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GEOCHEMICAL EXPLORATION FOR PLATINUM GROUP ELEMENTS IN WEATHERED TERRAIN

P252 FINAL REPORT

Volume I

*C.R.M. Butt, P.A. Williams, D.J. Gray, I.D.M. Robertson,
K.H. Schorin, H.M. Churchward, J. McAndrew,
S.J. Barnes and M.F.J. Tenhaeff*

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(CSIRO Division of Exploration Geoscience Report 332R, 1992.
Second impression 2001)

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RESEARCH ARISING FROM CSIRO/AMIRA YILGARN REGOLITH GEOCHEMISTRY PROJECTS 1987-1996

In 1987, CSIRO commenced a series of multi-client research projects in regolith geology and geochemistry which were sponsored by companies in the Australian mining industry, through the Australian Mineral Industries Research Association Limited (AMIRA). The initial research program, "Exploration for concealed gold deposits, Yilgarn Block, Western Australia" had the aim of developing improved geological, geochemical and geophysical methods for mineral exploration that would facilitate the location of blind, buried or deeply weathered gold deposits. The program commenced with the following projects:

P240: Laterite geochemistry for detecting concealed mineral deposits (1987-1991). Leader: Dr R.E. Smith.

Its scope was development of methods for sampling and interpretation of multi-element laterite geochemistry data and application of multi-element techniques to gold and polymetallic mineral exploration in weathered terrain. The project emphasised viewing laterite geochemical dispersion patterns in their regolith-landform context at local and district scales. It was supported by 30 companies.

P241: Gold and associated elements in the regolith - dispersion processes and implications for exploration (1987-1991). Leader: Dr C.R.M. Butt.

The project investigated the distribution of ore and indicator elements in the regolith. It included studies of the mineralogical and geochemical characteristics of weathered ore deposits and wall rocks, and the chemical controls on element dispersion and concentration during regolith evolution. This was to increase the effectiveness of geochemical exploration in weathered terrain through improved understanding of weathering processes. It was supported by 26 companies.

These projects represented 'an opportunity for the mineral industry to participate in a multi-disciplinary program of geoscience research aimed at developing new geological, geochemical and geophysical methods for exploration in deeply weathered Archaean terrains'. This initiative recognised the unique opportunities, created by exploration and open-cut mining, to conduct detailed studies of the weathered zone, with particular emphasis on the near-surface expression of gold mineralisation. The skills of existing and specially recruited research staff from the Floreat Park and North Ryde laboratories (of the then Divisions of Minerals and Geochemistry, and Mineral Physics and Mineralogy, subsequently Exploration Geoscience and later Exploration and Mining) were integrated to form a task force with expertise in geology, mineralogy, geochemistry and geophysics. Several staff participated in more than one project. Following completion of the original projects, two continuation projects were developed.

P240A: Geochemical exploration in complex lateritic environments of the Yilgarn Craton, Western Australia (1991-1993). Leaders: Drs R.E. Smith and R.R. Anand.

The approach of viewing geochemical dispersion within a well-controlled and well-understood regolith-landform and bedrock framework at detailed and district scales continued. In this extension, focus was particularly on areas of transported cover and on more complex lateritic environments typified by the Kalgoorlie regional study. This was supported by 17 companies.

P241A: Gold and associated elements in the regolith - dispersion processes and implications for exploration (1991-1993). Leader: Dr C.R.M. Butt.

The significance of gold mobilisation under present-day conditions, particularly the important relationship with pedogenic carbonate, was investigated further. In addition, attention was focussed on the recognition of primary lithologies from their weathered equivalents. This project was supported by 14 companies.

Most reports related to the above research projects were published as CRC LEME Open File Reports Series (Nos 1-74), with an index (Report 75), by June 1999. Publication now continues with release of reports from further projects.

P252: Geochemical exploration for platinum group elements in weathered terrain. Leader: Dr C.R.M. Butt.

This project was designed to gather information on the geochemical behaviour of the platinum group elements under weathering conditions using both laboratory and field studies, to determine their dispersion in the regolith and to apply this to concepts for use in exploration. The research was commenced in 1988 by CSIRO Exploration Geoscience and the University of Wales (Cardiff). The Final Report was completed in December 1992. It was supported by 9 companies.

P409: Geochemical exploration in areas of transported overburden, Yilgarn Craton and environs, WA.

Leaders: Drs C.R.M. Butt and R.E. Smith.

About 50% or more of prospective terrain in the Yilgarn is obscured by substantial thicknesses of transported overburden that varies in age from Permian to Recent. Some of this cover has undergone substantial weathering. Exploration problems in these covered areas were the focus of Project 409. The research was commenced in June 1993 by CSIRO Exploration and Mining but was subsequently incorporated into the activities of CRC LEME in July 1995 and was concluded in July 1996. It was supported by 22 companies.

Although the confidentiality periods of Projects P252 and P409 expired in 1994 and 1998, respectively, the reports have not been released previously. CRC LEME acknowledges the Australian Mineral Industries Research Association and CSIRO Division of Exploration and Mining for authority to publish these reports. It is intended that publication of the reports will be a substantial additional factor in transferring technology to aid the Australian mineral industry.

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FOREWORD

The CSIRO-AMIRA project "Geochemical Exploration for Platinum Group Elements in Weathered Terrain" had the broad objectives of gathering information on the geochemical behaviour of the platinum group elements (PGE) under weathering conditions and their dispersion in the regolith, and to apply this information to the development of concepts for use in exploration. It was anticipated that the Australian minerals industry would benefit from the improved data base on the weathering geochemistry of the PGE that would accrue from the laboratory and field studies, from the assessment of the data in terms of the potential for the formation of secondary PGE deposits, and from recommendations for the most appropriate geochemical exploration procedures for primary and secondary PGE mineralization in deeply weathered terrain. The findings of the project are described in full in the four volumes of this report.

The Project commenced under the leadership of Professor I.R. Plimer, Department of Geology, University of Newcastle, with Dr. P.A. Williams (Department of Inorganic Chemistry, University of Wales, Cardiff) and Dr. R.J. Knight (Division of Exploration Geoscience, North Ryde, NSW) as principal investigators. During the course of the project, Dr. Knight retired and the CSIRO commitment was transferred to the Weathering Processes Group of the Division of Exploration Geoscience at Floreat Park, WA, and Professor Plimer resigned from the University of Newcastle. Late in the project, Dr. Williams returned to Australia to become Professor of Chemistry at the University of Western Sydney, Nepean, NSW. These transfers interrupted the project and caused some delays, but gave the opportunity for field-based research to be carried out in Western Australia by a research group having considerable experience in regolith evolution, geochemical dispersion in the regolith and the problems of exploration in lateritic terrain. Some of the field research was conducted in parallel with similar studies of gold dispersion and secondary enrichment in Western Australia, and aspects of the petrographic studies, in particular, contribute both to this project and to CSIRO-AMIRA project 241A "Gold and associated elements in the regolith - dispersion processes and implications for exploration."

The personnel participating in the project were as follows:

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December, 1992.

TABLE OF CONTENTS

VOLUME I

FOREWORD	i
SUMMARY	xi
 CHAPTER 1 PROJECT OVERVIEW: GEOCHEMICAL EXPLORATION FOR PLATINUM GROUP ELEMENTS IN WEATHERED TERRAIN <i>C.R.M. Butt</i>	 1
1 INTRODUCTION	1
2 AQUEOUS GEOCHEMISTRY OF PLATINUM GROUP ELEMENTS	1
2.1 Background	1
2.2 Chloride complexes	2
2.3 Organic complexes	2
2.4 Sulphur oxyanion complexes	2
2.5 Arsenious acid	3
2.6 Summary	3
3 INTERACTION OF PGE WITH REGOLITH MATERIALS	4
4 FIELD STUDIES	4
4.1 Ora Banda sill, Western Australia	4
4.2 Tout intrusive complex, Fifield, New South Wales	6
4.3 Exploration procedures	7
 CHAPTER 2 CHEMICAL BEHAVIOUR OF THE PLATINUM GROUP ELEMENTS DURING WEATHERING <i>P.A. Williams</i>	 8
1 INTRODUCTION	8
2 PRIMARY MINERALOGY	8
3 MOBILITY AND ENRICHMENT OF PLATINUM GROUP ELEMENTS IN SURFACE ENVIRONMENTS - CASE HISTORIES	9
3.1 Platinum group elements in lateritic profiles	9
3.1.1 Perseverance (Leinster) nickel deposit, Western Australia	9
3.1.2 Gilgarna Rocks, Western Australia	11
3.1.3 Mt Keith nickel deposit, Western Australia	12
3.1.4 Other deposits	13
3.2 Stillwater Complex, Montana	14
3.3 Alluvial deposits	14
3.4 New Rambler Mine, Wyoming	16
3.5 Lac Sheen and Lac Long-Lac Montauban, Canada	16

4	POTENTIAL REACTION CHEMISTRY IN THE SECONDARY ENVIRONMENT	17
4.1	General	17
4.2	Complexes of the halides	18
4.3	Complex formation with other common inorganic ligands	22
4.4	Complexes with cyanide ion and organic ligands	23
4.5	Complexes of lower-valence oxyanions of sulphur	24
4.6	Sulphite and thiosulphate complexes of the platinum group elements	25
4.7	Complexes of other soft ligands	26
5	EXPERIMENTAL INVESTIGATIONS	26
	REFERENCES	27
CHAPTER 3	EXPERIMENTS CONCERNING NEW DISPERSION MECHANISMS FOR PGE IN WEATHERING SULPHIDES	30
	<i>P.A. Williams</i>	
	ABSTRACT	30
1	INTRODUCTION	30
2	EXPERIMENTAL	31
2.1	Metal blacks	31
2.2	Dissolution experiments	31
2.3	Synthetic and spectroscopic experiments	31
2.4	Instrumentation and analyses	33
3	RESULTS AND DISCUSSION	33
3.1	Thiosulphate dissolution experiments: Pt and Pd	33
3.2	Thiosulphate dissolution experiments: other PGEs	35
3.3	Sulphite and trithionate dissolution experiments	35
3.4	Dissolutions by arsenious acid	38
3.5	The nature of the thiosulphate species in solutions	39
4	CONCLUSIONS	40
	REFERENCES	41

CHAPTER 4:	THE SORPTION OF PLATINUM AND PALLADIUM ON SOILS AND REGOLITH MATERIALS	42
	<i>D.J. Gray</i>	
ABSTRACT		42
1	INTRODUCTION	43
2	MATERIALS	43
2.1	Soils	43
2.2	Synthesis of Pt, Pd, Au and Ag complexes	44
2.2.1	Humic complex	44
2.2.2	Thiosulphate complex	44
2.2.3	Iodide complex	46
2.2.4	Chloride complex	46
2.2.5	"Uncomplexed" ions	46
3	EXPERIMENTAL	47
3.1	Solution incubations of lateritic duricrust, Mt. Carnage	47
3.1.1	Dissolution experiments	47
3.1.2	Addition experiments	47
3.2	Addition of solutions to soils	47
3.2.1	Humate, thiosulphate and iodide	47
3.2.2	Chloride	47
3.2.3	Adsorption	48
3.2.4	Analysis of solutions	48
4	RESULTS AND DISCUSSION	48
4.1	MC 24 incubations of lateritic duricrust from Mt Carnage	48
4.2	Additions of Pt, Pd, Au and Ag to various regolith materials	49
4.2.1	Humic complex	51
4.2.2	Thiosulphate complex	57
4.2.3	Chloride complex	57
4.2.4	Iodide complex	58
4.2.5	"Uncomplexed" system	58
5	SUMMARY AND CONCLUSIONS	59
	REFERENCES	61

VOLUME IIA

CHAPTER 5	GEOCHEMICAL DISPERSION OF PLATINUM GROUP ELEMENTS IN LATERITIC REGOLITH, ORA BANDA SILL	1
	<i>C.R.M. Butt, I.D.M. Robertson, K.H. Schorin and H.M. Churchward</i>	
	ABSTRACT	1
1	INTRODUCTION	2
2	SAMPLING AND ANALYSIS	3
2.1	Mapping and Surveying	3
2.1	Sampling	3
2.1.1	Lag	3
2.1.2	Drill cuttings and core	4
2.2	Analysis	8
2.2.1	Sample preparation and chemical analysis	8
2.2.2	Mineralogy	8
2.2.3	Estimation of Al substitution in goethite	9
2.2.4	Petrography	9
3	GEOLOGY, GEOMORPHOLOGY AND REGOLITH	9
3.1	Geological setting.	9
3.2	Geomorphology	11
3.2.1	Regional setting	11
3.2.2	Regolith-landform units	13
3.3	Regolith	16
3.3.1	Regolith stratigraphy	16
3.3.2	Lag	21
3.3.3	Regolith mineralogy	22
4	GEOCHEMISTRY OF THE UNWEATHERED ROCKS	26
5	PETROGRAPHY OF DURICRUSTS AND LAGS	33
5.1	Introduction	33
5.2	Duricrust	33
5.3	Lag	34
5.3.1	Lag overlying peridotite	34
5.3.2	Lag overlying pyroxenite	35
6	GEOCHEMICAL DISPERSION IN THE REGOLITH	44
6.1	Introduction	44
6.2	Elements related to PGE mineralization: Pt, Pd, Rh, Ru, Os, Ir, Cu, S	44
6.3	Major elements: Si, Fe, Al	48
6.4	Alkaline earth elements: Ca, Mg, Sr, Ba	56
6.5	Alkali elements: Na, K, Cs, Rb	57
6.6	Lithophile elements: Cr, Sc, Ti, V, Zr, Ga	58
6.7	Base and transition metals: As, Pb, Co, Ni, Mn, Zn.	63
6.8	Rare earth elements: Ce, La, Y	65

7	MT. CARNAGE	65
7.1	Introduction	65
7.2	Regolith mineralogy	65
7.3	Regolith geochemistry	66
7.3.1	Major and trace elements	66
7.3.2	Platinum group elements	66
7.4	Primary lithology of hole MC 24	69
8	DISCUSSION AND CONCLUSIONS	71
8.1	Element distributions and regolith evolution	71
8.1.1	Introduction	71
8.1.2	Lateritic weathering under humid tropical climates	71
8.1.3	Weathering under semi-arid and arid climates	72
8.1.4	Regolith evolution	73
8.1.5	Origin of Fe-rich lateritic duricrust on peridotite	73
8.2	Implications for exploration	74
8.2.1	Supergene PGE mineralization	74
8.2.2	Primary PGE mineralization	75
8.2.3	Exploration procedures	75
8.2.4	Lithological discrimination	76
	ACKNOWLEDGEMENTS	76
	REFERENCES	79

VOLUME IIB

CHAPTER 5	GEOCHEMICAL DISPERSION OF PLATINUM GROUP ELEMENTS IN LATERITIC REGOLITH, ORA BANDA SILL - APPENDICES
I	Element distribution plots, Ora Banda
II	Comparative statistics for major and trace elements in different horizons of the regolith over peridotite and pyroxenite, Ora Banda
III	Ora Banda diamond drill core: data listings
IV	Ora Banda RAB drilling: data listings
V	Systematic petrography
VI	Lag geochemistry: traverses
VII	Lag geochemistry: contoured
VIII	Lag geochemistry: correlation matrix
IX	Lag geochemistry: frequency distributions
X	Lag and duricrust geochemistry and mineralogy: data listings
XI	Data listing and comparative statistics for major and trace elements in different horizons of the regolith, Mt. Carnage

VOLUME III

CHAPTER 6:	THE SELECTIVE EXTRACTION OF PLATINUM AND PALLADIUM FROM SOILS AND REGOLITH MATERIALS FROM MT. CARNAGE AND ORA BANDA	1
	<i>D.J. Gray</i>	
ABSTRACT		1
1	INTRODUCTION	2
2	IODIDE EXTRACTIONS	2
3	SELECTIVE EXTRACTION EXPERIMENT A - EASILY EXTRACTABLE PHASES	4
3.1	Experimental	4
3.1.1	Exchangeable cation phase (neutral ammonium acetate)	4
3.1.2	Carbonate phase (acid ammonium acetate)	4
3.1.3	Manganese oxide phase (dilute hydroxylamine)	5
3.1.4	'Amorphous' iron oxide phase (hydroxylamine)	5
3.1.5	Crystalline iron oxide phase (partial extraction; hydroxylamine then citrate/dithionite)	5
3.1.6	Residue dissolution	5
3.2	Major Element Results	5
3.3	Minor Element Results	7
3.4	Platinum and Palladium Results	8
4	SELECTIVE EXTRACTION EXPERIMENT B - IRON OXIDE PHASES	9
4.1	Introduction	9
4.2	Citrate Dithionite Scheme	9
4.2.1	Crystalline iron oxide phase (citrate dithionite)	10
4.2.2	Aqua-regia extraction	10
4.2.3	Residue analysis	10
4.3	Citrate Thiosulphate Scheme	10
4.4	General Results	10
4.5	Platinum and Palladium Results	13
5	EXPERIMENT C - HIGH GRADIENT MAGNETIC SEPARATION AND SELECTIVE EXTRACTION	14
5.1	Introduction	14
5.2	High Gradient Magnetic Separation	15
5.3	Differential X-ray Diffraction	16
5.4	Methods	16
5.4.1	Particle size analysis and separation	16
5.4.2	High gradient magnetic separation	17
5.4.3	Tamm's acid oxalate extraction	17
5.4.4	Citrate dithionite extraction	17
5.5	Particle Size Separation Results	17
5.6	High Gradient Magnetic Separation / Selective Extraction	21
5.7	D-XRD Investigation	25

6	SUMMARY	27
	REFERENCES	29
	APPENDICES	
I	Iodide Extraction Data	31
II	Selective Extraction Experiment A - Easily Extractable Phases (MC24)	33
III	Selective Extraction Experiment B - Iron Oxide Phases (MC24)	39
IIIA	Citrate-Dithionite Extractions	39
IIIB	Citrate-Thiosulphate Extractions	41
IV	High Gradient Magnetic Separation Method	42
V	Particle Size Separation and High Gradient Magnetic Separation Results	44
VA	Particle Size Separation - Percentage in each size fraction	44
VB	High Gradient Magnetic Separation - Percentage in each size fraction	44
VC	Elemental Compositions of Solid samples	45
VI	HGMS Samples - Extraction Results	48
CHAPTER 7:	GEOCHEMISTRY OF FRESH AND WEATHERED CHROMITE IN THE ORA BANDA SILL	50
	<i>I.D.M. Robertson, H.K. Schorin, S.J. Barnes and M.F.J. Tenhaeff</i>	
	ABSTRACT	50
1	INTRODUCTION	52
	1.1 Objectives	52
	1.2 Chromite Chemistry	52
2	STUDY METHODS	53
	2.1 Microprobe Analysis	53
	2.2 Statistical Analysis	53
3	MT. CARNAGE WEATHERED PROFILE	53
4	FRESH CHROMITES	55
	4.1 Fresh Chromite in OB DDH1 and DDH2, Ora Banda Prospect	55
	4.2 Multivariate Analysis of Fresh Chromite Data	57
	4.3 Discussion	60
5	LAG AND DURICRUST	63
	5.1 Objectives	63
	5.2 Chromite Compositions in the Lag and Duricrust	63
	5.3 Multivariate Analysis of Weathered Chromite Data	67
6	CONCLUSIONS	69
	6.1 Fresh Chromite	69
	6.2 Weathered Chromite	70

7	ACKNOWLEDGEMENTS	70
8	REFERENCES	71
APPENDICES		
I	Geochemistry and Statistics of Fresh Chromites - Ora Banda Prospect	72
II	Geochemistry and Statistics of Weathered Chromites - Ora Banda Prospect	78

SUMMARY

This report summarizes the results of over three years of research that had the objectives of (i) supplementing existing knowledge of the aqueous geochemistry of platinum group elements (PGE) in the weathering environment, (ii) obtaining information concerning the distribution of these elements in the lateritic regoliths and the potential for supergene enrichment, and (iii) establishing criteria for exploration in lateritic terrain. These objectives were met by conducting detailed laboratory experiments and field-based geochemical investigations.

Laboratory studies demonstrated that, in addition to chloride ion and organic compounds, thiosulphate ion and arsenious acid could mobilize the PGE under weathering conditions. Mobilization as thiosulphate complexes might occur in the vicinity of sulphides oxidizing under neutral to alkaline conditions, whereas arsenious acid could only mobilize Pd, and then only in acid environments. The potential for mobilization by these ligands has not previously been considered, but may have significance in appropriate environments. Studies were also made of the processes that cause immobilization of the PGE in the regolith. The PGE tend to be sorbed by most regolith materials, thus restricting their potential mobility, although in more organic samples, some redissolution occurred after a few months, possibly due to soluble organic species produced by biological activity. The results demonstrate that despite the theoretical models postulating mobility under specific physico-chemical conditions, the substrate will strongly influence the actual behaviour.

Field investigations on the distribution of PGE were carried out on the Ora Banda sill, Western Australia, and the Tout intrusion at Fifield, New South Wales. Lateritic regoliths are well preserved on the pyroxenites of the Ora Banda sill and the duricrusts locally contain 1-2 ppm Pt + Pd. There has been some relative loss of Pd in the duricrust and, particularly, the ferruginous lag derived from it, but otherwise there seems to have been little mobilization of the PGE. The PGE enrichment appears to be residual and occurs in similar horizons, and by a similar factor, as other relatively immobile elements such as Cr, Cu, V, Ti and Zr. No PGE minerals or alloys were found in the regolith and selective leaching experiments suggest that both Pt and Pd occur predominantly in the minus 2 μm fraction. Platinum is mainly associated with hematite throughout the profile, implying early release from its primary host; in comparison, Pd is present in goethite, but only high in the profile, and is presumed to be released from a primary phase (*e.g.*, chromite) late during weathering. Chromite compositions can discriminate between peridotite and pyroxenite in the regolith and could possibly be useful for indicating sulphide-rich zones within the bedrock. There has been rather greater secondary mobility of PGE, especially Pt, in the regolith over the serpentinized dunites of the Tout complex, but again no secondary PGE phase was located and the mechanism of remobilization could not be established, although organic or chloride complexes are most probable. PGE enrichment in alluvium is probably mechanical.

The surface exploration procedures of soil and lag sampling are effective in exploration in lateritic environments. Routine sampling of the laterite itself by shallow drilling may be the best general procedure, especially in areas where much of the laterite is buried. High Pt and Pd concentrations are themselves insufficient indicators, so that it is probably necessary to analyse selected samples for the other PGE. Copper, Cr and Ni are not effective pathfinder elements for none is necessarily associated with primary or secondary mineralization at either Ora Banda or Fifield. The restricted mobility of the PGE and lack of suitable pathfinder elements may pose problems to effective exploration of areas eroded to the saprolite or shallow fresh subcrop, since the target will be small and any enlargement is thus dependent on limited physical dispersion at the surface.

CHAPTER 1 PROJECT OVERVIEW: GEOCHEMICAL EXPLORATION FOR PLATINUM GROUP ELEMENTS IN WEATHERED TERRAIN

C.R.M. Butt

1 INTRODUCTION

The broad objectives of the research project were to gather information on the geochemical behaviour of the platinum group elements (PGE) under weathering conditions and to apply this to the development of concepts of use to exploration. A literature review of the occurrence of PGE in the weathering environment demonstrates that they may be mobile in aqueous solution under oxidizing conditions. However, detailed data are sparse and the mechanisms involved are not well understood; it could also be postulated that mechanisms other than those recognized could be significant in certain environments. In addition, the possibility that supergene concentrations of the PGE, similar to those of Au, could form in lateritic regoliths and some sedimentary environments was also worthy of investigation. Accordingly, the project had two principal components, namely:

1. laboratory studies to supplement existing knowledge of the aqueous chemistry of the PGE and its behaviour in the soil environment, and
2. field studies to establish the distribution of platinum group and associated elements in lateritic regoliths in selected localities, to determine the potential for the development of secondary deposits analogous to those of Au, and to establish criteria suitable for exploration for primary deposits in such terrain. The extent of these studies was limited, since few suitable field sites were available.

2 AQUEOUS GEOCHEMISTRY OF PLATINUM GROUP ELEMENTS

2.1 Background

There have been only a few studies of the geochemical dispersion of PGE during weathering, but examples exist from a range of environments, including temperate humid conditions in Canada and USA, cold semi-arid (USA), humid tropical lateritic (Sierra Leone, New Caledonia), and warm, semi-arid, (modified) lateritic in Western Australia. The data from these studies show that the metallic PGE and their alloys may be formed in oxidizing environments from alteration of their sulphides and other primary minerals. Supergene alteration of primary alloys during the formation of eluvial/alluvial placers and within the placers themselves is demonstrated by variations in mineralogy and composition (*e.g.*, by loss of Pd and Os). Nevertheless, some alloys and minerals (*e.g.*, sperrylite, PtAs₂) appear to be stable under most conditions. In summary, the existing studies show that:

1. differentiation of the PGE occurs during weathering, as shown, for example, by the differing distributions of Pt, Pd and Ir and the upward increase in the ratio Pt/(Pt+Pd) in lateritic regoliths;
2. weathering of PGE sulphides and primary alloys gives rise to secondary grains of the metals and their alloys;
3. the PGE can be chemically dispersed during intense weathering and may thus be either depleted or enriched.

The aqueous chemistry of the PGE with H_2O and OH^- is extremely limited and their mobility during weathering requires the formation of complex ions. Previous studies have suggested that the halides, dominantly chloride, and organic materials (particularly humic and fulvic acids) are the most probable ligands involved; the present study also demonstrates the potential significance of thiosulphate and arsenious acid complexes.

2.2 Chloride complexes

There is considerable data on the aqueous chemistry of PGE with chloride ions and these show that both Pd and Pt may be mobilized as chloro-complexes under acid, oxidizing conditions of the type that are encountered in the weathering environment, in an analogous manner to Au. However, it appears that Pd is mobile over a much wider range of supergene conditions than Pt, which may thus explain the depletion of Pd relative to Pt in lateritic profiles and placers, and the enrichment of Pd in some weathering horizons. Platinum may be mobile under more extreme conditions of high salinity, low pH and high Eh, similar to those known in parts of the Yilgarn Block. Experimental work conducted during this project suggests that, although Pt oxidizes, and hence dissolves, more slowly than Pd, Pt forms a stronger chloride complex and is less easily sorbed and hence could be more mobile. The other PGE also form chloride complexes and, except for Rh, could be mobile in very saline environments; the RhCl_6^{3-} ion is unstable and hydrolyses to the extremely insoluble $\text{Rh}(\text{OH})_3$, so that Rh dispersion is expected to be minimal.

2.3 Organic complexes

There is little information on the role of organic ligands in mobilizing PGE in the natural environment. However, cyanide ion forms stable complexes with Pd and Pt, and complexes or stabilized colloids of PGE form with fulvic and, probably, humic acids, so that these species may be significant in PGE dispersion, in an analogous manner to Au. Only limited experimental data were obtained during this project, since the PGE-rich lateritic samples from Ora Banda had very low contents of organic matter. However, some sorption experiments suggest that soluble organic species produced by biological activity could dissolve significant Pt, Pd and Au with time (Section 3).

2.4 Sulphur oxyanion complexes

Recent research has demonstrated the importance of thiosulphate ($\text{S}_2\text{O}_3^{2-}$) and, possibly, sulphite (SO_3^-) ions in the transport of Au from oxidizing sulphide mineralization. Available thermodynamic data suggest that these ions could also mobilize Pt, Pd and some other PGE during the oxidation of PGE-rich sulphide mineralization, but this possibility appears to have been overlooked in the geochemical literature. Accordingly, experimental investigations were instigated to examine whether thiosulphate, sulphite and polythionate complexes have potential significance in the supergene dispersion of Pt and Pd.

