



<http://researchspace.auckland.ac.nz>

ResearchSpace@Auckland

Copyright Statement

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage.

<http://researchspace.auckland.ac.nz/feedback>

General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the Library Thesis Consent Form.

**SURFACE ANALYSIS OF PARTICULATE EMISSIONS
BEFORE AND AFTER ATMOSPHERIC AGING**

by
Geoffrey Stephen Henshaw

A thesis submitted to
the University of Auckland
in fulfilment of the
requirements for the degree of
Doctor of Philosophy in Chemistry.

Auckland

December 1992.

ABSTRACT

The reactions and transformations of atmospheric primary particles have been studied using the surface analysis techniques of X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Scanning Electron Microscopy (SEM) and Secondary Ion Mass Spectrometry (SIMS).

Particles emitted from a steel mill were studied at their point of emission, during transport through the atmosphere and after deposition. The mill was located in a coastal region removed from other major industrial particle sources which made the identification of the mill particulate emissions possible in ambient samples. The mill utilizes indigenous titanomagnetite ironsand and coal as the raw materials. There is evidence of the surface enrichment of volatile trace elements such as Zn, S, Na, K and P from the raw materials in the particulate emissions.

Particle samples were collected from sites within the mill which represented different stages in the iron-making process, including the rotary kilns, electric melting furnaces and the vanadium recovery plant. This established an inventory of particulate emissions.

Mill sourced particles were then identified and studied in air samples collected downwind of the mill on silver-coated nucleopore filters. AES and SIMS depth profiling studies indicated the mill particles became surface enriched in sea salt components such as S, predominately as sulfate, Cl⁻ and Na⁺ after atmospheric aging. This was attributed to their coagulation with

the marine derived ambient aerosol. SIMS ion imaging and mass spectral analysis suggested a characteristic "fingerprint" of the mill emissions could be distinguished in the ambient aerosol up to 8 km downwind of the mill.

An experimental rig was constructed to model the interaction between the mill particles and the natural marine aerosol. A bubble nebuliser was developed to produce an artificial sea salt aerosol which was reacted with a metal powder in the fluidised bed of the rig. The metal powder was then aged under controlled relative humidity (RH) conditions. It was shown that an iron powder, after reaction and aging at 75 % RH, developed an aqueous surface layer which quickly led to electrochemical corrosion, dissolution and oxidation of the particle surface.

Evidence of this corrosion of metal particles occurring in the environment was found in a SEM-EDX study of the mill particles deposited on pine needles downwind of the mill. It was argued that these reactions would increase the bio-availability of the particle components.

A model which incorporated these observations was developed to describe the morphogenesis of atmospheric primary particles during aging in the New Zealand environment.

XPS was used to study ambient aerosols deposited on both botanical and artificial passive sampling surfaces. Plant leaves were shown to be excellent collectors of particulate material and were suited to analysis by XPS. Site differences in the atmospheric aerosol load and composition were detected on vine leaves located on a hill side (high NaCl) and at a roadside (high sulfate and silicates) in a rural area. Zn and Fe species were detected by XPS on pine needles up to 2 km downwind of the steel mill.

ACKNOWLEDGEMENTS

Firstly, I would like to thank my supervisor Dr Jim Metson for his warm enthusiasm, guidance and occasional humour.

I would also like to thank NZ Steel Ltd for their financial support and the staff in Technical Services, particularly Jeremy Batchelor, for their co-operation and interest in this work.

I am grateful for the University Grants Committee Postgraduate Scholarship which enabled me to undertake this project.

A number of people have been involved in this work at a technical level. Thanks to David Stringer for the SEM training and computer wizardry, Paul Van der Heide and Dr Margaret Hyland for the SIMS analysis, and Kevin McMahon for the impactor sampler. Thanks also to Michael Brajkovich, winemaker at Kumeu River Winery, for allowing sampling sites to be established within the vineyard.

To my colleagues, Paul Van der Heide and Alistair Gillespie, I am grateful for your friendships and help over the years and wish you well for the future.

There have been special friends with whom I have felt a kinship of spirit and mind and I wish acknowledge your support in this endeavour; Doug Cleverly with his wine, woman and crystalline emotion, Alan Cathro and his joie de vivre, Niall Parkes and Helen Moroney, my whanau, kia kaha. To my friends at Ponsonby Baptist Church, my turangawaewae, our lives are interwoven and we walk the journey together until Christ's return.

I wish to thank my family, Graeme, Sarah, Andrew, Joanne, Derek, Heyley and Alisdair for their encouragement, laughter and love.

