

10th International Tungsten Symposium

To be hosted by Zhuzhou Cemented Carbide Group Corp and China Minmetals Corp, the 10th International Tungsten Symposium will take place in the Dolton Resort Tongshenghu, Changsha in Hunan Province, CHINA. The event will begin on Monday 19 September and conclude with lunch on Wednesday 21 September.

The theme of the symposium will be "Evolution of the Tungsten Industry and the Major Challenges Ahead".

Registration forms, a list of papers and speakers, and the full programme may be downloaded from the ITIA website – www.itia.info.

Membership

Welcome to:

- ▼ Beralt Tin & Wolfram (Portugal) SA, producer of tungsten concentrates.
- ▼ CERATIZIT SA (Luxembourg), producer of hard materials such as tungsten carbide, ceramics or other products, whether for standard items or tailored solutions.
- ▼ Federal Carbide Co, a US company manufacturing sintered and precision ground tungsten carbide wear parts for mining, textile, oil, pharmaceutical, electronics, metrology, aerospace, food, construction and woodworking industries.
- ▼ JSC Polema Corp, a Russian company manufacturing metal powders. Its product range comprises more than 500 tungsten product items including large sized high purity (99.90-99.95%) tungsten sputtering targets and tungsten metal powder.
- ▼ SC Mining Co Ltd (Thailand), producer of ferberite concentrate, antimony concentrate and ingots.
- ▼ Zhangyuan Tungsten Co Ltd (China), producers and suppliers of wolframite (3 mines), APT, blue oxide, yellow oxide, tungsten powder and nanosized tungsten powder, tungsten carbide powder, RTP powders and cemented carbide products.

The ITIA does not often receive calls from TV producers but there has been excitement during the last year over the discovery of a lump of metal found in the West of England, after an article was published in "Materials World" in February 2004.

There is speculation that this lump is tungsten metal, possibly pre-dating its presumed discovery in 1783, and a further twist to the story suggests the involvement of that scientist, man of letters, bankrupt and thief, Rudolph Erich Raspe, the author of "The Travels of Baron Munchausen" to whom reference is made in the second article in this Newsletter. The story which follows explains.

The Trehiddle Tungsten Bloom

Did the earliest production of tungsten metal take place in Cornwall in the UK? The author of the article which begins on page 2 is Professor Thilo Rehren of the Institute of Archaeology UCL. He is also a trustee of the Institute of Archaeo-Metallurgical Studies (IAMS), a UK registered charity and a member of its Scientific Committee.

As IAMS has written:

"Men and Metals are synonymous. There is no sphere of Man's activities where metal has not played a major part – from the earliest weapons to the latest space age technology."

It is for this reason that the work of IAMS is so relevant today to all who have any connection with the metal industry and commerce. It is thanks to its supporters in the past that IAMS has been able over the past thirty years to draw together the threads of metallurgical activity that bind today's industry to its fascinating origins in the Late Neolithic Period."

Readers who would like to learn more about the Institute's work, or make a charitable contribution, should contact IAMS, 31-34 Gordon Square, London, WC1H 0PY, UK (Tel: +44 20 7387 7050, Fax: +44 20 7383 2572, Website: www.ucl.ac.uk/iams)

The Trewiddle Tungsten Bloom –

an initial report by Dr Ing habil Thilo Rehren FSA,
Professor of Archaeological Materials & Technologies, Institute of Archaeology UCL, London

Introduction

The recent find of a large and particularly heavy metal lump by D Coombe, from Trewiddle Farm near St Austell, sparked considerable interest in its origin and purpose; in particular once it had been identified as comprising considerable amounts of tungsten metal. Following on from initial analyses by Brian Earl, and an in-depth investigation by the BBC in co-operation with the Natural History Museum in London in October 2004, it became apparent that this is a rare example of early tungsten metal, and that it may hold clues about the early history of tungsten production or tungsten research in southwest Britain.

The aim of this first report is to characterise the material based on a few small samples removed in autumn 2004 from the side of the ingot, and the data provided by the Natural History Museum in London.

Macroscopic

The find is of dark to rusty colour, has a rough surface and is irregularly egg-shaped with a maximum length of around 20 cm (*fig 1*).

The quality of the surfaces varies slightly from more smooth and consolidated to rather rough and porous, almost fragmented (see the top surface in *fig 2* as compared to the side surfaces). This gives the find the feel of a worked piece rather than appearing as an un-treated waste product.



Fig. 1: Side view of the Trewiddle bloom, showing area of previous cutting attempts.

The weight of the find is approximately 17 kg, its volume was determined to about 1.7 litres, resulting in an apparent density of 10 g/ccm. Upon sectioning, a shiny metallic interior became visible, with large areas of dark inclusions (fig 2).



Fig. 2: Side view of the Trewiddle bloom, showing the surface freshly exposed from this study.

Initial assessment, and questions

The initial assays had identified the composition as being predominantly of metallic tungsten, leading to speculations that this piece may represent an early attempt to produce tungsten metal. One of the problems deriving from this assessment, though, lies in the fact that metallic tungsten has a density of around 19 g/ccm, as opposed to the 10 g/ccm measured for this object, and the rather high temperature necessary to melt tungsten, of around 3,300 C. Another fundamental question is that of the likely date of this object, which was found as a surface find with no supporting dating evidence.

To address the first two questions, a series of polished sections were produced from the slivers of metal removed during the initial investigation.

