Discovery of the element **nipponium** in 1908 and its **Re**-assignment to **rhenium**

Yoshi Maeno @ Kyoto University

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Ogawa's nipponium and its re-assignment to rhenium

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Ehime Prefectural Science Museum | Genesis Research Institute | Kyoto University

① Motivation: Issues over nipponium and rhenium

② Ogawa's discovery of nipponium

③ Yoshihara's identification of "nipponium" as rhenium

④ Our new evaluation of "nipponium" as rhenium (75 Re)

Introduction: at Mendeleev 150 conference (July 2019, St. Petersburg)

Japan: 日本 (Nihon or Nippon, both accepted)
Element 113 Nh (nihonium)

Morita, Enyo

Maeno, Scerri, Seaborg

Japan = 日本 = Nippon OR Nihon

Dr. Enyo gave a plenary talk on nihonium $_{113}$Nh.

Then, Dr. Eric Scerri commented :
"There is only weak evidence that Ogawa's nipponium was rhenium. I do not believe in that claim."

In fact, there are some reasons why Ogawa's work was not well evaluated yet.

We decided to re-evaluate previous studies.

Issues to assign Ogawa's nippoium as rhenium

1. Is there **solid evidence for rhenium**?
2. Is it really possible to extract nearly **100 mg of rhenium from the thorianite** mineral?
3. Why did Ogawa not report on detailed properties of nipponium after his first three papers, especially on **X-ray spectroscopic evidence** that became available in later years?
4. Why did Ogawa not re-assign nipponium as the element 75 himself even after the report by the Noddacks? And why did **Ogawa's colleagues in Japan** not report on such a re-assignment even after Ogawa's death?
5. Why is the absence of rhenium in the **zirconium silicate** often used as evidence against Ogawa's discovery?

International recognitions of Ogawa's nippoium as rhenium

Negative recognitions in the past:

・**Hevesy** (1925)
The silicate (supposedly) containing the new element nipponium, provided by Mr. R.-B. Moore, were composed, essentially, of zirconium silicate having a content of 2% of hafnium.

・**Noddack** *et al.* (1925)
They claimed the discovery of elements 43 (masurium) and 75 (rhenium), but did not cite Ogawa's work.

・**Van Spronsen** (1969)
He quoted Hevesy's report and continued that Ogawa's report did not satisfy the chemical properties to identify nipponium to hafnium.

Modern positive recognitions:

・**Theodore Gray** (2009) *The Element*

・**Fontani** et al. (2015) *The Lost Elements*,
They also criticize Western science community to accept Hevesy's misunderstanding.

・**Peter van der Krogt** "Elementymology & Elements Multidict" website

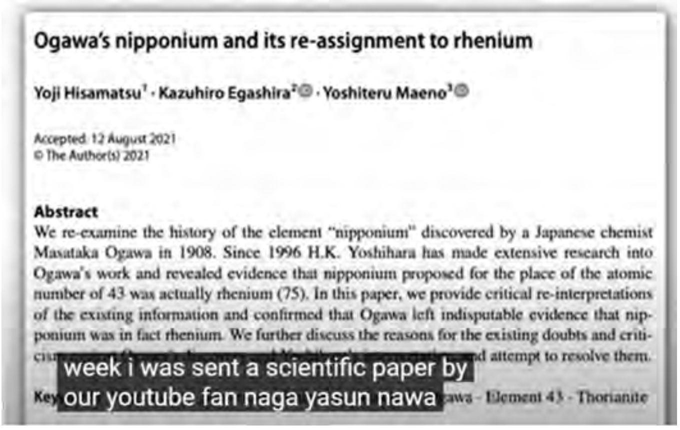
・**The Royal Society of Chemistry (RSC)** (2021) Periodic-Table website

・**John Emsley**'s book (2011)

Nipponium - The Element that Wasn’t –

Periodic Table of Videos

2021/12/13 (7:10) viewed 308,979 times



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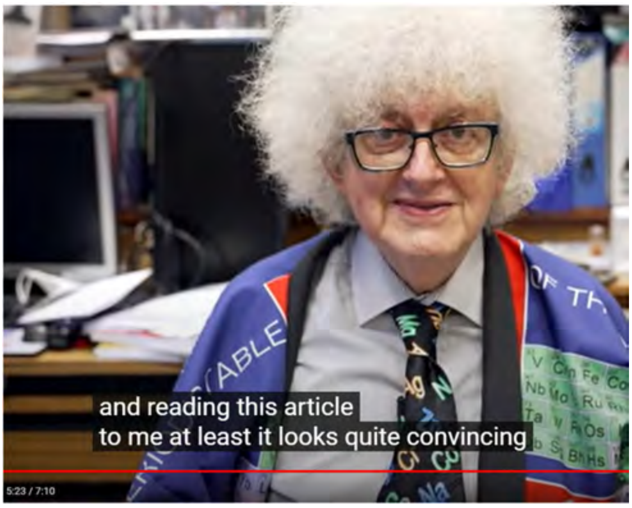
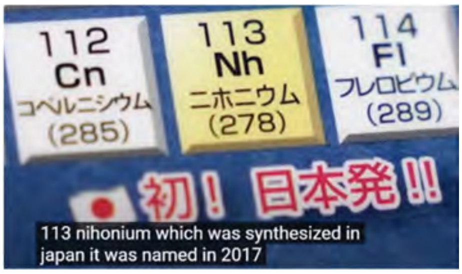
Abstract
We re-examine the history of the element “nipponium” discovered by a Japanese chemist Masataka Ogawa in 1908. Since 1996 H.K. Yoshihara has made extensive research into Ogawa’s work and revealed evidence that nipponium proposed for the place of the atomic number of 43 was actually rhenium (75). In this paper, we provide critical re-interpretations of the existing information and confirmed that Ogawa left indisputable evidence that nipponium was in fact rhenium. We further discuss the reasons for the existing doubts and criti[illegible]d attempt to resolve them.

