

## Chapter 2

# Radioactive Decay Chains

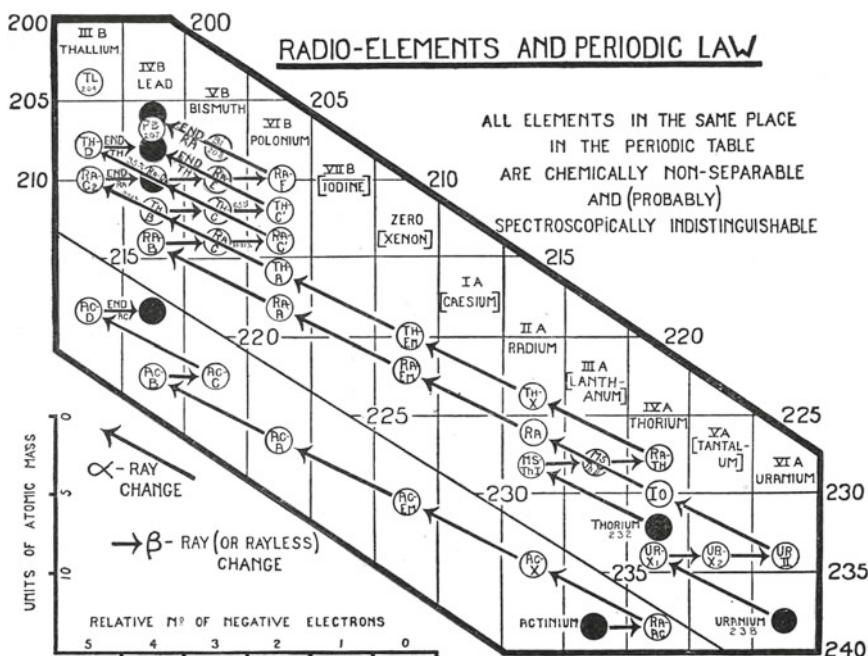
### 2.1 The Discovery of the Existence of Isotopes

Technically the discovery of isotopes should not begin before the concept of isotopes had been developed. However, since the discovery of radioactivity in 1896 many isotopes of the three naturally occurring radioactive decay chains were uniquely identified as separate substances without knowing the underlying physics. These so-called radio-elements were characterized by the type and energy of the emitted radiation and the half-life of their decay.

The detailed study and classification of the various substances and their relationships allowed Soddy [1] and Fajans independently in early 1913 [2] to finally understand and accept the fact that substances with different characteristics existed which were chemically identical. Soddy placed the substances in a two-dimensional grid of mass versus “relative number of negative electrons” [1, 3]. Each column represented an element so that the different isotopes for a given element lined up vertically and the rows corresponded to the mass. It can be considered as the first precursor of the chart of nuclides. It is interesting to note that a month earlier Russell had already placed the radio-elements correctly into element columns, however, he did not arrange them by mass [4]. Figure 2.1 shows the three radioactive decay chains as presented by Soddy in September 1913 at the 83rd meeting of the British Association for the Advancement of Science in Birmingham [5].

Soddy introduced the term isotope in December 1913 [6]. The name was derived from the Greek words *iso* (same) and *tope* (place) because the different radio-elements occupied the same place in the periodic table of elements.

Thus in principle Soddy should be credited with the discovery of all the isotopes he correctly identified and placed in his chart. However, it seems more appropriate to credit the discovery to the researchers who measured and characterized the unique properties of these isotopes for the first time although they did not yet understand the implications of their measurements.



**Fig. 2.1** Classification of the radio-elements presented by Soddy at the 83rd meeting of British Association for the Advancement of Science in Birmingham on September 16, 1913 [5]

In the following the discovery of the 46 radioactive isotopes of the three naturally occurring radioactive decay chains will be described divided into three time periods: (1) 1896–1904 when essentially nothing was known about the radiation and the exponential decay law was discovered [7], (2) 1904–1912 after Rutherford proposed the decay chain connections [8] and before Soddy established the concept of isotopes and (3) 1913–1961 after isotopes were established and the few missing connections and last branches of the decays were measured.

For the research of the isotopes of the radioactive decay chains several books and articles were consulted, for example, the 1908 edition of “Gmelin–Kraut’s Handbuch der anorganischen Chemie” [9], Soddy’s 1911 book “The Chemistry of the Radio-elements” [10], the 1913 edition of Rutherford’s book “Radioactive Substances and their Radiations” [11], and the 1933 article by Mary Elvira Weeks “The Discovery of the Elements. XIX. The Radioactive Elements” published in the Journal of Chemical Education [12]. In addition, the Wikipedia page on the radioactive decay chains was a good starting point [13].

## 2.2 Discovery of Radioactivity

The isotopes characterized by their decay within the first eight years of the discovery of radioactivity between 1896 and 1904 are listed in Table 2.1.

The credit for the discovery of the first two radioactive isotopes is granted purely on the observation of radiation. In 1896, Becquerel discovered radiation itself by placing uranium salt on a photographic plate covered with thick paper. When he developed the plate, he could see the silhouette of the salt. He concluded that the uranium salt emits radiation which passes through paper [14]. This radiation was mainly due to  $^{238}\text{U}$ .<sup>1</sup> Only in 1931, Aston demonstrated that  $^{238}\text{U}$  was the principal isotope of naturally occurring uranium [26].

Becquerel's observation of this new type of radiation which came only a few months after Roentgen discovered X-rays [27] was called uranium rays. Subsequently, many other substances were studied to search for a similar effect and it took two years before Schmidt in Erlangen, Germany, succeeded with thorium compounds. In addition to photographic plates he studied the effect of these thorium rays on an electroscope [15]. The radiation can be attributed to  $^{232}\text{Th}$ . Schmidt even estimated the atomic weight (atomic or mass number of the isotope) of the sources

