Marie Curie and the Discovery of Radium

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Abstract. Marie Curie gave outstanding contributions to science and society that were recognized still in her lifetime. In particular, the discovery of radium completely changed the therapeutic methods for treatment of cancer and other diseases, and allowed the development of radiotherapy and nuclear medicine. Radium was also used in many non-medical applications. Radium applications fostered the growth of uranium mining industry during the first half of 20th century. During the second half of the past century, with developments of artificial radionuclides production and particle physics, radium was gradually replaced by shorter-lived radionuclides and electron and photon beams in cancer therapy. In the 70s and 80s most radium sources in cancer hospitals were replaced while in non-medical applications radium had been substituted already. Notwithstanding, the avenue for medical use of radioactivity and radionuclides opened with Marie Curie discoveries and radium applications still goes on. This avenue is currently pursued in curietherapy and nuclear medicine.

Introduction

This year one completes the 100th anniversary of the Chemistry Nobel Prize awarded to Marie Curie in 1911 for the discovery of radium and polonium, two radioactive elements she identified and separated from uranium ore. These discoveries were made based on measurements of ionizing radiation emitted by the ore and they steered a fantastic number of scientific discoveries made during the first

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half of 20th century. Likewise, they paved the way to numerous radioactivity applications, particularly in medicine (NN 2011, Fevrier 2011).

In all the research she made, Marie Curie revealed a curious mind, open to novelty, while keeping an unfailing application of the scientific method in hypothesizing, planning experiments, interpreting results and reporting the findings. Furthermore, she combined that with perseverance, hard work, and thoroughness in the laboratory experiments, while fighting for research funding and teaching in the University. In those days these were not activities of easy access for a woman.

Marie Curie was also a woman sensitive to the problems of her time and, beyond her work for radium application in medicine, she was active in societal matters providing her direct contribution. Just two examples are given here. One, during the First World War, when she installed X-rays apparatus on cars, called the "little curies" and worked as volunteer radiographer in the screening of wounded to support medical surgery near the war front line. Other, when after the war she acted as one of the founding members of the Commission for the Intellectual Cooperation of the Society of Nations, which is an ancestor of UNESCO (NN 2011, Fevrier 2011, Curie E. 1938).

The history of scientific contributions given by Marie Curie has common roots with the uranium mining history. It is therefore appropriate to remind and celebrate her scientific discoveries here.

Marie Curie (1867–1934)

Borne Manya (Marie) Sklodowska, in Warsow, Poland, she was the youngest of the five children of a couple of school professors. In 1891 she travelled to Paris, joining her sister Bronya who had concluded studies in Medicine. In Paris, Marie Sklodowska followed courses in the Faculté de Sciences de Paris, and obtained her diploma in Physics in 1893, and in mathematics in the following year. Marie met Pierre Curie, Professor and researcher at the Paris University, in 1894 when she started research for her doctoral thesis in his laboratory. They married in 1895 and had two children, Eve and Irene. In 1898, with Pierre Curie, she discovered two new elements, polonium and radium. Pierre passed away in 1906, victim of an accident. She continued research isolating polonium and radium to fully demonstrate the existence of the elements discovered through their radioactive emissions. She was awarded two Nobel Prizes, one in 1903 together with Pierre Curie and Henri Becquerel for the discovery of radioactivity, and other in 1911 for the discovery of polonium and radium (Fig. 1). In 1910 she published her "Traité sur la Radioactivité". In 1914 the Institute du Radium de Paris was built, but with the start of the First World War, the opening was postponed. She helped, together with her daughter Irene as radiologists at the war front. After the war, she resumed her research on radioactive elements in the Institute du Radium. She visited the USA in two occasions, in 1921 and 1929, and received each time a donation of 1 g radium. The first she used in the Radium Institute in Paris and the second she

Fig. 1 Marie Curie aged 44, the year she received the Nobel Prize of Chemistry

offered to the Radium Institute in Warsaw. Marie Curie deceased in 1934 victim of leukemia caused by the exposure to ionizing radiation for many years. Her body ashes, as well as those of Pierre Curie, were transferred in 1995 to the Pantheon, in Paris (NN 2011, Fevrier 2011, Curie E. 1938).

