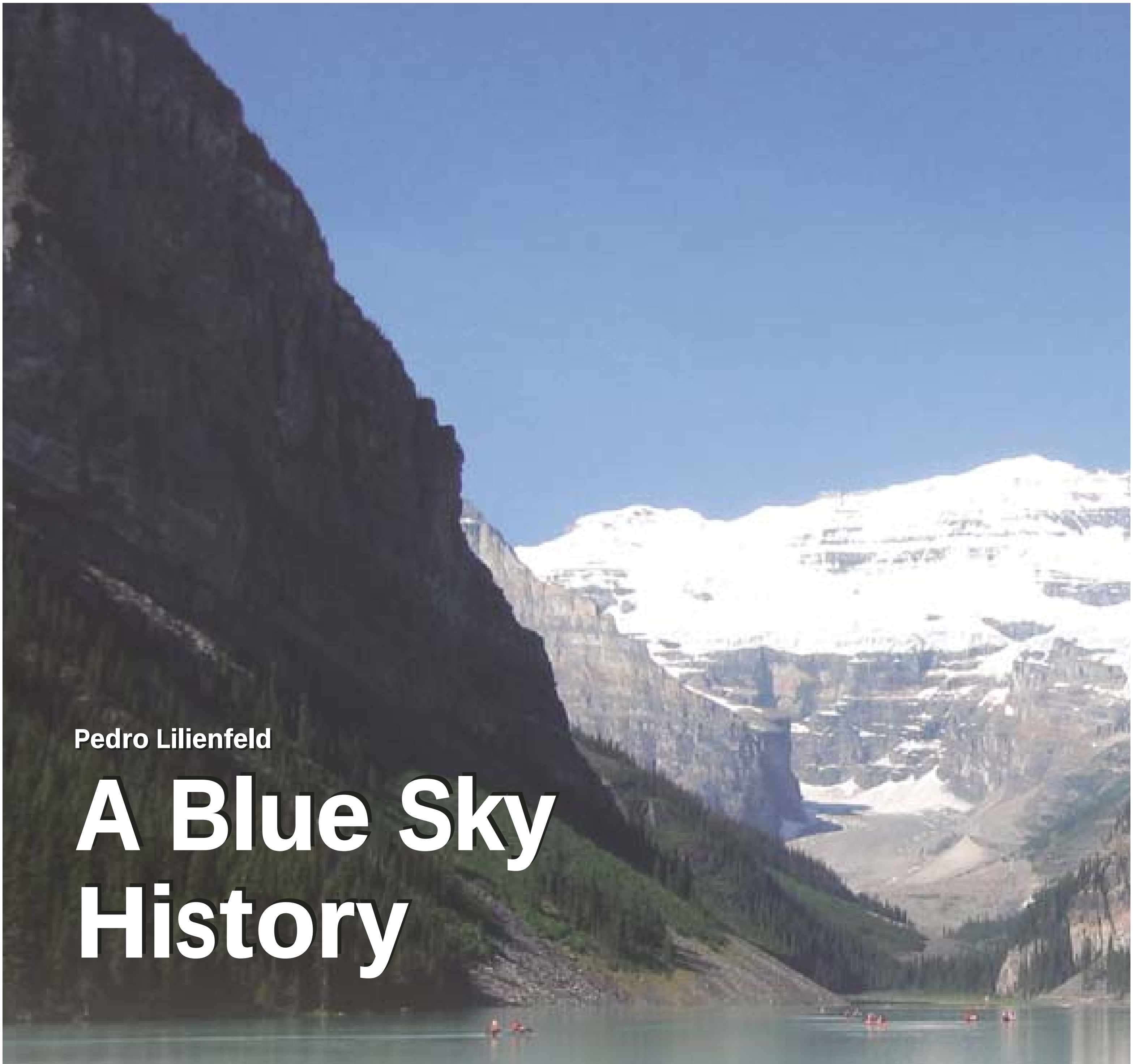

Pedro Lilienfeld

A Blue Sky History

One of the most pervasive of optical phenomena is the strikingly blue color of the clear daytime sky, a sight that, because of air pollution and urban sprawl, is becoming increasingly difficult to appreciate.

Throughout recorded history, people have taken note of the hues assumed by the sky under different viewing conditions; the most learned among them have sought to understand the physical origins of the colors that characterize it. In the ancient Greek Cyclades, sky blue was considered a fortuitous shade that could keep evil away, a superstition that continues to find expression in the form of blue church cupolas, blue trim around buildings and turquoise jewelry and clothing. Aristotle's elucubrations on the color of the sky were drafted 24 centuries ago. They are of great historical interest but show that the great thinker had little understanding of the origins of the sky's hue.