**Table 2.1** Isotopes observed during the initial studies of the radio-elements between 1896 and 1904. The submission date, first author and reference of the publication, as well as the method of identification or the measured half-life, and the presently accepted half-life are listed

| Date                    | First author | Ref. | Identification/ $T_{1/2}$ | Present $T_{1/2}$                          | Isotope           |
|-------------------------|--------------|------|---------------------------|--|-------------------|
| 02/24/1896 <sup>a</sup> | Becquerel    | [14] | Radiation                 | $4.468 \pm 0.003 \times 10^9 \text{ y}$    | $^{238}\text{U}$  |
| 03/24/1898              | Schmidt      | [15] | Radiation                 | $1.405 \pm 0.006 \times 10^{10} \text{ y}$ | $^{232}\text{Th}$ |
| 07/18/1898 <sup>a</sup> | Curie        | [16] | Chem. sep.                | $138.376 \pm 0.002 \text{ d}$              | $^{210}\text{Po}$ |
| 12/26/1898 <sup>a</sup> | Curie        | [17] | Chem. sep.                | $1600 \pm 7 \text{ y}$                     | $^{226}\text{Ra}$ |
| 09/13/1899              | Rutherford   | [7]  | $\sim 1 \text{ min}$      | $55.6 \pm 0.1 \text{ s}$                   | $^{220}\text{Rn}$ |
| 11/06/1899 <sup>a</sup> | Curie        | [18] | Few days                  | $3.8235 \pm 0.0003 \text{ d}$              | $^{222}\text{Rn}$ |
| 11/22/1899              | Rutherford   | [19] | 11 h                      | $10.64 \pm 0.01 \text{ h}$                 | $^{212}\text{Pb}$ |
| 05/03/1900              | Crookes      | [20] | Chem. sep.                | $24.10 \pm 0.03 \text{ d}$                 | $^{234}\text{Th}$ |
| 11/01/1900              | Hofmann      | [21] | Chem. sep.                | $22.20 \pm 0.22 \text{ y}$                 | $^{210}\text{Pb}$ |
| 09/15/1902              | Rutherford   | [22] | $\sim 4 \text{ d}$        | $3.66 \pm 0.04 \text{ d}$                  | $^{224}\text{Ra}$ |
| 02/16/1903 <sup>a</sup> | Debierne     | [23] | Few seconds               | $3.96 \pm 0.01 \text{ s}$                  | $^{219}\text{Rn}$ |
| 12/22/1903              | Rutherford   | [24] | 3 min                     | $3.098 \pm 0.012 \text{ min}$              | $^{218}\text{Po}$ |
|                         |              |      | 34 min                    | $26.8 \pm 0.9 \text{ min}$                 | $^{214}\text{Pb}$ |
|                         |              |      | 28 min                    | $19.9 \pm 0.4 \text{ min}$                 | $^{214}\text{Bi}$ |
| 2/1/1904                | Debierne     | [25] | 40 min                    | $36.1 \pm 0.2 \text{ min}$                 | $^{211}\text{Pb}$ |

<sup>a</sup>Date of presentation

<sup>1</sup>In modern nomenclature the element is uniquely identified by its symbol corresponding to a specific number of protons (Z). The superscript indicates the mass number (A) of the isotope. The number of neutrons can then be calculated as  $N = A - Z$ .

of the uranium and thorium rays: “It seems that these are related to the high atomic weight, 240 for uranium and 232 for thorium” [15]. Less than three months later [28] M. Curie independently reported the radioactivity of thorium [29]. Aston demonstrated only in 1932 that  $^{232}\text{Th}$  constituted the only thorium isotope of primordial origin [30].

While Becquerel and Schmidt primarily studied the radiation itself, Pierre and Marie Curie together with Bemond concentrated on the source of the radiation. In 1898, they analyzed the properties of a metal that they extracted from the original substance (pitchblende) which contained the radiation and concluded that it must correspond to a new element: “If the existence of this new metal is confirmed, we suggest to call it polonium, named after the country of origin of one of us” [16]. This discovery of the element polonium was due to the radiation of  $^{210}\text{Po}$ . Earlier M. Curie had already suggested the presence of a new element by observing strong activities in pitchblende and chalcocite [29]. In 1904/1905 Rutherford showed that the polonium activity, radio-tellurium (discovered in 1902 by Marckwald [31, 32]) and his radium F (originally named radium E) were the same ( $^{210}\text{Po}$ ) [33–35].

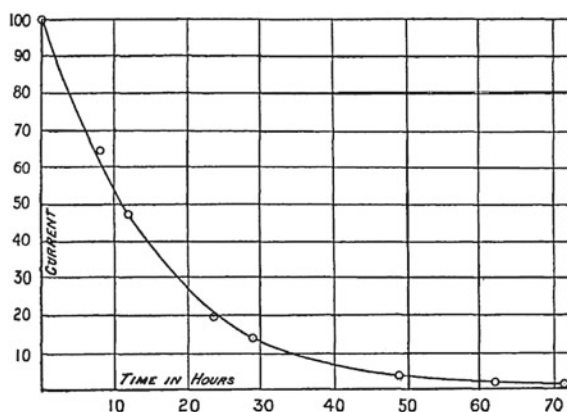
The Curies continued their chemical analyses of the radioactive substances and discovered the next new element only a few months later: “The new radio-active substance which we have found has all the chemical appearances of almost pure barium: it is neither precipitated by hydrogen sulfide nor by the ammonium sulfide, nor with ammonia; the sulfate is insoluble in water and in acids; the carbonate is insoluble in water, the chloride, very soluble in water, is insoluble in concentrated hydrochloric acid and alcohol. Finally, the spectrum of this substance is easily recognizable as barium... The various reasons we have enumerated lead us to believe that the new radioactive substance contains a new element, which we propose to name radium” [17]. The radiation of this new element was due to  $^{226}\text{Ra}$ .

The next important step was the realization that the radiation decreased with time. In 1899 Rutherford observed that thorium compounds emitted a radioactive substance which he called emanation. He noticed that “the intensity of the radiation has fallen to one-half its value after an interval of about one minute” [7]. His detailed measurements allowed him to derive the exponential decay law. The emanation corresponded to  $^{220}\text{Rn}$  and the measured half-life was quite accurate. The current accepted value is  $55.6 \pm 0.1$  s.

About at the same time Pierre and Marie Curie also reported a time dependence of radiation in the discovery of another radon isotope ( $^{222}\text{Rn}$ ) originating from radium: “Subtracting the contribution of the activated plate due to the radioactive substance, it remains radioactive for several days. However, the induced radioactivity is decreasing, first very rapidly, then slower and slower and tends to disappear asymptotically” [18]. They did, however, not quantify the time dependence any further. While Rutherford submitted his paper on September 13, the submission date of the Curie paper which appeared on November 6, was not given. Thus they probably should share the credit for the discovery of the element radon. It should be mentioned that sometimes the credit [36] is given to Ernst Dorn for his work on the emanation [37].

Only a couple of months later Rutherford detected another activity in the decay of thorium. From the decay curve shown in Fig. 2.2 he extracted a half-life of 11 h. This

**Fig. 2.2** Decay curve of radioactivity observed by Rutherford in 1899 within the decay chain of thorium [19]. The activity corresponds to  $^{212}\text{Pb}$  (Reprinted by permission of Taylor and Francis Ltd, [www.tandfonline.com](http://www.tandfonline.com), E. Rutherford, *Radioactivity produced in substances by the action of thorium compounds*, Philosophical Magazine 49 (1900) 161.)



activity was the direct cause of the previously discovered emanation [19]. Rutherford called this activity “excited radioactivity” and later on attributed it to ThA ( $^{212}\text{Pb}$ ) [8]. In 1902 Rutherford and Soddy continued their study of thorium and observed an activity with a half-life of about 4 days which they named ThX ( $^{224}\text{Ra}$ ) [22].