Key[illegible]awa · Element 43 · Thorianite

Nagayasu Nawa

Very surprisingly there have been huge arguments did Ogawa discover rhenium.



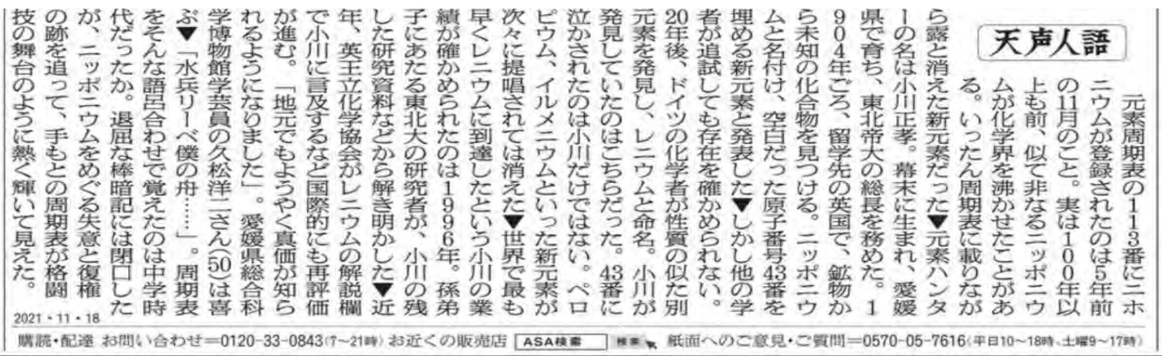


Japan = 日本 = Nippon OR Nihon

Special exhibition and citation in a very well-known newspaper column in Japan

Special exhibition
at Ehime Prefectural Science Museum
Oct. - Nov. 2020

Co-author
Yuji Hisamatsu



天声人語

元素周期表の113番にニホニウムが登録されたのは5年前の11月のこと。実は100年以上も前、似て非なるニッポニウムが化学界を沸かせたことがある。いったん周期表に載りながら露と消えた新元素だった▼元素ハンターの名は小川正孝。幕末に生まれ、愛媛県で育ち、東北帝大の総長を務めた。1904年ごろ、留学先の英国で、鉱物から未知の化合物を見つける。ニッポニウムと名付け、空白だった原子番号43番を埋める新元素と発表した▼しかし他の学者が追試しても存在を確かめられない。20年後、ドイツの化学者が性質の似た別元素を発見し、レニウムと命名。小川が発見していたのはこちらだった。43番に泣かされたのは小川だけではない。ペロピウム、イルメニウムといった新元素が次々に提唱されては消えた▼世界で最も早くレニウムに到達したという小川の業績が確かめられたのは1996年。孫弟子にあたる東北大の研究者が、小川の残した研究資料などから解き明かした▼近年、英王立化学協会がレニウムの解説欄で小川に言及するなど国際的にも再評価が進む。「地元でもようやく真価が知られるようになりました」。愛媛県総合科学博物館学芸員の久松洋二さん(50)は喜ぶ▼「水兵リーベ僕の舟……」。周期表をそんな語呂合わせで覚えたのは中学時代だったか。退屈な棒暗記には閉口したが、ニッポニウムをめぐる失意と復権の跡を追って、手もとの周期表が格闘技の舞台のように熱く輝いて見えた。

2021・11・18

購読・配達 お問い合わせ＝0120-33-0843(7~21時) お近くの販売店 ASA検索 紙面へのご意見・ご質問＝0570-05-7616(平日10~18時、土曜9~17時)

Asahi Newspaper
On the top page
2021/11/18

Ogawa and nipponium

Masataka Ogawa (1865 – 1930)

Masataka Ogawa (1865 –1930).

Taken in ca. 1911

1865 Born in Ehime

1889 Graduated from Imperial University (Univ. of Tokyo today)

1889 Entered its graduate school (advisor: Edward Divers)

1904 – 1906 Studied under William Ramsay*
at University College London (UCL)

* Ramsay: 1904 Nobel Prize in Chemistry
for his discovery of noble-gas elements

1908-1909 Published papers reporting the new element
nipponium Np, assigned as the element 43.