Chemical composition

One of the polished fragments was subjected to XRF analysis, using the Institute of Archaeology's SPECTRO XLab 2000 Pro and the 'alloy' methods. This indicates that the sample is comprised of about 40 to 45 wt% tungsten, c. 30 wt% tin, and c. 25 wt% iron. The main other component identified is silicon, probably present as silicon dioxide, at a few percent by weight. Of the trace elements, phosphorous is present at just above half of one percent, while sulphur, chromium and manganese are present at less than 0.1 percent. However, visual inspection of the sample clearly shows that it contains different parts and regions, most likely of different chemical composition, so that the values given here are not likely to be representative of the whole object.

Microscopic investigation

The metallic part shows a number of different phases, differentiated by their grey shades and hardness (*figs. 3 and 4*).

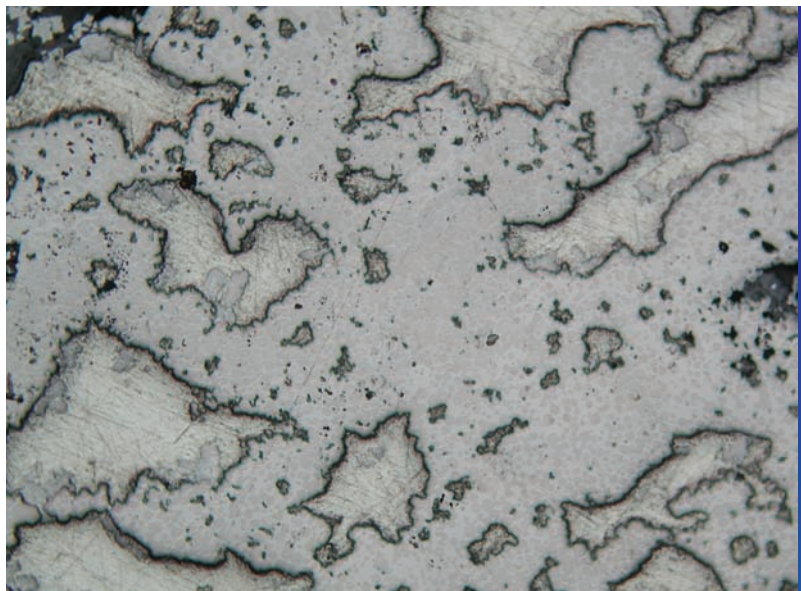


Fig 3: *Low-magnification overview of the metallic part of a sample from the Trewhiddle bloom. The silvery and rather scratched parts are metallic tin, often containing darker grey inclusions of tin-iron alloy (hard head). The matrix shows phases of different grey shades, as more clearly resolved in *fig. 4*.*

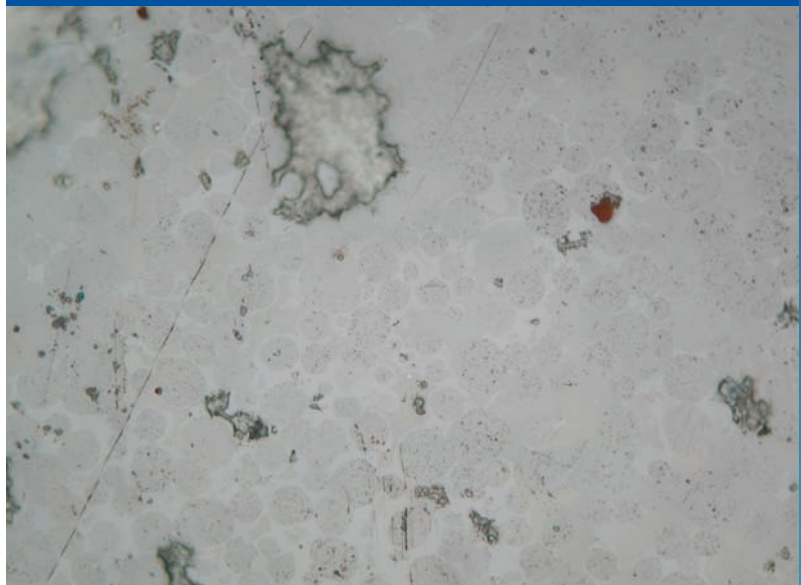


Fig 4: *Photomicrograph of the metallic matrix of the Trewhiddle bloom, with round particles of a hard and brittle phase (note the small dark specks), embedded in a slightly lighter matrix. In the lower right hand side, the matrix phase differs, having the same slightly darker grey shade as the round particles, but taking a better polish. Based on electron microprobe data from the Natural History Museum, the round particles are pure metallic tungsten, while the matrix phases are likely to be tungsten-iron alloys with and without phosphorous. Width of image c. 0.2 mm.*

The electron microprobe data from the Natural History Museum report almost pure tungsten for the round particles, with as little as 1/3 percent by weight of iron in it. The matrix phases appear to fall into two groups, one with about 63 wt% W, 34 wt% Fe and 3 wt% P, and another one with about 72 wt% W, 26 wt% Fe and 2 wt% P. The latter phase probably corresponds to the known phase W_5Fe_7 (theoretical iron content of c. 26 wt%), while the former may represent the known phase WFe_2 , which has a theoretical iron content of around 38 wt%. These phases are all known to form during the smelting of impure tungsten ore; and indeed, the presence of iron (and other metals such as nickel, cobalt and so on) greatly facilitates the formation of tungsten metal and intermetallic phases.

Other parts of the samples show large inclusions of slag (*fig. 5*) and charcoal (*fig. 6*); in particular the charcoal is dominating in the large dark inclusions already seen in the initial cut (*see fig. 2*).

