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# THE OCCURRENCE OF CARBON DIOXIDE[1]

## WITH NOTES ON THE ORIGIN AND RELATIVE IMPORTANCE OF SUBTERRANEAN CARBON DIOXIDE

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### OCCURRENCE

THE earliest scientific record of carbon dioxide seems to be that of Pliny,[2] who in his "Naturalis Historiae" says, "But, by Hercules! the history of the heavens themselves would not be more difficult to relate: the abundance of metals . . . the virtues of medicinal springs . . . the exhalation of deadly vapors (spiritus lethales) either emitted from caverns or from certain unhealthy districts; some of them fatal to birds alone as at Socrate, a district near the city; others to all animals, except to man, while others are so to man also." These openings were generally called vents and, by some persons, Charon's sewers, from their exhaling a deadly vapor. The account continues by telling of a place, in Asia, where no one can enter in safety, except the "priest of the great Mother of the Gods," and of prophetic caves, where those who enter are intoxicated with the rising vapor so that they can predict future events, as at Delphi.

There is to-day no doubt about the fact that Pliny was referring to the various carbonated water springs and carbon dioxide gas vents, such as the Grotta del Cane at Pouzzoles near Naples and the many similar grottos in various parts of the world. The Grotta del Cane is particularly interesting because it has been known since very early times. It is reported to yield a gas consisting of about 70 per cent. carbon dioxide, 24 per cent. nitrogen and 6 per cent. oxygen. Inasmuch as the ratio of the nitrogen to oxygen is exactly the ratio of these gases in the air, it seems reasonable to assume that there has been an unavoidable contamination with it either at the exit or somewhere deeper under ground.

[1] Address of the president of the Southwestern Division of the American Association for the Advancement of Science, Albuquerque, N. Mex., April 27, 1938.
[2] Pliny the Elder, 2, 95 (A.D. 77).

Flammarion[3] gives the following interesting account of the dog at the Grotta del Cane in his popular book "L'Atmosphère," Paris, 1872:

> The keeper has a dog whose legs he ties together to prevent his running way; he then places him in the middle of the grotto. The animal displays evident fear, struggles to escape, and soon appears to be dying. His master then takes him out into the open air, where he gradually recovers himself. One of these dogs has been used for this purpose more than three years.

This grotto is situated on the slope of a very fertile hill, near Lake Agnano. The entrance is closed by a locked gate. It has the appearance and shape of a small cell, the walls and vault of which have been rudely cut in the rocks. It is about one yard wide, three deep and one and a half high. It is difficult to judge from its appearance whether it is the work of man or of nature. The ground in the cavern is very rich and covered with a whitish mist of carbonic acid gas and water vapor. The stratum of gas is from ten to twenty-five inches high, representing an inclined plane, the highest part of which corresponds to the deepest portion of the grotto. The grotto being about on the same level as the opening leading into it, the gas finds its way out at the door, flows like a rivulet along the hill path, and may be traced for a long distance. A candle dipped into the gas at a distance of more than six feet from the grotto is extinguished at once. Flammarion states that a dog dies in the grotto in three minutes, a cat in four, and a rabbit in seventy-five seconds. A man could not live more than ten minutes if he were to lie down. It is said that the Emperor Tiberius had two slaves chained up there, and that they perished at once. Peter of Toledo, Viceroy of Naples, is reported to have killed two men condemned to death by placing them in the grotto.

On the borders of Lake Laacher, near the Rhine, and in Aigueperse, in Auvergne, there are two sources of carbonic acid so abundant that they give rise to accidents in the open country. The gas rises out of small hollows in the ground, where the vegetation is very rich; the insects and small animals, attracted by the richness of the verdure, seek shelter there and are at once asphyxiated. Their bodies attract the birds, which also perish.

Formerly accidents caused by this gas in caves, mines and even wells gave rise to the most extravagant stories. Such localities were said to be haunted, since no trace of lesion or bruise was to be found on the unfortunate persons who were suddenly struck down.

Lake Laacher in Germany, referred to above, is the water-filled crater of an extinct volcano. The Valley of Death in Java is also an old volcanic crater from whose fissures large amounts of carbon dioxide constantly come forth. The Stygian caves in the Yellowstone National Park contain concentrations of carbon dioxide sufficiently large to make them dangerous, although it has been stated that bears hibernate in them during the winter. The boiling springs and mud pots in the Yellowstone yield gases consisting principally of water vapor and carbon dioxide. This is also true of mud pots near the Salton Sea in the Imperial Valley in Southern California.

We are probably all most familiar with subterranean carbon dioxide when it comes to the surface in the form of carbonated water, as at Nauheim, St. Moritz, Altwasser and Saltzbrunn in Europe and at Saratoga Springs, New York, the Navajo and Ute Springs at Manitou, Colorado, the Hot Springs in Virginia and the Napa Soda Springs in California.

