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The history of the first germanium crystals along with a descendant of the novel "Bulgarians of old time"

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This article represents a review of studies on the determination of germanium and the intriguing history behind it. The purpose of this paper is to familiarize readers with one outstanding figure in Bulgaria on the second half of the 19^{th} century and his scientific activities - in particular, the Bulgarian trace in the discovery of the element Ge. The advantages of this research item are many and diverse, of course, but the main issue is to get closer for the umpteenth time to the chemistry that was created for us. Since then, the name of Stoycho Karavelov, the first Bulgarian metallurgical engineer, is quite forgotten and is not mentioned or spoken of today. Another positive issue is that inorganic chemistry during the germanium isolation is considered in depth herein including the foundations of chemical science in Bulgaria. In addition, the fascinating story of an incredible tradition and continuity among inorganic chemists in Bulgaria that lasted a hundred years, whose passing an ampoule of crystals from hand to hand is well worth telling.

Keywords: discovery of germanium, metallurgy, Clemens Winkler, Stoycho Karavelov, inorganic chemistry.

INTRODUCTION

In the Bulgarian National Polytechnic Museum in Sofia, a glass container is exhibited in a separate display case, in which a small glass ampoule with several germanium crystals is placed, accompanied by a donation inscription. In fact, these are some of the first experimentally obtained crystals of the chemical element germanium (Fig. 1).

We will try to tell you the exciting story behind which stands the first Bulgarian metallurgical engineer – Stoycho Dragoev Karavelov. Who is this Bulgarian about whom little is known today? *Quick overview*. He is the founder of the modern Bulgarian mining, born on August 1, 1865 in Koprivshtitsa (former Ottoman Empire), in the same house where the popular Lyuben Karavelov museum is located today. He comes from the famous Karavelov family and is first cousin of Lyuben and Petko Karavelov.

Figure 1. The house where Stoycho Karavelov (right photo and prof. Winkler - left photo) was born in Koprivshtitsa, as well as the glass container with the ampoule with the first experimentally obtained crystals of the chemical element germanium and the donation inscription.

