itia NEWSLETTER

INTERNATIONAL TUNGSTEN INDUSTRY ASSOCIATION

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19th Annual General Meeting

Tuesday 26 to
Thursday 28
September 2006
Hyatt Regency Hotel,
Boston, USA

The programme will begin on Tuesday evening with a Reception in the hotel jointly hosted by Tiberon Minerals and ITIA. Working sessions will be held on Wednesday and Thursday mornings and papers will include:

- **▼** HSE work programme
- ▼ Ganzhou's Tungsten Industry and Its Progress
- Geostatistics in the mid and long-term planning for the Panasqueira deposit (Nuno Alves, Beralt Tin and Wolfram)
- ▼ Paper by Zhuzhou Cemented Carbide
- ▼ Update on Tiberon's Development of Tungsten Mining in Vietnam
- ▼ Update on China's Tungsten Industry
- ▼ Update on US Tungsten Market (Dean Schiller, OsramSylvania Products)
- ▼ Review of Trends in 2006 (Nigel Tunna, Metal-Pages)

The principal focus this year will be on HSE Issues (Wednesday morning), with reports from the leaders of ITIA's extensive work programme and a short paper by Rheinmetall on Work Place Evaluation and

Toxicologic Assessment for the Production and Mechanical Processing of Materials containing Tungsten Heavy Metal. Not least will be an introduction to the formation of a Consortium to deal with the implications of REACH on behalf of the tungsten industry, both legal and financial.

Readers will recall that REACH will place an obligation on individual companies to submit a technical dossier and register any chemical substance manufactured or imported into the EU in quantities of more than 1 tonne.

In order to assist companies with the registration process, the Commission recommends the creation of industry Consortia. These Consortia will enable the joint development, submission and sharing of information with the aim of reducing the compliance burden on individual companies and preventing unnecessary additional animal testing.

Both members and non-members will be equally welcome to join the Consortium, saving themselves considerable amounts of money and time by so doing.

Registration and hotel reservation forms may be downloaded from the ITIA website (or contact the Secretariat).

NEW OFFICE PREMISES

Please ensure records are changed to reflect the move from London at the beginning of April of ITIA (and IMOA) to:

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Both Associations have always been registered under Belgian Law and the proximity to allied organisations will be advantageous.

Membership

Welcome to:

Queensland Ores Ltd,

an Australian company which owns Wolfram Camp near Cairns and plans to bring the mine back into production in 2007.

Rheinmetall Waffe Munition GmbH,

a German company producing an extensive array of large and medium calibre tungsten-based ammunition.

MINERALOGY OF THE ELEMENT TUNGSTEN

Wolf-Dieter Schubert and Erik Lassner

Institute of Chemical Technologies and Analytics - Vienna University of Technology

Tungsten does not occur in the earth's crust elementally but only in the form of chemical compounds (minerals). Tungsten minerals are quite rare because tungsten has a very low abundance in the universe (approx. 0.2 atoms W/10⁶ atoms Si) and, consequently, also on earth (approx.1 microgram per gram corresponding to 0.0001 %). Nevertheless, we know a variety of tungsten minerals. Economically important are only four of them: *wolframite*, *bübnerite*, *ferberite* and *scheelite* which occur in sufficient abundance and concentration in specific rocks. All others do not have any economical value, as they are rare and occur in small amounts only. They are generally called *minor tungsten minerals*.

CHEMISTRY OF TUNGSTEN MINERALS

In regard to their chemical composition the majority of tungsten minerals belong to the group of *tungstates*. We distinguish between *monotungstates*, as for example *scheelite - CaWO*₄, *ferberite - FeWO*₄ or *hübnerite - MnWO*₄, and *polytungstates* which themselves can be *iso*- or *beteropolytungstates*. *Isopolytungstates* contain polymerized tungstate species like $W_6O_{21}^{6-}$ or $W_{12}O_{46}^{20-}$.