1911 - Dean of the College of Science at Tohoku Imperial
University (Tohoku Univ. today, in Sendai)

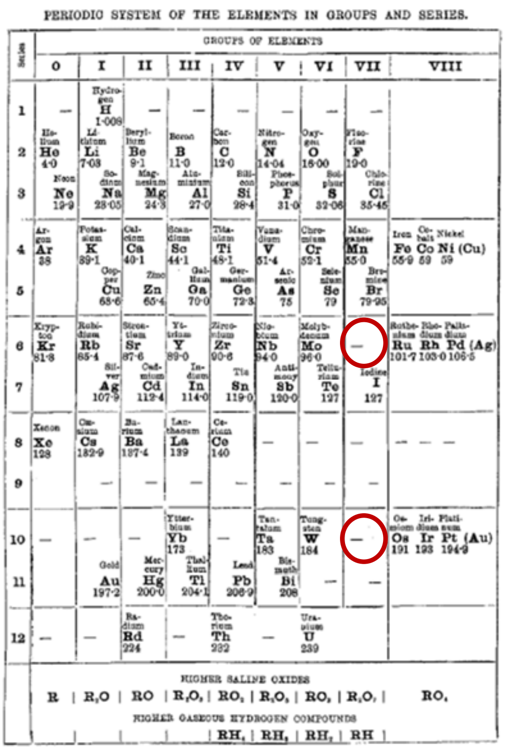
1919 - President of Tohoku Imperial University

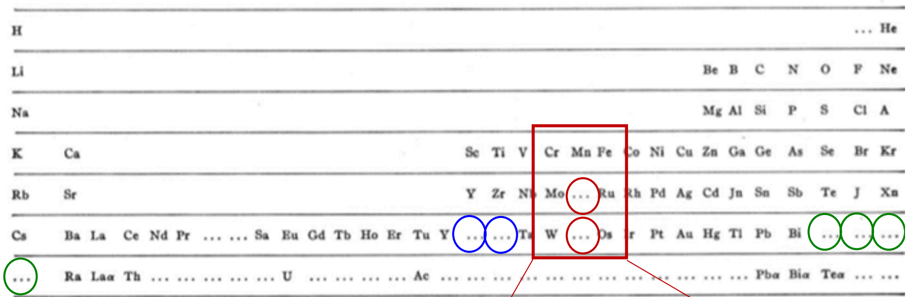
1930 Died of gallbladder disease

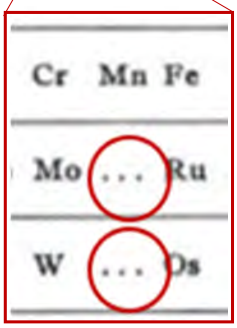
Periodic Tables as of 1905

Dmitri Mendeleev
Principles of Chemistry,
3rd ed., Longmans
(1905) .

Alfred Werner
Bericht. **38**, 914-921 (1905).







3d

4d

5d

Tokyo Electron

43 Tc technetium (1937 -)
75 Re rhenium (1925 -)

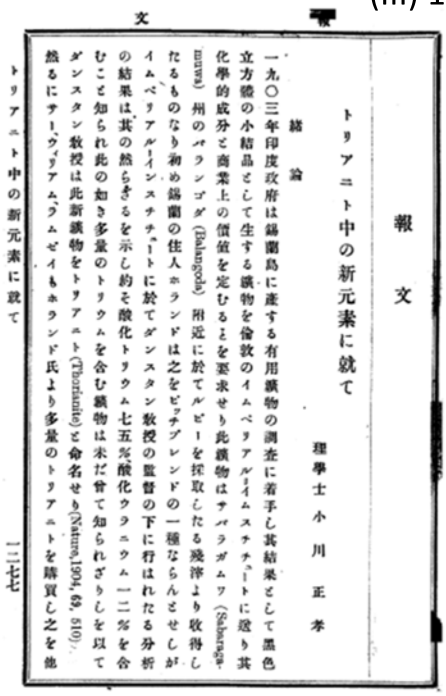
Ogawa's papers on nipponium

(I) Ogawa, M.: "Preliminary Note on a New Element in Thorianite".
J. Coll. Sci. Imp. Univ. Tokyo **25**, Art. 15, 1–11 (1908a)
(reprinted in Chem. News **98**, 249-251 (1908))

(II) Ogawa, M.: "Preliminary Note on a New Element allied to Molybdenum".
J. Coll. Sci. Imp. Univ. Tokyo **25**, Art. 16, 1–13 (1908b)
(reprinted in Chem. News **98**, 261-264 (1908))

(III) Ogawa, M.: "On New Elements in Thorianite".
J. Chem. Soc. Tokyo **30**, 1277–1299 (1909)
(only in Japanese)

(III) 1909


文　報

報文

トリアニト中の新元素に就て

理學士 小川正孝

緒論

一九〇三年印度政府は錫蘭島に產する有用鑛物の調查に着手し其結果として黑色立方體の小結晶として生する鑛物を倫敦のイムペリアル・インスチチュートに送り其化學的成分と商業上の價値を定むることを要求せり此鑛物はサバラガムワ(Sabaragamuwa)州のバランゴダ(Balangoda)附近に於てルビーを採取したる殘滓より收得したるものなり初め錫蘭の住人ホランドは之をピッチブレンドの一種ならんとせしがイムペリアル・インスチチュートに於てダンスタン教授の監督の下に行はれたる分析の結果は其の然らざるを示し約そ酸化トリウム七五%、酸化ウラニウム一二%を含むことを知られ此の如き多量のトリウムを含む鑛物は未だ曾て知られざりしを以てダンスタン教授は此新鑛物をトリアニト(Thorianite)と命名せり(Nature,1904, 69, 510)然るにサー、ウィリアム、ラムゼイもホランド氏より多量のトリアニトを購買し之を他

