

## FRANÇOIS STANISLAS CLOEZ

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Recibido: 12 de enero de 2017.

Aceptado: 10 de abril de 2017.

Palabras claves: aceite de tung, eucaliptus, fisiología vegetal, meteorito de Orgueil, nitrificación, nuez moscada, ozono, polen, química agrícola, química analítica, química mineral, respiración de plantas.

Keywords: agricultural chemistry, analytical chemistry, eucalyptus, mineral chemistry, nitrification, nutmeg, Orgueil meteor, ozone, plant physiology, plant respiration, pollen, tung oil

**RESUMEN.** François Stanislas Cloez (1803-1881), farmacéutico francés pionero en química y fisiología vegetal, química analítica y química orgánica, estudió el mecanismo de respiración de plantas acuáticas, la absorción de nitrógeno por las plantas, la nitrificación de los suelos, la fotosíntesis en plantas con hojas de color, los venenos de los batracios y salamandras, descubrió las primeras aminas etilénicas. (etiléndiamina, dietiléndiamina, and trietiléndiamina), separó e identificó el eucaliptol, el principal componente del aceite de eucaliptus, sintetizó la cianamida (junto con Cannizzaro), la tricloraacetamida, la primera acetamida clorada, hizo un análisis detallado del famoso meteorito de Orgueil, diseño un aparato para el lavado continuo de materiales pulverulentos o gelatinosos, etc.

**ABSTRACT.** François Stanislas Cloez (1803-1881), French pharmacist, pioneer in the chemistry and physiology of plants, analytical chemistry, and organic chemistry, studied the respiration mechanism of aquatic plants, the absorption of nitrogen by plants, soil nitrification, photosynthesis of colored leaves, the poisons of toads and salamanders, discovered the first ethyleneamines (ethylenediamine, diethylenediamine, and triethylenediamine), isolated and identified eucalyptol, the main component of eucalyptus oil, synthesized cyanamide (together with Cannizzaro), trichloroacetamide, the first chlorinated acetamide, made a detailed analysis of the famous Orgueil meteor, designed an apparatus for the continuous washing of pulverulent or gelatinous materials, etc.

### Life and career<sup>1-2</sup>

François Stanislas Cloez was born in Ors (Nord department, France) on June 24, 1817, within a family of farmers. He received his basic education at the Cateau and Valenciennes schools and then begun his pharmacy apprenticeship in Valenciennes and Tournay. Afterwards he moved to Paris and in 1841 won an internship in the Parisian hospitals, while simultaneously taking proper courses at the *École Supérieure de Pharmacie*. In 1846 he entered the *Museum d'Histoire Naturelle* as *préparateur* of Michel Eugène Chevreul (1786-1889) and begun a long and successful research and teaching career: In 1851 he was appointed *répétiteur* at the *École Polytechnique*, in 1867 professor of physics at the *École des Beaux-Arts*, replacing Louis Pasteur (1822-1895), and in 1872 *examineur de sortie* (students final examination) of the *École Polytechnique*, replacing Victor Regnault (1810-1878). He found enough time to pursue medical studies at the *Faculté de Médecine* of Paris. He did not seem to have been particularly interested in obtaining professional degrees because he waited for more than 20 years before presenting his thesis to the *School of Pharmacy*: In 1866 he was awarded the degree of *pharmacien de première class* by the *École Supérieure de Pharmacie* after successfully defending a dissertation about the oxidation of vegetable fats,<sup>3</sup> and in the same year he was awarded his doctorate *docteur ès sciences* from the *Faculté des Sciences* of the University of Paris, after defending a thesis about cyanic esters.<sup>4</sup> Not surprisingly, he found the time to study and pass all the exams required by the *Faculté de Médecine*, but did not complete the thesis for being awarded the degree. In 1844 he published his first memoir, in collaboration with Bouquet, on sulfo-arseniates, reporting for the first time the synthesis of acids containing simultaneously sulfur and oxygen as electronegative elements.<sup>5,6</sup> The *Société d'Agriculture* awarded him a gold medal for his work on the introduction of yellow horn poppy (*Glaucium flavum*) in non-cultivated terrains near the seashore and the *Académie des Sciences* the *Jecker Prize* for his work in organic chemistry (1877).<sup>1,2</sup>

In 1866 Cloez was appointed Chevalier of the Légion d'Honneur. He was a founding member of the Société Chimique of France and its treasurer and president (1868); in 1879 he was elected senior member of the Conseil d'Hygiène de la Seine, and in 1882 president of the same. In 1878 he was candidate to the chemistry section of the Académie, losing to Charles Friedel (1832-1899) and Louis Joseph Troost (1825-1911).<sup>1,2</sup>

Cloez passed away in Paris on October 12, 1883.

### Scientific work

Cloez wrote about 100 papers, booklets and books in the areas of chemistry and physiology of plants, analytical and organic chemistry, nitrification, animal poisons, metallurgy, etc. He also wrote a short booklet describing his academic activities and his research and results.<sup>7</sup> In addition to the subjects discussed below Cloez studied the extraction of a new acid from the mother liquor of mercury fulminant;<sup>8</sup> use of KI for the analysis of ozone;<sup>9</sup> non-existence of iodine in the atmosphere;<sup>10</sup> use of potassium permanganate as an oxidizing agent in the determination of sulfur in gunpowder and organic sulfur compounds;<sup>11</sup> the states of sulfur;<sup>12</sup> apparatus for continuous washing of precipitates;<sup>13</sup> introduction of yellow horn poppy (*Glaucium flavum*) in non-cultivated terrains near the seashore;<sup>14</sup> relative value of oil-producing plants;<sup>15</sup> a new method for the combustion of organic substances;<sup>16</sup> synthesis of a large number of cyanic ethers, their composition, and isomerization phenomena;<sup>4</sup> chemical composition of the dye green of China;<sup>17</sup> metallurgy,<sup>18</sup> etc.