With the advent of deep drilling for oil, carbon dioxide was discovered in various parts of the world at pressures up to about 1,000 pounds per square inch. In many cases the gas is practically one hundred per cent. carbon dioxide. Among the early discoveries of this nature was that in the Northern Tampico, Mexico, oil field. When we think of natural gas associated with oil, our first thought is that the gas consists of combustible hydrocarbons. At Tampico,[4] however, we have an area of about one hundred sixty-five square miles along the Rio Panuco, where oil is produced with a non-inflammable gas. Within this area lies the Isleta pool and the Herradura Oil Company Well No. 1. This well is reported to have come in as a salt-water gusher, yielding at the same time large quantities of carbon dioxide. As a result of the low temperatures produced by the expansion of the gas at the Corona Well No. 7 in this field, the carbon dioxide solidified as dry ice, in the heat of July, 1921, to a thickness of about an inch on the drill which was hanging in the casing.

On the eastern edge of the non-inflammable gas area lies the Quebracha field, which includes wells in Quebracha, San Isidro and Loma del Pozo. Although of no particular interest as an oil-producing field, it has attracted wide attention because of the tremendous non-combustible gas production, which runs as high as 98 per cent. carbon dioxide. The discovery well blew in from the Agua Nueva formation at a depth of about 3,000 feet in 1915, with an initial gas production rated at about 50,000,000 cubic feet per day. With favorable weather conditions the roar of the well could be heard at night for over seven miles. From 1923 to 1929 many large gas producers were discovered, at least four of which yielded one hundred fifty million cubic feet per day. Closed-in pressures were of the

[3] Flammarion, "The Atmosphere," translated by Pitman, Drallop Publishing Co., New York, 1896.

[4] Muir, "Geology of the Tampico Region, Mexico." Published by the American Association of Petroleum Geologists, 1936.

order of 1,000 pounds per square inch. The oil in the flow lines from the wells was often so cold that the moisture from the air froze on the outside for distances of almost a mile, giving an appearance similar to that of the ice on the coils in our electric refrigerators. A better notion of the magnitude of the gas flow can be obtained when we realize that if the daily production of 150,000,000 cubic feet of carbon dioxide were reduced to dry ice, we should have the enormous weight of about 9,000 tons.

According to Kemp,[5] the mineral springs at Saratoga, New York, were known as early as 1767, although it was not until 1870 that the first wells were drilled in an attempt to increase production. From 1892 to 1905 wells were drilled for the express purpose of extracting the carbon dioxide from the water. The gas was produced with water from depths as great as 600 feet from at least thirty wells. In the period from 1904 to 1908 as much as 5,000,000 pounds of carbon dioxide were produced annually. Pumping these wells resulted in the lowering of the water level at times by 150 feet. With the creation of a State Reservation at Saratoga in 1908 a legal restraint was placed on pumping, resulting in a decline of the industry.

In 1916 a gas well reported to have yielded 25,000,000 cubic feet of carbon dioxide per day was drilled in the Bueyeros field in Harding County, New Mexico, by the American Producers Corporation. The gas came from a depth of about 2,000 feet. This well, after flowing wide open for over a year, finally bridged itself and ceased flowing. The years 1925 and 1926 marked the discovery of several new carbon dioxide gas fields in New Mexico and Colorado. The California Oil Company encountered a non-combustible gas consisting chiefly of carbon dioxide on the Jaritas Dome in Colfax County, New Mexico, at a depth of 1,509 feet. Production was estimated at about 500,000 cubic feet per day. The Arkansas Fuel Company drilled a well on the Wagon Mound Anticline in Mora County, New Mexico, and after encountering gas at various levels completed the well at about 2,600 feet with a production of 26,000,000 cubic feet per day. The Estancia Company drilled a well on the Estancia Anticline in Torrance County, New Mexico, and encountered both oil and carbon dioxide, but the principal production in this area comes from some eight wells drilled since 1931 on the Wilcox Anticline northwest of Estancia. In 1926 when numerous gas wells were being discovered in New Mexico which were mostly devoid of oil, the Continental Oil Company completed a well on the McCallum Anticline in Jackson County near Walden, Colorado, which produced carbon dioxide reliably estimated at 50,000,000 cubic feet per day with some oil. In 1930 the Carbon Dioxice and Chemical Company completed a carbon dioxide well on the Farnham Anticline near Price in Carbon County, Utah. The Sierra Grande Oil Corporation drilled a well on the Sierra Grande uplift in Union County, New Mexico, in 1935 to a depth of 2,800 feet, encountering carbon dioxide of high purity at three levels, with a total volume estimated at 6,000,000 cubic feet per day. A total of nine wells have been drilled in the Bueyeros field, the deepest of which was the discovery well in 1916. Recently a well about one quarter mile from the discovery well has been completed which is reported to have a flow of 25,000,000 cubic feet per day at 700 pounds pressure. The producing sand has an estimated thickness of one hundred feet.

