Methodologies for the investigation of corroded iron objects: examples from prehistoric sites in South-eastern Arabia and Western Iran

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ABSTRACT
Ancient iron objects from early Iron Age archaeological sites are almost always severely corroded, which can severely limit the possibilities for their archaeometallurgical analysis. In this paper, a range of corroded iron objects from different sites and regions of the ancient Near East are investigated with the purpose of developing an integrated scientific approach to the investigation of such materials, outlining the capabilities and major technical limitations of currently available techniques. Specific objectives of the research include: (1) Assessing the state of degradation of ancient ferrous objects in respect to the portion of remnant carburized areas preserved; (2) Identifying metallographic structures and evaluating the carbon content from the observation of remnant carburized areas; (3) Developing an understanding of the representativeness of remnant carburized areas in corroded ferrous samples; and (4) Exploring the validity and technical constraints of SEM-EDS analyses of slag inclusions in corroded iron artefacts for the determination of provenance.

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1. Introduction
Many ancient ferrous artefacts, especially those dated to prior to the second half of the first-millennium BC (Agrawal et al. 1990; Pigott 1989; Rehren et al. 2013), are very poorly preserved due to corrosion. Corrosion acts to change the chemical content and physical structure of ancient ferrous artefacts (Neff et al. 2005), significantly complicating their archaeometallurgical analysis. Developing analytical approaches for the investigation of corroded objects therefore represents a perspective and relatively un-explored avenue. Although researchers are generally aware of the existence of remnant carburized structures (RSs) in the corroded iron artefacts (Knox 1963; Scott 1976; Stech-Wheeler et al. 1981), doubts about the representativeness of such RSs are sometimes expressed (Yahalom-Mack and Eliyahu-Behar 2015, 296), as some parts of corroded objects appear to be largely free of the pseudomorphs of former carburized areas (Scott 1989, 12). One of the primary goals of the present study is therefore to develop an understanding of different factors affecting preservation of RSs in the corroded iron artefacts, clarifying various aspects and potential outputs of such investigation.

The Near East is often referred to as the birthplace of iron metallurgy, which is thought to have originated somewhere in the South or Southeast of the Pontus region (Waldbaum 1978) in the second half of the second-millennium BC. According to some scholars (Muhly 2003), knowledge of iron smelting was mastered by the Hittites, with further diffusion of iron technology after the collapse of palatial centres during the Late Bronze Age (Yahalom-Mack and Eliyahu-Behar 2015, 299). By the late second and early first-
millennium BC, iron was used in various regions of the Near East including the Levant and Iran (Pigott 1980; Waldbaum 1999), and also appeared in neighbouring regions such as Greece, Cyprus and South Asia (Photos 1987; Sherratt 1994; Gullapalli 2014).

In Iron Age South-eastern Arabia, the situation regarding spread of iron technology is different: with the exception of Saruq al-Hadid (characterized by abundant ferrous remains, Weeks et al. 2017), few iron objects are known in the region despite the numerous excavated settlements. Although iron becomes more common in the late pre-Islamic period (300 BC–600 AD), the pace and process of the adoption of iron technology by the local population remains a matter of speculation.

Therefore, the present work highlights analytical approaches appropriate for the investigation of such corroded iron objects using examples from two regions of the Near East: Pusht-i Kuh in Western Luristan (Overlaet 2003), and the desert of Dubai and Sharjah in South-eastern Arabia, and discusses the technical capabilities and limitations of these approaches.

1.1. Selected archaeological assemblages

For this study, ferrous objects from six archaeological sites within South-eastern Arabia and Western Luristan were chosen for investigation (Figure 1), including the following samples:

a) From the site of Saruq al-Hadid located in the desert of Dubai: 10 medium- and large-sized iron objects (i.e. more than 1.5 cm thick) found within the upper deposits (Horizons I and II; Weeks et al. 2017) of the central sector of the site. Despite the wide chronological ranges of the metallurgical (copper) slag recovered from these deposits, the majority of the iron artefacts from Saruq al-Hadid can be clearly dated to the Iron Age II period (c. 1100–600 BC) by their poor preservation and typological characteristics. The latter can be traced through clear parallels with Iron Age (c. 1000–800 BC) swords from Luristan (Overlaet 2003: Fig. 131) and the recovery of two-lobed arrowheads at Saruq al-Hadid, whose appearance contrasts to the oblanceolate and trilobate arrow-

