The first polluted river? Repeated copper contamination of fluvial sediments associated with Late Neolithic human activity in southern Jordan

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Abstract

The roots of pyrometallurgy are obscure. This paper explores one possible precursor, in the Faynan Orefield in southern Jordan. There, at approximately 7000 cal. BP, banks of a near-perennial meandering stream (today represented by complex overbank wetland and anthropogenic deposits) were contaminated repeatedly by copper emitted by human activities. Variations in the distribution of copper in this sequence are not readily explained in other ways, although the precise mechanism of contamination remains unclear. The degree of copper enhancement was up to an order of magnitude greater than that measured in Pleistocene fluvial and paludal sediments, in contemporary or slightly older Holocene stream and pond deposits, and in the adjacent modern wadi braidplain. Lead is less enhanced, more variable, and appears to have been less influenced by contemporaneous human activities at this location. Pyrometallurgy in this region may have appeared as a byproduct of the activity practised on the stream-bank in the Wadi Faynan ~7000 years ago.

1. INTRODUCTION

Over the last few thousand years, civilisations have been underpinned by the use of metal-based technology, but the origins and roots of metal production are unclear and contested (e.g. Renfrew 1969; Craddock 2000; Golden et al. 2001; Hauptmann 2007; Radivojevic et al. 2010; Garfinkel et al. 2014; Golden 2014). One of the earliest documented metal extraction centres is the Faynan/Fidan orefield on the edge of the Wadi ‘Arabah in Southern Jordan, where unequivocal copper pyrometallurgy is documented from the 4th millennium BC (Hauptmann, 2007 and references therein). But even in this very well-researched area, the precursor activities to this established pyrometallurgy are far from clear.

The stratigraphy, palaeoenvironments and geochemistry of the later Quaternary deposits on the Faynan Orefield (Figure 1) in Southwest Jordan were evaluated during the Wadi Faynan Project (Barker et al. 2007a), which explored the history of desertification and its relationship with agricultural and industrial activity at the desert margin. At site WF5021, Grattan et al. (2007) recorded anomalously high concentrations of copper and lead in deposits attributed to the Faynan Member Upper Component (McLaren et al. 2004). These were dated by AMS radiocarbon to 7245-6994 cal. BP [Beta-205964] and are attributable to the local Late Neolithic (Hunt et al. 2007b). The Late Neolithic date is consistent with the regional lithostratigraphy, archaeological sequence and pollen biostratigraphy which are anchored by radiocarbon dates at other sites in the Faynan catchment (Grattan et al. 2007; McLaren et al. 2004; Hunt et. al. 2004, 2007a,b).

Stratigraphic and archaeological evidence (Grattan et al. 2007) suggested that the high concentrations of heavy metals in the Faynan Member – Upper Component at WF5021 are *in situ* and not the result of post-sedimentation events. 7000 calendar years is significantly older – typically 500-1000 years - than any pyrometallurgy from this region (Adams 1997, 1999; Adams et al. 2010; Barker et al. 2007a; Hauptmann 2000; 2007), or with global pollution signatures (Celine et al. 2008; Boutron et al. 1995; Muhly 1988; Neuninger et al. 1964; Thornton et al. 2010; Shotyk et al. 1998), although it is younger than contamination in the Keweenaw Peninsula, Michigan (Pompeani et al. 2013) and contemporary with instances in the Balkans (Radivojević et al. 2010). This study therefore examines a range of plausible explanations (Table S1), through

1. a reappraisal of the stratigraphy of the exposure
2. further geochemical analyses to test the original work and to clarify causes of these comparatively high concentrations (Figs. 2, 3)
3. comparative measurements in older, contemporary and modern regional sediments (Tables 1, S3, Figs. S3-S5)

FIGURE 1 HERE

2. STRATIGRAPHY AND DATING

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

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

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

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

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

[HD12335] were obtained (Hauptmann 2000) from the cliff section at respectively 4 m and 2.5 m below the cliff top adjacent to the archaeological site from fluvial deposits probably equivalent to the sediments studied in this paper.

3. PXRF, ICP-MS AND STATISTICAL STUDIES

The sedimentary sequences listed in Table1 are of inherently heterogeneous, variable materials. They reflect complex and changing geomorphic processes and a variety of sources. Therefore, this investigation has minimised issues with moisture and grain size and focused on the ranges, relativities and associations of copper and lead measured in the different deposits.

The number of geochemical analyses in this study was substantially increased beyond those of Grattan et al. (2007). At exposure WF5015, ICP-MS analyses following the procedures used by Grattan et al. (2007) were on sub-2 mm oven-dry material, in which low-power microscope inspection did not detect particles of metal ore. Most geochemical analyses were done, however, using a Niton® XLt Series 700 portable XRF analyser,

