THE SUPERFICIAL ALTERATION OF ORE DEPOSITS.¹

GENERAL FEATURES.

Scope of the subject.—The modern idea of ore deposits teaches that formations of this kind represent a process of concentration of mineral matter, either by chemical or physical means; in other words, that they are unusual localizations of certain minerals which are often found disseminated in smaller quantities in many common rocks, and that they differ from the same minerals situated in other conditions, only in their degree of concentration. These concentrations may take place at different times in the history of the rocks in which the deposits occur. If they occur in sedimentary rocks, they may sometimes be formed during the deposition of the rocks with which they are associated, as in the cases of placer gold, stream tin, and sometimes of other ores;

¹ The superficial alteration of ore deposits is a recognized principle of geology, in the same way as is the superficial alteration of any of the common rocks. Its importance in some classes of ore deposits is also well understood, as in many precious metal deposits; while in other classes, its importance has been proved in individual cases, as in the Lake Superior iron deposits. The causes and effects of superficial alteration in many classes of deposits, however, are not so generally understood, and it is the object of the present paper to show that such changes almost invariably give rise to exceedingly important chemical and physical phenomena, while in many deposits, the question as to whether they can or cannot be profitably worked, depends largely on the extent and character of this alteration.

The various treatises on ore deposits published in the United States and Europe make frequent mention of superficial alteration, but have not treated the subject fully. As early as 1854, however, before which time but little accurate information was had on the geologic nature of ore deposits, Professor J. D. Whitney in his classic volume, The Metallic Wealth of the United States, describes the alteration products, or gossans, in certain deposits and mentions others. On the more purely chemical side of the question, the work of Bischof, Daubrée, Roth, Rose, Hunt, Breithaupt, Blum, Julien, Deville, Debray, Volger, Moissan, Fremy, Lévy, Fouqué and others have afforded much valuable information and many useful suggestions. The chemical principles brought out by these various authors have been applied, to a certain extent, to the solution of the phenomena of the origin of ore deposits, but have not as yet been applied to anything like their possible extent to the solution of the phenomena of the alteration of ore deposits.

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while if they occur in igneous rocks, they may sometimes be the result of concentration by differentiation from fused magmas. More usually, however, ore deposits are a result of a concentration after the formation of the enclosing rock, whether the latter be of sedimentary or of igneous origin. The mineral matter represented in this concentration may be derived from the enclosing rocks or closely adjacent rocks, as in the case of many, if not most, iron ore deposits; or it may be derived from more distant sources, often from greater or less depths, as in some of the precious metal deposits. Occasionally, both these sources may be drawn on for mineral matter in one deposit. In this subject of the original source of an ore, we enter a field concerning which there has been much dispute of late years between the advocates of the lateral secretion theory and those who favor the idea of a deep-seated source for many ore deposits. It is not, however, the purpose of the present paper to enter into this discussion, and the following remarks are confined to what happens in the superficial parts of ore deposits, and to a less extent of allied formations, after the materials forming them have been brought into their present, or approximately their present, positions.

Relation of alteration in ore deposits and in country rocks.—Ore deposits are generally more or less changed in their upper parts by atmospheric influences, so that very rarely do the same mineralogical and physical features that are found in these parts, continue to very great depths. In considering this superficial alteration, we discuss a subject analogous to the secular decay of rocks. The latter, however, involves usually but a limited number of common rock-forming minerals, while the secular decay of ore deposits involves a great variety of minerals, not only the oxides, carbonates and silicates common in most rocks, but also sulphides, arsenides, tellurides, selenides, antimonides, chlorides, bromides, iodides, fluorides, sulphanes, phosphates, tungstates, molybdates, and numerous other classes of minerals, many of

1 This has been shown by J. H. L. Vogt (Zeitschrift für praktische Geologie, January, 1893) to be true of certain titaniferous iron ores and other deposits in the eruptive rocks of Norway. It may also be true of certain titaniferous iron ores in the United States.
which, under surface influences, give rise to intricate chemical changes. In discussing the subject of the superficial alteration of ore deposits, therefore, we treat a similar, but much less understood, subject than the superficial alteration of rocks.

Technical names of alteration products.—The altered surface outcrop of ore deposits is known by various names in different regions. Among the Cornish miners of England it is known as gossan, a name which has also been adopted into American mining nomenclature, though other special names are given in special classes of deposits. In France it is known as chapeau de fer; in Germany as eisener hut; among the Spanish Americans as pacos or colorados. As almost all deposits contain more or less iron minerals, the outcrops are usually stained brown from their oxidation, and hence the reference to iron in the French and German names. Sometimes, however, the outcrops are stained black by the oxidation of manganese carbonate or silicate, or green by copper minerals, or other colors by the formation of other compounds.

Agents of alteration.—The superficial alteration of ore deposits, as of any rock, results from a combination of mechanical and chemical disintegration, brought about by the combined action of the atmosphere, surface waters, changes in temperature, and the various organic and inorganic materials contained in the air and water. In nature, we never deal with perfectly pure water, but different waters contain different ingredients derived from the air and from the different materials with which they come in contact. Among the most important of these ingredients are oxygen, numerous organic acids like carbonic, oxalic, malic, citric, formic, propionic, butyric, acetic acids, etc., certain inorganic acids, such as sulphuric, nitric, hydrochloric, hydrobromic, etc., etc. Some of the acids mentioned occasionally occur in the free state, but most of them are generally combined with some of the bases present, such as the alkalies, lime, magnesia, iron, alumina, etc. These various ingredients, of course, are not all contained in the same waters, but are found in various associations in different waters. The organic acids mentioned represent
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Various stages of oxidation of materials from organic matter, but they all eventually, if allowed to become completely oxidized, pass into carbonic acid; while if they are in combination with different bases, these salts are eventually converted to carbonates.

