

Platinum stable isotope fractionation and adsorption on marine
ferromanganese oxide substrates

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Appendices

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Appendix A:

Chapter 2 Method development

A.1 SRM nodule standard and mean ferromanganese sediment element concentration.

Table A.1 Mean element concentration ($\mu\text{g/g}$) of three standard reference materials (SRM): US Geological Survey Manganese Nodule, USGS Nod-A-1, and USGS Nod-P-1, and Geological Survey of Japan (GSJ) Manganese Nodule, JMn-1, and a selection of the samples of ferromanganese crust and nodules from various ocean basins. Elements with no concentration data are left blank.

Element		Nod-A1	Nod-P1	JMn-1	Southern	Atlantic	Indian	N Pacific
		Mean	Mean	Mean	Mean	Mean	Mean	Mean
Fe/Mn	Iron/Manganese	0.61	0.20	0.39	0.94	1.44	1.31	0.74
Ag	Silver	0.17	0.21			0.20	0.37	0.10
Al	Aluminium	21700	24600			22000	18300	10100
As	Arsenic	310	86	76	226	308	207	389
Au	Gold	0.01	0.01	0.00		0.01	0.02	0.06
B	Boron	120	95	138		257	287	178
Ba	Barium	1666	3039	1642	1034	1556	1533	1938
Be	Beryllium	6	5	8		9	7	6
Bi	Bismuth	10	6	4	9	19	30	42
Br	Bromine	41	30	34		36	54	28
C	Carbon			905				
C(t)	Carbon total			905				

Table A.1. continued

Element		Nod-A1	Nod-P1	JMn-1	Southern	Atlantic	Indian	N Pacific
		Mean	Mean	Mean	Mean	Mean	Mean	Mean
Ca	Calcium	111917	22400			40300	22700	40300
Cd	Cadmium	7	22	16	4	4	4	4
Ce	Cerium	731	302	278	1166	1392	1469	1311
Cl	Chlorine							
Cr	Chromium	32	17	25	3205	47	22	28
Co	Cobalt	3305	2258	1721	4416	3608	3291	6655
Cs	Caesium	1	2	1			5	4
Cu	Copper	1181	11470	11212	885	861	1105	982
Dy	Dysprosium	23	27	28	40	47	56	59
Er	Erbium	13	13	14	20	28	29	31
Eu	Europium	5	8	7	11	12	13	12
F	Flourine			7430				
Fe	Iron	122144	58900	100283	168916	209000	223000	168000
Ga	Gallium	6	28	36		15	16	18
Gd	Gadollinium	26	29	29	51	58	67	56
Ge	Germanium		1	2		1	1	
Hf	Hafnium	5	4	6	9	9	10	9

Table A.1 continued

Element		Nod-A1	Nod-P1	JMn-1	Southern	Atlantic	Indian	N Pacific
		Mean	Mean	Mean	Mean	Mean	Mean	Mean
Hg	Mercury					0.09	0.04	0.01
Ho	Holmium	5	5	6		10	11	11
I	Iodine	48	31					
In	Indium			0.27		0.18	0.26	1
Ir	Iridium	0.02	0.01	0.29	0.01	0.01	0.01	0.01
K	Potassium	4945	10000			5400	6300	5400
La	Lanthanum	117	105	123	216	272	290	338
Li	Lithium	76	141	71		33	8	3
Lu	Lutetium	2	2	2	2	4	4	4
Mg	Magnesium	33805	20300			15800	12500	11000
Mn	Manganese	198777	296000	254022	179184	145000	170000	228000
Mo	Molybdenum	430	739	316	394	409	392	463
Na	Sodium	8660	17100			12600	15500	16300
Nb	Niobium	43	21	28	62	51	61	54
Nd	Neodymium	95	124	129	209	243	259	255
Ni	Nickel	6630	13500	12561	4179	2581	2563	4216
Os	Osmium			0.00		0.00	0.00	0.00

Table A.1 continued

Element		Nod-A1	Nod-P1	JMn-1	Southern	Atlantic	Indian	N Pacific
		Mean	Mean	Mean	Mean	Mean	Mean	Mean
P	Phosphorus	6715	2060			7500	3800	9700
Pb	Lead	741	517	441	1218	1238	1371	1636
Pd	Palladium	0.47	0.48	0.00		0.01	0.02	0.00
Pr	Praseodymium	25	32	31		64	66	61
Pt	Platinum	0.52	0.12	0.06	0.22	0.57	0.21	0.48
Rb	Rubidium	10	27	12		15	16	14
Re	Rhenium	0.00	0.00	0.00				
Rh	Rhodium	0.07	0.11	0.95		0.04	0.02	0.02
Ru	Ruthenium	0.02	0.01	0.01		0.02	0.02	0.02
S	Sulfur	3350	1000	940				
S(t)	Sulfur total			1080				
Sb	Antimony	34	53	37	18	51	40	41
Sc	Scandium	14	10	13		16	13	7
Se	Selenium	4	4	1		0.44	2	3
Si	Silicon	17400	58500			52100	68200	40400
Sm	Samarium	21	30	29	47	56	61	51
Sn	Tin	3	2	5		8	10	13

Table A.1 continued

Element		Nod-A1	Nod-P1	JMn-1	Southern	Atlantic	Indian	N Pacific
		Mean	Mean	Mean	Mean	Mean	Mean	Mean
Sr	Strontium	1732	673	784		1262	1201	1513
Ta	Tantalum	1	0.33	1	1	1	1	1
Tb	Terbium	4	5	5		9	10	9
Te	Tellurium	31	5	4		43	31	60
Th	Thorium	24	17	13	84	52	56	12
Ti	Titanium	2568	2720			9200	8800	11600
Tl	Thallium	114	178	135	103	104	95	160
Tm	Thulium	2	2	2		4	4	5
U	Uranium	7	4	5	10	11	10	12
V	Vanadium	735	541	426	598	849	634	642
W	Tungsten	87	58	41	69	79	80	89
Y	Yttrium	124	92	110	122	181	178	222
Yb	Ytterbium	14	13	14	17	24	25	29
Zn	Zinc	665	1638	1067	663	614	531	669
Zr	Zirconium	326	289	362	614	362	535	559

The standard reference material values are from Jochum et al., 2007, the Southern Ocean sample (U1335B) concentration data are from A. Plant, 2015, MSc thesis, and all other samples from Hein (unpublished).

A.2 Synthetic standard concentration

A synthetic standard was prepared based on the concentration of the major constituents (Fe, Mn, Mg, Ca, Ni, Co, Cu) of two of the SRM (USGS Nod-A-1 and USGS Nod-P-1). The GeoRem concentration (Jochum et al., 2007) value of Pt, 0.52 $\mu\text{g/g}$, was taken as the platinum concentration. The concentration of the major constituents of the two nodule standards are normalised to 0.15 $\mu\text{g/g}$ platinum, which was the desired end concentration of platinum. The mean normalised concentration of the two SRM are then used for the purposes of preparing the synthetic standard. Due to the low detection limit of the Element2 ICP-MS and MC-ICP-MS the major constituent concentrations can be scaled down and still result in an efficient standard, therefore, all majors were divided by 5.

The standard was prepared by combining aliquots of each aqueous single element certified reference material (CRM) and the Specpure® Precious Metals in a Savillex beaker and evaporated. The multi element standard was re-dissolved in 11 M HCl to convert all to chloride form and evaporated again. The multi element standard was then taken up in 0.5 M optima HCl to produce a 100 ng/mL solution ready for use.

Table A.2 Synthetic standard concentration

Element	Min. values from GeoRem		Normalised to 0.15µg/g Pt		Nod-A-1 & Nod-P-1 average (µg/g)	CRM (1000µg/g) /5 (scaler) (mL)	Solution prepared (mL)
	Nod-A-1 (µg/g)	Nod-P-1 (µg/g)	Nod-A-1 (µg/g)	Nod-P-1 (µg/g)			
Fe	110000	58000	31731	72500	52115	10.42	10.00
Mn	185000	293000	53365	366250	209808	41.96	40.00
Mg	28000	20000	8077	25000	16538	3.31	3.00
Ca	110000	22000	31731	27500	29615	5.92	6.00
Ni	7000	13600	2019	17000	9510	1.90	2.00
Co	3000	2300	865	2875	1870	0.37	0.50
Cu	1100	11500	317	14375	7346	1.47	1.50
Pt*	0.52	0.12					30.00

All single element aqueous certified reference materials (CRM) are commercial available solutions, with the exception of the platinum solution. The platinum solution used in the synthetic standard was the double spiked 60 ng/mL IRMM-010 solution (chapter 2). The minimum values are from GeoRem, Jochum et al., 2007.

A.3 Reagent grade and acid distillation protocols

To minimise the possibility of contamination from the reagents used in sample digestion and separation of platinum from the sample matrix, ultrapure reagents were used, with the exception of HCl and HNO₃. Due to the volume of HCl and HNO₃ that was required for this study, testing was undertaken on ‘lower’ grades and the ultrapure grades of HCl and HNO₃ to ensure that their platinum concentration, along with other metals, were low enough to not raise any potential contamination issues. Three grades of HCl and HNO₃ were analysed on the Element2 ICP-MS:

- 1) Once sub-boiled grade acid: analytical grade HCl (1 x sub-boiled HCl) and HNO₃ (1 x sub-boiled HNO₃) distilled in a Teflon still and a quartz still, respectively, in the ultra-clean laboratory at VUW (figure A.3). The acids densities were monitored after ca. 500mL and ca. 250mL for HCl and HNO₃, respectively, to ensure the desired concentration was attained.
- 2) Twice sub-boiled grade acid: 1 x sub-boiled HCl and HNO₃ are distilled again in a Teflon still and quartz still, respectively, which were solely used for the production of twice sub-boiled acids. Hereafter referred to as 2 x sub-boiled HCl and 2 x sub-boiled HNO₃. Similar to the 1 x sub-boiled acids, the density of the 2 x sub-boiled acids are monitored to maintain concentration.
- 3) Ultra-pure grade acid (optima), both HCl and HNO₃, with certified metal impurity levels > 100 pg/g. The optima acids used in this study have been purchased from Fisher Scientific (Optima) and SEASTARTM (Baseline).

