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

Cox, S., McKinley, J., & Rollinson, G. (2017). Mineralogical Characterisation to improve understanding of oral bioaccessibility of Cr and Ni in Basaltic Soils in Northern Ireland. DOI: 10.1016/j.gexplo.2017.02.006

**Published in:**

Journal of Geochemical Exploration

**Document Version:**

Peer reviewed version

**Queen's University Belfast - Research Portal:**

[Link to publication record in Queen's University Belfast Research Portal](#)

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1

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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17

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 oral 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<sup>®</sup>, 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

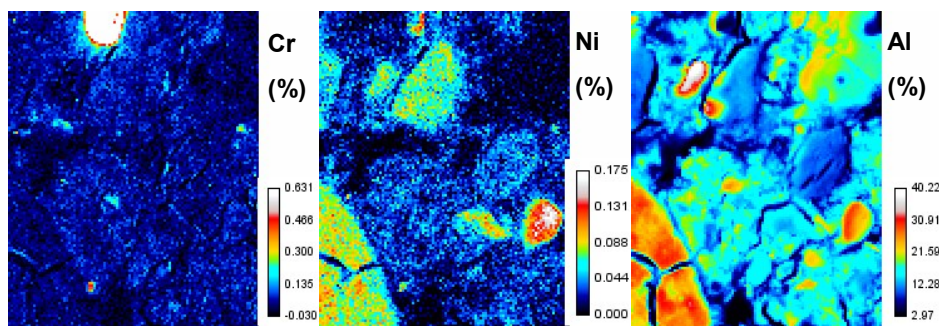
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38 **Graphical abstract**

39

40

41



42 **Highlights**

- 43 • Ni and Cr analysis of Basaltic soils overlying Antrim Basalts of Northern Ireland
- 44 • Combined chemical and mineralogical data for improved understanding
- 45 • High resolution analysis of samples, consistent across analytical methods
- 46 • Bioaccessible Ni in precursor clay minerals, secondary Fe-oxides and carbonates
- 47 • Low Cr bioaccessibility as Cr predominantly in chrome spinel and primary Fe-oxides

48

49 **Abbreviations**

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
73		

74 **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  $130\text{mg kg}^{-1}$  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 approximately 4 times greater for Ni and 2.5 times greater for  
109 Cr than the rest of Northern Ireland. However oral bioaccessibility 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<sub>2</sub>O<sub>3</sub>, indicating that Cr is  
113 predominantly present in phases associated with Fe<sub>2</sub>O<sub>3</sub> 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<sup>®</sup> 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.

133

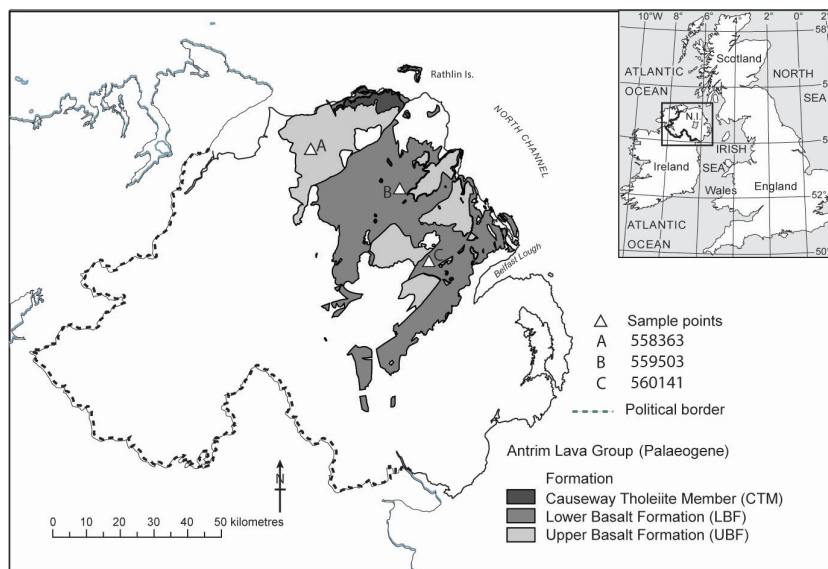


134 **2.0 MATERIALS AND METHODS**

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 km<sup>2</sup> (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 Tholeiite Member (CTM)) occurred (Mitchell, 2004). The Upper and  
148 Lower Basalts are composed principally of plagioclase feldspars (labradorite), Mg-rich olivine containing  
149 small spinel inclusions and pyroxene (augite) (Lyle, 1979) with magnetite, ilmenite and apatite also  
150 present as accessory minerals (Hill et al., 2001).

151



152

153 **Figure 1 Map showing the Antrim Lava Group.**

154

155 Figure 2a shows the spatial distribution of total Ni concentrations determined during the Tellus survey.

156 Median total Ni concentrations in the UBF and LBF were  $100 \text{ mg kg}^{-1}$ , with the highest Ni concentration

157 recorded in the Tellus Survey ( $334 \text{ mg kg}^{-1}$ ) reported for the LBF (Cox et al., 2013). 516 samples

158 overlying the Antrim Basalts (31%) have total Ni concentrations that exceed the “Suitable for Use Level”

159 (S4UL) for Ni ( $130 \text{ mg kg}^{-1}$ ) for a residential landuse (with homegrown produce) derived by Nathanail et

160 al. (2015).

