

AURORAL CHEMISTRY: THE RIDDLE OF THE GREEN LINE

Helge Kragh, University of Aarhus, Denmark

Introduction

The aurora borealis, also known as the northern light, rarely appears in works on the history of chemistry. The phenomenon is located in the upper atmosphere and is caused by streams of electrical particles originating from the sun. Hence the history of the subject may seem to belong to either the history of meteorology or astronomy; or, as far as the mechanisms are concerned, to the history of physics. Indeed, these three subdisciplines of history of science have their important share of the story of how the aurora became understood scientifically. What is missing from the picture, I suggest, is that chemistry, too, was significantly involved in the process. To my knowledge “auroral chemistry” has never been examined by historians of science, and yet even a cursory view at the development shows that problems of a chemical nature were an important part of the history that led to an understanding of the northern light. First and foremost, this was the case in the difficult problem of establishing the nature of the substances from which the colors of the aurora arose, which is largely the same as the problem of interpreting the auroral spectrum in terms of chemical elements.

The complex problem only received a satisfactory explanation in the 1920s, after more than 50 years of research. This essay examines the early phase of the development, up to about 1913, focusing on the problem of identifying the chemical nature of the elements

responsible for the northern light. Emphasis focuses on the uncertainty and many unfruitful hypotheses that characterized the development. It was a period of great change in the relationship between chemistry and physics, including a new definition of chemical elements and a greater understanding of the periodic system in terms of atomic theory. Attempts to find the origin of the spectral lines continued and eventually succeeded, in part because of more advanced experiments and their interpretations in terms of quantum theory (1).

The Green line and Astrospectroscopy

The general idea that the fascinating colors of the aurora are due to chemical elements in the higher atmospheric regions was expressed even before the invention of spectroscopy proper. Observing by means of a prism the colors produced by various elements subjected to electric sparks, an American researcher noted (2):

The colors also, observed in the aurora borealis, probably indicate the elements involved in that phenomenon. The prism may also detect the elements in shooting stars, or luminous meteors.

These were prophetic words, but they could only be turned into a scientific research program, chemical astrospectroscopy, after the invention of the spectroscope in 1860.

What was probably the first spectroscopic observation ever of the aurora was announced in 1868 by the

Swedish physicist Anders Jonas Ångström (3), who found a bright greenish line of wavelength 5567 in the units named after him ($1 \text{ \AA} = 1 \text{ \AA ngstr\o om} = 0.1 \text{ nm}$). Ångström's observations gave rise to a great deal of activity and many measurements of the spectrum of the aurora borealis. Observing an aurora visible in the Boston area in October, 1870, Alvan Clark and Edward Pickering suggested that two of the lines could be ascribed to hydrogen and one to the hypothetical substance assumed to make up the solar corona (4). Henry Procter of the Royal College of Chemistry, London, disagreed, arguing that some of the auroral lines could be produced in discharge tubes at low pressure. He thought that the green line had its origin in oxygen (5).

Another early auroral researcher was the Kiel astronomer and astrospectroscopist Hermann Carl Vogel, who in 1872 made a careful examination of the spectra

but without being able to identify the green line (7). (Figure 1).

During the 1870s many researchers were busy with studying the auroral spectrum. Among the chemists who took an early interest in the field were John Newlands and Arthur H. Church of the Royal Agricultural College (8). This kind of work resulted in more precise wavelength determinations and an extension of the number of lines, but not in a satisfactory understanding of the chemical nature of the substances responsible for the lines. By the late 1870s it was often assumed that the green line was due either to nitrogen or oxygen which, at the low pressure and temperature of the upper atmosphere, was excited by electrical actions coming from the sun. However, in spite of many attempts no one succeeded in reproducing the green line in the laboratory and thus its nature remained an unsolved problem.

