



Secondary Bismuth minerals

in the collection of the Australian Museum

Dieter Mylius

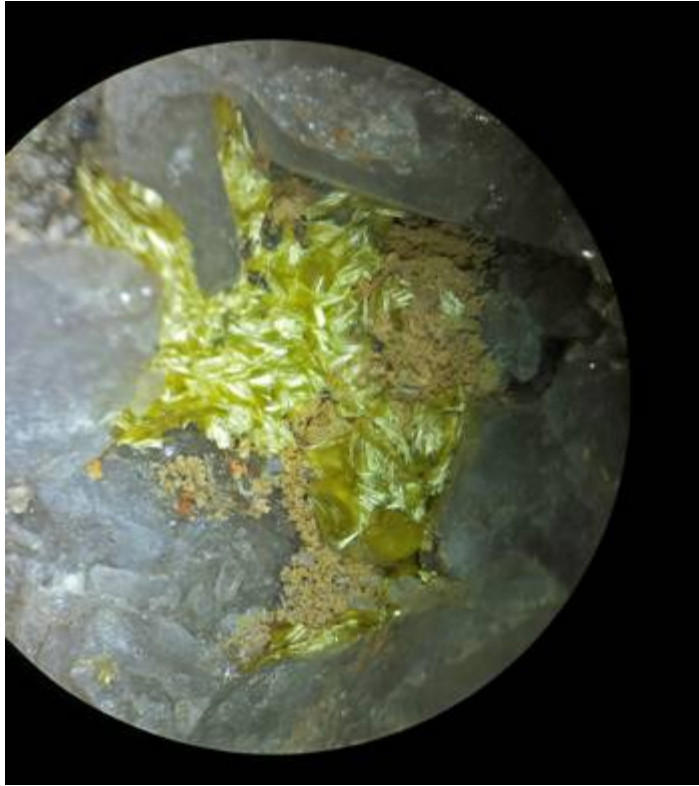
Bismuth, Deepwater, NSW

I have the privilege of being a volunteer at the Australian Museum in the Geoscience section headed by Ross Pogson.

The Australian Museum has many thousands of mineral specimens, many acquired well over 100 years ago, just waiting for someone to study them.

Like many collectors, to quote Ross,

“we usually accept what we are told when acquiring the specimen, unless we suspect otherwise, and time does not allow testing of every single specimen, but very often the collector or donor doesn’t know or suspect everything that is in the specimen either.”



Ferrimolybdate, Glen Eden, NSW

My original task was to check that all the specimens labelled as ferrimolybdate, were in fact ferrimolybdate. This was to be done using powder x-ray diffraction (XRD).

Most were ferrimolybdate.

However, koechlinite (Bi_2MoO_6) often popped up (especially in Kingsgate and other deposits where bismuth also occurred), so the testing naturally progressed to the secondary bismuth minerals.

Many specimens had been in the collection for many decades and identification at the time may have been “Bi oxides”, “bismuth carbonate”, or bismite.

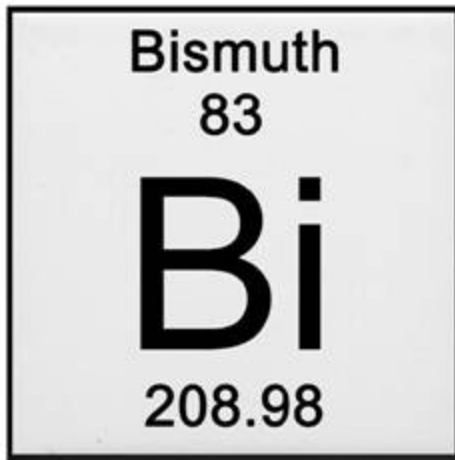
Many secondary bismuth minerals look remarkably similar to each other, or like the clay or weathered mica you or I would scrub off to see what more desirable minerals may lurk underneath. Many you would probably not even pick up.

Here we must thank the past generations for preserving what they thought was interesting and making it available to the museum.

I X-rayed 150 specimens, doing between 1 and 6 separate X-rays on each.

And I am sorry, but unlike ferrimolybdate, none of these minerals are high achievers in the looks department.





Bismuth

Bi, atomic number 83, atomic weight 208.980

Has a history of use to treat many illnesses. General cure-alls at beginning of 20th century (milk of bismuth), and other bismuth compounds used to treat syphilis.

Most of the original studies of Bi minerals were done in Europe, notably in the Erzgebirge, Germany in the 1800's and early 1900's. Many species have been known for a long time.

Main uses today:

Cosmetics, pigments, diarrhea remedies (bismuth subsalicylate) and other pharmaceuticals, low melting point alloys with lead, tin, etc., fire extinguishers, shot, ammunition & fishing sinkers.

But generally it is produced in small amounts as a by-product, mainly from China and Mexico

The dead give-away of Bi minerals is their weight if they are solid.

Native bismuth has a specific gravity (SG) of 9.7 or 9.8 and bismuthinite (Bi_2S_3) has an SG of about 6.8.

Bismutite ($(\text{BiO})_2\text{CO}_3$) is one of the most common Bi secondary minerals, and has an SG ranging from 6.7 to 7.4, which is 2.5 to 3 times the specific gravity of clays and micas which are typically 2 to 3.

However, if not solid or just coatings on quartz or the host rock, you do not have the advantage of weight to give you a hint

The minerals in this presentation fall into two groups just by their appearance

- a. There are clay-like ochres, oxides, carbonates that are a yellow to cream colour, which many of you may be familiar with.
- b. Then there are dark rims and blotches associated with native bismuth. These became increasingly interesting as testing went on.

If nothing else, I hope that this presentation will show that there is more going on in these specimens than may be apparent.