Dissolution experiments were conducted by adding carefully prepared metallic precipitates (metal blacks) of the PGE to aqueous solutions of sodium thiosulphate. Maximum dissolved concentrations of 111 ppm Pd (after 75 days), 20 ppm Pt (46 days), 200 ppm Ir (28 days), 1-2 ppm Ru (28 days) and 1 ppm Rh (28 days) were reached, demonstrating the effectiveness of thiosulphate ions in dissolving these PGE. Dissolution rates increased with decreasing concentrations of thiosulphate ion and were independent of pH in the range 6-9. Maximum observed rates were 20 ppm Pd per day and 0.5 ppm Pt per day. The differences in dissolution rates can be attributed, at least in part, to the well known slowness of reactions of Pt(II) compared to those of Pd(II). In comparison, in dissolution experiments with sulphite and trithionate, no Pt or Pd could be detected even after several weeks, even though the complexes have stabilities similar to those of thiosulphate. The low solubility is probably due to kinetic factors, *i.e.*, the reaction rates are very slow.

The geochemical significance of these results is that the PGE, like Au, are indeed soluble as thiosulphate complexes under conditions that prevail in certain weathering environments and thus may be chemically dispersed. A proviso, however, is that unlike Au, the PGE form oligomeric complexes with thiosulphate (*i.e.*, short chain polymers) which may rapidly be sorbed by iron oxides. Thiosulphate ions are formed when sulphides oxidize under neutral to alkaline conditions. Appreciable thiosulphate production can only occur if the oxidizing sulphide is buffered by alkaline species; for example, it has been calculated that 400-800 g CaCO_3 are required for every 240 g pyrite that is oxidized. This situation may exist in mafic-ultramafic complexes, particularly those having matrix or disseminated sulphides and, as for Au, where there is extensive carbonate alteration associated with mineralization, *e.g.*, in a shear. Appropriate conditions for thiosulphate formation may also be present in arid environments where sulphide oxidation is taking place in contact with alkaline groundwaters. Thiosulphate complexation thus provides a route for PGE mobilization under conditions that are largely complementary to those for chloride complexation.

2.5 Arsenious acid

Arsenious acid ($\text{As}(\text{OH})_3^0$) is an intermediate in the oxidation of arsenide to arsenate and may form during the weathering of As-bearing sulphide mineralization. The possibility that arsenious acid may act as a soft electron donor and coordinate with Pt and Pd under acid conditions ($\text{pH} < 6$) was investigated during this project. It was found that appreciable amounts of Pd were dissolved (maximum 170 ppm at pH 3 after 2 weeks), but negligible Pt, and it is inferred that, under appropriate acid, oxidizing conditions, arsenious acid could be effective in mobilizing Pd. Such conditions are intermediate between those required for thiosulphate and chloride complexation.

2.6 Summary

Although the PGE are generally considered to be resistant to weathering, past and present research has demonstrated that under appropriate conditions, they may be dissolved by one of several ligands:

- | | |
|---------------------|---|
| 1. Chloride ion | acid, highly oxidizing, saline (not Rh) |
| 2. Arsenious acid | acid, moderately oxidizing (only Pd) |
| 3. Organic matter | acid-alkaline, moderately oxidizing-weakly reducing |
| 4. Thiosulphate ion | neutral alkaline, mildly oxidizing-weakly reducing |

The stability ranges of the different possible ligands are broadly complementary, so that PGE mobility is potentially possible under most environmental conditions. However, mobilization by thiosulphate and arsenious acid only occurs in the vicinity of weathering sulphides. In lateritic environments, this implies that it takes place only at the weathering front or at the top of the supergene sulphide zone, either as the profile forms under humid tropical climates, or as it is modified, *e.g.*, during later arid phases. Similarly, neither thiosulphate nor arsenious acid can be implicated in alterations occurring in placer deposits. In comparison, mobilization as chloride or organic complexes is not dependent on the presence of oxidizing sulphides and can occur at any stage during the evolution of the regolith, including placer deposits, when appropriate conditions occur. Chloride complexation is probably insignificant during lateritization, due to the low salinity of groundwaters ($10^{-3.5}$ - 10^{-5} mole/L), but may have importance during subsequent arid periods, whereas organic complexation may occur at any stage, particularly in surficial horizons of the regolith. At the field sites examined during this project, however, only minor mobilization of the PGE has taken place. There is some depletion of Pd in the upper horizons of the lateritic regolith developed on the Ora Banda sill and local concentration of PGE in some Mn oxide segregations. The sill is sulphide-poor, hence unlikely to produce appreciable thiosulphate during weathering, and not in a highly saline or acid environment, so that chloride complexes are unlikely to form; the most probable mobilizing ligands are organic, which are likely only to be significant in near-surface

horizons. Some supergene enrichment of Pt is evident in saprolite at Fifield, but the mechanism of enrichment is not known.

3 INTERACTION OF PGE WITH REGOLITH MATERIALS

Although several soluble complexes of Pt and Pd may be formed during weathering, as described in Section 2, the processes that lead to the immobilization of the PGE complexes are less well known. The actual mobility of the PGE depends, in particular, on the inter-relationships of these complexes with regolith materials. These inter-relationships have been investigated by reacting thiosulphate, humate, chloride and iodide complexes of Pt and Pd with organic-, carbonate-, Fe oxide- and Mn oxide-rich samples under a range of different conditions and the results compared with those of similar experiments conducted previously with Au and Ag.

1. Platinum was sorbed only slowly onto the various regolith materials under a wide range of conditions. This implies that Pt, once dissolved, forms very stable soluble complexes that could have high mobility in the weathering environment.
2. Concentrations of dissolved humate-PGE complexes are very low in the reaction mixtures, suggesting strong sorption by the regolith materials. Peat moss was the least effective at sorbing the Pt, Pd, Au and Ag.
3. Concentrations of dissolved Pt and Pd thiosulphate complexes remained low in the reaction mixtures, even after three months. The low concentrations are possibly due to polymerization of the complex, resulting either in less soluble forms or highly negatively charged species that sorb readily on positively charged surfaces, such as those of Fe and Mn oxides. This suggests that PGE-thiosulphate complexes may have limited mobility during weathering.
4. In chloride-rich solutions, Pt and Ag were sorbed less strongly than Pd or Au, consistent with the high solubility of Pt (1, above). This does not, however, imply that Pt will be more mobile than Pd in saline environments, since Pd metal is much more readily oxidized and dissolved than Pt: *i.e.*, although the Pt complex is more stable, it is far less easily formed.
5. Weakly complexed PGE were rapidly sorbed by the regolith materials, but significant Pt, Pd and Au redissolved after three months in those mixtures having >0.2% organic matter in the solid. The dissolution is possibly due to soluble organic species produced by biological activity.

A conclusion of these studies is that the PGE mobility is strongly influenced by the nature of the substrate and that theoretical models postulating mobility under specific physico-chemical conditions may be in error if reactions with the regolith are ignored.

4 FIELD STUDIES

4.1 Ora Banda sill, Western Australia

The objective of this study was to describe the lateritic enrichments and nature of dispersion of the PGE in the regolith on the Ora Banda sill and to recommend appropriate exploration procedures for similar deposits or for concealed primary mineralization. The Ora Banda sill is a 2 km thick mafic-ultramafic intrusion, one of a number of highly differentiated sills in the Norseman-Wiluna Greenstone Belt known to contain anomalous PGE concentrations. The lower, ultramafic units of the sill have been deeply weathered and have given rise to lateritic enrichments of PGE similar to those of Au. The research was conducted at two prospects, at Ora Banda, the principal site, and at Mt. Carnage, west of Ora Banda. The region has moderate relief and variable preservation of

lateritic regolith. Preservation is greatest over the pyroxenites, which are characterized by the presence of partly dissected lateritic duricrusts. The peridotites are less dissected, but there is no complete lateritic cover and the soils are developed on saprolite. Remnant Fe-rich duricrusts on the peridotite at Ora Banda are partly transported and appear to be channel deposits. The pyroxenites and peridotites are weathered to depths of 40-60 m whereas, in contrast, the norite and gabbro-norite higher in the sill are essentially fresh at surface.

The basal ultramafic unit consists of peridotite (42 ppb Pt, 54 ppb Pd) overlain by pyroxenite (132 ppb Pt, 79 ppb Pd). There is a gradual increase in total PGE upwards through the peridotite, whereas in the pyroxenite, the PGE appear to be relatively enriched in the bottom 75 m and again towards the top. The sulphide distribution, indicated by Cu, suggests that S saturation corresponds to the base of the pyroxenite. No single horizon of PGE enrichment was located in the unweathered rocks by diamond drilling although, close to the contact, three RAB holes intersected a narrow zone in the regolith rich in several PGE (maxima over 1 m: 1800 ppb Pt, 1200 ppb Pd, 52 ppb Ru, 114 ppb Rh, 6 ppb Os, 20 ppb Ir).

The contents of all PGE in the regolith increase steadily towards the surface, with a total enrichment of three- to five-fold in the lateritic ferruginous zone over the pyroxenites. The highest concentrations occur in the ferruginous clays, lateritic horizons and calcareous lateritic soils on pyroxenite, and in calcareous saprolites and soils on peridotite. The maximum concentrations in the lateritic horizons are up to 2000 ppb total PGE at Mt. Carnage and 850-1150 ppb PGE at Ora Banda. The accumulations appear to be residual and are of the same order as other elements such as Cr, Zr and Cu that also appear to be immobile. The mean Pt/(Pt+Pd) ratio (expressed as percentage, Pt%) of unweathered rocks is approximately 45% in peridotite and 63% in pyroxenite. This difference is maintained in the regolith, particularly comparing the pyroxenites with the peridotites, and the relationship appears to distinguish the two lithologies reliably. There is an upward increase in Pt% in the profile, with the highest values (75-88%) in the PGE-enriched horizons (mottled clay, lateritic duricrust and derived soil) developed from the pyroxenite; greater values still are found in the lag derived from these duricrusts. The increase may be due either to further chemical reworking during lag formation or because Pt is preferentially concentrated in those components of the duricrust, such as ferruginous nodules, that comprise the lag. Chemical studies indicate that Pt is strongly associated with Fe oxides, especially hematite, in the regolith and is immobile, whereas Pd is located in a slow-weathering phase and may be leached as this is weathered. However, it is evident from the diamond drill core, and from samples of the deep saprolite, that fresh and partly weathered pyroxenite may have an initial Pt% of 75-85%, though usually in rocks containing <150 ppb Pt and <40 ppb Pd, so that a high ratio is not unequivocal evidence for loss of Pd. There is minor concentration of PGE in calcareous soil and saprolite, similar to Au in this region, but the relationship with pedogenic carbonate was not confirmed either by analysis of hand-picked material or by selective extraction. Despite loss of Pd, lag sampling effectively delineates the lateritic zones of PGE enrichment and the petrography and geochemistry of lag both discriminate between peridotite and pyroxenite.

There is no evidence for significant chemical dispersion of PGE in the regolith over the Ora Banda sill, with the minor exceptions of local concentrations in Mn oxides, loss of Pd in surface horizons and possible concentration in calcareous soils. The supergene behaviour of the PGE thus differs from that of Au in this region, for which secondary mobility has been shown to be quite pronounced, both during lateritization and subsequent arid periods, including the present. Gold mobility has resulted in widespread dispersion in lateritic horizons and some saprolite, secondary accumulation in pedogenic carbonates and leaching from the upper saprolite. Although significant enrichments of PGE have developed by residual accumulation during lateritic weathering, at Ora Banda, neither the concentrations nor the identified resource are sufficiently great to be exploitable. For supergene PGE concentrations in lateritic regoliths to be economic would probably require a rather higher initial PGE content and the possibility of chemical mobilization and reconcentration during

weathering. Such mobility might be promoted in rocks that have a greater sulphide content, or at sites where the regolith is saturated with hypersaline groundwater, thus permitting mobilization as thiosulphate or chloride complexes, respectively.

Attempts to isolate individual PGE minerals at Ora Banda and Mt. Carnegie were unsuccessful. Examination of panned concentrates and magnetic concentrates by scanning electron microscopy, and electron microprobe examination of chromites and other minerals yielded negative results. Selective extraction analyses indicate that, throughout the profile, Pt is dominantly associated with crystalline Fe oxides, particularly hematite, in the minus 2 μm fraction, and is only extracted when the Fe oxides themselves are dissolved. This implies that primary Pt is present in (or as) readily weathered phases, is rapidly incorporated in newly formed Fe oxides and essentially immobilized during subsequent evolution of the regolith. However, possible partial solution of the oxides in some shallow soils is indicated by release of Pt into some amorphous oxide phases. Up to 40% of the Pt in the plus 2 μm fraction remains unextracted and may represent primary Pt in coarser resistant phases. The host minerals have not been identified, although chromite is a possibility. Palladium has a different distribution to Pt. Extractable Pd occurs dominantly in the lateritic horizons, mainly in the minus 2 μm fraction, but less than half is associated with Fe oxides which, in this case, appear to be Al-goethite rather than hematite. This is interpreted to suggest that Pd is released from its primary phase late during weathering, perhaps even under present conditions, and is accumulating in more recently formed goethite. Manganese, Co, Cu, Cr, V and Ti also become associated with Fe oxides during weathering.

There are significant differences in the compositions of chromites associated with the peridotites and the pyroxenites. Chromites in the peridotite have very similar Cr-Al-Fe³⁺ compositions whereas those on pyroxenite are more widely scattered. The difference is probably related to the smaller size of the chromites in the pyroxenite, and their ability to react with the more abundant intercumulus liquid in these rocks. Chromite compositions also record the influence of cumulus sulphides, showing a trend of Al-depletion and Cr-enrichment in more sulphidic pyroxenite, compared to Al-depletion and Fe³⁺-enrichment in sulphide-poor pyroxenite. Chromium has been remobilized during lateritic weathering and partial extraction results show it to be associated with Fe oxides in the ferruginous upper horizons of the regolith. Some of the remobilized Cr may have been derived from Cr-bearing silicates, such as chromian augite, and some from weathering of chromites. Many chromites in the lateritic horizons and the lag have developed a reticulate crack pattern towards the grain margins, indicating that weathering has occurred. They have lower Fe³⁺ contents than most fresh chromites, but this may be because these surviving chromites are larger grains that were resistant to re-equilibration with the melt and originally poorer in Fe³⁺. Nevertheless, peridotite and pyroxenite can be distinguished in the regolith by chromite compositions. There is also potential for distinguishing between sulphide-poor and sulphide-rich units, but the low sulphide content of the parent rocks and absence of a suitable sample set in the regolith has meant that this potential could not be tested.

4.2 Tout intrusive complex, Fifield, New South Wales

The Tout intrusive complex is one of a number of mafic-ultramafic complexes in the Fifield area. In the eastern portion of the complex, Pt mineralization has been found in a weathered serpentinized dunite. The regolith consists of a lateritic profile typical of that developed on this lithology, namely a pisolitic laterite, ferruginous and silicified saprolite and clay-rich saprolite. Platinum and, to a lesser extent, Pd have been leached from the upper horizons and reconcentrated in the clay, giving erratic grades of 0.2-20 ppm Pt. No PGE minerals have been found and the variability is thus assumed to be inherent, rather than due to a "nugget" effect. The mechanism of PGE mobilization is not evident, although complexation with organic or chloride ligands would seem probable on theoretical grounds. Elsewhere, alluvium deposited prior to lateritization overlies the dunite. PGE enrichment occurs at the base of the alluvium, and a few grains of Pt-Fe alloys have been recovered.

This enrichment is probably mechanical in origin and not due to supergene chemical mobilization. No other elements appear to be pathfinders for primary or secondary PGE mineralization, other than those normally associated with dunites or specific weathering horizons.

4.3 Exploration procedures

The routine surface exploration procedures of soil and lag sampling have been effective in exploration for lateritic PGE mineralization at Ora Banda, followed up by shallow drilling of the lateritic enrichment itself. Sampling of the laterite itself by shallow drilling may be the best general procedure, especially in areas where much of the laterite is buried. Similar procedures would be effective in the Fifield area, followed up by drilling for supergene enrichments deeper in the profile. Laterite (and lag) sampling would also be suitable for exploration for primary mineralization, although care would be required within, or close to, areas of lateritic enrichment. High Pt and Pd concentrations are themselves insufficient indicators, so that it is probably necessary to analyse selected samples for the other PGE. Copper, Cr and Ni are not effective pathfinder elements. None is necessarily associated with primary enrichments and both Cu and Cr are residually enriched in lateritic horizons. The possibility that chromite compositions could distinguish sulphide-rich zones in the parent ultramafic rocks is worthy of further investigation. The apparent lack of chemical mobility of the PGE may pose problems to effective exploration of areas of saprolite, since the target will be restricted in size and any enlargement is thus dependent on limited physical dispersion at the surface. In extreme cases, where there is little regolith, element abundances in soil will be very low. Accordingly, careful regolith-landform mapping is essential and different threshold and anomaly limits need to be applied to each unit.

CHAPTER 2 CHEMICAL BEHAVIOUR OF THE PLATINUM GROUP ELEMENTS DURING WEATHERING

P.A Williams

1 INTRODUCTION

Equilibrium model calculations show that certain PGEs may be mobile in aqueous solution under oxidizing conditions. In particular, chloride complex formation provides a route for the well known separation of Pd from Pt in Kupferschiefer-type deposits, in placer deposits, oxide zones and laterites. However, important details of PGE geochemistry appear to have been overlooked; complexes of sulphite and thiosulphate may be involved in the transport of PGEs from oxidising sulphide ores. Arsenic(III) species may also be involved. Mechanisms for the formation of potentially economic secondary concentrations of the PGEs in the weathered zone may be drawn from the chemical literature. These involve dissolution and transport as complexes, and concentration of PGEs at a redox barrier owing to reduction and precipitation of metals.

This Chapter reviews these possible mechanisms for mobilization of PGE under oxidizing conditions. Experiments concerning the feasibility of thiosulphate, sulphite and arsenite complexes in this role are described in Chapter 3.

The platinum group elements (namely Ru, Rh, Pd, Os, Ir and Pt, referred to collectively as PGEs) occupy a central part in our understanding of inorganic and coordination chemistry in general. Extensive compilations of data and reactions [1-5] and reviews concerning the geochemistry of the PGEs [6-9] are available. A corresponding wealth of geological data has accrued [10-13]. Inevitably, geological and geochemical studies have concentrated on primary material and fewer data are available concerning the supergene geochemistry and mineralogy of the PGEs owing to their currently limited economic importance in surficial environments. For geochemical techniques to be applied in the search for new PGE deposits, such chemistry must be elucidated properly. Supergene chemistry is important in the development of placer PGE deposits and, potentially, other economically viable enrichments in the oxide zone.

The purpose of this section is to provide pertinent information on the mobilization, dispersion and enrichment of PGEs in oxidizing environments, with a view to developing appropriate geochemical exploration methods. The report examines the known geochemistry of the PGEs under weathering conditions, reviews the evidence for the supergene migration of the platinum group elements, and draws together some basic chemical data which have a bearing on these phenomena. Deficiencies in available knowledge are highlighted and other novel ideas have been experimentally explored.

2 PRIMARY MINERALOGY

Cabri [14, 15] has produced, in a series of detailed glossaries, a careful compilation of the accepted mineralogy of the PGEs. New species continue to be discovered [16-22]. The kinds of processes which might be important for the PGEs in the weathering environment may be inferred by examining the primary mineralogy and the redox chemistry of the elements.

The most striking feature is that many compounds of the PGEs occur as minerals, in addition to the native metals and their alloys. Thus, even in the primary environment, higher oxidation states appear to be achieved relatively easily. Hence, compound and complex formation in the secondary environment, in which higher oxidation potentials may arise, is to be expected.

Consideration of the kinds of chemical changes which can take place with these minerals in a weathering environment is hampered by a lack of thermochemical data for most of the reported primary minerals. Some data on the general chemistry of the PGEs with respect to geochemical applications are available [9], and examination of this does provide an overall chemical picture.

Simple sulphides can exist in a number of stoichiometries under reducing conditions (*i.e.* at lower values of redox potentials) but, at higher Eh values, the metallic elements are the thermodynamically stable phases. This situation results from the thermodynamics of the oxidation of sulphide or disulphide ion to sulphate.

Thus, the metallic PGEs and their alloys may be formed easily in oxidizing environments from their sulphides and, *inter alia*, sulphosalt minerals and congeners [9]. However, some compounds may be chemically stable. For example, sperrylite, PtAs₂, is resistant to oxidation, and persists in weathered material including gossans [14]. According to Figure 1, Os and Pd sulphides should be more easily attacked than Pt and Ir sulphides. Ruthenium sulphides appear to be the most resistant to weathering (ignoring Rh, which is dealt with below). On the basis of this cursory examination of reaction chemistry, it may be concluded:

- i mechanisms exist for the differentiation of the PGEs in the weathering environment;
- ii as PGE deposits are intensely weathered, chemical reactions of the PGEs may be involved in both dispersion and enrichment; and
- iii the weathering of fine-grained PGE sulphides in sulphide or ores will give rise to fine grains of platinum group metals or their alloys in the supergene zone.

3 MOBILITY AND ENRICHMENT OF PLATINUM GROUP ELEMENTS IN SURFACE ENVIRONMENTS - CASE HISTORIES

Before examining the likely aqueous chemistry of the PGEs in near-surface environments, it should be established that such chemistry has geological significance. Although the literature is not extensive, enough has been reported to show that the PGEs *are* mobile under oxidising conditions. Such suggestions were made several decades ago [23] but the necessary trace element analytical work has been carried out only in recent times. The advent of neutron activation analysis has helped this aspect of PGE chemistry.

3.1 Platinum group elements in lateritic profiles

3.1.1 *Perseverance (Leinster) nickel deposit, Western Australia*

This deposit is located at Leinster, 330 km north of Kalgoorlie and consists of a number of nickel sulphide bodies adjacent to the Perseverance fault in a zone of dunite-serpentine intrusions [24, 25]. Other major deposits occur nearby at Mt. Keith and the Six Mile. The supergene alteration of the deposit has been studied by Nickel *et al.* [25] who found that weathering extended to an irregular depth of up to 400 m below the surface, with the lower boundary transitional with the primary zone over perhaps some 250 m. Transition, violarite-pyrite and oxide zones were recognized.

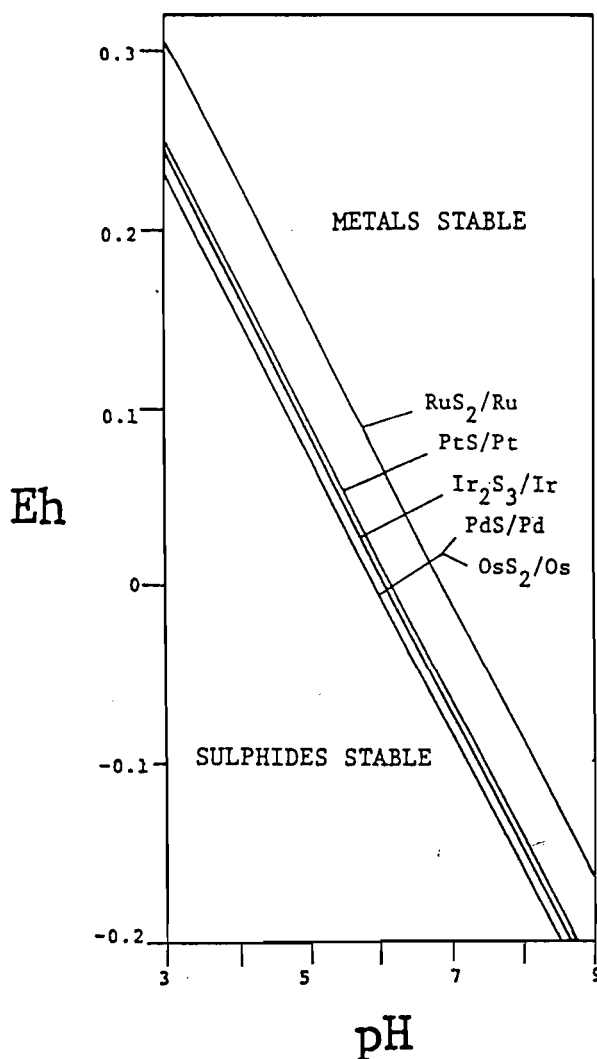


Figure 1. Partial Eh-pH diagram showing the relative stabilities of the platinum group metals and their sulphides at a sulphate activity of 1 at 25°C.

These are characterized, respectively, by pentlandite and pyrrhotite (partly altered to marcasite), and sulphides replaced by oxide and hydroxide minerals. Shoot 1 is a mineralized ultramafic body which outcrops at surface. Pronounced Ni enrichment is observed at 22-24 m from the surface associated with a nickel-rich pyroaurite phase; a lesser enrichment at 8-14 m depth is associated with a yellow-green montmorillonite. The latter zone is also enriched in Cu.

McGoldrick and Keays [26] have studied the distribution of a number of elements in the oxide zone developed over Shoot 1. Representative channel samples from a development shaft were analysed for (amongst other elements) Au, Ag, Pt, Pd and Ir. At this location, the base of the oxide zone is some 32.5 m below the surface. Their results are depicted in Figure 2. Data for grab samples are also shown. The results clearly indicates that Ir and Au are neither depleted nor enriched in the oxide zone. Silver values fluctuate markedly with depth but, by comparison with its abundance in bulk sulphides, Ag is generally depleted in the oxide zone. Both Pt and Pd are enriched in the oxide zone, with peak concentrations occurring towards the base of the zone by comparison with material both from near the surface and at depth. This pattern of Pt and Pd distribution must have resulted from the dissolution, transport in solution and redeposition of these elements while the deposit was being weathered. Apparently the chemistry of the groundwater present during weathering differentiated Pt and Pd from Au and Ir, but not Pt from Pd. No data are available for Ru, Os or Rh.

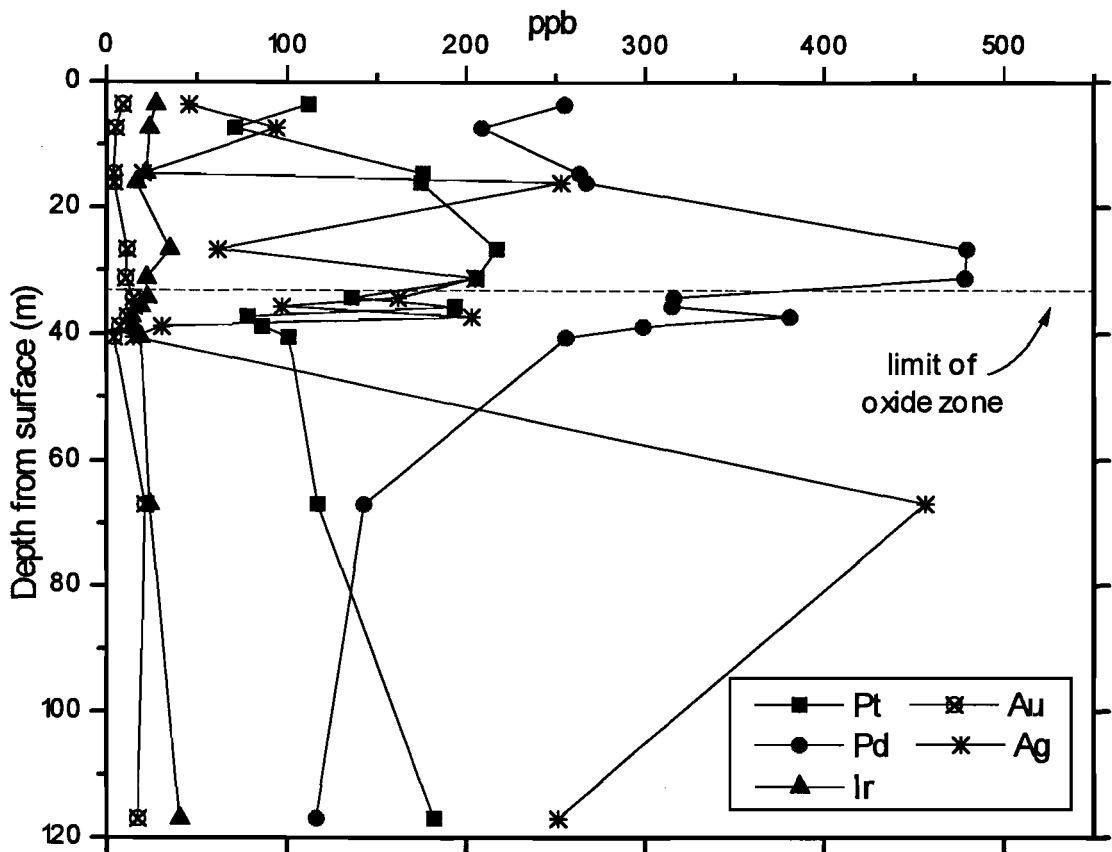


Figure 2. Distribution of PGEs with depth in the Metallurgical Shaft Perseverance Shoot No. 1. Data based on channel sampling of approximately 1.5 m intervals above 40 m and spot samples below 40 m.