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In fact, almost every Bulgarian student knows the cheerful and romantic love story of Pavlin and Lila from Lyuben Karavelov's novel "Bulgarians of Old Time", which refers to the time of the Bulgarian National Revival, in the 19th century. Considering the world historical periodization, we understand somehow why huge discovery of new elements started in the 19th century [1]. The characters behind this story are real people, close relatives and fellow citizens of Lyuben Karavelov. The prototype of Pavlin's image is Lyuben Karavelov's youngest uncle Dragoya, the father of the engineer Stoycho Karavelov. Dragoya Libenov Karavelov was born in 1820 and was the youngest son of Stoycho's grandfather Liben. Meanwhile, Lila was actually Paraskeva Ivanova Spasova, Nayden Gerov's niece. Nayden Gerov was a Bulgarian linguist, folklorist, writer and public figure during the Bulgarian National Revival. Dragoya and Paraskeva were married in 1842 and had nine children. The youngest one, Stoycho, was named after the father of Lyuben and Petko Karavelov. Generally, the book describes the flaws of Bulgarian society in those distant times, but also represents traditions and some essentials values. The main idea of the book is: "There is no, there is nothing in the world sweeter than to do good to a person." Little Stoycho started school at the age of 9 in his hometown. In 1878, his father had serious financial difficulties that forced him to settle the family somewhere around the town of Montana, where he died after only two years. Later, Stoycho studied II grade in Belogradchik and III grade in Tsaribrod. Left an orphan, he went to study up to the 7th grade at the real gymnasium in Lom located along the Danube River, where in 1885 he graduated with honors. The same year, 1885 he took part in the struggles for the Unification of Bulgaria and was also a volunteer in the Serbo-Bulgarian War. The Unification of Bulgaria was the act of unification of the Principality of Bulgaria and the province of Eastern Rumelia in the autumn of 1885. Both had been parts of the Ottoman Empire, but the Principality had *de facto* functioned independently whilst the Rumelian province was autonomous and had an Ottoman presence. Further on, he won a scholarship from the Ministry of Public Education to the Saxon Mining Academy in Freiberg, Germany, and the same year he went to study metallurgy. Freiberg today is home to the Technische Universität Bergakademie, which is the oldest mining and metallurgy university in the world, established by Prince Franz Xavier in 1765. During his studies in Freiberg (1885-1889), he was probably an assistant of Prof. Clemens Winkler, who was known to be the discoverer of the chemical element germanium. To be honest, it is not so clear how, and whether Stoycho Karavelov helped Winkler in the discovery of germanium, but he was obviously in some way connected to the scientific activity of the professor. It can only be asserted for sure that between our compatriot and the German scientist, there was more than a simple acquaintance or friendship, because in 1890 Prof. Clemens Winkler gave Stoycho some of the first germanium crystals. We cannot pass over the words of an American student who finished his studies in 1883, that – "He always did all of his experiments himself, rarely calling upon an assistant", which does not mean, however, that Professor Winkler could not count on help in his laboratory, because his "chemical feeling" is *sui generis* [2]. In those days in Freiberg, there were students from all parts of the world: North and South America, England, France, Russia, Sweden, Poland, Austria, Italia, Spain, Greece, Australia even Japan and the Philippine Islands. The first Japanese student studied at the Freiberg Mining Academy in the year 1873 and was followed by 44 more Japanese students until 1939 [2]. Among them was Watanabe Wataru in 1882 who became later the first Japanese professor for mining and metallurgy in Tokyo. For information, around 31.7 % of the students at the Mining Academy Freiberg were students from Russia (1900). The story is impressive for the way the students were taught with lots and lots of experimental work in the labs as no lectures were given in chemical analysis. However, each student was told to provide himself with a copy of C. Remigius Fresenius textbooks, do their task and consult the assistant when in doubt of something. Moreover, considering the enormous amount of laboratory work involved in obtaining this famous extract under the experimental conditions of that time, the crystals of germanium were truly priceless!

THE STORY OF THE FIRST GERMANIUM CRYSTALS

What exactly is a discovery of an element?

When the first germanium crystals appeared and how we can claim to know? In 1886, the German chemist, Professor of Inorganic Chemistry, Clemens Alexander Winkler from the Freiberg Mining Academy has received for analysis the newly discovered silver-rich mineral "argyrodite" from Albin Weisbach (Professor of Mineralogy) from the Himmelsfürst mine near Freiberg. From the start prof. Weisbach was somehow convinced of having a new species in front of him, found in the middle of September 1885, around 460 m underground (Ag_8GeS_6); because of the apparent high silver content prompted him to the undefined mineral as early as October 1, to give the characteristic name: argyrodite. In fact, it was Theodor Richter who first determined the exact silver content with the blowpipe to be 73.5 percent, but he also stated to have found some mercury, which was quite surprising owing to the fact that this heavy metal had never been found before in Freiberg ores [3]. Therefore, Prof. Weisbach was not so satisfied with this finding and kindly asked his cousin and friend Clemens Winkler for an analysis of this new mineral. Freiberg, which is located in present-day Saxony near Dresden on the Elbe River, is known as "die Silberstadt" or "The Silver City", due to its proximity to the Himmelsfürst mine that produced vast amounts of silver-containing ores. Germanium is usually recovered as a by-product from zinc and copper ores and coal. Moreover, the precise analysis shows that almost 7% of argyrodite weight consists of an unknown element. The balance of the contents was identified as silver (75%), sulfur (18%) and some minor impurities, i.e. trace amounts of mercury, iron, and zinc in the ore but all together these made up less than one percent of the composition. As a whole, currently about 30 germanium minerals are known to contain germanium ranging up to 70% in argutite, GeO_2. Many are sulfides, underlining the strong chalcophile character of germanium [4]. After doing a number of studies, as well as investigating its properties, after spending four months of solid work, on February 6th 1886, Winkler realized that he had discovered the missing element *eka*-silicon (Es) with properties intermediate between the metal tin and the non-metal silicon (the future germanium), Fig. 2. It is the third of the "big three" elements, i.e. element with sequence number 32 of Dimitri Mendeleev's Periodic Table of the elements today, whose place was left empty in 1871, in which the Sanskrit prefix meant "one". That is the element one row beyond silicon. One can see no more than four "?"-s in the first version (1869), left by Mendeleev vacant spaces "gaps" for future newcomers in the table, while nearly eleven " − "-s appeared in the second proposition from 1871 [5, 6].