In *beteropolytungstates* additional foreign anions like silicate, phosphate, etc. are part of the chemical composition. In all these compounds tungsten is present as a six-fold positively charged central ion (W⁶⁺) which is either tetrahedrally or octahedrally coordinated by double negatively charged oxygen ions (O²⁻). An example for isopolytungstates is the mineral *yttrotungstite* - *YW*₂*O*₆ (*OH*)₃ (*Fig.1*). Some of these minerals are very complex and the chemical formulas can be expressed in different, more or

less simplified ways. A typical respective example is the mineral **welinite**, the formula of which is given as either **Mn**₆[(W,Mg,Sb,Fe)O₃][(OH)₂|O|(SiO₄)₂] or as **Mn**₆(W,Mg)₂Si₂(O,OH)₁₄ in different publications. **Pinalite** is a rare example of a tungsten oxyhalide (**Pb**₃WO₃Cl₂).

Besides *tungstates* also *tungsten acids* and *bydrated tungsten oxides* can be found as minerals. Examples are *bydrotungstite - H2WO4·H2O (Fig.2), meymacite - WO3·H2O* and *tungstite - WO3·H2O*. They are characteristic weathering products of *scheelite* or *wolframite* as well as products of hydrothermal alteration. In presence of aluminium- or ironbearing solutions, *alumotungstite - (W,Al)(O,OH)*3 or *ferritungstite - (W,Fe)(O,OH)*3 (*Fig.3*) may form.

If the oxygen in tungstates is substituted by *sulfur* or *selenium* we talk about *thio*- or *selenotungstates*. *Kiddcreekite* is a member of that rare class: *CusSnW(S,Se)s*.

The last group of tungsten minerals belong to the **sulphides** with **tungstenite** - **WS**₂ (**Fig. 4**) as example. In this compound the tungsten atom is tetravalent (W^{4+}).

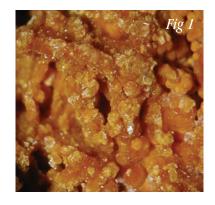


Fig. 1: Yttrotungstite – YW:04(OH): Kramat Pulai Mine, Malaysia; picture width 5 mm; copyright Thomas Witzke + Abraxas Verlag

Fig. 2: Hydrotungstite H.WO₁· H.O – Japan; picture width 5 mm; collection of NHM Wien; copyright V.M.F. Hammer

Fig.3: Ferritungstite (W,Fe)(0,0H)3 – Clara Mine, Rankacb Valley, Germany; picture width 2mm; copyright Stephan Wolfsried





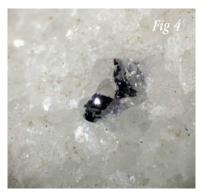


Fig. 4: Tungstenite WS₂ – Crevola d'Ossola quarry, Italy; 2 mm crude flakes; copyright Maurice de Graaf

The crystal structure of *scheelite* consists of distorted WO₄ tetrahedra linked to CaO₈ polyhedra *(Fig. 5)*. The crystals have tetragonal symmetry and appear as dipyramidal pseudo-octahedra *(Fig. 6)*. Colours range from golden yellow to orange, green to dark brown, reddish gray, dark blue to black and colourless (if chemically pure). Well-formed crystals are sought-after specimens for mineral collectors.

GENESIS OF MINERAL FORMATION

Most tungsten minerals form by crystallization from a hydrothermal liquid — the last liquid phase in the differential crystallization sequence of a magma (slow cooling process). Tungsten atoms, if present in magma, can not be incorporated in minerals of the first crystallization steps (basic rocks) because of the "wrong" size and charge of the tungsten ion (W^{6+}). Also tungstate ions can not substitute silicate or aluminate ions in the later acidic crystallization step. Therefore, if tungsten is present in magma it will be concentrated in the residual hydrothermal liquid which is a supercritical liquid (around 600 °C and high pressure). Tungsten may be encountered as *tungstate ion*, *tungstic acid*, *sodium tungstate* or *beteropoly acid*.

Depending on the presence and concentration of cations like Fe²⁺, Mn²⁺ and Ca²⁺ and the nature of the rocks surrounding the hydrothermal liquid, different tungsten minerals crystallize (precipitate). The usual mineral paragenesis is *ferberite*, *hübnerite* and *scheelite*. In case the surrounding rock is a limestone (i.e. CaCO₃) tungstate combines mainly with Ca forming *scheelite*.