161

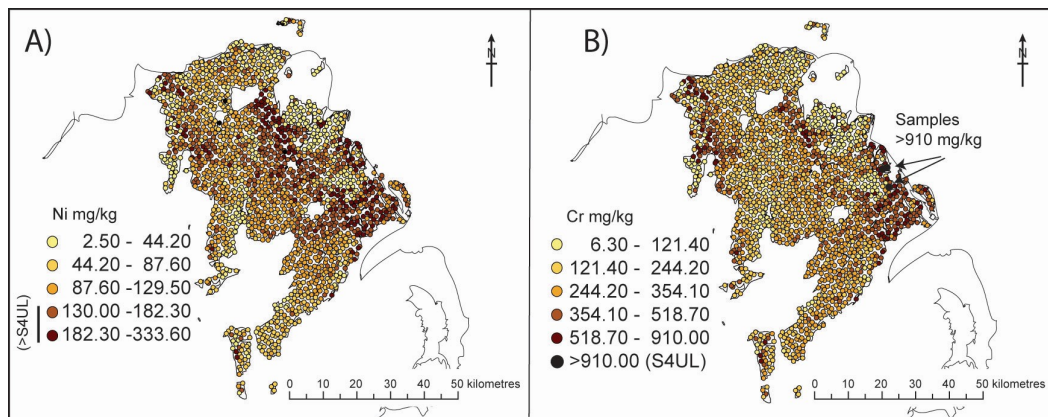
162 Similar trends are observed for total Cr concentrations (Fig. 2b), which are generally about 3 to 4 times

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<sup>-1</sup>, whilst 3 samples (0.18%) exceed the residential with gardens S4UL for Cr III of  
 167 910 mg kg<sup>-1</sup>.  
 168  
 169 Cox et al., (2013) reported that bioaccessible Ni and Cr were generally greater in gastric phase extracts  
 170 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<sup>-1</sup>), while the UBF showed greater  
 172 amounts of bioaccessible Cr (mean gastric phase concentration of 4.55 mg kg<sup>-1</sup>). 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



176  
 177 **Figure 2 Maps showing the spatial distribution of (A) total Ni and (B) total Cr (by XRF (mg kg<sup>-1</sup>))**  
 178 **for all Tellus soil samples overlying the Antrim Lava Group**

179  
 180

## 181 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 ( $\text{mg kg}^{-1}$ ) 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  $\mu\text{m}$  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.

201

202 **2.3 Quantitative XRD analysis**

203 Quantitative XRD analysis was undertaken by X-Ray Mineral Services Colwyn 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° 2θ (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.

220

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° 2θ (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  
235 total amount of <2 micron clay fraction. An indication of the clay minerals crystallinity was given by  
236 assessment of the peak width for each component.

237

238 **2.4 Mineralogical mapping**

239 Mineralogical mapping was undertaken using QEMSCAN<sup>®</sup>, 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<sup>®</sup> 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<sup>®</sup> 4300  
245 system.

246

247 During QEMSCAN<sup>®</sup> 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 µm 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<sup>®</sup> technique are discussed in detail in  
260 Andersen et al. (2009) and Rollinson et al. (2011).

261

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<sup>®</sup> 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<sup>®</sup> 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<sup>®</sup> analysis.

279

---

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

---



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

280 **Table 1 Mineral groupings used for reporting results of QEMSCAN<sup>®</sup> analysis**

281

## 282 **2.5 Elemental mapping**

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

284 using a JEOL JXA8530F electron probe microanalyser (EPMA), equipped with both a silicon drift

285 detector (SSD) energy dispersive spectrometer (EDS) and 5 wavelength dispersive spectrometers

286 (WDS). Results from the QEMSCAN<sup>®</sup> 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

288 representative examples of chrome spinel, iron oxide, calcite and apatite. Mapping was targeted on  
 289 areas of typical clay composition and where it was suspected olivine was weathering within the basalt.  
 290 Quantitative analysis of elemental concentrations was undertaken by WDS. Details of EPMA setup are  
 291 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 ( $\mu\text{m}$ )	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  $\text{Al}_2\text{O}_3$  (Amelia albite), Ca as CaO (Wollastonite), Cr as  $\text{Cr}_2\text{O}_3$ ,  
 297 Fe as FeO (Ilmenite), Mg as MgO (St John's Island Olivine), Mn as MnO, Na as  $\text{Na}_2\text{O}$  (Ameilia albite), P  
 298 as  $\text{P}_2\text{O}_5$  (Durango apatite), Si as  $\text{SiO}_2$  (St John's Island Olivine), Ti as  $\text{TiO}_2$  (Ilmenite), K as  $\text{K}_2\text{O}$  (Eifel  
 299 sanidine); Ni and NiO, Zn as ZnO, V as  $\text{V}_2\text{O}_3$  and Nb as  $\text{Nb}_2\text{O}_5$  ( $\text{LiNbO}_3$ ) and F as Durango apatite. V  
 300 was measured using an overlap correction, which subtracts the overlapping Ti K $\beta$  component based on  
 301 the intensity on the Ti K $\alpha$  line.

302

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  $\mu\text{m}$ .