The Discovery of Radium

Near the end of the 19th century, in 1895, Conrad W. Roentgen discovered the X-rays, the new type of radiation that allowed seeing internal structures of opaque bodies. This was followed by the discovery of the "uranic rays" made by Henri Becquerel in 1898, during his research on the phosphorescence of uranium salts.

When Marie Sklodowska, a young Polish lady that had completed the Degrees in Physics and Mathematics at the Sorbonne University in Paris, arrived in 1894 in Pierre Curie's laboratory at the Faculté de Sciences looking for a doctoral research subject, she considered first to work on X-rays. However, although very recent this subject had been already thoroughly investigated in comparison with the "uranic rays". Until late 1896 about 1000 articles and 50 books had been published already on Roentgen radiation (X-rays), while the Becquerel "uranic rays" were still mysterious and only 20 articles had been published on this subject. Furthermore, a new instrument recently invented by Pierre Curie and his brother Jacques, the Curie's electrometer that allowed much more precise measurements of the air ionization by radiations, might have contributed to Marie Sklodowska's selection of "uranic rays" as the subject for her research (NN 2011).

She started work in Pierre's laboratory in Rue Lhomond, Paris, using pitchblende uranium ore from the Joachimstal mine in Poland, at that time ruled by Austria. She tried to identify which substances and minerals besides pitchblende could also emit ionizing radiation. For this purpose she tested all compounds and minerals she could find in the Sorbonne University and noted that all uranium salts emitted radiation. She observed the same emission also with thorium salts, not being aware that in Germany another scientist had discovered the radiation emitted by thorium a few weeks before.

She focused her attention on the pitchblende from Joachimstal mine and noted that this rock emitted about 2.5 times more radiation than explained by the rock uranium content. She wrote on her laboratory note book: "I searched whether other substances, besides uranium compounds, could be susceptible of ionizing the air and allowing for electric conductivity". She found that all uranium salts and natural uranium phosphate were even more active than metallic uranium and about this she wrote: "This is an outstanding fact and makes one to think that these ores may contain another element much more active than uranium" Curie M. (1921).

Using another supply of uranium ore she initiated a lengthy and laborious chemical procedure to extract the mysterious radioactive element. Her husband Pierre Curie joined her in this research and they looked also into the collaboration of a chemist, Gustav Bémont, Professor at the École de Physique et Chimie de la Ville de Paris. For this work they could only use a shed in the university yard. There Marie treated the ore and, following Fresenius chemistry methodology, she separated several salt fractions and measured the radioactivity in each fraction (NN 2011, Fevrier 2011).

In the bismuth fraction, she measured a strong radioactivity emission, and they wrote about this in her article to the Académie des Sciences: "We believe that the substance extracted from the pitchblende contains an unknown metal with analytical properties close to those of bismuth. If the existence of this metal is confirmed we propose to name it Polonium, according to the name of the country of origin of one of us". The symbol Po is written for the first time in the laboratory note book on 13 July 1893 by the hand of Pierre Curie. The article published in the Comptes-rendus de l' Académie des Sciences announces the discovery of a new element, more radioactive than uranium, but not seen as yet. The word radioactive was used for the first time in this article (Curie & Curie 1898).

The research by the Curies on the radioactivity of uranium ore was not over yet. In the physical and chemical separation procedure applied to treat the uranium ore, they observed also high radiation emission in another chemical fraction containing barium. They hypothesized that eventually other substance with a chemical behavior close to barium could be present. They planned to check this hypothesis in a three step approach. Firstly, they checked that normal barium was not radioactive. Next, they found out that a radioactive substance could be concentrated through fractional crystallization starting with the radioactive barium chloride fraction obtained from the pitchblende. At last, they pursued this separation procedure until obtaining a chloride salt with 900 times more radioactivity than metallic uranium (Curie 1921).