Method and chemical effects of alteration.—Surface waters thus charged with various chemical ingredients percolate down into ore deposits, and there meet various materials which are even less stable under their influence than most of the common rocks. The alteration, therefore, is comparatively rapid, and, though only superficial, generally extends to much greater depths than in the surrounding country rock. From a chemical standpoint, the first effect of this superficial influence is usually the oxidation or hydration, or both, of certain ingredients, followed generally by the formation of other chemical combinations and by the leaching of certain materials. In the formation of these other chemical combinations, however, the base usually remains the same, and the alteration consists generally in a change of the materials associated with the base, that is, in the acidic portion of the mineral or the part that represents the acidic portion. Thus, iron sulphides are oxidized to iron sulphate, and then this is converted by further oxidation and by hydration to the hydrous sesquioxide. Copper sulphides may be oxidized to copper sulphate; and from the sulphate, by the agency of materials in surface waters, may be formed copper carbonates, haloid compounds, silicates, oxides, and even metallic copper; while from some of these, still other compounds may be produced. Similar reactions occur in many lead, zinc, silver, gold, and other deposits.

Occasionally, chemical changes may occur without previous oxidation, and sometimes, though rarely, surface influences under peculiar conditions may have a reducing effect, as in the formation of iron pyrites and copper pyrites from the sulphates of iron and copper, or in the formation of native copper by the action of a ferrous salt on certain copper salts, or in the formation of native silver in surface outcrops. In many of such cases, however, the chemical action is primarily one of partial oxida-
tion, and the reducing action follows as the effect of one of the partially oxidized compounds on the other, as in the case of copper just mentioned. In deposits, such as gypsum, a reduction, due sometimes to superficial influences, is seen in the occasional formation of sulphur from gypsum.

An important chemical effect of surface influences is the removal in solution of certain ingredients of the ore deposit which are soluble in surface waters; as the removal of the calcite gangue of many silver and other deposits; the oxidation and removal of the sulphur in various silver, lead, zinc, copper, and other deposits; the oxidation and removal of both the iron and sulphur of iron pyrites in auriferous quartz veins; the removal of silica from certain iron deposits, such as those in the Lake Superior region, etc. Probably many phosphate deposits are formed by the superficial leaching of carbonate of lime from calcareous beds, and the corresponding concentration of phosphate of lime once finely disseminated in the same beds.

Another chemical effect of superficial alteration is seen in the occasional formation of mineral deposits of importance by certain materials carried from outside sources and deposited in a rock of otherwise no commercial value. Thus certain phosphate deposits of the South Pacific Ocean, the West Indies and possibly of Florida, are formed by the leaching of soluble phosphates from guano, their transportation down into underlying limestone or coral reefs, and the precipitation of the phosphoric acid as tribasic phosphate of lime, which, being almost insoluble, arrests further escape of the phosphatic materials.

Again, another chemical effect is seen in the incrustations, and even extensive beds, of saline materials, like borax, nitre and the various alkaline salts of the western arid regions, formed by precipitation from water rising by capillary action through the soil, becoming evaporated on the surface and depositing the saline materials which they have dissolved from below. Many saline deposits are formed by the simple evaporation of surface waters, such as lakes, seas, etc., but certain deposits undergo only an initial concentration in this way, and are laid down with
clay, sand, and gravel, while further concentration is due to this capillary action. In the case of nitre, indeed, the saline material is very often, if not generally, formed in soils or guano beds and undergoes its first concentration by this capillary action.

In the various chemical changes mentioned above, the class of salts that remains, whether oxides, carbonates, haloid compounds, etc., varies with the nature of the bases affected. Thus, iron sulphides and copper sulphides are both oxidized and form sulphates. But here the similarity of their behavior ends, for the iron sulphate probably passes then into a basic sulphate and then into a hydrous sesquioxide, while the copper sulphate takes up carbonic dioxide and water and forms basic carbonates. The iron sulphate might, under certain conditions, form a carbonate in a similar manner, but this compound would be very unstable under the conditions existing in the alteration of sulphide deposits and would quickly go into the form of the hydrous sesquioxide, while the carbonate of copper is stable under existing conditions and remains.

In the same way, if silver sulphide and iron sulphide are both oxidized and then affected by waters carrying common salt or other chlorides in solution, the silver is converted to chloride, which is insoluble and remains; while the chlorides of iron are much less liable to be formed, as they are soluble, and some of them unstable, compounds, and even if they were formed, they would be leached out or oxidized. Hence, though chloride of silver is a common product of alteration in silver deposits, chloride of iron is never found, at least to any extent, as a product of alteration of iron deposits.

Again, it is frequently found that unaltered auriferous iron pyrites contains a certain amount of silver, while the altered part often carries almost none. In such cases, the gold has remained stable during the alteration, while the silver, in the absence of a chloride or other reagents to convert it to an insoluble compound, has been dissolved and carried away in solution by the acid materials generated during alteration.

Hence, the materials in surface waters affect different bases
differently, and, therefore, there is a great difference in the classes of salts formed by the same surface waters on the ores of different metals. In the same deposit there may be formed an oxide of one metal, a carbonate of another, a chloride of another, etc. In fact, in some of the silver deposits of southern New Mexico, there can be found hydrous sesquioxide of iron formed from iron sulphide, carbonates of copper formed from copper sulphides, and chloride of silver formed probably from silver sulphides, and yet in all probability the same surface waters produced all these changes practically simultaneously.

As a result of these various changes, certain materials are sometimes leached from the upper parts of ore deposits, which have become porous by alteration, and carried down to the less pervious unaltered parts. Here they are precipitated by meeting other solutions or in other ways, and hence the richest bodies of ore in a deposit often occur between the overlying altered part and the underlying unaltered part. This is not always the case, but it is true of some copper, silver, iron and other deposits.

*Physical effects of alteration.*—From a physical standpoint, the effect of superficial alteration is generally to make the deposit more open and porous, to cause it to shrink, and, in some cases, to convert it to a loose material of the consistency of sand and clay. In some cases, however, especially where considerable hydration goes on, an expansion may be caused. This is well seen in the formation of gypsum by the hydration of anhydrite, often causing an expansion sufficient to brecciate and fold the associated rocks,\(^1\) and amounting to about 33 per cent. of the original material.\(^2\) In the conversion of carbonate of iron to the hydrous sesquioxide of iron, or limonite, it has been found\(^3\) that there is a contraction of 19.5 per cent., giving the deposit the loose porous structure characteristic of limonite and forming the familiar

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limonite geodes. In this case carbon dioxide has been removed from the iron, but oxygen and water have been added. A porosity is also produced by the removal of certain ingredients in an ore deposit without the addition of others, as in the oxidation and leaching of iron pyrites in veins of auriferous quartz, leaving a loose, porous, spongy quartz mass.