![Figure 1. The artefact assemblage under study: South-eastern Arabia (Saruq al-Hadid, Muweilah), Luristan (Pusht-i Kuh region: Bard-i Bal, War Kabud, Ghaluli Gulgul, Sar Kabud).](image-url)
heads that characterize South-eastern Arabia during the subsequent periods, c.600 BC to AD 600 (Mouton 2008: Fig. 23; ElMahi and al-Jahwari 2005: fig. 9; Delrue 2007; Boucharlat and Lombard 1985, 60).

b) From the settlement of Muweilah, located in the coastal desert of Sharjah and dated to 1000–800 BC (Magee 2014): five iron objects. All Muweilah artefacts come from burnt contexts in Building II, where wooden roofing and columns were burnt when the site was destroyed. All objects are characterized by small size (i.e. no more than 7 mm in thickness) and typologically, include two double-edged blades, one tapering object with square cross-section (1 cm × 1 cm), six unidentified fragments that likely belong to a single artefact (as they were found in the same context) and an unidentified flake.

c) From the Iron Age II (1000–800 BC) cemetery of Bard-i Bal in the Pusht-i Kuh, Luristan: one small bracelet fragment (4 mm in cross-section) (Overlaet 2003, 194–197, 550, 556, pl. 183).

d) From the Iron Age III (800–600 BC) cemeteries of War Kabud (Haerinck and Overlaet 2004), Sar Kabud (Overlaet, forthcoming) and Ghaluli Gulgul (Overlaet, forthcoming) in the Pusht-i Kuh, Luristan: 11 fragments of ferrous blades and arrowheads. Many of these fragments are flakes, no more than 5 mm in thickness, removed from the surface of the objects during their excavation and conservation.

1.2. Environmental setting of South-eastern Arabia and Western Luristan

Since the processes affecting the corrosion of metal artefacts are primarily a function of the local burial environment, a brief note on the environmental setting of two regions considered in the present study should be provided.

Saruq al-Hadid is located in inland Rub‘ al-Khali desert, where dunes are composed of a mixture of quartz and low carbonate portion (Howari, Baghdady, and Goodell 2007). At the base of the site is a thick gypsum layer representing former sabkha or salt flat (Butler 1969) that can form both within the sand, and within the underlying bedrock. Sabkhas are common across the southern Persian Gulf coastal region and are characterized by halite deposited on the surface of the sabkha and subsurface precipitation of gypsum and aragonite from brines brought up from the water table via capillary action.

The site of Muweilah is situated in the coastal sand-dune belt of Sharjah Emirate, which according to Howari, Baghdady, and Goodell (2007) is characterized by a high carbonate content of the sand. The sand’s main sources are beaches at low tide meaning that salt is transported with the sand, and as aerosol. The “bedrock” at Muweilah consists of aeolinite formations, i.e. palaeo-dunes consolidated by evaporation. In contrast to the inland sabkha (rain) and coastal sabkha (high tide), the source of salt water (specifically, brackish groundwater) at Muweilah comes from below the surface due to the proximity to the sea. Overall, the salinity at the site is lower than at sabkha locations, which is confirmed by the high quantity of well-preserved animal hard tissue remains (bones and teeth) at Muweilah. Precipitation and humidity are however higher at Muweilah than at Saruq al-Hadid. Overall, the burial environments that existed at Saruq al-Hadid and Muweilah can be considered as highly corrosive for archaeological iron artefacts.

In contrast to South-eastern Arabia, Western Luristan is located in a non-arid environment. By analogy with soils of Eastern Luristan at the Sangtarashan archaeological site (Oudbashi, Hasanpour, and Davami 2016, 261), the soils of the Pusht-i Kuh region may be tentatively characterized as only moderately corrosive.

The burial environments experienced by the artefacts from Western Iran and South-eastern Arabia are critical for understanding and interpreting differences in the state of degradation of the artefacts from these regions.