The emission spectroscopy analysis of this salt revealed that the lines observed did not match any known element and their intensity increased along with radioactivity increase, i.e., with the purification of the chloride, while barium lines decreased in intensity. The Curies wrote: "There is a strong reason to believe that the substance obtained contains a new element. We propose to name it as Radium. This new radioactive substance obtained probably still contains a large amount of barium mixed therein, but radium radioactivity seems enormous" (Curie et al. 1898). In their laboratory notebook the word Radium, followed by a question mark, was first annotated on the 18 November 1898.

The acceptance of this discovery was dependent upon separation, purification and chemical characterization of the element with confirmation by spectroscopic emission that the element emission spectrum was different of known elements.

Marie Curie initiated then a lengthy procedure to isolate radium from uranium ore tailings from the processing of Joachimstal mine ore, given by Austria. Eventually she succeeded to obtain a precipitate of radium chloride of few milligrams obtained from one ton of ore.

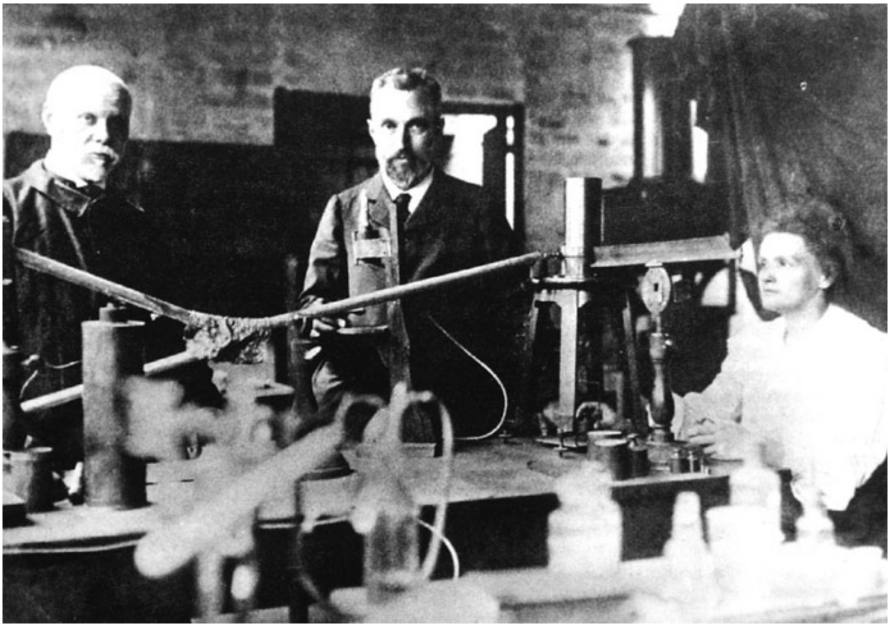

Fig. 2 Marie Curie, Pierre Curie (*at the center*) and their laboratory technician (*at left*) in the laboratory of rue Lhomond, Faculté de Sciences, Paris. On the bench, the Curie's electrometer used to measure ionization of the air by radioactivity

On 21 July 1902, Marie Curie using a sample containing 0.129 g of barium-radium chloride, which could contain probably only 1:1000 parts of radium in barium, made the first determination of the atomic mass of this new element, and obtained 223.3. Later she would correct this to 225 ± 1 and to 226.4 (actual value 226.0254). That chloride sample contained for the first time radium in visible amounts, and was 1 million times more radioactive than uranium (NN 2011).

In November 1903, Marie Curie presented her Doctoral Thesis, entitled "Recherches sur les Substances Radioactives" at the Sorbonne University, Paris. The same year the Swedish Academy awarded her, together with Pierre Curie and Henri Becquerel, the Nobel Prize of Physics for the discovery of radioactivity.

