Materials Science Forum
ISSN: 1662-9752, Vol. 1081, pp 137-142
doi:10.4028/p-s4jt77

Submitted: 2022-05-23
Revised: 2022-09-29
Accepted: 2023-01-12
Online: 2023-03-24

Direct Production of Tin Bronzes from Copper and Cassiterite

Roland Haubner[1,a*] and Susanne Strobl[1,b]

[1]TU Wien, Institut für Chemische Technologien und Analytik,
Getreidemarkt 9/164-CT, A-1060 Vienna, Austria

[a*]roland.haubner@tuwien.ac.at, [b]susanne.strobl@tuwien.ac.at

Keywords: bronze; cassiterite; archaeometallurgy.

Abstract. In the Bronze Age several possibilities for tin bronze production were available, namely direct from copper and cassiterite ore or by alloying copper with metallic tin. Cassiterite ores from two sources, Cornwall and Schlaggenwald, were available. It has to be noted that cassiterite from Schlaggenwald contained about 25 wt. % WO_3, presumably as wolframite. For the experiments, copper was melted at 1090 °C, covered with charcoal and then cassiterite and again charcoal was added. As is known from Sn smelting, the presence of tungsten reduces the yield of Sn. Thus, in our experiments the Sn content in the bronze was reduced. It can be confirmed by these experiments that the direct production of tin bronzes from copper and cassiterite ore is possible. In the Bronze Age the negative effect of tungsten should not have played a role, because at that time only the cassiterite deposits of Cornwall were known in Europe.

Introduction

The history of metallurgy began with the extraction and processing of copper, chronologically taking place in the late Neolithic and Early Bronze Age [1]. For the Alpine region, especially in Salzburg, Tyrol and Graubünden, this was at the end of the 3rd millennium BC. [2 - 4].

The Bronze Age in Central Europe was dominated by large chalcopyrite deposits at Mitterberg, Salzburg [5, 6]. Due to the different copper ores, different copper alloys were obtained from the smelting processes. Almost pure copper could be obtained from oxidic ores (e.g. cuprite, malachite) [7], arsenic bronzes were obtained when smelting fahlores [8] and copper with a certain sulfur and iron content was obtained from chalcopyrite ($CuFeS_2$) [6].

The Bronze Age began with the possibility of bronze production. With the term “bronze” usually tin bronze is meant and thus a discussion about the origin of tin is necessary [9, 10]. Cornwall is assumed to be the main tin deposit of this period.

Another question arises: how Sn was added to copper? The most likely variants are: (1) direct addition of cassiterite ore (SnO_2) to metallic copper [11]; (2) alloying copper with metallic tin.

Experiments were performed to verify the method of direct bronze production by adding cassiterite to molten copper.

Experimental Procedure

Cassiterite Ores. Cassiterite ores from Cornwall (England) (Fig. 1a - c) and Schlaggenwald (Bohemia) (Fig. 1d - f) were available.

X-ray fluorescence analysis (XRF) showed the composition of cassiterite ores (Table 1). The cassiterite from Cornwall contained about 81 wt. % SnO_2 as well as some Fe, Si, Ca, Ti and Al. In contrast, the cassiterite from Schlaggenwald contained only about 54 wt. % SnO_2 and almost 25 wt. % WO_3 and about 4 wt. % Bi_2O_3 should be mentioned as well.

The SEM Picture in Fig. 1f shows needle like crystals which could be identifies by SEM-EDX analysis as wolframite ($(Fe,Mn)WO_4$).

Melting Experiments. Two variants of alloying experiments were performed.

(a) Metallic copper and cassiterite were mixed and placed in self-made clay crucibles (Fig. 2), covered with charcoal and heated to 1090 °C in a box-type furnace.

(b) Metallic copper, covered with charcoal was molten at 1090 °C. After the 1090 °C had been reached cassiterite and once more charcoal had been added, heating was continued for about 15 minutes before the furnace was switched off and the crucible was cooled slowly.

Metallography. The bronze samples were sectioned with a cut-off machine and mounted in epoxide resin. Metallographic preparation started with plane-grinding, followed by polishing with 9 – 1 µm diamond. A Klemm 2 solution was used for etching. Light optical microscopy (LOM) and Scanning electron microscopy (SEM) with an energy dispersive x-ray analyzer (EDX) were used to characterize the samples.