310

Map No	Sample No	Width ( $\mu\text{m}$ )	Height ( $\mu\text{m}$ )	Step size ( $\mu\text{m}$ )
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

320 with the results of non-specific sequential extractions on these soils by Cox et al. (2013).

321

	Sample 558363	Sample 559503	Sample 560141	Average compositions <sup>1</sup>			
				Basalt (n=5)	Lithomarge (n=126)	Laterite (n=99)	Iron crust (n=10)
SiO <sub>2</sub> %	39.60	39.50	43.40	43.94	37.33	21.54	12.72
TiO <sub>2</sub> %	1.56	1.37	1.08	1.87	2.64	3.99	9.99
Al <sub>2</sub> O <sub>3</sub> %	13.10	14.70	13.50	15.15	27.86	33.78	17.51
Fe <sub>2</sub> O <sub>3</sub> %	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 <sub>2</sub> O %	0.30	0.60	0.60	2.24	0.37	0.15	0.07
K <sub>2</sub> O %	0.67	0.39	0.56	0.2	0.11	0.04	0.04
P <sub>2</sub> O <sub>5</sub> %	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. <sup>1</sup> Average concentrations of the main horizons within the laterite profile**

325 **(Hill et al., 2001)**

326

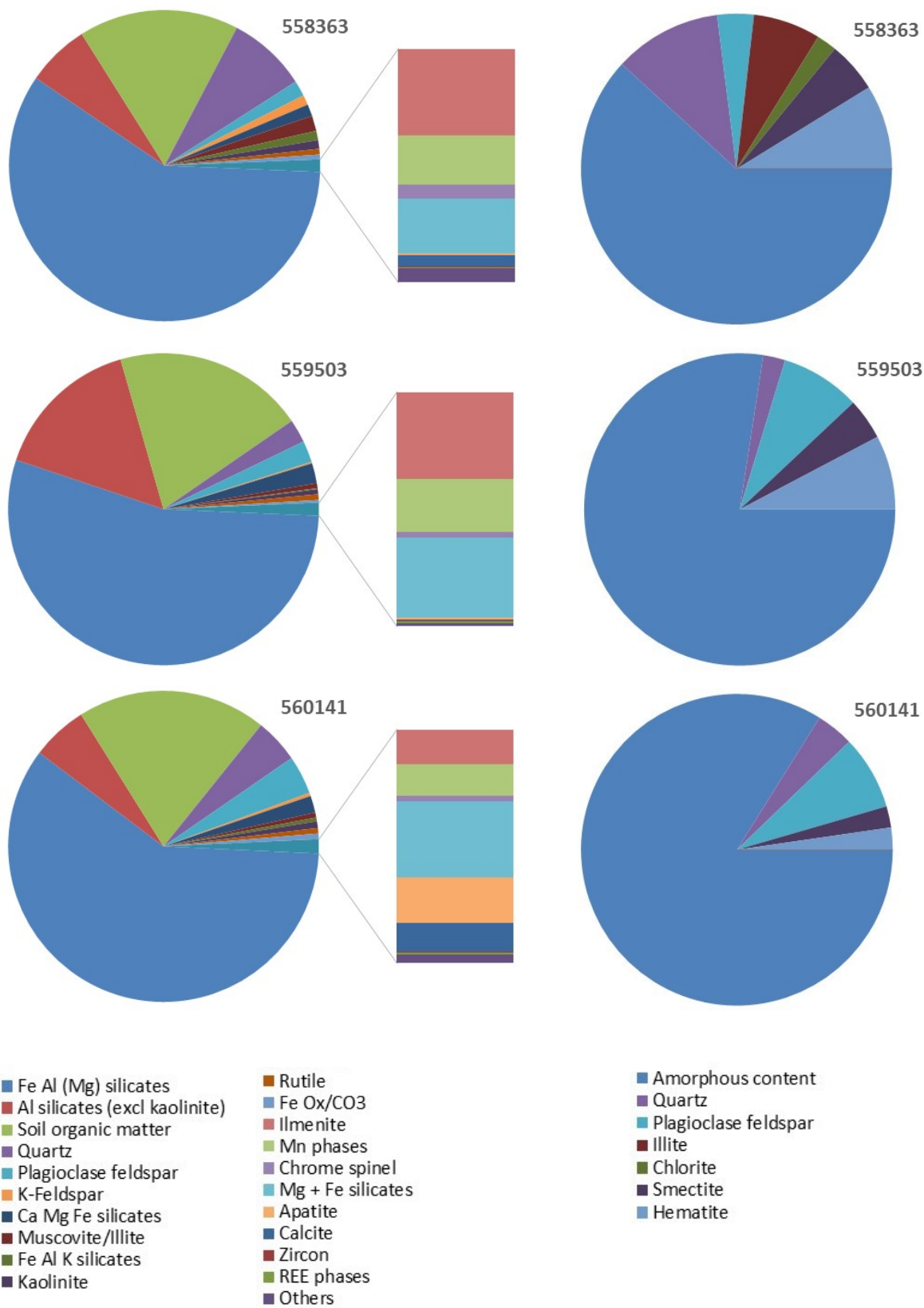
327 Comparison of the geochemical composition of the soils with composition data reported by Hill et al.

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.