Finally, my wife to be, Angela Kay Mollard. I have finished this despite your welcome diversion and now we begin a new life together. I thank you for your patience, fiestiness and unfathomable love. I have uncovered much over the course of this work but only now am I beginning to learn.



TABLE OF CONTENTS

TITLE	i
ABSTRACT	ii
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	v
LIST OF FIGURES	x
LIST OF TABLES	xv
GLOSSARY OF SYMBOLS	xvi

CHAPTER ONE INTRODUCTION

1.1	Particles in the atmosphere	1
1.1.1	The formation and physical properties of atmospheric particles . . .	2
1.1.2	Particle motion and deposition	7
1.1.3	The chemical composition of atmospheric particles	9
1.1.4	Heterogeneous chemistry of the atmospheric aerosol	12
1.2	Surface analysis techniques	15
1.2.1	X-ray Photoelectron Spectroscopy	15
1.2.2	Auger Electron Spectroscopy	17
1.2.3	The electron spectrometer - experimental conditions	20
1.2.4	Secondary Mass Spectrometry (SIMS)	22
1.2.5	The SIMS Instrument - experimental conditions	24

1.2.6	Conclusions and future prospects	25
1.3	Surface analysis in atmospheric environmental studies	27
1.3.1	Surface studies of the natural aerosol	28
1.3.2	Surface studies of primary particles from anthropogenic sources	29
1.4	Toxicological behaviour of aerosols	32
1.4.1	Toxicological studies of SO ₂ -aerosol mixtures	32
1.4.2	The effects of aerosols on vegetation	33
1.5	Aims of this study	37

CHAPTER TWO CHARACTERISATION OF PARTICULATE EMISSIONS FROM A STEEL MILL

2.1	Introduction	38
2.1.1	Studies of particles produced by high temperature industrial processes	39
2.1.2	The steel mill	42
2.1.1.1	<i>Rotary kiln</i>	44
2.1.1.2	<i>Melting furnace</i>	45
2.1.1.3	<i>Vanadium recovery plant</i>	45
2.2	Experimental methods	46
2.3	Results and discussion	48
2.3.1	Rotary kiln stack	48
2.3.1.1	<i>SEM-EDX analysis</i>	48
2.3.1.2	<i>XPS analysis</i>	54
2.3.2	Slag tap at the melting furnace	57
2.3.2.1	<i>SEM-EDX analysis</i>	57
2.3.2.2	<i>XPS analysis</i>	62
2.3.2.3	<i>AES analysis</i>	66
2.3.2.4	<i>SIMS analysis</i>	70
2.3.2.5	<i>Summary</i>	75

2.3.3	Vanadium recovery unit (VRU)	76
2.3.3.1	<i>SEM-EDX analysis</i>	76
2.3.3.2	<i>XPS analysis</i>	76
2.3.3.3	<i>AES analysis</i>	81
2.3.3.4	<i>Summary</i>	81
2.4	Conclusions	83

CHAPTER THREE SURFACE STUDIES OF MILL PARTICLES AFTER ATMOSPHERIC AGING

3.1	Introduction	84
3.2	Experimental methods	86
3.2.1	Sample collection and preparation	86
3.2.2	Instrumental methods	86
3.3	Results and discussion	89
3.3.1	AES analysis of individual mill particles - preliminary findings	89
3.3.2	AES depth profiling of individual mill particles - case studies . . .	92
3.3.2.1	<i>Fe oxide particle with a surface layer of marine components</i>	93
3.3.2.2	<i>Ca and Fe particle</i>	93
3.3.2.3	<i>Surface oxidised Fe-Si alloy particle</i>	96
3.3.2.4	<i>Vanadium particle</i>	101
3.3.2.4	<i>Summary of AES single particle study</i>	104
3.3.3	SIMS analysis of 150 μm diameter filter areas	105
3.3.3.1	<i>Mass spectra</i>	105
3.3.3.2	<i>Depth profiles</i>	108
3.3.3.3	<i>Ion images</i>	108
3.3.3.4	<i>Summary of the SIMS analysis</i>	116
3.4	Conclusions	118

CHAPTER FOUR LABORATORY STUDY OF METAL PARTICLE AND MARINE AEROSOL INTERACTIONS

4.1	Introduction	120
4.2	Experimental	121
4.3	Results and discussion	124
4.3.1	The artificial marine aerosol	124
4.3.2	The iron powder	126
4.3.3	Iron particle-marine aerosol interactions	132
4.3.3.1	<i>Iron particles aged at 0% relative humidity</i>	132
4.3.3.2	<i>Iron particles aged at 75% relative humidity</i>	137
4.4	Conclusions	143