1.3. Corrosion of ancient iron artefacts

Corrosion of archaeological artefacts takes place within the burial environment and is accompanied by the formation of specific products. All ferrous objects selected for the present investigation were found in soil, a complex burial environment (Neff et al. 2005) in which corrosion conditions can be affected by many different parameters including geological factors (soil types, pH, electrical resistivity, etc.), hydrological factors (water flow through ground layers) and soil chemical composition. Corrosion of archaeological iron objects in soil is known to develop through the formation of a three-layered structure consisting of the metal substrate, a dense product layer (DPL) containing well-crystallized and more compact corrosion products, and a transformed medium (TM) zone transiting between the DPL and the soil. The typical structure of the DPL is often schematically represented as striations or so-called marblings, which incorporate patches of magnetite (Fe3O4) and more rarely maghemite (γ-Fe2O3) within the general iron oxide-hydroxide matrix of the corroded artefact (Rémazellles et al. 2009). A variation in the portion of metal substrate, TM and DPL, is used in the present paper to assess the degree of degradation of ferrous artefacts, facilitating the development and validation of a robust and optimal methodological approach to their metallurgical analysis.
1.4. Study of remnant carburized structures

The usefulness of remnant carburized structures in ferrous objects relates to the fact that the original iron phases, including ferrite, pearlite and cementite, are often selectively or partially replaced with (different) iron oxides as a part of the corrosion mechanism. This observation was made as early as the 1960s (Knox 1963) and several subsequent works have utilized this characteristic of iron corrosion to identify RSs in archaeological ferrous specimens (e.g. Agrawal et al. 1990; Golfomitsou et al. 2017; Notis 2002; Tholander 1971; Scott 1976, 1989). However, probably because of the complex and highly variable nature of the corrosion process, the majority of these studies aim only at general characterization of RS (Knox 1963; Scott 1976; Golfomitsou et al. 2017), focus on analytical techniques (Notis 2002), or in attempt to explain preservation of RSs propose complex theories not backed by robust scientific evidence (Scott 1989, 13). The present study, therefore, aims to contribute to the debates on this subject, discussing mechanisms of formation of RSs based on the observations obtained from the investigation of corroded ferrous objects originating from different burial environments.

1.5. Investigation of slag inclusions in iron artefacts

In the past two decades, archaeometric provenance studies conducted on archaeological iron objects have become commonplace (Buchwald and Wivel 1998; Dillmann and L’Heritier 2007; Blakelock et al. 2009; Charlton et al. 2012; Disser et al. 2016). These studies often rely on the analysis of slag inclusions (SIs) incorporated into the metal during the formation of the bloom in the smelting furnace, and (partially) preserved in the iron object after its subsequent forging as slag “stringers”. Archaeometallurgical studies indicate that slag stringers are ubiquitous in pre-industrial era archaeological artefacts manufactured from both direct (i.e. bloomery process) and indirect (via production of cast iron and its subsequent remelting) processes of iron production (Buchwald and Wivel 1998; Dillmann and L’Heritier 2007). Elemental analyses of SIs can be used for the identification of an artefact’s provenance (Leroy et al. 2012), to characterize the compositional variation with an assemblage (Charlton et al. 2012) or to demonstrate the use of different reduction systems (Pągès et al. 2011). Depending on the research objective, analytical techniques may include SEM-EDS (Scanning Electron Microscopy with Energy-Dispersive Spectrometry) and/or L-ICP-MS (Laser Ablation Inductively-Coupled Plasma Mass Spectrometry; L’Heritier et al. 2016). Overall, the goal of the present work is to highlight important aspects and limitations of the methodology of analyses of SI from corroded objects, and compare this approach to that used to study un-corroded iron artefacts.