345

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

347 **(right). For details of mineral groupings used for QEMSCAN<sup>®</sup> see Table 1.**

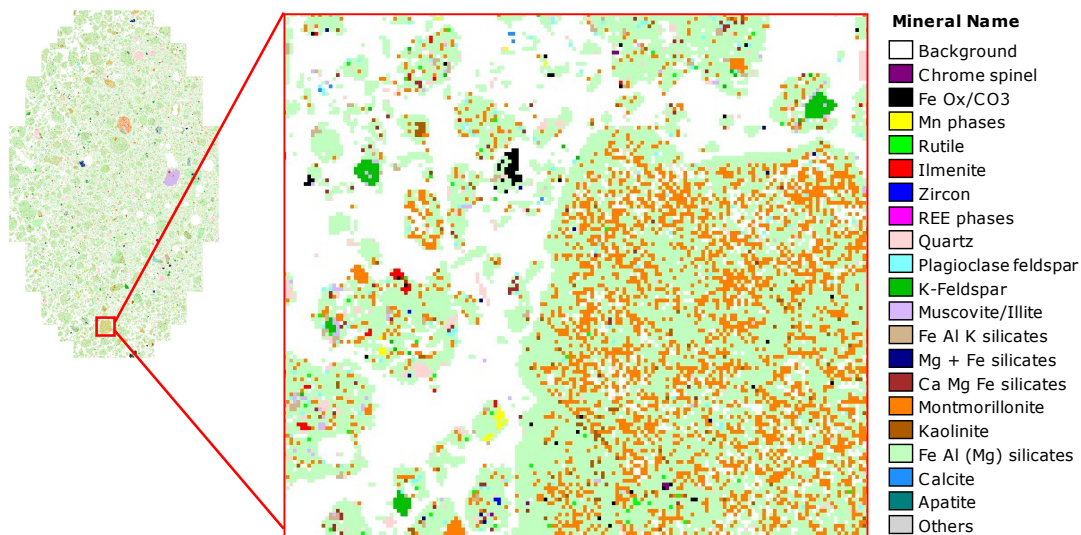
348

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<sup>®</sup> 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 crystallised chlorite, again supporting the hypothesis that weathering of the soils is  
359 incomplete.

360

361 QEMSCAN<sup>®</sup> 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<sup>®</sup> 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<sup>®</sup> also identified illite (<1.58%), mica (<0.97%) and kaolinite (<0.90%), with the greatest  
368 amounts of these minerals in sample 558363.



369

370 **Figure 4 A typical intergrown clay grain from sample 558363**

371

372 Quartz was found in all samples by both XRD (2-12%) and QEMSCAN<sup>®</sup> (2.43-8.25%) suggesting an  
373 input into the soils other than from the underlying basalts, perhaps due to movement of the glacial tills.

374 More plagioclase feldspar was identified by XRD (3.5-8.5%) than QEMSCAN<sup>®</sup> (1.63-4.01%), however

375 QEMSCAN<sup>®</sup> also identified K-feldspar (0.34-1.03%) and Ca Mg Fe silicates that are most likely

376 pyroxene (1.24-2.08%). Hematite were identified by XRD, as would be expected for soils overlying

377 basalt bedrock, however the quantities of hematite determined (2-9%) did not account for all the Fe

378 recorded in the geochemical analysis (8-12%) supporting the suggestion that the amorphous content

379 includes non-crystalline iron oxides. QEMSCAN<sup>®</sup> identified a variety of metal oxides and hydroxides,

380 at trace concentrations (<0.6%). These included titanium oxides, iron oxides, ilmenite, Mn-Fe oxides and



381 chrome spinels. Olivine was identified by QEMSCAN<sup>®</sup> 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%  
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<sup>®</sup> 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<sup>®</sup> allowed greater characterization of the significant quantity of amorphous material in the  
392 samples than XRD, but was unable to distinguish between polymorphs. QEMSCAN<sup>®</sup> 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<sup>®</sup>, as XRD is reported in wt % whilst QEMSCAN<sup>®</sup> 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

### 399 **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<sup>-1</sup>), 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.