Surface decomposition has also, in many places, not only affected the ore deposit itself, but also the country rock in the immediate vicinity, and has converted it into a loose material of a sandy or clayey consistency, as at Iron Mountain, Missouri, in the Batesville manganese region of Arkansas and in other localities described beyond. In the iron and manganese deposits of the Cambrian and Lower Silurian rocks in the Appalachian region, the limestones and shales, which once enclosed the ore bodies, have often been converted to clay in the same way as in the Batesville region; and, in fact, the common mode of occurrence of these deposits is as residual clays carrying irregular bodies and nodules of ore.

This decay of the country rock in immediate association with ore deposits, is generally more extensive than in similar rocks not associated with such deposits, and, therefore, requires further explanation than the simple action of ordinary surface waters. The explanation is, doubtless, in many cases, that the rock has decayed under the influence of the same waters that originally concentrated the ore; and as these waters differed from most waters in character and in the materials they held in solution, they often had an abnormal effect. Moreover, when subsequently the ore body is affected by surface influences, sulphuric acid is liberated from sulphides and carbonic acid from carbonates, as well as other acids from other minerals, and all these materials have an active effect on most rocks. Moreover, the porous nature of many ore deposits, after they have been altered on the surface, allows a freer percolation of surface waters than elsewhere in the same country rock, and, hence, a correspondingly greater decay.

Another physical effect of surface influences on ore deposits is seen in certain forms of brecciation due to physical or chemical causes, such as expansion by hydration, etc. Such brecciation, however, has usually occurred in the country rock before the concentration of the ore deposit; in fact, its existence, by offering favorable conditions for deposition, has often been the cause of the formation of the ore deposit in a given place. Though brecciation, therefore, is very important as a factor in the concentration of ore deposits, it does not belong, to any large extent, in a discussion of the surface alteration of ore deposits after their formation, and, therefore, it will not be treated further in this paper.

Depth of alteration.—Having thus discussed briefly the means by which superficial alteration in ore deposits is produced, and the results of this alteration, the next feature to be taken up is the depth to which it extends. As already shown, the alteration is primarily one of oxidation and generally of hydration; and, though either may occur without the other, they both very often occur together. When surface waters percolate into the rock, their influence is more active near the surface, because they carry large quantities of oxygen, and because the oxygen of the air itself also has some influence. As they sink deeper, the effect of the oxygen of the air becomes less active, and the oxygen dissolved in the water is consumed in oxidizing various materials which it meets on the way, until finally most of the oxygen is lost and active oxidation ceases. Theoretically, this oxidizing action may extend down as far as, and sometimes below, the level of the drainage of the surrounding country, which is called also the zone of permanent saturation. Above that level, there is a constant circulation of water from the surface downwards, thus affording means of active oxidation; but when the water reaches that level, not only has most of the oxygen contained in solution generally been used up, but also the circulation of the water is much more sluggish, so that oxidation is less active.¹

¹ It is possible that the oxidation near the surface is due largely to free oxygen in the waters, while, when this becomes exhausted at a depth, the oxidation may be due to the abstraction by mineral matter of the oxygen in combination with materials in solution.
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The process of hydration, when the materials affected do not require oxidation before they can become hydrated, may extend down indefinitely below the limit of oxidation; but when oxidation is necessary before hydration is possible, the latter process of course can extend no deeper than oxidation. Thus the silicate of alumina in feldspar may become hydrated and form kaolin without the intervention of oxygen. This is brought about by the action of carbonic acid and water, which react on the feldspar and form alkaline carbonates, kaolin and free or hydrous silica. Theoretically, therefore, kaolinization ought to go on to any depth that can be reached by water and its almost universal accompaniment, carbonic acid. In this case, however, the base in question is already in its peroxide condition (\( \text{Al}_2\text{O}_3\)), but when a base is not in this condition, it frequently requires oxidation previous to hydration. Thus sulphide of iron does not become hydrated until it is peroxidized, and this mineral, therefore, requires oxidation previous to hydration.\(^1\)

The various materials other than oxygen in surface waters have a very important effect on the mineral matter with which they come in contact, and their action sometimes takes place before that of oxidation, though it often requires at least a partial previous oxidation. The effect is both to form new chemical compounds with the materials involved, and to dissolve and bodily remove certain materials. As with oxygen, however, so with these other agents of alteration, they are more active above the drainage level of the country than below it, and an additional reason for this is that many of the materials affected require a primary oxidation before they enter into other chemical combinations. Thus sulphide of lead is oxidized to sulphate of lead before it can take up carbonic acid and form carbonate of lead; while on the other hand, carbonate of lime can be converted to sulphate of lime (gypsum) by the action of sulphuric acid or certain sulphates without any change in the degree of oxidation of the lime.

\(^1\)For a full discussion of this subject see H. Rose, Ueber den Einfluss des Wassers bei chemischen Zersetzungen, Pogg. Ann. der Physik und Chemic, 82 et seq.
It will thus be seen that in going from the surface downwards, we pass from a zone of active oxidation into a zone in which oxidation practically ceases. Below the level of permanent saturation, the waters may sometimes gradually sink to very great depths, even deep enough to become intensely heated and possibly dissociated. Such water may have a very important effect in the formation of ore bodies, though in a manner quite different from their action on the surface. The present discussion, however, relates not to this, but only superficial influences.

Though theoretically, therefore, alteration of one kind or another may extend down to, and in some cases much below the level of permanent saturation, and if given sufficient time would actually go to such depths; yet in many, if not most, cases it has not yet reached that level. The actual depth to which alteration does extend varies with the topographic conditions of the region, the chemical nature and the porosity of the deposits affected, the character of the climate, and other minor conditions.

The topography of a region affects the depth of alteration, because it is one of the principal features in determining the depth of permanent saturation. The chemical nature of the deposit affects the depth of alteration because on this depends the degree of resistance it will offer to the chemical effects of percolating waters. The porosity of the deposit affects the depth of alteration because, in deposits of similar kind but of different porosity, the more porous will be more accessible to surface influences, and will, therefore, be more affected, in a given time, than the less porous deposit.

