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Review

HISTORICAL FOUNDATIONS OF CHEMICAL GEOLOGY AND GEOCHEMISTRY

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SUMMARY

Roughly, the name chemical geology has been used for as long as chemistry has been applied in geology; the name geochemistry was introduced by Schönbein, in 1838. Whereas initially the names were often regarded as synonymous, in our century there is a tendency to make a distinction between the two on the basis of the way in which the subject is approached.

In the previous century most of the work dealt with mineral and rock analysis and the occurrence of geochemical cycles. Other fields of study, such as isotope "geology", physico-chemical petrology and crystal chemistry reached maturity early in the twentieth century. Somewhat later sedimentary geochemistry began to expand. The rise of geochemical prospection took place mainly in the nineteen thirties. In the meantime, a considerable progress was also achieved in the field of analytical geochemistry, particularly through the development of various new techniques.

INTRODUCTION

With the introduction of a new international journal to cover the wide interdisciplinary field between geology and chemistry, it is considered useful to devote a few pages to a reflection of how this field of scientific research began. It is fully realized that such a short article can only be somewhat arbitrary in the selection of its contents. It merely gives a few pictures of important moments in scientific history, without pretending to be a continuous, let alone a complete, story. In this sense there is a difference between a short and general historical account and the normal kind of review article. The present paper may serve (1) to show how a scientific discovery or development never stands on its own, but takes a place in an uninterrupted chain of intellectual human activities, and also (2) to show to whom modern workers in this interdisciplinary field owe the scientific basis with which they are so familiar that they take its presence almost for granted. It is in the nature of science to look into the future and to make use of the knowledge available to date mainly to produce further advances in the days and years ahead. This

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moment is chosen for some reflection about the path that is behind, and for paying a tribute to the founders of the scientific field which this journal hopes to serve. Those who wish to see a detailed survey of the state of knowledge in this field or in one of its components are referred to the various books mentioned in the list of references (e.g., Abelson, 1959; Fyfe, 1964; Goldschmidt, 1954; Mason, 1952; Rankama and Sahama, 1950; Smith, 1962. *Geochemical methods* : Adler, 1966; Ahrens and Taylor, 1960; Charlot, 1964; Ewald and Hintenberger, 1952; Feigl, 1963; Hermann and Alkemade, 1963;Kodama, 1963; Nakanishi, 1962; Ritchie, 1964; Samuelson, 1963; Smales and Wager, 1960. *Crystal chemistry* : Bragg, 1937; Buerger, 1960; Bunn, 1961; Evans, 1946; Hocart and Kern, 1959. *Silicate geochemistry* : Ahrens, 1954; Ahrens and Taylor, 1960; Eitel, 1954. *Physico-chemical petrology* : Bowen, 1928; Turner and Verhoogen, 1951. *Soil chemistry* : Gedroits, 1955; Jackson, 1958; Van Olphen, 1963; Winogradow, 1954. *Geochemistry of sedimentary rocks* : Degens, 1965. *Organic geochemistry* : Breger, 1963; Colombo and Hobson, 1964. *Petroleum geochemistry:* Dobryanskii, 1961; Nagy and Colombo, 1966. *Isotope geology* : Bowen, 1966; Hamilton, 1965; Rankama, 1954, 1963; Russell and Farquhar, 1960. *Geochemical exploration* : Ginzburg, 1960; Hawkes and Webb, 1962; Kudymov, 1962; Malayuga, 1963. *Hydrogeochemistry* : Alekin, 1948, 1953; Schoeller, 1956; Tageeva and Tihomirova, 1962. *Chemical oceanography* : Barnes, 1959. *Atmospheric chemistry* : Junge, 1963).

DEFINITION OF GEOCHEMISTRY

The word *geochemistry* was used first, in 1838, by the German chemist C.F. Schönbein, professor at the University of Basel, and the discoverer of ozone. He considered the task of geochemistry to consist of the investigation of the chemical and physical properties of all geological formations and of their age relationships. Four years later, he emphasized that a study of the chemical nature and origin of the masses composing the earth is of equal value to geology as the determination of the relative age and fossil content of geological formations.

Prior to Schönbein, such indications as chemistry of the earth or of the earth's crust and chemical geology had been used. These names remained in use also after the word geochemistry had been coined, partly as synonyms of geochemistry, partly as terms of a wider definition than was at that time given to geochemistry.

A definition of geochemistry which was much narrower than that by Schönbein, was given in 1924 by W.J. Vernadsky, who considered geochemistry as only the study of the chemical elements, i.e., the atoms, of the earth's crust and as far as possible of the earth in general, their history and their distribution in space in the present and past. He draw a clear-cut line with mineralogy which studies in the same way the compounds of the atoms i.e., the molecules and crystals.

In the same year, F.W. Clarke produced a wider definition, when he wrote: "Each rock may be regarded....as a chemical system, in which, by various agencies chemical changes can be brought about. Every such change implies a disturbance of equilibrium, with the ultimate formation of a new system, which, under the new conditions, is itself stable in turn. The study

of these changes is the province of geochemistry. To determine what changes are possible, how and when they occur, to observe the phenomena which attend them, and to note their final results are the functions of the geochemist... From a geological point of view the solid crust of the earth is the main object of study; and the reactions which take place in it may be conveniently classified under three heads – first, reactions between the essential constituents of the earth itself; second, reactions due to its aqueous envelope; and third, reactions produced by the agency of the atmosphere."

A compatriot and younger colleague of Vernadsky, A.E. Fersman, had given, in 1922, the following definition: "The purpose of geochemistry is the study of the element-atom in the conditions prevailing in the Earth's crust (as well as in the parts of the Cosmos accessible to our exact observations). Geochemistry studies: (a) the quantitative distribution of the chemical elements in the Earth's crust and their dispersion and local concentration; (b) the combinations of different elements in the different parts of the Earth's crust and their distribution in space and time under the influence of different chemical processes; (c) the migration of elements and the laws of such migration as determined by the different thermodynamic conditions of their environment; and (d) the behaviour of chemical elements either in the environment of the Earth's crust or as compounds and particularly as crystals. This may be expressed even more simply: geochemistry studies the history of chemical elements in the Earth's crust and their behaviour under different thermodynamic and physico-chemical natural conditions."

In a similar way V.M. Goldschmidt, in the years 1923–1937, formulated the task of geochemistry as the determination of the relative abundance of the elements and of the nuclids (isotopes), the distribution of the elements in the various spheres of the earth (atmosphere, hydrosphere, biosphere and lithosphere) and the detection of the laws which govern the abundance relationships and distribution of the elements.

