

Mineralogical Characterisation to improve understanding of oral bioaccessibility of Cr and Ni in Basaltic Soils in Northern Ireland

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2	MINERALOGICAL CHARACTERISATION TO IMPROVE UNDERSTANDING OF ORAL
3	BIOACCESSIBILITY OF Cr AND NI IN BASALTIC SOILS IN NORTHERN IRELAND
4	
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18 ABSTRACT

19 Underlying bedrock is often the source of elevated levels of potentially toxic elements (PTEs) (including 20 Ni and Cr) in soils, which can be at concentrations exceeding regulatory guidelines for the protection of 21 human health. However geogenic contaminants are often not significantly bioavailable to humans as 22 they are bound tightly within the soil matrix. Therefore or al bioaccessibility testing can be used to 23 refine human health risk assessment by quantifying bioaccessible PTEs in soils, but should be augmented 24 with soil mineralogy data to support its use in risk assessment. Elemental mapping using Electro Probe 25 Microanalysis (EPMA) and mineralogical mapping using QEMSCAN®, an automated mineral/phase 26 analysis system based on a scanning electron microscope, were combined with quantitative X-Ray 27 Diffraction (XRD) and previous oral bioaccessibility and non-specific sequential extraction (CISED) 28 results for 3 soil samples overlying Palaeogene basalt lavas in Northern Ireland, to determine the effect of 29 soil mineralogy on oral bioaccessibility of Ni and Cr. Results indicate that Cr concentrations are 30 principally related to recalcitrant chrome spinel and primary iron oxides, which explains the relatively 31 low bioaccessibility of Cr. In contrast, Ni is more widely dispersed within the soils, with a proportion 32 of total Ni found in carbonates and weathering products, including secondary iron oxides and precursor 33 clay minerals, leading to the higher oral bioaccessibility measurements recorded for Ni than Cr.

34

35 Suggested keywords

36 Nickel, Chromium, Oral bioaccessibility, Basalt, Mineralogical analysis, Elemental mapping

37



38 Graphical abstract

42 Highlights

43	• Ni and Cr	analysis of Basaltic soils overlying Antrim Basalts of Northern Ireland
44	• Combined	d chemical and mineralogical data for improved understanding
45	• High reso	lution analysis of samples, consistent across analytical methods
46	• Bioaccess	sible Ni in precursor clay minerals, secondary Fe-oxides and carbonates
47	• Low Cr b	ioaccessibility as Cr predominantly in chrome spinel and primary Fe-oxides
48		
49	Abbreviation	S
50	BAF	Bioaccessible Fraction
51	BARGE	Bioaccessibility Research Group of Europe
52	BSE	Backscattered Electron
53	CISED	Non-specific Sequential Extraction coupled with Chemometric Analysis
54	CTM	Causeway Tholeiite Member
55	EDS	Energy Dispersive Spectrometer
56	EPMA	Electron Probe Micro Analyser
57	G	Gastric Phase
58	GI	Gastrointestinal Phase
59	LBF	Lower Basalt Formation
60	LOI	Loss on Ignition
61	PTE	Potentially Toxic Element

- 62 QEMSCAN Quantitative Evaluation of Minerals by Scanning Electron Microscopy
- 63 S4UL Suitable for Use Level
- 64 SDD Silicon Drift Detector
- 65 SEM Scanning Electron Microscope
- 66 SGV Soil Guideline Value
- 67 SOC Soil Organic Carbon
- 68 UBF Upper Basalt Formation
- 69 UBM Unified BARGE Method
- 70 WDS Wavelength Dispersive Spectrometers
- 71 XRD X-Ray Diffraction
- 72 XRFS X-ray Fluorescence

1.0 INTRODUCTION

75	Elevated concentrations of nickel (Ni) and chromium (Cr) from both geogenic and anthropogenic sources
76	have been identified in soils throughout the world including Canada (Vasiluk et al., 2011), Brazil (Colin
77	et al., 1990), the Czech Republic (Quantin et al., 2008), Poland (Kierczak et al., 2007), Portugal (Costa et
78	al., 2011), UK (Barsby et al., 2012; Palmer et al., 2014; Wragg et al., 2014), Italy (Albanese et al., 2015)
79	and Greece (Albanese et al., 2015; Argyraki and Kelepertzis, 2014; Kelepertzis and Stathopoulou, 2013).
80	Total concentrations of these elements are often at levels exceeding regulatory guidelines suggesting they
81	may potentially cause harm to human health. Recently this has been compounded by new toxicological
82	advice (EFSA, 2015) which indicates that tolerable daily intakes of oral Ni are lower than was assumed
83	in derivation of many of these guideline values. On this basis the Environment Agency in England and
84	Wales withdrew the Soil Guideline Value (SGV) for nickel in 2015 and a new "suitable for use level"
85	(S4UL) for Ni of 130mg kg ⁻¹ was published by Nathanail et al. (2015) for a residential land use that
86	includes the production of home-grown produce. S4ULs indicate a level of minimal or tolerable level of
87	risk, indicating a site is suitable for the land use the S4UL has been derived for (Nathanail et al., 2015).
88	Concentrations of PTEs above S4ULs may require further assessment of risks to determine if any
89	remedial action is required.
90	
91	However, total concentrations do not reflect the amount of a contaminant that is actually bioavailable to
92	humans via the oral, inhalation and dermal pathways (Ruby et al., 1999). The use of oral

- 93 bioaccessibility testing provides risk assessors with an estimation of the amount of an element that will

94	become dissolved in the gastro intestinal tract (and is therefore accessible to humans via the oral
95	pathway), allowing assessors to more accurately consider potential risks posed to human health. The
96	Unified BARGE Method (UBM) was developed by the BARGE (Bioaccessibility Research Group of
97	Europe) research group (Wragg et al., 2011) and has been validated against in vivo studies for As, Pb and
98	Cd (Denys et al., 2012). However, as oral bioaccessibility can be affected by a number of factors
99	including mineralogy, particle size, solid-phase speciation and encapsulation (Cave et al., 2011; Ruby et
100	al., 1999), a "lines of evidence" approach (CIEH, 2009) is recommended to support oral bioaccessibility
101	testing, utilising information relating to soil mineralogy and the mobility and distribution of the
102	contaminant in the soil.
103	
104	McIlwaine et al. (2014) used data from the Tellus Geochemical Survey of Northern Ireland (Smyth,
105	2007) and geological mapping to identify domains (areas where a readily identifiable factor can be
106	shown to control the concentration of an element) for a number of PTEs in Northern Ireland. Soils
107	overlying the Antrim Lava Group were identified as a domain with elevated Ni and Cr, with median Ni
108	concentrations in the domain being were approximately 4 times greater for Ni and 2.5 times greater for
109	Cr than the rest of Northern Ireland. However oral bioaccessisbility testing undertaken by (Barsby et al.,
110	2012; Palmer et al., 2014) indicate the oral bioaccessibility of Cr and Ni in these soils is quite low (Cr <
111	5.5%; Ni < 44%). Investigations undertaken by Cox et al. (2013) found that bioaccessible Cr in the
112	basaltic soils of Northern Ireland is strongly correlated with total Cr and Fe ₂ O ₃ , indicating that Cr is
113	predominantly present in phases associated with Fe ₂ O ₃ that have relatively low bioaccessibility.