The climatic conditions, such as the amount and manner of occurrence of rainfall and other forms of atmospheric moisture, and the rate and degree of variation in temperature have a large influence on superficial alteration. On the amount of rainfall and other forms of atmospheric moisture depends the amount of moisture available as an agent of alteration; while on their mode of precipitation depends, other things being equal, the amount of water which would sink into the deposit, thus effecting alteration,
and the amount that would immediately run off the surface or be evaporated and thus have but little altering effect. The rate and degree of variation in temperature affect the amount of breaking in the rock by expansion and contraction, and, therefore, the accessibility of the rock to surface influences. The character of the climate also influences, to a certain extent, the nature and amount of vegetation, and from the vegetation are obtained many organic acids which assist the action of surface waters. In other ways, also, such as in the generation of nitric acid in the atmosphere, the character of the climate influences the agents of alteration.

As a result of all these influences, surface alteration is found to extend in different ore deposits to depths varying from only a few inches, or in fact only a fraction of an inch, to several hundred and even a thousand or more feet. In glaciated regions the products of decay have often been swept away by glacial action, and the time which has elapsed since then has not been sufficient for alteration to have extended to any great depths; while in regions of moist climates, the erosion sometimes, though not always, keeps pace with the alteration, so that the depth of the change is shallow. In those regions, however, which have not been recently glaciated and which have dry or only moderately moist climates, so that erosion is slight, or in places which have moist climates, but which, on account of their topography, are not subjected to very active erosion, the products of alteration collect, and the changes are traceable downwards often to great depths.

In the copper regions of Michigan, the deposits have been exposed to glaciation, and are still exposed to the active effects of erosion in a moist climate, so that here, though the native copper of the region is a material very easily affected by surface alteration, yet the only change observable is a slight stain of copper carbonate or oxide on the surface of some of the native copper, and even this is not always present. On the other hand, in the arid region of the west, most of which has not been recently glaciated and which has an exceedingly dry climate, the
residual products of alteration have accumulated to great thicknesses. This region, however, had once a much more moist climate than now, and some of the alteration may have occurred then. Many of the Arizona copper deposits in this region originally contained their copper in the form of copper pyrites, which, under similar conditions, is probably more resistant to surface alteration than the native copper of Michigan, and yet it has been changed to various other copper minerals for depths often reaching from 100 to over 700 feet. In Chile some of the copper sulphide deposits are said to have been altered to a depth of 1,500 feet, but it is very rare that much alteration extends in any ore deposits to greater depths than this. In the more moist climate of Tasmania, the results of alteration are also very marked.

The depth of alteration of ore deposits in unglaciated regions in the United States varies from a few feet to over 1,000 feet. In the Appalachian region, many of the deposits of auriferous quartz, iron pyrites, copper pyrites, etc., are altered to depths varying from less than one to a hundred feet or more. Many of the Clinton iron ore deposits are altered to still greater depths. The depth of alteration in these Appalachian deposits is usually much greater, other things being equal, south of the limit of glaciation than north of it. In the silver, lead, gold, and copper deposits of the Rocky Mountains and the western arid region, such as at Butte City, Leadville, Central City, Cripple Creek, Silver City, Lake Valley, Eureka, Virginia City, Park City, the Coeur d'Alene district, and elsewhere, the alteration has reached depths ranging from 50 to 600 or 700 feet, and in some rare cases still more. At Granite Mountain in Montana, signs of alteration are seen in the argentiferous quartz deposits of that region, even at depths of 900 feet, though of course at such depths the alteration is slight as compared with that nearer the surface.

Complete alteration rarely extends to these greater depths, and usually parts of a deposit which have as yet escaped alteration appear comparatively near the surface. These are at first very few and may be entirely enclosed by altered products, but with
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increased depth they become more numerous and continuous, until they predominate over the altered products, and finally, when the limit of alteration is reached, they entirely replace them. The planes of contact between an ore deposit and the country rock, that is the walls, afford, when well defined, easy passages for the downward percolation of surface waters, and therefore alteration frequently continues down along these lines for considerable distances after the limit of alteration in the main part of a deposit has been reached. Any other possible channels, such as the planes of contact of different minerals in banded deposits or the series of drusy cavities often found in the central parts of ore deposits, may act in the same way as passages for water. Hence the not infrequent abundance of alteration products, such as hydrous sesquioxide of iron, and native copper and silver, along the walls and elsewhere in certain deposits.

Classification of the products of alteration.—The products of superficial alteration may be divided into two general classes: (1) Those which occupy the same position as the materials from which they were derived, or are only slightly removed, and possess the same general environment. Thus the altered outcrops of auriferous quartz and iron pyrites, of argentiferous galena, of sulphides of copper and many other similar deposits, represent alteration-products occupying the same general position as the original sulphide ores; while the iron ore bodies of the Lake Superior region represent alteration-products changed somewhat in position from that occupied originally, but yet in the same series of rocks and sometimes with somewhat similar environment. (2) In the second class are included those deposits which have been entirely removed from their original position and redeposited under totally different environments. Thus, placer gold deposits, stream tin, most of the deposits carrying platinum and the allied metals, magnetic and chromite sand, the gravels and sands carrying precious stones, and many other similar deposits represent this class. They have been derived by the decay and erosion of veins, dikes or country rocks carrying the materials now concentrated in these fragmental deposits.
The materials in their original environment may or may not have been sufficiently concentrated to serve as commercial sources of supply, but the fragmental deposits mentioned almost always represent a further concentration. This class of deposits is of great importance, but the present discussion relates more especially to the superficial alteration of deposits that remain in situ, and therefore these will be treated more in detail than the other class, (No. 2), though the latter will be mentioned as occasion requires.

SUPERFICIAL ALTERATION IN DIFFERENT DEPOSITS.

Alteration in iron deposits.—It was once generally believed that most iron deposits were the result of direct precipitation from aqueous solution, or in rarer cases, were igneous masses. It has long since been shown, however, that most workable iron deposits are the result of a concentration subsequent to their deposition, while very few are due to a direct precipitation during the formation of sedimentary rocks, though some may be due to a process of differentiation in the cooling of eruptive magmas. The original presence of the iron in sedimentary rocks was doubtless due to a direct precipitation during the formation of the enclosing rock, but it was then in a finely disseminated condition, and it was only by being subsequently taken into solution again by percolating waters and concentrated, that it was converted into bodies of greater or less purity. Generally, though possibly not always, this process is superficial, and though it may extend to a depth of several hundred or even a thousand feet or more, it can be traced directly to surface influences, and its effects are seen to decrease gradually with depth. Shaler, in 1877, showed that some of the limonites of Kentucky, Ohio and elsewhere were concentrations of iron derived in solution from shales and other rocks and reprecipitated in underlying limestone.

