Discovery and Naming of the Isotopes of Element 91

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The history of the discovery and naming of the three naturally occurring isotopes of element 91 is outlined in order to eliminate contradictions to be found in the literature. Information about the nineteen isotopes of protactinium now known is listed.

THERE are several discrepancies in the literature concerning the discovery of element 91. For example, the statement in a recent obituary[1] of John Arnold Cranston . . . "In the course of his work he had discovered a new terrestrial element, protoactinium —element 91" . . . is misleading.

At the time of the placing of the radioelements in the periodic system it was predicted[2,3] that uranium X might be a mixture of two consecutive radioelements uranium X_1 and uranium X_2. This followed from the then newly established displacement laws, according to which the beginning of the uranium series should be formulated as

$$U_1 \xrightarrow{\alpha} UX_1 \xrightarrow{\beta-} UX_2 \xrightarrow{\beta-} U_{II} \xrightarrow{\alpha} Io$$

Periodic Group VI   IV   V   VI   IV

This is now known to correspond to

$$^{238}U \xrightarrow{\alpha} {}^{234}Th \xrightarrow{\beta-} {}^{234}Pa\,{}^{m} \xrightarrow{\beta-} {}^{234}U \xrightarrow{\alpha} {}^{230}Th$$

but no radioelement was known at that time in Group V at the place in the Periodic Table between thorium and uranium.

In attempting to find uranium X_2, Fajans and Göhring[4] applied the generalization[3] that after a beta transformation the daughter element is electrochemically more noble than the mother element. A solution of uranium X was placed in a lead dish, with the expectation that "ekatantalum" is more, thorium less, noble than lead. In fact, radioactive material was formed on the surface of the lead dish and its $\beta-$ activity decayed with the previously not known half life, 1.1 min. Its chemical nature was further confirmed[5] by its coprecipitation from solution with hydrous tantalum(V) oxide.
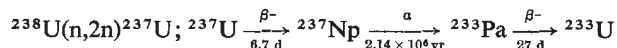
Because uranium X_2 occupied a previously vacant space in the periodic system (it constituted a new element), the nuclide received[6] the distinctive name brevium (Bv), suggested by its short life.

The discovery of the next isotope of element 91 was due to the search for the immediate precursor of actinium, which according to the displacement laws could be formed by an unknown radionuclide ? (Group V) $\xrightarrow{\alpha}$ Ac (Group III). Indeed, Soddy and Cranston[7], and independently Hahn and Meitner[8], separated from uranium minerals fractions having the chemical behaviour of brevium in which they found the production of actinium. The half life of the new radionuclide was initially estimated[8] to be between 1.2×10^3 and 1.8×10^5 yr; it is now known to be $3.2_7 \times 10^4$ yr. Hahn and Meitner named it protactinium (^{231}Pa) because it was the progenitor of actinium. This isotope is much more stable than UX_2, so Fajans[9] proposed that the name of element 91 be changed from brevium

to protactinium. This corresponded to the then common usage that the element's name was that of its longest lived isotope.

The third isotope of element 91 was discovered by Hahn[10] who found that UX_1 produces not only UX_2 but, to an extent shown later to be only 0.13%, also UZ of a half life of 6.7 h. It is not merely isotopic with UX_2 but has the same mass number 234 and the pair is considered as the first example of nuclear isomerism.

The three isotopes of protactinium ^{231}Pa, $^{234}Pa\,{}^{m}(UX_2)$ and $^{234}Pa(UZ)$ are those found in nature. ^{231}Pa is a member of the actinouranium $(4n+3)$ radioactive series and the pair of isomers belongs to the uranium–radium $(4n+2)$ series. Even the richest ores of uranium contain only about 1 part of Pa in 10^7. Nevertheless, in 1962 it was reported that well over 100 g of protactinium had been isolated by the United Kingdom Atomic Energy Authority from some 60 t of accumulated sludges from a uranium extraction process[13]. To be strictly accurate ^{233}Pa, a member of the $(4n+1)$ series, does occur in nature, but only to a tiny extent. It has been established[11] that minute amounts of ^{237}Np and ^{233}U are continuously produced in uranium ores by nuclear reactions brought about by neutrons resulting from spontaneous fission of uranium.

