1 **Revised version 1**

2 **Dissolution mechanisms of chromitite:**

3 **Understanding the release and fate of chromium in the environment**

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27 **ABSTRACT**

28   An understanding of the formation of toxic hexavalent chromium (Cr^{6+}) in Cr-containing

29   mine tailings and associated soils and sediments, requires an understanding of the underlying

30   dissolution mechanisms of chromitite, a common chromite-bearing rock in both ophiolites suites

31   and ultramafic intrusions. This study will examine dissolution mechanisms of chromitite in

32   various acidic, neutral and alkaline solutions containing cultivated bacteria, manganese oxides,

33   sulfates and phosphates. Dissolution of chromitite is non-stoichiometric under acidic, near-

34   neutral and alkaline pH conditions and involves the release of chromite nanoparticles and

35   complex dissolution/re-precipitation reactions. Chromitite samples are obtained from the Black

36   Thor chromite deposit in Northern Ontario, Canada; part of the 'Ring of Fire' intrusive complex.

37   The examined chromitite is composed of chromite, $(Fe_{0.5}Mg_{0.5})(Al_{0.6}Cr_{1.4})O_4$ and clinochlore;

38    $Mg_3[Si_4O_{10}(OH)_2] \times (MgAl_{1.33}(OH)_6)$, the latter phase contains ~3 wt% Cr in the form of chromite

39   nanoparticles. Bulk dissolution data are collected after dissolution experiments with chromitite

40   powders, and the chemical and mineralogical composition of treated chromitite surfaces is

41   characterized with a combination of surface analytical techniques (X-ray photoelectron

42   spectroscopy) and nano- to micro-analytical techniques (scanning electron microscopy,

43   transmission electron microscopy and focused ion beam technology). In the chromitite systems

44   studied here, the non-stoichiometric dissolution of clinochlore is the dominant reaction, which

45   results in the formation of a hydrous and porous silica precipitate that is depleted in chromite

46   nanoparticles relative to untreated clinochlore. Complete replacement of clinochlore by hydrous

47   silica on the surface of chromitite under acidic conditions promotes the release of chromite

48   nanoparticles and results in higher Cr:Si in solutions and in higher proportions of secondary Cr

49   species on its surface (secondary Cr species are defined as surface terminations that do not

50   occur on an untreated chromite surface, such as $-Cr^{3+}-OH_2$ and $-Cr^{6+}-OH$). Cultivated bacteria

51   from a sulfide-bearing acid-mine drainage system affect neither the degree of dissolution nor the

52   formation of secondary Cr species, whereas pyrolusite (MnO_2) particles, and adsorbed or

53   precipitated Fe- and Al-bearing hydroxide, -sulfate and -phosphate species, affect release and

54   re-adsorption of chromite nanoparticles and Cr-bearing species during dissolution of chromitite

55   under acidic, neutral and alkaline conditions. These results show that weathering of chromitite

56   and the release of Cr into the environment are strongly controlled by factors such as dissolution

57   rates of Cr-bearing silicates and chromite, the release of chromite nanoparticles, re-precipitation

58   of amorphous silica, the presence of particles in solution and the pH-dependence adsorption (or

59   precipitation) of Fe- and Al-bearing hydroxides and sulfates.

60   Keywords: chromite, clinochlore, dissolution, chromate, toxicity, Ring of Fire, X-ray

61   photoelectron spectroscopy, transmission electron microscopy, focused ion beam, bacteria,

62   pyrolusite

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64   **INTRODUCTION**

65   Effectively assessing the environmental risks posed by highly toxic hexavalent chromium

66   (Cr^{6+}) in Cr-containing mine tailings, as well as associated soils and sediments, requires an

67   understanding of (1) its occurrence and speciation in minerals and glasses (i.e., slags), (2) the

68   solubility and dissolution behaviour of such phases, (3) the complex redox chemistry of released

69   Cr species, (4) the chemical reactions that influence the mobility of Cr species in soils and

70   sediments; and (5) the occurrence and behavior of nano-scale chromite particles.

71   In a recent study at the nanoscale, Schindler et al. (2017) showed that chromite

72   nanoparticles are held within clinochlore and lizardite grains in chromitite ore from the Black

73   Thor chromium deposit in Northern Ontario, Canada and the Mistake mine, part of the

74   Franciscan Ophiolitic Complex. This is an important observation as the potential release of

75   chromite nanoparticles rather than Cr^{3+} aqueous species during the weathering of chromite-

76   bearing silicate minerals will have an impact on the environmental behavior of Cr^{3+} and its

77   potential oxidation to Cr^{6+}. The study by Schindler et al. (2017) did not address the dissolution of

78   the larger chromite grains or the roles of bacteria, manganese oxide particles and mineral

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79   surface coatings during dissolution and release of the Cr-rich silicates and chromite

80   nanoparticles, respectively. This study will further investigate the dissolution mechanisms of

81   chromitite from the Black Thor chromium deposit focusing on chemical reactions on surfaces of

82   millimeter-size slabs and the geochemical behavior of released elements and chromite

83   nanoparticles during the dissolution reactions.

84   Chromitite is an ultramafic rock composed predominantly of the spinel group mineral

85   chromite ($FeCr_2O_4$) with minor silicates phases (e.g., serpentine, chlorite, amphibole, pyroxene

86   and olivine groups). It is a common rock in both ophiolite suites and ultramafic intrusions, the

87   latter being exemplified by the Bushveld Igneous Complex in South Africa, the Stillwater

88   Igneous complex in Montana, and the current region of interest. Larger rock fragments, grains,

89   and particulate matter derived from chromitites may occur in soils and tailings piles in close

90   proximity to natural outcrops or mining activities, respectively (Pillay et al. 2003; Oze et al. 2004;

91   Tiway et al. 2005; Kien et al. 2010). Although the total amount of Cr in chromitite may be

92   controlled by the abundance of refractory chromite, the bioavailability of Cr and formation of

93   hexavalent Cr may ultimately depend on the weathering of serpentine and chlorite group

94   silicates, as they have been shown to be more susceptible to weathering (e.g., Oze et al. 2004,

95   2007; Fandeur et al. 2009; Hseu and Iizuka 2013; Morrison et al. 2015). For instance, elevated

96   Cr^{6+} concentrations in soil pore water and groundwater have been reported for serpentinite-

97   bearing soils and aquifers (e.g., Izbicki et al. 2008; Wood et al. 2010). On the contrary,

98   spectroscopic studies on the speciation of Cr in serpentine-derived soils from other locations

99   indicated the absence of detectable amounts of Cr^{6+} (Hseu and Lizuka 2013; Fandeur et al.

100 2009), and hence many aspects of this issue remain unresolved.

101   Understanding the redox chemistry of Cr is a critical aspect of determining its toxicity. As

102 a trivalent cation, chromium has relatively low toxicity, is a micronutrient, and is relatively

103 insoluble and immobile at neutral to alkaline pH. In contrast, hexavalent chromium is a

104 significant environmental toxicant, a human carcinogen, and is highly mobile at neutral-to-

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105   alkaline pH (e.g., Fendorf 1995). The complexity of Cr^{3+}/Cr^{6+} redox reactions in natural and

106   anthropogenic systems can make effective risk assessment difficult. For example, Cr^{3+} can be

107   readily oxidized to Cr^{6+} by naturally occurring Mn^{3+}/Mn^{4+}-oxides (Bartlett and James 1979; Eary

108   and Rai 1987; Fendorf 1995; Weaver and Hochella 2003; Oze et al. 2007), whereas Cr^{6+} can be

109   reduced to Cr^{3+} by organic carbon, bacteria (aerobic and anaerobic conditions), sulfides and

110   Fe^{2+}-bearing species and clay minerals (e.g., Kamaludeen et al. 2003; Parrhasarathy et al.

111   2003). Hence, understanding the dissolution mechanisms of chromitite under different pH

112   environments and in the presence of manganese oxides and/or bacterial organisms is critical for

113   assessing aspects of the health risks associated with chromitite-rich rocks, soils and tailings.

114   The dissolution mechanisms of chromitite in the presence of different types of acids,

115   bases, and oxidants at varying temperatures have been thoroughly studied to improve the

116   leaching efficiency of Cr from the ore at temperatures commonly above 100°C (e.g., Zhang et

117   al. 2016). A common process involves the dissolution of chromitite in oxidizing alkaline solutions

118   which results in the formation of water-soluble chromate species, allowing the physical

119   separation of Cr from the silicate minerals. Less soluble chromate phases, such as the

120   carcinogenic calcium chromate ($CaCrO_4$), remain with the silicate residue and require special

121   treatment or waste disposal. An alternative extraction process is the treatment of chromitite with

122   sulfuric acid, which results in the formation of amorphous silica on the surface of the chromitite

123   and in the simultaneous release of Cr, Al, Fe and Mg into solution (Zhao et al. 2014). This

124   process requires the separation of the latter elements, which can be achieved via the

125   precipitation of Fe-hydroxides at higher pH in the presence of an oxidant such as H_2O_2 (Zhang

126   et al. 2016).

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128   **Detailed objectives and approach**

129   The observation that Cr occurs in the form of chromite nanoparticles in silicate minerals

130   within high-grade chromitite ore from the Black Thor chromite deposit requires a unique multi-

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131   analytical approach to characterize the dissolution mechanisms of the ore at ambient Earth

132   surface temperatures. As such, this study will combine transmission electron microscopy with

133   surface sensitive methods such as X-ray photoelectron spectroscopy, and bulk dissolution data

134   to examine release, dissolution, re-adsorption and attachment of chromite nanoparticles and Cr-

135   bearing aqueous species during chromitite dissolution experiments. The occurrence of chromite

136   nanoparticles in solution and their proportion relative to Cr-bearing solutes will be addressed

137   elsewhere.

138   This study will aim specifically to examine whether:

        (a) the minerals in the ore samples dissolve stoichiometrically or non-stoichiometrically
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140   under conditions that may occur in potential mine waste environments;

141   (b) the amphoteric elements Al, Fe, and Cr behave similarly during dissolution in acidic,

142   neutral, and alkaline conditions;

143   (c) the chemical composition of solutions after the experiments can be directly linked to the

144   composition of altered ore mineral surfaces and *vice versa*;

145   (d) any secondary Cr species (i.e., those not found on untreated chromitite, such as

146   hydrated Cr^{3+} and Cr^{6+} species) occur on treated chromitite surfaces;

147   (e) bacteria from oxidized portions of sulfide-rich mine tailings affect the dissolution of

148   chromitite under aerobic acidic conditions and contain populations that grow

149   preferentially in Cr-bearing media;

150   (f) MnO_2 particles affect the dissolution of chromitite and specifically the proportion of

151   hexavalent Cr species, on both MnO_2 and altered chromitite surfaces;

152   (g) potential liming of tailings material through the addition of e.g., $CaCO_3$ affects the

153   dissolution mechanisms and the proportion of Cr^{6+} species on altered chromitite

154   surfaces.