1 See foot note on second page of present article.

Van Hise,\textsuperscript{1} in 1889, showed that the iron deposits of the Lake Superior region are concentrations of iron formerly disseminated in a siliceous rock containing carbonate of iron and other carbonates, and called by him cherty iron carbonate. This disseminated iron was taken into solution by surface waters, carried down until its passage was obstructed or impeded by less pervious rocks, often dikes, and there precipitated by meeting with other solutions of a different nature. These other solutions contained oxygen, while the iron-bearing solutions had been largely robbed of their oxygen and had been freed from silica by the large amount of carbonic acid they contained. When, therefore, the two solutions met, the iron in solution was oxidized and precipitated; while the silica, in the spot where this precipitation occurred, was, on account of the dilution of the carbonated waters with the other waters, and through the agency of alkaline carbonates, dissolved and carried off, thus gradually increasing the amount of iron and removing the silica. By this theory, the iron is largely a replacement of the silica of the cherty iron carbonates, and has been derived from the parts of the strata exposed to superficial influences. The deposits are, therefore, of only superficial extent, though they may reach over 1,000 feet below the surface, yet when they pass below the action of surface influences, the iron has not been concentrated and they are of too low grade to be mined for iron ore. The methods of local concentration proposed by Professor Van Hise for these Lake Superior iron deposits, are equally applicable to certain other iron deposits, and are a most valuable addition to our knowledge of chemical geology. They also bring out in a most prominent manner, the fact that even rocks composed of materials like silica, which are very resistant to surface influences, may, under proper conditions, be replaced on a large scale.

The iron deposits of the Mesabi Range in Minnesota, which have lately been described by H. V. Winchell are supposed to have had a somewhat similar origin to that given for the Michigan and Wisconsin ores by Van Hise. Winchell believes that they are due to the concentration by surface agencies of iron disseminated as oxides in a highly siliceous rock, and that in this concentration the silica has been replaced by iron.

The red hematites of the Clinton horizon of the Upper Silurian in the Appalachian region have been at least partly formed by superficial concentration which extends to only limited depths.

The iron deposits in other geologic horizons of the Appalachian valley, especially in the Cambrian, Lower Silurian and Carboniferous rocks, are also often much changed by the action of surface influences. Many of the deposits in the Cambrian and Lower Silurian can be clearly shown to be due to a superficial replacement of limestone, or even of more siliceous rocks like shales, by iron dissolved from ferruginous rocks in the neighborhood. In such cases, the iron in the original rock has been dissolved and carried off in carbonated surface water, and re-precipitated in the other rocks, all these stages being directly due to surface influences. Many of the carbonate iron ores of the Carboniferous rocks are rendered not only of higher grade, but also more easy to treat, by the oxidation of the carbonate to the sesquioxide and the removal of the carbonic acid. Moreover, these carbonate ores often occur as nodules, "kidney ores," in shale, and, on the surface, this shale has been softened by atmospheric conditions, thus facilitating mining; while away from the surface, the shale becomes harder and makes mining more expensive.

Surface influences on carbonate of iron have been made use of artificially in Styria, where a very hard spathic iron ore has been mined and spread out on a hill side for from 20 to 25 years. By this process the ore was oxidized and made more porous, and thus became very much more cheaply treated.²

² Letter from Mr. Charles E. Smith, Philadelphia, Pennsylvania.
At the celebrated Iron Mountain in Missouri, a large part of the ore came from conglomerates composed largely of fragments of iron ore, which had been weathered out of the pre-Cambrian rocks that had originally contained them. These conglomerates lie at the base of the Cambrian strata which overlie the pre-Cambrian rocks, and even in the latter rocks, where exposed, the original ore has been made much more easy to work by the decay of the enclosing material and its conversion to clay.

In the iron region of eastern Texas, the limonite ores are often a result of the solution of iron from the superficial oxidation of iron pyrites, iron carbonate and glauconite. Sometimes the sequel of this process is the downward passage of the solution to an underlying laminated clay, and the gradual replacement of this bed, forming a hard limonite, which still preserves the laminated structure of the clay.

In Mexico certain hematite deposits described by R. T. Hill as occurring in Lower Cretaceous limestone at or near the contact with intrusive masses of diorite, and sometimes even in the diorite itself, may, as Hill suggests, be the result of superficial concentration from the limestone.

Very large deposits of hematite also occur in Grant county, New Mexico, at the contact of limestone and an eruptive. The origin of this ore is as yet somewhat obscure, but is probably due to a concentration after the original deposition of the iron.

The iron deposits in the lakes of Sweden and Norway are most striking instances of a concentration of iron ore due to surface influences and going on at the present time. The iron is derived from the oxidation of the neighboring rocks, carried by carbonated surface waters to the lakes, and there, by further oxidation and hydration, precipitated as hydrous sesquioxide (limonite). The iron ore is dredged up and used, but the processes of nature gradually replace it, and, in the course of years, the lakes again accumulate a considerable thickness of ore.

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Many other similar cases of superficial enrichment in iron deposits might be mentioned, but the above are enough to illustrate the point in question, and it will be seen that, of the regions which are the active producers of iron ore in this country, almost all, if not all, owe the existence, or at least the availability of their large bodies of ore, to superficial concentration.

*Alteration in manganese deposits.*—Manganese deposits are affected by superficial influences in much the same way as iron deposits. Many of the manganese deposits in the Cambrian and Lower Silurian rocks of the Appalachian Valley were concentrated in a manner somewhat similar, though not always so, to the iron deposits in the same regions. 1

In the Batesville manganese region of Arkansas, the ore originally occurred in irregular masses in Silurian limestone, but surface decay has leached the carbonate of lime out of the limestone, leaving a red siliceous clay, which represents the less soluble part of the original rock. This clay now lies in hollows on the surface of the limestone and contains the masses of ore once disseminated through that rock. The removal of the carbonate of lime has concentrated the ore masses in the clay, and has also rendered them more easily mined; in fact, the only manganese ore that can now be profitably mined in this region is that in the residual clay. 2

The frequent occurrence of deposits of bog manganese ore in the areas of crystalline rocks, generally represents a concentration of manganese resulting from the oxidation of disseminated carbonate and silicate of manganese in the country rock. This oxidation product is taken into solution in surface waters, and transported until subjected to such conditions that it is oxidized and precipitated as a hydrous oxide.