Rankama and Sahama (1950), in their standard work, follow the definition of geochemistry as used by Goldschmidt. Their leading principle is not the subject of study but the viewpoint of the scientist attacking his problems. The geochemist deals largely with geological phenomena and geological subjects. However, his entire work is based on chemistry. His methods and his problems are those of a chemist or a physical chemist. On this basis, Rankama and Sahama draw the boundary line between geochemistry and chemical geology. "Conversely, the chemical geologist examines his problems from the viewpoint of a geologist. His is a geological material, and, when interpreting his observations, the analytical results, etc., he always has their geological application in his mind. For the geochemist, on the other hand, the geological observations, though based on the use of geological material, represent only a certain part of his results, which are intended to establish laws governing the abundance and distribution of the elements."

Mason (1952), is of the opinion, that "in the simplest terms, geochemistry may be defined as the science concerned with the chemistry of the earth as a whole, and of its component parts. At one and the same time, it is both more restricted and also more extensive in scope than geology."

There was already interest in the distribution of elements in the earth's crust even before the concept of chemical elements was clearly developed. This holds particularly true for ore geologists. Full development of geochemical work, however, only began in the first half of the nineteenth century.

As early as 1793, A. von Humboldt tried to derive the chemical composition of plants from their inorganic surroundings. Exact knowledge of the importance of plants in the geochemical cycle of the elements, particularly of carbon, oxygen, potassium and phosphorus, started with the work of J.A.B. Dumas (1837) and J. Boussingault (1851; Dumas and Boussingault, 1841) in France, and of K. Sprengel (1828, 1837) and J. von Liebig (1840) in Germany. In later years this subject made much advance in Russia, particularly by W.J. Vernadsky, who, in 1918, founded a biogeochemical research institute in Kiev.

The famous book of C.G.C. Bischof, *Lehrbuch der physikalischen und chemischen Geologie* (1846–1854) has been epoch-making in showing the importance of water for the distribution of the elements and in demonstrating that cyclic processes also occur in the inorganic world. The four-volume work presents a complete summary of the chemical work carried out by petrologists and other geologists in the pre-microscopic era. Bischof regarded the earth as a "vast chemical laboratory" and he questioned "whether there may be any other science of geology than that of a chemical and a physical geology". For several decades Bischof's book was a standard work. Only at the end of the century was it superseded by another geochemical classic, *Allgemeine und chemische Geologie*, by J. Roth, which appeared in 1879–1893. Further important works from that time are *Chemische Mineralogie*, by R. Brauns, issued in 1896, and *Treatise on Metamorphism* by C.R. van Hise, published in 1904.

Also in the twentieth century a great deal of important work has been done about geochemical cycles. Within the frame of this short review, however, only a few general points can be mentioned.

Goldschmidt (1926a, 1930, 1933b), when constructing a geochemical picture of the world ("Weltbild"), distinguished four stages of geochemical differentiation in the earth. The first stage includes all processes responsible for the differentiation of matter to form the geochemical spheres of which the earth is believed to be composed (see the section on the Geochemical structure of the earth). The second geochemical differentiation of matter is what happens when a magma crystallizes. The third differentiation chiefly comprises physico-chemical processes in aqueous solutions which result in the formation of the various sediments. Reactions between the biosphere, on the one hand, and the lithosphere, the hydrosphere and the atmosphere, on the other hand, form the fourth stage in the geochemical differentiation of the earth.

Rankama and Sahama (1949) distinguish between a minor or exogenic cycle in the migration of matter and a major cycle (Fig.1). The latter includes formation by chemical differentiation of both the primary igneous rocks and the sediments and their diagenetic products (stages two and three of Goldschmidt). At the deeper levels of the earth's crust, however, processes of still another kind take place which cannot be included under the concept of differentiation. Even though these processes tend to cause a chemical

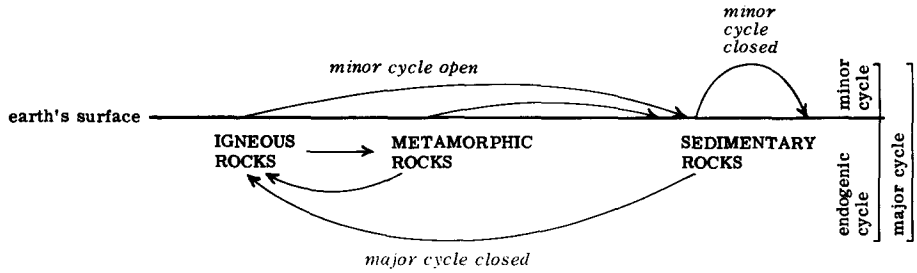

Fig.1. Very simplified representation of the major and minor cycles of matter

distribution of the elements among various rocks, they work essentially in the opposite direction, endeavouring to level-off the chemical differences already produced. They form the endogenic cycle of matter. The endogenic and exogenic cycles form the major cycle of matter. The minor or exogenic cycle, which starts from solid crystalline rocks and ends in sedimentary rocks, thus forms but a part of the major cycle of matter in nature. The minor cycle takes place under the direct influence of hydrospheric and atmospheric agents, and, unlike the major cycle, which is closed, it is largely open and takes place only in one direction; it is closed only for sedimentary rocks, but for all other rocks it is irreversible.

MINERAL AND ROCK ANALYSIS

Of fundamental importance to the development of geochemistry has been the chemical analysis of minerals and rocks. Progress in this field was closely connected with the development of analytical chemistry. Consequently, geochemistry was, to a certain extent, from the beginning an exact science, directed mainly to quantitative work. In 1821, J.J. Berzelius described mineralogy as the "chemistry of the earth's crust". Initially mineral and rock analyses were primarily carried out to establish the distribution of the main elements in the earth's crust. The first estimates about this distribution were made by Döbereiner, but these were little more than intelligent guesses. It was Berzelius and his school in Sweden who started the collection of basic data.

Valuable work in the collection of analytical data was also carried out by Boué (1843) and Élie de Beaumont (1847); both were interested in the qualitative as well as the quantitative aspects of the distribution of the chemical elements in the crust of the earth. A first attempt to express the average composition of the earth's crust in terms of minerals, was made by De Serres (1863).

A very important stage was the discovery of the spectral laws by G. Kirchhoff and R. Bunsen, in 1860–1861. This led to the discovery of several new elements, such as cesium (by R. Bunsen, in 1860–1861), rubidium (by R. Bunsen, in 1861), thallium (by W. Crookes, in 1861), indium (by F. Reich and H.T. Richter, in 1863), gallium (by L. de Boisbaudran, in 1875), scandium (by L.F. Nilson, in 1879). Study of the distribution of the trace elements was begun by W.N. Hartley and H. Ramage, in 1897, G. Eberhard, in 1908, and W.J. Vernadsky, in 1910.