ECONOMICALLY IMPORTANT MINERALS

Scheelite (Figs. 5-8)

The mineral was named after the famous Swedish chemist *Carl Wilhelm Scheele* (1742-1786). It is chemically *calcium tungstate*, *CaWO*⁴. It represents the most abundant tungsten mineral on earth. Approximately two thirds of the known tungsten deposits contain *scheelite*. *Scheelite* can be found in pegmatites, hydrothermal veins and areas of contact metamorphism often associated with the minerals *fluorite*, *muscovite*, *dolomite and molybdenite*.

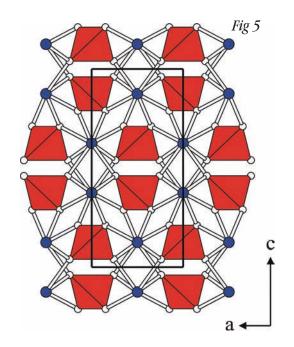


Fig. 5: The crystal structure of scheelite in projection along the b-axis with the unit cell outlined. Ca atoms are shown as blue spheres and oxygen atoms as white spheres with a black rim; the WO₄ tetrahedra are displayed as red polyhedra.



Fig. 6: Scheelite mineral specimens of different origin and colour; collection of NHM Wien; copyright V.M.F. Hammer orange (8×7×6 cm): Hiefelwand, Rauris, Austria (C.894) black (3×3×2 cm): Tae Wha, Korea (L.3572) green (4×3×5 cm): Fram Natas, Namibia (K.4611) transparent (5×5×5 cm): Felbertal, Salzburg, Austria (M.57)

Table 1:

Physical and chemical properties of scheelite.

Formula (pure) CaWO⁴ WO⁵ content [%] 80.6

Crystal structure tetragonal dipyramidal

Lattice parameters

 a [Å]
 5.24-5.26

 c [Å]
 11.37-11.40

 c/a
 2.163-2.169

 Cleavage
 (010) distinct

 Specific gravity
 5.9-6.1

Colour colourless, white, yellow, tan, orange, red, blue, black

Tenacity very brittle
Luster vitreous to resinous

Fracture uneven
Hardness (Mohs) 4-5
Magnetism nonmagnetic

Streak white
Diaphaneity transparent to translucent

Common form of occurrence pseudo-octahedral crystals, massive and in

small grains, pseudomorphic after wolframite, disseminated in small particles dispersed in

Important properties of *scheelite* are compiled in **Table 1**. *Scheelite* forms an incomplete solid solution series with *powellite* (*calcium molybdate*, *CaMoO*⁴), but natural *scheelite* contains only a very minor component of *powellite*, if at all. A very important property of the mineral is the bluish white fluorescence under short-wavelength UV radiation especially valuable in ore prospection and mining (*Fig. 7*). The colour of the fluorescence light is influenced by the molybdate content. With increasing Mo concentration in *scheelite*, its colour changes from blue to pale yellow and orange.

The refractive index of *scheelite* is high and with maximum birefringence and dispersion it results in high lustre and perceptible "fire" approaching that of diamond. Gemstones cut from transparent material are fragile yet attractive *(Fig. 8)*, but owing to the low hardness, however, they are best enjoyed unset as valuable collector pieces.





Fig. 7: Translucent brown scheelite (20 mm) on milky quartz with scattered tan dolomite;
Tae Wha Mine, Chungju, Korea; daylight illumination (left) and UV illumination (right);

courtesy of John Betts Fine Minerals (http://www.johnbetts-fineminerals.com/).

The mineral **stolzite** (*lead tungstate*, *PbWO*₄) is isotypic to *scheelite* and can occur as a result of hydrothermal alteration of scheelite (*Fig.9*).

Scheelite is the most important raw material for the production of all tungsten compounds and the metal itself.

The Wolframite Group

The *wolframite* group consists of iron and manganese tungstate minerals of varying composition. At higher temperatures of formation iron and manganese tungstates form a continuous solid solution series.

