ART. XXII.—*Genesis of Iron-ores by Isomorphous and Pseudomorphous Replacement of Limestone, etc.;* by JAMES P. KIMBALL.

IT is the object of the present memoir briefly to develop the following proposition, namely, that well recognized products of epigenesis, like siderite and ferro-calcite, in their several forms and wide distribution especially on a petrographic scale, are as a rule also products of direct pseudomorphous replacement of isomorphous calcic carbonate, like limestone, calcite, calc-sinter, calcareous sediments, calc-schutt, etc. This proposition is not new. But some of the conditions remain unsettled. So also some of the deductions which have been thought, or may seem, to follow. These it is my purpose briefly to discuss.

Contingent to this proposition, it follows that secondary or indirect replacement of calcic carbonate by ferric hydrate is wrought through alteration of pseudomorphous siderite or ferro-calcite, and also, through progressive alteration, by ferric oxide and even magnetic oxide. Hence proximate derivation from siderite of many occurrences of iron-ores which nevertheless are ultimate products of indirect or progressive pseudomorphism of calcic carbonate—itself often a product of epigenesis from basic silicates. Such occurrences may therefore be regarded as instances of double pseudomorphism, sometimes on a petrographic scale; that is, pseudomorphism in the first instance by substitution or replacement; in the second instance by alteration.

Again, ferric hydrate apparently directly pseudomorphous after limestone is produced by immediate, perhaps spontaneous, oxidation of ferrous carbonate, resulting from interchange or double decomposition between solutions of this salt or ferrous sulphate and calcic carbonate in place. All these permutations proceed from the same reactions, but differ in results according to atmospheric environment—whether oxidizing or not. The instable salt as first separated, it is scarcely necessary to add, is thrown down from solutions either of ferrous carbonate or ferrous sulphate indifferently, in reaction with dissolved calcic carbonate or other alkaline mono-carbonates. This salt however. it is important early to remark, is the hydrous salt, from which geologists, it seems, are not accustomed to distinguish the anhydrous carbonate which is almost, if not altogether, exclusively its natural form.

Other adventitious occurrences of brown and red ferric oxide well recognized as exotic, that is, neither in original

place, nor vicariously developed, form as such a separate class. These, however, as commonly understood, are products of like reactions between solutions of the same salts in circulating acidulous waters. These products, though sometimes accumulated under favorable conditions of environment and topography, are more commonly dissipated.

But for the instability of hydrous ferrous carbonate, it might be assumed to be transiently produced through reactions of ferrous salts and alkaline mono-carbonates in solution, not far from *loci* of replacement of calcic carbonate by siderite, as the result of transmission of solutions beyond range of reducing or preserving gases. Visible results of precipitation and spontaneous oxidation of this salt into ferric hydrate in these circumstances on the one hand, and direct precipitation of ferric hydrate through oxidation on the other hand, are identical. Hence the two processes in nature can seldom be distinguished.

The general proposition may now be advanced—that deposits of concentrated iron-ores occur far more extensively as pseudomorphous replacements than has hitherto been made to appear; and far more extensively than by original sedimentation of ferric hydrate in hydrographic basins (if indeed important deposits have ever been formed in this way), followed by chemical transmutations so far as essential to their plausible explanation upon theories of such a common genesis. In the present place, suffice it to indicate the impracticability of conceiving of sedimentation of ferriferous material without siliceous alternations: or of great accumulations of non-ferruginous, non-siliceous sediments at all, except in the case of marine limestones. These are preëminently the *habitat* or repositories of massive and stratiform iron-ores of all descriptions. Occurrences of iron-ores in this relation are often, and indeed generally, without transitions. On the other hand, it is easy to conceive, and in numerous instances to prove, effective replacement of limestones of all geologic periods. Among the great number of important stratiform occurrences of iron-ores —that *stratified* ores exist, there seems to me much reason to doubt—that is, homogeneous, non-laminated ores, formed in the natural order of succession of strata between which they are enclosed, and along with which they are commonly assumed, *prima facie*, to be imbedded.

