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Archaeometallurgical investigation of ancient artefacts' degradation phenomenon

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Archaeomaterials suffer from various degradation such as atmospheric corrosion, under-deposit corrosion and underwater corrosion etc.; however, the extent of degradation depends on the composition of materials, environment, manufacturing process and post-processing technology such as surface treatment like carburization etc. The corrosion (degradation) phenomenon of ferrous artefacts is very complex and has received significant attention for understanding the ancient metal technology and for designing the conservation pathway of historical artefacts. This review highlights the mechanism of degradation under different environments and also paves a path for the future studies by using different analytical techniques to advance the existing knowledge.

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INTRODUCTION

Archaeometallurgical examinations of ancient artefacts have been underway for a long time ago. However, application of modern characterization techniques is expected to provide some interesting fundamental mechanisms involved in the degradation of various metallic ancient artefacts. Archaeological studies combined with detailed metallurgical examination (which includes examination of artefacts' manufacturing processes, alloy composition and the types of ores utilized for the preparation of alloys) are required to understand the evolution of technology in the past and to suggest their conservation pathway from various degradation. It is noteworthy that ancient artefacts' deterioration (such as via corrosion) depends on various factors and composition of materials; manufacturing processes (such as hammering, forging etc.), exposed environments etc. are considered as important factors for the archaeomaterials' degradation. Ancient artefacts are known to be significant evidences of regional technological advancement that occurred in that region and are therefore expected to be persevered from corrosion; hence, understanding the corrosion mechanism of ancient artefacts is become an important field of research for metallurgists, material scientists, archaeologists and corrosion scientists. Our recent review articles describe emerging characterization techniques that are being used for corrosion mechanism investigation of metallic materials;^{1,2} however, in this review, our aim is to delineate the application of potential characterization techniques³ (destructive and non-destructive (in case one is allowed to destroy the samples depending on their requirement)) in order to find out the mechanism of various types of corrosion such as atmospheric corrosion, underwater corrosion, under-deposit corrosion etc. Apart from destructive techniques, certain non-destructive techniques are also available for structural and precipitates' morphological examination such as synchrotron X-ray diffraction and tomography, neutron diffraction and neutron radiography imaging and their application in artefact degradation mechanism investigations are suggested in this article later (Fig. 1).^{4–6}

ARTEFACTS EXPOSED TO ATMOSPHERE AND THEIR DEGRADATION MECHANISM (ATMOSPHERIC CORROSION)

Atmospheric corrosion is known to be a prominent degradation mechanism. Hence, in this section, various examples are included where atmospheric corrosion is found as the prominent way of degradation, and possible mechanisms of degradation are discussed.

Indian ancient artefact (Delhi iron pillar, India)

Delhi iron pillar is known for its corrosion resistance that has remained rust free for more than 1600 years⁷. The corrosion resistance property of the Delhi iron pillar has been delineated through two ways, i.e. (a) compositional aspect of the iron used and (b) based on Delhi's atmospheric condition. Some researchers believed that corrosion resistance is achieved due to Delhi's low humid environment throughout the year, whereas other researchers have highlighted the material composition aspect. Compositional theories are further divided into various aspects, which include the incorporation of P in the material, presence of slag particles in iron, absence of S and Mn in iron etc.^{8–12} Other theories signified the role of surface finishing and residual stress generation, absence of S from the atmosphere, surface coating (slag coating) done by the manufacturer etc. as the factors for rustless iron making.^{13–16} Although various theories are proposed in this regard, magic elemental composition of the iron has obtained significant attention by researchers. Similarly, the ancient Indian archaeological symbol, i.e. pillar at the sun temple Konark (Orissa, India) has remained rustless from the Gupta dynasty's period (300–500 AD). Compositional analysis of the iron made in the pre Gupta's dynasty confirmed the absence of P in the iron, which is found to be present in Gupta's dynastical iron. Delhi and Konark iron pillar (which still remained rustless) are known to be manufactured during this dynasty, and therefore advancement in the production of corrosion resistance iron happened during Gupta's period.¹⁷ This temple is also known to be established during Gupta's period and is assumed to undergo the similar iron making and processing technology. Microstructural analysis

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Fig. 1 Various imaging techniques available for archaeometallurgical artefact analysis. Reprinted with permission from ref. ⁴ (Atom probe tomography). Copyright 2007, Elsevier B. V. Reprinted with permission from ref. ⁵ (X-ray tomography). Copyright 2015, Royal Society of Chemistry. Reprinted with permission from ref. ⁶ (Neutron tomography). Copyright 2015, Royal Society of Chemistry

revealed the similarity between these two iron as reported by Puri et al.¹⁸ however, detailed in-depth investigation depicted the significant difference between the surface and internal layer's microstructure. Surface layer is found to consist of high amounts of carbon with the majority of ferrite phase surrounded by a small fraction of pearlite at the grain boundary, whereas in the central region, ferrite and pearlites were found to be present (in considerable amount) with an average grain size of around 10 μm . Interestingly, slag particles and unreduced FeO were also observed on the surface layer that is known as second-phase particles (Fe_2SiO_4 (fayalite)) (see Fig. 2 (1)).

The incorporation of slag particles in the iron is mainly related to the iron extraction techniques that are known to be performed with charcoal (solidstate reduction) during ancient times. It is assumed that the hammering operation, which usually happened to be performed after iron making, is found unable to remove the slag and unreduced FeO. Therefore these slag particles were found on the surface. Intriguingly, carbon content at the surface is found to be lower than the centre, whereas phosphorous (P) content is found to be high (with an overall presence of 0.25% as determined through wet chemical method). High P has also been detected at the interface of rust-metal and high P is found in the inner layer.