The Niton XLt 700 Analyser uses a low power (1.0 W) X-ray tube in tandem with an Ag anode target and Peltier-cooled Si-Pin x-ray detector. The possibility that contaminants had travelled down cracks or fissures in the sediments was addressed by ensuring that only sediments several cm away from such features were sampled. Likewise, the possibility of concentration of heavy metals having been concentrated by redox reactions or leaching was kept in mind during sampling, but features such as oxide staining, iron pans or manganese staining/concretions were not encountered. To minimise measurement variation caused by grain size and moisture variation (e.g. Ge et al. 2005; Kim et al. 2011), only dry, *in-situ* sand-size materials were analysed, while silt/clay-rich and gravelly horizons and locations with any visible clasts of copper ore or smelting slags were avoided. Since heavy metal concentrations are in general inversely related to grain-size (e.g. Kim et al. 2011), avoidance of silt/clay-dominated samples means that the possibility of sampling very high concentrations relating to the scavenging activities of clay minerals was minimised. To minimise variation caused by measurement distance, the pXRF analyses were all made on freshly-cleaned-back, planar exposures by placing the pre-cleaned window at the front of the instrument directly against the exposure to be analysed, with the axis of the instrument normal to the plane of the exposure. Measurement time was standardised at 30 or 60 seconds using the integral software in Soil Analysis mode, with five replicates for each measurement, following Haylock (2016) and similar to Shuttleworth et al. (2014). The exposed surfaces of the *in situ* and stratigraphically-separate fragments of Neolithic pottery investigated by PXRF at WF5021 at locations NP1 to NP3 appeared clean. Even so, they were brushed and further cleaned by blowing. Internal calibration followed the user guide (version 5.0 P/N500/905) using an Ag anode target within the hand-piece. Fundamental parameters eliminate the need for site-specific calibration utilising theoretical mathematics to predetermine inter-element coefficients rather than using matrix specific calibration standards (Kalnicky and Singhvi, 2001), and were used to interpret the fluorescence (secondary x-ray signal) into element identification and concentrations in ppm. Comparative testing of three reference materials, Till 4 (Natural Resources Canada, 2013), GSS-7 and NIM-D (Gorvindaraju, 1989) was used to quantify accuracy of measurement with this instrument (Haylock 2016). This showed that measurements of <10 ppm of copper and lead are best regarded as below the minima which can be identified with reliability and precision with this instrument. Above this threshold, the measurements differ systematically but to only a relatively modest degree (within 10%) from the results of parallel laboratory analyses by ICP-MS and/or AAS. This evaluation compares broadly with other comparisons between pXRF and other measurement techniques, which show reasonable concordance but by no means exact comparability (e.g. van Cott et al. 1999; Kalnicky and Singhiv 2001; Martin Pienado et al. 2010; Brown et al. 2010; Delgado et al. 2011; Shackley 2011; Shuttleworth et al 2014). Here, where sampling by both ICP-MS and pXRF on units has been carried out, Mann-Whitney tests show no significant difference between the two techniques (Table S4). Consequently, where both analyses have been carried out in the same stratum, pXRF and ICP-MS data are combined in the descriptive summary statistics shown in Fig. 4, Table 3, and in the statistical analyses of difference (Table S5). All the original measurements using ICP-MS or pXRF are plotted onto the illustrations of the lithostratigraphy in Figures 4–6 and are shown in Table S3.

TABLE 3 ABOUT HERE

The non-parametric Mann-Whitney U test (Siegel 1956) in MINITAB was used to determine the probability of the presence of statistically-significant differences between the measurements of the concentrations of (a) copper, and (b) lead, for the seven sediment bodies listed in Table 1. This calculated M-U statistic is appropriate to the limited and varying numbers of measurements possible. The results are displayed in Fig. 5 as two constellation diagrams, one for each heavy metal, following the approach of Andrews et al. (1985).

TABLE 1 here

4. NEW LITHOSTRATIGRAPHIC EVIDENCE

Re-examination of WF5021 in the 2009-2013 field seasons using the Lithofacies concept (Reading 1986) indicated that the alluvial sequence recognised by Grattan et al (2007) as the Faynan Member – Upper Component comprised two distinct and interbedded lithofacies. They are described and interpreted in Table 2 and shown stratigraphically in Figure S1.

TABLE 2 HERE

The new analysis indicates that the exposure of the Faynan Member – Upper Component can be summarised:

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

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

The exposure is evidently *not* a simple “layer-cake” accumulation whose varying properties can be adequately represented by description and sampling using a single column, as was done by Grattan et al. (2007). The *Fluvial-clastic lithofacies* and *Anthropogenic-fluvial lithofacies* essentially developed in parallel, both in space and time. Anthropogenic materials may have accumulated within the palaeochannel during low stage, only to be eroded by later strong flows, but there is remarkably little trace of this today other than sample I of Grattan et al. (2007).

The unrolled bones and pottery and evidence for recurrent wetness suggest that the ash and charcoal found within the *Anthropogenic-fluvial lithofacies* are unlikely to be the result of recurrent natural wildfire. Instead they *most likely* reflect fires lit episodically by people. In the absence of excavation, definitive evidence of hearths is, however, absent.

4. THE STRATIGRAPHIC DISTRIBUTIONS OF HEAVY METALS AT WF5021

Figs. 2 and 2 show the distribution of individual measurements of copper and lead in relation to the newly recognised lithofacies at WF5021. The distribution of copper measured by ICP-MS and pXRF appears broadly consistent, although as a result of the eroding exposure these were applied at slightly different places, on different dates.

