1.1 JOSIAH PARSONS COOKE (1827-1894): LINKS TO ATMOSPHERIC CHEMISTRY

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1. INTRODUCTION

So very difficult a matter it is to trace and find out the truth of anything by history. — Plutarch (AD 46?-120)

Atmospheric chemistry has become a well recognized area of atmospheric science in recent years, but this was not always the case. Tracing links into the past shows that we were surely influenced by the views and education of our academic ancestors and the experiences they passed down to us.

It has become fashionable in the chemistry community to determine chemical genealogies. The most notable of such databases is at the University of Illinois, Urbana-Champaign (http://www.scs.uiuc.edu/%7Emainzv/Web_Genealogy/index.htm). To honor J. Gaffney's thesis advisor, James N. Pitts, Jr., and to also explore our own roots, we recently constructed a chemical genealogy (Gaffney and Marley, 2002). During that process we found a very interesting academic ancestor who had an important influence on many chemists, including atmospheric chemists. This ancestor is Josiah Parsons Cooke (1827-1894).

In this paper, we revisit Cooke's life and show his connections with some leading atmospheric chemists in the United States.

2. EARLY LIFE AND EDUCATION

Josiah Parsons Cooke was born in Boston, Massachusetts, on October 12, 1827. His early education took place at the Boston Latin School. He later attended Harvard, where he obtained his A.B. degree in 1848. Cooke, an extraordinary fellow, was given the job of starting Harvard's chemistry department. Initially hired as a tutor in mathematics, in 1850 he was appointed Erving Professor of Chemistry and Mineralogy, a position he maintained until his death in 1894.

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3. COOKE, MINERALOGY, AND THE HARVARD DIAMOND

One of Cooke's first tasks was to upgrade the mineral collection at Harvard and restore it to order. The condition of the collection had suffered under the previous caretaker, Professor John Webster, who had recently been hanged for the murder of Dr. George Parkman. Webster was apparently indebted to Parkman for a large sum of money. Webster reportedly lured Parkman to the Medical School, where he committed the crime and attempted to dismember and burn the body. Through dental records and chemical analyses, the body was identified, and Webster was found guilty of the crime (Hauck, 1988).

To upgrade the mineral collection, Cooke asked for help from Benjamin Silliman of Yale (whom Cooke, at age 16, had heard lecture on chemistry). Silliman, the head chemist and mineralogist at Yale, spent several weeks aiding in reorganizing and setting up the collection at Harvard.

In 1860, Cooke married Mary H. Huntington. In later years, his wife's nephew, Oliver Whipple Huntington, came to live with the couple. Huntington obtained a doctorate in chemistry under Cooke's direction and ultimately landed a job as lecturer in chemistry and mineralogy. Cooke and Huntington were jointly handling the mineralogy collection when a number of significant gemstones were donated by James A. Garland, Sr., in 1892. Remarkable stones among the gifts included a "crystal clear," bluish-green crystal of beryl (aquamarine) weighing about a pound. Also included was the Harvard diamond, a yellow stone from the DeBeers Mine in South Africa, weighing over 86 carats (Conklin, 1988). This diamond was stolen from Harvard in 1962 and was never recovered.

Cooke conducted a number of scientific studies on minerals. A form of aluminosilicate quartz with the mineral formula $LiAl_4(Si_3Al)O_{10}(OH)_8$ was named "cookeite" after him.

4. HARVARD CHEMISTRY DEPARTMENT

Although he had no formal training in chemistry, Cooke was asked to establish a chemistry department at Harvard. He had attended Silliman's courses and also visited leading European chemists including Jean Baptiste Andre Dumas and Henri Victor Regnault, who, he indicated, influenced him greatly in his chemical thinking. Cooke successfully developed and directed a course in chemistry at Harvard that focused on incorporation of hands-on laboratory instruction. Indeed, he was the first to introduce this approach at a U.S. university. Though he invested a great deal of effort in teaching, he also found time to write a number of key contributions to chemical science, including the very popular *Religion and Chemistry* (Cooke, 1880). We discuss this book and the relationship to atmospheric chemistry in some detail in subsequent sections.