$$^{238}U(n,2n)^{237}U; \quad ^{237}U \xrightarrow[6.7\,d]{\beta-} {}^{237}Np \xrightarrow[2.14 \times 10^6\,yr]{\alpha} {}^{233}Pa \xrightarrow[27\,d]{\beta-} {}^{233}U$$

In thorium ores ^{233}Pa may be produced by reactions initiated by neutrons arising from the action of energetic α particles from the heavy elements on the nuclei of light elements, such as beryllium, present in the ore[12].

$$^{232}Th(n,\gamma)^{233}Th; \quad ^{233}Th \xrightarrow[22\,min]{\beta-} {}^{233}Pa \xrightarrow[27\,d]{\beta-} {}^{233}U$$
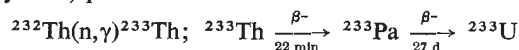
In addition to the radioisotopes of protactinium occurring in uranium minerals, many others have been prepared artificially. The lightest has mass number 216, the heaviest 238. First to be produced[14] was ^{233}Pa in 1938; the others were discovered from 1948 onwards. A list of the isotopes known now is given in Table 1. The half lives of the artificially produced radionuclides range between 5.7 ms (^{222}Pa) and 27 d (^{233}Pa). The latter is nearly 5×10^8 times longer than the former and nearly 5×10^5 times shorter than the half life of ^{231}Pa. Several isotopes of protactinium are constituents of well characterized collateral series[12,16,19-22].

The data for the isotopes listed in Table 1 correspond, with a few exceptions, to the following three rules found by Fajans[30] in 1913: (1) In a pleiad (the term isotope had not yet been used) which contains pure α and pure β emitters the former have a smaller mass than the latter. (2) For α emitters the half life increases with increasing mass. (3) For β emitters the half life decreases with increasing mass. Some more information about the application of these three rules can be found in the report K71-17 (1971) of a lecture at the Third International Protactinium Conference, 1969.

Pronounced exceptions to rule (2) had already been noticed in 1913, and these have proved of importance in the development of the modern theory of nuclear structure and radioactivity. In this context the nuclear characteristics of the lighter isotopes of protactinium merit brief discussion. For a smooth trough-like mass-energy surface a trend of increasing α disintegration energy with decreasing mass number is anticipated[31] and rule (2) may be expected to be obeyed. But

Table 1 Isotopes of Protactinium

Isotope	Half life	Type of decay, radiations and energies (MeV)	Year and place of discovery	Source	Reference
^{216}Pa	0.2 s	α 7.72, 7.82, 7.92	1971 Dubna	^{189}Os(^{31}P, 4n), ^{190}Os(^{31}P, 5n), ^{197}Au(^{24}Mg, 5n)	15
^{222}Pa	5.7 ms	α 8.16+8.18+8.21, 8.33, 8.54	1968 Berkeley	^{209}Bi(^{16}O, 3n), ^{206}Pb(^{19}F, 3n)	16
^{223}Pa	6.5 ms	α 8.01, 8.20	1968 Berkeley	^{208}Pb(^{19}F, 4n), ^{205}Tl(^{22}Ne, 4n), ^{209}Bi(^{20}Ne, α2n)	16
^{224}Pa	0.95 s	α 7.49	1958 Uppsala	^{232}Th(p, 9n)	17
^{225}Pa	1.8 s	α 7.20, 7.25	1951 Montreal	^{232}Th(d, 9n)	18
^{226}Pa	1.8 min	α 6.86, 6.82; EC	1949 Berkeley	^{232}Th(d, 8n)	19, 21
^{227}Pa	38.3 min	α 6.47, 6.42, 6.40, 6.36; EC; γ	1948 Berkeley	^{232}Th(d, 7n)	20, 19, 21
^{228}Pa	22 h	EC (α 6.11, others); γ	1948 Berkeley	^{232}Th(d, 6n)	20, 21
^{229}Pa	1.5 d	EC (α 5.67–5.32)	1949 Berkeley	^{230}Th(d, 3n)	23
^{230}Pa	17 d	EC; β⁻ 0.41 max; γ	1948 Chicago	^{232}Th(p, 3n)	24
^{231}Pa	3.27 × 10⁴ yr	α 5.02, 5.01, 4.95 (others); γ	1917 Aberdeen; Berlin–Dahlem	Natural source	7, 8
^{232}Pa	1.31 d	β⁻ 0.32, 1.34 max; γ	1949 Berkeley	^{232}Th(d, 2n)	25
^{233}Pa	27 d	β⁻ 0.26, 0.15, 0.57; γ	1938 Berlin–Dahlem	^{232}Th(n, γ),^{233}Th(β⁻)	14
^{234}Pa^m(UX₂)	1.17 min	β⁻ 2.29 (others); (IT; γ)	1913 Karlsruhe	Natural source	4, 5
^{234}Pa(UZ)	6.7 h	β⁻ 0.50, 0.19 (others); γ	1921 Berlin–Dahlem	Natural source	10
^{235}Pa	24 min	β⁻ 1.4 max	1950 Chalk River	^{234}Th(n, γ),^{235}Th(β⁻)	26
^{236}Pa	9.1 min	β⁻ 3.2 max; γ	1963 Amsterdam	^{238}U(d, α)	27 *
^{237}Pa	8.7 min	β⁻ 2.3 max; γ	1954 Berkeley	^{238}U(d, n2p)	28 *
^{238}Pa	2.3 min	β⁻ 2.9 max; γ	1968 Mainz	^{238}U(n, p)	29

