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1 **The first polluted river? Repeated copper contamination of fluvial sediments**

2 **associated with Late Neolithic human activity in southern Jordan**

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26 *Keywords*

27 Late Neolithic; environmental pollution; copper; lead; Jordan; pyrometallurgy

28

29 *Abstract*

30 The roots of pyrometallurgy are obscure. This paper explores one possible

31 precursor, in the Faynan Orefield in southern Jordan. There, at approximately 7000

32 cal. BP, banks of a near-perennial meandering stream (today represented by

33 complex overbank wetland and anthropogenic deposits) were contaminated

34 repeatedly by copper emitted by human activities. Variations in the distribution of

35 copper in this sequence are not readily explained in other ways, although the precise

36 mechanism of contamination remains unclear. The degree of copper enhancement

37 was up to an order of magnitude greater than that measured in Pleistocene fluvial

38 and paludal sediments, in contemporary or slightly older Holocene stream and pond

39 deposits, and in the adjacent modern wadi braidplain. Lead is less enhanced, more

40 variable, and appears to have been less influenced by contemporaneous human

41 activities at this location. Pyrometallurgy in this region may have appeared as a

42 byproduct of the activity practised on the stream-bank in the Wadi Faynan ~7000

43 years ago.

44

1.   INTRODUCTION

46 Over the last few thousand years, civilisations have been underpinned by the use of

47 metal-based technology, but the origins and roots of metal production are unclear

48 and contested (e.g. Renfrew 1969; Craddock 2000; Golden et al. 2001; Hauptmann

49 2007; Radivojevic et al. 2010; Garfinkel et al. 2014; Golden 2014). One of the

50 earliest documented metal extraction centres is the Faynan/Fidan orefield on the

51 edge of the Wadi 'Arabah in Southern Jordan, where unequivocal copper

52 pyrometallurgy is documented from the 4th millennium BC (Hauptmann, 2007 and

53 references therein). But even in this very well-researched area, the precursor

54 activities to this established pyrometallurgy are far from clear.

55   The stratigraphy, palaeoenvironments and geochemistry of the later Quaternary

56   deposits on the Faynan Orefield (Figure 1) in Southwest Jordan were evaluated

57   during the Wadi Faynan Project (Barker et al. 2007a), which explored the history of

58   desertification and its relationship with agricultural and industrial activity at the desert

59   margin. At site WF5021, Grattan et al. (2007) recorded anomalously high

60   concentrations of copper and lead in deposits attributed to the Faynan Member

61   Upper Component (McLaren et al. 2004). These were dated by AMS radiocarbon to

62   7245-6994 cal. BP [Beta-205964] and are attributable to the local Late Neolithic

63   (Hunt et al. 2007b). The Late Neolithic date is consistent with the regional

64   lithostratigraphy, archaeological sequence and pollen biostratigraphy which are

65   anchored by radiocarbon dates at other sites in the Faynan catchment (Grattan et al.

66   2007; McLaren et al. 2004; Hunt et. al. 2004, 2007a,b).

67   Stratigraphic and archaeological evidence (Grattan et al. 2007) suggested that the

68   high concentrations of heavy metals in the Faynan Member – Upper Component at

69   WF5021 are *in situ* and not the result of post-sedimentation events. 7000 calendar

70   years is significantly older – typically 500-1000 years - than any pyrometallurgy from

71   this region (Adams 1997, 1999; Adams et al. 2010; Barker et al. 2007a; Hauptmann

72   2000; 2007), or with global pollution signatures (Celine et al. 2008; Boutron et al.

73   1995; Muhly 1988; Neuninger et al. 1964; Thornton et al. 2010; Shotyk et al. 1998),

74   although it is younger than contamination in the Keweenaw Peninsula, Michigan

75   (Pompeani et al. 2013) and contemporary with instances in the Balkans (Radivojević

76   et al. 2010). This study therefore examines a range of plausible explanations (Table

77   S1), through

78   1.   a reappraisal of the stratigraphy of the exposure

79   2.   further geochemical analyses to test the original work and to clarify causes
80   of these comparatively high concentrations (Figs. 2, 3)

81   3.   comparative measurements in older, contemporary and modern regional
82   sediments (Tables 1, S3, Figs. S3-S5)

83

84   **Figure 1 here**

85

2. STRATIGRAPHY AND DATING

87 The exposure at site WF5021 (Figs. S1, S2) was described in McLaren et al. (2004),
88 Hunt et al. (2004, 2007) and Grattan et al. (2007). Previous work is described in the
89 SI and details of radiocarbon dates are given in Table S2. The exposure consists of
90 three major superposed components:

91 • Faynan Member (Lower Component): a basal trough cross-bedded light to
92   medium brown silty sandy gravel unit with silt and sand interbeds, one of which
93   was dated to 15,800±1,300 BP [Aber18/J8] by Optically Stimulated
94   Luminescence

95 • Faynan Member - Upper Component: an epsilon cross-bedded greyish-brown silt
96   and silty gravel unit, in places containing abundant potsherds and animal bone
97   fragments radiocarbon dated to 7245-6994 cal. BP [Beta-205964] (Grattan et al,
98   2007, sample G). Pollen in most of this unit was attributed by Hunt (2004, 2007)
99   to the PPA biozone, with the very top of the unit attributed to the PAP biozone.
100   The PPA biozone is dated at site WF5015 in the nearby Wadi Dana to 8310-7860
101   cal. BP [Beta111121]

102 • Tell Loam Member: a unit of irregularly planar but well-bedded light brown silts,
103   passing up locally into and overlying the remains of the mud-brick Late Neolithic
104   village of Tell Wadi Faynan (Najjar et al. 1990) which is dated to 7164-6892 cal.
105   BP [HD13775] and 7164-6796 cal. BP [HD12338] (Hauptmann 2000; Hunt et al
106   2007b). Contained archaeological finds suggest that the Tell Loam Member
107   accumulated until the Byzantine era (Barker et al. 2007b; McLaren et al. 2004). It
108   contains evidence for colluvial-aeolian sedimentation, aridification and episodic
109   contamination by smelting effluent (Grattan et al. 2007), but it is important to note
110   that the heavy metal contamination in these deposits is highly stratified (Grattan
111   et al. 2007) and shows no sign of vertical movement or the action of solutional
112   processes.

113 All these deposits are exposed in a steep cliff, 5–10 m high, at the edge of the
114 current Faynan braidplain. Dates of 7561-7025 [HD-10567] and 7420-7180

115 [HD12335] were obtained (Hauptmann 2000) from the cliff section at respectively 4

116 m and 2.5 m below the cliff top adjacent to the archaeological site from fluvial

117 deposits probably equivalent to the sediments studied in this paper.

118

119

120 ## 3. PXRF, ICP-MS AND STATISTICAL STUDIES

121 The sedimentary sequences listed in Table1 are of inherently heterogeneous,

122 variable materials. They reflect complex and changing geomorphic processes and a

123 variety of sources. Therefore, this investigation has minimised issues with moisture

124 and grain size and focused on the ranges, relativities and associations of copper and

125 lead measured in the different deposits.