These are all Australian Museum specimens

There are many ways to approach presenting the results but for mineral collectors the most useful is probably by locality

We will look at:

Kingsgate, New England, NSW
Deepwater & Dundee, New England, NSW
Elsmore, New England, NSW
Murrumbateman, near Canberra, NSW
Whipstick near Pambula, NSW
Barrier Ranges & Mt Gipps, western NSW
Halifax Bay, Qld
Biggenden & Mt Shamrock, Qld
Wolfram Camp, Bamford, Chillagoe area, Qld
Torrington area, New England, NSW

KINGSGATE



Bismutite with bismuthinite
D2967

Kingsgate, NSW

Registered 25 March 1892, but purchased from W H Yates in 1891



XRD results show that the secondary mineral is indeed bismutite $(\text{BiO})_2\text{CO}_3$ but mixed in with rooseveltite $\text{Bi}(\text{AsO}_4)$. They are not distinguishable.



A similar specimen from Kingsgate, D2978, turned out to be 50/50 mix of bismutite and preisingerite $\text{Bi}_3(\text{AsO}_4)_2\text{O}(\text{OH})$

The presence of arsenates is not surprising, as arsenopyrite is not uncommon at Kingsgate. Note: In general, specimens of bismite from Kingsgate, including replacement of bismuthinite, were found to be bismutite.



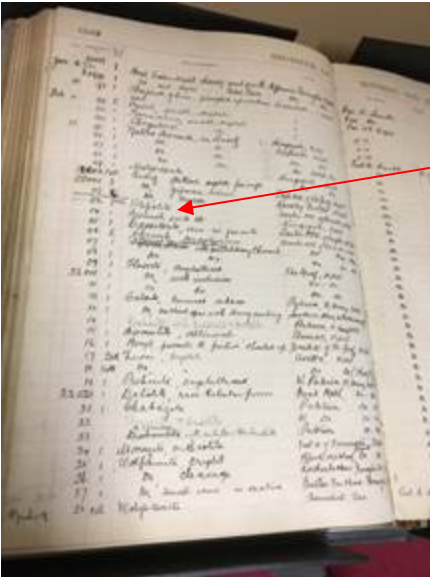
KINGSGATE

Bismuth oxide

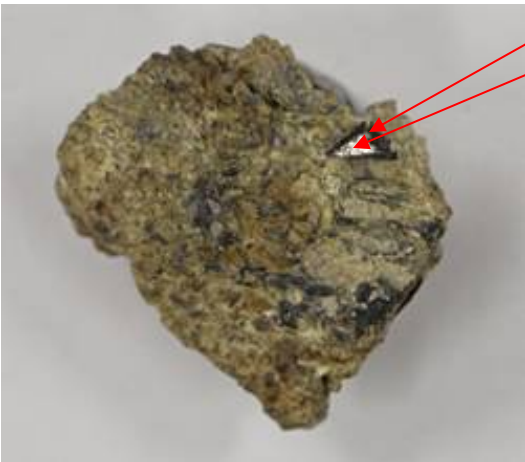
D22004

Kingsgate, NSW

Exchanged with George Smith, 13 Feb 1918

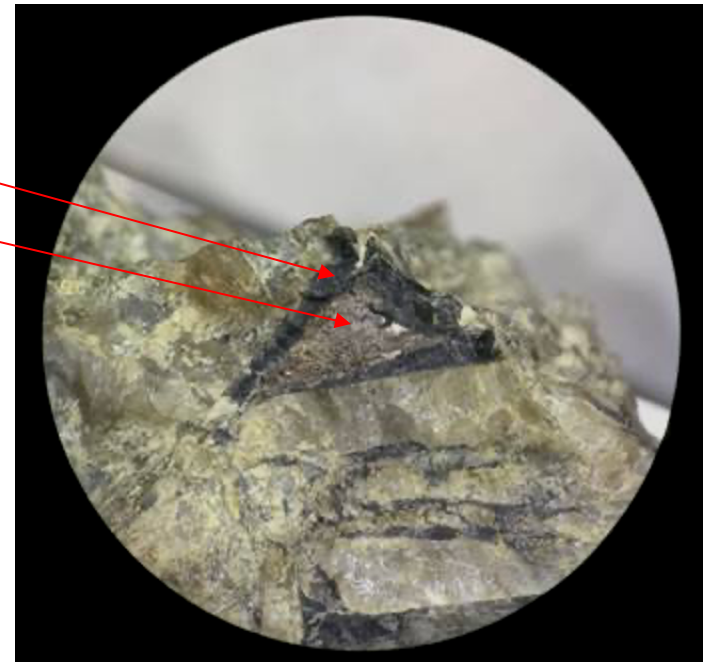


This specimen of bismuth oxide has euhedral grain of native bismuth surrounded by a dark grey, dull rim. This proved to be bismite (Bi_2O_3) with minor bismutite. This in itself was unusual as most specimens in this survey originally labelled as bismite, were in fact bismutite. Also the bismite is dark, not a pale colour.



Bismite
Bismuth

The yellowish matrix was thought to perhaps contain Bi secondaries, but proved to be just quartz with muscovite.



DEEPWATER AREA

AUSTRALIAN MUSEUM, SYDNEY.
Mineralogy Department.
D. 22246. Original No.
Bismutite.
Locality 14 miles N. of Deepwater,
N.S.W.
How acquired Exch. G. Smith.
64781-1 11.44

Bismutite

D22246

14 Miles N of Deepwater, NSW

Exchanged with George Smith on 12 September 1919

This specimen of bismutite $((\text{BiO})_2\text{CO}_3)$ from 14 miles north of Deepwater, was found to be largely what it claimed, in a granitic matrix.



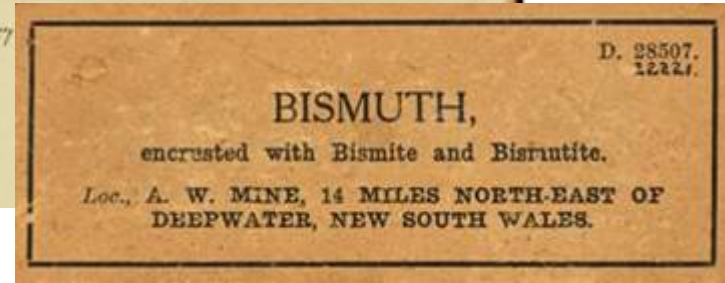
However, the dark grey patch was tested separately, and found to be zavaritskite $((\text{BiO})\text{F})$ with very minor tellurobismutite (Bi_2Te_3) , around a core of mostly altered native bismuth. The tellurobismutite may have been part of the primary core.