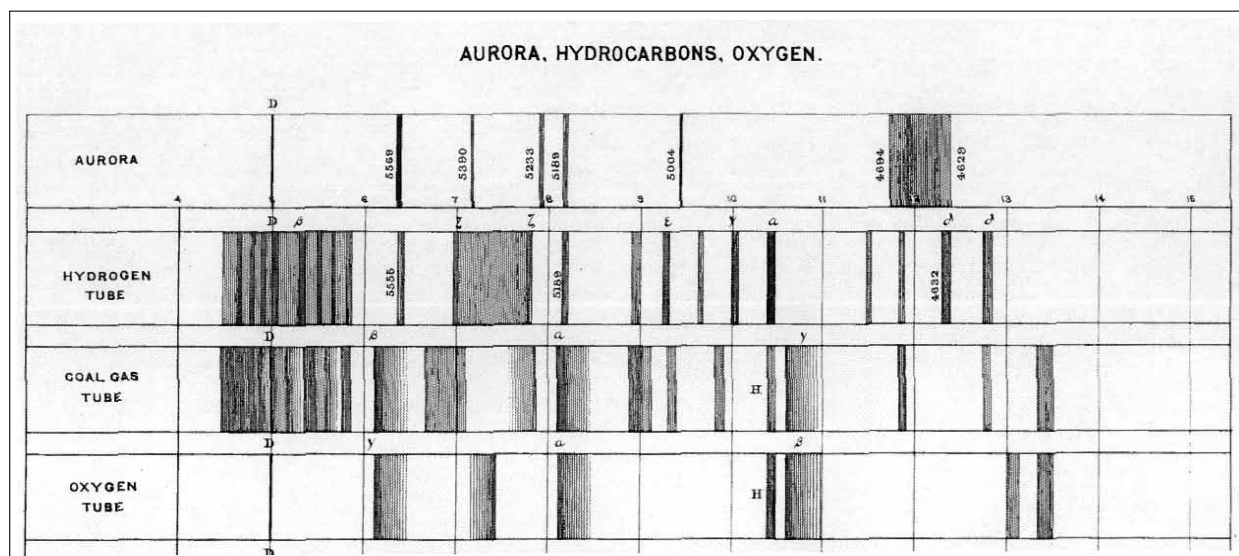


Figure 1. Rand Capron's comparison of the spectrum of the aurora with other spectra (Ref. 6).

of atmospheric gases and compared them with those of the aurora borealis (6). He suggested that some of the lines, possibly including the bright green line, were due to nitrogen and in general that the auroral spectrum was a modification of the spectra of the gases in the atmosphere—modified because of very different pressure and temperature conditions. However, he was unable to obtain a precise match between the green line and the lines produced in the laboratory. Vogel's research was followed up by John Rand Capron, an English businessman and accomplished amateur scientist. In a comprehensive monograph of 1879, he reported an extensive series of experiments on the spectra of gases in discharge tubes,

Hypotheses and Blind Alleys

Most suggestions related to gas molecules, but alternative explanations were discussed as well. One of them was that the green line had its origin in iron dust particles in the atmosphere of the earth, supposed to come from the combustion of meteorites, such as proposed by John Newlands, an industrial chemist who is better known as one of the precursors of the periodic system (8). Although the iron hypothesis was supported by a few researchers, it was never a serious candidate. Given the great number of iron spectral lines, the approximate coincidence with several auroral lines would be almost inevitable and hence of no real significance. A somewhat similar idea was

entertained by J. Norman Lockyer, according to whom the green line might be due to meteoritic manganese (9). However, neither did this hypothesis survive for long.

On a Danish expedition to Iceland 1899-1900, the meteorologist Adam Paulsen and his team succeeded in obtaining good photographs of the auroral spectrum, including 23 lines of which 12 were new and mainly located in the ultraviolet region. Paulsen reported on this work to the international congress of physics in Paris in 1900, leaving the origin of the lines unexplained. Based on Paulsen's Icelandic data and subsequent experiments with discharge tubes made in Copenhagen (10), the Potsdam astrophysicist Julius Scheiner concluded that "the auroral spectrum is absolutely identical with the cathode spectrum of nitrogen" (11). The Swedish physical chemist Svante Arrhenius agreed, stating that "the spectrum of the northern light is nothing but the spectrum of air which has been made luminous in the vicinity of a cathode" (12). However, the identity did not cover the characteristic green line, which resisted showing up in the laboratory experiments of Paulsen, Arrhenius, and other researchers. For example, experimenting with discharge tubes with air at very low pressure, S. D. Liveing and James Dewar found several of the auroral lines but no trace of the green one supposed to be the defining line of the polar light (13).

