Conference paper

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History of nihonium

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Abstract: Discovery of new element has been an impossible dream for Japanese people for over 100 years. Finally, in 2017, nihonium earned a permanent seat on Mendeleev's Periodic Table. The history of search for new elements in Japan is described here together with our challenges on the cosmological history of element genesis in the universe.

Keywords: element 113; Mendeleev 150; nihonium; Nishina; Ogawa; RI beam; RIBF; RIKEN.

Introduction: RIKEN, His Majesty's Research Institute

RIKEN, the birth place of nihonium was founded in 1917 as the first Japanese research institute for physical and chemical science. A part of the budget for its establishment was donated from the Emperor's family. With such honorable money to finance our research, we need to repay them with the very best research results, hopefully with national pride. We believe we have done that for the Emperor three generations later[1] with the discovery and naming of nihonium.

At the naming ceremony on the 14th of March 2017, just 100 years after the donation, Reiwa Emperor Naruhito (he was still the crown prince at the time of the ceremony) gave us a greeting with his personal story (see Fig. 1). When he was a high school student, he had to make 30 copies of Mendeleev's Periodic Table by hand as homework during summer vacation. He said, "It was very tough to draw so many copies of the Periodic Table, and I am very much impressed that one of the elements on the table now has a name after Nihon." Following this majestic greeting, the president of IUPAC, Natalia Tarasova, declared that the 113th element is named nihonium. It was a very touching moment.

Indeed, Japan is written with two Chinese characters which mean "the land of the rising sun". They are read as "Nihon" or "Nippon". "Japan" is a European dialect to pronounce Nippon. It is like Genève, Geneva or Genf, all of which are from the same verbal origin and officially allowed to be used in Switzerland (or Swiss). The supporters of our national teams of football, volleyball etc. often scream "Nippon cha cha cha", so the name Nippon became better known than Nihon. Nevertheless, we named the 113th element nihonium because of the story to be described later.

Thereafter, Japanese became fanatics of the Periodic Table. The mayor of Wako City where RIKEN is located, is one of them. He even created "Nihonium Avenue" as shown in Fig. 2. If you come to RIKEN, take a

1 Recent Japanese eras are; 123th Taisho Emperor Yoshihito Era from 1912, 124th Showa Emperor Hirohito Era from 1912, 125th Heisei Emepror Akihito Era from 1989 and 126th Reiwa Emperor Naruhito Era from 2019.

Article note: A collection of invited papers based on presentations at "Mendeleev 150": 4th International Conference on the Periodic Table endorsed by IUPAC, Saint Petersburg (Russia), 26–28 July 2019.

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Fig. 1: Majestic greetings from the crown prince Naruhito, now the Emperor of Japan (in front) at the nihonium naming ceremony. Back row from left, Kosuke Morita (the expermental group leader), Natalia Tarasova (the president of IUPAC) and Hiroshi Matsumoto (the president of RIKEN).

Fig. 2: Nihonium Avenue, 15 min walk from Wako-shi station to RIKEN, with 118 pavestones of element symbols from hydrogen to oganesson. On the way, you will find a three dimensional nihonium monument made by the local manufacture and at end of the avenue, you will reach a big monument of nihonium.

15 min walk from Wako City Station to RIKEN, the birth place of nihonium, by following Nihonium Avenue. This is the Walk of Fame for elements where you will see the paving stones like these from hydrogen to oganesson. Aside from these paving stones, you will also encounter a three-dimensional monument, beautifully made by a 3D printer. Finally, at the entrance of RIKEN, you will reach a big monument of nihonium. Wako City is now officially the city of elements.

Nipponium, the 43th element?

Thanks to the International Year of Periodic Table, so many articles have been submitted to the public, with scientific, educational or sometimes amusing contents. Among them, we have encountered one particular tweet [1] from the company Cefic, showing the Periodic Table with the country and date of discovery. Surprisingly, the table shows two Japanese flags in it.

One is the 113th element nihonium first discovered in 2004 and named after the country it originated from. The other Japanese flag can be seen in the background of the 75th element rhenium, labeled as discovered in 1908 and named after its birth place. Indeed, rhenium was discovered in 1925 in Germany, and the name came from Rhein River in Europe, not in Japan. There is an inside story to this that I would like to share on this occasion.

