

Cambridge University Press

978-1-107-63525-8 - The Preservation of Antiquities: A Handbook for Curators

Dr Friedrich Rathgen

Excerpt

[More information](#)

PART I.

THE CHANGES UNDERGONE BY ANTIQUITIES IN EARTH AND IN AIR.

THE greater number of those objects of antiquity which are composed of inorganic materials, such as limestone, earthenware, and metals, owe the commencement of any alteration in their character to the situation in which they are discovered, since they are buried in ground which has been at some period damp or wet, and has contained, moreover, salts soluble in water. Amongst these salts the most usual is sodium chloride (common salt), but this is mostly accompanied by potassium chloride, potassium sulphate, magnesium chloride, and calcium sulphate; in short, by those soluble salts which are found in sea-water. In the fine pores of Egyptian antiquities, especially, such salts occur, and their presence is readily explained by the fact that the land of Egypt was originally a sea-bottom.

The presence of salt in the soil of Egypt has been known for a considerable period. Thus Karabacek¹, quoting from Volney's "Travels in Syria and Egypt" (Jena, 1788, i. p. 13) :

"Wherever one digs one finds brackish water containing soda, sea-salt, and a small quantity of saltpetre. Indeed, when a garden has been flooded for irrigation

¹ "Mittheilungen aus der Sammlung der Papyrus Erzherzog Rainer." Vol. I. p. 118. See also Flinders Petrie, *Archaeological Journal*, Vol. XLV. 1888, p. 88.

Cambridge University Press

978-1-107-63525-8 - The Preservation of Antiquities: A Handbook for Curators

Dr Friedrich Rathgen

Excerpt

[More information](#)

2

THE PRESERVATION OF ANTIQUITIES

purposes, crystals of salt make their appearance on the surface after the water has evaporated or has been soaked up by the soil.”

In the dry climate of Egypt, objects saturated with salt keep better after their removal from the ground than in our climate, where the variations in the temperature and in the hygroscopic condition of the air produce a partial deliquescence in wet weather, and in dry weather a re-formation of crystals. The continued alternation of these processes gradually loosens the surface of limestone or earthenware, or induces certain chemical changes in objects of metal and in both cases leads to their destruction.

LIMESTONE AND CLAY.

The series of changes are particularly well illustrated by the Egyptian grave of Meten¹, the stones from which are now in the Royal Museum in Berlin. The three illustrations here given show: (1) an undecayed block of limestone, (2) a block with pitted surface, and (3) a block the surface of which was formerly covered with hieroglyphics, but which is now totally destroyed by flaking. The blocks of the latter kind were found in the lowest layer, or lowest but one, while those blocks which were above were the best preserved. As the amount of salt present scarcely varied, these specimens

¹ Aeg. 105. [This and similar notes have reference to the catalogue of the Egyptian (Aeg.) or Antiquarian (Ant.) sections of the Berlin Royal Museums.] The limestone blocks were brought from the Mastaba of Meten, at Abusir near Memphis, explored by Lepsius in 1846. Meten was one of the chief officials under King Snefru, B.C. 2800. The inscriptions relate to his possessions and official career, while the pictorial representations depict hunting scenes and the offering of the gifts for the dead. The statue of Meten was found in the grave and is now in the Egyptian department (No. 1106) of the Royal Museum. Comp. "Ausführliches Verzeichniss der aegyptischen Alterthümer," Berlin, 1899.

Cambridge University Press

978-1-107-63525-8 - The Preservation of Antiquities: A Handbook for Curators

Dr Friedrich Rathgen

Excerpt

[More information](#)



FIG. 1.

Limestone block, surface well preserved.



FIG. 2.

Limestone block with pitted surface.

1—2

Cambridge University Press

978-1-107-63525-8 - The Preservation of Antiquities: A Handbook for Curators

Dr Friedrich Rathgen

Excerpt

[More information](#)

4 THE PRESERVATION OF ANTIQUITIES

offer a striking illustration of the greater influence of moisture in the deeper soil than at the higher levels.