3.1.2 Gilgarna Rocks, Western Australia

Travis *et al.* [28] obtained results for complete lateritic profiles from Gilgarna Rocks, some 90 km north-north-east of Kalgoorlie. Two drill holes were sited on what was originally serpentinized dunite, one of which penetrated unweathered bedrock. The unweathered rock contained 2 ppb Pd and 2 ppb Ir - typical for Mg-rich rocks in Western Australia. The results for samples averaged over several metres for Pd and Ir plotted in Figure 3 show that Pd is depleted near the surface and concentrated in the lower level of the ferruginous zone, whereas Ir is concentrated higher in this zone. In both profiles, Pd follows the trends of Mn and Cu, and to a lesser extent Ni, Co and Zn, and Ir correlates best with Fe and Al oxides. Thus, Pd enrichment can be attributed to mobilization from other parts of the ferruginous zone and coprecipitation with Mn, Cu, Ni, Co and Zn. Owing to its comparative inertness, Ir is concentrated more in the residue upper section of the profile with Fe, Al and Cr when Mg, Si and other cations are leached out. The Ir enrichment in GRP1 is exceptionally high and is attributed to more extensive leaching of the laterite profile than for GRP6, which is more normal. The less marked concentration of Pd and Ir at the ferruginous zone-saprolite boundary in GR6 corresponds to a very much less well-defined boundary than in GRP1.

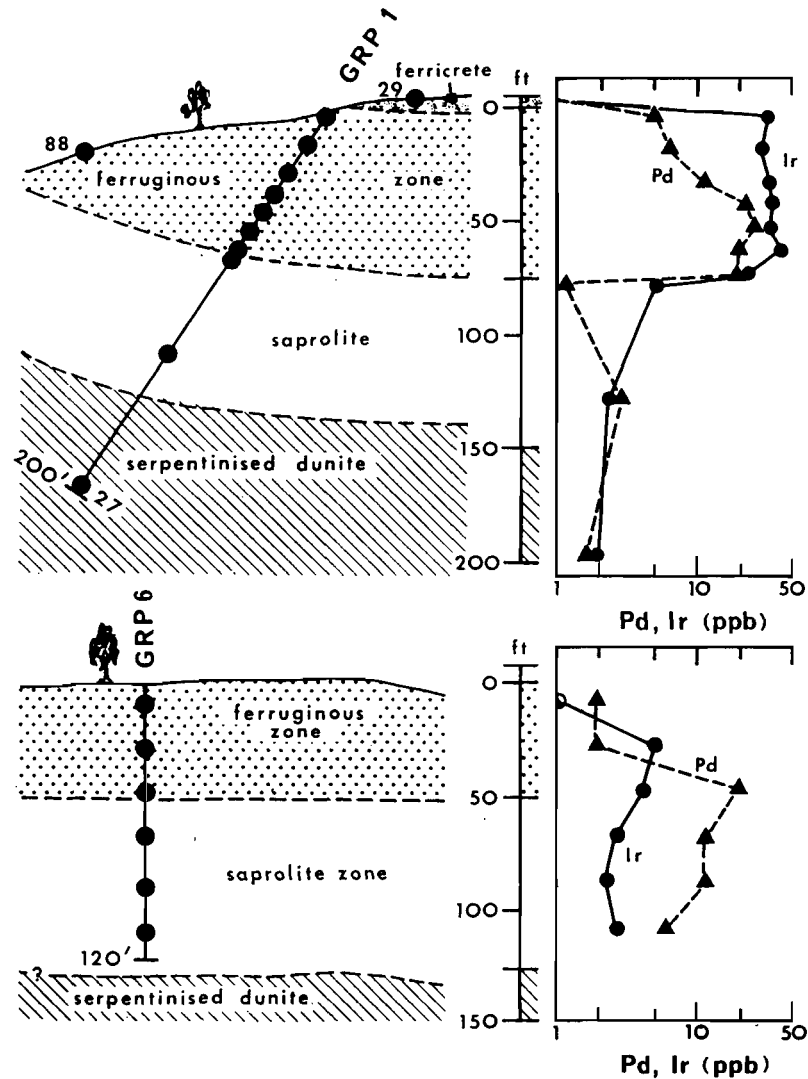


Figure 3. Distributions of Ir and Pd in laterite profiles (drill holes GRP 1 and GRP 6) at Gilgarna Rocks, W.A. (from Figure 4, Travis *et al.*, Ref. 28).

3.1.3 Mt Keith nickel deposit, Western Australia

The distributions of Pt and Pd in the lateritic regolith over the disseminated Ni sulphide deposit at Mt. Keith have been reported by Butt (113, 114). The deposit is about 400 km NNW of Kalgoorlie and is hosted by a serpentinitised dunite. The residual profile, which is buried by 30-40 m of transported overburden, is typical of that developed on this lithology. Thus, there is an *upper ferruginous horizon* of lateritic gravels and duricrust, with Mn oxide enrichment at the base, silicified saprolite, quartz pans and interstitial clay saprolite, with dolomite in voids (*quartz dolomite zone*), saprolite-saprock with secondary sulphides (*supergene zone*), and unweathered serpentinite (*primary zone*). The concentrations of Pt and Pd steadily increase upwards through the regolith, reaching maxima in the Mn-rich horizon of the ferruginous zone (Table 1). If concentrations are calculated isovolumetrically, however, the upward increase is less evident. There appears to be minor enrichment of the PGE in the supergene sulphides and dilution in the carbonate horizon, but the concentrations in the saprolitic quartz-dolomite zone, whether silicified or as clays, seem little different from those in the primary zone. Platinum and Pd are enriched by a factor of seven in the ferruginous zone, particularly where it is Mn-rich. However, some of the enrichment in this zone may be due to residual concentration and compaction rather than absolute accumulation during isovolumetric weathering. Similar calculations suggest that Ni and, to a lesser extent, Cu are

enriched about twofold in the supergene and quartz-dolomite zones and fivefold in the Mn-rich horizon. The Pd/Pt ratio remains more or less constant throughout the profile, but the lower value in the ferruginous horizon suggests some preferential loss of Pd. Overall, the data imply that Pd and Pt are relatively inert during weathering, but some chemical mobility is indicated by:

- minor enrichment in the supergene zone, probably associated with Ni in secondary sulphides;
- enrichment and a lower Pd/Pt ratio in the ferruginous zone;
- marked enrichment in the manganiferous horizon.

The enrichment in the profile at Gilgarna is also associated with the manganiferous horizon.

TABLE 1
Nickel, copper, platinum and palladium in the weathering profile, Mt Keith, W. Australia.
Data expressed as both mass and volume concentrations (from Butt, references 113,114)

		No.	Mass concentration				Volume concentration				Pd/Pt
			Pd ppb	Pt ppb	Cu ppm	Ni ppm	Pd mg/m	Pt mg/m	Cu g/m	Ni g/m	
Transported overburden		3	0-15	0-22	180	1030	0-38	0-55	500	2895	
Ferruginous zone	M	5	115	70	995	4760	325	195	2880	13980	1.65
	S		24	18	530	4745	87	54	1715	15180	
Manganiferous Horizon	M	2	295	125	1505	21595	850	360	4300	61745	2.33
	S		41	89	360	6420	150	240	875	16170	
Quartz-dolomite Zone	M	12	95	40	690	14420	140	80	1030	21010	2.35
	S		58	14	240	5520	65	35	240	5930	
Dolomite	M	3	37	14	260	8275	80	30	550	17375	2.62
	S		17	7	22	875	35	15	45	1840	
Supergene Zone	M	6	63	27	360	6020	150	65	870	14515	2.34
	S		17	6	53	1685	44	13	135	1440	
Primary Zone	M	5	47	19	295	4495	120	50	760	11785	2.47
	S		22	8	105	1320	55	18	275	3700	

M=mean; S=standard deviation

3.1.4 Other deposits

There are several reports of gossans in which residual concentrations of all PGEs are simply elevated [28-30]. Keays [28] noted that both Pd and Ir are enriched in the lower sections of the oxide zone and the violarite-pyrite zone at Kambalda, Western Australia. The sequence of alteration in these deposits has been studied [31, 32] and relationships similar to those occurring at Perseverance were found.

A few other deposits have been examined. Platinum and Pd are separated in lateritic soils in New Caledonia [33], where Pd is evidently more mobile under surface weathering regimes. There is probably little potential for the recovery of PGEs from laterites or gossans [33] but they have been worked in the past. Bowles [34] has described the development of PGE minerals in laterites in Sierra Leone. Both alluvial and eluvial deposits have been mined near the coast on the Freetown Peninsula. This locality represents a section of a basic layered intrusion consisting of repeated sequences of troctolite, gabbro and anorthosite [34]. PGE minerals have been recovered near the coast from lateritized gravels capped by duricrust. At Guma Water, PGE minerals are also present [35]. The source of the PGE minerals, which include platinum, platinum-iron alloys, Os-Ir-Ru alloys, tulameenite and the erlichmanite-laurite series, appears to be anorthosite [36], and the mobilization of the PGEs by surficial chemical processes seems probable. It has been concluded that the PGEs are derived from very sparsely disseminated deposits in which the role of thin veins can be

discounted on geological grounds. Crystalline, non water-worn growths of Pt in the streams have been observed [37]. Well-preserved crystals of PGE alloys and erlichmanite-laurite are also common and show regrowth and development of plates on previously etched surfaces [33]. The grains of PGE minerals reach a considerable size. It must be concluded that oxide zone chemistry involving aqueous solutions has been responsible for the development of these deposits. Bowles [34] explains this in terms of chloride complex formation.

The Sierra Leone laterites may be compared with a deposit at Yubdo, Ethiopia [38-40], where the possibility of supergene alteration has been the subject of some controversy. Current thinking leads to the conclusion that aqueous reaction chemistry *is* important in that setting as well [33], although it is now accepted that relic primary PGE phases are also present in the weathered material. Bowles [33] has pointed out "the important economic significance ... is that near-surface pockets high in platinum-group minerals may be found at appropriate horizons in laterites overlying basic or ultrabasic intrusions".

3.2 Stillwater Complex, Montana

Fuchs and Rose [27] examined the behaviour of Pt and Pd in soils near the No. 2 Showing in the Stillwater Complex. The mineralization occurs in a chromitite adjacent to small, later granite bodies. Although the amount of data reported is limited, Pd was found to be mobilized in the upper soil horizons where it occurred in a readily extractable form, and to occur to a greater extent in clay fractions. Platinum was relatively immobile. It was noted that Pt in chromite was relatively immobile because of that mineral's resistance to weathering. Some enrichment of Pd in the B horizon was evident and an interesting accumulation of Pd in *Pinus flexilis* was also reported. The differentiation of Pt and Pd was attributed to the relative ease of formation of their respective chloride complexes.

3.3 Alluvial deposits

Two important observations indicate that supergene alteration of PGE minerals does occur in alluvial deposits. The first is the large size of mineral grains observed, and the second is the conspicuous depletion of palladium in such deposits [41]. In addition, Os and Ir are relatively abundant in placer deposits. An excellent review by Cousins and Kinloch [41] places these facts in perspective and summarizes the known chemistry of alluvial deposits of PGE minerals. Platinoids usually occur predominantly as one of two alloys: Pt with various amounts of Fe, or Os-Ir alloys. The ratio (Os + Ir)/Pt may be used to assess the "degree of maturity" of platinoid placers [42]. There may be some relationship between this ratio and the salinity of the deposition environment [6, 43]. As Os-Ir alloys become "more mature" Os is depleted, especially from the rims of the grains. Arsenic enrichment (to form irarstite) is noted with many examples. Variations in mineralogy from primary to eluvial/alluvial placers, as shown in Table 2, are pronounced in certain cases and point to the role of aqueous PGE chemistry in the secondary environment.

TABLE 2
Variations of platinum group mineralogy from the primary horizons of the Bushveld Complex and eluvial and alluvial placers from several areas [41]

Merensky Reef	UG2 Chromitite	Placers
Braggite	Braggite	
Cooperite		
Sperrylite	Sperrylite	Sperrylite*
Laurite	Laurite-	Laurite-
	Erlichmanite	Erlichmanite
Pt-Fe alloys	Pt-Fe alloys	Tulameenite
		Pt (Fe, Pd, Rh)
Moncheite		
Kotulskite	Kotulskite	
Merenskyite	Merenskyite	
Micherinite		
Electrum		
Hollingworthite	Hollingworthite	
Irarstite		Irarstite
		Iridarsenite
Stibiopalladinite		
Arsenopalladinite		
Vysotskite	Vysotskite	
Potarite	Potarite	
Niggliite		
PtS.Sn		
PtRhCuNiCoIrS	PtRhCuIrS	
	PtRhCuNiS	
PtCuRhS	PbCuNiS	
PdPb	PdPb	
Polarite		
PdSnSbSAs		
PdPbTe		
PdBiFeTe**		
PdTe	PtCuFeAS	
		Osmium
		Iridium
		Osmiridium
		Iridosmine
		Rh(CuFeS)
		PtPdFe(Rh)
		RhAs

* Notoriously resistant to chemical attack.

** Kotulskite related phase (?) or borovskite (?).

Stumpfl and Tarkian have taken these considerations a step further [44]. Convincing proof of the reactivity of PGE minerals and the mobility of PGEs under surficial regimes was provided by a study of altered Pt-Fe and Os-Ir alloys in very young placers at Sorashigawa, Japan. Iridosmium grains were altered at the surface and along cracks to irarstite of singular purity, leading to the

conclusion that Os is removed in aqueous solution. Platinum grains show various stages of alteration, finally to cooperite. In other studies, Stumpfl observed platinum nuggets rimmed by niggliite and Pt replacing Pd in potarite [45]. These authors suggest that old placer grains in the Witwatersrand exhibit the same kinds of alteration phenomena described by Feather [46] and conclude that "the platinum group elements ... are neither inert nor insoluble".

Two more recent publications [47, 48] reinforce the conclusions drawn above. Platinum minerals, and particularly platinum-iron alloys, appear to persist together with Os - Ir - Ru alloys in placers. Palladium is conspicuously depleted, except where primary phases are included in unweathered centres of PGE mineral grains. This depletion of Pd is in accord with the known chemistry of the element, as further outlined below.

Supergene mobilization is, however, not always a feature of such environments. The concentration of PGE in lateritic duricrusts over pyroxenites of the Ora Banda Sill has been the subject of research in this project. Results (Volume IIA, Chapter 5) indicate that there has been minimal PGE mobility during weathering in this case.

3.4 New Rambler Mine, Wyoming

The New Rambler Mine is developed in a zone of mafic rocks, a somewhat different geological setting to those described above. The geology and mineralization of the deposit have been reviewed [49]. Gold-bearing quartz veins and pockets of high grade copper sulphides have been worked near a major shear. Nearby are gneisses and an irregular granite stock. Primary minerals reported include pyrite, pyrrhotite, cubanite, chalcopyrite, pentlandite, molybdenite, sphalerite, mackinawite, electrum, merenskyite, michenerite, kotulskite, moncheite, sperrylite, platinum and three unidentified Pd-containing phases. In the oxidized ore, a new Pd phase and sperrylite, both showing alteration, were found. Pt-Fe alloy was isolated from a sample of cuprite-malachite ore. No Pd minerals were identified in highly oxidized ore.

The distributions of the several rare elements in the gossan, oxide zone, supergene zone and the primary chalcopyrite ore are shown in Figure 4. Silver is depleted in the oxide zone and concentrated in the zone of secondary enrichment, a common observation in many kinds of oxidized base metal orebodies. Palladium is markedly depleted in the gossan and oxide zone, and Pt is enriched in the oxide zone. The chemical behaviour of Au mirrors that of Pd, and contrasts with that of Rh which is concentrated in the residual material in the upper horizons. Iridium and Ru were detected in only a few gossan samples.

3.5 Lac Sheen and Lac Long-Lac Montauban, Canada

Few data have been collected on groundwater and the dispersion of PGE from oxidizing ores. In a recent report [50], Wood and Vlassopoulos have commented on the preferential reaching of Pd with respect to Pt at two Cu-Ni-Pd-Pt occurrences in Quebec. It was found that at Lac Sheen, Pd was preferentially leached with respect to Au and Pt from soils overlying anomalous mineralization. This led to abnormally high Au and Pt levels in sediments. The observation was made that at least some Pd is transported in true solution, although some may be present in particulate form. Chloride, hydroxide and organic complexes were suggested as being important in the transport of palladium.

The authors concluded that in these environments Pd might profitably be used for regional geochemical surveys. Irrespective of its application in this sense, the findings provide further clear evidence of the differentiation of Pt and Pd by normal supergene processes.

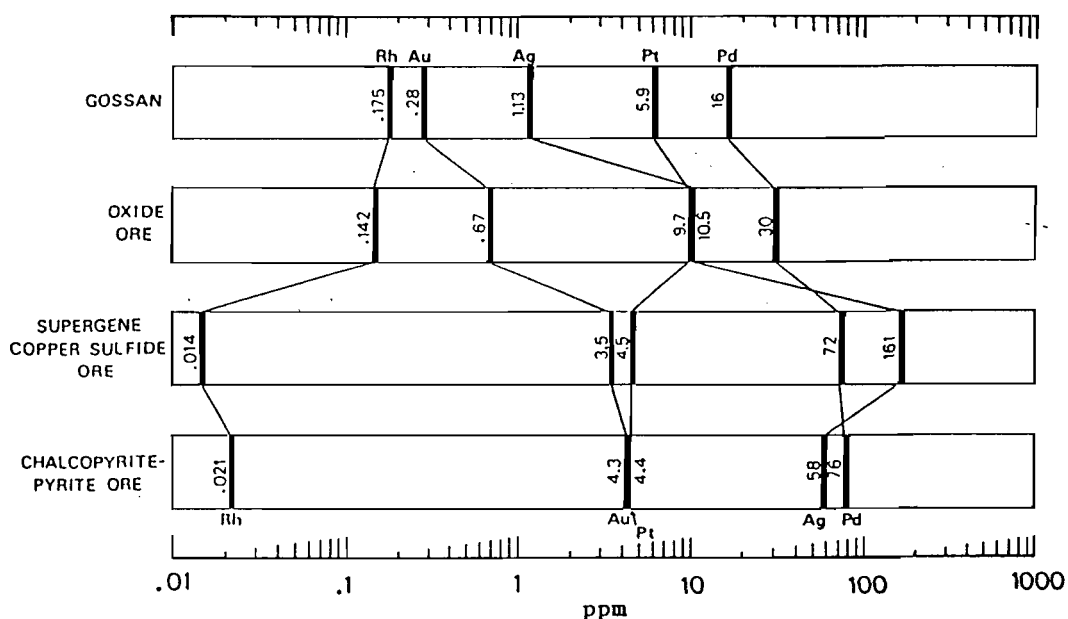


Figure 4. Schematic section of the New Rambler deposit showing the variation of average precious metal contents (in ppm) between horizons in the weathered profile (from Figure 6 [49]).

Other examples may be found in the general references given above to demonstrate that PGE are mobile in the supergene zone at low temperatures. Such geological and geochemical evidence shows that they may be differentiated in different ways, depending upon the chemical conditions prevailing at the time. An understanding of the mobility of the PGE in aqueous solution at ambient temperature is required to evaluate their dispersion in the vicinity of the oxidizing primary ores, or enrichment in placers. The chemical processes that might be responsible for this mobility need to be now considered.

4 POTENTIAL REACTION CHEMISTRY IN THE SECONDARY ENVIRONMENT

4.1 General

It has been pointed out above that an important change in PGE mineralogy on passing from primary to secondary environments is the generation of the appropriate metallic elements and alloys. The reactions of the PGEs in the secondary environment are of primary interest, notwithstanding the fact that certain minerals are inert towards weathering. In crude terms, the reactivity of the PGEs with increasing redox potential is given by their standard electrode potentials [51], as shown in Table 3. At first glance, it is seen that the third-row elements are more noble than their congeners of the second-row. The aqueous chemistry of the PGEs with H_2O and OH^- as ligands is *extremely* limited (especially with respect to Pt), and hence their behaviour in solution will be dominated by the formation of complex ions [1-5].

Only a few naturally-occurring ligands are available for complex formation. Few of those well-known in the laboratory are applicable to the natural environment (*i.e.* organic ligands such as phosphines and arsines).

TABLE 3
Standard electrode potentials (25°C) used in the calculations

Reaction	E°/volt	Ref.*
$\text{Ru}^{2+} + 2\text{e} = \text{Ru}$	+0.455	
$\text{Ru}^{3+} + \text{e} = \text{Ru}^{2+}$	+0.249	
$\text{OsO}_2 + 4\text{H}^+ + 4\text{e} = \text{Os} + 2\text{H}_2\text{O}$	+0.687	
$\text{Ru}(\text{OH})_4 + 4\text{H}^+ + 4\text{e} = \text{Ru} + 4\text{H}_2\text{O}$	+0.68	
$\text{Ru}(\text{OH})_4 + 4\text{e} = \text{Ru} + 4\text{OH}^-$	-0.15	
$\text{Rh}^{3+} + 3\text{e} = \text{Rh}$	+0.758	
$\text{Ir}^{3+} + 2\text{e} = \text{Ir}$	+1.156	
$\text{Pd}^{2+} + 2\text{e} = \text{Pd}$	+0.951	
$\text{Pt}^{2+} + 2\text{e} = \text{Pt}$	+1.188	
$\text{PdCl}^+ + 2\text{e} = \text{Pd} + \text{Cl}^+$	+0.771	see text
$\text{PdCl}_2^0 + 2\text{e} = \text{Pd} + 2\text{Cl}^-$	+0.634	see text
$\text{PdCl}_3^- + 2\text{e} = \text{Pd} + 3\text{Cl}^-$	+0.563	see text
$\text{PdCl}_4^{2-} + 2\text{e} = \text{Pd} + 4\text{Cl}^-$	+0.495	see text
$\text{PtCl}_4^{2-} + 2\text{e} = \text{Pt} + 4\text{Cl}^-$	+0.755	
$\text{PdO} + 2\text{e} = \text{Pd} + \text{H}_2\text{O}$	+0.917	
$\text{Pd}(\text{OH})_2 + 2\text{H}^+ + 2\text{e} = \text{Pd} + 2\text{H}_2\text{O}$	+0.897	
$\text{PdBr}_4^{2-} + 2\text{e} = \text{Pd} + 4\text{Br}^-$	+0.56	
$\text{PdI}_4^{2-} + 2\text{e} = \text{Pd} + 4\text{I}^-$	+0.18	
$\text{PtBr}_4^{2-} + 2\text{e} = \text{Pt} + 4\text{Br}^-$	+0.581	
$\text{PtI}_4^{2-} + 2\text{e} = \text{Pt} + 4\text{I}^-$	+0.40	
$\text{IrCl}_6^{3-} + 3\text{e} = \text{Ir} + 6\text{Cl}^-$	+0.77	
$\text{IrCl}_6^{2-} + \text{e} = \text{IrCl}_6^{3-}$	+0.86	
$\text{RuCl}_5^{2-} + 3\text{e} = \text{Ru} + 5\text{Cl}^-$	+0.601	
$\text{OsCl}_6^{3-} + 3\text{e} = \text{Os} + 6\text{Cl}^-$	+0.71	[9]
$\text{OsCl}_6^{2-} + \text{e} = \text{OsCl}_6^{3-}$	+0.452	
$\text{Rh}(\text{OH})_3 + 3\text{e} = \text{Rh} + 3\text{OH}^-$	0.0	
$\text{IrO}_2 + 4\text{H}^+ + 4\text{e} = \text{Ir} + 2\text{H}_2\text{O}$	+0.926	

* Ref. [51], except where noted.

4.2 Complexes of the Halides

The surface or near-surface transport of Au, the noblest of the elements, and its enrichment in oxide zones has long attracted the attention of geologists and chemists [78]. Much early work was stimulated by geological observations, particularly in the United States [79, 80], and these are summarized in Emmons' excellent review [23]. These observations are complemented by more recent work [81, 82] and the many observations of the enrichment of Au in organic-rich layers of soils around oxidizing auriferous deposits [68, 70, 83]. The behaviour of Au in lateritic environments has been summarized by Gray *et al.* [84].

The importance of the formation of suitable coordination complexes was realized and, for many years, attention was focussed on the formation of the complex anion $[\text{AuCl}_4]^-$ as the mobile species, with MnO_2 being the oxidising agent necessary to bring the gold into solution. Krauskopf [52] has elaborated the above chemistry and recent studies [85] have examined this system in further detail with respect to the growth of gold nuggets at room temperature from aqueous solutions. The half cell potential for the formation of the AuCl_4^- ion is given in Table 4, together with potentials for other species that have been proposed for the transport of Au in oxide zones and related

environments. Krauskopf calculated that significant amounts of Au will dissolve as AuCl_4^- with $[\text{Cl}^-] \geq 0.1 \text{ M}$ at $\text{pH} < 3$, when MnO_2 is the oxidant.

TABLE 4
Electrode potentials for the oxidation of gold in the presence of selected unidentate ligands [67, 89, 90]

	Reaction	$E^0(25^\circ\text{C})/\text{volt}$
$\text{AuCl}_4^- + 3\text{e}$	$= \text{Au} + 4\text{Cl}^-$	+1.00
$\text{AuBr}_4^- + 3\text{e}$	$= \text{Au} + 4\text{Br}^-$	+0.85
$\text{Au}(\text{SCN})_4^- + 3\text{e}$	$= \text{Au} + 4\text{SCN}^-$	+0.64
$\text{AuCl}_2^- + \text{e}$	$= \text{Au} + 2\text{Cl}^-$	+1.15
$\text{AuBr}_2^- + \text{e}$	$= \text{Au} + 2\text{Br}^-$	+0.96
$\text{AuI}_2^- + \text{e}$	$= \text{Au} + 2\text{I}^-$	+0.58
$\text{Au}(\text{SCN})_2^- + \text{e}$	$= \text{Au} + 2\text{SCN}^-$	+0.66
$\text{Au}(\text{CN})_2^- + \text{e}$	$= \text{Au} + 2\text{CN}^-$	-0.48
$\text{Au}(\text{S}_2\text{O}_3)_2^{3-} + \text{e}$	$= \text{Au} + 2\text{S}_2\text{O}_3^{2-}$	+0.15

The possibility that halide complexes of the PGEs control their dispersion in the natural environment has drawn the attention of many workers [9, 27, 34]. Considerable data concerning the complexes has accrued, and some stability constants are listed in critical compilations. In effect, chloride ion is the only halide that needs to be examined; fluoride concentrations are controlled by the low solubility of fluorite, CaF_2 , and although it is easier to oxidize the PGEs in the presence of the heavier halides (Table 3), most groundwaters contain only small concentrations of these ions [52, 53].