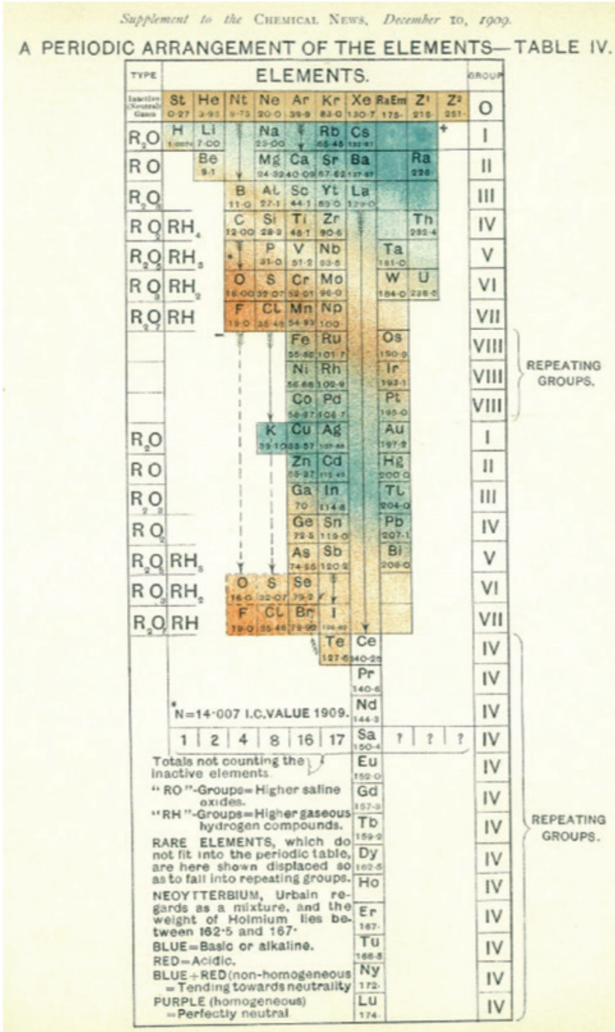

Fig. 3: The Periodic Table by F.H. Loring, Chem. News, 100 (1909) 281–287.

In 1908, a Japanese Chemist Masataka Ogawa published [2] that he had discovered the 43rd element and named it nipponium with the symbol Np. This, you can find in the old Periodic Table as shown in Fig. 3. Later, however, the 43rd element was found to be unstable, not existing in nature, and was synthesized in 1937 using an accelerator, and then named technetium (Tc). Consequently, nipponium (Np) disappeared permanently from the Periodic Table.

Later again, it was proven by the photo shown in Fig. 4 that the element which Ogawa had found was the 75th element [3]. Indeed, when they realized this, the 75th element had already been discovered in 1925 and named Rhenium. It was too late. Ever since this story, discoveries of element have been achieved through the synthesis of naturally non-existing elements by accelerator or by some other artificial means. Then came RIKEN's turn.

Np is Neptunium, not Nipponium

Yoshio Nishina, the godfather of physics in Japan, whom our research center was named after, was born in 1890. After graduating from the University of Tokyo, he became a researcher at RIKEN, and was sent to Europe. He invented the Klein–Nishina's formula [4] which describes scatterings of electron and photon, during his stay in Niels Bohr Institute. After returning to Japan, he became a chief scientist at RIKEN and

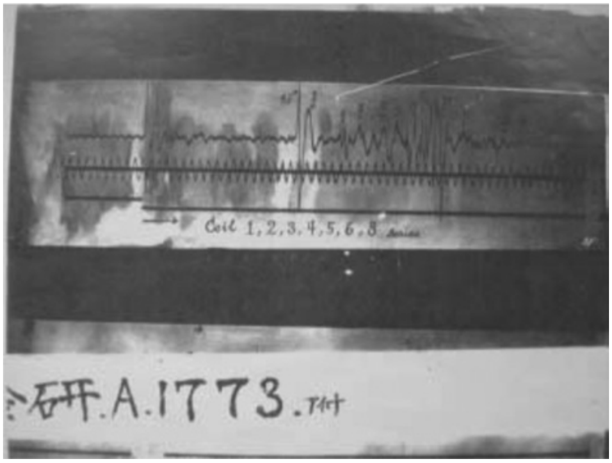

Fig. 4: The photo of X-ray analysys of Ogawa’s Nipponium taken by Shin-ichi Aoyama. This photo has been kept by his family, is now stored in Tohoku University.

started his own laboratory in 1931. His laboratory was joined by H. Yukawa,[2] S. Tomonaga,[3] and S. Sakata,[4] starting a lineage of Japanese Nobel Laureates.