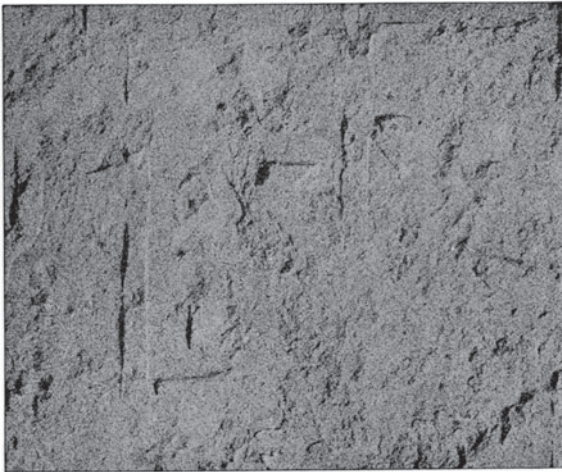


FIG. 3.

Limestone block showing destruction of surface.

Baked clay, particularly that of Egyptian ostraca (i.e. fragments of pottery showing inscriptions), exhibits similar changes, as is shown in the accompanying illustrations. The surface of some fragments is found to be almost completely covered with a layer of salt, which, apart from impurities of clay and dust and remains of the black lettering, consists of almost pure sodium chloride; only a trace of magnesium sulphate being found on analysis.

In contrast with this very loose superficial incrustation, the inner portions of the ostracoon contained considerable quantities of sulphates. Figure 4 represents a fragment

Cambridge University Press

978-1-107-63525-8 - The Preservation of Antiquities: A Handbook for Curators

Dr Friedrich Rathgen

Excerpt

[More information](#)

LIMESTONE AND CLAY

5

with granular efflorescences of sodium chloride, and also fine needles of magnesium sulphate¹. As a general rule the amount of salt is small compared with the bulk of clay or limestone: thus it was found by titration that three separate fragments contained 0.13, 0.20, and 0.48 % calculated as sodium chloride, and in one series the average of 16 fragments



FIG. 4.

Potsherd showing saline efflorescence of sodium chloride and magnesium sulphate.

was 0.13 %. But the percentage of sodium chloride has often been found higher, more especially in larger objects of baked clay, being in one instance as high as 2.3 %. The disintegration of the surface is due to the mechanical action of moisture which results in the scaling off of portions of the

Aeg. P. 4730.

Cambridge University Press

978-1-107-63525-8 - The Preservation of Antiquities: A Handbook for Curators

Dr Friedrich Rathgen

Excerpt

[More information](#)

6

THE PRESERVATION OF ANTIQUITIES

surface. This does not however exclude a chemical action of the salts upon the clay, especially when this has been only slightly baked. Thus by merely washing such fragments in cold distilled water, not only sodium and magnesium compounds but also those of aluminium and calcium may be removed. The soft powdery patches, which some limestones show instead of scales, are also evidences of chemical action; thus in one case a cuneiform tablet¹ of dolomitic stone showed decomposition at those spots where the salt was firmly deposited as an incrustation, and here the stone, elsewhere smooth and hard, was found, on washing away the salt, to be soft and porous.

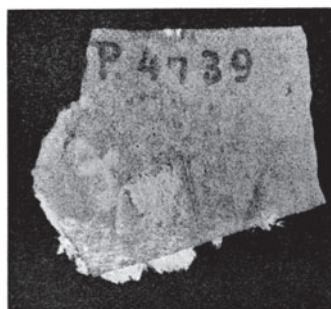


FIG. 5.

Pottery showing efflorescence of sodium nitrate.

Although, as has been already remarked, sodium chloride generally constitutes the bulk of the salts present, and only in rare cases, as I have for instance shown in an Egyptian Fayence and in several Greek clay vases, is the amount of sulphates greater, yet there are in collections clay objects (Fig. 5) covered with needles of sodium nitrate² (Chili saltpetre) where

¹ Aeg. V. A. 2846.² Aeg. P. 4739.

Cambridge University Press

978-1-107-63525-8 - The Preservation of Antiquities: A Handbook for Curators

Dr Friedrich Rathgen

Excerpt

[More information](#)

IRON

7

the nitric acid has been contributed by the decomposition of organic substances; and here the presence of nitrates proves inimical to antiquities just in the same way as a coating of limewash may be seen to be destroyed by the so-called wall-saltpetre¹.