In 1932 the Salton Sea Chemical Products Corporation started drilling wells in the Salton Sea basin in the Imperial Valley near Niland, California, and has brought in several good producers of very pure gas. Many other areas, such as Manitou and Delta, Colorado, as well as fields in the State of Washington and in Canada might be mentioned, but the above will suffice to indicate the rather wide-spread natural occurrence of pure carbon dioxide at relatively high pressures.

Although the present paper is largely restricted to a discussion of subterranean carbon dioxide, a few observations relative to its occurrence in general will serve to fix our ideas, while at the same time showing the tremendous reserves in the air, in water and in geologic structures. Our atmosphere consists of essentially 80 per cent. nitrogen and 20 per cent. oxygen, but contains in addition small amounts of numerous other gases. Among these is carbon dioxide to the extent of about three volumes in ten thousand, or 0.03 per cent. by volume. This very low concentration nevertheless represents a tremendous total mass which has been estimated to be of the order of two million million tons. Sea water constitutes another enormous reserve, as a result of its power to dissolve the gas in large quantities. The oceans may be regarded as vast regulative reservoirs which keep the concentration of carbon dioxide in the atmosphere constant. Although the solubility is dependent on the temperature, we may assume an average value of 0.05 per cent. by volume, which leads to a total weight thirty times as great as that in the atmosphere, or 60 million million tons. No one seems to have had the courage to estimate the reserve of carbon dioxide either free or combined which exists in the lithosphere. This is not surprising when we recall that such a large proportion of underground rocks consists of carbonates. The underground reserves surpass our powers of comprehension. Clarke[6] gives us a rough estimate of the total amount of carbon in the lithosphere including all forms such

[5] Kemp, *N. Y. State Museum Bull.*, 159, 1912.

[6] F. W. Clarke, *U. S. Geol. Surv. Bull.*, 795: 55, 1920.

as coal, oil and the carbonates when he states, "The known carbon of this lithosphere, if converted into carbon dioxide, would yield nearly twenty-five times the present mass of the entire atmosphere."

Although the carbon dioxide content of the air is at present very low, it is surprisingly constant when we consider the steady large additions to it by such phenomena as the combustion of all kinds of fuels, exhalations of the animal kingdom, emanations from the earth, the decay of organic matter and many industrial processes such as fermentation and lime burning. This balance is maintained in large measure by the solution of carbon dioxide in the oceans. The cold waters of the north reduce the carbon dioxide concentration of the air to very low values because the gas is more soluble in cold than in warm water. In other words, the partial pressure of carbon dioxide over cold water is less than over warm water. As the cooler waters of the oceans reach the warmer parts of the earth, the atmosphere is enriched with carbon dioxide. As warmer weather approaches and springtime comes to cold countries, the atmosphere is also enriched with carbon dioxide. Since plants live in part on carbon dioxide we may suspect a relationship between the luxuriant vegetation of springtime and the tropics, and the release of this gas from the waters where it was stored during the colder months. This process of using carbon dioxide for plant growth is known as photosynthesis. Some of the carbon dioxide stored by the water is used up by marine calcium-carbonate-forming organisms and is eventually deposited as limestone, and large amounts are used up in the weathering of rocks. Silicates are decomposed by carbonated water yielding carbonates. Calcium and magnesium carbonates are converted to bicarbonates. These bicarbonates are water soluble and may be carried long distances by underground water currents or surface water, only to be reprecipitated as normal carbonates when the carbon dioxide content of the water is reduced either by aeration or by heat.

## II. ORIGIN

To those of us interested in the physical sciences, the origin of such vast stores of carbon dioxide in the free state at great depths is of no less interest than the uses to which the gas can be put. Many theories have been advanced which are physically and chemically possible. However, when we attempt to reconcile some of them with the experimental fact that the gas exists underground at pressures approaching one thousand pounds per square inch, we are forced to question seriously whether the processes suggested could actually yield such pressures.

Fuller[7] discusses the origin and suggests the possibility of the gas coming from the chemical decomposition of the rock by its contact with igneous intrusion. He also suggests that it may result from the decomposition of carbonates by acids of the ground water. In 1906 Delkeskamp[8] published a rather exhaustive survey of the various theories which had been advanced for the origin and made a critical physical-chemical analysis of numerous characteristic examples. He also brought together the rather widely scattered literature on the subject which had been published up to that time. Under the title "Vadose and Juvenile Carbon Dioxide," he discusses the carbon dioxide which is formed by processes near the surface of the earth and that which has a volcanic origin. The latter he assumes to be a constituent of the molten magma, released as it slowly cools off, or trapped as inclusions in the solid stone. He believes that the vadose, or superficial carbon dioxide, may come either from the atmosphere or from some organic source such as lignite, peat or marsh beds. The possibility of chemical reactions on carbonates is also mentioned.

In support of Delkeskamp's suggestion of the carbon dioxide coming from the molten lava, we should mention the experimental fact that liquid carbon dioxide is often found as inclusions in spherical cavities in crystalline quartz. Although in general the solubility of gases in liquids is greater at low than at high temperatures, we know that a change of state such as that in going from liquid to solid may force the gas out of solution.