Due to definition one may distinguish between the following minerals:

Ferberite: iron tungstate **(FeWO₄)** with variable manganese tungstate concentrations, but always with a Fe:Mn ratio >1 **(Fig. 10)**. The mineral is named after the German mineralogist **Moritz Rudolf Ferber** (1805-1875) of Gera.

Hübnerite: manganese tungstate (MnWO₄) with variable iron tungstate concentrations, but always with a Fe:Mn ratio <1 (Fig.11), named after the German metallurgist Friedrich Adolf Hübner (1843-1905) of Chemnitz.



Fig. 8: Gemstones cut from transparent scheelite; collection NHM Wien; copyright V.M.F. Hammer



Fig. 9: Stolzite PbWO₄ - Clara Mine, Rankach valley, Germany; picture widths 3 mm; copyright Stephan Wolfsried





Fig. 10: Ferberite crystals with dolomite and quartz (6×4×2.5 cm); Yaogangxian Mine, Hunan, China; copyright Nik Nikiforou

Fig. 11: Hübnerite with quartz and scheelite (7.5×7×7 cm); Huayllapon Mine, Ancash, Peru; copyright M.K. Mayer

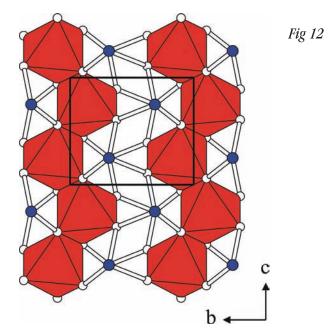


Fig. 12: The crystal structure of wolframite in projection along the a-axis with the unit cell outlined. Fe/Mn atoms are shown as blue spheres and oxygen atoms as white spheres with a black rim; the $W0_0$ octahedra are displayed as red polyhedra.



Fig. 13: Red, translucent bübnerite which forms at low iron concentrations; Pasto Bueno District, Ancash, Peru; picture width 5 mm; copyright O. Dziallas

Wolframite: (Mn,Fe)WO₄ is the group name for the complete solid solution series between the *ferberite* and *hübnerite* endmember compositions. In practice, the name *wolframite* is often used for the intermediate 20-80% range.

Although *wolframite* is not considered a valid mineral species by the International Mineralogy Association (IMA), the name is still used by

miners, collectors, technicians and scientists, especially if the Fe:Mn ratio of the *wolframite* ore is not known [1]. The name *wolframite* derives from the old German word *wolfram* or *wolfram*, which was used by the German tin miners already in the Middle Ages (see Newsletter June 2005).

The crystal structure of all members of the *wolframite* group consists of distorted WO₆ octahedra linked to (Fe,Mn)O₆ octahedra (*Fig.12*). The crystals have monoclinic symmetry, and usually form long prismatic crystals with sizes of up to 25 cm. Depending on the conditions of formation the crystal habit varies from bladed to needle-like. Frequently, the crystal faces are striated.

The colour of the minerals varies from densely black *(ferberite)* over brownish black *(wolframite)* to reddish-brown *(hübnerite)*. The latter can even be intensely red and transparent or translucent in case of low iron concentrations *(Fig. 13)*.

Although a complete solid solution between Fe^{2+} and Mn^{2+} exists, oscillatory zoning of successive Fe- and Mn-rich layers has been observed in some cases [1]. *Hübnerite* is the rarer mineral of the two end members. Most often natural occurrences belong to the 20-80% compositions within the wolframite group.

If the temperature during crystallization was lower than the limit for a complete solid solution series, *ferberite* and *hübnerite* can be found next to each other. Generally, *hübnerite* is deposited at higher temperatures of formation than *ferberite* and, therefore, the latter tends to be found further away from the source of the hydrothermal solution; *wolframite* lying approximately midway.

The majority of occurrences of *wolframite* minerals of pegmatitic-pneumatolytic or hydrothermal ranges are in quartz-rich veins and are associated with the minerals *cassiterite* (SnO₂), apatite, tourmaline, mica, topaz, scheelite, arsenopyrite, chalcopyrite, bismuth, galena and sphalerite. Alluvial and eluvial deposits of wolframite are also known. **Table 2** informs about the important properties of the three minerals.

