Radiochim. Acta **88**, 123−127 (2000)

The centenary of a controversial discovery: actinium†

By J. P. Adloff*

63 Rue Saint-Urbain, F-67100 Strasbourg, France

(Received October 20, 1999; accepted in revised form January 3, 2000)

History / Actinium / Emanium

Summary. André Debierne, collaborator of Pierre and Marie Curie, announced in 1900 the discovery of actinium, a third radioelement in pitchblende with properties resembling those of thorium. Four years later, Friedrich Giesel found a substance with a strong emanating power following lanthanum and which he called emanium. It become progressively clear that actinium and emanium were the same element. The arguments developed in the ensuing controversy are reviewed. Eventually Debierne was recognized as the discoverer of actinium, element 89 in the periodic table.

1. Introduction

In their discoveries of polonium and radium in July and December 1898, Pierre and Marie Curie were aided by Gustave Bémont. After a period of collaboration of about 6 months Bémont left the team for obscure reasons [1]. Marie Curie was aware that the spectroscopic analysis of radiferous barium, that revealed several lines of a new element, was not sufficient for the definitive proof of the existence of radium. The determination of the atomic weight was a prerequisite which required the treatment of tons of pitchblende. Marie Curie could not achieve this formidable task alone, inasmuch as she was primarily involved in pursuing fundamental investigations on the new elements and their radiation.

The Curies had a unique chance in replacing Bémont by André Debierne, who became famous for the discovery in pitchblende of actinium, a third, thorium-like element that was announced at the Academy of Science on April 2, 1900 [2]. Four years later, on April 23, 1904 the German radiochemist Giesel in turn claimed the discovery of emanium, a strongly radioactive substance, closely similar to lanthanum [3]. At this stage pitchblende contained two new elements besides polonium and radium. Were actinium and emanium distinct elements or were they in reality the same substance? In the affirmative, who should have the right to priority? The controversy lasted for several years and recalled the lengthy and stubborn dispute between Marie Curie and Willy Marckwald for the defense of their respectively so-called "polonium" and "radiotellurium" [1].

2. The protagonists

2.1 André Louis Debierne (1874, Paris – 1949, Paris)

After concluding his term at the Ecole Municipale de Physique et Chimie Industrielles where he was a student and admirer of Pierre Curie, Debierne became for a short time assistant of Charles Friedel at the University of Paris before joining the Curies in early 1899. Most of his career was at the Ecole, first as Chef de Travaux (like Bémont and Curie), and later as Professor (after Curie's death) and Director. He also held a chair at the Sorbonne and succeeded Marie Curie in 1934 as Director of the Institut du Radium until his death.

Debierne had an extremely shy and introverted character, but he was a very gifted chemist and a hard worker. He was the closest and most faithful friend of Pierre and Marie Curie, but otherwise quite unsociable. He could work for many years without indicating his state of progress or even the aim of his experiments, which became clear only after he obtained conclusive results.

In the Curie team, Debierne was essentially in charge of chemical research related to radioactivity and radioelements together with the production of radium on an industrial scale. Despite close collaboration he was co-author with Pierre in only four papers; they dealt mainly with the phenomenon of induced radioactivity. With Marie he published two papers in 1910: the first concerned measurement of the spectrum of polonium and the second the preparation of metallic radium. After 1914 Debierne's scientific career appears quite mysterious, and his publications almost ceased. Alone and isolated from other research scientists he worked, as he said himself, on very difficult experiments involving complex apparatus to verify ideas related to current theories. In one of his rare publications during this period he described new radioactive substances chemically very similar to radium, but which were not isotopes thereof since they could be separated. He attributed these "neo-radioelements" to the fine structure of the α rays, whereby an excited neo-radium chemically slightly different from

† Dedicated to the memory of Professor Alfred P. Wolf.

* E-mail: jpadloff@cybercable.tm.fr.

radium could be formed. In fact, the observed anomaly was due to isotopic impurities. Finally, Debierne gradually lost interest in the progress of science and in the contemporary social and political events [4].