Perhaps the earliest serious attempt to explain the sky's color was made by the Arab savant Aby Yusuf Yaquib ibn Ishaq al-Sabbah Al-Kindi (c. 800–873) who lived in what is now Iraq. He attributed the azure of the sky to "a mixture of the darkness of the night with the light of the dust and haze particles in the air illuminated by the sun."

If we choose to identify an individual as the father of skylight optics the distinction should be accorded to Leonardo da Vinci (1452–1519). The writings of the genius of the Renaissance contain tantalizing insights into the origins of the sky's blueness and the appearance of smokes and mists, including those generated under experimentally controlled conditions. Da Vinci's interest in such phenomena sprung from his keen artistic eye: his motivation in studying the sky

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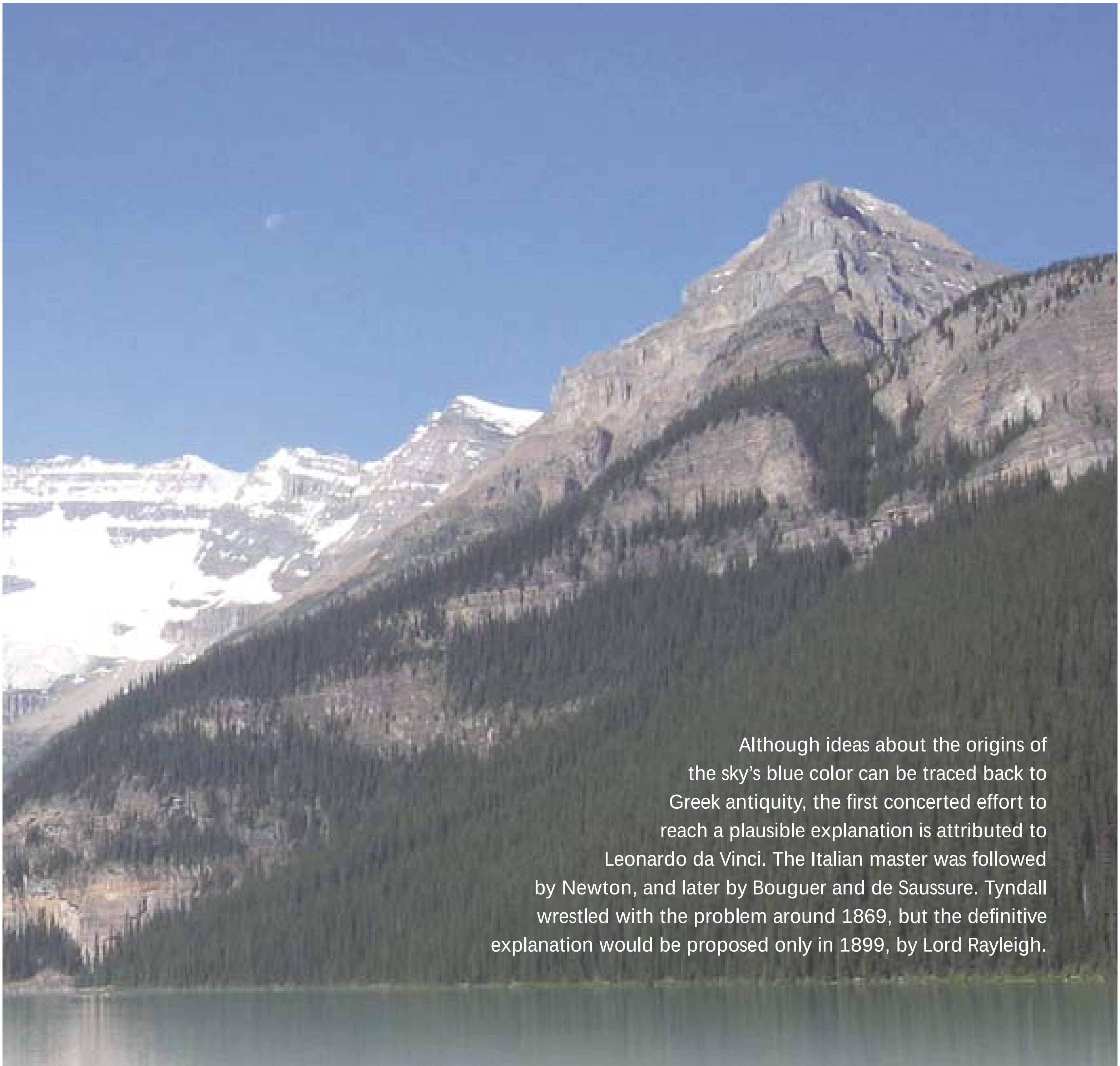