114	Non-specific sequential extractions (CISED), showed that the majority of Cr was present in oxides, with
115	a only a very small component present in clays (Cox et al., 2013). In contrast Cox et al. (2013) found
116	that bioaccessible Ni (both G and GI) was not strongly correlated with total Ni, most of the major oxides
117	or Soil Organic Carbon (SOC). Indeed, CISED extractions showed that bioaccessible Ni was related to
118	all identified soil components, including calcium carbonate, aluminium oxide, iron oxide and clay-related
119	components, suggesting weathering significantly affects nickel bioaccessibility but has a less significant
120	role in the bioaccessibility of Cr in these soils (Cox et al., 2013). However, without detailed data
121	relating specifically to soil mineralogy and element distribution within the soils, interpretation of the role
122	of mineralogy on the oral bioaccessibility of Ni and Cr was incomplete.
123	
124	The aim of this research is to further investigate the controls on oral bioaccessibility of PTEs in Ni and
125	Cr rich soils overlying the Antrim Basalts in Northern Ireland to provide evidence to support the use of
126	oral bioaccessibility testing both in Northern Ireland and internationally. To meet this aim: 1) the
127	mineralogy of soils overlying the Antrim Basalts is characterised using both quantitative XRD and
128	QEMSCAN® analyses combined with detailed geochemical data; 2) detailed elemental and mineralogical
129	mapping are compared to determine which minerals host total Ni and Cr; and 3) this information is
130	related to results of previous bioaccessibility testing (Barsby et al., 2012) and non-specific sequential
131	extractions (Cox et al., 2013) to elucidate how the oral bioaccessibility of both Ni and Cr is affected by
132	soil composition.

134 2.0 MATERIALS AND METHODS

135 **2.1** Study area

136 The Antrim Lava Group was formed in two cycles of volcanic activity that occurred about 60 million 137 years ago (Lyle, 1979). It extends across the north eastern corner of Northern Ireland (Figure 1), 138 covering an area of 4009 km² (Cruickshank, 1997). The first cycle of volcanic activity produced olivine 139 theoleiite lavas that formed the Lower Basalt Formation (LBF), whilst fractionation of this magma gave 140 rise to intermediate lavas towards the top of the Lower Basalts (Mitchell, 2004). The second cycle of 141 volcanic activity, approximately 5 million years later, formed the Upper Basalt Formation (UBF) (also 142 olivine theoleiites) (Mitchell, 2004). In the period between the formation of the Upper and Lower 143 Basalts, a period of extensive chemical weathering of the Lower Basalts occurred, which resulted in the 144 formation of the Interbasaltic Formation comprising of deeply weathered and lateritised basalts that are 145 found between the Upper and Lower Basalt Formations (Hill et al., 2001). Also during the period 146 between the cycles of volcanic activity that formed the Upper and Lower Basalts, eruption of the mainly 147 quartz tholeiites of the Causeway Tholeite Member (CTM)) occurred (Mitchell, 2004). The Upper and 148 Lower Basalts are composed principally of plagioclase feldspars (labradorite), Mg-rich olivine containing 149 small spinal inclusions and pyroxene (augite) (Lyle, 1979) with magnetite, ilmenite and apatite also 150 present as accessory minerals (Hill et al., 2001).



153 Figure 1 Map showing the Antrim Lava Group.



155 Figure 2a shows the spatial distribution of total Ni concentrations determined during the Tellus survey. Median total Ni concentrations in the UBF and LBF were 100 mg kg⁻¹, with the highest Ni concentration 156 recorded in the Tellus Survey (334 mg kg⁻¹) reported for the LBF (Cox et al., 2013). 516 samples 157 158 overlying the Antrim Basalts (31%) have total Ni concentrations that exceed the "Suitable for Use Level" 159 (S4UL) for Ni (130 mg kg⁻¹) for a residential landuse (with homegrown produce) derived by Nathanail et 160 al. (2015). 161 162 Similar trends are observed for total Cr concentrations (Fig. 2b), which are generally about 3 to 4 times 163 greater than total Ni concentrations (Cox et al., 2013). Cr speciation was not determined during the

- 164 Tellus survey, so both the S4UL for Cr (III) and Cr (VI) have been used for comparison. All samples
- 165 from the study area (1664 samples; 100%) have total Cr concentrations that exceed the residential S4UL

- 166 for Cr VI of 6 mg kg⁻¹, whilst 3 samples (0.18%) exceed the residential with gardens S4UL for Cr III of
 910 mg kg⁻¹.
- 168
- 169 Cox et al., (2013) reported that bioaccessible Ni and Cr were generally greater in gastric phase extracts
- than in the gastrointestinal phase, with samples overlying the LBF containing the greatest amount of
- 171 bioaccessible Ni (mean gastric phase concentration of 6.17 mg kg⁻¹), while the UBF showed greater
- amounts of bioaccessible Cr (mean gastric phase concentration of 4.55 mg kg⁻¹). Ni and Cr
- 173 bioaccessible fraction (BAF) was also greater in the gastric phase than in the gastrointestinal phase, with
- 174 Ni BAFs being up to 8 times greater than Cr BAF.
- 175





- 178 for all Tellus soil samples overlying the Antrim Lava Group
- 179

2.2 Collection, preparation and soil analyses

182	During the Tellus geochemical survey, samples were disaggregated and sieved to a <2 mm fraction
183	(Smyth, 2007), prior to being analysed for a range of elements and major oxides using X-ray
184	fluorescence (XRFS) as well as pH and soil organic carbon (SOC) (Smyth 2007). Barsby et al., (2012)
185	reported the results of oral bioaccessibility testing for these samples using the Unified BARGE Method
186	(UBM) (Denys et al., 2012; Wragg et al., 2011). Both the actual bioaccessibility of PTEs (mg kg ⁻¹) and
187	the bioaccessible fraction (BAF) (the ratio of bioaccessible concentration from the UBM test and total
188	concentration by XRFS), are reported in the gastric and gastrointestinal phase to allow discussion of all
189	four measurements. Quality control procedures employed for XRFS, pH and LOI analyses are
190	presented in Smyth (2007), and Barsby et al., (2012) provides full details of the use of reference materials,
191	duplicates and blanks for UBM testing.
192	
193	Three sieved and dried surface soil samples (558363, 559503, 560141), retrieved from areas overlying
194	the Antrim Lava Group were recovered from the Tellus archive for quantitative XRD analyses and
195	mineralogical and elemental mapping. For optical and e-beam microscopy, two samples (558363,
196	559503) were prepared as polished thin sections by embedding in epoxy resin followed by grinding and
197	polishing to 30 μ m thickness with ethane diol and aluminium oxide, with final cleaning undertaken using
198	alcohol. A third sample (560141) was prepared as a 30 mm diameter epoxy mount, and polished to a 1
199	micron finish using diamond media. For e-beam analysis, all samples were carbon coated with
200	approximately a 25 nm layer of carbon, to allow the electron beam to conduct across the sample surface.

202	2.3 Quantitative XRD analysis
203	Quantitative XRD analysis was undertaken by X-Ray Mineral Services Colywn Bay, UK, using a Philips:
204	PW1730 X-ray Generator, with copper anode tube equipped with a Philips PW1050 Goniometer and
205	graphite monochromator.
206	
207	2.3.1 Whole (Bulk) Rock Analysis
208	Samples were disaggregated using a pestle and mortar and 'micronised' using a McCrone Micronising
209	Mill to obtain a mean particle diameter of between 5 - 10 microns. This was mixed with water and the
210	resulting slurry was dried overnight at 80°C, re-crushed and homogenised to a fine powder and
211	back-packed into an aluminium cavity mount, producing a randomly orientated sample for presentation
212	to the x-ray beam.
213	
214	Samples were analysed between 2° and $70^{\circ} 2\theta$ (theta) with a step size of 0.05°/sec using x-ray radiation
215	from a copper anode at 35kV, 30mA. X-Ray Mineral Services "Traces" and "Search-Match" software
216	was used to compare the x-ray diffraction pattern from the unknown sample with the International Centre
217	for Diffraction Data PDF-4 Minerals database to identify unknown minerals. Amorphous content was
218	calculated by spiking with silicon (metal powder) and Siroquant software was used to quantify phases
219	identified in each sample.