126 The number of geochemical analyses in this study was substantially increased

127 beyond those of Grattan et al. (2007). At exposure WF5015, ICP-MS analyses

128 following the procedures used by Grattan et al. (2007) were on sub-2 mm oven-dry

129 material, in which low-power microscope inspection did not detect particles of metal

130 ore. Most geochemical analyses were done, however, using a Niton® XLt Series

131 700 portable XRF analyser,

132 The Niton XLt 700 Analyser uses a low power (1.0 W) X-ray tube in tandem with an

133 Ag anode target and Peltier-cooled Si-Pin x-ray detector. The possibility that

134 contaminants had travelled down cracks or fissures in the sediments was addressed

135 by ensuring that only sediments several cm away from such features were sampled.

136 Likewise, the possibility of concentration of heavy metals having been concentrated

137 by redox reactions or leaching was kept in mind during sampling, but features such

138 as oxide staining, iron pans or manganese staining/concretions were not

139 encountered. To minimise measurement variation caused by grain size and moisture

140 variation (e.g. Ge et al. 2005; Kim et al. 2011), only dry, *in-situ* sand-size materials

141 were analysed, while silt/clay-rich and gravelly horizons and locations with any

142 visible clasts of copper ore or smelting slags were avoided. Since heavy metal

143 concentrations are in general inversely related to grain-size (e.g. Kim et al. 2011),

144 avoidance of silt/clay-dominated samples means that the possibility of sampling very

145   high concentrations relating to the scavenging activities of clay minerals was

146   minimised. To minimise variation caused by measurement distance, the pXRF

147   analyses were all made on freshly-cleaned-back, planar exposures by placing the

148   pre-cleaned window at the front of the instrument directly against the exposure to be

149   analysed, with the axis of the instrument normal to the plane of the exposure.

150   Measurement time was standardised at 30 or 60 seconds using the integral software

151   in Soil Analysis mode, with five replicates for each measurement, following Haylock

152   (2016) and similar to Shuttleworth et al. (2014). The exposed surfaces of the *in situ*

153   and stratigraphically-separate fragments of Neolithic pottery investigated by PXRF at

154   WF5021 at locations NP1 to NP3 appeared clean. Even so, they were brushed and

155   further cleaned by blowing. Internal calibration followed the user guide (version 5.0

156   P/N500/905) using an Ag anode target within the hand-piece. Fundamental

157   parameters eliminate the need for site-specific calibration utilising theoretical

158   mathematics to predetermine inter-element coefficients rather than using matrix

159   specific calibration standards (Kalnicky and Singhvi, 2001), and were used to

160   interpret the fluorescence (secondary x-ray signal) into element identification and

161   concentrations in ppm. Comparative testing of three reference materials, Till 4

162   (Natural Resources Canada, 2013), GSS-7 and NIM-D (Gorvindaraju, 1989) was

163   used to quantify accuracy of measurement with this instrument (Haylock 2016). This

164   showed that measurements of <10 ppm of copper and lead are best regarded as

165   below the minima which can be identified with reliability and precision with this

166   instrument. Above this threshold, the measurements differ systematically but to only

167   a relatively modest degree (within 10%) from the results of parallel laboratory

168   analyses by ICP-MS and/or AAS. This evaluation compares broadly with other

169   comparisons between pXRF and other measurement techniques, which show

170   reasonable concordance but by no means exact comparability (e.g. van Cott et al.

171   1999; Kalnicky and Singhiv 2001; Martin Pienado et al. 2010; Brown et al. 2010;

172   Delgado et al. 2011; Shackley 2011; Shuttleworth et al 2014). Here, where sampling

173   by both ICP-MS and pXRF on units has been carried out, Mann-Whitney tests show

174   no significant difference between the two techniques (Table S4). Consequently,

175   where both analyses have been carried out in the same stratum, pXRF and ICP-MS

176   data are combined in the descriptive summary statistics shown in Fig. 4, Table 3,

177   and in the statistical analyses of difference (Table S5). All the original

178 measurements using ICP-MS or pXRF are plotted onto the illustrations of the

179 lithostratigraphy in Figures 4–6 and are shown in Table S3.

180 **TABLE 3 ABOUT HERE**

181 The non-parametric Mann-Whitney U test (Siegel 1956) in MINITAB was used to

182 determine the probability of the presence of statistically-significant differences

183 between the measurements of the concentrations of (a) copper, and (b) lead, for the

184 seven sediment bodies listed in Table 1. This calculated M-U statistic is appropriate

185 to the limited and varying numbers of measurements possible. The results are

186 displayed in Fig. 5 as two constellation diagrams, one for each heavy metal,

187 following the approach of Andrews et al. (1985).

188 **TABLE 1 here**

189   4. NEW LITHOSTRATIGRAPHIC EVIDENCE

190 Re-examination of WF5021 in the 2009-2013 field seasons using the Lithofacies

191 concept (Reading 1986) indicated that the alluvial sequence recognised by Grattan

192 et al (2007) as the Faynan Member – Upper Component comprised two distinct and

193 interbedded lithofacies. They are described and interpreted in Table 2 and shown

194 stratigraphically in Figure S1.

195

196 **TABLE 2 HERE**

197

198 The new analysis indicates that the exposure of the Faynan Member – Upper

199 Component can be summarised:

200   (i)   in-channel deposits of a near-perennial meandering stream (*Fluvial-clastic*
201   *lithofacies*);

202   (ii)   alluvial overbank-wetland-desiccation and interbedded anthropogenic
203   deposits (*Anthropogenic-fluvial lithofacies*);

204   The exposure is evidently *not* a simple "layer-cake" accumulation whose varying

205   properties can be adequately represented by description and sampling using a single

206   column, as was done by Grattan et al. (2007). The *Fluvial-clastic lithofacies* and

207   *Anthropogenic-fluvial lithofacies* essentially developed in parallel, both in space and

208   time. Anthropogenic materials may have accumulated within the palaeochannel

209   during low stage, only to be eroded by later strong flows, but there is remarkably little

210   trace of this today other than sample I of Grattan et al. (2007).

211   The unrolled bones and pottery and evidence for recurrent wetness suggest that the

212   ash and charcoal found within the *Anthropogenic-fluvial lithofacies* are unlikely to be

213   the result of recurrent natural wildfire. Instead they *most likely* reflect fires lit

214   episodically by people. In the absence of excavation, definitive evidence of hearths

215   is, however, absent.

216

217   4. THE STRATIGRAPHIC DISTRIBUTIONS OF HEAVY METALS AT WF5021

218   Figs. 2 and 2 show the distribution of individual measurements of copper and lead in

219   relation to the newly recognised lithofacies at WF5021. The distribution of copper

220   measured by ICP-MS and pXRF appears broadly consistent, although as a result of

221   the eroding exposure these were applied at slightly different places, on different

222   dates.

223   **Figures 2,3, here**

224   *The stratigraphic distribution of copper in the Anthropogenic-fluvial lithofacies*

225   High measurements extend through much of the exposure, vertically and horizontally,

226   beyond its original place of detection, although the highest values are near the

227   middle of the unit. Seven of the eight highest measurements (pXRF and ICP-MS) of

228   copper are located within the *Anthropogenic-fluvial lithofacies* (Figs. 2, 5, Table S3).