155   In typical studies of mineral dissolution, powders of known total surface area are used,

156   and the chemical reactions are deduced by subsequent bulk compositional analyses of

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157   solution and solid phase materials. Here, two types of experiments are conducted: (1)

158   utilizing powdered chromitite materials, and (2) using single slabs, manually cut from

159   chromitite rock pieces. Powder-based experiments result in the release of sufficient amounts

160   of ions to solution during the dissolution process, thereby facilitating quantification by

161   standard solution chemical analytical techniques. However, the relatively flat surfaces of the

162   slabs are better-suited for studying the chemical reactions occurring on mineral surfaces, as

163   similar locations on their surfaces can be examined with a multi-analytical approach,

164   integrating data from X-ray photoelectron spectroscopy (XPS), scanning electron

165   microscopy (SEM), *in situ* focused ion beam (FIB) sample extraction, and transmission

166   electron microscopy (TEM) techniques. Noteworthy disadvantages of working with chromitite

167   slabs, however, are that their surface composition, area, and roughness cannot be faithfully

168   reproduced between individual experiments, and the very low quantities of ions released

169   into solution are often below the detection limits of even the most sensitive analytical

170   methods. Hence, with material extraction from the same chromite sample, concurrent

171   dissolution experiments are run, one utilizing chromitite slabs and the other utilizing

172   chromitite powders. Comparing the results from both approaches allows greater

173   understanding of the overall, underlying dissolution mechanisms of chromitite ore.

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175   **METHODS**

176   A high grade chromitite ore sample was obtained from the Black Thor chromite deposit,

177   Ontario, Canada, through the Ontario Geological Survey. The Black Thor chromite deposit is

178   part of the Neoarchean 'Ring of Fire' Intrusive Complex, located in the Oxford-Stull Doman of

179   the Archean Superior Province, and interpreted as an intercratonic rift basin separating the

180   Mesoarchean North Caribou and Hudson Bay Terranes (Stott et al. 2010). Cumulate chromite

181   occurs throughout much of the deposit and occurs as a continuous, thickly-bedded chromitite

182   horizon at the transition from olivine-dominant to pyroxene-dominant lithologies (Weston and

183   Shinkle 2013; Laarman 2013).

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185   **Sample preparation**

186   Both powders and slabs were prepared from the same chromitite sample. Chromitite slabs

187   with dimensions of circa 5 x 5 x 3 mm^3 were prepared with a petrographic micro saw. Powders

188   (100 mg for each experiment) were prepared by crushing and milling the remaining rock sample

189   to an average grain size of 75 ±10 μm (determined by optical microscopy). All samples were

190   thoroughly washed with double-deionized water prior to initial analyses by optical microscopy,

191   SEM, XPS, TEM, X-ray diffraction (XRD), and X-ray fluorescence spectroscopy (XRF).

192   Experiments and analytics are carried out for chromitite slabs in the sequence (1) dissolution

193   experiment, (2) XPS, (3) SEM, (4) TEM and for powders in the sequence (1) dissolution

194   experiment, (2) ICP-OES (solution), (3) XPS (selected samples).

195   **Dissolution experiments with and without MnO$_2$ particles and bacteria**

196   Dissolution experiments were carried out on chromitite slabs and powders for four weeks

197   at the pH-values and chemical compositions listed in Tables 1-2 and A1-A3. Both initial and final

198   pH and Eh values were determined using a standard hydrogen electrode calibrated against pH

199   solutions of pH 4, 7 and 10 and a K-iodide standard. The standard deviation of individual

200   measurement pH and Eh measurements is circa ± 0.2 units, based on repeated measurements

201   of the standard solutions.

202   Manganese oxide phases containing Mn^{3+} (e.g., birnessite. (Na,Ca)$_{0.5}$(Mn^{4+}, Mn^{3+})$_2$O$_4$

203   (H$_2$O)$_{1.5}$ are commonly more reactive and stronger oxidants of Cr^{3+} than those containing

204   exclusively Mn^{4+} (e.g., pyrolusite, MnO$_2$) (Weaver and Hochella 2003). Manganese (III)-bearing

205   oxides are more common in soils, whereas Mn^{4+}-bearing oxides such as pyrolusite occur

206   predominantly in coal fly ashes and smelter waste products formed at higher T (Eary and Rai

207   1987). To better assess the alteration of chromitite in mine and smelter wastes, dissolution

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208 experiments were thus conducted with pyrolusite powder (US Research Nanomaterials,

209 average grain size 7.98 µm) under acidic, neutral and alkaline pH conditions (Tables 1-2).

210 Solutions during the dissolution experiments were not protected from solar radiation as Weaver

211 and Hochella (2003) showed that this had no effect on the oxidation of Cr^{3+} aqueous in the

212 presence of pyrolustite.

213   Bacteria sensitive or resistant to Cr^{6+} can reduce the ion to Cr^{3+} under aerobic and

214 anaerobic conditions, even if they have not been exposed to high concentrations of Cr in the

215 past (*e.g.,* Kamaludeen et al. 2003). At the Black Thor chromite deposit, chromitite is over- and

216 underlain by lithologies containing minor amounts of sulfides (pyrhotite, pyrite, chalcopyrite;

217 Laarman 2013). Hence, small proportions of the ore may become exposed to a sulfide-rich

218 environment in mine tailings. As such, dissolution experiments are carried out with bacterial

219 cultures, enriched from oxidized portions of sulfide-rich mine tailings in the Sudbury area

220 (Ontario, Canada). The growth of these cultures was completed in TK media (Tuovinen and

221 Kelly 1974) comprised of stock solutions A and B. Solution A contains 0.51 gL^{-1} $(NH_4)_2(SO_4)$,

222 $Mg(SO_4)(H_2O)_7$ and K_2HPO_4 and is adjusted with H_2SO_4 to a pH of 2.5. Solution B contains 33.5

223 gL^{-1} $FeSO_4(H_2O)_7$ and is adjusted with H_2SO_4 to a pH of 2.1 and mixed with solution A in a ratio

224 of 4:1 in the final TK media. Dissolution experiments under acidic conditions but without bacteria

225 were also carried out with the solutions A and B (using aseptic techniques) as this allowed a

226 better evaluation of the effect of bacteria on the dissolution of chromitite under acidic conditions.

227 Dissolution experiments simulating potential liming of chromitite-bearing mine tailings were

228 conducted with $CaCO_3$ powders in the presence and absence of pyrolusite particles.

229   The ionic strengths and degrees of undersaturation with respect to chromite in these

230 solutions were calculated with the software Visual MINTEQ 2.53 (Gustafsson 2012; Table A1).

231 The change in the microbial community during dissolution of a chromitite slab was analysed with

232 a microbial community profile (supplementary data B1).

233

234 **X-ray Photoelectron Spectroscopy (XPS)**

235   The near-surface composition of treated chromitite slabs and pyrolusite powder was

236 analyzed with a Kratos Axis Ultra X-ray photoelectron spectrometer (XPS) equipped with a

237 magnetic-confinement charge-compensation system. The advantages of this system for

238 insulators have been described in detail by Schindler et al. (2009a, b). A total of 10 high

239 resolution scans were collected for the Cr 2p photoelectrons using monochromatic Al $K\alpha$

240 radiation (1486.6 eV) and the charge-compensation system. Additionally, two survey spectra (0-

241 1100 eV) and three high-resolution scans were collected for the Mg 1s, C 1s, O 1s, Al 2p, Si 2p,

242 Mn 2p and Si 2p photoelectrons. High resolution scans were recorded with a step size of 0.1 eV

243 while survey spectra were collected with a step size of 0.5 eV. For all measurements, the

244 analyzer pass energy was 20 eV and the lens and aperture were in hybrid and slot mode,

245 respectively, which allowed the collection of photoelectrons from an area of circa 700 x 300 μm.

246   The electrostatic sample charging (which was not completely compensated by the

247 charge neutralizer) was corrected by setting the binding energy of the C 1s electrons of

248 adventitious C species on the sample surface equal to 285 eV (Wagner et al. 1979). In some

249 cases, the binding energy of the C 1s photoelectrons can vary with the type of substrate and

250 thus result in false shifts when referenced to other spectra. Hence, corrections applied to the Cr

251 2p spectrum were also applied to the Mg 1s spectrum, which varies over a smaller range in

252 binding energy for oxide and silicate surfaces (103-104 eV) than the Cr 2p peak (NIST database

253 2012). This procedure provided more confidence in the shift applied to Cr 2p spectra and is thus

254 crucial in terms of the determination of potential hexavalent Cr species on treated surfaces of

255 chromitite. A detailed summary of characteristic features in the Cr 2p spectrum and their

256 relationship to structural components on the surface of chromite are given in supplementary

257 data B2.

258   The inelastic mean free path (IMFP) of the Cr 2p electrons is calculated to be circa 1.3

259 nm, using the NIST XPS database (2012), the binding energy of the Cr 2p electrons (577 eV)

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260   and an average specific weight of 4.8 g cm^{-3} for a chromite surface layer. Information on the

261   chemical composition of a surface can be gained to a depth three times of the IMFP (3 x 1.3 =

262   3.9 nm, so called information depth) (Hochella 1988).

263   Both high-resolution and survey scans were processed and quantified using the Vision

264   2.2.6 software package. Peak fitting of the Cr 2p, Mg 1s, and C 1s was done using multiple

265   bands with constant full width at half maximum values (FWHM). The FWHM values used in the

266   fitting procedure were 1.2, 1.5 and 1.4 eV for the Cr 2p, Mg 1s and C 1s spectra, respectively.

267   Bands were only included in the fitting process if inflections points, shoulders or peaks indicate

268   the occurrence of multiplet splitting, variations in the chemical environment or changes in the

269   valence.

270   At least two sets of spectra were taken from each mineral surface (Table 1), whereby a

271   set of spectra includes high-resolution spectra of all major elements, C 1s and a survey scan.