### Vegetable principles

#### Eucalyptus

Cloez was the first chemist to report on the properties of the leaves and chemicals from eucalyptus. In his first paper on the subject he wrote that Ramel, the well-known traveller, had introduced in France a species of eucalyptus known as *Eucalyptus globulus*, a tree originating from Australia, which grew to very large height and had been discovered by the botanist Jacques La Billardièrre (1755-1834).<sup>19</sup> The parenchyma of the eucalyptus leaves were covered by a number of small transparent vesicles containing an essential volatile oil having a very pleasant aromatic odor.<sup>20</sup> Cloez subjected the leaves to a series of treatments to determine the physiological effects of the resulting materials. A steam distillation of the leaves yielded about 2% of the original weight as an essential colorless oil, lighter than water and having a more concentrated odor of the raw material. The water solution had a fresh, bitter, and agreeable taste and could be swallowed without consequences. Extraction with hot water produced a slightly colored infusion, bitter, astringent, and having a strong smell originating from the rupture of the cells by the high temperature. The solution produced a black precipitate with iron salts and was muddied by gelatin, indicating the presence of tannin. By evaporation it yielded a brown precipitate that the only effect it had on a small dog was an increase in appetite. Calcination and analysis of the precipitate indicated the presence of potassium and calcium salts. The residue of the water extraction was treated with alcohol and ether and the extract found to have similar properties than the aqueous one.<sup>20</sup>

The leaves were slowly burned in a pipe made of metal sheet and the resulting gas separated by successive washings in flasks containing distinct solutions. The different volatile components and the tar produced were found to produce an effect opposite to that of tobacco: more excitant than narcotic. According to Cloez his results indicated the leaves did not contain materials toxic to animals; they could be burned and aspired through the mouth without mayor consequences. The essence they contained seemed to have the same composition as turpentine, constituting another example of isomerism. It had a density of 0.896, boiled at 175°C, and its elemental composition corresponded to the formula  $C_{20}H_{16}$ , for four volumes of vapor.<sup>20</sup>

In a following paper Cloez he reported a more detailed study of the essence extracted from the leaves of eucalyptus.<sup>21</sup> From 10 kg of fresh leaves he obtained 275 g of the essential oil by steam distillation, that is, 2.75 % of the original weight. Using leaves taken from the trees in another geographic region he was able to obtain 489 g of essence from 8 kg of leaves, that is, near 6% of the original weight. These results showed that the oil enclosed in the vesicles was released very slowly. Anyhow, the properties of the oil were independent of the source; it was very fluid, almost colorless, and smelling similar to camphor. It begun boiling at 170°C and continued its distillation until above 200 °C. The first fraction collected, boiling between 170°C and 178°C, after purification with KOH and fused calcium chloride of calcium, was found to boil regularly at 175°C. According to Cloez, this material was a pure immediate principle, different from all other known chemicals, which he named *eucalyptol*. Eucalyptol had specific gravity 0.905 at 8°C; rotatory power +10.42° (for a length of 100 mm); did not freeze; at -18°C and its vapor, mixed with air, was fresh, agreeable when inhaled, and could be employed as a therapeutic agent. Eucalyptol was sparingly soluble in water and very soluble in alcohol; its alcoholic solution, when highly diluted, smelled like rose. An elemental analysis indicated that its composition corresponded to the formula  $C_{20}H_{20}O$  (vapor density 6.22). It was slowly attacked by nitric acid and produced, among others, a crystallizable acid, which did not contain nitrogen and was probably analogous to camphoric acid; treated with concentrated sulfuric acid it turned black and deposited a tarry substance, which by distillation generated a volatile hydrocarbon.<sup>21</sup>

Eucalyptol was attacked by phosphorus pentoxide producing several derivatives. One of them was a colorless liquid of density 0.836 at 12 °C and boiling at 165 °C; its composition seemed to be that of eucalyptol, less one equivalent of

water, that is,  $C_{20}H_{18}$ . Cloez named it *eucalyptene* and assumed it corresponded to cymene. Another product was a liquid boiling at above  $300^{\circ}C$  and decomposing at higher temperatures, which Cloez named *eucalyptolene*. Treating eucalyptol cooled to  $0^{\circ}C$  with a stream of dry HCl gas, it absorbed the gas abundantly and solidified to form a wet crystalline mass, which underwent spontaneous decomposition, into an aqueous solution of HCl and a hydrocarbon, boiling about  $168^{\circ}C$ , and apparently identical with eucalyptene.<sup>21</sup>

A third paper discussed the possible uses of the eucalyptus tree for forestation and construction purposes.<sup>22</sup>

#### Volatile oil from nutmeg

In 1864 Cloez wrote that the aromatic odor and stimulant properties of nutmeg was due to the presence of a significant amount of a volatile oil which had not yet studied and could be partially extracted from the crushed nuts by steam distillation. He believed that a better procedure was to extract the powdered nuts with carbon disulfide or ether, using standard equipment, followed by elimination of the solvent in a water bath and heating the buttery residue in an oil bath at  $200^{\circ}C$ . An even better procedure was to steam distill the residue and recover the essence in a cold recipient.<sup>23</sup>

As stated by Cloez, the resulting essence was not a pure substance because when heated it begun boiling at about  $160^{\circ}C$ ; the temperature remained constant at  $168^{\circ}C$  for some time and then increased to  $210^{\circ}C$ . About 95 % of the original material passed over above  $175^{\circ}C$ ; this distillate had all the characteristics of a hydrocarbon, which could be purified by treating it with pieces of KOH, followed by distillation over a small amount of sodium to eliminate the traces of an oxygenated contaminant that affected significantly its purity. The distilled essence was a very fluid colored liquid with an acrid and burning taste and odor resembling that of nutmeg; it had a density of 0.8355 at  $15^{\circ}C$ , rotational power  $-13.5^{\circ}C$ , and boiled regularly at  $165^{\circ}C$  without alteration. The composition of the essence of nutmeg was the same as that of the volatile oil of turpentine; it contained 87.664% of carbon and 11.814% of hydrogen, per 100 parts of liquid, corresponding to the formula  $C_{20}H_{16}$ . The oil was slightly soluble in water and totally soluble in alcohol.<sup>23</sup>

Exposed to air in a glass bell it slowly absorbed oxygen and lost its fluidity. It was lively attacked by chlorine, liberating HCl and becoming a chlorinated viscous and non-crystallizable matter. The behavior with bromine was similar. Treated with a stream of HCl it absorbed a large amount of the acid and the resulting combination was a well-defined hydrochloride colorless liquid of density 0.9827 at  $15^{\circ}C$  having a disagreeable odor and no rotational power. It was strongly attacked by nitric acid, releasing vapors. The final product contained ammonium oxalate and other non-identified components. Elemental analysis indicated it contained 69.99 % carbon, 10.25 % hydrogen, and 19.57 % chlorine, corresponding to the formula  $C_{20}H_{16}HCl$ .<sup>23</sup>