(1.) As deep-sea chemical precipitation of ferric hydrate is out of the question, the circumstance of the presence in limestone of important lenticular deposits of this material or its derivatives, including siderite upon one theory of its genesis, would suffice to prove the invasion of mid-sea or calcareous sediments by at least suspended material from sub-æerial rock-decay. This condition is obviously incompatible with the more important developments of Palæozoic iron-ores, whose relations in

the greater number of instances are with remarkably pure and persistent limestones, comparatively free from intercalations of argillaceous matter, also a residual product of rock-decay, and invariably accompanying ochreous matter in suspension. Again, replacement of limestone naturally progresses from exterior and divisional surfaces. This, as commonly observed, wherever incomplete, has invariably affected superficial or upper parts of formations under gentle dips, and seldom nether parts except under steep dips. Lenticular bodies of iron ores, not purely concretionary, are very rarely if ever found completely enclosed in pure limestone—that is, in any form corresponding to the filling of a hydrographic basin of marine limestone.

Conditions above briefly noticed are well illustrated, as I shall endeavor to show, by the more important developments of iron ores upon horizons of limestones and adjacent transition strata of all geologic periods.

(2.) The geologic importance of the phenomena of displacement of calcium-carbonate by ferrous carbonate was long since indicated by Bischof, mainly, as it appears, on mineralogic or *a priori* grounds.* Pseudomorphous siderite after calcite, occurring in drusy cavities in anamesite, as described by Blum and Sandberger, was attributed to removal of calcium carbonate by carbonated solutions of ferrous carbonate and deposition of this salt in its place. The same result, as well-known, is produced by reaction of solutions of ferrous sulphate, calcium sulphate being removed.

(3.) Pseudomorphic replacement of calcite by ochreous ferric oxyd was observed by Blum to have taken place indirectly, namely, first by substitution of ferrous carbonate followed by alteration of this comparatively unstable compound. As pointed out by Bischof, it seems probable indeed that pseudomorphs of this type are necessarily indirect—never direct.†

(4.) Aside from pseudomorphs by incrustation, pseudomorphous siderite commonly occurs by substitution of anhydrous isomorphous minerals. Pseudomorphism by alteration often succeeds pseudomorphism by substitution. Both processes, as inferred from relative densities, are attended with contraction. In the conversion of siderite into limonite, this, according to Hunt, amounts to nearly twenty per cent.‡ Hence the exhibition of cavities, anfractuosities and dislocations in products of either transformation, as witnessed both on a mineralogic and petrographic scale.

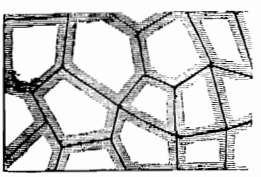
(5.) Whatever be the mode of accumulation of ferrous carbonate in various deposits, it can scarcely fail to be recognized as invariably a secondary product universally resulting from the decomposition of diffused proto-silicates of iron by means

* Bd. II, 1864, p. 154.
† Chem. Geol., Bd. III, 1866, 871.
‡ This Journal, xxvi, 1883, 202.

of carbonated waters; next in frequency, from solutions of ferrous sulphate in reaction with calcic carbonate; and, lastly, from like reactions with ferrous salts from reduction of ferric silicates.

(6.) The stability of this more or less alterable secondary product in fissures and deep-seated strata in an atmosphere of carbonic anhydride or reducing gases, was also long since pointed out by Bischof and W. B. Rogers, as well as its transformation into ferric hydrate through displacement of such gases by atmospheric air.

(7.) The frequent occurrence of limonite and hematite in limestone and their graduation into beds of this sedimentary material, as well as the presence of similar fossils in both, are facts adduced by Bischof to justify the conclusion that iron-ore deposits of this description have had their origin in replacement of limestone beds.* Yet, as by him remarked, replacement of amorphous limestone by ferric oxide obviously cannot be proved mineralogically as in the case of rare occurrences of incomplete pseudomorphs after calc-spar, like the specimen originally described by Blum. But every geologist has nevertheless observed ultimate replacement of limestone by brown and red ferric oxides, whether direct or indirect, among the more common phenomena of weathering. When as sometimes happens this is all but complete, and the original form of the limestone mass is preserved *in situ*, the replacement is likewise seen to be pseudomorphic—at least in a petrographic sense. Dana has given a good pictorial illustration of this kind in describing an occurrence in the Cone ore-pit at West Stockbridge.† The cut is here reproduced. Replacements of shells and parts of crinoids, still more common, are likewise pseudomorphic in the same limited sense.