The platinum concentration, in all grades, was below detection limit for the Element2 ICP-MS, with the exception of 2 x sub-boiled HNO₃, which had a concentration of 10 pg/g, however, the RSDs for that analysis are high at 17%. Due to the high volumes of acids required for the digestion of samples and platinum separation by column chemistry the 1 x sub-boiled HCl and HNO₃ acids were used for all steps of chemical processing.

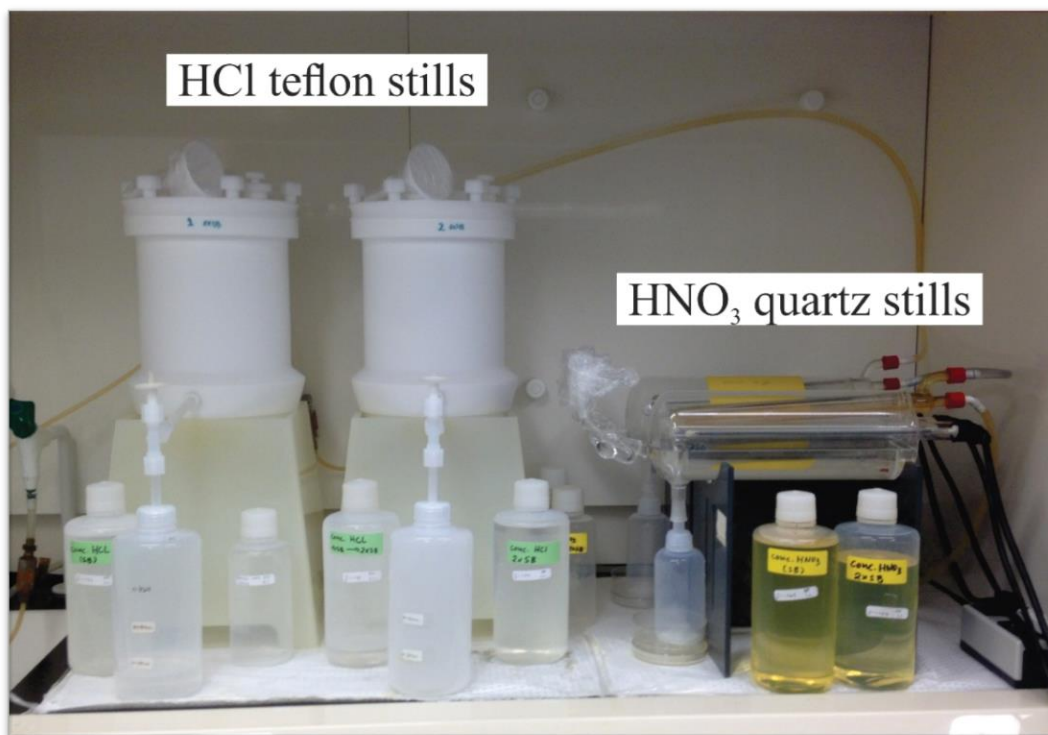


Figure A.3 Acid distillation stills within the ultraclean laboratory, VUW. The HCl Teflon stills on the right and the HNO₃ quartz still to the left. All acids that are distilled are collected into Teflon (PFA) bottles.

All final sample preparation for analysis on the Agilent ICP-MS or the Element2 ICP-MS was conducted in 2 x sub-boiled HCl, unless otherwise stated. The final preparation of the platinum cut solution for isotope analysis by MC-ICP-MS were performed in optima HCl, along with all standards for both ICP-MS and MC-ICP-MS. Final steps of beaker/bottle/centrifuge cleaning were completed with optima grade acids (see. Appendix A.4). All acid dilutions were made with Milli Q water and their molarities checked using a density meter.

Table A.3 Elemental concentration data (ng/g) on the three grades of HCl and HNO₃ acids and for the Milli Q water dispenser, located in the ultraclean laboratory, VUW. All data was collected on the Element2 ICP-MS.

Element	<u>HCl 1xsub-boiled</u>		<u>HCl 2xsub-boiled</u>		<u>HCl optima</u>		<u>HNO₃ 1xsub-boiled</u>		<u>HNO₃ 2xsub-boiled</u>		<u>HNO₃ optima</u>		<u>MQ H₂O</u>	
	ng/g	RSD	ng/g	RSD	ng/g	RSD	ng/g	RSD	ng/g	RSD	ng/g	RSD	ng/g	RSD
Na													0.02	0.96
Mg													0.17	0.78
Al													0.10	0.82
Si													n/a	n/a
Ca													0.06	0.96
Ti	0.09	23.67	0.07	35.11	0.10	12.06	0.02	47.98	0.13	15.15			0.01	3.23
V	0.01	4.17	0.01	5.15	0.01	7.15	0.01	7.53	0.04	2.89	0.01	8.35		
Cr														
Mn													0.00	4.55
Fe														
Co													0.00	20.25
Ni													0.07	1.78
Cu													0.00	5.05
Zn	0.05	23.49	0.31	0.70	0.27	3.65	0.49	0.68	0.57	2.13	0.30	2.63	0.03	1.31
Rb	0.00	11.62	0.01	50.14	0.00	6.60	0.00	6.69	0.01	4.68	0.00	0.43	0.00	12.52
Sr	0.02	1.61	0.23	1.29	0.02	3.09	0.05	2.06	0.03	1.17	0.02	2.06	0.00	6.75
Y									0.00	2.19				
90Zr	0.00	10.72	0.36	1.47			0.09	2.87	0.67	0.53	0.06	1.05	0.00	2.30
91Zr			0.36	1.93			0.08	2.56	0.66	1.80	0.05	3.80	0.00	4.64
Mo	0.03	3.05	0.05	2.66			0.00	16.38	0.01	8.56	0.01	5.90	0.00	2.88
Ru	0.00	27.24	0.00	1.66							0.00	9.02	0.00	120.45
Rh													0.00	105.34

Table A.3 continued

Element	<u>HCl 1xsub-boiled</u>		<u>HCl 2xsub-boiled</u>		<u>HCl optima</u>		<u>HNO₃ 1xsub-boiled</u>		<u>HNO₃ 2xsub-boiled</u>		<u>HNO₃ optima</u>		<u>MQ H₂O</u>	
	ng/g	RSD	ng/g	RSD	ng/g	RSD	ng/g	RSD	ng/g	RSD	ng/g	RSD	ng/g	RSD
Pd	0.00	20.81												
Ag			0.01	5.80			0.02	3.51	0.01	2.43	0.00	29.38	0.00	77.36
Ba	0.04	1.28	0.05	2.09	0.01	1.59	0.05	1.29	0.06	1.58	0.19	1.62	0.00	7.86
La	0.00	5.36	0.00	6.66			0.00	1.90	0.03	0.60			0.00	52.11
Ce	0.00	3.36	0.00	1.06			0.01	1.75	0.16	0.81	0.00	5.91	0.00	34.15
Gd									0.00	5.71				
Hf			0.01	9.12			0.00	8.43	0.01	1.41			0.00	10.75
Ta	0.00	23.17											0.01	8.00
W	0.05	2.78	0.01	18.61			0.10	1.39	0.29	1.53	0.06	4.02	0.02	2.13
Re														
Os													0.00	39.63
Ir									0.00	7.79			0.00	26.17
Pt									0.01	17.08				
Au													0.00	4.48
Tl	0.00	10.43											0.00	2.21
Pb	0.01	1.64	2.25	0.72	0.00	74.88	0.04	1.14	0.08	0.34	0.01	1.88	0.00	5.03

A blank space indicated below detection limit, n/a indicates an element not measured for that analyte.

A.4 Labware cleaning procedures

All labware used in this study was subjected to acid cleaning with the degree of cleaning changing depending on the end use of the labware in question. Below is a list of the variation to the cleaning procedures followed for the different types of labware used within this study:

Savillex beakers (PFA) – All beakers (7, 23, 60, and 90 mL) screw top Teflon beakers were used throughout all samples digestions and chemical separation processes. The beakers are wiped inside and out with methanol followed by rinsing with Milli Q three times. The beakers are then placed in a large glass beaker, 3 – 4 L capacity, and are completely submerged in analytical grade 6.5 – 7 M HCl and are placed on a hotplate for 24 hours at 80 °C. The HCl is then decanted and the beakers are rinsed with Milli Q water three times and re-submerged in analytical grade 7 – 8 M HNO₃. The beakers are placed back on the hotplate at 80 °C for a further 24 hours. The HNO₃ is decanted and the beakers are rinsed with Milli Q water three times, ensuring that the excess Milli Q water is removed following the final rinse. Freshly prepared optima aqua regia (3:1 optima HNO₃: optima HCl) is added to each beaker, ensuring that the base of each beaker is covered. The beakers are tightly sealed and placed on a hotplate to reflux at 120 °C for a minimum of 24 hours. The beakers are removed from the hotplate and allowed to cool. The optima aqua regia is then discarded and the beakers are individually rinsed three times with Milli Q water, ensuring that the excess Milli Q water is removed after the final rinse. The beakers are placed on a hotplate at 120 °C to completely dry. The beakers are ready for use.

