Recovery of Tungsten, Niobium and Tantalum occurring as by-products in mining and processing waste streams

(TARANTULA)

D2.3 Report on ore/gangue mineralogy and textures of sampled occurrences

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ABBREVIATIONS AND ACRONYMS

AMD	Acid Mine Drainage
BRGM	Bureau of Recherches Gèologiques et Minières
GIS	Geographic Information System
GKR	Global Knowledge Representation
ICP	Inductively Coupled Plasma
IT	Information Technology
LIPS	Laser-Induced Plasma Spectroscopy
NICT	National Institute of Information and Communication Technology
OECD	Organization for Economic Co-operation and Development
REE	Rare Earth Elements
SLO	Social License to Operate
SME	Small and Medium Enterprise
WGS	World Geodetic System
XRF	X-Ray Fluorescence

EXECUTIVE SUMMARY

Implementing the energy transition in Europe will require unprecedented quantities of rare metals. Metals will thus take over from oil in geopolitical strategies and the observed increase in international tensions amplifies the phenomenon.

Historically, Europe was the cradle of metallurgy supported by thousands of mines almost all of which are now forgotten. Will we have the metals needed to support the needs of our industries or will we have to import almost all of these metals as global demand exceeds production?

By relocating its industries, Europe has lost interest in mining activity since the 1990s. Exploration projects ceased and mines closed in very different economic and societal contexts. While we only exploited around ten metals until the 1980s, today we need all 86 metals in the periodic table of elements. Not recovered in historical operations, these metals can be found today in the waste from certain old mines. Can we identify them although they were never analysed before?

Furthermore, the new economy of these metals could redefine that of these abandoned operations while their deposits could contain unexploited resources. Should we reopen old mines for our supply of strategic metals?

Tungsten, niobium and tantalum are often concentrated in small, or even very small, deposits compared to deposits of metals such as iron, copper, zinc, ... They can also, like niobium and tantalum, be found in very small quantities in tin or titanium mines.

Until now, the mining economy has favoured the opening of “giant” deposits, the scale factor allowing operations with low metal contents. Open-air mining of very large quantities of very low-grade metals requires the management of huge quantities of waste. It is clear that the societal acceptability of such exploitations is not there in Europe.

Underground exploitation of small, rich deposits would limit the environmental footprint as much as possible. The full recovery of the metals contained, the recycling of water, the recovery of aggregates produced by underground infrastructure works and the in-situ burial of all mining waste are now proven techniques. The giant mine could give way in Europe to a network of SMEs, respectful of the environment and capable of greatly limiting our dependence on critical/strategic metals.

Selecting among the thousands of former mining operations those which would be likely to offer future mines is a complex task. Metals such as niobium and tantalum have practically never been analysed and a selection on the quantities of metals contained is therefore impossible. In the absence of chemical data, only mineralogical data can inform us about these potentials.

The notions of “gangue” and “ore” are exclusively linked to the economic conditions of former exploitation. Thus, we will find niobium and tantalum in the gangues of old exploitations, that is to say ultimately in the tailings of these historic works.

Knowledge of mineral associations in a metalliferous site is therefore essential to be able to evaluate:

- the nature of the metals contained in the deposit,
- their potential existence in the waste from old operations,
- the possibility of valorising these metals (impact on mineralurgical processing),
- predictable heavy metal hazards.

Task 2.2 aims to provide for each metalliferous site the mineralogical knowledge necessary to be able to prioritize the targets located in Deliverable D2.2.

These observations will be reported in the interactive map that accompanies this work. By explaining the other substances which could contribute to the economy of mineralurgical processes, they will constitute an essential guide for the direction of future research into primary or secondary production of tungsten, niobium or tantalum.

1. INTRODUCTION

The initial objective of task 2.2 was to provide Tarantula members with samples of tailings from old mines that could illustrate the main metallogenic models of tungsten, niobium and tantalum deposits.

The usefulness of these samples was of course conditional on their delivery from the first stages of its implementation.

A first sample from the tailings of the old Salau mine was submitted, but the arrival of the COVID 19 epidemic blocked all new sampling operations for a year.

To avoid any paralysis of the project, it was therefore decided to carry out the laboratory work using samples from mines controlled by the members of the consortium. This operation also removed the risks linked to the almost systematic refusal of mine owners (old or modern) to authorize sampling for fear of environmental repercussions.

Furthermore, from the first months of work within the framework of task 2.2, it was obvious that the lack of analytical data on old deposits would be an insurmountable handicap for hoping to obtain a suitable hierarchy of metalliferous sites, especially in the upstream stages of their development.

It is the community of mineralogists, made up of tens of thousands of passionate amateurs, which makes it possible to remove a large part of these obstacles. Indeed, the "hunting ground" of these amateurs is above all the old or very old mines, those which today constitute the bases of future mining research work. Their observations are generally gathered in the "Mindat.org" database which provides information on the mineralogy of hundreds of thousands of sites around the world.

The reinterpretation of metallogenic models of deposits based on mineralogical data was thus possible, and with it a refined hierarchy of metalliferous sites.