Two more radioactive substances were discovered in 1900 and identified by performing chemical separations and proving that they were different from previously observed radioactive materials. Crookes ensured that his new substance separated from uranium nitrate was different from polonium and radium and called it UrX [20]. UrX was later renamed UrX<sub>1</sub> and corresponds to  $^{234}\text{Th}$ . Hofmann and Strauss separated a radioactive substance from various uranium samples and determined that the radioactivity was still present when the substance consisted of lead only [21]. Later on it was realized that this “radiolead” was the same as the independently discovered RaD [33–35] corresponding to  $^{210}\text{Pb}$ . Aston’s 1927 claim of stable  $^{210}\text{Pb}$  [38] was later shown to be incorrect [39].

Once the concept of the radioactive decay law had become established it is reasonable to require a fairly accurate half-life measurement as a criterion to claim the discovery of a new isotope. This does not necessarily apply to the discovery of an element and affects the discovery of actinium. In 1902 Giesel reported the observation of a new active substance which could not be related to either uranium, radium or thorium [40]. Two years later he named this new element emanium [41]. It turned out that emanium was the same substance that Debierne had earlier called actinium [42] and Debierne is generally credited with the discovery of actinium. However, Kirby argued that Debierne could not have observed actinium in his first papers [42, 43] and thus credit should be given to Giesel [44]. Giesel did not measure the half-life of actinium so he is not credited for the discovery of the isotope ( $^{227}\text{Ac}$ ) responsible for the activity. The half-life of  $^{227}\text{Ac}$  was only measured in 1911 by M. Curie [45] who was credited with the discovery of this isotope (see next section).

A few months later Giesel then also reported a third type of emanation which he determined to be different from radium emanation and thorium emanation, however, he did not measure the half-life [46]. A month later Debierne independently

observed the actinium emanation ( $^{219}\text{Rn}$ ) and reported that it disappeared to half its value within a few seconds [23]. Debierne followed up his studies and a year later observed an additional activity: “I also found the radioactive decay law caused by the actinium emanation by measuring the induced activity in the same set-up, from the moment the emanation has ceased to act: The decay is regular, it reaches its half value in 40 min” [25]. Rutherford reproduced the observation by Debierne and named it actinium A [8]. It was later reclassified as AcB and corresponds to  $^{211}\text{Pb}$ .

Rutherford’s experiments with radium resulted in the discovery of three new activities in 1903: “An analysis of the decay curves of excited activity, produced for different intervals of exposure in the presence of the emanation, shows that there are three well-marked changes occurring in emanation X of radium. In the first change, half the matter is transformed in 3 min; in the second, half in 34 min; and in the third, half in 28 min” [24]. At the time Rutherford and Barnes did not name the activities which correspond to  $^{218}\text{Po}$ ,  $^{214}\text{Pb}$ , and  $^{214}\text{Bi}$ , respectively. Rutherford and Soddy had reported these activities labeled radium-excited activity I, II, and III already a year earlier without measuring the half-lives [47].

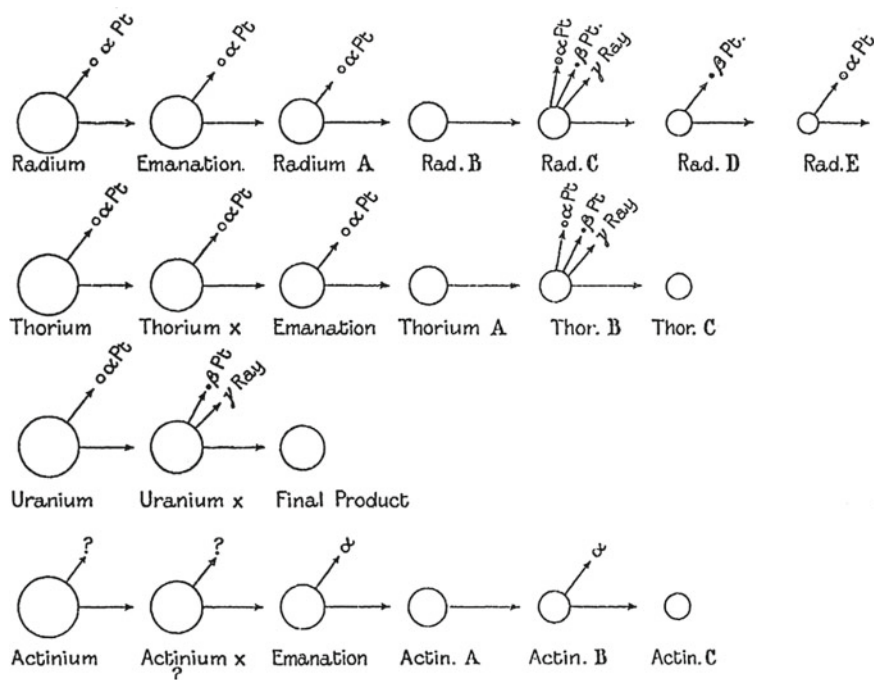
## 2.3 Discovery of Radioactive Decay Chains

At the beginning of 1904 the decay of 16 different substances (including actinium) had been measured. In his Bakerian lecture on May 19, Rutherford reported the discovery of two additional isotopes from thorium emanation ( $^{212}\text{Bi}$ ) and actinium emanation ( $^{211}\text{Bi}$ ) and presented for the first time a comprehensive scheme of four separate decay chains as shown in Fig. 2.3. In addition to placing the known activities into the chains, Rutherford had some evidence for the existence of AcX ( $^{223}\text{Ra}$ ) but referred to a later paper for the results and labeled it with a question mark in the figure [8]. The half-life of actinium was not yet known at the time.

Although the scheme was simple and offered valuable guidance for future researchers, the sequential naming of A, B, C, etc. was unfortunate. At the time the scheme was incomplete and several intermediate decay products were missing. As more and more additional isotopes were discovered in the following years, it became necessary to rename some of the isotopes which led to confusion until in 1913 Soddy introduced the concept of isotopes. Until then another 17 new isotopes were discovered (see Table 2.2).

The predicted actinium X activity ( $^{223}\text{Ra}$ ) was discovered within the year by Godlewski: “The activity increased in the first day after removal to about 15 % of its original value, and then decayed with the time according to an exponential law, falling to half value in about ten days” [48]. A year earlier Giesel had reported a new substance separated from emanium (actinium) [41] without any further more detailed measurements [63].