Teflon bottles (PFA) – all PFA bottles, 0.25 L, 0.5 L and 1 L, were used for all standard solutions and 2 x sub-boiled and optima acid solutions. Before use the PFA bottles are thoroughly rinsed three times with Milli Q water. A small volume (10 – 25 mL) of concentrated optima acid (acid used depended on end use of the bottle) was placed in each PFA bottle and swirled around the bottle to ensure it came in contact with all parts of the bottle. The concentrated optima acid would then be discarded and the process would be repeat two more times. A further small volume of concentrated

optima acid, to cover the base, is added to the PFA bottle. The PFA bottle is then loosely capped and placed on the hotplate at 120 °C for 24 hours. The PFA bottle is removed from the hotplate and the concentrated optima acid is then discarded. The PFA bottle is ready for use with concentrated acids. If the PFA bottle is to be used with a dilute optima acid solution it was further rinsed with the dilution of acid to be stored in the bottle.

High density polyethylene bottles (HDPE) – HPDE bottles, 125 mL – 2 L, were used for all 1 x sub-boiled acid solutions and oxide preparation for the incorporation experiments (appendix B). The HPDE bottles are rinsed three times with Milli Q water, the HPDE bottles are then place in a large, 3.5 – 4 L glass beaker, and fully submerged in ca. 5% 1 x sub-boiled HCl and placed on a hotplate for 24 hours at 80 °C. Once removed from the hotplate the acid is discarded and the HPDE bottles are rinsed three times with Milli Q water. The HPDE bottle are individually filled to the rim with ca. 5% 1 x sub-boiled HCl and capped tightly for a minimum of a 48 hours. The acid is then discarded and the HPDE bottle is rinse a further three times with Milli Q water. The HPDE bottles are ready for use.

Polypropylene centrifuge tubes (PP/PE) – PP centrifuge tubes, 10 mL and 50 mL, were used for all analytical sessions on the Agilent ICP-MS and the Element2 ICP-MS and for the leaching experiments (appendix B). The PP centrifuge tubes are rinsed three times with Milli Q water, with the PP centrifuge tube being capped (caps are polyethylene, PE) and shaken vigorously. The Milli Q water is decanted and a small volume of 1% 2 x sub-boiled HCl is placed in the PP centrifuge tube, the tubes are then capped and shaken vigorously. The acid is then discarded. The PP centrifuge tube is then filled with 1% 2 x sub-boiled HCl, so that all surfaces (including the cap) will be in contact with the acid. The PP centrifuge tubes are then capped and placed in large polypropylene sealable box for storage until required. Once required, the acid is decanted and the PP centrifuge tubes are rinsed three times with Milli Q water. The excess Milli Q water is removed and the PP centrifuge tubes are air dried in a fumehood in the Ultraclean laboratory.

Labcon centrifuge tubes (PP/PE) – 50 mL metal free centrifuge tubes were used solely during the incorporation experiments (appendix B). These metal free centrifuge tubes are certified to < 1 ppb for common trace metals; Ca, Mg, Zn, Fe, Mn, Cu, Al, Si, Ni, V, Na, P, Co, Cr, K, Li, and Pb. These metal free centrifuge tubes were rinsed three times with Milli Q water, with the tubes being capped and shaken vigorously. The metal free centrifuge tubes are then air dried before the sample is introduced.

Cetac ASX-100 auto sampler vials (PFA) – PFA vials, 4 mL and 20 mL, snap cap, round bottom vials were used solely with MC-ICP-MS analysis. The cleaning procedure involves rinsing the PFA vials three times with Milli Q water ensuring the Milli Q water reaches the rim of the PFA vial. A small volume of optima HCl (> 6M) is added and the PFA vials are placed on a hotplate at 120 °C overnight to reflux. The optima HCl is then removed and the vials are rinsed three times with Milli Q water. The PFA vials are then batched cleaned by fully submerging in 1 – 2 M optima HCl in a large, 1 L, PFA beaker and placed on a hotplate at 120 °C overnight. The PFA vials can remain submerged until required for analysis. When required the vials are removed from batch cleaning and rinsed three times with Milli Q water. A small volume of 11 M optima HCl is added to individual vials and placed on the hotplate to refluxing overnight at 120 °C. The 11 M optima HCl is then discarded and the vials are further rinsed three times with Milli Q water. Prior to the sample being introduced the vials are rinsed with 0.5 M optima HCl.

Shot glass (PE) – 30 mL flat bottom shot glasses are used throughout all chemical processing of samples and were cleaned immediately before use. The shot glasses are rinsed three times with Milli Q water. A small volume of the reagent that the shot glass will ultimately be used for is transferred to the shot glass and swirled to ensure all the interior surface area comes in contact with the reagent. This reagent is then discarded and the the shot glass is ready for use.

Transfer pipets (PE) – 1 mL and 2 mL transfer pipets were primarily used to either remove or add resin to the columns and are cleaned immediately before use. The very tip of the transfer pipet is submerged in a cleaned shot glass of Milli Q water and the Milli Q water is drawn up. This Milli Q water is then expelled from the transfer pipets and discarded. This is repeated an additional two times. If an acidified sample is to be transferred then a cleaned shot glass of the diluting acid of the sample, is drawn up and then expelled from the transfer pipet and discarded. The transfer pipet is ready for use.

Pipette tips (PP) – pipette tips (10 μ L – 5 mL) are used throughout all chemical processing of samples and were cleaned immediately before use. Pipette tips are attached to the pipette and the desired volume is selected. The very tip of the pipette tip is submerged in a cleaned shot glass of Milli Q water and the desired volume of Milli Q water is drawn up. This Milli Q water is then expelled from the pipette and discarded. This is repeated an additional two times. A cleaned shot glass of the diluting acid, of the sample that is to be pipetted, is then drawn up and then expelled from the pipette and discarded. The pipette tip is ready to use.

Luer lock syringe (PP/PE) – 20 mL PP syringes were used throughout the incorporation experiments. The plunger is removed from the barrel of the syringe and both components are rinse thoroughly under flowing Milli Q water, whilst the syringes are disassembled they are submerged in 1% 1 x sub-boiled HCl in large polypropylene sealable boxes for storage until required. The syringes are then removed from the 1% 1 x sub-boiled HCl with forceps and again rinsed thoroughly under flowing Milli Q water. The plunger is then re-inserted into the barrel and Milli Q water is drawn up from a cleaned shot glass and the Milli Q water is then expelled, this is repeated three times in total. Syringes are air dried in a fumehood within the ultraclean lab.

Whatman® Swin-lok filter holders (PP) – 25 mm reusable filter holders fitted with Viton® O-rings were used throughout the incorporation experiments. The filter holders are separated into its components (figure A.4) and placed into a 1 L glass beaker. The filter holder components are rinsed three times with Milli Q water. The filter holder components are submerged in 6 M 1 x sub-boiled HCl for 24 hours in a

fumehood. The filter holder components are removed and placed in another 1 L glass beaker and rinsed a further three times with Milli Q water. If the filter holders were required quickly for further filtration the excess Milli Q water is removed and the filter holder components are placed in a drying oven, Thermo Scientific Heraeus® heating and drying oven, at 50 °C until dry, approximately 30 – 60 minutes. Otherwise they would be left air dry on kimwipes in the fumehood. The filter holder components are then reassembled with the addition of the filter membrane. The filter holders are ready to use.

Vacuum Filtering System – used for the filtration of manganese oxide for the incorporation experiments (appendix B). The vacuum filtering system, which consisted of a 750 mL glass reservoir, glass sand core adapter, and a 1 L collecting liquid bottle (figure A.4), were initially rinsed well with running tap water. Each part of the vacuum filter was then rinsed three times with Milli Q water. The individual parts of the vacuum filter were then placed in large glass beakers, 3 – 4.5 L, and fully submerged in 5% 1 x sub-boiled HNO₃ and placed on a hotplate for 24 hours at 80 °C. The vacuum filter is then removed from the acid bath and rinsed three times with Milli Q water. The vacuum filter is placed in a drying oven at 50 °C until completely dry. The vacuum filter can now be reassembled with the addition of the filter membrane and the metal clamp. The vacuum filter is ready to use.

Lomb Scientific porcelain crucibles – 50mL, medium wall porcelain crucibles were used for nickel sulphide fire assay for bulk digestion of samples (chapter 2). The crucibles were initially cleaned under running Milli Q water followed by a solution of Citranox® and Milli Q water. The crucibles are then thoroughly rinsed with Milli Q water. The excess Milli Q water is then removed and the crucibles are placed in the drying oven at 50 °C until they are completely dry. The crucibles are ready for use.

Agate pestle and mortar – used for powdering the synthesised Fe-Mn oxide and oxyhydroxide. The agate pestle and mortar is cleaned thoroughly between uses with Milli Q water, methanol and grinding of pure quartz grains at least three times, followed by Milli Q water and methanol.

