LITERARY SURVEY ON CORROSION AND CORROSION PRODUCTS OF COPPER AND BRONZE OBSERVED IN ANCIENT ARTIFACTS

BY

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ABSTRACT

Copper is the most important of early metals since it could be alloyed with Sn and Sb to produce bronze. Bronze is a hard metal and was the first practical metal to be used for tools. Ancient artifacts have been exposed to different environments for very long times, as a result of which they have gone under considerable changes due to the surrounding factors. The corrosion and corrosion deposits formed by the corrosion process are stated to have resulted in formation of define minerals. A list of minerals identified in ancient copper and bronze artifacts is given. Conditions and mechanisms leading to formation of such minerals are described. Literary information has been put together.

A list of a considerable number of studies on corrosion of ancient copper and bronze artifacts is appended.

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INTRODUCTION

Archaelogists who find the remains of metal artifacts buried in the soil or immersed in water have observed the wide variety of products that encrust their surfaces. These encrustments are caused by the chemical interaction of the metal with the corroding agencies of soil, air and water. Many generations of different specialists have been concerned with the nature of these products. A few chemists have investigated metal corrosion crusts, and have been impressed by their diversity and complexity. Mineralogists have observed in the corrosion crusts crystalline compounds identical with the minerals of the earth's crust. Information about these inorganic mineral products in corrosion crusts is scattered far and wide in the scientific literature and in unpublished notes in museum files and laboratory notebooks.

The term "mineral" is used to designate the chemical elements or compounds occurring in the earth's crust as a product of natural inorganic processes. Minerals have more or less constant chemical composition and characteristic atomic structure, and hence characteristic crystalline form and physical properties.

The metals found in the ores of the earth are in a state of relative stability in respect to their environment. After these ores are reduced to a metallic form, they are used either in a pure state or as alloys. Being used for different purposes the metal reacts with its environment. Only with the more precious metals which are found in the placer state is there assurance that the metals will not corrode. Given the proper environment, any metal will corrode, for every metal resists attack by certain reagents and is prone to deterioration by others.

Corrision is the chemical and electrochemical reaction of the metal with its environment, which reaction may result in compounds brought about either by the destruction of the metal or to form a protective film of the most stable compounds of the metal.

In many cases minerals are formed which are duplicates of those found in nature, and serve as a protective coating of the basic metal. This is particularly true in works of art.

The mineral crusts on ancient objects are important for a number of reasons. Under certain circumstances the mineral alternation product formed on a metal adds interest and even beauty to an object. The artistic term "patina" is applied to the colorful, thin, but continuous corrosion films that form on the surface of copper and its alloys giving evidence of age and long use. I would like to quote here, H. J. Plenderleithe (1938 - 39) "... patina is a form of incrustation which is stable under normal conditions of temperature and humidity, is protective in proportion as it is hard and non-porous, and has often an aesthetic appeal in accordance with its hue or the play of colors of the minerals of which it is composed". Green and red patina on ancient bronzes is so admired that it is sometimes produced artificially on recent made objects to simulate appearance of age and authenticity. Unfortunately, however, most corrosion products on metals are ugly and disfiguring. Rust on iron and tarnish on silver have little appeal. Even copper and bronze are unattractive when covered with chloride-bearing corrosion crusts. The corrosion crusts are bearers of valuable historical and scientific information. In the mineral shell there may be evidence of metal composition, of age, and even of place of origin. The corrosion products sometimes have a layered structure containing two or more distinct minerals in which the outer more stable compounds can serve as natural protective coatings for less stable compounds lying beneath. Also,they may contain rare minerals unknown or little known to science.

Corrosion is usually regarded as destructive and undesirable. But it also has another side which is the constructive one. A glance at history shows that corrosion has stimulated much useful science and has been central to many useful processes. For example, corrosion products were used as pigments, inks and mordants, also removing superficial layers of products of prior corrosion, e.g., in pickling tarnished or heat blackened metals; "depletion guilding"; the chemical coloring of bronze, to roughen or to smooth a surface for decorative or technical purposes. Our knowledge for these processes comes from examination of archaeological objects and some ancient writings.

Being interested in ancient metal artifacts, i.e., their chemical composition, technological production, use and to some extent conservation and restoration problems, I decided that it would be appropriate for me to get acquainted with the literature on corrosion. I limited myself to the corrosion and corrosion products of copper and its alloys found in archaeological objects. The natural corrosion of copper and its alloys is also called natural patina.

The purpose of this project is an attempt, as far as possible, to put together and discuss and summarize different features on the nature and structure of natural patinas. I have been concerned mainly with literature that deals specifically with patinas, from mineralogical, physical and chemical points of view and also with mechanisms of corrosion reactions and influences of different environments.

The process used to generate the desired information was built around a two-fold approach which is reflected in the organization of the report. Initially, the phenomenon of corrosion was studied from scientific point of view, describing the mechanisms of the corrosion of copper and its alloys. The second part of the project deals with the corrosion products and their specific environments, where they occur relating in particular with ancient artifacts. Also, some techniques for studying corrosion are mentioned. The appendix includes the extra literature, not included in the references and some micrographs on corrosion products observed in the Laboratory for Research on Archaeological Materials at MIT.

CHAPTER I

HISTORY OF CORROSION

The ancient metallurgists were well aware of corrosion and they recognized that some metals are more stable than others, and also try to prevent the formation of corrosion products. Our literary information is based on Pliny's Natural History, in which one finds a description of oiled bronzes. (cf , Oliver, A. 1967): "In antiquity the appearance of the head of the boy was quite different, possessing then the golden color of bronze, and it was surely oiled - as the Roman writer Pliny said bronzes were - to prevent the surface from becoming tarnished)". Also, we find other statements made by Pliny.

The following are some quotations from Pliny's book:

XXXV.182 "Bitumen is used for staining copper and bronze and for casting statues. Smiths varnish iron and the heads of nails with bitumen."

XXXIV.160 "When copper vessels are coated with stagnum (alloy of silver and lead).... the formation of destructive verdigris (aerugo) is prevented."

XXXIV.99 "Copper or bronze objects become covered with copper rust more quickly when they are kept clean than when they are neglected, unless they are well greased with oil."

Corrision being a very complex subject and calling for a knowledge of many branches of natural sciences, there was little work carried on until the scientific period which began in the early 19th century.

The first explorator of the phenomena of corrosion is considered to be M. V. Lomonosov. At this time Stahl explained the oxidation of metals at elevated temperatures by the loss of "phlogiston" and Boyle, by combination with some material in the flame that, in his opinion, had the property of penetrating even the walls of retorts. Lomonosov, in 1756[1], conducted a strictly scientific experiment (accurately weighed metal heated in a sealed retort to a high temperature), which he described as follows:

"I conducted experiments in tightly sealed glass vessel to determine whether the weight of metals increases by heat alone. It was found that Robert Boyle's contention was false and that with exclusion of outside air, the weight of heated metal remains constant".

Lomonosov then stated that after heating the metal and opening the retort, air enters and increases the weight.[2] This proved that increase in weight of a heated metal is caused by its combination with air[3] and that the phlogiston explanation or that of the combination with some matter in the flame are not true. Seventeen years later in 1773 Lavoisier repeated these experiments and proved that the oxidation of metal is a chemical union of the metal with the most active element in the air, oxygen.

In his scientific work Thesis on the Action of Chemical Solvents in General (1743-1750), Lomonosov was the first to make broad systematic experiments on the study of the action of acids (nitric and hydrochloric) on metals (Ag, Cu, Fe, Au and others). He pointed out the high chemical resistance of the noble metals in comparison with the non-noble ones, he also described the passivation of iron in nitric acid. In 1790, J. Keir investigated and described in more detail the phenomenon of passivation of iron in nitric acid.

Austin in 1788 made a statement in which he stated that an originally neutral water tends to become alkaline during the corrosion process.

The first scientific study made by Sir Humphrey Davy in 1824, showed that sea water does not affect copper in the absence of oxygen. He proposed an electrochemical method using zinc protectors for preventing corrosion of cooper sheathing on ships bottoms.

In 1838, Mallet gave an electrochemical interpretation of corrosion.

Faraday (1830-1840) established a very important relationship between the amount of anodically dissolved metal and the current produced thereby. He also proposed the film-forming mechanism in the passivation of iron and the electrochemical nature of the processes of metal dissolution.

The actual science of corrosion, however, was formed at the beginning of the present century, and particularly in comtemporary times. A host of important works established the laws governing the electro-chemical mechanisms of corrosion. The names of the most prominent scientists are mentioned either in the references or in the appendix.

During the period between 1935-1955 societies of corrosion engineers were founded throughout the world. Books have been written, magazines and journals have been devoted entirely to the science of corrosion. It is a fast growing science and the underlying electrochemistry is already well understood.

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1. Menshutkin, B. N., The Biography of M. V. Lomonosov, Moscow: Academy of Sciences, 1947
2. The supposition of the nature of oxidation of metals was first explained by Lomonosov in a letter to L. Euler on July 5, 1748.
3. The complex composition of air had not yet been established at that time.

CHAPTER II

DEFINITIONS OF CORROSION

The term corrosion, as applied to metals as a precise definition, presents many difficulties and is, indeed, still a subject of controversy. In the case of non-metallic materials, "corrosion" invariably refers to their deterioration from chemical causes, but a similar concept is not necessarily applicable to metals.

Many authorities[1] consider the term "metallic corrosion" to cover all interactions of a metal (solid, liquid, or alloy) with its environment (non-metallic or metallic). This definition includes both the deliberate and profitable corrosion of a metal and its spontaneous deterioration and is referred sometimes to as the "transformation" definition. However, other authors of works on corrosion[2] have in general confined themselves to the consideration of the behavior of metals used in construction materials. The above definition of corrosion can be reformulated as all processes whereby a metal or alloy which is used as a material of construction is transformed from the metallic to a combined state by interaction with its environment.

Although there are obvious exceptions (e.g., the reaction of uranium fuel elements with carbon dioxide, formation of oxide films on molten metals, corrosion of objects d'art, etc.) it is considered that this definition is applicable to the majority of cases treated in a work of this nature.

On the other hand, corrosion has been more exclusively defined as "the undesirable deterioration" of a metal, i.e., an interaction of the metal with its environment which adversely affects those properties of the metal which it is desired to preserve[3]. This definition can be referred to as the "deterioration" definition- is also applicable to non-metallic materials, and embodies the popular conception of corrosion as a process which is always harmful and which demands prevention or control. The restriction of the definition to undesirable transformations has some limitations. This can be shown with the following examples. Iron when exposed to an industrial atmosphere reacts to form a loosely adherent reaction product (i.e., rust, $Fe_2O_3H_2O$) which is relatively unprotective, as it does not form an effective barrier between the metal and the environment. Copper, on the other hand, in this environment forms an adherent protective green patina (i.e., brochantite, $CuSO_4.3Cu(OH)_2$). If thin sections of iron were used, for example, as roofing sheet, it would become quickly perforated, whereas copper roofs installed 200 years ago are still performing satisfactorily. Clearly the formation of brochantite is not harmful to the function of copper as a roofing material - indeed, in this particular application it is considered to enhance the appearance of the roof, although similar patina on copper water pipes would be considered objectionable.