The following question remained unanswered yet as (a) what was the driving force for the development of small particle size corrosion products? The effect of manufacturing process in the corrosion resistance of iron making remained unclear as follows: (b) nanophase formation in corrosion products of Gupta's period artefacts; (c) information about the ion, which is described to occupy a position in the lattice of $\text{Fe}_{3-x}\text{O}_4$, remained unknown. Further to this, its impact on the corrosion resistance is expected to be explored using advance characterization techniques such as FIB SEM, TEM etc.^{19–21} Although the process of corrosion is known to be described in detail, no information is available about the driving force for the formation of delta-FeOOH. It is elucidated that the delta-FeOOH appeared as the amorphous phase with discontinuity

in the layer; however, the presence of P is known to enhance the formation of delta-FeOOH as illustrated by Misawa et al.²² however, delta-FeOOH is found to be enriched with Cu, Cr, etc. elements that were added for increasing the corrosion resistance. Balasubramaniam et al.¹⁷ highlighted the role of the amorphous layer in protecting the Gupta dynasty's iron from corrosion that was an interesting observation; however, stability of the interface between iron and the amorphous layer remained unexplained. Thermodynamic modelling of the interface formation between the iron and the phosphate phase is expected to suggest the stability of the interface under different conditions. Miedema^{23,24} model is a possible model that can be applied for the interface characterization.

In order to confirm the effect of Delhi's atmosphere on corrosion-phase kinetics, rust was collected from different locations of Delhi iron pillar, such as rust below the decorative bell capital etc.⁷ (see Fig. 2(2)). These rust samples were grounded into the fine powders that were then further analyzed with XRD, FTIR and Mossbauer spectroscopy. $\text{FeH}_3\text{P}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ formation was confirmed through XRD. It is worth to note that this phase was not found in the iron corrosion product; however, the same is found in the corrosion product in the powder form. Formation of this phase was explained by using thermodynamic theory. Since the free energies of FePO_4 and H_3PO_4 are found to be more negative than any other form of oxide or hydroxide, it supported the formation of $\text{FeH}_3\text{P}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$.⁷

It is noteworthy that P with 0.24 wt% in the Fe–P–O system, makes this system thermodynamically stable. It is observed that the size, shape and strain present in the particles may cause phase transformation. As in the earlier study, a characteristic diffraction peak for $\text{FeH}_3\text{P}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ was observed at $2\theta = 15.40$ instead of 12.75 (standard), which was speculated to be associated with the orientation of crystals; however, other possibilities such as degree of hydration etc. can also not be excluded. Delhi iron pillar was also investigated through non-destructive techniques (NDT) by Baldev Raj et al.²⁵ (see Table 1 for details).

Fig. 2 (1). Large pearlite presence with fayalite (Fe_2SiO_4) slag (observed by electron microprobe).¹⁴ Reprinted with permission from ref. ¹⁴. Copyright 2000, Elsevier B. V. (2). **a** Decorative bell capital from where rust samples were collected (**b**) after 1 year exhibited self-healing.⁷ Reprinted with permission from ref. ⁷. Copyright 2000, Elsevier B. V. (3). Mixed potential theory of Delhi iron pillar with and without slag inclusions.¹⁴ (4). Reprinted with permission from ref. ¹⁴. Copyright 2000, Elsevier B. V. Mixed potential theory of Delhi iron pillar with and without slag inclusions.¹⁴ Reprinted with permission from ref. ¹⁴. Copyright 2000, Elsevier B. V.

Table 1. Methods used for investigating Delhi's iron pillar and their outcomes with futuristic suggestions

Methods used for investigating Delhi's iron pillar	Outcome	Comments
FTIR	FeOOH (alpha, gamma and delta) was detected	Delta- FeOOH was the main component of the rust P offered help in the formation of $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (GI-XRD/synchrotron XRD with Rietveld analysis would be useful in quantitative analysis) ^{1,19}
Mossbauer spectroscopy	Doublet in the spectrum indicated the presence of fine particle size in the corrosion layer and assumed the formation of amorphous phases ¹⁴ Ion-doped magnetite formation was suggested; however, conclusive evidence is yet to be obtained. XPS, EXAFS or HRTEM STEM-DS ^{20,21} can be useful in this regard Pre-Columbian gold artefacts' microstructural features are successfully characterized with the help of TEM ²¹	No information is available whether FeOOH or $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ phase was amorphous. Synchrotron FTIR may consider a useful technique with improved spectra (good signal-to-noise ratio)
NDT (radiography and low-frequency ultrasonic testing (LFUT))	Aspect ratio of void was found to be higher in the axial direction (forging direction) Dent and fissures are observed in UFUT ²⁵	Ultrasonic test is not known to be very sensitive to microstructures, and therefore application of neutron tomography is expected to be performed for getting a clear idea about the size distribution of void and also the thickness of the corrosion layer
In situ metallographic examination	Large grains were found mainly in the lower end of the pillar Variation in the shape of inclusions was also observed ²⁵	Slags were found to be present in needle shape at the bottom region
In situ electrochemical study	Passive nature of rust ²⁵	It took 10–25 months in forming passive rust

Indian ancient artefact (Kodachadri Iron Pillar)
Another iron pillar is situated in Kodachadri (Karnataka, India).²⁶
Rougher surface is observed for the Kodachadri than the Delhi

iron pillar. Anantharaman et al.^{16,27} investigated the piece of the iron from this iron pillar and observed that the iron was made by tribes, commonly known as "Adivasi" in India with iron ore and

Table 2. Methods used for investigating Kodachadri's iron pillar and their outcomes with futuristic suggestions

Methods used for investigating Kodachadri's iron pillar	Outcome	Comments
XRF	Artefact (iron) contains 0.15–0.35 wt% Si and slag inclusion	Si-containing phase is yet to be confirmed
Metallography	Ferrite grain size was 30–300 μm . Ferrite and pearlite (around 15% volume fraction) were observed	Deformation featured as slip bands (sign of hammering)
NDT (ultrasonic testing)	Ultrasonic velocity was found in the range of 5500–5900 m/s, whereas the idealistic value for the pearlite–ferrite structure is 6000 m/s and indicated the presence of defects ²⁷	Type of defects and size and shape remained unknown Neutron tomography can be useful in this study
Mechanical hardness measurement	120–195 VHN (Vickers hardness no) hardness ²⁷	It is a destructive technique; however, synchrotron stress measurement methods can be useful

Table 3. Methods used for investigating Thanjavur cannon's iron pillar and their outcomes with futuristic suggestions