229   The highest ICP-MS measurement (1459 ppm) was just inside its outcrop. Five of

230   the highest measurements were associated with the former western stream-bank

231   (Fig. 2). Two were pXRF measurements: 446 ppm in a layer of silt with powder-

232   charcoal, and 277 ppm at the interface of grey silt/ash and grey silt. Two high

233   measurements were on the eastern stream bank (209 ppm and 193 ppm in grey silt

234 with plant-ash) – an area that was especially difficult and hazardous to reach and

235 work in, thus limiting the work that could be done there. The surfaces of three

236 stratigraphically separate potsherds (NP1, NP2 and NP3), exposed within this

237 lithofacies, had comparatively high copper (224-296 ppm by pXRF). The lowest

238 ~40% of measurements are comparable with those from the inter-quartile range of

239 the adjoining *Fluvial-clastic lithofacies* but 60% of measurements the *Anthropogenic-*

240 *fluvial lithofacies* exceed those of the upper quartile measurements in the *Fluvial-*

241 *clastic lithofacies* (Figure 5). Nevertheless, not all parts of the *Anthropogenic-fluvial*

242 *lithofacies* were notably enriched.   This work supports the observation (Grattan et al.

243 2007) that visible ash and charcoal is coincident with the presence of some

244 significant concentrations of copper, and hence they may be causally-related. This

245 may relate to the well-known ability of charcoal and other organic matter to act as a

246 cation sorb, but it cannot account for all of the raised values since most are in

247 relatively inorganic sands.

248 In the overlying Tell Loam Member, there was no indication from the highly-resolved

249 stratigraphically-related pattern of copper concentrations (the highest of which relate

250 to coherent horizons attributable on potsherd evidence to the Late Bronze Age and

251 Classical Period: Grattan et al. 2007 and Fig. 2) that desiccation cracks were routes

252 for contamination into the Faynan Member-Upper Component (although the few

253 visible cracks, avoided during sampling, showed no indication of groundwater or

254 sediment movement such as marginal discoloration, chemical precipitates or clay

255 linings). It is likely that shortly after the deposition of the Faynan Member - Upper

256 Component there was abrupt aridification and wadi incision, lowering regional

257 groundwater tables and desiccating the sediments. Thereafter the regional climate

258 was hyperarid, leading to the deposition of the Tell Loam Member (Hunt et al. 2010).

259 Rare surface wash is the predominant mode of movement of heavy metals in hyper-

260 arid environments (Sims 2010, 2011; Sims et al. 2013). The semi-indurated calcrete

261 palaeosol at the top of the alluvial sequence was perhaps a barrier to infiltration, as

262 calcretes often are (Gile et al. 1965) but did not show the enhanced heavy metals to

263 be expected if it had functioned as a barrier. The new surveys, like the original, did

264 not locate any visible fragments of copper ores within the alluvial sequence.

265

266 *The stratigraphic distribution of lead*

267 The distribution of lead at WF5021 (Fig. 3, 5) shows a general coherence between

268 measurements by ICP-MS and pXRF, but lead does not precisely parallel copper.

269 The highest concentrations of lead were not in stream-bank locations and the

270 potsherds (NP1-NP3) were not enriched in lead (Fig. 3).

271

272 5. COMPARATIVE DISTRIBUTIONS OF COPPER AND LEAD IN OTHER LATE

273 QUATERNARY DEPOSITS

274 The concentrations of copper and lead in other Late Quaternary sequences, are

275 listed in Tables 3, S3, Figures S3-S5.

276 *Late Pleistocene fluvial deposits and paludal deposits*

277 Concentrations of copper and lead were low (0-193 ppm Cu, 0-30 ppm Pb) in the

278 fine fraction of the Late Pleistocene Faynan Member – Lower Component underlying

279 WF5021 (Figs. 1, 2, 3; 5). Concentrations of copper and lead in the paludal-fluvial

280 Lisan Marls (Late Pleistocene) near Barqa el-Hetiye were also typically low, but

281 included two isolated higher measurements of 304 and 426 ppm copper. Lead was

282 0-40 ppm (Figures 1, 5). These sequences pre-date any known local human

283 impacts in this landscape.

284 *Early Holocene fluvial deposits in the Wadis Dana and Ghuwayr*

285 Concentrations of copper and lead were low and relatively uniform. WF5015 is

286 immediately down-channel and downslope of substantial outcrops of copper ores in

287 the Burj Dolomite Shales, but the deposits contained 21-31 ppm Cu and 9-19 ppm

288 Pb (Figures 1, 5, 7). In the slightly older WF5510 in the Ghuwayr gorge levels were

289 also low (38 – 52 ppm Cu, 7-18 ppm Pb) (Figs. 1, S3-S5).

290

291 **FIGURES 4 AND 5 HEREABOUTS**

292 *Modern braidplain of the Wadi Faynan*

293 Concentrations of copper and lead in the fine-fraction of the modern braidplain were
294 low (1-79 ppm Cu with an outlier of 147 ppm; 0-42 ppm Pb: Fig. 7).

295 *Summary*

296 Heavy-metal concentrations in other deposits in the catchment are consistently lower
297 than in the Faynan Member – Upper Component at WF5021, even where the
298 deposits were located adjacent to exposed ore-bodies (Tables 3, S3, S5) and are
299 consistent with the low levels in most bedrock formations in the area (Grattan et al.
300 2012).   Before and during early pastoralism and cultivation, only low concentrations
301 of copper and lead were deposited in the fluvial environment.

302 Overall, the fine-fractions measured on the modern braidplain adjacent to WF5021
303 have slightly lower concentrations of copper than those found in the adjacent
304 Pleistocene fluvial sequences, even though the braidplain sediments are only a few
305 kilometres downstream of an area of substantial surface pollution around Khirbet
306 Faynan (Fig. 1). This finding highlights the distinctiveness of the high concentrations
307 of copper in the Anthropogenic-fluvial lithofacies at WF5021

308 The levels and variability of lead in the *Fluvial-clastic lithofacies* and the
309 *Anthropogenic-fluvial lithofacies* are broadly comparable with those measured in the
310 Late Pleistocene and Early Holocene deposits, and across the adjacent modern
311 braidplain (Fig. 6). Overall the patterns differ from those of copper with no group of
312 higher concentrations having any particular sedimentary associations.

313 These patterns, inferred by visual inspection of the raw data and summary statistics
314 (Figs. 4, 5, Tables 3, S3) are also evident in Fig. 5 and Table S5, which displays the
315 probability of statistically-significant differences occurring between these various
316 deposits. There is statistically-significant difference between the concentrations of
317 copper in the Anthropogenic-fluvial lithofacies and all the other deposits studied.
318 Patterns of statistical significance differ for lead. Typically they are lower, supporting
319 the inferences drawn from visual inspection of distribution.