It follows from the "transformation" definition that any reaction of a metal with its environment must be regarded as a corrosion process irrespective of the extend of the reaction or of the rates of the initial and subsequent stages of the reaction. In deciding whether the corrosion reaction is detrimental to a metal in a given application the precise form of the attack on the metal (general, localized, intergranular, etc.), the nature of the reaction products, and the velocity and extent of the reaction must be taken into account.

Corrosion reactions are not always detrimental - the employment of many of the common and less-common reactive metals in certain environments is made possible by the formation of a thin film of corrosion product which interposes a barrier between the reactants so that the rate of the subsequent reaction is very slow. Expressions such as "preventing corrosion", "combatting corrosion", or even "fighting corrosion", are misleading, with the majority of metals, corrosion cannot be avoided and "corrosion control" rather than "prevention" is the desired goal.

It is necessary to observe that the scope of the term corrosion is continually extended. It is now considered that the term is applicable to certain solid/liquid metal reactions. Vermilyea[4] defined corrosion as a process in which atoms or molecules are removed one at a time, considers that evaporation of a metal into vacuum should be included in the definition as, atomically, it is similar to the other corrosion processes.

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CHAPTER III

MECHANISMS AND FACTORS IN THE FORMATION OF CORROSION PRODUCTS OF COPPER AND BRONZE

The subject of metallic corrosion is highly complex, and the understanding of the various phenomena involve many branches of pure and applied sciences. The mechanism of the corrosion process is considered to be of chemical and electro-chemical action. The gradual destruction of metals by mechanical wear or abrasion is termed erosion. The word corrosion comes from the Latin Corrodere, to gnaw away.

There is vast literature available on the subject of corrosion, treating it form various points of view. This project is concerned only with the basic characteristics of corrosion of copper and its alloys, found in ancient artifacts and reported in the literature.

1. General Information about Copper and its Alloys

Copper and copper alloys are among the earliest metals known to man, having been used from prehistoric times, and their importance at the present time is probably greater than ever. Their wide spread use depends on a combination of good corrosion resistance in a variety of environments, excellent workability, high thermal and electrical conductivities, and attractive mechanical properties at low, normal, and moderately elevated temperatures.

Copper is the first member of Group IB of the peridic table, having atomic number 29 and electronic configuration 2.8.18.1. Loss of the outermost electron gives the cuprous ion Cu^{+}, and the second electron may be lost in the formation of the cupric ion Cu^{2+}. Copper occurs in the uncombined state in nature and it is relatively easily obtained by the reduction of its compounds. It is not very active chemically and oxidizes slowly in air at ordinary temperatures. In the electro-chemical series of elements, copper is near the noble end and will not normally displace hydrogen, even from acid solutions. Indeed, if hydrogen bubbled through a solution of copper salts, copper is slowly deposited (more rapidly if the process is carried out under pressure, due to the thermodynamic considerations.). As copper is not inherently reactive element, it is not surprising that the rate of corrosion, even if unhindered by films of insoluble corrosion products, is usually low. Nevertheless, the breakdown of a protective oxide film on copper is not likely to lead to such rapid attack as with a more reactive metal such as say, aluminum. In practice the good behavior of copper (and more particularly of some of its alloys) often depends to a considerable extent on the maintenance of a protective film of oxide or other insoluable corrosion products. Many of the alloys of copper are more resistant to corrosion than is copper itself, owing to the incorporation either of relatively corrosion-resistant metals, such as nickel or tin, or of metals such as aluminum or beryllium, that would be expected to assist in the formation of protective oxide films.

The corrosion of metals is not only a serious industrial problem and a household nuisance but is also an interesting chemical pheonomenon. It is often a complicated process which produces several distinct products in intimate juxtaposition. Some of the best samples of the complexity of this process have been observed in the corrosion layer of bronze vessels and utensils excavated from the early graves of China. The diversity of copper and tin compounds disposed in the layered structures on their surfaces testify to the numerous factors that must enter into the formation of the mineral products. To the collector these structures and products are of interest, because their color and texture frequently enhance the value and reflect the age and authenticity of a piece, chemists and metallurgists study old bronze objects also because the formation and distribution of the corrosion products give information about the corrosion mechanism.

2. Corrosion Mechanism and Factors in the Formation of Corrosion Products

Beginning with Berthelot (1894) several investigators, including Rosenberg (1917), Fink and Polushkin (1936), Collins (1931), Caley (1941), Plenderleith (1938 - 39) and Gettens (1932 and 1937) have described the layered structure on the surface of ancient corroded bronzes and have suggested chemical and electro-chemical reactions and mechanisms to explain the formation of the several mineral products contained in them.

The corrosion of bronzes is based on the general electro-chemical theory of metallic corrosion, which give a true view on the mechanism by which metals and their alloys become corroded. According to this theory, the active corrosion of a metal or alloy occurs when the surface of a metal or alloy is sufficiently heterogeneous, and when this surface is in contact with a suitable electrolyte. Moreover, such a heterogeneous metal surface in contact with such electrolyte is considered to have upon it a large number of points or areas which are at different electrical potentials, so that numerous local electric currents pass between the numbers of pairs of these points or areas, and electro-chemical reactions of various kinds are produced at or near these places of different electrical potential by the current. Some of these electro-chemical reactions, those which occur at the points or areas which are anodic, are destructive to the metal, and various secondary chemical reactions may occur between the products of the primary reactions and the constituents of the electrolyte. The more heterogeneous the metal the greater will be the number of local currents, and the greater will be the rate of corrosion if other conditions remain constant.

Heterogeneity in the electrolyte, particularly when it arises from differences in the concentration of dissolved oxygen, may also cause electrolyte corrosion even when the metal itself is very homogeneous. Such heterogeneity may exist in effect when some parts of the metal surface are shielded by the presence of deposits of insoluable corrosion products from the action of the dissolved oxygen while other parts are exposed to the action of this agent.

Ancient bronze is usually very heterogeneous, and hence easily corroded, because of the presence in it of many kinds of impurities in considerable proportion. Other conditions being equal, the greater the variety of such impurities, the more heterogeneous the bronze, and greater the tendency for it to become corroded. In high tin content bronzes a separate alloy phase much richer in tin than the mass of the metal is usually present, the so-called delta bronze, being destributed throughout the body of the metal in the form of numerous minute crystallites or grains. With the existence of such a fundamental heterogeneity in the bronze cause the passage of more numerous electric currents than usual on contact of the surface of the bronze with an electrolyte, but it would cause larger currents than usual to pass because of the relatively large potential differences between the segregations of delta bronze and the mass of alpha bronze constituting the bulk of the alloy. Thus both the greater number and the greater intensity of these local currents would lead to more rapid corrosion than usual.

The nature of the electrolyte which comes into contact with surface of the bronzes also influences the rate at which the alloy undergoes corrosion. With buried ancient bronze this electrolyte is usually the local subterranean water. Other conditions being equal, the greater the concentration of dissolved salts in this water the higher the rate of corrosion. Moreover, certain dissolved salts or rather their ions, will accelerate the corrosion of bronze much more than others. Numerous experiments have shown that chloride ion in particular is effective in furthering the corrosion of copper and its alloys by aqueous solutions. (see expecially Gibbs, Smith and Bengough (1916) and Bengough and Hudson (1919)). Caley (1941, 84:720) in his paper on Corinthean corroded bronze also stresses this factor." As was shown by an analysis, the present subterranean water at Corinth is unusual in that it contains not only a high concentration of dissolved salts but also chloride ion in considerable concentration. Hence the kind of water which in all probability acted as the electrolyte in the corrosion of the bronze at Corinth was of such a composition that the corrosion of the bronze took place there at more rapid rate than similar bronze at other sites where the water that acted as the electrolyte had a more normal composition."

The nature of the chemical changes involved in the corrosion of bronze are also to a large extent determined by the chloride ion present in considerable concentration in some subterranean waters. The other ions such as sodium ion, calcium ion, and bicabonate ion are of little improtance in respect to the chlorine ion.

The explanation which follows is the theory of the chemical mechanism of the corrosion of any bronze which has undergone extensive alternation as the result of the action of soil or water containing chlorides.

Investigators have found that the places where corrosion starts and the paths subsequently taken by the corrosive action vary greatly in accordance with the composition and structure of the alloy, and probably in accordance with the nature of the corrosive agent. In general, however, regardless of where corrosion started, what path it subsequently followed, or the nature of the corrosive agent, the tin in the alloy not the copper, was always the first to be attacked. This is what would be expected from general electro-chemical principles since tin is the more electropositive metal of the two. The results of Fink and Polushkin (1936) do indicate that in ancient wrought bronze the places richest in tin were usually the first to be attacked. In almost all of the samples these places were the outside layers of the somewhat inhomogenous grains of alpha solid solution of which such bronzes are composed. Where such places are exposed on the surface of the metal object as edges of grains they are, because of their higher tin content, anodic in character, whereas the central parts of the exposed grains, which are poorer in tin, are cathodic. These edges of the grains, are therefore corroded by the action of the electrolyte, whereas the central parts are not corroded. The microscopic examination of specimens of ancient corroded bronze was shown that the corrosion of the outside layers of the grains of metal may extend far below the surface of the object while the central parts of the grains on the surface remain entirely uncorroded. From the standpoint of the electrolytic theory of corrosion, it is easy to understand why this corrosion of the outside layers of grains may occur far below the surface while most of the surface metal remains uncorroded. The outside layers of the grains are all of the same composition on the average so that the electrical potentials between these layers and the central parts of the surface grains are about the same whether these layers are on grains below the surface or on grains at the surface. Thus, corrosion of the outside layers of grains below the surface proceed in the same way as the surface providing the electrolyte can penetrate freely down between these grains. Since this so-called intergranular corrosion starts at the surface and proceeds inward with the formation of loose and porous corrosion products and with the formation of open spaces caused by the dissolution of some of these corrosion products, the electrolyte may penetrate more or less easily between the grains as their outside layers are corroded. However, the deeper the electrolyte penetrates into the body of the metal the less easily will it circulate and the longer will electrolyte remain in contact with the surfaces of the grains. Thus integranular corrosion probably tends to proceed at a slower and slower rate as if progressing into the body of the metal. The impurities in ancient bronze, which are often concentrated largely between the grains of metal play an important part in furthering this sort of initial corrosion. Some of these impurities may be cathodic toward the outside layers of the grains of metal with which they are in contact and so tend to accelerate the electrolythic corrosion of these layers. Other impurities may be easily oxidized to soluable corrosion products which are readily dissolved out, and in this way cavities or channels are formed between the grains that allow the electrolyte to penetrate the metal more freely.

