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Some new documents illuminating the controversy about the vestium-ruthenium discovery

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ABSTRACT

On 17 June 1808, Jna Sniadecki, Rector of University of Wilno, now Vilnius in Lithuania, sent a letter written in French to Jean-Baptiste Delambre, Perpetual Secretary of the *Académie des sciences*, to tell him, among other things, about the discovery by his brother Jedresz of a new metal, vestium, in native platinum. He asked that the *Académie* would express its opinion on his brother's discovery. This letter has recently been found in the *Académie* archives. This metal was the last found in the platinum mine. A report explaining the analytic method used was attached to the letter. Berthollet, de Fourcroy, Guyton de Morveau and Vauquelin, selected by the *Académie*, did not publicly express an opinion and did not reply to Sniadecki, who then stopped his research. Unfortunately, the report has disappeared. In 1845, Claus, Professor at the University of Kazan, announced the discovery of ruthenium, which was confirmed by Berzelius. Thus there is controversy about who was the true discoverer of vestium-ruthenium, Sniadecki or Claus. This is still under discussion today. Two documents written by Sniadecki, both dated, have been found these last years. They describe in a very similar way, the experiments conducted by Sniadecki. One is written in Polish; it consists of 27 printed pages, and is to be found in the library of Vilnius University. The other is in French, has eight hand-written pages, and was published in Poland in 1967; it had been sent to the Russian Academy of Sciences in Saint-Petersburg for publication. The coincidence between the dates of this second text, and the letter sent to Paris, as well as their translation into French, allows one to think that the report sent to Paris was identical to that sent to Saint-Petersburg. If discussion on the historical circumstances to decide the name of the discoverer continues, an exhaustive, critical analysis of the chemistry as described by Sniadecki has been hardly undertaken in a detailed manner. This study shows that Sniadecki was mistaken. Why? The mineral attack by aqua regia gives a solution and a residue. Sniadecki announced that he had found vestium in the solution, whereas ruthenium is totally insoluble in aqua regia and is today prepared for the residue. Sniadecki had isolated vestium in the form of a chloride insoluble in alcohol whereas ruthenium chloride is soluble in alcohol. Thus the discovery of ruthenium must be attributed to Claus.

RÉSUMÉ

Le 17 juin 1808, Jan Sniadecki, recteur de l'université de Wilno, aujourd'hui Vilnius en Lithuanie, envoyait une lettre écrite en français à Jean-Baptiste Delambre, secrétaire perpétuel de l'Académie des sciences, pour lui annoncer entre autres choses la découverte par son frère Jedresz d'un nouveau métal, le vestium, dans le platine natif. Il lui demandait que l'Académie se prononce sur la découverte de son frère. Cette lettre a été trouvée récemment dans les archives de l'Académie. Ce métal était le dernier découvert dans la mine du platine. Un rapport explicitant la méthode analytique utilisée avait été joint à la

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lettre. Berthollet, de Fourcroy, Guyton de Morveau et Vauquelin, désignés par l'Académie, ne se sont pas publiquement prononcés et n'ont pas répondu à Sniadecki qui a alors arrêté ses recherches. Malencontreusement, le rapport a disparu. En 1845, Claus, professeur à l'université de Kazan, annonçait la découverte du ruthénium qui a été confirmée par Berzelius. Il s'est alors établi une controverse sur le véritable découvreur du vestium-ruthénium, Sniadecki ou Claus. La discussion se poursuit encore de nos jours. Deux documents écrits pas Sniadecki, datés tous les deux, ont été retrouvés ces dernières années. Ils décrivent de façon très similaire les expériences réalisées par Sniadecki. L'un est écrit en polonais; il comporte 27 pages imprimées, et il se trouve à la bibliothèque de l'université de Vilnius. L'autre est écrit en français ; il comporte huit pages manuscrites et il a été publié en Pologne en 1967 ; il a été envoyé à Saint-Pétersbourg à l'Académie des sciences de Russie pour publication. La coïncidence des dates de ce deuxième texte et de la lettre envoyée à Paris, ainsi que leur rédaction en français, permet de penser que le rapport envoyé à Paris était identique au texte envoyé à Saint-Pétersbourg. Si la discussion sur les circonstances historiques pour décider du nom du découvreur continue, une analyse critique fine de la chimie telle qu'elle est décrite par Sniadecki n'a guère été entreprise de façon détaillée. Cette étude montre que Sniadecki s'est trompé. Pourquoi ? L'attaque du minerai par l'eau régale donne une solution et un résidu. Sniadecki annonce avoir trouvé le vestium dans la solution alors que le ruthénium est totalement insoluble dans l'eau régale et qu'il est préparé aujourd'hui à partir du résidu. Sniadecki a isolé le vestium sous la forme d'un chlorure insoluble dans l'alcool alors que le chlorure de ruthénium est soluble dans l'alcool. La découverte du ruthénium doit donc être attribuée à Claus.