In 1880, during his career at Harvard, Cooke began an investigation on the atomic weight of antimony. This work was continued by one of his students, Theodore Richards, who obtained his Ph.D. under Cooke's direction in 1888. Richards won the Nobel Prize in Chemistry in 1915 for weight determinations for a number of elements, as well as for his careful identification of isotopes of elements, notably lead.

Cooke was well known for his ability to perform careful mineral analyses and his identification of new minerals. He wrote numerous papers in the *American Journal of Sciences* and the *Proceedings of the American Academy of Sciences and Arts*, for which he also acted as an editor. He was elected in 1872 to the National Academy of Sciences and served as the president of that august society from 1892 until his death in 1894.

In 1873 Cooke published his *New Chemistry* textbook for classroom use. This work has been considered the earliest exposition of a consistent system of chemistry based on the principles of molecular mechanics. *New Chemistry* as a philosophy was widely accepted both in England and in Germany. The book was translated and found considerable success, with several subsequent editions.

Under Cooke's direction the Harvard chemistry department grew, and he directed a number of well known chemists to their doctoral degrees (despite never having earned one himself). Included were Frank Austin Gooch (analytical chemist), Henry Barker Hill (organic chemist who determined the amount of carbon dioxide in air), Charles Loring Jackson (organic chemist), and Theodore Richards. Both Jackson and Hill, after receiving their degrees at Harvard, studied with August Wilhelm von Hofman and were strongly influenced to become organic chemists, though they remained professors at Harvard. Cooke's real star and protégé was Richards, who won the Nobel Prize (as noted above) for work that clearly followed Cooke's lead. Richards also had a number of very successful students. Among these, Farrington Daniels was one of the first to investigate the nitrogen oxides and their production by high-temperature reactions in air. George Shannon Forbes, another Richards student, forged into the area of photochemistry and founded the genealogical line reported previously (Gaffney and Marley, 2002). Malcolm Dole obtained his Ph.D. in 1928 under Richards and dealt with the history of oxygen, among many other subjects.

Frank Thompson Gucker, another Richards student, studied the velocity of sound in gases and the penetration of gases into gas masks. Gucker produced the first measurements of light scattered by single aerosol droplets and compared his results to Mie scattering predictions, in a clear continuation of Richards' work on nephelometry in liquids. Other noteworthy Richards students in the Harvard chemistry department include Charles Phelp Smyth (Manhattan Project) and G.N. Lewis (Lewis acids, etc.).

5. RELIGION AND CHEMISTRY — CHAPTER 1

Cooke's treatise *Religion and Chemistry* (Cooke, 1880) makes a number of statements regarding the current state of religion (Christianity) and the pursuit of scientific study. Cooke makes the case that science and religion are mutually beneficial and supportive. Writing in conservative Boston in the late 19th century, during the aftermath of Darwinian evolution, he uses the atmosphere as an example of chemistry. The first chapter in *Religion and Chemistry* is titled "Statement of the Case — Testimony of the Atmosphere." In this chapter, he writes the following:

> *I shall ask you, in the first place, to study with me the physical condition of our atmosphere, and the properties of the various materials of which it consists; and I am sure we shall not fail to find in one and all abundant evidence of the wisdom, goodness, and power of God.*
>
> *Without seeking, therefore, to vindicate further the claims of my subject, I will at once enter upon the plan already proposed for this course of lectures, and will first ask your attention to the illustrations of the wisdom, goodness, and power of God, which may be discovered in the constitution of our atmosphere.*

Cooke goes on to describe the atmosphere and the relationships between height and air pressure. He also discusses the decrease in density with height and continues with the following description of the beauty of the air around us:

Consider, in the first place, the physical state of the atmosphere, its very aeriform condition. This air is as truly matter as the solid planks on which we are treading, or the granite rocks on which this building rests. It is far less dense, it is true, but then it has all the essential properties of matter. It fills space. It resists with an ever-increasing force all attempts to condense it; and, moreover, it has weight. But how different in condition from the solid rock! — so different that to the uneducated it hardly seems material; and in our common language we speak of a space which is filled only with air as empty. Its particles are endowed with such perfect freedom of motion, and yield so readily to the slightest pressure, that we move through it without feeling its presence. It is firm enough to support the wings of the lark as he mounts the sky, and yet so yielding as not to detain the tiniest insect in its rapid flight.