In 1911 again the Swedish Academy of Sciences awarded to Marie Curie the Nobel Prize, this time of Chemistry, for her discovery and characterization of the new elements radium and polonium (Curie 1911).

Following the adoption of the curie (in memory of Pierre Curie) as the unit of radioactivity, and upon request by the International Radium Standards Committee in 1911, Marie Curie prepared a radium standard with 21.99 mg of pure radium chloride in a sealed glass tube. The secondary certified radium standards for other countries were prepared and tested against this primary standard, now deposited in the Bureau International de Poids et Mesures in Sevres, near Paris (Curie 1912).

Radium Applications and the Dawn of Radiotherapy

Few years only after Becquerel's discovery of the "uranic rays", Ernest Rutherford and Frederick Soddy demonstrated that the radiation emitted by radioactive substances was indeed composed of three distinct types of radiation. These radiations behaved differently when under an electromagnet, and had very different energy. More of 80% of the emitted radiation was due to alpha particles with little penetrating power; beta radiation was also made of particles with electric charge but much smaller than alpha particles and with much higher energy and able to penetrate to a certain depth in the tissues. The third type of radiation were gamma rays (first identified by P. Villard in 1900), which accounted only for 1% of radiation with high energy, short wavelength and strong penetrating power (NN 2011, Mould R F (2007).

The idea of using radium in medicine to destroy tumors dates back to 1900, to the skin burns observed by two German scientists, Friedrich Walkoff and Friedrich Giesel, and to the incident of Henry Becquerel who carried a tube with a small amount of radium in the pocket of his waistcoat during 14 days. He developed a skin burn, and mentioned that to Pierre Curie. Pierre Curie amazed with the radium effect decided to confirm it and applied a small source of radium against his arm for 10 hours, obtaining a localized burn as well. That gave him the idea that radium could be used in medical work. Meanwhile, Becquerel's burn was serious and he went to see a dermatologist at the Hospital St Louis, Paris. The dermatologist, Dr. Ernest Besnier, noted that the Becquerel's radium burn was similar to X-ray burns and immediately thought that radium could be used in medical therapy such as the X-rays. He persuaded the Curies to lend a small amount of radium to a hospital colleague, Dr. Henri Danlos, who successfully used the radioactive material to treat lupus and other dermatological diseases and published his work in 1901 (Danlos & Bloch 1901).

Across the Atlantic, the first use of radium in therapy seems to have occurred by the same time, by the hands of a physicist, Francis Williams, in Boston. He was aware of the successful use of X-rays in the treatment of lupus and speculated that the radiation emission of the recently discovered radium could be used in treating this disease. In late 1900s, Francis Rollins seem to have prepared about 500 mg of radium chloride and placed them in a sealed capsule, and passed it over to his brother-in-law, Dr. William Rollins, for use in therapeutics (Mould 2007).

In his discussion of the first 42 cases treated with radiation from the encapsulated radium, William Rollins compared the results with the previous use of X-ay in similar therapy. He wrote: "The comparison at the present time is greatly to the advantage of radium.(…) When radium is employed for healing purposes no cumbersome apparatus is necessary: radium is portable and always ready for use. Further, the dose from radium is uniform; the strength of the output does not vary, so that the dose depends entirely on the length of exposure and the distance of the radium from the part to be treated. Radium may be applied to parts that are not readily accessible to the X-rays, such as the mouth or vagina. Furthermore, the healing action of the radium is more prompt". He also wrote about the severe burns that radium could cause in health tissues and the need for protection (Mould 2007, Danlos & Bloch 1901).

Since the very beginning, many medical doctors used radium in the treatment of tumors and malignant neoplasms, including for example the work in the Gussenbauer Clinic of Vienna (1902), the work at the Biological Laboratory of Radium in Paris by Louis-Frederick Wickham (1905); the work by Robert Abbe (1904) and William Morton (1914) in New York amongst many others, all testing improvements and innovation in radium therapy (Abbé R 1904, Eisenberg 1992).