As the anodic parts of the grains of an ancient bronze were first attacked by the local water acting as a corrosive agent, it is likely that the tin was more or less completely dissolved out superificially and that the copper was left behind as a porous layer or as loose powder. However, Fink and Polushkin (1936) conclude from their observations of the microstructure of ancient corroded bronzes that the metallic copper is certainly produced in the initial stages of the corrosion in such alloys.

The almost invariable occurence of cuprous oxide as an intergranular corrosion product in specimens that are otherwise sound shows that in ancient bronze generally, the corrosion of copper must begin shortly after the initial attack on the tin. It has been observed by Caley (1941) in experimental corrosion that copper corrosion products appear quickly after the beginning of the corrosive attack. So it can be concluded that in the natural corrosion of an ancient bronze, the corrosion of tin and copper began to occur simultaneously soon after the alloy was initially attacked.

The chemical mechanism of the corrosion of the tin in buried ancient bronze by the action of the subterranean water containing chloride ion can be discribed as follows. As the tin spontaneously dissolved in the water at anodic areas, the metal must have entered into solution almost entirely as stannous ions (Sn^{++}) and only to a very slight extent as stannic ions (Sn^{++++}) (it is known from numerous experimental observations). This process of solution at the anodic areas involves the release of two electrons for each stannous ion that enters the solution. The two electrons then become available at the cathodic areas in the centers of the surface grains, or at other cathodic areas, to combine with hydrogen ions, or more strictly speaking, with the hydrated hydrogen ions contained in the water in contact with these areas.

$$2\,e + 2\,H^{+} \rightarrow 2\,H$$

That the hydrogen which was so formed ever appears as molecular hydrogen gas at these cathodic areas of the metal grains is very unlikely in view of the almost certain presence in the subterranean water of dissolved oxygen which would immediately oxidize the hydrogen to water as soon as it has been formed. Indeed, if the hydrogen has not been so oxidized it would accumulate as a gas on the cathodic areas and probably would polarize them so that the electrolytic corrosive action could not proceed further.

As soon as the stannous ions diffused away from the metal surface, or are carried away from it by movement of the water, these ions are oxidized rather rapidly to stannic ions by the oxygen dissolved in the water, since the former ones are not stable.

$$2\ Sn^{++} + O_2 + H_2O \rightarrow 2\ S_n^{++++} + 4\ OH^-$$

By this oxidation of the stannous ions more electrons are released, two for each ion oxidized, so that still more hydroxyl ions accumulated in the solution. In the presence of the chloride ions in the solution, the stannic ions have transitory existance and combine very rapidly with chloride ions, forming stannic chloride.

$$Sn^{++++} + 4Cl^- \rightarrow Sn\ Cl_4$$

The stannic chloride formed in the solution exists for relatively short periods of time since this compound is readily hydrolyzed by water. This hydrolysis occurs in a series of stages, but the final products are hydrated stannic oxide and hydrochloric acid.

$$Sn\ Cl_4 + 4H_2O \rightarrow Sn(OH)_4 + 4H^+ + 4Cl^-$$

Thus, hydrochloric acid is released in the solution, and not only are the original chloride ions restored to the solution for further action, but an equivaten number of hydrogen ions are released at the same time, and these increase the rate at which the alloy corrodes. However, any such increase in rate of corrosion because of increased acidity must be, at the most, only local and temporary since most of this excess of hydrogen ions is soon neutralized by the equivalent excess of hydroxide ions also present in the solution, either through the diffusion of these ions toward each other or through the movement and consequent mixing of the liquid. Thus, the original neutrality of the water in contact with corroding alloy surface tends to be continually restored in spite of chemical reactions that produce local excesses of hydrogen and hydroxyl ions.

An important effect resulting from the local excess of hydroxyl ions produced at the cathodic areas causes the formation of hydrated stannous oxide. By mutual diffusion or through mixing of the solution, the hydroxyl ions produced at these areas come in contact with stannous ions produced at the nearby anodic areas before these metal ions became oxidized and form unsoluable hydrated stannous oxide.

$$Sn^{++} + 2OH^- \rightarrow Sn(OH)_2$$

This hydrated stannous oxide is one of the products formed in the natural corrosion of tin objects which have become corroded by the action of water or moist earth. It is not a mere transitory product but may persist for long periods as has been shown by analyses of corrosion products found on ancient objects composed of tin, and of alloys of tin

Bannister (1926), Smythe (1940), Caley (1941)).

The mechanism for the corrosion of tin in ancient bronze serves to explain why the ratio of the proportion of tin to the proportion of copper corrosion products found in ancient bronze artifacts, is much lower. Since, by reason of their known behavior, some of the intermediate products of the corrosion of the tin must have entered the water in contact with corroding bronze in either one of the collodial solutions, and because of their solubility a considerable proportion of these products are lost by diffusion, or by being carried away mechanically by the movement of the water. This is particularly true of the stannic chloride and of the products of its hydrolysis, including even the final product, hydrated stannic oxide. Thus, a considerable proportion of the tin that was corroded does not appear in the insoluble corrosion products attached to the metallic core. This behavior of the tin is in marked contrast to the behavior of the copper since when the copper corrodes it forms at once a sparingly soluable compound, and though this primary corrosion product is also hydrolyzed the products of the hydrolysis are compounds still more insoluable than this primary product. Thus, very little copper is lost in the course of the corrosion of bronze.

The mechanism of the corrosion of the copper in buried ancient bronze by the action of subterranean water will now be discussed.

Copper when it dissolves in diluted aqueous solutions of various sorts and from every relation involved in such processes, in contrast to the tin, enters into solution during corrosion largely in the higher valence state rather than lower. The equilibrium constant for the reaction, $Cu^{++} + Cu \leftrightarrows 2Cu^{+}$, is 0.5×10^{-4} at room temperature, which indicates that the concentration of cupric ions in a dilute copper solution is approximately a hundred times greater than the concentration of cuprous ions when these ions are in equilibrium with a surface of metallic copper. Hence, the metal that dissolves at anodic areas in the corrosion of the copper in the bronze has entered the water largely as cupric ions and only to a small extent as cuprous ions. This process of solution involves the release of electrons that enter the solution. These electrons then become available at the cathodic areas of the copper to produce, by the same mechanism as in the corrosion of the tin, hydroxyl ions that enter into solution. The result of the first stage in the corrosion of copper is, therefore, that cupric ions, accompanied by an apparently insignificant proportion of cuprous ions, enter into solution at the anodic areas and a excess of hydroxyl ions are accumulated at the cathodic areas of the corroding metal.

Although copper dissolves largely as cupric ion in the course of the corrosion of ancient bronze, cupric compounds do not appear as principal final corrosion products, nor are they formed to any extent even as primary corrosion products. The cause of this anomaly lies in the very low solubility of cuprous chloride in water as compared to that of cupric chloride, a difference that appears in determining the entire course of the chemical changes that occur when copper is corroded by the action of water containing chloride ion in sufficient concentraction, especially in sea water. Moreover, the solubility of cuprous chloride is reduced by the common ion effect that this salt tends to separate from the solution as an insoluble precipitate even when the cuprous ion concentration is very low. Because of the sharp difference in the soluability of the two chlorides of copper in very dilute chloride solution, based on theoretical grounds, cuprous chloride is formed as a principal solid corrosion product at the anodic areas in spite of the fact that the concentration of the cuprous ions at these areas are very low as compared to that of the cupric ions. In other words, the equilibria between the cupric ions, the cuprous ions, and the metallic copper are continuously upset by the removal of cuprous ions to form insoluble cuprous chloride, that this salt is formed as a principle corrosion product in spite of the fact that the metallic copper tends to dissolve almost entirely as cupric ions. Various observations and facts support this explanation of how cuprous compounds begin to form as corrosion products instead of cupric compounds (Evans (1946 p.365); Bengough and May (1924, 32:101-102); Caley (1941)). A few investigators have definitely identified cuprous chloride as a corrosion product of ancient bronze and copper objects which were known to have been corroded, or which were presumably corroded, in the presence of water containing chlorides (Rosenberg (1917), Gettens (1932), Caley (1955), who reports: "Most of the cuprous chloride in or on the objects from the well of the Athenian agora was soft, colorless, and translucent, and without crystalline form but was stained various shades of blue or green from the presence of small amounts of admixed cupric compounds, and some of it occurred in the form of small, brilliant, colorless translucent, tetrahedral crystals, which corresponded in every respect to the crystalline form of the rare mineral nantokite").

It has been observed by Gettens and Caley that the cuprous chloride in the corrosion products of ancient bronze and copper objects almost invariably occurs next to uncorroded metal and never in the outermost layers of these corrosion products. This, and the fact that cuprous chloride has never been found in the corrosion products of completely corroded bronze and copper objects, show clearly that cuprous chloride is an initial and unstable corrosion product. Indeed, it is such an unstable compound in the presence of oxygen and water that its survival is not to be expected under normal conditions even in objects that contain much uncorroded metal. In the presence of an abundant supply of oxygen and of moisture, cuprous chloride is so very unstable that its formation is probably only transitory in chloride solutions in which an abundant supply of air reaches the corroding metal. When copper is corroded in porous soil by the intermitten action of subterranean water containing chlorides, or in any other situation where oxygen may freely reach the surface of the corroding metal, cuprous chloride cannot therefore, be expected to survive long as corrosion product. Necessary also for the formation of cuprous chloride as more than a mere transitory product is the corrosion of the copper in somewhat restricted volume of water, since a volume of water, especially if renewed constantly, would certainly dissolve the cuprous chloride as fast as it was formed in spite of the low solubility of the salt in water. Actually the cuprous chloride decomposes by an abundant excess of water. Hence, its formation is not be expected in flowing water, nor in large volume of stagnate water, even when the supply of oxygen reaching the surface of the corroding metal is meager. The condition for the survival of cuprous chloride as a corrosion product of copper in water containing chloride ion is the submersion of the metal in a small volume of such water away from free access of air. Such a condition is obviously not of frequent occurence and, therefore, cuprous chloride has not been reported as a corrosion product often.