Spectroscopic examination of solar and stellar radiation, the chemical analysis of meteorites and the knowledge that was collected about the composition of the earth led already in the nineteenth century to the belief that the universe is chemically uniform, with the same elements occurring throughout the cosmos. Only once has an element been discovered, which was not previously known to occur on the earth. This was helium, first detected in the sun's spectrum by the astronomer Janssen, in 1868, and recognized as a new element by N. Lockyer, in 1869. Nearly thirty years later, in 1895, helium was identified on the earth by Ramsay, as the gas evolved when uraninite is heated with an inorganic acid. In fact, the evolution of an inert gas from uraninite had already been observed a few years earlier, by Hillebrand, but he thought it to be nitrogen.

The first published collections of chemical analyses of rocks were compiled by Roth (1861, 1869, 1873).

The need for complete analyses of minerals and rocks was firmly stressed by the American W.F. Hillebrand, who, in 1900, published one of the first accounts of silicate analysis.

A very important publication from this period is the summarising work of F.W. Clarke, of the U.S.Geological Survey, *The Data of Geochemistry*, published in 1908, and for several decades the standard reference work. Earlier Clarke had begun well by introducing the chemical investigation of the earth into America. This began in 1884, with his appointment as Chief Chemist to the U.S.Geological Survey. Before that time, this field of research was largely confined to the European continent. In 1922, Clarke issued, together with H.S. Washington, *The Average Chemical Composition of Igneous Rocks*, and in 1924 they published *The Composition of the Earth's Crust*. These works, together with a few other publications by Washington (1920, 1925) presented a reasonable approximation (though not unassailable) of the average chemical composition of the various rock types, the different parts of the lithosphere, and the lithosphere as a whole. Washington also showed that the average chemical composition of the rocks in the Pacific Ocean regions is almost identical to that of rocks from the Atlantic Ocean regions, but substantially different from the average for the total lithosphere. In 1924, also the last edition of *The Data of Geochemistry* appeared, more or less marking the end of a century of geochemical work dealing with the chemical assay of the directly accessible parts of the earth. In 1925, Clarke retired from his position in the U.S.Geological Survey.[1]

In the meantime, a new period in inorganic analytical geochemistry had already started in 1920. This period is characterized by the introduction of X-ray and optical spectrography. X-ray spectrography was first used to analyze trace elements by the Swede A. Hadding, in 1922. In the period 1923–1929, this technique was used very extensively for the analytical study

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[1] In recent years, the U.S. Geological Survey has been publishing a new edition of *The Data of Geochemistry*, in the form of a large number of separate monographic contributions, written by specialists in the various subjects.

Modern data about the abundance and distribution of elements in the earth's crust can also be found in Mason (1958), Taylor (1964), Vinogradov (1962) and Wedepohl (in press); data about the distribution of the elements in igneous rocks are given in Taylor (1964), Turekian and Wedepohl (1961) and Vinogradov (1962); for the distribution of elements in some sediments see Turekian and Wedepohl (1961). Data about the composition of meteorites are given by Mason (1962) and Vinogradov (1962).

of the distribution of rare elements in minerals, while X-ray crystallography furnished data on the atomic and ionic radii of the rarer elements (cf. the section on Crystal chemistry). The reason for concentrating on the rarer elements was, of course, that both analytical and structural data were lacking for many of them, so that determinations of such data naturally had a high priority among geochemical investigations (Goldschmidt, 1954). After 1929, X-ray spectrography was in many cases superseded by optical spectrography. The credit for having brought this method into fruition goes to V.M. Goldschmidt and the school which he led in Göttingen in the years 1929–1935. In most cases it has a much higher sensitivity and thereby the necessity of chemical concentration from the crude minerals or rocks could frequently be eliminated. Since then, non-destructive and instrumental techniques have strongly gained in importance, with further development of the X-ray spectrograph, flame photometer, and neutron activation.

The present stage in inorganic analytical geochemistry began with the development of the electron microprobe, by Castaing, in France, and introduced into petrology to a large degree by the Cambridge school of mineralogy and petrology. Focussing electrons in a way which is impossible with photons, enables the analyst nowadays to study a volume of material as small as $10^{-15}\,cm^3$. The use of electrons has also led to notable developments in the field of electron microscopy.

Our century has also seen the development of organic geochemistry (sometimes referred to as "biogeochemistry"). Its rise has, to an important degree, been determined by the discovery of the technique of chromatography. As early as 1903, chromatography was used by the Russian botanist Tswett, as a method of separating different natural substances, achieved by first placing them on adsorbent columns and then removing them selectively by elution with suitable solvents. Not until 1931, however, was the importance of chromatography fully realized. Major applications in chemistry did not take place until after World War II. By then column chromatography had been supplemented by paper chromatography (1943), which permitted a greater variety of separations from extremely minute samples. More recently, other thin-layer materials and gas chromatography have been introduced. All find application in modern geochemistry.

The importance of mass spectrometry also in the field of organic geochemistry should be emphasized. This technique, largely employed by petroleum geochemists, has found much application also by the students of meteorite organic matter, one of the most interesting new aspects of organic geochemistry. Polarimetry, and more recently spectro-polarimetry, have also found application in the detection and characterization of optically-active organic compounds in sedimentary rocks and carbonaceous meteorites.

CRYSTAL CHEMISTRY

Already in 1815, J.N. Fuchs had observed that in gehlenite iron and calcium could mutually replace each other; he also pointed out the analogy with potassium- and ammonium alum. Four years later, E. Mitscherlich observed the similarity in crystal form of the potassium and ammonium salts of arsenic and phosphoric acid. Several investigators afterwards concerned themselves with the problem of isomorphic replacement of elements in

crystals and proposed hypotheses for an explanation of the discoveries. However, a final solution could only be reached after M. von Laue's discovery of X-ray diffraction (for which he received a Nobel prize, in 1914) and the fuller interpretation thereof by W.H. Bragg and his son W.L. Bragg, in the years 1912–1913. This made possible the determination of the atomic structure of solid substances. But it took some time before geochemists realized the importance of this discovery. When the last edition of Clarke's *The Data of Geochemistry* appeared in 1924, it contained nothing about crystal-structure determinations. Once more, it was V.M. Goldschmidt who saw the importance of crystal chemistry, and in particular, the importance of ionic radii for geology, which is so much a science of solids. The entry of any atom or ion into the lattices of crystals was found to depend upon its size. The particles dissolved in a magma or in an aqueous solution are thus sorted by the lattices of crystallizing minerals according to their sizes, which can be defined with sufficient accuracy by their atomic or ionic radii. Goldschmidt found that standard values of these radii could be determined for the various particles which occur in crystal structures; the standard state chosen by Goldschmidt and later adopted by other scientists being that of the ions in a lattice of the sodium-chloride type (Goldschmidt, 1923, 1924, 1954).