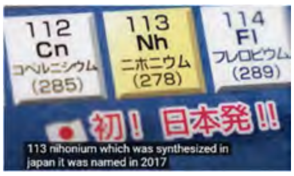
トリアニト中の新元素に就て　一二七七

nipponium by Ogawa

element Z = 43 ➡ Noddaks (1925) ➡ Tc (1937)

symbol Np ➡ neptunium Z = 90 (1940)

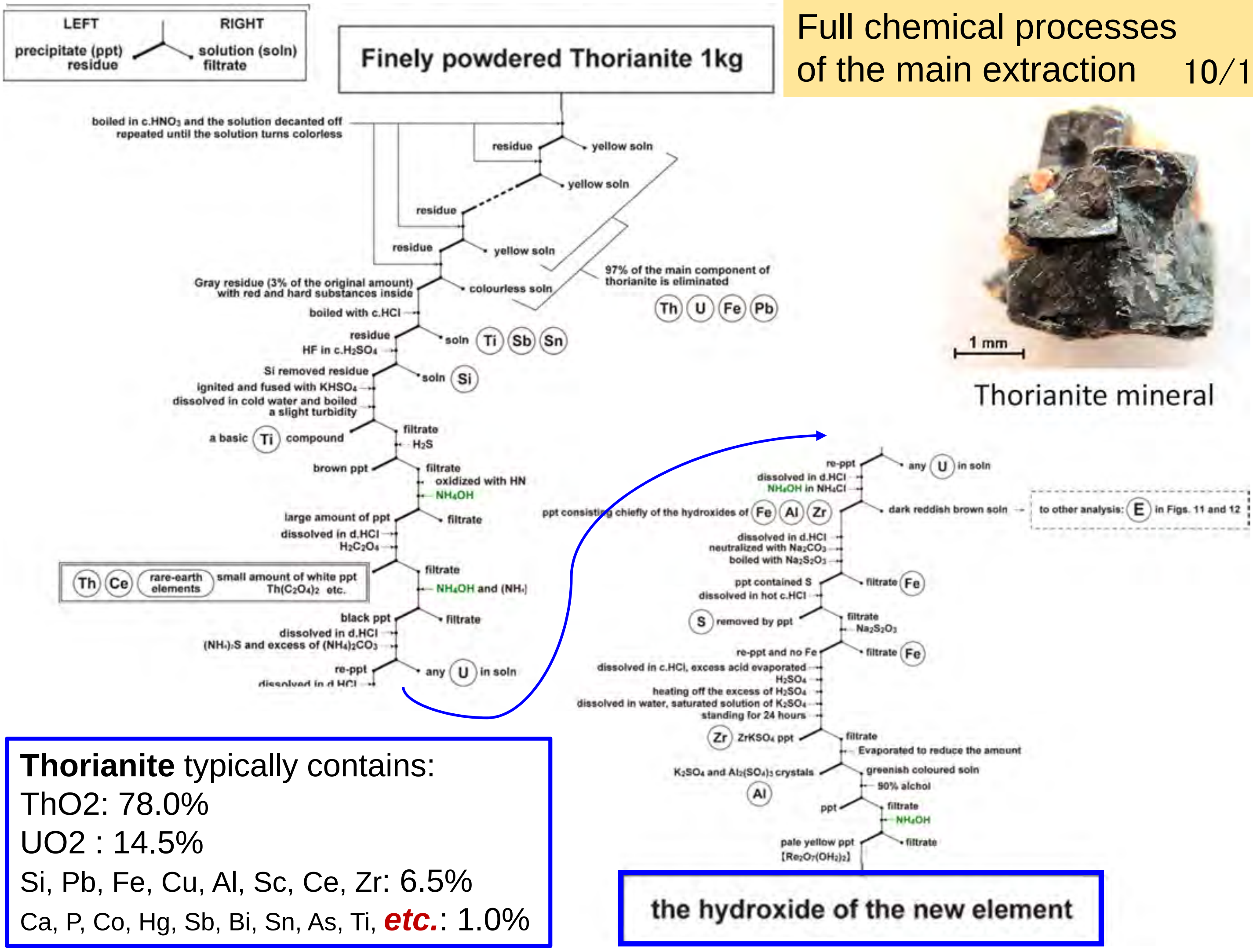
113 **nihonium** Nh



Japan = 日本
= Nippon OR Nihon

What did Ogawa actually found?