Potentials with respect to chloride complexes of Pt(II) and Pd(II) are well known (Table 3). Dubious values have been reported in the past for Pd(II) complexes [51] and reliance is placed here on a recent compilation of critical stability constants [54] for their calculation. Ultimately these depend on a value of $\Delta G^0(\text{Pd}^{2+})$ derived from the electrode potentials (Table 3) and well-established thermodynamic data [55]. Values from the latter compilation are used wherever possible. The significant difference between the following analysis and earlier conclusions concern reaction (1).



For the equilibrium (2),



$\log K = 15.4$ [54], a value somewhat higher than that previously reported. Using this value, together with $\Delta G^0(\text{Pd}^{2+}) = +183.53 \text{ kJ mol}^{-1}$ (from $E^0 = +0.951 \text{ volt}$ [51]), $\Delta G^0(\text{PdCl}_4^{2-})$ is found to be equal to $-429.48 \text{ kJ mol}^{-1}$ and thus ΔG^0 and E^0 values for (1) are $-95.60 \text{ kJ mol}^{-1}$ and $+0.495 \text{ volt}$, respectively.^{1*}

The potential for reaction (3) of $E^0 = +0.755 \text{ V}$ is well established.



¹ Unless stated, all values refer to 25°C (298 K).

It should be noted that stability constant data for $\text{PtCl}^+(\text{aq})$ and $\text{PtCl}_2^0(\text{aq})$ are *not* known with as much accuracy as their Pd(II) counterparts.

To examine these systems in detail, one may pick a chloride ion activity² and calculate the concentration of MCl_4^{2-} at equilibrium at a given potential. Alternatively, one may choose a representative concentration of MCl_4^{2-} and calculate the potential at equilibrium. Potential equations for the Pd(II)- Cl^- system are given in Table 5 and correspond to $E^\circ = +1.188\text{V}$ for the Pt/ Pt^{2+} couple [51] and $\log K = 14.54$ for equation (4).



TABLE 5
Electrode Potentials for the Pd/ PdCl_x^{2-x} System (activity corrections ignored)

$\text{PdCl}_4^{2-} + 2e = \text{Pd} + 4\text{Cl}^-$	
$E_4 = E_4^\circ - 0.02955 \log \{[\text{Cl}^-]^4/[\text{PdCl}_4^{2-}]\}$	
$\text{PdCl}_3^- + 2e = \text{Pd} + 3\text{Cl}^-$	
$E_3 = E_3^\circ - 0.02955 \log \{[\text{Cl}^-]^3/[\text{PdCl}_3^-]\}$	
$\text{PdCl}_2^0 + 2e = \text{Pd} + 2\text{Cl}^-$	
$E_2 = E_2^\circ - 0.02955 \log \{[\text{Cl}^-]^2/[\text{PdCl}_2^0]\}$	
$\text{PdCl}^+ + 2e = \text{Pd} + \text{Cl}^-$	
$E_1 = E_1^\circ - 0.02955 \log \{[\text{Cl}^-]/[\text{PdCl}^+]\}$	
$[\text{Cl}^-] = 1\text{M}$	$E_n^\circ(\text{Pt})$
$E_4 = 0.495 + 0.0296 \log [\text{PdCl}_4^{2-}]$	+0.755
$E_3 = 0.563 + 0.0296 \log [\text{PdCl}_3^-]$	+0.821
$E_2 = 0.634 + 0.0296 \log [\text{PdCl}_2^0]$	+0.907
$E_1 = 0.711 + 0.0296 \log [\text{PdCl}^+]$	+1.025
$[\text{Cl}^-] = 10^{-1}\text{M} (3550 \text{ ppm})$	
$E_4 = 0.613 + 0.0296 \log [\text{PdCl}_4^{2-}]$	+0.873
$E_3 = 0.651 + 0.0296 \log [\text{PdCl}_3^-]$	+0.910
$E_2 = 0.691 + 0.0296 \log [\text{PdCl}_2^0]$	+0.966
$E_1 = 0.801 + 0.0296 \log [\text{PdCl}^+]$	+1.055
$[\text{Cl}^-] = 10^{-2}\text{M} (355 \text{ ppm})$	
$E_4 = 0.731 + 0.0296 \log [\text{PdCl}_4^{2-}]$	+0.991
$E_3 = 0.740 + 0.0296 \log [\text{PdCl}_3^-]$	+0.998
$E_2 = 0.752 + 0.0296 \log [\text{PdCl}_2^0]$	+1.025
$E_1 = 0.830 + 0.0296 \log [\text{PdCl}^+]$	+1.084
$[\text{Cl}^-] = 10^{-3}\text{M} (35.5 \text{ ppm})$	
$E_4 = 0.850 + 0.0296 \log [\text{PdCl}_4^{2-}]$	+1.110
$E_3 = 0.829 + 0.0296 \log [\text{PdCl}_3^-]$	+1.087
$E_2 = 0.811 + 0.0296 \log [\text{PdCl}_2^0]$	+1.084
$E_1 = 0.896 + 0.0296 \log [\text{PdCl}^+]$	+1.114

* Corresponding E° values for the Pt/ PtCl_x^{2-x} system (volt).

² Approximately equal to concentration.

This value of log K differs from that at an ionic strength of 1.0, *i.e.* log K = 14.0 [54]. The reported stability constants for the Pt system have been increased by 0.5 log units to adjust them to zero ionic strength. Examination of Table 5 reveals that at *no* [Cl⁻] or for any chosen [MCl_x^{2-x}] species will Pt be more easily oxidized than Pd. Secondly, at low [Cl⁻], species other than MCl₄²⁻ predominate in aqueous solution, as expected from a consideration of equilibrium constants. Thus at [Cl⁻] = 10⁻³ mol/L (M; corresponding to a weakly saline groundwater), the major Pd species in solution are PdCl₂⁰ and PdCl₃⁻ (with the major Pt species being PtCl₃⁻ and PtCl₂⁰). The question of speciation is well-documented in the literature, but appears to have been mostly overlooked in geochemical work. The potential difference between corresponding Pt and Pd couples is large and provides a mechanism for the separation of these elements.

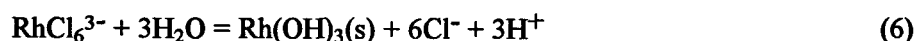
It is instructive to choose [Pt, Pd] concentrations deemed appropriate for mobility in the natural environment and calculate the Eh and pH conditions required. Most workers have picked 10⁻³ ppm, but here we take 10⁻⁹ M (~0.3 ppb) for individual complex chloride species. In groundwaters such as occur in arid environments [56], chloride ion concentrations are about 10⁻¹ M. We calculate that at the 10⁻⁹ M level, Pd will oxidize to PdCl₄²⁻ (predominantly) at E = +0.347 volt and Pt will oxidize to PtCl₄²⁻ at E = +0.607 volt in 10⁻¹ M (=3550 ppm) solutions. Thus at low pH values (<5) where hydrolysis of Pt and Pd does not occur to any significant extent [57], both Pt and Pd may be mobilized as chloro-complexes under oxidizing conditions, if the (relatively high) appropriate potentials are achieved [58, 59].

The geological and geochemical ramification of these calculations is that Pd is mobile over a much wider range of supergene solution conditions than Pt, and a reasonable explanation for the depletion of Pd in placer (alluvial and eluvial) deposits relative to Pt and enrichment of Pd in oxide zones is thus available. Platinum might be mobile when [Cl⁻] is much higher.

The other PGEs also form chloro-complexes. The potentials in Table 3 show that Rh is the least noble of the PGEs. However, Rh forms a *remarkably* insoluble hydroxide, long the bane of synthetic coordination chemists. Earlier workers [60, 61] have given the solubility product of Rh(OH)₃(s) as 4.8 × 10⁻²³ but associated experimental work was bedevilled by complications due to the formation of chloro-complexes. A better estimate is obtained from the potential measurements for equation (5),



given in Table 3, from which ΔG⁰ of Rh(OH)₃(s) is -492.0 kJ mol⁻¹ and K_{SP} = 3.72 × 10⁻³⁹. Then, for equilibrium (6),



ΔG⁰ = -280.3 kJ mol⁻¹ and K = 10^{49.1}. From this, (7) is derived.

$$\log [\text{RhCl}_6^{3-}] = -49.1 + 6 \log [\text{Cl}^-] + 3 \log [\text{H}^+]. \quad (7)$$

Thus, RhCl₆³⁻ is thermodynamically unstable with respect to Rh(OH)₃(s). Rate effects are important (especially in the laboratory) but in geological terms, ample time is available for complete hydrolysis. The conclusion to be drawn is that even though Rh metal may be easily oxidized in aqueous solution containing chloride ion, *it will be quickly and profoundly immobilized by the precipitation of the hydroxide*. This chemical evidence supports the observations of McCallum *et al.* [49], (Figure 4), who found Rh enriched in gossan at the New Rambler mine, while Au, Ag and Pd were remarkably depleted. More data are needed on the distribution of Rh in weathered environments. It is anticipated that the formation of Rh(OH)₃ will dominate the chemistry of Rh during gossan formation, and perhaps generally.

Iridium has a stable oxide IrO_2 [2], but this is not expected to be formed in natural aqueous systems as its range of stability lies above the redox limit of aqueous solutions. IrCl_6^{3-} has an appreciable stability field only at very high chloride activities ($[\text{Cl}^-] = 1\text{M}$, and $[\text{IrCl}_6^{3-}] = 10^{-9}\text{ M}$).

The potentials for forming MCl_6^{3-} for $\text{M} = \text{Ir}$ and Os are about equal, so they might be expected to persist as native elements in the secondary environment. This would explain why Ir and Os , and their alloys, are commonly found in placer deposits [42]. However, chloride complex formation does *not* explain why osmiridium and irodsosmine nuggets are frequently depleted in osmium at their surfaces. The lattice energy of IrAsS *versus* OsAsS might provide some clue, but this is not convincing. It is necessary to look to other complex chemistry for the answer to this phenomenon.

Ruthenium appears to be oxidized comparatively easily in chloride solutions. Data on the chemical behaviour of Ru in the supergene environment are scanty, but the results of McCallum *et al.* [49] tend to support such a suggestion.

4.3 Complex formation with other common inorganic ligands

Possible interactions of PGE ions with other simple naturally-occurring inorganic ligands such as carbonate, silicate and sulphate are limited by the fact that the former are "soft" and the majority of the latter are "hard". Thus, negligible stability attends the interactions. No PGE silicate complexes are known. Carbonato complexes of Pd(II) and Pt(II) are known, but these are stabilized only by exotic (in the environmental sense) phosphine ligands [3].

Of the *thermodynamically stable* ligands in the natural environment, only sulphate appears to be worthy of attention. Some known species are listed in Table 6 [1-5]. As far as Pd(II) and Pt(II) are concerned, the sulphate ion is a weaker ligand than water, and hence complex formation is not favoured. The footnotes to Table 6 indicate that the known compounds are not likely to be stable in, and would have little, if any, relevance to the natural environment. Some stability constant data for Ru sulphate complexes are given in Table 7. The log K values indicate that these complex ions will have only a small effect on Ru mobility.

Iridium is unusual among the PGEs in forming phosphate compounds [2], but these have little relevance to natural systems. Aqueous phosphate species have been reported for Ir(IV) . Evidence for the species $\text{Ir(PO}_4)_3^{5-}$ or $\text{Ir(HPO}_4)_2(\text{PO}_4)_2^{4-}$, $\text{Ir}_2\text{O}_3(\text{H}_2\text{PO}_4)_6^{4-}$, $\text{Ir}_2\text{O(OH)}_4(\text{HPO}_4)_6^{10-}$ and $\text{Ir}_4\text{O}_3(\text{OH})_8(\text{H}_2\text{PO}_4)_{10}^{8-}$ has been advanced [62], but the nature of some of these species is questionable and they are unlikely to occur in the supergene zone.

Two recent reviews by Mountain and Wood [63, 64] have dealt exhaustively with halide complexes of the PGEs. Although the main emphasis of these papers concerns the hydrothermal transport of PGEs, calculations have mostly concerned conditions at 25°C . The authors conclude that chloride complexing would be important only under highly oxidizing, acidic and saline conditions. Nevertheless, the studies do indicate broad agreement with the conclusions reached above with respect to the supergene environment, and thus it seems clear that other mechanisms must be involved for the transport of the PGEs under near-surface conditions.

TABLE 6
Some simple sulphate complexes of the platinum group elements^a

$\text{PdSO}_4(\text{s})^{\text{b}}$
$[\text{M}(\text{SO}_4)(\text{NH}_3)_2(\text{H}_2\text{O})], \text{M} = \text{Pt}, \text{Pd}^{\text{c}}$
$[\text{RuO}_2(\text{SO}_4)_2]^{2- \text{d}}$
$[\text{RuO}_2(\text{SO}_4)_2]^{\text{b}}$
Ill-defined polymeric complexes of Ru(IV/III) [4].
$\text{Rh}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}^{\text{e}, \text{f}}$
$[\text{OIr}_3(\text{SO}_4)_9]^{10- \text{g}}$
$[\text{Ir}(\text{SO}_4)_2(\text{H}_2\text{O})_2]^{-}$
$[\text{Ir}(\text{SO}_4)_2] \cdot n\text{H}_2\text{O}$
$[\text{Ir}(\text{SO}_4)_3]^{3- \text{h}}$

^aComplexes with "exotic" ligands such as phosphines are not included. Some simple salts are added for completeness. ^bVery soluble in water; decomposes. ^cDissociate instantly in water to give free sulphate ions. ^dReacts to give Ru(IV) species in water. ^eProbably polynuclear oxo- or hydroxo-bridged species. ^fComplexes in solution are not particularly stable. ^gFrom boiling sulphuric acid. ^hBy fusion with KHSO_4 of Ir(III) salts.

TABLE 7
Stability constants for some ruthenium sulphate complexes at 298.2 K

Reaction	log K	Ref.
$\text{Ru}^{2+} + \text{SO}_4^{2-} = \text{RuSO}_4^0$	2.72 ^a	[54]
$\text{Ru}^{3+} + \text{SO}_4^{2-} = \text{RuSO}_4^{+}$	2.04 ^b	[54]
$\text{Ru}^{3+} + 2\text{SO}_4^{2-} = \text{Ru}(\text{SO}_4)_2^{-}$	3.57 ^b	[54]
$\text{RuO}^{2+} + \text{HSO}_4^{-} = \text{RuOSO}_4^0 + \text{H}^{+}$	2.24	[69]
$\text{Rh}(\text{NH}_3)_5^{3+} + \text{SO}_4^{2-} = \text{Rh}(\text{NH}_3)_5\text{SO}_4^{+}$	0.0 ^c	[69]

^a20°C. ^bI = 2.0. ^cI = 4.0.

4.4 Complexes with cyanide ion and organic ligands

Cyanide forms very stable complexes with Pd(II) and Pt(II). The elements dissolve in water in the presence of the ligand with the evolution of hydrogen. The best current estimates for stability constants of $\text{Pd}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{CN})_4^{2-}$ respectively are 10^{63} and 10^{80} [65, 66], although the values are somewhat suspect. The availability of CN^{-} ion as a naturally occurring ligand is discussed in an extensive review on the chemistry of gold in the weathering cycle [67]. It was concluded that "gold cyanide offers the most feasible form of soluble gold in soils". About 1000 species of plants produce cyanoglycosides which can hydrolyse to produce cyanide. Certain fungi and invertebrates also produce cyanide. However, the amounts produced are very small and the above conclusion was made prior to the development of an understanding of other feasible chemical processes for the transport of Au (*vide infra*). In any case, should cyanide be important, it would hardly explain why Pt is relatively inert, geochemically speaking, as compared with Pd.

Similar arguments can be applied to most other "simple" naturally occurring organic ligands such as amines and aminoacids, for which the synthetic chemistry with PGEs is well known [65]. The likely concentrations in the weathered zone are just too low in general, and also, most such ligands are quickly metabolized.

PGE complexes, or stabilized colloids, with humic and fulvic acids may be formed [68], as has been suggested for Au by many workers [70], and these may be important with respect to the mobility of the PGEs. Cousins and Kinlock [41] have argued for PGE - organic complex formation by analogy with the work on Au but pointed out that platinoids may be transported by organic materials in a colloidal form [71, 72]. Halide complexes may be protected by absorption by organic material. A recent report on the generation of Pt grains compositionally similar to native material from a silica gel-chloroplatinic acid mixture may be of some application in this respect [73]. However, there would be little reason to invoke organic complexation when comparatively simple inorganic chemistry can explain what little is known of the supergene behaviour of the PGEs. Nevertheless, Wood [74] has recently reported experiments concerning the interaction of Pt^{2+} with natural fulvic acid in an attempt to assess the likelihood of such materials being involved in the transport of Pt in soil pore waters and stream waters. In experiments involving such fulvic acids and synthetic organic analogues, it was found that the possibility of transportation as an organic complex was established, although the formation of colloidal or colloidally protected species was probably important. Further experimental work is required to establish the role of humic and fulvic acid transport of PGE in the natural environment.

4.5 Complexes of lower-valence oxyanions of sulphur

Complex formation with sulphur oxyanions in low oxidation states, particularly sulphite, SO_3^{2-} , and thiosulphate, $\text{S}_2\text{O}_3^{2-}$, which may be formed as intermediates during oxidation of sulphides are potentially important for PGE ion differentiation in the weathering zone. The conversion of sulphide (S^{2-} or S_2^{2-}) to the thermodynamically stable end-product, SO_4^{2-} , involves, respectively, 8 and 14 electron oxidation steps and therefore must proceed *via* intermediate species. Intermediate oxidation products have been shown to be present [75-77] and thiosulphate and sulphite ions play key roles [75]. These ions are present during the oxidation of sulphide minerals over a considerable pH range.

Listova *et al.* [86] advanced the idea that thiosulphate species may be important in the leaching of Au in nature and more recent experimental work [87] has confirmed that such species are likely to be involved in the supergene chemistry of Au. Gold forms the stable thiosulphate complex $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ and the electrode potential for the $\text{Au}/[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ couple is + 0.15 V. Many common oxidants [O_2 , Fe(III), Cu(II)] could effect the dissolution of Au as the thiosulphate complex. It seems probable that this species is the important one for the transport of Au in the oxide zone of base metal sulphide orebodies, and could lead to secondary enrichments.

Garrels and Naeser [88] have calculated that for a total dissolved S concentration of 10^{-1} M at 25°C , the maximum concentration of $\text{S}_2\text{O}_3^{2-}$ achieved in a metastable equilibrium would be of the order of 10^{-6} M (about 0.11 ppm). Taking free $[\text{S}_2\text{O}_3^{2-}]$ to be 10^{-6} , 10^{-7} and 10^{-8} M, the equilibrium concentrations of the $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ ion would be respectively $10^{-1.5}$, $10^{-3.5}$ and $10^{-5.5}$ M, assuming $[\text{Fe}^{2+}] = [\text{Fe}^{3+}]$. These concentrations are quite appreciable and illustrate that this complex anion is capable of transporting Au during weathering. Data concerning the actual concentrations of $\text{S}_2\text{O}_3^{2-}$ in aqueous solutions in oxide ore bodies are limited but some numbers are available for spring waters. Boyle [70] has observed concentrations of up to 5 ppm in neutral and alkaline waters leaching gold deposits. Average levels of about 1 ppm have been reported for a series of Japanese hot springs [91], and a maximum concentration of 37 ppm was found. The occurrence of thiosulphates and polythionates in hot springs has been reviewed [92, 93]. In anoxic marine environments, significant thiosulphate levels are present in pore waters. There is little reason to

doubt that sufficient thiosulphate ion may be present in oxidising sulphide ores for complex formation to play a significant role in gold transport.

4.6 Sulphite and thiosulphate complexes of the platinum group elements

The evidence for the mobility of Au as thiosulphate and possibly sulphite complexes as discussed above leads directly to an examination of the potential role of these ligands in PGE mobility.

The sulphite ion acts as a bidentate in the well-known anionic complex $[\text{Rh}(\text{SO}_3)_3]^{3-}$ [95] but the existence of the normal salt $\text{Rh}_2(\text{SO}_3)_3 \cdot 6\text{H}_2\text{O}$ is doubtful. A mixed sulphate-sulphite species, $[\text{Rh}(\text{SO}_3)_2(\text{SO}_4)]^{4-}$ has been reported [96, 97]. Quantitative calculations of the possible role of these complexes in weathering are precluded by a lack of stability constants.

Mixed complexes containing thiosulphate or sulphite and ammonia or amines have been reported for Ru, Rh, Pt and Pd [98-105]. Such species are not relevant to the natural environment but they do provide a guide to the coordination chemistry of the elements involved.

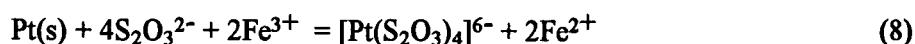
Simple sulphite complexes of Pt and Pd include $[\text{Pd}(\text{SO}_3)_4]^{6-}$, $[\text{Pt}(\text{SO}_3)_4]^{6-}$, $[\text{Pt}(\text{SO}_3)_2]^{2-}$, $[\text{Pt}(\text{SO}_3)_2\text{Cl}_2]^{4-}$, $[\text{Pd}(\text{SO}_3)(\text{H}_2\text{O})_3]$ and $[\text{Pd}(\text{SO}_3)_2(\text{H}_2\text{O})_2\text{O}]^{2-}$ [106]. Corresponding thiosulphate complexes exist, some known from the earliest work [107, 108], and are supposed to include such species as $[\text{Pt}(\text{S}_2\text{O}_3)\text{Cl}_2]^{2-}$, *cis*- and *trans*- $[\text{Pt}(\text{S}_2\text{O}_3)_2]^{2-}$ (bi- and unidentate behaviour being well-established [109]), $[\text{Pt}(\text{S}_2\text{O}_3)_3]^{4-}$, $[\text{Pt}(\text{S}_2\text{O}_3)_4]^{6-}$, and its Pd(II) congener, and $[\text{Pd}(\text{S}_2\text{O}_3)_2]^{2-}$.

Measurements of the standard redox potentials for reactions involving these species [66], shown in Table 8, indicate that a number of geochemically common oxidants, besides O_2 , would dissolve Pt and Pd in the presence of sulphite or thiosulphate.

TABLE 8
Electrode potentials for some Pd(II) and Pt(II) complexes of sulphite and thiosulphate

Reaction	E°/volt^*
$\text{Pd}(\text{SO}_3)_4^{6-} + 2e = \text{Pd} + 4\text{SO}_3^{2-}$	+0.058
$\text{Pd}(\text{S}_2\text{O}_3)_4^{6-} + 2e = \text{Pd} + 4\text{S}_2\text{O}_3^{2-}$	-0.116
$\text{Pt}(\text{S}_2\text{O}_3)_4^{6-} + 2e = \text{Pt} + 4\text{SO}_3^{2-}$	+0.001
$\text{Pt}(\text{S}_2\text{O}_3)_4^{6-} + 2e = \text{Pt} + 4\text{S}_2\text{O}_3^{2-}$	-0.170

To illustrate this fact (on the basis of this reported data, taking E° for the Fe(III)/Fe(II) couple as +0.77 volt at 298.2K) E° and log K for the equilibrium (8)



are calculated to be +0.94 volt and 31.8, respectively. Assuming $[\text{Fe}^{2+}] = [\text{Fe}^{3+}]$ for simplification, the amount of Pt dissolved as $[\text{Pt}(\text{S}_2\text{O}_3)_4]^{6-}$ at equilibrium in the presence of 10^{-8} M free thiosulphate is 0.63 M. Comparable concentrations may be calculated for $[\text{Pd}(\text{S}_2\text{O}_3)_4]^{6-}$, and for $[\text{Pt}(\text{SO}_3)_4]^{6-}$ and $[\text{Pd}(\text{SO}_3)_4]^{6-}$. Despite the assumptions made in the above calculations (activities of anion and iron species, supply of sufficient thiosulphate and the attainment of equilibrium), it seems evident that these sulphur oxyanions could play an important role in the mobilization of Pt and Pd in oxidizing PGE-rich sulphide ores. Similar chemistry may also apply to some other PGEs. This possibility appears to have been largely overlooked in the geochemical literature. Formation of such

complexes could explain some of the enigmatic enrichment patterns reported for weathered environments.

Thiosulphate complexes of the other PGEs may also prove to be important in geochemical systems. Little data are available in the literature, but there is a recent report [110] of a simple Os complex $[\text{OsO}_2(\text{S}_2\text{O}_3)_2]^{2-}$. The coordination geometry of the Os(VI) centre is tetrahedral, as expected, with the two oxo ligands and two sulphur atoms of unidentate thiosulphate ions completing the coordination sphere.

As far as applications to real geochemical systems is concerned, the potential of thiosulphate as a ligand has been recognized previously [63, 111] but no new experimental data were given. Attention has been focussed on Pt and Pd because of their far greater abundances in natural materials.

4.7 Complexes of other soft ligands

Few other "soft" ligands can be envisaged as occurring in the natural environment and thus as being candidates for the complexing and transport of the PGE in weathering regimes. The most probable are the Se and Te analogues of lower valency sulphur oxyanions, since these two elements do occur in a number of PGE minerals. However, there is virtually no information concerning their application to geochemical systems available in the literature.

A further species containing As remains for consideration. Like S, As exists in primary minerals in lower oxidation states (arsenides, sulpharsenides and other sulphosalts) which are not thermodynamically stable when exposed to a weathering environment, and oxidation ultimately leads to the As(V) species AsO_4^{3-} , or its conjugate acid anions. An important intermediate in the oxidation sequence involves As(III) in one of the forms of arsenious acid, $\text{As}(\text{OH})_3^0$. Arsenites, polyarsenites and hydrogen arsenites are certainly formed in oxide zones. Indeed, some nineteen secondary As(III) minerals are reported from such environments [112].

Arsenious acid exists in a pyramidal form and the soft arsenic donor is thus available for coordination to metal ions. This possibility has been completely overlooked by geochemists in the past and it may be that arsenious acid does form very stable complexes with soft metals. This possibility, however, remains to be explored.

5 EXPERIMENTAL INVESTIGATIONS

As part of AMIRA Project P252, the gathering of information concerning the possible transport of PGEs in the supergene zone prompted us to undertake a number of experimental studies to ascertain whether it was likely that some hitherto unsuspected complexes might be important. Part of the reason for this is simply that while thermodynamic predications may be sound, kinetic constraints may make the formation of certain chemically attractive complexes meaningless in a geological sense. In other cases, no information was available whatsoever. Experimental investigations have centred on:

- (i) The formation of complexes of thiosulphate, sulphite and polythionates of Pt and Pd;
- (ii) Interaction of Pt and Pd with arsenious acid in aqueous solutions.

The decision was made to concentrate on Pt and Pd in view of elemental abundances of the PGEs. The results of those experimental studies are described in Chapter 3 and lead to the inevitable conclusion that thiosulphate and arsenite complexes of the platinum group elements may have a profound effect on their mobilization in the weathering environment. These studies in turn provide a new insight into the geochemical behaviour of the PGEs.