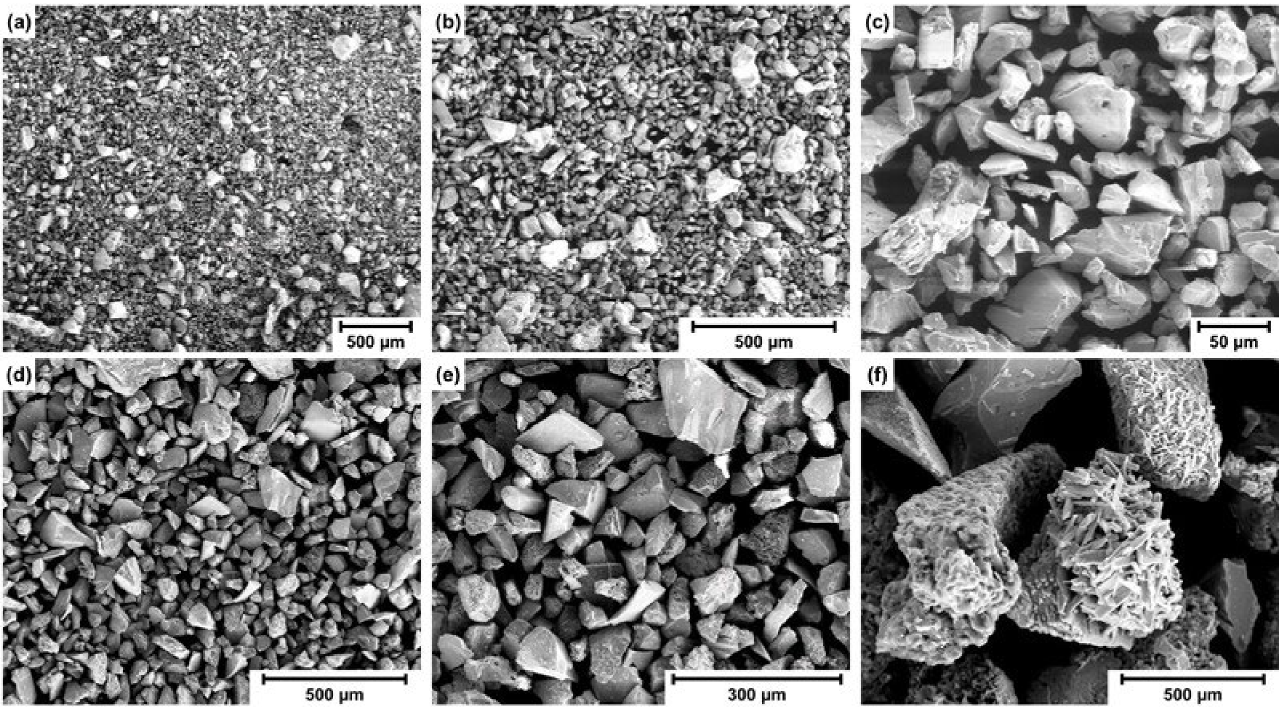

Fig. 1 Cassiterite ores in SEM at different magnifications. (a - c) Cornwall, (d - f) Schlaggenwald, (f) particles with wolframite.

Table 1 XRF results of the cassiterite ores

wt. %	**Cornwall**	**Schlaggenwald**
SnO_2	**80.78**	**53.7**
WO_3	**0.23**	**24.91**
Fe_2O_3	5.29	7.07
Bi_2O_3	0.11	4.05
MnO	0.04	1.54
SiO_2	3.73	1.98
CaO	2.18	0.48
Al_2O_3	1.42	1.96
TiO_2	2.17	0.91
CuO	0.09	1.04
S	0.43	0.08

Fig. 2 Self-made clay crucibles after an experiment.

Results and Discussions

Adding cassiterite (Schlaggenwald) to metallic Cu before melting. Amount of 70 g of metallic Cu and 7 g of SnO_2 (Schlaggenwald) were placed in the crucible together with charcoal and melted at 1090 °C (Fig. 3). After metallographic preparation of the sample and Klemm 2 etching a dendritic structure was observed (Fig. 3a - c). The dendrites themselves show a homogeneous etching pattern but strong differences in brightness. The interdendritic areas are surrounded by a seam with phases inside.