272   Using the optical imaging camera of the XPS system, the two sets of spectra were taken from

273   areas with a higher and lower proportion of clinochlore. Proportions of Mg, Al, Si, Mn, Cr, and Si

274   are based on high resolution scans and were calculated without considerations of the

275   proportions of C, O, S and P on the surface (Table 1, A2). As experiments under acidic

276   conditions were carried out in phosphate-bearing sulfuric acid solutions (Tables 1-2 and A1-A3),

277   elemental ratios between Fe and (S + P) were also determined using the Fe 2p, S 2p and P 2p

278   peaks in the survey scans.

279   Table 1 lists selected elemental ratios of an untreated surface and treated surfaces

280   analyzed with multiple sets of XPS spectra and the number of recorded sets (*N* XPS). The

281   standard deviation of a ratio between the atomic proportions of two elements is circa ±0.1 and is

282   based mainly on the uncertainty of the size of the quantification area in a spectrum. Table A2

283   lists the normalized atomic proportions of Cr, Mg, Si, Al and Fe for the untreated and treated

284   surfaces of the chromitites.

285

286 **Inductively coupled plasma optical emission spectrometry**

287   The elemental concentrations of Mg, Al, Si, Cr, and Fe in the solutions after the

288 experiment with the chromitite powders were determined with solution-mode inductively coupled

289 plasma optical emission spectrometry (ICP-OES) at a commercial lab (AGAT labs, Sudbury,

290 Ontario, Canada). Blanks, sample replicates, duplicates and internal reference materials, both

291 aqueous and geochemical standards are routinely used in the laboratory as part of the quality

292 assurance. Tables 2 lists atomic ratios between selected elements in solution and Table A3

293 their corresponding concentrations.

294

295 **X-ray fluorescence spectroscopy and determination of loss on ignition**

296   The loss on ignition (LOI) for untreated chromitite powders was assessed prior to

297 analysis by X-ray fluorescence. The LOI gives the proportion of volatile elements or compounds

298 in a sample (H, H_2O, S, N) and was determined by heating the sample to 100°C under nitrogen

299 atmosphere, and to 1000°C under oxygen atmosphere, until a constant wt. % was reached. The

300 sample was subsequently fused with a borate flux to produce a glass bead for characterization

301 by X-ray Fluorescence Spectroscopy (XRF). A dilution factor of chromitite to borate flux of 1:24

302 ensured that no Cr-oxide exsolved from the glass matrix during cooling. The glass bead was

303 subsequently analyzed with a Panalytical Axios Advanced XRF spectrometer. Table A4 lists the

304 average concentrations for the major elements in chromitite (on the basis of two

305 measurements).

306

307 **Scanning electron microscopy, X-ray diffraction (XRD), X-ray fluorescence spectroscopy**

308   Scanning electron microscopy was conducted with a JEOL 6405 at 20 kV, equipped with

309 both backscattered (BSE) and secondary electron (SE) detectors and an energy dispersive X-

310 ray spectrometer (EDS). Powder X-ray diffraction of an untreated chromitite samples was done

311 with a Philips PW 1729 X-ray diffractometer using Cu Kα radiation (1.5418 Å) at a voltage and

312   current of 40 kV and 30 mA, respectively. Spectra from powdered samples were collected over

313   a scan range of 5-75° 2θ with a step size of 0.02 °2θ and a dwell time of 4 seconds. The XRD

314   patterns are given in supplementary data A5.

315

316   **Focused ion beam extraction, high-resolution transmission electron microscopy, and**

317   **scanning transmission electron microscopy**

318   A FEI Helios 600 NanoLab Focused Ion Beam (FIB) microscope, equipped with an *in*

319   *situ* extraction probe, was used to extract two sections of the sample treated with solution A at

320   pH 2.5 for subsequent imaging and analyses by TEM. One section was extracted from inside

321   the chromitite sample, representing an unaltered environment, whereas the other was extracted

322   from along the altered surface (Schindler et al. 2017). Upon extraction, samples were lifted

323   using a platinum gas-glue and thinned to electron transparency by ion gas milling (Ga^+ ions).

324   Nanoscale mineralogical and chemical compositions of untreated and treated areas

325   were characterized using a JEOL 2100 field thermionic emission analytical TEM at the Virginia

326   Tech National Center for Earth and Environmental Nanotechnology Infrastructure (NanoEarth).

327   All measurements were taken with an accelerating voltage of 200 kV and a beam current of

328   approximately 107 μA. EDS point analyses and maps were acquired with the instrument

329   operating in scanning transmission electron microscope (STEM) mode using a JEOL BF

330   detector, and selected area electron diffraction (SAED) patterns were acquired using a Gatan

331   Orius SC200D detector.

332

333   **RESULTS**

334   The examined chromitite consists of the major elements Cr, Fe, Mg, Al, Si, O and H,

335   minor Ti and traces of Ca, Ba, K, Mn, Na and V (Table A4). Elemental ratios relevant to the

336   following discussion include Cr:Si = 18.7:1, Cr:Al = 4.7:1 and Cr:Fe = 2.13:1. Chromite and

337   clinochlore are the only two minerals with modal abundances exceeding 1% (on the basis of X-

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338   ray powder diffraction). The latter silicate is the most common mineral of the chlorite mineral

339   group and commonly forms through the chemical alteration of pyroxenes and amphiboles. The

340   average chemical composition of the clinochlore (on the basis of five analyses with SEM-EDS)

341   is $Mg_3[Si_4O_{10}(OH)_2]$ x $(MgAl_{1.33}(OH)_6)$. Areas composed of clinochlore contain an average of 3

342   wt% Cr (most likely in the form of chromite nanoparticles) with Cr:Si, Cr:Al and Cr:Fe of 1:14,

343   1:3 and 2.2:1, respectively.

344   The chromite is Mg- and Al-rich and has the average composition $(Fe_{0.5}Mg_{0.5})$

345    $(Al_{0.6}Cr_{1.4})O_4$ (N = 5 with SEM-EDS). On the basis of the average compositions of both minerals

346   (SEM-EDS) and the bulk composition of the ore sample (XRF), the modal ratio between

347   chromite and clinochlore is circa 15:1. Chromite occurs as rounded to angular grains in thin

348   section (Fig. 1a) and is massive in hand samples. Anhedral grains can be up to 5 mm in

349   diameter and display a cumulate texture. Clinochlore appears colourless, anhedral, and displays

350   third order interference colours in thin section. The mineral occurs between individual chromite

351   grains in areas ranging in size from lower (~1 μm) to upper micrometers (400-500 μm) (Fig. 1a).

352   Schindler et al. (2017) showed that clinchlore in chromitite from the Black Thor chromite

353   deposit contains chromite nanoparticles (Fig. 1b-d). Similar average Cr:Fe in clinochlore (2.2:1,

354   (SEM-EDS)) and chromite (2.3:1 (SEM-EDS)) suggest that Cr and Fe occur in clinochlore

355   predominantly as chromite nanoparticles. On the basis of this assumption, the modal ratio

356   between chromite and clinochlore (15:1) and the average concentration of Cr in clinochlore (3

357   wt%), the calculated mass ratio between the chromite nanoparticles in clinochlore and the

358   micrometer-size grains of chromite is circa 1:180.

359

360   **The chemical composition of the untreated chromitite surface**

361   Two XPS spectra were taken from areas with a higher and lower proportion of

362   clinochlore on the surface of an untreated chromitite (Tables 1 and A1). The Cr:Fe varies in the

363   range of 3.0-3.2 (N = 2) to 2.7-3.2 (N = 2) in areas containing a lower and higher proportion of

364   clinoochlore, respectively. These ratios are higher than those observed by SEM for chlorite

365   (2.2:1) and chromite (2.3:1) and with XRF for the bulk chromitite sample (2.1:1). Similarly the

366   average Mg:Si for chromitite determined with XPS (0.7:1) is much lower than the ratio in the

367   bulk structure (4.7:1). These observations indicate that the sensitivity factors for elements listed

368   in the database of the Vision software package (which were determined using anhydrous

369   minerals) are not appropriate to determine exact elemental ratios for spectra of rocks containing

370   hydrous minerals such as clinochlore. This observation is in agreement with those by Schindler

371   *et al.* (2009), who showed that the use of the sensitivity factor for Si of 0.325 (Vision 2.2.6) for

372   hydrated mineral samples (amorphous silica, uranyl minerals) results in larger Si:M (M = metal)

373   and Si:O with respect to the bulk composition of the minerals. The authors showed, however,

374   that relative changes in the elemental ratios determined for hydrous minerals with XPS can be

375   used to monitor changes in elemental ratios as a function of surface treatment. Hence, changes

376   in Cr:Si, Cr:Fe and Al:Si between the various dissolution experiments are still considered in this

377   study (Table 1) as they provide insights into chemical changes on chromitite surfaces under

378   various conditions.

379

380   **Stoichiometric and non-stoichiometric dissolution features on altered chromitite**

381   **surfaces at the micrometer and nanometer scales**

382   Non-stoichiometric dissolution commonly yields altered surfaces that differ in their

383   chemical composition from the unaltered mineral, whereas stoichiometric dissolution results in

384   etch features on surfaces with similar elemental ratios as an unaltered surface.

385   Stoichiometric dissolution features occur on the surface of chromite grains. Although

386   rare, they occasionally occur in the form of symmetrical etch pits (Fig. 2a) and asymmetrical

387   etch features (Fig. 2b). EDS-SEM chemical distribution maps for Si on a chromitite surface

388   treated with solution A indicate the occurrence of non-stoichiometric dissolution features on the

389   surface of clinochlore grains (Fig. 2d). These areas are often highly altered and enriched in Si

15

390   and depleted in Mg, Al, Fe and Cr (all < 1 wt%) with respect to the chemical compositions of

391   clinochlore and chromite (Fig. 2c).

392   The absence of diffraction spots and rings in SAED patterns taken from the silica-rich

393   areas indicate the occurrence of an amorphous silica modification (Schindler et al. 2017). STEM

394   images indicate the occurrence of fragments of clinochlore in areas composed mainly of silica

395   (Fig. 3a). Chemical distribution maps for Si, Cr and Mg indicate a higher abundance of chromite

396   nanoparticles (green) in the clinochlore fragments than in the surrounding silica (Fig. 3b and c).