According to Mindat there are only two other recorded occurrences of zavaritskite in NSW and Australia, Fielders Hill near Torrington and Elsmore, both in the New England area.

DEEPWATER

Date	Registration No.	No. of Specimens	Name of Description	Locality	Collector	Date
Jan 6	D: 28502	1	Bismuth	Kangaroo, NSW	Prof Geo Smith Esq.	3/31/1927
		3	do	do		
		4	do in Quartz	do		
		5	do with goethite	do		
		6	do with Bismutite in Quartz	do		
		7	do encrusted with Bismite & Bismutite	do		
		8	do	do		

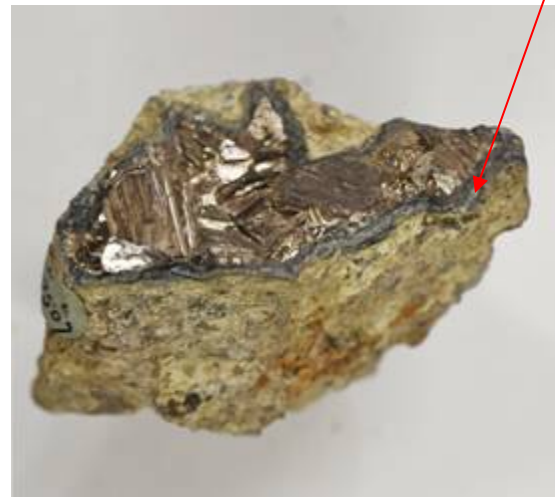
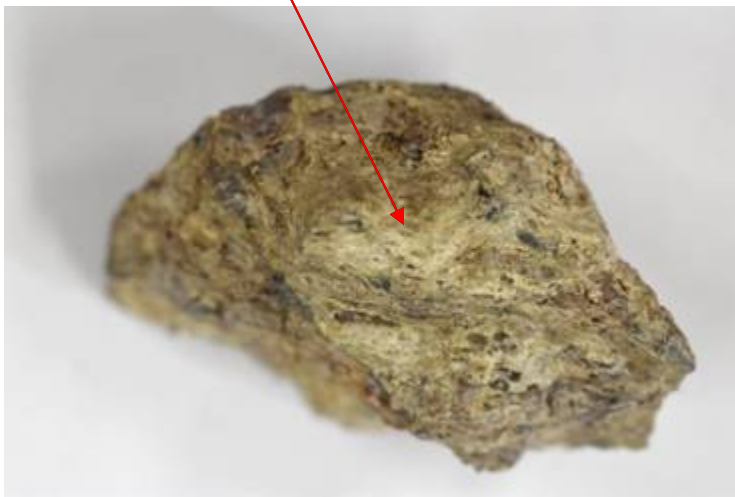


Bismuth encrusted with Bismutite and Bismite
D28507 A.W. Mine, 14 Miles NE of Deepwater, NSW
Purchased from George Smith on 6 January 1928

The outside of the specimen was nothing to look at, but its weight would have been a give away. Once cracked open, fantastic crystallised native bismuth was revealed.

The yellowish material proved to be koechlinite (Bi_2MoO_6) with some bismutite.

The dark grey rim around the bismuth proved to be bismite with bismutite



AUSTRALIAN MUSEUM, SYDNEY.
Mineralogy Department.
D. 35450. Original No. S:164.
Bismuth changing to bismite.
Locality Rare Metals Mine, Dundee,
N.S.W.
How acquired Pres. G. Smith.
64781-1 11.44

DUNDEE

Bismuth changing to bismite
D35450

Rare Metals Mine, Dundee, NSW.

Presented by George Smith on 17 April 1939



These pieces of bismuth were found to be coated with bismite, also containing bismutite



The bismuth secondary on a another specimen D23974, labelled Bismite in granite, from the Rare Metals Mine at Dundee proved to be koechlinite

ELSMORE

Elsmore, New England area, NSW is a little different.

Several boxes of pea-sized secondary cream-coloured bismuth “gravel” was variously labelled as bismoclite and bismutite.

A random sample of 10 pebbles were tested and all came back as bismoclite (BiOCl), often crusting a water-worn crystal of brown cassiterite.

Many of the Bi secondary minerals have been found at Elsmore, but the bismoclite is not unusual.

MURRUMBATEMAN

Murrumbateman is between Canberra and Yass, in NSW and includes claims such as Bullman’s, Hay Mair’s and MacCheeney’s.

Several specimens labelled as bismutite were tested, and were mainly bismutite but in places included beyerite ($\text{Ca}(\text{BiO})_2(\text{CO}_3)_2$), again visually indistinguishable from bismutite.

WHIPSTICK

A specimen, D21661, from the Mt Metallic Mine at Whipstick, near Wyndham in southern NSW was labelled as bismite with molybdenite, but proved to be koechlinite (Bi_2MoO_6). Interestingly, much of the matrix included spessartine, the Mn garnet. There was an indication of the rare mineral atelestite ($\text{Bi}_2(\text{AsO}_4)\text{O}(\text{OH})$), but this would need further work.



MT GIPPS

Bismutite (kettnerite added recently by hand)
D15637
Mt Gipps, Barrier Ranges
purchased from D A Porter on 16 July 1901



Mt Gipps is about 10km E of Broken Hill. This was the station for which Charles Rasp was a boundary rider, when he found some ore at Broken Hill.

The specimen does not look like much and is predominantly bismutite, but also contains a small amount of kettnerite - CaBiCO_3OF

These minerals are visually indistinguishable.



A similar specimen, D15628 from the Barrier Ranges, also listed as bismutite, gave the same of results of bismutite with minor kettnerite.



BIGGENDEN

Bismutite in magnetite

D31014

Biggenden, Qld

Presented by family of the late W H Yates on 10 April 1931



Pale cream patches of this specimen originally just labelled Bi carbonate in magnetite, was tested in a number places, and all proved to be a mixture of preisingerite ($\text{Bi}_3(\text{AsO}_4)_2\text{O}(\text{OH})$) as the major mineral, with more minor bismutite.