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CHAPTER 3 EXPERIMENTS CONCERNING NEW DISPERSION MECHANISMS FOR PGE IN WEATHERING SULPHIDES

P.A. Williams

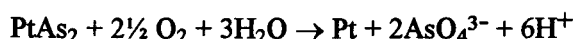
ABSTRACT

Patterns of dispersion in placers and in the profiles above sulphide deposits demonstrate that platinum group elements are mobile during weathering. Given the limited role of chloride complexes of these elements, except under conditions of extremely high Eh, low pH, and high salinity, it was deemed desirable to investigate other potential ligands. Leaching experiments have illustrated the effectiveness of thiosulphate and arsenite solutions in dissolving certain platinum group elements (PGE). Maximum concentrations were 111 ppm Pd in 75 days, 20 ppm Pt after 46 days, and 200 ppm Ir after 28 days. Dissolution rates increase with decreasing concentrations of $S_2O_3^{2-}$ and are independent of pH in the range from 6 to 9. Arsenious acid is effective in mobilizing Pd at lower pH values.

Synthetic and NMR studies have proven useful in elucidating the true nature of species formed in solutions containing thiosulphate. The species $Pt(S_2O_3)_4^{6-}$ formed in synthetic experiments, is unstable with respect to *S* - bridged oligomeric species, $(S_2O_3)_2Pt[(-S_2O_3)_2Pt]_n(S_2O_3)_2^{x-}$, in aqueous solution.

1 INTRODUCTION

In Chapter 2 (this volume), it was demonstrated that thermodynamic predictions could be made that indicated the course of breakdown of primary PGE minerals under oxidizing conditions. In essence, it can be predicted that during the first phases of oxidation, sulphides, sulphosalts and the like are oxidized to give the free metallic elements. Although the metals themselves are formally reduced, the overall reaction is an oxidation in terms of anion formation. For example, the initial oxidation of sperrylite, $PtAs_2$, to give native platinum can be described by the following equation:



Thus, it was simply reasoned that the limiting measure for testing the effectiveness of a given ligand for dispersing PGE from oxidizing sulphide ores containing PGE minerals would concern the ability of the ligand to dissolve the metals in aqueous solution in the presence of O_2 as oxidizing agent. In particular, the dissolution of Pt and Pd metal blacks (finely divided metals to maximize surface area for reaction) in aqueous solutions of thiosulphate and sulphite (as key intermediates in the oxidation of sulphides) have been investigated. Additional experiments involving arsenious acid, $As(OH)_3$, as an intermediate in the oxidation of arsenide to arsenate, were also carried out.

In this connection, it is worth noting here a recent observation (P.A. Williams, unpublished results) of the oxidation of sperrylite to native platinum in oxidized ore samples from deposits near Broken Hill, NSW.

2 EXPERIMENTAL

2.1 Metal blacks

Two methods were used to prepare the finely-divided metal blacks used in the dissolution experiments. The first method [1] was as follows: 2.0 grams of K_2PdCl_4 (or K_2PtCl_4) and 25 cm³ of water were stirred in a cooled 100 cm³ Ehrlenmayer flask until the salt dissolved and the solution reached approximately 10°C. To the solution was added 7.5 g (7 cm³) of 37% formaldehyde in water. To this solution was added, drop-wise over 20 minutes, 15.3 g of 50% KOH. The solution temperature was kept at approximately 0°C during the addition. The resulting metal blacks were exhaustively washed by decantation with H₂O, and stored under H₂O. The second method, which was used to precipitate Rh, Ir and Ru, involves the reduction of a metal salt by reaction with sodium borohydride [2]. The rate of reaction is more difficult to control than is the case with the first method and is quite variable for the different PGE. The procedure was as follows: one gram of sodium borohydride was dissolved with stirring in 45 cm³ of water in a 125 cm³ Ehrlenmayer flask. Temperature was maintained at 25°C. Into this solution was added, drop-wise, 5 cm³ of a 0.1 mol/L (M) solution of the appropriate salt. The metal blacks were washed and stored as outlined above.

2.2 Dissolution experiments

The metal sample was added to 500 cm³ Ehrlenmayer flasks containing aqueous sodium thiosulphate solutions of varying concentrations. Most experiments were buffered using "hard" ligands to minimise their complexing with the PGE. Carbonate buffer was used in the pH range 8 to 9, and phosphate buffer in the pH range 6 to 8. Thiosulphate-free solutions were investigated to monitor the effect of the phosphate buffer on solubility. Metal concentrations brought into solution for these blanks were below detection limits (< 0.2 ppm). For some experiments, Cl⁻ was added (as dissolved NaCl) to determine whether it enhanced solubility. The flasks were covered with an oxygen-permeable membrane and submersed in a water bath at 25°C.

From time to time, 10 cm³ aliquots were removed from the reaction mixtures and their pH measured to verify that the buffer was still effective. The pH increased gradually through the experiments after the first few weeks. However, for the measurements listed in Table 1, the final pH was usually within half a unit of the initial pH. The aliquots were filtered using Whatman GF/F fibreglass filter paper prior to analysis. Pure metals were determined using ICP-AES techniques.

With atomic absorption, there are significant matrix effects involving thiosulphate; its presence (0.1 M $S_2O_3^{2-}$) results in 10 to 20 percent higher absorbance values than standards prepared in chloride. ICP-AES techniques are preferable, although cross-checking and standardization would permit the use of AAS methods. Accuracy is estimated to be 10 percent.

For leaching experiments involving arsenious acid, the metal blacks were added to solutions that were 0.05 M in sodium arsenite, NaAsO₂. The pH was adjusted by additions of NaOH or HCl over the range of pH from 2 to 9. Samples were removed from the mixtures from time to time, filtered and analysed as above.

Unbuffered leach runs involving the addition of metal blacks to aqueous solutions of sodium sulphite (0.1 M) or potassium trithionate (0.1 M) were treated similarly.

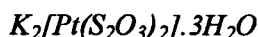
2.3 Synthetic and spectroscopic experiments

In order to understand the nature of species in aqueous solution, generated by the leaching/dissolution experiments, a number of likely products were synthesised. Spectroscopic

measurements, principally using NMR (nuclear magnetic resonance) spectroscopy, have helped to elucidate the main complexes formed.

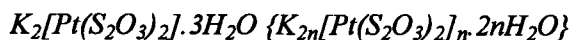


K_2PtCl_4 (0.5 g, 1.205 mmol) dissolved in H_2O (15 cm³) was added to a solution of $Na_2S_2O_3 \cdot 5H_2O$ (2.99 g, 12.05 mmol). The mixture was left to stand for 18 hours. To the resulting pale, lemon yellow solution was added $[Co(NH_3)_6](NO_3)_3$ (1.735 g, 5.00 mmol) dissolved in H_2O (250 cm³), dropwise. A dense, lemon yellow precipitate formed immediately. The product was collected at the pump, washed copiously with H_2O , then with ethanol and diethyl ether, and air dried. Yield: 0.86 g (69%). Analysis: calculated for $H_{40}N_{12}S_8O_{14}Co_2Pt$: H, 4.0; N, 16.8%. Found: H, 3.8; N, 16.4%. An infra-red spectrum confirmed the presence of water of crystallization.



K_2PtCl_4 (0.1 g, 0.24 mmol) and $Na_2S_2O_3 \cdot 5H_2O$ (0.12 g, 0.48 mmol) were dissolved in H_2O (3 cm³) and the mixture left to react at room temperature. The solution became cloudy after some 7 hours and after 7.5 hours a bright, lemon yellow precipitate had formed. The product was collected at the pump on a glass sinter, washed with a minimum of cold water, and air dried. Yield: 26.5%. The complex salt is somewhat soluble in H_2O , and very soluble in aqueous solutions of thiosulphate. Longer reaction times result in the formation of a second product (*vide infra*). Analysis: calculated for $H_6O_9S_4K_2Pt$: Pt, 35.4; S, 23.3%. Found: Pt, 35.3; S, 23.6%. This complex corresponds to the soluble "cis" isomer isolated by Ryabchikov [9, 10], but differs in the number of molecules of water of crystallization.

If the solid is left in contact with the solution for some time it turns black. This product has not, as yet, been identified. This decomposition process occurs in all reactions carried out with platinum and thiosulphate.



This compound was prepared in exactly the same way as that reported immediately above, except that the reaction time was prolonged. The initially precipitated, lemon yellow complex slowly turns a yellow ochre colour and more material is precipitated. At intermediate reaction times, mixtures of the two isomeric salts can be isolated, with the less soluble salt being ultimately obtained by repeated washing of the mixtures by water. The yellow ochre salt also corresponds to material reported by Ryabchikov [9, 10], but again differing in the degree of hydration. It is virtually insoluble in water or aqueous solutions of thiosulphate.

The product was collected at the pump on a glass sinter, washed with a minimum of cold water, and air dried. Yield: 81 mg (63%; mechanical losses are significant). Analysis: calculated for $H_6O_9S_4K_2Pt$: Pt, 35.4; S, 23.3%. Found: Pt, 35.3; S, 24.0%.



K_2PdCl_4 (0.214 g, 0.66 mmol) dissolved in H_2O (2 cm³) and $Na_2S_2O_3 \cdot 5H_2O$ (0.325 g, 1.31 mmol) dissolved in H_2O (2 cm³) were cooled to 0°C in an ice bath. The solutions were rapidly mixed, whereupon an orange precipitate quickly formed. The reaction mixture was allowed to stand at 0°C for two hours. The solid was collected at the pump, washed with ice water, sucked as dry as possible, then finally dried *in vacuo* over silica gel at room temperature. Yield: 0.27 g (95%). Analysis: calculated for $H_2O_7S_4K_2Pd$: S, 30.7; Pd, 24.9%. Found: S, 30.0, Pd, 24.8%.

If the solid is left in contact with the solution for some time, it turns black. The final black product has not, as yet, been identified. This decomposition process occurs in all reactions carried out with palladium and thiosulphate.

2.4 Instrumentation and analyses

Sulphur was analysed gravimetrically as BaSO_4 . Most of the complexes are extremely difficult to bring into solution prior to analysis. An effective dissolution method involves the reaction of complexes with 50/50 (v/v) 100 vol. H_2O_2 / 9 M aqueous NH_3 . The reaction mixture is heated on a steam bath until the excess ammonia is expelled, and after cooling, the pH is adjusted with dilute HCl to 6.3-6.6. It is important that this pH is maintained, because if the solution is too alkaline, hydroxy compounds will precipitate; if it is too acidic, sulphur is not completely precipitated. The reaction mixture is further warmed on the water bath and an excess of BaCl_2 added. Precipitated BaSO_4 is digested overnight, to give a denser, more filterable compound and the solid is collected at the pump on a pre-weighed glass sinter (which has been kept under vacuum), washed with H_2O , and dried to constant weight at 100°C ; cooling is effected *in vacuo* over silica gel to constant weight, before weighing. The same decomposition technique was used for samples analysed by ICP.

Carbon, H and N analyses were performed by Mrs A. Dams of the School of Chemistry and Applied Chemistry, UWCC. Pt and Pd analyses were carried out using the ICP method.

Infra-red spectra were recorded using a Perkin Elmer 783 spectrophotometer. During synthetic procedures, pH was monitored using a Radiometer PHM85 instrument fitted with a Radiometer combination electrode. The ^{195}Pt NMR spectra were recorded at 21°C using a Bruker WM 360 spectrometer operating at 77.29 MHz and a Jeol FX90 instrument operating at 19.21 MHz and 27°C , employing K_2PtCl_4 as an internal standard (d 0 ppm). AAS measurements were carried out on a Varian AA-275 spectrometer.

3 RESULTS AND DISCUSSION

3.1 Thiosulphate dissolution experiments: Pt and Pd

The results of the dissolution experiments are reported in Table 1 and Figures 1-3. Table 1 covers $\text{Pd/S}_2\text{O}_3^{2-}$ runs alone. Other experiments are discussed individually. The most significant results concerned the high concentrations of the PGE, especially Pd, that were achieved. Maximum solubilities observed were: 111 ppm after 75 days for Pd; 23 ppm after 46 days for Pt (Figure. 1). The difference in dissolution rates can be attributed at least in part to the slowness of reactions of Pt(II) compared to those of Pd(II) , an effect which has been documented by numerous authors [3].

The capacity of the solutions to continue to dissolve Pd diminished with time, and dissolved concentrations eventually reached a plateau. Initially, the solutions were a pure lemon yellow colour, but became brown with the approach to the plateau and finally turned opaque. In some aliquots, brown material settled out, leaving a clear solution behind. It appears that the diminished capacity to dissolve Pd is associated with decomposition of the Pd thiosulphate complex. The rate of decomposition increased for both decreasing pH and decreasing concentration of thiosulphate. Both these factors are known to have the same effect on the rate of decomposition of free thiosulphate [4,5].

Aliquots removed from the reaction flasks containing Pd retained their lemon yellow colour much longer, although this phenomenon is also pH dependent. After 8 months of storage in plastic-stoppered, glass specimen containers, the aliquots from Experiment 3 (pH = 10) still retained their yellow colour, whereas those from Experiment 6 (pH = 8.5) turned brown and opaque. It is suggested that decomposition rates are catalysed by both the metal black and decomposition products in the reaction mixtures, the latter being important for free thiosulphate, as noted above.

TABLE 1
Pd concentration (ppm) for dissolution experiments

DAYS ELAPSED	EXP 3	EXP 6	EXP 7	EXP 8	EXP 11	EXP 12	EXP 13	EXP 15	EXP 18	EXP 29
1			2	4	10	6	6	0	14	20
2			5	9	0	0	0	12	25	
3					19	22	17	16		
4	22	36			22	26	22	21	20	30
6					27	31	26	27	25	
8			23	25	32	38	33			35
14	43	70	29	28	33	46	44	36	32	
17		73			0		0	0		
20	46	76	32	32	0		54	50		
23					32		56	53	41	
26	54	81	35	37						
31			37	42						
32	62	97								
37	67	99								
40			41	49						
46	69	102							56	
60			42	57				75		
66	84	106								
75	84	111								
[S ₂ O ₃ ²⁻]	0.1	0.1	0.1	0.1	0.05	0.05	0.05	0.05	0.01	0.001
LOT	1	1	4	4	4	4	4	4	4	4
METAL*										
pH	10	8.5	8.2	9.0	5.9	6.9	8.5	8.7	8.9	8.9

*Particular batch of metal black.

The experiments demonstrate that the initial rates of dissolution (before onset of the decomposition of the complex) are essentially independent of pH in the range 6 to 9.

1. The dissolution rates for experiments carried out in 0.1 M S₂O₃²⁻ solutions are shown in Figure 1. Experiments 7 and 8 use the same lot of metal and the same type of buffer, and differ only in pH. They have quite similar dissolution rates for the first 30 days. Experiments 3 and 6 differ from the previous two in the lot of metal used and show higher rates of dissolution. The solution at pH 10, which was self-buffered, shows a smaller capacity for dissolution than the solution at pH 8.5. The dissolution course for Pt in 0.01 M S₂O₃²⁻ is included here for comparison. Platinum dissolves more slowly than Pd.
2. The dissolution rates for solutions containing 0.01 M S₂O₃²⁻ at various pH values are shown in Figure 2. All were run with the same buffer and the same lot of metal, with pH ranging from 6 to 8.5. Similar dissolution rates are observed for the first 10 days. The low pH solution concentrations then levels off to a plateau quite rapidly, followed by the solution at pH 7. The pH 8.5 solutions continued to dissolve metal until the experiments were discontinued. Experiment 15 is identical to Experiment 13 except that, in addition to buffer and thiosulphate,

0.01 M Cl^- was added. It demonstrates that the solubility of Pd is not enhanced in the presence of Cl^- under these conditions.

The capacity of the solutions at pH 6 to dissolve metal is of particular interest. The decomposition rate of thiosulphate increases dramatically with decreasing pH. However, under our experimental conditions, this critical pH is somewhat less than 6.

The effects of varying the concentration of thiosulphate on dissolution rates are illustrated in Figure 3. There is a marked tendency for the dissolution rate to increase with decreasing molality. The concentration of dissolved Pd after 24 hours is 4 ppm for 0.1 M $\text{S}_2\text{O}_3^{2-}$, 6 ppm for 0.05 M, 14 ppm for 0.01 M, and 20 ppm for 0.001 M. Such behaviour is expected if the ligand forms surface bonds with the metal, thus shielding it from oxidation. Figure 3 also demonstrates the effect of thiosulphate concentrations on the decomposition rate of the complex, the experiment with the lowest concentration (No. 29) reaching a plateau after only 6 to 8 days.

3.2 Thiosulphate dissolution experiments: Other PGEs

Preliminary investigations of the dissolution of Ru, Rh and Ir in aqueous thiosulphate solutions were carried out. Because these elements exist predominantly in oxidation state(III) in supergene environments, they prefer octahedral coordination. Consequently, mixed $\text{S}_2\text{O}_3^{2-}$ and Cl^- ligand complexes may be more important than for Pt(II) and Pd(II), which prefer square planer coordination. In order to explore this possibility, the metal blacks were reacted with both 0.01 M $\text{S}_2\text{O}_3^{2-}$ and mixed 0.01 M $\text{S}_2\text{O}_3^{2-}$ and 0.01 M Cl^- solutions.

All three elements were detectable in solution by ICP after some time. Only one aliquot from each experiment, collected at 28 days, was analysed. The fine-grained Ru gave approximately 1 to 2 ppm in thiosulphate alone; Ru in the solution containing both thiosulphate and chloride was twice as concentrated. The coarser-grained Rh black yielded approximately 1 ppm in solution for the chloride-free aliquot, and approximately 1.5 ppm in the mixed ligand solution. With Ir, a pale yellow solution was obtained with an Ir concentration of 200 ppm. These experiments thus demonstrate there to be a true potential for thiosulphate and mixed thiosulphate-chloride complexing of all PGE in natural systems.

3.3 Sulphite and trithionate dissolution experiments

Leaching experiments with sulphite and trithionate gave rather quite different results, in that no Pt or Pd could be detected over a period of weeks in solutions above the metal blacks. These results are of interest in the two respects.

Firstly, it is known that sulphite complexes of Pt and Pd have stabilities that are comparable to those with thiosulphate [3]. The fact that neither metal was dissolved under comparable conditions in the presence of sulphite indicates that kinetic factors in this system are such that any reactions are very slow. Indeed, this provides an excellent example of kinetic *versus* thermodynamic stability. *Secondly*, complexes of Pt and Pd with sulphite are indeed well-known and for Pt(II) the tetrakis sulphito complex, $\text{Pt}(\text{SO}_3)_4^{6-}$, is more stable than the corresponding thiosulphate complex. This has been confirmed in separate experiments in which sodium sulphite was added to solutions of the tetrakis thiosulphato complex of Pt(II). In this complex, the thiosulphate ligands are labile and the sodium salt of the corresponding Pt sulphite complex is comparatively insoluble in aqueous solution. After a short time, the yellow thiosulphate complex reacts to give a white precipitate of the well-known species $\text{Na}_6[\text{Pd}(\text{SO}_3)_4] \cdot 1.5 \text{H}_2\text{O}$, which was isolated and identified by comparison with an authentic sample synthesised separately [6, 7].

In addition, indirect mineralogical evidence is available for the existence of polythionates. Thus, $\text{Hg}_3\text{S}_2\text{Cl}_2$, corderoite (and its congeners), is known to be formed by the reaction of the trithionate ion with HgCl_2 . Such a reaction would explain the formation of these minerals in the oxidized zones of a Hg of mercury-bearing sulphide ores. It is also likely that perrouditite, $\text{Hg}_5\text{Ag}_4\text{S}_5(\text{Cl, I, Br})_4$, could be formed by a similar mechanism. Furthermore, Pt(II) and Pd(II) form stable complexes with polythionates, as judged simply by observations of the reaction mixtures when $\text{S}_3\text{O}_6^{2-}$ or $\text{S}_4\text{O}_6^{2-}$ is added to aqueous solutions of MCl_4^{2-} ($\text{M}=\text{Pt, Pd}$).

It may be the case that complexes of these ligands do play a role in transporting Pt and Pd in the natural environment. However, this prediction is made on the basis of equilibrium calculations alone. It appears that these compounds are present when sulphides oxidize at appropriate pH values [8]. However, the leaching experiments indicate that, because of kinetic reasons, the contribution that sulphite (and polythionates) could make to the mobilization of PGEs in oxidizing sulphides would be negligible in comparison with that concerning the thiosulphate ion alone.

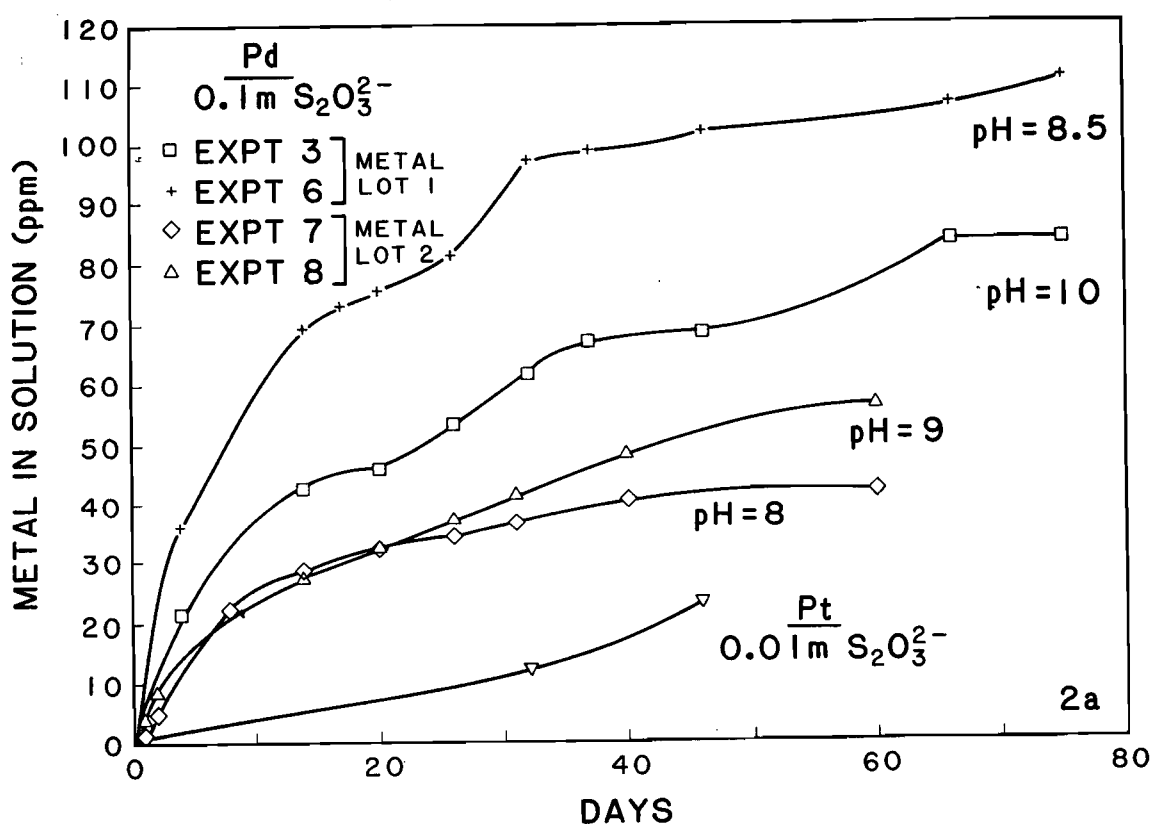


Figure 1. Course of dissolution of Pd black and Pt black in aqueous sodium thiosulphate solutions at 25°C with varying pH. Here, concentrations (m) are molal (mol kg^{-1}). For the runs, however, this is almost identical to the molar (M) scale (same for Figures 2 and 3).

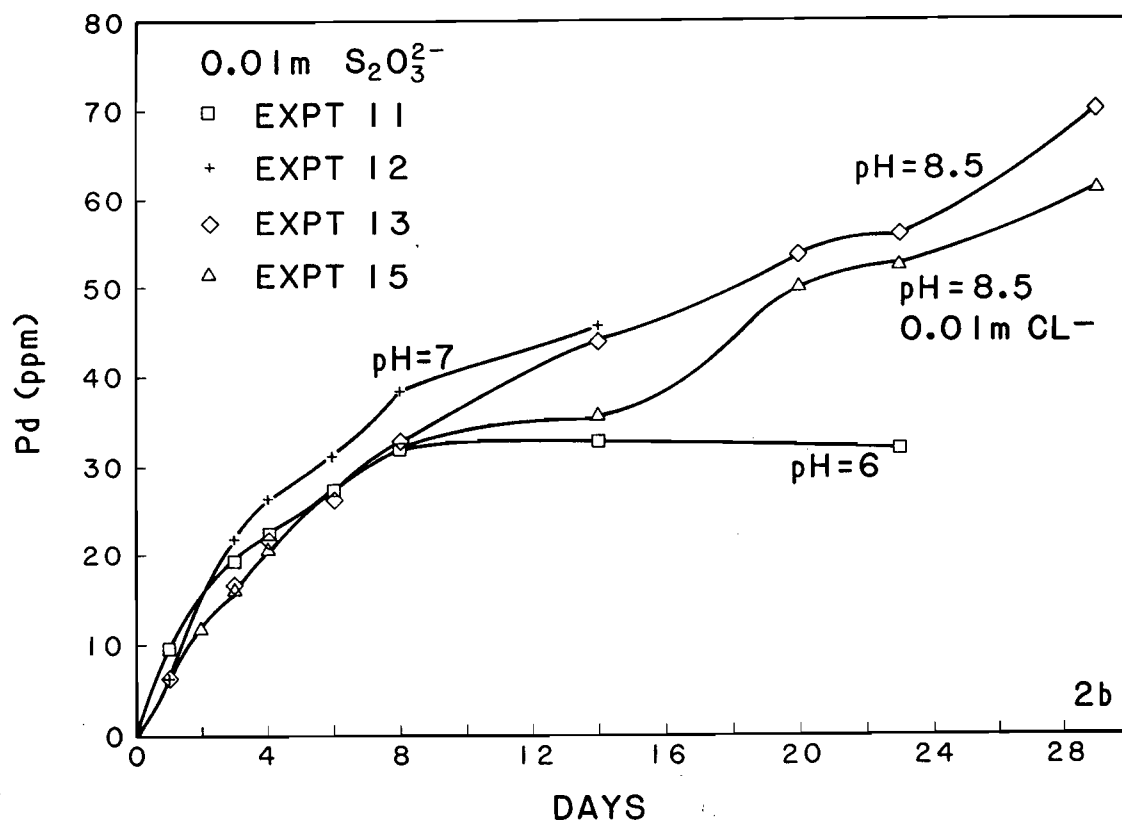


Figure 2. Course of dissolution of Pd black in aqueous $S_2O_3^{2-}$ (0.01M) at 25°C and with varying pH and chloride additions.