* Wolzak and Morinaga[27], who are credited with the discovery of protactinium-236, pointed out that the same activity had been observed earlier by Crane and Iddings[28] who had assigned it to ^{237}Pa. Protactinium-237 may be prepared[29] by the nuclear reactions ^{238}U(n, pn) and ^{238}U(γ, p). EC, Electron capture; IT, isomeric transition.

amongst heavy elements a discontinuity in atomic masses occurs at the closed nucleon configuration occurring with a neutron number of 126, and this causes a related discontinuity in the α decay energies[12]. Therefore isotopes of protactinium with 126 or fewer neutrons are expected to have lower α disintegration energies and enhanced α partial half lives (Fig. 1). The only isotope in that region for which definite experimental evidence is available is ^{216}Pa, discovered in 1971 by Sung-Chin-Yang et al.[15] in osmium targets bombarded with 200 MeV ^{31}P^{5+} ions and in gold targets bombarded with

146 MeV ^{24}Mg ions, and which has a half life of 0.2 s. This represents a striking increase in stability over that of the protactinium isotopes of mass numbers 222 and 223.

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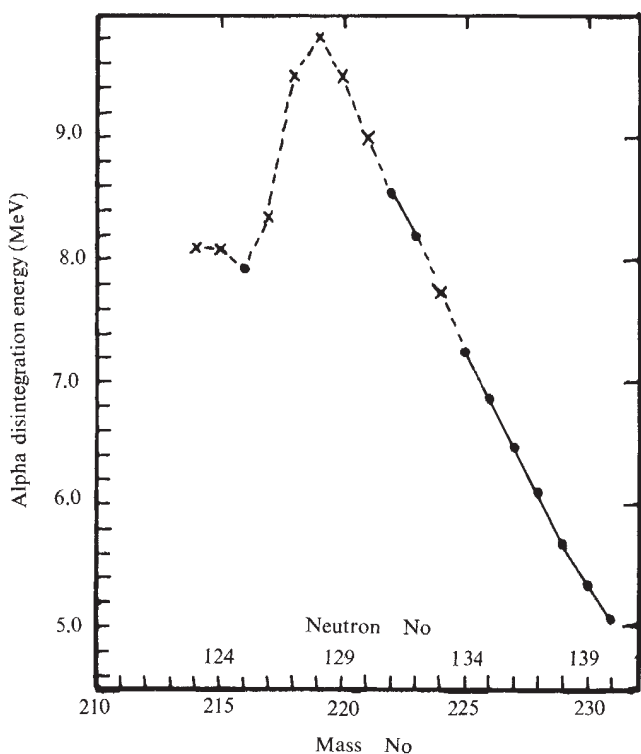32 Valli, K., Borggreen, J., and Hyde, E. K., Phys. Rev., C, 1, 2115 (1970).

Fig. 1 Alpha particle energy (for ground-state transition) as a function of mass number of protactinium isotopes. ●, Experimental data; ×, predictions[16,32].