On 13 June 1808, Jedresz Sniadecki, Professor at Wilno University (today Vilnius, Lithuania), lectured at this Russian imperial university, presenting an analytical work on crude natural platinum which led him to claim the discovery of a new element he called Vestium. On 17 June 1808, his brother Jan Sniadecki, Rector of Wilno University, sent a letter to his friend Jean Baptiste Delambre, Perpetual Secretary of the French Academy of Sciences in Paris, which was then named Institut National des Sciences et des Arts. First of all Sniadecki announced to Delambre that he had been elected a Wilno University Honorary Member. Jan Sniadecki was a renown astronomer, as was Delambre; he reported in his letter some astronomical observations. Moreover, on behalf of his brother Jedresz, he announced the discovery of a new metal found by Jedresz in natural platinum grains as the result of a long and careful chemical analysis of this ore. The letter is written in French. A translation of the part of interest is given:

> ''As a Colleague, please be kind enough to present to the Institute the enclosed report of my brother, a former student of the famous (Joseph) Black of Edinburgh. It is a detailed summary of a long work describing the analysis of platinum in which he found a new metal which he named Vestium the specific properties of which are given and for which the name Vestium is proposed, of the new planet Vesta. French chemists are requested to check the reported facts.''

This handwritten letter has been found in May 2011 in the archives of the French Academy of Sciences. The report mentioned above has unfortunately disappeared.

The letter has been read at the weekly meeting of the Academy on Monday 11 July 1808 as is indeed reported in the minutes of this meeting. The Academy set up an ad hoc Committee of four chemists to look at Sniadecki's findings. It was made of Claude Berthollet, of Antoine de Fourcroy, of Louis Guyton de Morveau who developed with Lavoisier the first comprehensive chemical nomenclature, and of Nicolas Vauquelin who discovered chromium a few years before in 1797.

On 13 July 1808, Delambre acknowledged the letter of Jan Sniadecki. It took two months to reach Wilno. There is no copy in the archives. On 18 October 1808, after having received the acknowledgment of Delambre, the Rector Jan Sniadecki sent a second letter in French to Delambre. It has been also found in the archives. He announced some new astronomical observations. One can also read the following sentence, which is translated:

> ''Be kind enough and let me know what your Chemists of the Institute have done with the report on platinum analysis.''

Clearly the Sniadeckis received no news from the four appointed French chemists. Nothing about the check of Vestium discovery has been found in the weekly minutes of the Academy, neither in 1808, nor in 1809. Jedresz Sniadecki was very probably disappointed. He had also written a detailed report of his work; it is a printed 27-page document written in Polish which may be found at the library of Vilnius University [2]. The title is translated: ''Report on a new metal found in crude platinum.'' One can read on the front page that it has been read at a public meeting on 28 June 1808 (Julian calendar). He also translated this document into Russian and sent it to Saint-Petersburg to be published [2]. Then he stopped working on platinum chemistry; it has been reported that he was finally himself not so sure about his findings [3,4].

What can we think, or deduce, or guess once those facts are related?

One may imagine that the four French Chemists came to the conclusion that the proposal of Sniadecki about Vestium was not correct. Then they might have wondered how to publish their conclusions; they remained silent,

unless some documents to be discovered prove the opposite. However, one can read in the July 1808 issue of the *Journal de Physique, de Chimie, d'Histoire Naturelle et des Arts* [5] the following translated paragraph:

> "One writes from Germany that a chemist has discovered a metal in platinum grains. It has been named Vestium from the name Vesta given to the last planet discovered by Olbers."

Let us remark that news came from Germany and from an unidentified source while Sniadecki announced his discovery in Russia. Moreover the name of the discoverer is not given. Finally it is not signed. The "*Journal de Physique, de Chimie, d'Histoire Naturelle et des Arts*" was edited privately by Delamétherie; it means that it was not the official journal of the Academy of Sciences. Perhaps the Editor heard about the discovery and wanted to publish some kind of a scoop; indeed this announcement was published with a date which coincides with the arrival date of Jan Sniadecki letter. Thus it cannot be taken as the conclusion of the four French chemists.