Full chemical processes of the main extraction



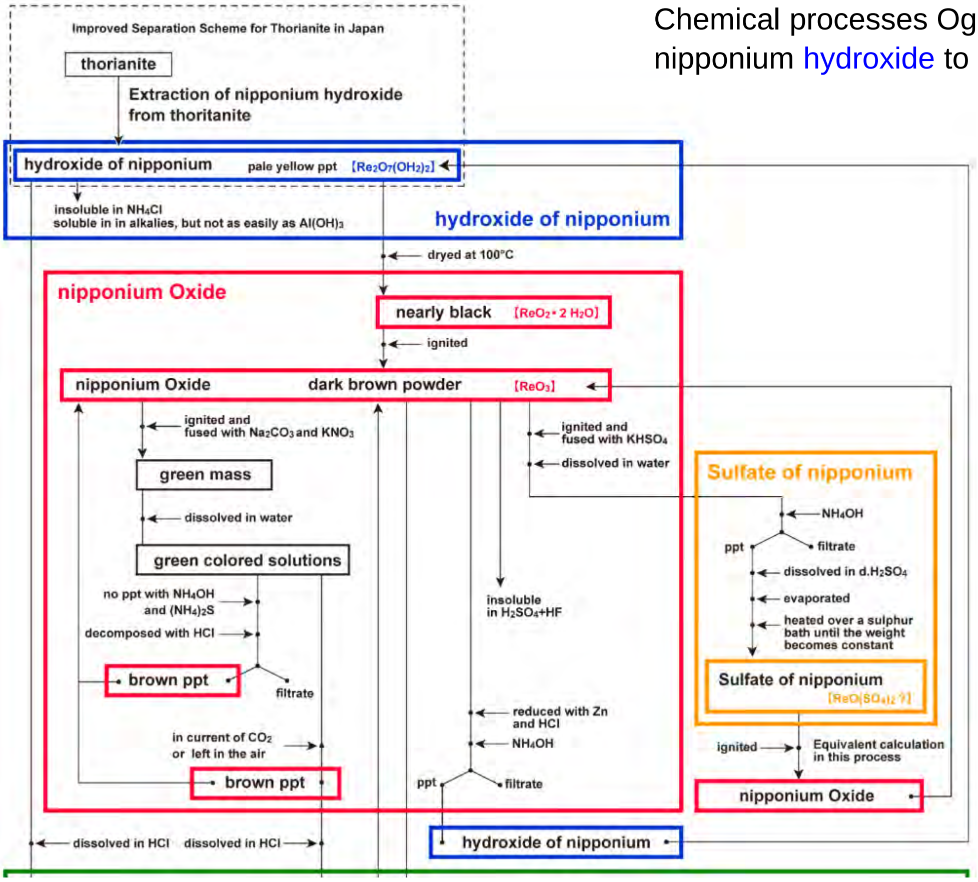
Thorianite mineral

Thorianite typically contains:
ThO_2: 78.0%
UO_2 : 14.5%
Si, Pb, Fe, Cu, Al, Sc, Ce, Zr: 6.5%
Ca, P, Co, Hg, Sb, Bi, Sn, As, Ti, ***etc.***: 1.0%

Ogawa's attempts to identify nipponium

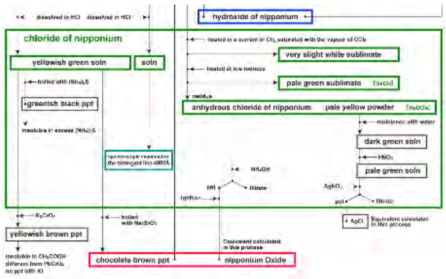
"Ogawa's Nipponium and Its Re-assignment to Rhenium"

Y. Hisamatsu, K. Egashira, Y. Maeno, Found. Chem. (Oct. 2021) DOI: 10.1007/s10698-021-09410-x



Chemical processes Ogawa adopted to convert nipponium hydroxide to the oxide, chloride, and sulfate.

Thorianite mineral



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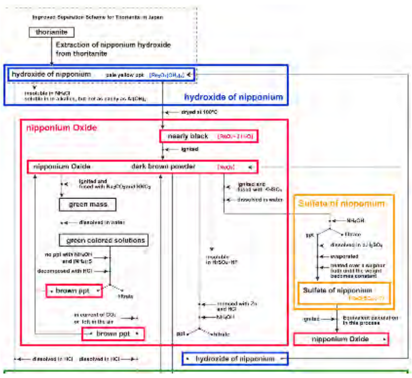
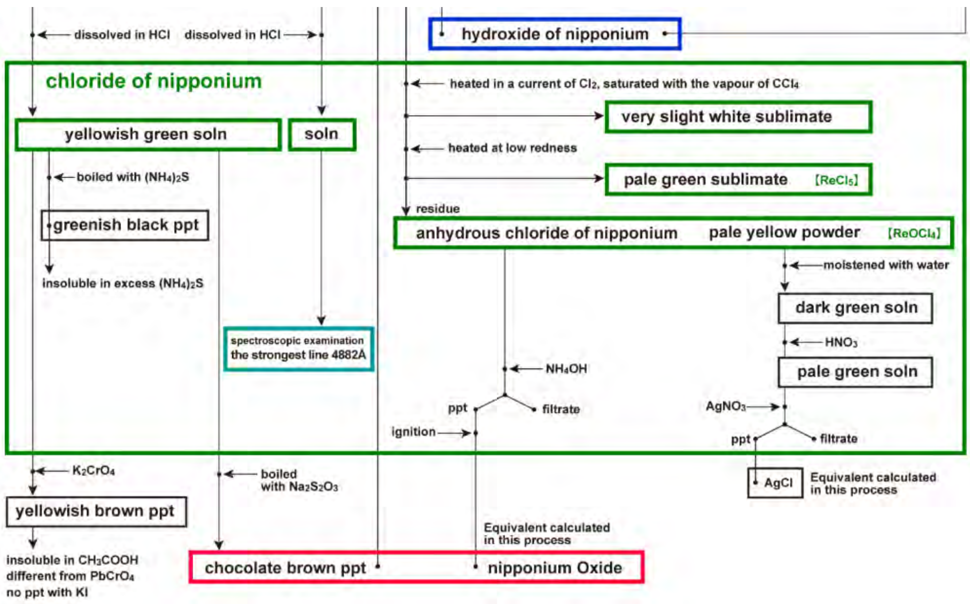


From the mass ratios of the oxide, chloride, and sulfate, Ogawa deduced the atomic mass of 100 for nipponium, and concluded it as the element 43.