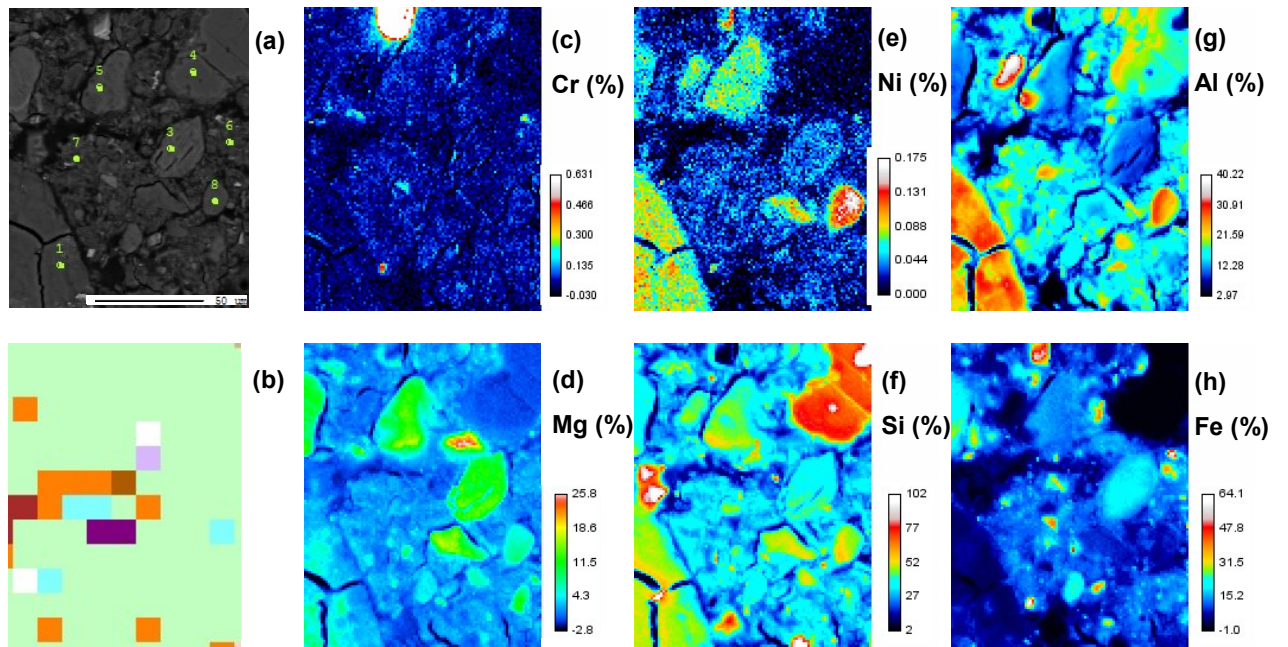
408

### 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  
412 by QEMSCAN<sup>®</sup>, if these Cr concentrations are typical of chrome spinels in the sample, chrome spinels  
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  
417 chrome spinel. 500 to 2500 mg kg<sup>-1</sup> of Ni and 1300 to 11000 mg kg<sup>-1</sup> V was identified in all chrome  
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.