2.2 Friedrich Oskar Giesel (1852, Winzig, Silesia – 1927, Braunschweig)

Giesel was the leading pioneer of radiochemistry in Germany. He studied in Berlin and became assistant and collaborator of the famous organic chemist Karl Liebermann, who was reputed for the synthesis of alizarine. In 1878 he was appointed chief chemist at the quinine factory in Braunschweig (Brunswick), a position that he held until the end of his life. Giesel had a wide interest in science, particularly for aspects that appeared promising for new discoveries. In such cases he could not resist becoming involved. When he learned about the discoveries of the Curies in 1898, he decided to produce radium in Germany from pitchblende residues rather than from the costly mineral itself. He had strong support from the de Haën Chemical Company, which produced uranium for the glass industry. Using the procedure established by the Curies, he started the production of radium within a few months and offered it at a nominal price. This was the beginning of his prolific "secondary" profession as a radiochemist. In over 30 publications he reported many important discoveries and first observations, for example, the scintillations produced by α particles in zinc sulfide, the magnetic deflection of β particles, the flame spectrum of radium, the radioactivity of lead from pitchblende, the physiological effects of radium (a sample held before a closed eye produced the sensation of light). Giesel's last publication appeared in 1910. His scientific career ceased with the outbreak of the World War and the difficult post-war period. But for years Giesel remained the supplier of rare radioactive preparations.

For his achievements, Giesel received the title of Professor, a very seldom distinction for chemists outside of universities. However, he had little interest in honours and in social life. He considered facts more important than forms. He was a poor speaker and his timidity was a severe obstacle to his official duties [5].

Like many pioneers in the early history of radiochemistry, both Debierne and Giesel died from the pernicious effects of radium and other radioelements [6].

3. The actinium puzzle

The properties of the natural isotope of the element 89, i.e., ^{227}Ac, were not conducive to its discovery and identification. In 1910, about ten years after the discovery, doubts and uncertainties were expressed by Frederick Soddy in the following terms: atomic weight, unknown; half-life, unknown; radiation emitted, none; precursor, unknown. This sombre description arose from several unfortunate circumstances. First, the equilibrium ratio of actinium in uranium is very small (0.2×10^{-9}). The amount of actinium in pitchblende, the only source of the element at that time, is 0.6×10^{-3} that of radium. The chemical properties of actinium are closely similar to those of the rare earths, which are often contained in considerable amounts in uranium ores. In the extraction procedure actinium is always mixed with these elements in which it can be concentrated by tedious fractional precipitations.

The main obstacle is that ^{227}Ac can hardly be detected. The very soft β radiation (the end point of the spectrum is about 40 keV) was not observed until the mid-30's and a rare (1.2%) α branching was discovered only in 1939. In the second edition (1935) of Marie Curie's treatise "Radioactivité" it is still stated "actinium itself does not have an observable radiation" and the half-life is given as "about 10 years", much below the present value of 21.7 years.

Accordingly, actinium can only be measured by the radiation emitted by the daughters. The first descendants are 18.7 d ^{227}Th (Radioactinium, RdAc, in the early terminology) and 11.4 d ^{223}Ra (AcX) identified 6 or 7 years after the discovery of the element. ^{223}Ra is the progenitor of the radioactive emanation 3.96 s ^{219}Rn (actinon) whose main daughter in the active deposit is 36.1 min ^{211}Pb (AcB). For quantitative determination, actiniferous samples had to be sealed into a tight cup to avoid loss of emanation and measured after radioactive equilibrium was attained, which required about 3 months.

4. First clue: a titanium-like radioactive substance

Debierne started the processing of several hundred kg of uranium-free pitchblende residues and simultaneously, following Pierre Curie's advice, he searched for other radioactive substances which might be hidden in pitchblende.

For this purpose, Debierne could only rely on the properties of polonium and radium. His reasoning was straightforward: separate chemically the two already known radioelements and search for other radioactive substances which would behave in a different way, i.e., which did not precipitate with hydrogen sulfide but could be carried down completely by ammonia. Since the radioactive substances (measured with the ionization chamber coupled to a quadrant electrometer set up by the Curies) were expectedly present in very small amounts, a large quantity of the material was required − this was precisely what Debierne had on hand.

In the precipitate of hydroxides, the most active fraction contained titanium and analogous elements. Using a procedure which he never described in detail, Debierne eventually separated a substance whose solution exhibited the main properties of titanium and a fraction of the material had an activity 100 000 times (emphasized by Debierne) greater than that of uranium. He stated that the new substance could not be radium or polonium.