221 2.3.2 Clay Mineral analysis

222	The <2 micron fraction of a 5 gram split of disaggregated sample, was separated by ultrasound, shaking
223	and centrifugation. The total weight of clay extracted was determined by removing a 20ml aliquot of
224	the final clay suspension and evaporating to dryness at 80°C. Clay XRD mounts were obtained by
225	filtering the clay suspension through a Millipore glass microfiber filter and drying the filtrate on the filter
226	paper. The samples were analysed as an untreated clay, after saturation with ethylene glycol vapour
227	overnight and following heating at 380°C for 2 hours and 550°C for one hour. The initial scan for these
228	four treatments was between 3° and 35° 2 θ (theta) at a step size of 0.05°/sec using x-ray radiation from a
229	copper anode at 40kV, 30mA. The untreated sample was also analysed between 24-27° 2θ at a step size
230	of 0.02 °/2 sec to further define kaolinite/chlorite peaks.
231	
232	Diffractograms from the four clay treatments were overlain to identify the clay mineral assemblages

233 present. Peak intensities were measured to calculate the relative amounts of clay minerals present, which

- 234 were subsequently used to quantify the clay minerals with respect to the whole rock by reference to the
- total amount of <2 micron clay fraction. An indication of the clay minerals crystallinity was given by
- assessment of the peak width for each component.

237

238 2.4 Mineralogical mapping

239 Mineralogical mapping was undertaken using QEMSCAN[®], an automated mineral/phase analysis system
240 based on a scanning electron microscope (SEM) that provides rapid determination and quantification of

241	the mineralogy, chemical composition (through defined databases) and grain size of a sample (Gottlieb et
242	al., 2000; Haberlah et al., 2011). QEMSCAN [®] is a mature technique that is over 40 years old and has
243	been used in a variety of research projects (Pirrie and Rollinson, 2011; Santoro et al., 2014). Analysis
244	was undertaken at the Camborne School of Mines, University of Exeter, using a QEMSCAN® 4300
245	system.
246	
247	During QEMSCAN [®] analysis an electron beam is rastered across the sample surface producing a
248	Backscattered Electron (BSE) image and X-rays which are used to identify the mineralogy. For this
249	investigation, samples were analysed using the Fieldscan mode using iMeasure software, which
250	measured each sample in fields (1.5mm squares) at a 10 μ m X-ray pixel spacing, with the resin media
251	ignored due to being below a pre-set BSE threshold. Data processing was undertaken using iDiscover
252	software, which is an involved process that requires checks of the mineral database and refinement of the
253	data specific to the context of the sample type. The resultant fields are then recombined (stitched) to
254	give an overall false colour mineral map with corresponding data tables for mineral abundances and
255	associations. The advantage of Fieldscan mode was that it examined the entire sample area providing
256	excellent spatial modal mineralogy with between 1.3 and 2.4 million analysis points. However, pixel
257	resolution was carefully designed to avoid excessive measurement time, thus minerals or textures less
258	than the pixel resolution (10 microns) are poorly represented but compensated for by the BSE and
259	element maps. The advantages and limitations of the QEMSCAN® technique are discussed in detail in
260	Andersen et al. (2009) and Rollinson et al. (2011).

262	Standard operating conditions were 25kV and 5nA using a tungsten filament operating under a
263	customized high vacuum. X-ray collection rate was 1000 counts combined from four EDS Bruker
264	Silicon Drift (SDD) detectors, with a maximum X-ray resolution of around 1 micron. Operation of
265	QEMSCAN® followed quality control procedures developed at the Camborne School of Mines,
266	University of Exeter, for sample preparation, instrument calibration, operation and data processing. See
267	Rollinson et al. (2011) for further details.
268	
269	Minerals with similar chemical composition were grouped together and groups were described either by
270	the elemental composition, or in some cases the minerals deemed most likely to be present as shown in
271	Table 1. QEMSCAN® cannot separate polymorphs (minerals with the same chemistry but different
272	crystallography) as its analysis is based on chemical spectra and minerals/phases with very similar or
273	overlapping chemical spectra can be difficult to separate. Very fine grained material such as mixed
274	clays (less than 5 microns) may also be difficult to separate chemically due to the beam excitation
275	volume effects (Rollinson et al., 2011) and only elements that are greater than approx. 3% in
276	concentration at each analysis point may be detected (Andersen et al., 2009). Total percentages for each
277	mineral group reported here, have been corrected to include soil organic carbon (SOC) as measured
278	during the Tellus survey, as SOC is not quantified by QEMSCAN [®] analysis.
279	
	Mineral Category Mineral Description
	Background All resin/mounting media and related edge effects

Mineral Category	Mineral Description
Background	All resin/mounting media and related edge effects

Chrome spinel	Includes any phase with Cr, Fe, Al and Mg; such as Chromite, Chrome
	metal and Chrome Spinel
Fe Ox/CO ₃	Fe oxides and carbonates such as Siderite, Hematite, Magnetite,
	Ti-Magnetite, Fe Metal and any other Fe-Oxide/Carbonate.
Mn phases	Includes Mn Silicates and Mn Fe Oxides
Rutile	Any phase with Ti and O; includes Rutile/Anatase/Brookite
Ilmenite	Any phase with Fe, Ti and O
Zircon	Any phase with Zr, Si and O
REE phases	Includes Monazite (Ce Phosphates)
Quartz	Quartz and other silica minerals
Plagioclase	Plagioclase Feldspars: phases with Na, Al, Si and O to Ca, Al, Si and O.
feldspar	May include a boundary effect with Quartz and Al oxide polishing media
	(mixed spectra looks like Albite)
K-Feldspar	Any phase with K, Al, Si and O; includes Orthoclase/Microcline/Sanidine
Muscovite/Illite	Muscovite Mica, may include Illite (K, Al, Si and O)
Fe Al K silicates	Any phase with Fe, Al, K and Si; such as Biotite Mica and any other Mica
	except Muscovite, may include Glauconite
Mg + Fe silicates	Any phase with Mg, Fe and Si; such as Olivine, Talc, Serpentine Group,
	includes Fe Silicates
Ca Mg Fe silicates	Any phase with Ca, Mg, Fe and Si (with or without Fe and Al); such as
	Hornblende, Tremolite, Augite, Diopside, Actinolite, maybe Amphiboles
	and Pyroxenes
Al silicates	Any phase with AI, Si and O; separated from Kaolinite by the AI-Si ratio.
(excluding	May contain low amounts of other elements such as Fe, Mg and Ca. May
kaolinite)	
Kaolinite	Al silicates such as Kaolinite/Halloysite/Dickite and Topaz, and any other Al silicate
Fe Al (Mg)	Any phase with Fe, Al and Si, with or without Mg; such as Chlorite/
silicates	Clinochlore, Nontronite, Vermiculite
Calcite	Any phase with Ca, O and C
Apatite	Apatite and any other Ca Phosphates
Others	Any other mineral not included above. Boundary/polishing effects

280 Table 1 Mineral groupings used for reporting results of QEMSCAN[®] analysis

282 2.5 Elemental mapping

283 Elemental analysis and mapping was undertaken at the School of Earth Sciences, University of Bristol

- using a JEOL JXA8530F electron probe microanalyser (EPMA), equipped with both a silicon drift
- detector (SSD) energy dispersive spectrometer (EDS) and 5 wavelength dispersive spectrometers
- 286 (WDS). Results from the QEMSCAN[®] analysis were used to identify locations for quantitative element
- 287 point analysis and areas for elemental mapping on each of the three samples. Point locations included

²⁸¹

representative examples of chrome spinel, iron oxide, calcite and apatite. Mapping was targeted on
areas of typical clay composition and where it was suspected olivine was weathering within the basalt.
Quantitative analysis of elemental concentrations was undertaken by WDS. Details of EPMA setup are
summarised in Table 2.