Figures 2,3, here

The stratigraphic distribution of copper in the Anthropogenic-fluvial lithofacies

High measurements extend through much of the exposure, vertically and horizontally, beyond its original place of detection, although the highest values are near the middle of the unit. Seven of the eight highest measurements (pXRF and ICP-MS) of copper are located within the *Anthropogenic-fluvial lithofacies* (Figs. 2, 5, Table S3). The highest ICP-MS measurement (1459 ppm) was just inside its outcrop. Five of the highest measurements were associated with the former western stream-bank (Fig. 2). Two were pXRF measurements: 446 ppm in a layer of silt with powder-charcoal, and 277 ppm at the interface of grey silt/ash and grey silt. Two high measurements were on the eastern stream bank (209 ppm and 193 ppm in grey silt with plant-ash) – an area that was especially difficult and hazardous to reach and work in, thus limiting the work that could be done there. The surfaces of three stratigraphically separate potsherds (NP1, NP2 and NP3), exposed within this lithofacies, had comparatively high copper (224-296 ppm by pXRF). The lowest ~40% of measurements are comparable with those from the inter-quartile range of the adjoining *Fluvial-clastic lithofacies* but 60% of measurements the *Anthropogenic-fluvial lithofacies* exceed those of the upper quartile measurements in the *Fluvial-clastic lithofacies* (Figure 5). Nevertheless, not all parts of the *Anthropogenic-fluvial lithofacies* were notably enriched. This work supports the observation (Grattan et al. 2007) that visible ash and charcoal is coincident with the presence of some significant concentrations of copper, and hence they may be causally-related. This may relate to the well-known ability of charcoal and other organic matter to act as a cation sorb, but it cannot account for all of the raised values since most are in relatively inorganic sands.

In the overlying Tell Loam Member, there was no indication from the highly-resolved stratigraphically-related pattern of copper concentrations (the highest of which relate to coherent horizons attributable on potsherd evidence to the Late Bronze Age and Classical Period: Grattan et al. 2007 and Fig. 2) that desiccation cracks were routes for contamination into the Faynan Member-Upper Component (although the few visible cracks, avoided during sampling, showed no indication of groundwater or sediment movement such as marginal discoloration, chemical precipitates or clay linings). It is likely that shortly after the deposition of the Faynan Member - Upper Component there was abrupt aridification and wadi incision, lowering regional groundwater tables and desiccating the sediments. Thereafter the regional climate was hyperarid, leading to the deposition of the Tell Loam Member (Hunt et al. 2010). Rare surface wash is the predominant mode of movement of heavy metals in hyper-arid environments (Sims 2010, 2011; Sims et al. 2013). The semi-indurated calcrete palaeosol at the top of the alluvial sequence was perhaps a barrier to infiltration, as calcretes often are (Gile et al. 1965) but did not show the enhanced heavy metals to be expected if it had functioned as a barrier. The new surveys, like the original, did not locate any visible fragments of copper ores within the alluvial sequence.

The stratigraphic distribution of lead

The distribution of lead at WF5021 (Fig. 3, 5) shows a general coherence between measurements by ICP-MS and pXRF, but lead does not precisely parallel copper. The highest concentrations of lead were not in stream-bank locations and the potsherds (NP1-NP3) were not enriched in lead (Fig. 3).

5. COMPARATIVE DISTRIBUTIONS OF COPPER AND LEAD IN OTHER LATE QUATERNARY DEPOSITS

The concentrations of copper and lead in other Late Quaternary sequences, are listed in Tables 3, S3, Figures S3-S5.

Late Pleistocene fluvial deposits and paludal deposits

Concentrations of copper and lead were low (0-193 ppm Cu, 0-30 ppm Pb) in the fine fraction of the Late Pleistocene Faynan Member – Lower Component underlying WF5021 (Figs. 1, 2, 3; 5). Concentrations of copper and lead in the paludal-fluvial Lisan Marls (Late Pleistocene) near Barqa el-Hetiye were also typically low, but included two isolated higher measurements of 304 and 426 ppm copper. Lead was 0-40 ppm (Figures 1, 5). These sequences pre-date any known local human impacts in this landscape.

Early Holocene fluvial deposits in the Wadis Dana and Ghuwayr

Concentrations of copper and lead were low and relatively uniform. WF5015 is immediately down-channel and downslope of substantial outcrops of copper ores in the Burj Dolomite Shales, but the deposits contained 21-31 ppm Cu and 9-19 ppm Pb (Figures 1, 5, 7). In the slightly older WF5510 in the Ghuwayr gorge levels were also low (38 – 52 ppm Cu, 7-18 ppm Pb) (Figs. 1, S3-S5).

FIGURES 4 AND 5 HEREABOUTS

Modern braidplain of the Wadi Faynan

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

Summary

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

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

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

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

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

The distributions of copper and lead measured at different times across the eroding exposure at WF5021 (Figs. 2,3) suggests that the ICP-MS and pXRF investigations produced broadly similar results, supporting the comparative investigations of Haylock (2016). Application of Mann-Whitney tests for significant differences between ICP-MS and pXRF copper data from samples in single lithological units where both methods were applied shows no significant differences between the means of the two methods (Table S4). It is clear, however, that exact comparisons between the methods cannot be made (e.g. Brown et al. 2010; Delgado et al. 2011; Hu et al. 2014).

The geochemical anomaly in this sequence (Grattan et al. 2007) is now shown to be principally copper, which is not in parallel with the distribution of lead. The distribution of lead in all the studied sequences appears to have been predominantly influenced by geomorphological processes, since it is not raised beyond the general level found in older and contemporary comparatives (Table S3, Fig. 5). Analysis I at WF5021 of Grattan et al. (2007) remains atypical. The simplest explanation for this outlier is the unwitting analysis of a particle of lead-rich ore.