Recognition of nipponium as rhenium by Yoshihara (1996)

Kenji Yoshihara
(Prof. Emeritus,
Tohoku University,
1929 -)

Ogawa (1908) assumed that Np (nipponium) was divalent, deduced the atomic weight of 100, and concluded the element as 43rd.

Instead of divalent NpO, $NpCl_2$, $NpSO_4$,
Yoshihara assumed hexavalent $\mathit{R}O_3$, **$(\mathit{RO})ClO_4$**, $(\mathit{R}O)(SO_4)_2$.
Then, the values in Ogawa's papers lead to the atomic weight of $_{75}$Re.

Note that Yoshihara assumed **$(\mathit{RO})Cl_4$**, NOT $\mathit{R}Cl_6$.

Yoshihara found the X-ray photographic plate of 1930 that had been kept by Ogawa's family.

Yoshihara recognized a strong peak of Re.

Yoshihara, H.K.:

"Nipponium, the Element Ascribable to Rhenium from the Modern Chemical Viewpoint," Radiochim. Acta **77**, 9-13 (1997).

"Nipponium as a new element (Z = 75) separated by the Japanese chemist, Masataka Ogawa: a scientific and science historical re-evaluation", Proc. Jpn. Acad. B **84**, 232-245 (2008).

Yoshihara also collected a large variety of evidence on Ogawa's nipponium, including oral evidence from Ogawa's colleagues.

Key compounds in Ogawa's study

Key compounds and reactions to obtain the equivalence in Ogawa's paper, compared to Yoshihara's and our re-assignments.

Conversions	Mass ratio (g)	Ogawa (1908)	Yoshihara (1997)	Our paper
Hydroxide to Oxide	–	$Np(OH)_2$ / NpO	ReH_2O_3 / (ReO_2 + Re_2O_7)	$Re_2O_7(OH_2)_2$ / ReO_3
"Chloride" to Oxide	0.1092 / 0.0742	$NpCl_2$ / NpO	$ReOCl_4$ / (ReO_2 + Re_2O_7)	$ReOCl_4$ / ReO_3
Sulfate to Oxide	0.1253 / 0.0747	$NpSO_4$ / NpO	$ReO(SO_4)_2$ / (ReO_2 + Re_2O_7)	$ReO(SO_4)_2$ / ReO_3
"Chloride" to AgCl	0.0652 / 0.1120	$NpCl_2$ / 2AgCl	$ReOCl_4$ / 2AgCl	$ReOCl_4$ / 2AgCl

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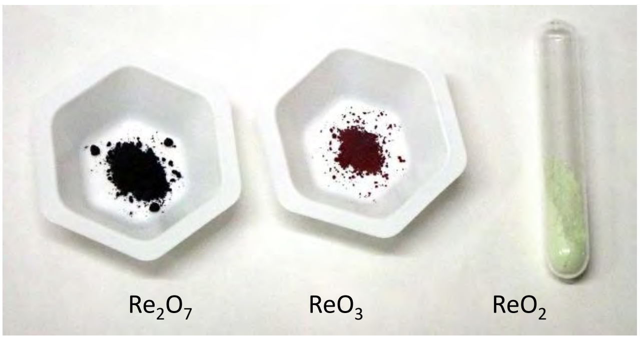
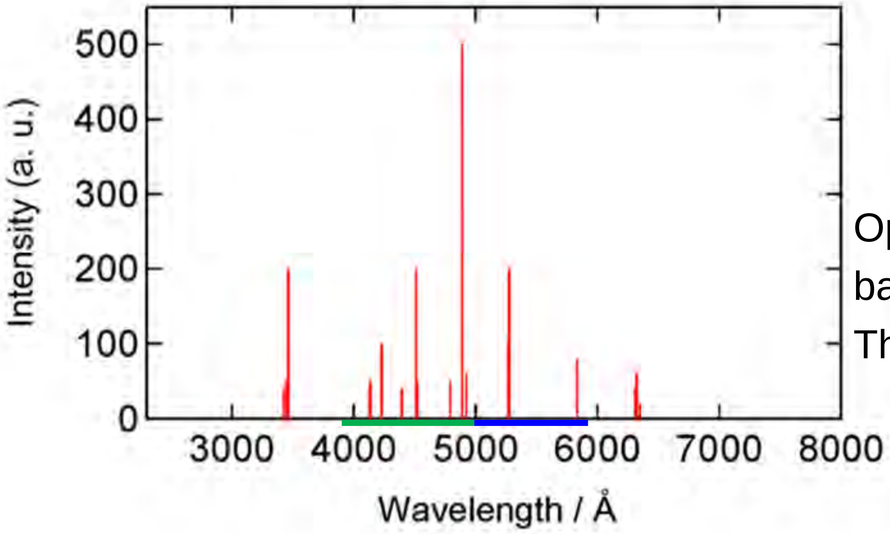


Optical emission spectrum of $_{75}$Re (rhenium)