292

	Major and trace elements (stable mineralogy)	Major elements (unstable mineralogy)	Trace elements (unstable mineralogy)	Major and trace elements (apatite)	Major and trace elements (calibration of maps 0043, 0059, 0061 and 0063)	Major and trace elements (calibration of maps 0029-0032)
Acceleration voltage (kV)	20	20	20	20	20	20
Probe current (nA)	40	2	40	2	40	40
Beam size (µm)	1	10	1	15	1	1

293 Table 2 Acceleration voltages, probe currents, beam size and dwell times for quantitative

294 analyses

295

```
296 The crystals and standards used were Al as Al<sub>2</sub>O<sub>3</sub> (Amelia albite), Ca as CaO (Wollastonite), Cr as Cr<sub>2</sub>O<sub>3</sub>,
```

297 Fe as FeO (Ilmenite), Mg as MgO (St John's Island Olivine), Mn as MnO, Na as Na₂O (Ameilia albite), P

as P₂O₅ (Durango apatite), Si as SiO₂ (St John's Island Olivine), Ti as TiO₂ (Ilmenite), K as K₂O (Eifel

sanidine); Ni and NiO, Zn as ZnO, V as V₂O₃ and Nb as Nb₂O₅ (LiNbO₃) and F as Durango apatite. V

300 was measured using an overlap correction, which subtracts the overlapping Ti Kb component based on

301 the intensity on the Ti Ka line.

303	The distribution of Mn, Ca, P, Mg, Ti, K, Si, Fe, Na, Al, Cr and Ni was determined using elemental
304	mapping. Mn, Ca, P, Mg, Ti, K, Si and Fe were mapped using EDS, and Na, Al, Cr and Ni were
305	mapped using WDS, with Ni mapped on two spectrometers. For the WDS elements a peak map and an
306	upper background map was collected providing net count maps. The EDS maps are total counts. The
307	maps were then calibrated using a calibration curve determined from a series of quantitative point
308	analyses undertaken within each mapping area. The size of the measured areas for each map are shown in
309	Table 3. All maps were measured with a step size of 1 μ m.

310

Map No	Sample No	Width (µm)	Height (µm)	Step size (µm)
0029	558363	100	128	1
0030	558363	100	128	1
0031	559503	128	100	1
0032	559503	100	128	1
0043	558363	200	256	1
0059	560141	100	128	1
0061	560141	100	128	1
0063	560141	140	180	1

311 Table 3 Measured area and step size for each elemental map

312

313 3.0 RESULTS AND DISCUSSION

314 3.1 Geochemical data

315 Major element data (Table 4) shows that between 80 to 85% of the soils comprise Si, Al, Fe and SOC.

316 The contribution these elements make to the soil is similar between all three soils reflecting that they

317 overlie bedrock of similar origin. Ca and Mg are present in all soils at concentrations of approximately

318 2%, as would be expected given the presence of plagioclase feldspars and pyroxene in the underlying

319 bedrock (Lyle, 1979). Sample 560141 contained more Ca than the other 2 samples, which is consistent

	Sample	Sample	Sample		Average co	mnositions	1
	558363	559503	560141	Decelt	Lithomarga	Latarita	Iron orust
				(n=5)	(n=126)	(n=99)	(n=10)
SiO ₂ %	39.60	39.50	43.40	43.94	37.33	21.54	12.72
TiO ₂ %	1.56	1.37	1.08	1.87	2.64	3.99	9.99
A12O3 %	13.10	14.70	13.50	15.15	27.86	33.78	17.51
Fe ₂ O ₃ %	11.24	11.42	8.68	13.61	18.03	25.03	45.51
MnO %	0.22	0.27	0.11	0.34	0.18	0.1	0.06
MgO %	2.40	2.60	2.10	6.94	2.32	0.37	0.4
CaO %	1.76	2.53	3.10	9.32	1.8	0.45	0.59
Na ₂ O %	0.30	0.60	0.60	2.24	0.37	0.15	0.07
K ₂ O %	0.67	0.39	0.56	0.2	0.11	0.04	0.04
P ₂ O ₅ %	0.32	0.56	0.41	0.15	0.2	0.13	0.07
SOC %	16.62	19.89	19.70	3.39	14.22	17.35	9.78
Ba (ppm)	238	207	250	53	87	81	248
Ce (ppm)	26	26	26	22	35	27	26
Cr (ppm)	448	300	293	205	384	572	832
Cu (ppm)	93	142	72	87	189	197	89
Nb (ppm)	8	8	9	3	6	18	74
Ni (ppm)	175	167	122	205	557	404	88
Pb (ppm)	21	16	22	<3	<3	6	10
Rb (ppm)	19	13	10	3	4	5	9
Sn (ppm)	3	2	3	<8	<8	< 8	<8
Sr (ppm)	42	82	116	233	87	30	67
Th (ppm)	2	2	2	<2	<2	4	13
U (ppm)	2	1	1	<2	<2	<2	3
V (ppm)	260	259	233	278	389	627	1227
Zn (ppm)	127	176	127	88	98	77	72
Zr (ppm)	166	106	95	84	90	142	173

322 Table 4 Geochemical composition of each soil sample (as determined by XRF analysis

323 undertaken during the TELLUS survey) and averages geochemical composition for fresh and

324 altered Antrim basalt. ¹ Average concentrations of the main horizons within the laterite profile

325 (Hill et al., 2001)

326

327 Comparison of the geochemical composition of the soils with composition data reported by Hill et al.

328	(2001) (Table 4) for the underlying basalt and the deeply weathered and lateritised basalts of the
329	Interbasaltic Formation found between the Upper and Lower Basalt Formations, shows the soils are
330	consistent with the weathered basalt, particularly the lithomarge layer from the laterite profile (Si, Ca,
331	Mg and Na are all similar). Hill et al. (2001) report that the lithomarge is predominantly comprised of
332	clays, which are mostly kaolinite and meta-halloysite at the top of the lithomarge profile, but also
333	includes a layer of "saprock" at the base of the profile that contains montmorillonite and vermiculite (Hill
334	et al., 2001).
335	
336	3.2 Mineralogy
337	Quantitative XRD analysis determined that the amorphous content of the samples was between 65 to
338	80% (Figure 3). This very high amorphous content is likely to relate to organic materials (SOC was
339	greater than 15% for these samples) and non-crystalline weathering products such as amorphous iron
340	oxides (perhaps intergrown with clay minerals), and other precursor minerals for clays. The presence of
341	large amounts of amorphous iron oxides would explain why significant amounts of the Fe identified by
342	geochemical analysis was not identified by XRD. In their study of serpentine soils from the Czech
343	Republic, Quantin et al., (2008) also found that sequential extractions revealed significant amounts
344	(nearly 50%) of iron was present in iron (hydr)oxides that were not detected by XRD analysis.