Our comparative investigations provide insights into heavy metal cycling during parts of the Late Pleistocene and Early Holocene in this landscape. At the comparative sites, the levels of copper are typically less than 100 ppm (Tables 3, S3), even when adjacent to and/or downstream/downslope of ore body outcrops. These observations suggest that generally Late Pleistocene erosion and Neolithic cultivation had little impact on the levels of copper in fluvial aggradations. Possibly, climatically-mediated enhanced erosion during the Late Pleistocene, leading to minor placer-like concentrations of silt-sized metal ore, might account for the small number of outliers in the Lisan Marls, the down-wadi “terminus” for storm runoff from the catchment.

Analyses by Mohamed (1999) show that the organic matter contents of the epsilon cross-bedded Faynan Member – Upper Component at sites WF5021, WF5015 and WF5051 lie between 6 and 12% with very similar levels at the three sites. Grain size analyses of the same sites show relatively similar patterns at all three, with the basal deposits being clay-rich (45-88% clay), and the upper parts being sandier. In these deposits, therefore, the different levels of copper cannot be attributed to differences in grain size or organic matter content, particularly as sand layers were selected in all possible cases.

Within the *Anthropogenic-fluvial lithofacies*, levels of copper are typically double the interbedded in-channel *Fluvial-clastic Lithofacies* and up to an order of magnitude higher than in the other early Holocene and Late Quaternary sequences sampled (Figure 5; Tables 3, S3). Careful checking of samples suggests this does not reflect copper ore clasts in the sediments. Stratigraphically-constrained patterns of contamination in the Tell Loam Member indicate that the infiltration of contamination from the upper parts of this unit did not occur – and in fact the overall levels of copper contamination in the Tell Loams are lower than in the Anthropogenic-Fluvial Lithofacies (Figs. 2,3, Tables 3, S3; Grattan et al. 2007). High levels of copper in the Anthropogenic-Fluvial Lithofacies are sometimes apparently causally-associated with the presence of ash and charcoal but it is unlikely that this resulted from the burning of naturally-occurring heavy-metal-rich biomass (while some high values are in inorganic sands presumably reflecting spatially-discrete episodes of human activity). Whilst bioaccumulation occurs today in plants growing on late Prehistoric to medieval contaminated materials in the Faynan area (Gilbertson et al. 2007; Grattan et al. 2007; Pyatt et al. 1999, 2000, 2005; Pyatt and Grattan 2001, 2002), there is no evidence for soils containing high levels of copper close to Tell Wadi Faynan at ~7ka BP. The remarkable regional extent of heavy-metal contaminated land in modern times is a product of post-Neolithic pyrometallurgy (Gilbertson et al. 2007; Grattan et al. 2007; Hunt and el-Rishi 2010). Seven thousand years ago, outcrops of copper ore and consequent copper-enriched biomass would have been relatively small, and several kilometres up-wadi.

Thus, natural processes do not explain the copper levels in the *Anthropogenic-fluvial lithofacies*. This points to anthropogenic causes and in turn suggests a modification of the original anthropogenic explanation (Grattan et al. 2007). We can hypothesise that approximately seven thousand calendar years ago, people repeatedly introduced copper ores gathered from exposures several kilometres away into purposefully-lit and very hot fires. They did this on stream margins most likely using locally-gathered, uncontaminated fuel, close to the contemporary settlement of Tell

Wadi Faynan. The contamination of the accreting sediments might have been produced by: (i) minute residual ores particulates, too small to be detected by visual inspections; and/or (ii) condensation onto surface sediments and residual burnt biomass of copper-rich fumes emitted during burning. The geomorphic-habitat properties that attracted people to this location also led to the preservation of the evidence of the repeated fires and the recurrent contamination.

The motivations of these contaminating activities are unclear. Copper ores were collected at Tell Wadi Faynan (Najjar et al. 1990) and dust, possibly from bead-making (e.g. Bar-Yosef Meyer and Porat, 2008) in a precursor settlement may have introduced contamination. Such dust, introduced initially accidentally into very hot fires during the making of the lime plasters such as those found by Najjar et al. (1990) at Tell Wadi Faynan, may have led to further dispersal of copper contamination. This would have created multi-coloured flames, especially at night (Fig. S6) and may have been repeated for some combination of fun, enquiry, ritual and/or spiritual reasons (see Budd and Taylor 1995) and may help to explain occasional high values of copper associated with ash and charcoal. Such activities *do not* necessarily imply a local direct precursor of the purposeful smelting of copper. But a scenario of this general type could easily have led to pyrometallurgy if people had become aware that such activity sometimes produced copper and the metal was of interest. A very unlikely and at the moment untenable hypothesis might be that the raised levels of copper reflect very early crucible-based smelting of copper in charcoal fires, which leaves very little slag, as occurred in Anatolia, Iran and possibly the Caucasus during the 5th millennium BC (Craddock 2000; Thornton 2009; Garfinkel et al. 2014). The complete absence of archaeological remains militates against this suggestion, however, and it would require controlled excavation to substantiate.