Y. Hisamatsu, K. Egashira, Y. Maeno,
Found. Chem. (Oct. 2021) DOI: 10.1007/s10698-021-09410-x

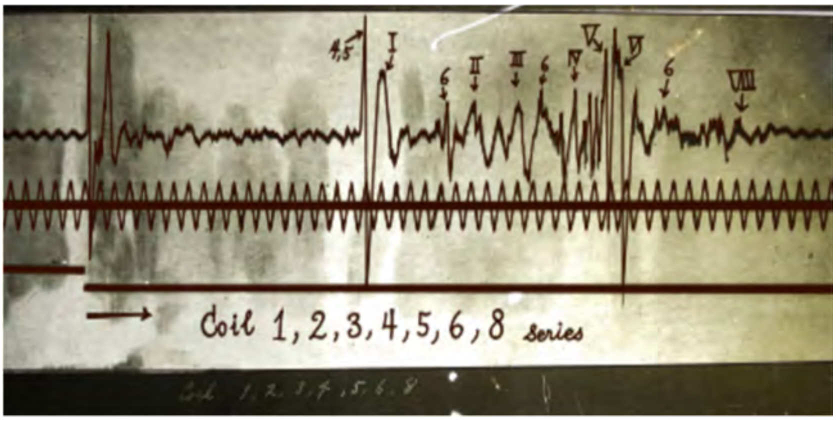
Ogawa's description (1908) for his nipponium sample:
"three spectral lines in the green-blue region
with the strongest peak at 4882 ± 10 Å".



Optical spectrum of rhenium based on Meggers (1931).
The strongest peak at 4889.2 Å.

This is essentially different from reports claiming new elements based on their X-ray spectra after the "correct answer" became known beforehand from Moseley's law (1913).

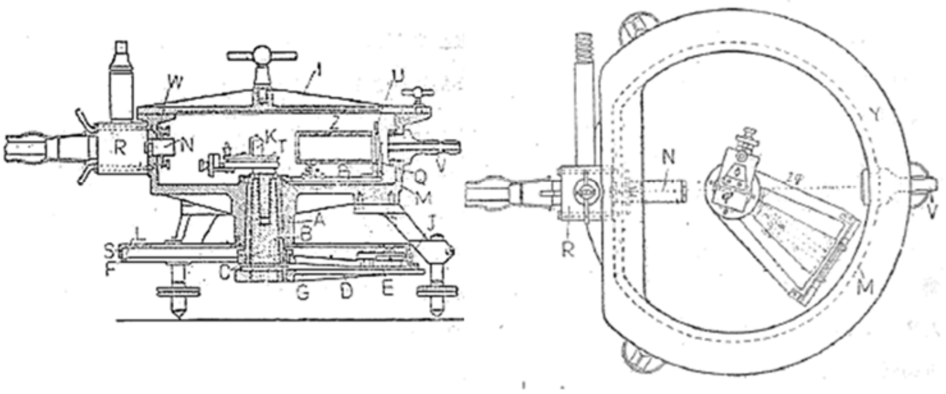
X-ray spectrum of Ogawa's nipponium sample



It shows an unusual spectral shape. Instead of a peak, **a pair of positive and negative peaks** appears.

It must have been a "Differential output" of a peak signal.

Photographic plate of the X-ray spectrum by S. Aoyama at Tohoku Imperial Univ. (1930). Reference elements were added to the "nipponium" sample by Ogawa.

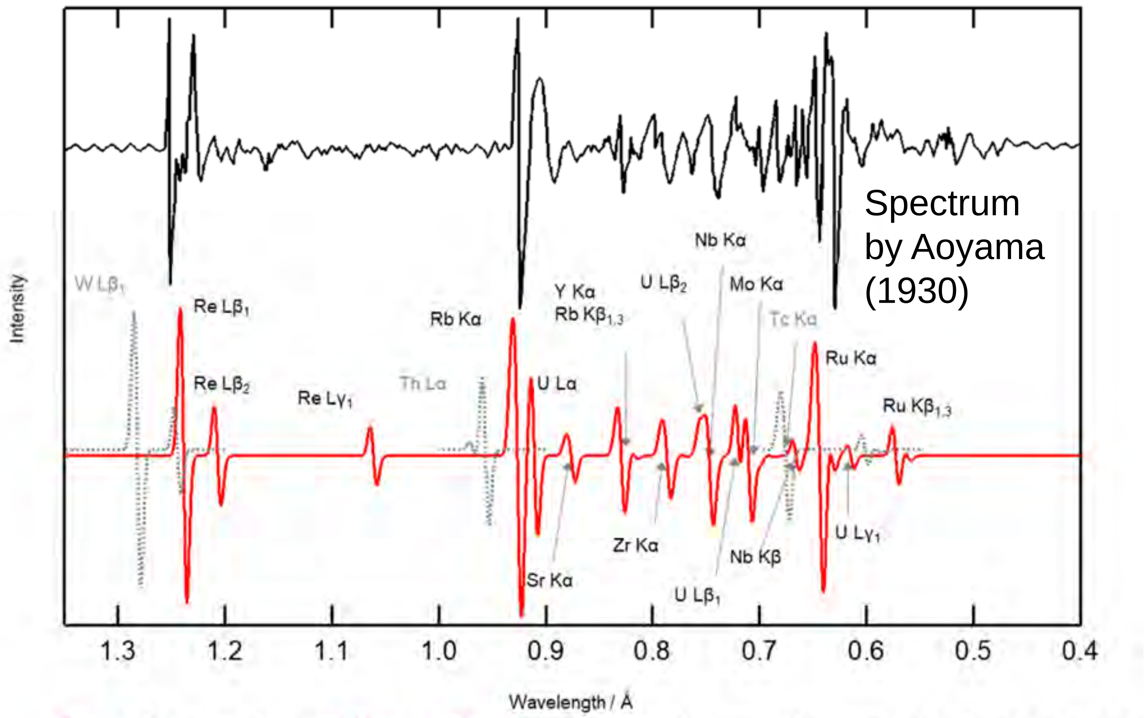


Siegbahn-type
X-ray Spectrometer

Became available in Japan in 1929-1930.