At certain deposits in Central Africa (Uganda, Rwanda, Zaire) but also in the Yamaguchi Prefecture in Japan *ferberite* occurs as pseudomorphs after *scheelite*. In this case the primary *scheelite* was transformed into polycrystalline *ferberite* through the interaction with iron-rich solutions [2].

This kind of *ferberite* is called *reinite* (named after *Johannes Justus Rein* — the "father" of geology in Japan — 1835-1918) and in some cases even the tetragonal crystal shape of the *scheelite* was still maintained *(Fig. 14)*. On breaking a *reinite* "crystal" the

Table 2: Physical and chemical properties of wolframite group minerals.

Property	Ferberite	Wolframite	Hübnerite
Formula (pure)	FeWO4	(Fe,Mn)WO4	MnWO ₄
WO3 content [%]	76.3	76.5	76.6
Mn content [%]	0-3.6	3.6-14.5	14.5-18.1
Fe content [%]	18.4-14.7	14.7-3.7	3.7-0
Crystal structure	monoclinic	monoclinic	monoclinic
Lattice parameters			
a [Å]	4.71-4.76	4.77-4.79	4.85
<i>b</i> [Å]	5.68-5.70	5.73-5.74	5.77
c [Å]	4.92-4.95	4.98-4.99	4.98
β	90°	90°26'	90°53'
Cleavage	(010) perfect	(010) perfect	(010) perfect
Density [g·cm³]	7.5	7.0-7.5	7.2-7.3
Colour	black	dark grey to black, brownish black	Red, reddish brown to black
Tenacity	very brittle	very brittle	very brittle
Luster	submetallic to metallic	submetallic to metallic	submetallic adamantine
Fracture	uneven	uneven	uneven
Hardness (Mohs)	4.5-5	4-5.5	4.5
Magnetism	sometimes feebly magnetic	slightly magnetic	
Streak	dark brown, black	dark brown	brownish red to greenish yellow
Diaphaneity	opaque to translucent in cleavage plates	opaque	opaque to translucent
Common form of occurrence	well defined crystals, massive crystalline	irregular masses radiating groups of bladed crystals	radiating groups of thin-bladed crystals

Minor Tungsten Minerals

As already mentioned above they are usually very rare in Nature and, therefore, they do not have any economic value. However, for mineralogists and mineral collectors they are as valuable and important as wolframite or scheelite. Last not least, because of their rarity and the beautiful colours of some of them. **Table 3** summarizes the secondary tungsten minerals as currently approved by the International Mineralogy Association. Some of the formulas reflect the highly complex chemistry of the solutions from which these tungstates have formed. Figs. 16-18 demonstrate examples of the exceedingly rare minerals Rankachite, Tungstibite and *Manganokhomyakovite* – each is known from only one locality.

inside is seen to consist largely of a yellow to white mass commonly referred to as *tungstic ochre*, which consists of a number of secondary tungsten minerals, such as *alumotungstite*, *anthoinite*, *ferritungstite* or *cerotungstite* (see **Table 3**). In some pseudomorphs the ochre has been leached away leaving behind a porous network of polycrystalline *ferberite* [2].

The rare mineral **sanmartinite** - $(Zn,Fe)WO_4$ (Fig. 15)—named after the province of San Martin in Argentina where it was found for the first time – ("zinc-wolframite") also belongs to the wolframite series.

Wolframite ore is the number two raw material for tungsten and tungsten compounds production. About one third of the presently known tungsten ore deposits consist of these minerals.