SEM-EDX measurements showed approximately 5 wt. % Sn in the bronze, indicating that Sn from the ore was largely incorporated into the bronze. SEM pictures nicely show the dendritic microstructure and also the precipitates in the interdendritic areas (Fig. 3d, e). EDX measurements again showed that these phases are Cu_2S (dark gray phase) and Bi_2S_3 (bright phase). This means that Sn and Bi from the ore have dissolved in the molten copper, but tungsten was absent.

Enrichments of W, Sn and O were found at the edge of the regulus (Fig. 3f). This could be a Sn-W-O compound, because a reaction between W and Sn is known to make Sn unavailable for bronze formation [12].

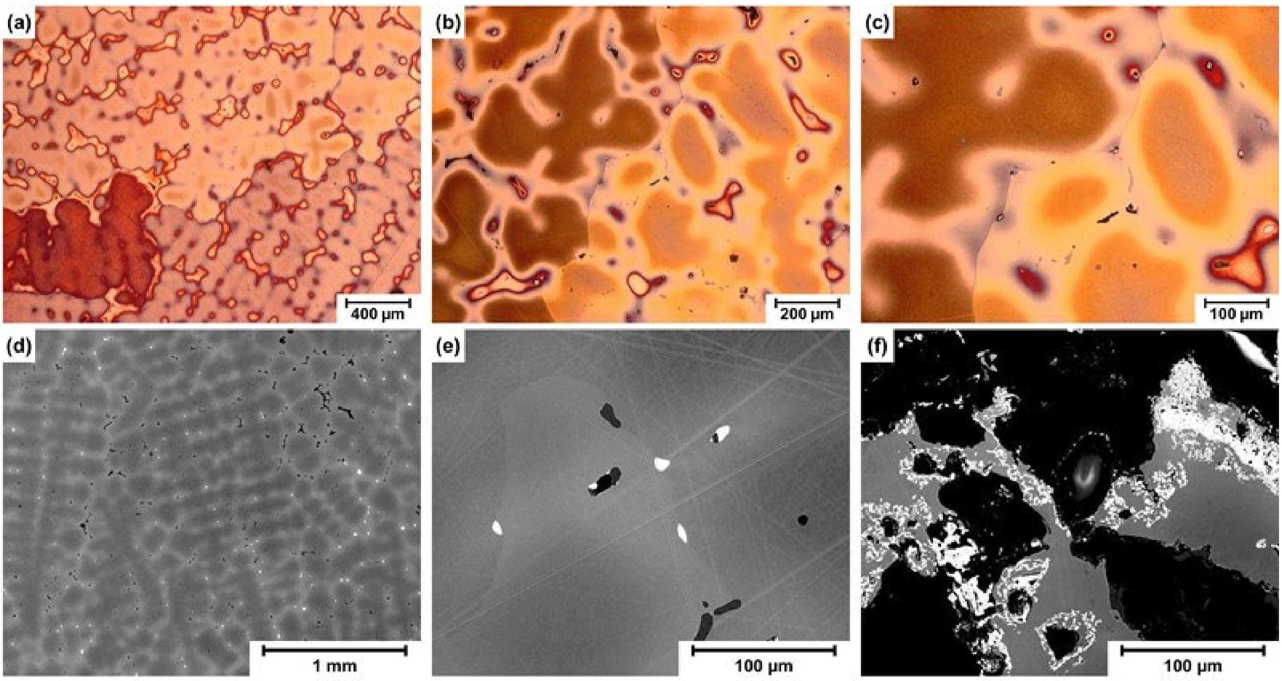

Fig. 3 Bronze, obtained after melting of metallic Cu and cassiterite (Schlaggenwald).
(a - c) LOM after Klemm 2 etching, (d - f) SEM micrographs.

Adding cassiterite (Cornwall) after melting metallic Cu. 50 g of metallic Cu were placed in the crucible and after melting at 1090 °C 5 g of cassiterite ore (Cornwall) and some charcoal were added (Fig. 4).

After etching with Klemm 2 a typical dendritic microstructure was observed (Fig. 4a - c). The interdendritic areas appear sharply outlined.