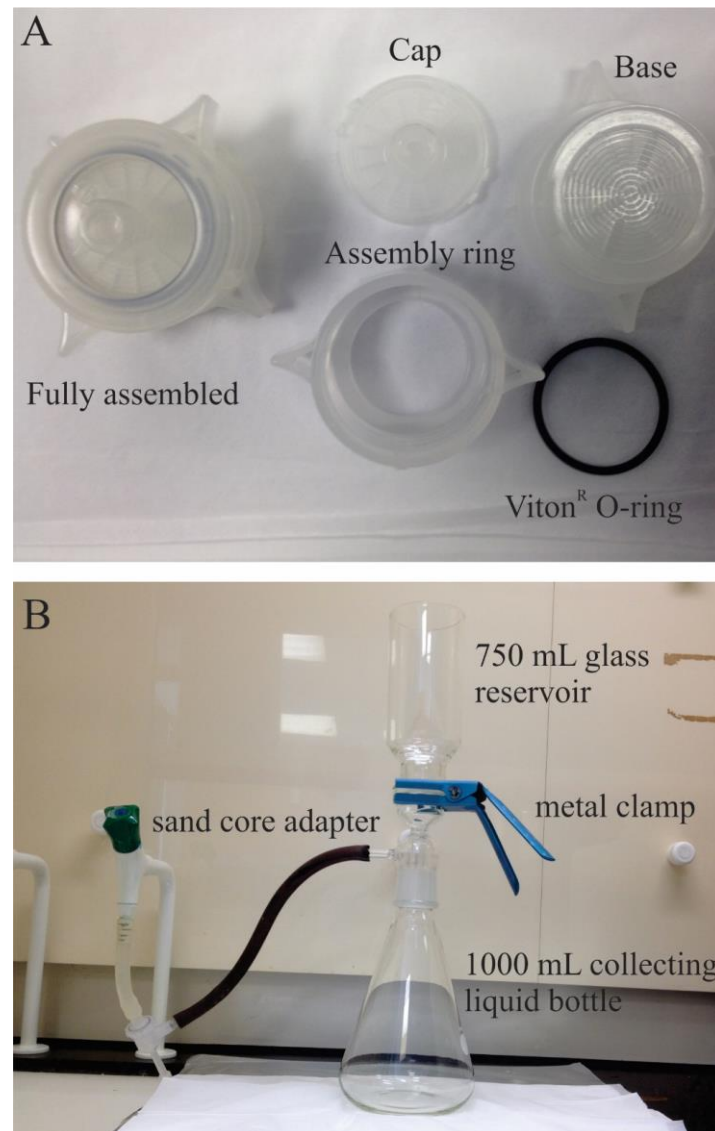


Figure A.4 A) Whatman® 25 mm Swin-lok reusable filter holders (PP), fully assembled on the left and disassembled to its components on the right; cap, base, assembly ring, and a Viton® O-ring. B) Glass vacuum filtration system with parts labelled; glass reservoir, glass sand core adapter, clamp, and collecting liquid bottle.

A.5 Oxidation and reduction of the authigenic component of nodule standards

Following initial elution profile data determined on the Agilent ICP-MS at VUW, discussed in detail in chapter 2.3 (i.e. double elution peak), three separate steps were undertaken on samples prepared by authigenic digestion method (chapter 2.2.2); oxidation with aqua regia, oxidation with nitric acid and hydrogen peroxide (H_2O_2), and reduction with Tin (II) chloride (SnCl_2). These three steps were performed on nodule standards that were fully digested by 11 M HCl, centrifuged and then evaporated to dryness.

Oxidation with aqua regia – nodule standards were taken up in 4 mL aqua regia and refluxed overnight on a hotplate at 120 °C and then evaporated to dryness. This aqua regia step is repeated again. The nodule standards are then converted to chloride form by drying down in 11 M HCl. A small volume of 0.5 M HCl is added to the nodule standard and dried down, a further 10 mL is added to the nodule standard and the beakers are closed tightly and refluxed for 24 hours. The nodule standard is ready for loading onto the anion exchange column for platinum separation.

Oxidation with HNO_3 and H_2O_2 – nodule standards were taken up in 4 mL HNO_3 and H_2O_2 (1:1, HNO_3 and H_2O_2) refluxed overnight on a hotplate at 120 °C and then evaporated to dryness. This HNO_3 and H_2O_2 step is repeated again. The sample is then treated the same as the aqua regia samples i.e. convert to chloride form and redissolving in 0.5 M HCl for anion exchange column for platinum separation.

Reduction with SnCl_2 – follows a method described by Handler (1998). 20 mL of 1 M HCl is placed in a Milli Q water cleaned 100 mL glass beaker and warmed on a hotplate. To this 4 g of SnCl_2 is added and dissolved while stirring. A watch glass is placed over the beaker and the solution is brought to the boil. When the solution is boiling 200 μL of tellurium is added and the solution is left to simmer while covered for 15 minutes. The Te will remove any PGE from the SnCl_2 solution, in the form of a black precipitate, resulting in a clean SnCl_2 solution to reduce the nodule standard

without the possibility of contamination. A 0.5 mL aliquot of the cleaned SnCl_2 solution is added to the nodule standard sample and the dried down. The sample is redissolved in 2 – 5 mL 11 M HCl and dried down twice. The nodule standard is taken up in 10 mL 0.5M HCl and refluxed overnight. The sample is ready for anion exchange column.

These additional oxidation and reduction steps after authigenic digestion (HCl digest) were not successful in removing the ‘double peak’ elution observed in the natural samples. However, the proportion of where was eluted from the column. For example, with a single acid HCl digest 20 – 25 % of the platinum eluted with 11 M HCl and the remainder with 15 M HNO_3 , the platinum cut. However, with the addition of SnCl_2 the platinum eluted with 11 M HCl decreased to ~ 15 %. The platinum elution profile data for these three additional oxidation and reductions steps are given in the electronic appendix (appendix E).

A.6 IRMM-010 reproducibility

Individual analysis are given in Appendix E.

Table A.6. Mean session and analysis for IRMM-010

	Mean $\delta^{198}\text{Pt}$	Mean $\delta^{198}\text{Pt}$ 2se	$\delta^{198}\text{Pt}$ 2sd	# of analysis
<i>IRMM-010 VUW</i>				
All analysis	-0.002	0.062	0.032	62
Session 1	-0.002	0.061	0.018	23
Session 2	-0.002	0.054	0.053	5
Session 3	0.000	0.055	0.033	19
Session 4	-0.003	0.074	0.040	15
Session mean	-0.002	0.061	0.036	-
<i>IRMM-010 UoC</i>				
All analysis	0.000	0.018	0.022	117
Session 1	0.000	0.019	0.029	12
Session 2	0.000	0.018	0.019	22
Session 3	0.000	0.018	0.021	29
Session 4	-0.001	0.018	0.023	21
Session 5	0.001	0.017	0.028	16
Session 6	-0.001	0.018	0.012	17
Session mean	0.000	0.018	0.022	-
<i>IRMM-010 VUW & UoC all analysis</i>				
Combined	-0.001	-0.001	0.025	179

A.7 Baker reproducibility

Individual analysis are given in Appendix E.

Table A.7. Mean session analysis of double spiked Baker standard.

	Mean $\delta^{198}\text{Pt}$	Mean $\delta^{198}\text{Pt}$ 2se	$\delta^{198}\text{Pt}$ 2sd	# of analysis
<i>Baker VUW</i>				
All analysis	0.086	0.052	0.027	4
<i>Baker UoC</i>				
All analysis	0.097	0.017	0.016	15
<i>Baker VUW & UoC</i>				
Combined	0.094	0.025	0.016	19

Appendix B:

Chapter 3 The platinum stable isotope fractionation associated with the surface adsorption of platinum onto synthetic Fe and Mn oxyhydroxide and oxide surfaces

B.1 Time required for pH to equilibrate during the adsorption experiment

Table B.1 Time required for goethite, ferrihydrite and δ -MnO₂ to reach pH equilibrium with the addition of the platinum bearing solution.

Oxide and weight	starting pH	1 hour	3 hours	5 hours	7 hours	9 hours	12 hours	24 hours	30 hours	36 hours	48 hours
<i>Goethite</i>											
0.509	2.00	2.27	2.30	2.43	2.41	2.43	2.4	2.45	2.41	2.39	2.41
0.507	4.00	7.56	7.67	7.74	7.77	7.76	7.7	7.76	7.76	7.72	7.73
0.509	6.00	7.76	7.79	7.79	7.84	7.84	7.81	7.84	7.83	7.73	7.75
0.507	8.00	8.06	8.01	8.02	8.01	7.99	7.96	7.99	7.95	7.95	7.95
<i>Ferrihydrite</i>											
0.515	2.00	2.98	3.09	4.73	5.18	5.51	5.66	5.83	5.93	6.01	6.03
0.508	4.00	6.90	7.33	7.45	7.47	7.51	7.51	7.56	7.57	7.54	7.53
0.505	6.00	7.38	7.55	7.58	7.61	7.6	7.6	7.6	7.6	7.56	7.56
0.511	8.00	7.62	7.61	7.63	7.61	7.63	7.59	7.6	7.61	7.58	7.59
<i>δ-MnO₂</i>											
24.067	2.00	2.46	2.50	2.45	2.46	2.47	2.45	2.42	2.46	2.43	2.45
24.536	4.00	4.54	4.53	4.53	4.56	4.53	4.48	4.51	4.53	4.5	4.52
24.532	6.00	6.11	6.13	6.16	6.15	6.19	6.23	6.22	6.26	6.29	6.29
24.557	8.00	6.72	6.78	6.82	6.82	6.9	6.89	6.94	6.96	6.97	6.96

B.2 ICP-MS and MC-ICP-MS adsorption weights and pH values

Table B.2 Synthesised minerals weights for ICP-MS analysis and the pH values obtained throughout the experiment. The starting pH is the initial platinum bearing solution. The pH was adjusted at 48 hours for the 4 day series, at 48 and 96 hours for the 7 and 14 day series, and 48 hours and 10 days for the 21 day series.