7. CONCLUSIONS

A lithofacies-based based approach and pXRF survey has yielded useful results. There is a general coherence between the stratigraphic distribution of copper measured by ICP-MS and by pXRF across the Early Holocene Faynan Member –

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

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

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

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

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

Copper in the *Fluvial-clastic Lithofacies* at WF5021 is generally raised compared with levels in regional Late Pleistocene and Early Holocene deposits and with levels in the modern braidplain, all of which probably reflect the regional geochemical background (Tables S2, S3). Analysis I in the Fluvial-clastic Lithofacies remains atypical. It likely reflects an undetected minute particle of copper ore which had toppled into the channel from an area of human activity on the riverbank. Distribution of lead in riverine sequences seems likely to reflect mostly fluvial processes.

The following inter-related hypotheses are thus suggested.

1. Human activity adjacent to Tell Wadi Faynan during the Late Neolithic created a distinctive *Anthropogenic-fluvial lithofacies* at the margins of a perennial meandering stream, in a riparian-wetland habitat within steppic lowlands.

2. The episodic use of fires was associated with notable, but patchy, contamination of the steam banks with copper. Copper levels were often high in comparison to those measured in interbedded in-channel sediments, which appear to reflect more closely the natural background levels of copper and lead.

The motivations of the people who lit the hot fires on the stream margins are unknown: but they appear to have left the earliest (currently) known heavy-metal contamination of a alluvial-wetland environment. Further evaluation would benefit from controlled excavations and an approach using ICP-MS and an enrichment-factors approach.

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CAPTIONS TO FIGURES

Figure 1. The Wadi Faynan catchment around Khirbat Faynan (probably ancient Phaeno) in the Faynan Orefield of southern Jordan showing locations of Faynan Member – Upper Component Early Holocene fluvial deposits at Tell Wadi Faynan (WF 5021). Fluvial sites of broadly similar age and lithology at WF5015 in the Wadi Dana and WF5510 in the Wadi Ghuwayr are close to outcrops of copper-rich ores but uncontaminated by heavy metals. Fluvial and paludal deposits of Late Pleistocene age, respectively, were studied at WF 5021 and in gullies in deposits of Lisan Marls (Raab'a 1994) near Barqa el-Hetiye. Some of the many ancient mines and smelting sites are indicated – these are younger than the exposures studied at WF5021, WF5015 and WF5510. Modern annual precipitation near Tell Wadi Faynan is variable, typically 50-100 mm p.a. Permanent groundwater-fed springs occur in the wadis Ghuwayr and Dana but only the very largest floods bring surface water as far downstram as Tell Wadi Faynan (el-Rishi et al. 2007; Hunt et al. 2007a; Palmer et al. 2007). Site-codings follow the catalogue in Barker et al. (2007a).

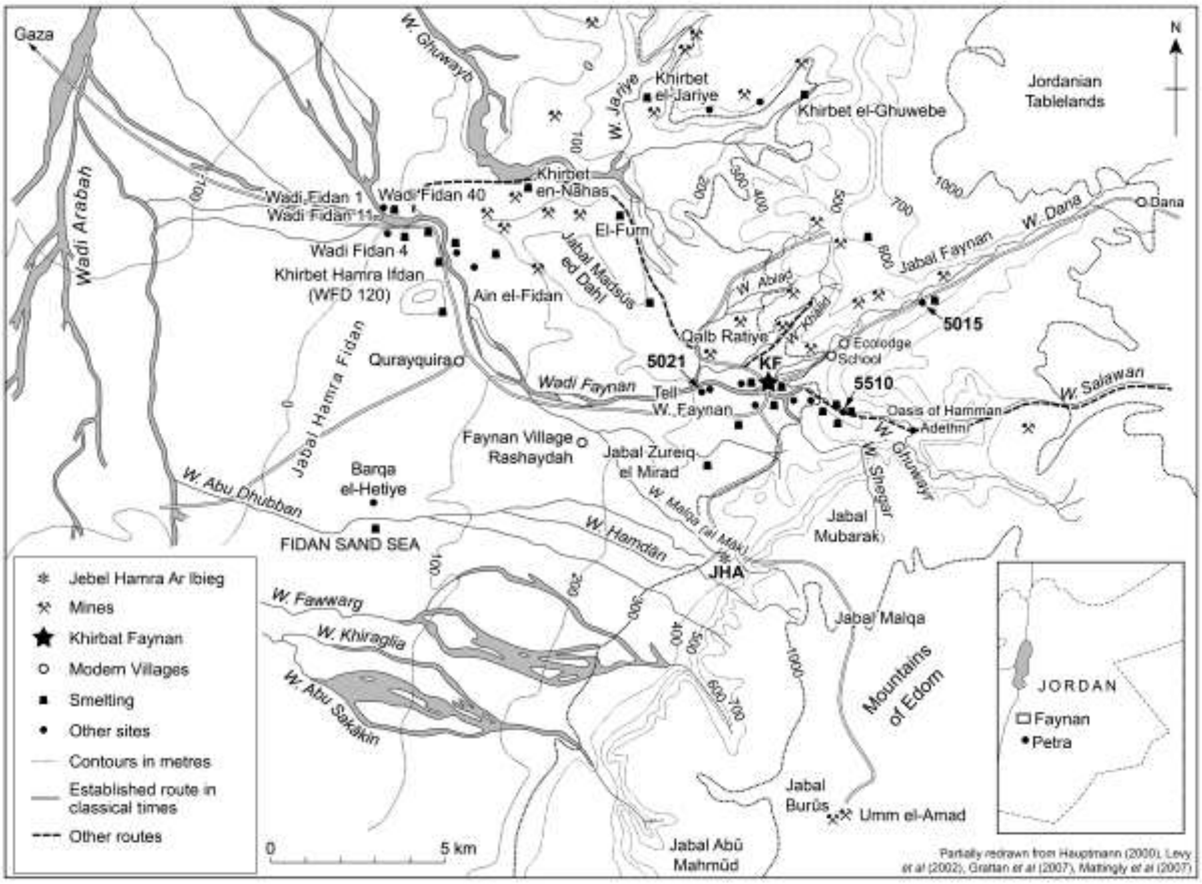


Figure 2. Plots of measurements of the concentrations of copper superimposed onto the stratigraphy shown in Figure S1 of the Late Quaternary sequence at WF5021 adjacent to Tell Wadi Faynan.