In 1937, Nishina completed the construction of the first cyclotron in Japan in his laboratory in RIKEN. In 1938, he irradiated 238-Uranium (atomic number is 92) by fast neutrons created with his cyclotron and synthesized 237-U with neutron knockout reaction and observed its beta decay. This means 237[93] was created via

$$^{238}U + n -> {}^{237}U + 2n -> {}^{237}[93] + \beta^- \text{ (see Ref. [6]).}$$

Second beta decay from $^{237}[93]$ was not observed because the half-life of $^{237}[93]$ is 2.14 million years long. In 1939, the USA group led by McMillan discovered the 93rd element via neutron capture reaction $^{238}U + n -> {}^{239}U -> {}^{239}[93] + \beta^-$, and successfully observed the beta decay of $^{239}[93]$ whose life-time is 2.4 days [7]. They earned the naming rights and named the 93th element neptunium with the symbol Np, which was once the symbol of nipponium. Nishina just missed his chance.

So, earning a seat on the Periodic Table has been a 100-plus-year-long impossible dream for Japanese, with some historical background of great accomplishments with regrettable results by the two senior master scientists. From RIKEN’s view point, the best way to repay the Emperor had been in vain.

A long and winding road leading to the RI Beam Factory and the Nihonium experiment

While conducting experiments with the first cyclotron, Nishina started to build the second one, the largest cyclotron in the world at the time. In building these cyclotrons, Nishina learned a great deal from Ernest Lawrence, the inventor of cyclotron. Nishina and Lawrence built the accelerators shown in Fig. 5 in America

2 Hideki Yukawa, Nobel Prize Winner in 1945 for his prediction of the existence of mesons on the basis of theoretical work on nuclear forces.

3 Shin-ichiro Tomonaga, Nobel Prize Winner in 1967 for his fundamental work in quantum electrodynamics, with deep-ploughing consequences for the physics of elementary particles.

4 Shoichi Sakata missed out on Nobel Prize in spite of his many distingudhed Nobel-class work. Makoto Kobayashi and Toshihide Maskawa, Nobel Laureates in 2008, are Sakata’s students.

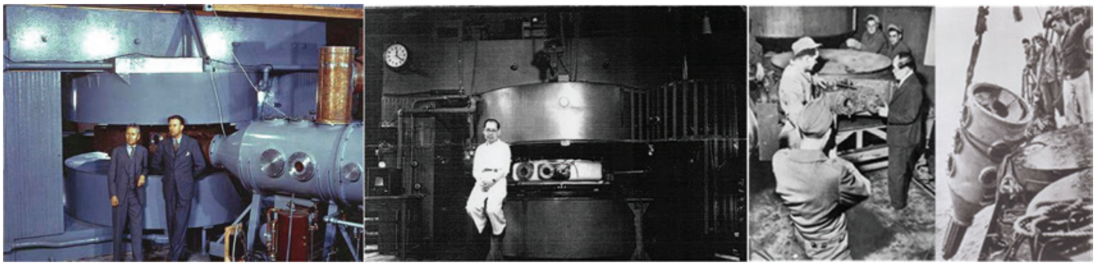

Fig. 5: From left to right. Ernest Lawrence and his cyclotron, Yoshio Nishina and his cyclotron, and the scenes taken of Nishina's cyclotron being abandoned.

and in Japan. They even shared the procurement together. These cyclotrons were thus like brothers and look very similar to one another.

Lawrence's cyclotron contributed in making a history of great discoveries. So many new elements were synthesized and discovered by this machine. However, the story of Nishina's cyclotron completed just before the end of the World War II was that of a tragedy. After the war, American army came, disassembled the cyclotron and threw them into Tokyo bay. It was a regrettable incident which halt the advancement of nuclear science in Japan.