2. Experimental methods

The selected analytical protocols include standard procedures of epoxy resin mounting, abrasion and polishing using a range of abrasive pastes, chemical etching, and reflected light optical microscopy to investigate the microstructures of corroded iron matrices. Metallography was performed on rare surviving islands of un-corroded iron by etching them in a 5% nitric solution. Exposed metal structures were used as a reference point for the interpretation of Figure 2. Appearance of some typical corrosion phases under the SEM (a) and optical microscope (b). (a) SEI. War Kabud. WK.B172-6_8-2a. Magnetite (Mt) appears as light-grey cubic crystals with dark-grey iron oxide-hydroxide (FeO(OH)) filling the interstitial matrix. Metallic copper (Cu, white), present close to the surface of the original artefact, is presumably due to the galvanic corrosion between adjacently buried iron and copper objects. Remnant carburized structures are not visible because the composition of original metal is pure ferrite, as deduced from etching of preserved islands of metallic iron. (b) Optical microscopy (un-etched). Saruq al-Hadid. SF13024. Layer of magnetite developed in the object (running upper left to lower right) and characterized by cubic crystals. The darker grey-blue area below the magnetite layer is iron oxide-hydroxide (FeO(OH)).
of RSs found within the same object. Remnant carburized areas were commonly investigated in their un-etched state, as they were largely unaffected by nital etching, with the exception of few objects, in which prolonged (c.30–60 sec.) etching by nital allowed RSs within a magnetite matrix to be contrasted. Once the optical micrographs of RSs were taken, a standard graphical software was used to increase the contrast between pseudomorphs replacing different metallic components.

Energy-Dispersive Spectrometry (SEM-EDS) on a JEOL-6010 Scanning Electron Microscope was used for high-resolution microscopic observation and compositional analyses of SIs. Differences in optical properties and in the oxygen and iron contents of corrosion phase components allowed optical microscopy (Figure 2(b)) and SEM-EDS (Figure 2(a)) to tentatively differentiate between at least two components: marbled areas primarily composed of magnetite and surrounding matrix primarily composed of oxi-hydroxide. Marbled areas appear in electron imaging as a light grey component of higher relief, while surrounding matrix appears as a dark-grey component of lower relief. Additionally, cubic crystals of magnetite comprising scales of hot oxidation (similar to those reported by Balos, Benscoter, and Pense 2009 and Golfomitsou et al. 2017) were identified along the cracks and on outer surfaces of some ferrous objects (Figure 2(b)).

3. Results and discussion

3.1. Investigation of the state of degradation of ferrous objects

The present study indicates different preservation of RSs depending on different factors such as overall state of the degradation, mass of the object, location of the sample within the corroded body and dominance of specific metallographic structures.

Analyses reveal that the objects from Saruq al-Hadid and Muweilah are significantly distorted (i.e. bloated) from their original shape by corrosion, which is likely a reflection of their specific burial environment enriched in carbonate salts. Additionally, chlorine was likely to be present in the burial environment at Saruq al-Hadid, because this element was detected by the SEM-EDS in the vicinity of un-corroded metallic substrate in concentrations of up to 0.8 wt.% in four out of ten artefacts.

Six out of ten artefacts from Saruq al-Hadid and four artefacts from Muweilah are the most heavily degraded, which is reflected in their low proportions of magnetite “marblings” (5–20% of the total specimen surface area), small surviving islands of un-corroded iron (30–150 µm) and the relatively rare areas with observable remnant structures in the samples: Muweilah 5–10%, Saruq al-Hadid 10–20%. A greater amount of RSs in Saruq al-Hadid objects is due to their larger size and mass, compared to Muweilah objects. The remaining four objects from Saruq al-Hadid, and one artefact from Muweilah, show larger “marblings” (30–60% of the total specimen surface area), larger areas of RSs (10–40% of the total specimen surface area) and larger islands of un-corroded iron (c.100–1000 µm in their largest dimension).

In addition, four Muweilah samples feature magnetite rims (30–100 µm) at their exterior indicating oxidizing heating as a potential cause, which confirms “burnt contexts” from which the artefacts originated.

The Iranian objects appear to be better preserved than the majority of the Arabian specimens, despite their small dimensions and superficial location within the original object (Figure 3(b)). This better preservation is represented by the presence of larger areas

![Figure 3](image_url)
of un-corroded metal islands (up to 30% of the total specimen surface area) and magnetite "marblings" (30–70% of the total specimen surface area). Remnant structures also usually occupy significant areas (c.10–50% of the total specimen surface area) within Luristan ferrous samples. The high variation in the amount of their RSs is due to the difficulties of identifying RSs in the objects of predominantly ferritic composition, as discussed below.