The result was published on October 19, 1899 with the title "On a new radioactive matter" [7]. This announcement did not produce the excitement that followed the discoveries of the Curies, possibly because no name was proposed for the new element. However, the discovery was a landmark in the history of radiochemistry since it represented the first among the multitude of radioactive substances to be found during the following 20 years. It preceded by a few months the discovery of thorium emanation by Owen and Rutherford and of uranium X by Crookes [8].

5. Second clue: a thorium-like radioactive substance

Although Debierne had indicated that he would report soon on the new substance, it was only six months later that a second paper contradicted the previous result: the new substance now followed thorium. In acidic solution it was precipitated by sodium thiosulfate and in neutral solution by hydrogen peroxide. In particular, it could be separated from titanium: the freshly precipitated active hydrate was insoluble in potassium fluoride or hydrofluoric acid, contrarily to the case of titanium. Finally, the activity co-precipitated with barium sulfate and accompanied the rare earths upon precipitation with oxalic acid. However, Debierne added cautiously (and, in a certain sense, in a premonitory manner) "I cannot guarantee that it [the new substance] will follow thorium in all its reactions". This comment was later exploited in the dispute with Giesel.

Spectroscopic analysis of the most active fraction performed by Eugène Demarçay (who had identified the new lines pertaining to radium) confirmed that thorium was the major constituent, as expected from the reactions used in the procedure, but no unknown lines could be detected. Since the activity was definitely not due to radium or polonium, Debierne assumed the presence of a new, very active, element which he decided to call *actinium* [2]. The name from the Greek *aktis*, *aktinos* meaning "ray" was ill-founded since, as seen, actinium scarcely emits any observable radiation. Since it was known that thorium salts are only slightly radioactive and actinium seemed to be an element close to thorium, Debierne added "it may be supposed that the radioactive property observed in thorium compounds does not belong to the element, but to a foreign substance … I intend to search whether it is possible to deprive thorium compounds of the radio-active property, or to extract from these compounds a substance similar to the actinium extracted from pitchblende." Several years passed and the intention was not carried out before Giesel's discovery of emanium.

In the light of the present knowledge of the chemical and radioactive properties of the uranium daughters the question has been raised whether Debierne actually discovered the element actinium as it is now known. The stated activity of the titanium preparation as being 100 000 times that of uranium was incredibly high with respect to the strongest activities reported in 1898 by the Curies for polonium and radium, i.e., 400 and 900 times that of uranium, respectively. The first titanium preparation probably did not contain any actinium and the activity reported in the second paper (without further indication on the strength) was very likely a mixture of the naturally occurring isotopes ^{230}Th (ionium) and ^{227}Th (RdTh) in the ^{238}U and ^{235}U series. The absence of rare earths in the spectroscopic analysis indicates that actinium could not have been more than a very minor constituent of Debierne's "new radioactive element" [9, 10].

Several years later, in 1907, the debate resurged with the discovery of ionium by Bertram Borden Boltwood. The latter was searching for the parent of radium and, misled by Debierne's statement that the chemistry of actinium was similar to that of thorium, he assumed from his experiments that actinium was the intermediate product between uranium and radium. Of course this was wrong and Boltwood eventually identified ionium as the true progenitor of radium. He felt extremely vexed by "Debierne's perfectly rotten statements in the matter" and added "I think that Debierne has probably had the stuff [ionium] in his hands for years and has not had the sense to identify it" [11]. He also took the opportunity to claim that his student Clifford Langley submitted in June 1899 a bachelor's thesis with the conclusion that pitchblende contained another radioelement differing from uranium, polonium and radium, which was really ionium. Debierne, said Boltwood, had a mixture of ionium and actinium but believed he had a single element.

Rutherford congratulated Boltwood for the discovery of ionium: "You deserve to get the last of the radioactive family [of uranium]. I never felt that Debierne deserved much credit for actinium − he could'nt miss it. As a matter of fact, if there had been a dozen elements with actinium, he had not enough radioactive sense to find it out". Acerbic and ironic comments on colleagues were not exceptional in the history of radiochemistry [12].