422

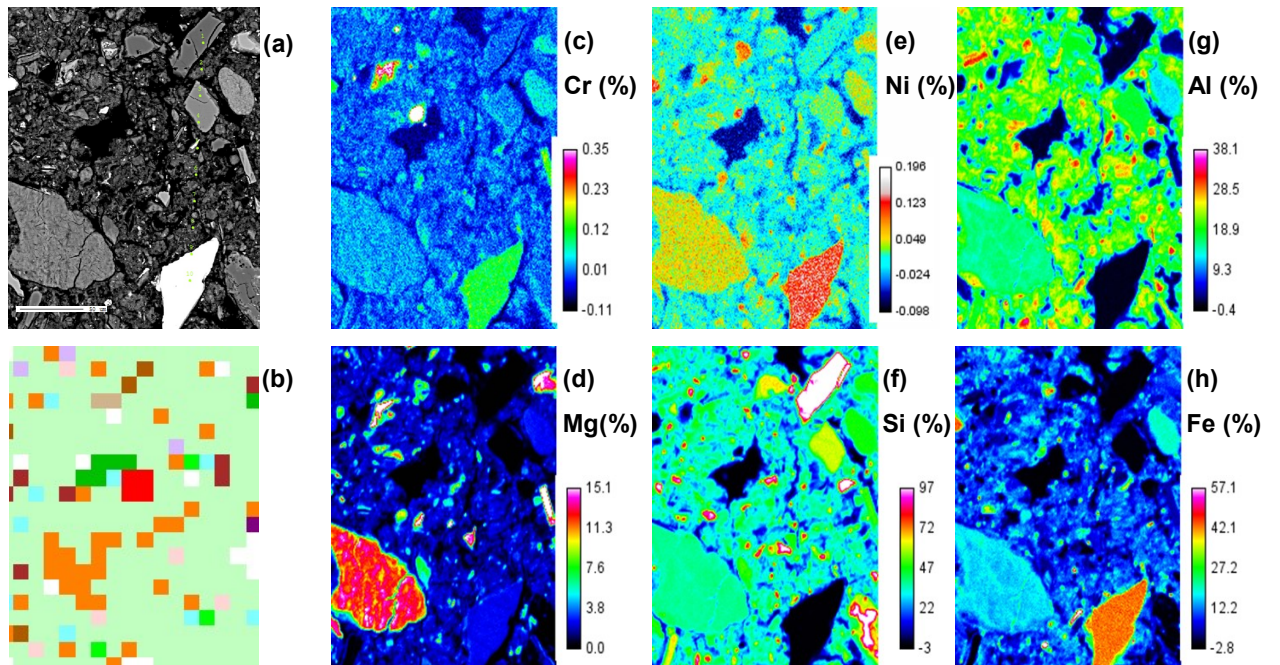


423

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

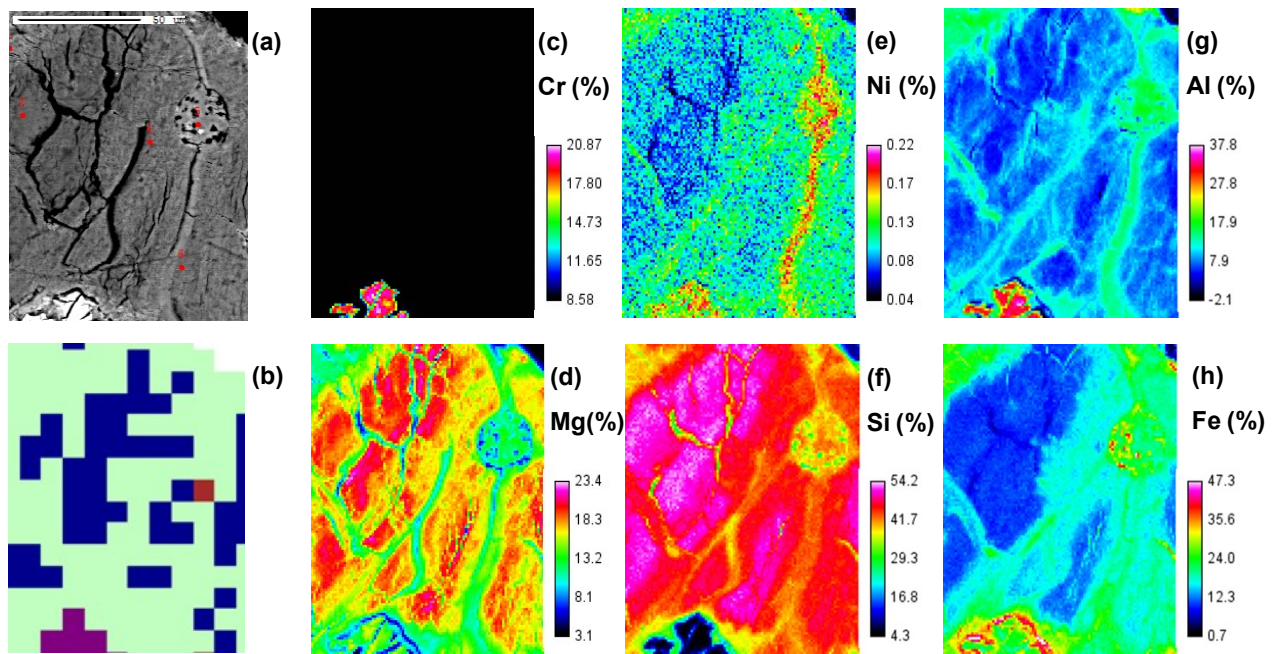


428

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.**

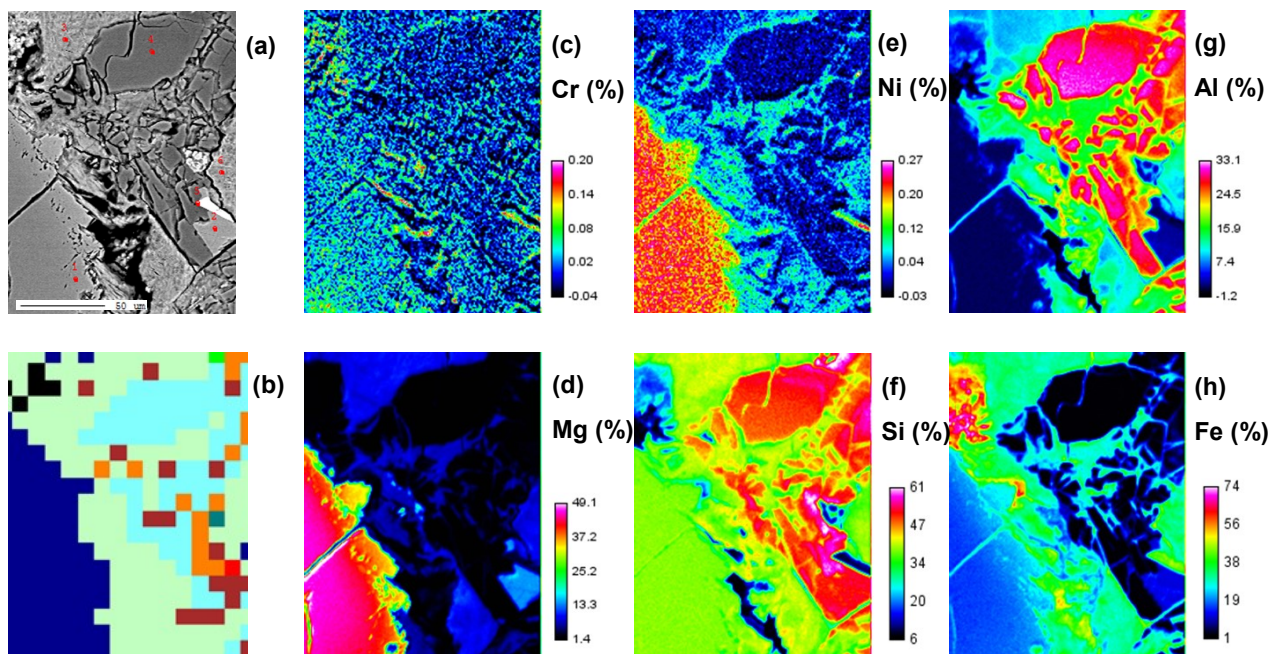




432

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.**

441

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<sup>®</sup> 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<sup>-1</sup>, with the exception of Cr in primary iron oxides which was

453 greater than 2000 mg kg<sup>-1</sup> in two out of the four primary iron oxides tested. Ni concentrations were also