According to Cloez, the results of his experiments proved that the volatile oil of the essence of nutmeg was a well-defined product, having the same composition as the essence of turpentine but very different properties.<sup>23</sup>

#### Tung oil tree

As described by Cloez, the Tung oil tree of China (*Elæococca vernicia*) is a plant of the family of the Euphorbiaceae that produces a large amount of fruits carrying oily seeds. The seeds submitted to strong pressure in the cold, yield about 35 % per cent of liquid oil, colorless, inodorous, and almost insipid, of density 0.9362 at  $15^{\circ}C$ , and thickening at  $-18^{\circ}C$  without losing its transparency or crystallizing. Cold extraction with ether yielded 41 % of slightly colored oil having all the characters of the oil obtained by pressure. Extraction with carbon disulfide followed by evaporation of the solvent at  $100^{\circ}C$  left a residue that solidified on cooling forming a number of small kidney-shaped masses having a clear crystalline texture, melting at about  $34^{\circ}C$  and possessing the same elementary composition as the liquid oil obtained by pressure.<sup>24</sup>

Cloez found that the difference between the oil separated by mechanical means or with cold ether, and the one extracted with hot carbon disulfide, was a combined effect of heat and air absorption. The properties and composition of the resulting solid were different from the primitive material; it did not melt at  $200^{\circ}C$  and was sparingly soluble in carbon disulfide or ether. The oil extracted by cold mechanical expression had the curious property of solidifying rapidly under the influence of the most refrangible rays of the spectrum (yellow and violet) in the absence of contact with air. The oil of *Elæococca* was the most drying of all known oils; spread on a plate of glass or metal it dried in a few hours on exposure to the air. It was saponifiable by all the caustic alkalis; the resulting soap was crystallizable. Decomposed by phosphoric acid it separated into two phases; the solid one was composed of rhomboidal lamellæ melting at about  $44^{\circ}C$ .<sup>24</sup>

In a second paper, Cloez recalled his previous finding that the oil extracted from *Elæococca* by cold mechanical pressure remained indefinitely liquid when kept in the dark, even at temperatures below  $0^{\circ}C$ , but exposed to sunlight in a closed tube it slowly solidified without changing its weight. The liquid oil and the resulting solid were perfectly neutral; they did not contain free fatty acids and did not release glycerin in contact with water. The alkaline soaps of the oil were decomposed by phosphoric acid producing glycerin and a mixture of two fatty acids. Cloez was able to separate partially both acids by pressing the mixture between sheets of blotting paper.<sup>25</sup>

The solid fatty was purified by successive crystallizations from its alcoholic solution and found to be new chemical compound, which Cloez named *elæomargarolic acid* (elæomargaric acid). The liquid fat was purified by converting it into calcium soap, followed by decomposition with a hot solution of HCl. Cloez named it *elæolic acid*. Cloez

believed that these two new acids seemed to originate from two neutral immediate principles, *elaolin* and *margarolin*, which together constituted the largest part of Tung oil. Margarolic acid crystallized in rhomboidal lamellæ, melting at 48°C; was insoluble in water and very soluble in ether, carbon disulfide, liquid hydrocarbons, and alcohol. Exposed to air it abundantly absorbed oxygen turning in to soft transparent mass, which hardened with time into a resinous varnish. Elemental analysis indicated that it contained, by weight, 71.50% carbon, 10.94% hydrogen, and 17.56% oxygen, corresponding to the formula  $C_{34}H_{30}O_6$ .<sup>25</sup>

In a following paper Cloez described the modifications experimented by elæomargaric acid under the influence of light and heat.<sup>26</sup>

## Plant physiology

### Composition of pollen

As stated by Edmond Frémy (1814-1894) and Cloez, previous researchers had shown pollen to be essentially built of external membranes enveloping an internal substance, which had been named of *fovilla*. The composition of fovilla was very complex; it contained a dense liquid, oily drops, small granular corpuscles, and sometimes starch. Frémy and Cloez decided to carry on a chemical examination of pollen to determine the composition of the membranes covering the grain, and the fatty and viscous substances that were enclosed in this membrane, or on its surface. The latter caused the grains of pollen to adhere one to another.<sup>27</sup>

For their objectives they chose the pollen of the orange lily (*Lilium croceum*) known to contain an amount of this fatty external substance that was extracted easily with ether without altering the grain of pollen. This pollen was of a deep yellow color, unctuous and sticky, insoluble in water, sparingly soluble in cold and boiling alcohol, easily dissolved in ether, non crystallizable, neutral to colored reagents, often holding a powerful waxy odor, and saponifiable with difficulty by alkalis. Elemental analysis of the material showed it contained 79.53-79.65 % of carbon, 12.00-12.09 % hydrogen, and 8.26-8.46% oxygen. The yellow substance coloring the external fatty body of pollen was found to decompose rapidly in contact with the air, under the influence of even diffused light. These results indicated that the external fatty substance of pollen presented a certain analogy to yellow wax; it was not a pure immediate principle for it was formed of a yellow coloring matter, a fatty body saponifiable by alkalis, and of another fatty body, which resisted the action of concentrated KOH.<sup>27</sup>

Additional experiments done with the pollen of white and yellow lily showed it was not affected by cold water but boiling water generated a yellow solution charged with a gummy substance, which proved to be dextrin; prolonged action of heat transformed the dextrin into glucose. These results proved clearly the presence of starch in the interior of pollen and of a ferment (enzyme), which acted on the starch in the same manner as diastase. A nitrogenous substance was also found to be present. Extraction of the pollen with ether or alcohol indicated the presence of an oily substance, easily saponifiable, and containing 75.56 % carbon, 12.90 % hydrogen, and 11.74 % oxygen, a composition very similar to the fatty oil extracted from oleaginous grains. Treatment with several chemical reagents showed the external membranes of the pollen were not formed of cellulose; they resisted the action even of concentrated sulfuric acid, which colored them black but did not dissolve them. Further analysis showed that the nitrogenous substance contained 50.06 % carbon, 7.28 % hydrogen, 30.20 % oxygen, and 12.46 % nitrogen, a composition resembling that of albuminous bodies.<sup>27</sup>

Frémy and Cloez also examined the pollen of two species of pines (*pinus mughus* and *pinus austriaca*) and two species of cattails (*typha latifolia* and *typha angustifolia*), and found that although their shape was different from the pollen of the lilies, they had essentially the same chemical composition.<sup>27</sup>