Fig. 14: Reinite (ferberite pseudomorphous after scheelite); courtesy of the Toboku University Museum, Japan



Fig. 15: Sanmartinite (Zn,Fe)WO₁ – Rwanda; wbite/grey masses on dark background; collection of NHM Wien; copyright V.M.F. Hammer

Table 3: Minor Tungsten Minerals

for more detailed information see www.mindat.org or www.webmineral.com/

Colour

white

grey

yellow

yellow-white

emerald green

yellow brownish

orange to red

grey, brown

orange-red

white

vitreous

yellow

yellow

black

brown

brown, yellow

pale yellow to green

yellowish, greenish

lead grey to black

yellow to green

yellow, orange

yellow to orange

orange

green to dark green

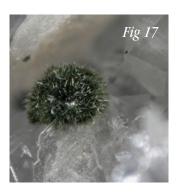
orange red, red brown

pale yellow

yellow brown

dark/metallic lustre





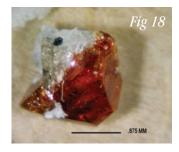


Fig. 16: Rankachite (table 3) – Clara Mine, Rankach valley, Germany; picture widths 3 mm; copyright Stephan Wolfsried

Fig. 17: Tungstibite (table 3) — Clara Mine, Rankach valley, Germany; picture widths 2 mm; copyright Stephan Wolfsried

Fig. 18: Manganokbomyakovite (table 3)

– Poudrette quarry, Québec, Canada;
copyright Doug Merson

Name Formula* **Alumotungstite** $(W,AI)(0,OH)^3$ **Anthoinite** $(W,AI)(0,OH)^{3}$? **Catamarcaite** Cu₆GeWS₈ Cuprotungstite $Cu^2[(OH)^2 \mid WO^4]$ WO3-0.5H2O Elsmoreite **Farallonite** Mg2W2SiO9·nH2O **Ferritungstite** $(W,Fe)(0,OH)^3$ W03-2H20 **Hydrotungstite** lixianite Pb(W,Fe)2(0,OH)7 Johnsenite-(Ce) $Na^{12}(Ce,REE,Sr)^{3}Ca^{6}Mn^{3}Zr^{3}W(Si^{25}O^{73})(OH)^{3}(CO^{3})\cdot H^{2}O$ Khomyakovite $Na_{12}Sr_3Ca_6Fe_3Zr_3W(Si_{25}O_{73})(0,0H,H_2O)_3(0H,CI)_2$ **Kiddcreekite** Cu₆SnWS₈ **Koragoite** $(Mn,Fe)^3(Nb,Ta,Ti)62(Nb,Mn)^2(W,Ta)^2O^{20}$ Mn-Khomyakovite $Na_{12}Sr_{3}Ca_{6}Mn_{3}Zr_{3}W[Si_{25}O_{73}](0,0H,H_{2}O)_{3}(0H,CI)_{2}$ Meymacite W03-2H2O **Mporoite** AIWO3(OH)3.2H2O **Ovamboite** Cu20 (Fe, Cu, Zn) 6W2Ge6S32 Paraniite-(Y) Ca₂Y(AsO₄)(WO₄)₂**Phyllotungstite** CaFe3H[WO4]6·10H2O **Pinalite** Pb3WO3Cl2 **Qitianlingite** (Fe,Mn)2(Nb,Ta)2WO10 $(V^{4+}, V^{5+})(W, Fe)^2O^8(OH) \cdot (Ca \times H^2O_Y)$ Rankachite Raspite Pb[WO4] Russellite (BiO)2[WO4] Sanmartinite (Zn,Fe)WO4 Stolzite Pb[W04] **Tungstenite** WS₂

Further Information:

For more detailed information on the different minerals in regard to optical properties, localities of occurrences, classification, etc. as well as on companies selling mineral specimens the reader is referred to the following web sites:

Tungstibite

Tungstite

Welinite

Uranotungstite

Yttrotungstite-(Ce)

Yttrotungstite-(Y)

Sb2O3·WO3

W03·H20

http://webmineral.com/ http://www.mindat.org/

Literature:

 R.J. King, The wolframite series, Geology Today, Vol.21, No.1, 2005.
 Th.G. Sahama, The Secondary Tungsten Minerals, The Mineralogical Record (March-April 1981) 81-87. Acknowledgements:

 $(Fe,Ba,Pb)(UO_2)_2[(OH)_2 \mid WO_4]\cdot 12H_2O$

 $Mn_6(W,Mg)_{0.7}[(0,OH)_3 | SiO_4]$

 $(Ce,Nd,Y)W_2O_6(OH)_3$

YW206(OH)3

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