320

321   6.   NATURAL AND HUMAN CAUSES OF STRATIGRAPHIC PATTERNS OF
322   HEAVY METAL CONTAMINATION

323 The distributions of copper and lead measured at different times across the eroding

324 exposure at WF5021 (Figs. 2,3) suggests that the ICP-MS and pXRF investigations

325 produced broadly similar results, supporting the comparative investigations of

326 Haylock (2016). Application of Mann-Whitney tests for significant differences

327 between ICP-MS and pXRF copper data from samples in single lithological units

328 where both methods were applied shows no significant differences between the

329 means of the two methods (Table S4). It is clear, however, that exact comparisons

330 between the methods cannot be made (e.g. Brown et al. 2010; Delgado et al. 2011;

331 Hu et al. 2014).

332 The geochemical anomaly in this sequence (Grattan et al. 2007) is now shown to be

333 principally copper, which is not in parallel with the distribution of lead. The

334 distribution of lead in all the studied sequences appears to have been predominantly

335 influenced by geomorphological processes, since it is not raised beyond the general

336 level found in older and contemporary comparatives (Table S3, Fig. 5). Analysis I at

337 WF5021 of Grattan et al. (2007) remains atypical. The simplest explanation for this

338 outlier is the unwitting analysis of a particle of lead-rich ore.

339 Our comparative investigations provide insights into heavy metal cycling during parts

340 of the Late Pleistocene and Early Holocene in this landscape. At the comparative

341 sites, the levels of copper are typically less than 100 ppm (Tables 3, S3), even when

342 adjacent to and/or downstream/downslope of ore body outcrops. These

343 observations suggest that generally Late Pleistocene erosion and Neolithic

344 cultivation had little impact on the levels of copper in fluvial aggradations. Possibly,

345 climatically-mediated enhanced erosion during the Late Pleistocene, leading to minor

346 placer-like concentrations of silt-sized metal ore, might account for the small number

347 of outliers in the Lisan Marls, the down-wadi "terminus" for storm runoff from the

348 catchment.

349 Analyses by Mohamed (1999) show that the organic matter contents of the epsilon

350 cross-bedded Faynan Member – Upper Component at sites WF5021, WF5015 and

351 WF5051 lie between 6 and 12% with very similar levels at the three sites. Grain size

352 analyses of the same sites show relatively similar patterns at all three, with the basal

353 deposits being clay-rich (45-88% clay), and the upper parts being sandier. In these

354 deposits, therefore, the different levels of copper cannot be attributed to differences

355 in grain size or organic matter content, particularly as sand layers were selected in

356 all possible cases.

357 Within the *Anthropogenic-fluvial lithofacies*, levels of copper are typically double the

358 interbedded in-channel *Fluvial-clastic Lithofacies* and up to an order of magnitude

359 higher than in the other early Holocene and Late Quaternary sequences sampled

360 (Figure 5; Tables 3, S3). Careful checking of samples suggests this does not reflect

361 copper ore clasts in the sediments. Stratigraphically-constrained patterns of

362 contamination in the Tell Loam Member indicate that the infiltration of contamination

363 from the upper parts of this unit did not occur – and in fact the overall levels of

364 copper contamination in the Tell Loams are lower than in the Anthropogenic-Fluvial

365 Lithofacies (Figs. 2,3, Tables 3, S3; Grattan et al. 2007). High levels of copper in the

366 Anthropogenic-Fluvial Lithofacies are sometimes apparently causally-associated with

367 the presence of ash and charcoal but it is unlikely that this resulted from the burning

368 of naturally-occurring heavy-metal-rich biomass (while some high values are in

369 inorganic sands presumably reflecting spatially-discrete episodes of human activity).

370 Whilst bioaccumulation occurs today in plants growing on late Prehistoric to

371 medieval contaminated materials in the Faynan area (Gilbertson et al. 2007; Grattan

372 et al. 2007; Pyatt et al. 1999, 2000, 2005; Pyatt and Grattan 2001, 2002), there is no

373 evidence for soils containing high levels of copper close to Tell Wadi Faynan at ~7ka

374 BP. The remarkable regional extent of heavy-metal contaminated land in modern

375 times is a product of post-Neolithic pyrometallurgy (Gilbertson et al. 2007; Grattan et

376 al. 2007; Hunt and el-Rishi 2010). Seven thousand years ago, outcrops of copper

377 ore and consequent copper-enriched biomass would have been relatively small, and

378 several kilometres up-wadi.

379 Thus, natural processes do not explain the copper levels in the *Anthropogenic-fluvial*

380 *lithofacies*. This points to anthropogenic causes and in turn suggests a modification

381 of the original anthropogenic explanation (Grattan et al. 2007).   We can hypothesise

382 that approximately seven thousand calendar years ago, people repeatedly

383 introduced copper ores gathered from exposures several kilometres away into

384 purposefully-lit and very hot fires. They did this on stream margins most likely using

385 locally-gathered, uncontaminated fuel, close to the contemporary settlement of Tell

386 Wadi Faynan. The contamination of the accreting sediments might have been

387 produced by: (i) minute residual ores particulates, too small to be detected by visual

388 inspections; and/or (ii) condensation onto surface sediments and residual burnt

389 biomass of copper-rich fumes emitted during burning. The geomorphic-habitat

390 properties that attracted people to this location also led to the preservation of the

391 evidence of the repeated fires and the recurrent contamination.

392 The motivations of these contaminating activities are unclear. Copper ores were

393 collected at Tell Wadi Faynan (Najjar et al. 1990) and dust, possibly from bead-

394 making (e.g. Bar-Yosef Meyer and Porat, 2008) in a precursor settlement may have

395 introduced contamination. Such dust, introduced initially accidentally into very hot

396 fires during the making of the lime plasters such as those found by Najjar et al. (1990)

397 at Tell Wadi Faynan, may have led to further dispersal of copper contamination.

398 This would have created multi-coloured flames, especially at night (Fig. S6) and may

399 have been repeated for some combination of fun, enquiry, ritual and/or spiritual

400 reasons (see Budd and Taylor 1995) and may help to explain occasional high values

401 of copper associated with ash and charcoal. Such activities *do not* necessarily imply

402 a local direct precursor of the purposeful smelting of copper. But a scenario of this

403 general type could easily have led to pyrometallurgy if people had become aware

404 that such activity sometimes produced copper and the metal was of interest. A very

405 unlikely and at the moment untenable hypothesis might be that the raised levels of

406 copper reflect very early crucible-based smelting of copper in charcoal fires, which

407 leaves very little slag, as occurred in Anatolia, Iran and possibly the Caucasus

408 during the 5th millennium BC (Craddock 2000; Thornton 2009; Garfinkel et al. 2014).

409 The complete absence of archaeological remains militates against this suggestion,

410 however, and it would require controlled excavation to substantiate.

411

412 ## 7. CONCLUSIONS

413 A lithofacies-based based approach and pXRF survey has yielded useful results.

414 There is a general coherence between the stratigraphic distribution of copper

415 measured by ICP-MS and by pXRF across the Early Holocene Faynan Member –

416   Upper Component at WF5021; i.e. the analytical techniques broadly replicate each
417   other at a reconnaissance level.

418   This study recognises two components in the Faynan Member – Upper Component,
419   both dated to ~7000 cal. BP: the overbank *Anthropogenic-fluvial lithofacies* and the
420   in-channel *Fluvial-clastic Lithofacies.* These lithofacies developed in parallel in
421   space and time.