The formation of cuprous chloride at the anodic areas of the corroding metal is in accordance with the following equation:

$$Cu^{+} + Cl^{-} \rightarrow Cu\,Cl$$

The mode of occurence of cuprous chloride, indicates that cuprous chloride is formed as initial solid corrosion product of ancient bronze and copper objects, which have undergone corrosion in water containing chloride ion, and that all the other corrosion products are formed from this salt. In view of the nature of the ground conditions the cuprous chloride formed during the corrosion, decomposes soon after it is formed. This decomposition in the presence of water and oxygen occurs both by hydrolysis and oxidation. The rate of decomposition and the nature of the products varies greatly according to the conditions under which the decomposition takes place. In the decomposition of cuprous chloride by distilled water containing oxygen in the form of dissolved air, the nature of the products varies according to temperature, time, concentration of oxygen and ratio of the mass of the salt to the mass of the water. In natural corrosion processes, the decomposition of cuprous chloride takes place at an indefinitely long time, the concentration of dissolved oxygen, the temperature and the ratio of the masses of the salt and the water are important factors. It has been shown by Gröger (1901) that cuprous chloride decomposes even by water free from oxygen. The residue resulting from the complete decomposition of the salt consists mostly of cuprous oxide.

Apparently when the supply of oxygen is restricted, the decomposition of the cuprous chloride salt proceeds largely by hydrolysis and autoxidation, but when the supply of oxygen is ample, the decomposition proceeds largely by oxidation. Actually, the effect of a large excess of water is furthering the hydrolytic decomposition of the salt by making possible the free diffusion of the hydrogen and chloride ions, formed on hydrolysis away from the immediate neighborhood of the decomposing salt, so that these products do not accumulate there in considerable concentration and thus hunder the further decomposition of the salt by hydrolytic action.

During the decomposition of the cuprous chloride formed in the course of the natural corrosion of copper, the process occurs under the presence of water containing chloride ion and also in the presence of a surface of metallic copper. The concentration of the chloride ion is important in determining the nature of the ultimate products of the decomposition. When the chloride ion concentration is very high, as in sea water, cuprous oxide does not form, but the product always formed is basic cupric chloride ion. The very high concentration of chloride represses the hydrolytic decomposition of the cuprous chloride and no Cu_2O is formed. With decreasing concentration of the chloride ion more and more cuprous oxide and less and less basic cupric chloride appear as decomposition products, provided always that the volume of the water is large. In the presence of copper surface, cupric ions do not appear in noticeable amount as a decomposition product of cuprous chloride. The product of the decomposition is mixture of cuprous oxide and basic cupric chloride. In general, the relative proportion of cuprous oxide and basic cuprous chloride in the corrosion products of ancient bronze and copper objects which have undergone corrosion by the action of water containg chlorides may provide a valuable clue to the ground conditions that prevailed during the corrosion of such objects.

The hydrolytic decomposition reaction may be represented by the equation

$$2\ CuCl + H_2O \rightarrow Cu_2O + 2H^+ + 2Cl^-$$

As indicated by the equation, hydrochloric acid is released in the solution, and not only are the original chloride ions restored to the solution, but an equivalent number of hydrogen ions are released at the same time, and these have the tendency to increase, locally and temporarily, the rate of the corrosion of a bronze in the same way as the hydrogen ions released by the hydrolysis of the stannic chloride produced in the course of the corrosion of the tin. These hydrogen ions are soon neutralized by the hydroxyl ions present in equivalent amount at the cathodic areas of the corroding copper, either through the diffusion of these ions toward each other or through the movement and consequent mixing of the liquid.

Some cupric ions arising from the dissolution of the metal or from the autoxidation of cuprous ions are always present in the film or layer of solution around the corroding copper. Additional cupric ions are undoubtedly formed to some extent by the oxidation of cuprous ions by the oxygen dissolved in the subterranean water, especially in parts of the film or layer of solution not immediately next to the metal suface. This oxidation is represented by the following equation:

$$4\ Cu^{+} + O_2 + 2\ H_2O \rightarrow 4\ Cu^{++} + 4\ OH^{-}$$

The hydroxyl ions so produced unite almost at once with part of the cupric ions to form slightly soluable hydrated cupric oxide:

$$Cu^{++} + 2\ OH^{-} \rightarrow CU(OH)_2$$

In the presence of the other cupric ions and the chloride ions present in abundance in the solution, this compound does not long exist and combines with some of these ions, forming the more stable and still more insoluable basic cupric chloride, atacamite:

$$3\ Cu(OH)_2 + Cu^{++} + 2\ Cl^{-} \rightarrow 3\ Cu\ OH)_2 \cdot CuCl_2$$

From the frequent occurrence of basic cupric chloride as a principle corrosion product on the exterior of highly corroded bronze and copper objects in which cuprous oxide is the predominant substance in the corrosion as a whole, it is probable that some basic cupric chloride is often formed by the alternation of cuprous oxide. Cuprous ions arising from the dissolution of cuprous oxide in a film or layer of water surrounding a buried object of this sort are oxidized by air or dissolved oxygen with the subsequent formation of the basic cupric chloride by much the same mechanism as was described for its more direct formation. Because of the very low solubility of cuprous oxide, this change is very slow in spite of the unusually favorable conditions for the oxidation of cuprous ions at the outside surface of a highly corroded object.

Because of their insolubility and marked chemical stability, cuprous oxide and basic copper chloride, undergo little or no transformation into other compounds in the course of the centuries, even into the very stable copper carbonate, malachite. In cases where transformation has occured, it is based on the following chemical reaction:

$$Cu\ Cl_2 \cdot 3\ Cu(OH)_2 \cdot H_2O + CO_2 \rightarrow \underset{\text{(malachite)}}{Cu\ CO_3 \cdot 3\ Cu(OH)_2 \cdot 2\ H_2O} + 2\ H\ Cl$$

Results of investigations by Gettens and Caley show that basic copper carbonate is not formed as primary corrosion product in the presence of water containing chloride ion in sufficient concentration, even when much bicarbonate ion is also present in the water. They show, moreover, that malachite is formed only in small amounts as a secondary product when copper corrodes under these conditions. Numerous investigations show that basic copper carbonate is not even the principle component of the green patina formed on bronze and copper objects which have been exposed for a long time in the open air. The principle component of this green patina is basic copper sulfate, basic copper chloride, or an intimate mixture of the two.

The chemistry of the corrosion of the tin and the chemistry of the corrosion of the copper in ancient bronze have been considered separately as though the chemical changes which occured during the corrosion of the one metal took place quite independently of those which occured during the corrosion of the other. In reality, these two sets of chemical changes do not take place independently. The chemical properties of the two metals and the chemical properties of some of the corrosion products of these metals being such that certain chemical interactions occur. Interactions occur between one of the metals and certain of the corrosion products of the other, between solid solutions or compound of the two metals and certain corrosion products of either metal, and between certain corrosion products of the two metals. As a specific example of such interaction is the formation of redeposited copper which is:

$$Cu^{++} + Sn \rightarrow Sn^{++} + \underset{\text{(redeposited copper)}}{Cu.}$$

It occurs as a result of cupric ions in contact with Cu - Sn eutectoid. In this way some copper which already dissolved was precipitated on the surface of the corroding alloy. That such precipitation of copper does occur is indicated sometimes by the occasional presence of bright crystals of copper next to, or near to, the metallic core of bronzes which have undergone severe corrosion. It must be admitted that the existence of such copper crystals is not conclusive proof that they originated in this particular way. They could also be formed by the auto-reduction of cuprous chloride or by the action of local currents generated from inequalities in the concentration of copper ions in the liquid around the corroding alloy. Sooner or later such precipitated copper must have again dissolved and passed through the same stages in corrosion as any other copper in the alloy. However, these chemical interactions do not really change the general course of the chemical changes which occur during the corrosion of the tin and the copper. For this reason it does not seem necessary to discuss all these possible interactions in detail.

In bronzes with low lead content as compared to the tin and the copper, changes which occur during its corrosion has little effect on the main course of the corrosion of bronze and on the composition and structure of the princial product of corrosion. Lead enters into solution almost entirely as plumbous ions. All the lead ions combine almost at once with hydroxyl ions to form insoluble hydrated lead oxide as an intermediate corrosion product. By the action of the bicarbonate and carbonate ions in the water this intermediate product is then transformed more or less rapidly into basic lead carbonate, the final product of the corrosion of the lead. A few other lead corrosion products are reported in Chapter IV, but their formation does not change drasticly the main course of the corrosion mechanism. They are formed as a result of chemical reactions with the environment.

Another metal which occurs in some ancient bronze as a minor component is iron. Much of the iron may actually be in the form of ferric oxide before corrosion starts, either because it enters the bronze in this form or because it is oxidized to this compound during the fabrication of the objects from the prepared alloy. In the course of corrosion any elementary iron in the bronze must enter into solution largely as ferrous ions with the production of an equivalent quantity of hydroxyl ions. Most of these ferrous ions are oxidized rapidly to ferric ions by presence of oxygen (dissolved oxygen in subteranean water). Some of these ions may be combined first with hydroxyl ions to form nearly insoluble hydrated ferrous oxide as an intermediate corrosion product. The ferric ions produced by the direct oxidation of ferrous ions, or those produced by the oxidation of ferrous ions which had first combined to form hydrated ferrous oxide, then combined rapidly with hydroxyl ions to form a hydrated ferric oxide as immediate final corrosion product. This compound loses water gradually until a less hydrous ferric oxide is formed as the final product of the corrosion of the iron. Some chemical interactions involving these minor components and their corrosion products take place, but these interactions are insignificant as compared to those which take place between the major components of the alloy and their corrosion products.

Another found element in ancient bronzes is arsenic and those bronzes are called arsenical bronzes. They have been found extensively in the Early and Middle Bronze Age periods. Presence of arsenic leads to the formation of protective film on copper, dulling the surface and considerably retarding subsequent corrosion. Arsenical copper has been recognized as having superior corrosion and erosion resistance to other copper alloys. These sorts of statements appear in some sources: Collins (1931), J. A. Charles (1967) and others, but I have not been able to find any explanation as to the cause of the process, which occurs during the corrosion of arsenical bronzes. It is a well known factor that As is a useful deoxidizing agent in casting of copper and improves its mechanical properties. Evans (1960) mentions the use of small amounts of arsenic for preventing dezincification of brasses.

Though the various chemical reactions which occur during the corrosion of buried bronze constitutes the most important changes that take place in the transformation of metal into corrosion products, these reactions are by no means the only changes which occur. Various physical changes also occur , such as, for example, change in the state of aggregation of such particles, and changes in the relative positions of the different kinds of particles and aggregates.

The general composition of the corrosion products or patina of an ancient bronze may be satisfactorily explained on the basis of chemical changes. The arrangement of the individual corrosion products in relation to each other, or the general structure of the patina, often cannot be satisfactorily explained on the basis of such changes alone, but has to be explained in part on the basis of physical changes. The occurrence in particular physical changes during the corrosion of an ancient bronze cannot ordinarily be established with the same degree of certainty as the occurrence in a particular chemical change. However, certain types of structure may be adequately explained on the basis of chemical considerations. This explanation is based on the factor that certain chemical reactions proceed more readily under one set of conditions and others more readily under another set of conditions. In other words corrosion proceeds at all times, but in accordance with the alternations in the conditions. Certain reactions will predominate and determine the course of the corrosion and the nature of the final products at one time and other reactions will predominate and determine the course of the reactions and the nature of the final products at another time.

