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RELATIONS BETWEEN
LOCAL MAGNETIC DISTURBANCES
AND THE
GENESIS OF PETROLEUM

BY

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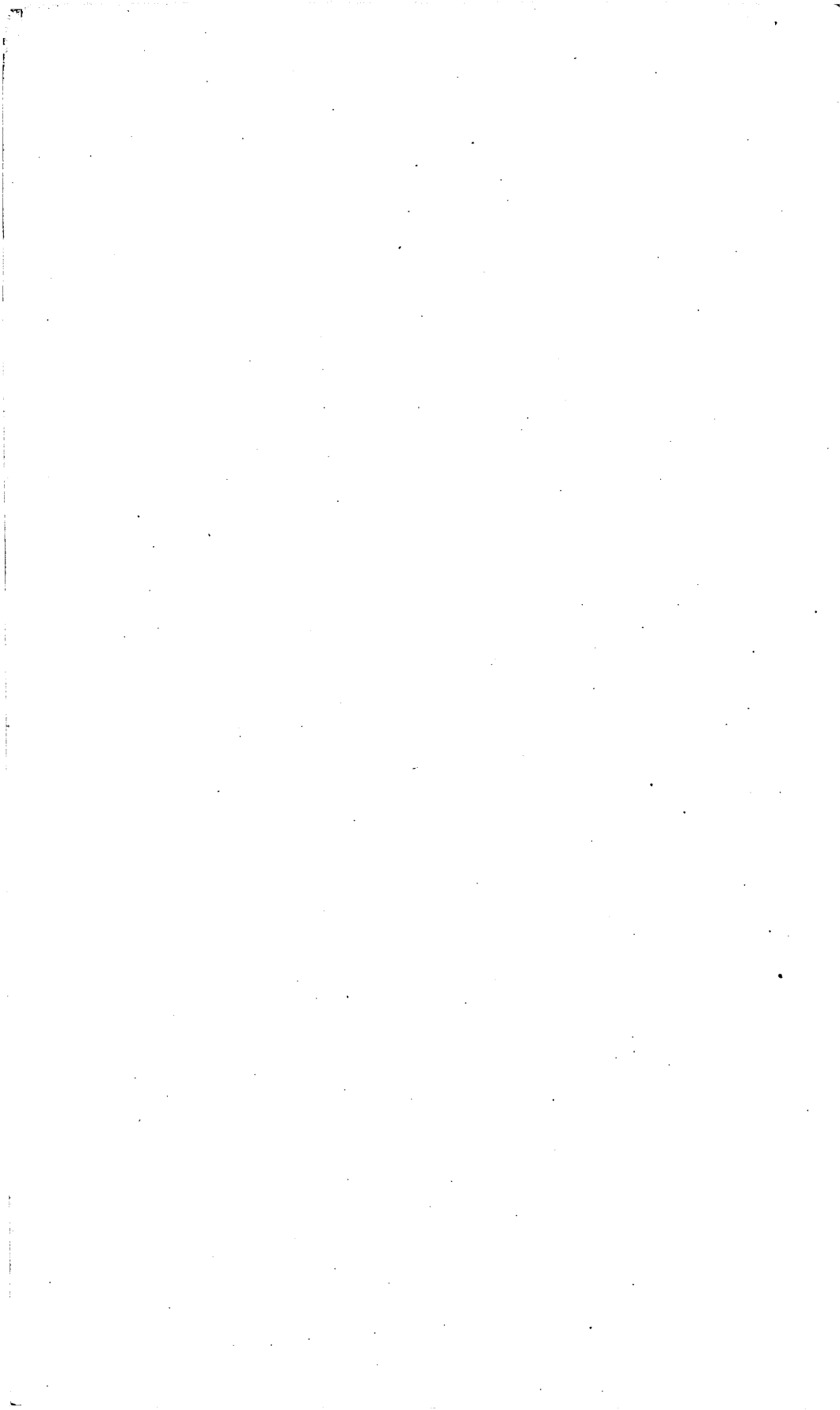
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CONTENTS.

	Page.
Very questionable origin of the hydrocarbons.....	5
Argument for organic origin.....	5
Argument for inorganic origin.....	7
Digression on the origin of ammonia.....	7
Associations of hydrocarbons.....	9
Conclusion, that hydrocarbons accompanying igneous rocks are inorganic.....	12
Importance of inorganic hydrocarbons.....	14
Theories of inorganic genesis all unsatisfactory.....	15
Facts bearing on carbide of iron theory.....	19
Irregular compass declination in petroleum fields.....	22
Conclusions.....	24

ILLUSTRATION.

	Page.
PLATE I. Map showing petroleum deposits and lines of equal magnetic declination for 1905	22



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By GEORGE F. BECKER.

VERY QUESTIONABLE ORIGIN OF THE HYDROCARBONS.

No question in geology is more obscure than that of the origin of the numerous natural hydrocarbons commonly classified as asphalt, ozokerite, petroleum, and natural gas. Certain facts of occurrence and certain results of experiment are indeed established, but the interpretation to be placed upon them is so doubtful that the conclusion reached may almost be said to depend on predilection. A great number of the more important hydrocarbons found in petroleum can be produced artificially from organic substances, such as coal, wood, and fish oil, while identical or closely allied hydrocarbons result from the interaction of inorganic substances, such as cast iron and chlorhydric acid. In many places petroleum is closely associated with fossiliferous strata; but hydrocarbons likewise exist in meteorites and in volcanic gases; they are even expelled by heat from granite and basalt. The most orthodox opinion at the present day is that a part of the natural hydrocarbons is of organic origin and a part also of inorganic origin; but when it comes to estimating the relative importance of the two portions there is no approach to unanimity. Before making a suggestion, which in this connection appears to be of interest, it may be well to outline the arguments for the opposing views.

ARGUMENT FOR ORGANIC ORIGIN.

Mr. Clarke has given an excellent digest of the evidence of organic origin in his "Data of geochemistry." It will be still more briefly summarized here. That hydrocarbons are produced by the destructive distillation of either vegetable or animal matter has long been known. The manufacture of illuminating gas from coal exemplifies the process. In 1865 Warren and Storer^a made paraffins, olefines,

^a Mem. Am. Acad., 2d ser., vol. 9, 1865, p. 177.

and aromatic compounds in mixture (thus practically manufacturing petroleum) from saponified fish oil; and in 1888 Mr. Engler^a formed similar compounds under pressure from unsaponified fish oil. Later^b the same chemist obtained hydrocarbons by distillation from vegetable oils. All of these results have been abundantly confirmed by other experimenters.

Many observed associations also point to organic genesis. Marsh gas (fire damp, methane) is the most volatile member of the paraffin series. It is generated in swamps and in coal beds and forms the greater part of natural gas. Rotting seaweeds likewise emit it, and there is some reason to believe that salt water by delaying putrefaction is favorable to the formation of hydrocarbons; at any rate brine and petroleum are often associated. Some petroleum, especially those of California, contain nitrogen bases, which tends to show that the oil has been derived from animal matter. According to Mr. F. Hornung,^c the hydrocarbons of the Zechstein formation in the Harz region are derived from fish remains. In his opinion the fish were killed by brines of salt lagoons and their fats saponified by salts of lime, magnesia, and ammonia. If so, Warren and Storer's experiments completely illustrate the process.