Foundation of the Radium Institute in Paris

Encouraged by the successful therapy applications of radium, particularly those of Henri Danlos in Paris, the foundation of the Radium Institute was agreed in 1909 between the Pasteur Institute and the University of Paris. The Radium Institute was set up to further develop the research on radioactivity started by the Curies and to foster their application in medicine and biology. The Radium Institute would house two laboratories, the Curie Pavilion for research on physics and chemistry of radioactive elements under the direction of Marie Curie, and the Pasteur Pavilion for research on radium applications in biology and medicine and treatment of patients with Claudius Regaud, a biologist from Lyon, as director Fevrier (2011).

The construction of the Radium Institute started in 1911 and it was nearly ready in 1914 when the First World War started. The opening of the Institute was postponed and took place only after the war, becoming fully operational in 1919. The Radium Institute was renamed Institute Curie in 1932 and was leaded by Marie Curie until she died in 1934 Fevrier (2011).

The medical treatments achieved using radium inspired the foundation of radium institutes in many other countries. The treatments performed with radium rapidly increased in number and the demand for this element increased as well.

The Radium Mining Industry

Following the pioneer work carried by doctors in Paris and Vienna immediately after the discovery of radium, the use of this radioactive element in therapy rapidly expanded. In Europe, around 1913 the use of radium therapy was already widespread, but still little used in USA. Most American radiologists performed therapy with X-rays. This was due to the availability of the newly invented high energy X-rays and to short radium supply in USA (Mould 2007).

During the first two decades of the 20th century the radium commercially available was mainly produced from the Joachimstal mine, in Bohemia, and some small mines in France, Portugal, and a few other countries. Joachimstal in 1913 contributed alone to about 80% of the world radium supply. Nevertheless, the amounts produced were modest, rendering radium salts price astronomically high.

The search for other sources led to discovery of radium in carnotite, in Colorado, USA. The Standard Chemical Company, founded by Joseph Flannery of Pittsburgh, purchased the Colorado mines in 1911 and began to supply radium in 1913. This company published from 1913 to 1925, a bulletin entitled Radium, to publicize the radium production but where most of the knowledge and applications of this element were abstracted as well (Mould 2007).

In 1910 in USA was founded also the National Radium Institute that jointly with the US Bureau of Mines set up a radium recovery plant in Denver. The production by this plant substantially decreased the cost of radium and made it more available in the USA. By 1922, some 80% of the world's supply of radium was produced already in the USA.

A few years later, a turning point in radium industry took place with the discovery of the richer uranium ores of the Chinkolobwo mine in the Haut Katanga Province, in Belgian Congo. Large amounts of radium from Congo ores were produced in Oolen, Belgium, and this nearly closed radium production in American and European mines (Mould 2007).

In the beginning of last century most radium supply was from the mines of Joachimstal in Poland and nearby, that produced 100 g radium from 1899 to 1940. The Colorado, New Mexico and Utah mines in USA, produced about 200 g between 1900 and 1926. Port Radium in Canada, produced 60 g between 1933 and 1937, while Haut Katanga mines in Belgium Congo, produced 50–100 g per year from 1922 to 1940 (total between 900 and 1800 g). Radium productions in other countries were of a few grams or even less (Mould 2007).

In the beginning of the 20th century, radium price was at $ 180,000 per gram (about 1.8 million Euros today). In 1921, when a subscription was made in the USA to offer 1 g radium to Marie Curie, this amount did cost $ 100,000 (about 1 million Euros today) and it was produced from the uranium mines in Colorado and Utah. Later, with the discovery of uranium in Katanga, the prices dropped to $ 70,000 per gram. After the Second World War, other mines were exploited and together with the decreasing use of radium in medicine and industry the price of 1 g dropped to $ 25,000 in the fifties (Fevrier 2011, Mould 2007).

The availability of radium from the 1920s and the decrease in market price definitively enabled the adoption of radium therapy in many medical centers. This allowed for the development of therapeutic methods and increased reporting of successful healings in many countries.