In addition to discovering the relations between crystal structure and the sizes of atoms and ions, Goldschmidt also devised a research plan which led to a maximum of results in a minimum of time. Together with his associates at the University of Oslo, he determined the crystal structure of many compounds, in the years 1922–1926. He thereby established the extensive basis on which the general laws which govern the distribution of elements in crystalline substances had to be founded. The results were laid down in a series of nine papers, under the collective title *Geochemische Verteilungsgesetze der Elemente* (Goldschmidt, 1923, 1924; Goldschmidt and Thomassen, 1924; Goldschmidt et al., 1925a,b, 1926a,b; Goldschmidt, 1926b, 1937a); notwithstanding the title, most of the contents of the first eight of these papers concern the crystal structures of inorganic compounds. The ninth paper summarizes the information, then collected, on the abundance and distribution of individual elements. An excellent summary of the first eight articles can be found in Goldschmidt (1929b).

The appearance, in 1937, of *Atomic Structure of Minerals*, by W.L. Bragg, may be considered as the real introduction of crystal structures to workers in the geo-sciences.

More recent publications in crystal chemistry include Azároff and Buerger (1958), Buerger (1942, 1960), Bunn (1961), Evans (1963), Gay (1959), Hocart and Kern (1959).

PHYSICO-CHEMICAL PETROLOGY

The first experiments in geology were carried out by Sir James Hall, a contemporary and compatriot of Hutton. The theoretical considerations of the latter were the direct inducement to Hall's experiments, but he received no support from Hutton. "There are superficial reasoning men, who without truly knowing what they see, think they know those regions of the earth which can never be seen, and who judge of the great operations of the mineral kingdom from having kindled a fire and looked into the bottom of a little crucible" (Hutton, 1795, p.251).

Hall (1812, p.72) remained convinced of the progress which would become possible in geology because of the increasing knowledge of chemistry. He continued his experiments, however, only after the death of Hutton.

According to Hutton's theory, crystalline granites and basalts crystallized from a melt. In order to test this, Hall (1805), in his first series of experiments, melted and cooled basalts and lavas. After the first melting, these solidified to glaseous substances, but after a second melting and a gradual cooling, by slowly extinguishing his coal fire, he did, indeed, obtain crystalline products.

A second series of experiments dealt with the effects of heating under pressure (Hall, 1812). He wished to test whether high pressure could prevent the disintegration of limestone when heated, and could make melting possible. He did his experiment in melted-up barrels of rifles, and from limestone powder obtained crystalline marbles which could not be distinguished from natural marbles even by stone masons.

Guthrie, who had developed the theory of eutectic (synchronous crystallization), was the first to suggest that this theory could be applied to the crystallization of granite (Guthrie, 1884), and Teall (1888) interpreted graphic granite as an eutectic structure. This study was continued by the Norwegian Vogt (1884, 1888, 1890, 1904, 1908, 1921–1923). He investigated metallurgical slags and compared these with natural rocks. It was established in this way that a relationship exists between the chemical composition of a melt and the nature of the minerals which crystallize out of it. Vogt also studied the influence that the addition of various oxides has on the nature of these minerals and on the order of their separation. His works on the formation of melilite, åkermanite, gehlenite, wollastonite, pyroxene and olivine are well-known and form one of the foundation stones of modern physico-chemical petrology (Loewinson-Lessing, 1954).

Up until 1904, when Vogt's classic work appeared, he based his opinions on the idea of liquid-magmatic differentiation. Later, however, he changed his view and became a protagonist of the crystallization-differentiation theory, with which the name of Bowen is closely associated.

Another very important application of physical chemistry to geochemistry and geology, around the turn of the century, was the monumental work of J.H. van 't Hoff on the formation of salt minerals from evaporating sea water and the metamorphic processes connected with it. His work was continued, on a more general basis, by Boeke (1915), one of his students.

Although classical thermodynamics was already well developed by the middle of the nineteenth century, through the work of, for example, J.P. Joule, K. Clusius and Lord Kelvin, it lasted until 1911 when it was introduced into the earth sciences through the famous doctorate thesis of, again, V.M. Goldschmidt, *Die Kontaktmetamorphose im Kristianiagebiet*, presented at the University of Oslo (at that time still called Christiania). In this work, Goldschmidt applied the phase rule to the mineral changes which are induced by contact metamorphism in shales, marls, and limestones. He showed that the changes can be interpreted in terms of the principles of chemical equilibrium. Until 1922, Goldschmidt did much more work on the subject of rock metamorphism, and this also stimulated other Scandinavian researchers to work on related problems.

Another most important institute, where the line of phase-equilibrium research was further developed in petrology, was no doubt the Carnegie

Institution of Washington. In 1910, N.L. Bowen came to that Institution, where he started a phase-equilibrium study of a silicate system. The results which he obtained enabled him to get a doctor's degree and this stimulated him to continue this kind of research, which he did for forty years. He followed the successful system of making experimental studies in the laboratory first and then carrying these results into the field to check them with the rocks themselves, thus evaluating the factors that lead to failure of equilibrium under natural conditions, together with the magnitude and direction of their effects. The experiments provided him with a chemical basis for hypotheses on rock genesis and the field tests helped to modify the hypotheses to give a closer approach to the mechanism of rock genesis. As such he has given a classical example of fundamental geo-scientific work. The book which he published in 1928, *The Evolution of the Igneous Rocks*, is still the best introductory literature to those interested in the origin of the igneous rocks. In addition to Bowen, also scientists like F. Schairer, O.F. Tuttle and H.S. Yoder have contributed to the reputation of the Carnegie Institution as a leading geochemical research center.

In order to classify and group the great variety of metamorphic rocks systematically, Eskola (1915, 1920), following a study of the saturation diagrams of Van 't Hoff, introduced the concept of mineral facies or metamorphic facies. In a particular facies, he includes all rocks which exhibit a unique and characteristic correlation between chemical and mineralogical composition, in such a way that rocks of a given chemical composition always have the same mineralogical composition, and differences in chemical composition from rock to rock are reflected in systematic differences in their mineralogical composition (cf. Winkler, 1965, p.16). The concept became widely known through Barth et al. (1939). Here Eskola states that the significance of this principle is based on the observation that the mineral paragenesis of metamorphic rocks in many cases conforms to the laws of chemical equilibrium. Numerous international discussions and elaborations were the result, and the concept was enlarged especially by F.J. Turner. Since Eskola defined his five original facies (sanidine, hornfels, greenschist, amphibolite and eclogite), a division into subfacies has in some cases been found to be necessary, while several additional facies have also been proposed. The control of the mineralogical composition of rocks by their chemical composition could be illustrated by means of triangular composition diagrams. The apices of the diagram represent the three components that mainly account for the observed mineralogical variation within the facies. These components, as used by Eskola, are Al_2O_3, CaO, and (Mg,Fe)O, and he named the diagrams themselves as triangular ACF diagrams.