422   The work of Grattan et al. (2007) is corroborated by the new data. High levels of
423   copper are relatively widespread in, and systematically and probably causally
424   associated with, the *Anthropogenic-fluvial lithofacies.* This unit does not contain
425   visible fragments of copper ore. The high levels of copper do not seem to result from
426   infiltration from overlying strata in which the contamination is highly stratigraphically
427   constrained, or by the reworking of ores from underlying deposits, as these contain
428   notably lower concentrations of copper. Comparison with local Pleistocene and
429   Early Holocene sequences suggests that Neolithic agriculture did not impact on the
430   relative abundance of copper. Low copper values in the modern braidplain give a
431   partial analogue for the situation at WF5021, where overbank sediments are
432   enhanced in copper, but in-channel sediments are generally not.

433   The highest concentrations of copper are associated repeatedly with clear
434   indications of localised episodic human activity and fire, thus suggesting
435   contamination causally associated with human-mediated fire or fire products. Loose
436   and friable materials survived because they were buried by overbank muds from
437   slow-moving floodwater among reedbeds. Concentrations of copper are typically 1-2
438   orders of magnitude greater than in contemporary in-channel sediments and other
439   older deposits.

440   The close association of copper enhancement with fire and human activity in a
441   wetland environment makes it unlikely that natural wildfires led to the anomaly. The
442   biological resources of this wetland habitat were most likely exploited by people, who
443   might have come from the adjacent settlement at Tell Wadi Faynan where fragments
444   of copper ores occur in Late Neolithic deposits. Lime plaster there indicates the
445   capability for very hot fires but there is no evidence for pyrometallurgy.

446 Copper in the *Fluvial-clastic Lithofacies* at WF5021 is generally raised compared

447 with levels in regional Late Pleistocene and Early Holocene deposits and with levels

448 in the modern braidplain, all of which probably reflect the regional geochemical

449 background (Tables S2, S3).   Analysis I in the Fluvial-clastic Lithofacies remains

450 atypical. It likely reflects an undetected minute particle of copper ore which had

451 toppled into the channel from an area of human activity on the riverbank. Distribution

452 of lead in riverine sequences seems likely to reflect mostly fluvial processes.

453 The following inter-related hypotheses are thus suggested.

454 1. Human activity adjacent to Tell Wadi Faynan during the Late Neolithic created a

455 distinctive *Anthropogenic-fluvial lithofacies* at the margins of a perennial meandering

456 stream, in a riparian-wetland habitat within steppic lowlands.

457 2. The episodic use of fires was associated with notable, but patchy, contamination

458 of the steam banks with copper. Copper levels were often high in comparison to

459 those measured in interbedded in-channel sediments, which appear to reflect more

460 closely the natural background levels of copper and lead.

461 The motivations of the people who lit the hot fires on the stream margins are

462 unknown: but they appear to have left the earliest (currently) known heavy-metal

463 contamination of a alluvial-wetland environment. Further evaluation would benefit

464 from controlled excavations and an approach using ICP-MS and an enrichment-

465 factors approach.

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475   9. REFERENCES

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756   CAPTIONS TO FIGURES

757   Figure 1. The Wadi Faynan catchment around Khirbat Faynan (probably ancient

758   Phaeno) in the Faynan Orefield of southern Jordan showing locations of Faynan

759   Member – Upper Component Early Holocene fluvial deposits at Tell Wadi Faynan

760   (WF 5021). Fluvial sites of broadly similar age and lithology at WF5015 in the Wadi

761   Dana and WF5510 in the Wadi Ghuwayr are close to outcrops of copper-rich ores

762   but uncontaminated by heavy metals. Fluvial and paludal deposits of Late

763   Pleistocene age, respectively, were studied at WF 5021 and in gullies in deposits of

764   Lisan Marls (Raab'a 1994) near Barqa el-Hetiye. Some of the many ancient mines

765   and smelting sites are indicated – these are younger than the exposures studied at

766   WF5021, WF5015 and WF5510. Modern annual precipitation near Tell Wadi

767   Faynan is variable, typically 50-100 mm p.a. Permanent groundwater-fed springs

768   occur in the wadis Ghuwayr and Dana but only the very largest floods bring surface

769   water as far downstram as Tell Wadi Faynan (el-Rishi et al. 2007; Hunt et al. 2007a;

770   Palmer et al. 2007).   Site-codings follow the catalogue in Barker et al. (2007a).
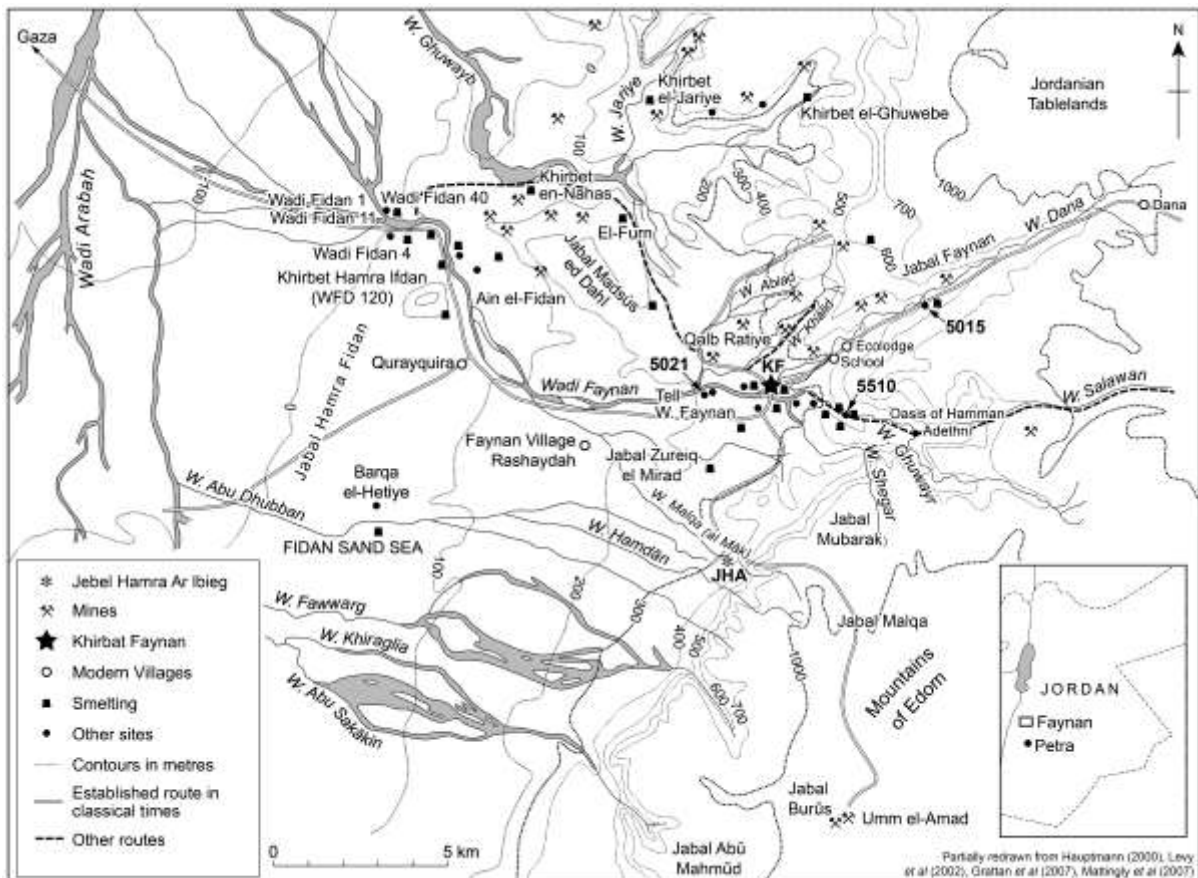