According to Mindat, preisingerite has not previously been recorded from Biggenden.



MT SHAMROCK

Mt Shamrock is about 15km NW of Biggenden. It was a small gold mine, producing gold and gold tellurides (hessite), but also contained bismuth and molybdenum.

Specimen D2976 (registered in the 1890's) from there was labelled as Bi carbonate, but was found to be a mixture of bismoclite (BiOCl) and rooseveltite (Bi_2AsO_4) with possible minor koechlinite, which was also found on a more recent specimen from Mt Shamrock (D31048).



Note: These photos are of a specimen I had linked to D2976, but cannot be 100% that is correct (currently no access to the specimens). I cannot find a reference to a "Centre Cobalt Pipe" in the Biggenden area, although cobaltite is listed in Mindat as occurring in the Biggenden Mine.



HALIFAX BAY

Bismutite with Bismuth

D31010

Halifax Bay, NE Qld,

Presented by family of the late W H Yates on 10 April 1931

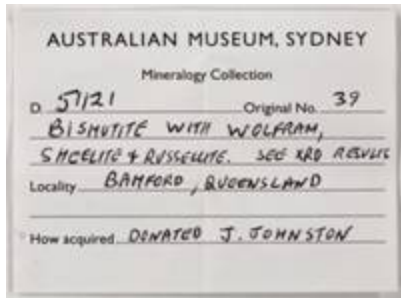
Halifax Bay is a broad coastal area north of Townsville in Qld. Possibly referred to mines inland to the N and NW, which may include Wolfram Camp area, whose ores were possibly taken to the coast for shipping.

Depending on where samples were taken from specimen, bismutite was present, but also bismite and bismoclite.

It is also one of the specimens in which an unnamed mineral, bismuth iron oxide ($\text{Bi}_{24}\text{FeO}_{40}$), was found. It is close to bismite with a little Fe present, but with a different XRD pattern.



BAMFORD



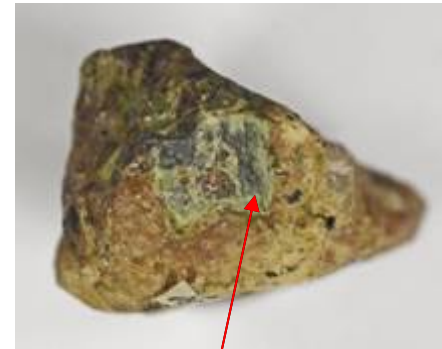
Bismutite

D51121

Bamford Qld

Donated by J Johnston, registered on 21 January 1997

Bamford is basically at Petford on the Burke Development Rd between Dimbula (Wolfram Camp) and Almaden, about 140km west of Cairns in Qld. Well and truly in the W, Mo, Bi area, it's the type and only locality for the rare green mineral, Bamfordite ($\text{Fe}^{3+}\text{Mo}_2\text{O}_6(\text{OH})_3 \cdot \text{H}_2\text{O}$).



Old note in box suggested "arsenbismutite",
But XRD showed yellow coatings on
wolframite indicated koechlinite with minor
russellite (Bi_2WO_6)

The grey-green material
proved to be a mixture of
bismutite and scheelite
(CaWO_4)

LINEDALE, CHILLAGOE ?



Bismuth
D29019

Linedale, West Chillagoe, Qld

Presented by Mrs B G Englehardt on 1 June 1928



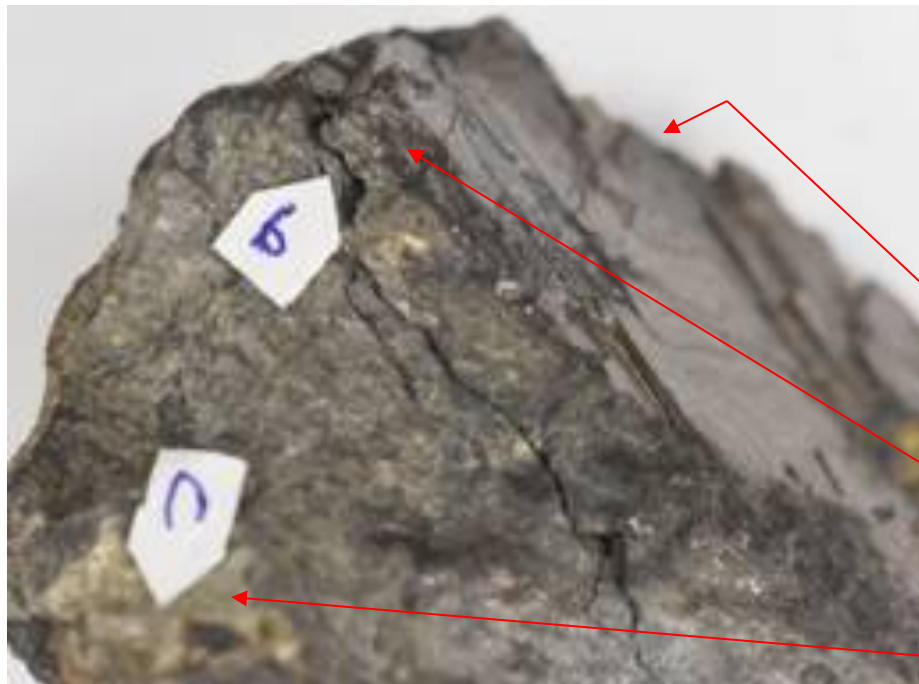
The locality is enigmatic, as I can find no record of it. It appears there was a Linedale syndicate working in the Chillagoe area (Trove, Northern Miner, July 12, 1895), but it focussed on copper. It also refers to the Linedale's West Chillagoe company. It may have had an interest in a deposit further east near Dimbula and Wolfram Camp.

The specimen is a beautiful 40mm cleavage plane of native bismuth in matrix, with a black rim around the Bi.



A similar specimen D29131 labelled as bismutite from Chillagoe, Linedale W, was found to contain koechlinite (Bi_2MoO_6) together with preisingerite ($\text{Bi}_3(\text{AsO}_4)_2\text{O}(\text{OH})$), showing arsenic is present.