The nature of the slag inclusions has not yet been studied in much detail; the presence of large clusters of pure silica and the overall glassy nature of the slag indicate that it is rich in silica, but may contain iron oxide and calcium oxide as well. It is hoped that the composition of this slag can be compared to published tin slag analyses, to test whether the Trewiddle bloom originates from tin smelting, or has its own unique slag composition, and hence may be the result of a special smelting operation.

The use of charcoal as fuel for the smelting operation is interesting, and may help us to determine the approximate date of production for the bloom, either by radiocarbon dating, or by study of historical records and an understanding of the general use of charcoal and mineral coal / coke in Cornish metallurgy.

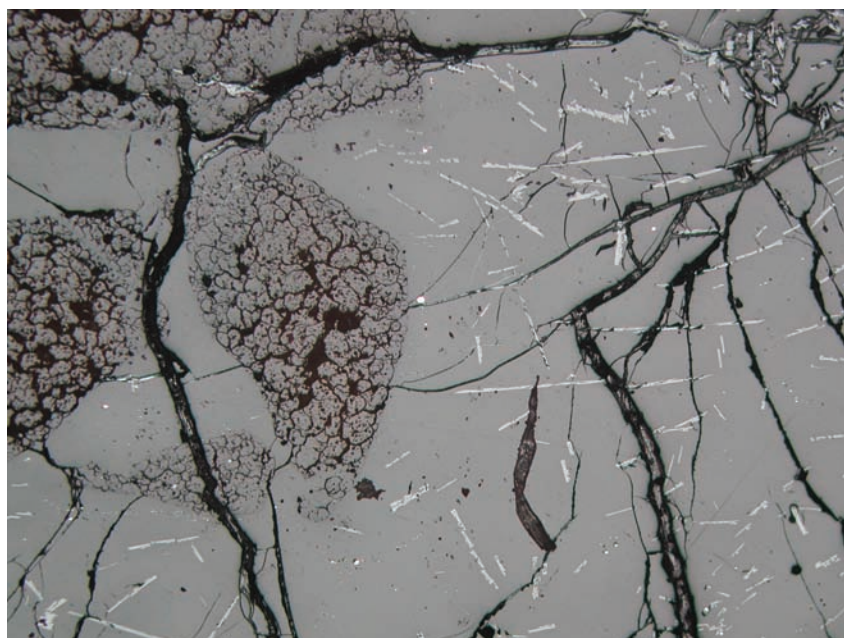


Fig. 5: Photomicrograph of a slag inclusion from the Trewiddle bloom. The cloudy areas at the left and upper left part of the image are silica (probably former quartz from the host rock), while the slag itself is predominantly glassy (grey area) with a scatter of bright needle-like crystals of metal oxide. Width of image c. 1 mm.

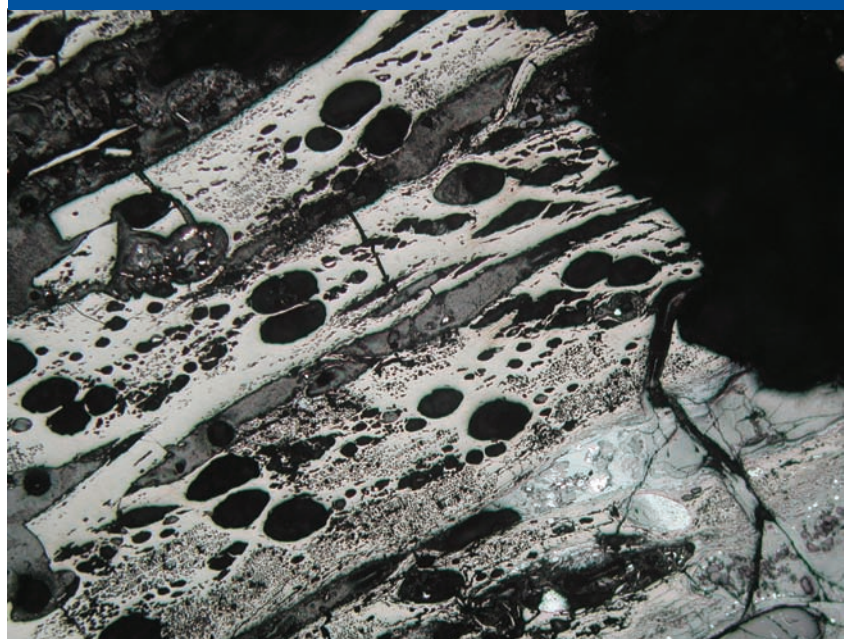


Fig. 6: Charcoal inclusion in the Trewiddle bloom. The cellular structure of the wood is well preserved, while the close association of the charcoal with the slag (lower right hand corner) confirms that the charcoal was in direct contact with the slag while the latter was still liquid.

Preliminary interpretation

There is little doubt that the metal originates from a mixed tin - tungsten ore; the association between the two is too intimate and the amounts present too high. Tin and tungsten ores occur often together in nature, not least in Cornwall, and iron is a typical impurity in both ores. Even back in the 16th and 17th century, smelters in central Europe were aware of the occurrence of some unwanted material during tin smelting; they gave it the name of *wolfram* ('wolf spittle' in English), clearly on a negative note. However, it was not before the late 18th century (1783) that two brothers in Spain isolated and identified the new metal tungsten / wolfram. In the mid 19th century, the addition of tungsten to steel was patented first in Austria (which has large tungsten deposits of its own) and soon also in England. It is this period of metallurgical enquiry, experimentation and discovery in which we are interested in the context of the Trewhiddle bloom, as it may be an early witness of the Cornish attempts to elucidate the nature and potential use of this material which they produced inadvertently during tin smelting.