The work of W. Nernst in Germany and of G.N. Lewis in the U.S.A. gave us the concept of "the minimum of free energy", which defines the trend of all physico-chemical changes in nature, and thus, as emphasized especially by A.E. Fersman, governs the formation and stability of minerals and rocks (Goldschmidt, 1954).

Bowen and his associates generally did not include water as a component in their experiments. In later years, the opinion has gained ground that a better insight can be obtained into the processes which have been possible in the earth, if experiments are made with natural materials, including water Wyart and Sabatier (1959) used, apart from synthetic materials, clayish sediments, which they heated to 800°C and a water pressure of 1800 atm.

They found that melts of granitic composition originated in equilibrium with crystals of (Fe,Mg)minerals. Extensive experiments have also been carried out by Winkler (1957) and Winkler and Von Platen (1958, 1960, 1961a,b).

ISOTOPE "GEOLOGY"

It was Rutherford and Soddy (1902), who through a study of thorium, developed the disintegration theory of radioactive elements. Among the first to contribute to an experimental proof of this theory was Boltwood (1905a,b, 1907). He determined the amounts of uranium and lead present in primary minerals from different geological formations and thus of different geological ages, and found that the amount of lead per gram of uranium increased with increasing age of the formation from which the analyzed minerals were collected. Since he believed firmly in the disintegration theory and since he has observed that lead is present in all radioactive minerals, Boltwood came to the conclusion that all of the lead might be the final disintegration product of uranium.

Strutt, later Lord Rayleigh, found that the amount of radium present in a variety of minerals was proportional to the amount of uranium and also that helium was present only in uranium and thorium-bearing minerals (Strutt, 1905). Some years later, he observed that the helium/uranium ratio is also related to geological age (Strutt, 1908, 1909a,b, 1910), but he had to note that while high values were not found in geologically young deposits, low values were found in old formations, indicating loss of helium. Holmes (1913) used the lead/uranium ratio for measuring geological age, by assuming a decay rate of 1 mole of lead replacing 1 mole of uranium in 8,200 million years. In the meantime, Joly had begun determining geological ages by investigating the pleochroic halos which surround radioactive minerals in micas (Joly, 1907, 1922, 1923; Joly and Rutherford, 1913). These halos had already been discovered in 1873, but until Joly (1907) explained their origin as being due to radioactivity, their nature and origin were the subject of much speculation.

In an attempt to connect radium and uranium, Boltwood (1907) discovered ionium. He found that the latter was chemically inseparable from thorium, despite the obvious difference between their atomic weights (thorium 232, ionium 230). This led to the concept of isotopes, individual members of a single chemical type. The name was suggested by Soddy (1912), to express that these members occupy the same (isos) place (topos) in the periodic classification.

The next major analytical advance in isotope research was made by Aston (1927), who for the first time, used the mass spectrograph to study the isotopic composition of lead.

The natural radioactivity of potassium and rubidium had already been discovered in 1905, but not until the last few decades were methods of dating based on it. Libby and associates proved, in 1947, that the radioactivity of ^{14}C could be detected and might also be used as a method of dating.

In recent years the expansion of isotope geology, also known as nuclear geology, nuclide geology or nuclear geochemistry, has been enormous. Its applications now cover a wide range. Isotope studies help in solving problems of the mechanism and products of geological and geochemical processes.

Radiometric dating of rocks and minerals has become a standard procedure. Much important information has been obtained, through isotope studies, on the age and the mode of formation of meteorites and about the conditions of their habitats during their making. Oxygen isotopes are used in palaeotemperature analysis. Studies of stable isotopes are also of practical importance, for example, the ratio of sulphur isotopes may help to understand the genesis of some sulphide ore deposits. Artificially produced radionuclides are increasingly applied to the different branches of geology and to the related pure and engineering sciences. For further details reference is made to Rankama (1954, 1963).

GEOCHEMICAL STRUCTURE OF THE EARTH

After A. Boisse, in 1850, had suggested for the first time that meteorites might give information about the bulk composition of the earth, several hypotheses about the chemical composition and structure of the earth were published, of which a few should be mentioned in this survey

Suess (1885–1909), following earlier work of the Frenchman A. Daubrée, introduced the distinction between nife (the nickel-iron core of similar composition as the iron meteorites), sima (a zone of dark and heavy rocks, chemically rich in silica, with magnesia in second place) and sial (the outer zone of the earth, forming the continental crust to a depth of several kilometers, and consisting of light rocks very rich in silica with alumina as the most abundant of the remaining chemical constituents).

Washington (1925) assumed the earth to consist of a central core enveloped by five shells of different composition. The core should consist of metallic nickel-iron, comparable to the metal phase of the meteoritic irons. The core merges on its outside into the lithosporic shell (700 km) with scattered segregations of ferromagnesian orthosilicate, which decrease in number towards the next, the ferrosporic shell (700 km), which corresponds to the chondritic stony meteorites. The peridotitic shell (1,540 km) would be comparable in composition to the achondritic stony meteorites. The two outermost shells are the basaltic (40 km) and the granitic (20 km) shells.

Goldschmidt (1922a,b, 1933b) distinguished only three shells. First, around the nickel-iron core or siderosphere, a sulphide-oxide shell (1,700 km), next an eclogite shell or chalcosphere (1,080 km) consisting of compressed silicates, and on the outside, the 120 km thick silicate crust or lithosphere. Goldschmidt compared the earth both with meteorites and with the products of an ore-melting furnace.

Kuhn and Rittmann (1941) proposed a completely different hypothesis. They assumed that the earth originated as a hot gaseous globe composed of undifferentiated solar material. Cooling, through heat radiation and escape of hydrogen and helium from the earth's gravitational field, caused an increase in specific weight of the outer parts and convection currents established themselves, carrying heavy material down and bringing light material to the surface. However, the convection currents did not reach the earth's core and this should still consist of undifferentiated solar material. The discontinuity, which seismic research had revealed to exist at a depth of 2,900 km was thought not to represent a change in chemical composition

but a sudden change in physical properties as a result of a sudden decrease of viscosity because of reduction of silica by hydrogen where the reaction of $SiO_2 + 2H_2 \longrightarrow Si$ (in solution) $+ 2\ H_2O$ takes place with increasing temperature. Despite, or probably because of, its revolutionary nature this hypothesis has received comparatively little attention. "In spite of its ingenious features, Kuhn–Rittmann's earth model involves such striking mistakes that, in our opinion, it is unnecessary to refute it." (Egyed, 1957). The latter author thinks it likely, that the differentiation of the earth is restricted to a zone having a maximum depth of 900 km; and that all the rest of the earth is of homogeneous composition, with the geophysical discontinuities being phase boundaries.