LINEDALE, CHILLAGOE



Back to the bismuth, the specimen has dark grey to black rim where the bismuth is in contact with the “matrix”.

Three tests showed:

- Dark rim (back of specimen) – tetraroseveltite $\text{Bi}(\text{AsO}_4)$
- Dark rim mainly tetraroseveltite with some bismuthinite (Bi_2S_3)
- Pale patch was also tetraroseveltite.

Tetraroseveltite is the tetragonal dimorph of rooseveltite, which is monoclinic. Rooseveltite has been found in many deposits around the world.

According to Mindat, tetraroseveltite has only been found at the type locality, the Moldava deposit, Teplice District, Czech Republic, back in 1994. The deposit also contains bismuth, bismuthinite and preisingerite.

Very little information available, but Timothy Murphy in his thesis on “Bismuth in the Supergene Environment” also noted that it has only been found in the Czech Republic.

However, John Ranklin (pers. com.) found tetraroseveltite in one specimen at Elsmore.

WOLFRAM CAMP



Bi Carbonate

D31450

Wolfram Camp, Dimbulah, Qld.

Presented by family of the late W H Yates



Wolfram Camp is well known as a source of fine specimens of molybdenite, bismuth and "wolframite", often quite large in size and well crystallized.

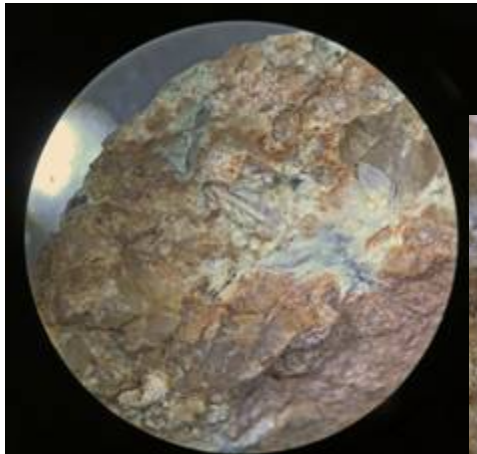
This specimen is rather nondescript. It was labelled as Bi carbonate, but testing revealed a specimen that is far from boring. It is quite fractured and had broken into two pieces at some time in the distant past.

WOLFRAM CAMP

D31450



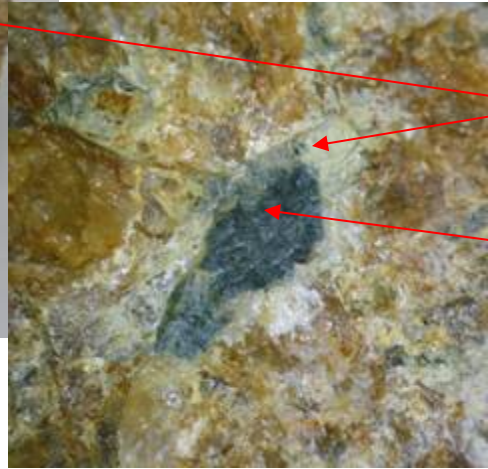
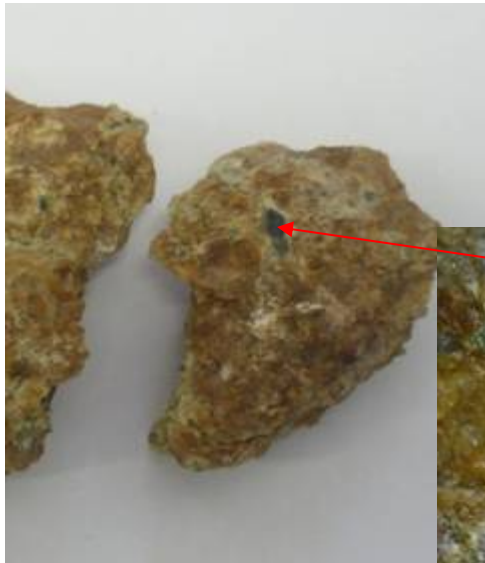
1. One corner was tested, and this indicated bismutite, but with massive and slightly foliated scheelite (CaWO_4). The scheelite fluoresces a slight off-white, rather than a blue-white, so there may be some powellite in the mix, although this was not evident in the XRD. On the basis of this unexpected result, other parts of the specimen were tested.



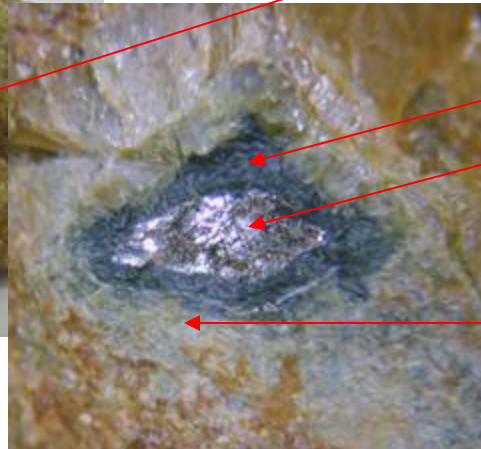
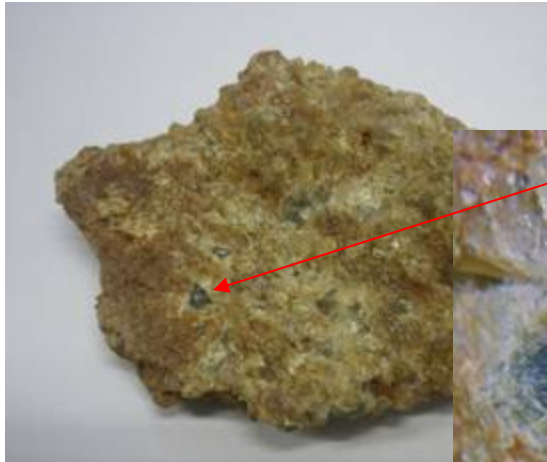
2. A platy, cream coloured mineral that appeared to be a replacement of molybdenite (seen edge on), proved to be powellite (CaMoO_4).

WOLFRAM CAMP

D31450



3. A greenish cream patch with darker mineral behind, proved to be koechlinite coating, and in part obscuring, bismuth oxifluoride, zavaritskite, BiOF.