6. Third clue: a rare earth-like radioactive substance

At about the same time, early in 1900, Rutherford discovered the thorium emanation and the phenomenon of induced activity, also observed by the Curies for radium. In 1901 Ernst Dorn discovered radon, the emanation of radium.

In a paper submitted in October 1901 and published during the first days of the following January, Giesel reported the discovery of a third emanation, released by a substance concentrated with the rare earth fraction from pitchblende [13]. In his investigation, Giesel was the first to use the phosphorescence induced by α particles impinging on a screen of zinc sulfide, also known as Sidot's blende, which happened to be very convenient for the detection of the emanations. Giesel called *Emanationskörper* (emanating body) the strongly emanating substance carried with the rare earths. The latter contained mainly elements of the cerium group and the activity could be concentrated by fractional crystallization of the oxalates. Since this procedure had similarities with that described by Debierne in the discovery of actinium, Giesel commented that "it seemed a good opportunity to investigate Debierne's actinium". The proposal was not innocuous, since Giesel's radioactive substance behaved quite differently from that reported by Debierne for actinium: it contained very little thorium. The separation methods for thorium, in opposition to Debierne's observation, yielded not more, but *less* active precipitates.

In Giesel's mind this was enough to raise doubts about Debierne's discovery of actinium. During the next two years he pursued a meticulous investigation of the chemical behaviour of his *Emanationskörper*, which clearly showed that it was a rare earth. The substance had been concentrated and purified to a point where lanthanum was the chief impurity and thorium could no longer be detected. Nevertheless, in his January 1903 publication Giesel was still reluctant to state firmly that the emanating body was

different from actinium [14]. It took him one more year to accumulate definitive proofs for the discovery of a new element: "I will try to isolate from the best lanthanum preparations the new radioactive rare earth. From now on I will name *emanium* the strongly active element, probably close to lanthanum, contained in the *Emanationskörper*" [3]. The name itself was chosen because the main characteristic of the new substance was its exceptional property to illuminate a screen of Sidot blende to an extent "visible throughout a large auditorium". However, it was as ill-named as actinium, since emanium itself was not the direct cause of the emanation.

Giesel was probably incited to take this step because Debierne had never responded to his publications nor answered his letters. He was confident in his own discovery because the behaviour of lanthanum could not be confused with that of Debierne's thorium-like actinium. A further strong argument was the release of the emanation which, to Giesel's knowledge, was never reported by Debierne. In this respect he was wrong, because he had missed Debierne's papers published during 1903 in which the author described the emanation produced by actinium and the accompanying induced activity [15, 16]. He had already mentioned (in the publication reporting the discovery) that actinium produces very weak induced radioactivity [2].

7. The confrontation

The only way to settle the controversy was to compare the properties of actinium and emanium. After Giesel had repeatedly and vainly invited Debierne to provide a small sample of actinium, and sent to Marie Curie a sample of his own product, he decided to take the initiative and bring his lanthanum preparation to Paris together with a Sidot screen for a side-by-side comparison with actinium. The test was performed in June or July 1904. Debierne stated laconically: "We [together with the Curies] made a few comparative observations on the characteristic of phosphorescence produced by the emanations of the two products and the results were identical". For Giesel the experiment was very frustrating since no further comparison of the chemical properties of the two elements could be performed. In particular, Debierne's previous thorium-like substance on which he had founded the discovery was no longer available; the later sample at Paris consisted of rare earths from the cerium group with a composition similar to that of Giesel's material.

After his four-year long black-out on actinium, Debierne then hastened to set the issue in order in the *Comptes Rendus* [17]. Interestingly enough, this paper was translated into German and received by the Editor of the *Berichte* on September 30, 1904, just a few days before the presentation at the Academy of Science in Paris [18]. Debierne admitted that thorium carries a rather small part of the actinium contained in pitchblende, but the element was readily concentrated with the rare earths. He took care in pointing out that in the discovery paper he had warned that the activity would not necessarily follow thorium in all its reactions.

Debierne stated that, owing to the striking similarities between emanium and actinium, he was convinced from the beginning that the two products were identical. "In no way can it be doubted that M. Giesel's active lanthanum contains the same radioactive substance as the active thorium which I had prepared previously. Thus, only the name *actinium* should be used to designate this radioactive substance and all work published on the *Emanationskörper* and *emanium* refer to the radioactive element actinium".