397

398   **Secondary Cr-species on treated chromitite surfaces**

399   The changes in the chemical environments of Cr on the surfaces of the treated

400   chromitite surfaces can be determined through examination of the binding energies of the

401   various bands in the Cr $2p_{3/2}$ spectrum (supplementary data B2). The Cr $2p_{3/2}$ spectra taken from

402   altered chromitite surfaces are shifted to higher binding energy relative to the spectra recorded

403   from unaltered surfaces (Fig. 4a-c). Spectra with smaller shifts in binding energy display similar

404   multiplet splitting and peak shape (Fig. 4b), while those with larger shifts in binding energy

405   depict more asymmetric peak shapes (Fig. 4c). Quantification of the proportions of Cr^{3+} and Cr^{6+}

406   species in Cr $2p_{3/2}$ spectra displaying multiplet splitting is complicated by the fact that bands

407   corresponding to anhydrated and hydrated Cr^{3+} and Cr^{6+} surface terminations may overlap

408   (supplementary data B2). However, the identification of the exact nature of the surface

409   terminations is not a requirement for the quantification of the degree of alteration on a treated

410   chromitite surface. As indicated in supplementary data B2, the covalency of *M*-O bonds

411   decreases with the degree of protonation of the O atom. As such, a higher number of

412   protonated surface terminations on the chromite surface (i.e., lower electron densities around

413   the Cr^{3+} atoms) results in a shift of the Cr $2p_{3/2}$ spectrum to higher binding energies (Fig. 4-c).

414   Similarly, a higher number of Cr^{6+}-bearing surface terminations would also result in a shift of the

415   Cr $2p_{3/2}$ spectrum to higher binding energies. Hence, the degree of chromite surface alteration

16

416   can be related to the abundance of either protonated surface terminations or Cr^{6+}-bearing

417   surface terminations (e.g., $^{[6]}Cr^{3+}$-OH_2 or $^{[4]}Cr^{6+}$-OH); both such configuration types are defined

418   here as secondary Cr species, which are presumably absent on the untreated surface.

419   The proportion of secondary Cr species on a treated surface can be calculated from the

420   weighted average binding energy of the Cr $2p_{3/2}$ spectra (i.e., the total sum of the binding

421   energies of the bands multiplied by their respective proportions within the envelope), assuming

422   a linear relationship between the proportions of secondary species on the surface and the

423   weighted average binding energy. Using this approach, we define the weighted average binding

424   energy of an untreated chromite surface (577.0 eV) and the average binding energy for Cr^{6+}

425   components (579.4 eV) listed in the NIST database (2012) as the lower (0%) and upper limit

426   (100%) of secondary Cr-components, respectively. The proportion of secondary Cr-

427   components, and thus the degree of surface alteration, is then given by the equation

428   *secondary Cr-components [%] = 41 * weighted binding energy Cr 2p spectrum –*

429   *23694.7* [1]

430   where the numbers *41* and *23694.7* are the slope and intersection with the y-axis of the linear

431   plot, respectively

432

433   **Changes in chemical composition on the treated chromitite surfaces: dissolution**

434   **features in the absence and presence of bacteria and pyrolusite particles**

435   Quantification of the XPS spectra indicates that treated chromitite surfaces commonly

436   have lower Cr:Si, Al:Si and Cr:Fe than untreated surfaces (Fig. 5a, Table 1). Surfaces treated

437   with a TK solution, which contains Fe^{2+}, P, and S, have lower Cr:Fe and higher proportions of S

438   and P than those treated without TK solutions (Table 1). For example, the surface treated with

439   solution A + bacteria + TK solution (pH 2.3) has the lowest observed Cr:Fe (1.7:1) and the

440   highest proportion of S and P (Fe:(S+P) is 1.1:1 with P >> S) of all surfaces treated with acidic

441   solutions (Table 1). The latter surface has also the lowest proportion of secondary Cr species

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442 (13%). On the contrary, for all surfaces treated with acidic solutions (either Solution A or TK with

443 or without bacteria), the final Cr:Si and Al:Si on chromitite are similar (Table 1) and thus, the

444 addition of cultivated bacteria had a negligible effect on this aspect of the chomitite surface

445 chemistry.

446 The correlation between Cr:Si and Al:Si indicates that (a) surfaces treated with near-

447 neutral and alkaline solutions are enriched in Si relative to surfaces either untreated or treated

448 with acidic solutions, and (b) similar changes in the proportions of Cr and Al relative to Si occur

449 between surfaces treated with near-neutral and acidic solutions (Fig. 5a). A plot of Cr:Si versus

450 the proportion of secondary Cr species [%] indicates that the majority of the data follows a linear

451 trend with higher proportions of secondary Cr species occurring on surfaces with higher Cr:Si

452 (Fig. 5b). Exceptions to this trend are the surface compositions of the untreated surface (grey

453 data point) and the surface treated with a 0.1 $molL^{-1}$ MnO_2 solution of pH 6.2 (Table 1, Fig. 5b).

454

455 **Proportion of Cr- and Mn-components on the surfaces of MnO_2 particles and chromitites**

456 Optical examinations and XPS spectra recorded after dissolution experiments with MnO_2

457 powders show that the proportions of attached pyrolusite particles and Mn on the surfaces of

458 the chromitite slabs are significantly higher after treatment with near-neutral ($pH_{initial}$ 6.2) than

459 after treatment with acidic ($pH_{initial}$ = 2.5) or alkaline ($pH_{initial}$ = 8) solutions containing 0.1 $molL^{-1}$

460 MnO_2 (Table 3). XPS studies of pyrolusite particles separated from the chromite powder indicate

461 the presence of detectable amounts of Cr- Fe-, Si- and Al-bearing species (or particles) on the

462 surfaces of the pyrolusite grains. For example, concentrations of Cr on the surface of the

463 pyrolusite particles can be up to 8.3 at% Cr, whereby the Cr:Fe on the respective surfaces

464 (2.0:1-2.8:1) are similar to the ratio on the untreated chromitite surface (Tables 1 and 3).

465

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18

468 **Microbial community composition in dissolution treatments**

469   The initial microbial inoculum was a known mixed community containing at least 60%

470   Fe-oxidizing bacteria including *Acidithiobacillus ferrooxidans*, *Alicyclobacillus* sp. and acidophilic

471   heterotrophs including *Acidiphilium* sp. The 1 mL inoculums that were added with and without

472   TK solution B were sampled at the end of the dissolution experiment. Only the solution from

473   1mL bacteria + TK full solution had sufficient biomass to extract DNA with a yield of 2.3 ngμL^{-1}.

474   The community profile indicated a loss of most of the Fe-oxidizing bacteria (supplemental Table

475   A6) (0.1% abundance of *Alicyclobacillus* sp. remained) with the vast majority of the community

476   represented by heterotrophic acidophiles, > 98% *Acidiphilium* sp. This indicates that no Fe- or

477   S- oxidizing chemolithotrophs were sustained through the duration of the experiment and the

478   population likely declined after the Fe^{2+} from the TK media was consumed.

479

480   **Chemical composition of the solutions after the experiments**

481   Linear correlations are observed between the elemental concentrations of Al and Cr

482   (Fig. 6a) and Si and Cr (Fig. 6b), with the highest concentration of Cr consistently occurring in

483   solutions treated with the acidic solution A (Table A3). In both correlations, concentrations of Cr

484   in solutions containing pyrolusite particles are below the observed trend. Table 2 lists the Cr:Al,

485   Cr:Fe and Cr:Si in chromitite and clinochlore as well as in the final solutions; however, the Cr:Fe

486   is only meaningful for experiments in which additional Fe^{2+} was not introduced (i.e., those

487   without TK and bacteria solutions). Closer inspection of Cr:Al, Cr:Fe and Cr:Si in the solutions

488   shows that dissolution of chromitite was non-stoichiometric in all dissolution experiments, with

489   all solutions being enriched in Si relative to the Si:Cr in the bulk material (Table 2). It is also

490   apparent that Cr:Al and Cr:Fe in solutions after experiments carried out under acidic conditions

491   and deionized water, respectively, are similar to those observed in clinochlore.

492

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19

494   **DISCUSSION**

495   Laarman (2013) described the abundance, morphology and chemical composition of chlorite

496   group minerals from the Black Label, Black Thor and Big Daddy chromite deposits. The author

497   argues that these minerals are the product of retrogressive, hydrothermal alteration of chromite

498   and amphiboles and that the Mg, Al and Cr contents of clinochlore reflect that of the primary

499   chromite. For example, chlorites with elevated Cr_2O_3 either replace Cr-rich tremolite, occur as

500   interstitial material in massive chromitites, or occur in fractures where Cr becomes relatively

501   mobile with fluid influx. Laarman (2013) also reports that in minerals of the chlorite group, the

502   Cr_2O_3 concentration ranges from 1 to 10 wt%, with minerals occurring in fractures having the

503   highest concentrations of Cr.

504   The identification of chromite nanoparticles in clinchlore by Schindler et al. (2017)

505   suggests that the high Cr contents in many chlorites at the Black Label, Black Thor and Big

506   Daddy chromite deposits are the result of the presence of these nanoparticles and not as

507   commonly assumed a result of the replacement of Al^{3+} by Cr^{3+} in the structure of minerals of the

508   chlorite group (Lapham 1958).

509   In the next sections, we will address first non-stoichiometric dissolution features

510   observed on the surfaces of the treated chromitites, followed by discussions on the occurrence

511   of surficial secondary Cr-species, links between the chemical compositions of surfaces and

512   solutions and the effect of pH, pyrolusite particles and bacteria on the degree of chromitite

513   dissolution.

514

515   **Non-stoichiometric dissolution of chromite**

516   Both major constituents of chromitite, chromite and clinochlore, appear to undergo non-

517   stoichiometric dissolution under the investigated conditions. According to Zhang et al. (2016),

518   the non-stoichiometric dissolution of chromite, especially under strongly oxidizing conditions,

519   results in the removal of Cr as $Cr^{6+}_{(aq)}$ and in the re-precipitation of $Fe^{2+}_{(aq)}$ as Fe^{3+}-hydroxides.

520 Evidence for a similar mechanism on the chromitite surfaces treated with near-neutral and

521 alkaline solutions is seen in lower Cr:Fe and Cr:Al values relative to the untreated surface

522 (Table 1), which are consistent with the presence of Fe- and Al-hydroxide species precipitated

523 or adsorbed to the chromitite surface.