The observations performed on the archaeological materials suggest that the burial environment (as well as object’s size and mass) is the major factor affecting the degradation of metal and the formation of identifiable RSs. The samples from South-eastern Arabia are generally more degraded than the contemporary samples from Luristan, which must be ascribed to the strongly corrosive sabkha environment rich in evaporitic salts that characterizes the coasts and deserts of the lower Persian Gulf. Among the salts comprising sabkas, sulphates and chlorides are known to promote corrosion of iron (Gerwin and Baumhauer 2000, 76). Moreover, the poor preservation of archaeological plant remains (Tengberg 2002) at archaeological sites within the Persian Gulf region also reflects the deteriorating effects of local burial conditions.

The variation in preservation of objects from Saruq al-Hadid (primarily manifested by the different amounts of magnetite present), nevertheless, requires explanation. The observation about the majority of ferrous objects at the site containing only up to 10% of magnetite among their corrosion products is further supported by data obtained from the study by the authors of this paper of several dozen additional objects from Saruq al-Hadid that were not included within the present study (unpublished data). While leaving this question open for the future investigations, it is worth emphasizing that the formation of magnetite can occur not only due to natural processes of corrosion, but also as a result of oxidation during heating of the object, for example during the manufacturing process in a blacksmith’s hearth (Rémazeilles et al. 2009, 2938).

Overall, results of the present investigation show that the degree of degradation of the samples of ancient ferrous objects and the amount of preserved RSs can be assessed, based on the amount of marbled areas in the DPL and the total area of un-corroded metal. This, combined with the knowledge of other parameters such as location of the sample in the corroded object and the likely amount of ferritic areas, permits to evaluate the reliability of the characterization of its carbon content.

3.2. Types of remnant carburized structures

Based on comparison with structures of etched un-corroded metal from the analysed samples, RSs within the range of hypoeutectoid steels (0–0.7% C) can be more or less clearly identified in the archaeological materials under study (Figures 4–6). Regarding the mechanisms of formation of remnant structures, several types of replacement of metallic phases by oxides were observed: (1) intergranular corrosion, in which corrosion progressed along the ferrite (or former austenite) grain boundaries leaving them intact or replacing them with an oxygen-poor component such as magnetite (Figures 4(a) and 7b); (2) inverse intergranular corrosion, in which grain boundaries were replaced by an oxygen-rich component such as oxy-hydroxide (Figure 4(b)); (3) pearlite corroded in

![Figure 4. Optical Microscopy.](image-url)
preference to ferrite, in which pearlite was largely replaced with an oxygen-rich component, while ferrite was replaced with an oxygen-poor component (Figures 5(a) and 6(a)); (4) ferrite corroded in preference to pearlite, in which ferrite was replaced with oxygen-rich component, while pearlite was replaced with an oxygen-poor component or was only partially corroded leaving its cementite intact (Figures 5(b) and 6(b)).

These types of RSs are commonly observed to co-exist within the same sample and in close proximity to each other, indicating the complex character of corrosion processes.

In the case of inverse intergranular corrosion of largely ferritic structures or low-carbon structures in which ferrite corroded in preference to pearlite, cubic zoning, which is sometimes preserved within former
ferrite grains, may serve as a diagnostic feature of such RS (Figures 4(b) and 5(b)). Nevertheless, the identification of low-carbon (<0.1% C) structures is often seen as questionable due to the fact that former ferrite grains are not clearly outlined because of the absence of a cementite network. In a few cases, however, traces of cold-working (grains elongated in one direction) with or without annealing (equiaxed grains) were identifiable in low-carbon samples (Figure 7(a,b)).

With regard to high-carbon structures, RSs of 0.7–0.9% C are not common for artefacts in the present study. This may be due to either the limited production of such steels during the early Iron Age or, more likely, by the analogy with low-carbon RSs, due to the analytical challenges of recognizing thin (or absent) networks of hypereutectoid cementite (Figure 6(b)). Although optical microscopy can be used for identifying RSs of close-to-eutectoid composition, backscattered electron imaging allows for better recognition due to a greater contrast between residual cementite (or pearlite) and the corroded iron oxide matrix, as shown in former studies (Notis 2002; Golfomitsou et al. 2017) and confirmed by the present investigation.