The first question therefore is whether this is a purposefully produced material, or whether it is just a waste of tungsten metal accumulated in the tin slag during repeated smelting and processing. At present, this is difficult to answer; however, there are some indications (primarily based on the investigation done by the Natural History Museum) of near-original ore minerals being present, both tungsten-iron oxides and tin oxide. If this is confirmed by further analyses, then there are good reasons to argue that this is unlikely tungsten accumulated over a period of time in a tin smelter, but is indeed the result of processing impure tungsten ore for the tungsten. The same goes for the presence of charcoal, which is – if present in larger quantities within the object – indicating direct smelting efforts, and not the accumulation of heavy tungsten metal, presumably at the bottom of a tin smelter. For further clarification, however, it is necessary to see how much charcoal there actually is in this piece. The overall low density of around 10 g/ccm (as compared to the expected 19 for tungsten and about 8 of tin metal, resulting in at least an average 13 or 14

so for a block of equal quantities of tin and tungsten) indicates that there is a significant amount of charcoal (or other very light material) trapped inside.

The second issue concerns the actual possibility of forming solid tungsten at a time when it was technically impossible to melt tungsten metal, or its alloys. Here, we have to resort to the known principle of solid state metal reduction, as e.g. routinely done in the bloomery process of early iron smelting; in this, the iron metal was also never liquid, but still formed a solid block or billet after sufficient forging. Chemically, tungsten ore is even easier to reduce to tungsten metal than iron ore to iron metal; the surrounding presence of tin and iron metal will have helped to agglomerate and separate the metal from any forming slag. The visually gained impression that this object underwent some hammering and consolidation would also point towards the intentional – probably experimental – production of this metal, and attempts to work or refine it.

In reference to the established term 'bloom' for the semi-finished product of solid-state direct iron smelting, I suggest to call also this find a bloom rather than an ingot; an ingot would be a trade item of acknowledged proportions and properties, which at present seems not to be what can be said about this unique and semi-finished find. Whether it was something which the local smelters did after the discovery of tungsten metal in Spain in 1783, or whether they tried to work, isolate and possibly develop this long-known un-identified by-product of tin smelting even before that, is at present impossible to say. For this, we would need a more reliable date of manufacture for this find, and / or insight into the activities of the tin smelters during the last century or so of their operation in this region. I certainly hope to contribute to this discussion with further research.

The ITIA's Technical Consultancy continues its series on the many aspects of tungsten with a look at its early days.

THE HISTORY OF TUNGSTEN (WOLFRAM)

*Erik Lassner and Wolf-Dieter Schubert
Vienna University of Technology*

PART I: THE BIRTH OF THE ELEMENT AND THE EARLY DAYS OF EXPLORATION

GENESIS – THE FORMATION OF TUNGSTEN ATOMS

Tungsten like all the elements having a higher atomic number than iron ($Z > 26$) cannot be formed by nuclear fusion processes in stars, as is the case for those elements with lower atomic numbers, but originate only by neutron or proton absorption of already existing bigger nuclei. These processes with extremely high fluxes of neutrons and protons occur exclusively in massive stars (> 8 times the solar mass) during the end of their life cycle. Massive stars end in a supernova explosion (**Fig. 1**) whereby certain amounts of their mass are distributed to the surrounding space, including also the tungsten atoms formed. It is assumed today that during the early life of our galaxy (the Milky Way) the formation of massive stars and the subsequent supernova events took place much more often than today and consequently larger amounts of their "ash" were distributed to interstellar space.

Due to the fact that elements with higher atomic mass than 26 are formed only during short times, the probability of their formation is low and consequently the average abundance of those elements is low too. For tungsten it corresponds to 0.2 to 0.3 atoms W/ 10^6 atoms Si in the cosmos and 0.127 for the solar system.

About 4.6 billion years ago, our solar system started its formation from an interstellar cloud which contained besides hydrogen and helium also parts of the "ash" of one or more exploded stars and consequently also tungsten atoms. We cannot be sure if these remnants stem from one or more supernova explosions and moreover whether the atoms have undergone one or more star cycles. Also the time of their birth is not known. We only may say – it must be within the limits of 14 billion years ago (early stars in the Milky Way galaxy) and 4.6 billion years ago (formation of the solar system).

This corresponds to a span of about 10 billion years.