771

772 Figure 2. Plots of measurements of the concentrations of copper superimposed onto
773 the stratigraphy shown in Figure S1 of the Late Quaternary sequence at WF5021
774 adjacent to Tell Wadi Faynan.
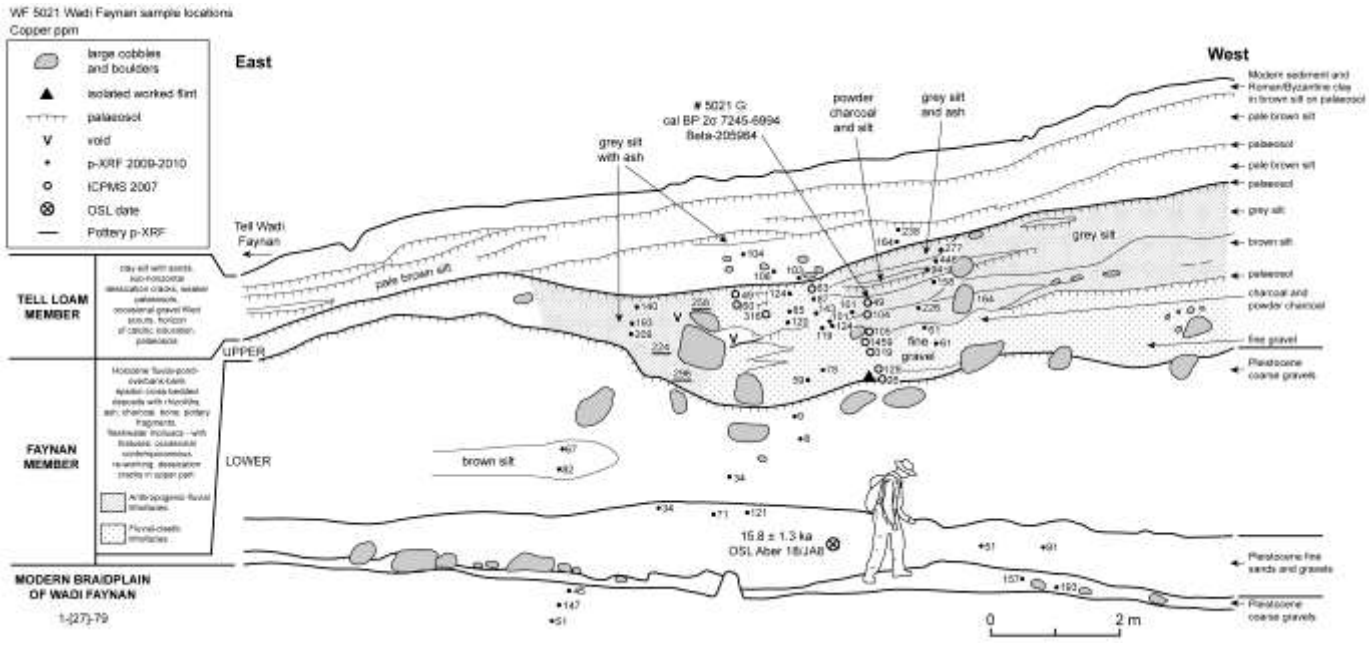
775

776 Figure 3. Plots of measurements of the concentrations of lead superimposed onto
777 the stratigraphy shown in Figure S1 of the Late Quaternary sequence at WF5021
778 adjacent to Tell Wadi Faynan.
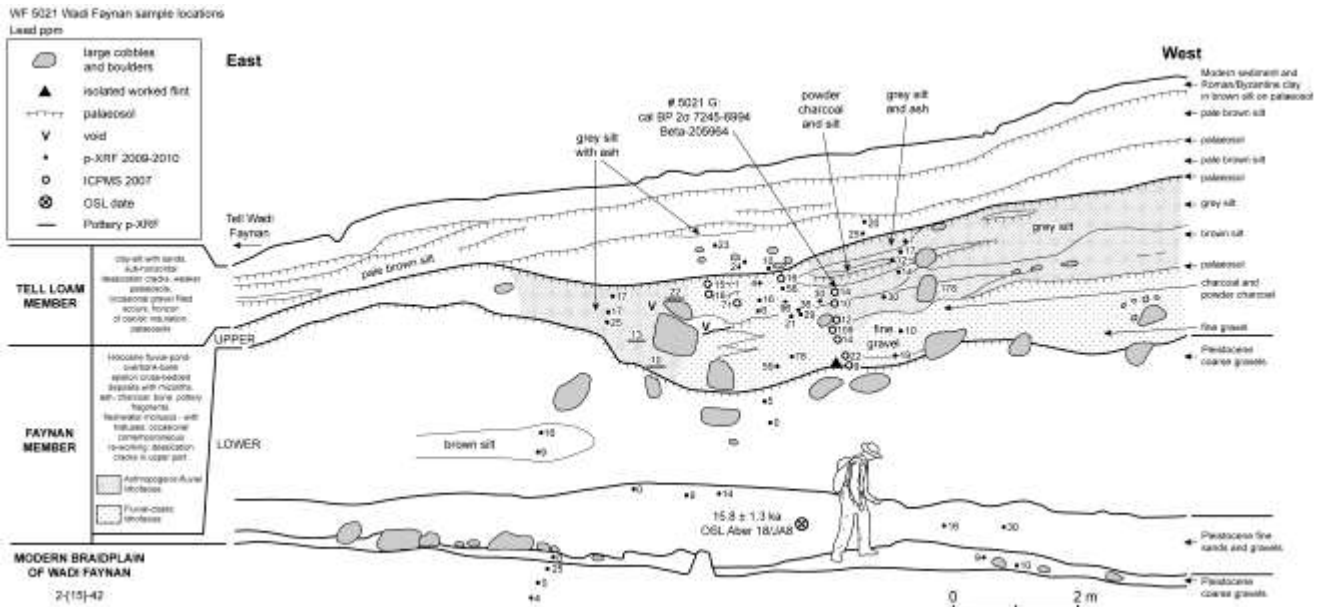
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780

781   Figure 4. Summary of the concentrations of copper and lead measured by ICP-MS

782   and/or pXRF: - in the fine-grained sediments of the ~7,000 cal. years BP

783   Anthropogenic-fluvial lithofacies and Fluvial-clastic lithofacies at WF5021; at the

784   accessible lower parts of the overlying Tell Loam Member at WF5021; in the lowest

785   1.3m of closest exposure of the Tell Loam member at Tell Wadi Faynan; across the

786   modern braidplain of the Wadi Faynan; in underlying Late Pleistocene fluvial

787   sequence at WF5021; the lower parts of exposures of Pleistocene paludal Lisan

788   Marls, (Raab'a 1994) at Barqa el-Hetiye; and in early Holocene fluvial sequences

789   exposed in the Wadis Dana and Ghuwayr. These sites are located in Figure 1.