346 Figure 3 Proportion of mineral components by QEMSCAN[®] (vol %) (left) and XRD (wt %)

349	XRD analyses also showed that smectite, illite and chlorite constitute up to 15% of the samples (Figure
350	3), with the greatest clay content in the sample with the lowest amorphous content (558363), suggesting
351	this soil is more weathered than the other samples. Although the amorphous content of the sample was
352	high and it was suspected that a significant proportion of this was 'clay like' material (including
353	precursor clay minerals and protoclays), the percentage of soils recovered for clay XRD analysis (<2
354	microns) was relatively low (1-8%). Images from QEMSCAN [®] and EPMA showed this was because
355	the vast majority of the agglomerations in the soil were larger than 2 microns. Clay XRD showed that
356	68% of clay sized particles in sample 558363 and all clay sized particles in 559503 and 560141 were
357	found to be a randomly interstratified illite/smectite, and the remainder of the clay fraction of sample
358	558363 was a poorly crystalised chlorite, again supporting the hypothesis that weathering of the soils is
359	incomplete.
360	
361	QEMSCAN [®] analysis added further support to this hypothesis as it determined that all three samples
362	were composed primarily of minerals initially identified as Fe Al (Mg) silicates and Al silicates (65-70%)
363	that were often identified at the scale of individual pixels (Figure 4), suggesting they may in fact reflect
364	amorphous protoclays of variable content. Mineral association data from QEMSCAN [®] supports this, as
365	Al silicates are significantly more likely to touch Fe Al (Mg) silicates than any other mineral. Therefore
366	from this point on, these minerals have been grouped together into an 'amorphous protoclay' group.

- 367 QEMSCAN[®] also identified illite (<1.58%), mica (<0.97%) and kaolinite (<0.90%), with the greatest
 - **Mineral Name** Background Chrome spinel Fe Ox/CO3 Mn phases Rutile Ilmenite Zircon REE phases Quartz Plagioclase feldspar K-Feldspar Muscovite/Illite Fe Al K silicates Mg + Fe silicates Ca Mg Fe silicates Montmorillonite Kaolinite Fe Al (Mg) silicates Calcite Apatite Others
- amounts of these minerals in sample 558363.

370 Figure 4 A typical intergrown clay grain from sample 558363



381	chrome spinels. Olivine was identified by $QEMSCAN^{\text{(B)}}$ to be present at low concentrations (<0.5%) in
382	the soil, reflecting the fact that although it is present in the underlying basalt bedrock in significant
383	concentrations (Lyle, 1979), it is very easily weathered (Delvigne et al., 1979). Significantly more
384	apatite (0.29%) and calcite (0.19%) were recorded in sample 560141, than the other two samples (0.01%) and calcite (0.19%) were recorded in sample 560141.
385	apatite and <0.07% calcite), which supports the finding by Cox et al. (2013), using the CISED
386	methodology, that significantly more carbonate was present in Sample 560141 than the other 2 samples.
387	
388	Overall results from XRD and QEMSCAN [®] analyses are consistent, within the limitations of each
389	method as set out by (Boni et al., 2013), and suggest a mineralogical makeup similar to "saprock" which
390	Hill et al. (2001) found at the base of the lithomarge layer in the underlying Interbasaltic Formation.
391	QEMSCAN [®] allowed greater characterization of the significant quantity of amorphous material in the
392	samples than XRD, but was unable to distinguish between polymorphs. QEMSCAN [®] also allowed
393	identification and mapping of trace mineralogy at concentrations below the detection limits of XRD. It
394	should be noted that quantification analyses by XRD cannot be directly compared with measurements by
395	QEMSCAN [®] , as XRD is reported in wt % whilst QEMSCAN [®] results refer to modal abundance (vol %),
396	as accurate densities of each mineral were uncertain in this study and so wt % were not calculated (Boni
397	et al., 2013).
398	

3.3 Distribution of Cr and Ni within minerals

400 Ni was generally dispersed throughout element Maps 0031, 0032 and 0061 (which had the lowest

401	maximum Ni concentrations), with areas of elevated Ni concentrations associated with individual
402	minerals being more obvious in Maps 0029, 0030, 0043, 0059 and 0063 (which had the highest
403	maximum Ni concentrations). Similarly less Cr was identified in element Maps 0032 and 0061 (<900
404	mg kg ⁻¹), where it was generally dispersed throughout the maps and could not be attributed to specific
405	minerals. Insignificant quantities of Cr were identified in map 0031. As Map 0029 duplicated what is
406	shown in Maps 0059 and 0063, results from Maps 0030, 0043, 0059 and 0063 are presented in Figures 5
407	to 8. All results from elemental analysis are presented as wt % of the relevant oxide.

409 **3.3.1** Chrome spinel

410 Quantitative analysis of 11 individual points within chrome spinels revealed that concentrations of Cr 411 were typically in the range 18 to 40%. Given the proportion of chrome spinel identified in each sample by QEMSCAN[®], if these Cr concentrations are typical of chrome spinels in the sample, chrome spinels 412 413 contribute between 20 and 80% of total Cr in each sample. Fe, Al and Mg contents in chrome spinels 414 were typically 14 to 50%, 5 to 30% and 3 to 17% respectively, with Ni content being positively 415 correlated with Mg content and negatively correlated with Ca and Mn content. Si concentrations were 416 generally less than 0.02% while Ti was only elevated (9% and 14%) at two of the points identified as chrome spinel. 500 to 2500 mg kg⁻¹ of Ni and 1300 to 11000 mg kg⁻¹ V was identified in all chrome 417 418 spinels. Given that chrome spinels had been investigated by point analysis, only one map (0059, Figure 419 7) was selected to include a chrome spinel, and in this case, Cr and Ni concentrations were both within 420 the range noted in the point analysis. Map 0043 (Figure 6) also revealed what appears to be a small Cr

421 spinel of Fe-Mg oxide with elevated Cr.





424 Figure 5 Detailed mapping of sample 558363 (Map 0030): (a) shows a BSE image of the map area;

- 425 (b) shows mineralogical mapping of the map area (key for this map shown in Figure 4); and, (c), (d),
- 426 (e), (f), (g) and (h) show elemental mapping for Cr, Ni, Al, Mg, Si and Fe.
- 427





429 Figure 6 Detailed mapping of sample 558363 (Map 0043): (a) shows a BSE image of the map area;

- 430 (b) shows mineralogical mapping of the map area (key for this map shown in Figure 4); and, (c), (d),
- 431 (e), (f), (g) and (h) show elemental mapping for Cr, Ni, Al, Mg, Si and Fe.



433 Figure 7 Detailed mapping of sample 560141 (Map 0059): (a) shows a BSE image of the map area;

- 434 (b) shows mineralogical mapping of the map area (key for this map shown in Figure 4); and, (c), (d),
- 435 (e), (f), (g) and (h) show elemental mapping for Cr, Ni, Al, Mg, Si and Fe.
- 436



437

438 Figure 8 Detailed mapping of sample 560141 (Map 0063). (a) shows a BSE image of the map

- 439 area, (b) shows mineralogical mapping of the map area (key for this map shown in Figure 4), whilst
- 440 (c), (d), (e), (f), (g) and (h) show elemental mapping undertaken for Cr, Ni, Al, Mg, Si and Fe.