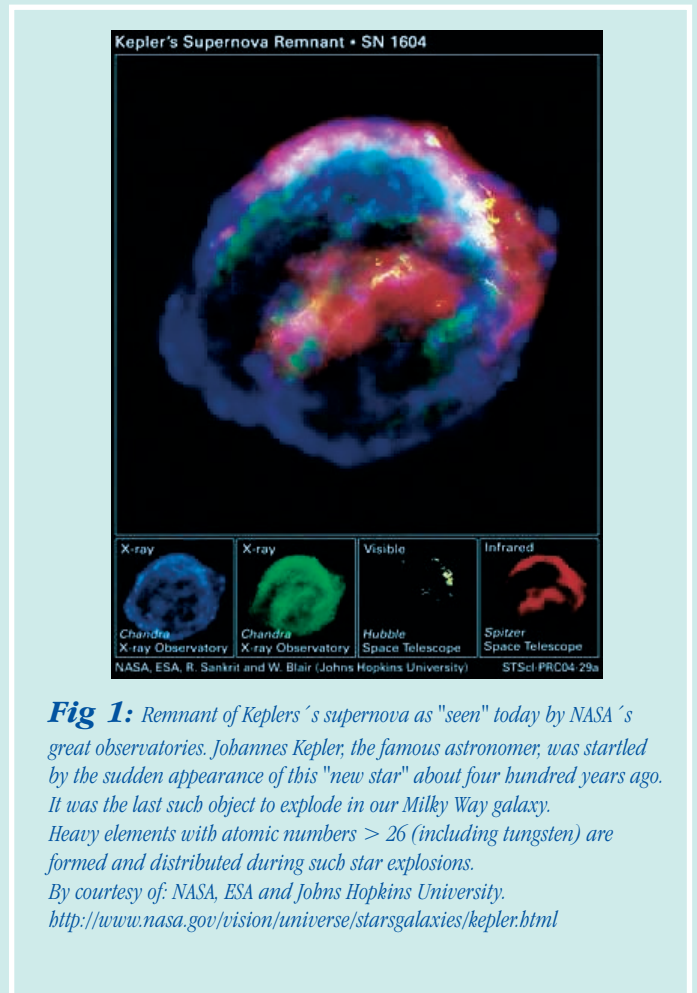


Fig 1: Remnant of Kepler's supernova as "seen" today by NASA's great observatories. Johannes Kepler, the famous astronomer, was startled by the sudden appearance of this "new star" about four hundred years ago. It was the last such object to explode in our Milky Way galaxy. Heavy elements with atomic numbers > 26 (including tungsten) are formed and distributed during such star explosions. By courtesy of: NASA, ESA and Johns Hopkins University. <http://www.nasa.gov/vision/universe/starsgalaxies/kepler.html>

METAMORPHOSIS – PARTITION AND ENRICHMENT

The part of material remaining outside the sun forming the earth has undergone different processes, such as oxidation, accretion, melting, segregation, fractional crystallization and separation of the iron-nickel core. Depending on the local oxygen concentration tungsten can be present in the metallic form (reducing conditions - tungsten atoms are *siderophile*) or as the oxidized, hexavalent ion (oxidizing conditions – tungsten trioxide or corresponding tungstates are *lithophile*).

During the core segregation most of the metals including tungsten migrated to the iron -nickel core. Partly and locally oxidizing conditions during the segregation process are the reason why we can

find tungsten at all in the earth crust. Igneous processes within the crust are responsible for a local enrichment of tungsten by 3 and sometimes also by 4 magnitudes, which we call deposits. Within those, tungsten is concentrated from the average abundance of about $1 \mu\text{g/g} = 0.0001 \%$ to some tenth and sometimes to a few percents.

These processes are best described by the magmatic-hydrothermal model – a partial and fractional crystallization of the magma – due to the decreasing temperature. By that an enrichment of certain elements occurs locally and temporarily in different fractions. Most tungsten deposits are therefore connected to ancient volcanism.

During the cooling of magma of any composition and source, changes in chemical and physical properties take place. Temperature and pressure gradually drop and differential crystallization starts. After crystallization of the main part of rock forming minerals, the hydrothermal liquid (rich in silica, volatiles and metals) remains. Metals present in the magma originally in very low concentrations are now concentrated and therefore minerals can be formed during the following crystallization steps. Tungsten is contained in the hydrothermal liquid as tungstate ion, tungstic acid, sodium tungstate and heteropoly-acid and crystallizes at the high temperature side, frequently together with tinstone (**Fig.2**).

DISCOVERY BY HUMANS – EVOLUTION OF NAMES - BIRTH OF TUNGSTEN CHEMISTRY

Tungsten is not the only one, but is among the group of elements having different names depending on language and respective country. In regard to a number of countries, WOLFRAM is the prevailing name. But because in the Anglo-Saxon nomenclature it is called TUNGSTEN this name is also very common, especially

because English is today's most frequently used language in the scientific and technical literature.

A complete list of the names used for the element in different countries can be found under:
<http://elements.vanderkrogt.net/>

The name **WOLFRAM** was recommended in 1949 as the scientific name for the element by the Commission on Nomenclature of Inorganic Chemistry of the International Union of Pure and Applied Chemistry (IUPAC) but this recommendation was withdrawn only shortly after due to heavy protests by the scientific community. No decision has yet been made. Nevertheless, the use of the name **TUNGSTEN** for the chemical element and of **W (WOLFRAM)** for the respective chemical symbols seems a reasonable "compromise".

In the following, let us go back to the roots of the two names and follow their history up to the present.

THE ROOTS OF WOLFRAM

The dawn of a conscious contact between humans and tungsten leads us to the end of the Middle Ages and the beginning of modern times in Europe. For sure in those times, nobody knew anything about that element or its minerals. Although people knew a lot about ores (fossils) and their smelting, they in general had in our sense often quite curious imaginations and explanations in regard to minerals and their behaviour, and respective names are closely related to that. But we should always keep in mind that, in those times, modern natural and technological sciences had not yet been "invented", but the experiences, observations and skills of our ancestors formed the basis on which sciences could be built up and develop further.

The name **WOLFRAM** is closely related to today's important tungsten mineral wolframite. Already in the Middle Ages (16th century) tin miners in the Saxony-Bohemian Erzgebirge in Germany reported about a mineral which often accompanied tin ore (tinstone). By experience it was known that the presence of this mineral reduced the tin yield during smelting. Foam appeared on the surface of the tin melt and in this foam much of the valuable tin could stay as droplets. It was said – the mineral (the wolf) eats up the tin. **Georgius Agricola** was the first to report about this new fossil in his book on "*De Natura Fossilium*", published in 1546.