The state of art in auroral spectroscopy in the early twentieth century may be inferred from a detailed article on the aurora polaris in the 1911 edition of *Encyclopedia Britannica*. According to this article, written by the British geophysicist Charles Cree, the most complete record of the spectrum was obtained by Swedish scientists on Spitsbergen, who found no fewer than 158 auroral lines. By far most of these had wavelengths between 3684 Å and 5205 Å, many of them coinciding with oxygen and nitrogen lines (14). However, measurements were ambiguous and interpretations even more so. At about the same time the spectroscopic expert Heinrich Kayser, professor at Bonn University, concluded that "We know nothing at all about the chemical origin of the lines of the polar light" (15).

In the early part of the twentieth century the recently discovered gas krypton appeared to be a good candidate for several of the auroral lines. This possibility was first suggested by Arthur Schuster, who noted that the green line coincided with an intense krypton line. Determining the wavelength of the krypton line to 5570.4 Å, the German physicist Carl Runge agreed that the match with the auroral line of $\lambda = 5571.0 \text{ \AA}$ was sufficiently close

to make the identification convincing (16). W. Marshall Watts, an English meteorologist, was even more confident; in 1907 he concluded (17):

There seems now little doubt that the chief line of the aurora, i.e., Ångström's green line, must be assigned to krypton.

The optimism, however, was premature as well as problematic. For one thing, krypton was known to be a very rare constituent of air and it was difficult to imagine why such a relatively heavy gas (atomic weight 83.80 u) should appear in the upper atmosphere; for another thing, not all of its bright lines could be found in the spectrum of the aurora. Although provisionally assuming the identity of the green line with the krypton 5570 line, William Ramsay, the discoverer of krypton, cautiously concluded that the question remained undecided (18).

Peirce's Auroral Element

Given the many unsatisfactory attempts to identify the green line with known substances, it was natural to look at another possibility, namely that the green line and perhaps also some of the other auroral lines were due to an element unknown to the chemists. Having reviewed the various ideas of the origin of the green line, Scheiner suggested as much (19):

It appears more plausible to ascribe the existence of the green northern light line to an unknown gas which, perhaps because of its small specific weight, only turns up in the high regions of our atmosphere.

This may seem to be a far-fetched hypothesis, but it made sense at the time and fitted well with contemporary developments in astrospectroscopy and speculative chemistry. The early examinations of the auroral spectrum coincided with Mendeleev's introduction of the periodic system; yet this system in no way precluded the existence of new elements that only existed in the heavens. By accident, Ångström's discovery of the green line occurred at the same time as Lockyer detected a yellow line, denoted D_3 , in the chromosphere of the sun. Lockyer, as well as a few other scientists, believed that the line had its origin in a new element, soon known as helium, that existed only in the sun and possibly had an atomic weight smaller than that of hydrogen (20). If helium were accepted as real, why not an auroral element?

Helium was not the only hypothetical element ushered into the Victorian era as a result of astrospectrography. In investigations of the sun's corona, the American astronomer Charles Young found in 1870 a green line of

wavelength 5316 \AA , which he suggested might be due to a rare gaseous element, generally known as "coronium." Young speculated that the hypothetical element "must be something with a vapor density below that of hydrogen itself" (21). Although coronium never became part of chemistry, it found its way to at least one version of the periodic system, proposed by Benjamin Emerson (22). In 1919 two American chemists even thought they had found traces of it in a helium gas well (23). Because of the apparent similarity between the aurora and the rarefied solar corona, the two phenomena were often thought to be related.

The first suggestion of a distinct auroral element came from an unlikely source, the later eminently famous American philosopher and logician, Charles Sanders Peirce. As a young man Peirce worked as an assistant at the Harvard College Observatory (1868-1875), just at the time when spectroscopy began to transform astronomy in a more physical and chemical direction. He had at that time considerable interest and competence in chemistry, witnessed by a brief paper published anonymously in the *Chemical News* of 1869, dealing with the classification of the elements according to their atomic weights and chemical characters (24). In this little known paper he presented a table with 50 elements ordered in two series, which he called "artiads" and "perissads." As he pointed out, there was a close correspondence between elements belonging to the two series. In fact, the correspondence amounted to a classification of groups of elements which in some cases were the same as those proposed by Mendeleev the same year. Although Peirce's "pairing" scheme of elements has not attracted attention among historians of chemistry, it clearly has a place in the history of the periodic system.