Oxide, time step, starting pH	pH check 1	pH check 2	Final pH	Starting sample (g)	Final sample (g)
<i>Goethite 24 hours</i>					
2	-	-	2.45	0.50	0.50
4	-	-	7.74	0.51	0.49
6	-	-	7.96	0.50	0.50
8	-	-	8.03	0.50	0.49
<i>Goethite 48 hours</i>					
2	-	-	2.45	0.51	0.50
4	-	-	7.69	0.51	0.51
6	-	-	7.90	0.51	0.51
8	-	-	7.99	0.51	0.50
<i>Goethite 4 days</i>					
2	2.41	-	2.03	0.51	0.47
4	7.73	-	4.21	0.50	0.49
6	7.75	-	6.19	0.50	0.48
8	7.95	-	7.88	0.51	0.51
<i>Goethite 7 days</i>					
2	2.43	2.04	2.08	0.51	0.50
4	7.65	4.26	4.10	0.52	0.50
6	7.94	6.21	6.01	0.51	0.49
8	8.08	7.96	8.02	0.51	0.50
<i>Goethite 14 days</i>					
2	2.44	2.03	2.03	0.50	0.49
4	7.72	4.18	4.03	0.50	0.48
6	7.86	6.22	5.99	0.51	0.51
8	8.13	7.95	7.83	0.50	0.49
<i>Goethite 21 days</i>					
2	2.39	2.1	2.05	0.51	0.55
4	7.39	4.91	4.49	0.51	0.50
6	7.84	6.52	6.11	0.51	0.51
8	7.99	7.92	7.83	0.51	0.71

Table B.2 continued

Oxide, time step, starting pH	pH check 1	pH check 2	Final pH	Starting sample (g)	Final sample (g)
<i>Ferrihydrite 24 hours</i>					
2	-	-	4.61	0.50	0.37
4	-	-	7.50	0.50	0.37
6	-	-	7.55	0.50	0.36
8	-	-	7.65	0.52	0.37
<i>Ferrihydrite 48 hours</i>					
2	-	-	5.24	0.52	0.37
4	-	-	7.52	0.51	0.37
6	-	-	7.58	0.51	0.37
8	-	-	7.59	0.51	0.37
<i>Ferrihydrite 4 days</i>					
2	6.03	-	2.31	0.52	0.36
4	7.53	-	4.73	0.51	0.36
6	7.56	-	6.64	0.50	0.36
8	7.59	-	7.82	0.50	0.35
<i>Ferrihydrite 7 days</i>					
2	5.51	2.45	2.28	0.51	0.34
4	7.49	4.81	4.87	0.52	0.36
6	7.52	6.54	6.33	0.50	0.38
8	7.63	7.89	7.84	0.50	0.33
<i>Ferrihydrite 14 days</i>					
2	4.47	2.4	2.27	0.51	0.33
4	7.29	5.1	4.76	0.50	0.36
6	7.57	6.33	6.41	0.50	0.34
8	7.61	7.87	7.75	0.50	0.36
<i>Ferrihydrite 21 days</i>					
2	5.39	2.48	2.26	0.51	0.33
4	7.35	5.48	4.73	0.51	0.36
6	7.44	6.64	6.61	0.51	0.37
8	7.55	7.76	7.80	0.51	0.36
<i>δ-MnO₂ 24 hours</i>					
2	-	-	2.39	24.58	0.002
4	-	-	4.47	24.57	0.005
6	-	-	5.88	24.57	0.006
8	-	-	6.64	24.61	0.002

Table B.2 continued

Oxide, time step, starting pH	pH check 1	pH check 2	Final pH	Starting sample (g)	Final sample (g)
<i>δ-MnO₂ 48 hours</i>					
2	-	-	2.40	24.07	0.002
4	-	-	4.48	24.54	0.004
6	-	-	5.97	24.53	0.002
8	-	-	6.60	24.56	0.002
<i>δ-MnO₂ 4 days</i>					
2	2.45	-	2.02	24.57	0.000
4	4.52	-	4.04	24.51	0.002
6	6.29	-	6.12	24.47	0.001
8	6.96	-	7.82	24.34	0.001
<i>δ-MnO₂ 7 days</i>					
2	2.44	2.00	2.03	23.74	0.003
4	4.44	4.00	4.02	24.14	0.004
6	6.01	6.07	6.00	24.15	0.001
8	6.92	7.8	7.76	24.12	0.002
<i>δ-MnO₂ 14 days</i>					
2	2.5	2.05	2.04	24.96	0.002
4	4.54	4.03	4.02	24.83	0.002
6	6.04	6.05	6.08	24.87	0.002
8	6.76	7.55	7.70	24.89	0.004
<i>δ-MnO₂ 21 days</i>					
2	2.4	2.1	2.03	24.58	0.002
4	4.47	3.99	3.99	24.58	0.001
6	6.39	6.03	6.12	24.34	0.001
8	6.89	7.45	7.80	24.50	0.001

B.3 Synchrotron adsorption

Table B.3 Synchrotron sample weights and pH and concentration values. The starting pH is the initial platinum bearing solution pH and the final pH is the pH after 14 days when the solids were removed from the platinum bearing solution. The * signifies which samples underwent analysis at the Australian synchrotron and by MC-ICP-MS. Red text represents samples of insufficient mass to undergo XAS or MC-ICP-MS analysis.

Oxide and starting pH	48 hours pH	Final pH	Final sample (g)	Aliquot for ICP-MS (g)	Pt in aliquot (μg)	RSD Pt ng aliquot (%)	Pt ($\mu\text{g/g}$)	Sample remaining	XAS analysis	MC-ICP-MS analysis
<i>Goethite 0.5g</i>										
2	2.05	2.14	0.40	0.040	3.15	0.36	0.08	0.36		
4	7.33	4.95	0.49	0.027	5.37	0.14	0.20	0.46		
6	7.54	6.93	0.54	0.030	3.84	0.35	0.13	0.51	*	
<i>Goethite 1.0g</i>										
2	2.03	2.33	0.76	0.031	1.66	0.52	0.05	0.73		
4	7.55	4.84	1.14	0.040	4.15	0.48	0.10	1.10		
6	7.75	6.79	1.32	0.051	3.01	0.44	0.06	1.27		
<i>Ferrihydrite 2g</i>										
2	2.51	2.48	0.12	0.013	1.14	0.09	0.09	0.11		
4	7.28	3.97	0.10	0.009	9.88	1.05	1.12	0.09		
6	7.47	5.05	0.11	0.014	19.38	0.19	1.35	0.10		
4	7.48	4.29	0.21	0.010	5.45	0.28	0.53	0.20	*	*
6	7.83	5.92	0.20	0.008	7.10	0.15	0.89	0.19	*	*

Table B.3 continued

Oxide and starting pH	48 hours pH	Final pH	Final sample (g)	Aliquot for ICP-MS (g)	Pt in aliquot (μg)	RSD Pt ng aliquot (%)	Pt ($\mu\text{g/g}$)	Sample remaining	XAS analysis	MC-ICP-MS analysis
<i>Ferrihydrite 4g</i>										
2	3.10	2.59	0.23	0.018	1.37	0.37	0.08	0.21		
<i>$\delta\text{-MnO}_2$ 100 mL</i>										
2.00	2.52	2.65	0.01	0.01	5.48	0.34	0.47	n/a		
4.00	4.98	4.32	0.04	0.02	2.94	1.06	0.18	0.03		
6.00	7.58	6.13	0.01	0.01	2.69	0.28	0.32	n/a		
<i>$\delta\text{-MnO}_2$ 500 mL</i>										
2	3.12	2.05	0.10	0.005	5.41	0.72	1.01	0.09	*	*
4	5.26	4.18	0.20	0.007	3.66	0.30	0.53	0.20	*	*
6	7.31	5.02	0.05	0.006	3.44	0.22	0.58	0.05	*	*

B.4 Platinum adsorption onto the surface of goethite.

Table B.4 Concentration of platinum adsorption onto the surface and remaining in the platinum containing solution. The mass balance is determined by normalising the concentration of platinum remaining in solution and platinum adsorbed onto the surface to the ID calculated concentration of the initial platinum bearing solution for each pH (appendix B.8). Sample with no concentration data are left blank.

Starting pH and time (hours)	Pt conc solid ($\mu\text{g/g}$)	RSD (%)	Pt in solution ($\mu\text{g/mL}$)	RSD (%)	Solids normalised to total Pt	Solutions normalised to total Pt	Sum for mass balance
<i>Goethite, pH = 2</i>							
0			9.56		0.00	1.00	1.00
24	12	2.87	8.42	0.13	0.02	0.88	0.90
48	10	1.19	8.19	0.75	0.02	0.86	0.88
96	10	2.61	8.26	0.54	0.02	0.86	0.88
168	15	0.29	8.40	0.41	0.03	0.88	0.91
336	11	0.8	8.52	0.42	0.02	0.89	0.91
504	8	2.64	8.44	0.41	0.02	0.88	0.90
<i>Goethite, pH = 4</i>							
0			8.67		0.00	1.00	1.00
24	34	0.29	7.62	0.15	0.08	0.88	0.96
48	29	0.25	7.94	0.23	0.07	0.92	0.98
96	46	0.64	7.45	0.29	0.10	0.86	0.96
168	33	0.73	7.58	1.02	0.08	0.87	0.95
336	38	0.88	7.84	0.23	0.08	0.90	0.99
504	45	1.00	7.22	1.45	0.10	0.83	0.94

Table B.4 continued

Starting pH and time (hours)	Pt conc solid ($\mu\text{g/g}$)	RSD (%)	Pt in solution ($\mu\text{g/mL}$)	RSD (%)	Solids normalised to total Pt	Solutions normalised to total Pt	Sum for mass balance
<i>Goethite, pH = 6</i>							
0			8.67		0.00	1.00	1.00
24	32	0.25	8.22	0.39	0.07	0.95	1.02
48	34	1.36	7.26	0.23	0.08	0.84	0.92
96	80	0.78	7.16	1.11	0.18	0.83	1.00
168	66	0.73	7.21	0.26	0.15	0.83	0.98
336	122	0.77	5.92	1.35	0.29	0.68	0.97
504	138	0.17	5.43	0.21	0.32	0.63	0.95
<i>Goethite, pH = 8</i>							
0			8.81	-	0.00	1.00	1.00
24	139	0.06	5.33	0.77	0.31	0.61	0.92
48	134	0.85	5.56	0.70	0.31	0.63	0.94
96	144	0.75	5.01	0.62	0.34	0.57	0.90
168	109	0.73	6.14	0.48	0.25	0.70	0.94
336	173	0.72	4.68	0.44	0.39	0.53	0.92
504	106	0.34	4.98	0.14	0.34	0.57	0.91

B.5 Platinum adsorption onto the surface of ferrihydrite.