Thus, for example, silver melted in the presence of air dissolves large quantities of oxygen from the air. If the melt is allowed to cool to its solidification temperature, the outside becomes solid, while the center is still liquid. The oxygen at the surface escapes easily, but once the surface has solidified, the oxygen from the inside has no way of escaping except by breaking through the hard layer. This it does, producing the phenomenon known to metallurgists as spitting or sprouting. Jets of gas with liquid metal come to the surface, making fantastic forms on the crust. When the surface layer becomes thick enough, the gas no longer breaks through but remains as inclusions. As a result of this, objects of silver can not be cast except in atmospheres devoid of gases which are appreciably soluble.

Lindgren and Ransome,[9] in a volume on the "Geology and Gold Deposits of the Cripple Creek District of Colorado," devote a chapter to the study of mine gases and report analyses in metal mines running as high as 14.7 per cent. carbon dioxide. Pointing out that exhalations of gases composed of carbon dioxide,

[7] M. L. Fuller, "Mineral Resources," 21: 1259, 1905.

[8] Rudolf Delkeskamp, *Z. prakt. Geol.*, 14: 33, 1906.

[9] Lindgren and Ransome, *U. S. Geol. Surv. Professional Paper*, 54: 252, 1906.

nitrogen and sometimes hydrogen sulfide always take place after volcanic eruptions, and that they frequently continue for a long time after the cessation of the igneous outbursts, the authors conclude that the mine gases of the Cripple Creek region represent the last exhalation of the extinct Cripple Creek volcano.

Guilleaume,[10] in an article on "Natural Carbon Dioxide" published in 1926, mentions the various possible organic and inorganic origins, but concludes that none of these could account for the large volumes found in the many European vents and mineral springs. After an exhaustive survey of the existing deposits in France and Germany, he calls attention to the fact that in every case there is a close relationship to basal outcrops and evidence of rather recent volcanic activity. He does not suggest thermal decomposition of carbonates, but does raise the question of the possible decomposition of carbonates dissolved in ground water coming in contact with igneous rocks, and also the combustion of carbonaceous material. Guilleaume leaves one with the impression that he favors a strictly primary origin of the gas which is in solution in the molten magma. He states that in nature, lava flows continue to give off carbon dioxide for a very long time. Lohmann[11] states that carbon dioxide from the earth's interior may be the last sign of former volcanic activity, or that it may result from thermal or acid decomposition of carbonate stones. The acids involved he believes to be silicic, from weathering processes, and sulfuric, formed from sulfides.

The occurrence of carbon dioxide in coal seams has in recent years led to a great deal of study as a result of the numerous fatal explosions caused by its sudden release. S. Bubnoff[12] published a series of articles on the geological aspects of this problem and Potonié,[13] Ruff,[14] and Tammann and Seidel[15] studied the chemical aspects. Bubnoff suggests three possibilities for the origin: (1) the carbon dioxide is the result of normal carbonization; (2) it is the result of abnormal carbonization, that is, an enrichment as a result of the rock pressure and a chemical dynamic metamorphism; and (3) the carbon dioxide does not come from the coal, but is juvenile, coming from inside of the earth. It is the third possibility which he says must be accepted, as the various experimental facts fail to give support to the first two suggestions. The strongest arguments for a juvenile origin are the facts that these carbon dioxide explosions also occur in salt mines and that the greatest pressures of the gas are found in those coals which have been most completely carbonized. Potonié concludes that the carbon dioxide is held in the crevices in the coal by adsorption on the surface, but Ruff insists that the gas is held in solution in the coal. Both agree that the gas does not originate in the coal seams, but that it has been trapped and held there in its escape from below. In this connection it is interesting to note that carbon dioxide is more soluble in coal than is methane or marsh gas. According to data obtained by Ruff, a given mass of coal will dissolve three times as much carbon dioxide as it will methane when these gases are in contact with the coal at a pressure of ten atmospheres, or about one hundred fifty pounds per square inch.

R. F. Selden,[16] of the U. S. Bureau of Mines, in an article published in 1934 on "The Occurrence of Gases in Coals," states that whenever carbon dioxide is the principal gas evolved, the consensus of opinion seems to support the theory of an exterior source where the gas is supposed to have been generated by intrusions of igneous rock into underlying strata containing limestone or other carbonates. If intrusions are always to be found below coal beds impregnated with carbon dioxide he suggests three possibilities: (1) The limestone was decomposed thermally; (2) the carbon dioxide accompanied the igneous rocks in its ascent into the upper strata; and (3) the carbon dioxide was formed, along with new minerals, by reactions between the carbonates and some of the constituents of the intruded rock. All these hypotheses involve the retention of the gas in the coal beds and adjacent strata for long periods. Selden dismisses the possibility of thermal decomposition of limestone on the basis of the fact that at the assumed temperature of 1,000° C. of the intruded igneous rocks, the pressure of carbon dioxide resulting from the decomposition of the stone would be only four atmospheres absolute or about forty-five pounds gauge pressure. Moreover, he doubts whether the mass of intruded rock is great enough to heat an appreciable thickness of the limestone. These calculations are based on the assumption that the only carbonate present in sufficient quantities in the neighborhood of coal seams is that of calcium. The situation would be materially changed in the case of magnesium carbonate or dolomitic limestone. The fact that in some instances there is no evidence of purely thermal metamorphism of limestone adjacent to the intrusive magma is also offered as an argument against this theory.[17]