454 generally less than 100 mg kg<sup>-1</sup>, however elevated Ni concentrations (between 100 and 400 mg kg<sup>-1</sup>) 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<sup>-1</sup>) and Ni (500-1900 mg kg<sup>-1</sup>) 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<sup>®</sup> 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<sup>-1</sup>) and Cr (500-3500 mg kg<sup>-1</sup>) were identified in mineral grains in Map  
473 0032 (2 No) and 0043 (Figure 6) (2 No) that contained Si (approx. 50%), Al (2-14%), Fe (5-10%), Ca  
474 (8%) and Mg (10-15%), with no Na or K present. Both grains on map 0043 were identified by  
475 QEMSCAN<sup>®</sup> as Ca Mg Fe silicates, but both grains on Map 0030 (Figure 5) were smaller than the  
476 QEMSCAN<sup>®</sup> pixel size and were therefore not categorised. Given the underlying geology is basalt and  
477 that concentrations of Si, Al, Fe, Ca and Mg fall within the range reported for pyroxenes in Deer et al.  
478 (1992), it is likely that all 4 grains are pyroxene, which is known to host elevated Ni and Cr. In  
479 contrast significant areas of Map 0029 were identified as Ca Mg Fe silicates by QEMSCAN<sup>®</sup>, but did not  
480 contain significantly elevated Cr or Ni.

481

482 **3.3.4 Olivine**

483 Between 1000 and 2500 mg kg<sup>-1</sup> 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<sup>®</sup> 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<sup>-1</sup> Ni was recorded in Map 0063  
490 (Figure 8) in an area with 48% Mg and 1000 mg kg<sup>-1</sup> Ni in Map 0029 in an areas with 25% Mg.

491

492 **3.3.5 Clay like minerals**

493 Clays and other clay like minerals were generally identified by visual inspection as specific grains with  
494 mottled or dappled surfaces or the secondary minerals that appear to make up the matrix in large  
495 agglomerations. Although these minerals appeared to be ubiquitous, it was impossible to visually  
496 identify which contained elevated Ni and Cr and therefore point analysis did not reveal significantly  
497 elevated concentrations of Cr and Ni in clay-like minerals. Typically concentrations of Cr and Ni  
498 identified during point analysis of clay-like grains were between 100-400 and 300-800 mg kg<sup>-1</sup>  
499 respectively. In contrast mapping revealed concentrations of Ni of up to 2200 mg kg<sup>-1</sup> in some claylike  
500 minerals whilst no significantly elevated Cr was identified in any of these materials, other than wisps of  
501 elevated Cr (approx. 2000 mg kg<sup>-1</sup>) 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.

504

505 Elevated Ni concentrations (up to 2200 mg kg<sup>-1</sup>) were hosted in what appeared to be clay-like materials  
506 (generally identified as as Fe Al (Mg) silicates by QEMSCAN<sup>®</sup>). 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<sup>-1</sup>) throughout the  
514 whole map in some of the grains that were identified as Fe Al (Mg) silicates by QEMSCAN<sup>®</sup>. A  
515 particularly large grain in the bottom left of Map 0030, hosting 1300 mg kg<sup>-1</sup> of Ni, was identified as a  
516 mixture of Fe Al (Mg) silicates and kaolinite by QEMSCAN<sup>®</sup>. 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<sup>-1</sup> Ni and a smaller grain QEMSCAN<sup>®</sup> identified as Fe Al (Mg) silicates mixed with illite, hosting  
519 500-600 mg kg<sup>-1</sup> 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<sup>-1</sup>) 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<sup>®</sup> 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<sup>®</sup> as Fe Al (Mg) silicates and are likely to be phyllosilicates that are initial alteration products of  
528 olivine. The highest concentrations of Ni (up to 2000 mg kg<sup>-1</sup>) 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<sup>-1</sup> of Ni that is enclosed within  
534 a soil grain that was shown to also include feldspars and Fe Al (Mg) silicates using QEMSCAN<sup>®</sup>. 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 ( $<90 \text{ mg kg}^{-1}$ ) were identified in all but two of these 14 samples, with  $360 \text{ mg kg}^{-1}$  of Ni found in 2  
544 calcite points and 200 and  $400 \text{ mg kg}^{-1}$  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<sup>®</sup> analysis,  
546 however no elevated Ni or Cr was identified.

547

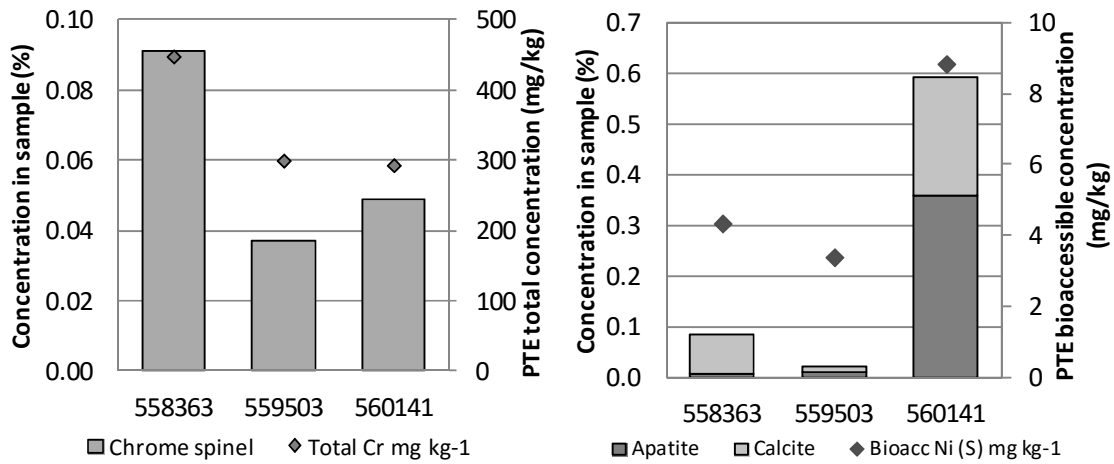
### 548 **3.4 Relation of results to oral bioaccessibility**

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 ( $9.94 \text{ mg kg}^{-1}$  (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<sup>®</sup> 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.