The association of petroleum with sedimentary strata is well known; in fact, oil is found in large quantities only in stratified rocks. In a word, as Mr. Clarke^d says:

Wherever sediments are laid down, inclosing either animal or vegetable matter, there bitumens may be produced. The presence of water, preferably salt, the exclusion of air, and the existence of an impervious protecting stratum of clay seem to be essential conditions toward rendering the transformation possible. Seaweeds, mollusks, crustaceans, fishes, and even microscopic organisms of many kinds may contribute material to the change. In some cases plants may predominate; in others animal remains; and the character of the hydrocarbons produced is likely to vary accordingly, just as petroleum varies in different fields.

Granting the organic origin of petroleum, its accumulation may be accounted for in some measure by flotation, since it is lighter than water; but capillary displacement by water appears from the studies of Mr. David T. Day to be much more efficient than buoyancy. The presence of organic hydrocarbons in massive rocks might be ascribed either to capillary infiltration or to the incorporation by massive rocks of strata carrying organic matter. Similarly it is possible that the evolution of hydrocarbons in volcanic gases depends upon the distillation of organic matter by volcanic heat, and the same explanation may be applied to the marsh gas which is brought to the

^a Ber. Deutsch. chem. Gesell., vol. 21, 1888, p. 1816.

^b Cong. internat. du pétrole, Paris, 1900, p. 20.

^c Ber. Deutsch. geol. Gesell., vol. 57, 1905, p. 538.

^d Data of geochemistry, 1908, p. 640.

surface by hot springs with or without boracic acid. Even the asphalt lake of Trinidad may owe its origin to distillation or eliquation.

ARGUMENT FOR INORGANIC ORIGIN.

Of the rival hypotheses, that which ascribes to oil an inorganic origin is the less fashionable, and for that reason I shall discuss it somewhat more fully, though without any attempt at exhaustive treatment. Very famous men of science, however, have adopted this explanation as the more probable, and of these observers the first, so far as I know, was Alexander von Humboldt.

On August 12, 1805, Humboldt and Gay-Lussac witnessed a great eruption of Vesuvius; and at times they found the prevailing smell wafted from the crater bituminous. Humboldt had also noted in literature three cases in which a pleasant smell (*Wohlgeruch*) attended eruptions. "I put these few observed facts together," he says, "because they help to confirm the close connection of all manifestation of volcanic activity, the connection of brine-naphtha wells with real volcanoes."^a This was a very long shot, even though aimed by the eye of genius.

Much evidence in favor of Humboldt's view has accumulated during the past century, however, and I think it can now be shown that such hydrocarbons as are immediately associated with volcanic or intrusive phenomena have an inorganic origin. The relative economic importance of the organic and inorganic oils is another matter. So also is the chemical theory of the relations of inorganic oils to other minerals.

DIGRESSION ON THE ORIGIN OF AMMONIA.

Most intimately connected with the origin of hydrocarbons is the derivation of the ammoniacal compounds emanating from volcanoes. In ordinary experience the source of ammonia is organic, and it is impossible to pass a stable without being reminded that ammonia is one of the commonest products of decay. It was therefore very natural that the pioneers in the investigation of volcanoes, such as Bunsen, should have regarded the ammoniacal fumes and the incrustations of ammonium chloride so abundant at active vents as due to the action of hot lavas on organic matter; but a comparatively recent investigation by Mr. J. Stocklasa seems to demonstrate that the ammonia is of inorganic origin, as others had suspected from less complete evidence.

^a *Cosmos*, vol. 4, p. 274. This volume appeared in 1858. Whether Humboldt had referred to the matter in any earlier publication I do not know. I assume that his opinion was formed at the date of his observation. L. von Buch noted the smell of volatilizing petroleum (Bergoehl) at Vesuvius nearly a year before Humboldt (*Geog. Beob.*, vol. 2, 1809, p. 216), but did not draw any general inference.

Mr. Stocklasa ^a made chemical tests in the field during the progress of the eruption of Vesuvius in April, 1906, supplemented later by laboratory work. He found that the gases emitted always contained chlorhydric acid and ammonia; that the glowing lavas are shrouded in a veil of ammonium chloride vapor even far away from any vegetation; that lava still hot from the crater yields (when powdered and leached with water) notable quantities of ammonium chloride; that the yellowish smoke forming the "pine tree cloud" above the crater of Vesuvius consisted chiefly of ammonium compounds; and, finally, that from the more solid fresh lavas, especially the olivine bombs, ammonia may be expelled by heat alone.

Though eruptions break out at various points on the cone of Vesuvius, analogy justifies the belief that it has but a single conduit or neck through which the eruptions of many thousand years have reached the surface. Any fossiliferous strata through which the conduit may pass must have been baked out long ago and must have yielded up any products of distillation with which the sediments could part. It thus seems quite impossible that the immense ammoniacal product of this volcano can have an organic origin.

Mr. Stocklasa considers it probable that the origin of the ammonia is referable to nitrides, especially that of silicon, which is easily prepared, but not known as an actual mineral. A nitride of iron, however (now known as silvestrite), was found at Etna by Orazio Silvestri ^b in 1875.

Others had preceded Mr. Stocklasa in maintaining that the ammoniacal emanations of volcanoes are due to the presence of nitrides in the magmas; for example, Mr. Armand Gautier ^c and Mr. A. Brun.^d The last obtained ammonium chloride by calcination from all lavas, acidic or basic, with which he experimented. His list included specimens from Krakatoa, Chimborazo, Bourbon Island, and Hecla, as well as a long suite from the Mediterranean. Mr. Brun also anticipated Mr. Stocklasa in asserting that the smoke of volcanoes is largely composed of chlorides.

Ammoniacal compounds appear to be almost or quite invariably present in volcanic emanations. They are also found, I believe, without exception in boric acid springs, or suffoni, and in many other thermal springs. If ammonia were only occasionally associated with volcanic phenomena and igneous rocks, its presence might be at-

^a Ber. Deutsch. chem. Gesell., vol. 39; 1906, p. 3530.

^b Pogg. Annalen, vol. 157, 1876, p. 165. Silvestri lays especial emphasis on the formation of ammonium chloride within the great crater of Etna where, he says, an organic origin for this substance is not to be thought of.

^c Bull. Soc. chim., 3d ser., vol. 29, 1903, p. 191.

^d Arch. sci. phys. et nat., vol. 19, 1905, pp. 439, 589.

tributed to adventitious organic matter. The evidence of the inorganic origin of the ammonia emitted by volcanoes is cumulative but conclusive.^a

ASSOCIATIONS OF HYDROCARBONS.