Later in this first chapter, Cooke described in elegant detail the discovery of atmospheric pressure. He also detailed Torricelli's experiments and discovery and Pascal's experiments at various heights to show that a mercury barometer reading changes because of the size of the column of air over it. Cooke described the physical state of the atmosphere as follows:

The density of the atmosphere may be said to depend upon four conditions: first, on the inherent nature of the substance which we call air itself; secondly, on the intensity of gravity; thirdly, on the total quantity of air on the globe; and, lastly, on the temperature. The influence of the first condition is not understood, but that of the last three we can readily trace. If the intensity of the force of gravity at the surface of the earth were to change, other circumstances remaining the same, the density of the atmosphere would change in the same proportion. Thus, for example, if the intensity of gravity on the earth were as great as it is on the surface of the sun, the density of the atmosphere would be twenty-eight times as great as at present; or if this intensity were reduced to that which exists on the surface of the moon, the density would be diminished to one-sixth of the existing density.

Cooke then discussed how biological organisms and humans were designed to survive in just this environment:

Consider next what these relations imply. Reflect that the intensity of the force of gravity depends upon the mass of the earth. Remember that the mean temperature depends upon the distance of the earth from the sun, and you will see that not only the actual size of the earth, but also its distance from the sun, and the quantity of air on its surface, were all necessary conditions in order that the atmosphere should have its present density, and thus become the fit abode for the actual families of organic beings. If any one of these conditions had been different, the same result would not have been attained, and man, as he exists, could not have lived on this globe.

6. RELIGION AND CHEMISTRY — CHAPTER 2

Cooke's Chapter 2, "Testimony of the Atmosphere — Concluded," details the scattering of light in the atmosphere:

I will merely bring before you a few facts, drawn from these departments of knowledge, which illustrate the adaptations of the atmosphere to its appointed ends.

The atmosphere, although very much more pervious to light than any kind of solid or liquid matter, is far from being perfectly transparent. Indeed, the reverse is sufficiently evident from our daily experience. Every one has noticed that distant objects appear less distinct in proportion as they are removed, their colors become fainter, the contrast between light and shade less marked, and that they seem as if covered with a pale blue veil. This effect, always noticed on distant mountains, is owing to a partial absorption of the light while passing through the atmosphere; for, were the passage of the rays wholly unimpeded, all objects, although reduced in size in proportion to their distance, would appear equally distinct, and their colors equally brilliant.

Cooke discussed in detail the importance of diffuse light in our lives:

Indeed, the atmosphere is as much an essential condition of our seeing as of our breathing, and the immeasurable pleasure which we derive from our sense of vision depends upon its adaptation to the organization of the eye. Were it not for the diffusive effect of the atmosphere on the sun's light, the contrast between light and shadows would be so greatly increased that, while objects directly illuminated by the sun would shine so brilliantly as to dazzle the eyes, all surrounding objects would be in darkness, and the interior of our dwellings would be as dark as night. Our eyes, as little fitted to such conditions as our lungs, would be blinded by the sudden alternations, and distinct vision would be impossible.

Cooke then put forth a rather faulty hypothesis for why the sky is blue:

I have thus far spoken only of the influence of the atmosphere in softening the intensity of the rays of *light, and in diffusing their action; but the atmosphere has also, under certain conditions, the power of decomposing the sun's rays, and thus producing, not only those displays of gorgeous tints which we witness in the sunset clouds, but also the pure blue which colors the dome of heaven.*

In regard to the precise means which are employed by nature to produce these results, scientific men are not agreed. It has been proved that the blue color of the sky is seen by reflected light, and it is probable that the color is caused by repeated reflections of the sun's rays from the surfaces of the innumerable small water-bubbles which are constantly floating in the atmosphere. You have all noticed the blue color of the soap-bubble shortly before it breaks. This color is caused by the action of the very thin film of water in decomposing the light reflected from its surface, and it is supposed to be an action of the same sort, only very much increased by repeated reflections, which gives to the sky its azure hue.