Among various metallic phases that can be formed in non-equilibrium conditions, only the structure of spheroidized cementite was identified in samples in the present study (Figures 8(a) and 10(a,b)). Such structures may indicate prolonged annealing after cold-working (Gordon and Van Der Merwe 1984, 112). No quenched structures were identified, which primarily must be due to the limited use of quenching during the Early Iron Age, which to our knowledge was known only in Cyprus at this period (Tholander 1971). However, following Knox (1963), failure to identify quenching may also reflect the difficulties in recognizing acicular (martensitic) structures in fully corroded matrices comprising iron oxides.

3.3. Validity of investigation of remnant structures in corroded iron artefacts

Considering the varying expression and preservation of remnant structures commonly noted within analysed archaeological samples (Scott 1989; Yahalom-Mack and Eliyahu-Behar 2015), questions arise regarding the representativeness of the metallographic data. Specifically, can an artefact’s carbon content and smithing techniques be adequately
An attempt to validate the proposed approach was undertaken using an example of a severely corroded fragment of iron knife from Saruq al-Hadid (SF31145, Figure 9). Morphologically, the artefact is a fragment that has both ends fractured and an asymmetrical cross-section characterized by faces of different lengths, i.e. 1.2 and 1.5 cm (Figure 9, left), that might identify the longer face as hosting the cutting edge. One (broken) end of the object is tapering and more flattened compared to its other end. In order to comprehend the patterns of carbon distribution within the specimen, its RSs were systematically investigated and the carbon content was mapped (Figure 9, right), similarly to the procedure proposed for un-corroded iron artefacts by Pagès et al. (2011: Fig. 4).

Within the corrosion layers (Figure 9, right) of the section, the DPL occupies most of the area of the sample, while the TM (incorporating quartz grains intruded from the surrounding environment) is rather thin (0.5–1.5 mm) and developed only locally. Magnetite “marbling” occupies only a small area (less than 5% of the total specimen surface area) in the core of the sample. Remnant structures, comprising c.10–20% of the total sample area, are largely evenly distributed in the core of the sample, decreasing in proportion towards the object’s exterior surfaces. Nevertheless, the distribution of RSs within SF31145 allows for assessment of the carbon content on the long edge, in the core, and on the short edge, and indicates:

1) Spheroidization of cementite in the area of the short edge (Figure 10(a,b)), resulting from prolonged annealing/heating of this part of the blade. Such prolonged heating could reflect a range of activities, but is most likely due either to intentional softening/annealing of the back side of the blade or to heating of the blade in order to recycle it, as has been suggested for archaeological iron objects from Northern Transvaal (Miller, Boeyens, and Küsel 1995, 43).

2) Slightly lower carbon content (0.2% C) of the areas located closer to the core part of the object (Figure 10(c)).

3) Slightly higher carbon content (0.3–0.4% C) of the areas located near the surface of the long and short edges and along the main radial (axial) crack (Figure 10(d)), which might have resulted from intentional or unintentional carburization from contact with charred material.
Overall, the investigation of RSs in the blade confirms that the short (back?) edge, on account of its structure, was characterized by lower hardness than the long edge (where cementite was not spheroidized), which may support the identification of the long edge as the primary cutting edge. The correlation of carbon content with the location of RSs may be tentatively interpreted as evidence for the intentional use of the cementation technique for the manufacture of the blade, or at least as carburization in the smithing hearth happening at the contact between the artefact’s surface and the charcoal. The possible use of the cementation/carburization technique at Saruq al-Hadid needs to be confirmed or rejected by further analyses of other artefacts.

Despite the impossibility of fully reconstructing the metallographic structure of this corroded sample (as only 10–20% of RSs are preserved), it is possible to successfully assess the carbon content of a variety of components that are important from the practical perspective, such as cutting edges, justifying the use of invasive study (cf. Golfomitsou et al. 2017). However, the objective assessment of carbon content in samples of a small size (and hence more vulnerable to corrosion), and which originate from a highly aggressive burial environment (such as in South-eastern Arabia), represents a significant challenge, due to the lower proportion of preserved remnant areas (5–10% in the samples that are less than 7 mm in thickness).