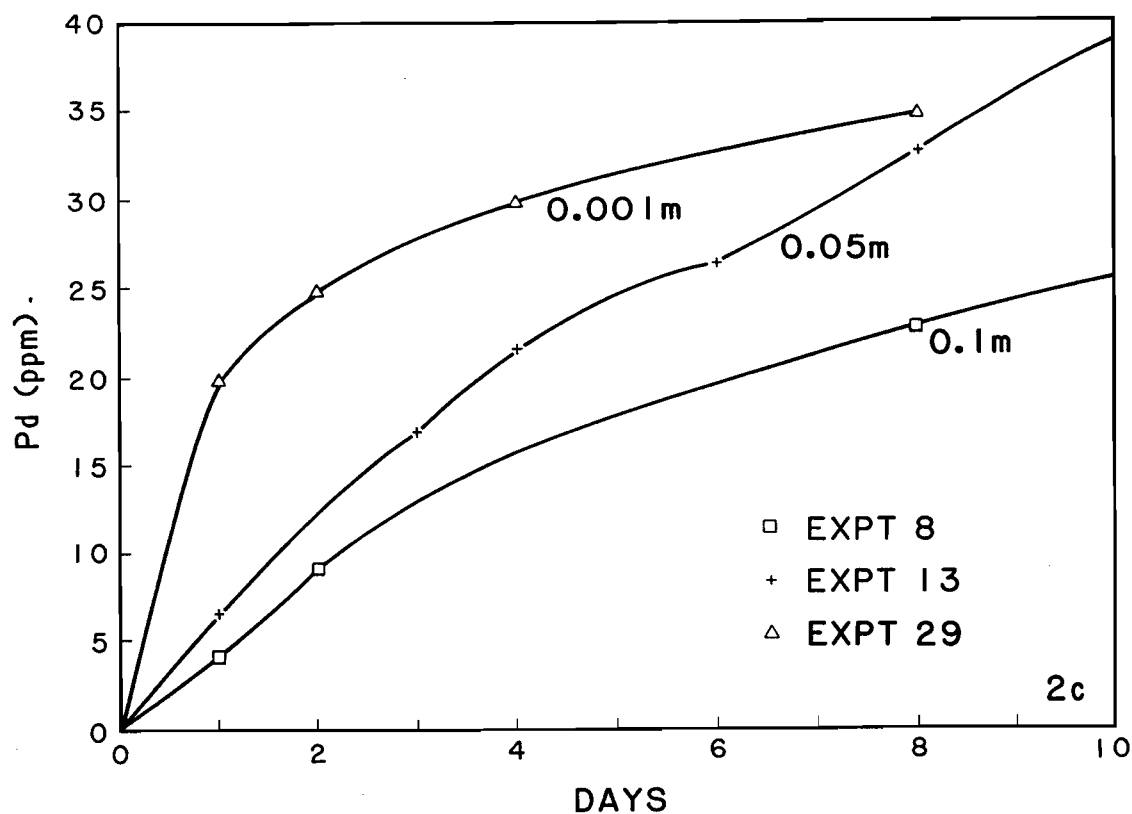


Figure 3. Dissolution of Pd black with varying $S_2O_3^{2-}$ concentrations at pH about 8.5.

3.4 Dissolutions by arsenious acid

Because of the instability of thiosulphate in acid solutions, it was worth examining the chemistry of arsenious acid towards Pt and Pd under comparable leach conditions. The reason for this is related to the first "dissociation" of arsenious acid, in that it does not involve, truly, the loss of a proton. Rather, the reaction shown in (1) takes place as pH is increased.



Because the first conjugate base of arsenious acid is the tetrahedral anion containing four hydroxide groups, the acid loses its coordinating abilities as the pH rises; the addition of the fourth OH⁻ group to the arsenic centre prohibits its coordination. Thus, if arsenious acid were to play a role in coordinating Pt and Pd in oxidizing sulphide ores containing arsenic, such reactions would have to take place at pH values less than about 6, because of the pK_a of the acid.

In the leach experiments, aliquots were taken from solutions of varying pH after two weeks and analysed for Pt and Pd. Negligible Pt was found to be dissolved in any of the experiments, but appreciable amounts of Pd were brought into solution. The results obtained at different pH values are given in Table 2.

Because Pd metal will dissolve in concentrated hydrochloric acid alone, blank experiments were carried out with Pd and acid in the absence of any arsenic species. Results for these runs are also included in Table 2 (for higher pH values phosphate buffers were used). Subtraction of the appropriate blanks from the results obtained for leach runs using arsenious acid show that the As(III) species is effective in leaching Pd over a range of pH values less than seven.

Again, kinetic factors are important in this chemistry. Addition of arsenious acid to solutions of PtCl₄²⁻ and PdCl₄²⁻ gives pale yellow solutions of complex species in which the arsenic centre must be bonded to the transition metal ion. No mention appears to have been made of such complexes in the literature, and no attempt has been made to characterize the species present in

TABLE 2
Dissolution of Pd in aqueous As(III) solutions (0.05 M)
at 25°C over 2 weeks at various pH values

pH	total Pd(ppm)	blank Pd (ppm)*
2	90	20
3	174	3
4	16	<1
5	5	<1
6	6	<1
7	7	<1
8	5	<1
9	5	<1

*Prepared in HCl/NaCl or phosphate buffers. The blank was free of arsenious acid.

solution further. It is pointed out that both Pt and Pd form complexes, in contrast to their behaviour in the preliminary dissolution experiments. It seems inescapable that given the appropriate

conditions (such as in weathering sulphides containing As), arsenic-bonded complexes may be formed in the natural environment and that these may play a role in the mobilization of certain of the PGEs in the supergene zone.

3.5 The nature of the thiosulphate species in solutions

Ryabchikov [9, 10] proposed the existence of four complexes of Pt or Pd with thiosulphate alone; Pt $(S_2O_3)_2^{2-}$ (cis and trans)¹, Pt $(S_2O_3)_3^{4-}$ and Pt $(S_2O_3)_4^{6-}$, as well as mixed ligand species such as Pt $(S_2O_3)Cl_2^{2-}$.

¹⁹⁵Pt NMR spectra for near-saturated solutions of thiosulphate and PtCl₄²⁻ were recorded for solutions of stoichiometric ligand: metal ratios of 2:1, 3:1, 4:1 and 10:1 (ligand : metal). The initial spectra collected shortly after mixing the solutions showed a resonance corresponding to the starting material and another at -2103 ppm relative to the PtCl₄²⁻. The latter is due to the formation of a Pt(II)-thiosulphate complex. Surprisingly, given Ryabchikov's work, all of the experiments using the different molar ratios yielded only these two peaks, together with that of a minor intermediate at about -1600 ppm, indicating that there is only one dominant aqueous species of Pt(II) with thiosulphate.

The experiment with the large excess of thiosulphate showed that the peak at -2103 ppm is due to the Pt $(S_2O_3)_4^{6-}$ species, which was isolated as a complex salt from such solutions (as detailed in the experimental section), and gives the same NMR signal. The minor peak observed at -1600 ppm is inferred as being due to the intermediate complex Pt $(S_2O_3)_2Cl_2^{4-}$. In solutions with ratios of ligand to metal equal to 2:1, the lemon solid K₂[Pt $(S_2O_3)_2$].3H₂O precipitated after several hours. If left in contact with the aqueous solution from which it is formed, this salt turns to a yellow ochre colour, but the new material has the same formula as that from which it was derived.

Two points need to be noted. The first is that these two solids are not particularly important as far as natural systems are concerned. Experiments carried out with the sodium ion as the sole other simple cation in the solution led to no formation of precipitated complexes of Pt. Instead, the solutions containing Pt $(S_2O_3)_4^{6-}$ slowly darkened with age. This is a feature of all solutions studied, although the rate of colour darkening is slower when an excess of thiosulphate ligand is present in solution. In addition, as the colour of the solution changes from canary yellow to orange-brown, the signal in the NMR due to the tetrakis complex disappears. Thus it is evident that this species is not thermodynamically stable in aqueous solution under ambient conditions.

It is concluded that, given the extremely insoluble nature of the yellow ochre complex mentioned above, the thermodynamically stable species in solution are S-bridged oligomers and that these species are formed quickly in aqueous solution for Pd than for Pt. It is noticed that an analogous bis ligand salt for Pd can be synthesised (see experimental section). It has a virtually superimposable infra-red (IR) spectrum with respect to that of the Pt(II) analogue. The oligomers are the species $(S_2O_3)_2M[(-S_2O_3)_2M]_n(S_2O_3)_2^{x-}$; analogues are known for Cu(II) and Cd(II) [3].

¹ Cis species have the ligands adjacent to each other; the trans species have them opposite each other.

4 CONCLUSIONS

1. Dissolution experiments using aqueous sodium thiosulphate solutions in the presence of oxygen show that this medium is strikingly effective with respect to the dissolution of a number of the platinum group elements. Maximum concentrations in solutions were over 100 ppm Pd, 20 ppm Pt, and 200 ppm Ir.

The experiments confirm the predicted efficacy of PGE thiosulphate complexes based on the thermodynamic stability, and show that kinetic parameters for the reactions are favourable for the observation of large concentrations of PGE elements being dissolved in aqueous solution even for short reaction times.

2. Initial dissolution rates are independent of pH in the range of 6 to 8.5. Decreasing the concentration of $S_2O_3^{2-}$ increases the initial dissolution rates by a factor of about two for each order of magnitude of decrease in ligand concentration. Maximum rates observed were approximately 20 ppm per day for Pd in 10^{-3} M $Na_2S_2O_3$ and 0.5 ppm per day for Pt in 10^{-2} M $Na_2S_2O_3$. Experiments with the highest initial rates do not necessarily yield the highest total metal concentration because lower ligand concentrations appeared to hasten the decomposition of metastable species in solution.
3. Use of ^{195}Pt nuclear magnetic resonance spectroscopy and synthetic studies indicate that S-bridged species are thermodynamically stable complexes in these systems.
4. Thiosulphate complexes would be stable in a low Eh, high pH environment. The stability fields for chloride complexes are complementary: they predominate in a high Eh, low pH environment. The available data on distribution of the PGE in weathered profiles demonstrate mobility of Au, Ag, Pd, Pt and, rarely, Ir in the highly oxidised portion of some laterites and gossans. Gossan formation can take place under conditions favourable for chloride complexing but it is not yet clear whether gossan development and PGE mobility are simultaneous or superposed events.
5. Arsenious acid, $As(OH)_3^0$ is also effective in mobilizing Pd under more acid conditions than those outlined above for thiosulphate.
6. These results provide the background for new mechanisms for the mobilization of the PGE in weathering sulphide ores.

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CHAPTER 4: THE SORPTION OF PLATINUM AND PALLADIUM ON SOILS AND REGOLITH MATERIALS

D.J. Gray

ABSTRACT

Sorption is a poorly understood aspect of PGE chemistry, particularly in comparison to the better known chemistry of Au and Ag. Sorption has been investigated by reacting synthesised Pt and Pd complexes with a range of different soils. The particular species studied were the thiosulphate, humate, chloride and iodide complexes of Pt and Pd, and results were compared with studies on Au and Ag chemistry (Gray, 1990a). Soil and regolith materials included organic-, carbonate-, Fe oxide- and Mn oxide-rich samples. The experimental conditions were designed to study as many feasible water-soil interactions as possible. Results indicate the critical effect of both the form of the Pt and Pd, and the soil material with which it is interacting, on the mobility of these metals. Particular observations were that:

- (i) Platinum sorbed at a slow rate (even when eventually being removed from solution) onto a wide range of soil and regolith materials, in a number of differing solutions, implying a high mobility if dissolved during weathering;
- (ii) Humate PGE complexes were found to maintain only low concentrations in solution, suggesting a weak interaction between PGEs and humate or a strong sorption of the complex;
- (iii) Platinum and Pd thiosulphates were strongly sorbed, possibly due to the high negative charge of the complex, or a tendency to polymerize to less soluble forms. The sorbed forms did not redissolve from the soils;
- (iv) In a chloride-rich solution, Ag and Pt had a much higher mobility than Au or Pd, again consistent with the high initial mobility of Pt;
- (v) After three months, the poorly complexed, iodide complexed and humate complexed mixtures showed redissolution of previously sorbed Pt, Pd and Au, while sorbed Ag did not redissolve. Such redissolution reactions are possibly due to soluble species with a high affinity for these metals being produced by biological activity, and appears only to occur in organic-rich environments.

Similar mechanisms as discussed may be conducive to PGE mobility in natural environments. The observed redissolution of sorbed Pt, Pd and Au may represent an important mechanism for soil redistribution of these noble metals.

1 INTRODUCTION

The chemical re-distribution of PGEs in soils is controlled by physico-chemical factors that determine the nature of the processes that may cause mobilization and precipitation. Mobilization is initiated by dissolution of primary and secondary PGE minerals. Such dissolution may occur during weathering of accessory sulfides, either by thiosulphate during neutral weathering or by arsenious acid in acid conditions, or by other mechanisms as discussed previously (Volume I, Chapter 2, Section 4), including dissolution as chloride complexes in acid/saline environments, in a similar manner to that observed for Au (Gray, 1990b). Soil studies (Gray *et al.*, 1990a) have shown that Au is mobilized in soils by as yet undetermined, probably organic, ligands, presumably produced by bacterial activity. A number of investigations (Friese, 1931; Baker, 1973, 1978; Boyle *et al.*, 1975; Gray *et al.*, 1990b) have also suggested Au mobilization via the humate complex. Such biological mechanisms may also control PGE mobilization in organic-rich soils.

The varying PGE complexes, if they exist in nature, may be formed by some of the different processes introduced above. The processes leading to the immobilization of the PGEs, and how they are influenced by factors such as the complexing ligand, water chemistry and soil mineralogy are less well understood than the processes of dissolution. This chapter reports studies into the inter-relationships of these factors, and how they affect the sorption¹ and mobilization of Pt and Pd, and relate this to the better understood chemistry of Au and Ag. The particular species studied were the thiosulphate, humate, chloride and iodide complexes of Pt and Pd, and results were compared with studies on Au and Ag chemistry (Gray, 1990a). Soil samples² included organic-, carbonate-, Fe oxide- and Mn oxide-rich samples. The experimental conditions were designed to study as many feasible water-soil interactions as possible. Results indicate the critical effect of both the form of the Pt and Pd, and the soil material with which it is interacting, on the mobility of these metals.

2 MATERIALS

2.1 Soils

Ten soils were selected. These were:

- (i) MC 24 0-1m (soil and laterite, Mt Carnage);
- (ii) MC 24 1-2m (lateritic duricrust, Mt Carnage);
- (iii) MC 24 3-4m (lateritic duricrust, Mt Carnage);
- (iv) Peat moss: 4% commercially purchased Yates Peat Moss mixed with 96% crushed quartz;
- (v) 1467: organic-rich soil sample 1467;
- (vi) 1468: Fe oxide-rich soil sample 1468;
- (vii) 1470: carbonate-rich soil sample 1470;
- (viii) Std. 7: Fe oxide-rich standard 7;
- (ix) Mount Keith (MKD): Mn oxide-rich Mount Keith Shaft 44 m saprolite;
- (x) Ora Banda (OB): Mn oxide-rich segregation, Siberia.

¹ The terms "sorption" and "sorbed" are used as umbrella terms to describe all reactions that may remove metals from solution. This could include adsorption, precipitation, decomposition of the ligand by agents released from the soil, or bacterial uptake, amongst others.

² Note that, for simplicity, the term soil is used in this chapter to include various regolith materials.

The elemental compositions and mineralogies of these samples are tabulated in Tables 1 and 2. Profile MC 24 is from the Mt. Carnage site and is described in detail in this report (Volume IIA, Chapter 5, Section 7). The sample taken from 0-1 m is carbonate-rich, whereas the other two samples are dominantly iron oxide. All three of these samples are organic-poor. Samples 1467, 1468 and 1470 were taken from a Au rich profile within the Bounty Pit, at Mt. Hope (Lintern, 1989), while Std. 7 is an Fe-rich material from surface scrapings near Holleton. The chemistry of some these samples, particularly in regards to Au, have been studied extensively (Gray *et al.*, 1990a).

2.2 Synthesis of Pt, Pd, Au and Ag complexes

Solutions were made up, prior to addition to the soils, so as to contain approximately 1 mg/L Pt, 1 mg/L Pd, 10 mg/L Au and 10 mg/L Ag, complexed with a particular ligand. Four different solutions were synthesized:

2.2.1 Humic complex

1.25 g of Aldrich Humic Acid, sodium salt, tech. (cat. no. H1,675-2³) were added to approximately 100 mL deionized water, then Pt, Pd, Au and Ag standards added. The solution pH was maintained above 6 by addition of sodium hydroxide (NaOH) solution. The solution was made up to 250 mL final volume, stored in glass in the dark, and passed every three days through a 0.45 µm membrane filter until there was no solid residue. The final solution was expected to contain 5000 mg/L humate (the humic acid being converted to humate at neutral pH), 1 mg/L Pt, 1 mg/L Pd, 10 mg/L Au and 10 mg/L Ag (less any metal precipitated). Actual measured concentrations were 0.25 mg/L Pt, 0.48 mg/L Pd, 3.4 mg/L Au and 2.55 mg/L Ag. On the completion of the filtering the solution had an Eh of 430 mV (*i.e.*, moderately oxidizing) and a pH of 6.7.

2.2.2 Thiosulphate complex

0.248 g sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) was mixed with approximately 50 mL deionized water, with N_2 bubbling. The pH was raised to 10 with NaOH solution, then Pt, Pd, Au and Ag standards added. As the addition of the standards will tend to lower the pH of the solution, and thus destabilize the thiosulphate, this was done dropwise, and interspersed with addition of NaOH solution so as to maintain neutral to alkaline conditions. Following this, another 0.248 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ was added, the solution taken to pH 7, made up to 100 mL final volume, and stored in glass in the dark. The final solution was expected to contain 20 mmol/L (mM) $\text{S}_2\text{O}_3^{2-}$ (less any decomposition), 1 mg/L Pt, 1 mg/L Pd, 10 mg/L Au and 10 mg/L Ag (less any metal precipitated). Actual measured concentrations were 0.63 mg/L Pt, 0.73 mg/L Pd, 9.55 mg/L Au and 8.8 mg/L Ag.

³ Properties of this material are detailed in MacCarthy and Malcolm (1987).

TABLE 1
Elemental Compositions of Samples.

	Sample									
	MC24 0-1m	MC24 1-2m	MC24 3-4m	Moss	1467	1468	1470	Std. 7	MKD	OB
pH	7.86	4.46	nd	6.52	8.21	8.83	9.51	6.39	7.50	6.33
OC	<0.1	<0.1	0.15	1.31	1.06	0.69	0.26	1.22	<0.1	<0.1
SiO ₂	28.1	25.0	20.0	97.3	72.0	57.7	35.6	47.7	61.8	40.6
Al ₂ O ₃	12.9	17.1	15.8	0.12	13.7	15.9	13.6	18.4	0.42	4.2
Fe ₂ O ₃	31.9	43.6	45.1	0.84	10.0	17.7	15.8	31.6	18.2	27.4
MgO	1.86	0.08	0.01	0.05	1.43	2.26	12.6	0.23	0.55	1.50
CaO	6.7	0.01	0.00	0.26	0.72	4.41	20.5	0.24	0.23	0.13
Na ₂ O	0.30	0.37	0.42	0.00	0.26	0.33	0.78	0.07	0.10	0.21
TiO ₂	0.63	0.85	0.79	0.04	0.64	0.73	0.56	1.67	0.03	1.32
P ₂ O ₅	0.00	0.00	0.00	0.05	0.03	0.00	0.00	0.00	0.05	0.12
SO ₃	3.16	1.43	0.58	0.04	0.03	0.04	0.14	0.07	0.03	0.17
Pt	0.85	0.68	0.69	nd	nd	nd	nd	nd	nd	nd
Pd	0.44	0.41	0.44	nd	nd	nd	nd	nd	nd	nd
Au	0.00	0.00	0.00	0.00	1.01	3.56	6.07	0.67	0.00	0.00
Ba	120	28	6	20	113	193	214	42	31300	17300
Ce	26	15	7	1.6	29	31	22	10	388	202
Co	262	26	19	0.7	27	27	22	11	33900	15400
Cr	2809	5190	10071	6	640	1250	1200	465	550	4840
Cu	639	710	741	9	73	137	148	58	2840	267
La	19	11	17	1	17	18	14	6	197	132
Mn	1500	988	1232	46	539	589	479	207	25400	80100
Ni	803	808	907	8	180	202	148	49	49300	54500
Pb	6	0	0	0	11	19	13	26	0	7
Rb	15	7	2	0	40	36	26	14	1	8
Sr	95	20	5	6	54	127	824	15	120	2410
V	176	250	310	2	201	402	405	950	16	1100
W	0	2	0	0	4	5	5	14	308	203
Y	11	8	5	1	12	16	12	7	48	25
Zn	57	107	115	0	34	36	20	22	624	35
Zr	79	70	48	29	141	151	116	219	3	46

Corrected to dehydrated weight, all oxides and OC (organic carbon) in wt %, other elements in mg/kg.

nd: not determined.

TABLE 2
Mineralogy of Samples

Mineral phase	Formula	MC 24 0-1m	MC 24 1-2m	MC 24 3-4m	Moss	1467	1468	1470	Std. 7	MKD	OB
Smectite	#	-	-	-	-	xxx	xxx	-	-	-	-
Kaolin	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	xxx	xxx	xxx	-	xxx	xxx	xx	xxx	-	-
Quartz	SiO_2	x	x	x	xxx	xxx	xx	x	xx	xxx	xx
Goethite	FeOOH	xx	xxx	xxx	-	x	xx	x	x	-	-
Hematite	Fe_2O_3	xxx	xxx	xxx	-	?	?	?	xxx	xxx	xxx
Cryptomelane	$\text{KMn}_8\text{O}_{16}$	-	-	-	-	-	-	-	-	-	xxx
Lithiophorite	$(\text{LiAlCoMn})\text{OOH}$	-	-	-	-	-	-	-	-	xxx	xx
Anatase	TiO_2	-	-	-	-	x	?	-	-	-	-
Rutile	TiO_2	-	x	x	-	x	?	-	-	-	-
Calcite	CaCO_3	xx	-	-	-	-	xx	x	-	-	-
Dolomite	$\text{MgCa}(\text{CO}_3)_2$	-	-	-	-	-	x	xxx	-	-	-
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	xx	-	-	-	-	-	-	-	-	-
Feldspar	$(\text{K,Na})\text{AlSi}_3\text{O}_8$	-	-	-	-	-	-	x	-	-	-

Highly variable. A general formula is:
 $(\frac{1}{2}\text{Ca,Na})_{0.35}(\text{Al,Mg,Fe})_{2.3}[(\text{Si,Al})_4\text{O}_{10}](\text{OH})_2 \cdot n\text{H}_2\text{O}$.

xxx major component
 xx minor component
 x trace component
 ? possible component
 - below detection

2.2.3 Iodide complex

0.166 g potassium iodide (KI) was mixed with approximately 50 mL deionized water, and Au and Pt standards (though not Pd and Ag, because of the low solubility of AgI and PdI₂) were added. The pH was then raised to 7 with NaOH solution, the solution made up to 100 mL final volume, and stored in glass in the dark. The final solution was expected to contain 10 mM I⁻, 1 mg/L Pt, and 10 mg/L Au (less any metal precipitated). The actual measured concentrations were 0.92 mg/L Pt and 9.0 mg/L Au.

2.2.4 Chloride complex

14.61 g NaCl (58.44 g molecular weight) was mixed with approximately 100 mL deionized water, then Pt, Pd, Au and Ag standards added. The solution was made up to 250 mL final volume, and stored in glass. The final solution was expected to contain one mole/L (M) Cl⁻, 1 mg/L Pt, 1 mg/L Pd, 10 mg/L Au and 10 mg/L Ag (less any metal precipitated), and to have a pH below 3. Actual measured concentrations were 0.97 mg/L Pt, 1.20 mg/L Pd, 9.0 mg/L Au and 8.0 mg/L Ag.

2.2.5 "Uncomplexed" ions

Solutions of weakly complexed noble metals were used in order to quickly precipitate metals in soil/water mixtures. These were produced by using concentrated (10 - 1000 mg/L, depending on requirements) noble metal standards in 1 M HCl, which were then diluted in the solution required, thus ending up with the noble metals in a dilute Cl solution, which will have a poor complexing capacity.

3 EXPERIMENTAL

3.1 Solution incubations of lateritic duricrust, Mt. Carnage

3.1.1 Dissolution experiments

This experiment was conducted to see if *in situ* Pt and Pd could be dissolved from soils over time in a similar manner to Au (Gray *et al.*, 1990a). The regolith materials used in this experiment were Fe-rich samples MC24 0-1m, MC24 1-2m and MC24 3-4m. Fifty grams of material were weighed into a 350 mL glass bottle and 100 mL of deionized water added, the bottle sealed and placed on an automatic shaker in the dark. For each sample, four mixtures were prepared, for analysis after one day, one week, two months and six months. At these specified times the bottles were taken off the shaker, 5 mL solution filtered through a 0.45 μm ⁴ membrane filter, and the filtrate digested in aqua regia. The solution was then made up to 10 mL in 1 M HCl / 0.3 M HNO₃ for analysis for Pt and Pd by ICP-MS.

3.1.2 Addition experiments

A series of soil/water mixtures was prepared to observe the effect of adsorption of 'uncomplexed' Pt, Pd, Au and Ag (Section 2.2.5) onto samples MC24 0-1m, MC24 1-2m and MC24 3-4m. Fifty grams of soil were weighed into a 350 mL glass bottle and 90 mL of deionized water was added. Platinum, Pd, Au and Ag were added as concentrated standards to yield a solution of 900 $\mu\text{g/L}$ Pt, 440 $\mu\text{g/L}$ Pd, 500 $\mu\text{g/L}$ Au and 500 $\mu\text{g/L}$ Ag in a dilute sodium chloride (NaCl) solution. The mixture was taken to pH 7 with sodium hydroxide, made up to 100 mL solution with deionized water, and the bottle then sealed and placed on an automatic shaker in the dark.

After one day, one week, two months and six months, the bottles were opened and 5 mL aliquots of the mixtures were taken. The aliquots were centrifuged, filtered through a 0.45 μm membrane filter, and the filtrate digested with aqua-regia. The solution was then made up to 10 mL in 1 M HCl / 0.3 M HNO₃ for analysis for Pt, Pd, Au and Ag by ICP-MS.

3.2 Addition of solutions to soils

The soils used in this series of experiments were Peat moss, 1467, 1468, 1470, Std. 7, MKD and OB, which represented a wide range of materials.

3.2.1 Humate, thiosulphate and iodide

These experiments were designed to test the capacity of various species to maintain Pt, Pd, Au and Ag in solution, when contacting soil and regolith material. Fifty grams of soil were weighed into a 350 mL glass bottle and 90 mL of deionized water added. Following this, 10 mL of the stock humate, thiosulphate or iodide solution (Sections 2.2.1 - 2.2.3) was added, the bottle sealed and placed on an automatic shaker in the dark. The initial concentration of the ligands, and the metals in the mixtures, was 0.1 times that of the stock solution.

3.2.2 Chloride

A series of soil/water mixtures were prepared to simulate the interaction of Pt-, Pd-, Au- and Ag-rich acid saline waters with soil. Fifty grams of soil were weighed into a 350 mL glass bottle and 50 mL of 1 M NaCl solution added. Sufficient HCl was added to ensure the mixture had a pH below 4 even after several days equilibration (this required considerable acid for carbonate-rich samples 1468 and

⁴ For the purposes of simplicity dissolved metals are taken to include any aqueous phases that pass through 0.45 μm membrane filters; this could thus include various non-ionic and/or colloidal forms as well as true dissolved metals.

1470), and then 10 mL of the Pt/Pd/Au/Ag chloride stock solution (Section 2.2.4) was added. The solution was made up to 100 mL with 1 M NaCl, the bottle was sealed and placed on an automatic shaker in the dark. The initial concentration of the metals was 0.1 times that of the stock solution, with Cl^- concentration of about 1 M, and a $\text{pH} < 4$.

3.2.3 Adsorption

A series of soil/water mixtures was prepared to observe the effect of adsorption of 'uncomplexed' Pt, Pd, Au and Ag onto the soils. Fifty grams of soil were weighed into a 350 mL glass bottle and 90 mL of deionized water was added. Platinum, Pd, Au and Ag were added as concentrated standards to yield a solution of 0.1 mg/L Pt, 0.1 mg/L Pd, 1 mg/L Au and Ag in a dilute NaCl solution. The mixture was made up to 100 mL with deionized water, and the bottle then sealed and placed on an automatic shaker in the dark.