CHAPTER FIVE SURFACE ANALYTICAL STUDY OF PASSIVE AIR SAMPLERS

5.1	Introduction	144
5.2	Experimental methods	146
5.2.1	Sampling sites	146
5.2.2	Artificial passive samplers	149
5.2.3	Biological samples and sample preparation	149
5.2.4	Analysis techniques	153
5.3	Results and discussion	154
5.3.1	Kumeu passive samplers	154
5.3.1.1	<i>XPS results</i>	154
5.3.1.2	<i>SEM-EDX results</i>	164
5.3.1.3	<i>Summary of results from the analysis of the Kumeu passive air samplers</i>	167
5.3.2	Glenbrook sites	169
5.3.2.1	<i>XPS analysis of the artificial sampling substrates</i>	169
5.3.2.2	<i>Summary of results from the analysis of the Glenbrook</i>	

	<i>artificial air samplers</i>	175
5.3.2.3	<i>Kiwifruit skins</i>	175
5.3.2.4	<i>Pine needles</i>	177
5.3.2.5	<i>Summary of results from the analysis of Glenbrook biological samplers</i>	186
5.4	Conclusions	187

CHAPTER SIX CONCLUDING REMARKS

6.1	Model for the atmospheric aging of primary particles in the New Zealand environment	190
6.2	Future work	193

APPENDICES

Appendix A	SIMS quantification by the RSF method	195
Appendix B	AES single particle spectra	197

LIST OF REFERENCES	214
-------------------------------------	-----

LIST OF FIGURES

Figure		Page
1.1	Schematic of the atmospheric size distribution showing the three modes and their main sources and sinks.	4
1.2	Schematic diagram showing mechanisms of aerosol formation in the atmosphere.	6
1.3	Schematic picture of an aged atmospheric particle.	11
1.4	Schematic diagram of the Auger emission process.	18
1.5	Diagram of the Kratos XSAM 800 electron spectrometer.	21
1.6	Schematic diagram of the Cameca IMS 3f ion microscope.	24
1.7	Stylised diagram of the uptake resistances through a leaf for atmospheric species.	35
2.1	Schematic diagram of ash formation and behaviour in coal combustion.	40
2.2	Map of the Glenbrook environs showing the position of the steel mill.	43
2.3	SEM micrograph of the rotary kiln particles on the glassfibre collection filter.	49
2.4	XRD pattern of the rotary kiln sample.	51
2.5	Graph showing the fractional removal efficiency of particulate emission control equipment as a function of particle size.	53
2.6	XPS spectrum of the rotary kiln particles.	55
2.7	SEM micrographs of the slag tap particles.	58
2.8	SEM micrograph of a ruptured slag tap particle.	59
2.9	SEM micrographs of slag tap particle crystallinity	60
2.10	SIMS ion image of slag tap particles.	61

2.11	XRD patterns of the slag tap particles.	63
2.12	S 2p and Si 2p XPS regions of the slag tap particles.	65
2.13	AES spectra of sulfur compounds showing the S LMM region.	67
2.14	XPS S 2p spectra of Na ₂ SO ₄ .	68
2.15	AES S LMM spectra of individual slag tap particles.	69
2.16	AES depth profile of a slag tap particle.	71
2.17	SIMS relative elemental concentrations in slag tap particles.	72
2.18	²⁷ Al ⁺ and ⁴⁸ Ti ⁺ ion images of a slag tap particle.	73
2.19	⁶⁴ Zn ⁺ ion image of a slag tap particle.	74
2.20	SEM micrograph of the VRU particles.	77
2.21	XPS spectrum of the VRU particles.	79
2.22	P 2p region of the VRU particles.	79
2.23	AES spectra of an agglomerated VRU particle.	82
3.1	Beam geometry around a spherical particle in the Kratos XSAM spectrometer.	80 87
3.2	Diagram showing etch rates as a function of ion beam angle of incidence.	87
3.3	AES spectra of a mill particle collected downwind of the mill.	90
3.4	AES spectrum of a Zn particle collected downwind of the mill.	91
3.5	AES spectrum of a 5 μm particle collected downwind of the mill.	94
3.6	AES depth profile of the 5 μm particle.	94
3.7	AES spectrum of a 16 μm particle collected downwind of the mill.	95
3.8	AES depth profile of the 16 μm particle.	95
3.9	AES spectrum of a 6 μm particle collected downwind of the mill.	98
3.10	AES spectrum of particle after etching.	98
3.11	AES depth profile of the 6 μm particle.	99
3.12	AES Fe LMM spectra of the 6 μm particle.	100
3.13	AES spectrum of a 8 μm particle collected downwind of the mill.	102
3.14	AES depth profile of the 8 μm particle.	102