524   Micrometer-thick silica-enriched surfaces are visible by SEM (Fig. 2d) on surfaces of

525 clinochlore grains after treatment under acidic (but not near-neutral) pH conditions. This

526 observation is in accord with previous observations on the formation of silica-rich surfaces on

527 chlorite-group minerals treated with acidic solutions (Brandt et al. 2003) and on chromitite

528 samples treated with sulfuric acid solutions at higher T (Zhao et al. 2014). As the sole possible

529 source of Si in the studied system is chlinochlore, the occurrence of the Si-rich layer indicates

530 complete dissolution of chlinoclore followed by re-precipitation of amorphous silica within an

531 interfacial fluid film on the surface of the mineral (Hellman et al. 2002, 2012, Putnis and Ruiz-

532 Aguda 2013).

533   The solubilities of clinochlore and chromite are significantly different in aqueous

534 solutions. Chromite is a refractory mineral and sparingly soluble at room temperature, whereas

535 the solubility of chlorite group phases depends on solution pH and the activities of its constituent

536 ions. In a natural environment, the latter may be largely controlled by the presence of secondary

537 minerals such as gibbsite and kaolinite (Kittrick 1982). The absence of these minerals and their

538 higher solubility in an acidic environment (*e.g.*, pH 2-3) suggest that the dissolution of

539 clinochlore has been likely controlled by the solubility of amorphous silica in the experiments

540 under acidic pH conditions (pH = 2-3, Faure 1998). The effect of the higher solubility of

541 clinochlore relative to chromite is consistent with the final Cr:Si ratios observed in the reacted

542 solutions (Table 2). The mean Cr:Si in solution is 1:7.7, which is much closer to the value

543 measured in clinochlore (1:14) than that measured in the bulk chromitite (18.7:1; Table 2).

544   The occurrence of a visible layer of amorphous silica at low pH indicates the formation of

545 a higher proportion of amorphous silica on the surface of chromitites treated under acidic than

21

546   near neutral pH conditions. However, higher concentrations Si in solution after the experiments

547   under acidic conditions (Table 2) indicate that the re-precipitation of amorphous silica is not a

548   complete reaction (most likely due to the high solubility of amorphous silica, Faure 1998).

549   Hence, with increasing dissolution of clinochore, the total amount of Cr and Fe on the chromitite

550   surface remains relatively constant (due to the low solubility of chromite), while the total

551   amounts of Al, Si and Mg on the treated surfaces decrease. As the loss of Al on the surface is

552   somewhat mitigated by the relatively insoluble chromite, the loss of Si is greater, resulting in the

553   observed increases in Al:Si and Cr:Si with decreasing pH value in solution (Fig. 5a, Table 1).

554

555   **Secondary Cr species on treated chromitite surfaces of treated chromitites**

556   Figure 5b shows an increase in the proportions of secondary Cr species on chromite

557   with increasing dissolution of the chromitite (the latter increases as a function of Cr:Si). An

558   exception to this trend is the chromitite surface treated with a 0.1 molL^{-1} MnO$_2$ solution (pH$_{initial}$ =

559   6.2; Table 1). This surface has the lowest Cr:Si of all treated surfaces (even lower than that

560   treated with deionized water), but the proportion of secondary Cr species approximates that of

561   surfaces treated with acidic solutions (Table 1, Fig. 5b).

562   A likely reason for this observation is the presence of a high proportion of pyrolusite

563   particles on the surface of the chromitite after the experiment (Table 3). Particle attachment to

564   mineral surfaces is favored where surfaces and particles have opposing electrostatic charges.

565   The points of zero charge (PZC) for amorphous silica, clinochlore, pyrolusite and Al-rich

566   chromite are 4.1, 4.7, 5.9 and 7.4 respectively (Kosmulski 2009a, b; Alvarez-Silva 2010;

567   Christiano et al. 2011). Hence in a solution of pH 6.2, the surfaces of amorphous silica, and

568   clinochlore are negatively-charged, surfaces of pyrolusite are slightly negatively-charged, and

569   those of chromite are slightly positively-charged and the attachment of pyrolusite particles to the

570   surface of chromite is thus favored at pH 6.2.

22

571   The presence of pyrolusite particles on the surface of chromitite may also be related to

572   particle agglomeration and aggregation. Agglomeration is commonly favored when the surface

573   of the particles has a minimum charge, which is the case when either (1) the pH is close to the

574   PZC, or (2) when adsorbed species neutralize positive or negative surface charges (e.g., Hotze

575   et al. 2010). The surface charges listed above indicate that attachment, agglomeration, and

576   heteroaggregation of pyrolusite particles on the surface of chromite is favored in the solution of

577     $pH_{initital}$ = 6.2, as compared to the solutions of $pH_{initital}$ = 2.5 and 8.0, in accord with the

578   observations in this study (Table 3).

579   The higher abundance of pyrolusite particles on the surface of chromitite treated with a

580   solution of $pH_{initial}$ = 6.2 likely provided a higher number of adsorption sites for aqueous species

581   such as $Cr(OH)^{2+}$ and $Cr(OH)_2^+$, which are the predominant Cr^{3+}-bearing aqueous species in

582   weakly acidic conditions (Fendorf 1995). The presence of such species on the surface of the

583   attached pyrolusite particles may explain the observed elevated proportions of secondary Cr

584   species on the chromitite surface treated with a 0.1 $molL^{-1}$ MnO_2 solution of pH 6.2 (Fig. 5b).

585   Chromate species such as $(HCr^{6+}O_4)^-$ and $(Cr^{6+}O_4)^{2-}$ form predominantly under alkaline

586   pH conditions in solution but can also form through oxidation of Cr^{3+} by Mn^{3+}/Mn^{4+}-bearing Mn-

587   oxides under acidic conditions (Eary and Rai 1987, Fendorf 1995). The occurrence of adsorbed

588   chromate species on the surface of the treated chromitite cannot be completely ruled out

589   because Al-rich chromite and Fe-hydroxide species (or precipitates) that form during dissolution

590   experiments with $CaCO_3$-bearing solutions have net-positive surface charges under acidic to

591   near-neutral pH-conditions, which would promote the adsorption of the negative charged

592   chromate species.

593   The observation that no Fe- and S-oxidizing bacteria were sustained during the

594   dissolution experiments indicates that the bacteria were either (1) not resistant to the presence

595   of Cr^{6+} aqueous species, or (2) did not gain enough energy from the potential oxidation of

596   released Fe^{2+} and Cr^{3+} species. This observation may explain the similarities in the proportions

23

597   of secondary Cr-species after the dissolution experiments under acidic conditions in the

598   presence and absence of bacteria (Table 1, Fig. 5b).

599

600   **Linking surface composition of chromitite slabs and pyrolusite particles with the**

601   **chemical composition of solutions**

602   Comparison between the compositions of surfaces (chromitite and pyrolusite) and

603   solution shows that the concentrations of Cr in solution are controlled by (1) the initial release of

604   chromite nanoparticles during clinochlore dissolution, (2) the adsorption of chromite

605   nanoparticles (and other Cr-bearing aqueous species) to the surfaces of pyrolusite particles,

606   and (3) the potential oxidation of Cr^{3+} to Cr^{6+}.

607   In addition to the formation of silica-enriched surface layers during dissolution/re-

608   precipitation processes, the dissolution of clinochlore will likely release chromite nanoparticles to

609   solution. This conclusion is in accord with the following four considerations and/or observations:

610   (1) In a dissolution-re-precipitation process, all components (including chromite

611   nanoparticles) are initially removed from the surface;

612   (2) The highly hydrous and porous character of the hydrous silica layer easily allows the

613   diffusion and transport of aqueous species and nanoparticles (Schindler et al 2009c;

614   Putnis and Ruiz-Aguda 2013, Schindler and Hochella 2017);

615   (3) Chromite nanoparticles occur in lower abundance in the hydrous amorphous silica layer

616   relative to the unaltered clinochlore grain (Fig. 3b and c, Schindler et al. 2017);

617   (4) Elevated Cr:Si in acidic, as opposed to near-neutral and alkaline solutions likely result

618   from (a) a higher release rate of chromite nanoparticles and (b) a higher degree of

619   alteration of the surficial chromite grains (higher proportion of secondary Cr species)

620   (Table 2, Fig. 5b).

621   In experiments with pyrolusite particles present, solutions are depleted in Cr, relative to

622   Al and Si (Fig. 6a-b) with Cr:Al and Cr:Si as low as 1:8.4 and 1:145, respectively (Table 2). This

24

623   depletion in Cr and Cr:Fe of 2:1 to 3:1 on the surfaces of the pyrolusite particles suggest

624   preferential sequestration of chromite nanoparticles over Al- and Si-bearing aqueous species by

625   the pyrolusite particles (Table 3). Conversely, similar Cr:Al in acidic solutions and a similar

626   Cr:Fe in deionized water as in clinochlore indicate that neither Cr, Al, nor Fe have been

627   preferentially removed from the respective solutions though adsorption and precipitation

628   processes.

629   In solutions after experiments with $CaCO_3$ in solution, Cr:Al and Cr:Fe are greater than

630   those in the initial clinochlore (Table 2). This indicates an enhanced adsorption or precipitation

631   of Al and Fe-species under alkaline pH conditions (see above). Preferential adsorption or

632   precipitation of Al and Fe relative to Cr occurs commonly when Cr is in the hexavalent oxidation

633   state, as the geochemical and crystal chemical properties of Cr^{3+} are sufficiently similar to those

634   of Al^{3+} and Fe^{3+} to not result in a significant difference in their environmental fate (Fendorf

635   1995). Although the XPS studies could not unequivocally identify Cr^{6+} species on the surfaces of

636   the altered chromitites, the latter conclusion is in accord with the observed higher stability of

637   chromate aqueous species under alkaline pH conditions (Fendorf 1995; Zhang et al. 2016).

638   In conclusion, chemical and mineralogical features on the surfaces of chromitite and

639   pyrolusite particles and the compositions of the respective solutions show that the

640   concentrations of Cr in solution are controlled by the release of chromite nanoparticles, the

641   adsorption of chromite nanoparticles or Cr-bearing aqueous species to the surfaces of

642   pyrolusite particles and the potential oxidation of Cr^{3+} to Cr^{6+}.