### Coloring matter of flowers

In a following publication Frémy and Cloez reported the results of their study of the substances coloring flowers. In the introduction they wrote that although many chemists had studied this problem it still remained one of the most obscure subjects in vegetable chemistry. It was accepted that flowers owed their color to non-crystallizable substances that changed their color according to the reagents employed to isolate them and that plants having the most vivid tints contained a very small amount of coloring substance. The color was caused by two substances a blue called *cyanic* and a yellow called *xanthic*. For some time the blue color of blue flowers had been attributed to presence of indigo; but Michel Eugène Chevreul (1786-1889) had disproved this claim by showing that cyanic was always reddened by acids.<sup>28</sup>

Frémy and Cloez isolated the blue principle by extracting the petals of bluebonnet, violet, or iris with boiling alcohol. The blue color of the alcoholic liquid disappeared slowly and was replaced by a yellow brown, a change caused by the prolonged action of the alcohol; the tint reappeared on evaporating the alcohol in the air or by adding water to the concentrated solution. The result of the last operation precipitated a resinous substance while the coloring matter remained in solution and could be precipitated by lead acetate. The green precipitate was washed with a large amount of water and the excess lead acetate eliminated with hydrogen sulfide. Further treatment with alcohol and ether precipitated the blue color in bluish flocks. The resulting blue color, which Frémy and Cloez named *cyanine*, was non-crystallizable; acids turned it red, alkalis green; it combined with lime, baryta, lead oxide, etc., forming green substances insoluble in water; and was decolorized by SO<sub>2</sub>, phosphorus pentoxide, and alcohol. The color reappeared through the presence of the oxygen of the air.<sup>28</sup>

The rose coloring matter was obtained by alcohol extraction of the petals of roses, peonies, some dahlias, etc., similar to the one used to extract the blue color. Frémy and Cloez found that it was a modification of cyanine produced by the action of plant juices: those having an acid character changed the blue cyanine to red while those of blue flowers were neutral. In the presence of alkalis, the rose or red color became first blue and then green.<sup>28</sup>

Frémy and Cloez found that the yellow coloring matter had no relation to cyanine and was composed of two different substances, one totally insoluble in water, *xanthine*; the other very soluble, *xantheine*. The xanthine was mainly extracted from sunflower; it was insoluble in water, soluble in alcohol and ether, had all the properties of a resin and mixed with cyanine it produced in flowers an orange color, a scarlet, and a red. The xantheine was obtained from certain dahlias, it was soluble in water, alcohol and ether, did not crystallize, and alkalis changed it to a very rich brown color and of considerable strength, while acids caused the brown color to disappear. Xantheine combined with metallic oxides forming insoluble yellow or brown lacs.<sup>28</sup>

#### **Decomposition of CO<sub>2</sub> by plant leaves**

It was accepted that foliated plants under the influence of light assimilated carbon by the reduction of CO<sub>2</sub>, giving cause to the disengagement of oxygen. The parts of the plants exposed to the light had various colors, of which green was predominant and typical of young stems, bracts, calyx, etc., and should be considered as essential to the parts that decomposed CO<sub>2</sub>. Certain foliated plants seemed apparently to be deprived of green; their leaves were brown, red, dark purple, etc. Nevertheless, a close inspection of their leaves indicated the presence of green matter. According to Cloez his experiments proved conclusively that by virtue of this part alone they decomposed CO<sub>2</sub> and gave place to plant growth. The fact that the non-green parts of the plant, for example, the wood, roots, most of the petals, the white spots of the leaves, and the leaves, which became totally red or brown in autumn, did not exhale oxygen, did not require accepting Nicolas Theodore de Saussure's (1767-1845) or Benjamin Corenwinder's (1820-1884) opinion that the green color was an essential characteristic of the parts that decomposed CO<sub>2</sub>. These researchers had reached this conclusion from an experiment done with *Atriplex hortensis* (orache), where all the green parts were replaced by red or purple ones. This plant, under water, had provided in five hours seven or eight parts of oxygen, which contained only 15% of nitrogen.<sup>29,30</sup> Cloez reproduced this experiment and obtained the same results but found that the tissue of the red leaves of orache contained a certain amount of green matter masked by a violet red principle.<sup>31</sup>

To prove his hypothesis, Cloez carried on additional experiments using *Amaranthus tricolor*, a species of ornamental amaranth having leaves dotted with green, yellow, and red spots. He separated the different spots with a pair of scissors and subjected them under conditions as similar as possible to the action of light while submerged in degassed water containing a small quantity of CO<sub>2</sub>. The results indicated that only the green parts were able to produce oxygen. The yellow and red spot showed no gas disengagement during twelve hours exposure to sunlight. To further substantiate his results Cloez repeated the experiment using the leaves of *Amaranthus caudatus* where the three colors (green, red, and yellow) are intimately mixed. As expected, the leaves of *Amaranthus caudatus* released a much smaller amount of oxygen (148 cm<sup>3</sup>) than the green spots of *Amaranthus tricolor* (245 cm<sup>3</sup>).<sup>31</sup>

#### **Respiration by submerged plants**

In 1850 Georges Ville (1824-1897) published a paper reporting his findings on the assimilation of nitrogen by plants and the possible influence exerted by ammonia on vegetation.<sup>32</sup> In his experiments Ville planted a certain number of seeds in pots filled with a bed made of equal parts of white sand and powdered brick, which had previously been calcined for several days in order to eliminate all the possible organic matter they contained. The bed was mixed with 5% its weight of ashes produced from plants originated from the soil where the seeds normally developed. The pots thus seeded were put under a glass bell closed hermetically. The internal gas atmosphere was renewed daily with fresh air enriched with CO<sub>2</sub> and the emerging stream analyzed for ammonia content. According to Ville, the results of his experiments demonstrated that the plants assimilated directly atmospheric nitrogen and atmospheric ammonia played no sensible role.<sup>32</sup>

In an additional series of similar experiments a certain amount of ammonia was put inside the glass bells. In this situation Ville observed that there was a clear influence of ammonia, the leaves of the plants had taken a greener and more vivid color, the stems had grown higher, and more branches had developed and carried a larger number of leaves, particularly with cereals.<sup>32</sup>