Three additional isotopes had to be inserted into the actinium chain. In 1906, Hahn discovered radio-actinium ( $^{227}\text{Th}$ ) in between Ac and AcX [50] and two years later Hahn and Meitner determined that AcC ( $^{207}\text{Tl}$ ) was radioactive and not the end of the



**Fig. 2.3** Rutherford's radioactive decay chains based on the 18 radio-elements (including actinium but not actinium X) known by 1904 [8]

decay chain [55]. Geiger then added a new isotope ( $^{215}\text{Po}$ ) between the emanation and AcA in 1911: "It has been shown that the actinium emanation is complex, consisting of two products each of which emits  $\alpha$  rays. The first one—the emanation—with a period of 4 seconds emits  $\alpha$  rays of a range of 5.7 cm. The second product emits  $\alpha$  rays of range 6.5 cm, and has a period of the order of 1/500 of a second" [60]. It was the first time that such a short half-life was measured. Earlier Geiger and Marsden had established an upper half-life limit of 0.1 s for this activity [58]. The addition of a new AcA required the renaming of the subsequent isotopes including Hahn and Meitner's AcC which was renamed AcD and later AcC".

Another member of this series was discovered by Antonoff in 1911, but he did not connect it to the actinium chain [59]. Since he observed the new activity from a uranium nitrate sample he speculated that it was another decay branch of uranium naming it UY ( $^{231}\text{Th}$ ). In the same year, M. Curie measured the half-life of  $^{227}\text{Ac}$  [45]. This actinium activity had been known since 1902 (see previous section). It is interesting to note that Marie Curie is listed as Mme. P. Curie as the author of the paper. For all the isotopes of the actinium series see Fig. 2.6.

Five of the six additional isotopes of the thorium decay chain were discovered by Hahn. In 1905, he observed another substance that decayed to thorium emanation which he called radiothorium ( $^{228}\text{Th}$ ). Hahn was not able to extract the half-life; he only stated that the radioactivity did not show any reduction after two months [49].



**Table 2.2** Isotopes of the radio-elements discovered between 1904 and 1912. The submission date, first author and reference of the publication, as well as decay chain, the measured half-life, and the presently accepted half-life are listed

| Date                    | First author | Ref. | Chain | Measured $T_{1/2}$ | Present $T_{1/2}$               | Isotope           |
|-------------------------|--------------|------|-------|--------------------|---------------------------------|-------------------|
| 08/20/1904              | Rutherford   | [8]  | Ac    | 1.5 min            | $2.14 \pm 0.02$ min             | $^{211}\text{Bi}$ |
|                         |              |      | Th    | 55 min             | $60.55 \pm 0.06$ min            | $^{212}\text{Bi}$ |
| 01/02/1905              | Godlewski    | [48] | Ac    | 10 d               | $11.43 \pm 0.05$ d              | $^{223}\text{Ra}$ |
| 01/24/1905              | Rutherford   | [34] | Ra    | 6 d                | $5.012 \pm 0.005$ d             | $^{210}\text{Bi}$ |
| 03/07/1905              | Hahn         | [49] | Th    | “long”             | $1.9116 \pm 0.0016$ y           | $^{228}\text{Th}$ |
| 03/27/1906              | Hahn         | [50] | Ac    | 20 d               | $18.68 \pm 0.09$ d              | $^{227}\text{Th}$ |
| 04/07/1906              | Hahn         | [51] | Th    | ~sec.              | $0.299 \pm 0.002$ $\mu\text{s}$ | $^{212}\text{Po}$ |
| 03/23/1907              | Hahn         | [52] | Th    | 7 y                | $5.75 \pm 0.03$ y               | $^{228}\text{Ra}$ |
| 09/09/1907              | Boltwood     | [53] | U/Ra  | 1900 y             | $75380 \pm 300$ y               | $^{230}\text{Th}$ |
| 03/07/1908              | Hahn         | [54] | Th    | 6.5 h              | $6.15 \pm 0.02$ h               | $^{228}\text{Ac}$ |
| 08/28/1908              | Hahn         | [55] | Ac    | 5.1 min            | $4.77 \pm 0.03$ min             | $^{207}\text{Tl}$ |
| 01/22/1909              | Hahn         | [56] | Th    | 3.1 min            | $3.053 \pm 0.004$ min           | $^{208}\text{Tl}$ |
| 09/20/1909              | Hahn         | [57] | Ra    | 1–2.5 min          | $1.3 \pm 0.3$ min               | $^{210}\text{Tl}$ |
| 11/14/1909              | Geiger       | [58] | Th    | 0.14 s             | $0.145 \pm 0.002$ s             | $^{216}\text{Po}$ |
| June 1911               | Antonoff     | [59] | Ac    | 1.5 d              | $25.52 \pm 0.01$ h              | $^{231}\text{Th}$ |
| July 1911 <sup>a</sup>  | Geiger       | [60] | Ac    | 2 ms               | $1.781 \pm 0.004$ ms            | $^{215}\text{Po}$ |
| 08/27/1911              | M. Curie     | [45] | Ac    | 21 y               | $21.772 \pm 0.003$ y            | $^{227}\text{Ac}$ |
| March 1912 <sup>a</sup> | Geiger       | [61] | U/Ra  | 200,000 y          | $245,500 \pm 600$ y             | $^{234}\text{U}$  |
| 06/07/1912              | Fajans       | [62] | Ra    | $10^{-6}$ s        | $164.3 \pm 2.0$ $\mu\text{s}$   | $^{214}\text{Po}$ |

<sup>a</sup>Publication date

Subsequently, Hahn determined that radiothorium is a decay product of thorium and that two other isotopes—mesothorium I ( $^{228}\text{Ra}$  [52, 64]) and mesothorium II ( $^{228}\text{Ac}$  [54])—exist between these two isotopes.

Hahn also extended the thorium chain when he discovered in 1906 that ThA emitted  $\alpha$ -particles with two distinctly different energies [51]. Following Rutherford’s convention he named the new activity thorium C ( $^{212}\text{Po}$ ). A few years later Hahn observed together with Meitner yet another activity towards the end of the thorium decay chain. They determined the half-life of the activity accurately but assumed incorrectly that it sequentially followed the decay of ThB and ThC [56]. The logical conclusion was to name the new activity ThD. Later it was reclassified as ThC” ( $^{208}\text{Tl}$ ).

The last isotope within the thorium chain was identified by Geiger and Marsden in 1909 with a new method to measure very short times between two successive  $\alpha$ -particle emissions. They let the radioactive substance diffuse between two closely spaced scintillation screens which were viewed from opposite ends by two microscopes: “The scintillations, which were viewed by two observers on the corresponding screens over a period of several minutes, were registered via an electromagnetically operated pen onto the same paperstrip of a chronograph. The velocity of the paperstrip was in most cases 0.5 cm per second.” With this set-up they were able to



determine a lifetime of about 0.2 s from the thorium emanation [58]. A year later Rutherford and Geiger placed this activity ( $^{216}\text{Po}$ ) between the thorium emanation and ThA [65]. At the same time they suggested that Hahn's ThB and ThC activities were not sequential. As a consequence they renamed the old ThA to ThB, and indicated that ThC consists of ThC<sub>1</sub>, and ThC<sub>2</sub>. To confuse the situation even further, later on ThC<sub>2</sub> and ThD were renamed one more time to ThC' and ThC''.