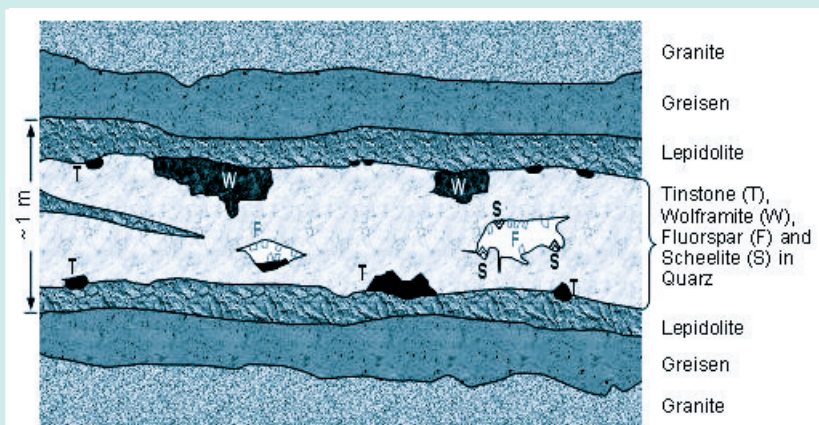


Fig. 2: Schematic drawing of a one meter broad wolframite-cassiterite vein formed in the granite of Zinnwald (Erzgebirge; Germany); wolframite and - to a minor extent also scheelite - occur besides tinstone; R. Beck: Z. prakt. Geol. 1896, 148-150.



effe facta, ut suo loco dicam. Quinetiam niger quidam lapis inuenitur prorsus colore similis illi ex quo cōflatur candidum plumbum: fed adeò leuis, ut mox intelligas inanem esse, & in se habere nullum metallum. hunc nostri appellant lupi spumam. Vt autem æs, si cum

Translation from latin into English:

One also finds a black stone with a colour similar to that from which one smelts white lead (tin). But it is so light that one might believe that it is empty (unsubstantial) and does not contain any metal. This we call *Spuma Lupi*

Fig. 3: Georgius Agricola (1494-1555); painted by Karl Pindl; <http://www.cbemnitz.de/>

Agricola was the first to mention WOLFRAM as a new mineral, which accompanied the tinstone in the tin veins of the Erzgebirge.

In his work "De Natura Fossilium" (published in 1546) Agricola used the Latin expression *Spuma Lupi* (wolf's foam). This term has subsequently caused some confusion as it is hardly appropriate to the mineral in question. For sure, the miners had already realized that the mineral was as heavy as the tinstone, although "mousse" formation during smelting will have occurred

He named it "*Spuma Lupi*" (Latin) - corresponding to **Wolfsschaum** in German or Wolf's Spittle in English (**Fig.3**).

The German teacher and priest **Johann Mathesius** ("Sarepta oder Bergpostill") was the first to name the mineral as **Wolform** (1551; third prayer), **Wolfrumb**, **Wolfsschaum** as well as **Wolffshar** – "darumb das es schwartz und lenglicht ist" – obviously related to the longish, hair-like appearance of the mineral (ninth prayer; 1559).

The names **Wolfferam** and **Wolffram** were used by Lazarus Ercker (1569, 1574) in his work "Aula Subterranea alias Probiere Buch des Herrn Lazari Erckers". He assumed the mineral to be an iron and arsenic containing tin ore.

Similar names, which were used in the later literature, are: **Wolfarth**, **Wolferam**, **Wolfram**, **Wolfort**, **Wolfert**, **Wolf(e)rig**, **Wolferan**, **Wolfish**, **Woolfram**, **Wolframit**, **Wolframicum**, but also **Lupus Jovis**.

In principle, the name **WOLFRAM** (chastisement of the mineral) can be derived from the German words **WOLF** (English: *wolf*) and **RAHM** = *Geifer* or *Schaum* (English: *spittle, foam*), or, more likely, from the Middle High German word **RAM** = *Schmutz*, *Dreck* (English: *dirt, ream, dross*), which seems to be the more correct term in regard to the problems which occurred during tin smelting.

The term **Spuma Lupi**, as used by Agricola in 1546, has caused some confusion in relation to the appropriateness of the term *foam*, mainly because of the high density of the mineral *wolframite*. Probably the term *wolfram* or *wolfferam*, as used by the smelters (and also by Lazarus Ercker), was erroneously latinized by Agricola into "spuma lupi" and then again erroneously re-germanized into *wolfsschaum*. The density of the mineral is about the same as that

of tinstone, and that of liquid tin ($\sim 7 \text{ g/cm}^3$), which will have caused considerable difficulties during mineral concentration and subsequent tin smelting. As the *wolframite* is more fragile than the hard tinstone, we can expect that during breaking of the ore-leading rock, fine *wolframite* particles were introduced into the tin smelting process, where they remained to the most part in the slag, forming a *mousse* with a higher density and viscosity, and being more difficult to separate from the liquid tin during tapping. In such case also small metallic droplets of tin (prills) will have remained within the slag.

Re-use of the slag through the miners, as described by Agricola in his "De Re Metallica" (Book IX) will have brought back the "wolfram" into the tin smelting process, and we can expect that under certain smelting conditions (high temperatures; high iron concentrations) part of the "wolfram" was reduced to the metallic (and intermetallic) form. In such cases the "wolfram" is drawn into the metallic phase together with the iron, and settles to the bottom of the melting furnace, due to its extremely high density ($\sim 19 \text{ g/cm}^3$), forming a high viscous mass together with the iron and tin ("hardhead"). Finally, a residue will be built-up at the bottom (German: *Ofensau*), which has to be removed to render the further tapping of the tin melt. As such residues must have had a much higher density as compared to metallic tin or iron we can expect that the smelters were aware of something exceptional, but could not use it.