While the blue color of the sky appears to result from changes in the white light of the sun caused by reflection, it is equally probable that the sunset tints arise from changes in the same white light caused by an unequal absorption of its different colored rays during their transmission through the atmosphere. Here, again, the vapor in the air is supposed to be the active agent; and the theory is, that the tints are produced while the vapor is condensing into clouds, a change which naturally occurs at sunset. But this is a mere theory, and our whole knowledge on these subjects is very imperfect.

The chapter finishes with a crescendo of text on sound and light in the atmosphere, as well as considerable discussion of electricity, heat, and other issues dealing with the overall perception of order and pleasantness on the earth, as understood by science and religion alike.

7. CHAPTERS 3 AND 4 — TESTIMONY OF OXYGEN

Cooke's Chapters 3 and 4 deal with an analysis of the chemical composition of air and its importance to us. In Chapter 3, "Testimony of Oxygen," Cooke reported the composition of air as follows:

	Composition of the Atmosphere (%)
Oxygen	20.61
Nitrogen	77.95
Carbonic Dioxide	0 .04
Aqueous Vapor (average)	1.40
Nitric Acid, Ammonia, and Carburetted Hydrogen	traces
Total	100.00

	Composition in Billions of Tons
Oxygen	1,233,010
Nitrogen	3,994,593
Carbonic Dioxide	5,287
Aqueous Vapor	54,460

Cooke discussed in detail the importance of oxygen in the chemistry of the atmosphere, soil, plants, and animals. He then discussed the differences in density between the two most abundant gases and noted that the two gases are well mixed throughout the atmosphere:

Oxygen gas, like all other forms of aeriform matter, tends to expand, and can be prevented from obeying this natural tendency only by enclosing it in an air-tight receiver. As it exists in our glass jars, under the ordinary conditions of temperature and pressure, one cubic foot of oxygen weighs 590.8 grains, although in its more expanded state, as it exists in the atmosphere at the surface of the globe, it has but one-fifth of this density. One cubic foot of nitrogen gas weighs, under the same circumstances, 517.5 grains; but although there is such a decided difference between the specific gravities of the two gases, yet so perfectly are they mixed together throughout the whole extent of the face of the earth, and the lighter nitrogen floating above it? Simply because gases, unlike the other forms of matter, have the property of ''diffusing'' through each other, and existing together in the same space. The presence of one gas does not prevent the entrance of another into the space which it occupies, and if two open jars, containing different gases, are placed together, mouth to mouth, each gas will expand until it fills the whole volume of both receivers. Moreover, the greater the difference between the densities of the gases, and the greater consequent disposition to separate, the stronger is their tendency to mix together. This process is known as ''diffusion,'' and plays a very important part in the plan of creation. Were no such *law in operation the two gases composing air would have separated partially, and the atmosphere have become unfitted for many of its important functions.*

Cooke continued with a discussion of the reactivity of oxygen with living organisms and its relationship to fire and combustion:

A single spark of fire will change the whole character of this element, and what was before inert and passive becomes in an instant violent and irrepressible. The gentle breeze which was waving the corn and fanning the browsing herds, becomes the next moment a consuming fire, before which the works of man melt away into air.

And here I must correct an erroneous, although very common impression, that there is something substantial in fire. This is one of those ideas, originating in an illusion of the senses, which we have inherited from a more ignorant age, and which our modern science cannot wholly dispel from the popular mind. Fire was formerly regarded as one of the elementary forms of matter, and all burning was supposed to consist in the escape of this principle of fire, previously pent up in the combustible substance. In support of this doctrine the old philosophers confidently pointed at flame as the visible manifestation of the escaping fire-element; and, childish as this doctrine may seem, it was the prevalent belief of the world for at least two thousand years.