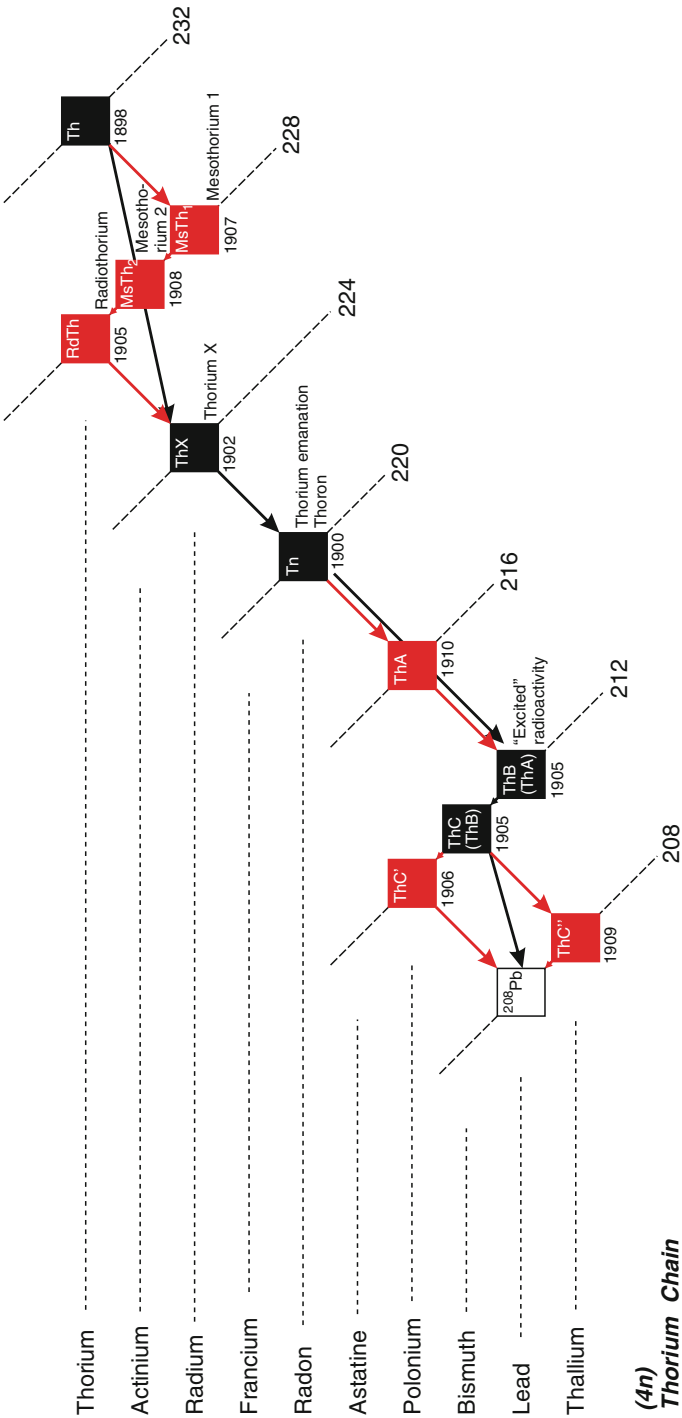
The thorium decay chain was completely known at the time when Soddy developed the isotope concept. Figure 2.4 shows all radio-elements of the chain. Isotopes known to Rutherford in 1904 and his suggested decay paths are shown in black. Isotopes known to Soddy in 1913 and the modifications to the decay paths are shown in red.

The radium decay chain was even more complicated than the other two. It already contained two more isotopes at the time Rutherford presented his overview in 1904. A year later Rutherford reported that he had overlooked an activity in RaD which he then named D<sub>1</sub> ( $^{210}\text{Bi}$ ) [34]. In a paper submitted four months later Rutherford renamed radium D<sub>1</sub> to radium E and the old radium E to radium F [35]. In October 1904, Hofmann et al. [66] had identified a  $\beta$ -emitter chemically separated from radiolead (radium D,  $^{210}\text{Pb}$ ) which Rutherford acknowledged [35], however, the extracted half-life of about six weeks was incorrect.

Shortly after Hahn and Meitner encountered in 1909 the difficulty explaining the two different  $\alpha$ -decays in ThC (see above [56]) they determined that RaC also consists of two substances which they called RaC<sub>1</sub> and RaC<sub>2</sub> [57]. RaC<sub>2</sub> was later called RaC'' ( $^{210}\text{Tl}$ ) while RaC<sub>1</sub> remained RaC. Hahn and Meitner also indicated that there might be yet another unknown activity present. This was confirmed by Fajans three years later who deduced that RaC<sub>1</sub> (or RaC) branches off into RaC<sub>2</sub> and RaD—via the new RaC' ( $^{214}\text{Po}$ )—with a ratio of 3/10,000 which agrees with the currently accepted ratio of 2.1/10,000 [62]. His estimate of an extremely short half-life ( $10^{-6}$  s) was too short and is actually about 100 times larger.

The other remaining open question of the radium decay chain was its relation to the uranium chain. It had been realized early on that due to the relatively short half-life radium could not be the origin of a radioactive decay chain and Soddy proposed a uranium as the ultimate origin of the radium series in 1905 [67]. The first step bridging the gap between radium and uranium was presented by Boltwood in 1907: "...there is good cause for believing that uranium minerals contain an element emitting  $\alpha$  rays, which is different from the other elements that have been identified, which produces no emanation, and which resembles thorium in its chemical properties" [53]. Later in the year Boltwood suggested the name "ionium" ( $^{230}\text{Th}$ ) for the new substance [68, 69]. His estimate of the half-life (1900 y) was somewhat short.

In 1912 Geiger and Nuttall discovered a second uranium isotope ( $^{234}\text{U}$ ): "Uranium I therefore, which has a period of  $5 \times 10^9$  years, emits  $\alpha$ -particles of range 2.5 cm in air at atmospheric pressure and at 15 °C, and is followed by another  $\alpha$ -ray product, uranium II, which has a period of about  $2 \times 10^6$  years and emits  $\alpha$ -particles of range 2.9 cm" [61]. Earlier, the existence of a second  $\alpha$  emitting uranium isotope was suspected from the number of emitted  $\alpha$ -particles per uranium atom [70, 71]. Geiger and Nuttall did not make the connection to ionium. For all the isotopes of the combined radium/uranium series see Fig. 2.7.