Regarding the second possibility, namely, that the

[10] Charles Guilleaume, *Rev. universelle mines,* 10: 169, 1926.

[11] W. Lohmann, "Mineralwasser,—Fabrik," 34: 823, 859, 915, 939, 1930.

[12] S. Bubnoff, *Z. Berg-, Hütten-, Salinenwesen,* 1924, 1926, 1928.

[13] R. Potonié, *Z. angew. Chem.,* 43: 767, 1930.

[14] O. Ruff, *Z. angew. Chem.,* 43, 1038, 1930.

[15] G. Tammann and K. Seidel, *Z. anorg. algem. Chem.,* 205: 209, 1932.

[16] R. F. Selden, U. S. Bur. of Mines Dept. of Investigations, 3233, 1934.

[17] W. Lindgren, *U. S. Geol. Surv. Professional Paper,* 43, 1905.

carbon dioxide accompanied the igneous rock in its ascent, Selden states that he is not aware of any definite evidence either for or against the theory, but quotes a personal communication from L. H. Adams, of the Geophysical Laboratory, that in his opinion the rock magma does not of itself contribute any important quantity of carbon dioxide to adjacent strata.

The third hypothesis, which suggests that the carbon dioxide was formed, along with new minerals, by reactions between carbonates and some of the constituents of the intruded rocks, offers many possibilities. It is the opinion of some geologists that the magma had considerable gaseous water entrapped in it at the time of the flow. If this were the case, many reactions would become possible which otherwise would have to be excluded. Thus Van Hise,[18] and Leith and Mead,[19] attribute the metamorphic changes in limestone to the action thereon of hot water solutions and the constituents of the intruded magma. Although little is known about such systems, we do know that the pressures of carbon dioxide would be greater at a given temperature than would be the case in purely thermal decomposition.

In 1932 Tammann and Seidel[20] published an article on the subject of carbon dioxide explosions in mines in which they state that the recent carbon dioxide explosions in coal and salt mines made it necessary for the scientists of Germany to investigate the physical-chemical conditions which brought them about. Regarding the origin, they admit that it is external to the coal seams and salt beds. They oppose the belief of some geologists that the origin is in the molten magma, a belief held because of the assumption that silicates act on carbonates only at the beginning of fusion. Tammann and Grevemeyer[21] showed that calcium oxide begins to act on orthoclase and leucite at 500° C., so that low temperature reactions previously unsuspected may be taking place as the result of lava flows. Tammann and Seidel, however, do not believe that carbon dioxide had its origin as a result of the action of anhydrous silica on dry carbonates, since rocks containing these substances do not occur in nature. However, they suggest that marl strata consisting of calcium and magnesium carbonate, iron and aluminum silicates, silicic acid and water which are wide-spread, may well give rise to gas pressures such as are encountered in nature.

In order to obtain evidence in support of this conclusion they pulverized three samples of dolomitic marl taken from shell limestone outcrops near Göttingen, Germany. The samples were placed in closed containers both with and without an admixture of water and heated to 100° C. After correcting for the vapor pressure of water, they found the pressure of carbon dioxide developed in twenty hours was three centimeters of mercury for the dry and five centimeters for the wet sample. Although these pressures are low, we must compare them with those over pure dry calcium carbonate, which shows no measurable pressure at 100° and at 500° C. is still of the order of one tenth of a millimeter of mercury. With this wide discrepancy at 100°, it becomes plausible that extremely high temperatures are by no means necessary to produce pressures encountered in nature. Experiments similar to those on dolomitic limestone are being carried out by Germann and Ayres in the physical chemistry laboratories in Boulder on oolitic limestone, and pressures of the same order of magnitude as those obtained by Tammann and Seidel on dolomitic limestone are being obtained.