Since the formation of a fine stratified structure in the patina of an ancient bronze is connected with seasonal or climatic changes, it seems possible that the number and thickness of the layers in the patina may somehow serve as an index of the length of the time the bronze was buried, or of the prevalence of certain climatic conditions at certain times during the period of burial. Too many factors of uncertain or unknown effects are involved in the formation of these layers. Hence, the possibility of attaching any chronological significance to the number of these layers must exist only for objects of the same composition buried at a given site, and even for these the number of the layers may be only of relative and of absolute chronological significance.

It has been observed in ancient bronzes that the rate and mechanism of corrosion are different, based on the fact of whether the metal is cast or cold worked. It was mentioned before that the eutectoid in bronzes is usually more easily chemically attacked, and hence corrodes to much greater depth below the surface of the metal than is the α - phase generally. Also, in some soils the tin-rich phase is corroded first, leaving spongy copper filled with tin oxide. In the process of the corrosion course copper turns to Cu_2O and eventually to malachite. If the alloy has lead constituent, the lead is one of the first to be attacked by the corrosion process as a result of the electrochemical reaction with the environment. Usually, it is the Cu - rich phase that is less easily attacked by the corrosion process due to its homogeneity.

In cold worked bronzes another type of corrosion is observed, called STRESS CORROSION, which is caused by the simultaneous action of the corrosive medium and mechanical stress. Stress can be cyclic or non-cyclic, or is applied by an external load, or is the result of residual internal stresses. Another type of stress corrosion, called STRESS CORROSION CRACKING, is due to static external and internal tensile stresses.

After bronze has been hammered, its crystals undergo great external and internal physical stresses. But, if the metal is annealed, these physical stresses are released to a certain extent. If the annealing is done at higher temperatures (usually around 600° C) the internal stresses left are of a lower degree, compared to those left from annealing at lower temperatures (about 200° C). During the hammering process the cast crystals are broken and during the annealing recrystallization occurs, as a result of which new smaller twinned crystals are formed. The presence of internal stresses increases the tendency to corrosion. The corrosion forms sort of geometric pattern along the planes of the crystals. The corrosion product is duplex, leaving a stripe of different mineral in the middle probably because of differing amounts of tin oxide in the corrosion products formed at different times. When the last process performed on a bronze object is hammered, slip bands are noticed on the microstructure of the alloy. The internal and external stresses have not been released and one notices that thin corrosion layers appear around areas with slip bands if the rest of the metal core is not attacked by corrosion. This shows that the stresses in those areas are big and areas with such stresses tend to corrode first.

The microbiological corrosion of copper alloy has received much less attention than other types of corrosion, because of the mistaken viewpoint that copper ions formed by microbial corrosion are always lethal to the organisms. For example, Jones and Roche[1] have determined the toxicity of copper to marine bacteria. Copper concentrations of 10^{-5} to 10^{-6} M proved slightly stimulatory to the marine bacterial community in a sea-water-agar containing 0.5% peptone and 0.1% yeast extract. In some cases the colonies tolerated copper concentration as high as 10^{-3}M. Certain fungi are very resistant both to high hydrogen ion concentrations and to high copper ion concentrations. In particular, ACONTIUM VELATUM Morgan and a dark green organism belonging to the DEMATIACEAE grow at pH 0.1 and in media saturated with copper sulfate[2].

Corrosion by microbial action can be brought about in various ways: 1) by direct action, for example, by the production of corrosive substances such as CO_2, H_2S, NH_3, and organic and inorganic acids; 2) by the metabolism of the organism, producing organic substances that can act as depolarizers or catalysts for the corrosion reaction, 3) by the activites of sulfate- reducing bacteria, under some conditions of which the corrosion reaction is an intergral part of the metabolic cycle of the bacteria; and 4) by the deposition or formation of a slime or solid mass that can be the basis of an oxygen or other concentration cell. In some conditions the corroding medium may be generally infected with the offending organisms. If they produce substances that are able to catalyze corrosion reactions, it is possible for the medium to remain abnormally corrosive even after the microorganisms have died, become dormant, or been removed.

A very good study by Rogers[3] shows the promotion and acceleration of copper alloy corrosion by microorganisms. There also are few studies[4-10] that show different properties of the microbial corrosion, but there has to be more work done in this area to explain the complete mechanism and classifications which microorganisms are corrosive catalysis, which are not. This is very important for the archaeologists, due to the fact that a lot of the ancient artifacts have been found in sea waters.

Summary:

CORROSION ENVIRONMENTS

In summary, the environments which bring about corrosion of metals are as follows:

Air
Soil
Natural Waters
Sulphur Compounds
Acids
Oxidizing agents
Alkalies
Chemical Salts and brines
Organic materials and food products
High Temperatures

From this list, the three important ones to archaeologists are water, air and soil.

Water, of course, is essential to corrosion and the conductivity of the water is governed by the amount of dissolved chemicals in the water. These chemicals, usually liquid, are called electrolytes. Most natural water is a good conductor of electricity.

Air carries moisture, carbon dioxide and other gases including sulphur and nitrogen.

Although there are a large number of chemical elements in soil, most of them are difficultly soluable compounds therefore, they have little influence on corrosion.

Soil corrosion is brought about to a great extent by the penetration of air and water in porous soils, consequently, the older artifacts would be found under the non-porous clays.

However, in soils carrying a low amount of air, the corrosion pits are often very deep because the corrosion products are in the reduced condition and are precipitated away from the point of attack.

The sulphur-reducing bacteria found in soils reduces sulphates to hydrogen sulphide. Hydrogen sulphide is corrosive to all of the known ancient metals except gold.

Electric currents are generated in soils between adjoining areas having a different electric potential and between the metal and the soil.

In the case of ancient metals having been found in comparatively dry climate and dessert areas, which at one point have experienced big floods, resulting in either a covering of clay to retard corrosion, or the addition of salts to accelerate corrosion. Sodium chloride, or common salt, found in the ocean, is an extremely strong electrolyte.

METHODS OF STUDY:

The present day methods used for studying corrosion products have advanced, using rather poweful tools.

Usually, a low power binocular microscope is used for visual analysis. Also, very oftenpolarized light in optical microscopes, which helps to determine the color of the corrosion products.

Wet chemical analysis are available for studying corrosion films, but their disadvantage is that one needs a rather large quantity of sample, which is not the case with ancient metals.

Chemical microscopy and microchemistry are of some help.

Spectrographic analysis can determine the cations present.

The x-ray diffraction methods are greatly used to determine the compounds from which the corrosion products are made of.

X-ray fluorescence methods are very valuable, because they are nondestructive, i.e., compositions of films and metals can be obtained directly on the object.

Metallography methods are used to show the stages of corrosion process in cross sections of the metal. This method is greatly used by the engineers for studying corrosion in the industry. dealing with ancient metal artifacts, samples are obtained either from broken pieces or through cutting of very small samples that are not visible. The samples should be mounted in such a mounting medium which does not need big changes in temperature. The latter one, if it is very different from that of the piece may cause some corrosion reactions to appear on the metal surface.

Usually metallographic studies combined with x-ray diffraction and fluorescence methods lead to satisfactory results for the composition of products.

Laser and electron-micro analyses have also been used lately for study of corrosion products.

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CHAPTER IV

CORROSION PRODUCTS OF COPPER AND ITS ALLOYS

The products formed as a result of the chemical and electrochemical reaction of the metal with the environment are the so called corrosion products and also very often called mineral alternation products. The most common ones formed from copper and its alloys are: oxides, sulphides, carbonates, chlorides, silicates and sulphates. The formation of different products is due mainly to the environmental conditions. For example, metals exposed to air would form oxides, carbonates and sulphates according to the impurities and moisture in the air. When a copper or bronze artifact is buried in soil or immersed in water, the corroding environment is vastly different. The change of the surface of an artifact depends upon many factors including the composition of the metal, kind of concentration of the chemically active agencies (especially of oxygen and of salt anions), pH or degree of acidity or alkalinity, temperature, seasonal changes and also the physical character of the products of chemical change.

All of the following minerals in which copper is found in nature have been identified as corrosion products on copper or bronze articles.

OXIDES		
Cuprite	Cu_2O	Ruby Red
Tenorite	$Cu O$	Black
CARBONATES		
Malachite	$Cu_2(OH)_2CO_3$	Green
Azurite	$Cu_3(OH)_2(CO_3)_2$	Blue

SULFIDES		
Covelite	$Cu S$	Indigo Blue
Chalcocite	$Cu_2 S$	Blackish-lead gray
Chalcopyrite	$Cu Fe S_2$	
Bornite	$Cu_3Fe S_3$	Bronze-brown with purpulish tarnish
Enargite	$Cu_3As S_4$	Grayish-black
CHLORIDES		
Atacamite	$Cu Cl_2 3Cu (OH)_2$	Bright to dark green
Nantokite	$Cu Cl$	Colorless to white/ grayish
Battallacite	$Cu_2(OH)_3Cl H_2O$	Grayish-blue
SULFATES		
Brochantite	$Cu_4(SO_4) (OH)_6$	Bright Green
Connellite	$Cu_{19}(SO_4) Cl_4(OH)_{32} \cdot 3H_2O$	Bright blue
SILICATES		
Chrysocolla	$Cu SiO_3 2H_2O$	Bluish green

1. Copper Oxides The most frequently reported and widely occuring copper oxide is the red cuprous oxide, Cu_2O, called CUPRITE. Very often most of the cuprite is found beneath the green and blue basic salts of copper and seems to be an intermediate compound in the corrosion process. A cuprite underlayer is also revealed when the outer green oxidation is removed by mechanical or partial chemical cleaning. In cast bronzes cuprite sometimes forms along grain boundaries or in seams that penetrate deeply into the metal core, but more often it occurs in coarsely

crystalline masses of cube-shaped crystals. A fractured or scaled surface of cuprite on bronze occasionally has a sugary appearance caused by reflection of light from numerous small crystal faces. This crystalline cuprite is usually cochineal red in color but sometimes fine grained cuprite in inner or intermingled layers is quite orange-red or even yellow. In copper objects made out of smelted copper, cuprite is often found in small globules among the copper crystal grains. This is not a corrosion product but is cuprite formed under inadequate reducing conditions at the time of smelting.