After Humboldt's qualitative detection of hydrocarbons at Vesuvius their study seems to have been neglected for a long time. Bunsen^b indeed looked for hydrocarbons at Hecla, but in vain. In 1856 Ch. Sainte-Claire Deville found them on the flank of Etna near Aci Reale as gaseous emanations.^c In the main crater he detected no hydrocarbons, a fact which he attributed to combustion in the volcanic hearth. Fouqué first actually collected hydrogen and marsh gas from an incandescent crater, that of Santorin.^d He considered the circumstances at this locality peculiar in that the atmosphere had uncommonly little access to the gases on their way to the vent. As a rule, in his opinion, a volcanic cone is so porous and so charged with air that combustible gases are consumed in the heart of the mountain. He thus agrees with Deville, and Mr. Stocklasa holds a similar opinion. From this point of view an ordinary volcano would resemble a Bunsen burner in which the flame has "struck back." Since Deville's first investigations hydrocarbons have been found at Vesuvius, Etna, Santorin, Terceira Island (in the Azores), and at Pélee by Fouqué, Gorceix, Silvestri, and Moissan.^e Hydrocarbons have also been detected spectroscopically in the gases of Kilauea by Jannssen^f and by Libbey.^g Mr. Stocklasa, whose investigations on the ammoniacal products of Vesuvius were referred to above, promised a special paper on the hydrocarbons, but this I have not succeeded in finding. He states, however, that the lavas contain hydrocarbons, and he attributes to their combustion the steam and carbon dioxide of the vapors.^h In short, it seems only needful to look for hydrocarbons under favorable conditions at volcanic vents to find them in the gases.

Ch. Sainte-Claire Deville was a pioneer in the examination of the gases liberated by heat from massive rocks. "Obsidians," he says, "are well known to be due to the rapid cooling of lavas, especially those rich in silica. Now, the greater part of the obsidians still retain water, sodium chloride, and bituminous or ammoniacal substances,

^a Mr. Clarke, remarks Stocklasa, "has clearly shown that the nitrogen of lava is an original constituent and not of organic origin." *Data of geochemistry*, p. 222.

^b *Annales chim. phys.*, 3d ser., vol. 38, 1853, p. 215.

^c *Compt. Rend.*, Paris, vol. 43, 1856, p. 359.

^d *Santorin et ses éruptions*, 1879, p. 225.

^e Mr. F. C. Lincoln (*Econ. Geology*, vol. 2, 1907, p. 258) gives 50 analyses of emanations with references.

^f *Compt. Rend.*, Paris, vol. 97, 1883, p. 602.

^g *Am. Jour. Sci.*, 3d ser., vol. 47, 1894, p. 371.

^h *Chem. Zeitung*, 1906, p. 740.

and if they are rapidly heated to a temperature well below the melting point, they swell up, becoming extremely porous, passing, in short, into the condition of pumice."^a Mr. Brun has repeated and extended this investigation.^b From a Lipari obsidian he dissolved out with ether a vaseline-like grease, and by the same method he obtained an oil from Vesuvian ash of 1904 which floated on water. He found hydrocarbons abundant in Stromboli lavas of 1901 and in Santorin andesite of 1866. Even an obsidian from Plomb du Cantal (Auvergne), the date of which is of course unknown, yielded hydrocarbons copiously. In later investigations Mr. Brun^c found hydrocarbons in the ash or cinder of two volcanoes in the Canary Islands and of four volcanoes on the Island of Java. The portion of Java north of the volcanic belt contains numerous pools of petroleum, and Mr. Brun says he is forced to admit that this petroleum is of eruptive origin, but he does not give his reasons for this conclusion. Silvestri actually found bubble-like pockets in the lava of Etna containing solid paraffins and liquid oil.^d

It is difficult to draw the line between active volcanism and solfatarism. Most of the cases in which hydrocarbons can be shown to escape in volcanic districts are to be classed as solfataric, for incandescent vents are hard to approach, and the gases if present would inflame. The bitumens of the Auvergne are probably solfataric. The association of lava and bitumen in that region is very close, and the basaltic tuffs, or peperites, which in many cases form volcanic necks, are heavily impregnated with hydrocarbons. The most famous of these rocks is the bituminous tuff of Puy de la Poix. It is noteworthy that the volcanoes of the Auvergne rest on a great granite massive, and in this rock actual veins of bitumen occur.^e Solfataric, too, are the occurrences of bitumens at quicksilver deposits, for hot water and gases pour through some of them, while the extreme similarity of most of these ore deposits indicates community of origin. In every quicksilver-producing district in California bitumens are present, usually and perhaps always members of the paraffin series. They are found with the ore embedded in hydrous silica. Bitumens also accompany the quicksilver ores in Texas, in Rhenish Bavaria, at Idria, at Monte Amiata, and at Almaden.^f There is an especial and unexplained affinity between bitumen and cinnabar,^g an ore which has undoubtedly been brought to the surface in solution from great depths.

^a Sur les émanations volcaniques, Paris, 1857, p. 14.

^b Arch. sci. phys. et nat., 4th ser., vol. 19, 1905, p. 589.

^c Bib. univ. arch. des sciences phys., vol. 27, 1909, p. 113.

^d Gazz. chim. ital., vol. 7, 1877, p. 1.

^e See De L'Apparent, Traité de géologie, 5th ed., 1906, pp. 541, 1786; also Geikie, Text-book, p. 357.

^f Quicksilver: Mineral Resources U. S. for 1892, U. S. Geol. Survey, 1893.

^g Paraffins partially precipitate mercuric sulphide from its solutions in alkaline sulphides.

The diamonds of South Africa occur in volcanic necks, and it is now generally acknowledged that the gems are native to the subsilicic, peridotitic rock known as kimberlite.^a In this rock Moissan found carbonado and graphite, which was more abundant than diamond.^b Sir Henry Roscoe also examined the kimberlite. A quantity of it was powdered and digested with ether. "On filtering and allowing the ether to evaporate," he says, "a small quantity of a crystalline, strongly aromatic body was obtained. This substance was very volatile, burned easily with a smoky flame, and melted at about 50° C."^c There can be no doubt, I take it, that these necks extend downward to a depth of many miles.

The famous Tuscan boracic "suffoni," or fumaroles, emit gases. They were examined as early as 1858 by Deville and Le Blanc,^d and without exception they were found to contain hydrocarbons. They have repeatedly been analyzed since that time, with a similar result.^e All the suffoni appear to carry ammoniacal compounds also, while boric acid is characteristically of volcanic origin. If any line can be drawn between suffoni and the boric, ammoniacal asphalt lake of Trinidad I do not know how to do it.

Massive rocks at a distance from active volcanoes or distinctly solfataric phenomena contain hydrocarbons. At some points masses of solid or liquid oils exist in ancient massive rocks, but these may perhaps be derived from extraneous sources. Mr. W. A. Tilden^f showed, however, that granite and gabbro, as well as basalt, when heated to redness, give off gases in volumes several times as great as that of the rock itself, methane being one of the educts. The granite developed about a twelfth of its own volume of marsh gas and gabbro an eighth. Mr. Armand Gautier^g has also analyzed the gases driven off by a red heat from granite, granitoid porphyry, and ophite, getting about one volume of methane to seven of the rock. If the unit volume is taken as a cubic mile, these figures become impressive. In what form the hydrocarbon exists in the rock before heating is uncertain, but it can hardly be merely adsorbed (or condensed on surfaces), for pulverization scarcely reduces the quantity. This behavior seems inconsistent with the idea that the presence of methane is due to the diffusion of a gas of organic origin or to the infiltration of exotic oils.