The above proposition affords grounds for a ready and complete explanation of the common association of iron ores with limestone as far from accidental. This association would obviously be still more common had all replacements of thin limestone beds been only partially effected, as in replacements of thick limestone, which are necessarily incomplete or relatively superficial. Occurrences of the latter kind justify the conclusion that thin beds of limestone have in fact in numerous instances been wholly or pseudomorphously replaced. Hence frequent occurrences of lenticular beds of siderite and of its derivatives in place of thin limestones, of which no trace may remain except

* Bd. III, 1866, 873.

† This Journal, xiv, 1877, p. 136. See, also, Rep. Tenth Census, xv, 292, 296, 297, 299, 396.

form, and perhaps character of insoluble contents, on the one hand; and local developments of iron-ores, void of anything like regular form, within the compass of a thick limestone formation, and graduating into that material, on the other hand. The latter modes of occurrence (and by inference the former also) are particularly well illustrated by numerous stratiform iron-ore developments in strata of the Carboniferous period. These strata are understood by all to have accumulated under specially favorable conditions of environment for the production of the materials of iron-ores through internal chemical transmutations; and to have since subsisted under equally favorable atmospheric conditions for the preservation of alterable kinds of material produced, like siderite and sphærosiderite.

(8.) The possession of many physiographic characters by stratiform iron-ores in common with deposits *in situ*, formed in the natural order of strata between which they are imbedded, or rather enclosed, has naturally led geologists to seek an explanation of at least Carboniferous iron-ores of this description on theories of direct deposition either chemical or mechanical: that is, according to one theory, in original form of ferrous carbonate; or, according to another theory, as the product of transmutation of ferric hydrate in place into the same compound, through successive deoxidation and carbonating agencies, the potential influence of which in the development of this particular series of strata it may not seem difficult to imagine on grounds of either theory. As to further alteration from weathering action, regulated by circumstances of topography and environment, all are agreed.

The same agencies however may well be believed to have been equally potential in clearly recognized processes resulting in pseudomorphous replacement of limestone by ferrous carbonate, especially in the preliminary work of decomposing diffused clastic ferrous and ferric silicates, dissolving their soluble products, and in the generation and preservation unaltered of anhydrous ferrous carbonate in concrete form however produced.

(9.) While dissolved alkaline mono-carbonates, as well known, readily precipitate instable hydrated ferrous carbonate from solutions of ferrous salts, no artificial method appears to have been proposed for the production at ordinary temperatures of anhydrous ferrous carbonate.

(10.) The generation of this natural compound in the form of siderite and sphærosiderite is sometimes attributed to direct precipitation and concentration of hydrous ferrous carbonate in the presence of reducing gases, or of an atmosphere of carbonic anhydride. This presupposes dehydration at ordinary temperatures by some natural process as yet unexplained.

Upon another theory, commonly entertained as a collateral theory by the same geologists who employ the one just stated, its derivation is also attributed to direct deposition through volatilization of free carbonic acid from aqueous carbonated solution—likewise in atmospheres of hydro-carbon gases and carbonic anhydride.

(11.) No natural occurrence and therefore no mineral species of hydrous ferrous carbonate seems to have been recognized by mineralogists. A moderately instable white, earthy amorphous hydrate said by Massieu to have occurred in the mineral lode of Pontpéon, France,* seems to have possessed the same characteristics as an occurrence beneath an ochreous deposit of a carbonated spring near Laacher-See in the Eifel, but described by Bischof as siderite or the anhydrous salt.† The same locality is famous for exhalations of carbonic acid. Preservation of the artificial product appears to be impracticable except in an atmosphere displaced by carbonic anhydride, or, as easily supposable, by reducing gases.