From Shibata, Mizushima, **Kimura**,
"Spectral Chemistry" (1945).

X-ray spectrum of Ogawa’s nipponium sample



Red: Simulated **differential**-peak spectrum with anticipated intensity ratios.

Y. Hisamatsu, K. Egashira, Y. Maeno,
Found. Chem. (Oct. 2021) DOI: 10.1007/s10698-021-09410-x

Why Ogawa and his colleagues could not re-assigne nipponium as rhenium

By the chemists in Japan

At least a few chemists who most probably knew that nipponium was rhenium never published such results even after Ogawa’s death.

The science in Japan was not matured enough

Considering the **imperial fame Ogawa received**, it must have been difficult to disclose the unwanted truth in that period in Japan.

By Ogawa himself

1906–1912: during the publications
1913–1925: before the report by the Noddacks
1925–1930: after the report by the Noddacks

We explained how Ogawa’s work was often incorrectly cited and we attributed such misunderstanding to the fact that he published some key results only in Japanese.

As a scientist who searches for and identifies a new element.
Ogawa’s strength: his superb ability to extract minute element contents from the minerals by traditional wet-chemistry processes.

Ogawa’s weakness: he insisted on such an approach alone and did not organize a **team with multiple expertise** necessary to identify new elements.

It must have been Ogawa’s **insistence** to search for the 43rd element that prevented him from reconsidering the re-assignment as the 75th element perhaps until just before his death in 1930 (when he was told about the results of X-ray spectra) .

Conclusions

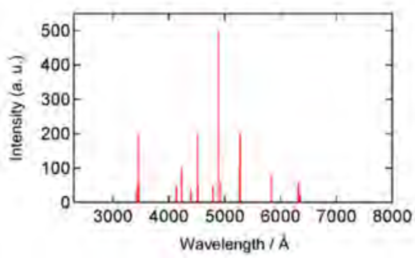
"Ogawa's Nipponium and Its Re-assignment to Rhenium"

Y. Hisamatsu, K. Egashira, Y. Maeno, Found. Chem. (Oct. 2021) DOI: 10.1007/s10698-021-09410-x

We have reexamined the works by Ogawa and Yoshihara and conclude that
Ogawa's nipponium is indeed re-assigned to the 75th element, rhenium (Re).

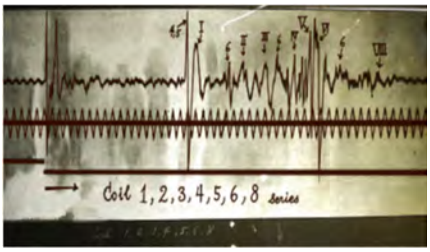
(0) We made detailed diagrams of the chemical processes, described in Ogawa's papers only in words.

(1) The **weight changes** reported by Ogawa, after interpreted with the actual chemical reaction, lead to the correct atomic weight of rhenium.



(2) The **optical emission spectrum** described by Ogawa is consistent with that of rhenium

(3) The **X-ray photographic plate** for a nipponium sample shows clear peaks of rhenium.



(4) We examined the reasons why Ogawa himself and his colleagues could not identify nipponium as the 75th element (Re).

Thank you.

Table 4 Elemental assignments of the X-ray photograph features in Fig. 6 and the corresponding wavelengths

Aoyama (1930)	Yoshihara (2004)	This paper		
		Assignment	Wavelength (Å) at the zero-crossing in Fig. 6b	Wavelength[*1] (Å)
	Re Lβ_1	Re Lβ_1	1.245	1.239
	Re Lβ_2	Re Lβ_2	1.225	1.207
4, 5 (Th, Pa?)	Th Kα	Rb Kα	0.926[*2]	0.926
I (Rb)	Rb Kα	U Lα	0.898	0.911
	U Lα	Sr Kα	0.875	0.876
6 (U)	Sr Kα	Y Kα	0.829	0.829
II (Sr)	Y Kα	Zr Kα	0.790	0.787
III (Y)	Zr Kα	Nb Kα	0.745	0.747
6 (U)	Nb Kα, U Lβ_2	U Lβ_1	0.706	0.719
IV (Zr)	Mo Kα, U Lβ_1	Mo Kα	0.683	0.710
V (Nb)	Nb Kβ	Ru Kα	0.647	0.644
VI (Mo)	Ru Kα, Th Lγ	(Ru Kα)	0.631	–
6 (U)	U Lγ	Ru K$\beta_{1,3}$	0.580	0.573
VIII (Ru)	Ru Kβ	–	0.493	–

[*1] Wavelengths in the literature (Deslattes et al. 2005). [*2] Adjusted so that this value coincides with that of the literature