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Observation of the negative ions: Ra^-, Pa^-, and Pu^-

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The negative ions of the isotopes ^{226}Ra, ^{231}Pa, and ^{244}Pu have been observed by means of accelerator mass spectrometry and their properties compared with the negative ions of Th and U. The electron affinities of all these elements have been estimated to be similar and greater than 50 meV.

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The discovery of stable calcium negative ions [1,2] has stimulated a substantial activity in negative ion studies of group IIA elements. The results of other theoretical calculations published more recently [3–5] have not only confirmed the stability of Ca^-, but also predicted that Sr^-, Ba^-, and Ra^- with similar configurations (ns^2np) should all be stable. The electron affinity of Ca^- has now been measured again to high precision by two different methods [6,7], and the negative ions of Sr and Ba have been observed [8]. The experimental study of Ra^- possesses a challenge due to the fact that no stable radium isotope exists. To avoid elaborate radiation protection, it is necessary to work with natural amounts or very low abundance of the α emitter ^{226}Ra. This requires the use of a very sensitive method for detecting $^{226}Ra^-$, such as accelerator mass spectrometry (AMS) [9], which is at present the only method for measuring $^{226}Ra^-$ at low levels. We report here the successful exploitation of a heavy-element AMS system for the observation of $^{226}Ra^-$ by using high-grade uranium ore material as the natural ^{226}Ra source, where the isotope ratio of ^{226}Ra to ^{238}U is no more than 3.58×10^{-7}. In addition the negative ions of Pa and Pu were also observed using the same apparatus.

In this experiment, a Cs sputter ion source [10] was used for producing $^{226}Ra^-$ and other negative ions. As a result of the expected exponential variation of negative ion current with electron affinity [11], the yield of $^{226}Ra^-$ was expected to be small due to the anticipated low electron affinity of radium. Furthermore, due to the low abundance of Ra in the sample, the $^{226}Ra^-$ signals were expected to be rare events, which could not be simply analyzed by using a set of electric and magnetic analyzers without any further means of background elimination. This is because the signals of $^{226}Ra^-$ could be overwhelmed by the interfering molecular ions of the same mass and by the scattering tails and decaying products of the potentially more intense $^{226}RaH_n^-$ ions. These interferences, which have been found to be serious in many cases, are completely removed by using the heavy-element AMS system described in Refs. [12,13].

$^{226}Ra^-$ ions, after being extracted from a Cs sputter ion source, were first analyzed by a pair of electric and magnetic analyzers, and then accelerated by a tandem accelerator. In the stripping canal at the central electrode, negative ions undergo charge-changing processes. This results in multiply charged positive ions which are further accelerated back to ground potential. After acceleration, positive ions of ^{226}Ra, with a particular charge state, were first selected by an electric analyzer and then analyzed further by a pair of post-acceleration magnetic and electric analyzers with higher resolution. Finally, the selected positive ions of ^{226}Ra were observed by a gas ionization detector.

With this method, all the molecular interferences are eliminated if $^{226}Ra^{+q}$ ions with a charge state q higher than 3 are selected. This is because highly charged molecular ions quickly break up due to Coulomb repulsion and have lifetimes too short for them to reach the final detector. However, if the resulting fragments have the same m/q and E/q ratios as those of $^{226}Ra^{+q}$ ions, where m and E are the mass and energy of the fragments, they can pass through all the post-acceleration electric and magnetic analyzers to reach the final detector, together with $^{226}Ra^{+q}$ ions. Since these fragments must have lower energies, they are readily separated from $^{226}Ra^{+q}$ ions by the ionization chamber if their intensities are not excessive. In fact, the molecular fragments from the charge-changing process $^{113}In_2^- \rightarrow {}^{113}In^{+2}$ can be used as a pilot beam in setting up the AMS system to detect $^{226}Ra^-$ through the charge-changing process $^{226}Ra^- \rightarrow {}^{226}Ra^{+4}$. The small difference in the m/q ratios of the two processes, due to nuclear mass defects, can be resolved by the post-acceleration magnet with mass

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resolving power $M/\Delta M = 2600$, which can therefore be calibrated uniquely by scanning the field over the peaks of the two processes. During such a scan, the potentially interfering $^{226}Ra^{+4}$ ions from the injection of hydride negative ions ($^{226}RaH^- \rightarrow {}^{226}Ra^{+4}$) can also be resolved from the process of interest. The major difficulty of the experiment is to achieve a sufficient counting rate of $^{226}Ra^{+4}$ ions, from $^{226}Ra^-$, to carry out the scan of the post-acceleration magnetic field to obtain data with an adequate statistical significance.