Of greater importance in the present context is that Peirce made spectroscopic observations and, as early as April 1869, studied the auroral light. According to the *Annals* of the Harvard College Observatory (25):

On April 15, 1869, the positions of seven bright lines were measured in the spectrum of the remarkable aurora seen that evening; the observer being Mr. C. S. Peirce.

The same year, Peirce wrote an insightful review of the eminent English chemist Henry Roscoe's *Spectrum Analysis*, a subject with which he was thoroughly familiar, both with regard to its astronomical and chemical aspects. Peirce's comments on the use of the spectroscope in auroral research are not well known and they deserve to be quoted at some length (26):

The spectrum of the aurora, as usually seen, consists of a single yellowish-green line, which belongs to no substance with which we are acquainted. As the aurora is held to be above the ordinary atmosphere (and this is confirmed by its showing no nitrogen lines), it follows that there is some unknown gas reaching above the other constituents of the atmosphere. According to the laws of gravity and diffusion of gases, this substance must extend down to the surface of the earth. Why, then, have not chemists discovered it? It must be a very light elastic gas to reach so high. Now, the atomic weights of elementary gases are proportional to their density. It must, then, have a very small atomic weight. It *may* be as much lighter than hydrogen as hydrogen is than air. In that case, its atomic weight would be so small that, supposing it to have an oxide of the type of water, this oxide would contain less than one per cent of it, and in general it would enter into its compounds in such small proportions as almost infallibly to escape detection.

As an example Peirce suggested that the auroral gas might have an atomic weight of 0.07 u. If it were divalent and combined with oxygen as X_2O , it would make up only 0.87% of the compound.

This was the first suggestion that the green auroral line might be due to an unknown chemical gas with atomic weight smaller than that of hydrogen.

Although an interesting speculation, it attracted very little attention, which is scarcely surprising in view of the fact that it was published as an unsigned review in an obscure American journal. Peirce did not himself return to the hypothesis, but a few other scientists toyed with the idea of "aurorium," an appropriate name for Peirce's element but not one he used. The spurious element "aurorium" only appeared in the chemical literature in 1923, when it was mentioned by B. Smith Hopkins, a chemistry professor at the University of Illinois (27).



Figure 2. Charles Sanders Peirce

Wegener's Geocoronium

With the gradual completion of the periodic system, and especially after the incorporation of the new group of inert gases, it appeared increasingly difficult to find a place for new gaseous elements. However, there still remained the possibility of subhydrogenic elements, such as proposed by Peirce. Indeed, in his revised system of 1903 Mendeleev considered the existence of two such elements, one of which he thought might be identical with coronium, and the other, even lighter element, to be the same as the physicists' world ether (28). Among his inspirations was an address to the British Association for the Advancement of Science, in which Dewar had suggested that some of the auroral lines "may perhaps be due to some volatile element which may yet be discovered in our atmosphere" (29). According to Mendeleev (30):

This is only a few steps from the yet more distant regions of space, and from the necessity of recognizing the existence of a still lighter gas capable of permeating and filling space and thus giving a tangible reality to the conception of the ether.

That is, the Russian chemist entertained the idea of a very light auroral element in the form of an intermediate between the ether and ordinary gases.

The hypothesis of an auroral element was also suggested by Alfred Wegener of drifting continents fame. Primarily a meteorologist and astronomer, Wegener had a strong interest in the composition of the upper atmosphere, including its chemical and physical aspects (31). Measurements showed that the intensity of the unknown 5570 line increased with the height of the aurora and completely dominated the high-altitude steady arcs,

which Wegener took as evidence that the line originated in a light gas only found in the uppermost regions of the atmosphere. He first made the suggestion in a paper of 1910, where he speculated that the gas might be lighter than hydrogen and be analogous to the substance of the solar corona (32). The following year he went a step further, suggesting that the hypothetical gas was a new chemical element.

