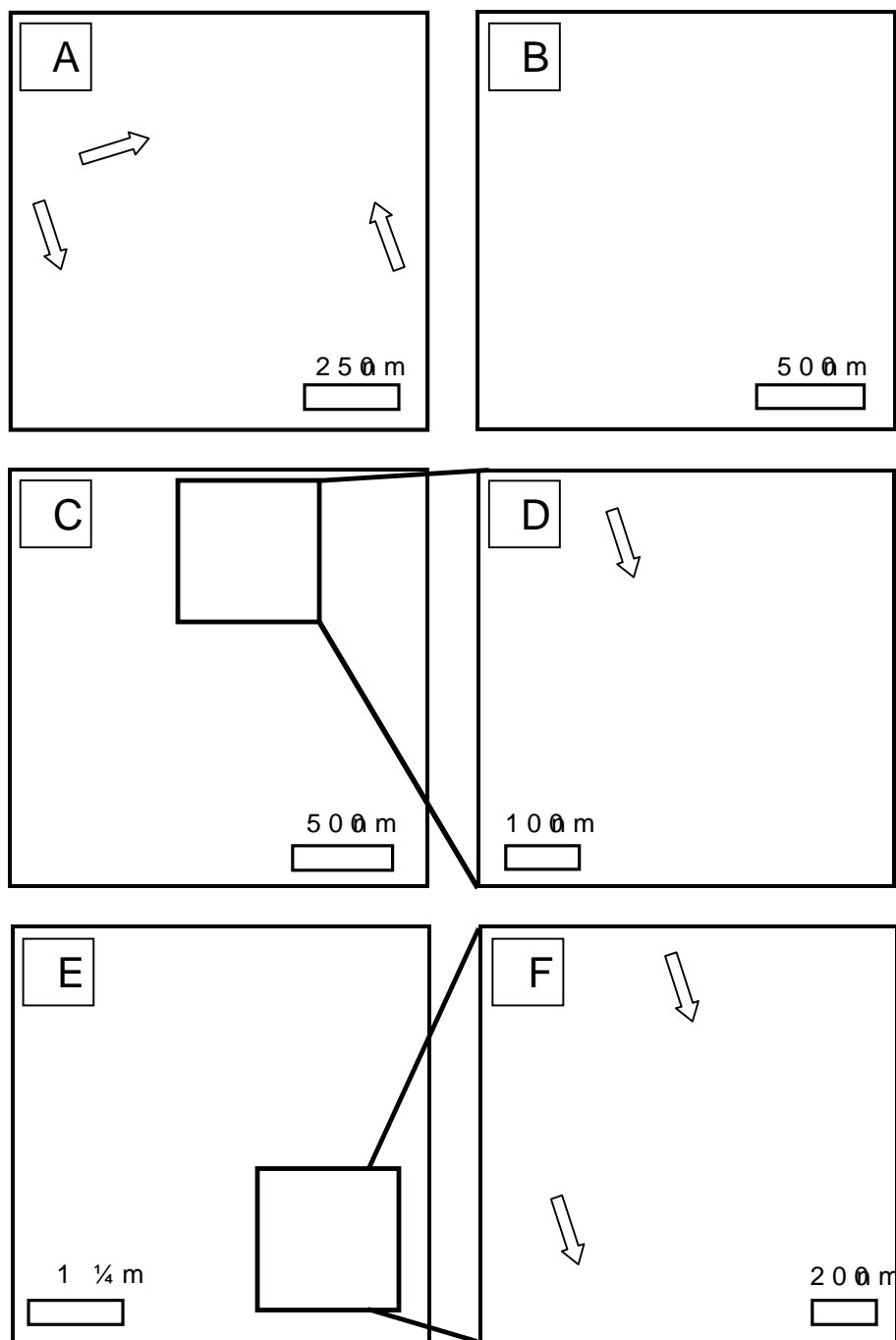


Figure 3.6. TEM micrographs of cells immobilized with $5000 \mu\text{M}$ Pt (1000 $\mu\text{g Pt/L}$). A: 1 min (whole mount) (ultra-thin section has been immobilised at the cell envelope and within the cell); B: 1 min (whole mount) (ultra-thin section has been immobilised at the cell envelope); C: 1 day (whole mount) (ultra-thin section has been immobilised at the cell envelope); D: 1 day (whole mount) (ultra-thin section has been immobilised at the cell envelope); E: 1 day (whole mount) (ultra-thin section has been immobilised at the cell envelope); F: 1 day (whole mount) (ultra-thin section has been immobilised at the cell envelope). Arrows indicate immobilised Pt. Pt becomes more pronounced at longer incubation times (C-F).