It has been suggested that the four French Chemists did not answer because one or more of them desired to protect a work in progress [6]. That might be an explanation. Indeed in 1804 de Fourcroy and Vauquelin were studying raw platinum [7] at the time of the announcement of the discovery of iridium, osmium, palladium, and rhodium by Tennant and Wollaston [8]. In the black residue left after aqua regia reaction on raw platinum, they observed facts which pushed them to think about the occurrence of a new element. They indeed wrote, a translation is given: "About raw platinum, about the occurrence of several metals, and about a new metallic species found in this ore". However they did not reach a definite conclusion and they made no proposal. The first publication after 1808 on the topic of platinoids seems to be by Vauquelin in 1814 [9]. Actually, there are two papers dealing with chemical properties of osmium and iridium. Vauquelin points out the discovery anteriority of Tennant. However, there is nothing about Vestium or about a new metal, not a word about the Sniadecki proposal. Interestingly, in one of these papers, Vauquelin described a compound in chloride solution which has an intense blue color. We know today that ruthenium is left in the black solid residue together with osmium, rhodium, and iridium once platinum grains have been treated by aqua regia. This blue compound might well be the mixed valence compound $[Ru_3Cl_{12}]^{4-}$. Vauquelin did relate this blue compound neither to Vestium nor to a new metal.

In the January 1809 issue of the "*Journal de Physique, de Chimie, d'Histoire Naturelle et des Arts*" [10], one can read the following short paragraph which is translated:

> "About Vestium. This is the name given to a new metal which is said to have been extracted from platinum grains; however those experiments have not been done again; thus one has to wait for new work."

Once more those few lines are not signed and the source is not given. Let us emphasize that it has been written elsewhere [11] that "experiments were not reproducible". Actually the translation was not correct; the French wording is "*les expériences n'ont pas été répétées*".

As said above Jedresz Sniadecki wrote a 27-page document in Polish language describing his chemical analysis of platinum grains [1]. Sniadecki prepared a handwritten eight-page summary in French language. It is entitled "On a new metal found in platinum grains". There is a date on this document, 15 May 1808. It has been sent to the Councillor de Fuss, Perpetual Secretary of the Academy of Sciences of Saint-Petersburg. It has also been presented during a lecture at Wilno University on 1 June 1808, as written on the document. Twelve days have to be added because the Gregorian calendar was not yet in use in Russia at that time. This summary has been found and published in Poland [12].

Considering the coincidence of dates of this document and of the first letter sent to Paris by the Rector Sniadecki, considering that it is written in French, considering that it announced the discovery of Vestium, it strongly suggests that the document sent to Paris was identical to this one sent to Saint-Petersburg.

It is not the purpose of this paper to describe once more the discussions about the discoverer of vestium-ruthenium [12,13]. Having this French eight-page and this Polish 27-page documents at hand, the author of this paper felt strongly pushed to compare them and to try to understand the chemistry herein described. It seems indeed a good way to make clear whether Jedresz Sniadecki was right or not. As a matter of fact it has been written without any explanation "There is no doubt that he has isolated ruthenium" [13].

The French language is clear with a few clumsy sentences which require a careful and critical study. The ink handwriting is partly erased in some places adding some difficulties to read it. Finally, a few words do not belong today to the French language but one can guess what they mean from the context. The Polish document has been translated in French; it was not an easy task because it is old Polish language. Despite these difficulties a thorough lecture is possible and it makes possible a conclusion in light of what we know today about ruthenium chemistry. Although it appears that Sniadecki was a good chemist, he was mistaken. Why?

Before looking at details, what are the main differences between the Polish 27-page document and the French eight-page document? They both describe aqua regia reaction on raw platinum: it is called saltpeter-salt acid in the Polish one, that is nitric-chlorhydric acid, and nitromuriatic in the French one, i.e. the translation given by Sniadecki himself. It yielded a red solution and a black residue. The French document limits the discussion on the black residue to half a line while the Polish document devotes six pages to its study. The descriptions of the red solution analysis are about the same in both documents.