Methods used for investigating Thanjavur cannon's iron pillar	Outcome	Comments
Atomic emission spectroscopy (AES)	Low S (< 500 ppm) with Cr (0.01 wt%), 0.026 wt% Ni, 0.003 wt% Mo, 0.042 wt% p and 0.411 wt% C	Very low S and P content as compared with Delhi iron pillar
Metallography	High volume of slag was detected	Slag plays a vital role in micro-segregation of P. Quantification of slag phase is required to get a better understanding on segregation phenomenon
Electrochemical testing	Mild steel (which was studied for comparison) and cannon iron both behaved similarly at pH 7.0 (active) and at pH 7.62 (passive and stable) The pH was adjusted with 0.01 M NO_3 , 0.05 H_3BO_3 and 0.05 < $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, respectively.	Presence of alpha, delta and gamma-FeOOH and magnetite were confirmed through FTIR analysis
Micro-XRD	150- μm thick rust. Goethite and magnetite were found in the inner section of rust. Beta-FeOOH (akagaenite) was also noticed with the presence of Cl	Lepidocrocite was identified as the main phase

charcoal. However, it is worth mentioning that there are different aboriginal tribes living in India, which are known to be famous for iron making, such as Agaria, Gonda etc. The dimensions and types of the furnaces used by these communities are different from each other. It was noticed that the top portion of the pillar was hammer forged, whereas this similar process was not followed in Delhi iron pillar manufacturing as observed by Ananthraman et al.²⁷ see Table 2 for further details.

Indian ancient artefact (Thanjavur cannon)

“Thanjavur” was known in the world for sword making. The best example of sword technology is Tipu Sultan's sword (the famous emperor of India).^{28–30} Thanjavur cannon is known for its size and weight as it is considered as the world's largest cannon. It was made by forge welding manufacturing process and observed that the fabrication of parts was done individually as chamber and barrel, and later got joined together. Still the information about manufacturing technology of chamber is unclear in terms of pre- and post-processing technology. The effect of mechanical working on corrosion resistance of materials has been highlighted elsewhere,¹ see Table 3 for further details.³⁰ The following key aspects still remained unclear: (a) the mechanism of corrosion of cannon from materials processing point of view, (b) driving force for multilayer corrosion product formation and (c) location of Cl in the lattice of the corrosion product because phase evolution kinetics depends on the Gibbs free energy that justifies the phase stability, and therefore it is important for corrosion and materials scientists to develop an in-depth understanding on this phenomenon.

Indian ancient artefact (Vidarbha Cannon)

The cannon situated in western Maharashtra (India) is investigated by Deshpande et al.³¹ The authors speculated that rings were fabricated separately and later joined through forge welding. Similar observation was also made by Balasubramaniam et al.³⁰ for Thanjavur cannon as illustrated earlier in this review. These studies delineated the ancient cannon construction technology in India and established the forge welding as the manufacturing technology for cannon manufacturing. All the cannons were specifically designed with a large ring diameter. A large ring diameter offered high fracture toughness. Reddish-golden layer was observed on the surface, which was assumed due to the P in iron. Only pitting corrosion was observed in the atmospheric condition. We believe that this phenomenon happened due to the microsegregation of P in the presence of slag particles. Balasubramaniam³² noticed a sign of cannon ball that stroked on the DIP and observed originated several cracks around the hitting spot. No detailed corrosion studies are available yet and therefore are suggested as future study.

Ancient objects found in Vidarbha, Maharashtra, India were examined by Deshpande et al.³³ Layer structure was noticed and further indicated that no forging technology was followed. This is further confirmed by observing slag. Iron carbide particles were evident in metallography. Park and Shinde et al.³⁴ have investigated the iron from Vidarbha's cannon by using SEM and EDS. The presence of pearlite structure with fine interlamellar spacing that contains dispersed carbide particles (Fe_3C) is noticed. It is interesting to note that the morphology is found similar to the martensite (with low hardness than original martensite ($H_v = 438$ (H_v —Vickers hardness))). This is likely to be associated with post heat treatment such as tempering and quenching. Interestingly,

Vidarbha and South Korean (southern coastal area peninsula) irons are found the same (typologically and technologically). The ancient slag analysis done by Park et al.³⁵ has suggested the presence of wustite and fayalite. Fayalite is found with Ca; however, in Delhi iron pillar and Gupta Period, iron has not exhibited the presence of Ca. The EDS analysis remained consistent and depicted the presence of Ca and P. The presence of these elements has confirmed the different process of manufacturing followed in Delhi iron pillar and South Korean artefacts (southern coastal area peninsula), and therefore it is very likely that its degradation mechanism is expected to be different than other artefacts. XRD analysis of slag has also confirmed the presence of wustite, magnetite and fayalite; however, the amount of phase fraction has not been reported yet, which is required for developing the phase diagram of slags. Synchrotron XRD analysis is expected to be useful in determining secondary or segregated phases that are expected to be formed on iron as well as in slags. It is worth mentioning that basic atmosphere is required for removing P, but in this iron, P is present in slag along with the Ca. Therefore, it confirms that basic atmosphere was maintained in the furnace while iron making.³⁶

French artefacts (Amiens cathedral)

Medieval period's hypo-eutectoid steel from Amiens cathedral (13th century) was found suffering with atmospheric corrosion. Micro-XRD and Micro-Raman analysis were used for the investigation of phase and corrosion products' compositional analysis followed by macro EXAFS, which suggested the presence of maghemite, ferroxyhyte and ferrihydrite. Micro-Raman and micro-XAS (X-ray absorption spectroscopy) have further confirmed the analysis done by EXAFS. Micro XRF elucidated the presence of Cl at the crack site, whereas other elements were found dispersed in the rust. Localized segregation of Cl in the crack site is still not explained. Similarly Ca and S are found migrating towards the scale. Detection of P was presented as a challenge, and P insertion in ferrihydrite phase is not well explained; however, it is suggested that two situations are likely to occur: (a) stand-alone formation of ferrihydrite and (b) ferrihydrite and phosphate simultaneous precipitation; however, XANES analysis is found unable to confirm any of these hypotheses. We believe that application of synchrotron XRD (specifically in situ, with the application of Vegard's law³⁷) with simultaneous electrochemical examination can help researchers in this regard.

ARTEFACTS BURIED UNDERGROUND AND THE MECHANISM OF DEGRADATION (UNDER-DEPOSIT CORROSION)

In this section, artefacts excavated from the underground (buried in land) are reviewed, and the mechanism of their degradation process is discussed.