Figure 3. XANES spectra of bacteria reacted with 5×10^{-4} M Pb^{2+} for 1, 2, 4, 8, 16, and 28 days. The line corresponds to the Pb^{2+} standard. The shift in the Pb^{2+} edge energy that is observed over the 28 days, indicating that synchrotron energy did not

energy for either immobilised platinum species, indicating did not detect a change in platinum oxidation states. It is important to note that at least 10% of the immobilised platinum synchrotron radiation would detect the change in speciation are representative of the XANES spectra (data not shown).

Figures 3.8 and 3.9 show the XANES and EXAFS spectra with 5000 μM ($1000 \mu\text{g}/\text{mL}$) Pt^{2+} peaks. Similar spectra were obtained from reactions with 5000 μM ($1000 \mu\text{g}/\text{mL}$) Pt^{2+} and Pt^{4+} solutions (data not shown). Examination of the EXAFS demonstrated that the Pt fingerprint decreased in intensity over time, indicating that the chlorine $^{2+}$ was displaced by another binding partner. This indicates that the replacement was immediate, as the short time between bonds occurred within 1 min; however, gradual Pt^{2+} with substitution of chlorine continued over the 4 week period. The Pt bond length is best matched to oxygen on a carboxyl group, indicative of Pt on carboxyl groups is $\sim 2.06 \text{ \AA}$, which compares to 2.07 \AA and 2.08 \AA bonded distances (Cotton and Murrells 2000; Murrells et al 2009).

PtCl fingerp

Figure 3.8. EXAFS spectra of bacteria reacted with PtCl_4^{2-} for 1, 3, 7, and 28 days. The arrow indicates the Pt-L edge, which decreases over time. There is a shift in the Pt-L edge from 150.0 eV to 150.5 eV over the 28 days, indicating that synchrotron energy did not deter

Figure 1. XAFS spectra of bacteria reacted with 5000 ppm (1000 $\mu\text{g/g}$) Pb. Arrows show the first shell binding energy of Pb.

3.4. Discussion

The interaction of platinum with bacteria resulted in a variety of bacterial responses: cell death and cytolysis, plasmid nanosphere formation, which were directly proportional to platinum time (Table 3.2).

The literature lacks consistent experimental data on the potential of platinum complexes in the interactions system. Under Pt²⁺ PtCl₄²⁻. Likely compounds include PtCl₄²⁻ and PtCl₆⁴⁻ but very little data exists for the latter (Beveridge and Murray 1980; Nies 1992; Azar et al 2001; Coleman 2008). EXAFS confirmed that to be the dominant aqueous species prior to bacterial uptake of the Pt²⁺ complexes from solution is consistent with the literature uptake of other metals, by bacterialisation on the cell envelope within the cytoplasm (Beveridge and Murray 1980; Nies 1992).

Platinum sorption through and then immobilisation and immobilisation occurred and the cell surface reactivity controlled by the proton exchange-capacity (CEC) of the cell wall (IR-OP₃ and (R₂PO₂H) amine-NH₃⁺ and hydroxyl (R-OH) functional groups on the membrane but the 500 μM threshold concentration of carboxyl groups would be a negatively charged and available reaction with oxidised polyamine and hydroxyl groups remained protonated and positive. The conditions consistent with the acidity of aqueous solutions used in the experiment.