An average Sn content of about 6 wt. % was measured in the alloy by SEM-EDX. Due to the slightly higher Sn content in the bronze and a segregation during solidification, in the interdendritic areas the intermetallic phase $Cu_{41}Sn_{11}$ was formed (Fig. 4d - i). $Cu_{41}Sn_{11}$ is part of a eutectoid microstructure. By SEM-EDX the dark gray phases were identified as Cu_2S.

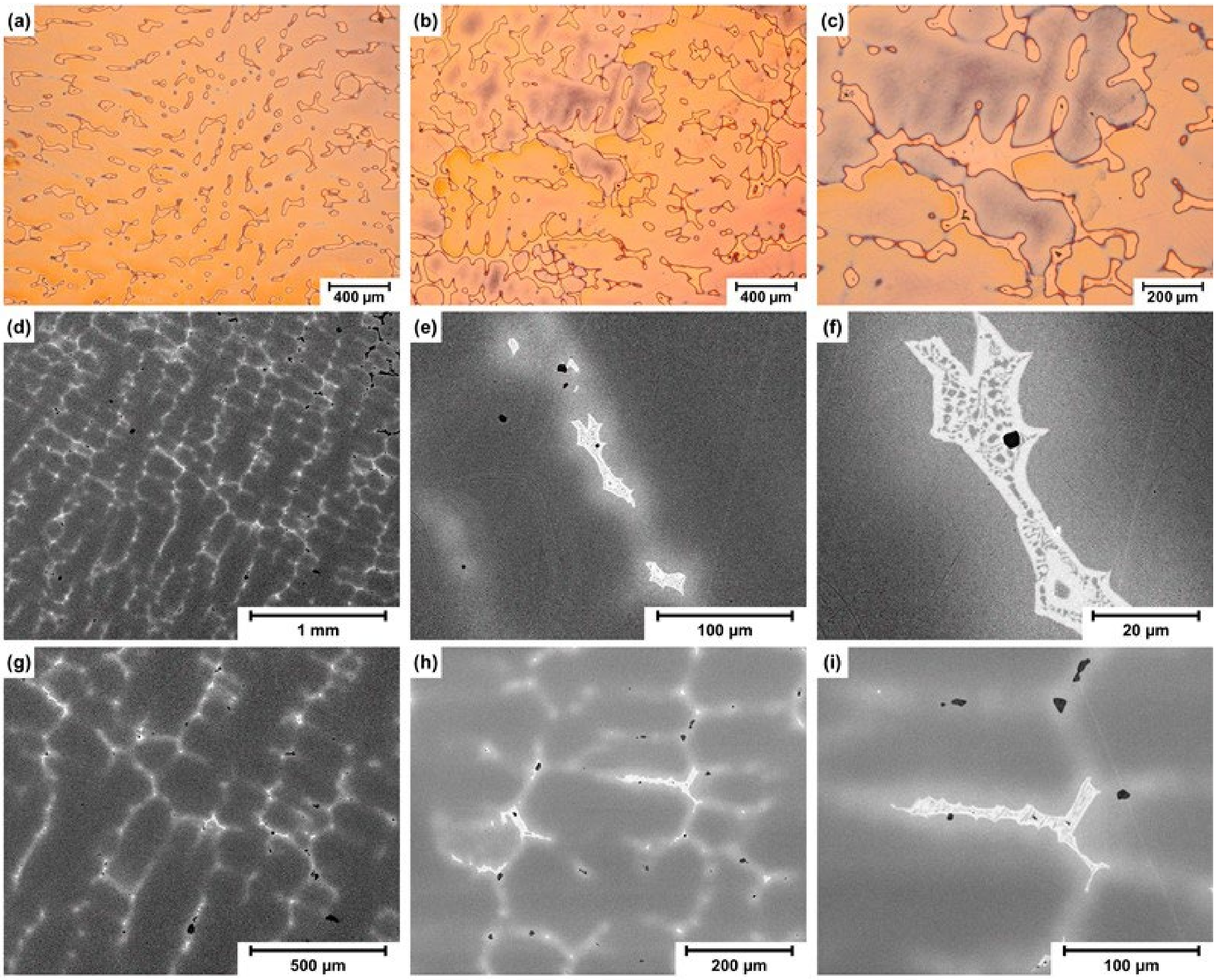

Fig. 4 Bronze, obtained after adding cassiterite (Cornwall) to molten Cu. (a - c) LOM after Klemm 2 etching, (d - i) SEM micrographs.

