

Supplementary Material

Natural cobalt–manganese oxide nanoparticles: speciation, detection and implications for cobalt cycling

Owen P. Missen^{A,B,}, Stuart J. Mills^A, Thebny Thaise Moro^{C,D}, E. Eduardo Villalobos-Portillo^{E,G}, Hiram Castillo-Michel^E, Thomas E. Lockwood^F, Raquel Gonzalez de Vega^C and David Clases^C*

^AGeosciences, Museums Victoria, GPO Box 666, Melbourne, Vic. 3001, Australia

^BCentre for Ore Deposit and Earth Sciences, University of Tasmania, Hobart, Tas. 7001, Australia

^CInstitute of Chemistry, University of Graz, Graz, AT-8010, Austria

^DDepartamento de Química, Campus Trindade, Universidade Federal de Santa Catarina, Florianópolis, SC 88040-900, Brazil

^EEuropean Synchrotron Radiation Facility, Grenoble, Cedex 9, F-38043 France

^FHyphenated Mass Spectrometry Lab, University of Technology Sydney, NSW 2007, Australia

^GPresent address: ALBA Synchrotron, Cerdanyola del Valles, Barcelona E-08290, Spain

*Correspondence to: Email: owen.missen@utas.edu.au

Table S1. Full results by individual sampling site for bulk Co and Mn concentrations and single particle ICPMS data, including ToF (when possible).