Ville's results were strongly criticized by Cloez and Louis Pierre Gratiolet (1815-1865). In their immediate reply<sup>33</sup> they wrote that they had been conducting researches on vegetation for more than three years and had not desired to publish their results until they had attained the greatest degree of accuracy and extent of which they were susceptible. They had performed their experiments in Chevreul's laboratory, in the Museum of Natural History, and under his auspices. It was well known that the green part of plants decomposed CO<sub>2</sub> and disengaged the oxygen from it. This process was particularly fast in submerged aquatic plants, and they separated more oxygen in a given time than most other plants. For this reason they selected for their experiments different species of *Potamogeton*, *Naias*, *Ceratophyllum*, *Myriophyllum*, and *Conferva*. The results of their experiments indicated that (1) oxygen was disengaged rapidly in sunlight, insensibly in diffused light, and not at all in darkness. In the latter case, no CO<sub>2</sub> whatever was given off by plants, contrary to what was generally supposed; (2) decomposition was most rapid under

colorless unpolished glass; followed by yellow glass, colorless transparent glass, red, green, and lastly, blue glass; (3) the decomposition of CO<sub>2</sub> by aquatic plants exposed to light in a temperature raised gradually from 4°C did not begin until the temperature had increased to 15 °C, reaching a maximum at 30 °C. The decomposition of CO<sub>2</sub> by plants exposed to light in a temperature that was lowered from 30°C continued when the temperature was lowered all the way down to 11°C and stopped completely at 10 °C; (4) vegetation of submerged plants continued for several months in water of the Seine aerated and renewed every day. In river water degassed by boiling and containing CO<sub>2</sub> in the same proportion as Seine water, and also renewed every day, decomposition was initially very active, then slowed somewhat and ceased entirely at the end of 4 or 5 days. After this time the green color of the plants was clearly less intensive, and (5) the phases of this phenomenon were remarkable. The gas initially formed was mixed with a certain quantity of nitrogen, which diminished little by little, so that the last portions of disengaged oxygen were nearly pure. The total quantity of nitrogen disengaged was much larger than the volume of the plant. For equal weights of the plant it was found that it contained less nitrogen than another portion of the same plant not submitted to the experiment. These facts proved that in the vegetation of submerged plants nitrogen was produced from the decomposition of their very elements; a fresh supply was therefore necessary and that nitrogen, free or combined, constituted an *article of food* essential to the life of an aquatic plant.<sup>33</sup>

Another series of experiments was devoted to study the influence of ammonia and its salts in the vegetation process. The results indicated that ammonia and its salts, dissolved in 10,000 times their weight of water, were always harmful. The decomposition of CO<sub>2</sub> diminished, and ceased at the end of a few hours. The obvious conclusion was that nitrogen dissolved in water was directly assimilated by the plants employed in our experiments.<sup>33</sup>

An interesting result was that independently of the position of the leaves of a Potamogeton were placed in water, calcium carbonate was constantly deposited on the upper, and never on the lower surface of the leaves (upper and lower being used in their botanical sense). This result seemed to show that CO<sub>2</sub> was essentially absorbed by the upper surface of leaves. The oxygen produced by the decomposition of CO<sub>2</sub> had a perfectly defined course: It constantly descended from the leaves towards the roots.<sup>33</sup>

The detailed memoir published a year later started with an historical review of the knowledge about the physiological role of leaves of submerged plants under different conditions of temperature, light, and salts present in the liquid. This was followed by a thorough description of the different pieces of equipment and experimental procedures employed for studying the different phenomena accompanying vegetation, as well as tables providing quantitative results for the different conditions, for example, effect of glasses of different colors, influence of the media and the temperature, vegetation of aquatic plants growing in natural water constantly renewed, water degassed by boiling and artificially impregnated with a little of CO<sub>2</sub>, movement of the elements absorbed and released by the plants, etc.<sup>34</sup>

Cloez and Gratiolet reached the following conclusions: (1) the green parts of submerged plants decompose CO<sub>2</sub> only under the influence of light; (2) no CO<sub>2</sub> is produced in the darkness; (3) the influence of light filtered through a colored glass decreases in the order colorless and frosted, yellow, colorless and transparent; red, green and blue; (4) a certain temperature is needed for the phenomenon to occur, when the temperature is increasing it starts at 15 °C, when it decreases it can continue all the way down to 10°C; (5) the salts and air dissolved in natural water are indispensable for the duration of the process; (6) the gas released by the plant contains oxygen and a certain amount of nitrogen. The latter originates mostly from the decomposition of the plant itself; (7) the nitrogen from the air dissolved in the water seems to repair this loss; its presence is indispensable; (8) ammonia and its salts dissolved in the water up to 1/10,000 parts led rapidly to the death of aquatic plants, (9) absorption of CO<sub>2</sub> takes place in the upper face of the leaves; and (10) the oxygen produced by the decomposition of CO<sub>2</sub> descends from the leaves to the roots through the intercellular passages.<sup>34</sup>

In a later paper Cloez provided additional experimental results proving that the gas released by aquatic plants was nitrogen pure, and not a mixture with combustible gases.<sup>35</sup>

### Nitrification

It so happened that Cloez was present during the test of Ville's results conducted at the Museum of Natural History, under the inspection of a committee of the Academy of Sciences. The phenomena observed led him to consider in a more general way the question of the assimilation of nitrogen by vegetables. He asked himself if plants were able of directly absorbing the nitrogen in the state of simple gas, as it existed in the atmosphere, or could they assimilate it only when it was in the form of a binary combination, as ammonia and nitric acid, or were they were able to derive their nitrogen simultaneously from both these sources. His experiments about the property possessed by plants exposed to the light of disengaging oxygen by the decomposition of water and CO<sub>2</sub> had led him to consider the possibility that the nitrogen present in plants could originate principally from the nitrates which existed, or could be formed in the soil in which they grew.<sup>36</sup>

Cloez understood that the natural conditions favored the formation of nitric acid: nitrogen and oxygen in the atmosphere, moisture, alkaline substances in the ashes added to the soil, a porous structure, etc. For these reasons he decided to conduct a series of carefully conducted experiments to test this possibility. In his experiments he passed a current of air, free of acid and ammonia vapors, through a series of flasks filled with fragments of a porous substance, impregnated with an alkaline or earthy carbonate. Previous to admission, the air was purified by bubbling

successively through a series of wash flasks containing an alkaline carbonate to eliminate acid vapors, dilute sulfuric acid for absorbing ammonia, and concentrated sulfuric acid to retain the humidity. The purified air was passed through 20 flasks filled with pieces of different porous materials (e.g. new brick previously calcined, pumice, calcined porous bones, calcareous marl, chalk, kaolin, clay, etc.) mingled with pure or mixed chemicals (e.g. carbonates of calcium, magnesium, potassium, etc.), dried or in solution. All the porous materials had been properly treated to eliminate all nitrogenous or ammoniacal substances. For example, pumice was first calcined with sulfuric acid, afterwards washed with distilled water, and then again heated to redness, without the addition of acid. The experiment was commenced on September 15, 1854, and concluded towards the end of the following April, at which time saline efflorescence appeared in some of the flasks.<sup>36</sup>