For the sake of completeness, the presence of methane in thermal springs not referable with certainty to volcanic action may be men-

^a I could not find the least evidence of change even in the sharpest splinters of shale embedded in the lava. *Science*, vol. 6, 1897, p. 664.

^b *Compt. Rend.*, Paris, vol. 116, 1893, p. 292.

^c *Proc. Manchester Lit. and Phil. Soc.*, vol. 24, 1885, p. 8.

^d *Compt. Rend.*, Paris, vol. 47, 1858, p. 317.

^e For example, by Mr. R. Nasini (*Gazz. chim. ital.*, vol. 28, 1898, p. 100).

^f *Chem. News*, vol. 75, 1897, p. 169.

^g *Annales des mines*, 10th ser., vol. 9, 1906, p. 316.

tioned. There is a growing belief that springs of high constant temperature and constant flow emanate from points below the level to which stratified rocks usually extend, and that the water is either "juvenile" (i. e., of recent formation) or magmatic. This opinion is founded on the impossibility of accounting for the composition of such springs as those of Bohemia on the hypothesis that the waters are vadose.^a Mr. F. W. Clarke^b has thrown new light on this subject by showing that all the sodium of the sea and the sedimentary strata might be supplied by a shell of igneous rock, enveloping the globe, with a thickness of half a mile at the very most. Supposing the relative areas of land and sea always to have been substantially the same as at the present day, and making any reasonable allowance for erosion, the mean thickness of stratified rocks in continental areas can be only a fraction of a mile. Mechanically, also, it is most difficult to conceive how the purely superficial action of erosion and decomposition could ever result in burying the primeval rocks under detritus to an average depth of many thousand feet. Hence it would seem that typical hot springs must come from beneath the sediments. Now great numbers of hot springs in France, Germany, Austria, and elsewhere carry methane. This gas seems too common in such springs to be attributed to fortuitous association with organic deposits, and it is reasonable to regard it as magmatic.

**CONCLUSION, THAT HYDROCARBONS ACCOMPANYING IGNEOUS
ROCKS ARE INORGANIC.**

Of all the associations of hydrocarbons briefly enumerated above, perhaps not a single one is incapable of explanation on the hypothesis that the hydrocarbons are of organic origin. It is possible to conceive that in exceptional circumstances an obsidian should have been kept melted within a few thousand feet of the earth's surface in an atmosphere of organic hydrocarbons until it had occluded as much of such material as can now be expelled from it by heat. So, too, it can be imagined that at the Puy de la Poix a fissure extends through the granite to some distant accumulation of organic bitumen and that this has merely been distilled into the peperites. So long as only a few isolated cases of the presence of hydrocarbons in volcanic educts and massive rocks were known, such explanations might suffice. They no longer seem sufficient or plausible. The cases of association are so numerous and their character is so diverse as to break down the hypothesis of merely fortuitous collocation. The evidence is indeed mainly cumulative; but it has so accumulated and is so consistent as to leave only a negligible probability that the con-

^a Vadose waters are those which have infiltrated from the earth's surface.

^b Data of geochemistry, p. 29.

nection is not genetic. I see no logical way of avoiding the conclusion that much the greater part of the hydrocarbons associated with eruptions or occluded in massive rocks has an inorganic origin.

Evidence similar to that here adduced has carried conviction to the minds of some of the highest geological authorities of the day. Sir Archibald Geikie in his text-book seems to make only a single reference to the hypothesis of the organic origin of the hydrocarbons attending volcanic phenomena. From the association of hydrocarbons with igneous rocks he says: ^a "The opinion has been formed that these emanations do not proceed, as has generally been supposed, from the decomposition of coal or other sedimentary material of carbonaceous composition and vegetable origin, but rather point to the existence of vast quantities of carbon combined in the interior of the earth with such metals as iron and manganese." In another passage he remarks: ^b "The association of mineral oil, marsh gas, and other hydrocarbons, and of carbonic acid in old volcanic districts, may thus point to the continuous decomposition of such carbides by access of water."

Mr. de Lapparent is even more decided in the expression of his views. "In short, there is no doubt," he says, ^c "that the lavas of Santorin in a state of pasty fusion were accompanied to within 100 meters of their point of emergence by combustible gases originally imprisoned in their mass." So, again: ^d "It seems, then, that the basaltic emissions of the Miocene, forming a prelude to the great volcanic activity of the Auvergne, were accompanied by abundant outflows of hydrocarbons."

More than thirty years ago Mr. Tschermak ^e gave his assent to the hypothesis that volcanic gases are derived from the interior of the earth, likening eruptions to the tremendous outbursts which cause sunspots.

Mr. Eduard Suess ^f has happily characterized as *juvenile* the newly formed products of reactions which occur in volcanoes or solfataras and which accompany allied manifestations of energy. He thus classifies the carbon dioxide and the aqueous vapor of volcanoes as well as the formic acid detected by Fouqué at Santorin. In his opinion the carbon and the hydrogen are oxidized at eruption and, though he does not make the statement, it may be inferred that he supposes these elements to have been combined as hydrocarbons. Mr. Suess disclaims originality for the theory of juvenility, assigning the credit to the group of French scientists whose work has been referred to

^a Text-book of geology, 4th ed., 1903, p. 86.

^b Idem, p. 270; see also p. 185.

^c Traité de géologie, 5th ed., 1906, p. 448.

^d Idem, p. 1786.

^e Sitzungsber. Akad. Wien, vol. 75, 1877, p. 151.

^f Ueber heisse Quellen: Verhandl. Gesell. deutsch. Naturf. und Aerzte. 1902, p. 133.

above; but he gives it his hearty adhesion, reinforced by observations of his own.

This list of authorities might be extended, but that seems superfluous since it could not be improved.

IMPORTANCE OF INORGANIC HYDROCARBONS.

No direct means has yet been found of determining quantitatively the amount of hydrocarbons brought to the surface by eruptions. Much of it must burn while some escapes to make "a pleasant smell." It would seem to me that careful quantitative work on obsidians would be most likely to furnish data for estimating the percentage content of the magmas. If any considerable part of the water and carbon dioxide of eruptions is due to the combustion of hydrocarbons, as Sainte-Claire Deville, Fouqué, Messrs. Suess, Stocklasa, and others have inferred, the total must, of course, be enormous. By examining the accounts of experiments it appears that ammonium chloride and hydrocarbons are generally referred to in similar terms, as if at least the order of magnitude of the two kinds of emanation were the same. In fact I am unable to guess from the published investigations whether ammoniacal compounds or hydrocarbons predominate in obsidians and recent lavas. Now, according to Mr. Stocklasa, a large part of the emissions of Vesuvius consists of ammoniacal compounds. When the scale of a Vesuvian eruption is borne in mind, it appears that the total quantity of these salts expelled is immense. Thus even if the quantity of hydrocarbons attending eruption were only a very moderate fraction of the ammoniacal output, volcanism must be competent to yield exceedingly valuable quantities of hydrocarbons.^a

Even if petroleum of organic origin were exceptional, the distribution of oil might resemble its actual disposition. An accumulation of inorganic oil within reach of vadose water would be driven toward the surface by capillary displacement and buoyancy. If the surrounding rocks were intersected in all directions by cracks, the oil would be expelled at least in part through springs. Only an impermeable sheet of rock could prevent this expulsion, and the only rock found in sheets impervious to liquids is moist clay. Hence it is to be expected that inorganic oil when it occurs in considerable quantity should impregnate the rocks underlying clays. But such rocks are usually stratified and frequently fossiliferous. Oils of organic origin would behave in the same way and would also accumulate, if at all, beneath clay. Hence the well-known fact that petroleum is found in these circumstances proves nothing whatever as to its origin.