Delhi iron pillar and Eran's samples analysis

Delhi iron pillar is also encountered by under-deposit corrosion because a significant portion of the pillar is buried inside the ground. Various researchers have analyzed the rust from the top and bottom portion (buried underground), and rust was found with silica and clay. XRD examination has revealed the formation of gamma-FeOOH with alpha-FeOOH and $\text{Fe}_{3-x}\text{O}_4$. Ghosh et al.³⁸ cut the samples for metallographic analysis from the bottom portion of the iron pillar, which was then exposed to air for 1.5 years, and later Lahiri et al.³⁹ have used this sample for XRD analysis, which has confirmed the alpha- and gamma-FeOOH formation. In this way, researchers were able to get metallographic and corroded phase information. Alpha-, gamma- and delta-FeOOH were further confirmed by FTIR done by Balasubramaniam et al.⁷ The presence of Fe_3O_4 is deduced as a responsible factor for making the Delhi iron pillar protective enough for atmospheric

conditions. Kumar et al.¹⁷ have investigated the Eran ancient iron's rust that has confirmed the presence of crystalline magnetite (which appeared in diffraction), whereas the corrosion product of Delhi iron pillar ($\text{Fe}_{3-x}\text{O}_4$) has been found amorphous. Both the rusts were formed in the Gupta dynasty's iron, and therefore further analysis of rust by using modern sophisticated instruments, such as HRTEM with the EDS and EELS (electron energy loss spectroscopy), is expected to be useful for atomistic mechanism of under-deposit corrosion. These analyses would be helpful for understanding the insertion of foreign ion, such as P in the lattice of $\text{Fe}_{3-x}\text{O}_4$, which is observed through Mossbauer spectroscopy. Application of EXAFS is known to be useful for getting an idea of the occupied position in the lattice (in this case, P in the lattice of $\text{Fe}_{3-x}\text{O}_4$). Design of this new study would also be useful to understand the effect of dislocation and/or defects in the occupation of P in the lattice. HRTEM morphological analysis of the two different rusts from two different heritage sites (Delhi Iron Pillar and Eran iron object) would enable us to visualize the fundamental differences in terms of size and shape of the rust particles, including the differences in morphologies, particularly in the case of under-deposit corrosion. Insertion of foreign atom in the lattice is known for the strain development, and this phenomenon can be identified through Vegard's law (change in the lattice parameters) as discussed earlier in this review. Since oxygen exposure to Eran's iron clamp is more limited than the Delhi iron pillar (which is completely exposed to the atmosphere), formation of crystalline $\text{Fe}_{3-x}\text{O}_4$ in Eran's iron is expected; however, the driving force for this formation is still not clear. The mechanism responsible for this phenomenon of formation of crystalline $\text{Fe}_{3-x}\text{O}_4$ is not yet understood. Mossbauer spectroscopy is another technique, which is used to confirm the presence of $\text{FeH}_3\text{P}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ formation in Eran's artefact, which is earlier affirmed by using XRD. Eran's rust is found containing ferrous ion, whereas Delhi iron pillar is found with ferric iron (see Fig. 2(3) (a, b)).

Dillmann et al.⁴⁰ have used microprobe technique to analyze rust of ancient iron. Application of a microprobe is decided because (a) inhomogeneity in the composition of the Indian iron can be identified, (2) one of the corrosion products delta-FeOOH is formed as a discontinuous product and (3) ancient iron contains slag particles, commonly known as second-phase particles, which are known to be easily analysed by using microprobe techniques. For Delhi iron pillar, the role of slag particles is investigated in detail, and its effect on electrochemical performance through Evans diagram was examined. High exchange¹² current for cathodic reaction was noticed as shown in Fig. 2(4).

PIXE is used to investigate the trace-element analysis, and this technique has confirmed the P content, which was around 570–2300 ppm. Lower P is found just below the scale. Metal-slag interface contained high P. Micro-XRD detected goethite (alpha-FeOOH), magnetite and $\text{Fe}_2(\text{PO})_4\text{OH}$. This has confirmed the matrix site containing high P content, led to the formation of amorphous phases and the vice versa was also true. Another study of artefacts under-deposit corrosion is done by Balasubramaniam et al.¹⁰ for the Delhi iron pillar where analysis of the bell capital and main body joint is performed. The presence of lead (Pb) in the joint is reported. This provides an evidence of sound knowledge of Indian blacksmiths about joining technology. This is further confirmed through XRD, and phases like PbCO_3 , $\text{Pb}(\text{OH})_2 \cdot \text{H}_2\text{O}$ (lead carbonate hydroxide hydrate) and lead oxide carbonate (Pb_2CO_4),⁴¹ are obtained in diffraction pattern. Thermodynamic theory has also confirmed the formation of lead oxide carbonate as the corrosion product because of its low free energy of formation. Balasubramaniam et al.⁴² have also investigated the growth kinetics of passive film formation on Delhi iron pillar. This study provided the fundamental information about the presence of P in metal–rust interface, which happened due to the slag inclusion. This led to the protective film formation. The formation

of delta-FeOOH (amorphous) phase is assigned as a responsible factor for promoting high corrosion rates (initially). Various kinetics models such as parabolic law by Warnglen et al.⁴³ linear corrosion kinetics by Bardgett and Stanners⁴⁴ etc. were employed. Flaws associated with these models are (a) corrosion process, which occurred in Delhi iron pillar (DIP), is treated as unique throughout; however, this is not the case in real time. (b) Thickness of magnetite was selected as model film thickness, which was based on the assumption that magnetite is the most corrosion-resistant phase that formed in DIP, but this may or may not be true as consideration of phosphates may be argued. (c) Mass metal effect is another important area of concern. It is important to highlight that small coupons cannot be true representatives of 600 kg of iron pillar with 1800-cm² surface area. Therefore, following are the steps associated with the film formation in Delhi iron pillar: (1) formation of initial hydrated oxyhydroxides (high corrosion rate), (2) protective delta-FeOOH formation (low corrosion rate observation) and (3) formation of phosphate layer at the interface of rust and metal (low corrosion rate), and later crystallization of phosphate layer due to drying and wetting cycles (low corrosion rate).