4. A small patch of dark-grey to black mineral with a sub-metallic lustre, surrounding a lustrous metallic, but slightly tarnished central core, also proved to be zavaritskite with a core being native bismuth.

This in turn was surrounded by a mixture of bismutite and koechlinite, which could not be differentiated visually.

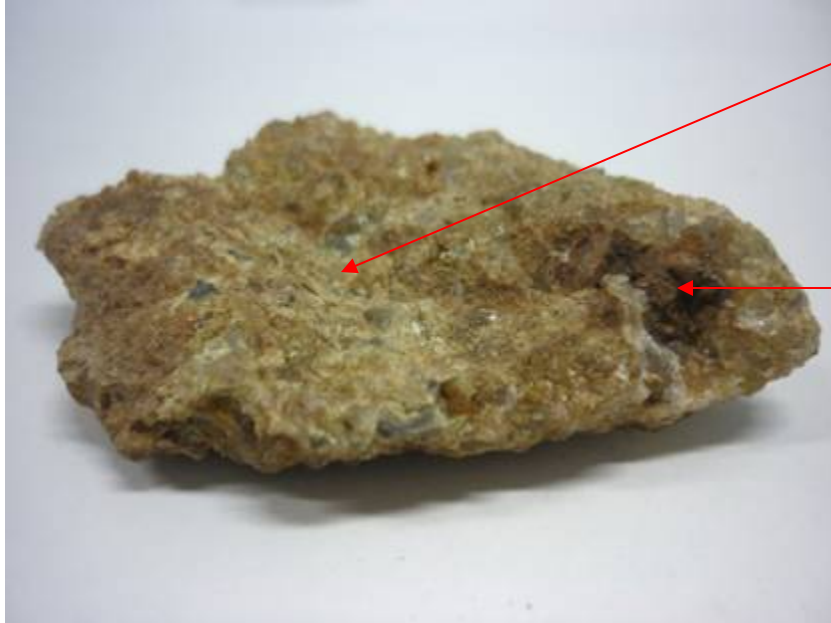
WOLFRAM CAMP

D31450

5. A sample of the quartz matrix was tested and proved to be quartz, with minor koechlinite.

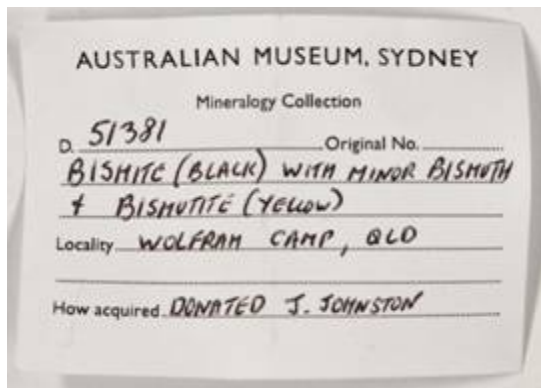
6. A brownish crust or stain to one part of specimen, gave the result of powellite, koechlinite and quartz, with minor preisingerite

The Bi, W and Mo minerals and elements listed for Wolfram Camp, certainly provide the raw materials to form the range of secondary minerals encountered, with fluorite present in the gangue as a potential source of fluorine.



Minerals found in addition to the quartz matrix in this specimen:

bismuth, zavaritskite, bismutite, koechlinite, preisingerite, scheelite, powellite



WOLFRAM CAMP

Bismite on Wolframite

D51381

Wolfram Camp, Qld.

Donated by J Johnston (registered on 21 March 1997)



Here the yellowish coating proved to be bismutite with minor bismuth iron oxide ($\text{Bi}_{24}\text{FeO}_{40}$).

The old entry in the register suggested wolframite, but the black material is in fact bismite.



WOLFRAM CAMP



Bismutite with Bismuthinite

D21847

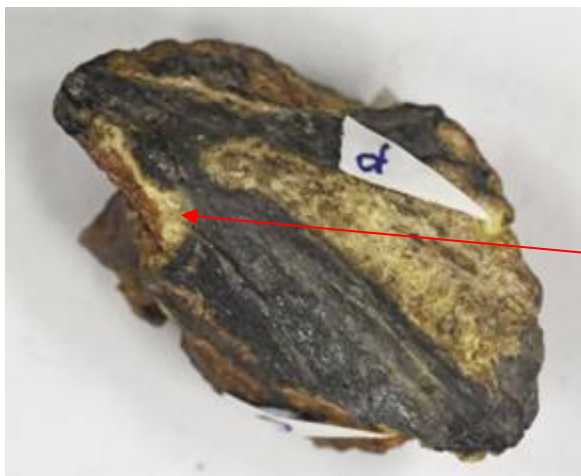
Wolfram Camp, Dimbulah, Qld

Presented by Louis Algiers on 14 February 1917



Small specimen, about 25-30mm long, again with a lot happening. The grey mineral is bismuthinite

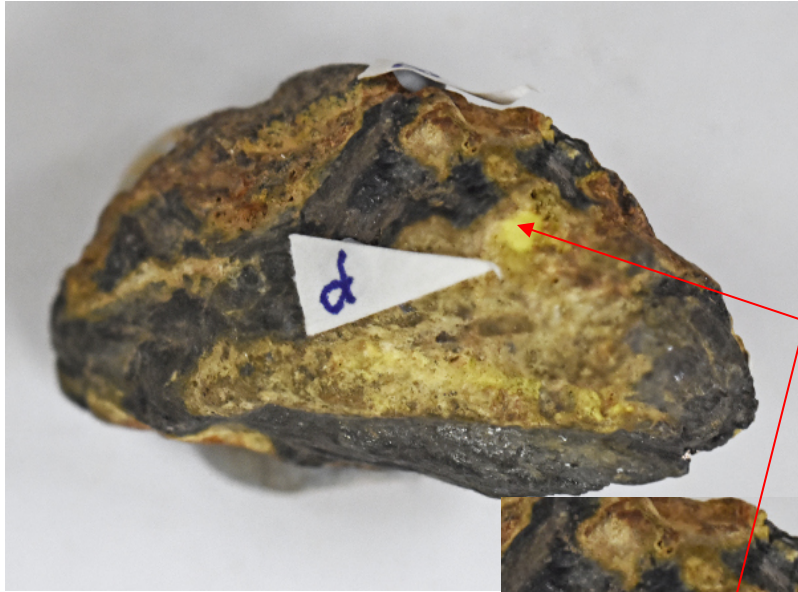
Dark massive patch proved to be a mixture of bismite, koechlinite and bismoclite