It was no wonder that Giesel's violent reply followed rapidly, on November 7 [19]. He refuted most of Debierne's arguments and assessed his own rights of priority for a number of chemical and radioactive properties of "actinium", in particular that the element followed lanthanum and that the intense action on the Sidot screen was still unknown to Debierne at the time of the Paris experiment. He concluded with the statement "I shall not permit a disparagement of the discoveries that I made entirely on my own". [Eine Schmälerung meiner vollständig unabhängig gemachten Entdeckungen werde ich nicht zulassen.]

8. Actinium or emanium?

It was natural that Debierne did not doubt that actinium and emanium were identical. In his first publications, Giesel sincerely pondered over a possible identity of the elements before opting for emanium. This decision was both for subjective (Debierne's contempt for his work) and scientific reasons. The joint Paris experiment, that was merely qualitative, favoured Debierne's standpoint, but an ultimate test would be clearly provided by the half-lives of the emanation and of the excited activity (i.e., that of the active deposit) for both elements. In 1904 Debierne gave the values of 3.7 s and 41 min for the two half-lives, respectively. The same year, Hariett Brooks carried out a similar determination on a sample of emanium 250 times more active than uranium, sent by Giesel to Rutherford in Montreal [20]. She obtained about the same values for the half-lives and Rutherford commented that "there can be no doubt that the emanating substance of Giesel and the actinium of Debierne contain the same radioactive constituent. The name actinium will thus be used to denote the emanating substance of Giesel" [21]. The following year, Sir William Ramsay in London, aware of the controversy between Debierne and Giesel, asked for a sample from both authors. For the first time, it was possible to measure actinium and emanium under strictly similar conditions. The experiment performed by Otto Hahn and Otto Sackur showed that the half-lives of the emanation and of the induced activities were so nearly identical that actinium and emanium were undoubtedly the same element [22]. At the same time, Marckwald reported the opposite conclusion: actinium and emanium were not identical but linked genetically: the lanthanum-like emanium decayed into thorium-like, strongly emanating, actinium [23]. Of course, Marckwald was wrong. The matter was finally settled after the elucidation of the decay products of actinium and the discoveries of ^{227}Th and ^{223}Ra, the latter being the true progenitor of ^{219}Rn, the "actinium" emanation.

Conclusion

The discovery of actinium by Debierne in 1900 was accepted without criticism and, for a time, the element was

not further mentioned, even by its presumed discoverer, until Giesel's first publication in 1902. In fact, researchers were much more interested in radium, which became rapidly available free of charge from the Curies or could be purchased from de Haën or Giesel at a reasonable price. Thorium was also available commercially and became a source of intensive research.

Debierne's silence with respect to the Giesel *Emanationskörper* may be traced to his odd character and to his involvement in more urgent work. Criticisms which are now directed towards his first two actinium-related publications should be mitigated when one considers the state of radiochemistry at the beginning of the 20th century. Radioactive decay and transformations were unknown, chemical behaviour at the tracer level could not be imagined, and the chemistry of rare earths and of the heaviest elements was still unfamiliar. Debierne commented that "the various reactions [described in the text] cannot yet be considered specific of the new radioactive substance … I rather believe they must be considered as resulting from carrier reactions …". As said, spectroscopic analysis of the most active fraction isolated by Debierne showed the lines of thorium. At least part of the activity belonged to thorium isotopes but the carrying of radionuclides homologues of other elements such as rare earths present in non-detectable amounts cannot be excluded. In any event, nobody can contend that Debierne's substance *did not* contain actinium.

For his own part, Giesel can be credited with the first preparation of a radiochemically pure product. He proved that emanium accompanied lanthanum rather than thorium and thus he identified the element with atomic number 89, the first actinide in the periodic table, and the homologue of the first lanthanide. Giesel held a possessive sentiment for "his" element and pursued for several years research on emanium and its daughters, whereas Debierne left the topic.

After the identity of actinium and emanium had been demonstrated, it was obvious that Debierne's claim for priority should be accepted. The name emanium was discarded, eventually by Giesel himself in 1907, but before relinquishing he recalled "Debierne's statement that actinium is close to thorium must now be corrected. In a mixture of the rare earths from pitchblende, actinium never precipitates with thorium, but, as I have discovered, remains with the ceric earths, in particular with lanthanum" [24].