The initial stage of corrosion is assigned by linear rate because the film was not found protective. The formed film was unable to prevent oxygen and moisture ingress. The challenge with the Delhi iron pillar's kinetic study was the formation of different rust with different thickness. Therefore, the use of a micromechanical model is a good option, which takes the porosity into account including composition, rust area etc. This model is described by Stratmann et al.⁴⁵ These parameters such as porosity, surface area, composition etc. are experimentally verified. Second-stage growth is explained by parabolic kinetic law and is described the diffusional phenomenon. Logarithmic law ($y = K \log t$) is another possible option for defining the later stage of corrosion process; however, this law is only found applicable in specific conditions, i.e. humidity < 50% and that is associated with diffusion of ion under an electric field (thin oxide film in non-aqueous environment).⁴⁶

Nydam Mose (Denmark) and Saint Louis (France) samples

Soheb et al.⁴⁷ have studied the two sites of iron, Nydam Mose (Denmark) and Saint Louis (France). No transformed media, such as soil contaminants, SiO₂ etc., were observed for Nydam Mose objects. The morphology for corrosion layers was measured 0.5–5-mm thick and remained the same for all the samples with the presence of Ca (0.5–4 wt%), P (< 1.5 wt%), S (< 1 wt%) and Mn (< 1 wt%). Siderite and goethite were identified as corrosion products; however, some poorly crystallized phases are also noticed. These poorly crystallized phases are assumed as either ferrihydrite or delta-FeOOH. Their formation mechanism under the exposure of soil is still unclear. The artefacts, which are received from the site named Saint Louis, exhibited the formation of iron hydroxycarbonate (Fe₂(OH)₂CO₃), which was assigned as the main corrosion product. Nydam Mose (Denmark) site's iron including Glinet's iron (Seine Maritime, France) was studied by Remazeilles et al.⁴⁸ The artefacts were found in anoxic environment and under high CO₂ partial pressure (0.1 atm at Glinet and 0.5 atm at Nydam Mose). The analysis has confirmed the presence of S-rich zone that was in contact with the porous, less-adherent rust layer. The micro-XRD and Raman spectroscopic results of Nydam Mose have elucidated the presence of FeCO₃. The presence of mackinawite, nanocrystalline FeS, goethite and Fe(III)-containing mackinawite were also confirmed in Glinet artefact samples.

Artefacts that were excavated from four excavation sites of France (which comprises different types of soils) were studied through micro-beam techniques. The analysis has elucidated the presence of Cl at the metal–rust interface. Micro-XRD and micro-Raman spectroscopic results were agreed about the formation of

beta-FeOOH (akaganeite) with 5–8% Cl (mass). The zone where Cl was present (15–20% by weight), formation of beta-Fe₂(OH)₃Cl was confirmed and verified by XANES (X-ray absorption near-edge spectroscopy). The edge shift towards the lower energy was observed, which was known to be an indication of phase transformation from beta-FeOOH (Fe(III)) to beta-Fe₂(OH)₃Cl (Fe(II)). In this study, formation of mixed Fe valency phases also appeared, which are thermodynamically not favourable. Therefore, a detailed investigation regarding the formation mechanism of metastable-phase formation is suggested to be performed in future because the driving force for formation still remains undescribed. Interface thermodynamics analysis is to be performed in the future for evaluating the impact of soil particles on corrosion process,⁴⁹ and the interface between the soil (including composition and humidity of soil) and artefacts (particularly the phases of artefacts) is described as an important field of investigation.

Glinet (France artefact)

The effect of soil on corrosion of iron was also observed for the artefacts excavated from Glinet (France). Characterization technique known as nuclear microprobe technique (with ¹⁸O) was utilized for the analysis of artefacts. Three samples were immersed into the distilled water with ¹⁸O (1.2 atm) for 4, 11 and 19 weeks. ¹⁸O was found to be increased in concentration at the metal–oxide interface. ¹⁸O is found migrated through the pores in the corrosion products and also supported the O reaction. Based on the experimental results, the dissolution of O in water (present in the pores of the corrosion products) is promoted as the potential corrosion mechanism as studied by Vega et al.⁵⁰ The effect of soil was examined for the artefacts recovered from French archaeological sites (Cabaret, Glinet, Mountbaron, Montreuil en Caux and Avrilly). The pH of the soil was measured for all the sites. Cabaret and Montbaron had a higher pH than the other sites, whereas the lowest pH was observed for Montreuil en Caux. All the steels were hypo-eutectoid steels with a heterogeneously distributed pearlite zone. The highest P content (at the crack, see Fig. 3(1)) was observed for Glinet whereas it was the lowest for Cabaret. The corrosion occurred through slag inclusion and grain boundaries. In the dense product layer, goethite and magnetite were assigned as the main corrosion products. Micro-Raman spectroscopy, micro-XRD and XANES were utilized for the dense product layer's characterization (see Fig. 3 (2)). The exact transformation kinetics in the second-phase formation with respect to soil properties is identified as a potential challenge. A study has explained the formation of carbonates, chlorides and oxyhydroxides as corrosion products.⁵¹ It is yet to delineate the corrosion-phase formation mechanism to the soil's characteristics.

German ancient artefacts (Anreppen Buttstadt)

Soil effects were also noticed in the case of German ancient artefacts excavated from Anreppen Buttstadt, Ladenburg, Pommern and Xanten.⁵² The soil properties were extensively studied, and varying particle size is extensively noticed in all the sites. Anreppen and Xanten have exhibited low silt and clay, whereas Buttstadt site has exhibited the high silt content with loamy texture. Weak alkaline soils were found in Buttstadt (rich in organics); Pommern and Ladenburg are known for exhibiting high electrical conductivity, whereas strong acids were found to be present in Anreppen and some Xanten site's artefacts. Chloride and sulfates were identified (as shown in Fig. 4). This study has concluded the highest corrosion rate for Ladenburg, whereas the lowest corrosion rate was for Buttstadt. Sandy sites such as Anreppen and Xanten exhibited more corrosion, which was further confirmed by Neff et al.⁵¹ In this review, authors have illustrated the segregation of Cl in cracks; however, the mechanism behind this phenomenon is yet to be discovered. Observation

Fig. 3 (1) Elucidated the P content on cracks at DPL.⁵¹ Reprinted with permission from ref. ⁵¹ Copyright 2005, Elsevier B. V. (2). DPL characterization of **a** Montreuil en Caux, **b** Cabaret and Montbaron, **c** Avrilly and **d** Glinet with the help of EDS/EPMA*, micro-XRD/micro-Raman**, micro-XANES***.⁵¹ Reprinted with permission from ref. ⁵¹ Copyright 2005, Elsevier B. V.

of corrosion products through scanning electron microscope and EDS (energy-dispersive spectroscopy) is presented as future study, which needs to be performed for confirming the presence of cracks and compositional variation at the crack site. Further investigation on the O incorporation (along with the valency that oxygen travels through the pores and sits on the pore at cracks in the corrosion layer) is required to be examined, which is known to be offered through cathodic reaction as mentioned earlier.