442 3.3.2 FeOx

443	Fe oxides were easily identified and therefore could be examined in detail using point analysis.
444	Individual point analysis of 18 points identified as iron oxides in QEMSCAN® analysis, revealed these
445	minerals were a combination of primary iron oxides and iron oxides intergrown with clays, that are
446	known to be alteration products of both the weathered olivine (Delvigne et al., 1979) and pyroxene
447	(Noack et al., 1993) that originated in the underlying basalt. Fe oxides intergrown with clays were
448	identified by their textured appearance on BSE images and the presence of Si at concentrations of greater
449	than 1.5%. Primary oxides by comparison had Si concentrations of $<1.5\%$ and were smooth.
450	Generally the highest Fe concentrations (>65%) were encountered in the primary oxides, while lesser
451	concentrations (30 to 65%) were present in intergrown oxides and clays. Cr concentrations in these
452	minerals were generally less than 150 mg kg ⁻¹ , with the exception of Cr in primary iron oxides which was
453	greater than 2000 mg kg ⁻¹ in two out of the four primary iron oxides tested. Ni concentrations were also
454	generally less than 100 mg kg ⁻¹ , however elevated Ni concentrations (between 100 and 400 mg kg ⁻¹) were
455	identified in 5 of the 18 points tested, 4 of which were associated with intergrown oxides. Quantin et
456	al.'s (2008) observation that only secondary Fe-Mn-oxides (and not secondary Fe-oxides) contained
457	elevated Ni, was not confirmed in secondary iron oxides in this study as all secondary Fe-oxides
458	contained some Ni, and Mn concentrations in none of the Fe-oxides exceed 1.5%.
459	
460	Elemental mapping revealed similar results, with minerals with high Fe content not necessarily

461 coinciding with areas of significantly elevated Cr and Ni (Figures 5 to 8). However mapping did

462	highlight a number of minerals with elevated Cr (450-2000 mg kg ⁻¹) and Ni (500-1900 mg kg ⁻¹) with
463	high Fe (>30%) and Ti (>10%) and zero Si concentrations. These minerals were identified as primary
464	Fe-Ti oxides. Although these minerals contained elevated Ti, inspection of Figures 5 to 8 showed Ti
465	was not necessarily correlated with either elevated Cr or Ni. No secondary iron oxides intergrown with
466	clays, containing elevated Ni or Cr were identified during elemental mapping. This was not surprising
467	as mapping did not specifically target Fe oxides identified in QEMSCAN® analysis, as these had been
468	extensively investigated by point analysis. The primary oxides noted above are very small particles that
469	were obvious due to their elevated Fe concentration.
470	
471	3.3.3 Pyroxene
472	Elevated Ni (500-1000 mg kg ⁻¹) and Cr (500-3500 mg kg ⁻¹) were identified in mineral grains in Map
472 473	Elevated Ni (500-1000 mg kg ⁻¹) and Cr (500-3500 mg kg ⁻¹) were identified in mineral grains in Map 0032 (2 No) and 0043 (Figure 6) (2 No) that contained Si (approx. 50%), Al (2-14%), Fe (5-10%), Ca
472 473 474	Elevated Ni (500-1000 mg kg ⁻¹) and Cr (500-3500 mg kg ⁻¹) were identified in mineral grains in Map 0032 (2 No) and 0043 (Figure 6) (2 No) that contained Si (approx. 50%), Al (2-14%), Fe (5-10%), Ca (8%) and Mg (10-15%), with no Na or K present. Both grains on map 0043 were identified by
 472 473 474 475 	Elevated Ni (500-1000 mg kg ⁻¹) and Cr (500-3500 mg kg ⁻¹) were identified in mineral grains in Map 0032 (2 No) and 0043 (Figure 6) (2 No) that contained Si (approx. 50%), Al (2-14%), Fe (5-10%), Ca (8%) and Mg (10-15%), with no Na or K present. Both grains on map 0043 were identified by QEMSCAN [®] as Ca Mg Fe silicates, but both grains on Map 0030 (Figure 5) were smaller than the
 472 473 474 475 476 	Elevated Ni (500-1000 mg kg ⁻¹) and Cr (500-3500 mg kg ⁻¹) were identified in mineral grains in Map 0032 (2 No) and 0043 (Figure 6) (2 No) that contained Si (approx. 50%), Al (2-14%), Fe (5-10%), Ca (8%) and Mg (10-15%), with no Na or K present. Both grains on map 0043 were identified by QEMSCAN [®] as Ca Mg Fe silicates, but both grains on Map 0030 (Figure 5) were smaller than the QEMSCAN [®] pixel size and were therefore not categorised. Given the underlying geology is basalt and
 472 473 474 475 476 477 	Elevated Ni (500-1000 mg kg ⁻¹) and Cr (500-3500 mg kg ⁻¹) were identified in mineral grains in Map 0032 (2 No) and 0043 (Figure 6) (2 No) that contained Si (approx. 50%), Al (2-14%), Fe (5-10%), Ca (8%) and Mg (10-15%), with no Na or K present. Both grains on map 0043 were identified by QEMSCAN [®] as Ca Mg Fe silicates, but both grains on Map 0030 (Figure 5) were smaller than the QEMSCAN [®] pixel size and were therefore not categorised. Given the underlying geology is basalt and that concentrations of Si, Al, Fe, Ca and Mg fall within the range reported for pyroxenes in Deer et al.
 472 473 474 475 476 477 478 	Elevated Ni (500-1000 mg kg ⁻¹) and Cr (500-3500 mg kg ⁻¹) were identified in mineral grains in Map 0032 (2 No) and 0043 (Figure 6) (2 No) that contained Si (approx. 50%), Al (2-14%), Fe (5-10%), Ca (8%) and Mg (10-15%), with no Na or K present. Both grains on map 0043 were identified by QEMSCAN [®] as Ca Mg Fe silicates, but both grains on Map 0030 (Figure 5) were smaller than the QEMSCAN [®] pixel size and were therefore not categorised. Given the underlying geology is basalt and that concentrations of Si, Al, Fe, Ca and Mg fall within the range reported for pyroxenes in Deer et al. (1992), it is likely that all 4 grains are pyroxene, which is known to host elevated Ni and Cr . In
 472 473 474 475 476 477 478 479 	Elevated Ni (500-1000 mg kg ⁻¹) and Cr (500-3500 mg kg ⁻¹) were identified in mineral grains in Map 0032 (2 No) and 0043 (Figure 6) (2 No) that contained Si (approx. 50%), Al (2-14%), Fe (5-10%), Ca (8%) and Mg (10-15%), with no Na or K present. Both grains on map 0043 were identified by QEMSCAN [®] as Ca Mg Fe silicates, but both grains on Map 0030 (Figure 5) were smaller than the QEMSCAN [®] pixel size and were therefore not categorised. Given the underlying geology is basalt and that concentrations of Si, Al, Fe, Ca and Mg fall within the range reported for pyroxenes in Deer et al. (1992), it is likely that all 4 grains are pyroxene, which is known to host elevated Ni and Cr . In contrast significant areas of Map 0029 were identified as Ca Mg Fe silicates by QEMSCAN [®] , but did not
 472 473 474 475 476 477 478 479 480 	Elevated Ni (500-1000 mg kg ⁻¹) and Cr (500-3500 mg kg ⁻¹) were identified in mineral grains in Map 0032 (2 No) and 0043 (Figure 6) (2 No) that contained Si (approx. 50%), Al (2-14%), Fe (5-10%), Ca (8%) and Mg (10-15%), with no Na or K present. Both grains on map 0043 were identified by QEMSCAN [®] as Ca Mg Fe silicates, but both grains on Map 0030 (Figure 5) were smaller than the QEMSCAN [®] pixel size and were therefore not categorised. Given the underlying geology is basalt and that concentrations of Si, Al, Fe, Ca and Mg fall within the range reported for pyroxenes in Deer et al. (1992), it is likely that all 4 grains are pyroxene, which is known to host elevated Ni and Cr . In contrast significant areas of Map 0029 were identified as Ca Mg Fe silicates by QEMSCAN [®] , but did not contain significantly elevated Cr or Ni.