Debierne is now recognized by most historians as the discoverer of actinium one hundred years ago. However, owing to the prevailing confusion that related the event, the question of priority is still not unequivocal [9]. At least Giesel has his own *post mortem* recognition with the engraving "Entdecker des Aktiniums" on his tombstone in Braunschweig.

Acknowledgments. The author thanks Professor Emeritus Masanobu Sakanoue of Kanazawa University, Japan, for his invaluable help in providing documents and for enlightening discussions on the early history of radiochemistry. Thanks are also due to Dr. John MacCordick for comments and revision of the manuscript.

References

1. Adloff, J. P., MacCordick, H. J.: The dawn of radiochemistry. Radiochim. Acta **70/71**, 13 (1995).
2. Debierne, A.: Sur un nouvel élément radioactif: l'actinium. Compt. Rend. **130**, 906 (1900).
3. Giesel, F.: Über den Emanationskörper (Emanium). Ber. Deut. Chem. Ges. **37**, 1696 (1904).
4. Haïssinsky, M.: Pseudo-discoveries in the history of Science. 13th International Congress on the History of Science, Moscow (1971).
5. Hahn, O.: Friedrich Giesel. Phys. Zeitsch. **29**, 353 (1928).
6. Rona, E.: Laboratory contamination in the early period of radiation research. Health Phys. **37**, 723 (1979).
7. Debierne, A.: Sur une nouvelle matière radioactive. Compt. Rend. **120**, 593 (1899).
8. Adloff, J. P.: The "X"-compounds, a breakthrough in the early history of radioactivity. Radiochim. Acta **77**, 1 (1997).
9. Kirby, H. W.: In: *Gmelin Handbook of Inorganic chemistry*, 8th Edition, Actinium, Supplement volume 1, Springer-Verlag (1981).
10. Kirby, H. W.: The early history of radiochemistry. MLM-1960, TID-4500, USAEC (1972).
11. Boltwood, B. B.: Letter to Rutherford, E., 23 Sept. 1907. In: *Rutherford and Boltwood, Letters on Radioactivity*, L. Badash, Ed., Yale University Press, New Haven and London (1969).
12. Rutherford, E.: Letter to Boltwood, B. B, 20 Oct. 1907. In: *Rutherford and Boltwood, Letters on Radioactivity*, L. Badash, Ed., Yale University Press, New Haven and London (1969).
13. Giesel, F.: Über Radium und radioaktive Stoffe. Ber. Deut. Chem. Ges. **35**, 3608 (1902).
14. Giesel, F.: Über den Emanationskörper aus Pechblende und über Radium. Ber. Deut. Chem. Ges. **36**, 342 (1903).
15. Debierne, A.: Sur la radio-activité induite provoquée par les sels d'actinium. Compt. Rend. **136**, 446 (1903).
16. Debierne, A.: Sur la production de la radioactivité induite par l'actinium. Compt. Rend. **136**, 671 (1903).
17. Debierne, A.: Sur l'actinium. Comptes Rendus **139**, 538 (1904).
18. Debierne, A.: Über das Aktinium. Phys. Zeitsch. **5**, 732 (1904).
19. Giesel, F.: Über Aktinium-Emanium. Phys. Zeitsch. **5**, 822 (1904).
20. Brooks, H.: The decay of the excited radioactivity from thorium, radium, and actinium. Phil. Mag. **8**, 373 (1904).
21. Rutherford, E.: The succession of changes in radioactive bodies. Phil. Trans. Roy. Soc. London, A **204**, 168 (1905).
22. Hahn, O., Sackur, O.: Die Zerfallskonstante der Emanationen des Emaniums und Actiniums. Ber. Deut. Chem. Ges. **38**, 1943 (1905).
23. Marckwald, W. : Über Actinium und Emanium. Ber. Deut. Chem. Ges. **38**, 2264 (1905).
24. Giesel, F.: Über die ersten Zerfallprodukte des Aktiniums (Emaniums), über eine neue Emanation und über Bildung von Helium aus Aktinium. Ber. Deut. Chem. Ges. **40**, 3011 (1907).