In recent years attempts are being made to collect more direct information about the interior of the earth, in particular about the outermost 1,000 km of the earth's radius, that part of the earth whose processes most influence the development of the earth's crust. V.V. Beloussov, president of the International Union of Geodesy and Geophysics, proposed the execution of an international scientific programme, the Upper Mantle Project. The period 1960–1963 was devoted primarily to the planning and organization thereof. At the I.U.G.G. meeting in Berkeley, Calif., in August 1963, an International Upper Mantle Committee (U.M.C.) was constituted that could "...encourage and develop international cooperative investigations of the upper mantle, its relationships to and influence upon the development of the earth's crust". At its first major meeting, in May 1964, the U.M.C. resolved that "... all national committees are urged to consider the period from 1 January 1965 to 31 December 1967 as Phase II of the International Upper Mantle Project, a period during which definite accomplishments should be achieved in the main international and interdisciplinary programs emphasized by the Upper Mantle Committee".

Deep-drilling programmes are carried out principally by the U.S.S.R. and by the U.S.A. (Mohole Project). Although in both countries unforeseen difficulties of financial, technical and other nature delayed the original plans, progress is being made, with the U.S.S.R., at is seems now, in the lead. Also Canada, China, Germany, Japan and South Africa incorporated plans for deep drilling in their proposed programmes for the Upper Mantle Project. Deep holes have two major scientific aspects: first, the materials from otherwise inaccessible depths become available for study by the powerful methods of laboratory physics and chemistry; second, the hole itself provides a means for introducing instruments for the observation of physical properties in place.

CHEMICAL OCEANOGRAPHY

The presence of common salt in solution in sea water was already known from very ancient times, as the Chinese some time prior to 2200 B.C. extracted it from sea water. The discovery of other elements in sea water is of much more recent date. Thus, bromine was first noted, around the year 1825, by the Frenchman A.J. Balard, in bitterns obtained after the salt had been precipitated from the water of salt marshes near Montpellier.

Modern chemical oceanography may be considered to have started with the work on the English physician A. Marcet, in 1819, the Danish chemist

G. Forchhammer, in 1865, and the German-born chemist W. Dittmar, who worked with 77 water samples collected by the famous British deep-sea expedition with the "Challenger" (1872–1876). Forchhammer worked for 20 years to complete the analysis of 200 samples of water collected for him by friends, ship captains and naval officers. The analyses of Dittmar took 9 years to be completed. He determined the percentage composition of the dissolved solids (chloride, sulphate, sodium, calcium, magnesium, and potassium) in each of the samples. His results supported the findings of his two predecessors that these six constituents make up as much as 99% of the dissolved salts in sea water and that the ratio of any one of the major constituents to the total dissolved solids is nearly constant in the sea, even though the total concentration of dissolved solids may vary from place to place.

Since then workers from all parts of the world have continued the study of sea water, but because of the size and complexity of the dynamic ocean system, no exact, universal description of ocean water can be given and it is doubtful whether this will ever by the case.

Knowledge of the mineralogical and chemical composition of the sea-floor deposits started in 1851, with the collection of samples by the U.S.Coast Survey off the Atlantic coast of the U.S.A., with which the name of J.W. Bailey is connected. For the deep-sea deposits the "Challenger" expedition, and particularly its geologist J. Murray, again did pioneering work.

GEOCHEMISTRY OF SEDIMENTS

The original constituents of the earth's crust, the igneous rocks and their minerals, are to a large extent unstable as regards the atmosphere and hydrosphere. The interaction of the latter two on the lithosphere leads to sedimentation, including such aspects as weathering, erosion, deposition, and diagenesis. The central problem in the geochemical side of sedimentation is, therefore, the chemical breakdown of some minerals and the formation of others. Also at the origin of this branch of geochemistry, one will encounter the name of the genius V.M. Goldschmidt.

The understanding of the distribution of elements in the sedimentary sequence was greatly facilitated by the introduction of the concept of "ionic potential". This is the quotient of ionic charge and radius. It was Goldschmidt who first pointed out that this ionic potential provides a measure for the behaviour of an ion in water: the hydration of an ion being proportional to its charge and inversely proportional to its radius.

The fixation of ions by crystalline clay minerals is governed to a large extent in both soils and sediments by the interaction of polarization forces arising from the electrical fields associated with the surfaces of the clay particles and more or less polarizable ions or ion hydrates (cf. Goldschmidt, 1954). As shown in the nineteen thirties, by Noll (1930, 1931, 1932, 1934) and by Jenny (1932a,b, 1941), not only is the size of the ions involved in ion exchange and adsorption on clay particles important, but also their polarizability.

Sedimentary geochemical processes take place at low and intermediate temperatures and are often connected with reactions in aqueous solutions. Goldschmidt (1928) realized, therefore, that the study of the dielectric properties of water is of great importance, because more or less oriented layers of polarized water must be formed on the surface of the layer lattice of clay

minerals due to their electrical fields and those of their adsorbed ions. The combination of layer lattices and a dipole liquid is the cause of the plasticity and bonding properties of clay aggregates, and these properties are, therefore, closely dependent on all kinds of ion exchange (Goldschmidt, 1954).

In the early stage of sedimentary geochemical work, it was believed that hydrolysis was the most important process in sediment decomposition. It was Correns and Von Engelhardt (1939), who demonstrated that both acid and alkaline solutions possess a more strongly decomposing action and are therefore more important agents in weathering.

The many investigations into rare elements, in the period of the nineteen twenties and the first half of the thirties, also led to such analytical studies of sediments. Goldschmidt and Peters (1931a,b, 1932a,b,c,d, 1933a, b,c, 1934; Goldschmidt, 1935; Goldschmidt et al., 1933a,b) published several papers, during the Göttingen period of the former, in which they demonstrated the presence of many rare elements in the ash of certain coals. Presumably this is due to the concentration of rare elements in certain plant products (e.g., forest litter) and in the uppermost zones of forest soils.

Basic studies have been made by Brenchley (1926; Brenchley and Warrington, 1927; Brenchley et al., 1927), Byers et al., (1938a,b), Mitchell (1944, 1945, 1948; Mitchell and Scott, 1947), on the distribution of trace elements in soils. This subject is of direct practical value because of the nutritional importance of these elements for plants, animals and man, and their toxicity when present in excessive amounts. How health of animals and man is linked to the mineral balance of the soil is explained by, among others, Voisin (1959). A survey of the trace-element contents of soils, arranged by elements, can be found in Swaine (1955).