Sample code	Latitude (S)	Longitude (E)	Co (ppm)	Co NPs ($n\text{ g}^{-1}$ soil)	s.d.	Concentration of Co NPs (ng g^{-1} soil)	s.d.	Co NPs/total Co (%)	Mn (ppm)	Mn NPs ($n\text{ g}^{-1}$ soil)	s.d.	Concentration of Mn NPs (ng g^{-1} soil)	s.d.	Mn NPs/total Mn (%)	Molar ratio of Co:Mn in NPs (ToF data)	Average per location
QS1	-20.082502	140.15301	6130	3.14E+08	5.26E+06	1261.57	21.12	0.021%	868	4.80E+07	3.15E+06	5.48	0.36	0.001%	0.23	
QS2	-20.082215	140.152866	10000	9.77E+07	2.90E+06	1390.35	41.37	0.014%	836	5.23E+07	3.23E+06	7.04	0.45	0.001%	1.79	
QS3	-20.08219	140.152828	10000	1.53E+08	3.71E+06	1236.00	29.86	0.012%	603	7.85E+07	4.06E+06	11.44	0.56	0.002%	0.66	
QS4	-20.082234	140.152835	376	3.12E+08	5.23E+06	70.67	1.18	0.019%	612	9.00E+07	4.27E+06	14.16	0.64	0.002%	0.13	0.70
MC1	-21.737239	140.493096	3650	1.00E+08	2.86E+06	866.89	24.76	0.024%	316	7.13E+07	3.62E+06	12.74	0.68	0.004%	1.79	
MC2	-21.737409	140.492969	343	3.93E+08	5.67E+06	87.15	1.27	0.025%	217	4.97E+07	3.06E+06	5.89	0.34	0.003%	-	
MC3	-21.737519	140.492963	42.7	2.29E+08	4.46E+06	29.94	0.63	0.070%	249	3.85E+07	2.77E+06	4.26	0.27	0.002%	-	
MC4	-21.737599	140.492946	383	4.95E+08	6.89E+06	88.64	1.19	0.023%	479	2.26E+07	2.24E+06	6.33	0.60	0.001%	-	
MC5	-21.737385	140.493308	628	1.09E+07	9.91E+05	108.45	9.91	0.017%	343	1.76E+08	6.05E+06	30.13	1.03	0.009%	0.61	
MC6	-21.737488	140.493502	571	2.73E+08	4.63E+06	240.48	4.04	0.042%	458	3.28E+07	2.43E+06	6.31	0.49	0.001%	0.13	
MC7	-21.737544	140.493788	540	1.77E+08	3.86E+06	180.82	3.92	0.033%	434	6.75E+07	3.58E+06	9.70	0.52	0.002%	0.23	0.69
PHill1	-32.092566	141.194506	29.5	7.42E+07	2.68E+06	13.53	0.50	0.046%	154.5	5.27E+07	3.46E+06	17.23	1.10	0.011%	-	
PHill2	-32.092704	141.194519	41.1	1.69E+07	1.21E+06	1.87	0.09	0.005%	127	1.35E+07	1.64E+06	1.99	0.27	0.002%	0.26	
PHill3	-32.092731	141.194404	21.7						63							
PHill4	-32.092755	141.194252	60.4	1.81E+08	4.13E+06	27.31	0.58	0.045%	256	4.75E+07	3.20E+06	9.23	0.58	0.004%	0.19	
PHill5	-32.091932	141.194528	20.4	1.11E+07	1.05E+06	6.62	0.62	0.032%	353	5.85E+07	3.66E+06	20.39	1.23	0.006%	-	
PHill6	-32.092709	141.193885	55.4	1.57E+07	1.20E+06	4.36	0.29	0.008%	238	4.84E+07	3.21E+06	5.37	0.38	0.002%	-	
PHill7	-32.092221	141.194624	53.8	6.33E+07	2.28E+06	7.82	0.26	0.015%	430	4.66E+07	2.97E+06	11.07	0.68	0.003%	-	0.22
YCP1	-31.119777	138.675712	8.1	2.47E+07	1.55E+06	13.47	0.80	0.166%	423	9.10E+07	4.50E+06	12.32	0.60	0.003%	-	
YCP2	-31.119773	138.675833	6.28	3.34E+06	5.45E+05	0.94	0.18	0.015%	305	9.02E+07	4.27E+06	13.74	0.64	0.005%	-	
YCP3	-31.119752	138.675892	5.93	4.85E+06	6.28E+05	0.69	0.08	0.012%	250	1.25E+08	4.81E+06	18.20	0.68	0.007%	0.30	0.30
Copp1	-17.062826	137.816865	191.5	4.47E+07	2.06E+06	5.96 ^A	0.30 ^B	0.003%	2650	4.03E+07	2.97E+06	11.15	0.79	0.000%	-	
Copp2	-17.062773	137.816926	148	1.17E+08	3.27E+06	13.95 ^A	0.38 ^B	0.009%	2150	1.03E+08	4.66E+06	35.64	1.61	0.002%	-	
Copp3	-17.06257	137.816797	70.8	1.08E+08	3.16E+06	11.67 ^A	0.38 ^B	0.016%	1490	1.12E+08	4.94E+06	69.68	3.07	0.005%	-	
Copp4	-17.062683	137.816599	39.1	2.37E+08	4.82E+06	128.71	2.63	0.329%	612	8.60E+07	4.40E+06	110.70	5.67	0.018%	0.10	
Copp5	-17.062821	137.816802	126.5	1.35E+08	3.42E+06	20.00 ^A	0.54 ^B	0.016%	1125	6.03E+07	3.47E+06	20.17	1.17	0.002%	-	0.10
Calv1	-17.19355	137.48983	179.5	2.08E+08	4.31E+06	18.59	0.37	0.010%	16750	8.76E+07	4.24E+06	486.48	23.51	0.003%	-	
Calv2	-17.193394	137.489842	31	1.63E+07	1.17E+06	1.62	0.09	0.005%	12100	2.06E+08	6.24E+06	342.68	10.33	0.003%	-	
Calv3	-17.19359	137.489869	324	1.37E+08	3.43E+06	12.33	0.27	0.004%	32900	1.92E+08	6.10E+06	245.72	7.83	0.001%	0.10	0.10
			Co (ppm)	Co NPs ($n\text{ g}^{-1}$ soil)		Concentration of Co NPs (ng g^{-1} soil)		Co NPs/total Co (%)	Mn (ppm)	Mn NPs ($n\text{ g}^{-1}$ soil)		Concentration of Mn NPs (ng g^{-1} soil)		Mn NPs/total Mn (%)	Mn/Co ratio	
Queen Sally Prospect, Qld			6626.50	2.19E+08	4.28E+06	989.65	23.38	0.016%	729.75	6.72E+07	3.68E+06	9.53	0.50	0.0014%	3.26	
Mount Cobalt, Qld			879.67	2.40E+08	4.19E+06	228.91	6.53	0.034%	356.57	6.55E+07	3.39E+06	10.77	0.56	0.0032%	3.66	
Pyrite Hill, NSW			40.33	6.04E+07	2.09E+06	10.25	0.39	0.025%	231.64	4.45E+07	3.02E+06	10.88	0.71	0.0045%	1.36	
Young's Co Prospect, SA			6.77	1.10E+07	9.08E+05	5.03	0.356	0.064%	326.00	1.02E+08	4.53E+06	14.75	0.64	0.0049%	0.11	
Copperado, NT			115.18	1.28E+08	3.34E+06	36.06	0.85	0.075	1605.40	8.05E+07	4.09E+06	49.47	2.46	0.0053%	1.60	
Calvert, NT			178.17	1.20E+08	2.97E+06	10.84	0.24	0.0065	20583.33	1.62E+08	5.53E+06	358.29	13.89	0.0022%	0.74	

^AAverage minus outlier = 12.90.

^BAverage minus outlier = 0.40