Collins (1934) and Gettens (1951) showed that the black patina on some Chinese bronzes consists of cuprous oxide. The former one examined 3rd - 10th century A.D. bronzes. They were chemically tested, showing them to be in the speculum metal range, with tin content varying between 19.25 and 26.97%. He reported that the black patina was unaffected by alkalis and by acids when cold. On another specimen the patina was raised in blisters. X-ray analysis data showed close resemblence to cuprite, but the crystal form was not identical with known cuprites. Metallographic studies showed that the "mirror black" patina consists of cuprous oxide perhaps with a thin film of cupric oxide on its surface. The lead content (less than 2.5%) was not considered to play an effective part in the formation of the patina, although lead content up to 50% in some Chinese bronzes produces a black patina as does silver sulphide. Gettens' sample was from an ancient bronze ceremonial vessel of the Chou period (112-225 B.C.) with high-tin content (above 20%) also. He observed a few corrosion zones formed above the metal core. In the zone immediately contiguous with uncorroded metal, unattacked densities of the α - bronze (copper-rich) phase are surrounded by a black eutectic (tin rich) phase. Because it is so intimately mixed with uncorroded alpha it was impossible to isolate the black material for microchemical tests. Some samples (chips) were isolated for x-ray diffraction analysis. The powder pattern showed mainly presence of copper lattice and faint cassiterite ($Sn\ O_2$) lines. Tin oxide was plentifully seen in the outer corrosion layers. The faintness of the cassiterite lines indicates that the tin oxide is in crypto-crystalline state. The presence of the black color is not clear, but there is possibility that it is stained black with cupric oxide, and it is well known that some forms of cupric oxide (melachonite) are so nearly amorphous that they give indistinct diffraction patterns or none at all. If the black is cupric oxide it is doubtful if it is formed by direct oxidation of copper especially under the reducing conditions that seem to prevail in the interior after corrosion attack is well along. In the zone of completely mineralized products, the innermost layer is a grayish soft waxy layer of cuprous choloride (nantokite). Next is a narrow zone of redeposited metallic copper that is compact but crystalline as in electroplate; strangely it is not continuous but intermittent. Redeposited copper occurs also in tiny pockets throughout the initial penetration zone among dendrites of residual alpha. Next comes a thick band of cuprous oxide (cuprite).

The density and compactness of the cuprite layer is probably an important factor in preventing the complete oxidation of cuprous chloride. Tin oxide seems to form no distinct separate interior layer. At high magnifications, however, white tin oxide is seen deposited mainly in little disconnected seams through the cuprite. Ghosts of the original dendritic structure in places still persist in the white tin oxide.

The tin corrosion product, unlike the copper, does not migrate, because after formation immediately becomes unsoluble. The initial products of copper corrosion, which are slightly soluble in the corrosion liquid, either deposit cuprite around the tin oxide, or they are blacked out leaving a nearly solid tin oxide patina, as is often seen on ancient Chinese bronze mirrors, cast from speculum metal (alloy of 2/3 copper and 1/3 tin). In certain areas on the surface, copper is all dissolved out leaving a smooth solid tin oxide, which gives the reflecting surface of the high tin content bronzes.

Speculum owes its resistance to corrosion to its high proportion of fine-grained duplex ($\alpha+\delta$) structure. Cuprite does not always change to malachite for reasons unknown. The fine lustre of the patina is due to the original polishing of the bronze and to the thinness and evenness of the corrosion layer. The terms "quick-silver" or "silver" applied to speculum metal patina are erroneous, as the silvery color is due to the alloy.

In advanced corrosion, cuprite sometimes is interlaced with seams or lenses of white tin oxide. Bronze converted internally to cuprite is brittle and easily shattered. Gettens (1970) reports "in the transformation of the copper to cuprite the calculated volume increase is nearly 1:2. In spite of the substantial theoretical volume increase, the original shape of a fairly heavily corroded bronze object is often well retained in the cuprite layer. The increase in volume appears to be accomodated by transfer of copper from within to outside the original surface, where some of the copper is deposited as low density basic salts."

TENORITE: The black cupric oxide is seldom reported. It is easily produced artificially by heating copper in air. However, it has been reis sometimes seen on ancient bronze pieces that have been cleaned down and polished. Occasionally, malachite is observed on bronzes in delicate fibrous aggregates, sheaflike in form.

AZURITE, $Cu_3(OH)_2(CO_3)_2$, similar in composition to malachite, its color ranges from bright blue to dark indigo. Like malachite it sometimes appears on objects as a thin compact layer but it is more often observed in fine blue crystal aggregates scattered among patches of malachite. In nature azurite is less abundant than malachite and as a corrosion product the same is also true. Azurite is most often encountered on the interior surfaces of hollow vessels where less humid conditions may favor azurite formation. Occasionally, a bronze will appear to be completely transformed to crystalline azurite.

Malachite and Azurite are formed by contact of the object with soil water or even rain water charged with carbonic acid gas in the presence of atmospheric oxygen. Gettens (1970) observes that "carbonated bronzes seem mostly to have lain long in humid closed spaces such as underground tombs". Lewin (1973) reports the summary of investigations that have been performed on the conditions of formation and stability of malachite and azurite.

CHALCONATRONITE, $Na_2Cu(CO_3)_2\ 3H_2O$, has been reported by Gettens and Frondel (1955) who discovered a bluish-green corrosion product found on several Egyptian bronzes in the Fogg Museum of Art. This mineral seems to be product peculiar to the arid soils of Egypt. According to the authors the formation of chalconatronite on the objects appears to have resulted from their contact with the very special conditions that prevail in the soils which contain alkali carbonates like natron, $Na_2CO_3\ .\ 10\ H_2O$, or trona, $Na_2CO_3.\ H_2O$. The mineral product, not reported before ported by Perinet (1961) among the products found in the inner layer of a corroded copper nail recovered from a sunken 2nd century B.C. Greek vessel found in 1952 in the islet of Grand Conglouie in the Mediteranean. Fink and Polushkin (1936) in their study argue that in all cases where corrosion is merely an oxidation process, resulting only in the formation of oxides and carbonates, the inner-most layer of patina is always cuprite, or cuprite and tenorite. Formation of cuprite starts during the initial corrosion. Even in the presence of other corrosive agents such as chlorine, cuprite is frequently found in the first corroded layer in association with other products. Their argument is supported by microscopic examination of grains attacked by corrosion disclosing accumulations of cuprite at the boundaries or along cleavage planes of these grains. If the primary product was anything else, e.g., malachite, malachite would have been found at the boundaries or along cleavage planes of the attacked grains.

It appears that tenorite, even though as a seldom occuring corrosion product has been underconsideration. It does form as a separate corrosion layer but it is found with other corrosion products, most often in conjunction with cuprite.

2. Copper Carbonates

Malachite and Azurite, both basic carbonates of copper, are perhaps the most familiar natural alternation products on copper artifacts.

MALACHITE, $Cu_2 (OH)_2CO_3$, sometimes occurs as a smooth dark green compact layer on the surface of a bronze and gives it an enameled appearance, but more often it is seen in scattered rounded masses described as mammallary, or as botryoidal because of their resemblance to clusters of grapes. The banded structure characteristic of large malachite masses has been discovered also on an Egyptian bronze group in the Freer Gallery of Art.

This is a proof that the form and chemical composition of the corrosion products on an ancient metal object may reflect its past history. They may tell us something about its former surroundings, and even its approximate topographical origin. The occurance of chalconatronite on these bronzes certainly confirms their origin to the few exceedingly arid places of the world and supports the stylistic and historic evidence of their Egyptian provenance.

3. Copper Chlorides

Ancient copper and bronze objects found after long contact with the saline soils of dessert regions or buried in the sea, are covered with green corrosion crusts which are usually a mixture of the chlorides of copper. They do not have desirable patina on bronzes but are ugly and disfiguring.

ATACAMITE, $Cu_2(OH)_3Cl$, the most common copper chloride mineral, gets its name from the dessert of Atacama in northern Chile where it occurs in secondary copper ore deposits. Since sodium chloride is highly reactive with copper and its alloys, ancient artifacts of these metals exposed to it are usually fissured and nearly distorted. The color of the mineral ranges from emerald to blackish green. On the surface of many bronze objects from Egypt and Mesopotamia atacamite occurs as a continuous, sugarlike coating of dark green glistening crystals.

Rooksby and Chirnside (1934), using x-ray powder diffraction method show that a basic copper chloride equivalent to atacamite is produced by the action of 5% solutions of sodium, potassium, calcium and magnesium chlorides on copper, also by the action of sea-water on copper, and by the action of sodium chloride solution on a copper-nickel alloy, by addition of dilute ammonia to 2% $CuCl_2$ and by hydrolysis of Cu_2Cl_2.

Often crystalline atacamite is associated with a paler green powdery product which gives the x-ray diffraction pattern of PARATACAMITE, a mineral identical in chemical composition, but having hexagonal crystal form, whereas atacamite is orthorhombic. Such related minerals are called dimorphs. Although both atacamite and paratacamite are observed most commonly on bronzes from arid areas, they may also be found on bronzes from regions of normal rainfall. Otto (1959) cites the occurrence of both minerals on bronzes from Germany and other parts of Europe, and he reports that paratacamite occurs much more frequently than hitherto realized. It is also found on bronzes from Anyang and other parts of central and Eastern China. Frondel (1950) cites the occurence of atacamite crystals up to 0.5 mm in size on Egyptian bronze bull of the XIX Dynasty in association with malachite, chessylite, and cassiterite. Paratacamite has been found only as dense to powdery coatings and not as distinct crystalls.

Paratacamite is the pulverulent green product of hydrolysis and oxidation of synthetic cuprous chloride in moist air. It is also the green powder that forms on chloride-corroded bronzes when the inner unstable nantokite (cuprous chloride) layer is exposed to air by cross sectioning of mechanical cleaning. It is not stated clearly in mineralogical books which of the dimorphs is more stable; but in museum reports, it appears that paratacamite is the initial product of rapid nantokite transformation, and atacamite (perhaps mixed with malachite) is the final one. The formation of paratacamite is the manifestation of what is called "bronze disease".

BOTALLACKITE, $Cu_2(OH)_3 Cl \cdot H_2O$, is another basic copper chloride. It was found originally at the Bottallack mine, St. Just, Cornwall, England and was first described by A. H. Church (1865). The first occurance as a corrosion product was reported by Frondel (1950) found on the interior of an Egyptian bronze figurine of the deity Bastet in the Fogg Museum of Art. Another occurrence on an artifact has been observed by Gettens (1970) in the Walters Art Gallery, Baltimore. Botallackite may occur on ancient bronzes more commonly than is suspected.

NANTOKITE, Cu Cl, cuprous chloride.

Cross section studies on bronzes massively coated with cuprite sometimes reveal an inner layer of a pale gray waxy looking substance which has been shown to be cuprous chloride. It corresponds to the unstable mineral called nantokite named after the first noted occurence at Nantoko, Copiapo, Chile. Caley (1941) found that nantokite was one of the principal alternation minerals of the extensively corroded bronze and copper objects recovered from deep wells at the site of the Athenian Agora, and from the fountain Pierene at Corinth. Various investigators have shown that nantokite is the parent substance of both paratacamite and atacamite and that is the cause of "bronze disease". Gettens (1932) describes the occurence of nantokite in corroded copper nails from the second millenium B.C. Mesopotamian site of Nuzi (Iraq). Later he (1951) proposed a series of chemical reactions to explain the complex processes that are involved in the transformation of nantokite to cuprite and alternately to atacamite. Essentially nantokite rapidly hydrolizes and oxidizes when exposed to moist air and forms simultaneously red cuprous oxide and basic cupric chlorides. Organ (1963) has given a new review of the chemical reactions involved in chloride corrosion of copper, and describes various methods used by the British Museum Research Laboratory for stopping them.