We were disappointed but didn't give up. We have had a tradition to climb on top of the completed cyclotron and take a picture. Figure 6 shows a glimpse of our history of building cyclotrons where one can see the size of the cyclotrons getting bigger. In 2006, the 9th cyclotrons since Nishina's first one, was completed at the heart of our facility, and Nishina's impossible dream was once again realized. At present, using 5 cyclotrons in cascade (from 5th to 9th), with two linear accelerators as injectors, the RIKEN Nishina Center operates the RI Beam Factory (RIBF), the world's best facility in accelerating heavy elements. Under the RIBF project, we

Fig. 6: RIKEN's cyclotrons at a glance. From left top to right bottom; Nishina's second cyclotron, now sunk in Tokyo Bay. The fourth cyclotron completed in 1966, is now the monument in RIKEN's Wako Campus. The fifth cyclotron completed in 1986, is still active. The ninth cyclotron completed in 2006, is the largest superconducting cyclotron in the world.

have upgraded every corner of the facility and the linear accelerator achieved enough power to compete in the race to discover new elements.

Utilizing a beam generated by the linear accelerator, we will go to the limit of the Periodic Table, and with a beam generated by the 9th cyclotron, we will elucidate the origin of elements, i.e. how all the elements of the Periodic Table were created.

Nihonium was created with a fusion of zinc (Z = 30) and bismuth (Z = 83) nuclei. We accelerated zinc as a beam up to about 10 % of the speed of light in order to overcome repulsive Coulomb force between the two nuclei. When fused, the excited nucleus of nihonium (Z = 113) emits one neutron and goes down to the ground state. Neutron emission is limited to only once due to the energy conservation law. This is called the "cold fusion" process and the nuclear processes are well identified as below.

$$\begin{bmatrix}\text{Mass number N+Z}\\ \text{Atomic number Z}\end{bmatrix}\text{Symbol}: {}^{70}_{30}\mathrm{Zn} + {}^{209}_{83}\mathrm{Bi} \rightarrow {}^{279}_{113}\mathrm{Nh} \rightarrow {}^{278}_{113}\mathrm{Nh} + n$$

This is easier to write than to do in real life. Imagine looking at the golf green at the top of Mt. Fuji. You are in Tokyo, 100 km away. You putt the golf ball by aiming at the hole with just the right speed, high enough to climb the Coulomb's hill but not so much as to overrun. The mathematical probability is one in a quadrillion (10^{15}). This requires a powerful accelerator with high intensity, a rotating target system to cool the target down, efficient detectors to detect alpha decays of the product, etc.

The search for the element started in 2003, with the first event followed by 4 alpha decays observed in 2004, the second event with 4 alpha decays again occurring in 2005, and finally the history-making third event observed in 2012 followed with beautiful 6 alpha decays as described below.

$${}^{278}_{113}\mathrm{Nh} \xrightarrow{\alpha\,\text{decay}} {}^{274}_{111}\mathrm{Rg} \xrightarrow{\alpha} {}^{270}_{109}\mathrm{Mt} \xrightarrow{\alpha} {}^{266}_{107}\mathrm{Bh} \xrightarrow{\alpha} {}^{262}_{105}\mathrm{Db} \xrightarrow{\alpha} {}^{258}_{103}\mathrm{Lr} \xrightarrow{\alpha} {}^{254}_{101}\mathrm{Md}$$

The third event was obtained during the aftermath of the Tohoku earthquake and the Fukushima nuclear disaster when the electric power supply was still very limited. The paper on the third event was published with the hope that pride and faith in science would replace the lost trust of those who had suffered from the tragic incident. In 2012, we claimed the discovery of element 113 to IUPAC. In 2015, we earned the naming rights to it, and in 2017, we named the element nihonium. Due to the historical turn of events as described previously, we couldn't use the name nipponium and the symbol Np. The experimenters thus chose nihonium with the symbol Nh, paying homage to their predecessors.

In Table 1, we summarized the "brothers" of nihonium, i.e. isotopes. Morita et al. discovered ^{278}Nh in RIKEN, while Oganessian et al. discovered five different isotopes of nihonium at Flerov Laboratory of Nuclear Reactions (FLNR). It was thus indeed very lucky for the Japanese team that they earned the naming rights for nihonium. We were a little bit faster than the rivals in obtaining a proof beyond a reasonable doubt as published in Pure and Applied Chemistry [5] by the IUPAC/IUPAP Joint Working Party which considers claims for discovery and naming of new chemical elements.

