ANTIMONY also known as STIBNITE

(Antimony sulfide)

This website was recently asked about the above and as this writer had never heard of Stibrite decided to produce a page or two with some information as to what it is and how it was used.

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The following is information gathered from various sources – usually shown
There is a web article giving some details - www.chemicool.com/elements/antimony.html

A part of this information is given below

Antimony is a silver white metaloid found in a solid state, it melts from 631-904 degrees C (approx). The symbol for it is Sb

Ancient Egyptian hieroglyphics from 1890BC show the processional arrival of Stibium.

Antimony alloys are also used in batteries, low friction metals, type metal and cable sheathing, among other products. Antimony compounds are used to make flame-proofing materials, paints, ceramic enamels, glass and pottery. The ancient Egyptians used antimony, in the form of stibnite, for black eye make-up.

People have been making use of antimony's compounds for thousands of years. It is likely that the Roman author Pliny used the name stibium in the first century AD. We get the modern element symbol for antimony, Sb, from the word stibium. According to Pliny, the mineral stibnite was found most commonly among silver ores.

Pliny described how stibnite could be used as a medicine and how, if heated too strongly, it would turn to lead. We understand now that the 'lead' described by Pliny is actually the element antimony, produced by heating its ore. (2)

In the first half of the 1500s, Italian metallurgist Vannoccio Biringuccio wrote the alchemical work: "Concerning Antimony and Its Ore." He describes antimony sulfide as either "a monstrosity among metals" or "a material that is about to reach metallic perfection but is hindered from doing so by being mined too soon." [This was not chemistry as we know it!]

Biringuccio does get it right when he warns against heating antimony sulfide too strongly, because this will produce a substance that, "although this is very white and almost more shining than silver, it is much more brittle than glass." This is a clear description of the element antimony. (3)

Clearly alchemists had produced antimony in its elemental state by the 1500s.

French chemist Nicolas Lémery wrote his Treatise on Antimony in 1707 and took a scientific leap — backwards. In his writings, Lémery describes how acids prick the tongue because

they contain spiky particles, while metals dissolve in acids because the sharp points of acids tear the metal particles apart. [4]

The name “antimony” is derived from two Greek words: ‘anti’ and ‘monos’ which mean ‘not alone.’

Stibnite occurs in massive forms in gneiss and granite. It is also found in limestone, presumably deposited by hot springs. Significant deposits of stibnite have been located in Hunan province, China; on the island of Shikoku, Japan; and in the western United States (Idaho, California, and Nevada).

The name was given because antimony is rarely found native; it is usually combined with sulfur or with heavier metals such as copper, lead and silver.

Harmful effects:

Like arsenic, which sits directly above it in the periodic table, the toxicity of antimony and its compounds varies according to the chemical state of the element. Many of the salts are carcinogenic.

The metallic form is considered to be less active whereas stibine (SbH_3) and stibnite (Sb_2S_3) are extremely toxic.[5] Antimony is toxic and immediately dangerous to life or health at 50 mg m^{-3} or above. [6]

Exposure to 9 milligrams per cubic meter of air (mg/m^3) of antimony as stibnite for a long time can irritate your eyes, skin, and lungs. Breathing 2 mg/m^3 of antimony for a long time can cause problems with the lungs (pneumoconiosis) heart problems (altered electrocardiograms), stomach pain, diarrhoea, vomiting and stomach ulcers. People who drank over 19 ppm of antimony in one sitting vomited. [7

There is no reason to assume that antimony as used in Britannia Metal is harmful at all. It will change some of its properties in mixture with other metals, it is only a small percentage being used, there is no recorded instance of any harm. – This was the answer to the website question that gave rise to this short article.

Characteristics:

Antimony is metalloid, so it has some metallic properties but not enough to be classified as a true metal. Physically, it behaves like sulfur while chemically it is more metallic. [1]

Antimony’s electrical and thermal conductivity are lower than most metals’ conductivities.

Antimony is a brittle, fusible, crystalline solid. It is easily powdered.

Antimony also has the unusual property that (like water) it expands as it freezes. Four other elements expand when they freeze; silicon, bismuth, gallium and germanium.

Uses of Antimony

The major use of antimony is in lead alloys – mainly for use in batteries – adding hardness and smoothness of finish. The higher the proportion of antimony in the alloy, the harder and more brittle it will be. Alloys made with antimony expand on cooling, retaining the finer details of molds. Antimony alloys are therefore used in making typefaces for clear, sharp printing.

Babbit metals, used for machinery bearings, are alloys of lead, tin, copper and antimony. These metals are hard but slippery and so ideal for use as bearings. (8)

Antimony is used in the semiconductor industry as an n-type dopant for silicon.