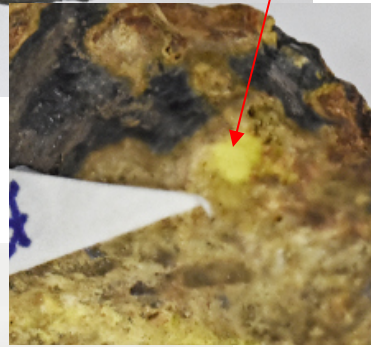
A yellow band running through the specimen proved to be russellite (Bi_2WO_6) and preisingerite ($\text{Bi}_3(\text{AsO}_4)_2\text{O}(\text{OH})$)

WOLFRAM CAMP

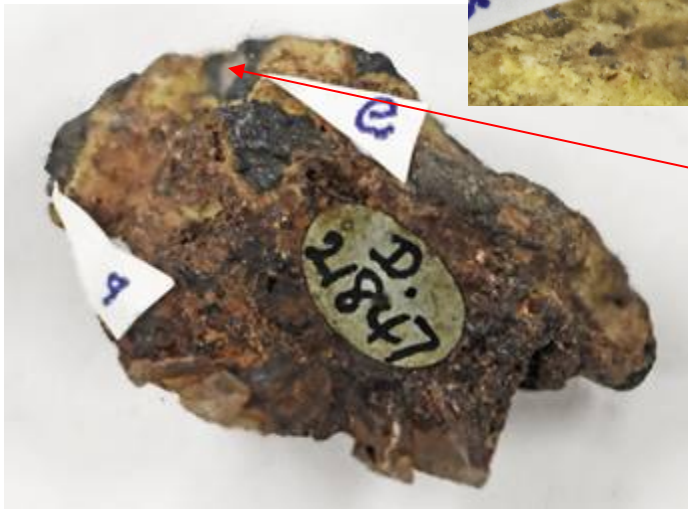
D21847



A bright yellow patch on one surface proved to be
Betpakdalite-NaNa,
 $[\text{Na}_2(\text{H}_2\text{O})_{16}\text{Na}(\text{H}_2\text{O})_6][\text{Mo}_8\text{As}_2\text{Fe}_3\text{O}_{33}(\text{OH})_4]$
No bismuth at all

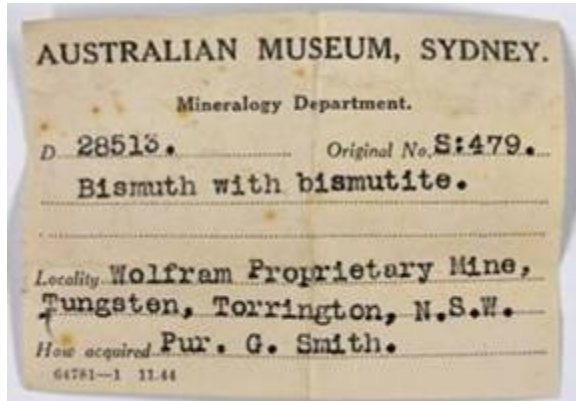


Yellow patch in the bismuthinite was a
mixture of russellite and bismutite



So this was another Wolfram Camp specimen
with a multitude of minerals present

TORRINGTON



Bismuth with bismutite

D28513

Wolfram Proprietary Mine, Tungsten, Torrington, NSW

Purchased from George Smith on 6 Jan 1928



An earthy, but heavy, nodule with a core of native bismuth. D28513 - Torrington - listed as bismutite, was mainly sillénite ($\text{Bi}_{12}\text{SiO}_{20}$) with some bismutite.



Sillénite is an uncommon mineral but is represented on every continent. It's type locality is in Durango in Mexico. In Australia it was also recorded at Elsmore by John Rankin, et al. back in 2002.

TORRINGTON

Several other Torrington specimens were tested.

Bismuth oxide and carbonate from the Bismuth Mine at Torrington (D22702) was found to be zavaritskite (BiOF) (dark grey) with bismutite, minor preisingerite and topaz

Bismutite and bismite from Torrington (D29744 & 29745) was found to be a mixture of russellite (Bi_2WO_6)/koechlinite (Bi_2MoO_6) and bismutite with minor preisingerite. It is sometimes quite difficult to differentiate between russellite and koechlinite based on an XRD pattern.

Bismutite and bismite from Heffernan's Mine in Torrington (D29746) was also found to be russellite/koechlinite and bismutite

TORRINGTON

Bismuth oxide
D22106

Rockvale (Wolfram) mine, Tungsten, 5km N of Torrington, E of the Silent Grove Rd, NSW

Exchanged with George Smith on 21 June 1918



A rather nondescript specimen from this mine at Tungsten (not to be confused with the Rockvale mine near Armidale) contains several small submetallic, dark grey to black grains within the coarse grained granitic rock. These proved in part to be zavaritskite, BiOF. Here there was no visual evidence of primary native bismuth.

1918		REGISTER OF				MINERAL AND ROCKS.		1918
Date	Registration No.	No. of Specimens	Name or Description	Locality	How Acquired	Reference to Papers	Disposition	Remarks
June 21	D: 22106	1	Bismuth oxide	Rockvale Mine, Tungsten Mts	Exch. Geo. Smith	Am. J. Sci. 1918	T 24	
	22107	1	baesite, nugget	Nuggety quarry, The Gulf, NSW	" "		Exch. Ward, 11739/28	
		1	Do. crystals immature	4 miles W. of The Gulf, NSW				

TORRINGTON

D22106



Two of the grains that were analysed by XRD also indicated the presence of the bismuth fluoride, gananite, BiF_3 , which given the presence of the bismuth oxyfluoride zavaritskite, is perhaps not surprising.