643

644   **Effect of the pH, solution composition and bacteria on the degree of chromitite**

645   **dissolution**

646   The occurrence of multiple chemical and physical processes on the surfaces of the

647   treated chromitites makes evaluating the combined effects of solution composition, pH and

648   bacteria presence on the degree of dissolution of chromitite difficult. The higher concentrations

25

649   of Cr and more pronounced dissolution features on the chromitite slabs after the dissolution

650   experiments under acidic than under neutral or weak basic conditions indicate that a decrease

651   in pH likely enhances the degree of dissolution and the release of associated chromite

652   nanoparticles. This is supported by the observations that the formation of silica-rich alteration

653   layers on silicate minerals is commonly favoured under acidic rather than near neutral and

654   alkaline pH conditions (*e.g.* Brantley 2003). Higher concentrations of Cr after dissolution

655   experiments in solution A (sulfate-phosphate-bearing solution without Fe^{2+}) than in solution TK

656   (Fig. 6, Table A3) suggest that the absence of Fe^{2+}-bearing aqueous species (and thus a higher

657   degree of undersaturation with respect to chromite; Table A1) has an effect on the degree of

658   dissolution. However, this is not apparent when considering the respective compositions of the

659   treated slabs (where higher Cr:Si and higher proportions of secondary Cr species occur after

660   the experiments with the TK solution than solution A, Table 1).

661   The role of bacteria is also unclear during these dissolution experiments as their

662   abundances seem to be controlled primarily by the initial amount of Fe^{2+} in solution rather than

663   by the amount of Fe^{2+} released during the dissolution of the chromite nanoparticles.

664

IMPLICATIONS

666   Evaluation of the potential fate of Cr in contaminated soils, tailings, and waste rock piles

667   is a complex issue requiring a thorough characterization of the mechanisms in operation during

668   the non-stoichiometric dissolution of chromitite ore. An understanding of these dissolution

669   mechanisms is fundamental to being able to accurately predict (1) the compositional evolution

670   of aqueous solutions in contact with chromitite, particularly related to formation of the highly-

671   toxic chromate Cr^{6+} species; (2) the compositional, structural, and mineralogical changes

672   occurring on the surface of the affected minerals (i.e., clinochlore and chromite); and (3) the

673   behaviour of nanoparticles upon their release from the dissolving clinochlore phase, thereby

674   affecting the transport, reactivity, and bioavailability of chromium.

26

675   Elucidation of dissolution features of chromitite is facilitated in this study by a multi-

676   analytical approach, utilizing methods capable of nano-scale imaging and chemical

677   characterization such as XPS, SEM and TEM. The comprehensive data set collected here

678   shows the importance of factors such as dissolution rates of Cr-bearing silicates and chromite,

679   the release of chromite nanoparticles, re-precipitation of amorphous silica, the pH-dependence

680   adsorption (or precipitation) of Fe- and Al-bearing hydroxides and sulfates. It also shows that

681   chemical signatures of aqueous solutions in contact with chemically complex rocks such as

682   chomitite can be only explained when considering physical, chemical and mineralogical

683   characteristics of each phase present in the rock. Bacterial activities and species appear to

684   have no direct effect on the release of Cr species or on the surface composition of altered

685   chromitites. However, their presence in tailings, mine waste piles and soils may control pH and

686   Eh due to their ability to either oxidize or reduce redox-sensitive ions such as S^{2-}, $(SO_4)^{2-}$, Fe^{2+},

687   Fe^{3+}, Mn^{2+} and Mn^{4+} and thus control indirectly degrees of chromitite alteration and the $Cr^{3+}:Cr^{6+}$

688   redox-chemistry in solution.

689   The existence of chromite nanoparticles in silicate minerals associated with chromite

690   deposits at the Ring of Fire in Ontario, Canada and the Mistake mine in California, USA

691   suggests a widespread occurrence of chromite nanoparticle in Cr-rich rocks and minerals. The

692   ultimate release of these nanoparticles during either natural weathering or mine-related rock

693   processing and waste disposal may, therefore, be a significant vector of chromium introduction

694   into the environment. Here, we show that the magnitude of this release can only be assessed by

695   considering the dominant geochemical conditions (e.g., pH, Eh, and counter-ion chemistry) that

696   are driving chromitite dissolution and re-precipitation and adsorption processes. The

697   observations in this study suggest that release of chromite nanoparticles during alteration of

698   chromitite ore fragments in future mine tailings would be favoured at low pH values in a sulfide-

699   rich environment as acidic pH conditions favour the non-stoichiometric dissolution of the

700   associated Cr-silicates. The results of this study also suggest that released chromite

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701 nanoparticles will be effectively sequestered by larger colloids or particles in pore solutions

702 within mine tailings settings. Neutralization of acidic pore solutions towards near neutral pH

703 conditions through liming and the use of barriers or linings composed of clays or hydroxides

704 should be then sufficient to limit the amount of chromite nanoparticles released into the

705 environment. Further work would be required to assess the ability of chromite nanoparticles to

706 ultimately control the abundance of $Cr^{6+}_{(aq)}$ in soils and outcrops proximal to mining activities

707 and tailings.

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718

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833   FIGURE CAPTIONS

834   Figure 1 (a) SEM image of chromitite from the Black Thor chromite deposit, the occurrence of

835   clinochlore in the interstices of chromite grains is indicated with arrows; (b) TEM image of the

836   clinochlore matrix indicating the presence of chromite nanoparticles; (c) high-resolution TEM

837   images of an individual chromite nanoparticle depicting lattice fringes with d = 2.05 Å (400); (d)

838   SAED pattern of clinochlore indicating the presence of a single crystal of clinochlore (diffraction

839   spots) and chromite nanoparticles (diffraction rings).

840

841   Figure 2 (a) SEM image in BSE mode of a nearly symmetrical etch pit on the surface of a

842   chromite grain treated with a bacteria + TK solution of pH 2.0; (b) SEM image in BSE mode of

843   asymmetric etch features along an edge of a chromite grain after treatment with solution A of pH

844   2.5; (c)-(d) BSE image in BSE mode and corresponding chemical distribution map for Si of a

845   chromitite grain treated with solution A of pH 2.5; highly-altered clinochlore and silica-rich

846   patches on the chromitite surface are indicated with arrows.

847

848   Figure 3 (a) STEM image of a selected area in a FIB section extracted from a surface treated

849   with solution A at pH 2.5; areas composed of chromite, clinochlore and amorphous silica are

850   labelled accordingly, a fragment of clinochlore within the amorphous silica matrix depicted in (b)

851   and (c) is encircled; (b)-(c) STEM-EDS chemical distribution maps for (b) Si (red) and Cr (green)

852   and (c) Mg (blue) and Cr (green).

853

854   Figure 4 Cr 2p$_{3/2}$ spectra for various chromitite surfaces: (a) untreated; (b) treated with a bacteria

855   + TK solution; (c) treated with a 0.1 molL^{-1} MnO$_2$ solution; a vertical grey-shaded bar indicates

856   the location of the peak at the lowest binding energy of the spectrum for the untreated surface.

857

858   Figure 5 (a) plots of the Cr:Si versus Al:Si determined with XPS for untreated (grey data point)

859   and treated (black data points) chromitite surfaces; (b) Cr:Si versus proportion of secondary Cr

860   species on the surface of untreated (grey data point) and treated surfaces, , data points

861   representing surfaces treated with acidic solutions in the presence and absence of bacteria are

862   indicated with black squares and circles, respectively; data points representing surfaces treated

863   with near neutral and alkaline solutions are depicted with black triangles pointing up and down,

864   respectively.

865

866   Figure 6 (a)-(d) plots with the concentrations of (a) Al versus Cr and (b) Si versus Cr in solutions

867   after experiments with chromitite powders; solid lines indicates calculated linear regression

868   curves; symbols for data points are the same as for Figure 5

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890 Table 1 Results from dissolution experiments with chromitite slabs (0.5 x 0.5(1) x 0.1cm) in 25 mL solution for four weeks: selected

891 elemental ratios between major elements and proportion of secondary Cr species on the surface of the treated samples determined

892 with XPS after the experiment; N (XPS): number of spectra taken from the surface; the uncertainty of the pH and Eh (mV) is ±0.1

Experiment	Cr:Si	Cr:Fe	Al:Si	Fe:(P+S)	Secondary Cr species [%]	N XPS	$pH_{initial}$ pH_{end}	$Eh_{initial}$ $Eh_{initial}$
Untreated	1.8:1	3.0:1	2.1:1	n.a.	0	4		
1 mL bacteria TK + 24 mL TK	1.4:1	2.0:1	1.8:1	2.4 S >> P	19	2	$2.3_{initial}$ 2.4_{end}	0.6 0.5
25 mL TK	1.3:1	1.9:1	1.6:1	2.0 S >> P	17	2	$2.3_{initial}$ 2.4_{end}	0.6_i 0.5
25 mL solution A	1.3:1	3.5:1	1.4:1	2.4 S ~ P	15	2	$2.5_{initial}$ 2.6_{end}	0.6 0.5
1 mL bacteria TK + 24 mL solution A	1.2:1	1.7:1	1.5:1	1.1 P >> S	13	2	$2.3_{initial}$ 2.4_{end}	0.6 0.5
deionized water	1.1:1	2.25:1	1.5:1	n.a.	6	2	7 6.7_{end}	0.6 0.5
25 mL Solution A 0.1 molL^{-1} MnO$_2$	1.25:1	2.9:1	1.6:1	n.d.	19		$2.5_{initial}$ 4.5_{end}	1.1 0.7
0.1 molL^{-1} MnO$_2$	0.73:1	2.0:1	1.2:1	n.a.	21	2	$6.2_{initial}$ 6.0_{end}	0.6 0.5

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0.1 molL^{-1} MnO$_2$ + 0.05 molL^{-1} CaCO$_3$	1.0:1	2.4:1	1.5:1	n.a.	8	2	8.0 initial	0.6
							6.5$_{end}$	0.5
0.05 molL^{-1} CaCO$_3$	1.1:1	3.0:1	1.7:1	n.a.	14	2	9.2 initial	0.6
							6.3$_{end}$	0.5

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896   Table 2 Elemental ratios in chromitite and clinochlore and elemental ratios in the solutions after

897   the bulk dissolution experiments with 100 mg chromite powder in 25 mL solution for four

898   weeks(with pH value)