Cooke discussed the erroneous phlogiston theory and indicated that accurate weight determinations had revealed the importance of oxygen in combustion, crediting Lavoisier with the discovery. He commented on the balance of chemistry in the atmosphere with a statement concerning smoke:

Moreover, this smoke, though so long unnoticed by man, was not overlooked by the Author of nature. It is a part of his grand and beneficent design in the scheme of organic nature. No sooner do the products of that wood burning on the hearth escape into the free expanse of the outer air, than a new cycle of changes begins. The carbonic dioxide and the aqueous vapor, after roving at liberty for a time, are absorbed by the leaves of some wide-spreading tree, smiling in the sunshine, and in the tiny laboratory of their green cells are worked up by those wonderful agents, the sun-rays, into new wood, absorbing from the sun a fresh supply of power, which is destined, perhaps, to shed warmth and light around the fireside of a future generation.

Cooke concluded Chapter 3 with a lengthy discussion of how oxygen is bonded to many elements to compose the myriad mineral types seen in the earth.

In Chapter 4, "Testimony of Oxygen — Concluded," Cooke discussed the chemistry of decay processes and indicated that the same forces are at hand in rotting wood and fire. He followed with analogies to religious beliefs and then detailed some of the slower oxidation reactions of oxygen and their importance, focusing on respiration.

Cooke also noted the importance of a new form of oxygen — ozone — and related its remarkable properties:

One of the most striking characteristics of this new modification of oxygen is its peculiar odor, and hence Schönbein calls it ozone, from a Greek verb signifying to smell. It frequently happens that a great discovery supplies the wanting links between a number of obscure facts, and thus adds quite as much to our knowledge by its indirect bearings as by the positive additions it makes to the general stock. So it has been with the discovery of ozone. Every one who has used an electrical machine must have noticed the peculiar smell which follows the electrical discharge. This was formerly supposed to be the odor of the electrical fluid itself; but as soon as ozone was discovered, the odor was recognized at once as belonging to this new agent, and it was soon ascertained that electricity is one of the most efficient means of modifying the oxygen of the air.

It certainly seems probable that decay and respiration, which are also examples of slow combustion, may act on the air in the same way. Moreover, the inference that ozone is the active agent in these processes is also supported by the fact that it is always present, to a greater or less extent, in the atmosphere, although, at most, in exceedingly minute quantities. Ozone, being so highly corrosive, cannot be present in the atmosphere in perceptible quantities without producing important effects, and some persons have thought not only to refer to it the various processes of slow combustion, but also to trace a connection between the prevalence of various contagious diseases and the excess or deficiency of this agent in the air of the infected district; but these speculations are not as yet based on sufficient evidence, and are not worthy of serious attention.

Little did Cooke know that the chemistry of the atmosphere would be dominated by the study of the slow oxidation reactions of species derived from ozone, OH, and O(1D), and that ozone would be used as a disinfectant for water in future years.

8. CONCLUDING REMARKS

Cooke continued with a discussion of the importance of water vapor in the atmosphere and its unique properties, followed by chapters on carbon dioxide and nitrogen. The rest of the treatise *Religion and Chemistry* (Cooke, 1880) pointed out the balance of the system and how well ordered the earth is with regard to water, air, and the beings on it. Considerable discussion follows on Darwin's theory and how science and religion actually work hand in hand. The reader is referred to the original text for further insight into Cooke's thoughts in this area.

Clearly, Cooke was a remarkable man who was very much intrigued by the atmosphere and its components. This interest must have been transmitted to Cooke's students and to Theodore Richards. Richards' student Forbes, one of the first photochemists, taught Philip A. Leighton. Leighton wrote *Photochemistry of Air Pollution* and trained Francis Blacet, a noted photochemist who pointed out the importance of the photochemistry of nitrogen dioxide in production of tropospheric ozone. Blacet trained James N. Pitts, Jr., and Jack Calvert, among others, who were also well known atmospheric chemists. One of us, JG, was a doctoral student under Pitts.

Cooke's contributions to atmospheric chemistry are apparent in his academic descendents and the continued interest in that area at Harvard. Cooke had to be a truly outstanding individual to establish one of the best known chemistry departments in the world, without the benefit of actual formal training in chemistry. Those who have Cooke for an academic ancestor (including the authors) are certainly in his debt.

9. ACKNOWLEDGEMENT

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