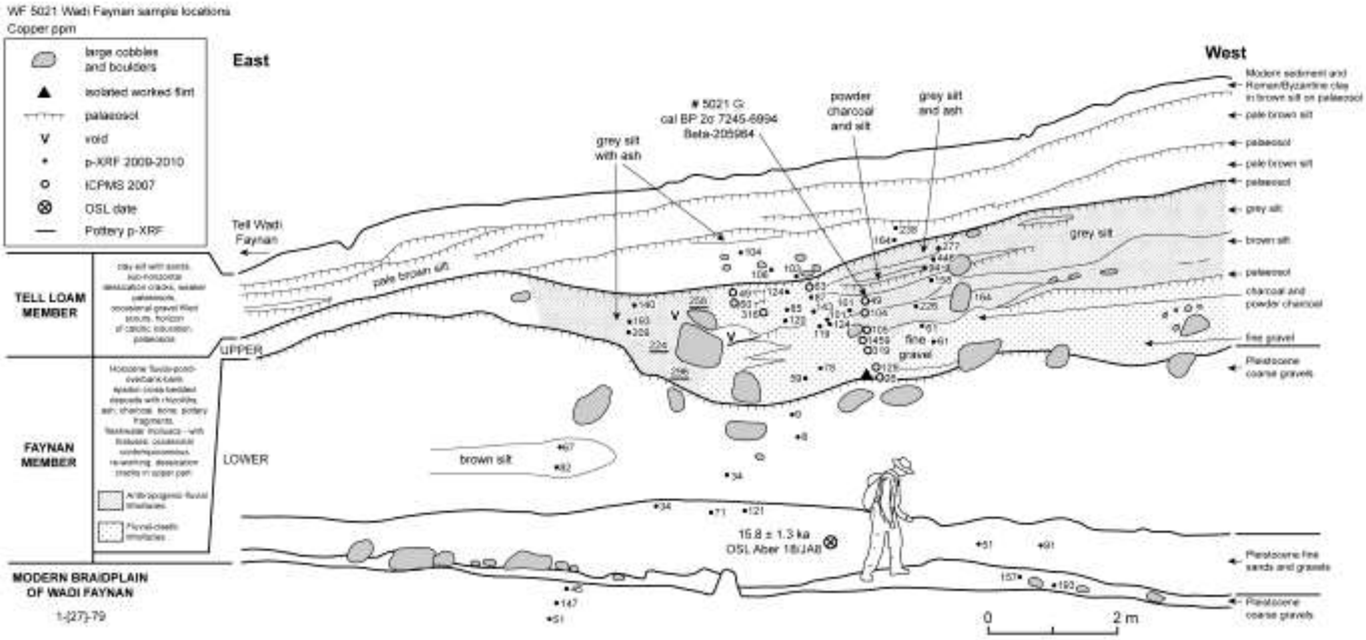


Figure 3. Plots of measurements of the concentrations of lead superimposed onto the stratigraphy shown in Figure S1 of the Late Quaternary sequence at WF5021 adjacent to Tell Wadi Faynan.