Murray 1980; Elisei 1997; Gutina 2006) XANES and EXAFS spectra clearly show the replacement of chlorine for oxygen on carboxyl binding mechanism. Noting that the mobilised platinum occurs as organo platinum complexes at the cell surface and in the cytoplasm, organo platinum complexes may be preferred to inorganic complexes. This process has been demonstrated by the fact that carboxyl functional groups on soluble organic acids are able to react with platinum complexes (Vlastakis 1999; Wood 2000; Webdal 1992; Kubrakova 2011).

As suggested by Berne and Murray (1980), platinum binding to the cell envelope likely proceeded first as a stoichiometric event, where platinum and then as a nucleation event, where nanoparticles formed non-stoichiometrically, which continued at a slower pace. That occurs in a progressive staining of the cell formation of nanoparticles at increasing times and concentrations indicated that this process may be a necessary step in the system. Platinum in a cell was also observed. The rapid uptake of platinum may have occurred via membrane transport proteins that regulate the entry of these particles into the cell. All complexes freely enter the cell driven by the concentration gradient that exists (Nascos 1999). The entry of platinum into the cell by passive diffusion would have ceased once platinum concentrations within the cell equalled the platinum concentration within the extracellular medium. Aqueous platinum that is neutral at the neutral pH of the cytoplasm

bound to deprotonated functional groups or as a complexed group (Fiserl et al 1997; Gutierrez 2006)

Bacterial cells that remained viable following exposure to platinum would have presumably initiated a biological response, an attempt to survive in which cells inhibit the function of important proteins and bind to important functional groups, or alter important physiological processes. Detoxification responses include chemical reduction or complexation of metal to a less toxic state and/or the excretion of the metal. The cell's mitigation response drains the cell of energy and causes a decline in growth and continued cell death at long term exposure (Girvan et al 1996, Nishikawa et al 1999). XANES did not indicate platinum reduction, therefore it appears as if the nanometre platinum is in the cytoplasm (and at the cell membrane) and evidence that some platinum reduction occurred.

The relationship between toxicity and immobilization is shown in a comparison of Tables 4.3 and Tables 3.5. For a particular platinum species, immobilisation generally corresponds to a reduction in cell death. The more platinum that was immobilised, the more resistant the cells were. Figure 4.1, 5000 μM Pt⁴⁺ demonstrates that the toxicity experienced by the cells is not directly proportional to the amount of platinum due to a platinum effect. Similarly, cell death was immediate at 1000 μM and 5000 μM Pt⁴⁺, but when cells were exposed to pH 4.0 comparable solutions of HCl, corresponding to the same amount of platinum (not shown). Intuitively, acidic solutions will induce some

results demonstrate that platinum immobilization triggered toxicity is important and dead cells cannot actively pump out platinum. Immobilisation of cells at 5000 μM solution killed bacteria within 1 minute and platinization. Dead cells no longer metabolise and the proton motive force is not maintained. Consequently, there is less competition for platinum groups (Urrutia *et al.* 2002). The reactivity of metallic platinum is known to be higher than the reactivity of platinum (Guyana 2007). In this situation, the appearance of new reactive sites from denatured cytoplasmic contents likely contributed to the continued death of cells even when cell death was not observed.

Further examination and comparison of Tables 3.2 to 3.5 reveal differences between the reaction systems. First, reactions involving Pt^{2+} are more toxic than Pt^{4+} . Perchlorate as an acidic Pt^{4+} solution as a test that remained viable following exposure have been able to neutralise and capture Pt^{4+} cations. The metalloid trivalent cation efflux ATPase is used by the bacterium to help it highly oxidise the platinum and attempt to neutralise it internally. However, it brought about a fatal oxidative stress (N 2009). It is also important to note that bacteria were able to tolerate more platinum in Pt^{2+} solutions than in Pt^{4+} solutions. From a concentration and character of platinum vs. hydronium, platinum systems were tested by approximately 2 orders of magnitude and generally

concentration in P^{H} systems. They would have easily displaced hydronium for carboxyl binding sites where heads are more competitive and therefore less opportunity to be bound and immobilised.