Analysis of the contents showed the presence of a considerable amount of nitrates in the flasks containing brick, calcined pumice and ordinary pumice; a small amount of the same salts in the flasks containing chalk, pure calcareous marl, the marl containing alkaline carbonate; and none in the pots containing calcined bones, or clay. According to Cloez, the results of his experiments showed clearly that a current of air freed from acid and ammoniacal vapors, in passing through porous matters, may give rise, in certain cases, to the formation of nitric acid and nitrates.<sup>36</sup>

In a class given to the member of the Société Chimique de France in 1861, Cloez gave an historical review of the theories regarding nitrification and the role of nitrates on vegetation, and a more detailed explanation of the experimental equipment and procedure, results, and analysis of the same.<sup>37,38</sup> Two interesting consequences were that plants did not assimilate nitrogen directly from the atmosphere and that porosity alone was not enough to induce the synthesis of nitric acid, even in the presence of water and alkalis. He could not explain it but assumed that in the case of bricks it could be due to the presence of an oxidizable substance, such as iron sulfide.<sup>37,38</sup>

### Oxidation of drying oils

As mentioned before, one of the theses presented by Cloez to the École Supérieure de Pharmacie de Paris to obtain the degree of pharmacist of first class was devoted to the study of the oxidation of drying oils.<sup>3</sup> It was preceded by the publication of several short memoirs describing part of his results.<sup>3,39-41</sup>

The first publication reported the experiences done previously by Chevreul about the action of air upon vegetable fats and their confirmation and extension by Cloez.<sup>39</sup> Cloez wrote that during two years he had carried on 208 experiments on oils derived from 140 species of plants belonging to different families. As an example, he reported in detail the measurements he had performed on the fruits of African oil palm (*Elaeis guineensis*). These included the analyses of the hulk and the grain (humidity at 100°C, incineration residue, percent of solid fatty material, and density at 15 °C).

Cloez wrote that it was well known that fatty materials exposed to the air changed more or less rapidly and that the alteration was due to the absorption of oxygen. For these reasons oils were classified arbitrarily into drying and non-drying oils; the first class included the oils that became dry in contact with air.<sup>3,40,41</sup> Cloez's experimental program was devoted to study (a) the action of air at atmospheric temperature on 50 species of vegetable oils, (b) the action of an air stream on four different oils, two drying (linseed, and poppy oil) and two non-drying (sesame and castor), heated to 100°C, (c) the influence of darkness and light of different colors on the oxidation rate of the same oils, exposed to air at room temperature, (d) the influence of pure oxygen on these oils at room temperature and at 150 °C, (e) the action of ozonized air, hydrogen peroxide and other oxidative reagents, and finally (f) the products resulting of the oxidation of oil after a long exposure to air. In every case he determined the weight of a given volume of the particular grain, the water lost by drying at 100°C, the percentage of fatty material present in 100 g of grains in their normal state and at 100°C, the amount of ashes produced by incineration of 100 g of the grains, the specific weight of the solid or liquid fat at 15 °C, and the solidification point. He took all the necessary precautions to assure that the different experiments were conducted, as much as possible, under the same conditions. He provided a detailed description of the procedures for determining the weight of the grains, their drying, the extraction of the fatty material, incineration, and determination of the specific gravity of the fatty substances. The experiments on the influence of light and heat were conducted in cages built of colorless, red, yellow, green, or blue glass, or in the darkness. The pertinent results were summarized in tabular form, expressing the outcome of the exposure of 50 different grains after exposure to air for 150 days. Before initiation of the process each fat was analyzed for its content in carbon, hydrogen and oxygen.<sup>3,40,41</sup>

Cloez summed up the results of his investigations as follows: (1) All fatty oils, without exception, absorbed oxygen from the air and increased in weight; an interesting characteristic of this phenomenon was that the increase in weight was not continuous until the end of the process: it increased up to a maximum and then it began to decrease. The pertinent graph showed a curve going up to a maximum point followed by a slow decrease down to a line parallel to the abscissa (time); (2) elevation of temperature exerted a strong influence of the rate of oxidation; the oxidation could be very much accelerated without the application of heat, by the simple addition of a small quantity of oil of the same kind, which had been previously thickened by exposure to the atmosphere, thus oil for painting could be prepared so as to be perfectly colorless, and consequently to produce no diminution of the brilliancy of the colors; (3) the intensity of light also had a marked influence on the progress of the phenomenon; (4) light transmitted through colored glass retarded more or less the oxidation of the oil by air. Starting from colorless glass, as the term of comparison, the decrease in the rate of oxidation was in the order is increased by colored glass in the order blue,

violet, red, green, and yellow; that is, oil covered with yellow glass, oxidized most slowly; (5) In the dark the oxidation progressed very slowly; it started later and progressed slower than in light; (6) The presence of various matters and the contact with certain substances accelerated or retarded this effect; (7) the resinification of oil occurred with loss of both carbon and hydrogen and absorption of oxygen; part of the disappearing carbon appeared as CO<sub>2</sub> and the rest as acrid and suffocating vapors, which gave the odor called *rancid* to the oil; some of the components of the emanation were formic, acetic, acrylic, and butyric acids, and probably acrolein. Most of these arose from the decomposition of glycerin; butyric acid was the only component resulting from the oxidation of the fatty acid. During oxidation in a confined space acid vapors accumulated and produced ill effects on animals or individuals who breathed them; (8) the oxidation of various oils in oxidizing furnished in general the same products; gaseous and volatile compound acids, unchanged solid and liquid fatty acids, and a solid, insoluble matter, which appeared to be a definite immediate principle. Oils oxidized in the air no longer contained glycerin; (9) drying oils and non-drying oils were not chemically distinguishable, all contained the same glyceric proximate principles but in different proportions; and (10) as assumed previously, the presence of albuminoidal matter, mucilage, etc., in vegetable oils did not promote their oxidation. Oils perfectly free from such matters oxidized as rapidly in the air as those contaminated by them. Boiling water had little action on the oxidized oil; alcohol and ether dissolved out a thick fatty matter, which, among other substances, contained unchanged margaric and oleic acids.<sup>3,39-41</sup>