Ion-source targets made of a compressed mixture of powered Cigar Lake uranium ore material (20–60 wt % of U_3O_8) and Nb powder, in the ratio of 0.69 g/g and 0.31 g/g, respectively, have been used as the ^{226}Ra source. The charge-changing process $^{226}Ra^- \rightarrow {}^{226}Ra^{+4}$ at 1.25 MV terminal voltage was used for the observation. A low tandem voltage of 1.25 MV was used because of the limited magnetic rigidity (1.5 T m) of the post-acceleration magnet. Consequently, the experiment had to be carried out by detecting $^{226}Ra^{+4}$ ions with a low energy (6.27 MeV). The counting rate of $^{226}Ra^{+4}$ ions also had to be greater than 1 count per 1000 s, which was the base background level due to the electronic noise of the system. In the experiment, counting rates more than ten times higher than the background were obtained and an adequate energy resolution ($\sim 13\%$) of the ionization chamber was achieved for detecting 6.27 MeV $^{226}Ra^{+4}$ ions.

With the counting rate greater than 10 counts per 1000 s, a scan of the post-acceleration magnetic field was possible in order to show that the detected $^{226}Ra^{+4}$ ions resulted from the injection of $^{226}Ra^-$ ions instead of $^{226}RaH^-$. Figure 1 shows a typical result of such a scan of the post-acceleration magnetic field, which was subsequently calibrated by using $^{113}In_2^- \rightarrow {}^{113}In^{+2}$. The post-acceleration magnetic field was also calibrated by the detection of $^{223,235,238}U^-$ and $^{230,232}Th^-$ ions through a charge-changing process similar to that of $^{226}Ra^-$.

Under the same conditions, $^{231}Pa^-$ was also observed from the uranium ore targets. The Cigar Lake uranium deposit is known to be well contained and geologically ancient, so its decay chain of uranium is expected to be at equilibrium. Therefore the relative abundances of the isotopes ^{226}Ra, ^{230}Th, ^{231}Pa, and $^{234,235,238}U$ in the targets are known, and so these can be used to estimate the relative electron affinities of the four elements through a systematic measurement of the intensities of $^{226}Ra^-$, $^{230}Th^-$, $^{231}Pa^-$, and $^{234,235,238}U^-$. Since these negative ions are produced from the same target, the conditions on the target surface can be assumed to be identical for generating them. If the same transmission efficiency is also assumed for detecting these negative ions and their mass differences are neglected, the negative ions yield (Y) is then a simple exponential function of the electron affinity (A) [11], $Y = K_1 e^{K_2 A}$, where K_1 and K_2 are positive constants. When corrected for the lower abundances, the relative negative ion yields of these negative ions were measured within $\sim 10\%$ uncertainty [13] to be

$$^{226}Ra^-:{}^{230}Th^-:{}^{231}Pa^-:{}^{234}U^- \approx 1.3:4.0:1.0:1.0:1.0 ,$$

and so the electron affinities of these elements should be

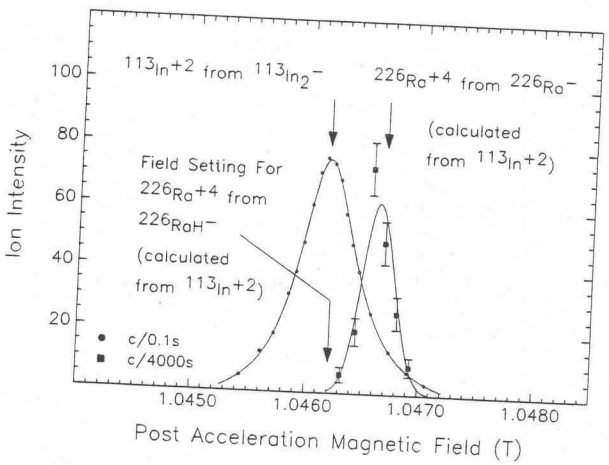

FIG. 1. Typical results of scans of the post-acceleration magnetic field are shown, which identify the detection of the charge-changing process $^{226}Ra^- \rightarrow {}^{226}Ra^{+4}$ in comparison with its pilot process $^{113}In_2^- \rightarrow {}^{113}In^{+2}$, where $^{113}In_2^-$ is a diatomic negative ion. The $^{226}Ra^{+4}$ counting rate is fitted with a Gaussian distribution, and each point is weighted by the square root of its total counts. The arrow, showing the detection of the negative ion $^{226}Ra^-$ and the potential detection of the ion $^{226}RaH^-$, are positioned at the field values where these processes are expected to occur, according to the mass-defect calculations with respect to the measured central field (also pointed to by an arrow) of the $^{113}In_2^-$ pilot process. The intensity units are either counts per 0.1 s or counts per 4000 s as indicated.

of similar magnitude, assuming the same number of bound quantum states for all the negative ions.