Antimony trioxide is used as a flame retardant in adhesives, plastics, rubber and textiles.

Source: Most antimony is produced from stibnite (antimony sulfide, Sb_2S_3). It is also extracted as a by-product of copper, gold and silver production.

The Dutch Pewter Society offer the following comments –

From an analysis one cannot say whether it was added in pure or in sulfide form. Purification was already possible in the 15th C.

it was hardly used in the Middle Ages, although mined in Devon and Cornwall:
- John Blair and Nigel Ramsay (ed.), English Medieval Industries The Hambledon Press 1991, p. 82 and 84, found in a latten effigy and other objects;
- Brian Spencer, Pilgrim Souvenirs and Secular Badges, Museum of London 1998, p. 11, found in a bell, to improve its sonority.

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AUTUMN 2014 PAGE 6 JOURNAL OF THE UK PEWTER SOCIETY

James VI Scottish Enamel Bossed Dishes BY Peter Spencer Davies and David W. Hall
Dishes analysed including the partner to the one in the National Museum of Scotland (the Neish Collection Dish) were approx found to be - tin 83.9% lead 12% copper 1.13% antimony 2.7%
Antimony was not used in London until the middle of the 17th Century.
The Weir Dishes (said to be Royal Dishes) are of similar content to a known faked tappit hen.
The article continues to establish that the marks differ from those struck and that some of such enamel bosses have been found to be faked.
The article states there is no recorded Scottish provenance.

The interest in this Antimony article is the assertion that the presence of Antimony is sufficient evidence for doubt as to authenticity as it would not be found in Scottish dishes (if they were Scottish) at a date in the early 1600s.

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USE OF ANTIMONY

The article above does not detail the rules of the English Guild c1600. We can only assume that antimony was not used as that is by inference perhaps the evidence of other pieces analysed.

We cannot assume that Edinburgh obeyed English Guild Rules or more especially that the Court of James VI (Scotland) 1st (England) did.
What can be quoted is this translation by Robert Vetter in about 1930-34 of an article about the Pewter of Denmark.

The year 1685 is an important one in the history of the pewter of these two countries, for in it King Kristian V, of Denmark gave a new Charter to the craft. This Charter made pewter-marking compulsory for the first time; regulated the qualities of the various alloys, confirmed existing customs and regulations and it is essential that we note some of the more important of these - even at the risk of becoming a little wearying - for they are so essential to a right understanding of our story.

King Kristian's charter sets up three standards of alloy, with distinctive markings as follow;

1. ENGELSK TIN (English tin). This was to have no lead and was to be marked with an angel in addition to a second touch of a crowned Rose bearing the Town Arms on the rose. This second touch must bear also, the name or initials of the maker and the year of his admission to the Guild. If he was already a member in 1685, such date to be added.

Engelsk Tin examples are of a beautifully white, though softish metal; they are exceptionally free from allotropic decay and the absence of lead or antimony from the alloy, seems to be borne out by the good appearance of the metal.

What the above seems to tell us is that in the best tin there was neither lead nor antimony **AFTER 1685**. Robert Vetter quotes several leading Danish Museum Curators as his sources for his document.

Why should Denmark be relevant?
James VI married Anne of Denmark in 1589. Ann had good relationships with several of her siblings.

QUEEN ANNE (OF DENMARK)
Below the list of her parent's children (Frederick II of Denmark Sophie Mecklenburg-Güstrow) and hence her siblings (who survived to adulthood)

1. Elizabeth (25 August 1573 – 19 June 1626), married in 1590 to Henry Julius, Duke of Brunswick-Lüneburg.
2. Anne (12 December 1574 – 2 March 1619), married on 23 November 1589 to King James VI of Scotland (later James I of England)
3. Christian IV of Denmark and Norway (12 April 1577 – 28 February 1648)
4. Ulrik (30 December 1578 – 27 March 1624 in Rühn), last Bishop of the old Schleswig see (1602–1624), and as Ulrich II Lutheran Administrator of the Prince-Bishopric of Schwerin (1603–1624), married with Lady Catherine Hahn-Hinrichshagen
5. John August (1579–1579), died in infancy
6. Augusta (8 April 1580 – 5 February 1639), married on 30 August 1596 to Duke Johann Adolf of Holstein-Gottorp
7. Hedwig (5 August 1581 – 26 November 1641), married on 12 September 1602 to Christian II, Elector of Saxony
8. John, Prince of Schleswig-Holstein (9 July 1583 – 28 October 1602)

It is surely likely then that the pewter of Denmark and Northern Germany (at least) were known to the Scottish Court and the ourt Pewterer.
It is surely likely that the best pewter of Denmark before 1685 contained lead – and antimony.