Table B.5 Concentration of platinum adsorption onto the ferrihydrite surface and remaining in the platinum containing solution. The mass balance is determined by normalising the concentration of platinum remaining in solution and platinum adsorbed onto the surface to the ID calculated concentration of the initial platinum bearing solution for each pH (appendix B.8). Elements with no concentration data are left blank.

Starting pH and time (hours)	Pt conc solid ($\mu\text{g/g}$)	RSD (%)	Pt in solution ($\mu\text{g/mL}$)	RSD (%)	Pt of total solution $\mu\text{g/g}$	Solids normalised to total Pt	Solutions normalised to total Pt	Sum for mass balance
<i>Ferrihydrite pH = 2</i>								
0			9.56		239	0.00	1.00	1.00
24	61	0.25	7.66	0.31	191	0.09	0.80	0.90
48	112	0.52	6.99	0.12	175	0.17	0.73	0.90
96	177	0.98	4.58	1.1	114	0.27	0.48	0.75
168	55	1.32	7.05	1.83	176	0.08	0.74	0.82
336	44	1.05	7.22	0.53	180	0.06	0.76	0.81
504	70	1.18	6.95	0.14	174	0.10	0.73	0.82
<i>Ferrihydrite pH = 4</i>								
0			8.67		217	0.00	1.00	1.00
24	82	1.02	6.47	0.37	162	0.14	0.75	0.89
48	85	0.26	6.87	0.98	172	0.14	0.79	0.94
96	198	0.61	4.69	0.93	117	0.32	0.54	0.87

Table B.5 continued

Starting pH and time (hours)	Pt conc solid ($\mu\text{g/g}$)	RSD (%)	Pt in solution ($\mu\text{g/mL}$)	RSD (%)	Pt of total solution $\mu\text{g/g}$	Solids normalised to total Pt	Solutions normalised to total Pt	Sum for mass balance
<i>Ferrihydrite pH = 4</i>								
168	230	0.06	4.93	0.05	123	0.39	0.57	0.95
336	269	0.11	4.58	0.45	114	0.45	0.53	0.98
504	317	0.77	3.25	0.38	81	0.52	0.38	0.90
<i>Ferrihydrite pH = 6</i>								
0			8.68		217	0.00	1.00	1.00
24	102	1.56	6.78	0.27	170	0.17	0.78	0.95
48	108	0.13	6.47	0.94	162	0.19	0.75	0.93
96	199	0.07	4.82	0.25	121	0.33	0.56	0.89
168	200	0.69	6.07	0.47	152	0.35	0.70	1.05
336	322	0.2	3.60	0.31	90	0.50	0.41	0.91
504	352	0.07	2.97	0.17	74	0.60	0.34	0.94
<i>Ferrihydrite pH = 8</i>								
0			8.81		220	0.00	1.00	1.00
24	313	0.64	3.22	0.31	80	0.52	0.37	0.89
48	280	1.25	3.33	0.55	83	0.47	0.38	0.84
96	366	0.08	3.20	0.48	80	0.58	0.36	0.95
168	250	0.48	4.49	1.27	112	0.37	0.51	0.88
336	391	1.31	2.81	0.09	70	0.64	0.32	0.96
504	417	0.26	2.03	0.29	51	0.67	0.23	0.91

B.6 Platinum adsorption onto the surface of δ -MnO₂.

Table B.6 Concentration of platinum adsorption onto the ferrihydrite surface and remaining in the platinum containing solution. The mass balance is determined by normalising the concentration of platinum remaining in solution and platinum adsorbed onto the surface to the ID calculated concentration of the initial platinum bearing solution for each pH (appendix B.8). Elements with no concentration data are left blank.

Starting pH and time (hours)	Pt conc solid (µg/g)	RSD (%)	Pt in solution (µg/mL)	RSD (%)	Pt of total solution µg/g	Solids normalised to total Pt	Solutions normalised to total Pt	Sum for mass balance
<i>δ-MnO₂ pH = 2</i>								
0			10		239	0.00	1.00	1.00
24	16	1.48	8	0.49	205	0.00	0.86	0.86
48	42	22.2	9	0.22	217	0.00	0.91	0.91
96	570	11.48	8	0.74	201	0.00	0.84	0.84
168	12	0.33	8	0.90	201	0.00	0.84	0.84
336	34	7.04	8	0.78	204	0.00	0.85	0.85
504	31	4.26	8	1.89	209	0.00	0.87	0.87
<i>δ-MnO₂ pH = 4</i>								
0			9		217	0.00	1.00	1.00
24	95	1.31	8	1.84	209	0.00	0.87	0.88
48	71	0.27	8	0.46	201	0.00	0.84	0.84
96	113	0.54	8	0.35	191	0.00	0.80	0.80

Table B.6 continued

Starting pH and time (hours)	Pt conc solid ($\mu\text{g/g}$)	RSD (%)	Pt in solution ($\mu\text{g/mL}$)	RSD (%)	Pt of total solution $\mu\text{g/g}$	Solids normalised to total Pt	Solutions normalised to total Pt	Sum for mass balance
168	49	0.94	8	0.92	208	0.00	0.87	0.87
336	112	0.38	9	0.22	217	0.00	0.91	0.91
504	182	0.53	7	0.66	184	0.00	0.77	0.77
<i>$\delta\text{-MnO}_2$ pH = 6</i>								
0			9		217	0.00	1.00	1.00
24	272	0.9	9	0.80	216	0.01	0.90	0.91
48	550	1.25	8	0.37	204	0.00	0.85	0.86
<i>$\delta\text{-MnO}_2$ pH = 6</i>								
96	846	0.30	8	0.24	209	0.00	0.87	0.88
168	426	0.24	8	1.19	212	0.00	0.89	0.89
336	513	0.05	8	0.18	188	0.00	0.79	0.79
504	481	0.67	8	0.84	202	0.00	0.84	0.85
<i>$\delta\text{-MnO}_2$ pH = 8</i>								
0			9		220	0.00	1.00	1.00
24	5342	1.12	8	0.91	198	0.05	0.83	0.88
48	7423	0.75	8	0.68	192	0.06	0.80	0.87
96	3720	0.36	8	1.10	204	0.02	0.86	0.88
168	1307	0.28	9	0.38	214	0.01	0.90	0.91
336	1348	0.91	8	0.87	204	0.02	0.85	0.88
504	1873	0.07	8	0.63	210	0.01	0.88	0.89

B.7 Linear combination fitting

Table B.7 Linear combination fitting of the platinum standards to the platinum adsorbed onto the surface of the synthetic samples. The linear combination fitting was performed in the Athena software. The embolded text represents the linear combination fitting that was used as the most appropriate fitting (chapter 3).

R factor	X ²	Reduced X ²	<u>PtCl₂</u>		<u>PtCl₄</u>		<u>PtO₂·H₂O</u>		<u>Na₂PtCl₆·6H₂O</u>		
			weight	error	weight	error	weight	error	weight	error	
<i>Goethite pH = 6</i>											
0.0028	0.0008	0.1457	-	-	0.191	0.041	0.496	0.025	0.313	0.032	
0.0028	0.0008	0.1478	0.000	0.046	0.210	0.094	0.481	0.026	0.309	0.135	
0.0034	0.0010	0.1815	0.064	0.071	-	-	0.504	0.027	0.432	0.032	
0.0039	0.0011	0.2067	-	-	-	-	0.483	0.039	0.517	0.028	
0.0044	0.0012	0.2336	-	-	0.296	0.018	0.704	0.032	-	-	
0.0073	0.0021	0.3866	0.127	0.059	-	-	0.873	0.013	-	-	
<i>Ferrihydrite pH = 4</i>											
0.0009	0.0002	0.0348	0.047	0.002	0.712	0.009	0.227	0.014	0.013	0.001	
0.0014	0.0003	0.0545	0.049	0.003	0.739	0.010	0.212	0.015	-	-	
0.0034	0.0007	0.1283	0.049	0.004	0.759	0.018	-	-	0.192	0.018	
0.0038	0.0008	0.1466	-	-	0.775	0.017	0.207	0.020	0.018	0.003	
0.0048	0.0010	0.1835	-	-	0.819	0.016	0.181	0.032	-	-	
0.0058	0.0012	0.2221	0.497	0.034	-	-	0.503	0.010	-	-	