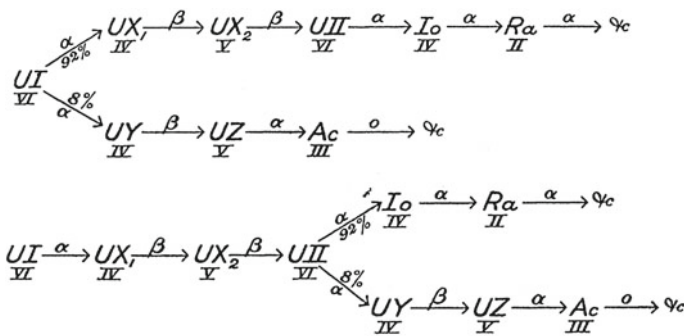
**Fig. 2.4** Isotopes and decay paths of the thorium decay chain. The chain includes isotopes which have a mass number which is a multiple of four ( $A = 4n$ ,  $n = 52-58$ ). Isotopes known to Rutherford in 1904 and his suggested decay paths are shown in *black*. Isotopes known to Soddy in 1913 and the modifications to the decay paths are shown in *red*

## 2.4 Completing the Radioactive Decay Chains

In the February 1913 issue of the Chemical News, Soddy sorted the radio-elements for the first time in a chart as a function of mass and charge [1]. He placed the 25 known isotopes of the uranium (14) and thorium (11) decay series correctly and predicted the existence of eka-tantalum ( $^{234}\text{Pa}$ ) connecting the radium with the uranium series. The existence of  $^{234}\text{Pa}$  had also independently been predicted as  $\text{UX}_2$  by Fajans [2] and Russell [4]. However, he incorrectly placed the 8 at the time known isotopes of the actinium series at the same location as the uranium series starting at  $^{230}\text{Th}$  [1, 3].

Eka-tantalum or  $\text{UX}_2$  ( $^{234}\text{Pa}$ ) was discovered by Fajans and Göhring already one month later [72]. In a subsequent paper with Beer, Fajans realized that it corresponded to the first observation of a new element and named it brevium: “The reason to name the short-lived element which O. Göhring and I discovered is that it is the only element which fits in the location of the fifth group of the last horizontal row of the periodic table. However, for the radioactive characterization the name  $\text{UrX}_2$  is preferred, because it immediately clarifies its genetic relation” [73]. Fajans and Göhring’s discovery also corresponds to the first observation of an isomeric excited state. The ground-state of  $^{234}\text{Pa}$  was discovered by Hahn in 1921 who named it at first Z [74] and then UZ [75].

Following the discovery of eka-tantalum, Soddy realized that the radium and actinium chains were not identical starting from ionium/radioactinium and subsequently placed the actinium series separately from the other two without any mass assignment (see Fig. 2.1 [5]). In the 1913 Chemical Society Annual Report he proposed two solutions shown in Fig. 2.5. Both options predicted the existence of another isotope UZ connecting UY with actinium. In the first and second solution actinium would have an atomic weight of 230 and 226, respectively [76]. The connection of UY to the actinium series had previously already been suggested by Antonoff [77].



**Fig. 2.5** Possible connections of the uranium and actinium chain proposed by Soddy in 1913 [76]

**Table 2.3** Isotopes of the radio-elements discovered between 1913 and 1961. The submission date, first author and reference of the publication, as well as decay chain, the identification method or measured half-life, and the presently accepted half-life are listed

| Date                    | First author | Ref. | Chain | Identification/T <sub>1/2</sub> | Present T <sub>1/2</sub> | Isotope                        |
|-------------------------|--------------|------|-------|---------------------------------|--------------------------|--------------------------------|
| 03/15/1913              | Fajans       | [72] | U/Ra  | 1.1 min <sup>a</sup>            | 1.17 ± 0.03 min          | <sup>234</sup> Pa              |
| 09/03/1913              | Marsden      | [78] | Ac    | α-particle range                | 0.516 ± 0.003 s          | <sup>211</sup> Po              |
| 03/16/1918              | Hahn         | [79] | Ac    | 1,200–180,000 y                 | 32,760 ± 110 y           | <sup>231</sup> Pa              |
| 07/12/1935              | Dempster     | [80] | Ac    | Mass-spectroscopy               | 7.04 × 10 <sup>8</sup> y | <sup>235</sup> U <sup>b</sup>  |
| 10/21/1935 <sup>c</sup> | Preiswerk    | [81] | U/Ra  | 4 min                           | 4.202 ± 0.011 min        | <sup>206</sup> Tl              |
| 07/03/1939              | Hulubei      | [82] | U/Ra  | X-rays                          | 1.5 ± 0.3 s              | <sup>218</sup> At              |
| 01/09/1939              | Perey        | [83] | Ac    | 21 ± 1 min                      | 22.00 ± 0.07 min         | <sup>223</sup> Fr              |
| 12/30/1943              | Karlik       | [84] | Ac    | α-particle range                | 100 ± 20 μs              | <sup>215</sup> At              |
| 05/20/1948              | Studier      | [85] | U/Ra  | Sequential α-decay              | 35 ms                    | <sup>218</sup> Rn <sup>d</sup> |
| 12/17/1952              | Hyde         | [86] | Ac    | 8 min                           | 7.6 ± 0.2 min            | <sup>215</sup> Bi              |
|                         |              |      | Ac    | 0.9 min                         | 56 ± 3 s                 | <sup>219</sup> At              |
| 04/29/1961              | Nurmia       | [87] | U/Ra  | 7.5 ± 1.0 min                   | 8.32 ± 0.07 min          | <sup>206</sup> Hg              |

<sup>a</sup>Isomeric state

<sup>b</sup>See also Sect. 3.2

<sup>c</sup>Date of presentation

<sup>d</sup>See also Sect. 9.3

With the exception of the placement and the ultimate origin of the actinium series all main decay branches of the three decay chains were established by early 1913. It took another 48 years before the last isotope of one of these three naturally occurring decay chains was identified. Table 2.3 lists the 12 remaining isotopes discovered between 1913 and 1961.

The proposed isotope UZ (<sup>231</sup>Pa) was discovered in 1918 by Hahn and Meitner [79]. A few months earlier Soddy and Cranston had demonstrated the existence of UZ but did not measure any properties of UZ or its decay. In contrast, Hahn and Meitner had determined the range of the α-particles and determined a half-life between 1,200 and 180,000 years. They are generally given equal credit for the discovery [12]. Hahn and Meitner named the new substance protactinium [79, 88], however, Soddy quoted them with the name protoactinium [89, 90]. Both names were subsequently in use until the name protactinium was officially selected at the 15th IUPAC conference in Amsterdam in 1949 [91, 92].

Once it was demonstrated that brevium (<sup>234</sup>Pa) and protactinium (<sup>231</sup>Pa) belonged to the same element, Fajans withdraw the right to name the element: “Protactinium occurs in the periodic system in the same location as uranium X<sub>2</sub>, and since it is the by far longer-lived element which determines the name, the term brevium is no longer needed” [93]. In 1973, Fajans and Morris reflected on the discovery and naming of protactinium [94].