Although ideas about the origins of the sky's blue color can be traced back to Greek antiquity, the first concerted effort to reach a plausible explanation is attributed to Leonardo da Vinci. The Italian master was followed by Newton, and later by Bouguer and de Saussure. Tyndall wrestled with the problem around 1869, but the definitive explanation would be proposed only in 1899, by Lord Rayleigh.

was related to the problems of aerial perspective he faced in landscape painting. The perspicacious mind of the great master is evident in the following excerpts from his notebooks:

You know that in an atmosphere of equal density the remotest objects seen through it, as mountains, in consequence of the great quantity of atmosphere between your eye and them appear blue and almost of the same hue as the atmosphere itself when the sun is in the East. Hence you must make the nearest building above the wall of its real color, but make the more distant ones less defined and bluer; thus, if one is to be five times as distant, make it five times bluer. And by this rule the buildings which above a [given] line appear of the same size will plainly be distinguished as to which are the most remote and which are larger than the others.

Another of da Vinci's writings gives voice to an early interpretation of atmospheric turbidity as manifested by the whitening of the sky near the horizon:

And if the sky, as you see it, ends on a low plain, that lowest portion of the sky will be seen through a denser and whiter atmosphere, which will weaken its true color as seen through that medium, and the sky will look whiter than it is above you, where the line of sight travels through a smaller space of air charged with heavy vapor.

Da Vinci became aware that the sky became darker as one ascended the Alps. He correctly attributed the phenomenon to the thinning of the air as a function of altitude, concluding that above the atmosphere the sky must appear black. His interpretation of the origin of the sky's blue color, however, proved to be only partially correct. He wrote:

> *I say that the blue which is seen in the atmosphere is not its own color, but is caused by the heated moisture having evaporated into the most minute imperceptible particles, which the beams of the solar rays attract and cause to seem luminous against the deep intense darkness of the region … above them. And this may be seen, as I myself saw it, by anyone who ascends Mon Boso,* a peak of the Alps that divides France from Italy … And I saw the atmosphere dark overhead, and the rays of the sun striking the mountain had far more brightness than in the plains below, because less thickness of atmosphere lay between the summit of this mountain and the sun.*

The preceding paragraph is truly striking in its insights, except of course for the idea that minute water droplets dispersed through the atmosphere constitute the scattering medium that yields the sky's blue color, a misconception that would persist for another 400 years, until the very end of the 19th century.

Isaac Newton (1642–1727) was unable to provide a better explanation for the sky's blue color than that provided by da Vinci almost two centuries earlier. Still, the great English mathematician had a far more thorough understanding of optical phenomena. He suggested an early awareness of the spectral dependence of light scattering on particle size in what came to be known, two-and-a-half centuries later, as the Rayleigh regime:

> *The blue of the first Order, though very faint and little, may possibly be the Colour of some Substances; and particularly the azure Colour of the Skies seems to be of this Order. For all Vapours when they begin to condense and coalesce into small Parcels, become first of that Bigness, whereby such an Azure must be reflected before they can constitute Clouds of other Colours. And so this being the first Colour which Vapours begin to reflect, it ought to be the Colour of the finest and most transparent Skies, in which Vapours are not arrived to that Grossness requisite to reflect other Colours, as we find it is by Experience.*

* Believed to be Monte Rosa.

I saw the atmosphere dark overhead, and the rays of the sun striking the mountain had far more brightness than in the plains below, because less thickness of atmosphere lay between the summit of this mountain and the sun.

— Leonardo da Vinci

The Age of Enlightenment

The expansion of the sciences in the 17th century set the stage for them to take hold on a much broader scale in the 18th century. As experimentation unburdened by medieval preconceptions began to prevail, methodologies became more rigorous and even quantitative. In the field of atmospheric visibility and light transmission in the 1700s, two scientists stand out: Bouguer and de Saussure.