Experiment	Cr:Al	Cr:Fe	Cr:Si	pH initial	pH end
Chromitite	4.5:1	2.1:1	18.7:1		
Clinochlore	1:3	2.2:1	1:14		
Bacteria + TK solution[1]	1:2.5	1:1492	1:3.2	2.1	2.18
TK solution[1]	1:2.5	1:1607	1:3.3	2.1	2.36
Solution A	1:2.8	1:1	1:4.5	2.5	2.35
Bacteria + Solution A	1:2.9	1:17.5	1:4.4	2.1	2.2
H_2O	2.3:1	2.0:1	1:14.9	7	6.7
TK solution[1] + 0.1 mol L^{-1} MnO_2	1:8.4	1:1461	1:11.5	2.1	2.27
Solution A +0.1 molL^{-1} MnO_2	1.3:1	1:1.6	1:145	2.1	4.28
0.1 molL^{-1} MnO_2	1.4:1	1:1.3	1:135	6.2	6.7
0.1 molL^{-1} MnO_2 + 0.05 molL^{-1} $CaCO_3$	5.6:1	3.7:1	1:18	8.0	7.65
0.05 molL^{-1} $CaCO_3$	3.0:1	16.3:1	1:12.6	9.2	7.81

899   [1] contain Fe^{2+}-sulfates
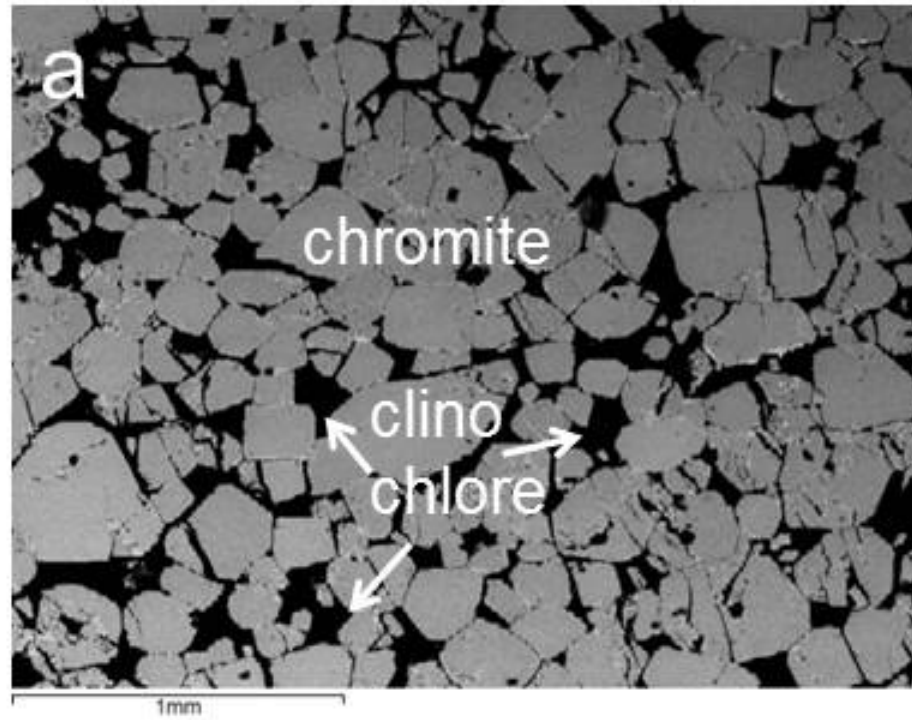
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906   Table 3 Results of the XPS measurement after dissolution experiments with pyrolusite powders

Experiment	pH	Mn [at%][1] on the surfaces of chromitite	Cr [at%][1] on the surfaces of MnO_2 particles	Fe [at%][1] on the surfaces of MnO_2 particles
0.1 molL^{-1} MnO_2 0.05 molL^{-1} $CaCO_3$	8.0$_{initial}$ 6.5$_{end}$	2.0	6.3	3.1
0.1 molL^{-1} MnO_2	6.2$_{initial}$ 6.0$_{end}$	22.1	6.4	2.9
Solution A 0.1 molL^{-1} MnO_2	2.5$_{initial}$ 4.5$_{end}$	3.6	8.3	2.9