The occurence of chloride minerals on artifacts from areas of fairly heavy rainfall, such as Europe and eastern China as noted above, is interesting but puzzling. This would be an interesting subject for further investigation by soil chemists.

4. Copper Sulfates

The bright green basic sulfate of copper corresponding to the mineral BROCHANTITE, $Cu_4(SO_4)(OH)_6$, is seldom reported on artifacts although it might be expected on bronzes, exposed to sulfate bearing waters. Otto (1961) however, reports the occurence of this mineral on bronze artifacts from German graves. Gettens (1933) found evidence of basic copper sulfate in the green corrosion crusts of a bronze statue of Nathan Hale in Hartford, Conn. Brochantite occurs commonly on outdoor bronze statuary and on copper roofs exposed to the urban atmosphere.

At the beginning it was thought that the green patina on copper roofs and outdoor bronze statues to be basic copper carbonate, identical with malachite. In the late 1920's Vernon and Whitby carried an extensive research on the green of copper roofs in London and other parts of England. They found that the main constituent of the green alternation product is basic copper sulfate and it corresponds to the mineral brochantite when it has been exposed long enough to attain full basicity. Kosting (1937) also found that the green on a 10 year exposed copper roof in Washington, D. C., is brochantite over a layer of cuprite He further notes that only ANTLERITE ($3\ CUO.SO_3\ .\ 2H_2O$) was detected in the patina from copper that was formed by accelerated weathering in the laboratory. It has been proven that brochantite is formed from sulphur compounds produced in the burning of coal and fuel oil.

CONNELLITE, ($Cu_{19}(SO_4)\ Cl_4(OH)_{32} \cdot 3H_2O$), rare mineral, found on rings made of bronze sheets from the only group of graves of the La Tène Period in Southwestern Germany, reported by Otto (1963). The bright blue needlelike crystals of connellite occur mixed with other copper minerals in the bronze corrosion crusts.

5. Copper Sulfides

Sulfides are not often reported as occuring on copper artifacts, but they might be expected where objects have been in contact with sulfur-bearing waters. Both Rogers (1903) and Clarke (1924) mention the investigations of A. G. Daubree (1875, 1881) and others who examined Roman coins and medals recovered years ago from French mineral springs and report occurrences of CHALCOCITE, Cu_2S, CHALCOPYRITE, $Cu\ Fe\ S_2$, BORNITE, $Cu_5\ FeS_4$ and THETRAHEDRITE, $(Cu, Fe)_{12}\ Sb_4S_{13}$. They also mentioned that Daubree (1875) noted the occurrence of indigo blue COVELLITE, $Cu\ S$, reported by Calley (1971), among the other sulfide minerals in the corrosion crusts of coins. The latter one believed the sulfide in the thermal spring water came from the reduction of soluble sulfates by bacterial action on vegetable material. Gettens (1970) talks about it, "Covellite seems to be an especially abundant corrosion product on copper and bronze artifacts recovered from wrecks of old wooden ships found at the edge of the sea. This may seem strange because there is little or no sulphide ion in sea water. The sulphide ion, however, appears to come from sulphate reducing bacteria harbored in decaying wood, which act on sulphates in sea water. Sulphate ion makes up about 7.7 per cent of the salt content of sea water". Other reported copper sulfides as corrosion products are CUPREINE, a black form of chalcocite with metallic lustre, and DIGENITE (Cu_9S_5). The last one has been cited by Perinet (1961) among the alternation products on copper nails.

6. Copper Nitrates

The occurence of heavy metal nitrates in nature is rather rare because of their solubility in water, although the nitrates of the alkali metals, sodium and potassium, which are especially soluble, occur abundantly in certain dessert regions. Aoyama (1960, 1961) has identified basic copper nitrate, $Cu(NO_3)_2 \cdot 3Cu(OH)_2$, among green corrosion products on copper electric powerlines in Japanese mountain areas. Although x-ray diffraction data is given, the exact mineralogical species is not named.

7. Copper Phosphates

Bone and horn materials buried in direct contact with copper and bronze are often found stained blue-green with copper phosphate salts formed by action of copper salt solutions on calcium phosphate of the bone. Geilmann and Meisel (1942), on the basis of x-ray diffraction studies, identified as LIBETHENITE ($Cu_2(PO_4)(OH)$ a green blue mass on bronze spiral which had been in contact with bone in a German grave. Otto(1959) cites three occurrences of copper phosphate on artifacts. He does not call this alternation product Libethenite, but gives the formula as $Cu_3(PO_4)_2 \cdot 3H_2O$, a compound which he claims is not known to occur in nature.

8. Other Copper Minerals

No occurrence of the natural silicate of copper CHRYSOCOLLA, $CuSiO_3 \cdot 2H_2O$, seems to have been reported. REDEPOSITED COPPER sometimes occurs among the inner layers of heavily chloride-encrusted bronzes. It is formed by reduction of cuprous chloride (nantokite) by the more electropositive high-tin phases of bronze alloys. Redeposited copper can occur in isolated pockets or patches or as a continuous inner layer. It is sometimes revealed in the form of little scales beneath the green corrosion crusts when they are stripped from the bronze surface with forrenic or other mild organic acids. Often the flakes are intermingled with cuprite.

Considerable amount of research has been done, but much remains to be learned about corrosion products and corrosion processes of copper and its alloys. Investigators for the industry have been much concerned with corroding agencies and corrosion prevention, but they have given little attention to corrosion products themselves. They are usually described as worthless and uninteresting end products of corrosion reactions.

9. Tin Oxide

Tin is a metal of prime importance in archaelogy, not as an individual material but as a necessary adjunct to the making of bronze. Tin oxide is an important alternation product on surface of ancient high-tin bronze objects. Gettens (1949) reported stannic oside, SnO_2, as major constituent of the smooth gray-green patina on Chinese bronze mirrors and ceremonial vessels. It also occurs on high-tin Etruscan and other European bronzes. This alteration product, which may penetrate into the bronze for a distance of 1 to 2 mm, may be hydrous form of a stannic oxide. The pale greenish color is a stain caused by a small impurity of copper. Under certain conditions of soil contact, the copper is dissolved away from the surface of the bronze and replaced, atom by atom without volume change, by stannic oxide. This phenomenon, explained by Gettens is identical with pseudomorphic substitution of elements in mineralogy. The tin oxide encasing corroded high-tin bronzes is sometimes compact and translucent like ceramic glaze. Gielmann (1950 and 1956) has published the analyses of a dozen Bronze Age artifacts from Europe in which tin oxide resulting from alternation is the principal constituent. These were all originally bronze objects in which copper has been pseudomorphically replaced by a brownish colored hydrous tin oxide. This type of patina formation seems to occur principally on bronzes buried in sandy soils. Copper in alloy is dissolved by both the carbonic and humic acids, leaving the stannic oxide. In some other occurences the tin oxide is powdery and friable. Gettens (1970) reports that "x-ray diffraction patterns of tin oxide from bronzes are identical in spacing to those of naturally occuring cassiterite, but the lines are broader and more diffuse, which indicates that the bronze corrosion product is much more finely divided than the cassiterite of tin ore deposits".

It has been found that there is a close resemblance between the diffuse x-ray diffraction pattern of tin oxide alteration product on bronzes and that of the yellow tin mineral VARLAMOFFITE, discovered in the Maniema region of Belgium Congo by the mineralogist N. Varlamoff. Another occurence of Varlamoffite from Cornwall, England, has been described by Russel and Vincent (1950 - 52).

F. Lihl (1962), as well as Plenderleith and Organ (1953) have reported evidences of stannous oxide as well as stannic oxide among corrosion crusts on tin objects, but there is no mineral of stannous oxide listed in the current edition of Dana's System of Minerology.

Much has to be done before the mechanism of the solution of copper and its replacement by tin oxide on bronze surfaces is completely understood.

The rarity of metallic tin may be a physical change called "tin pest" whereby tetragonal metallic white β-tin is transformed to cubic powdery grey α-tin by allotropic modification at equilibrium temperature about 13.2° C. The behavior is well described by Lihl (1962) and by Plenderleigth and Organ (1953), who admit the existence of allotropic modification but minimize its importance in respect to the decay and disappearance of ancient tin objects. They agree that often what appears to be "tin pest" is nothing more than inter-granular oxidation of tin with formation of mixed stannous and stannic oxides. This view is strongly supported by the x-ray diffraction analysis investigation carried out by Lihl on old corroded tin sarcophagi in Vienna.

10. Lead Corrosion Products

Among ancient metals, lead, next to copper forms the widest variety of corrosion products. It also forms some double salts with copper. Lead is an important constituent of many ancient bronzes, but it does not alloy easily with copper. Lead usually segregates in copper-tin solid solution in the form of lead inclusions. The amount of lead in bronzes varies, and it is a well known fact that Chinese bronze objects have rather high percentage, over 25%.

The commonest alteration product of lead is CERUSSITE, or lead carbonate, Pb CO_3. This is the dense, adherent, warm-gray deposit usually seen on old lead seals, sarcophagi, statuary, and on all sorts of buried lead objects. Cerussite, seems to form a protective layer on lead and prevents its progressive and complete disintegration. In the Freer Gallery collection of ancient Chinese bronze ceremonial vessels those with high lead content frequently have cerrissite as a mineral alternation product among the corrosion constituents. (This has been observed by Gettens (1969).) On some of the vessels it covers large areas with smaller ugly grayish crusts with patches of reddish lead oxide (LITHARGE) and malachite. It is not uncommon to find cerussite as a distinct layer underlying malachite. In some occurences, cerussite is found as well-formed crystals with glistening crystal faces, in others it occurs as rounded excrescences much like malachite, and in some early bronze vessels cerussite took the form of the original bronze surface much as tin oxide does when it replaces copper pseudomorphically. Cerussite often reveals itself on ancient bronze by its pinkish yellow fluorescence in long wavelength ultraviolet light.

Next to the carbonates the several oxides of lead seem to be the most common occurring lead minerals. Caley (1955) has identified MASSICOT or yellow lead monoxide PbO, on lead objects excavated at the Agora in Athens. He also found dark brown patches of lead dioxide or PLATTNERITE, PbO_2, in a thin layer next to the lead metal. Another form of the lead monoxide is called LITHARGE. The third common oxide of lead called MINIUM (red lead) is found also in nature, but its occurence on an artifact has not been reported. The last two minerals have been used as pigments in ancient times.