Complete calculations of the total quantity of sediments on earth were published by Goldschmidt (1933a). He obtained a value of about $3 \cdot 10^8$ km^3. Clarke, in the last edition of *The Data of Geochemistry* (1924), found 84,300,000 cubic miles (approx. $3.5 \cdot 10^8$ km^3) to be the highest possible value for the volume of decomposed igneous rocks. Kuenen (1941), basing his calculations on the rate of deposition of sediments on the ocean bed (Kuenen, 1937), assumed a total volume of $13 \cdot 10^8$ km^3. He revised this value later (Kuenen, 1946) to $7 \cdot 10^8$ km^3 as the outcome of geochemical calculations for all sedimentary materials. The volume of continental sediments is about $2 \cdot 10^8$ km^3 and, consequently, the deep-sea deposits occupy about $5 \cdot 10^8$ km^3. Other calculations gave slightly different values for the latter, but all are of the same order of magnitude.

Ronov (1948), using a new volumetric method, found that, in the European part of the U.S.S.R., limestones and dolomites constitute on the average 55% by volume of the total sediments in the Russian platform, whereas in the geosynclines surrounding the Russian platform the carbonate rocks are less abundant (Ural geosyncline 30%, Donetz geosyncline 28%, Great Caucasus Alpine geosyncline 25%).

Fig.2 shows that considerable variation occurs in the percentage of carbonate and clastic rocks of the Russian platform. The diagram indicates a periodic character of the sedimentation, with the beginning of each new cycle of sedimentation being determined by the end of the preceding tectonic cycle and uplift which stimulated the erosion. Similar periodic changes of relative amounts of carbonate and clastic sediments were also observed, by Ronov, in the Russian geosynclines.

On the basis of the findings by Ronov and an examination of the stratigraphic columns of various parts of the world, Chilingar (1956a) estimated the abundance of carbonate rocks in the continental sediments at 25% by volume. This is higher than the values obtained by geochemical calculations (Clarke, 1924; Goldschmidt, 1933a;

Kuenen, 1941). The example shows that a mutual checking of data obtained by geochemical and other geo-scientific methods should be carried out wherever possible.

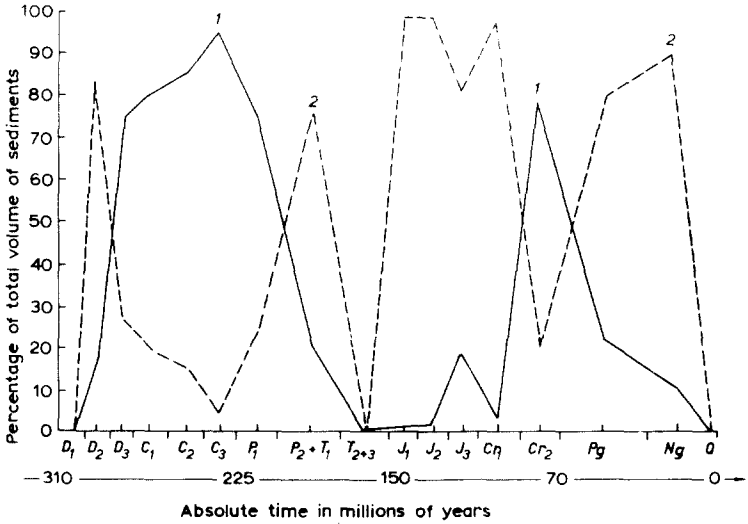

Fig.2. Variation in percentage of (*1*) carbonate rocks and of (*2*) clastic rocks of the Russian platform. (After Ronov, 1948, p.480.)

An important subject in sedimentary geochemistry is the formation of dolomite. Already Daly (1910) demonstrated that the abundance of dolomites declines in younger rocks. Chilingar (1956b) showed that superimposed on this general decline in number of dolomites (or increase in average Ca/Mg ratio) in going up the geological column, periodic fluctuations occur. A possible explanation of this phenomenon may be the periodic formation of dolomites. The first stage of the cycle would involve accumulation of Mg in the oceans and a simultaneous deposition of calcitic limestones. The second stage would be the formation of dolomites and dolomitic limestones when the Mg content of the oceans reaches a certain limit. The formation of dolomites would eventually impoverish the sea water of Mg and a new cycle, with accumulation of Mg, would start (Chilingar, 1956b). Other possible explanations for the periodic formation of highly dolomitic limestones include variations in depth and temperature of basins of deposition.

A brief survey of the present status of knowledge in sedimentary geochemistry can be found in the book by Degens (1965).

ORGANIC GEOCHEMISTRY

Closely interrelated with sedimentary geochemistry is organic geochemistry of which some information was given already earlier, in the section on mineral and rock analysis. This is the branch of geochemistry which studies all naturally occurring carbonaceous substances. Under the realm of organic geochemistry falls also the study of those mineral substances (for example, calcium and magnesium carbonates) formed in nature through biologic processes, or accumulated as a result of the special function of organic substances.

Over the last 20 years, interest in organic geochemistry has been growing fast, as demonstrated by the increasing number of published works on subjects ranging from lipids in Precambrian rocks, to the nature of kerogen, the origin and evolution of petroleum and coal, and to organic matter in carbonaceous chondrites. It is right to say that organic geochemistry would not be such an active field today, if it were not for the major efforts made by those geochemists dealing particularly with petroleum and, to a smaller extent, with coal.

Surveys of the recent progresses made by organic geochemistry can be found with Breger (1963) and Colombo and Hobson (1964).

GEOCHEMICAL EXPLORATION

For as long as man has been using metals, he has been trying to find mineral deposits. His prospecting was guided by what he could observe with the naked eye on the surface of the earth. Geochemical exploration techniques, however, were not applied in essence before well into the twentieth century and most are still in a stage of development. Of course, the advance of geochemical exploration has been strongly dependent upon the development of analytical methods (spectrography, X-ray fluorescence, chromatography, etc.), especially where these made a prompt and inexpensive determination possible of small quantities of elements, as these occur in plant ashes, soils, stream sediments, etc. Especially in the Soviet Union has geochemical work been particularly directed towards the search for and exploitation of mineral raw materials, and with great success.

Biogeochemical prospecting

As early as medieval times mineral prospectors were guided by certain kinds of vegetation to find copper and other pyrite ores. In Scandinavia, the occurrence of "pyrite plants" (kisplant), was used in prospecting for copper, in the Altai, U.S.S.R., "copper grass" (*Gysophila patrinii*) was known, as was a zinc flora in Belgium and in the Rhine area. This zinc flora comprises the galmei violet *Viola lutea* var. *calaminaria* and penny cress (*Thlaspi calaminare*). It had also been noted that European holly has an affinity to rocks rich in aluminium (Malayuga, 1963). The Russian scientist M.V. Lomonosov reported in 1763 that vegetation growing over ores or other mineral deposits was poor and unhealthy. The chromite deposits in Maryland and Pennsylvania were discovered, in 1810, because of the presence of a depressed flora on ore-bearing serpentinites (Singewald, 1928).