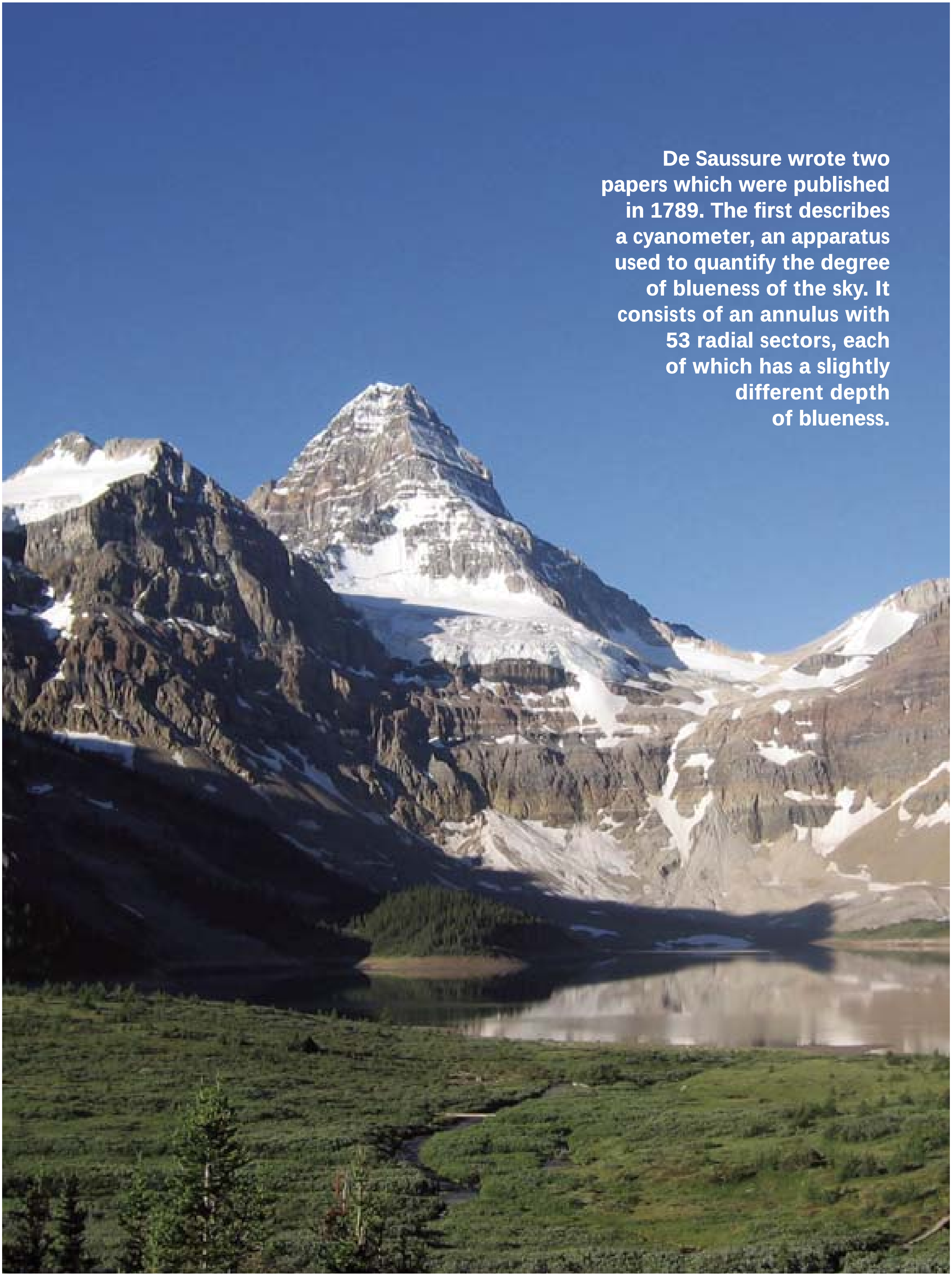
Pierre Bouguer (1698–1758) is known principally for the exponential attenuation law for light traversing a homogeneous medium, also known as the Bouguer-Lambert-Beer law (Bouguer predated both Lambert and Beer). This contribution secures Bouguer's place as a founding father of atmospheric optics. The great scientist was a child prodigy, having succeeded—at the age of 15—his father as Royal Professor of Hydrography upon the latter's death in 1713.

November 23, 1725, can be considered the birthday of atmospheric photometry. It was on that day, in Brittany, that Bouguer first quantified the light attenuation of Earth's atmosphere. The method he used was ingenious, constrained as he was by having as his only light sensor the human eye. Bouguer assumed that, if he used the moon as the source of illumination, Earth's atmosphere could be considered a thin plate. He further surmised (correctly) that if he could measure the atmospheric brightness of moonlight at two different angles, he could determine the atmospheric transmission. Bouguer used the light of a candle as a reference to compare the brightness of the moon at the two angles. Remarkably, he circumvented the nonlinearity of the human eye's irradiance response by varying the distance to the candle and using Kepler's inverse square law to quantify the changes in brightness. Bouguer was thus able to determine that the pre-Industrial Revolution air in Brittany was indeed, by our standards, of pristine purity.

Bouguer's method exemplifies the general approach to measurement used over several centuries before the availability of sensors and detectors. This method consisted of using one of the human senses as a relative measurement device, i.e., comparing the perceived magnitude of the sensory stimulus against a reference. Bouguer went on to make significant contributions to other areas of science and technology. He distinguished himself as the principal participant in an eight-year-long scientific mission, sponsored by the Académie Royale des Sciences, to what is now Ecuador, to determine the spheroidal shape of Earth.