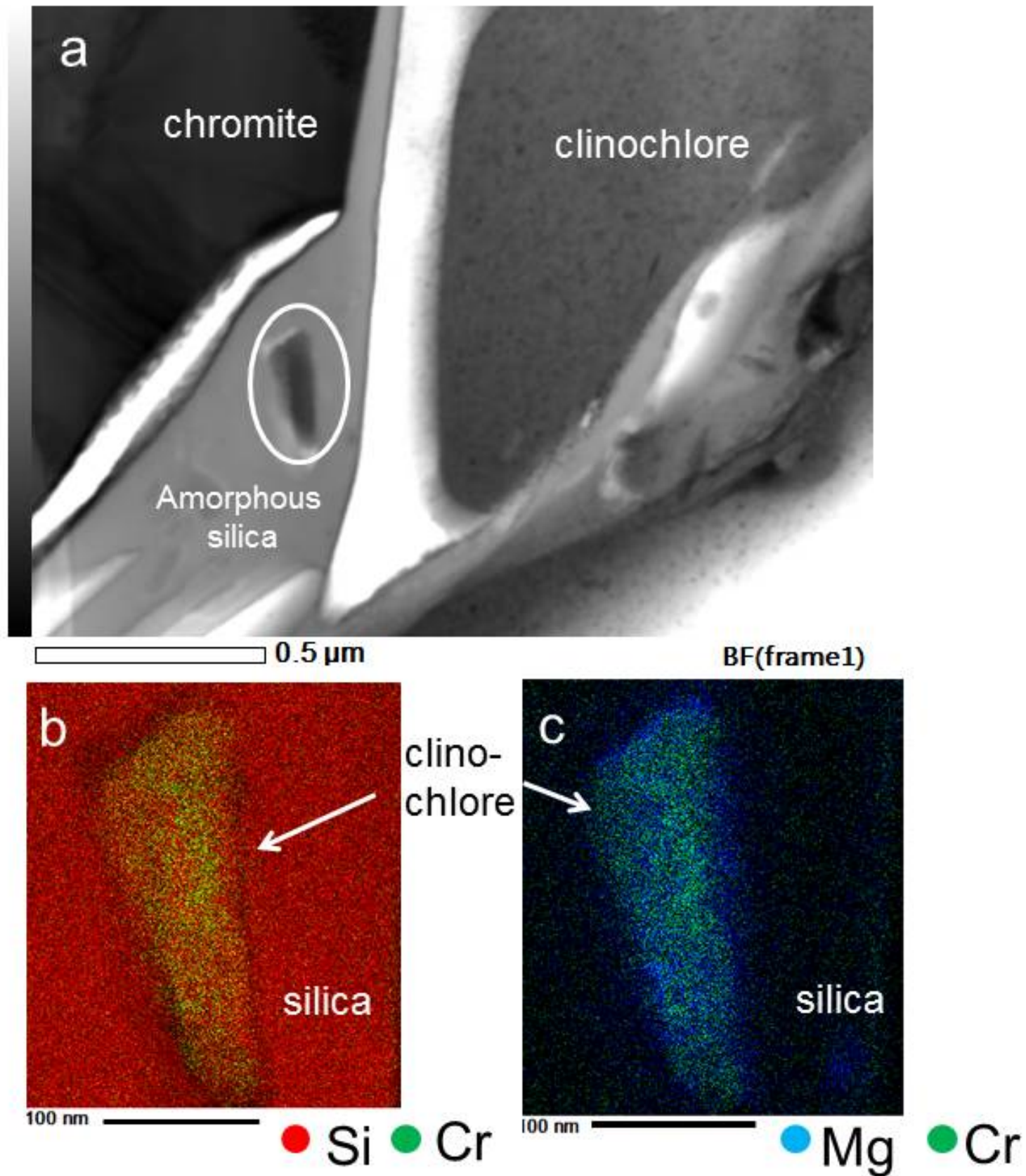907   1. percentage relative to all other cations (O and H not included in quantification)
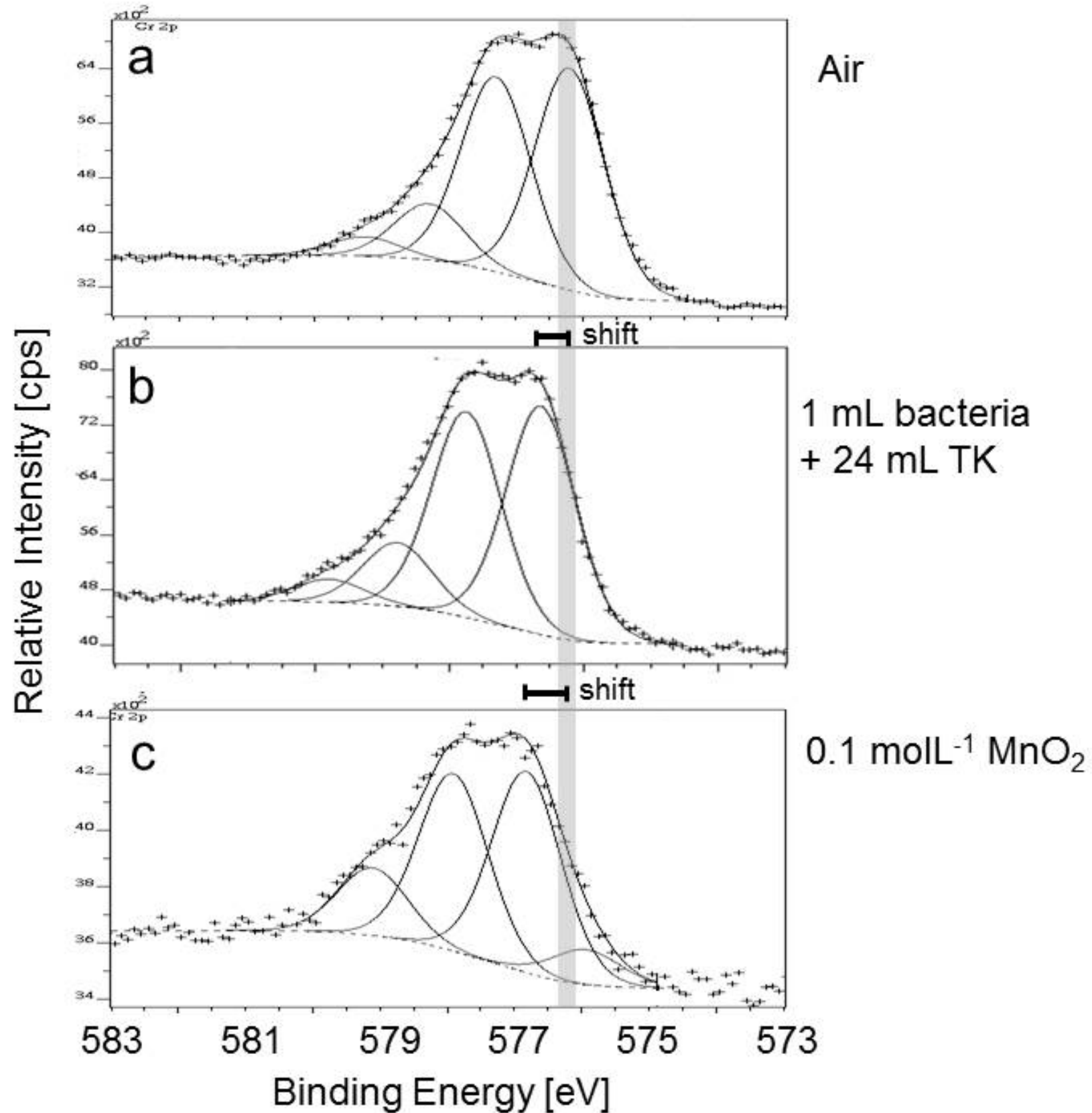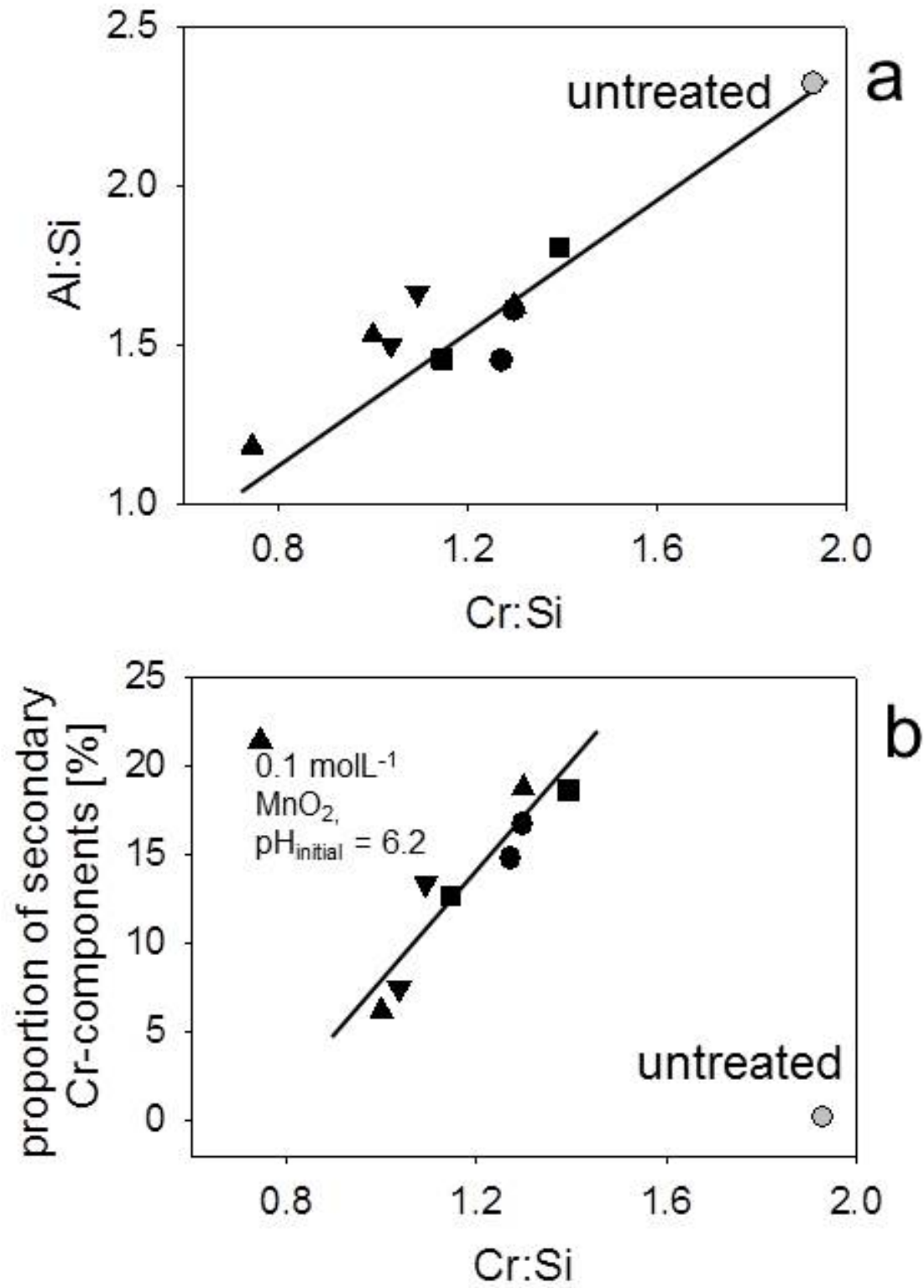
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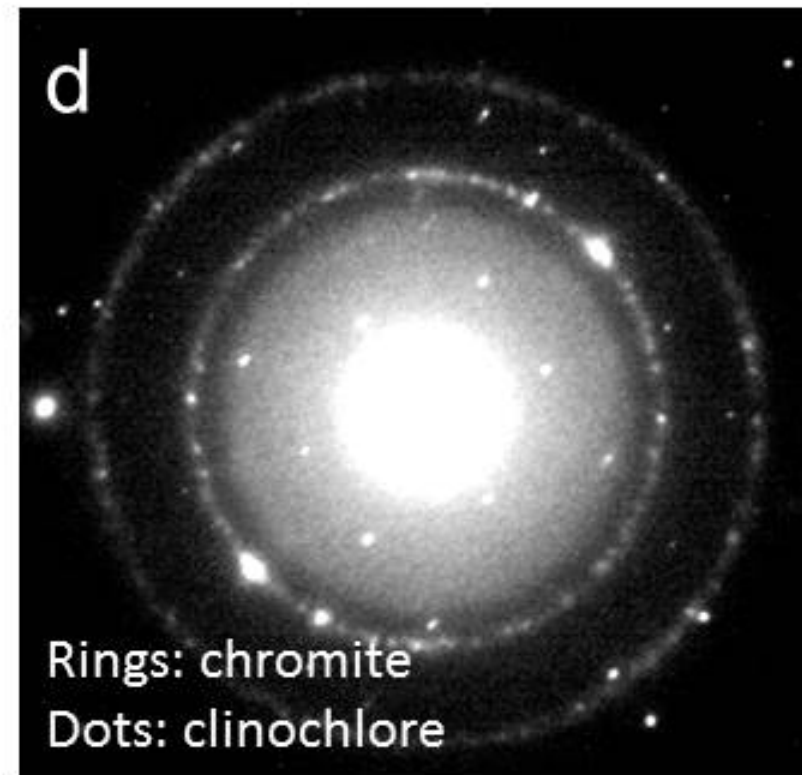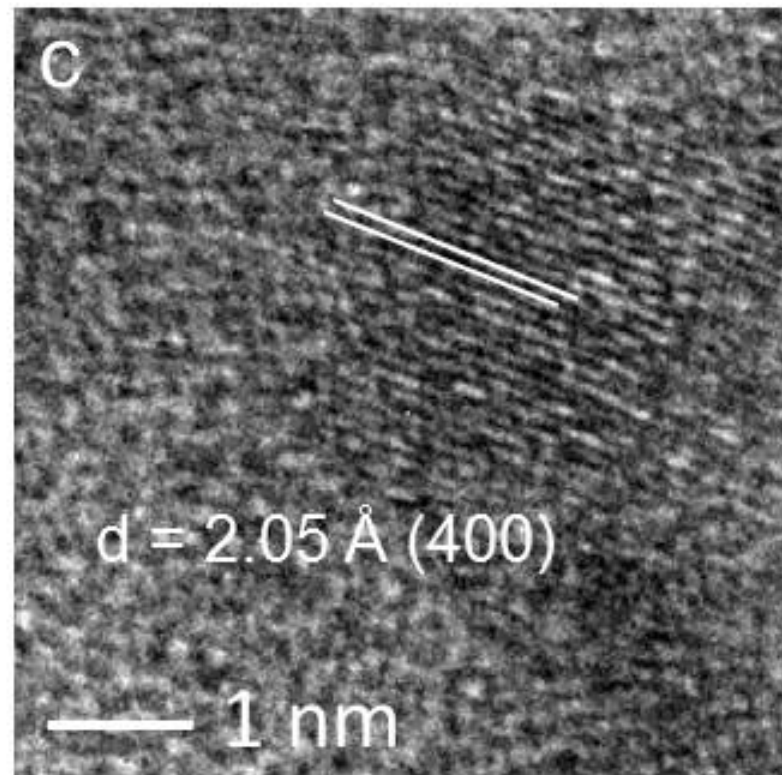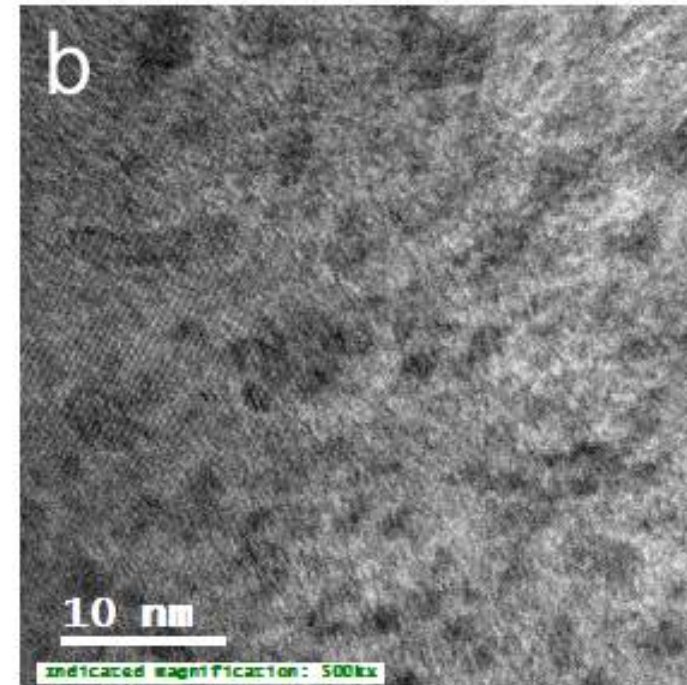
Fig. 1

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Fig. 5

Fig. 6