(12.) Siderite pseudomorphous after crystalline anhydrous calcic carbonate not uncommonly occurs both in hexagonal and trimetric forms, though isomorphous only in the former case. This fact goes far to show that the phenomena of replacement of calcic carbonate by anhydrous ferrous carbonate are not simply those of isomorphism. Yet it is true that in crystalline as well as in amorphous siderite ferrous carbonate is extremely apt to be partially replaced with isomorphous carbonates of lime, magnesia, manganese and zinc. The first three, and sometimes all four, of these carbonates are freely developed even where sparry siderite distinctly occurs as a product of epigenesis, particularly in drusy cavities and fissures in basic rocks inaccessible to atmospheric air.

(13.) The much greater tendency to precipitation of ferric hydrate from aqueous solutions of ferrous carbonate than of the salt itself by dissipation, as assumed, of carbonic acid, is well exhibited by Roth in the case of numerous mineral waters and deposits of mineral springs, as well as the relative and proportional precipitation of alkaline and manganous carbonates.‡

The existence of stable siderite in calcareous sinter points to replacement of calcic carbonate previously deposited. Away from oxidizing atmospheres, anhydrous ferrous carbonate, if ever directly deposited, which there seems much reason to doubt, is probably by reaction of solutions of ferrous salts with these anhydrous carbonates, and at ordinary temperatures in no other way. But as all known reactions of this kind result in hydrous ferrous carbonate from which passage into the anhydrous carbonate at ordinary temperatures is difficult to

* Compt. Rend., lix, 238. † Chem. Geol., Bd. I, 1863, 550.
‡ Chem. Geol., Bd. I, 565, 577.

imagine, the problem still remains.—Whence the production of the anhydrous carbonate?

(14.) In this question one is confronted by the remarkable fact that writers within the field of chemical geology habitually fail to discriminate between the two carbonates either in noting rare occurrences of hydrous carbonate, if such they really be, developed in reactions commonly yielding this extremely alterable or evanescent form; or in tracing epigenesis of comparatively stable anhydrous carbonate, either crystalline or amorphous, from like reactions. On the contrary, it seems to have been assumed that chemical reactions, geologically considered, producing hydrous carbonate, might equally serve, at least eventually, to produce anhydrous carbonate. As in many other unexplained instances of dehydration, conceivable only at ordinary temperatures, this phenomenon has probably been supposed to be an effect of inscrutable operations of time Bischof, for instance, to whom we owe what still stands as the fullest conspectus of this subject, fails to distinguish as such the hydrous carbonate, which as yet appears to be exclusively the product of well understood reactions.

(15.) Now there seems much reason to doubt that anhydrous ferrous carbonate is ever directly deposited from acid solutions of ferrous salts except in circumstances of contact with isolated or solid anhydrous alkaline mono-carbonates, probably at the point of double decomposition, or in the nascent state of the ferrous salt. Such a mode of development, if assumed, must be considered due to the well known isomorphous relations of anhydrous ferrous carbonate and its pseudomorphic tendencies. This explanation appears at least consistent with the phenomena of replacement, both isomorphous and pseudomorphous, of amorphous calcic carbonate; and may perhaps be found adequate to explain most occurrences of crystalline siderite on the theory of its epigenic origin in all cases. Some of these points will now be further considered.

(16.) It is remarkable that although in the earlier volumes of his great work, Bischof was the first, I believe, to point out the importance of replacement of limestone as one mode of genesis of siderite, he assumes in his supplementary volume stratiform developments of this epigenic compound, particularly in Carboniferous series of strata, to have been directly deposited from its carbonated water solution as an effect of volatilization of carbonic acid, and to have been preserved from oxidation by hydro-carbon gases. Yet the constant association in these strata of carbonic acid along with those gases is remarked by Bischof in the same place.* Even by loss of half-combined carbonic acid, however difficult to imagine as taking place in an atmosphere impregnated with the same gas, it is extremely

* Chem. und Phys., Geol. Suppl., Band 1871. p. 64.

doubtful whether the anhydrous salt would be deposited. A no less important difficulty arises as to the *locus* of deposition. If this take place at the surface, the presence of these gases can scarcely be imagined; and if below—conditions are precluded for lenticular accumulations. Beneath the surface conditions exist for deposition by segregation or replacement only.

(17.) In any theory of the genesis of siderite, it becomes necessary first of all to explain occurrences of siderite in lenticular form, as widely distributed: that is, as a product of direct superficial deposition in hydrographic basins; or else of chemical replacement of lenticular beds originally deposited in that manner. Between these alternatives the former seems to me to be quite impracticable.