With similar procedures, $^{244}Pu^-$ was observed from a target made of compressed mixture of powders of ^{244}Pu attached to charcoal (0.13 g/g) and Nb (0.87 g/g). The target contained ~ 17 mg total sample material, which was estimated to contain $\sim 10^{13}$ ^{244}Pu atoms, so the ^{244}Pu concentration was similar to that of $^{226}Ra^-$. The sputter rate of the ^{244}Pu target was also found to be similar to that of the uranium ore targets, ~ 0.75 mg hr^{-1}, by measuring the weight of targets before and after a few hours of sputtering with the same level of Cs^+ current. The properties of $^{226}Ra^-$, $^{231}Pa^-$, and $^{244}Pu^-$ could therefore be compared with the negative ions of Th and U. As both Th and U negative ions were not dissociated by a 5 MV/m electric field in an electric dissociator [14], and as their normalized negative ion intensities were similar to the values for Ra, Pa, and Pu, the electron affinities of all these elements have been estimated to be greater than 50 meV.

It must be pointed out, however, that the experimental method described above cannot distinguish between the observed negative ion being in a bound state or in a metastable state. A few comments should be made about the possibility of Ra^- in a metastable state.

The lowest excited state of Be^- is known to be the $2s2p\ ^4P$ quartet [15]; its autodetachment to the ground state $2s^2\ ^1S$ of the atom is a forbidden transition on L-S coupling, but it decays to the neutral Be ground state via the spin-orbit-induced Coulomb autodetachment with a long lifetime (the latest experimental result is 45 ± 5 μs [16]). Another possible excited state is $2p^3\ ^4S$ which de-

cays to $2s2p^2\,^4P$ by an $E1$ transition. Other long-lived excited states are rare and are not likely to survive longer than the $2s2p^2\,^4P$. The situations for Mg^- to Ra^- are expected to be similar, but as the ion gets heavier the spin-orbit interactions are expected to be larger and autodetachment rates greater. It is predicted [17] that the lowest configuration in Mg^- is $3s3p^2\,^4P$ and the lifetimes of the $J=\frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$ levels are calculated to be 7.8, 9.8, and 1.6 ns, respectively. The last two values are supported by another calculation [18]. These estimated lifetimes of Mg^- are therefore too short for the ion to survive the AMS injection, and indeed no signal from Mg^- has been observed with the AMS system [19]. The situation for the Ca^- $4s4p^2\,^4P$ metastable state is complicated. Ca^- ions in the $4s4p^2\,^4P$ metastable state were reported to have been observed ~ 4 μs after their formation [6], but the autodetachment of the ^4P $J=\frac{3}{2}$ and $\frac{5}{2}$ states of Ca^- was calculated [18] to be very fast (0.822 and 0.0865 ns, respectively). Though more experimental studies are required to clarify this matter, one cannot expect such a dilemma for the AMS observation of the heavier negative ions, Sr^-, Ba^-, and Ra^-, which take $\sim 50-100$ μs from their formation to arrive at the terminal of the tandem accelerator. We therefore conclude that, with the evidence presented above, the stable negative ion of radium has been observed, with a binding energy estimated to be greater than 50 meV, confirming the theoretical predictions [3–5].

No information is available on the possible metastable states of the negative ions of protactinium and plutonium. However, it is very likely that the observed negative ions of protactinium and plutonium are in bound states. Theoretical estimates of the affinities of lanthanide and actinide negative ions that were based on the assumption that the extra electron goes to the $(n-1)d$ or $(n-2)f$ orbital suggested that Nd, Pm, Eu, Dy, and Pu cannot form stable negative ions [20,21]. This assumption is questionable in light of a systematic experimental observation of the lanthanide negative ions [19] and now the observation of $^{244}Pu^-$ ions. More detailed studies are needed on the roles of the $(n-1)d$, $(n-2)f$, and possibly the $(n)p$ orbitals in forming the negative ions of lanthanide and actinide elements. The importance of $(n)p$ orbitals for stable negative ion formation, in a number of cases, has been stressed recently [22].

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