No attempt, other than normal clean laboratory practice, was made to exclude organisms during preparation and bottling of the mixtures. It is thus feasible that "exotic" bacteria could contaminate the mixtures. However, it is more likely that most organisms present in the mixtures would have been derived from the samples themselves, which would be expected to have significant populations of *in situ* biota.

3.2.4 Analysis of solutions

After two weeks, and after three months, the bottles were opened and 10 mL aliquots of the mixtures were taken. The aliquots were centrifuged, filtered through 0.45 μm membrane filter, and the filtrate digested with aqua-regia. The solution was then made up to 10 mL in 1 M HCl / 0.3 M HNO_3 for analysis for Pt, Pd, Au and Ag by ICP-MS. Subsamples of the various stock solutions (Section 2.2) were also analysed in the same manner, so as to provide a direct comparison for determination of the amount of metals removed from solution.

4 RESULTS AND DISCUSSION

4.1 MC 24 incubations of lateritic duricrust from Mt Carnage

The samples and methodology are described in Sections 2.1 and 3.1. There was NO observed dissolution of *in situ* Pt or Pd from the samples over the six month period. This contrasts with the observed dissolution of Au in organic- and carbonate-rich soils (Gray *et al.*, 1990a). As will be discussed in Chapter 5, this may be due to Pt and Pd occurring in very different mineral phases than Au in the regolith.

Results for the sorption of Pt, Pd, Au and Ag are illustrated in Figures 1 - 4. Palladium (Figure 2) showed virtually complete sorption onto the three soils within one day, whereas Au (Figure 3) took up to one week to be completely sorbed. In contrast, Ag and Pt (Figures 1 and 4) were sorbed much more slowly, in most cases taking up to two months for total sorption, with Pt sorption on MC 24 3-4m being only 80% complete after six months. The sorption rate for Ag and Pt decreased with depth, possibly due to the effect of carbonate in maintaining high pH values in the shallow samples.

The enhanced solubility of Pt may be related to the slow rate of ligand exchange for this ion: thus, Pt may only sorb on the soils once the PtCl_4^- complex has been hydrolysed, which might well take many weeks. On the other hand, the enhanced Ag solubility may be related to the tendency of this ion to remain oxidized, even under relatively reducing conditions (Gray, 1988). Although these hypotheses are provisional, the data suggest that Pt, if dissolved as the PtCl_4^- complex, should have a high mobility. Note that, once sorbed, the metals did not redissolve over the six month period. This appears to be due to the organic-poor nature of these materials, and may be compared with the results for addition of these metals to organic-rich soils, described in Section 3.2.

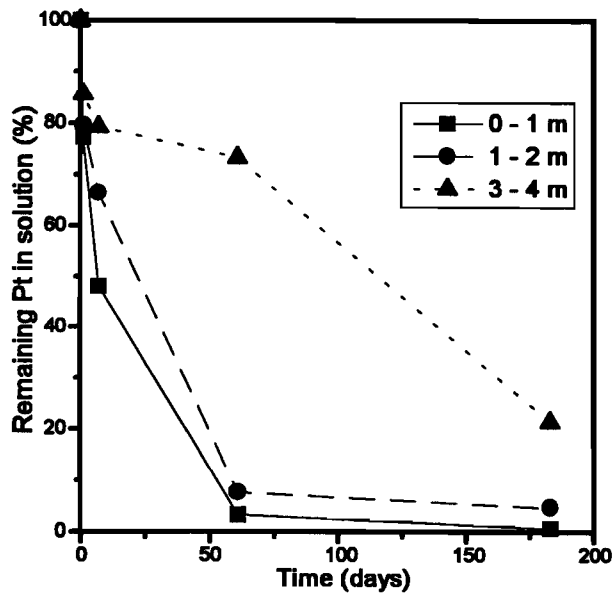


Figure 1: Percentage dissolved Pt in contact with MC 24 soils over six months.

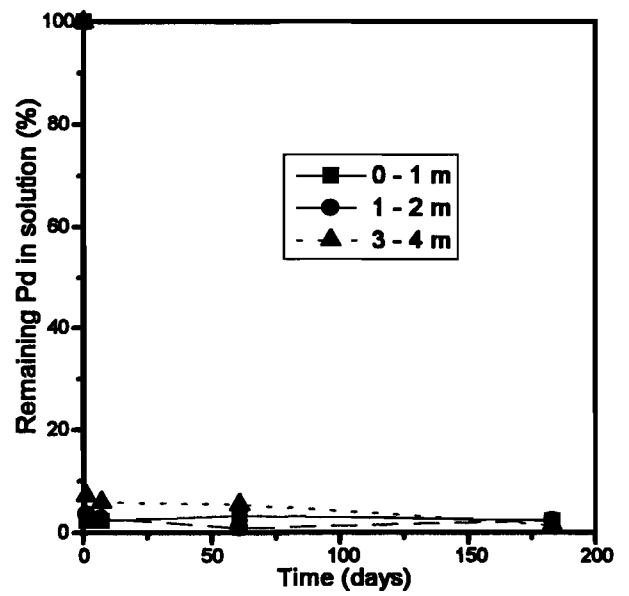


Figure 2: Percentage dissolved Pd in contact with MC 24 soils over six months.

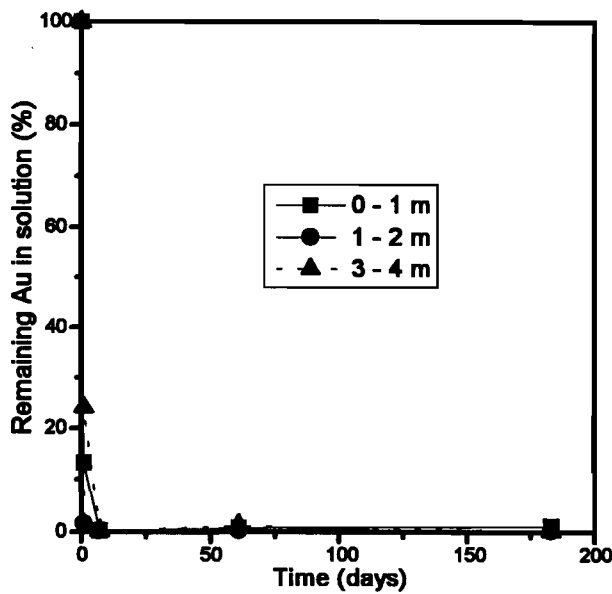


Figure 3: Percentage dissolved Au in contact with MC 24 soils over six months.

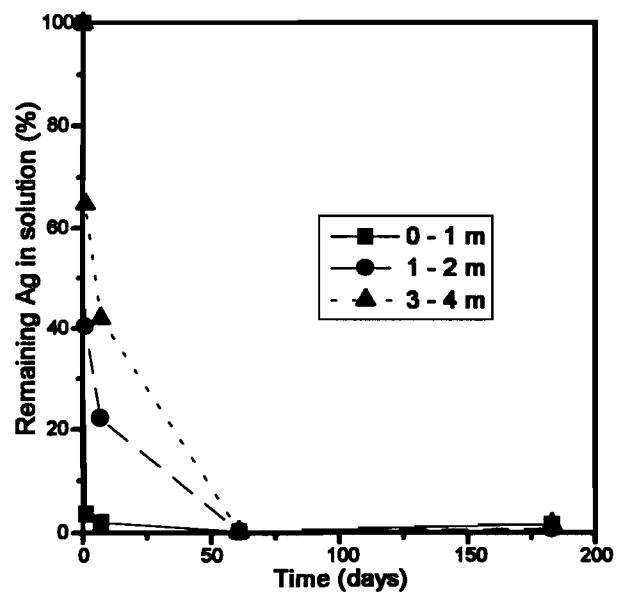


Figure 4: Percentage dissolved Ag in contact with MC 24 soils over six months.

4.2 Additions of Pt, Pd, Au and Ag to various regolith materials

The samples and methodology are described in Sections 2 and 3.2, and results are given in Tables 3 to 6. Note that results for Au and Ag have been previously reported in Gray (1990a). Direct comparisons of the behaviour of all of the metals are shown in Figures 5 to 15, which best illustrate the experimental results.

TABLE 3
Sorption Results for Pt

Complex	Initial Conc. (µg/L)	Time	Percentage Remaining in Solution						
			Moss	1467	1468	1470	Std. 7	MKD	OB
Humic	25	2 weeks	10	30	20	0	30	0	50
		3 months	32	2	2	8	2	2	2
Thiosulphate	63	2 weeks	8	12	12	4	8	0	0
		3 months	32	2	3	1	1	1	1
Iodide	92	2 weeks	3	0	5	11	0	0	8
		3 months	21	14	11	10	1	1	7
Chloride	97	2 weeks	21	10	26	36	31	10	5
Water	100	2 weeks	0	10	0	20	10	3	5
		3 months	9	10	8	4	1	2	1

TABLE 4
Sorption Results for Pd

Complex	Initial Conc. (µg/L)	Time	Percentage Remaining in Solution						
			Moss	1467	1468	1470	Std. 7	MKD	OB
Humic	48	2 weeks	16	0	0	0	0	0	11
		3 months	17	1	1	6	1	1	1
Thiosulphate	73	2 weeks	0	0	0	3	0	0	0
		3 months	25	3	3	1	1	1	1
Chloride	120	2 weeks	4	0	0	0	0	0	4
Water	100	2 weeks	5	0	0	0	5	3	0
		3 months	6	17	12	8	1	2	1

TABLE 5
Sorption Results for Au

Complex	Initial Conc. (µg/L)	Time	Percentage Remaining in Solution						
			Moss	1467	1468	1470	Std. 7	MKD	OB
Humic	340	2 weeks	40	1	1	1	3	1	3
		3 months	24	3	0.3	14	0.3	9	8
Thiosulphate	850	2 weeks	17	6	10	63	25	1.0	<0.5
		3 months	19	<0.1	0.3	9	<0.1	<0.1	<0.1
Iodide	900	2 weeks	11	7	1	1	1	1	67
		3 months	24	31	51	24	3	0.7	55
Chloride	900	2 weeks	2	3	2	1	4	1	36
		3 months	<1	<1	nd	nd	<1	<1	<1
Water	1000	2 weeks	1	2	0.5	2	1	5	0.5
		3 months	5	26	20	9	<0.1	2	<0.1

nd: not determined (due to breakage of sample bottles).

TABLE 6
Sorption Results for Ag

Complex	Initial Conc. (µg/L)	Time	Percentage Remaining in Solution						
			Moss	1467	1468	1470	Std. 7	MKD	OB
Humic	255	2 weeks	24	4	4	4	6	<2	6
		3 months	16	<0.4	<0.4	<0.4	0.8	<0.4	<0.4
Thiosulphate	880	2 weeks	13	1	<0.6	45	1	0.6	<0.6
		3 months	16	0.2	<0.1	1	0.1	<0.1	<0.1
Chloride	800	2 weeks	4	93	100	98	100	96	100
		3 months	<1	38	nd	nd	44	53	59
Water	1000	2 weeks	2	2	1	1	2	1	2
		3 months	8	0.8	0.2	<0.1	<0.1	<0.1	<0.1

nd: not determined (due to breakage of sample bottles).

4.2.1 Humic complex

Gold is presumably complexed by a number of biologically generated ligands in the soil environment, but of a complex range of possible ligands, only the humate ligand was explicitly tested in these experiments.

After two weeks of shaking, more than 90% of the Pd, Au and Ag from the humate solution was sorbed onto the soils in all of the mixtures, with the notable exception of the Peat Moss mixture (Figure 5). This would suggest that the humic complexes with Pd, Au and Ag are not strong and that the humate complex is readily immobilized. The lesser sorption by the Peat Moss is possibly because the competition for the metals is only between soluble humic matter and solid organic matter, in the absence of other soil minerals (*e.g.* Fe oxides, carbonates, Mn oxides) that are present in the other soils.

Platinum showed much lower sorption in the humate solution than the other three metals after two weeks. Based on the high sorption of Pt after three months, this represents a slow speed of sorption, rather than a ultimately lesser degree of sorption than the other metals. As observed in the previous experiment (Section 3.2), and corroborated by observations detailed below, the sorption of Pt when complexed by halide ligands (*e.g.*, Cl⁻, I⁻) by soils was very slow, even in very dilute solutions. It is possible that the slow sorption of Pt in the humate solution is due to Pt remaining in ionic form, which is only slowly sorbed by the various soils.

After three months, at the conclusion of the experiment, some significant variations were observed (Figure 6). All of the metals were still only partially sorbed in the Peat Moss mixture, whereas, for most of the other soils, Pt, Pd, Au and Ag were all virtually totally sorbed. However, there appeared to be a small amount of redissolution of previously sorbed metals: of Au in the manganiferous samples MKD and OB, and of Pt, Pd and Au in the calcareous sample 1470. The mechanism causing this could be alteration of the soluble humate into a form that dissolves Au more strongly. More graphic indications of this effect are observed for the iodide and uncomplexed treatments (see below).

The important observations for the humate tests are:

- (i) the strong sorption of Pd, Au and Ag by all soils except the Peat Moss;
- (ii) the slow rate of sorption of Pt, consistent with other experiments;
- (iii) the minor redissolution of sorbed Au, Pt and Pd (with Ag remaining insoluble) over time for manganiferous and calcareous samples.

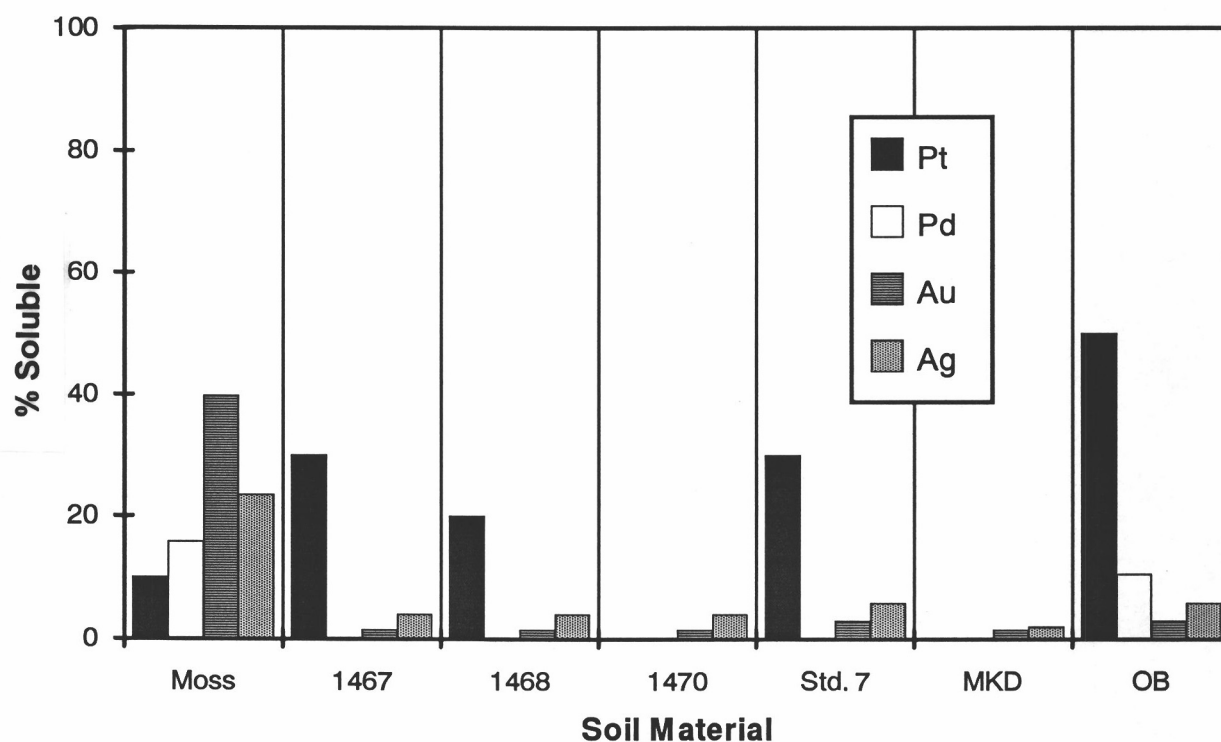


Figure 5: Concentration of Pt, Pd, Au and Ag in humate solution, mixed with various soils, after two weeks. See Section 2.1 for sample compositions.

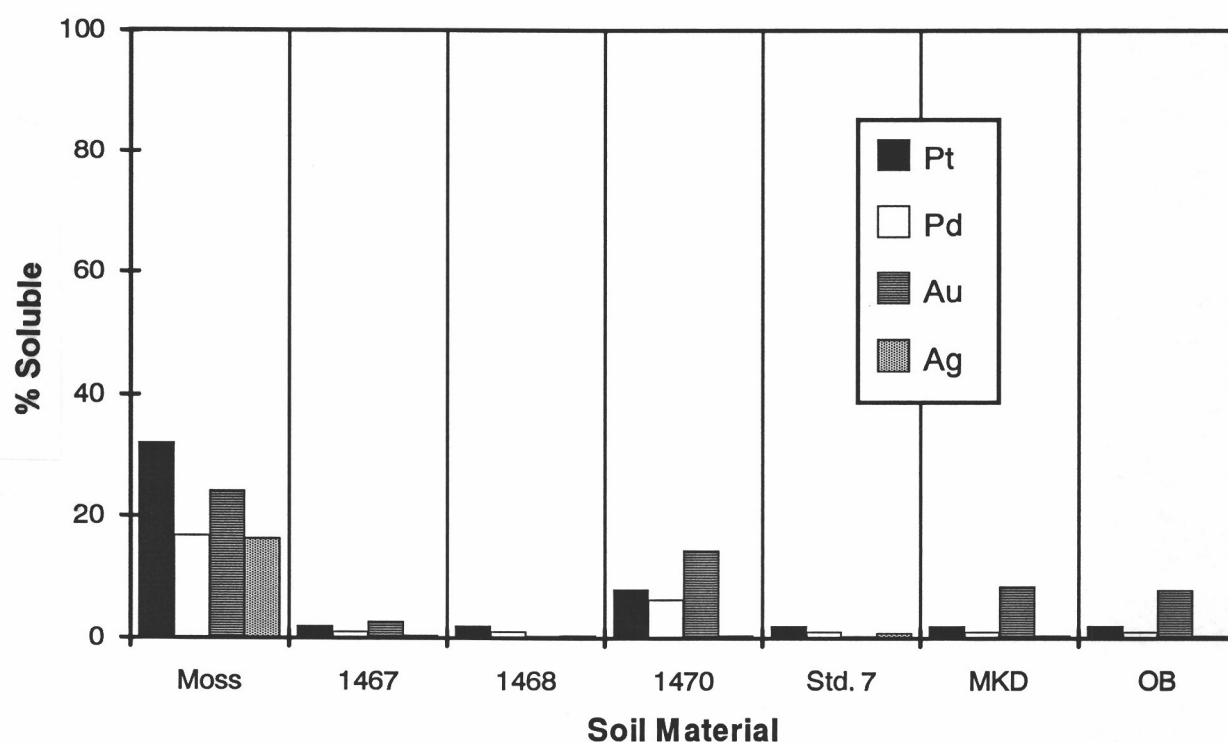


Figure 6: Concentration of Pt, Pd, Au and Ag in humate solution, mixed with various soils, after three months. See Section 2.1 for sample compositions.

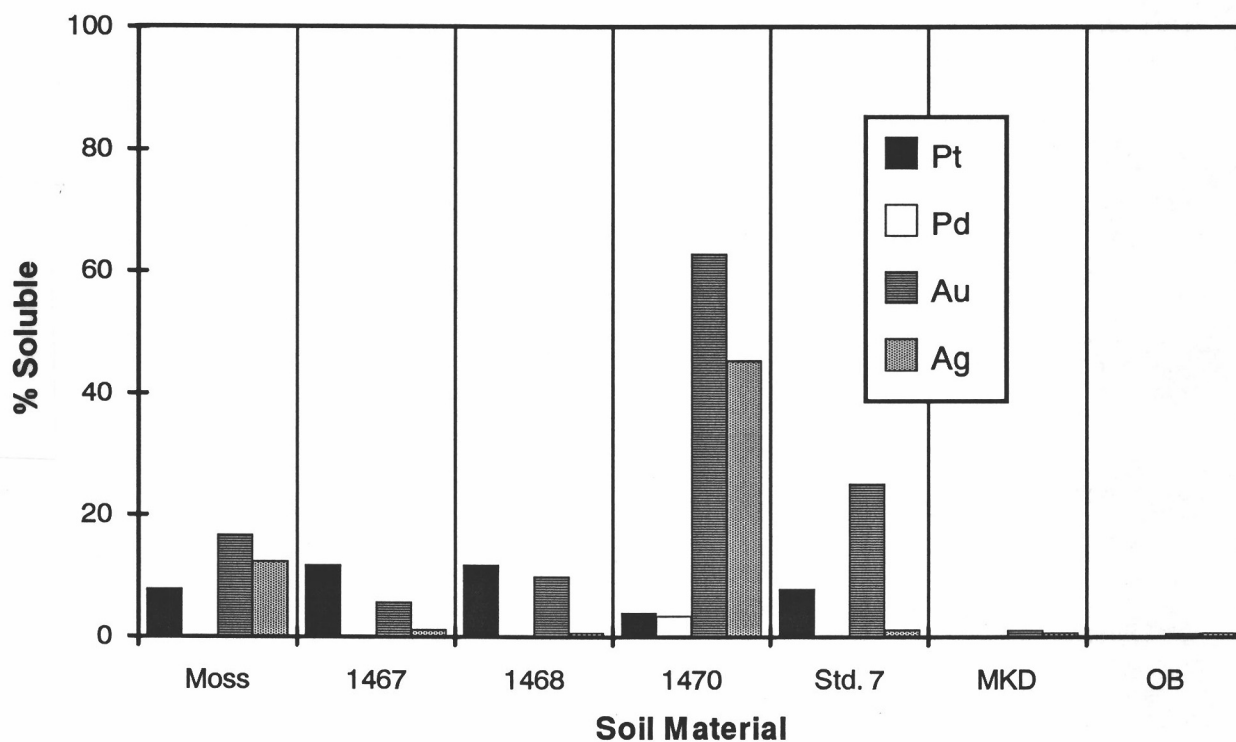


Figure 7: Concentration of Pt, Pd, Au and Ag in thiosulphate solution, mixed with various soils, after two weeks. See Section 2.1 for sample compositions.

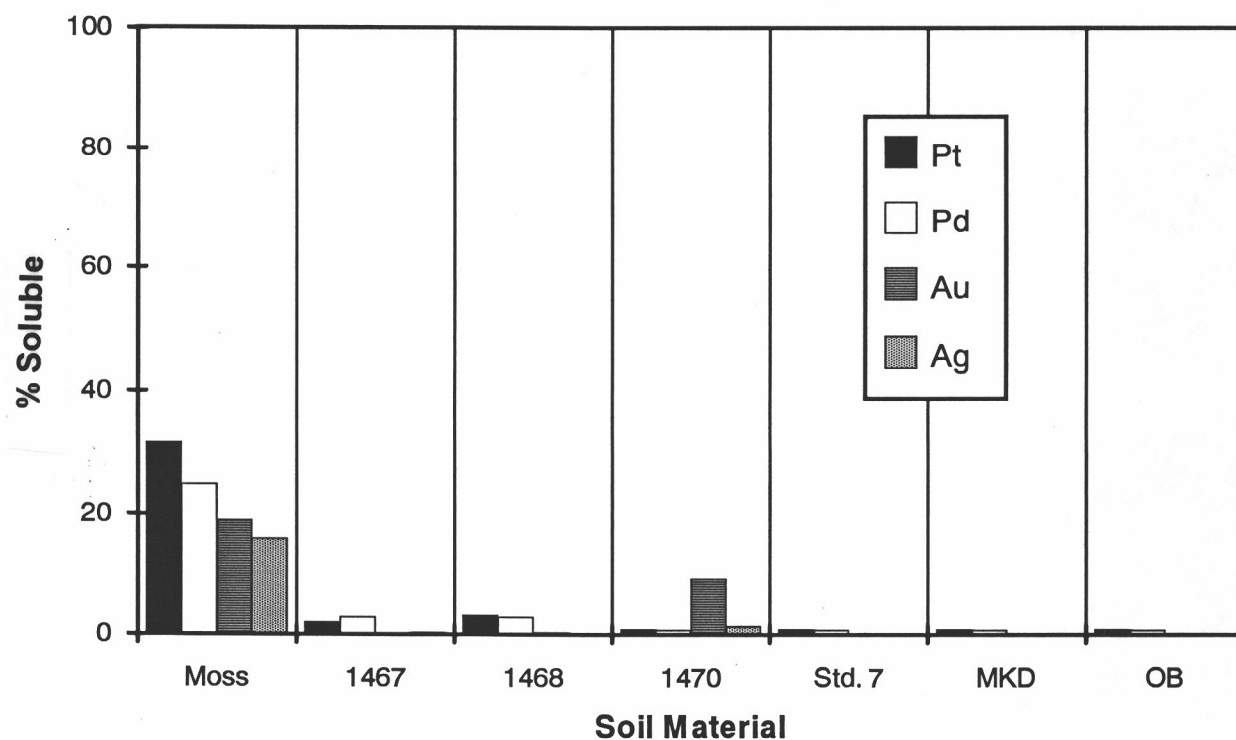


Figure 8: Concentration of Pt, Pd, Au and Ag in thiosulphate solution, mixed with various soils, after three months. See Section 2.1 for sample compositions.

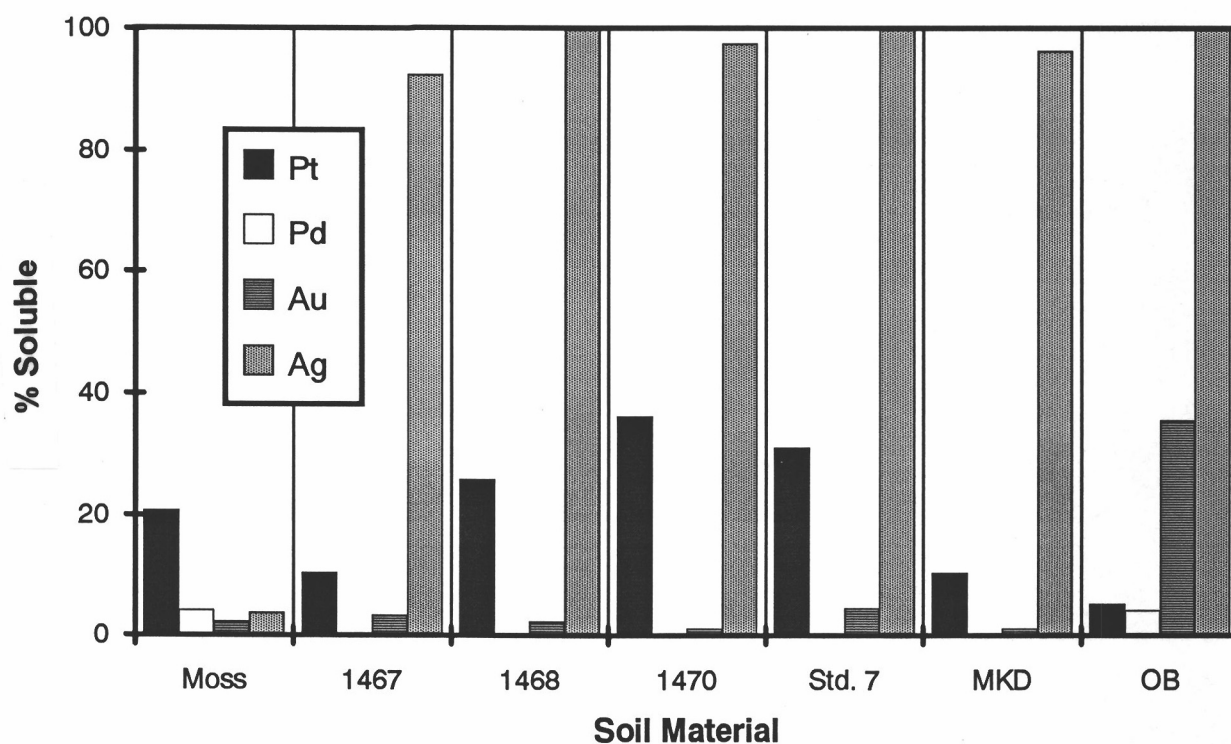


Figure 9: Concentration of Pt, Pd, Au and Ag in chloride solution, mixed with various soils, after two weeks. See Section 2.1 for sample compositions.