The discovery of UZ (<sup>231</sup>Pa) still did not resolve the question of the placement of the actinium series. In his Nobel lecture in 1922 Soddy mentioned the possibility that it could be a completely independent series which initiated from another uranium

isotope [95]. In 1929 Rutherford predicted the existence of actino-uranium ( $^{235}\text{U}$ ) [96] based on Aston's extrapolation of 231 for the mass of protactinium as the precursor of  $^{207}\text{Pb}$  [97]. It was experimentally only resolved with the mass determination of  $^{231}\text{Ac}$  in 1934 [98] and the discovery of actino-uranium ( $^{235}\text{U}$ ) in 1935 by Dempster in his mass spectrograph [80].

In addition to solving this major mystery of the origin of the actinium series, several small side branches of this decay chain were observed after Soddy published his chart in 1913.

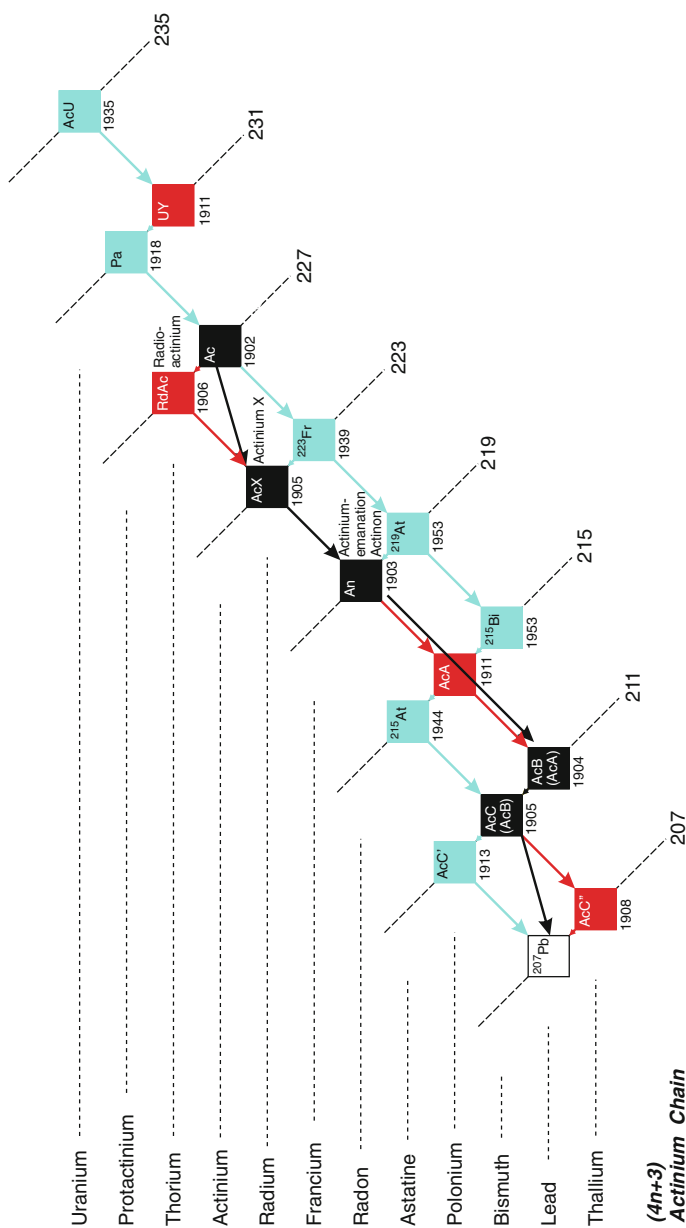
At the end of 1913 Marsden and Wilson detected another  $\alpha$ -decay from AcC which had been expected in analogy to the thorium and radium series: "The results showed that in addition to the  $\alpha$ -particles of actinium C with a range of 5.4 cm, a small number, about 1 in 600, can penetrate as far as about 6.45 cm. Special experiments showed that the long-range  $\alpha$ -particles could not be due to radium or thorium impurity, and they must therefore be attributed to the expected new branch product" [78]. This activity—later named AcC'—corresponds to  $^{211}\text{Po}$ .

The next branch point was reported 26 years later and corresponded to the discovery of the new element francium. Perey discovered  $^{223}\text{Fr}$  as an  $\alpha$ -decay branch of  $^{227}\text{Ac}$  in 1939 [83]. She determined the branching to be 1% [99]. In 1952, Hyde and Ghiorso explored the continuation of this parallel branch, explored the  $\alpha$ -decay of  $^{223}\text{Fr}$ , and discovered  $^{219}\text{At}$  and  $^{215}\text{Bi}$ : "The observed branching rate is ca.  $4 \times 10^{-5}$ , and the  $\text{At}^{219}$  daughter decays predominantly by the emission of 6.27-Mev alpha-particles with a half-life of 0.9 min to the new isotope  $\text{Bi}^{215}$ , which in turn emits  $\beta^-$  particles with a half-life of 8 min" [86]. In the same paper, Hyde and Ghiorso questioned Karlik and Bernert's claim for the observation of  $^{215}\text{At}$  in the actinium series. Karlik and Bernert had deduced the discovery of  $^{215}\text{Ac}$  from the measurement of the  $\alpha$ -particle energy. The value agreed with the extrapolated value for mass number 215 in a plot of the decay energy as a function of the mass number for atomic number 85 and they quoted a  $\beta$ -decay branch of  $5 \times 10^{-4}\%$  from AcA ( $^{215}\text{Po}$ ) [84]. In a note added in proof Hyde and Ghiorso mentioned that the work by Karlik and Bernert on  $^{215}\text{At}$  had been confirmed [100].