Adding cassiterite (Schlaggenwald) after melting metallic Cu. Again, 50 g of metallic Cu were melted in a crucible and then 5 g cassiterite ore (Schlaggenwald) were added (Fig. 5). However, no bronze was obtained in this experiment because no Sn could be detected in the copper by means of SEM-EDX.

After Klemm 2 etch a coarse dendritic structure became visible, which can be attributed to the accumulation of impurities at the grain boundaries (Fig. 5a - c).

In SEM light and dark phases were observed at the grain boundaries (Fig. 5d - f). The light phase is Bi_2S_3 and the dark phase is Cu_2S. The presence of Bi in the copper shows that the ore has reacted with molten copper but tin has not been incorporated. One reason for this could be the presence of tungsten.

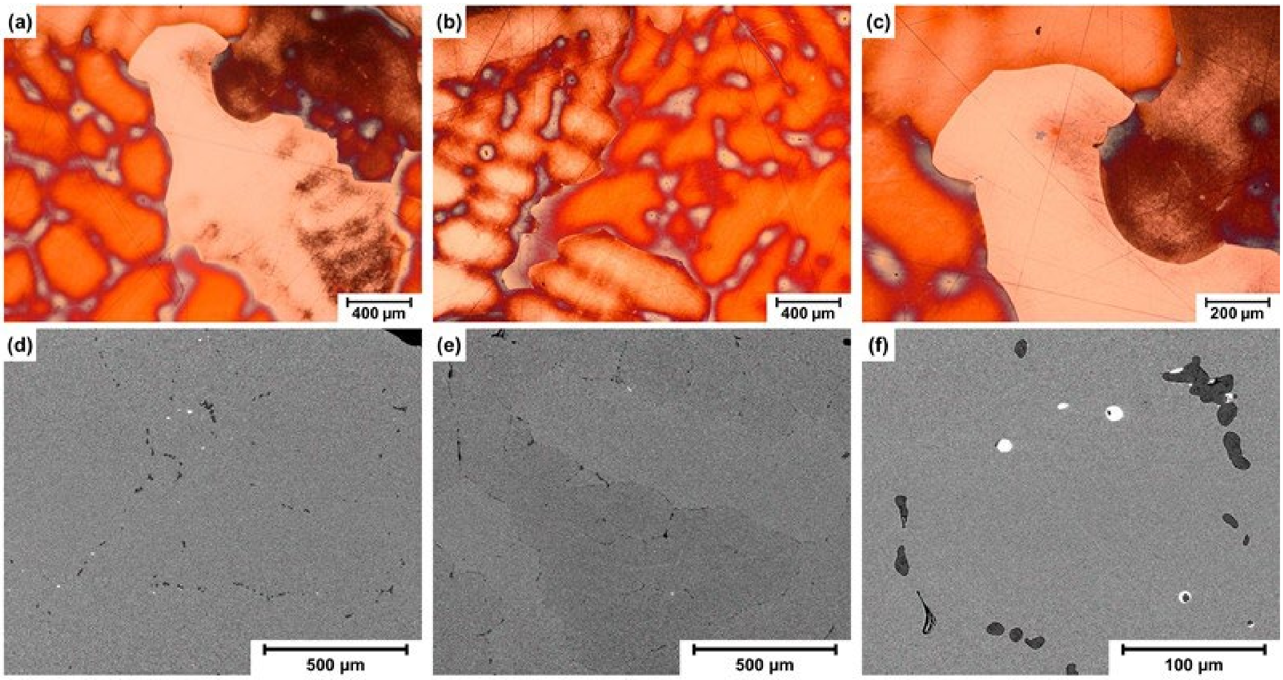

Fig. 5 Bronze, obtained after adding cassiterite (Schlaggenwald) to molten Cu. (a - c) LOM after Klemm 2 etching, (d - f) SEM micrographs.

In the Early Middle Ages German miners knew that an accompanying substance in the ore greatly reduced the tin yield [12 - 14]. Since tungsten was still unknown in the medieval, this accompanying substance in Sn ores was called "Wolf rahm" (Wolffrahm, wolf saliva, scum, foam or dross) by German medieval miners, meaning a wolf devouring the lambs (the Sn). Georgius Agricola was the first to report about this “Spuma Lupi” [15, 16]. In England a lump from Sn production was examined, which showed an extremely complex structure. However, no concrete compound containing Sn-W could be identified [17].