Lenticular deposits from either chemical or mechanical precipitation are formed exclusively at the surface, that is, in hydrographical basins or bottoms where conditions essential to stability of hydrous ferrous carbonate can not ordinarily be set up, or at least long maintained. Besides, wherever this salt is separated from standing water it must be assumed to pass spontaneously into a higher state of oxidation. Not only does it appear, then, that lenticular developments of ferrous carbonate can not have been superficially deposited, but that this compound can not have been derived from direct precipitation.

(18.) Senft's theory of the genesis of siderite and sphærosiderite seems to have been founded on special occurrences of stratiform and nodular clay-ironstone enclosed in clays and shales. These are explained as epigenic products resulting from saturation of buried argillaceous sediments with acid solutions of ferrous carbonate, supposed to yield the neutral salt upon evaporation; or again by interchange with stronger bases like lime. Spathic carbonates are likewise supposed by Senft to proceed from absorbents like calcareous material, clay or marl.* However applicable may seem parts of this theory to concretionary lenses and nodules of clay-ironstone contained in beds of residual clay and shales, it must be seen to be incompatible with the composition of spathic siderite of considerable purity, that is, when comparatively free from earthy admixtures, as well as with conditions of deposition in the form of lenticular beds. Like other explanations, it rests on the assumption that anhydrous ferrous carbonate may be separated by evaporation as well as by precipitation from acid solutions of ferrous carbonate, a reaction probably true only in a limited sense as above pointed out.

The reaction however incidentally mentioned by Senft, namely, the isolation of ferrous carbonate by interchange of solutions of ferrous salts with stronger bases like lime, is

* Gesteins und Bodenkunde, 1877, 28.

probably the prevailing one in the circumstances cited. For alkaline mono-carbonates, likewise resulting from decomposition of silicates, may safely be assumed to be present partly in undissolved or diffused form wherever ferrous oxide is available, or wherever ferrous salts are displaced from solution.

(19.) While such reactions may be readily believed to take place in fissures, particularly in contact with segregations of calcic carbonate, they can hardly be assumed with Senft also to extensively obtain in clay bottoms of standing water, or beneath peat-bogs and marshes, still less in a manner to result in direct deposition in bedded form from water. In such circumstances not the anhydrous salt but the hydrated ferrous carbonate, if either, would be deposited; this however quickly passing into ferric hydrate. Still more likely, ferric hydrate would be directly deposited from solution through dissipation of free carbonic acid. Yet I am not prepared to deny that from the condition of ferric hydrate however accumulated anhydrous ferrous carbonate may eventually be formed by de-oxidation and by carbonating processes. If so, this could be only after the original deposits are buried deep below superficial sediments and so excluded from atmospheric oxidation.

(20.) Hence, perhaps, the more commonly received metamorphic theory of the genesis of stratiform siderite, generally assumed to be stratified. This theory, based on the assumption of relative origin corresponding to the natural order of enclosing strata, involves, in short, alteration *in situ* of ferric hydrate commingled with vegetable matter originally accumulated in hydrographic basins. This process is also supposed to be excluded from atmospheric air under cover of successive sediments.

(21.) Some of the objections to this theory as a general explanation of the genesis of siderite will appear farther on. Especially will it, as I think, be found to fail to explain the prevailing occurrence of siderite and ferro-calcite in association with limestone, or on horizons of limestone, or in lenticular form otherwise than concretionary.

(22.) On the other hand, a theory of its derivation in such circumstances at least, by isomorphous and pseudomorphous replacement of calcareous material *in situ*, not only seems to fit the greater number of familiar occurrences of siderite, and thus to explain the almost universal association of this secondary product with limestone, and the graduation into each other of these two materials of widely opposite derivation; but to be alone adequate to explain the epigenesis and indeed existence of the anhydrous salt. Where of course limestone has been completely transformed into siderite, and all immediate evidences of their relation have disappeared, it may sometimes be found practicable to identify lenticular developments of siderite

with horizons of limestone by stratigraphic relations. Impracticable though this may be in certain cases, it should not fail to be considered that as the thinner and less persistent limestones are the only ones liable to complete replacement, actual stratigraphic or even inferential identification is not in all cases to be expected.