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Chapter 4

Conclusions

The traditional notion that platinum is inert has been a biogeochemical paradigm (Anthony and Williams 1994). The transport of platinum from the mantle to the crust and its subsequent transport to air and water is a complex process. The presence of platinum in primary magmatic host rocks is an incomplete metallogeny of platinum. Subsequent to magmatic dissolution, transportation and precipitation, biological and abiotic processes potentially are now considered to be key components in placer platinum formation (Fulford and Ross 1974; Bowles and Azarova 2001; Hanley et al. 2005, 2009). The structural and chemical examination of platinum grains, revealing dissolution and biogeochemistry of candidate platinum compounds have demonstrated more to learn about the mobility of platinum in natural systems. This has highlighted the importance of identifying platinum compounds in platinum exploration, which could lead to applications for

With respect to the current controversy regarding platinum precipitation and growth of platinum grains (Fulford 2009), this work on Australian platinum grains, which provides clear evidence that platinum found in natural systems ultimately comes from primary magmatic material, supports the dissolution-precipitation model. This work highlights the importance of examining platinum grains in secondary imaging before, more classic, cross polishing to

mineral grains. Deep weathering scars, pits and cavities of platinum grains are important sites of mechanical and weathering. SEM micrographs show delicate mineral structures that could be lost by polishing and wouldn't be as obvious in a TEM image, which does not achieve the same resolution as SEM. The dissolution of the bulk nugget around these minerals demonstrates a homogenous, reflecting the geological conditions of the mineral. The mineral left in the regolith or the alluvium. The presence of iron oxides provides evidence that acidic conditions occur and presents a possible mechanism for chemical dissolution (Guilbert 1986, 2005).

For future work on this system, the next step in characterization from Fifield requires that they be investigated using the same techniques as was used to study their surfaces. Any weathering features and the bulk, interior of the nugget needs to be characterized for heterogeneity, from the periphery of platinum grains to the interior. Preferential weathering of the bulk grain is a real possibility; cubic grains are more susceptible to weathering than other shapes. Trace element mapping using synchrotron element mapping could be used to identify interior morphological features noted in microscopy with TEM. Element mapping would likely be required with a spot size of 100 nm to detect the chemical gradient from surface to interior and precipitation processes affecting platinum grains.

A large number of microorganism have been implicate cycling of arte\$al surface or surface conditions (Southam and Reith a2009; Southam 2009). The precipitation of secondary bacteria has been well documented (Southam and Beveridge 2006, 2009; Lengen and Southam 2007). A c micromediated mobilisation of platinum was hypothesized chemical similarity of gold and platinum, but did not occur et al1990; Coats 2007). *Whiplash* is a metal resistant soil bacterium that has been reported to mobilise platinum (Reith a2006; 2009) mobilised appreciable amounts of platinum quantities by mass (see Tables 3.4 and 3.5) in platinum immobilised appreciable amounts of secondary platinum. TEM clearly d immobilised at the cell envelope and within the cytoplasm immobilisation was determined by synchrotron radiation (existing as platinum bound to exposed hydroxyl groups on the cell wall and within the cytoplasm (Beveridge 1986, Mountain and Wood 1992, Wood 1997, Zarog et al 2001; Goiné 2006). Although platinum reduction was not synchrotron methods, the reduction of at least some of the particles of elemental platinum was observed in a number of ubiquitous nature of bacteria in natural environments and the h both ^{2+}Pt and ^{4+}Pt for organically derived carboxyl functional groups suggests that platinum must be important in natural systems.

bearing materials are exposed to weathering conditions, platinum in association with organic acids and the biosphere.

Work into understanding the biosphere's influence on biogeochemical cycles of platinum continue. Recommendations for future experiment include: exposing to aqueous platinum species for periods of time (months) to promote and examine platinum precipitation. et al (2006a) exposed cyanobacteria to platinum for up to a month and reported immobilisation of platinum particles. Given that consortia of other microbes should be tested for their ability to immobilise platinum. Likely, many bacteria are able to precipitate platinum. The combined presence in weathering profiles may provide evidence for platinum transformation. Also, bacterial interactions are likely not responsible for the immobilisation of aqueous platinum species in the weathering profiles of platinum-bearing material in primary ore deposits. The sulphur-oxidising bacterium *Acidithiobacillus thiooxidans* and sulphur-oxidising bacterium *Acidithiobacillus ferrooxidans* contribute to the supergene enrichment of platinum via metal oxidation and sulphuric acid production (Stumm 1970; Lizama et al 1985; Sillitoe 2006). As platinum is the main PGE in most world's platinum deposits, including the Merensky Reef in the Bushveld Igneous Complex, bacteria may be able to enhance platinum in the host rocks (Macdonald 1987; Teluk 2001).