Horace-Bénédict de Saussure was born near Geneva, Switzerland, in 1740. He attended the Académie de Genève, where at the age of 19 he produced his thesis "Dissertation on the Nature of Fire" (*Dissertatio physica de igne*). At the age of 22, he became a professor of physics and philosophy. Perhaps history's first scientific mountaineer, de Saussure was responsible for the first ascent to the summit of Mont Blanc in the Alps, where he carried out barometric pressure and atmospheric transparency measurements.

De Saussure wrote two papers which were published in 1789, the year of the French Revolution, that have seminal relevance to the field of atmospheric photometry. The first describes a cyanometer, an apparatus used to quantify the degree of blueness of the sky. It consists of an annulus with 53 radial sectors, each of which has a slightly different depth of blueness. The colors progress from pure white (the absence of blue) to deep,



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1400s

Milestones in the understanding of the origin of the blue color of the daytime sky.

A page from Leonardo da Vinci's *Codex Leicester* manuscript.

1480–1519
Leonardo da Vinci's manuscripts.

Sir Isaac Newton. *(From a 1725 portrait by John Vanderban.)*

1700s

1704
Isaac Newton's *Opticks*.

1725
Bouguer measures atmospheric transmission.

Pierre Bouguer.

Prussian blue, on to mixtures of intense blue and gradually increasing amounts of India ink black. This range of color gradations was intended to simulate the gamut from a milky (perhaps polluted) sky to the appearance of the sky above the atmosphere. The steps of increasing blueness were based on a visual threshold determination normalized against a visibility contrast referenced against a black-on-white target. De Saussure defined these minimum color discrimination steps as "nuances." He reported simultaneous "measurements" (by visual matching of the sky's blueness with one of the wheel's sectors) at three different sites: Geneva, Chamonix and on the slope of Mont Blanc at an altitude of 3,436 meters. Both zenith and horizontal observations were tabulated. The data of the zenith measurements clearly indicated the deeper blueness of the sky as seen from the elevated Mont Blanc site. Remarkably, de Saussure interpreted his results as proof that "the color of the sky determined by the cyanometer is the measure of the quantity of concrete vapors in suspension in the air," defining such "concrete vapors" (i.e., particles in suspension) by contrasting them with "vapors that are dissolved" in the air (i.e., in the gas phase, in modern terminology).

The 19th century

Dominique François Arago (1786–1853) made major contributions to various branches of physics, including postulation of the definitive test to decide between the corpuscular and the undulatory theories of light. (The test, ultimately performed by Foucault in 1850, confirmed the wave nature of light. Today's accepted wave-particle duality concept was derived by means of de Broglie's quantum mechanical analysis in the 1920s.) A significant advance of the early 19th century was Arago's discovery, in 1809, of the polarization of daytime skylight at 90 degrees to the direction of the sun.

Yet Arago's observations introduced an element of confusion into the interpretation of the optical process underlying the skylight phenomenon. Rudolf Clausius (1822–1888), noted for his contributions to thermodynamics, pointed out that refraction within macroscopic droplets could not explain the color of the sky; he postulated the presence in the atmosphere of minute water bubbles, an explanation inconsistent with Arago's observation. Sir John Herschel (1792–1871), son of the famous astronomer William Herschel, struggled with the observed 90-degree polarization in these terms:

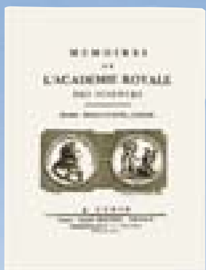
> *The cause of the polarization is evidently a reflection of the sun's light upon something. The question is, On what? Were the angle of maximum polarization 76°, we should look to water or ice as the reflecting body, however inconceivable the existence in a cloudless atmosphere on a hot summer's day of unevaporated molecules (particles?) of water. But though we were once of this opinion, careful observation has satisfied us that 90°, or thereabouts, is a correct angle, and that therefore, whatever be the body on which the light has been reflected, if polarized by a single reflection, the polarizing angle must be 45°, and the index of refraction, which is the tangent of that angle, unity; in other words, the reflection would require to be made in air upon air!*

Complete elucidation of the vexing polarization effect could not be achieved by means of the macroscopic optics of refraction and reflection as understood during the first half of the 19th century: it had to await Lord Rayleigh's molecular scattering theory of 1871.