The principal objection to a purely thermal origin for carbon dioxide is based on the assumed maximum temperature of 1,000° C. of the intrusive rocks and the value of about four atmospheres pressure which is developed by the decomposition of powdered, pure calcium carbonate, such as found in nature as calcite. In the first place, the temperature of 1,000° is only an estimate and is based on certain assumptions of pressure which might prevail in the interior of the earth. It is quite obvious that these assumptions should lead to different values from those obtained for the temperature of the same molten magma when extruded at the surface of the earth. If the gas pressures of the order of 1,000 pounds per square inch, such as are at times encountered in carbon dioxide gas wells, could be accounted for by the assumed temperatures, there would be no objection to accepting the theory of purely thermal decomposition. A very careful study of the decomposition of pure calcite has been made by Smyth and Adams,[22] which shows that at the eutectic temperature of 1,240° C., the pressure begins rising rapidly with an increase of temperature, going from about 40 atmospheres at this temperature to 70 atmospheres at 1,275° C. This is a rise of thirty atmospheres for a temperature increase of only 35° C. Moreover, seventy atmospheres is equal to 1,029 pounds per square inch, which is at least as high as any recorded in carbon dioxide gas wells.

Remembering that pressure begins increasing rapidly at the fusion point, and that these values were those for pure calcite, we turn now to the actual cases found in nature. Here we are dealing with impure

18 C. H. Van Hise, *U. S. Geol. Surv. Monograph*, 47: 652, 1904.

19 C. K. Leith and W. J. Mead, "Metamorphic Geology." Henry Holt and Co., 1915.

20 G. Tammann and K. Seidel, *Z. anorg. algem. Chem.*, 205: 209, 1932.

21 G. Tammann and C. F. Grevemeyer, *Z. anorg. algem. Chem.*, 136: 114, 1924.

22 F. H. Smyth and L. H. Adams, *Jour. Am. Chem. Soc.*, 45, 1167, 1923.

carbonates of calcium, with mixtures of carbonates of calcium and magnesium, as well as with mixtures of all of these with the various silicates. For pure magnesium carbonate, Manchot and Lorenz[23] find that the pressure increases from a value too low to measure at 400° C. to one atmosphere at 540° C. Moreover, they calculate from their equation that the pressure would reach a value of 473 atmospheres or about 7,000 pounds at 700° C. Marc and Simek[24] obtained considerably higher values for the lower temperatures, and state that traces of water vapor when present greatly increase the speed of pressure rise. This increase in pressures as well as increase in speed of dissociation may be explained by what is known to chemists as hydrolytic dissociation. By this is meant a chemical reaction of the carbonate with water in such a way as to form magnesium hydroxide, commonly known as milk of magnesium, and carbon dioxide. This is the reverse of the reaction which normally takes place at atmospheric temperatures and pressures, in which case magnesium hydroxide takes up carbon dioxide from the air with the formation of magnesium carbonate. The behavior of a mixture of impure carbonates containing shells, all possible combinations of minerals in small amounts, and water, such as studied by Tammann and Seidel, and Germann and Ayres, is thus very easily explained, and the development of high pressures at temperatures well below 1,000° C. is to be expected. It would therefore seem reasonable to assume that the carbon dioxide found to accompany the flow of lava and to be dissolved in it may have come from the solution of this gas in the magma under high internal pressures, the carbon dioxide itself having resulted from the thermal decomposition of carbonates in contact with the heated rock. Since it is a well-known fact that the solubility of a gas in a liquid increases with pressure, large quantities would be dissolved at pressures of 1,000 pounds. As the melt came to the surface, the pressure would be reduced and the gas would come out of solution, sometimes violently, with the blowing off of volcanic ash, sometimes slowly, giving rise to the very porous lavas. This theory would seem all the more reasonable in the light of the difficulty of explaining the presence of carbon dioxide in the interior of the earth.

New Mexico, with its abundance of evidence of volcanic activity, carbon dioxide wells and limestone caves, offers a most interesting outdoor laboratory for the study of natural carbon dioxide. We may visualize the picture in the following manner. Assuming the original limestone beds to have been formed, volcanic activity visited the state, with the resulting changes in level and faulting in the various strata, subterranean intrusions of lava, lava dikes and lava flows. The igneous intrusions caused the thermal decomposition of calcareous and dolomitic rocks and the liberation of carbon dioxide and calcium and magnesium oxide. As the carbon dioxide was liberated, some dissolved in the heated rock, came to the surface, and was responsible for the formation of volcanic ash and the accompanying violent eruptions. Some moved away from the region where it was formed along the openings in the strata to higher levels, and escaped to the surface through faults. Some encountered water, in which it dissolved to form carbonic acid. These acid waters traveled underground and dissolved the carbonate rocks, forming bicarbonates which finally reached the surface in solution. As the rock was dissolved, the underground passages became larger and our underground rivers developed. Finally the supply of surface water became less and the underground streams dried up, leaving our large caves. If these caves had openings to the outside, the water which still entered slowly from the top would gradually evaporate, lose its carbon dioxide and deposit its lime in the form of stalactites on the roof and stalagmites on the floor. As a result of these processes we have vast underground passages such as the incomparable Carlsbad Caverns. Still another part of the liberated carbon dioxide was caught in the strata where it was held in underground domes, or sealed in by dikes or faults just as oil and the hydrocarbon gases are held. In New Mexico we find the gas trapped at various levels in sand strata, and the log of one well shows that from 1,995 to 2,055 feet a large flow was encountered in what was described as lime shells and sandy red shale. In some cases gas sands 100 feet thick have been found. In the drilling of these wells caves are frequently encountered, giving evidence of the removal of limestone by water charged with carbonic acid.