Thus we asked the Dutch and German Pewter Society's for their comments as to if the best pewter of 1600 contained Antimony (Stibrite)

DUTCH RESPONSE, –

I asked a knowledgeable man about antimony. He tells me that from an analysis one cannot say whether it was added in pure or in sulfide form. Moreover, I learned that purification was already possible in the 15th c. https://www.chemicool.com/elements/antimony.html
So, in or not in - does not deliver proof or the contrary of any point of view.

Only if the piece contains pure antimony one might conclude that it cannot be older than 19th c. If it contains sulfide mineral stibnite it can be older. Thus it could be proved.

A chemist should tell whether the two minerals can be distinguished when the alloy is researched on composition. I know there exists (and I worked with) an instrument which determines the composition of metals.

It is like a GSM which you hold against the piece; no sample ought to be taken. On a screen you can read the percentages of the various minerals. It is used by used-metal dealers and by the Rijksmuseum in Amsterdam and costs some 30.000 euros.
German literature does not help a lot. Ludwig Mory, Schoenes Zinn, Munich, 3rd edition 1972, p. 27: 'Zugleich mit dem Zinnbarren wird auf einem zweiten Ofen eine geringe Menge Kupfer und Antimon (frueher Blei) verschmolzen.' (At the same time as the tin ingots were melted a second oven was used to melt a small quantity of copper and antimony (formerly lead).
H.-U. Haedeke, Zinn, Brunswick 1963, p. 11:' Der Zusatz von Antimon wurde seit Ende des 19. Jahrhunderts ueblich; diese Legierung ist unter der Bezeichnung Britanniametal und Kayserzinn (so genannt nach der Herstellungsfirma) bekannt.' (The addition of antimony came into use since the end of the 19th c.; this alloy is known as Britanniametal and Kayserzinn (after their producers)). Note: Brunswick is Northern Germany as you know from the British royal family.

GERMAN RESPONSE -

Antimony in pewter is certainly an interesting topic, but I must admit that I do have very little knowledge here. Here in southern Germany pewter alloys were always very pure, only pewter with a small addition of lead allowed. The guild rules are very strict about it.

But I do know that antimony was used in other German areas. Frankfurt is the first town that comes to my mind, but that was mainly an 18th century development.

I cannot rule out, that there was antimony in the alloy in early northern German pewter, but so far I have not given it much thought. However, I cannot remember to have ever heard of antimony containing alloys as early as 1600.

CONCLUSION – Antimony has been used for a long time. Unknown and unrecorded practices and rules do not enable us to be conclusive about dating other than if the Antimony used was – pure- then probably it was 19th century or later.

This article has set out a little of what is recorded as to Antimony and its use. Whilst raising various questions, that appear unanswered, it does not contradict the conclusions of the article quoted.

Those testing the dishes mentioned could have tested other pewter – said to be English – likely used at the Scottish/English Court in the period around 1600-1615 – known as the very scarce - and unusual for British – finely cast decorated pewter. This pewter has a 'whiteness' the dishes do not have.
Additional comment by sophisticated long term collector author and authority –

The salient points are that when Jacques Taudin arrived in London from Bordeaux, be brought with him the secret of how pewterers there were making pewter for use in flatware. Antimony is a hardening agent, and more effective than copper. The plates that he made were clearly more lustrous, and he was able to command a higher price for them. Hi success, as an incomer, clearly annoyed the London pewterers, which is why he suffered harassment. He would not reveal how he made them, but laid a false trail by saying that the alloy was 'double-refined' – which is quite meaningless. Eventually the secret came out and in the late seventeenth century, other pewterers were using his formulation and stamped their wares 'French Metal' or ' Hard Metal'. The Worshipful Company gave recognition and decreed that Hard Metal was to be stamped with a crowned X. You can follow the story in Welch. By the end of the eighteenth century, Vickers recognised that by increasing the antimony further he could produce an alloy that could be rolled and worked in thin sheets – Britannia Metal, and the development of the Sheffield BM factories.

Nothing to do with fake Scottish dishes. One Collector made the observation that the composition of such a is exactly what one might expect from pewter bought from a scrap metal merchant ie from the melt of the range of items sold to them.

The critical thing is that flatware does not have the mechanical strength of hollowware made in the round- and hence the need for the hardest metal they could make, to avoid bending. Flatware always had a tin content of well above 90% (even in Scotland!) to create an alloy with the hardest possible strength. QED