On February 8, 1886, the editors of the *Berichte der deutschen chemischen Gesellschaft* received Winkler's article, in which he informed the scientific community about the discovery of this chemical element [7]. He wrote about this discovery as follows: *After several weeks of laborious searching, I can today say with certainty that the argyrodite contains a new element very similar to antimony, but sharply differentiated from it, to which the name "germanium" may be given*. However, at first, Winkler assumed that his new element should chemically be similar to antimony because argyrodite and antimony minerals behaved similarly, but the chemists have to forgive him for the mistake, which was relatively quickly spotted by others. First Victor von Richter, and then Lothar Meyer, pointed out that, according to the plot of atomic volumes, germanium should be low-melting as well as volatile, and identified with *eka*-silicon, prognosticated fifteen years ago by Mendeleev [8].

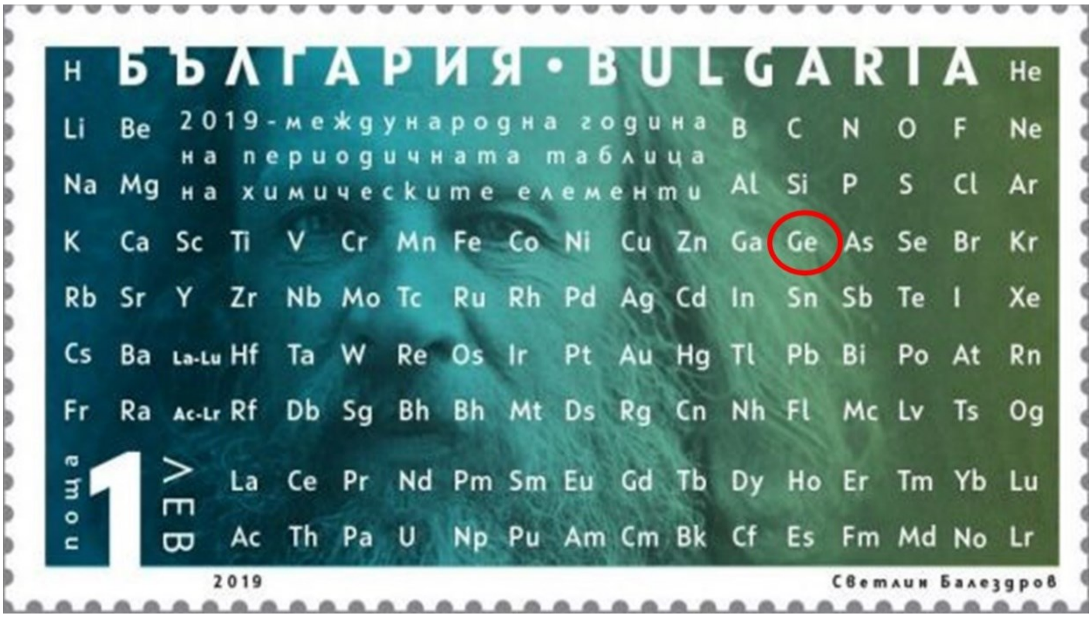

Figure 2. International Year of the Periodic Table stamp issued by the Bulgarian Post on 24.06.2019. (The author of the stamp which has a circulation of 5.500 pieces, is Assistant Professor Dr. Svetlin Balezdrov from the National Academy of Arts. It depicts the Periodic Table over the face of Dmitri Mendeleev).