562

563 **Figure 9 Percentage composition of the trace minerals (a) chrome spinel (including chromite) and**

564 **(b) apatite and calcite (including other Ca carbonates and phosphate) plotted with (a) total Cr**

565 **concentration and (b) bioaccessible Ni concentration.**

566

567 Al-oxides were not identified by either QEMSCAN or XRD analysis in this study, suggesting that the Al

568 dominant component that contained significant amounts of bioaccessible Ni identified by Cox et al.

569 (2013) is likely to be an amorphous proto clay or precursor mineral that is dispersed within the soil matrix.

570 This precursor mineral was shown by Cox et al. (2013) not to contain bioaccessible Cr. However other

571 clay-like minerals hosted significant quantities of both bioaccessible Ni and to a lesser extent

572 bioaccessible Cr. Although they varied significantly in composition, Ni was found to accumulate in

573 many (but not all) of these clay-like minerals. Hill et al. (2001) observed similar accumulation of Ni in

574 the lithomarge within laterites in the Antrim Lava Group, which they postulated was due to substitution

575 of Ni in montmorillonite or vermiculite in the lithomarge. As substituted Ni would be readily released

576 in the stomach, Ni present in these clay-like minerals is likely to be bioaccessible.

577

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<sup>-1</sup>) 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

594

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

600 Mineralogical investigation of the samples by quantitative XRD and QEMSCAN<sup>®</sup> was generally  
601 consistent within the limitations of each method. QEMSCAN<sup>®</sup> allowed greater characterization of the  
602 significant quantity of amorphous material in the samples than XRD, but was unable to distinguish  
603 between polymorphs. QEMSCAN<sup>®</sup> 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  
608 by both XRD and QEMSCAN<sup>®</sup>, however QEMSCAN<sup>®</sup> also identified K-feldspar, pyroxene and olivine.  
609 Hematite was identified by XRD, whilst QEMSCAN<sup>®</sup> identified a variety of metal oxides and hydroxides,  
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<sup>®</sup>, 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<sup>-1</sup> Cr in some primary iron oxides and up to  
616 3500 mg kg<sup>-1</sup> Cr in pyroxene. Surprisingly Cr was identified at concentrations of up to 400 mg kg<sup>-1</sup> 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<sup>-1</sup>), primary iron oxides (up to 1900 mg  
625 kg<sup>-1</sup>), Mg rich olivine (up to 2500 mg kg<sup>-1</sup>) and pyroxene (up to 1000 mg kg<sup>-1</sup>), Ni was distributed more  
626 widely throughout the samples than Cr, with concentrations of up to 400 mg kg<sup>-1</sup> identified in the  
627 amorphous secondary iron oxides (especially those intergrown with clays) and concentrations of up to  
628 2200 mg kg<sup>-1</sup> 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  
636 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,  
640 allowing increased understanding of the bioaccessibility of PTEs in soils.

641

## 642 **5.0 ACKNOWLEDGMENTS**

643 Geochemistry data were provided by the Geological Survey of Northern Ireland as part of the Tellus  
644 Project, which was funded by the Department of Enterprise, Trade and Investment of Northern Ireland  
645 and by the EU 'Building Sustainable Prosperity' programme of the Department of Agriculture and Rural  
646 Development. QEMSCAN<sup>®</sup> and EPMA analysis was supported by the EU INTERREG IVA-funded  
647 Tellus Border project. The authors express their thanks to Ben Buse at University of Bristol and  
648 Jonathan Wilkins at X-Ray Mineral Services for assistance with EPMA and XRD analysis.

649

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752 **Supporting information**

	<b>558363</b>	<b>559503</b>	<b>560141</b>
<b>Total Ni by XRF (mg kg<sup>-1</sup>)</b>	174.50	166.50	121.60
<b>Bioacc Ni (G) (mg kg<sup>-1</sup>)</b>	4.34	3.39	8.84
<b>Ni BAF (G) (%)</b>	2.49	2.04	7.27
<b>Bioacc Ni (GI) (mg kg<sup>-1</sup>)</b>	2.45	1.80	5.00
<b>Ni BAF (GI) (%)</b>	1.41	1.08	4.11
<b>Total Cr by XRF (mg kg<sup>-1</sup>)</b>	447.70	299.70	293.10
<b>Bioacc Cr (G) (mg kg<sup>-1</sup>)</b>	9.20	4.54	3.20
<b>Cr BAF (G) (%)</b>	2.06	1.51	1.09
<b>Bioacc Cr (GI) (mg kg<sup>-1</sup>)</b>	7.39	3.00	1.83
<b>Cr BAF (GI) (%)</b>	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).**