At the same time, the abundance of radium and popular believes that this element could in small amounts be miraculously beneficial to health, lead to the invention of a high number of side applications marketed for public use. In that time were commonly advertised and used beauty products such as face powders and skin creams, hygiene products such as toothpaste, and radioactive water to the benefit of stomach. All these products contained added radium and were available for unrestricted use (Mould 2007).

Other radium applications were invented, such as the use in phosphorescence quadrants of wrist watches, alarm clocks, night reading instruments, including industrial, aviation and military instruments. NN 2011 (Fevrier 2011, Mould 2007).

The Onset of Radium in Medicine and Other Applications

The noxious effects of radiation emission from radium were noticed early, and Marie Curie herself noticed also how easily instruments and clothes became contaminated with radium in the laboratory. She encouraged the use of caution to her collaborators and students. However, the radiation protection as a science was not born yet, and sadly she was victimized by the element she discovered and handled for so many years.

The radiation protection knowledge was progressively accumulated and led to improved protection measures and regulations today used worldwide in research laboratories, hospitals, mining and chemical industry, and nuclear power plants Fevrier (2011).

Radiation protection considerations and the carcinogenic potential of prolonged exposure to radium led to abandon the use of radium in applications for public use, such as luminescent dials. In medicine, with the discovery of artificial radioactivity, fission products such as cobalt-60 and cesium-137 with much shorter half-lives than radium and high energetic radiation replaced radium allowing for safer applications in teletherapy. In curietherapie other radionuclides, such as iridium-192, gradually replaced the radium needles. After several incidents with lost radium needles, an international program was implemented to recuperate these needles and dispose them safely. Production of radium sources for use in medicine ended in the 1970s (Mould 2007, Eisenberg 1992).

The improved knowledge on biological effects of ionizing radiations and approval of international basic safety standards against the harmful effects of ionizing radiation, led also to improved mining and milling waste management and to the concept of environmental remediation of former radium and uranium producing facilities (IAEA 2005).

The life cycle of radium applications was than completed.

Medical applications of radium were developed for about 70 years, many patients underwent radiotherapy, many successful healings were achieved and human lives extended. During those years many technologies and new sciences started with radium use. Although artificial radioisotopes have already replaced radium to increase the benefits of ionizing radiation and reduce the radiological and environmental risks, and new technologies such as photon and electron beams produced by linear accelerators, and nowadays using proton emission technology (PET), have in turn taken their place, the way was opened with the discovery of radium (IAEA (2009).

Radiation therapy and nuclear medicine continue developing today, making use of much shorter lived radioisotopes, and using as radionuclide carriers organic compounds tailored to specifically bind to certain cells and tissues. The outcomes are much improved radio diagnostic and less invasive therapy techniques along with better targeted cancer treatments.

It shall be remembered that this path was opened also by the Curie family with the discovery of artificial radioactivity by Frederic and Irene Joliot-Curie, Nobel Prize of Chemistry in 1935.

What Future?

During the first half of the 20th century, radium was used in exciting applications, which drove the uranium mining to grow. Today, radium has no major applications and it is not the aim for mining industry. Nevertheless, the mining of radioactive ores and uranium for energy production continues.

The radium applications particularly in medicine, devised by Marie Curie and other scientists of her time, were continued and refined generally through the use of radionuclides with shorter half-lives. The curietherapy is still a method currently applied in medicine to treat cancer tumors, with recent developments in the treatment of prostate and gynecological cancers.

For a while at least, radium is left now in peace by human kind. In nature radium continuously provides a significant contribution to the maintenance of mild temperatures that allowed and sustain human and non-human life on Earth. Nevertheless, applications of radium isotopes are not over. Naturally-occurring radium isotopes are currently used as natural tracers in hydrogeology and in the investigation of groundwater discharges into the oceans. Most likely, other applications or uses of radium isotopes will be invented.

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