These negative experiences with the mineral *wolframite* during tin smelting and the experience that the value of smelted tin was reduced through contamination remained up to the middle of the 19th century, when first applications for the chemical element tungsten appeared on the horizon. However, now and then, smelters might have tried to use this material before, but the time was still not ripe for the next stages: *isolation, refining and application*.



XII.
Chymische Untersuchung des reinen stahlberben Wolframs von Zinnwalde auf der Sächsischen und Böhmischen Gränze.

Fig. 4: Johann Gottlob Lehmann (1719-1767)

German geologist and director of the Imperial Museum at St. Petersburg, Russia. Lehmann was the first to thoroughly investigate the mineral **wolfram**. His results were published in 1761 in the form of 82 pages of outstanding scientific quality in the **physikalisch-chemische Schriften**. He obtained tungstic acid (as later named so by Scheele), but did not identify the new chemical element behind it.

Even today problems of dross formation are known from the tin smelting industries in cases where wolframite was not sufficiently separated from the tinstone prior to smelting.

In Cornwall, the mineral wolframite was known for centuries to the Cornish tin miners, who called it *Call* or *Mock Lead* because of its high weight and the suspicion that it contained lead.

ADVANCES IN MINERALOGY AND CHEMISTRY

200 years later, in the 18th century, the knowledge of humans in Chemistry throughout Europe had increased enormously. Geology, Mineralogy and Chemistry had grown into real sciences, and a series of new minerals and chemical elements were discovered. Systematic experiments revealed that the mineral *wolfram* must contain a new, still unknown element.

The German geologist and mineralogist **Johann Gottlob Lehmann (Fig. 4)** was the first in 1761 to fuse pure *wolframite* crystals with sodium nitrate. He then dissolved the melt cake in water, and observed a green solution which, on addition of sulphuric acid, formed a white precipitate turning yellow after longer standing. In 1779, **Peter Woulfe**, a chemist and mineralogist of Irish origin, cooked the mineral with hydrochloric acid and found a rich yellow colour.

Today we know that in both investigations tungstic acid was formed, but the authors failed in identifying the new chemical element within the mineral.

THE ROOTS OF TUNGSTEN

The name **tungsten** can be deduced from the other important tungsten ore, which is called today *scheelite*. In 1750 this heavy mineral was discovered in the Bispsberg's iron mine in the Swedish province Dalecarlia. The first person to mention the mineral was **Axel Frederik Cronstedt** in 1757, who called it **TUNGSTEN** {composed of the two Swedish words **tung** (heavy) and **sten** (stone) due to its density close to 6. In his famous book: "*Försök till mineralogie eller Mineral-Rikets Upställning*", published in 1758, he classified *tungsten* to be a calcium-containing iron ore (*Ferrum calciforme*).

In 1781, the outstanding Swedish chemist **Carl Wilhelm Scheele (Fig. 5)** published the results of his experiments on the mineral *tungsten* in *Kongl. Vetenskaps- Academiens Nya Handlingar*, with the title: "*The Constituents of Tungsten*". In this work he demonstrated that the mineral contains lime and a still unknown acid, which he called tungstic acid. In the same issue of the Journal ("*Appendages about Tungsten*") **Torbern Bergman (Fig. 6)**, a professor in Uppsala, suggested preparing the corresponding metal by charcoal reduction of the obtained acid. He also proposed to call the mineral *Lapis Ponderosus* (heavy stone) or, in Swedish, tungsten. In 1811, **Martin Heinrich Klaproth** recommended the name *scheelium* (*Scheelerz*- referring to B. R. Werner) in honoring the great chemist Scheele.



Fig. 5: Carl Wilhelm Scheele (1742-1786)

Scheele, who was one of the greatest experimental chemists of all times, was the first to demonstrate that the mineral *tungsten* (later: *scheelite*) is composed of lime and a new acid, which he called tungstic acid. Reproduced courtesy of the Library & Information Centre, Royal Society of Chemistry

Fig. 6: Torbern Olof Bergman (1735-1784)

Professor at University of Uppsala; painted by the Swedish artist Lorens Pasch the Younger, in 1778. Owner: Uppsala University Art Collections; photographer: Bo Gyllander.

Professor Bergman was one of the leading analytical chemists in the 18th century. Already in 1781 he proposed to reduce the "acidic earth" in "*tungsten*" by charcoal to obtain the new metal.



SCIENTIFIC AND CULTURAL EXCHANGE IN EUROPE

Biographies of the most prominent scientists of the 18th and 19th century indicate to us today the vivid scientific and cultural exchange which already existed in Europe in these times. Two important examples are demonstrated below.



Fig. 7: Juan José and Fausto Jermin de Elhuyar
Special issue stamp on the bicentenary of the discovery of tungsten in 1783.

The de Elhuyar brothers clarified the constitution of the mineral wolframite and were the first to obtain the new metal (following the advice of the Swede Bergman). They named it WOLFRAM, in consideration of the mineral from which it was extracted.

JUAN JOSE D´ELHUYAR – Discoverer of Tungsten

During 1781/1782, a Spanish nobleman, **Juan José D´Elhuyar** studied metallurgical chemistry with **Professor Bergman** in Uppsala. He had been before to Freiberg in Saxony (Germany) during the years 1778-1781 together with his brother **Fausto Jermin (Fig. 7)**. There, they had attended lectures by the famous **Abraham Gottlob Werner** in geology, and also had traveled through Austria and Hungary to study geological formations, smelters and refineries. Juan Jose was attracted to Sweden, and Professor Bergman was willing to take him as a student. There, he also visited **Carl Wilhelm Scheele** in his pharmacy in Köping. During his stay in Sweden he gathered information about the work on the mineral *tungsten*.