790   Analysis H at 170 ppm Pb (ICP-MS) in the Fluvial-clastic lithofacies is distinct from

791   all other measurements where there is a maximum of ~90 ppm.
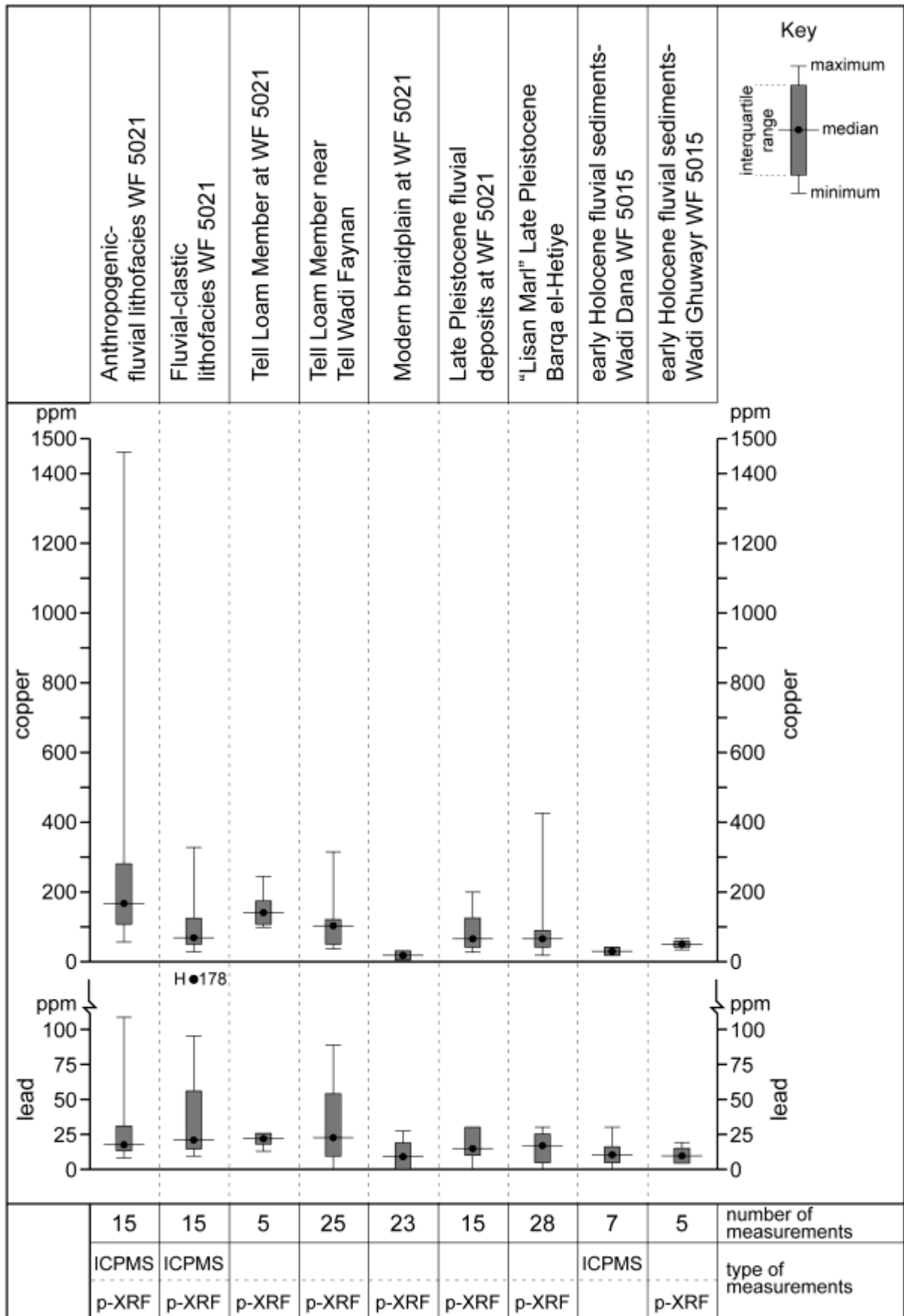
793 Figure 5. Constellation diagrams showing the probabilities of the absence of
794 significant differences determined by the Mann-Whitney U test in the concentrations
795 of: (a) copper, and (b) lead, between the seven different bodies of Late Quaternary
796 deposits described in Table 2. Where the calculated probabilities of the M-U statistic
797 are high (i.e. þ is in the range 0.0000 to 0.01) they suggest a statistically-significant
798 difference exists between the measurements at each body of sediment. This
799 relationship is shown by the "open" linking rectangles and the dashed lines. The
800 other end of the probability scale, where calculated þ is in the range 0.5 to 1 is
801 shown by black rectangles. The small numbers of measurements and geomorphic
802 similarity of the early Holocene fluvial deposits in the Wadis Dana and Ghuwayr led
803 to their combination in these diagrams.
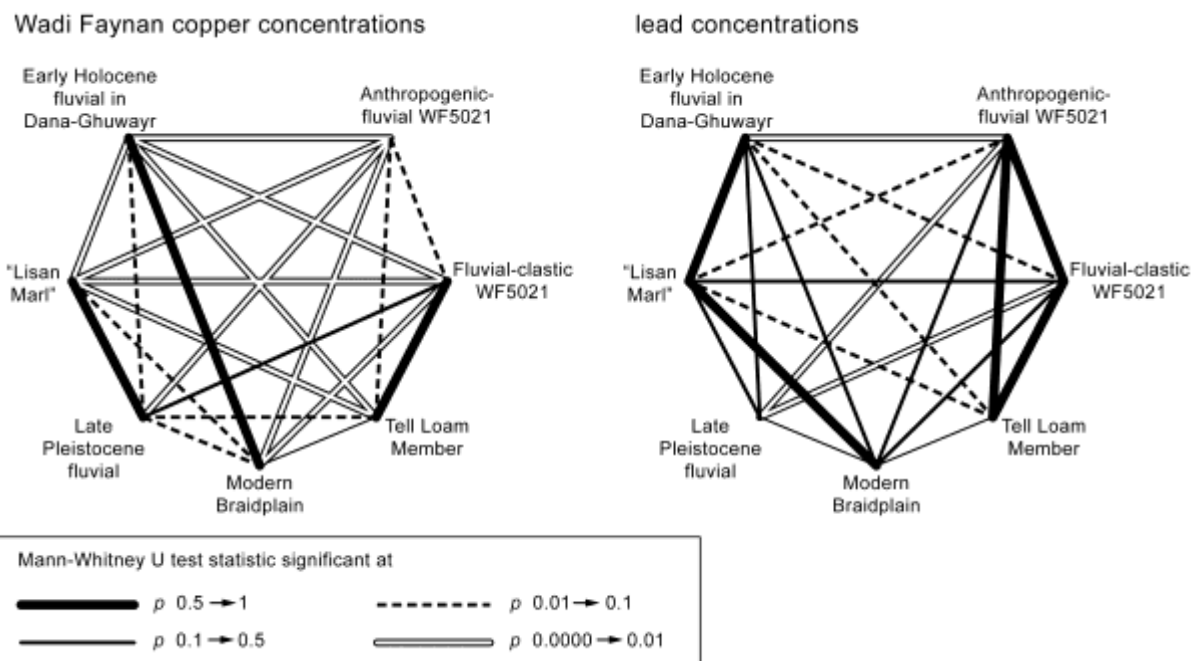
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811   CAPTIONS TO TABLES