According to Wegener, whereas the atmosphere consisted of a nitrogen-oxygen mixture up to about 80 km, at very high altitudes it was quite differently composed. Hydrogen would be abundant but mixed with the new gas which he proposed to call "geocoronium" (33). Wegener calculated that at a height of 200 km the atmosphere would consist of equal amounts of hydrogen and geocoronium, whereas at a height of 500 km the distribution would be 93% geocoronium and 7% hydrogen. In a paper published in the *Zeitschrift für anorganische Chemie*, he expressed the belief that "in this way it is possible, for the first time, to establish some order in the confusing chaos of contradictory observations and opinions" (34). (Figure 3).

Wegener was aware of Mendeleev's earlier speculations, which he considered to provide support for his hypothesis. Assuming geocoronium to

be monoatomic, with an atomic weight of 0.4 u (a value he took from Mendeleev), and with a partial pressure at height 200 km equal to that of hydrogen, he found that the atmosphere at sea level should include 0.00058% geocoronium according to volume. This was a small amount indeed, but not very much smaller than the amount of hydrogen. "A direct detection cannot be ruled out," he commented (35). As to the nature of the new gaseous envelope of the earth, he thought it might be similar to or perhaps identical with the solar coronium. Although the bright aurora line did not coincide with the coronium

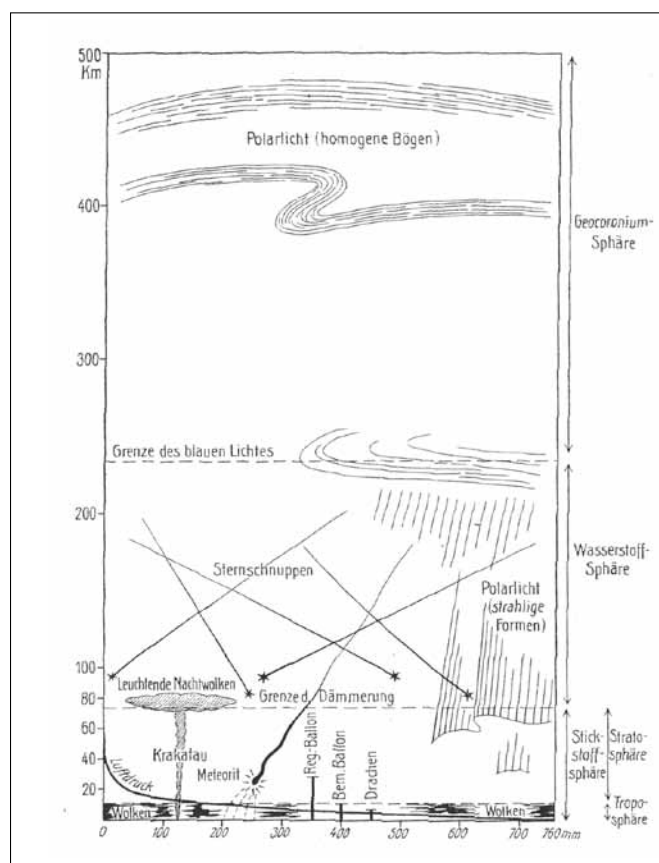


Figure 3. Wegener's picture of the atmosphere, as reproduced in his textbook of 1911 (Ref. 33).

line, he argued that the difference might be ascribed to different excitation mechanisms in the solar and terrestrial coronas. He therefore concluded that the two gases were very likely identical.

Published in a monograph and in two of the leading journals of physics and chemistry, the geocoronium hypothesis was noticed by contemporary scientists. However, it was coolly received. Among the few supporters of the hypothesis was the German geophysicist Gustav Angenheister, according to whom the lower auroral region consisted of about 64% hydrogen, 33% geocoronium, and 3% helium (36). Most chemists were unwilling to consider new elements of the kind proposed by Mendeleev and Wegener, and meteorologists and other specialists in the aurora thought that the green line could be explained without the drastic assumption of a new gas enveloping the earth (37). There was no independent evidence for geocoronium, and so the hypothesis might seem to be based on a circular argument. The Norwegian pioneer in auroral research, Kristian Birkeland, found Wegener's hypothesis interesting, but his former assistant Lars Vegard rejected it as speculative and unnecessary (38).