### 3.4. Analyses of SIs in corroded iron objects

As expected (Scott 1976), SIs were encountered in the corroded ferrous artefacts from different burial environments such as South-eastern Arabia and Western Iran. SIs represent an additional avenue for research into corroded iron artefacts, particularly their provenance, although they too can be affected by corrosion processes. Compositional analyses of the SIs in these artefacts indicate the dominance of the following three mineralogical types: SIs composed of glass + olivine ± wustite; SIs composed of pyroxene + glass (Figure 11); and SIs dominated by a single glassy phase. Other mineral phases, such as herzenite, ulvite, leucite and calcium phosphate, that have been recorded in ancient iron slags (Kronz 1998) and sometimes in SIs of iron artefacts (Dillmann and L’Héritier 2007, 1815; Gordon and Van Der Merwe 1984, 122), were largely absent in SIs of the artefacts from South-eastern Arabia and Western Iran. This is most likely a reflection of the specific raw materials that were used to make the iron found in these regions.

Overall, in accordance with the results of previous studies (Buchwald and Wivel 1998; Dillmann and L’Héritier 2007), the data obtained for the present assemblage suggest that variations in the iron concentrations of SIs directly affect their mineralogy. At high iron concentrations (FeO 30–60 wt.%), SIs tend to be dominated by olivine, iron-rich glass (FeO 20–40 wt.% ± wustite). As the total iron concentration of the SI decreases (FeO 2–35 wt.%), their mineralogy changes, giving way to crystallization of pyroxenes and glass (of varying FeO). Following further decrease in FeO (<25 wt.%), some SIs become dominated by a single glassy phase, while other SIs with FeO < 20 wt.% break down into pyroxenes and low-Fe glass.

As an example, the bulk and single-phase analyses of different types of SIs from a longitudinal section of an artefact SF13054 from Saruq al-Hadid are presented in Table 1. Although individual single-phase analyses

![Figure 11. BSEI. Example of a slag inclusion composed of pyroxene + glass. Pyroxene (Px, light grey) is represented by two generations of clinoferroilite crystals (as deduced from their monoclinic crystals and chemical composition, Deer, Howie, and Zussman 1997: Table 3, cols. 33–35): large idiomorphic crystals, and fine microcrystallites. Glass (Gl, black) fills the interstitial areas. Saruq al-Hadid. SF13048.](image)

### Table 1. SEM-EDS analyses of different types of SIs within artefact SF13054. Saruq al-Hadid.

| SI No. | Phase/area analysed | Na₂O | MgO | Al₂O₃ | SiO₂ | K₂O | CaO | TiO₂ | MnO | FeO |
|-------|---------------------|------|-----|-------|------|-----|-----|------|-----|-----|
| 1     | Olivine             | 0.5  | 12.8| 1.4   | 28.7 | 0.2 | 2.5 | 0.1  | 53.6|
|       | Glassy matrix       | 0.5  | 1.1 | 11.1  | 46.4 | 1.8 | 20.8| 1.1  | 17.2|
|       | Whole SI            | 0.6  | 5.2 | 7.5   | 42.3 | 1.9 | 10.4| 0.6  | 31.3|
| 2     | Ferroaugite         | 0.4  | 8.6 | 8.1   | 46.0 | 1.1 | 17.3| 0.8  | 17.6|
|       | Glassy matrix       | 0.6  | 3.7 | 13.9  | 46.4 | 3.1 | 13.1| 0.7  | 18.3|
|       | Whole SI            | 0.4  | 6.9 | 9.1   | 46.4 | 2.0 | 16.5| 0.9  | 17.7|
| 3     | Monophase glassy SI | 0.5  | 6.0 | 7.4   | 51.8 | 2.8 | 12.1| 1.0  | 18.2|
of multi-phase SIs show significant compositional heterogeneity, a principal components analysis plot (Figure 12) reveals that the bulk analyses of multi-phase SIs, and spot analyses of monophase glassy SIs, form a common cluster along the vectors FeO, SiO₂, and CaO in the PC1-PC2 (Figure 12(a)) or PC1-PC2-PC3 system (Figure 12(b)). Altogether, these results can be summarized as follows:

1) Despite the fact that single-phase analyses of multi-phased SIs can sometimes be used for qualitative information about the presence or absence of certain elements in the slag, only whole-inclusion bulk analyses are fully representative of the chemical signature of the object, as observed in the studies performed on un-corroded objects (Buchwald and Wivel 1998; Dillmann and L’Héritier 2007).