(23.) Calling attention to the possible application of the theory of the formation of ore-deposits by replacement or substitution, Emmons expresses the possibility that "in the older and more crystalline rocks, where the calcareous beds are of limited extent, metallic deposits in large masses like those of iron, may have so completely replaced the calcareous material that little or no trace of it remains."* Complete ultimate replacement of isolated masses of emerged coral-reef by ferric oxide on the island of Cuba was described by me in 1884. To this example I shall again take occasion to refer.

"The limits of the actually demonstrated application of the theory of the formation of ore deposits," as remarked by Emmons in the paper just quoted, "are being every day extended, not only by studies of new districts, but by more careful and unbiased studies of old districts in which a different method of formation had previously been determined upon."

(24.) Argillaceous shales and other miscellaneous ferriferous sediments commingled with carbonate of lime, originally accumulated, or resulting from decomposition of component basic silicates or left behind from evaporation of circulating waters, may in whole or in part be transformed into clay iron-stone or siderite, containing insoluble residues of the original beds. This process is again one of replacement. Divisional parts or prisms of such beds separated by planes of cleavage and stratification, and by anfractuosities from shrinkage, pass by progressive superficial oxidation into concretionary or nodular limonite. This process has often been described.†

(25.) Diffused ferrous carbonate resulting from replacement of calcic carbonate, also diffused and more or less commingled with clay containing other insoluble residues of sub-aerial decay of basic rocks, may, especially in sediments as yet unindurated, be involved in what may be termed the extra-molecular tendency of fine clays to form concretionary aggregations. Thus it appears that impure ferrous carbonate in nodular form, so frequently imbedded in clays, shales and grits, is probably a product of secular metasomatic interchange and substitution under genetic conditions varying only slightly with circumstances of environment from conditions governing replacement of limestone beds by siderite.

* Trans. Am. Inst. Min. Eng. 1886. Extract p. 7.

† See Hunt, this Jour., xxvi, 1883, pp. 202, 206.

(26.) In the foregoing remarks no discrimination between limestone and dolomite has seemed necessary, nor specific reference to analogous compounds of magnesium in isomorphous relations to those of calcium. Nor, on the other hand, has it seemed important to refer to relations of the same kind subsisting between corresponding compounds of manganese and iron. For the sake of brevity, the same course will generally be followed throughout the present memoir. Yet it will not fail to be considered that epigenesis of compounds of manganese is practically in common with those of iron, and that in fact epigenesis of a given compound of one metal often involves that of a corresponding compound of the other. Quantitatively considered, this according to M. Dieulafait* appears in relative degree to depend less on the distribution of the two metals in the composition of silicates from which epigenesis proceeds, than might be supposed.

(27.) This chemist observed that the heat of combination developed in the production of (hydrous) ferric oxide and (hydrous) ferrous carbonate from ferrous oxide to be respectively 26·6 and 10·0 calories (Fr). In corresponding reactions resulting in the production of manganic oxide (hydrate) and (hydrous) manganous carbonate 21·4 and 13·6 calories were developed.†

When oxygen and carbonic anhydride both in excess come in contact with minerals containing ferrous and manganous oxides, the latter, as may therefore be inferred, will be converted into ferric oxide (hydrate) and manganous oxide (hydrate) and no carbonate will be formed. It is also inferred by Dieulafait that if these gases come in contact with the producing minerals slowly and in quantity insufficient to transform both oxides, the products will be insoluble ferric oxide (hydrate) and soluble (hydrous) manganous carbonate. This serves to explain at least the formation of ferric hydrate comparatively free from manganic hydrate, as well as the separate generation of manganic hydrate comparatively free from ferric hydrate—perhaps in another *locus* of deposition after further transmission of solutions.

Again it is inferred, that as much more heat is developed when ferrous oxide is converted into ferric oxide (hydrate) than when converted into (hydrous) ferrous carbonate, the latter can be formed only in circumstances where atmospheric air is displaced by reducing gases or carbonic anhydride, to the exclusion of oxygen.

* Comptes Rendus, ci. 609, 644.

† The parentheses are mine, the observer ignoring the distinction between hydrous and anhydrous compounds.