The current value of platinum has nearly matched gold prices in the highs over the last few years. Continued exploration and mining

these prices and companies will look for more effective ways and processing techniques to boost the amount of minerals they use once inaccessible minerals dissolved in mine waste rock piles could improve efficiency for mining companies. Furthermore, some of the minerals and precious metals, microbes may one day be used as bioplutonium emitters (Corbisier 1997, ORCID).

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Appendix Chapter 2

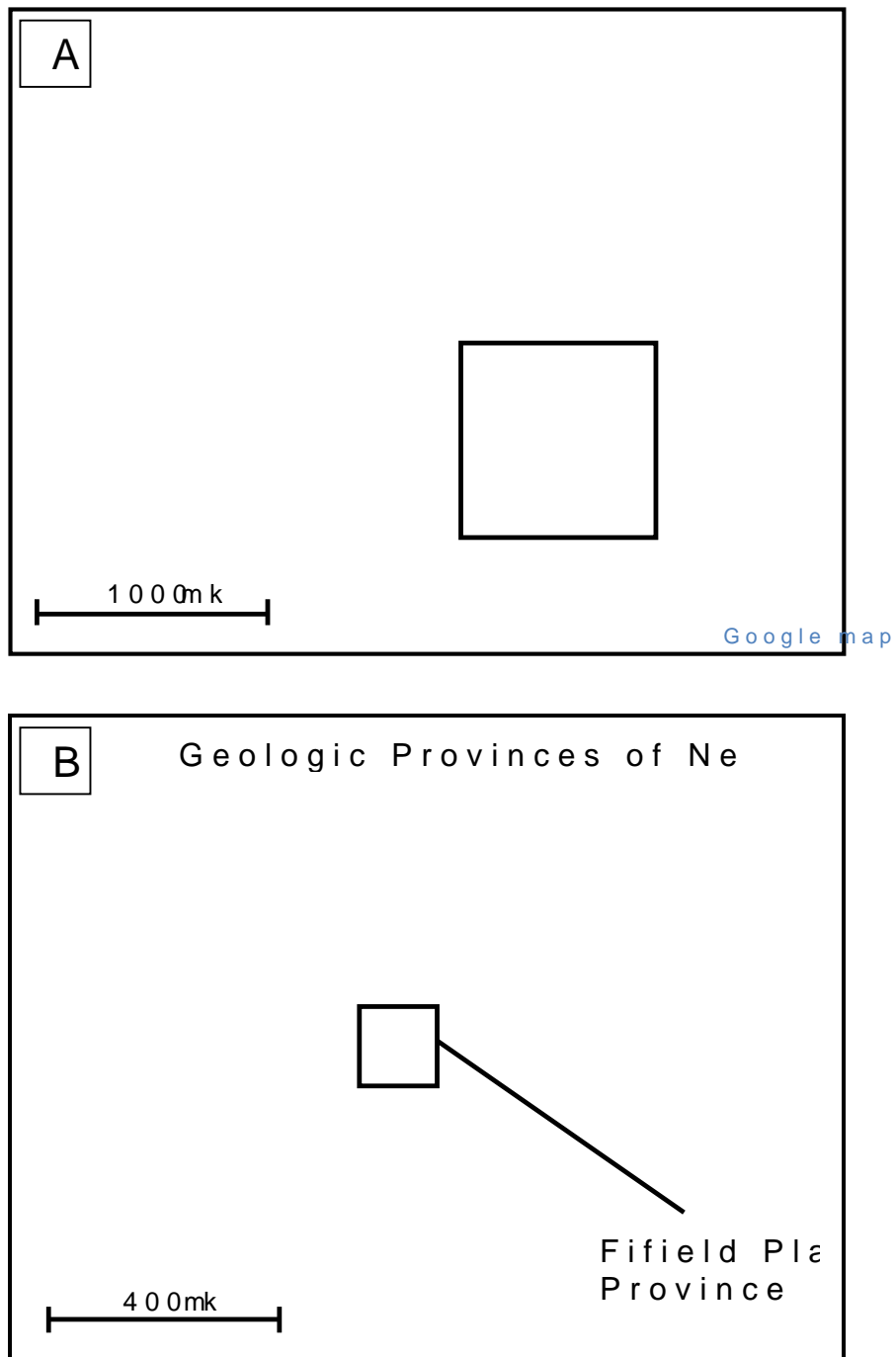


Figure 2.1A: Map of Australia with state of New South Wales and geologic provinces of New South Wales and squared area noting the location of the Fifield Plateau Province (Xiet al. 2009)

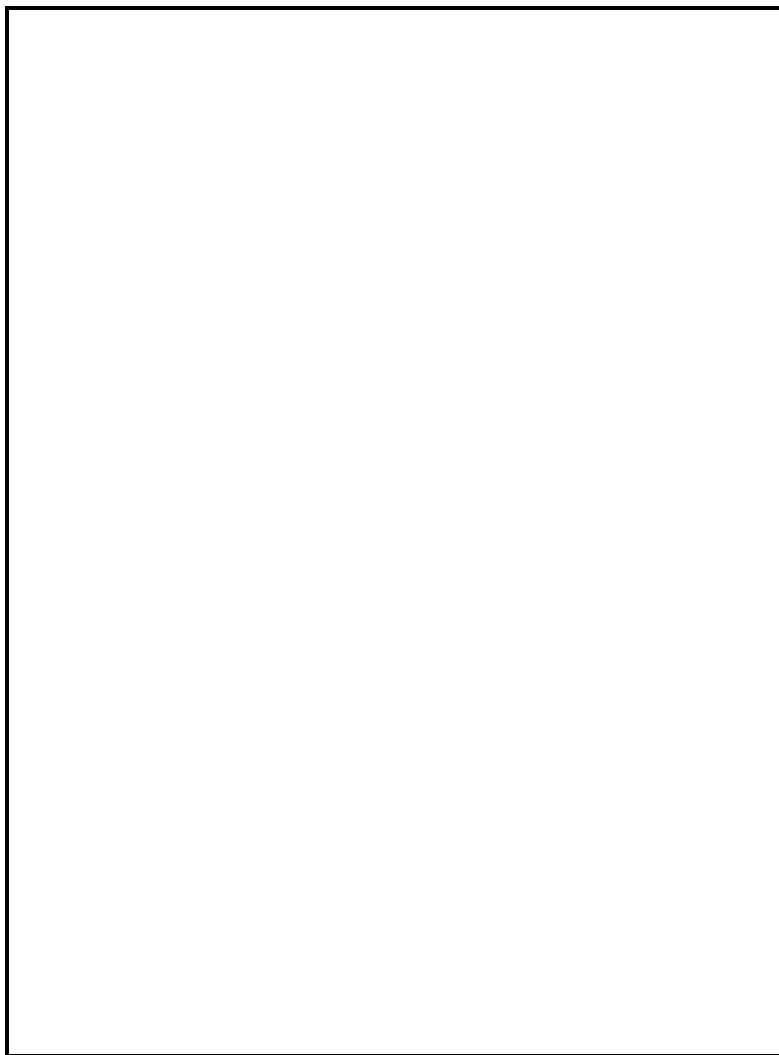


Figure A.2 Schematic profile of Fifield Platinum Province la
Platinum is found in high grade goethite zone.

μ XRD of Pt₃Fe

- Isoferroplatin (PDF# 09020716) (↑)
- Isoferroplatin (PDF# 09020716) (↓)

Figure μ XRD of platinum grain in Figure 2.3 AFETabloy, ulle rgnáíedisa (Pt₃Fe).

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