For instance, applying the so-called "Freiberger digestion" in order to analyze the argyrodite, upon digestion process, a soluble sodium thiogermanate is formed that dissolves when water is added after the performed heating process. While, at the same time, the silver sulfide does not dissolve [3, 9]:

$2Ag_8GeS_{6(s)} + 2Na_2CO_{3(s)} + 3S_{(s)} \rightarrow$
$2Na_2GeS_{3(s)} + 8Ag_2S_{(s)} + 2CO_{2(g)} + SO_{2(g)}$

However, the aqueous extract also contained the thiosalts Na_3AsS_4 and Na_3SbS_4 because naturally, the ore in use was contaminated with both elements, i.e. arsenic and antimony. The essential key to isolating the germanium salt was to separate it from these two contaminants. This was somehow ultimately achieved by weakly acidifying the aqueous solution with hydrochloric acid, allowing the solution to sit overnight to form precipitates. Further, the final isolation of germanium was achieved by slow acidification of the obtained inorganic material. Generally, the three anions AsS_4^{3-}, SbS_4^{3-}, and GeS_3^{2-} are present in solution and the process of slow acidification will result in the precipitation of the two sulfides As_2S_5 and Sb_2S_5, respectively, while the GeS_3^{2-} ion remains in solution [3, 9]. Perhaps, here it is good to recall the memory of the student from Princeton: "*You see*, Prof. Winkler said, *the precipitation was not complete. Hereafter, when you have occasion to throw out of a solution a substance, see to it that the proper reagent is added in moderate excess*." [2]. The main difficulty in isolating this new element, experienced by Winkler, stems from the unusual fact that the sulfide is soluble in dilute acids and water but insoluble in concentrated acids. Therefore, the following addition of excess mineral acids HCl or H_2SO_4 then leads to the precipitation of germanium(IV) sulfide:

$GeS_3^{2-}{}_{(aq)} + 2\ HCl_{(aq)} \rightarrow GeS_{2(s)} + H_2S_{(g)} + 2\ Cl^-{}_{(aq)}$

The sample of GeS_2, initially obtained by Winkler, was sealed in a glass tube and is currently exhibited at the Bergakademie (the Mining Academy, the Institute for Inorganic Chemistry) in Freiberg, shown in Fig. 3 [3]. Moreover, a second ampoule ended up in the hands of a Bulgarian student as a gift. It was later determined that washing the solid product of GeS_2 with sulfuric acid and then alcohol would prevent it from undesirable re-dissolving in water. Moreover, the element itself could be isolated from the sulfide by roasting in oxygen followed by reduction of the resulting oxide by hydrogen gas [3]:

$GeS_{2(s)} + 3O_{2(g)} \rightarrow GeO_{2(s)} + 2SO_{2(g)}$
$GeO_{2(s)} + 2H_{2(g)} \rightarrow Ge_{(s)} + 2H_2O_{(g)}$

Figure 3. Winkler's sample of GeS_2 from February 6, 1886, and his gift.

Think of a sulfide which possesses the unique chemical property of being insoluble in strong acids but soluble in dilute acids and water! No wonder why Winkler experienced such difficulty in obtaining it [2]. Thankfully, from this chemical stage on, all was likely more easily. Fortunately, the managing director of the Himmelsfürst mine, Eduard Neubert, was generous and provided Winkler with a total of 5.34 kg of argyrodite, with the stipulation that the silver obtained from this material would be returned [9]. This worthwhile ore ended up yielding about 100 g of germanium. In five months of intense research, Prof. Winkler was able to obtain the majority of the compounds of the element for which Mendeleev had made some predictions. The properties of elemental germanium and those of its compounds agreed very well with those predicted by Prof. Mendeleev, including the determination of its atomic weight of 72.32 g/mol from $GeCl_4$, as well as the oxide GeO_2, the sulfides GeS and GeS_2, as well as the iodide GeI_4, Table 1. Thus, surely one of Mendeleev's greatest triumphs, and perhaps the one that he is best remembered for forever, is the correct prediction of the existence of several new elements [10, 11].