GALENA, PbS, naturally abundant mineral of lead has not been reported as corrosion product.

Gettens (1970) cites that "Some rather interesting rare lead minerals have been found, like the COTUNNITE, lead chloride, $PbCl_2$ reported by A. Lacroix on lead plates in the sunken Roman ship found off

Mahdia, Tunis, in 1907. Lacroix also noted PHOSGENITE, lead chlorocarbonate $Pb_2(CO_3)\ Cl_2$, on a Roman lead pipe from the same source. I had the good fortune to find phosgenite on the column of an old Persian lamp now in the Freer study collection. I also found on the same object, in contact with the phosgenite, deep blue crystals of the even more rare mineral COMENGITE, a complex copper-lead basic chloride, $(Pb_4\ Cu_4\ Cl_8\ (OH)_8 \cdot H_2O)$".

Other lead-copper minerals may occur but they have not been observed or reported.

Small deposits of ANGLESITE, $Pb\ SO_4$, mixed with phosgenite were observed by Perinet (1961) on lead plates from the ancient sunken ship found off Grand Congloue.

11. Zinc Corrosion Products

Brass, an alloy of copper and zinc has been used by the Romans, and later by the Chinese and Indians in the Middle Ages, it was not put in great use in Europe until the 18th Century. Brass is the least corrosion resistant copper-base alloy. One might expect to find HYDROZINCITE, $Zn_5(OH)_6\ (CO_3)_2$, or ROSASITE ($(Cu, Zn)_2\ (OH)_2\ CO_3$), similar in outward form to botryoidal malachite, but bluer in tone. Also another possible alternation product might be SMITHSONITE, $Zn\ CO_3$.

CONCLUSIONS

Doing this survey on literature on corrosion in copper and bronze objects I found there are quite a few questions and problems, which researchers have asked themselves and some of them are still unanswered.

Even J. Davy in 1826 addressed himself to the questions of:

1. The identification of the constituents presend in patinas.
2. Their relationship to the chemical composition of the underlying metal.
3. The possibility of utilizing the patina to distinguish modern fraudulent productions from authentic ancient artifacts.

The same questions have been re-investigated by numerous workers since then and continue to be pursued to the present day. Although a substantial body of information has been developed, these questions cannot yet be considered to have been satisfactorily resolved.

Other fundamental problems relating to natural patinas that have been the subject of scientific study are the following:

4. Can the structure of certain patinas (e.g., the occurrence periodically alternating stratification) provide means of deducing the age of the patina, and hence of the object?
5. What is the sequence and mechanism of formation of the various compounds found in natural patinas?
6. Is there a characteristic structure in the inter-zone between residual metal and the natural corrosion products that is diagnostic of the authenticity of the latter?
7. What can the quantitative composition of patinas reveal with respect to the character of the environment in which the object corroded?

A fair amount of information now exists in the literature bearing on these matters and certainly very helpful insights have been gained, critical consideration of the available facts can only lead to the conclusion that these questions, too, remain largely unresolved.

This rather ambiguous state of affairs might seem to be inconsistent with the great power, versatility, and sophistication of modern scientific methods, as well as with the often astounding successes which have been achieved in resolving questions of far greater complexity than those just cited. However, progress in the study of corrosion has been, and is still, severely circumscribed by factors beyond the control of the investigator. The most interesting and potentially informative corrosion products have been found only after very long periods of exposure to mildly corrosive environments (e.g., several centuries to millennia). Until relatively recent times the metal composing an artifact of such intrinsic value that when the object ceased to serve its original purpose (as a tool, weapon, or symbol of power, wealth or religion) it was reworked into another form or object. Consequently, the only objects of this kind that have persisted since antiquity are those which were lost or hidden and forgotten. Hence, there is, in general, no objective historical record available. The majority of ancient metal artifacts have come to light under uncontrolled conditions, i.e., accidentally, or in "treasure-hunting" forays and only recently have archaeological expeditions adopted rigorous control procedures for recording and preserving all pertinent data that can aid in interpreting the state of the artifacts. Furthermore, most of the available ancient metal objects have passed through many hands (local peasants, collectors, dealers) before reaching a permanent museum collection, and have been subjected to more or less drastic cleaning (often, over-cleaning, followed by attempts of artificial patination to regain the appearance of antiquity). There is rarely any reliable record available of the type and extent of cleaning and restoration suffered by ancient objects. Hence, very few objects have been available that have been suitable for the proper, detailed investigation of patinas.

Nevertheless, a significant number of ancient objects with corrosion in their pristine state have been studied. Unfortunately, the scientific techniques available for the identification and characterization of the relatively complex types of substances present in corrosion products, have until now, not been adequate to the task, and furthermore, the workers in this field have in general been unaware of that inadequacy. This point may perhaps be most explicitly shown by means of a specific case.

Malachite is a naturally occuring copper-containing mineral that is found in good purity and generous quantity in numerous places on the surface of the earth, and has been well-known and characterized by mineralogists and chemists for over 200 years. Before the advent of x-ray diffraction as a tool for identification of crystalline phases (first applied by Bragg in 1913),but not used as a routing analytical technique until several decades later), malachite could be identified as such only if it were present (a) in large enough quantity so that the stoichiometric proportions of copper hydroxide, and carbonate could be determined by classical wet chemistry, and (b) in a sufficiently well-crystallized form so that its optical constants could be determined by the methods of petrographic analysis through polarization microscopy. One or both of these desiderata are generally not satisfied in patinas, and it has been common for workers in this field simply to assume that any green product on copper or bronze that gave a qualitative reaction for carbonate (viz., signs of gas evolution when treated with drop of acid) was malachite. Since many other basic copper compounds are green the presence of carbonate in any form in a patina would conduce to the overestimation of the occurence of malachite in these corrosion crusts.

Another problem is the unreliability of some of the literature on the composition of the mineral alternating products is also evidenced by the often uncorrect formulas assigned to the constituents. For example, malachite has a well-defined and unique crystal structure, the unit cell of which contains 8 copper (11) ions, 8 hydroxyl ions and 4 carbonate ions (Ramsdell and Wolfe, 1950). This corresponds to the stoichiometric formula $Cu_2(OH)_2CO_3$, which could also be written, according to the conventions employed in the older literature, either as $Cu(OH)_2 \cdot CuCO_3$, or as $2CuO \cdot CO_2 \cdot H_2O$. The following tabulation shows the formulas that have been given as representing malachite in the literature pertaining to corrosion:

FORMULA	REFERENCE
* $6CuO.3CO_2 \cdot 4H_2O$	Gröger (1900)
$2CuO \cdot CO_2 \cdot H_2O$	Pickering (1909)
$CuCO_3 \cdot Cu(OH)_2$	Fowles (1926) Imhoff (1953)
* $3CUCO_3 \cdot 3CU(OH)_2 \cdot H_2O$	Labanukrous (1929)
* $2CuO \cdot CO_2$	Chaplet (1936)
$Cu_2(OH)_2CO_3$	Otto (1959)

Those formulas marked by asterisks give an incorrect stoichiometry for malachite.

A similar situation exists with respect to the other copper compounds that are important constituents of patinas, like brochantite and antlerite. The situation with respect to the suejate containing copper compounds is further complicated by the fact that it is now known that there are at least eight different such compounds which can form when copper or its alloys corrode in the presence of sulfur compounds. The only way in which these substances can be distinguished from each other in corrosion products is through x-ray diffraction studies. Similar ambiguities surround the question of the occurence of the chloride-contiaining minerals.

Thus, the rather limited present-day understanding of the nature and structure of patinas on metal is the consequence of the availability of only a small body of suitable study material, coupled with considerable complexity of the chemical systems involved, necessitating x-ray diffraction and similarly sophisticated investigational techniques.

Reading the available information, I also found out that there are different ambiguities, contradictions and lacunae in our knowledge. Attention may be called to the following interesting cases.

1. A question that has concerned many is whether the ancients intentionally patinated some of their decorative objects. It does not appear to be any solid evidence at present upon which to base either an affirmation or denial of this question.

2. Intergranular corrosion, some investigators think of it as a specific feature of the slow corrosion processes occuring under natural conditions, and its presence in an object was asserted to be a conclusive proof of antiquity. However, intergranular corrosion has been reported to be absent in cases of natural patinas on metal. The matter has not been

sufficiently investigated to permit the presence of intergranular corrosion under a patina to be accepted as proof positive of antiquity, and its absence as proof of fraudulence.

3. Other criteria which have been cited as diagnostic of authenticity of objects proving to have been patinated during long burial in earth are the presence of a substantial thickness of cuprite immediately next to the residual metal and the presence of a banded structure of alternate layers of cuprite and/or tin oxide and malachite and/or atacamite in the cross section of the patina. However, in some cases of ancient objects the cuprite layer is thin or non-existent or separated from the metal by another substance. Banded stratification of patinas is not observed in many authentic ancient corrosion crusts; furthermore, banding or periodicity of precipitation of corrosion products can be produced artificially. It does appear, though, that at the present time the art of forging patinas has not yet reached the stage where thick, adherent, crystalline cuprite layers covered by malachite or atacamite, or stratified layers, can be artificially grown on copper or bronze. The presence of such a patina, free of any trace of a binder or adhesive, can be taken as indicating a high probability of antiquity of the object. However, the absence of these features cannot be considered per se to cast doubt on the authenticity of the object.

4. In the corrosion of buried copper or bronze, the first product formed on the metal, which in turn is converted into the other substances found in patinas, is asserted to be cuprite by Noggerath (1825), Auger (1914), Collins (1931), Plenderleith (1941), Feitknecht (1952) and Fink and Polushkin (1936), even in the presence of much chloride in the surroundings. However, if chloride is available, the first species formed is claimed to be cuprous chloride by Bengough and May (1924), Gettens (1933, 1936 and

1951), Caley (1941), May (1953 - 54), and Organ (1961).

There appears that cuprite is the primary product formed on copper and bronze in pure air, and in pure water. The primary corrosion product in other environments may be one of the other species mentioned in Chaper IV, but this cannot be considered as having been reliably established.

5. The colors and textures of the various species present in patinas vary so much that appearance cannot be depended upon as an indication of composition.

6. The assumption that patina components can be equated with well defined mineral species, may not be entirely valid. It has been shown that the sulfides of copper are non-stoichiometric compounds and the same may be true of copper hydroxysulfates and hydroxychlorides. It is consequently reasonable to expect that the extent of deviation of the composition of these species from simple, integral atomic relative proportions may contain important clues to the age and rate of formation of patina.

7. The rate of corrosion of the individual metals in alloys depends both on the nature of the metals and the composition of the surroundings.

8. It is evident that much remains to be done in the investigation of natural corrosions before we can hope to employ the above features of ancient metal objects as keys to their detailed understanding.

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