

igneous action of any recency in the vicinity, or anywhere else in the eastern United States; and he especially rejected the volcanic knob at Schuylerville because he believed it at least Mesozoic in age (recent radium-lead measurements of the rock by Dr. A. C. Lane have shown it to be of Ordovician age as the present writer proposed at first). He concluded that the waters were mixed and in part may be connate and also of metamorphic origin, as urged by Ruedemann.<sup>4</sup> It was the writer's opinion that the carbon dioxide and some of the salts may originate in the eastern mountain regions where deeply buried sediments may still be undergoing metamorphism and impure limestones are still crystallizing into schists and producing free carbon dioxide. This is especially probable, as the source of the waters is clearly to the east and north-east.

Later, Dr. Paul Haertl, a German expert from Kissingen, who was twice called to Saratoga, in discussion with the writer recognized three possible

origins of the carbon dioxide, *viz.*, volcanic, chemical (by reaction of limestone and sulfuric acid producing anhydrite and gypsum) and metamorphic by metamorphosing of limestone under pressure and heat. In his final report he favored the volcanic origin and accepted the metamorphic origin as an alternative. Dr. Herbert Ant, chemist of the Saratoga Commission, held for some time the view of the chemical origin of the gas and salts of the water in the thick deposits of Canajoharie shale, overlying the limestone and dolomite. Dr. R. J. Colony in his report to the Saratoga Springs Commission finally advanced the unusual view that the carbonic acid gas and minerals may be derived from a cooling batholith deep down below the sediments.

Dr. Brewer and Dr. Baudisch, for the first time among experts, seem now to be able to give a positive clue to the origin of at least one important element of the mineral salts, clearly pointing to a marine origin.

## CHEMICAL CLUES TO THE ORIGIN OF THE SARATOGA MINERAL WATERS

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DIFFERENT investigators have often attempted to unfold the mystery of the origin of the Saratoga waters. These attempts could, however, remain only mere speculations, since a direct tracing of the water by special indicators was out of reach. Even the most basic and vital question whether the water comes from magmatic deep-seated sources or whether it is of meteoric origin remained unsolved.

The latest intensive geological investigation of the Saratoga basin was carried out by the late Professor R. J. Colony, of Columbia University, in 1929.<sup>5</sup> Colony believes that most of the constituents of the waters, including sodium and potassium, are derived from deep-seated primary rock out of which the elements are dissolved by the meteoric water super-saturated with carbon dioxide.

About barium, Colony writes: "It is possible that the barium, too, have a deep seated course, but I am not sure of it."

Colony did not like the marine hypotheses of the origin of the water; the rejection of it he expresses boldly in the following sentence: "It is inconceivable that *sulphate-free* waters can have been derived from any marine source."

The fact that the Saratoga waters do not contain sulfates has been a puzzle to most of its investigators, and it was always the reason why the marine origin

of the waters had been rejected. We will see later that the absence of sulfates in the waters is easily explained and does, in fact, harmonize well with its marine origin.

Potassium, which in amount ranges from 72.33 to 750.19 parts per million, is in itself an important constituent of these waters. That Saratoga water is of marine origin can be demonstrated by studying the isotopes of the element in the different strata from which the waters come and from the water itself. In comparison with sea water, it is interesting to note the amount of sodium and potassium which has entered and remained in solution in sea water.<sup>6</sup>

PER KG. OF SEA WATER

|          | Supplied | Present | Percentage |
|----------|----------|---------|------------|
| Na ..... | 16.8 g   | 10.70 g | 66.0       |
| K .....  | 15.0 g   | 0.37 g  | 2.5        |

Potassium is very important for the life process of marine algae, and we find it in some specimens concentrated in remarkable amounts. The abundance ratio for isotopes of potassium in ocean water all over the world has been shown by Brewer to be 14.20 to 14.25.<sup>7</sup>

As shown in a recent paper of A. Keith Brewer and Oskar Baudisch on "The Isotopes of Potassium and

<sup>6</sup> V. M. Goldschmidt, *Jour. Am. Chem. Soc.*, April, 1937.

<sup>7</sup> A. K. Brewer, *Jour. Am. Chem. Soc.*, 58: 365-370, 1935.

<sup>4</sup> N. Y. State Mus. Bull. 169, p. 165ff.

<sup>5</sup> R. J. Colony, Legislative Document, No. 70, 1930.