IRON.

If in some cases it may be uncertain whether the destruction of antiquities of limestone or earthenware has been due to mechanical or to chemical influences, this uncertainty is excluded in the case of metallic objects, of which those of bronze and iron chiefly come under the notice of the antiquary.

From the first piece of metallic iron which he possessed man must have soon become acquainted with its untoward property of rusting, but even at the present day opinions differ as to the origin of rust, and the cause of its rapid spreading. It has long been known with certainty that iron containing but little carbon (wrought iron) rusts with greater ease than iron which is rich in carbon (cast iron or steel), and that the rust is a compound of iron with hydrogen and oxygen (hydroxide). That rust is of variable composition may be inferred from the variations of shade from yellow to dark brown which are met with.

Widely different views are held on the question of the production of rust. Some² maintain that iron rusts only in the presence of water containing free oxygen and carbonic acid (CO₂) in solution, a ferrous bicarbonate being first formed; the bicarbonate is then converted into ferrous carbonate, which finally yields the hydrate with evolution of

¹ It may be here mentioned that, as is well known to chemists, the efflorescences which often go by the name of "wall-saltpetre," in most cases do not contain any saltpetre, but consist of sodium sulphate.

² Crum Brown, "Chem. Centralblatt," 1890, i. p. 212; E. Simon, "Ueber Rostbildung u. Eisenanstriche," p. 4.

Cambridge University Press

978-1-107-63525-8 - The Preservation of Antiquities: A Handbook for Curators

Dr Friedrich Rathgen

Excerpt

[More information](#)

carbonic acid. This carbonic acid continues to attack further areas of metallic iron. Others¹ maintain that, while the formation of rust *may* proceed as described, carbonic acid is not necessary, and that free oxygen *alone* causes rusting when atmospheric moisture is condensed upon the surface of iron. That iron remains free from rust when in a solution of caustic potash or soda is said to be due to the absence of free oxygen and not to the removal of carbonic acid. Spennrath holds, in opposition to the opinion of Axel Krefling², that rust once formed cannot act as an oxidising agent, except by virtue of its power of condensing water and retaining it in its pores. Similarly E. Simon finds the chief cause of the corroding action of rust in the property of absorption, that is surface-condensation of gases. This condition is comparable to that of liquefaction, and produces rapid chemical action. Under certain circumstances ferrous hydrate is formed instead of ferric hydrate, particularly when iron is subjected to vibrations, as Tolomei³ has observed in iron rails etc. Stapff⁴ believes that mixtures of ferric hydrate with ferroso-ferric oxide, which possess a similar composition to forge scale, are formed under the influence of thermal waters. According to Irvine⁵ rusting proceeds rapidly when two kinds of iron, such as cast and wrought, are in contact, since their electro-chemical relations may result in a voltaic couple. The electric current brings about the decomposition of the water, and the evolved hydrogen, being in the nascent state, combines with the nitrogen dissolved in the water to form ammonia, as had

¹ J. Spennrath, "Verhandlungen d. Vereins zur Beförd. d. Gewerbeleissens," 1895, p. 245.

² "Christiania Videnskabs-Selskabs Forhandling" for 1892, No. 16, p. 8.

³ "Chemische Zeitung. Repetitorium," 1895, p. 289.

⁴ "Chem. Centralblatt," 1895, i. p. 441.

⁵ Id., 1891, i. p. 860.

Cambridge University Press

978-1-107-63525-8 - The Preservation of Antiquities: A Handbook for Curators

Dr Friedrich Rathgen

Excerpt

[More information](#)

FORMATION OF RUST

9

been previously observed by Akermann¹. Similarly, electric currents are said to be caused by the contact of ferroso-ferric oxide with metallic iron, thus causing a further oxidation of the iron².

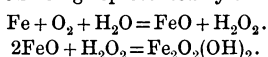
¹ "Berg- und Hüttenmännische Zeitung," 1882, p. 469.

[² It may not be out of place here to give the main conclusions, drawn from a long series of experiments by Prof. W. R. Dunstan ("Proc. Chem. Soc.," xix. 150, 1903).

(a) Pure iron is not oxidised in the presence of gases and water-vapour only, but for the appearance of rust the presence of water in the liquid state is necessary.