As Morita said in his video message at the beginning of my talk, he participated in the experiment conducted by Yuri Oganessian many years ago. Oganessian has been a mentor of Kosuke Morita of RIKEN

Table 1: Nihonium isotopes discovered. Nobody has ever observed 279-Nh to 281-Nh. FLNR stands for Flerov Laboratory of Nuclear Reactions.

Place	**RIKEN**		**Nobody has seen yet**		**FLNR**	**FLNR**	**FLNR**	**FLNR**	**FLNR**
Symbol	${}^{278}_{113}\mathrm{Nh}$				${}^{282}_{113}\mathrm{Nh}$	${}^{283}_{113}\mathrm{Nh}$	${}^{284}_{113}\mathrm{Nh}$	${}^{285}_{113}\mathrm{Nh}$	${}^{286}_{113}\mathrm{Nh}$
#proton	113	113	113	113	113	113	113	113	113
#neutron	165	166	167	168	169	170	171	172	173

for many years. Morita learned the ABCs of superheavy element experiments from Oganessian. This is the most important foundation which eventually earned one seat in the 7^{th} row of the Periodic Table for Japan or in another word Nihon. If the 118^{th} element named oganesson is a son of Oganessian, the 113^{th} element named nihonium can be called Oganessian's grandson. Please note that Mendeleev himself had a Japanese granddaughter.

Is nihonium only man made?

All the recent element discoveries required syntheses using an accelerator. Has the universe ever created nihonium? This question is relevant to the quest for the origin of all the elements in the universe.

Figure 7 shows a nuclear chart made of LEGO. It is displayed in the exhibit room called Cyclopedia in the RIKEN Nishina Center. It doesn't really show periodicity, but instead is a 3-dimensional expression of a nuclear chart with bars showing possible combinations of protons and neutrons. The black, red and yellow bars represent stable nuclei, unstable nuclei, and unstable nuclei yet to be discovered, respectively (the green bars are the unstable nuclei discovered at RIKEN). Today, 118 elements are known to exist, but as a core of elements, we already know about 3000 nuclei (red) of which only 270 are stable (black). We expect that 172 elements may exist and 6000 nuclei may exist (yellow). How were these stable nuclei on the earth created? We believe we know the answer: Big Bang.

The universe was born 13.8 billion years ago with the Big Bang. In the first 1 ms after the Big Bang, quarks & gluons were created, and were bound to protons and neutrons. In the first 3 min, strong forces worked between protons and neutrons, and they were bound to make small nuclei.

It took about 400 thousand years for the universe to become less dense and cooler enough to allow atoms to exist, the bound states of electrons and nucleus. This caused the cleanup of the universe, i.e. photon being able to traverse long distance across the universe.

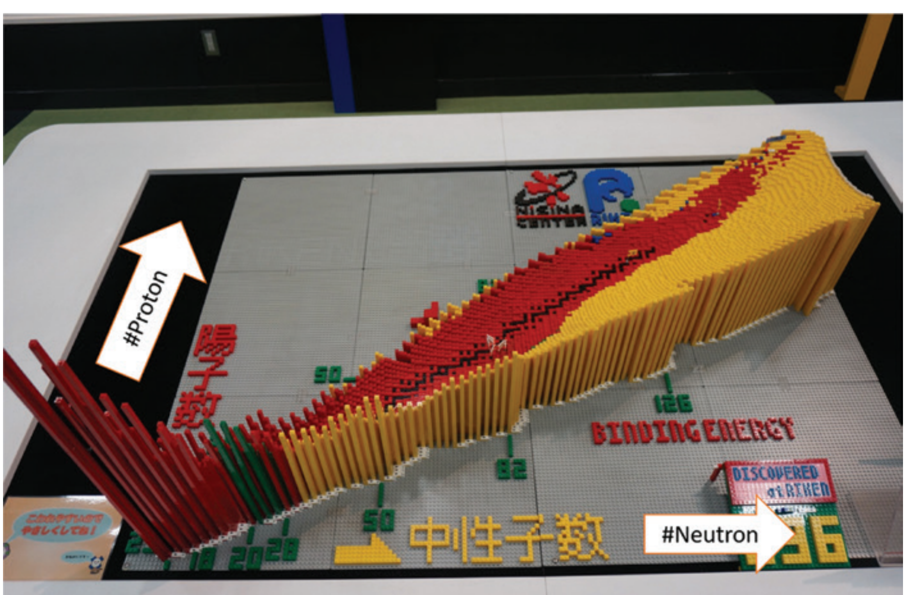

Fig. 7: The three-dimensional nuclear chart made of LEGO, displayed in the exhibit room called Cyclopedia in the RIKEN Nishina Center. The black bars along the valley are stable nuclei, the red bars are unstable nuclei, and the yellows are unstable nuclei yet to be discovered. The green bars are the unstable nuclei discovered at RIKEN. The height of bars shows the weight (i.e. energy) per nucleon (proton + neutron).