^a Mr. Brun asserts that the Javanese petroleum is of eruptive origin, but does not offer detailed evidence that it is so. Java oil is not unlike that of Pennsylvania.

From another point of view also the argument that the genesis of petroleum is organic because oil is associated with fossils may be pushed too far. In swamps the accumulation of vegetable matter is enormous, as everyone knows. In the open sea conditions are very different. The Atlantic coast of Virginia is one long beach plentifully strewn with shells, but not one in thousands of these contains a shellfish, and the seaweed driven up by a storm disappears with wonderful rapidity. It is safe to say that an acre of the Dismal Swamp carries more organic matter than 10,000 acres of Virginia beach. Even in tropical seas, where life is most abundant, dead animals and plants are rarely to be found. For the most part, living things there are consumed *while* they die. An ooze is derived from organisms which have perished at the surface, and their remains must in many cases take weeks to reach the bottom. What fatty tissue surface scavengers and the deep-sea fauna do not assimilate must be almost completely decomposed by bacteria during the long journey to the grave and the slow process of burial beneath the remains of survivors.^a The simplest and best proof that there are no great accumulations of dead organic matter in the sea is that the ocean is not a stinking pool, but a great reservoir of purity. Hence, where notable quantities of oil are found in sandstones and limestones associated with marine fossils, as is commonly the case, there is ground for suspecting that the oil is at least exotic, if not inorganic. In shales, on the other hand, the presumption is the other way. Many mud flats are full of dead organisms, a part of which may in time be hermetically sealed by argillaceous matter; moreover, when a small amount of induration has taken place without desiccation the mass becomes impervious to allothigenetic oil.

It now appears certain that bituminous compounds are derived in part from organic matter and in part from azoic magmas. There is satisfactory evidence also that neither portion is economically insignificant.

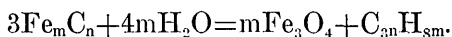
THEORIES OF INORGANIC GENESIS ALL UNSATISFACTORY.

In the foregoing pages the attempt has been made to set forth the facts with as little reference to hypotheses as practicable. Study of the associations of the hydrocarbons leads irresistibly to the conclusion that notable quantities of inorganic hydrocarbons exist in nature, but does not indicate whether or no they are juvenile, or if juvenile how hydrogen and carbon came to unite. The present state of knowledge and speculation on this subject can be briefly set forth.

^a It is reasonable to suppose that the fecundity of the abysmal fauna keeps pace with the food supply which reaches the bottom; "broth," as William B. Carpenter called it. For a lucid discussion, see Mr. A. Agassiz's *Three Cruises of the Blake*, Mus. Comp. Zool. Bull. 14, 1888.

Mr. N. V. Sokoloff ^a has maintained that the bitumens are of cosmic origin, that they were inclosed in the mass of the earth and have since been emitted. In short, he supposes the hydrocarbons as such to be magmatic and to exist within the earth in solution, solid or gaseous. Various other writers either take this view or do not expressly dissent from it. More widely held is the hypothesis that the carbon exists within the earth in the form of carbides of metallic bases. Most of those who adopt it appear also to suppose that the hydrogen of the hydrocarbons is derived from water, though this does not seem a necessary complement of the carbide theory.

Mendeléef ^b was the first to suggest that in nature hydrocarbons were made from carbides, viz, those of iron. Experimentally he relied for support on the well-known fact that artificial irons, cast or wrought, if dissolved in chlorhydric or sulphuric acids, develop hydrocarbons. He held that the earth had an iron nucleus similar in composition to siderolites and believed that water at high temperatures and pressures would react as follows:



That steam at high temperatures produces a coating of magnetic oxide on iron is well known, and it is most likely that the nascent hydrogen would unite to some extent with the combined carbon of hard irons; but Mendeléef does not seem to have demonstrated this. Moissan objected ^c to this theory because cementite (Fe_3C), the only well-known iron carbide, is not decomposed by pure water or by sea water at 150° . It is nearly certain, however, that there are several iron carbides, and Moissan does not appear to have tried steam at higher temperatures.

Even the existence of the natural, terrestrial carbides of iron demanded by Mendeléef's hypothesis has been questioned, but it will be shown a little later that this objection at least is not well taken.

That carbon irons digested with acids evolve hydrocarbons was first shown by J. L. Proust ^d more than a hundred years ago. He experimented both on cast iron and on iron sponge reduced at a relatively low temperature in glass. The most elaborate investigation is by Stanislas Cloëz. ^e He produced a long series of hydrocarbons from cast iron by solution in chlorhydric and sulphuric acids. From specular iron (which contains much manganese) he was also able to

^a Bull. Soc. imp. nat. Moscou, new ser., vol. 3, 1890, p. 720.

^b Ber. Deutsch. chem. Gesell., vol. 10, 1877, p. 229. This is a report of a meeting of the Russian Chemical Society, where Mendeléef made his views known in January, 1877. See also Mendeléef's Principles of Chemistry, vol. 1, 1905, p. 402.

^c Traité de chimie, vol. 2, 1905, p. 374.

^d Nicholson's Jour. Nat. Phil. Chem., etc., vol. 5, 1803, p. 100, quoting from Jour. de physique, ed. by de Lamétherie, vol. 56, 1802, p. 276.

^e Compt. Rend., Paris, vol. 78, 1874, p. 1565; vol. 85, 1877, p. 1003; vol. 86, 1878, p. 1248.

evolve hydrocarbons by the action of water at a low red heat, and from ferromanganese by water at only 100° . Mendeléef, too, made from manganiferous pig iron, by the action of chlorhydric acid, a mixture of hydrocarbons indistinguishable from naphtha. Of course this is interesting and important, but native irons seem to contain the merest traces of manganese.

As is well known, Moissan^a produced in the electric furnace and studied in some detail a long series of metallic carbides. The carbides of the metals of the alkalis and the alkaline earths when brought into contact with water yield acetylene which has not been found in petroleum. The carbide of aluminum gives methane and that of manganese equal volumes of methane and hydrogen, whereas the carbides of iron, nickel, and cobalt in water do not emit hydrocarbons at ordinary temperatures. Moissan^b was led by this investigation to believe that carbides, other than those of iron, exist in the interior of the earth and that their decomposition by water yields a part of the petroleum. (The bituminous schists of Autun, on the other hand, he thought organic.)

This hypothesis has much to recommend it. That temperatures of well over $2,000^{\circ}$ exist within the earth I think almost certain, because the temperature of the earth at its consolidation must have approximated to a condition of convective equilibrium. There seems no known reason why carbides besides those of iron might not have formed in the earth, especially those of aluminium and manganese. None have been found as yet, however. Possibly they may exist in a state of solid solution, and thus have escaped recognition. Until they are recognized, Moissan's theory is only plausible.