Table 1. Predicted and observed properties of *eka*-silicon (germanium).

Properties	1871	1886
Relative atomic mass	72	72.32
Density, g/cm^3	5.5	5.47
Specific heat	0.073	0.076
Atomic volume, cm^3	13	13.22
Color	dark grey	grayish-white
Vaporization energy, J.°C^{-1}.g^{-1}	0.31	0.32
T_f, °C	high	960
Oxide	RO_2	GeO_2
Oxide density, g/cm^3	4.7	4.703
Chloride	RCl_4	$GeCl_4$
Boiling point of tetrachloride, °C	100	86

Furthermore, Lecoq de Boisbaudran also received a good sample of germanium and was so eager to subject it to the action of the induction spark, consequently, he is the first person that measured germanium's spark spectrum. A very beautiful spectrum was produced which contains two lines whose brilliancy is above all remarkable: a blue and a violet at 468 and 422 nm, respectively. These lines lay midway between similarly determined lines for silicon and tin, Fig. 4. "*I have measured the two rays with an accuracy already sufficient to enable me to apply my formulas relating the wavelengths of the homologous rays and the atomic weights of bodies which produce them*, *i.e. 72.27*" [12].

As a matter of fact, Ge as an element is somewhat more reactive and more electropositive than Si, as it slowly dissolves in hot concentrated H_2SO_4 and HNO_3 acids but does not react with water or with dilute acids or alkalis unless an oxidizing agent such as H_2O_2 or NaOCl is present; fused alkalis react with incandescence to give germanates. Germanium is oxidized to GeO_2 in air at red heat and both H_2S and gaseous S yield GeS_2. Both Cl_2 and Br_2 yield GeX_4 on moderate heating, while HCl gives two compounds, $GeCl_4$ and $GeHCl_3$ [13].

Despite its spectacular increase in availability during the past few decades from a laboratory rarity to a general article of commerce, Ge and its compounds still are more or less relatively expensive [14]. Actually, germanium, along with selenium, tellurium and helium, is one of the few non-metallic elements to carry the '-ium' suffix in English [5, 10].

Further, Clemens Winkler wrote to Mendeleev in a letter dated February 26, 1886 [8]: *Your Excellency! Allow me to transmit to you this separate reprint of a report according to which I have discovered a new element, germanium, in a silver mineral found here. Initially, I was of the opinion that this element fills the gap between antimony and bismuth in the very ingeniously compiled by you periodic table, that is, that it, therefore, represents your eka-antimony; however, everything points to the fact that here we are dealing with the eka-silicon predicted by you. I hope soon to be able to give you details on a new extremely interesting body; today I will confine myself to informing you of this new triumph of your ingenious research and to pay you my highest respect.*

In June 1886, Dr. G. Quesneville, the editor of the French journal *Moniteur Scientifique*, accused Prof. Winkler of bringing nationalism into science, and insisted that Winkler should give up the name germanium as opposed, no doubt, to that of gallium, and that the new element should keep the name *eka*-silicon, since that was Mendeleev's name for this predicted element and so the naming of it should be up to him [15].

Over and above, C. Winkler kindly asked Mendeleev, if it was possible to name the element germanium: a manifestation of great respect [8, 11, 16], Fig. 5. Not long after that, the two scientists, the predictor of a new element and the real discoverer of said element, had the opportunity to meet each other in 1900 on the occasion of the 200th anniversary of the Prussian Academy of Sciences, Berlin. In fact, four countries, situated in Europe, have chemical elements named after their lands, i.e. Fr, Ga, Ge, Po and Ru. So, France has not only two elements, but its capital Paris (Lutetia) also gave the name of the element No 71 in the Periodic Table [16].