Usually carbonate and phosphate are known for decreasing the corrosion rate as described earlier in the case of Delhi iron pillar (DIP), but the artefacts obtained from Ladenburg are found containing significant amounts of phosphate and carbonate and offered severe corrosion. These phosphate and carbonate materials are assumed to be incorporated from the garbage deposition such as bones etc. (as the site is located in the urban area). The carbon dating of bones and other stuffs obtained from the near vicinity of the excavated sites is suggested to guide us about the origin of the phosphate and carbonate in the samples (whether they were inherently present on the soil or came through garbage and human activity in recent past).⁵²

Iceland artefacts

Viking Age Chieftain's farmstead (Hrisbru, Mosfeuvally, Iceland) is an archaeological site in Iceland, and various artefacts were excavated from this site. These artefacts are considered as highly corroded artefacts that were excavated from the church, surrounding grooves and the cremation site. Four knives were excavated from Longhouse, which contained extensive corroded layers, and therefore analysis by using metallography was not possible. Knife blade, which is excavated from church building, is found to exhibit the sandwich structure of wrought iron, which are welded together around high carbon steel. The sample underneath the church floor exhibited the Fe₃O₄ flakes that are considered as an indication of hammering scale. As illustrated

earlier, the sand composition, properties of sand (such as pH and conductivity), type of sand etc. are known to alter the corrosion kinetics, and therefore experiments are expected to investigate these factors in the case of Iceland's (as mentioned) ancient artefacts.⁵³

Egyptian artefacts

Under-deposit corrosion is also noticed in ancient Egyptian artefacts that are excavated from two burials in Gerzeh, northern Egypt.⁵⁴ Application of time-of-flight neutron diffraction (ToF ND) has elucidated no Bragg diffraction peak, and even the no sign of Fe was noticed. It is therefore concluded that the iron was heavily corroded. It is also assumed that the Fe was converted into iron oxide or hydroxide in the amorphous form. Prompt gamma-activation analysis (PGAA) has also been used, which exhibited the presence of Fe and O as the major components. The presence of iron as a major element along with Ni (5 wt%), and Cu, Pb, As, Zn and Mn as trace elements, is found to be confirmed by using PIXE. An effort was made to confirm the presence of iron phosphide phase, which is known to be a characteristic of meteoritic iron, but it was not possible. Surprisingly P content in the artefact was found significantly high (0.3 wt%), but still no phosphide was detected. Hammering and heating operations are assigned as responsible factors for no phosphide formation, and it is believed that Fe₃P got destroyed due to these operations.

Artefacts from Japan

Under-deposit corrosion is also evinced in the Japanese ancient artefacts, which are known as "Tetsutei", and were excavated from Nara (Uwanabe Kofun), Japan. X-ray tomography, which is a non-destructive technique, is used to locate the pits (as shown in Fig. 5), which are known to be occurred due to the pitting corrosion. XRD analysis has suggested the presence of goethite and

Fig. 4 Average degree of corrosion of artefacts excavated from the respective places.⁵² Reprinted with permission from ref. ⁵² Copyright 2000 Elsevier B. V.

magnetite that are identified as corrosion products; however, the mechanism of pitting is still unknown. Intriguingly, it was observed that 1 mm of rust layer had 0.35 mm of iron in the case of magnetite, whereas 0.14 mm for goethite including akaganeite and lepidocrocite.⁵⁵

ARTEFACTS EXCAVATED FROM SEAWATER AND RIVER SIDE AND THE MECHANISM OF UNDERWATER CORROSION

In this section, we have reviewed the artefacts that are excavated from the sea and river. The mechanism involved in artefacts' degradation process is discussed.

Artefacts from Switzerland

Two sword blades and iron slag products are received from the northern part of Switzerland, which are analyzed through X-ray microprobe analysis. These swords were excavated from the lake sites, Murten BE (known as water sword) and grave at Conthey Daillon VS. Similarly, slags are excavated from Naftenbach ZH. Intriguingly, the presence of Ni, As and P along with Fe in the water sword is confirmed. This study has highlighted the ancient piling technique where sandwich structure (alternate layer of soft and hard materials) is known to be built for designing the structures with good elasticity. Micro-EXAFS (extended X-ray absorption fine structure spectroscopy) is used for probing the oxidation state of As, which is identified to be present with reduced oxidation state. This brings as an interesting observation about the processing technology. Iron-manufacturing techniques (including furnaces), which are followed during the "Swiss Iron Age", are expected to provide exact information on the maximum operating temperature and conditions for Graveyard sword. P, As and Ni are further confirmed by using micro-XRF (X-ray fluorescence), which has confirmed the "di" oxidation states of these elements. The outer shell of slag is suggested the cold oxidation, whereas the inner shell of slag has been found indicating the hot oxidation. Mixed Fe valencies are observed, which is speculated as either the presence of mixed phases or the presence of mixed valency phase such as magnetite.⁵⁶

Artefacts from eastern Australia

Iron cannon, which was lying under the sea on the eastern coast of Australia for more than 225 years ago, is excavated in 1969. The cannon was found fully covered with corals, which were removed by using hammering that led to the detection of black corrosion layer formed at pH at around 8.0. The composition analysis has confirmed the presence of C (3.5 wt%), Si (0.5 wt%), Mn (1.1 wt%),