Beginning with the second half of the nineteenth century and especially during the present century, more systematic data on the geochemical affinity of plants were collected. Linstow (1929), who wrote the first major review of the subject, cites many examples of relationships between plant species and geological soil conditions, as these were gathered by scientists in the course of almost a century. The first attempt to provide a scientific basis for this phenomenon was made by the Russian botanist Karpinskii (1841).

Starting in 1936, the Swedish Prospecting Co. has for several years carried out biogeochemical surveys in conjunction with its regular

geophysical services to mining companies. During the uranium boom (1948–1956) the U.S.Geological Survey conducted a substantial volume of biogeochemical prospecting work in the western U.S.A. (Hawkes and Webb, 1962). In Canada, particularly Warren and co-workers have done important work in biogeochemical prospecting (e.g., Delavault and Warren, 1950, 1955; Howatson and Warren, 1947).

Drainage surveys

In his *Pirotechnia*, first published in 1540, Vannoccio Biringuccio says: "There are some who praise highly as a good sign certain residues that waters make where they are still, and after having stood for several days, frequently warmed by the rays of the sun, they show in some parts of their residues various tinctures of metallic substances. There are others who usually take this water and cause it to evaporate or dry up entirely by boiling it in a vessel of earthenware, glass, or some other material, and they test the gross earthy substance that remains at the bottom by testing, by the ordinary fire assay, or in some other way that pleases them. In this way (although they do not have an exact proof) they approach some sort of knowledge of the thing." (quoted from Hawkes and Webb, 1962, p.5). This seems to be the first written account of the possible application of chemical tests of stream water to prospecting.

The Russians, apparently, were the first, in the early nineteen thirties, to see the importance of chemical analysis of stream sediment. They used spectrographic techniques to determine the tin content of the fine fraction of stream sediments as a method of finding bedrock deposits of cassiterite (Hawkes and Webb, 1962). The pioneering study in the western world was a large drainage survey in eastern Canada, in 1954, in which the readily soluble heavy-metal content was determined from samples of stream sediments collected over an area of approx. 70,000 km^2 (Hawkes et al., 1956).

Metallometric or soil surveying

In 1932, Soviet geologists made the first chemical analysis of systematically collected samples of soil and weathered rock, to see what indications these could give in mineral exploration (cf. Fersman, 1939; Sergeyev, 1941). The first results were promising, and three years later the geological staff of the Central Geological and Prospecting Institute, in Moscow, had developed sampling procedures for routine geochemical surveys of soils and other sediments and had at their disposal good spectrographic equipment to analyze the collected material. They called their method "metallometric surveying". Several field projects were carried out in search of tin, others to prospect for copper, lead, zinc, nickel, chromium, wolfram, molybdenum and boron.

In the western world, experimental work on geochemical soil surveying started in 1947, by the U.S.Geological Survey (Hawkes and Webb, 1962). This organization has since carried out an active programme of field investigation. Rapid and simple techniques of colorimetric analysis were developed. In the early nineteen fifties several large mining companies also began to apply routine geochemical soil surveys.

Making use of the American experience (Webb, 1953), British geochemists at that time started an extensive programme of research and development, primarily in Africa and the Far East, but also in their own country (Webb, 1958a,b). A dominant role was played in this by the Geochemical Prospecting Research Center at the Imperial College of Science and Technology, London (Williams, 1956; Hawkes and Webb, 1962).

Geochemical prospecting for petroleum

In connection with petroleum drilling and production, which started in the second half of the nineteenth century, it was noted that petroleum is generally associated with saline water. No particular attention was paid to this water. One of the first scientifically important papers on the subject was that by Rogers (1917). He found that oil-field waters are not necessarily high in salinity and showed that near the surface sulphate waters are likely to occur, that at intermediate depths bicarbonate waters are common and that at depth, in waters most closely associated with petroleum, chloride is generally the dominant anion.

Minor (1925, 1934) focussed attention on geochemical differences in water at a horizontal plane and demonstrated that isolated patches of saline waters occur within a zone of alkaline waters 75 miles wide parallel to the Gulf Coast; these patches were proved to overlie salt domes. Minor then raised, as the first one, the idea that such geochemical anomalies might be related to oil fields.

Laubmeyer (1933) investigated micro-seepages of gas from 1 and 2 m deep holes, and noted that these soil gases were richer in methane over known oil fields than they were in adjacent barren areas. Horvitz (1939) supposed that soils could be enriched by migrant hydrocarbons and tried to demonstrate that these would form a halo-type (ring-shaped) anomaly around the margins of an oil field. This is a remarkable phenomenon, since at first sight, a gas anomaly with the highest concentration of hydrocarbons at its center should be expected directly on top of the petroleum deposit. McDermott (1939) showed that whereas liquid hydrocarbons were never present in soils in barren areas in a weight percentage of more than 0.2, this percentage could go up to 2 in similar soils over oil fields. Rosaire (1940) maintained that a hydrocarbon halo is only one of the possible patterns that could develop at the surface over an oil field. The pattern depends on the mechanism of hydrocarbon migration and this is governed by the occurrence of zones of lower pressure. Precipitation of carbonates, sulphides and even silica in the cap rock which is in contact with oil would reduce the permeability of the sediment, thus restricting hydrocarbon effusion to the fringe of a petroleum reservoir and would so lead to the formation of a halo pattern. Soli (1957) assumed a relationship between hydrocarbon concentration and bacterial activity. In the central part of the field they keep the amount of hydrocarbon gases low, but with hydrocarbon concentration diminishing towards the edges, there will be a point where this is insufficient for the support of specific bacteria. If it is assumed that the permeability on top of the petroleum deposit is reduced as a result of reduction of the sulphates to sulphides by sulphate-reducing bacteria, then the gases will take the path of least resistance and form a halo-shaped anomaly. Mogilevskiy (1959) based his hypothesis

on the fact that nitrogen and carbon dioxide are usually present with the hydrocarbon gases and that the concentration of carbon dioxide in excess of 10% tends to depress the activity of hydrocarbon microflora. Inasmuch as a higher carbon-dioxide concentration is usually near the periphery of the structure, where it tends to decrease the bacterial activity, the hydrocarbon concentration is greater at the periphery. On the other hand, in the central part of the structure where the concentration of non-combustible gases is at a minimum, the hydrocarbons are oxidized by bacteria. Thus, a minimum concentration of hydrocarbons occurs at the center, and the gas surveys produce a halo-type gas anomaly.

Blau (1943) and De Ment (1947) developed the estimation of fluorescent matter in soils, which was based on the assumption that bacteria thriving on ascending hydrocarbons were the medium that produced the fluorescent compounds. When continuous account was taken of the mycological content of the soils, this method was found to produce good results. In 1954, Horvitz presented the gas-sampling technique of petroleum exploration.

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