Let's recall that on August 27, 1875, the French chemist Lecoq de Boisbaudran had also discovered the predicted by Mendeleev *eka*-aluminum, i.e. gallium. Mendeleev's prognosis concerning the existence of *eka*-boron also became somehow the truth [17]. In other words, this element was discovered by the Swedish chemist Lars Frederic Nilson in 1879: scandium. It should be mentioned that in a ten-year period from 1880 to 1890 only 6 new chemical elements were discovered, germanium being the only one different among the isolated lanthanoids (Gd, Pr, Nd, Dy and Sm) at that time [1].

Unfortunately, the years following the discovery of Ge did not lead to any major scientific findings or technological applications for this rare, greyish-white, expensive, brittle and metal-like element which has a bright lustre with a diamond structure. It is a metalloid with a similar electrical resistivity to Si at room temperature but with a substantially smaller band gap [18, 19]. As a whole, more than one-half century elapsed after the isolation of germanium before its first commercial application in diodes and transistors [20]. To remind a reader that the chemical element In was also discovered by German scientists Ferdinand Reich (physicist) and Hieronymus Theodor Richter (chemist) during a spectrographic analysis of sphalerite ore samples again from the mines around Freiberg [21], just two decades earlier, 1863. However, they decided to name the element indium after the distinctive indigo-blue line in its emission spectrum. One more time, indium remained only a scientific curiosity for years following its discovery and unfortunately little was known about its occurrence apart from the Freiberg ore too [20].

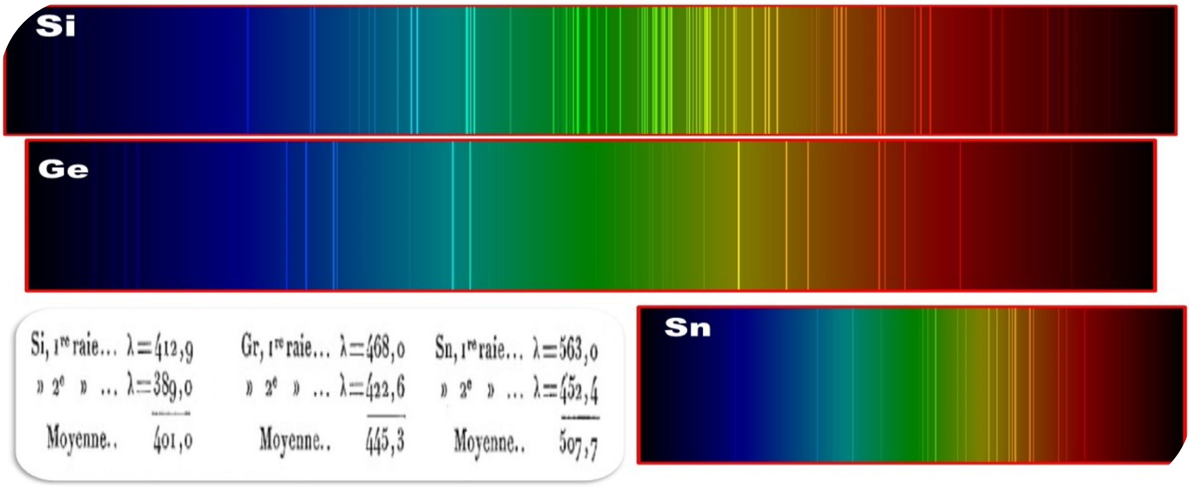

Figure 4. Spectral lines of Si, Ge and Sn in the visible spectrum at about 400-700 nm as well as the observed spark spectra applying Boisbaudran's new experimental apparatus.

Figure 5. Winkler and Mendeleev in Berlin in 1900. Monument in honor of Clemens Winkler in Freiberg (Wikipedia).