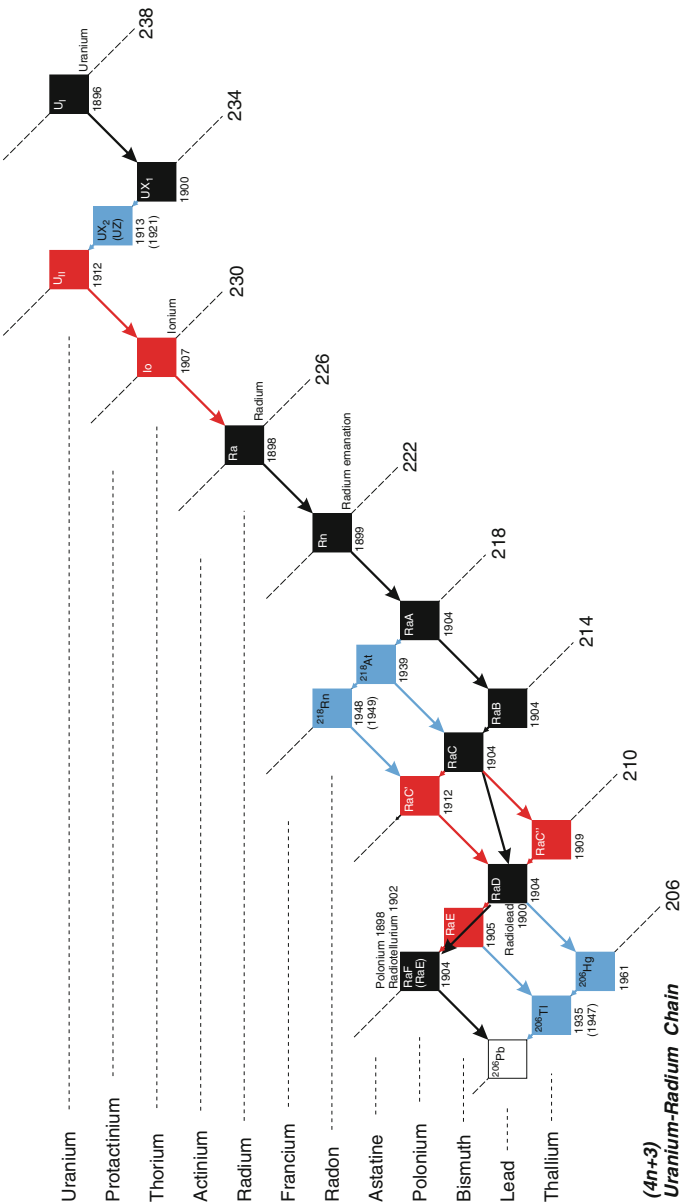
The discovery of  $^{219}\text{At}$  and  $^{215}\text{Bi}$  by Hyde and Ghiorso completed the actinium series in 1953. The complete chain is shown in Fig. 2.6. Isotopes known to Rutherford in 1904 and his suggested decay paths are shown in black. Isotopes known to Soddy in 1913 and the modifications to the decay paths are shown in red. All subsequently discovered isotopes and decay paths are shown in light blue.

Once the connection between the uranium and radium series had been established only four additional small side branches were discovered. The complete chain is shown in Fig. 2.7 and the explanation for the different colors are the same as in Fig. 2.6. For  $^{234}\text{Pa}$  the discovery of the isomer ( $\text{UX}_2$ ) and the ground-state ( $\text{UX}$ ) are indicated. Two of the isotopes ( $^{206}\text{Tl}$  and  $^{218}\text{Rn}$ ) were discovered before they were identified as a decay branch in the uranium chain. For these isotopes the date of discovery as well as the date when they were linked to the chain are listed.

The discovery of  $^{218}\text{At}$  has been extensively debated. In an overview paper in 2010, Thornton and Burdette [101] pointed out that Hulubei and Cauchois reported evidence for the observation of  $^{218}\text{At}$  already in 1939. Hulubei and Cauchois had



**Fig. 2.6** Isotopes and decay paths of the actinium decay chain ( $A = 4n + 3$ ,  $n = 51 - 58$ ). Isotopes known to Rutherford in 1904 and his suggested decay paths are shown in *black*. Isotopes known to Soddy in 1913 and the modifications to the decay paths are shown in *red*. All subsequently discovered isotopes and decay paths are shown in *light blue*.



**Fig. 2.7** Isotopes and decay paths of the uranium/radium decay chain ( $A = 4n + 2$ ,  $n = 51 - 59$ ). Isotopes known to Rutherford in 1904 and his suggested decay paths are shown in *black*. Isotopes known to Soddy in 1913 and the modifications to the decay paths are shown in *red*. All subsequently discovered isotopes and decay paths are shown in *light blue*



reported the observation of three X-rays which were close to the predicted values for eka-iodine (astatine) [82]. These X-rays were observed from a  $^{222}\text{Rn}$  sample and the astatine lines could only originate from  $^{218}\text{At}$  populated either by  $\alpha$  and  $\beta$ -decay through  $^{218}\text{Po}$  or by  $\beta$  and  $\alpha$ -decay through  $^{222}\text{Fr}$ . The acceptance of the Hulubei and Cauchois discovery of  $^{218}\text{At}$  places the discovery of this isotope before the discovery of the element astatine. The discovery of astatine has been credited [102] to Corson, MacKenzie, and Segrè for their observation of the  $\alpha$ -decay of  $^{211}\text{At}$  in 1940 [103, 104]. It is justified to give Hulubei and Cauchois credit for the discovery of the isotope but not the element because they lacked chemical proof [101].

The observation of a weak  $\beta$ -decay branch of  $^{218}\text{At}$  in 1949 linked  $^{218}\text{Rn}$  to the uranium decay chain. Walen reported a 1 % branch in a paper submitted on November 24, 1948 claiming the discovery of the new isotope  $^{218}\text{Rn}$  [105]. He probably was not aware of the paper by Studier and Hyde submitted six months earlier. They had identified  $^{218}\text{Rn}$  in the artificially produced protactinium decay chain beginning at  $^{230}\text{Pa}$  (see Sect. 9.3) [85].

In 1947, Broda and Feather reported a  $5 \times 10^{-5}$  %  $\alpha$ -decay branch from  $\text{RaE}$  ( $^{210}\text{Bi}$ ) linking  $^{206}\text{Tl}$  to the uranium series [106]. At time the existence of  $^{206}\text{Tl}$  was well established. It had been discovered in 1935 by Preiswerk and von Halban when they irradiated metallic thallium and thallium nitrate with neutrons from an 800 mCi radon-beryllium source.  $^{206}\text{Tl}$  was formed in the neutron capture reaction on  $^{205}\text{Tl}$  and decayed to  $^{206}\text{Pb}$  with a half-life of 4 min [81].

The last isotope of the radium series was discovered in 1961 by Nurmia et al..  $^{206}\text{Hg}$  was observed in the  $\alpha$ -decay of  $^{210}\text{Pb}$  with a branching ratio of  $1.8 \pm 0.5 \times 10^{-6}$  % and decayed with a half-life of  $7.5 \pm 1.0$  min to  $^{206}\text{Tl}$  [87].

The fourth possible radioactive decay chain with  $A = 4n + 1$  does not exist in nature. It is called the neptunium series after the isotope with the longest half-life ( $^{237}\text{Np}$ ,  $T_{1/2} = 2.1 \times 10^6$  y) discovered in 1948 by Wahl and Seaborg [107] (see Sect. 5.2). The majority of the chain was discovered by Hagemann et al. in 1947 [108] (see Sect. 7.2).

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The Discovery of Isotopes

A Complete Compilation

Thoennessen, M.

2016, XIII, 413 p. 107 illus., 21 illus. in color., Hardcover

ISBN: 978-3-319-31761-8