S (0.03 wt%), P (0.6 wt%) and Ti (0.04 wt%), and the material was identified as grey cast iron. The presence of Ti is uncommon nowadays in the grey cast iron. It is suggested that the corrosion occurred due to the formation of galvanic coupling between pearlite (anode) and graphite flake (cathode). It is observed that the pearlite started corroding and left the corrosion product. The whole phenomenon is noticed as graphitized corrosion. High Ca and chloride along with some sulfur-based products were found at the interface of cannon and coral rust that are found to contain Fe_3O_4 . The corrosion process is accelerated due to the sulfate-reducing bacteria (*Sporovibrio desulfuricans*). Carbon flakes are speculated as a catalyst for the formation of Fe_3O_4 .⁵⁷ The surprising aspect of the study is about the presence and the role of Ti in grey cast iron. It is important to unveil the iron-making technology followed in grey iron making. Similarly, it is also important to identify the post-processing heat treatment and mechanical processing that are used to make the iron corrosion mechanically compatible. Application of neutron tomography (for detecting the pores, pits and corrosion layer thickness) and neutron diffraction (for directional stress detection in order to identify the mechanical forming operation) are suggested as tools that are required to be used for investigating the hidden mechanism.

Artefacts from Israel

Underwater corrosion is also observed in the ship wreck excavated from Dor lagoon, Israel (1995). The microstructural observation has exhibited the presence of ferrite, pearlite and Widmanstatten ferrite-pearlite. Products are known to be made by using bloomer furnace that remained famous for wrought iron making during ancient era. The FeO (wustite) is observed as slag, and carburization of iron is confirmed by using Vickers hardness. Appearance of forging lines is exhibited in the iron artefacts that confirmed the type of mechanical forming process used.⁵⁸ Optical emission spectroscopy (OES) has suggested the compositional (chemical) similarities between both the anchors (with low Mn content) with the formation of equiaxed grains (as noticed for both the anchors). However, no directional orientation of grain is noticed, which is known to discard the possibility of forge-welding process. As observed, both the artefacts are found with a large amount of pearlite, which is known as the responsible factor for corrosion, and acted like an anodic site. It is found interesting to note the appearance of equiaxed grains of slag. The effect of slag in corrosion process is universally accepted.⁵⁹ Hence, improved corrosion resistance is expected to be achieved as a combination of grain boundary engineering, slag layer presence and surface treatment operation like carburization.

Artefacts from the United States

Christopher J McNamara designed a study to observe the effect of bacterial composition on the VSS Arizona, Pearl Harbor, Hawaii. This study has suggested a group of microorganisms such as flavobacteria and protobacteria as responsible for the corrosion of naval monument; however, detailed examination is required for investigating the mechanism of corrosion process of VSS Arizona.⁶⁰

Federated state of Micronesia artefacts

In situ corrosion studies are performed on world war (II) ship wreck and sunken aircraft (Chuuk Lagoon, federated state of Micronesia). The corrosion analysis has explained the iron decay that was dependent on the water depth (logarithmically) upto 20 m and was also found dependent on the dissolved oxygen flux. Localized corrosion and roughness were found to be correlated with the in situ pH measurement. Increment in the roughness with

Fig. 5 Pitting corrosion on the surface of Tetsuie.⁵⁵ Reprinted with permission from ref. ⁵⁵ Copyright 2008, Elsevier B. V.

decreasing pH is observed, which happened due to the oxygen flux.⁶¹

Artefacts from western Australia

Macleod et al.⁶¹ have studied the effect of heat on the microstructures of wrought iron of Rapid (1811) (which is a wrecked found on the northwest coast of Western Australia) and observed that the interior of the hook contained pearlite and ferrite phases. The inclusions are found segregated around the ferrite. The iron was described as containing P and due to the burning of oak timber. It is speculated that the iron phosphide is transformed into the phosphate ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), which is also noticed in the case of Delhi iron pillar as the corrosion product. The corrosion rate was found to be 0.042 mm/year (which was 60% lesser than the general decarburized iron). The presence of high P content, silica and decarburization can be assigned as responsible factors for improved corrosion resistance. The slag is found containing dual-phase FeO and $2\text{FeO} \cdot \text{SiO}_2$. An interesting aspect of this study is the formation of crystalline ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), whereas in the case of Eran (Gupta dynasty iron), phosphate was found amorphous as illustrated earlier in this review, whereas the crystalline phosphates were observed in the case of Delhi iron pillar, which is speculated due to the hydration–dehydration cycle. The following questions remain intriguing for the fundamental studies on the corrosion mechanism: (1) whether the temperature (developed due to the burning of oak timber) is the factor responsible for the phosphate formation? This is expected to be answered by using thermodynamic modelling of phase stability; however, exact heat development due to oak timber's heating is hard to be known, but a rough estimation is sufficient enough for unveiling this phenomenon: (2) what was the role of Si in phosphate formation? Did it act like a catalyst, as studied by Yang et al.⁶² This study has suggested the importance of Si/SiO₂ in the phosphate formation; however, the mechanism of corrosion product formation is still unknown. Detailed XPS and XANES studies are expected to unveil the role of Si in the phosphate

formation, which is not only an interesting aspect for ancient article's corrosion, but the study's outcome is expected to be valuable for catalysis, material science and process engineering.⁶³

Artefacts from Israel

Dor 2002/2 wreck is excavated from Mediterranean coast of Israel. The ring bolt was manufactured via forge welding, which was a technique followed in the case of Delhi iron pillar as described earlier. The metallography has elucidated the presence of significant amounts of slag inclusions along with the ferrite. Slag inclusions were oriented in one direction, surrounded by equiaxed ferrite matrix. Chain links are found in the iron oxide layer (as a corrosion product). It is interesting to note that chain links and ring bolts both contain significant amounts of P, i.e. 0.7–1.2 wt% and 0.2 wt%, respectively, which is also a characteristic of Indian Gupta's dynasty iron. Phosphate formation and corrosion resistance of these artefacts are not yet uncovered. Slags are found containing 5.2 wt% P including Si (5.7 wt%) and Mn (6.2 wt%). The chain link contained orange-brown corrosion product. The oxide layer is observed with cracks as also observed in the case of Glinet, Mountbaron, Montreuil en Caux and Avirity sites' excavated iron artefacts.⁵¹ P was observed in the cracks; however, the mechanism of crack formation in the corrosion product and P diffusion and/or segregation in the cracks are not well understood and required further experiments to be conducted. Signification of orientation, morphology and chemical composition of slag on the corrosion resistance are also required to be investigated.⁶⁴