The first germanium crystals in Bulgaria. A little more of the story of engineer Stoycho Karavelov.

In 1890, Stoycho Karavelov returned to Bulgaria and joined the Mining Department of the Ministry of Finance as a mining engineer. In 1893, the Department was transferred to the newly created Ministry of Commerce and Agriculture. In the following years, he held various positions: chemical engineer for mines, head of the chemical laboratory, head of the chemical engineering laboratory, metallurgical engineer, director of mines, head of the department for mines, etc. As an outstanding expert, he was also the main author of the Basic Law on Mines in Bulgaria [22]. This law regulates the relations between mining enterprises and the state. In other words, the state reserves the right to exploit the main mineral resources on its own. As a person with broad interests, Karavelov also participated in the establishment of the first balneological organization for the use of mineral waters in Bulgaria. The engineer is the author of numerous articles providing information about the state of mining production in the world and in our country, about the production of precious metals in the world, as well as various statistical data on that topic. The works of the engineer also include the translations from German into Bulgarian language of the two books: "Guide to the determination of minerals with the help of the bellows" by Prof. Dr. C. W. C. Fuchs (translation 1892) and "Tables for the determination of minerals by external signs" by Prof. Dr. A. Weisbach (translation 1899), Fig. 6. Of course, these works were extremely important for that time, as they were the first serious scientific materials on metallurgy and mining in our country and for a long time they satisfied the glaring needs for such kind of literature in the young Bulgarian state. Eng. Stoycho Karavelov was repeatedly authorized to represent Bulgaria abroad [23], e.g., in the making of coin dies, and as state comptroller in the minting of coins at the mints of Vienna and Berlin. For his extraordinary work, Eng. Karavelov was awarded with several medals: "St. Alexander" 5th degree (1892) and "St. Alexander" 4th degree (1905), as well as the medal for Civil Merit 4th degree (1898) and Civil Merit 3rd degree (1914). Examples of medals, that Eng. Stoycho Karavelov was awarded are shown in Fig. 7, as described in his personal business list [24].

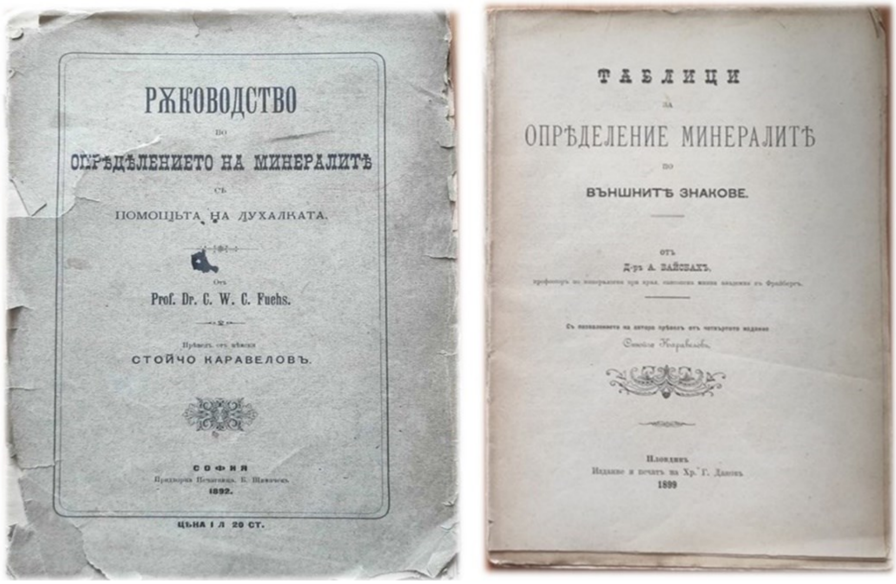

Figure 6. Photos of the two books.

Figure 7. Stoycho Karavelov's medals.