3.15	SIMS elemental concentrations of the 2 km sample.	106
3.16	SIMS elemental concentrations of the 8 km sample.	106
3.17	SIMS depth profiles of the 2 km filter.	107
3.18	SIMS ion images of the downwind sample.	109-111
3.19	SIMS ion images of the upwind sample.	112-114
4.1	Nebuliser for the production of a sea salt aerosol.	122
4.2	Mixing rig for the metal powder and sea salt aerosol.	123
4.3	SEM micrograph of the sea salt particles produced by the nebuliser.	125
4.4	XPS spectrum of the sea salt particles produced by the nebuliser.	125
4.5	SEM micrograph of the BDH Fe powder.	127
4.6	XPS spectrum of the BDH Fe powder.	127
4.7	C 1s region of the BDH Fe powder.	128
4.8	Fe 2p _{3/2} region of the BDH Fe powder.	128
4.9	O 1s region of the BDH Fe powder.	130
4.10	Fe 2p depth profile of the BDH Fe powder.	131
4.11	O 1s depth profile of the BDH FE powder.	131
4.12	SEM micrographs of the Fe powder after reaction and aging in a desiccator.	133
4.13	XPS spectrum of the Fe powder after reaction and aging in a desiccator.	134
4.14	Fe 2p _{3/2} region of the Fe powder after reaction and aging in a desiccator.	135
4.15	O 1s region of the Fe powder after reaction and aging in a desiccator.	135
4.16	Fe 2p depth profile of the Fe powder after reaction and aging in a desiccator.	136
4.17	SEM micrographs of the Fe powder after reaction and aging at 75 % relative humidity.	138
4.18	Fe 2p _{3/2} region of the Fe powder after reaction and aging at	

	75 % relative humidity.	139
4.19	O 1s region of the Fe powder after reaction and aging at 75 % relative humidity.	139
4.20	Fe 2p depth profile of the Fe powder after reaction and aging at 75% relative humidity.	140
4.21	O 1s depth profile of the Fe powder after reaction and aging at 75 % relative humidity.	140
4.22	Schematic diagram of the corrosion of the Fe powder by Cl ⁻ at 75 % relative humidity.	142
5.1	Map of the Kumeu region showing sampling sites.	147
5.2	Map of the Glenbrook region showing sampling sites.	148
5.3	Passive air sampling device.	150
5.4	XPS spectra of the sampling substrates before atmospheric exposure.	151
5.5	Cu 2p region of the Kumeu copper substrates.	156
5.6	XPS spectra of the Kumeu silver substrates.	157
5.7	XPS spectra of the Kumeu copper substrates.	158
5.8	XPS spectra of the Kumeu graphite substrates.	160
5.9	XPS spectra of the Kumeu leaf samples.	163
5.10	SEM micrographs and x-ray analysis of crystalline features on the silver substrate from Kumeu site 3.	165
5.11	SEM micrographs and x-ray analysis of particles on the surface of the silver substrate from Kumeu site 3.	166
5.12	C 1s regions of the silver and copper substrates from the Glenbrook site 3.	172
5.13	Graph of XPS atomic concentrations versus etch time for the silver substrate from Glenbrook site 4.	173
5.14	XPS spectra of stained and unstained regions on kiwifruit.	176
5.15	EDX maps of the stained kiwifruit skin.	178
5.16	SEM micrograph of a mill particle on a kiwifruit skin.	179

5.17	SEM micrographs of pine needles collected 2 km from the mill.	181
5.18	SEM micrographs of pine needles collected 5 km from the mill.	182
5.19	SEM micrograph and x-ray analysis of mill particles on the pine needles.	183
5.20	SEM micrograph of a particle, on a pine needle, exhibiting corrosion morphology.	184
6.1	Chemical structure and evolution of a mill particle at emission, during atmospheric transport and after a period of aging in the atmosphere.	191