It is a mystery to me why Mendeléef and Moissan should have relied for the decomposition of their carbides on water alone. Volcanic eruptions are regularly accompanied by the emission of vast quantities of ammonium chloride and free chlorhydric acid. According to Mr. Suess, the amount of free chlorhydric acid is sometimes so great that volcanic rains seriously injure vegetation over wide areas. Again, ammonium chloride splits up into ammonia and free chlorhydric acid at a temperature approaching 350° under atmospheric pressure. Visible red heat begins near 500° , so that except in the cooler parts of a volcano none of the chlorhydric acid near the surface is neutralized by ammonia. Even in solution ammonium chloride may be partially dissociated, ammonia escaping and leaving a certain amount of free chlorhydric acid. Hence it would seem that volcanic waters would in most cases be acid and competent to evolve hydrocarbons from iron carbides.

^a *Traité de chimie*, vol. 2, 1905, p. 259.

^b *Proc. Roy. Soc., London*, vol. 60, 1896-97, p. 156.

Water, however, is not essential to the formation of hydrocarbons from carbides even as a solvent for acids. Mr. Brun^a reports his results on this subject in the following terms:

The chemical reactions in volcanoes proceed without the cooperation of water; this the writer has confirmed anew from observations on Pico de Teyde and Timanfaya, in the Canaries. In discussing the formation of hydrocarbons (which are very common in volcanic ash) it is evident that the reactions between carbides and ammonium chloride, always present in abundance, must be taken into consideration. Salvadori^b produced methylamine and acetylene from calcium carbide and ammonium chloride; and the writer observed during the same reaction the appearance of fluorescing hydrocarbons resembling crude petroleum. With iron carbide a paraffin-like substance was obtained, accompanied by gaseous hydrocarbons and free hydrogen. With aluminium carbide methane and hydrogen were evolved.

Artificial irons differ so considerably from the native metal that it seemed very desirable to test the action of dry ammonium chloride on Greenland iron. Mr. G. P. Merrill was good enough to supply me with a few grams from a specimen of an Ovifak iron, which is about as hard as the best tool steel, but very brittle, and which contains a large amount of combined carbon. The powdered metal was heated with pure ammonium chloride in an atmosphere of nitrogen. Of the educts a small portion condensed at zero degrees to a pasty grease, somewhat thicker than vaseline; a second portion, not condensable in ice water, was absorbed by bromine water, which was bleached as the absorption progressed. The gases escaping from the bromine water, after being freed from bromine, were passed over hot copper oxide and the carbon dioxide formed was caught as barium carbonate. Both saturated and unsaturated hydrocarbons were thus present in the educts. The gases which passed the bromine water will burn in air almost without luminosity and must consist mainly of hydrogen and methane. More of the carbon seems to be represented by the saturated volatile hydrocarbons than by the condensable oils or the bromine compounds, and the pasty grease therefore probably contains paraffin. The unsaturated hydrocarbons are perhaps due to the cracking of paraffins. I see no reason to doubt that cracking may occur in some solfataric oil deposits and that marked differences in the composition of oils from different pools may be thus accounted for. The combined carbon of the iron appears to be completely converted into hydrocarbons, for there is an approximate quantitative relation, and no graphite was detected in the residues from the metal. A brownish-gray, nonmagnetic powder remains behind which probably consists of iron nitrides.^c Large quantities of nearly colorless crystals of ferrous chloride also form.

^a Chem. Zeitung, vol. 32, 1908, p. 302.

^b Gazz. chim. ital., vol. 32, 1902, p. 496.

^c Either metallic iron or ferrous chloride heated in an atmosphere of ammonia yields silvestrite or other iron nitrides; Hintze, Handbuch der Mineralogie, vol. 1, 1898, p. 189.

These experiments were made for me by Mr. George Steiger, who will publish when completed such quantitative determinations as the amount of material available enables him to make. In the meantime it is established that solid, liquid, and gaseous hydrocarbons are copiously evolved by the action of dry ammonium chloride on native iron. There seems no reason to suppose that pressure would interfere with this evolution. It follows that the formation of hydrocarbons from inorganic substances may very probably take place at depths far greater than those to which vadose waters penetrate, far greater also than those at which stratified rocks are prevalent.

FACTS BEARING ON CARBIDE OF IRON THEORY.

That iron carbides exist in artificial iron is well and definitely known. Cementite, Fe_3C , was first prepared in a pure state by Moissan^a in 1897, but seems to have been recognized as a distinct compound by Sir F. Abel in 1885. It is probable that several other carbides exist in smelted iron, but their study is attended by great difficulties.

Most modern metallographers accept, so far as its general features are concerned, Roozeboom's phase-rule diagram of iron constitution. As so represented, all uncombined carbon is graphite and the combined carbon is all combined in carbides. In respect to matters of detail, however, there are differences of opinion. It has been held by a number of metallographers that at ordinary temperatures the most stable mixture consists of ferrite (pure iron) and graphite; or, in other words, they believe that cementite tends to dissociate into graphitic carbon and iron. But two recent investigations by Mr. G. B. Upton^b seem to disprove this view. He concludes that the most stable mixture consists of ferrite and Fe_3C accompanied by no graphite unless carbon is present in excess of the proportion represented by this carbide. In a higher metastable phase, as everyone acknowledges, cementite exists; but by very slow cooling Fe_3C is resolved, according to Mr. Upton, into Fe_2C and Fe. "Stead's brittleness" is referred to this change.

Among other confirmations of his views Mr. Upton cites the magnetic permeability of the soft, gray cast iron employed in the construction of electrical apparatus. He finds that this is only about half as great as it should be were the castings composed of graphite and magnetically "soft" ferrite.

In 1889 Mr. E. Weinschenck^c discovered in the Magura meteorite a compound to which he gave the name cohenite. Its formula is

^a *Traité de chimie*, vol. 4, 1905, p. 392.

^b *Jour. Physical Chemistry*, vol. 12, 1908, p. 507, and vol. 13, 1909, p. 388.

^c *Annalen Naturh. Hofmus. Wien*, vol. 4, 1889, p. 94. I find some erroneous references in the literature to cohenite as FeC_3 . The density of cohenite is 7.227. Moissan found the density of cementite 7.07.

(Fe,Ni,CO)₃C. This may be regarded as a cementite in which a part of the iron is replaced by nickel and cobalt, or cementite may be considered as a cohenite free from cobalt and nickel. Cohenite has since been identified in several meteorites and also in the terrestrial iron of Greenland at Ovifak and Niakornak, localities separated by about 100 miles.

The large amount of combined carbon in the Greenland iron has frequently been commented upon. Daubrée,^a who found 3 per cent in one specimen from Ovifak, said: "The presence and abundance of carbon in these masses, combined carbon as well as that in a free state," is remarkable. J. Lawrence Smith^b also found 2.34 per cent combined carbon in iron extracted in small particles from the basalt of Ovifak. His comment is: "The very large percentage of carbon in a state of combination in the iron of Ovifak, without traces of graphite, is a very interesting fact and demands a special chemical investigation." Although there was no graphite in the iron, Smith noted its presence in the basalt. In the Niakornak iron he found 1.74 per cent carbon, all combined. Mr. Carl Hintze^c expresses his belief that the carbon of Smith's irons existed as cohenite.