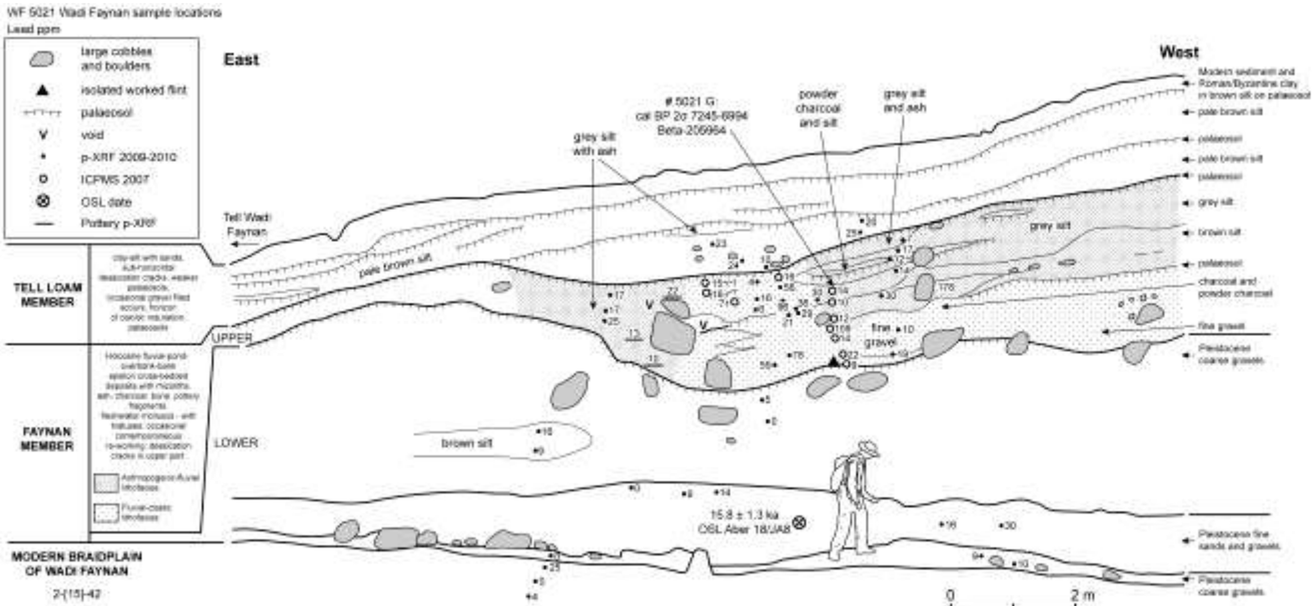


Figure 4. Summary of the concentrations of copper and lead measured by ICP-MS and/or pXRF: - in the fine-grained sediments of the ~7,000 cal. years BP Anthropogenic-fluvial lithofacies and Fluvial-clastic lithofacies at WF5021; at the accessible lower parts of the overlying Tell Loam Member at WF5021; in the lowest 1.3m of closest exposure of the Tell Loam member at Tell Wadi Faynan; across the modern braidplain of the Wadi Faynan; in underlying Late Pleistocene fluvial sequence at WF5021; the lower parts of exposures of Pleistocene paludal Lisan Marls, (Raab'a 1994) at Barqa el-Hetiye; and in early Holocene fluvial sequences exposed in the Wadis Dana and Ghuwayr. These sites are located in Figure 1. Analysis H at 170 ppm Pb (ICP-MS) in the Fluvial-clastic lithofacies is distinct from all other measurements where there is a maximum of ~90 ppm.

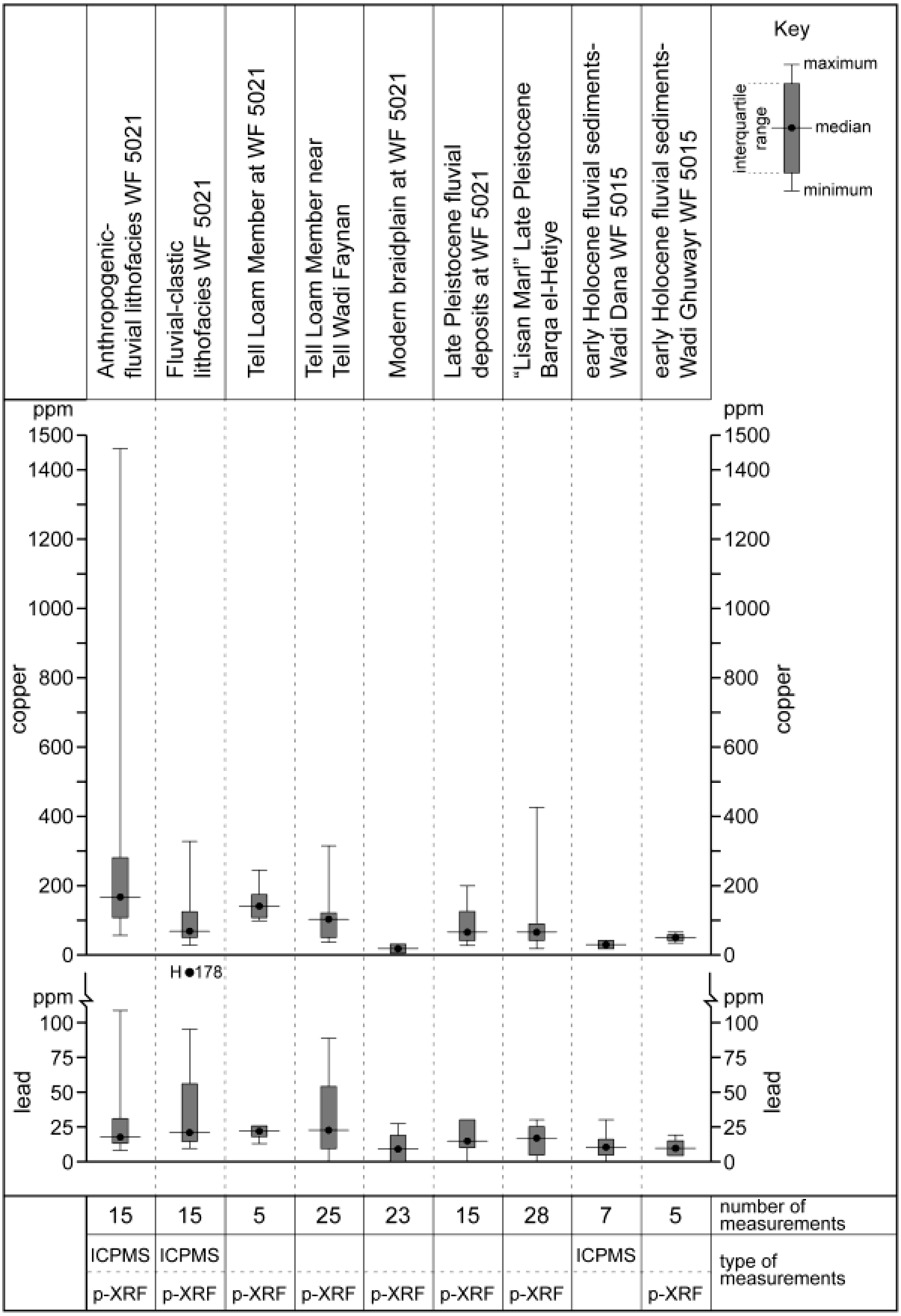
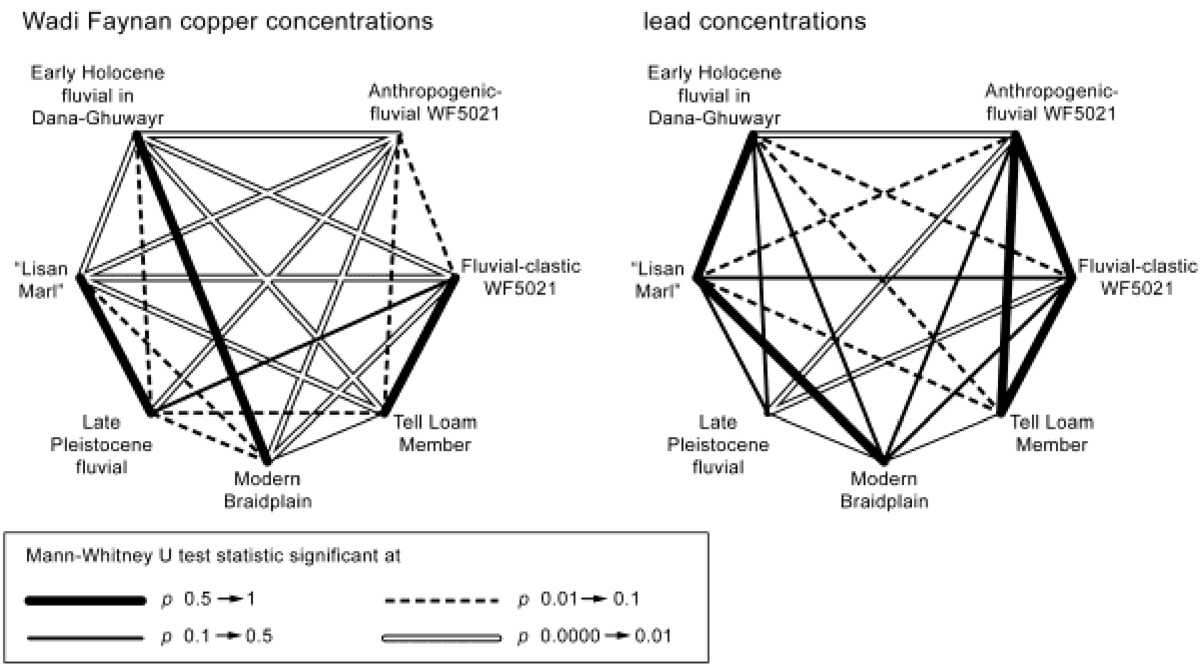