Visually, the ganonite cannot be distinguished from the zavaritskite.

To my knowledge, gananite has not previously been recorded from Australia.



Gananite is a brown-black to green-black, submetallic isometric mineral. The type and only locality for gananite is the Laikeng tungsten mine, Ganzhou, Jiangxi, China a Bi, W, Mo mine where the gangue includes fluorite. The mine produces fine wolframite and bismuth specimens.

The XRD pattern for the Torrington gananite is nearly identical to metacinnabarite (HgS), which being a more common mineral, would have been a possible choice. But it was considered unlikely that there be any mercury in this deposit.

The sample was tested for mercury by John Rankin, who also X-rayed the sample on a different XRD at WSU, with the result being no mercury, and the pattern suggesting gananite.



Summary of species found, in order of date first described (not necessarily under current name)

There are many bismuth minerals (~240), some of which are very pretty in hand specimen and under the microscope ... but not these.

Bismutite	$(\text{BiO})_2\text{CO}_3$	1805 (Luftsaures Wismuth)
Tellurobismutite	Bi_2Te_3	1815 (Tellur-Wismuth)
Atelesite	$\text{Bi}_2(\text{AsO}_4)\text{O}(\text{OH})$	1832
Bismuthinite	Bi_2S_3	1880
Powellite	CaWO_4	1889
Koehlinite	Bi_2MoO_6	1914
Bismoclite	BiOCl	<1921
Beyerite	$\text{Ca}(\text{BiO})_2(\text{CO}_3)_2$	1921 (Bismutosphaerite), 1943
Russellite	Bi_2WO_6	1938
Bismite	Bi_2O_3	1943
Sillénite	$\text{Bi}_{12}\text{SiO}_{20}$	1943
Rooseveltite	Bi_2AsO_4	1946
Kettnerite	CaBiCO_3OF	1957?
Betpakdalite-NaNa	$[\text{Na}_2(\text{H}_2\text{O})_{16}\text{Na}(\text{H}_2\text{O})_6][\text{Mo}_8\text{As}_2\text{Fe}_3\text{O}_{33}(\text{OH})_4]$	2011 (1961)
Zavaritskite	BiOF	1962
Preisingerite	$\text{Bi}_3(\text{AsO}_4)_2\text{O}(\text{OH})$	1981
Gananite	BiF_3	1984
Tetrarooseveltite	Bi_2AsO_4	1994
Bismuth Iron Oxide	$\text{Bi}_{24}\text{FeO}_{40}$	

Take Home Value

The "hidden collection" is alive and well, and probably exists in most collections. You may not be able to identify what you have, but you can put it aside to ask someone.

This is especially true if you have a specimen or specimens from places such as Wolfram Camp, Kingsgate, Biggenden and Torrington. Look at them closely to see if there is anything that looks different to what you expect.

Have a look at your native bismuth specimens. On the basis of this study, if there is a dark semi-metallic or dull rim around the outside it may be bismite if Kingsgate, or bismite or zavaritskite if Wolfram Camp, Deepwater or Torrington areas.

Most of these minerals are rarely found as crystals, mostly massive or as pseudomorphs.

In general, you cannot distinguish between the many cream to yellow coloured Bi secondary minerals by eye or even under the microscope, but bismutite and koechlinite are most common.

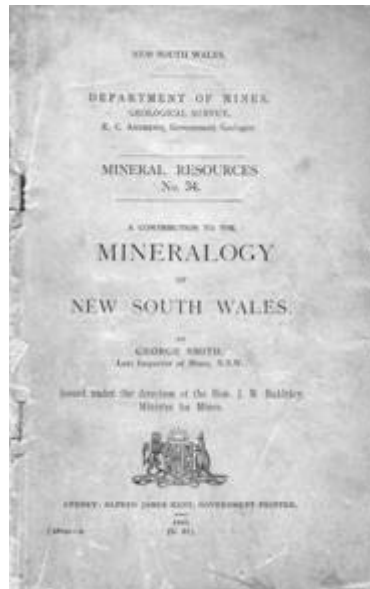
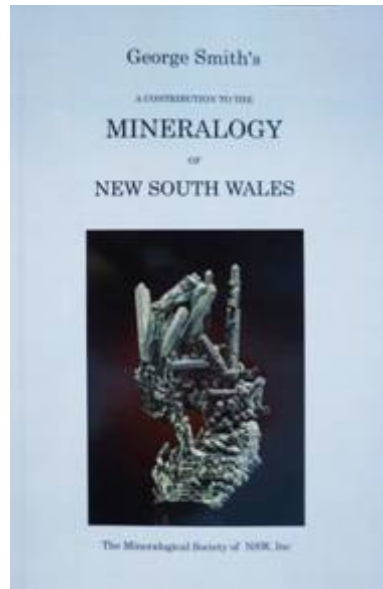
More often than not, if you have something labelled bismite (Bi oxide) in your collection, chances are it will actually be bismutite (the carbonate).

This study has found tetraroseveltite for the second time in Australia, namely from a place, or from a company called “Linedale, W Chillagoe”. The first was at Elsmore in NSW. The locality of this second occurrence is not certain.

It is also the first recording of gananite (BiF_3) in Australia, namely from the Rockvale Mine near Torrington in NSW, and possibly the second in the world.

Zavaritskite (BiOF) appears to be more common than originally thought. It seems closely associated with native bismuth where the deposits contain fluorine-containing minerals such as fluorite and topaz.

The number of times the name George Smith comes up as the person donating or selling a specimen to the museum is noteworthy. He had an extraordinary eye for fine specimens and things out of the ordinary. It's worth training our eyes for such things when we go out fossicking.



Acknowledgments:

Ross Pogson and the Australian Museum for allowing access to the mineral collection and the XRD for testing. He also provided training in using the machine and interpreting the results, as well as verified many of the results.

Dayna McGeeney at the Australian Museum for accessing and sending out additional information to help prepare this presentation during the current time of lockouts at AM.

John Rankin and David Colchester for additional testing and interpretation of results.

“Bismuth in the Supergene Environment”, Timothy D. Murphy, BSc (Hons), UWS published PhD thesis, available online.