At the time Wegener proposed the geocoronium hypothesis, other scientists suggested that the new and exciting phenomenon of radioactivity might throw a much needed new light on the aurora and its spectrum. For example, Vegard suggested a detailed theory of the aurora borealis according to which the characteristic drapery bands were caused by alpha rays emitted from the sun. Although he expressed great confidence in the new theory, he had to admit that it failed to offer an explanation of the green line. Forty-four years after Ångström had pioneered auroral spectroscopy, "the origin of the most conspicuous line with a wave-length $\lambda = 5570$ is still unknown" (39).

The Green Line Identified

From about 1920, Vegard, the period's foremost authority in auroral spectroscopy, started a series of systematic investigations in order to establish the origin of the green line. He had at the time become convinced that the green line belonged to an unusual form of nitrogen, possibly in the form of crystalline dust. To vindicate the hypothesis, he made a series of low-temperature experiments with solid nitrogen exposed to cathode rays which made him conclude that the puzzle of the green line had finally been solved (40). However (and to make a long story short), Vegard's discovery claim was disputed by similar experiments made in Toronto by John McLennan and Gordon

Shrum in 1925 (41). The Canadians demonstrated that the green line did not have its origin in solid nitrogen, but that it was due to a "forbidden" transition in atomic oxygen. This has remained the accepted explanation.

Although Vegard failed to explain the green line, his extensive work in auroral spectroscopy was not wasted. Vegard did his first scientific work in physical chemistry (42) and kept an interest in borderline problems between physics, chemistry, and meteorology. He published a couple of important papers on X-ray spectroscopy in the *Journal of the Chemical Society*. While a professor of physics in Oslo he was primarily occupied with the aurora, but he also did much work on the structure of crystals of alums and other compounds. As a consequence of his failed interpretation of the green line, he extended this work to the crystal structure of solid nitrogen and other gases in the solid state (43). This line of work, mostly published in the *Zeitschrift für Kristallographie*, was important to the new field of solid state chemistry.

With respect to the green auroral line ("aurorium"), there is a noteworthy analogy to three other elements, only one of which is real: helium, coronium, and nebulium. The evidence for these hypothetical elements was unidentified spectral lines in the heavens, either from the sun or from the distant nebulae. The status of helium changed drastically in 1895, when the gas was found in terrestrial sources. No such change occurred in the cases of coronium and nebulium. While the main coronium line was eventually identified as due to iron in a highly ionized state (Fe^{13+}), the nebulium lines were explained in a way similar to the green auroral line, namely as transitions between metastable states in doubly ionized oxygen. The resolution of the nebulium puzzle dates from 1927, two years after the green line had been understood, whereas the coronium puzzle was delayed until the late 1930s before it was resolved (44). Of course, in this period no one seriously believed in the existence of new gaseous elements of low atomic weight.

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ABOUT THE AUTHOR

Helge Kragh is professor of history of science at the University of Aarhus, Denmark. His research covers the development of the physical sciences after 1850, including physics, chemistry, and cosmology. He serves currently as president of the European Society for History of Science.

February 13, 2010 To the Editor:

I enjoyed John Plater's article in the most recent issue of the *Bulletin* (**2010**, 35(1), 40-45) on serendipity. Though, in his discussion of the use of lithium salts to retreat mania, he mentioned several mineral waters, such as Perrier and Vichy, which naturally contain small concentrations of lithium ion, he failed to mention one of the more famous commercial soft drinks that tried to cash in on the original lithium craze – 7 Up. First created by Charles Leiper Grigg of St. Louis in 1920 under the name of "Bib-Label Lithiated Lemon-Lime Soda," it was originally formulated with lithium citrate as one of its active ingredients. Since Grigg was a professional designer of soda flavors rather than a pharmacist, it is unclear from the accounts I have read just what the original motive was for adding the lithium salt, nor is it obvious whether the current soda still contains any lithium citrate, since apparently the brand has been sold and resold several times to various companies and has also been reformulated in the process. But of greater interest is the name "7 Up" which rapidly displaced Grigg's original tongue twister. I have never come across an explanation of its origins but have always wondered whether "Up" was a reference to the idea that lithium could act as a pick-me-up and that 7 was a reference to the atomic weight of Li. Perhaps this explanation is too cleverly chemical to be true. Nevertheless, I would be interested in knowing whether the readers of the *Bulletin* might have some insights into this question.

William B. Jensen, Oesper Professor of the History of Chemistry, University of Cincinnati