Lithium in Saratoga Mineral Water and Cryptozoon,"<sup>8</sup> for the first time in the history of the geological studies of the Saratoga basin, an isotope of an element in solution, namely,  $K^{41}$ , has furnished a direct indication of the origin of the water. The result of the work of Brewer and Baudisch shows an appreciable concentration of  $K^{41}$  in the mineral water and a small concentration in the Cryptozoon formations. The overlying shale, however, does not differ appreciably in its content from that normally present in rocks of this type.

The abundance ratio of mineral waters is  $13.85 \pm 0.1$ ; of Cryptozoon,  $13.95 \pm 0.1$ .

Brewer has first published the most important and spectacular discovery that isotopes can be enriched by life processes.<sup>9</sup> In the last or fourth stage of evolution, we may consider that the processes of concentration of elements of the earth's crust are due to the action of living organisms. Many such processes are well known to science. For instance, certain marine organisms concentrate iodine up several hundred thousand fold as compared with sea water. According to Brewer's investigations, kelp and agar, in comparison to ocean water, possess an appreciably higher concentration of  $K^{41}$ . These marine organisms in fact concentrate the heavy potassium out of the ocean water, a most spectacular life process. By further investigations, Brewer and Baudisch demonstrated also that the marine organisms of the Cambrian Age—the Cryptozoon algae—have concentrated the heavy potassium in an appreciable amount. We find most of the potassium leached out of the Cryptozoon limestone into the water of Saratoga.

The hypothesis of the *marine origin* of the water based on this discovery is now more than mere speculation. Since we are now on solid ground and know that the Cryptozoon reefs and the Saratoga water have

a direct correlation to each other and that the minerals in solution are derived at least in part from this source, we are able to say something about the appearance of barium ions in the water.

The remarkable concentration of barium by marine algae (*Fucus vesiculosus*) has been discovered in recent years.<sup>10</sup> While the ocean water contains only 0.02 per cent. of Ba, in the marine algae this element is concentrated several hundred fold. Among the primary rocks which contain only very small amounts of barium, the syenite with 0.2 per cent. BaO is quite outstanding. It seems to be no accident that much syenite is found in the vicinity of the Saratoga basin and barium in the Saratoga waters.

Since we find in all the different mineral springs small amounts of barium chlorid, naturally we can not expect any sulfates in the waters. Through the enrichment of barium by the life process of growing algae, the sulfur in these marine organisms must have been chemically bound to this element during geological time. Some of the sulfur is found in the Cryptozoon in the form of pyrite. In studying the constituents of Cryptozoon limestone by spectral analysis,<sup>11</sup> we found the following elements: Ca, Na, K, Li, Rb, Mg, Sr, Si, B, Mn, Fe, Cu and Ag. We did not find even traces of barium in the samples investigated. It is conceivable that the salty water in course of time has leached out all the barium from the Cryptozoon rocks.

The concentration of different elements and their isotopes in marine organisms of ancient and modern times furnishes a striking example of the ability and selective power of living organisms in obtaining constituents necessary for their existence.

The further study of Saratoga water and its constituents should be of scientific value not only for geochemistry but also for medicine.

## OBITUARY

### FRANK NELSON BLANCHARD

HIS colleagues record with a sense of intimate personal loss the untimely death of Frank Nelson Blanchard, associate professor of zoology in the University of Michigan, after an illness of two months of bacterial endocarditis, on September 21, 1937. He was forty-eight years old. His passing leaves a conspicuous gap in the personnel of his institution.

Dr. Blanchard was born on December 19, 1888, of New England stocks which began their career in America in 1639 and 1643. Son and grandson of printers and publishers and editors, young Frank

showed no inclination to follow in the ancestral footsteps. In grade school he showed great interest in batteries and other electrical devices. In high school his chief passion was for chemistry, and he fitted up a laboratory in the home cellar and busied himself in it for several years. Because of city residence, the only indication in early years of his later interest in natural history was his devotion to gardening. That devotion persisted throughout his life. In a diary which he began at the age of sixteen, and in which thereafter never a day's activities failed to be recorded,

<sup>8</sup> Brewer and Baudisch, *Jour. Am. Chem. Soc.*, 59: 1578, 1937.

<sup>9</sup> A. K. Brewer, *loc. cit.*

<sup>10</sup> Wolf von Engelhardt, "Chemie der Erde," Vol. 10, 187, 1936.

<sup>11</sup> Oskar Baudisch, *Arkiv Kemi, Min. och Geol.*, Bd. 12B, No. 9, Stockholm (Sweden). (1935.)