Akko Tower wreck was excavated from Israel in 2012. Analysis of iron artefacts has exhibited the Fe and O in the corrosion product along with the P (0.5 wt%), Al (1.3 wt%) and Cl (2.4 wt%). Pure Fe contained 0.6 wt% P. However, role of P in the formation of phosphate is suggested to be confirmed by using XRD. Ian MacLeod et al.⁶¹ and Balasubramaniam et al.⁶⁵ have observed the crystalline phosphate formation and suggested mechanisms (oak wood burning and drying and weathering cycle), which are further to be confirmed by using complementary techniques done on different artefacts. The role of Cl in the formation of akaganeite phase is confirmed in some studies; however, the driving force of Cl and P segregation in the vicinity of cracks is yet to be confirmed. Application of XRD and Raman spectroscopy can be found useful in uncovering the hidden mechanism.⁶⁶

APPLICATION OF ADVANCED ANALYTICAL TECHNIQUES

In this section, we have listed out some important experimental and computation approaches that are assigned as useful techniques for ancient artefact's corrosion analysis (see Table 4).

CONCLUSION

This review provides information on the archaeometallurgical factors responsible for ancient artefacts' degradation. Artefacts suffered from various types of corrosion such as atmospheric corrosion, under-deposit corrosion, underwater corrosion etc. Numerous earlier studies were chosen in this review as examples to describe the degradation phenomenon in detail. The challenges in analyzing the artefact sample for probing the artefacts' degradation mechanism are described in detail, and future experiments are suggested for getting the mechanistic insight on the degradation of corrosion. Occasionally, fundamental questions are raised, which is expected to be useful in paving the future investigation direction in ferrous artefacts' degradation mechanism. Authors have suggested various analytical and computational techniques that can be used for investigating the degradation phenomenon of archaeological artefacts at various length scales such as at nano- and microscale.

Table 4. List of the techniques that can be used for different artefacts' corrosion investigation

Type of technique	Name of the technique	Role in finding mechanism/benefits	Limitation
Computational technique	Monte Carlo simulation ⁶⁷	X-ray Monte Carlo techniques can be used in the quantification of spectra; XRD spectrum with the simulation results can be useful for getting a mechanistic insight into the degradation phenomenon of the ancient artefacts	As XRD only reveals the crystalline phases, this technique limits to crystalline phases only
Computational technique	Finite-element modelling ⁶⁸	It is used in predicting the wreck degradation timeline of VSS Arizona. It is delineated that by 2020, 20% of hull steel will be lost, whereas by 2050, loss is expected to be 30%. By 2021, complete loss is expected. It is an excellent technique in assessing the risk of ancient artefact's degradation	The technique becomes difficult when more than one corrosion agent works (such as in atmospheric corrosion, microbial-influenced corrosion etc.)
Computational technique	Cellular automata	Useful in finding the mechanism of steel's oxidation. Possible to get information about the grain boundary diffusion of Fe in oxide layer. ⁶⁹ This tool is very useful in understanding the micro- and macro scale phenomena that occurred in corrosion such as morphology variation, preferential dissolution and development of active sites. ^{70,71} It is found useful in predicting pitting ⁷² corrosion and for predicting the roughness of the interface between metal and electrolyte depending on the reaction kinetics. ⁷³	This captures the phenomenon very well at the mesoscopic length scale, whereas finds difficulty in capturing microscopic and nanoscopic phenomena associated with corrosion
Computational technique	Other commercial techniques	Corrosion mitigation, change in the shape of substrate, electrochemical transport, reaction kinetics etc. can be investigated via the COMSOL package ⁷⁴	In-built equation creates a problem in defining the real system, although the interface user is friendly
Experimental technique	ToF–neutron diffraction	This technique can be used in getting the diffraction pattern at a fixed scattering angle. This is particularly useful for archaeological samples where samples have irregular shapes. This technique captures the simultaneous microstructural properties due to the deeper penetration depth of the neutron. Japanese armours, ⁷⁵ Greek coins, ⁷⁶ bronze artefacts ⁷⁷ (for texture analysis ⁷⁸) etc. have already been investigated by using this technique	It is not extensively surface sensitive, and therefore if the corrosion layer is very thin, then ToF–neutron diffraction would not be possible
Experimental technique	Deep proton activation analysis	Used in analyzing the chemical composition beneath the surface of the alloy. ⁷⁹ This offers minimum contribution from the surface and very limited use for ancient artefacts analysis	Long-term exposure makes the sample radiative. Surface composition would not be detected
Experimental technique	Prompt gamma-activation analysis	It is used in elemental analysis of big size and irregularly shaped archaeological samples. ⁸⁰ It is a non-destructive method	This may also cause radiation damage in the sample; radiation-induced transformation in the sample may take place. Experimental
Experimental technique	Peptide mass fingerprinting	The technique is not very popular; however, Caroline Solazzo et al. ⁸¹ have used peptide mass fingerprinting for the analysis of fibre products obtained from the corrosion layer of Cu alloy, which was buried in Mangolia, and delineated the potential of this technique in artefacts' corrosion investigation	Limited application (restricted upto fibre's product analysis)

It is necessary to understand the mechanism of corrosion of ancient artefacts to preserve those valuable artefacts. Archaeometallurgical characterization would not only provide the mechanism of their degradation but also assist to design the policy of conservation as elucidated in this review.

In summary, (a) mechanistic studies at various length scales on the archaeometallurgical degradation phenomenon are necessary to prevent the degradation of the historical monument and to design the conservation strategies. (b) Challenges such as radiation damage (activation of samples and heating) of the sample, instrumental artefacts development etc. are required to be taken

into account while designing experiments with intense beams such as synchrotron and neutron beam lines. (c) Instrumental limitations are to be known before performing experiments, such as many characterization methods include sophisticated sample preparation such as for TEM, XPS, etc. (d) Enormous opportunities exist in archaeomaterials' degradation mechanism investigation by using advanced surface and spectroscopic characterization, including in situ methods and modelling at different length scales.

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D.D. has designed the contents and wrote the paper, obtained necessary permissions. J.M. has provided supervision, read the paper and provided an expert opinion.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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