Following out the idea of a decomposition of the carbonate rocks by means of water and elevated temperatures, we have a picture similar to the one above, except that in this case the slightly soluble calcium or magnesium hydroxide is slowly carried away by the water, in place of being removed as bicarbonates. On reaching the air and absorbing carbon dioxide, the insoluble carbonates would again be formed and be reprecipitated as crystalline calcium or magnesium carbonates.

For many years after the discovery of our vast carbon dioxide resources, little hope was held out for their commercial exploitation. The reasons for this were: (1) the wells were so far from railroads that it was thought necessary to construct long pipe lines, a risky financial venture because of the uncertain life of the gas supply; (2) the cost of shipping liquid carbon dioxide in steel tanks to the markets was such

[23] W. Manchot and L. Lorenz, *Z. anorg. algem. Chem.*, 134: 297, 1924.

[24] R. Marc and A. Simek, *Z. anorg. Chem.*, 82: 17, 1913.

as to make the margin of profit small; (3) the dry ice industry had not developed to a point where the markets were great, and the science of its transportation was in its infancy. To-day the picture is much more encouraging, since specially insulated trucks can load up at the well with either the liquid in tanks, or the dry ice and deliver the load to points within a radius of 1,000 miles in one to three days. Specially designed refrigerator cars loaded with dry ice will lose no more than 1.25 per cent. per day, which means that even though air transportation were available at a comparable price, the advantage of speed would mean very little. Regions remote from large centers of population will find the production and transportation of dry ice made from natural carbon dioxide much more advantageous than the shipment of liquid carbon dioxide in cylinders. If the consumer wishes to have the liquid rather than solid gas, he has only to place a block of the ice in a specially designed container, screw on a lid and allow the ice to melt.

The production of both liquid and solid carbon dioxide in the large industrial centers must always be regarded as a real competitor of the natural carbon dioxide industry, since industrial gases may be used as the source of the gas. Since the production of carbon dioxide by chemical processes is dependable and may be carried out as long as we have fuel to burn, an industry based on them is apt to be much more stable than one based on the problematic life of the natural carbon dioxide supply. This means that the profits must be greater in the latter case if the investment of capital is to be warranted.

We are really just awakening to the commercial possibilities of dry ice. Its use in the packing of ice cream obviates the use of the heavy pails with the ice and salt and hence makes it possible for a truck to carry a much more valuable load. Trucks and freight cars refrigerated with dry ice not only carry a much larger payload, but the upkeep of the carrier is very materially reduced because of the absence of salt and water. Flowers packed with dry ice for shipment seem to be literally put to sleep and to remain stationary in their development until they are unpacked. The same is true in part in the storage of fruits and vegetables, although in this case the results are not always uniformly good. A great deal of research is, at the present time, in progress in the field of the preservation and rapid freezing of meats, fish and fruits, so that the future offers great things for the dry ice industry.

The rôle of carbon dioxide in plant metabolism deserves much more attention from a commercial point of view than it has received in the past. Priestley and Scheele, the discoverers of oxygen, observed oxygen exchange taking place between plants and the atmosphere, but it remained for Ingenhousz to observe in 1779 that plants give off oxygen in the light and absorb it in the dark. Later Senebier showed that the oxygen given off in the light came from the decomposed carbon dioxide which was being absorbed. In 1804 Theodore de Saussure sprouted seeds in the light and in the dark, and found that the dry weight increased in the case of the seeds in the light and decreased in the case of those in the dark, thus proving that plants need the carbon taken from the carbon dioxide as food for growth. During all this time the "humus theory" of plant growth, which assumed that the plant roots not only took up water and salts from the soil but also organic matter, was generally accepted. This theory was, however, definitely overthrown by Liebig and Sachs, who demonstrated that plants could be grown and made to bear ripe fruit in pure water and quartz sand, provided that certain mineral salts were present in the water and that the leaves were in an atmosphere containing carbon dioxide. To-day we may visualize oxygen absorption as a combustion process liberating carbon dioxide, water and energy as in the reaction

$$C_6H_{12}O_6 + 6\ O_2 = 6\ CO_2 + 6\ H_2O + \text{energy}.$$

Similarly, liberation of oxygen is the result of assimilation in which carbon dioxide and water, with the aid of the energy derived from light, are combined to form plant tissues as in the reaction

$$6\ CO_2 + 6\ H_2O = \text{energy} + C_6H_{12}O_6 + 6\ O_2.$$

Granting that the air must contain carbon dioxide if plants are to grow, the question arises if the normal concentration is sufficient to grow the maximum crops in a given length of time. We find the answer to this question, in part, in many of the older references to natural carbon dioxide gas vents and springs, where mention is made of the very abundant vegetation to be found in the environment. Numerous experiments along this line have been carried out and it has been shown that, depending on the nature of the plant studied, the concentration of carbon dioxide of the air may be increased from its normal value of three hundredths of 1 per cent. to as much as 8 per cent. without injury and with increased assimilation. Studies conducted under glass have shown increase in leaves and stalk of from 50 to 300 per cent., blooming and ripening of fruit speeded up by 10 to 25 per cent., and hence maturing one to two weeks earlier, finer flowers and, in the case of tomatoes, an increase of almost 300 per cent. ripe fruit. Experiments carried out in the open air, making use of the purified flue gases from a steel mill, have shown a 50 per cent. increase in yield in the case of beets. All this suggests that we have been overlooking what appears to be a most promising possibility.