482 3.3.4 Olivine

483	Between 1000 and 2500 mg kg ⁻¹ of Ni and insignificant quantities of Cr were observed in maps 0029 and
484	0063 (Figure 8) in distinct areas in agglomerations within the soil matrix. These areas, that were
485	composed of 30-40% Si, 10-35% Fe, 25-50% Mg but no Al, were identified as Mg and Fe silicates
486	(which includes olivine) by QEMSCAN [®] and have a composition that is consistent with and Mg rich
487	olivine (Deer et al., 1992). Mg rich olivine is known to host both Ni and Cr, but generally Cr is present
488	as minute plates of chromite (Deer et al., 1992). Increasing amounts of Mg are often associated with
489	increased Ni (Wedephol, 1978), and this is observed as 2500 mg kg ⁻¹ Ni was recorded in Map 0063
490	(Figure 8) in an area with 48% Mg and 1000 mg kg ⁻¹ Ni in Map 0029 in an areas with 25% Mg.
491	
., -	
492	3.3.5 Clay like minerals
492 493	3.3.5 Clay like mineralsClays and other clay like minerals were generally identified by visual inspection as specific grains with
492 493 494	3.3.5 Clay like minerals Clays and other clay like minerals were generally identified by visual inspection as specific grains with mottled or dappled surfaces or the secondary minerals that appear to make up the matrix in large
492 493 494 495	3.3.5 Clay like minerals Clays and other clay like minerals were generally identified by visual inspection as specific grains with mottled or dappled surfaces or the secondary minerals that appear to make up the matrix in large agglomerations. Although these minerals appeared to be ubiquitous, it was impossible to visually
 492 493 494 495 496 	3.3.5 Clay like minerals Clays and other clay like minerals were generally identified by visual inspection as specific grains with mottled or dappled surfaces or the secondary minerals that appear to make up the matrix in large agglomerations. Although these minerals appeared to be ubiquitous, it was impossible to visually identify which contained elevated Ni and Cr and therefore point analysis did not reveal significantly
 492 493 494 495 496 497 	3.3.5 Clay like minerals Clays and other clay like minerals were generally identified by visual inspection as specific grains with mottled or dappled surfaces or the secondary minerals that appear to make up the matrix in large agglomerations. Although these minerals appeared to be ubiquitous, it was impossible to visually identify which contained elevated Ni and Cr and therefore point analysis did not reveal significantly elevated concentrations of Cr and Ni in clay-like minerals. Typically concentrations of Cr and Ni
 492 493 494 495 496 497 498 	3.3.5 Clay like minerals Clays and other clay like minerals were generally identified by visual inspection as specific grains with mottled or dappled surfaces or the secondary minerals that appear to make up the matrix in large agglomerations. Although these minerals appeared to be ubiquitous, it was impossible to visually identify which contained elevated Ni and Cr and therefore point analysis did not reveal significantly elevated concentrations of Cr and Ni in clay-like minerals. Typically concentrations of Cr and Ni identified during point analysis of clay-like grains were between 100-400 and 300-800 mg kg ⁻¹

500 minerals whilst no significantly elevated Cr was identified in any of these materials, other than whisps of

501 elevated Cr (approx. 2000 mg kg⁻¹) within what appeared to be a claylike weathering products on the

502	boundaries of a distinct grain of olivine in map 0063 (Figure 8) which appear to be associated with
503	depleted Mn and Fe.

505	Elevated Ni concentrations (up to 2200 mg kg ⁻¹) were hosted in what appeared to be clay-like materials
506	(generally identified as as Fe Al (Mg) silicates by QEMSCAN®). This mineral contained 14-24% Si,
507	5-16% Al, 6-20% Fe and up to 9% Mg, with increasing Ni concentration being weakly correlated with
508	increasing Fe. Delvigne et al. (1979) reported that during weathering in shallow media under both
509	hydrated and oxidizing conditions, iron enters into the chlorite lattice forming a mixed structure of
510	goethite and magnesium smectite.
511	
512	Maps 0030 (Figure 5) and 0043 (Figure 6) were targeted on areas of what appeared to be agglomerations
513	containing claylike minerals. Map 0030 shows elevated Ni (1000 to 1750 mg kg ⁻¹) throughout the
514	whole map in some of the grains that were identified as Fe Al (Mg) silicates by QEMSCAN [®] . A
515	particularly large grain in the bottom left of Map 0030, hosting 1300 mg kg ⁻¹ of Ni, was identified as a
516	mixture of Fe Al (Mg) silicates and kaolinite by QEMSCAN [®] . Less Ni was present in clay like
517	minerals in map 0043, with a large grain, identified as Fe Al (Mg) silicates by QEMSCAN, hosting 700
518	mg kg ⁻¹ Ni and a smaller grain QEMSCAN [®] identified as Fe Al (Mg) silicates mixed with illite, hosting
519	500-600 mg kg ⁻¹ Ni.
520	

521 Map 0059 (Figure 7) surveyed an area of what appeared to be olivine, that was in places significantly

522	weathered, enclosing a chrome spinel. Elevated Ni was encountered throughout the grain, with the lowest
523	concentrations (400-1000 mg kg ⁻¹) observed in Mg rich areas (18-25% Mg) at the centre of the grain.
524	These areas have very little Al, and were identified as Mg Fe silicates by QEMSCAN® and are likely to
525	be predominantly unweathered olivine. Concentrations of Ni increase in surrounding areas, which also
526	show increased Al and Fe and decreased Mg compared with the olivine. These are identified by
527	QEMSCAN® as Fe Al (Mg) silicates and are likely to be protoclays that are initial alteration products of
528	olivine. The highest concentrations of Ni (up to 2000 mg kg ⁻¹) are found in fractures within the grain
529	that also have the highest Al (up to 25%) and Fe (up to 28%) and lowest Mg (approximately 10%)
530	concentrations, suggesting Ni and Fe are accumulating in the alteration products of olivine, which are
531	likely to be clay-like minerals.
532	
533	Map 0063 (Figure 8) includes an olivine grain (50% Mg) with 2500 mg kg ⁻¹ of Ni that is enclosed within
534	a soil grain that was shown to also include feldspars and Fe Al (Mg) silicates using QEMSCAN [®] . Ni is
535	present in lower concentrations (400-1000mg/kg) within a fracture in the olivine and the surrounding
536	material. These areas also have greater concentrations of Al (15%) and Fe (30%) indicating they are
537	alteration products of the olivine.
538	
539	3.3.6 Carbonates
540	10 analysis point were undertaken on calcite minerals and 4 analysis points were undertaken in apatite

541 minerals from sample 560141. Generally Ca concentrations ranged from 20 to 60% at these points,