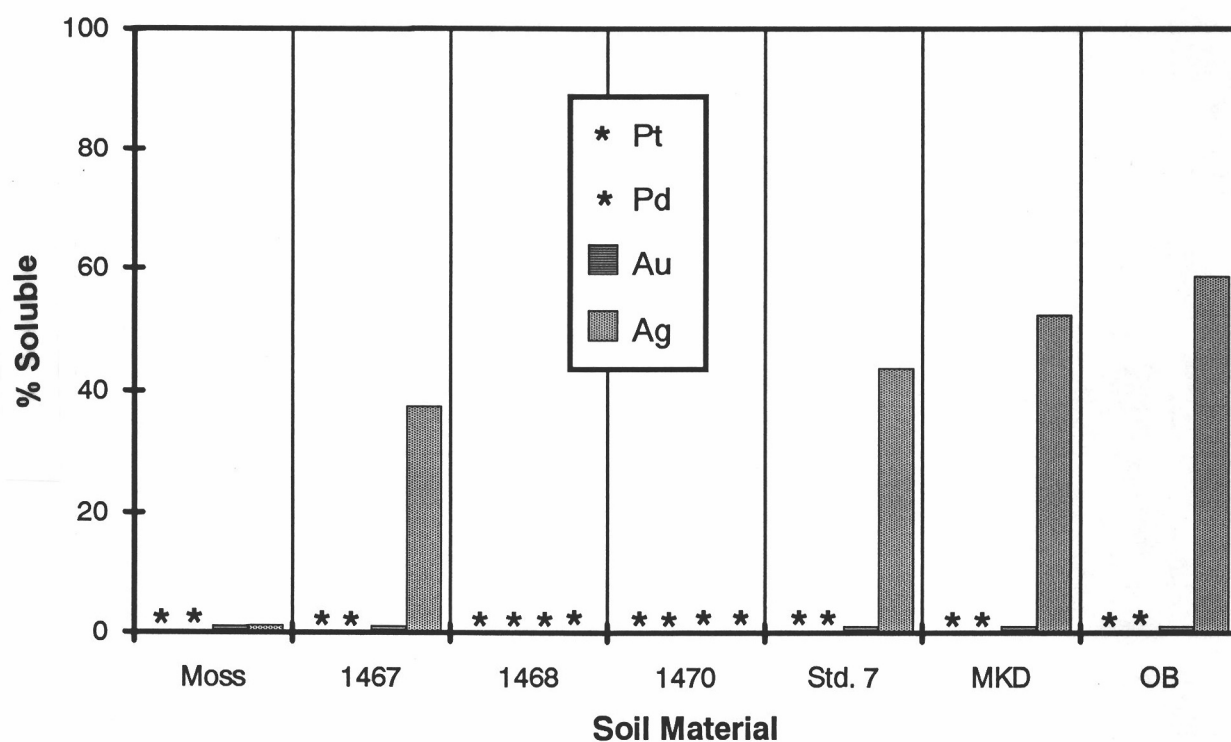


Figure 10: Concentration of Au and Ag in chloride solution, mixed with various soils, after three months. See Section 2.1 for sample compositions. (Asterisks indicate that solubility was not determined.)

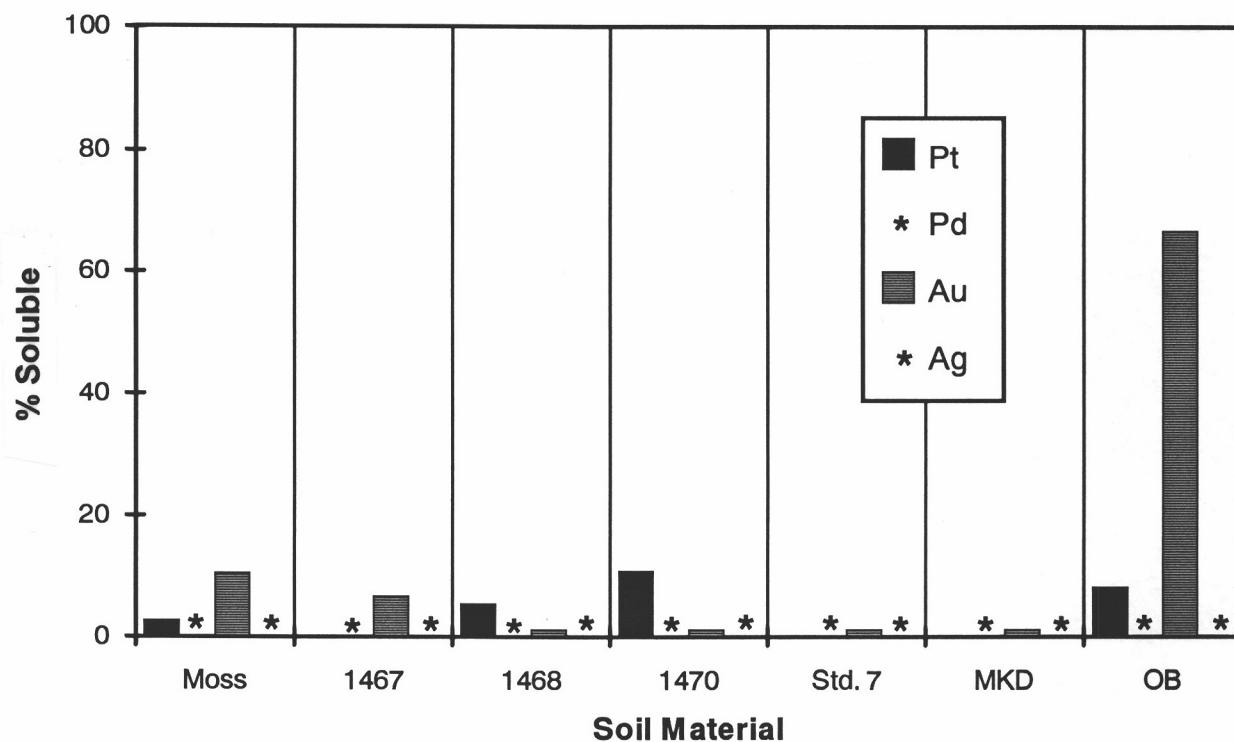


Figure 11: Concentration of Pt and Au in iodide solution, mixed with various soils, after two weeks. See Section 2.1 for sample compositions. (Asterisks indicate that solubility has not been determined.)

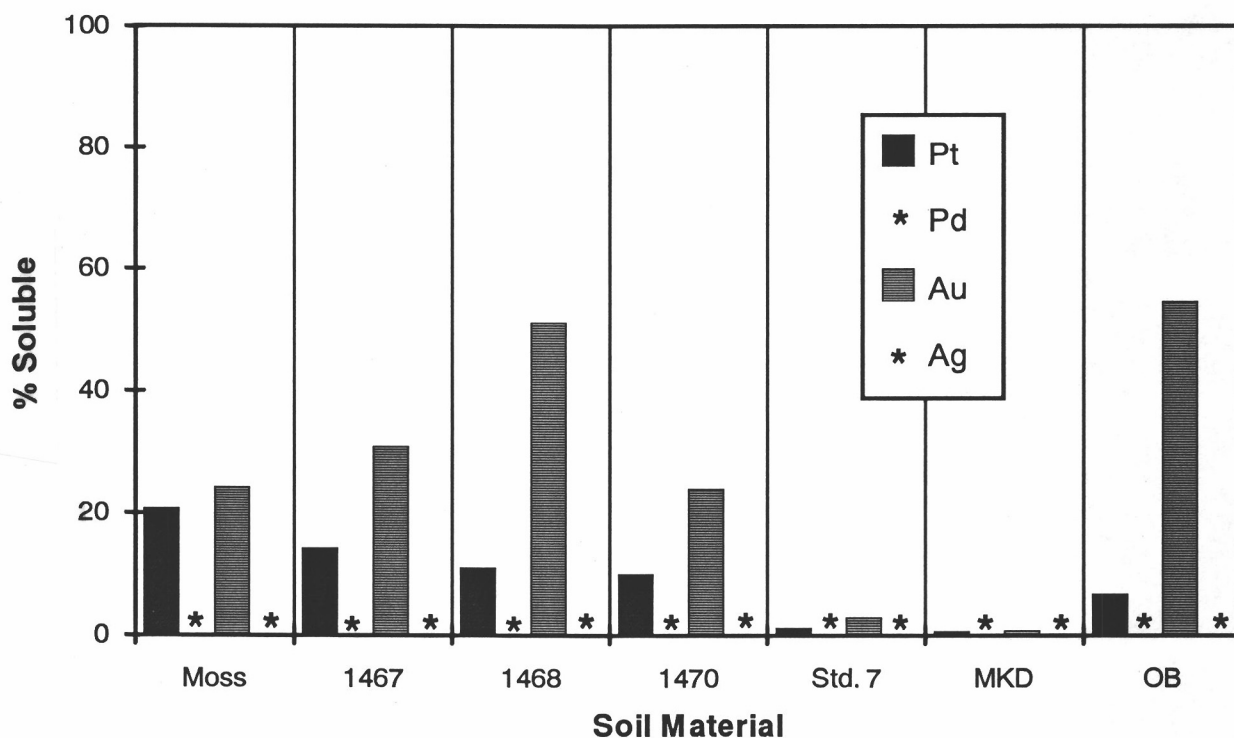


Figure 12: Concentration of Pt and Au in iodide solution, mixed with various soils, after three months. See Section 2.1 for sample compositions. (Asterisks indicate that solubility has not been determined.)

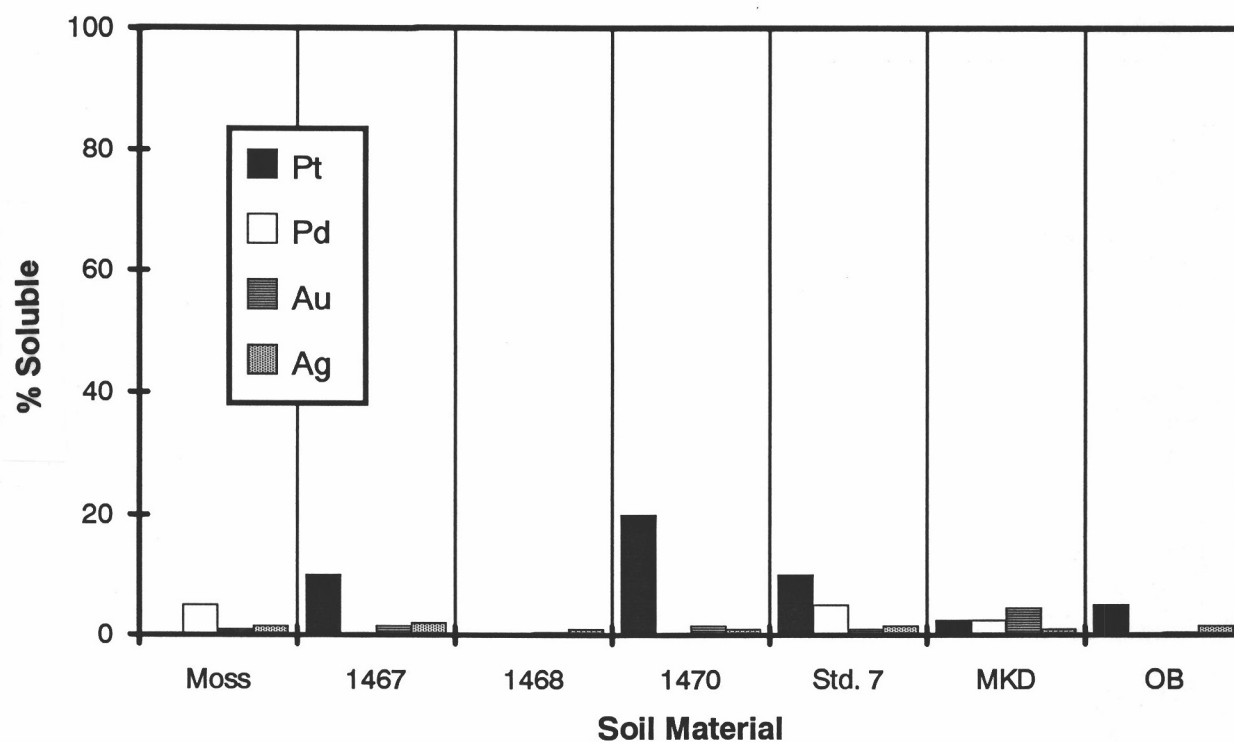


Figure 13: Concentration of Pt, Pd, Au and Ag in water, mixed with various soils, after two weeks. See Section 2.1 for sample compositions.

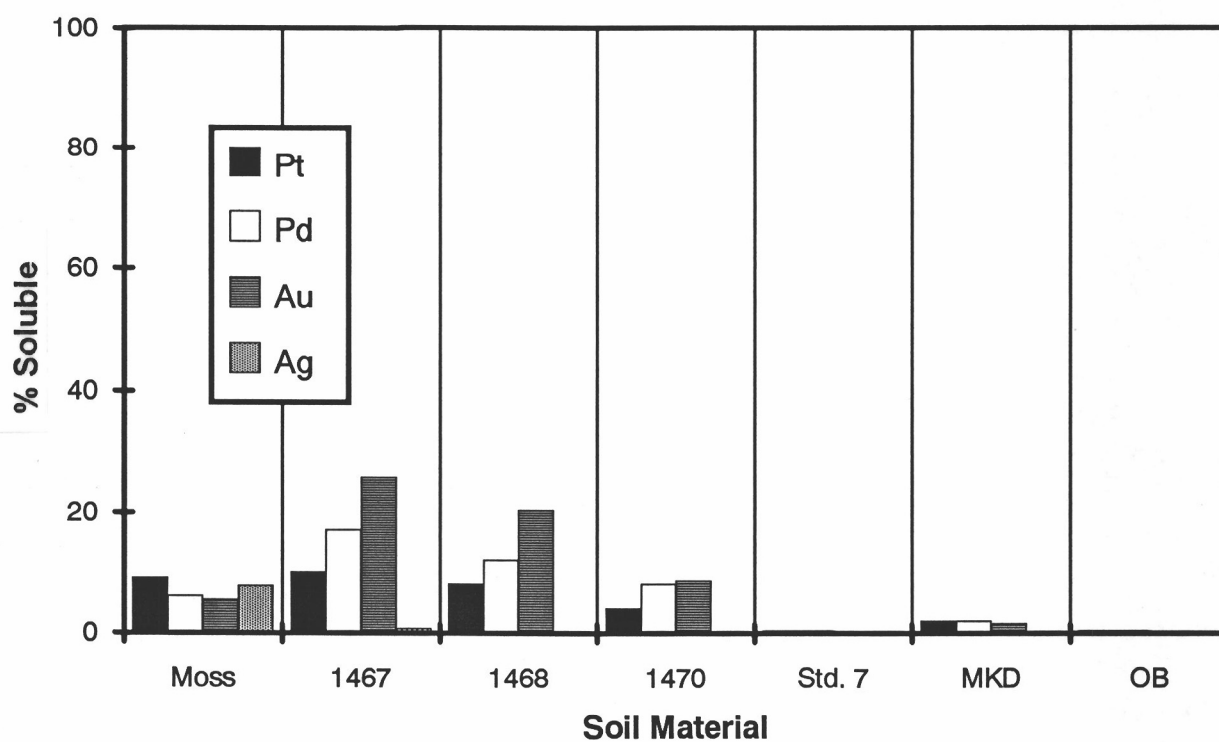


Figure 14: Concentration of Pt, Pd, Au and Ag in water, mixed with various soils, after three months. See Section 2.1 for sample compositions.

It should be noted that these results may not apply to other organic ligands. Other species such as cyanide or amino acids may mobilize noble metals more strongly than humate, and Pt, Pd, Au and Ag could still have high mobilities in organic-rich soils, due to their influence.

4.2.2 Thiosulphate complex

Thiosulphate is generated during neutral to alkaline weathering of sulphides (Granger and Warren, 1969; Goldhaber, 1983; Mann, 1984; Webster, 1984). Thus, thiosulphate complexation of the noble metals represents a mobilization mechanism that would occur at depth in specific deeply weathered environments.

After two weeks of shaking with the various solids, the thiosulphate solutions (Figure 7) showed a lesser sorption for Au and Ag than did the humate solutions (Figure 5). Conversely, Pt and Pd were more strongly sorbed than in the humate mixtures although, as before, Pt was more weakly sorbed than Pd. The greater sorptions of Pt and Pd are presumably a consequence of the chemistry of the thiosulphate complex. Whereas Au and Ag form the stable and soluble $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ and $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ complexes, Pt and Pd form the highly charged $\text{Pt}(\text{S}_2\text{O}_3)_4^{6-}$ and $\text{Pd}(\text{S}_2\text{O}_3)_4^{6-}$ ions which are more likely to adsorb on positively charged surfaces such as iron oxides, and may tend to polymerize into less soluble forms (Volume I, Chapter 3, Section 3.5).

After three months, marked changes were observed (Figure 8). The concentrations of the metals in the solution shaken with the Peat Moss increased, again indicating the low affinity of the noble metals for solid organic matter, while most of the other soils showed virtually 100% sorption of Pt, Pd, Au and Ag. The results imply that the sorption reactions for the various thiosulphate complexes are kinetically slow, and not that the complexes are soluble when in contact with these soils.

The concentrations of dissolved Pt, Pd and Au for the thiosulphate solutions shaken with soils for 3 months were significantly lower than those observed for the "uncomplexed" mixtures (see below; Figure 14). This implies that the thiosulphate complexes are sorbing in a form that is not readily redissolved.

In summary, the general characteristics of the sorption of the thiosulphate complexes are:

- (i) Pt and Pd are sorbed more quickly than Au and Ag;
- (ii) solid organic matter, on its own, only partially immobilizes the metals;
- (iii) the metal thiosulphate complexes are sorbed in a form that is not readily redissolved.

4.2.3 Chloride complex

A number of texts (Gray, 1988 and references given therein; Gray, 1990b) have indicated the importance of the Au chloride complex in the mobilization of Au in acid/saline environments, and it is entirely reasonable that Pt and Pd may also be mobilized in such environments. The chloride solution/soil mixtures were prepared using acid ($\text{pH} < 4$) and saline (Cl^- concentration approximately 1 M or 35000 mg/L) solutions to simulate interaction of soils with acid/saline waters. After 2 weeks (Figure 9), the various noble metals had very different solubilities under these experimental conditions. With the exception of the Peat Moss mixture, sorption of Ag was only minor, while between 60 and 95% of the Pt was sorbed in the various mixtures, with this incomplete sorption possibly being a consequence of a slow rate of sorption (see above and Section 4.1), rather than the final expected sorption. In comparison, both Pd and Au were strongly sorbed by all of the soil mixtures, with the exception of the OB sample, for which Au was still moderately soluble (discussed in Gray, 1990a). The greater solubility of Ag, compared with Au, is entirely consistent with previous discussion on the geochemical separation of these two elements during weathering (Mann, 1984). The greater solubility of Pt, relative to Pd, is unexpected although consistent with the other experiments described in this Chapter. It suggests that if Pt and Pd were dissolved together

then Pt would be more mobile than Pd. However, it should be noted that Pd would still be depleted relative to Pt in a weathering profile if Pd is more readily dissolved.

No redissolution of Au was observed after 3 months (Figure 10), unlike the humate (Figure 6), iodide (Figure 12) or uncomplexed mixtures (Figure 14). This could be due to the suppression of biological activity or because other potentially important Au ligands, such as thiosulphate or the S-containing amino acid cysteine (Korobushkina *et al.*, 1983), are unstable in acid conditions.

Thus, the behaviour of Pt, Pd, Au and Ag in the acid/chloride solution is markedly different from that for the other ligands tested, in that:

- (i) the order of the sorption is $\text{Ag} < \text{Pt} < \text{Au} < \text{Pd}$;
- (ii) Au is completely sorbed except when in contact with the Mn-rich sample OB (as with the iodide complex), whereas for Pt, sorption is highest for the OB mixture;
- (iii) there is no redissolution of sorbed Au during the experiment.

4.2.4 Iodide complex

The iodide complex was included as part of this experiment because field studies at the Panglo deposit, near Kalgoorlie, have indicated that iodide complexation of Au may dominate over chloride in some saline groundwaters (Gray, 1990b), and such effects could also be important for Pt and Pd. Only the Pt and Au iodide complexes have been tested, due to the low solubility of Pd and Ag iodides. After 2 weeks of shaking (Figure 11), 90% or more of the Pt and Au was sorbed, except for Au contacting the Mn-rich OB sample which was poorly sorbed. This trend was also observed for Au chloride (see above), implying this to be a general phenomenon for Au halides.

After 3 months (Figure 12), the OB mixture still poorly sorbed Au. Significant amounts (10 - 50%) of the Pt and Au that were sorbed at 2 weeks in the mixtures with the Peat Moss and the soil samples 1467, 1468 and 1470 were redissolved, with even small amounts redissolved for the Std. 7 mixture. These observations of Au redissolution can be directly compared with previous work on the shaking of Au with soils 1467, 1468 and 1470, as discussed in Gray *et al.* (1990a). The redissolution was considered to be due to biological activity because it was reduced when the soil mixtures were sterilized by irradiation. This conclusion is consistent with sample MKD not showing any redissolution of Pt or Au, for, unlike the surface soil samples 1467, 1468, 1470 and Std. 7, sample MKD is derived from 44m depth and contains very little organic matter (< 0.05 %, Table 1).

The major observations for the iodide solutions are:

- (i) as in other experiments, Pt shows slow sorption kinetics;
- (ii) Au iodide is weakly sorbed when contacting the Mn rich OB material, but is strongly sorbed by the other soils;
- (iii) sorbed Pt and Au redissolves from the Peat Moss, 1467, 1468 and 1470 mixtures after 3 months, possibly because of biological production of ligands.

4.2.5 "Uncomplexed" system

Shaking diluted metal standards with the soils (Section 2.2.5) results in a initial solution in which the Pt, Pd, Au and Ag are very weakly complexed by the small amounts of chloride present (calculated to be approximately 2.5 mM, or 100 mg/L). After 2 weeks shaking of the mixtures (Figure 13), the Pd, Au and Ag were, as expected, virtually totally sorbed. As observed in the other experiments, Pt was only incompletely sorbed.

After 3 months (Figure 14), significant redissolution of the Pt, Pd and Au was observed for the mixtures with Peat Moss, 1467, 1468 and 1470 soils. Silver was only redissolved in the Peat Moss

mixture. The observed redissolution pattern was very similar to that for the iodide mixtures (Figure 12), suggesting similar mechanisms in both cases.

These results indicate a major capacity for organic-rich soils to dissolve Pt, Pd and Au and to maintain these metals in solution, presumably as a result of biological activity, when the soil is saturated with water over extended periods. In comparison, Ag remained undissolved, implying either that Ag is being precipitated in a highly insoluble form, or that the ligands are highly selective for Pt, Pd and Au. The latter hypothesis seems more likely, and is possibly a function of the high affinity of these 'soft' metals for chemically 'soft' ligands, such as those containing the sulphide (R-S⁻) group, which may be part of a number of soluble molecules released during biological activity. Previous results, for both added and *in situ* Au, supports this hypothesis (Gray *et al.* 1990a). In general, the present results suggest that in biologically active soils, the PGEs should be considered moderately mobile elements, rather than as noble metals.

In summary, the critical observations for the uncomplexed system were:

- (i) rapid sorption of Pd, Au and Ag, and the slower sorption of Pt;
- (ii) the significant redissolution of Pt, Pd and Au but, with the exception of the Peat Moss mixture, not Ag, after 3 month shaking, presumably due to release of ligands from the soil;
- (iii) the similarity in the redissolution of the Pt, Pd and Au when added in the uncomplexed form, and when added as the iodide complex.

5 SUMMARY AND CONCLUSIONS

The differing behaviours of the various metal complexes demonstrate the critical influence of the chemical complexation on the mobility of Pt and Pd within the soil profile.

Under a wide range of conditions, Pt sorbed very slowly onto the soil and regolith materials tested (Section 4). Such a result, though clearly observed in this report, is not clearly understood, though it may be due to strong binding between the Pt metal and the dissolved ligand causing kinetic inertness. The critical implication of this observation is that Pt could well have a high mobility if dissolved during weathering

Humate complexes were found to be effectively sorbed by most of the soils (Section 4.2.1), suggesting a weak interaction between PGEs and humate or a low solubility of the complex. In addition, the Peat Moss material, which only contained organic matter and quartz (Section 2.1), was least efficient at sorbing the Pt, Pd, Au and Ag, indicating poor affinity for these metals relative to other soils phases such as carbonates, Fe or Mn oxides. Such results suggest that the importance of humic material in mobility of noble metals in soil horizons is less would be commonly expected: *i.e.*, other phases such as halides, thiosulphate or amino acids would be more important than soluble humic matter in dissolving the PGEs; and solid humic matter does not sorb dissolved PGEs as efficiently as other soil phases. Note that other, smaller, phases derived from biological activity, such as amino acids, cyanide or various reduced S compounds may well be very important for dissolution of PGEs in soils

Platinum and Pd thiosulphates had a low mobility when contacting soils, possibly due to the high negative charge of the complex, or a tendency to polymerize to less soluble forms. The sorbed Pt and Pd did not redissolve after 3 months. Other work (Volume I, Chapter 3) has suggested a major affinity of thiosulphate for Pt and Pd, under laboratory conditions. However, the dissolved PGE thiosulphates could well have a low mobility in oxidized regolith and soil horizons, due to their affinity to positively charged surfaces, commonly observed for minerals such as Fe oxides.

In a chloride-rich solution, Ag and Pt were sorbed much less strongly than Au or Pd, again consistent with a high initial solubility of Pt. However, this does not necessarily imply that Pt will be more mobile than Pd in chloride-rich environments, as Pd metal is much more readily oxidized than Pt metal. Common observations of depallidation of PGE-rich materials (Volume I, Chapter 2, Section 3) infer that the higher initial solubility of Pd outweighs the greater solubility of Pt once dissolved.

The 'uncomplexed' metals were readily sorbed by the soils but after three months, a number of the 'uncomplexed' mixtures contained significant quantities of dissolved Pt, Pd and Au (but not Ag). This is possibly due to soluble species, with a high affinity for these metals, produced by biological activity. Redissolution effects were also observed for the iodide and humate mixtures. There was no observed redissolution for the sorption experiments on the organic-poor lateritic soils (Section 4.2; Figures 1-4), suggesting that this redissolution will only occur in organic-rich (> 0.2 %) soil horizons. Similar mechanisms may be conducive to PGE mobility in natural soils, and this may be an important mechanism for soil redistribution of PGEs.

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