Table B.7 continued

R factor	X ²	Reduced X ²	<u>PtCl₂</u>		<u>PtCl₄</u>		<u>PtO₂·H₂O</u>		<u>Na₂PtCl₆·6H₂O</u>		
			weight	error	weight	error	weight	error	weight	error	
<i>Ferrihydrite pH = 6</i>											
0.0005	0.0001	0.0256	0.007	0.016	0.533	0.023	0.438	0.032	0.021	0.014	
0.0005	0.0001	0.0257	-	-	0.549	0.017	0.434	0.010	0.018	0.013	
0.0005	0.0001	0.0260	0.003	0.012	0.551	0.016	0.445	0.009	-	-	
0.0005	0.0001	0.0260	-	-	0.558	0.006	0.442	0.012	-	-	
0.0017	0.0004	0.0815	0.290	0.028	-	-	0.521	0.018	0.189	0.020	
0.0026	0.0006	0.1212	0.317	0.007	-	-	0.683	0.013	-	-	
<i>δ-MnO₂ pH = 2</i>											
0.0074	0.0027	0.5195	-0.154	0.025	0.154	0.000	-	-	1.000	0.000	
0.0240	0.0087	1.6805	-	-	-	-	0.449	0.080	0.551	0.080	
0.0247	0.0090	1.7280	-	-	0.000	0.0637	0.324	0.123	0.676	0.105	
0.0276	0.0101	1.9327	0.020	0.000	-	-	-0.020	0.000	1.000	0.000	
0.0280	0.0102	1.9598	0.000	0.029	-	-	-	-	1.000	0.029	
0.0280	0.0102	1.9605	-	-	0.000	0.061	-	-	1.000	0.061	
<i>δ-MnO₂ pH = 4</i>											
0.0033	0.0010	0.1881	0.0159	0.0055	-0.067	0.063	0.415	0.029	0.635	0.055	
0.0035	0.0010	0.1999	-	-	-0.045	0.049	0.421	0.028	0.624	0.040	
0.0039	0.0012	0.2242	0.0027	0.0041	-	-	0.402	0.030	0.596	0.096	
0.0039	0.0012	0.2248	-	-	-	-	0.404	0.029	0.596	0.095	
0.0062	0.0019	0.3539	0.0329	0.0000	-0.033	0.005	-	-	1.000	0.000	
0.0077	0.0023	0.4406	-	-	0.010	0.005	-	-	0.990	0.091	

Table B.7 continued

R factor	X^2	Reduced X^2	<u>PtCl₂</u>		<u>PtCl₄</u>		<u>PtO₂·H₂O</u>		<u>Na₂PtCl₆·6H₂O</u>		
			weight	error	weight	error	weight	error	weight	error	
<i>δ-MnO₂ pH = 6</i>											
0.0048	0.0016	0.2971	0.000	0.011	-0.054	0.126	0.518	0.084	0.536	0.087	
0.0056	0.0018	0.3510	-	-	-0.042	0.068	0.680	0.042	0.362	0.041	
0.0091	0.0029	0.5671	-	-	-	-	0.546	0.046	0.454	0.046	
0.0101	0.0033	0.6267	0.000	0.009	-	-	0.705	0.050	0.295	0.069	
0.0102	0.0033	0.6375	0.069	0.000	-0.069	0.034	-	-	1.000	0.000	
0.0111	0.0036	0.6894	0.034	0.000	-0.034	0.034	1.000	0.000	-	-	

B.8 $\delta^{198}\text{Pt}$ of the initial platinum bearing solution

Table B.8 The $\delta^{198}\text{Pt}$ of the initial platinum bearing solution at pH = 2, 4, 6, and 8.

Control solution pH	$\delta^{198}\text{Pt}$	$\delta^{198}\text{Pt}$ 2se	ID ($\mu\text{g/g}$)	E2 ($\mu\text{g/g}$)	ID/E2
pH = 2	0.051	0.022	9563	8422	1.14
	0.043	0.027	9563	8422	1.14
	0.042	0.032	9563	8422	1.14
pH = 4	0.030	0.021	8669	8240	1.05
	0.028	0.021	8669	8240	1.05
	0.037	0.019	8669	8240	1.05
pH = 6	0.050	0.025	8677	8295	1.05
	0.037	0.026	8676	8295	1.05
	0.019	0.023	8677	8295	1.05
pH = 8	0.029	0.023	8811	8403	1.05
	0.031	0.019	8811	8403	1.05
	0.025	0.019	8810	8403	1.05

B.9 $\delta^{198}\text{Pt}$ of the platinum adsorbed onto the goethite surface and the platinum remaining in the solution.**Table B.9** $\delta^{198}\text{Pt}$ and concentration of the adsorption pair on the goethite surface.

Solid	$\delta^{198}\text{Pt}$	$\delta^{198}\text{Pt}$ 2se	ID ($\mu\text{g/g}$)	E2 ($\mu\text{g/g}$)	ID/E2	Solid	$\delta^{198}\text{Pt}$	$\delta^{198}\text{Pt}$ 2se	ID ($\mu\text{g/g}$)	E2 ($\mu\text{g/g}$)	ID/E2
Goethite solid, pH = 2						Goethite solution, pH = 2					
24	0.013	0.018	10	12	0.91	24	0.024	0.015	238	210	1.13
168	0.058	0.016	14	15	0.90	168	0.070	0.018	228	210	1.09
504	0.069	0.016	9	8	1.03	504	0.166	0.052	226	211	1.07
Goethite solid, pH = 4						Goethite solution, pH = 4					
24	-0.200	0.015	30	34	0.90	24	0.090	0.019	218	190	1.15
168	-0.207	0.016	32	33	0.98	168	0.070	0.018	215	190	1.14
504	-0.303	0.014	47	45	1.05	504	0.103	0.020	202	181	1.12
Goethite solid, pH = 6						Goethite solution, pH = 6					
24	-0.221	0.015	31	32	0.95	24	0.092	0.020	225	205	1.10
168	-0.331	0.018	66	66	1.00	168	0.104	0.022	174	180	0.97
504	-0.297	0.016	135	138	0.98	504	0.281	0.021	135	136	0.99
Goethite solid, pH = 8						Goethite solution, pH = 8					
24	-0.241	0.018	145	139	1.05	24	0.146	0.021	166	133	1.25
504	-0.235	0.017	125	105	1.20	504	0.283	0.019	140	124	1.13

B.10 $\delta^{198}\text{Pt}$ and concentration of the adsorption pair on the ferrihydrite surface**Table B.10** $\delta^{198}\text{Pt}$ of the platinum adsorbed onto the ferrihydrite surface and the platinum remaining in the solution.

Solid	$\delta^{198}\text{Pt}$	$\delta^{198}\text{Pt}$ 2se	ID ($\mu\text{g/g}$)	E2 ($\mu\text{g/g}$)	ID/E2	Solid	$\delta^{198}\text{Pt}$	$\delta^{198}\text{Pt}$ 2se	ID ($\mu\text{g/g}$)	E2 ($\mu\text{g/g}$)	ID/E2
Ferrihydrite solid, pH = 2						Ferrihydrite solution, pH = 2					
24	-0.321	0.016	57	61	0.94	24	-0.029	0.016	207	191	1.08
168	-0.304	0.019	54	55	0.97	168	0.041	0.017	191	176	1.08
504	-0.268	0.016	71	70	1.02	504	0.06	0.02	192	174	1.11
Ferrihydrite solid, pH = 4						Ferrihydrite solution, pH = 4					
24	-0.274	0.018	87	82	1.05	24	0.034	0.019	194	162	1.20
168	-0.262	0.015	229	230	0.99	168	0.163	0.017	136	123	1.10
504	-0.221	0.018	328	317	1.04	504	0.343	0.021	91	81	1.11
Ferrihydrite solid, pH = 6						Ferrihydrite solution, pH = 6					
24	-0.364	0.018	107	102	1.05	24	0.084	0.015	181	170	1.07
168	-0.314	0.019	209	200	1.04	168	0.146	0.022	148	152	0.97
504	-0.212	0.017	363	352	1.03	504	0.421	0.018	80	74	1.08
Ferrihydrite solid, pH = 8						Ferrihydrite solution, pH = 8					
24	-0.092	0.025	355	313	1.13	24	0.143	0.021	88	80	1.09
168	-0.256	0.019	262	250	1.05	168	0.219	0.023	124	112	1.10
504	-0.17	0.019	431	417	1.03	504	0.51	0.016	57	51	1.12

B.11 $\delta^{198}\text{Pt}$ and concentration of the adsorption pair on the $\delta\text{-MnO}_2$ surface**Table B.11** $\delta^{198}\text{Pt}$ of the platinum adsorbed onto the $\delta\text{-MnO}_2$ surface and the platinum remaining in the solution.

Solid	$\delta^{198}\text{Pt}$	$\delta^{198}\text{Pt}$ 2se	ID ($\mu\text{g/g}$)	E2 ($\mu\text{g/g}$)	ID/E2	Solid	$\delta^{198}\text{Pt}$	$\delta^{198}\text{Pt}$ 2se	ID ($\mu\text{g/g}$)	E2 ($\mu\text{g/g}$)	ID/E2
$\delta\text{-MnO}_2$ solid, pH = 4						$\delta\text{-MnO}_2$ solution, pH = 4					
24	-0.303	0.028	93	95	0.98	24	0.031	0.018	212	209	1.01
168	-0.430	0.029	55	49	1.12	168	0.037	0.018	210	208	1.01
504	-0.465	0.030	207	182	1.14	504	0.017	0.014	193	184	1.05
$\delta\text{-MnO}_2$ solid, pH = 6						$\delta\text{-MnO}_2$ solution, pH = 6					
24	-0.362	0.031	263	272	0.97	24	0.049	0.018	215	216	1.00
168	-0.537	0.035	420	426	0.99	168	0.029	0.018	222	212	1.05
504	-0.528	0.030	580	481	1.21	504	0.038	0.016	213	202	1.05
$\delta\text{-MnO}_2$ solid, pH = 8						$\delta\text{-MnO}_2$ solution, pH = 8					
168	-0.499	0.035	1295	1307	0.99	168	0.030	0.016	218	214	1.02
504	-0.566	0.036	2448	1873	1.31	504	0.054	0.018	217	210	1.04

Appendix C:

Chapter 4 Effects of leaching on the platinum isotopic composition: approximating weathering in an oxic environment

C.1 Leaching experiment samples mass and Pt concentration

C.2 Leaching experiment final mass and the concentration of platinum that is leached.