Anthropogenic-fluvial lithofacies WF 5021
Fluvial-clastic lithofacies WF 5021
Tell Loam Member at WF 5021
Tell Loam Member near Tell Wadi Faynan
Modern braidplain at WF 5021
Late Pleistocene fluvial deposits at WF 5021
"Lisan Marl" Late Pleistocene Barqa el-Hetiye
early Holocene fluvial sediments-Wadi Dana WF 5015
early Holocene fluvial sediments-Wadi Ghuwayr WF 5015
Key
maximum
interquartile range
median
minimum
ppm
copper
1500
1400
1200
1000
800
600
400
200
0
H 178
ppm
lead
100
75
50
25
0
15
15
5
25
23
15
28
7
5
number of measurements
ICPMS
ICPMS
ICPMS
p-XRF
p-XRF
p-XRF
p-XRF
p-XRF
p-XRF
p-XRF
p-XRF
type of measurements

Figure 5. Constellation diagrams showing the probabilities of the absence of significant differences determined by the Mann-Whitney U test in the concentrations of: (a) copper, and (b) lead, between the seven different bodies of Late Quaternary deposits described in Table 2. Where the calculated probabilities of the M-U statistic are high (i.e. þ is in the range 0.0000 to 0.01) they suggest a statistically-significant difference exists between the measurements at each body of sediment. This relationship is shown by the “open” linking rectangles and the dashed lines. The other end of the probability scale, where calculated þ is in the range 0.5 to 1 is shown by black rectangles. The small numbers of measurements and geomorphic similarity of the early Holocene fluvial deposits in the Wadis Dana and Ghuwayr led to their combination in these diagrams.



CAPTIONS TO TABLES

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, beds10–50 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

Table 2. Description and interpretation of the ~7000 cal. BP alluvial sequence at WF5021 (Figure S2; see also Grattan et al. 2007; Hunt et al. 2004; 2007a,b; 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/6.1), 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.	Finegrained units contain rare *in situ* rhizome-casts of *Phragmites*, reed rhizoliths, and aquatic molluscs.	Contains anomalous sample I. 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 clay/silt-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 Fluvial-clastic lithofacies; sometimes with steeper, but less distinct contacts.	The finer sediments contain *in situ* rhizome-casts and rhizoliths 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.

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