Let us focus on the solution. Sniadecki found 400 g of platinum grains [1]. Taking into account the 1808 year, it is clear that this platinum came from South America since platinum grains were found in the Tagil river in Ural mountains around 1819 [11,14]. Sniadecki wrote that he used a "rather large amount of this ore" [12], indeed 200 g [1]. Grains have been treated with nitromuriatic acid

understood as aqua regia. In the Polish document, it is described as a mixture of three parts of nitric acid with one part of sodium chloride. A red solution and a black solid residue have been obtained. Let us focus on the solution. After some chemical treatments, Sniadecki separated some insoluble red crystals by using "wine alcohol", i.e. ethanol. In the alcoholic solution, he found platinum, rhodium, palladium, and iron. Sniadecki considered those insoluble red crystals as the sign of a new element; he prepared the new metal by reducing insoluble Vestium chloride with iron, zinc, and mercury. Surprisingly he also used potassium carbonate under heating. He gave the name Vestium, from the just discovered planet Vesta by Olbers. He wrote that this metal was easily molten than platinum (1772 °C) which fits with ruthenium (2310 °C). Unfortunately he also wrote: "It dissolves only in oxygenated muriatic acid and in nitromuriatic acid much more easily than platinum." This is not a property of ruthenium metal known to be completely insoluble in aqua regia. A good way to react it is a chlorine stream at a few hundreds of degrees [14a,15]. It has been argued that due to its small amount ruthenium might have been carried to the solution and then found with the other elements, platinum, palladium, rhodium, iron. But it should have been only a minute part of ruthenium already in small amount in platinum grains and red insoluble chloride crystals would have been isolated as a minute amount making them extremely insoluble. But Sniadecki got enough metal to look at its melting behavior. Moreover, osmium and iridium occur in a larger amount than ruthenium, then why they have not been also carried into the solution? As a matter of fact, it has been observed that the aqua regia reaction on a platinum-iridium alloy may carry some iridium into the solution [16,19]; Sniadecki did not observed it. Let us suggest that the insoluble red crystals taken by Sniadecki as the sign of a new element might actually be some iridium(III) chloride, maybe mixed with another chloride.

Let us now look at the black solid residue. In the eight-page French document, Sniadecki wrote that he found iridium, osmium, and chromium without any explanation. In the 27-page Polish document, six pages deal with the analysis of the black powder describing in details the chemical separation of osmium, iridium, and chromium; nothing is said about a new metal, and it should have been the right place to find vestium-ruthenium. Sniadecki separated 10.4 g of black powder called osmides in the XIXth century [1]. Two chemical analyses are reported by Ste Claire Deville and Debray; osmides came from a British factory and from a French factory [16]. The black powder should have contained approximately 3.5 g of osmium, 5.8 g of iridium, and 0.6 g of ruthenium considering the first analysis. The second analysis reported no ruthenium at all. It is then understandable that Sniadecki overlooked it. Let us point out that the black powder should have also contained some rhodium, known as insoluble in aqua regia. It has not been observed by Sniadecki since he found it only in the solution resulting from the aqua regia reaction on raw platinum.

After having discussed this separation procedure, let us have a look at chemical properties as given by Sniadecki. One of them is chosen. He wrote that Vestium chloride was not soluble in alcohol: "It can be seen that one of the main differences between platinum and vestium is that the muriate of this last one (understood as Vestium chloride) does not dissolve in alcohol". It is actually just the opposite, red ruthenium(III) chloride is quite soluble in ethanol [17]. Moreover ruthenium chloride is deliquescent, a feature not mentioned by Sniadecki, a careful chemist.

Several features written above about the chemistry are in agreement with the comments of Marshall and Marshall published in 2010 and 2011 [11,18]. However, it seemed of interest to repeat in detail those comments because of the still going on controversy about allegated ruthenium discovery by Sniadecki [13,14]. The chemical results of Sniadecki are rarely thoroughly discussed and compared with what we know today. Indeed it looks to be the best key to come to a conclusion.

It seemed valuable to present in details some new documents recently found in Poland and in Paris written by the Sniadecki brothers. They give more insight on the wrong announcement of a new element Vestium by Jedresz Sniadecki. It clearly demonstrates how difficult it was to prove the discovery of a new element with the limited chemistry knowledge and the limited means of the time. Karpenko presented a long list of about 130 allegated new elements which proved later on to be more or less erratic proposals [20].

Let us summarize the end of the story which has been detailed in several occasions [11,13,14,18]. A few years later, in 1828, Osann became interested in platinoids. He claimed the discovery of three new elements, pluran, ruthen, and polin [21]. Berzelius did not confirm these findings, and Osann withdrew his proposal. In 1840, Carl Claus, Professor at Kazan University, tackled the problem again. In 1819, platinum grains had been found in Ural mountains; platinum was used by the Russian Mint to make coins and wastes were carefully kept in which the five spurious platinoid metals got enriched. Claus used those wastes. He worked out a very careful chemical study and isolated ruthenium [22]. He met some difficulties to convince Berzelius who finally confirmed the work of Claus in 1845. Claus chose the name ruthenium, from the old name of Little Russia, as he wrote: "I named the new body in honor of my motherland ruthenium".

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