* Certified reference value less the platinum (ng) in the leachate

Time (hours)	Starting sample (g)	Final sample (g)	Sample lost (%)	Pt leachate (ng)	RSD Pt leachate (%)	Pt leached residue* (ng)
<i>SARM-76 1% HNO₃</i>						
96	1.029	0.893	13.27	-	-	-
168	1.005	0.895	10.97	-	-	-
336	1.029	0.908	11.74	-	-	-
504	1.009	0.881	12.68	-	-	-
5760	-	-	-	-	-	-
<i>SARM-76 5% HNO₃</i>						
96	1.035	0.783	24.34	77.66	0.89	3638
168	1.065	0.782	26.60	62.91	0.65	3762
336	1.020	0.736	27.81	28.02	0.86	3633
504	1.007	0.730	27.57	37.56	0.47	3578
5760	-	-	-	-	-	-
<i>SARM-76 10% HNO₃</i>						
96	1.058	0.790	25.35	85.02	3.36	3712
168	1.010	0.752	25.50	265.78	4.55	3359
336	1.016	0.719	29.23	226.09	1.40	3420
504	1.014	0.717	29.26	144.92	1.64	3495
5760	1.020	0.670	34.28	213.92	3.62	3448
<i>PTA-1 1% HNO₃</i>						
96	1.038	1.023	1.41	-	-	-
168	1.265	1.246	1.51	-	-	-
336	1.010	0.965	4.41	-	-	-
504	1.019	0.994	2.44	-	-	-
5760	-	-	-	-	-	-

Table C.2 continued

Time (hours)	Starting sample (g)	Final sample (g)	Sample lost (%)	Pt leachate (ng)	RSD Pt leachate (%)	Pt leached residue* (ng)
<i>PTA-1 5% HNO₃</i>						
3	1.026	1.001	2.47	-	-	-
168	1.042	1.011	2.97	0.96	3.42	3178
336	1.012	0.935	7.62	0.19	4.18	3085
504	1.011	0.953	5.70	0.61	0.95	3082
5760	-	-	-	-	-	-
<i>PTA-1 10% HNO₃</i>						
96	1.073	1.031	3.92	-	-	-
168	1.053	1.013	3.77	3.99	1.60	3207
336	1.046	0.987	5.59	-	-	-
504	1.040	0.979	5.92	1.96	0.99	3172
5760	1.012	0.706	30.26	4.59	5.52	
<i>WPR-1 1% HNO₃</i>						
96	1.021	0.904	11.49	-	-	-
168	1.025	0.918	10.43	-	-	-
336	1.009	0.860	14.80	-	-	-
504	1.042	0.914	12.24	-	-	-
5760	-	-	-	-	-	-
<i>WPR-1 5% HNO₃</i>						
96	1.044	0.825	21.00	0.58	7.00	297
168	1.072	0.811	24.32	0.60	5.83	305
336	1.028	0.746	27.48	0.04	3.72	293
504	1.078	0.727	32.57	0.28	0.72	307
5760	-	-	-	-	-	-
<i>WPR-1 10% HNO₃</i>						
96	1.041	0.784	24.63	5.13	0.76	291
168	1.024	0.735	28.22	4.02	3.20	288
336	1.017	0.692	31.96	3.85	0.98	286
504	1.059	0.657	37.98	4.11	1.49	298
5760	1.003	0.483	51.87	20.68	2.68	265

C.2 Leaching experiment $\delta^{198}\text{Pt}$

C.2 Leaching experiment $\delta^{198}\text{Pt}$, $\Delta^{198}\text{Pt}$, $\alpha^{198}\text{Pt}$ and associated errors

Time (hours)	Leachate $\delta^{198}\text{Pt}$	Leachate $\delta^{198}\text{Pt}$ 2se	Residue $\delta^{198}\text{Pt}$	Residue $\delta^{198}\text{Pt}$ 2se	$\Delta^{198}\text{Pt}$	$\Delta^{198}\text{Pt}$ 2se	$\alpha^{198}\text{Pt}$	$\alpha^{198}\text{Pt}$ 2se
<i>SARM-76 5% HNO₃</i>								
96	1.936	0.094	-0.011	0.022	1.947	0.097	0.99806	0.0001
168	2.800	0.100	0.109	0.027	2.691	0.104	0.99732	0.0001
504	1.940	0.210	-1.628	0.050	3.568	0.216	0.99644	0.0003
<i>SARM-76 10% HNO₃</i>								
168	0.961	0.080	0.058	0.026	0.903	0.084	0.99910	0.0001
336	1.368	0.084	-0.110	0.022	1.478	0.087	0.99852	0.0001
504	0.959	0.069	0.084	0.054	0.875	0.088	0.99913	0.0001
5760	1.478	0.051	0.006	0.029	1.472	0.059	0.99853	0.0001
<i>WPR-1 10% HNO₃</i>								
5760	5.440	0.120	0.118	0.063	5.322	0.136	0.99471	0.0002

Appendix D:

Chapter 5 Stable platinum isotopic composition of modern ferromanganese crusts and nodules

D.1 The $\delta^{198}\text{Pt}$ of a global suite of FMN and FMC

D.1 The $\delta^{198}\text{Pt}$, concentration, and Fe/Mn ratio of a range of FMN and FMC from a number of ocean basins.

Sample	Ocean	Type of deposit	$\delta^{198}\text{Pt}$	$\delta^{198}\text{Pt}$ (2se)	Pt ng/g	Fe/Mn ratio
<i>Ferromanganese nodules</i>						
Nod-A-1	Atlantic	Diagenetic	0.322	0.018	487	0.59
Nod-P-1	Pacific	Diagenetic	0.158	0.037	126	0.20
JMn-1	Pacific	Diagenetic	0.163	0.041	137	0.39
U1365B	Southern	Hydrogenetic	0.126	0.026	284	0.94
<i>Ferromanganese crust</i>						
ALV 539	Atlantic	Hydrogenetic	0.417	0.017	383	1.54
ANT 109D	Indian	Hydrogenetic	0.082	0.045	93	1.13
DODO 232D	Indian	Hydrogenetic	-0.075	0.031	71	1.14
CD 29-2	Pacific	Hydrogenetic	0.081	0.027	120	0.87
D11-1	Pacific	Hydrogenetic	0.088	0.026	191	0.73
TAN 19-B1/2	Pacific	Mixed	0.264	0.025	289	2.67
TAN 19-B2/2-S1	Pacific	Mixed	1.281	0.035	181	1.07
TAN 19-B2/2-S2	Pacific	Mixed	-0.274	0.027	251	1.06
TAN 19-B2/2-S3	Pacific	Mixed	-0.446	0.040	260	1.32
TAN 19-R-S3	Pacific	Mixed	0.336	0.026	90	1.99
CR 19 B	Pacific	Mixed	-0.236	0.032	128	2.15

D.2 Predicted $\delta^{198}\text{Pt}$ of seawater

D.2 Seawater $\delta^{198}\text{Pt}$ was calculated using using the $\alpha^{198}\text{Pt}$ equation, $\delta^{198}\text{Pt}_{(\text{seawater})} = [\alpha^{198}\text{Pt} * (\delta^{198}\text{Pt}_{(\text{FMC,FMN})}/1000)] - 1$, where the $\delta^{198}\text{Pt}$ referees to the measured $\delta^{198}\text{Pt}$ of the FMN and FMC samples and the $\alpha^{198}\text{Pt}$ of $\delta\text{-MnO}_2$ at pH = 8 (1.00058 ± 0.00005)

Sample type	Ocean	Digest	Split	$\delta^{198}\text{Pt}$	$\delta^{198}\text{Pt}$ (2se)	seawater
FMN Diagenetic						
<i>USGS Nod-A-1</i>	Atlantic	35-1		0.678	0.022	1.25
		35-2		0.500	0.022	1.07
		36-1	A	0.308	0.016	0.88
		36-1	B	0.312	0.017	0.88
		36-2	A	0.067	0.016	0.64
		36-2	B	0.067	0.018	0.64
<i>USGS Nod-P-1</i>	Pacific	36-1	A	0.145	0.035	0.72
		36-1	B	0.123	0.036	0.69
		36-2	A	0.187	0.041	0.76
		36-2	B	0.178	0.035	0.75
<i>GSI JMn-1</i>	Pacific	35-2		0.156	0.040	0.73
		36-1	A	0.196	0.043	0.77
		36-1	B	0.125	0.047	0.70
		36-2	A	0.121	0.039	0.69
		36-2	B	0.142	0.039	0.71
FMN hydrotgenetic						0.57
<i>U1365B</i>	Southern	M- 27855		0.126	0.026	0.70
FMC hydrotgenetic						0.57
<i>ALV 539</i>	Atlantic			0.417	0.017	0.99
<i>ANT 109D</i>	Indian			0.082	0.045	0.65
<i>DODO 232D</i>	Indian			-0.075	0.031	0.49
<i>CD 29-2</i>	Pacific			0.081	0.027	
<i>D11-1</i>	Pacific			0.879	0.026	1.45
FMC mixed						0.57
TAN 19-B1/2	Pacific			0.264	0.025	0.83
TAN 19-B2/2-S1	Pacific			1.281	0.035	1.85
TAN 19-B2/2-S2	Pacific			-0.274	0.027	0.30
TAN 19-B2/2-S3	Pacific			-0.446	0.040	0.12
TAN 19-R-S3	Pacific			0.336	0.026	0.91
CR 19 B	Pacific			-0.236	0.032	0.33

Appendix E:

Electronic Appendices