Figure 8. The eminent Bulgarian inorganic chemists, in whose hands has been the ampoule with the first germanium crystals.

In 1915, however, he resigned for health reasons and the following year (October 8) he died in Sofia, only 51 years old, from lung cancer. To mention, on the same date, but 11 years earlier, Professor Clemens Winkler died also because of lung cancer: October 8, 1904.

However, what is the route of the germanium ampoule and how did it reach to the Bulgarian National Polytechnic Museum? In 1898, Eng. Karavelov decided to give the ampoule with the first germanium crystals to the First Higher School in Bulgaria, probably to the Chemical Institute of the Faculty of Physics and Mathematics. The ampoule was placed in a glass jar (along with a handwritten donation inscription of Eng. Karavelov) and was kept by some of the distinguished Bulgarian chemists for a whole century. This peculiar relic is carefully preserved to this day. An incredible but real fact that all chemists in Bulgaria highly appreciate (Fig. 8). Prof. Nikola Dobrev, (head of the "Inorganic and Analytical Chemistry" Department in the period 1889-1909) handed it over to Prof. Zahari Karaoglanov (head of the same department in the period 1909-1922), who carefully hid the precious ampoule. Further, in 1922, the department was divided into two: "Inorganic Chemistry" and "Analytical Chemistry". Thus, the ampoule was handed over for safekeeping, completely naturally, to the head of the "Inorganic Chemistry" Department, Prof. Dimitar Balarev, who, following the tradition, handed it over to his best student, Prof. Nikola Kolarov. In fact, as an assistant professor, Mr. Kolarov had the opportunity to observe how Prof. Balarev showed the ampoule with germanium to the students, emphasizing with great pride that Winkler gave the first received crystals to a Bulgarian. Since 1958, Prof. Kolarov kept it in the Department of "Inorganic Chemistry" of the State Polytechnic, and later at the Higher Institute of Chemical Technology, nowadays University of Chemical Technology and Metallurgy. Upon his retirement in 1977, he entrusted it to his successor, Prof. Ivan Mladenov, one of the first assistants in the department from 1947 remained until 1953 when he moved in order to be a PhD student in the Department of Plastics Technology. Later, he became the founder and first rector of the Higher Institute of Chemical Technology in the city of Burgas. In July 1993, both Prof. Nikola Kolarov and Prof. Mladenov decided to give the ampoule for storage at the National Polytechnic Museum, thus ending this beautiful tradition and continuity among the inorganic chemists in Bulgaria. Recorded in the inventory book of the museum under No. OF 06564, the ampoule with germanium and the corresponding donation inscription became part of the permanent exhibition today. The exact text of the donation inscription reads: "*Germanium isolated in 1886 by Prof. Winkler in Freiberg. − Gifted in 1890 to Mr. Karavelov by Mr. Winkler. − Gifted to the Higher School by St. Karavelov 1898 – 31/I.*"

CONCLUSION

While the name of the eminent German chemist Clemens Winkler is loudly heard among chemists in Germany, that of the Bulgarian is almost forgotten or is little mentioned today. For example, in the present days the Clemens-Winkler gold medal is awarded by the Division of Analytical Chemistry of the German Chemical Society every two years. Undoubtedly, it was a real privilege to study under the direction of an eminent man like Winkler, who inspired his students. *A university has no doctrine to teach. Its special purpose is to investigate what is true in any field. It is the special gift of the great teacher to open the mind of the pupil*. − Jeremiah W. Jones [2]. The intertwining of historical facts and events with the life stories of existing people and/or literary characters from Bulgarian literature makes the experience herein even more memorable, brings the museum narrative to life, makes the memories lasting, and emotional for almost all people, not only students or chemists, but also foreigners. Accordingly, science education should emphasize the major landmarks in our understanding of the natural world, and the major figures and events in the history of science and the cultural significance of scientific achievement as a primary argument. It is our pleasure to recount the past 130 years related to the Bulgarian footprint in the history of germanium.

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