*Alteration in copper deposits.*—In many copper deposits superficial alteration has produced very remarkable chemical and economic results, and this is especially well seen in the copper

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sulphide deposits of Arizona, Chile and elsewhere. In Arizona the upper parts of the deposits are composed of brown or black ferruginous masses, with brilliantly colored oxidized copper minerals, as cuprite, malachite, azurite, chrysocolla, etc.; while below, at depths varying from a few feet to several hundred feet, the deposits usually pass into a mixture of copper pyrites and iron pyrites, the latter usually being far in excess. Sometimes other copper sulphides occur, either mixed with copper pyrites or free from it, and they may or may not have been derived from it. Here the carbonates and some of the other alteration minerals contain not only more copper than the unaltered copper pyrites, but they are also in a much more concentrated condition than the sulphide which is disseminated through iron pyrites. The total amount of copper has not been increased, in fact it may be decreased by leaching, but it is in a more concentrated form, and therefore the ore obtained from these concentrations averages from eight to thirty per cent. or more in copper, while the mixture of unoxidized copper pyrites and iron pyrites below averages only about five per cent. in copper. Moreover, the altered ores are much more cheaply treated than the unaltered ones, and are therefore still more desirable. It will thus be seen that the economic value of the deposits as a whole has been greatly increased.

In the surface alteration of these deposits, the copper sulphides have first been converted to copper sulphate and then, by the action of surface waters and the materials contained in solution in them, they pass into the forms of copper carbonates, oxides, silicates, and occasionally to the chlorides and bromides, and sometimes to native copper. The iron sulphide is first converted to sulphate and then this, through other stages, is converted into the hydrous sesquioxide (limonite), though the iron sometimes now occurs in the form of the anhydrous sesquioxide (hematite). This may have been derived from the limonite by dehydration, or, under certain conditions, may have been formed directly by the oxidation of iron pyrites. The oxidized copper minerals in the upper part of
the ore deposit have been concentrated partly by segregation during alteration, and partly by the leaching of the associated materials. As a result of this, these minerals occur as seams, pockets or irregular bodies, often a hundred feet or more in diameter, generally enclosed by, and often intimately associated with, the oxidized iron materials which represent the gangue.

In the case of the Arizona deposits, alteration has progressed just far enough to increase greatly the value of the deposits without to any extent injuring it. Such products of alteration, however, are more or less soluble in surface waters containing various organic and inorganic compounds, so that in a moist climate there is a constant tendency to leach them out and leave only the less soluble parts of the gangue. In Arizona, this stage has not yet progressed to a noticeable degree, and one reason for this may be the extreme dryness of the climate, which affords opportunity for only comparatively slight percolation of surface waters.

In the copper deposits of Montana and the Appalachian region, however, a further stage of alteration is often observable. The copper deposits at Butte City, Montana, are composed largely of chalcocite, with copper pyrites, bornite, enargite, iron pyrites and other minerals in a siliceous gangue. On the surface the copper in these deposits has been almost entirely oxidized and leached out, and the ore consists of a porous, rusty, siliceous mass which was once mined for the small percentage of silver it contained. As depths were reached, the oxidized copper minerals began to appear, and eventually the sulphides formed the mass of the veins. In this case, a further stage of alteration is seen than that in Arizona.

At Ducktown in eastern Tennessee, deposits of mixed iron and copper pyrites occur and have been altered in a somewhat similar manner on the surface. The copper minerals have been leached out of the ferruginous gangue in the upper parts of the deposits, and for a depth of from 20 to 80 feet or more, the deposits are composed simply of a porous mass of more or less

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Hydrous sesquioxide of iron. Below this a part of the copper, which has been leached from above, has been carried down and deposited as a dark material, probably composed largely of oxides and sulphides of copper, and averaging sometimes 20 to 25 per cent. or more in metallic copper. This material immediately overlies the unoxidized mixture of copper and iron pyrites, which averages only from 2 per cent. to 4 or 5 per cent. in copper. The commercial copper mined in this region came from the part of the deposit below the iron capping and above the unoxidized sulphides. When this was exhausted, the mines had to be closed, for the unaltered sulphides were too poor to be utilized.

In Chile, Peru, and elsewhere in South America, changes in copper deposits, somewhat similar to those described in the United States, frequently occur. In fact, the great reputation which Chile once had as a copper producer, was largely due to this surface alteration, for the oxidized ore once supplied a rich and easily treated source of copper, but when the mines reached the unoxidized sulphides, the ores became poor in copper and more difficult to treat, so that the copper industry of Chile began to decline. In that region, however, the oxidation has in some places extended down as far as 1,500 feet.

Alteration in lead deposits.—In the case of lead deposits, the mineral galena, which is the commonest ore, is frequently more or less altered on its surface outcrops and converted to the sulphate (anglesite) and the carbonate (cerussite). The first product of oxidation is anglesite, but this is a soluble compound and readily unites with carbonic acid or soluble carbonates in surface waters, forming the carbonate of lead, or cerussite. In rarer cases, other lead minerals, like phosphates, may also be formed.

Alteration in silver deposits.—Galena deposits often contain silver, possibly sometimes in the same condition of sulphide as the galena, and this material is altered at the same time as the lead, with the formation of native silver, chloride of silver (cerargyrite), bromide of silver (bromyrite), iodide of silver (iodyrite),
and various other minerals. The native silver is formed, probably, only after a preceding oxidation of the sulphide. Deposits carrying other unaltered silver-bearing minerals, such as the various silver sulphides, arsenides, antimonides, tellurides, etc., are, when exposed to surface influences, affected in much the same way as the silver in argentiferous galena.

Alteration of zinc deposits—In the case of zinc, the most common ore is the sulphide known as blende. This mineral, like galena, is generally oxidized on the surface, and forms by other chemical changes the carbonate (smithsonite), the basic carbonate (hydrozincite), and the basic silicate (calamine), in a manner similar to that described in copper and lead ores.