542	with elevated P (30 to 35%) recorded in apatite samples. Insignificant amounts of Cr ($<60 \text{ mg kg}^{-1}$) and
543	Ni (<90 mg kg ⁻¹) were identified in all but two of these 14 samples, with 360 mg kg ⁻¹ of Ni found in 2
544	calcite points and 200 and 400 mg kg ⁻¹ of Cr found in a point analysed on apatite and a point on calcite
545	respectively. Map 0061 was selected to include areas identified as apatite during QEMSCAN® analysis,
546	however no elevated Ni or Cr was identified.
547	
548	3.4 Relation of results to oral bioaccessibility
549	Total Ni concentrations were approximately 50% greater in samples 559363 and 559503 than in sample
550	560141, but the greatest amount of bioaccessible Ni (9.94 mg kg ⁻¹ (gastric phase)) was observed in
551	sample 560141. In contrast approximately 50% more total Cr was observed in sample 558383 than the
552	other 2 samples, with gastric (G) and gastrointestinal (GI) Cr showing similar trends. Total and
553	bioaccessible Ni and Cr for the three samples as measured during the Tellus survey and by Barsby et al.
554	(2012) are provided in in Table S1 in the supporting information.
555	
556	Using non-specific sequential extraction (CISED) undertaken on the same soil samples, Cox et al. (2013)
557	identified carbonate, Al rich, clay and Fe oxide components that contained bioaccessible Ni.
558	QEMSCAN® analysis identified the presence of greater amount of Ca carbonates (calcite) and
559	phosphates (apatite) in Sample 560141 than the other soils (Fig. 9(b)). This supports the results of
560	previous CISED extractions (Cox et al., 2013) which attributed more bioaccessible Ni (37%) to Ca
561	dominated phases in this soil than the other 2 soils.



578	As predicted by Cox et al. (2013) EPMA point analysis in this study identified Fe oxides with high Al
579	and Si content that were identified as Fe oxides intergrown with clays. This intergrown oxides
580	contained elevated Ni that would be likely to be bioaccessible. Small quantities of Cr were present in
581	these minerals, accounting for the small amount of bioaccessible Cr identified in Fe-oxides in Cox et al.
582	(2013).
583	
584	Cox et al. (2013) reported that the majority of Cr in these soils was not bioaccessible. In this study, total
585	chromium was found to be strongly correlated to the presence of chrome spinel in all samples (Figure
586	9(a)). Chrome spinels are highly recalcitrant minerals, which is reflected in the low bioaccessibility
587	(approx 2%) for each of these samples (Cox et al., 2013). Elevated Cr concentrations were also
588	identified in primary metal oxides which are also highly recalcitrant and therefore unlikely to contribute
589	significantly to oral bioaccessibility. Some elevated Cr (approximately 200 to 400 mg kg ⁻¹) was
590	identified in weathered olivine and clays and some calcite and apatite, which are likely to be more
591	bioaccessible. Cr concentrations were generally low in most calcite, apatite, feldspars and iron oxides
592	intergrown with clays.
593	

595 4.0 CONCLUSIONS

596 The geochemical composition of the 3 soils is similar reflecting that they overlie bedrock of similar 597 origin. Geochemical and mineralogical data indicate the soils are consistent with the weathered basalt, 598 particularly the "saprock" within the lithomarge layer from the laterite profile (Hill et al., 2001). 599 Mineralogical investigation of the samples by quantitative XRD and QEMSCAN[®] was generally 600 consistent within the limitations of each method. OEMSCAN[®] allowed greater characterization of the 601 602 significant quantity of amorphous material in the samples than XRD, but was unable to distinguish 603 between polymorphs. QEMSCAN[®] also allowed rapid identification and mapping of trace mineralogy 604 at concentrations below the detection limits of XRD. Results of both techniques indicate significant 605 amorphous content (>60%) in the samples, which has been attributed to organic materials and 606 non-crystalline weathering products such as amorphous iron oxides and precursor minerals for clays, 607 suggesting that weathering of the soils is incomplete. Quartz and plagioclase feldspar were identified by both XRD and QEMSCAN[®], however QEMSCAN[®] also identified K-feldspar, pyroxene and olivine. 608 Hematite was identified by XRD, whilst OEMSCAN[®] identified a variety of metal oxides and hydroxides, 609 610 at trace concentrations (< 0.6%). These included titanium oxides, iron oxides, ilmenite, Mn-Fe oxides and 611 chrome spinels. Whilst apatite and calcite were identified in all samples by QEMSCAN[®], significantly 612 more was recorded in sample 560141, than the other two samples. 613

614 Cr was identified by EPMA in chrome spinel at concentrations that could account for up to 80% of the Cr

615	in each sample. EPMA also identified up to 2000 mg kg ⁻¹ Cr in some primary iron oxides and up to
616	3500 mg kg ⁻¹ Cr in pyroxene. Surprisingly Cr was identified at concentrations of up to 400 mg kg ⁻¹ in 2
617	out of 14 of the apatite and calcite points investigated during point analysis by EPMA. Limited Cr was
618	identified in secondary Fe oxides, olivine and clay like minerals. The existence of the majority of total
619	Cr in highly recalcitrant chrome spinel and primary metal oxides, and to a lesser extent olivine and
620	pyroxene, explains the very low Cr bioaccessibility recorded in these samples, whilst the slightly elevated
621	Cr identified in secondary iron oxides, clay like materials, calcite and apatite is likely to be more
622	bioaccessible.
623	
624	Although Ni was identified in chrome spinel (up to 2500 mg kg ⁻¹), primary iron oxides (up to 1900 mg
625	kg ⁻¹), Mg rich olivine (up to 2500 mg kg ⁻¹) and pyroxene (up to 1000 mg kg ⁻¹), Ni was distributed more
626	widely throughout the samples than Cr, with concentrations of up to 400 mg kg ⁻¹ identified in the
627	amorphous secondary iron oxides (especially those intergrown with clays) and concentrations of up to
628	2200 mg kg ⁻¹ in some of the amorphous clay-like minerals that are likely to be protoclays or precursor
629	clay minerals. Although it was impossible to visually identify which of these materials contained
630	elevated Ni, elemental mapping revealed that some elevated Ni appeared to be associated directly with
631	alteration products formed due to weathering of olivine (although this was not always the case) and
632	increasing Ni concentration appeared to be weakly correlated with increasing Fe in "clay-like" minerals.
633	The greater amount of Ni than Cr present in secondary oxides and other weathering products is likely to
634	originate from weathered olivine (which contained insignificant amounts of Cr), explaining the higher

- 635 bioaccessibility of Ni than Cr in these soils. Calcite and apatite were also found to host significant
- amounts of bioaccessible Ni in 1 of the 3 samples.
- 637
- 638 The combined analysis approach adopted in this investigation, utilising mineralogical analysis, elemental
- 639 mapping and standard chemical analysis, allows the minerals hosting PTEs to be clearly identified,
- allowing increased understanding of the bioaccessibility of PTEs in soils.
- 641

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- 649

650 6.0 REFERENCES

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752 Supporting information

	558363	559503	560141
Total Ni by XRF (mg kg ⁻¹)	174.50	166.50	121.60
Bioacc Ni (G) (mg kg ⁻¹)	4.34	3.39	8.84
Ni BAF (G) (%)	2.49	2.04	7.27
Bioacc Ni (GI) (mg kg ⁻¹)	2.45	1.80	5.00
Ni BAF (GI) (%)	1.41	1.08	4.11
Total Cr by XRF (mg kg ⁻¹)	447.70	299.70	293.10
Bioacc Cr (G) (mg kg ⁻¹)	9.20	4.54	3.20
Cr BAF (G) (%)	2.06	1.51	1.09
Bioacc Cr (GI) (mg kg ⁻¹)	7.39	3.00	1.83
Cr BAF (GI) (%)	1.65	1.00	0.62

Table S1 Total Ni and Cr concentrations measured by XRF during the Tellus survey and bioaccessible Ni and Cr

concentrations measured using the UBM method by Barsby et al. (2012).