James David Forbes (d. 1868), principal of the University of St. Andrews and inventor of the seismometer, made the observation that the sun appeared red when viewed through a section of the steam plume of a locomotive. When he repeated the experiment in the laboratory using a small steam boiler, he found that white light shining through the just-condensing detached part of the visible steam plume underwent a similar reddening. He concluded that this observation recreated the optical process underlying crimson sunsets, where the blue components have been preferentially scattered out of the primary beam.

An outstanding contributor to the understanding of atmospheric light scattering was John Tyndall (1820–1893), who is also remembered for his remarkable work in other fields. Among Tyndall's many achievements are some

1800s | **1890-1900s**



Issue of the *Mémoires de l'Académie Royale de Turin* that contains de Saussure's papers on atmospheric photometry.

1789
De Saussure's papers on atmospheric transmission and blueness of the sky.

John Tyndall.

1809
Arago discovers skylight polarization.

1869
Tyndall and Herschel fail to explain the blue sky.

1871
Lord Rayleigh's scatter theory.

Lord Rayleigh.

1890
Lorenz's scatter theory.

1899
Lord Rayleigh's definitive explanation of the blue sky.

1913
Cabbanes' laboratory air scatter experiment.

that are of major relevance to 21st century science. They include the invention of the light pipe, which led to the development of fiber optics, and pioneering work on the trapping of infrared radiation by various atmospheric gases, in other words, the "greenhouse" effect. Tyndall visited the Swiss Alps many times. It is worth nothing that, like da Vinci and de Saussure, Tyndall was stimulated by these alpine excursions to investigate atmospheric optical phenomena. He pursued this interest in the context of his work on particle light scattering, in particular the examination of small particles in suspension.

His most notable contributions are the first detailed observations of scattering phenomena by particles smaller than the wavelength of the incident light, as well as those the size of which approaches that wavelength. He is also known for the first determination of the dependence of scattering irradiance on particle size (the Tyndall effect) in what was later to be called the Rayleigh regime. The first systematic observations of the effects of particle size on the color and angle of scattered white light are also credited to Tyndall.

Yet Tyndall was unable to resolve the persistent question with which his predecessors and contemporaries had grappled without success: the true nature of the scattering medium that gives the sky its blue color. Influenced by Leonardo da Vinci and Newton, he continued to attribute the phenomenon to scattering by minute water droplets in the high atmosphere. Based on laboratory experiments he concluded in 1869 that:

> *When the air was so sifted as to entirely remove the visible floating matter, it no longer exerted any sensible action upon the light, but behaved like a vacuum.*

This sentence suggests that he did not realize the integrating effect of a long—on the order of kilometers—path through a purely molecular atmosphere which is required to yield a visibly blue scatter. As late as 1869, in reference to the color and polarization of skylight, Tyndall had to admit "these questions constitute, in the opinion of our most eminent authorities, the two great standing enigmas of meteorology."

The solution would in fact have to await Rayleigh's rigorous mathematical treatment and its subsequent interpretation. Tyndall's unsuccessful search for the source of the blue color of the daytime sky can be attributed to his reliance on elegant, heuristic conjecture as a means to explain natural phenomena rather than on rigorous mathematical analysis. Nevertheless, credit is due to Tyndall in that his detailed and insightful experiments and observations provided the foundation for the next generation of scientists to achieve the necessary breakthroughs by applying the heretofore insufficient methodological rigor.

The solution to the enigma

The next breakthrough required the mathematical solution of the scattering of light by particles with dimensions smaller than and comparable to the incident wavelength. A discussion regarding the primacy of attribution of these solutions would immerse us in a veritable minefield. It involves a cast of well known and lesser known scientists working during the second half of the 19th and the first half of the 20th century: Clebsch, Lorenz, Maxwell, Rayleigh, Mie, Debye and others. The debate over who was the first to develop workable theories on the scattering of light by small spheres is beyond the scope of this article.

The contributions of Ludwig Valentine Lorenz (1829–1891) have received due recognition since the 1980s. His name is cited with that of Gustav Mie in connection with the generalized theory of electromagnetic scattering (i.e., Lorenz-Mie scattering). He is best known to today's physicists for the Lorentz-Lorenz equation that relates the refractive index to the dielectric constant of a medium. (Hendrick Lorentz developed the equation independently, nearly concurrently, in 1870).

Lorenz's principal contribution to the study of the optics of aerosols is found in an 1890 memoir in which he solves the problem of the scattering of light by a dielectric sphere. For molecular sized spheres, he derived the inverse fourth power wavelength relationship that agreed with the derivation made by Rayleigh in 1871. Lorenz's contributions, however, were largely ignored, presumably because he chose to publish his memoir in his native language, Danish.