Now that atoms are charge neutral, they started to clump together with gravity. Finally, stars were created. It took one billion years after the Big Bang. In stars, large scale nucleosynthesis took place. Like in our sun, protons and deuterons were fused into helium. Later, they are fused into beryllium, then carbon. This process can continue until iron. Why?

Figure 8 is the LEGO nuclear chart again but viewed from the heavier element side. The heights of the bars represent the weight per nucleon. In other words, energy per nucleon. At the bottom of this valley, there are iron, chromium and nickel. They are energetically most stable nuclei. So, in stars, nucleosynthesis can go on until around iron. Keep in mind that nature favors iron, the most stable nucleus.

Then the big question arises. How can we have heavier nuclei than iron? The answer lies in other cosmological events like the Big Bang. Recently, gravitational waves were observed. They are from neutron star or black hole mergers. We believe neutron star mergers or super nova explosions are the source of heavy elements.

In such a circumstance, iron nuclei at the bottom of the valley are absorbing neutrons around them, getting fat like a snowman. Inside the snowman, neutrons convert to protons, increasing the atomic number. So symbolically, the process goes like the arrows shown in Fig. 8, climbing the slope of the valley and reaching to at least uranium. This process is called r-process (rapid process). Figure 9 is the r-process simulation by Wanajo et al. showing how such process can evolve in a merger of two neutron stars [8]. In this calculation, the r-process provided by a neutron star merger seemingly reaches the region of the super heavy elements. Even though the process reaches the super heavy elements, since most of them are unstable, they decay down to the valley, i.e. back to the more stable domain.

They fall into the hole of "stable nuclei" (black bars along the valley of Figure 8) where decays are terminated. These holes are created due to the nuclear structure which is very discrete and has a semi-periodic structure called "magic numbers".

We know that the age of the universe is 13.7 billion (13.7×10^9) years. This is the time scale of nucleosynthesis. While ^{208}Pb is the heaviest stable nucleus, ^{209}Bi can also be considered to be stable since its lifetime is 2×10^{19} years, longer than the age of the universe. The lifetime of ^{238}U is 4.4 billion years which is comparable to the age of the universe, so they barely remain on the earth even though they are unstable. All short-lived nuclei had disappeared.

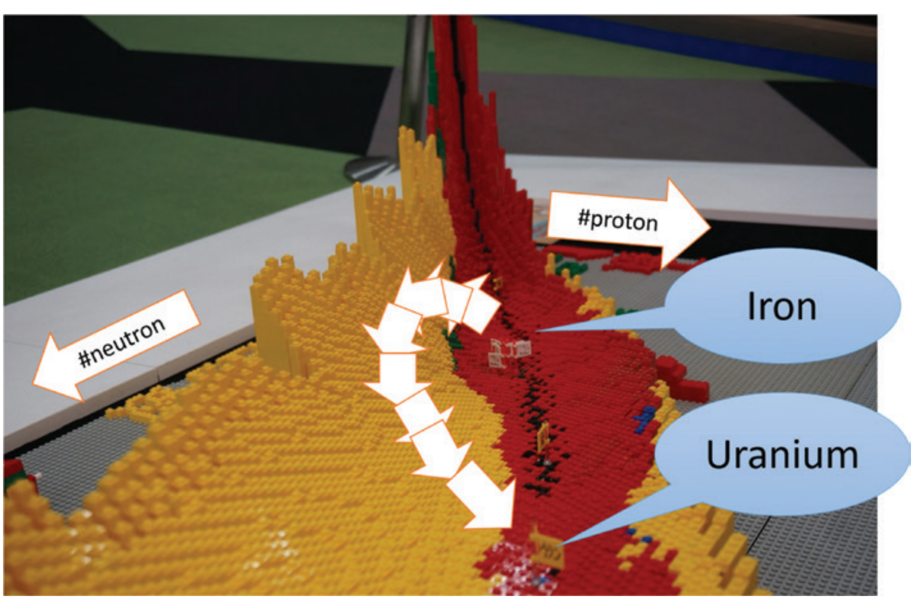

Fig. 8: The LEGO nuclear chart again viewed from the heavier element side. At the bottom of the valley, there exist iron. Chromium and nickel, which are most energetically stable nuclei. The allows show the path on which nuclei grow in neutron-star mergers or super-nova explosions.