LIST OF TABLES

Table		Page
1.1	Deliquescence points of some salts found in the atmospheric aerosol particles.	2
1.2	Mean atmospheric lifetimes and travel distances of atmospheric aerosol particles.	9
1.3	Survey of surface analysis techniques.	26
2.1	Sampling methods and conditions at the steel mill.	46
2.2	XPS and SEM-EDX analyses of the rotary kiln particles.	50
2.3	XRD data for the rotary kiln particles.	52
2.4	Auger parameters of Zn compounds.	56
2.5	XPS and SEM-EDX analyses of the slag tap particles.	64
2.6	XPS and SEM-EDX analyses of the VRU particles.	78
2.7	Auger parameters for sodium compounds.	81
4.1	XPS composition of the laboratory sea salt aerosol.	124
5.1	Meteorological data for the Kumeu region during the sampling period.	146
5.2	XPS analysis of the Kumeu substrate surfaces.	155
5.3	Na:Cl ratios for the Kumeu substrates.	161
5.4	N 1s binding energies for nitrogen species.	162
5.5	Description of the atmospheric aerosol at the Kumeu sites.	168
5.6	XPS analysis of the Glenbrook substrate surfaces.	170
5.7	Na:Cl ratios for the Glenbrook sites.	171
5.8	Silver Auger parameters for various silver compounds.	174
5.9	XPS concentrations of elements on stained and unstained regions of a kiwifruit skin.	176
5.10	XPS concentrations of elements on pine needles collected from sites downwind of the mill.	180

LIST OF TABLES

Table		Page
1.1	Deliquescence points of some salts found in the atmospheric aerosol particles.	2
1.2	Mean atmospheric lifetimes and travel distances of atmospheric aerosol particles.	9
1.3	Survey of surface analysis techniques.	26
2.1	Sampling methods and conditions at the steel mill.	46
2.2	XPS and SEM-EDX analyses of the rotary kiln particles.	50
2.3	XRD data for the rotary kiln particles.	52
2.4	Auger parameters of Zn compounds.	56
2.5	XPS and SEM-EDX analyses of the slag tap particles.	64
2.6	XPS and SEM-EDX analyses of the VRU particles.	78
2.7	Auger parameters for sodium compounds.	81
4.1	XPS composition of the laboratory sea salt aerosol.	124
5.1	Meteorological data for the Kumeu region during the sampling period.	146
5.2	XPS analysis of the Kumeu substrate surfaces.	155
5.3	Na:Cl ratios for the Kumeu substrates.	161
5.4	N 1s binding energies for nitrogen species.	162
5.5	Description of the atmospheric aerosol at the Kumeu sites.	168
5.6	XPS analysis of the Glenbrook substrate surfaces.	170
5.7	Na:Cl ratios for the Glenbrook sites.	171
5.8	Silver Auger parameters for various silver compounds.	174
5.9	XPS concentrations of elements on stained and unstained regions of a kiwifruit skin.	176
5.10	XPS concentrations of elements on pine needles collected from sites downwind of the mill.	180

GLOSSARY OF SYMBOLS

Symbol	Definition	Units
<i>A</i>	Isotope abundance	
<i>C</i>	Slip correction factor for particle velocity	
<i>d</i>	Overlayer thickness	Å
<i>D</i>	Particle diameter	μm
<i>D</i>	Fick's diffusion co-efficient	
<i>D*</i>	Critical diameter for growth through homogeneous nucleation	μm
<i>D_a</i>	Aerodynamic diameter	μm
<i>E_b</i>	Binding energy	eV
<i>E_k</i>	Kinetic energy	eV
<i>F_r</i>	Resistance force acting on a particle due to laminar flow of air	N
<i>hν</i>	Photon energy	eV
<i>I</i>	Intensity	counts per sec (cps)
<i>j</i>	Total angular momentum quantum number	
<i>J</i>	Flux of particles	cm ⁻² s ⁻¹
<i>l</i>	Particle mean free path through the air	μm
<i>m</i>	Atomic mass	amu
<i>N_a</i>	Number concentration	cm ⁻³
<i>r</i>	Uptake resistance	s.cm ⁻¹
<i>s</i>	Spin orbital quantum number	
<i>z</i>	Atomic charge	

GREEK

α	Auger parameter	eV
η	Gas viscosity	$\text{m.l}^{-1}.\text{s}^{-1}$
λ	Inelastic mean free path of an electron through a solid	Å
ρ	Density	g.cm^{-3}
τ	Atmospheric residence time	day
ϕ	Spectrometer work function	eV

ABBREVIATIONS

AES	Auger Electron Spectroscopy
FWHM	Full Width Half Maximum
LAMMA	Laser Microprobe Mass Analysis
RH	Relative Humidity
RSF	Relative Sensitivity Factor
SEM-EDX	Scanning Electron Microscopy with Energy Dispersive X-ray analysis.
SIMS	Secondary Ion Mass Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
UHV	Ultra High Vacuum