In 1897 Emil Cohen^d discovered that although Greenland irons disintegrate with great rapidity, the decomposition is not complete. In fact, unattacked metallic grains remain, and these can be practically freed from extraneous matter. Parcels of such grains, both from Ovifak and Niakornak, were analyzed for him by Mr. Sjöström and their composition found to correspond very satisfactorily to cohenite.^e

This identification seems to me of great importance. Not only do the Greenland irons contain carbides, but cohenite must be stable at ordinary temperatures. The Greenland basalts unquestionably took decades to cool from the temperature of fusion, say 1,100° or 1,200°, to that of the atmosphere. No experimenter can hope ever to attain so gradual a cooling, and since the iron reached atmospheric temperatures it has had thousands of years to complete molecular readjustment. Cohen concluded that chalybite, or Fe₂C, does not exist in the Greenland irons. These facts, however, are not, to my thinking, necessarily inconsistent with Mr. Upton's conclusions. The nickel may make all the difference, and perhaps some of the good qualities of nickel steel are due to the stability of cohenite under conditions such that cementite would split up.

^a Compt. Rend., Paris, vol. 74, 1872, p. 1542.

^b Annales chim. phys., 5th ser., vol. 16, 1870, p. 452.

^c Handbuch der Mineralogie, vol. 1, 1898, p. 190.

^d Meteoritenkunde, heft 2, 1903, p. 226.

^e Cohen remarks that these Greenland cohenites are identical with meteoric cohenite in their behavior to acid and neutral solutions as well as in composition.

For the present purpose the vital point is that all investigations of the Greenland terrestrial irons show the presence of iron carbides in abundance.

Mendeléef, in supporting his hypothesis, expressed his belief that the nucleus of the earth is composed of metallic iron, and it was from the action of water on this nucleus that he derived his hydrocarbons. The idea of an iron nucleus, long familiar, has grown in favor during the last half century. It is probable, indeed, that with such internal densities as are implied by the known mean density and surface density of the globe, stability would be impossible unless the intrinsic density of the nucleus were great. On the other hand, this nucleus, the barysphere, must lie far below the surface, several hundred miles assuredly, possibly a thousand; and it is improbable that surface influences of any kind are sensible at any such depths. Vadose water in particular is confined to an extremely superficial shell.

These considerations, however, involve only a very slight modification of the iron-carbide theory. If the earth, like meteorites, consists of metallic iron and rock, the rock must overlie the iron as slag does in a blast furnace, and it may be taken for granted that this slag contains "shot metal," that this rock contains entangled metallic particles which presented so much surface per unit volume as to prevent their sinking to the bottom of the viscid, lithoid magma. Such "particles," too, might have considerable dimensions and even weigh tons, since no provision was made in the world-building process for mobile slags and clean separation. It is thus rather to clouds of iron particles suspended in the lithoid shell of the globe than to an iron nucleus that advocates of the carbide of iron hypothesis of petroleum must appeal.

Native terrestrial iron or nickel iron has been found in many parts of the world, but nowhere in such abundance or in masses of such size as at Disco Island and the neighboring mainland of Greenland. Long before Nordenskiöld discovered this wonderful locality, Andrews had found specks of iron in the basalt of Antrim, Ireland. Irons supposed to be terrestrial have since been detected in every quarter of the globe, and though a meteoric origin is suspected for some of them, many are beyond question natives of this planet. At some points again a reduction by burning seams of coal or lignite is probable, but there are also many undoubted instances in which the metal is a component of a massive rock. Curiously enough, however, the native metals in which nickel predominates carry no appreciable amount of carbon. So far as carbides are concerned, therefore, awaruite, josephinite, and souesite must be ruled out, for all of them contain from 60 to 75 per cent of nickel.

In the United States native iron was first discovered by G. H. Cook^a in New Jersey. "Native iron," he reported, "could be obtained from any of the specimens we had from the various ridges of trap in the red sandstone region of New Jersey." This iron evolved hydrogen with acids and precipitated copper from acid sulphate solution. In 1877 G. W. Hawes^b found native iron embedded in magnetite in New Hampshire, and reported that he had also detected it in the fresh trap rocks of the Connecticut River.

In 1898 Mr. F. L. Ransome examined for me a series of several hundred thin sections of subsilicic rocks from various parts of the country, with a view to detecting metallic iron. The sections were uncovered, cleaned, and immersed in copper sulphate solution. It was found difficult to distinguish very minute particles of metallic copper from ferric oxide under the microscope, even in direct sunlight. After all doubtful cases had been rejected, only six sharply determinable occurrences from the United States remained. Of these four were olivine basalts from northern California, one a saxonite from Riddles, Oregon, and one a peridotite from Elliot County, Kentucky.^c Had we been able to dispose of hand specimens by crushing them and extracting the magnetic particles, it is presumable that more localities would have been detected.

IRREGULAR COMPASS DECLINATION IN PETROLEUM FIELDS.