In the cases of both lead and zinc, oxidized ores are very desirable for metallurgical purposes, and are much sought after. To be sure, the carbonates, sulphates, etc., of lead and zinc contain less of these metals than the pure sulphides, but they occur in a more concentrated form than the sulphides, and, therefore, the ores containing them frequently carry as much or more of the metals than the ores containing the sulphides. Moreover, the oxidized ores are much more easy to treat and, therefore, have an additional value over the sulphide ores.

Alteration in gold deposits.—In the case of gold deposits, surface alteration has a most marked effect, and probably in no class of deposits is the change of more geologic and economic importance. The typical unaltered condition of gold in nature is in association with iron pyrites in quartz, the gold being sometimes in such association with the pyrites that it cannot be separated by mechanical means, while in rarer cases, it can be so separated. The effect of surface oxidation on such a deposit, is first to convert the iron pyrites into a hydrated sesquioxide of iron, which permeates the white quartz, with which the pyrites is usually associated, and turns it into a rusty brown mass. The next stage is the gradual leaching out of the hydrous sesquioxide by the action of surface waters. The iron is, in this way, finally removed altogether, and the remaining product is a pure white quartz, containing the gold which was originally in the
iron pyrites, and which has remained stable during the oxidation and leaching of that mineral. Such quartz is usually porous and spongy, and is filled with cavities which represent the shapes of the original crystals of iron pyrites, and which, during an intermediate stage, have been partly filled with hydrous sesquioxide. This leaching, however, is rarely complete, and the quartz is usually stained brown on the surface.

In gold deposits of this kind, other minerals, such as copper pyrites, galena, blende, etc., frequently occur, and when the deposit is affected by surface influences, these minerals act in the manner already described under copper, lead, and zinc. It is not uncommon to see gold-bearing quartz stained green by oxidized copper minerals, or black by manganese minerals. Sometimes, especially in the Rocky Mountain region, gold occurs in the form of a telluride instead of in iron sulphide, and in such cases, the telluride is oxidized and the gold set free from its combined state. The gold, in being freed from pyrites or other minerals, is not only concentrated by the removal of certain ingredients of the deposits, but it is brought into a condition in which it is much easier to treat than the unaltered part of the deposit, and, therefore, the upper parts of most gold-bearing veins are greatly enhanced in value. The ore from these parts is known as "free milling" ore, because it can generally be ground and the gold extracted by direct amalgamation with mercury; while the ore in the unaltered parts of the deposit cannot usually be thus easily extracted, but must be smelted or treated by chlorination or some other more or less expensive process.

When such deposits as those described are eroded, the particles of gold separate from the quartz and are concentrated in the streams as placer gold. These detrital deposits are the source of a large part of the gold of commerce, and, in fact, were once the source of most of it. Now, however, many of the richest placer deposits known have been exhausted; and besides, the methods of treating the ores in the original deposits are better understood, so that the latter are supplying yearly a larger and
larger percentage of the gold production of the world. Hence, it will be seen, that in gold deposits, surface alteration not only plays an important part in freeing the gold from the iron pyrites, but also in forming placer deposits. Detrital deposits similar to gold placers and carrying various other materials are not at all uncommon, as in the cases of the platinum group of metals, cassiterite, diamonds and many other gems, chromite and magnetite sands, and, in fact, even with some of the more common ores, as with the iron conglomerate at Iron Mountain, Missouri.

*Alteration in tin deposits.*—In tin deposits, the typical mode of occurrence of the metal is in veins, dikes, or country rocks, in the form of the oxide known as cassiterite. Cassiterite is not easily affected chemically by surface influences, so that it is not much changed by superficial alteration, but for this very reason, its concentration is most markedly affected by surface alteration, for in the erosion of tin-bearing deposits the masses of cassiterite are broken up and carried off mechanically by surface waters, to be deposited somewhere else in the form of gravel beds, instead of being dissolved and possibly disseminated. In this transition, the fragments of cassiterite are largely separated from the accompanying materials by reason of their greater specific gravity, and hence, gravel deposits rich in cassiterite frequently occur. These represent the stream tin of the miner, and have been formed in much the same manner as have the placer gold deposits. Some chemical action, however, has gone on in the tin ore itself, but this seems to have been simply a process of solution and redeposition, as is seen in the pseudomorphs of cassiterite after other minerals and in the impregnations of animal remains in Cornwall, such as antlers, with oxide of tin.1

*Alteration in antimony deposits.*—In many antimony deposits, alteration similar to that described in some of the deposits already mentioned frequently occurs. The metal occurs most commonly as the sulphide known as stibnite. By alteration, however, this passes into the oxides valentinite, senarmontite, cervantite, stibiconite, etc., or into the combined sulphide and oxide known

as kermesite. Valentinite and senarmontite have the same chemical composition but differ in their crystalline forms. Native antimony sometimes occurs, and this also, by alteration, gives rise to the oxides.

Alteration in bismuth deposits.—The allied metal bismuth occurs most commonly as native bismuth, though the sulphide (bismuthinite), the selenide (guanajuatite), the telluride (tetradyrite), etc. also occur. Native bismuth, by alteration, forms the carbonate (bismutite) and probably also the oxide (bismite) and the silicate (eulytite).

Alteration in mercury deposits.—In the case of mercury the metal commonly occurs as the sulphide (cinnabar), though other mercury minerals also occur. By the alteration of cinnabar and some of the other mercury minerals, metallic mercury is set free and occurs as globules or filling cavities in the ore.

Alteration in molybdenum deposits.—Another case of surface alteration in metalliferous deposits is that seen in molybdenite. This mineral is the sulphide of the metal molybdenum, and often occurs in quartz or calcite veins in the crystalline rocks of parts of Canada, and in many ore deposits of the Rocky Mountains and elsewhere. By surface oxidation, molybdenite passes into a brilliant yellow oxide of molybdenum, commonly known as molybdate or molybdic ocher, which, in the Canadian region, occurs as a powdery coating on the cleavage planes of the molybdenite.