(b) The reagents which prevent the rusting of iron are those in the presence of which hydrogen peroxide is decomposed, and which are consequently inimical to its formation: among such reagents the following are given—sodium chloride, sodium sulphate, ferrous sulphate and potassium nitrate.

(c) The action of H_2O_2 on metallic iron leads to the production of red basic ferric hydroxide, which is identical with ordinary rust. The composition of rust may therefore be represented by the formula $\text{Fe}_2\text{O}_2(\text{OH})_2$, the reaction being represented by the equations:

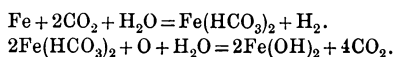


These views are however combated by Moody ("Proc. Chem. Soc.," xix. 157 and 239) who concludes that aerial rusting must be regarded as a change involving the interaction of iron and carbonic acid and the subsequent formation of rust by oxidation of the ferrous salt.

He also states that those salts which do not combine with and which are not decomposed by CO_2 have no retarding influence on the formation of rust, e.g. sodium chloride, sodium sulphate, etc.

On the other hand substances which absorb and combine with carbonic oxide (e.g. sodium carbonate or hydroxide, ammonium carbonate, calcium hydroxide), or which are decomposed by carbonic acid (potassium and sodium nitrites), inhibit rusting, which may therefore be regarded as a change involving the interaction of iron and acid and the subsequent formation of rust by the oxidation of the ferrous salt.

O. Kröhnke ("Wochensch. Brauerei," xvii. 233) gives the following equations:



Cambridge University Press

978-1-107-63525-8 - The Preservation of Antiquities: A Handbook for Curators

Dr Friedrich Rathgen

Excerpt

[More information](#)

The presence of certain neutral salts, especially sodium chloride (common salt), has a very marked influence on the destruction of iron¹.

When iron filings are exposed to air and moisture, oxidation takes place; the action is, however, according to Krefting, far more intense in the presence of an alkaline chloride. A mixture of iron filings and sodium chloride exposed to moisture is converted in a few days into a black powder which has the following composition:—11.4% FeO, 80.0% Fe₂O₃, 8.6% H₂O, thus resembling the “iron-black” of Lemery; on extraction with water the filtrate is found to be alkaline

Comp. also Dammer, “Handbuch der anorg. Chem.,” Vols. III. and IV. (supplement).

Considerable attention has also been directed to the influence of bacteria upon iron. Thus the growth of *Crenothrix* may cause much trouble in waterworks, vide “Centralblatt für Bakterien und Parasitenkunde,” II. 12, 681. A variety, *Chlamydothrix* (*Gallionella*) *ferruginea* (Mig.) appears to play an important part in the formation of rust (comp. Zopf, “*Crenothrix polyspora* die Ursache der Berliner Wasser-Calamität,” Berlin, 1879. De Vries, “Unter. der *Crenothrix* Commission,” Rotterdam, 1887 and 1890).

Neufeld (“Chem. Centralblatt,” 1904, I. 1621—abstracted from “Zeitschrift für Untersuchung der Nahrungs- und Genussmittel,” VII. 478) gives particulars of three varieties: *Crenothrix polyspora*, which separates iron; *Cr. ochracea*, which separates aluminium and some iron; and *Cr. manganifera*, which separates manganese.

Jackson (“Journal of Society of Chemical Industry,” 1902, p. 681) gives micro-photographs of these varieties. Microscopically the masses of *Crenothrix* are seen enclosed in a gelatinous sheath, in which is imbedded the precipitated metallic hydrate. It is anaërobic and its action is favoured by absence of light. In the absence of dissolved oxygen, the bacillus appears to take its iron from the pipes. *Cr. polyspora* is found however (“Zeitschrift für analytische Chemie,” XLII. 590) to separate the iron not from the ferrous carbonate (FeCO₃) but from iron organically combined. See also Winogradsky, Ueber Eisenbakterien, “Bot. Zeit.,” 1888, and “Chem. Centralbl.” 1904, II. 1332. Transl.]

¹ Wagner in Dingler’s “Polyt. Journal,” CCXYIII. p. 70. Axel Krefting in the above-quoted “Forhandlinger,” p. 4.