2) Ratios of non-reducing components (Blakelock et al. 2009, K, Mg, Si, Al, Ca, Ti, P and Mn) in the bulk SI from corroded objects remain constant regardless of their FeO contents, as reported for SIs from un-corroded iron (Buchwald and Wivel 1998; Dillmann and L’Héritier 2007).

3) The variation in iron concentrations in SIs and the resulting presence of different mineralogical types suggests that locally variable reducing conditions existed in the smelting furnace or in the smithing hearth, for example at zones of direct contact with charcoal.

4) SIs from corroded iron are therefore broadly similar to SIs from un-corroded iron. However, despite these similarities, SIs from corroded iron objects are sometimes subject to a significant alteration, which will be discussed in the section below.

3.5. Alteration of SIs

The present study reveals that in corroded iron objects, SIs dominated by wustite and fayalite (characterized by FeO contents >60 wt.%) are the most subjected to degradation, as opposed to the monophase glassy SIs (characterized by <25 wt.% FeO). The degradation happens upon the interaction of aqueous solution with the SI and is revealed through the formation of new oxygen- and iron-rich phases in the SIs, as well as leaching and disintegration of the originally existing silica network. Specifically, glass leaches (Figure 13) and hydrates (Figure 14(a)), fayalite incorporates extra oxygen and is replaced by ferric fayalite, ferrifayalite or laihunite Fe²⁺Fe³⁺(SiO₄)₂ (Figure 13), as confirmed by Martin et al. (2011) and Hauptmann (2007, 178), while wustite can be recrystallized (as magnetite?) at the interface between the metal matrix and the SI (Figure 14(b)).

In contrast to iron-rich SIs, monophase glassy SIs (FeO 3–25 wt.%) are less prone to degradation and are therefore more often found relatively un-altered in corroded ferrous artefacts (Figure 15). Nevertheless, fragmentation and cracking, as well as formation of a leached zone at the interface of the SI, are often observed. The leached zone is composed of several layers, all usually characterized by increased O, Fe and diminished K and Na relative to the pristine glass. At different layers of the leached zone, enrichment or depletion of Mg, Mn, Si, Al, P, Ti and Ca relative to the pristine glass is also observed.

Overall, during the analyses of monophase glassy SIs, the major and considerable challenge affecting
the quality of the data is the reduction of their pristine area. This can be particularly noticeable in the case of small SIs (diameter <5 µm), as the minimum diameter of the SEM beam is usually around 1–2 µm and any surviving area of pristine glass can be too small for analysis.

Figure 13. BSEI and EDS-elemental maps of O, Fe, Si, Al and K. Partial alteration (pronounced in the upper part of the photo) of an SI composed of glass + fayalite. Elemental maps allow witnessing the difference between the composition of altered (upper) and unaltered (lower) parts of the SI. Saruq al-Hadid. SF13238.

Figure 14. BSEI. Degradation of wustite-rich SIs through hydration and formation of new oxygen- and iron-rich phases. Saruq al-Hadid. (a) The light-grey areas surrounding the wustite dendrites (white) are a result of the hydration and Fe enrichment of the surrounding unresolved matrix (mid-grey) of fayalite and glass whose bulk FeO content is ~60 wt.%. SF13024. (b) Degradation of SI located near the ferrite grain boundary (GB, seen in the lower right part of the photo) through recrystallization of Fe oxide (light-grey) at the interface of the ferrite grain (white) and the slag inclusion. The bulk FeO content of the pristine silicate matrix (dark-grey) is ~50 wt.%. SF20407.
in the burial environment, SIs from corroded iron can be a subject to partial or complete chemical degradation which can be a barrier for provenance studies. Nevertheless, the identification of these alteration processes and their physical and chemical manifestation in corroded iron objects allows for the identification of un-altered SIs that are suitable for archaeometallurgical provenance determinations.

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Disclosure Statement

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