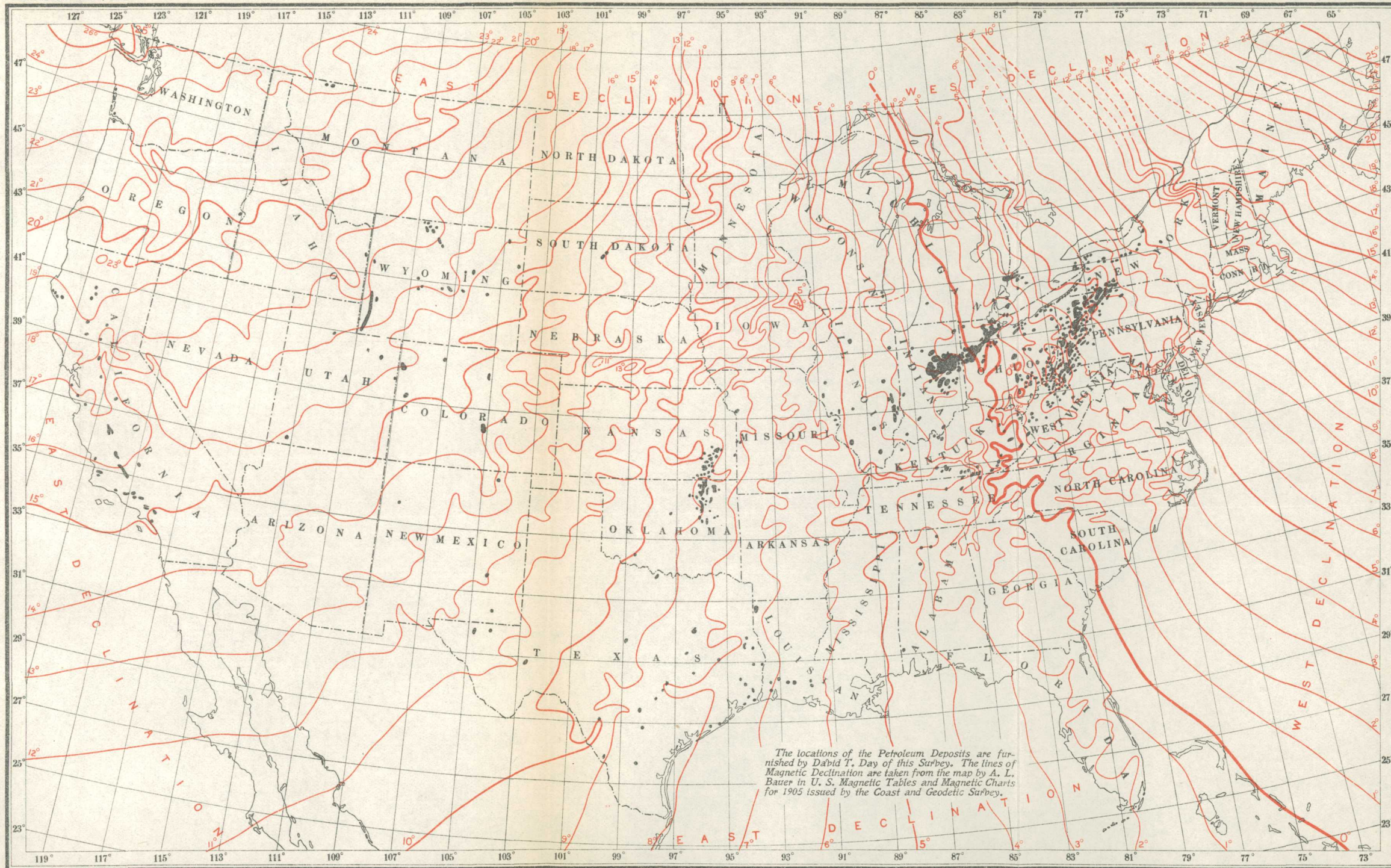
In the foregoing pages the condition of knowledge with reference to the origin of petroleum and other bituminous substances has been reviewed. The result is thoroughly unsatisfactory. Some oils are undoubtedly organic and some are beyond question inorganic. The evidence shows that neither variety can properly be regarded as unimportant. This review, however, does not elucidate the source of the principal deposits, the great petroleum pools. They may have been derived from carbonaceous matter of vegetable or animal origin, and they may have been derived from carbides of iron or other metals. It is also barely possible that the hydrocarbons exist as such in the mass of the earth.

In thinking over this situation it occurred to me to inquire whether any relation could be detected between the behavior of the compass needle and the distribution of hydrocarbons. Not very much could be expected from a comparison of these phenomena, for magnetite

^a Ann. Rep. New Jersey Geol. Survey, 1874, p. 56.

^b Am. Jour. Sci., 3d ser., vol. 13, 1877, p. 33.

^c The basalts are (1) No. 369 Ps., H. W. Turner collection, Downieville quadrangle, 2.8 miles west by south from Mount Jackson; (2) No. 909 S. N., H. W. Turner collection, fragment from basaltic Tuscan tuff, Chico quadrangle, 4 miles a little east of south from Inskip; (3) No. 1789 C. R., J. S. Diller collection, 1.5 miles southwest of Lassen Peak; (4) No. 1168 M. S., J. S. Diller collection, 18 miles north of Mount Shasta, in Siskiyou County. The saxonite and peridotite have both been described by Mr. Diller.



PETROLEUM DEPOSITS AND LINES OF EQUAL MAGNETIC DECLINATION FOR 1905

exerts an attraction on the needle whether this ore occurs in solid masses or is disseminated in massive rocks; and again, as was first shown by Messrs. Brunhes and David,^a many if not all volcanic rocks possess polarity, so that repulsions are involved as well as attractions. Even if the iron carbide theory of genesis were known to be correct, and exclusively correct, no one would think of maintaining that all bodies of magnetite have a connection, however remote, with the occurrence of petroleum. Hence any indications of iron carbides and associated petroleum which the compass might be supposed to afford would be obscured by the local attraction of independent masses of magnetite. Earth currents are also to some extent local and thus produce irregularities in declination.

Nevertheless, on glancing at Mr. Bauer's map of the magnetic declination^b in the United States for January 1, 1905, with this idea in mind, I saw that the irregularities of the curves of equal declination were strongly marked in the principal oil regions. When this map was compared with one prepared by Mr. David T. Day^c showing in detail the known hydrocarbon deposits of the United States the coincidences recognized became more striking and other agreements became evident.

The chart accompanying this paper is merely a compilation from the two maps of Messrs. Bauer and Day. The red lines are the isogonal loci, and the black dots or blots represent deposits of hydrocarbons. The most marked agreement is found throughout the great Appalachian oil field, which is the area of greatest variation in declination. In California, also, strong deflections of the isogonal lines accompany the chain of hydrocarbon deposits. In the interior of the country the coincidences are less marked, but they are very noticeable, as may be seen by inspection of the map.

There are other systematic irregularities, wrinkles in the isogonic topography as I may call them, which can not be connected with oil. One such wrinkle runs down the Atlantic coast and contains the New Jersey native iron as well as known deposits of magnetite. Another lies near latitude 47° and is doubtless due to the great northern iron belt.

No detailed chart of the magnetic declination in the petroleum fields of the Caucasus has yet been prepared. Mr. Bauer informs me, however, that great magnetic disturbances exist in that region, so that relations not dissimilar to those in this country are probable.

^a Compt. Rend., Paris, vol. 133, 1901, p. 155.

^b A line of equal declination, also called an "isogonal line," is one along which the compass needle everywhere makes a particular angle with the geographical meridian. A magnetic meridian differs in toto from an isogonal line. The map referred to appeared in U. S. Coast and Geodetic Survey magnetic tables and magnetic charts for 1905, chart 1.

^c Mr. Day was kind enough to place this map in manuscript at my disposal. It will appear in Mineral Resources U. S. for 1908, U. S. Geol. Survey, 1909.

Study of the map accompanying this paper justifies the statement that the coincidences between the occurrence of petroleum and local disturbances of the compass needle are too numerous to be attributable to mere accident or chance. There must therefore be a direct or an indirect historical connection between the two phenomena in the regions of coincidence.

CONCLUSIONS.

None of the hypotheses of petroleum genesis is proved by the relations shown on the map. These relations, however, are compatible with the supposition that the great oil deposits are generated from iron carbides either by or without the agency of water. Of these alternatives the latter is the more plausible.

What the map does prove is that petroleum is intimately associated with magnetic disturbances similar to those arising from the neighborhood of minerals possessing sensible magnetic attraction, i. e., iron, nickel, cobalt, or magnetite. Henceforth no geological theory of petroleum will be acceptable which does not explain this association.

No one doubts the vast industrial importance as well as the deep geological interest of the petroleum question. As time elapses it will grow more and more important, for the pinch of dwindling coal resources will probably affect children of those already born. In the interest both of the development and the conservation of our natural resources all the means at the command of science should be brought to bear on this mysterious subject. A geologist and a chemist each of the highest order should be coupled in the long and difficult investigations needed to elucidate the genesis of petroleum. The expense would be considerable but the economy would be enormous.