812   Table 1. Locations of geochemical investigations of the comparative sequences.

Location	Unit	Details	Investigatory methods
WF5021 and adjacent to Tell Wadi Faynan	Faynan Member – Upper Component	The accessible parts of the WF5021 exposure dated to *c.* 7000 cal. BP, exposed in 2009-2010 (Figure 2), with reference to two lithofacies – the *Anthropogenic-fluvial lithofacies*, and the *Fluvial-clastic lithofacies* (Table 3)	p-XRF and ICPMS. P-XRF includes the surfaces of three separate potsherds exposed by erosion.
	Tell Loam Member	The lowest 1.3 m of the closest accessible exposure of this unit at Tell Wadi Faynan	p-XRF
	Faynan Member – Lower Component	Late Pleistocene gravels underlying the Faynan Member – Upper component at WF5021 and adjacent exposures (Fig. 2).	p-XRF
Wadi Faynan Braidplain	Modern braidplain	Fine fractions at regular intervals across the 400 m of the modern Wadi Faynan braidplain gravels, adjacent to WF5021 – at the surface and at 15 cm depth. The transect is just over 1 km downstream from the ancient major copper-metallurgical centre at Khirbat Faynan, active from Bronze Age to late Classical times (perhaps briefly in medieval times) and still highly contaminated with heavy metals (Barker and Gilbertson 2002; Barker et al. 2007a,b; Geerlings 1985; Gilbertson et al. 2007; Grattan et al. 2007; 2013; Hauptmann 1989, 2000, 2007; Hauptmann and Weisgerber 1992; Hauptmann et al. 1992; Hunt and el-Rishi 2010). The gravels are derived from Cainozoic and Mesozoic limestones and basalts, Palaeozoic sandstones and Pre-Cambrian igneous rocks (Figs. 1 and 2).	p-XRF
Near prehistoric Barqa el-Hetiye.	Previously undescribed Late Pleistocene deposits attributed provisionally to the Lisan Marls, (Raab'a 1994; see Bender 1965).	Gully-wall exposures, beneath contaminated Bronze age sediments, ~10 km west of Tell Wadi Faynan (Figure 1: Adams et al. 2010; McLaren et al. 2004), of plane bedded paludal silts greater than 1 – 1.5 m thick, beds 10–50 cm thick, lacking visible fossils. They are part of the infill of a very large shallow basin at the confluence of wadis draining the Mountains of Edom.	p-XRF
Wadi Dana Gorge	Faynan Member	Early fluvial Holocene silts and sands at WF5015 (Figs. 1 and 4), immediately adjacent to outcrops of the heavy metal-rich Burj Dolomite-Shale Formation (Barjous 1992; Hauptmann 2007). Exposures elsewhere in the Dana gorge (Hunt et al. 2004) were avoided because observation suggested they might be affected by emissions from 4WD vehicles or campsites.	ICPMS
Wadi Ghuwayr Gorge	Faynan Member	Early Holocene fluvial silts (Unit 2 in Hunt et al. 2004) at WF5510 (Figures 1 and 5), predate by ~750 years the deposits at WF5021. The Umm 'Ishrin Sandstone Formation, parts of which were mined for copper, outcrops ~0.5 km up the gorge. The outcrop was largely lost to erosion in May 2014.	p-XRF

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814 Table 2. Description and interpretation of the ~7000 cal. BP alluvial sequence at
815 WF5021 (Figure S2; see also Grattan et al. 2007; Hunt et al. 2004; 2007a,b;
816 McLaren et al. 2004)

Lithofacies	Thickness	Description	Boundaries	Palaeoecology	Anthropogenic Indicators	Age	Interpretation
Fluvial-clastic lithofacies	1-2 m	Epsilon cross-bedded, pale-grey (2.5YR/7.1; 7.5YR/7.1, 10YR/8.1), well-sorted silts, sands and fine gravels, some stony-silt diamicts. Bedding planes and desiccation surfaces with low, but variable dips are fewer in number than in the adjacent Anthropogenic-fluvial lithofacies.	Sharp upper boundary with the Tell Loam Member, marked by a thin clayey-silty palaeosol in the western part, with very occasional desiccation cracks. Sharp, erosive lower boundary, with the Pleistocene deposits, undulating to broadly concave-upwards and associated with a lag of rounded/sub-rounded boulders to 0.7m diameter, resembling those in the underlying deposits. Often interfingers west and east with the Anthropogenic-fluvial lithofacies, and passes beneath it westward. Sometimes with steeper, but less distinct, contacts between the units.	Fine-grained units contain rare in situ mizome-casts of Phragmites, reed mizoliths, and aquatic molluscs.	Contains anomalous sample 1. One worked chert. Immediately overlay the Pleistocene gravels. No other material – worked stone, potsherds or slag - were found	~7000 cal. BP	Episodically deposited in-channel sediments of a near-perennial meandering stream.
Anthropogenic-fluvial lithofacies	1-2 m	+/- Plane-bedded, often grey (7.5YR6/1, 7.5YR7/1 to 7/4; 10YR6/1) well-sorted silts and fine sands, occasional lenses of well-sorted fine gravels, stony-silt diamicts, with lenses or thin layers of unsorted friable ash and charcoal. In some silty layers, disseminated charcoal-powder gives darker grey tones. Surfaces of desiccation or induration present, from which descend desiccation cracks. Occasional sub-rounded to rounded boulders to 0.8 m diameter, probably derived from underlying Pleistocene gravels.	The upper surface is often marked by a clayish-rich, +/- indurated palaeosol in the basal Tell Loam Member. Often this boundary is stratigraphically - sharp; including above the position of the original heavy-metal anomaly. Further east this upper contact is transitional. The lithofacies often interdigitates laterally with and overlies the Fluvia-clastic lithofacies; sometimes with steeper, but less distinct contacts.	The finer sediments contain in situ charcoal and mizome-casts of Phragmites, and rare aquatic molluscs	Contains sometimes very common ash, charcoal, potsherds and bone fragments, occasional worked flints, with minimal or no rounding. No visible smelting slag, but anomalous levels of heavy metals occur in some samples.	~7000 cal. BP	Overbank deposits of a meandering stream, with ample evidence for human activity. The stream banks were often wet, sometimes flooded, occasionally eroded, with overbank deposition that incorporated charcoal, bones, pottery and worked chert among areas of reedswamp and shorter vegetation. At times of lower discharge, the stream banks dried and desiccation-cracks formed. This lithofacies results from the interaction of human action and fluvial geomorphic processes.

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818   Table 3. Summary statistics for levels of copper in the sampled units

	N	Mean	Std. Deviation	Median	Minimum	Maximum	Range
Lisan Beds	28	77.3929	86.84355	55	13	426	413
Faynan Member Lower Component	12	68.1667	39.13342	70	8	134	126
Ghuweir E Holocene	5	46.8	5.35724	49	38	52	14
Dana E Holocene	7	25.4286	3.64496	26	21	32	11
Fluvial-Clastic facies	17	105	65.19011	89	26	318	292
Anthropogenic-Fluvial facies	14	264.1429	357.997	148.5	49	1459	1410
Tell Loams	49	137.7551	186.7366	90	18	1166	1148
Modern braidplain	17	45.9412	33.78696	43	1	147	146

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