### Poisons of the salamander and toad

Gratiolet and Cloez wrote that it was a very ancient and widely spread opinion among the people that the salamander (*Lacerta Salamandra*, Linn.) possessed a very subtle venom, and a strong bitterness was attributed to the viscid and milk-looking liquid secreted by the cutaneous pustules of this animal. The accidental observation that some frogs put in a tub with some salamanders were found dead after a week led these two chemists to study in detail the supposed venom of the salamander.<sup>42</sup>

The liquid withdrawn from the cutaneous pustules of the salamander was white and had a very powerful foul odor. At the moment of extraction from the pustule it flowed like thick milk, but it soon coagulated. Addition of alcohol caused its immediate coagulation. Put under the skin of the wing or thigh of a small bird did not seem to possess the causticity attributed to it, but after a short time the bird became highly perturbed and rapidly died. A similar behavior was observed with other small and large birds, showing that all birds submitted to the action of the milky liquid of the salamander suffered epileptiform convulsions. Small mammals such as guinea pigs and mice showed a different behavior: After about 10 minutes, all of them manifested great anguish, their respiration became rapid and painful, they slept every instant and their sleep was interrupted by slight convulsions, like electrical shocks. But at the end of a few hours these symptoms disappeared and the wounded animals were restored to health. These results showed that the symptoms experimented by mammals were not mortal.<sup>42</sup>

Gratiolet and Cloez completed their experiments examining the milk-looking liquid contained in the dorsal and parotid pustules of the common toad (*Rana bufo*). This yellowish liquid was thick and viscid; it had a foul smell and an intolerable nauseous bitter taste and powerfully acid reaction. Birds inoculated with it died in five or six seconds, without convulsions; the same results were obtained with the dried liquid. Gratiolet and Cloez did not conduct a pathological examination of the birds but believed they had died of cerebellar apoplexy.<sup>42</sup>

In a following publication Gratiolet and Cloez reported that they had dried the poisonous liquid of the toad and found that after one year it still kept its deadly properties. This significant result led them to try to isolate the active component present in the poison. The dry substance was extracted with ether and the resulting solution evaporated. A microscopic examination of the residue showed it was formed of oily granules containing small crystal shaped needles. This residue was found to be a very powerful and mortal poison; it killed birds in less than four minutes. Separation and testing of the oily substance showed it was not poisonous. The crystalline solid poison was purified by extraction with alcohol and crystallization from the alcoholic solution. It was found to be completely soluble in water strongly acidified with HCl; this solution produced a yellow precipitate with platinum dichloride and an abundant white precipitate with HgCl<sub>2</sub>. The latter results indicated the possible presence of an alkaloid; for this reason it was treated with ammonia and the resulting flocculent precipitate was found to be insoluble in water and soluble in acetic acid. The acetic solution was evaporated and the crystalline residue injected to a linnet (*Carduelis cannabina*). After sometime the bird became paralyzed and died after suffering a large number of tetanus attacks.<sup>43</sup>

## Chemistry

### Cyanamides

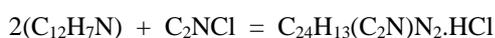
In 1838 Amand Bineau (1812-1861) described the synthesis of a large number of ammonia derivatives, among them ammonium chlorocyanide. He reported that the gases cyanogen chloride (CICN) and ammonia reacted almost immediately to produce white crystals of ammonium chlorocyanide, which he believed was represented by the formula C<sub>4</sub>N<sub>2</sub>Cl<sub>2</sub>·2N<sub>2</sub>H<sub>6</sub>.<sup>44</sup> In a paper published in 1851 Cloez and Stanislaw Cannizzaro (1826-1910) reported that the results they had obtained while trying to synthesize the new bases of Charles-Adolph Würtz (1817-1884) by reacting cyanogen chloride with ammonia,<sup>45</sup> had led them to re-examine the results of Bineau about ammonium chlorocyanide. They promptly realized that this substance was actually a mixture of ammonium chloride and an

amide having the formula  $C_2H_2N_2$  (the actual formula is  $CH_2N_2$ , using the modern values of the atomic mass of carbon and nitrogen), which they named *cyanamide*.<sup>46</sup>

They described cyanamide as a white crystalline substance, melting at  $40^\circ C$ . At about  $150^\circ C$  the liquid suddenly solidified with a large release of heat and became a compound having the same composition of cyanamide, but different properties. Cloez and Cannizzaro believed that the solid had the same properties of melamine and should be considered the amide of cyanuric acid (*cyanuramide*). Cyanuramide was stable in contact with dry air and soluble in water, anhydrous alcohol, and ether. Evaporation of the aqueous solution left a solid residue, almost insoluble in water, which Cloez and Cannizzaro believed was cyanuramide.<sup>46</sup>

The experimental results of Cloez and Cannizzaro indicated that the volatile bases discovered by Würtz, and a large number of organic bases, behaved in the same manner as ammonia with cyanogen chloride, the resulting product was the hydrochloride of the base and the corresponding cyanic amide (cyanomethylamide,  $C_4H_4N_2$ , cyanoethylamide,  $C_6H_6N_2$ , and cyanamylamide  $C_{12}H_{12}N_2$ ). Cyanamide was easily prepared by bubbling dry gaseous cyanogen chloride through an ethereal solution of ammonia. The precipitate of ammonium chloride formed was separated by filtration and the filtrate distilled to dryness over a water bath.<sup>46</sup>

August Wilhelm Hofmann (1818-1892), found that the reaction between aniline and cyanogen chloride resulted in the formation of the hydrochloride of a base containing the double equivalent of aniline where one "molecule" of hydrogen and been replaced by one "molecule" of cyanogen (*melaniline*)<sup>47</sup>:

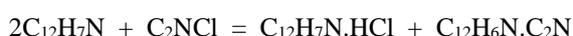


Cahours and Cloez compared this result with one obtained by Cloez and Cannizzaro, where ammonia and cyanogen chloride produced a mixture of crystalline ammonium chlorine and cyanamide:



and decided to investigate if ammonia or aniline were an exception to the ammonia conjugated bases.<sup>48</sup>

Bubbling pure and dry cyanogen through an ether solution of aniline contained in a vessel surrounded with crushed ice, formed a crystalline deposit of pure aniline hydrochloride and evaporation of the residual liquid left reddish translucent mass resembling colophony, which after purification proved to be *cyanic anilide*:



Heating an equimolar mixture of aniline hydrochloride and cyanic anilide resulted in formation of a solid substance having all the properties of melaniline. The same results were obtained with toluidine and naphthalidam. Methylaniline, ethylaniline, amylaniline, methylamine, ethylamine, amylamine, diethylamine, methylethylamine, and diamylamine, yielded the corresponding cyanic alkylanilide. All these compounds proved to be weak bases, capable of combining with concentrated acids and forming compounds, which decomposed in the presence of an excess of water. Cahours and Cloez concluded that all these reactions could be represented by the general formula



At the conclusion of their paper Cahours and Cloez described a very simple process for preparing cyanogen chloride: 100 g of mercuric cyanide and 4 liters of water are introduced into a bottle of capacity 6 liters and then the water saturated with chlorine at  $0^\circ C$ . A considerable amount of HCl is formed and the mercuric cyanide is converted in the course of 24 hours into mercuric chloride, which precipitates, and cyanogen chloride, which remains dissolved. Heating the remaining solution releases the cyanogen chloride, which is purified by passing over of turnings of copper and a calcium chloride.<sup>48</sup>

### Oxidation of benzene

In 1858 Cloez and Charles-Ernest Guignet reported that potassium permanganate was able to convert nitro derivatives into potassium nitrate. Among the many examples, they mentioned that nitrobenzene was converted into a salt crystallizing as large rhomboidal blades, which were little soluble in water.<sup>49</sup> The details of this particular reaction were discussed in another paper where they reported that boiling nitrobenzene with potassium permanganate precipitated manganese oxide and left a solution containing potassium carbonate, potassium nitrate, potassium oxalate, and a potassium salt containing an acid sparingly soluble in water. This acid precipitated when adding HCl to the solution separated by filtration. Cloez and Guignet mentioned that the oxidation of nitrobenzene was unruly and for this reason decided to exchange potassium permanganate by a mixture of nitric acid and potassium dichromate. This new reaction took place smoothly and was terminated when the orange color of the dichromate changed to the green of chromium nitrate. Similar results were obtained with a mixture of potassium dichromate and dilute sulfuric acid. The new potassium salt was soluble in nitrobenzene and precipitated upon cooling. The resulting crystals were purified by solution in ammonia, precipitated again with HCl, and by water washes.<sup>50</sup>

The purified acid had a piquant acrid taste and could be further purified by sublimation. The resulting crystals were sparingly soluble in cold water and more soluble in boiling water. They dissolved easily in alcohol, ether, nitrobenzene, and acetic acid. Elemental analysis indicated that its global formula was  $C_{18}H_7(NO_4)O_6$ , which Cloez and Guignet believed corresponded to an oxidation product of nitrocinnamic acid. They also mentioned that they had conducted the reaction with commercial nitrobenzene and thus the acid could have originated from the oxidation of an impurity.<sup>50</sup>

### The Orgueil meteor

On May 14, 1864, at eight in the evening, a large meteor, "about half the size of the moon", split into many pieces, which fell in the neighborhood of the village Orgueil (southwest of France). A piece of the meteor was partially analyzed by Gabriel-Auguste Dubrée and then in detail by Cloez.<sup>51-53</sup> A first examination indicated the stone in contact with water disintegrated completely into extremely small particles that remained suspended in the liquid for a long time. This disintegration was the result of the dissolution of the abundant saline matter (about 5.3 % of the total weight) present in the meteor, which acted as a sort of cement. The saline matter contained ammonium, potassium and sodium chlorides, magnesium and calcium sulfates, etc. Absolute alcohol produced the same effect. Heating a sample in a small tube resulted in the release of water vapor, which condensed in the cold end of the tube. At a higher temperature a deposit of ammonium chloride and ammonium carbonate deposited slightly above the zone being heated. The sample examined was black and had a density of 2.567; in contact with air the color changed to ochreous red. The black color of the stone suggested the presence of carbon in the state of graphite, and maybe also in the state of organic matter. Combustion of the sample yielded  $CO_2$  in an amount of carbon corresponding to 5.92 % of the original weight. Hydrochloric acid dissolved most of the sample with the simultaneous release of hydrogen sulfide; the resulting solution was colored yellow green and contained ferrous oxide and iron sesquioxide. The stone was strongly attracted by a magnet, indicating the presence of a substantial amount of magnetic iron. Additional analysis indicated the presence of a very small amount of nickel and chromium.<sup>51</sup>

Cloez looked first for the presence of water and noticed that this substance was retained in the hygroscopic state. Heating various samples to  $110^{\circ}C$ , under vacuum and in the presence of sulfuric acid, showed a decrease in weight from 5.2 to 6.9 %. About 8 to 10 % of water was also present in a combined state and could be released only at temperatures above  $200^{\circ}C$ ; more water was produced when heating the sample to about  $300^{\circ}C$  in a tube containing an oxidizing substance, probably originating from the partial combustion of the hydrogen present in a humic organic substance. Analysis of the latter indicated that it contained, by weight, 63.45 % carbon, 5.98 % hydrogen, and 30.57 % oxygen. According to Cloez, this composition was very similar to the turf formed in bogs by the decomposition of aquatic plants. A more detailed analysis of the meteorite indicated the presence of 5.975 % hygroscopic water, 24.475 % silicic acid, 2.195 % sulfuric acid, 4.369 % sulfur, 0.073 % chlorine, 1.175% alumina, 0.225 % chromium oxide, 13.324 % ferric oxide, 17.924 % ferrous oxide, 2.450% nickel oxide, 0.085% cobalt oxide, 1.815% manganese oxide, 8.163 % magnesium oxide, 2.18 3% calcium carbonate, 1.244 % sodium, 0.307% potassium, 0.098 ammonium, 6.027 % humic substance, 7.345% combined water, and traces of phosphorus (for a total of 96.442 %). Another analysis indicated that the meteor contained carbon in the amount equivalent to a little over to 0.5 % weight.<sup>51,52</sup>

The presence of organic matter in the Orgueil meteor gave place to a hot scientific discussion about the possibility that it might have a biological origin. Cloez himself wrote "la composition de cette matière charbonneuse semble indiquer l'existence de êtres organisés dans les corps célestes (the composition of these carbonaceous matter seems to indicate the existence of organized organic beings in celestial bodies).<sup>7,53</sup>

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