Summary

The investigations have shown that it is very easy to produce tin bronze from cassiterite ore (SnO_2) and metallic copper. Thus, the probability is high that in the Bronze Age the same procedure for bronze production was used.

- The cassiterite ore from Cornwall, with a SnO_2 content of about 81 wt. %, could be processed into tin bronze without any problems.
- When the cassiterite ore from Schlaggenwald, with about 54 wt. % SnO_2, 25 wt. % WO_3 and 4 wt. % Bi, was added to molten copper a Sn-W compound could have been formed and Sn was unavailable for bronze formation. Bi was observed in the interdendritic areas. In contrast, when solid Cu and W-containing cassiterite were heated simultaneously, bronze formation was not influenced by tungsten.
- In the Bronze Age the W-problem for the bronze production was not relevant, because it is assumed that the used cassiterite has its source in Cornwall.

Acknowledgement

The authors would like to thank Hannes Herdits (Burgenländisches Landesmuseum, Eisenstadt) for providing the Cassiderite from Cornwall and Philipp Burski (TU Wien) for experimental help.

References

[1] C. Pare, Bronze and the Bronze Age, in: Metals Make The World Go Round, C. Pare (Ed.), 2000, 1-38, Oxbow Books, Oxford.

[2] B. Höppner, M. Bartelheim, M. Huijsmans, R. Krauss, K.-P. Martinek, E. Pernicka, R. Schwab, Prehistoric copper production in the Inn Valley (Austria), and the earliest copper in Central Europe, Archaeometry 47, 2, (2005), 293-315.

[3] K.-P. Martinek, W. Sydow, Frühbronzezeitliche Kupfermetallurgie im Unterinntal (Nordtirol), Der Anschnitt, Beiheft 17 (2004) 199-211.

[4] R. F. Tylecote, A History of Metallurgy, The Metals Society, Mid County Press London, 1976.

[5] E. Pernicka, J. Lutz, T. Stöllner, Bronze age copper produced at Mitterberg, Austria, and its distribution, Archaeologia Austriaca, by Österreichische Akademie der Wissenschaften, Wien, 100 (2016) 19-55.

[6] H. Herdits, Die ostalpine bronzezeitliche Kupfererzeugung im überregionalen Vergleich am Grundbeispiel eines Hüttenplatzes in Mühlbach/Sbg., Dissertation an der Universität Wien, 2017.

[7] R. Haubner, Die prähistorische Kupfermetallurgie – allgemeine Betrachtungen, BHM Berg- und Hüttenmännische Monatshefte, 166 (2021) 343-351.

[8] R. Haubner, F. Ertl, S. Strobl, Examinations of a Bronze Ingot Made of Fahlore, Practical Metallography, 54 (2017) 107-117.

[9] J. D. Muhly, Sources of Tin and the Beginnings of Bronze Metallurgy, American Journal of Archaeology, 89 (1985) 275-291.

[10] I. Baranyi, Betrachtungen über die Herkunft des Zinns in der Bronzezeit, carolinea, 58 (2000) 115-124.

[11] H. Herdits, J. Keen, M. Steinberger, Wie kommt das Zinn in die Bronze? Ein Beitrag zur experimentellen Archäologie, Archäologie Österreichs, 6 (1995) 78-85.

[12] T. Young, S. Taylor, 'Wolf rahm': archaeological evidence for the veracity of an old term, Historical Metallurgy 49 (2015) 96-109.

[13] H. Louis, Metallurgy of Tin, McGraw-Hill book Company, 1911.

[14] P. Wagner, Die mineralogisch-geologische Durchforschung Sachsens in ihrer geschichtlichen Entwickelung, Sitzungsberichte und Abhandlungen der Naturwissenschaftlichen Gesellschaft Isis in Dresden, (1902) 63-128.

[15] Georgius Agricola, in: De Natura Fossilium, 1546.

[16] E. Lassner, W.D. Schubert, The history of tungsten (Wolfram), ITIA Newsletter, June (2005), 6-11.

[17] T. Rehren, The Trewhiddle Tungsten Bloom, ITIA Newsletter, June (2005), 2-5.