Back to Spain in 1783, Juan José analyzed a *wolfram* specimen from a tin mine in Zinnwald/Saxony (where he had stayed before, together with his brother) and showed it to be an iron and manganese salt of a new acid. He also concluded that *wolfram* contained the same acid as Scheele had gained from *tungsten*.

He then reduced the synthesized oxide to the new metal by heating it with charcoal, as had been recommended by his teacher Bergman.

His discovery was published together with Fausto in September 1783 by the Royal Society of Friends of the Country in the City of Vitoria (*"Análisis químico del volfram, y examen de un nuevo metal, que entra en su composición por D. Juan José y Don Fausto de Luyart de la Real Sociedad Bascongada"*).

Juan José was the true discoverer of the metal tungsten; even so Fausto assisted him in his investigation, and later received the honors from scientific centers after Juan José arrived in New Grenada (America) in 1784, leaving Spain forever. The new metal was named **WOLFRAM** after the mineral used (*"Daremos á este nuevo metal el nombre de volfram, tomándolo del de la materia, de la qual lo hemos sacado"....Este nombre le corresponde mejor que el de tungsto ó tungsteno....."*).

In their work, the two brothers also described the reaction of tungsten with pig iron which resulted in a greyish-white, hard and brittle material. This may be regarded as the first (reported) preparation of ferrotungsten.

THE PROSPECTOR

Another interesting contribution to the formation of the metal and to its alloys occurred in the northern part of Europe. **Rudolf Erich Raspe**, a German geologist, curator, essayist, translator, embezzler and author of *"The Adventures of Baron Munchausen"* had come to London to work for Cornwall mining industrialist **Matthew Boulton**. In 1783 he left for Cornwall where he worked as an Assay Master to conduct investigations into Cornish soil.

During this period, Raspe investigated two heavy minerals which were brought to him from the mines (i.e. wolframite and scheelite). He identified them as *"tungstein"* (referring to Scheele) and obtained a greyish-white fine-grained hard *"king"*, which he analyzed as a mixture of tin, iron and a "semi-metal". He also revealed the identity of the acid and the reduced metal from both minerals: *"If I am not mistaken, the two "kings" (metals) are identical. . . . It (the "king") cuts glass like hardened steel and ought to be suitable for the manufacturing of hard tools"*. This is obviously a foreboding of the enormous success in the field of tool materials and stands contrary to a statement of the D´Elhuyar brothers, which at first did not sound as promising: *"No use has yet been found for the new metal, but we must not conclude that it is entirely worthless"*.

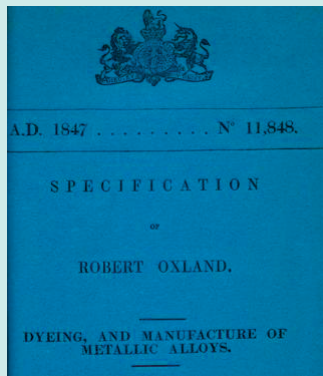


Fig. 8: Robert Oxland patented his manufacturing process for sodium tungstate, tungstic acid and tungsten metal in 1847. A second patent followed on tungsten steel in 1857 (No. 3114). Oxland opened the way for the industrialization of tungsten. Interestingly, the first application he referred to was the use of sodium tungstate as a substitute of tin usually employed as mordant in dyeing cloth.

Raspe also described the bright yellow colour of the tungsten oxide and proposed its use as artists' colour ("*in beauty it exceeds Turner's well known yellow by far*") as well as the wealth of Cornwall in terms of rich "tungstein" ore deposits (*...this area has more abundance than any other in the world*).

Only recently, the find of a heavy metal bloom containing tungsten at Trehiddle farm near St. Austell has drawn attention to these early days of mining and smelting in Cornwall (see previous article).

<http://www.bbc.co.uk/insideout/southwest/series6/tungsten.shtml>

STILL AN EXOTIC ELEMENT

Thereafter, an increasing number of scientists dealt with the new chemical element and its compounds. Further improvements in metal preparation were suggested by **Henri Louis Duhamel du Monceau** already in 1786. He also proposed to use the metal for the hardening of steel. In 1816, **Jöns Jacob Berzelius** (who favored the name wolfram over the term tungsten, although a Swede) described the lower tungsten oxides, and in 1824 **Friederich Wöhler** produced the so-called *tungsten* bronzes and recognized their application. However, the price for the metal was still far too high, and the time not yet ripe for promising applications.

In 1847, a patent was granted to the engineer **Robert Oxland** related to "*Improvements in Dyeing, certain Parts of which Improvements are applicable to the Manufacture of Metallic Alloys (Fig. 8)*". This included the preparation of sodium tungstate, formation of tungstic acid, and the reduction to the metallic form by oil, tar or charcoal. The work constituted an important step further to modern tungsten chemistry, and opened the way to industrialization.

Due to **Friedrich August Breithaupt** (1820) the name *wolframite* was adopted for the mineral $(\text{Fe,Mn})\text{WO}_4$, the former WOLFRAM (although the term wolfram is still in use for the

mineral in the English speaking countries). In 1821, **Karl Caesar von Leonhard** suggested the name *scheelite* for CaWO_4 , formerly TUNGSTEN. These two names remain valid today, whereas the names WOLFRAM and TUNGSTEN are in use for the chemical element, as indicated above. The mineral *ferberite* (FeWO_4), discovered in Spain in 1863, was named after the German mineralogist **Moritz Rudolf Ferber**, and the mineral *huebnerite* (MnWO_4) after the German metallurgist **Adolph Huebner**.

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PART II of the history will appear in the December Newsletter. It will be devoted to the early applications of the metal and of its alloys.

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