Alteration in other deposits.—Superficial alteration like that already described in various deposits, occurs also in many others not yet mentioned, as in aluminum, nickel, cobalt, chromium, tungsten, and many rarer deposits, but the changes already described show the general features of the subject. It may be said, however, that one of the important ores of aluminum, known as bauxite, is probably derived from the alteration of feldspar under certain conditions; and its source, therefore, is not altogether unlike that of the hydrous sesquioxide of iron derived from the alteration of certain silicates. The conditions during formation, however, were probably quite different.
THE FORMATION OF HALOID COMPOUNDS IN ORE DEPOSITS IN ARID REGIONS.

The formation of chlorides and other haloid compounds has already been mentioned as one of the phenomena of superficial alteration in ore deposits. As soluble chlorides and sometimes other haloid compounds are common in surface waters, chlorides and the allied compounds are not at all uncommon as alteration products, especially in such cases as that of silver, where the chloride, bromide and iodide are insoluble compounds, and are not leached out. For this reason, chloride ores of silver are found to a greater or less extent in almost all silver districts in America, Europe, and elsewhere, but the occurrence of such compounds in very large quantities in certain parts of North and South America deserves special explanation.

Over a large part of the arid region of the west, lying between the Rocky Mountains and the Sierra Nevada, ores containing chloride of silver (cerargyrite) are abundant, and sometimes the bromides and iodides also occur; in fact, parts of this region are characterized by chloride ores. They are especially well developed in parts of New Mexico, Arizona, Utah, Nevada and other states and territories, and it seems probable that their abundance can be traced to the effect of the peculiar climatic conditions which have prevailed in that region in late geologic times. Most of this arid country was once covered with numerous bodies of water, some of them of great size. In late geologic times, however, these began to dry up, until their waters no longer rose high enough to have outlets, and then, as a natural result, they became highly impregnated with salt and other saline matter. Finally, they became desiccated, leaving deposits of various earthy and saline materials in their old basins, and among the most common of these was common salt. It seems probable that the abundance of chloride ores is due to the action of this salt on the pre-existing ore deposits of the region, in the basins of the lakes, and that the smaller quantities of bromides and iodides were formed by a similar action of the soluble
bromides and iodides in association with the salt. Such ores, in some of the mines that have gone to sufficient depths, have passed into various other silver compounds, such as the sulphide (argentite), argentiferous galena, etc., which represent the original condition of the ores. This transition proves the chlorides and other haloid compounds to be of only superficial extent.

This transition to haloid compounds is not confined to silver ores, for the basic chloride of copper (atamite) occurs at Jerome in Arizona, and both chlorides and bromides of copper occur in the Bloody Tanks district west of Globe in Arizona, though here, as elsewhere in Arizona, the other copper minerals already mentioned, such as carbonates, sulphides, etc., form the bulk of the copper deposits.

In parts of Mexico, Chile, and Peru, where saline materials have collected in a manner somewhat similar to that in the arid regions of the United States, the chloride of silver is one of the important ores mined, and it sometimes occurs intimately mixed with chloride of sodium, or common salt, forming the mineral huantajayite or the lechedor of the miners. The bromides of silver are also abundant in Chile, and, in fact, at the mines of Chañarcillo, a common ore is the double chloride and bromide known as embolite. Again, the atamite, or basic chloride of copper, from the Desert of Atacama is well known.

It seems probable that this transformation of the silver and copper minerals did not necessarily occur exclusively while the deposits were covered by saline lakes, but may have occurred even more actively afterwards, when the surface waters were highly impregnated with chlorides from the residue left by the lakes, and when oxidation in the ore deposits was much more active than when they were covered by water. This seems all the more likely when we consider that the original silver and copper minerals probably had to be oxidized before they were converted to chlorides, etc. Of course the oxidation may have partly occurred before, or during, the existence of the lakes, but
in many cases it probably also occurred after they were desiccated.¹

SUMMARY.

It will be seen from the above discussion that:

(1) After the deposition of ore deposits and their subsequent exposure to surface influences, such as air, water and the materials contained in it, changes of temperature, etc., chemical and physical alterations occur which cause a total change in the mineralogical condition, and generally in the economic value, of the ore deposit.

(2) The process of this alteration is primarily one of oxidation and generally of hydration, and both of these actions may go on alone, but generally both have their effect on the same material. The other materials in solution in surface waters also react on the substances in the ore deposit, either before or after the oxidation of the latter, though generally after at least partial oxidation, and form various compounds different from those originally in the deposit. The difference, however, with few exceptions, is not in the metal or other base which forms the important feature of the deposit, but in the acidic portion or material representing this portion of the mineral. Thus, sulphide of copper may be altered to carbonate of copper, but the base remains the same. The action of surface influences is in rare cases one of reduction, which, however, often follows a previous oxidation. The process of alteration also frequently causes a leaching of certain ingredients of the ore deposit, either with or without previous oxidation, as in the removal of iron pyrites, calcite, etc. It also sometimes renders a hitherto worthless material valuable by the introduction of a valuable constituent, as in the replacement of carbonate of lime by phosphate of lime. It also causes the concentration, by capillary action in soils, of certain deposits like nitre, etc. The compounds formed with different ore deposits vary with the ores affected and the sta-

¹ Chlorides of other materials than silver and copper may also have been formed by a similar process, but the solubility of many metallic chlorides would prevent their being accumulated in any but very dry regions.
Superficial alteration of ore deposits.

The physical effect of superficial alteration is generally to make the deposit more open and porous, to cause it to shrink, and, in some cases, to convert it to a loose material of the consistency of sand and clay. In some cases, however, especially where hydration is active, and expansion may be caused.

Superficial alteration extends downwards as far as surface influences are able to act, though generally alteration is not complete down to the possible limit. The depth of alteration depends on the topography of the region, the nature of the rocks, and on the climate. In glaciated regions, the glacial action has swept away the products of alteration, and sufficient time has not yet elapsed since then for alteration to have gone on to any great extent, but in many other regions the products of alteration have accumulated to considerable depths. The depth of alteration, under different conditions, varies from a fraction of a foot to 1,500 feet, or possibly more.

Superficial alteration is well illustrated in iron, manganese, copper, lead, zinc, silver, gold, tin, and many other deposits. For special descriptions see text.

The accumulation of soluble saline materials, like salt, on the surface has a very important effect in converting certain materials in underlying ore deposits to chlorides, etc.

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