He showed little interest in communicating his results to physicists in other countries and chose not to base his work on Maxwell's recently developed electromagnetic propagation theory. Another of Lorenz's idiosyncrasies was his phenomenological view of physics; he sought to keep ontological hypotheses and physical assumptions out of physical theory. This may account for the fact that Lorenz, unlike Rayleigh, does not seem to have related his mathematical conclusions about light scattering by very small particles to real atmospheric phenomena such as the blue color of the sky.

We have now arrived at one of the most remarkable players in the field of light scattering, John William Strutt, Third Baron Rayleigh (1842–1919). The span of Lord Rayleigh's scientific work was exceedingly wide. Considered by some to be the last of the great Victorian polymaths, his research ranged over nearly the entire field of physics of the late 19th century: sound, wave theory, color vision, electrodynamics, electromagnetism, light scattering, fluid flow, hydrodynamics, density of gases, viscosity, capillarity, elasticity, photography and electrical standards (ohm, ampere, volt). Among the many honors he received was the 1904 Nobel Prize in Physics for his contribution to the discovery and isolation of argon. In 1905 he was elected president of the Royal Society. Rayleigh wrote some 450 papers and retained his mental powers until the end, working on scientific writings until his death in 1919.

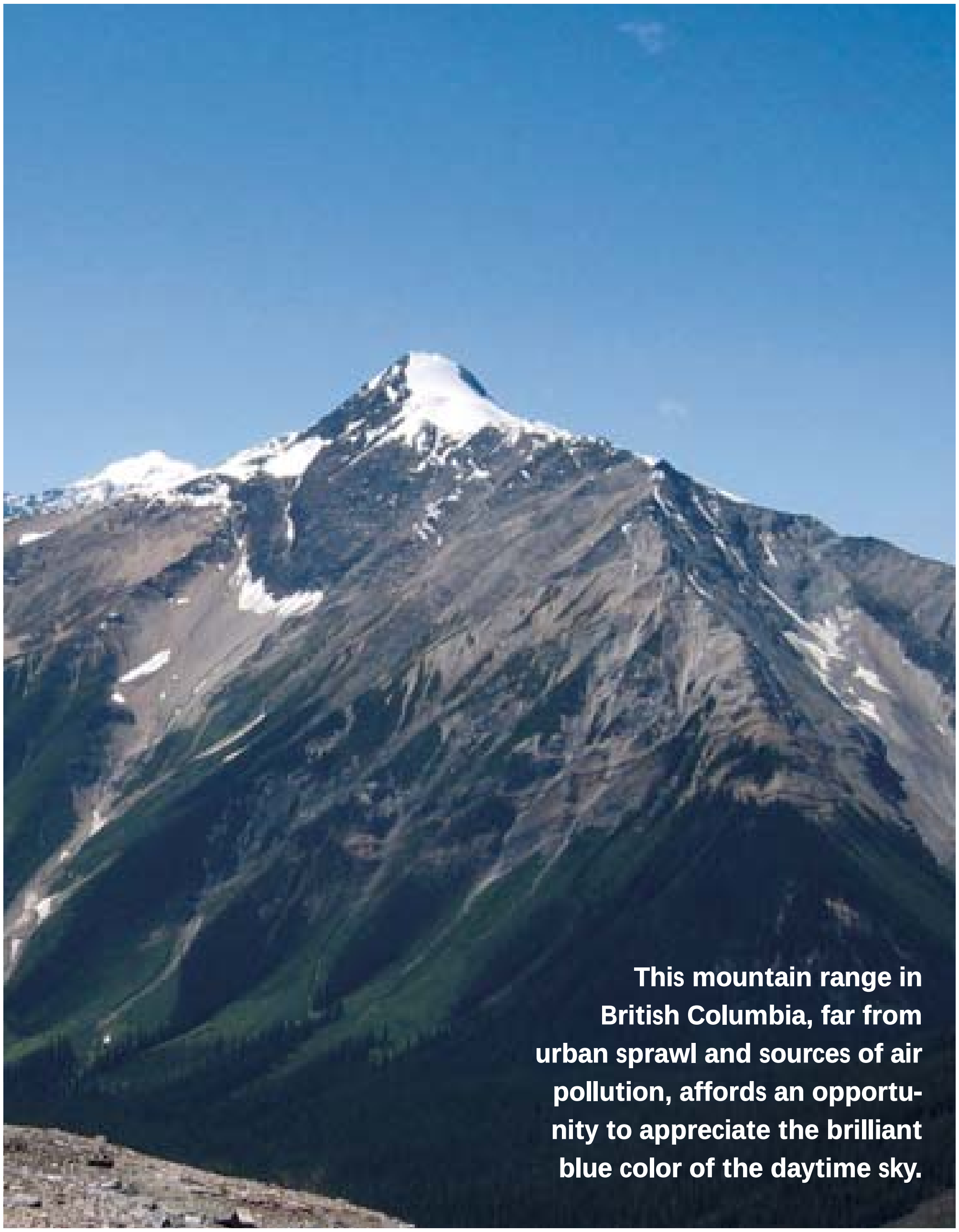
In 1871, Rayleigh published his first paper on the subject that concerns us: "On the light from the sky, its polarization and colour," followed immediately by another entitled: "On the scattering of light by small particles." This early work was based on elastic-wave equations where, as expected for that period, ether is the oscillating medium. This was a natural extension of Rayleigh's interest in the behavior of sound. In the first of these papers, Rayleigh develops for the first time his now famous equation:

$$I/I_0 = \frac{9\pi^2}{2}\left(\frac{\varepsilon-1}{\varepsilon+2}\right)^2(1+\cos^2\theta)\frac{nV^2}{\lambda^4 r^2}$$

where I_0 and I are the incident (unpolarized) and scattered irradiances, ε is the dielectric permittivity of the particle relative to the surrounding medium, θ is the scattering angle, n is the number of scattering particles, V is the particle volume, λ is the wavelength of the incident light, and r is the distance between the scattering particles and the observer (or detector). This equation explains the entire scattering behavior of particles the size of which is negligible with respect to the wavelength: the strong size dependence (the sixth power of diameter), the angular symmetry and polarization and, most importantly, the inverse fourth power dependence on wavelength. As we shall see, the latter was to lead Rayleigh, 18 years later, to the definitive explanation of the blue color of the sky.

A decade later, Rayleigh had incorporated Maxwell's electromagnetic theory of light into his own writings. In 1899 he published perhaps his most famous paper, which settled the puzzle once and for all. It appears from Rayleigh's own assertion that he may have been led to the origin of the sky's blue color as a result of a letter that he received from Maxwell in 1873 which, in turn, had been inspired by Rayleigh's 1871 paper. It is worth citing Rayleigh's introductory remarks to his 1899 paper:

This subject has been treated in papers published many years ago. I resume it in order to examine more closely than hitherto the attenuation undergone by the primary light on its passage through a medium containing small particles, as dependent upon the number and size of the particles. Closely connected with this is the interesting question whether



This mountain range in British Columbia, far from urban sprawl and sources of air pollution, affords an opportunity to appreciate the brilliant blue color of the daytime sky.

the light from the sky can be explained by diffraction from the molecules of air themselves, or whether it is necessary to appeal to suspended particles composed of foreign matter, solid or liquid. It will appear, I think, that even in the absence of foreign particles we should still have a blue sky.*

The latter was a remarkably cautious statement about the definitive solution to the centuries old enigma. It is worthy of note that today we have come to the complementary realization that the presence of such "particles … of foreign matter" actually degrades the blueness of the sky.

Finally, Rayleigh reaches an important, insightful qualitative conclusion, fully supported by modern theoretical analysis:

If the view, suggested in the present paper, that a large part of the light diffracted from the molecules themselves, be correct, the observed incomplete polarization at 90° from the Sun may be partly due to the molecules behaving rather as elongated bodies with indifferent orientation than as spheres of homogeneous material.

It is of interest that, as late as 1908, Rayleigh's definitive identification of the medium that causes the sky's blueness was still being questioned, and alternative explanations such as ozone fluorescence were still being postulated.

The actual experimental confirmation that air molecules do scatter light was apparently achieved for the first time by Jean Cabannes (1885–1959) in 1913.

Postscript

Why is the clear daytime sky blue and not violet, since violet has an even shorter wavelength? The blue color is the result of the combined effects of the incoming solar irradiance spectrum, the inverse fourth power scattering dependence and the photopic response of the human eye. As da Vinci postulated centuries ago, the blue appearance requires the dark background of empty space beyond the atmosphere. Thus, the irradiance from a background of sun-lit clouds overwhelms that caused by the blue molecular scattering.

Since the blue of the sky is not an intrinsic color of air, the color of any planetary atmosphere viewed against the black of space and illuminated by a sun-like star will also be blue, on condition that Lorenz-Mie scattering and wavelength-selective absorption processes do not predominate, as in the case of Mars with its thin atmosphere and reddish suspended dust, or Venus with its thick sulfuric acid aerosol cloud cover.

Most surprisingly, more than a century after Rayleigh published his solution, present day understanding of the origin of the sky's blueness remains imperfectly disseminated. Respected sources, such as the Encyclopedia Britannica, still misattribute the cause of this phenomenon.

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* Rayleigh's "diffraction" in this context is most probably equivalent to our concept of scattering.