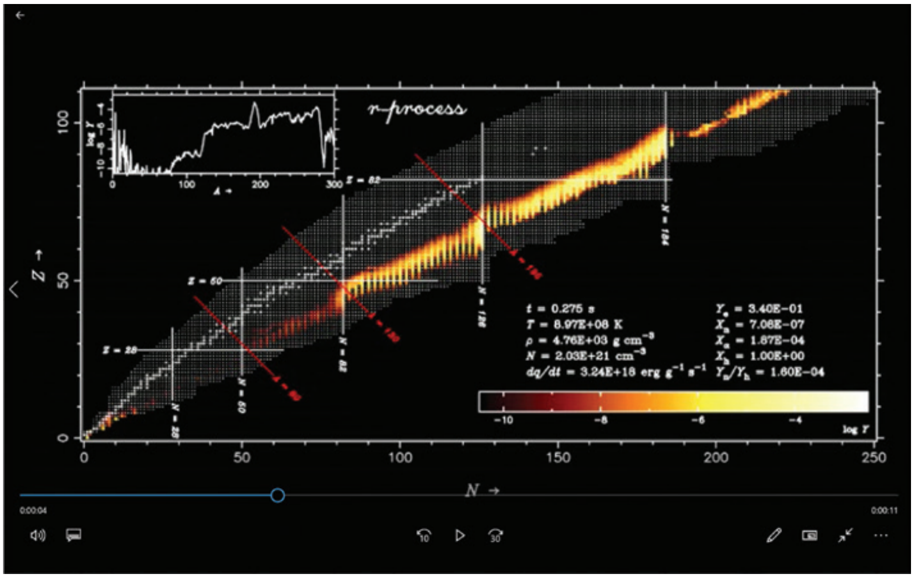

Fig. 9: Nucleosynthesis simulation by S. Wanajo et al. mapped on the nuclear chart. The horizontal axis is the number of neutrons and the vertical axis is the number of protons. The yellow band shows nuclei on the r-process path, at the given time after the neutron-star merger.

Summary

Let me think again, how can the universe ever create nihonium? To reach nihonium, the r-process must be retained by nuclei on the path which must have a lifetime long enough to absorb neutrons or to decay to nuclei with a higher atomic number (via beta decay). Competing losing processes are spontaneous fissions and alpha decays, or the process falls over the "neutron drip line", the limit of the maximum neutron number with a given atomic number. So precisely speaking, we do not know yet whether neutron star mergers could create nihonium or not, due to lack of knowledge of very-neutron-rich unstable nuclei. At our facility, the RI Beam Factory, we will thus continue with our researches to synthesize superheavy elements to investigate the limit of atomic number, and to study the characteristics of neutron-rich nuclei to the neutron drip line to understand the cosmological nucleosynthesis.

Since December 2018, we have started an experiment to search for the 119^{th} element with a vanadium beam on a curium target. We hope to be able to inform you of our discovery in the near future.

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[2] M. Ogawa. *Chem. News* **98**, 249 (1908).
[3] There was a discussion in my presentation about the scientific significance of whether the element which Ogawa had extracted was the 75th element or not. There are some articles on this question as follows. Some are only in Japanese so we should make the English translation for the future study on this matter, although the author thinks there are sufficient proofs to believe as I have written here. "Nipponium as a new element (Z=75) separated by the Japanese chemist, Masataka Ogawa: a scientific and science historical re-evaluation" by Kenji Yoshihara, Proc. Jpn. Acad., Ser. B84 (2008) 232. "On the nipponium by Masataka Ogawa (in Japanese)" by Kenji Yoshihara, Chemistry and Chemical Industry Vol. 66–67 p. 540, 2013. "On nipponium (in Japanese)" by Kenji Yoshihara, Kagakushi, Vol. 42 (2015) pp. 206–209. "A Tale of Seven Elements" by Eric Scerri, Oxford press, 2013, ISBN: 9780195391312.

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