Our vast reserves of carbon dioxide should be put to work in increasing our crop production. In properly constructed greenhouses we could not only raise our materials in water fed with the appropriate salts, as has been done in California, but we could also feed the leaves with carbon dioxide from our gas wells. Conducting the gas over the fields is not as easy nor as economical as in enclosed places. However, since the density of the gas is greater than air, it tends to hang close to the soil where it is most needed, so that even a moderate amount let loose near the ground has a very beneficial effect. Most natural gas coming from deep wells requires no purification. The natural pressure will carry it long distances, requiring only the laying of pipe lines. Some day we shall no doubt wonder why it took so long for us to awaken to this important use of a natural resource which had been permitted to go to waste.

The Southwest is blessed with much sunshine and natural carbon dioxide; soil and water conservation projects are everywhere under way. With these assets of water, sunshine and carbon dioxide, the finest fruit and vegetable crops can be grown. When to this we add that the vast store of natural carbon dioxide may also be converted to a refrigerant, it is obvious that not only can the finest products be raised, but they may be shipped in prime condition to the nation's markets from the Atlantic to the Pacific. The history of some of the gas wells which have been permitted to blow off into the atmosphere uncontrolled leads us to believe that the life of these wells will be long. Moreover, experience has shown as a rule that the deeper we drill, the higher gas pressure we encounter. We may well ponder over these facts and ask ourselves if we do not have here the nucleus which may some day lead to an enterprise more profitable than mining has ever been. We may confidently anticipate that in the not distant future, capital looking for a good place to go to work may seize upon this project as one giving great promise of ultimate reward.

# OBITUARY

## WILLIAM PENN BROOKS

AT its sixty-second commencement exercises, in 1932, Massachusetts State College conferred upon a member, who had received his first degree as a member of its fifth class, the honorary degree of doctor of agriculture. Never was the degree of doctor with all the ideals and knowledge which that word should signify—never was this title more fittingly bestowed than it was upon Dr. William Penn Brooks. In the death of this man science has lost a worker who devoted forty years of constant application to studying, improving and teaching agriculture. His death occurred on March 8 at the age of 86.

Starting life on a Massachusetts farm, he took a natural interest in agriculture, an interest which he first pursued in the newly incorporated land-grant college of that state. He graduated from Massachusetts Agricultural College with its fifth class and spent two succeeding years there in graduate study of botany and chemistry. Still not firmly enough grounded for his satisfaction, Dr. Brooks traveled to Halle, Germany, where for his year's work in agriculture, botany and philosophy the Friedrichs Universität awarded him the Ph.D. degree.

From the first Dr. Brooks had shown his remarkable talent for organizing and teaching. Before his first year in college he had already taught secondary schools for two terms. In college he helped to found the national fraternity of Phi Sigma Kappa. Yet it is worthy of notice that this young scholar was called directly from Halle halfway around the globe to the Island of Sapporo, Japan, in order that he might aid in the establishment upon a sound, scientific basis of the Imperial College of Agriculture. For eleven years he fostered the growth and welfare of that institution, acting as president for some time and earning for himself the honorary degree Nogaka Hakushi, and later the decoration of the Fourth Order of the Rising Sun.

After this productive eleven-year sojourn in the Orient, Dr. Brooks returned to his Alma Mater, where he taught agriculture as professor and lecturer from 1889 to 1918. Twice he was president *ad interim* of that college, and from 1906 to 1918 he was director of the Massachusetts Agricultural Experiment Station. During the whole period of his thirty years of active work at Amherst, he was associated with this station and was a leader both in experiment and organization. The results of his research and scholarly efforts he published in numerous reports to the bulletins of the experiment station, the state board of agriculture and to the Massachusetts Horticultural Society. He was also the author of the annual reports of the experiment station for twelve years. He published a three-volume text, entitled "Agriculture," which treated of soils, manure and crops and animal husbandry. All these works, together with his several writings for the Imperial College of Agriculture, in Japan, were constant sources of contemporary reference and had a profound influence upon the trend of agricultural instruction in all the land-grant colleges of the United States.

It was only under the compulsion of a Massachusetts law that the venerable Dr. Brooks retired in 1921 at the age of 70. Keen and progressive to the end (his death was the result of a fall), Dr. Brooks flew across