2. TASKS DESCRIPTION AND RESULTS

This report explains the different stages of the method used to identify and prioritize refractory metal resources in Europe based on the mineralogical associations of the ore and the gangue.

The first step is to establish an economic classification of the minerals which constitute the ore and gangue of the deposits. This classification is based on the probability of being able to valorise the mineral.

The second step consists of establishing the exhaustive list of minerals described for each metalliferous site. This list will be used by the GKR algorithms to hierarchize the potential of each of these sites.

The third step consists in establishing a mineralogical filter which makes it possible to select from the candidates selected during Task 2.2, those which present indications on the presence of Niobium and Tantalum. This particularly important step consists in establishing for each mineral deposit the paragenesis (mineral association) not only of the ore but also that of the gangue which will be found in the mining discharges of the old exploitations.

The fourth step is to generate the "Mineralization" section in the GKR record. This section explains the economic impact of the observed paragenesis.

The fifth step is to anticipate the environmental impact of the reopening of an old mine or the recycling of dumps. For this, it will be necessary to look for the contaminants in the minerals present in the ore or the gangue. For this, we integrate into the study the results of the economic syntheses obtained in Task 2.2

The sixth step consists of generating a specific tooltip in the interactive Google Earth map to distribute the complete list of minerals present in the metalliferous sites, indicating their classification in the GKR system.

It is possible to select sites likely to offer recoverable mining waste, or failing that, which generate an environmental hazard strong enough to justify studies on the feasibility of their rehabilitation.

2.1 MINERALOGY OF THE W, NB, AND TA DEPOSITS

2.1.1 REMINDERS ON MINERALOGY

An ore is a mineral or a rock from which one or more elements can be extracted with profit.

However, this lapidary definition is ambiguous. Indeed,

- For the mineralogist, the ore is the mineral that contains the element to be recovered: scheelite ($CaWO_4$) for tungsten, cassiterite (SnO_2) for tin, ... It is ore in the strict sense.
- For the miner, on the other hand, the ore designates the mass of material mined as a whole, and not the only recoverable mineral: it is ore in the broad sense. A cassiterite quartz is thus a tin ore, and a skarn impregnated with scheelite a tungsten ore, although the proportion of "real" ores, cassiterite and scheelite, is at most a few percent.

In the case of gold, the ore is often a sulphide and gold quartz, in which the strict ore, native gold, represents only a few grams per tonne. This broader meaning is very close to the definition in the Larousse dictionary (“rock containing useful minerals in significant proportion”), and has no connotation of exploitation. This notion of ore joins those of deposit and content, which have an essential economic dimension.

Ore minerals generally have a relatively simple chemical formula that reflects their crystal structure. This formula is called stoichiometric, for example SnO_2 for cassiterite, principal, not to say unique, ore mineral of tin.

However, in nature, the crystal lattice of a mineral very often admits foreign ions to the stoichiometric formula as long as the ionic radius and / or valence are compatible. These substitutions can thus lead to minerals which can be considered as metal ores which are not part of their theoretical chemistry. ***Tantalum can thus replace tin in cassiterite up to a maximum of 4%.*** Without an in-depth mineralogical study (electron microscopy, laser ablation, microprobe, etc.), it will sometimes be difficult to establish whether these metals "foreign" to the basic formula are incorporated into the crystal lattice, or if they meet at the within other specific minerals included in the "host" ore in the form of inclusions; these inclusions sometimes having a size of the order of a micron and becoming impossible to separate by the way of a conventional mineralurgy.

Sometimes two or more metals can come in varying proportions within the same crystal structure, forming a solid solution between two or more poles, each having saturation in one of these metals. Each pole will then take the name of a mineral. Thus we will name wolframite the mineral of composition $(Fe,Mn)WO_4$ which can contain up to 100% either of iron, the mineral then takes the name of ferberite, or of manganese and the mineral will take the name of hübnérite.

The more complex the mineral formula, the more possible the substitutions; families of minerals are thus defined, composed of groups, themselves capable of admitting sub-groups, enclosing species which may present varieties. The family of pyrochlores is a good example of this complexity.

Depending on the crystal structures that the minerals will acquire during these substitutions, new species will be named. Each of these species is likely to react differently during mineralurgical treatments and their early diagnosis is a necessity.

Thus, mineralogy is the main parameter that will control the mineralurgy. Schematically, the recovery rate of a treatment line will depend on two main factors:

- Recovery of the mineral(s) contained in the ore (rock)
- Presence or absence of minerals also containing the desired metals but refractory to the treatments applied.

The mere chemical analysis of the process input content and that of the final concentrate alone will not allow us to specify the relative proportions of these two factors.

Ores and gangues

If the term ore presents an ambiguity, the term gangue which accompanies it, is more precise. These are non-valued minerals which accompany ores in the mineralogical sense within the ore (the exploited rock). This set of minerals represents more than 95% of the tungsten or tin ore; their nature will be dictated by the deposit model. They will be rejected during the various stages of mineral processing.

In our approach aiming to recover old mine wastes and to promote the integral valuation of the ores, the study of this gangue is decisive because minerals containing the new high-tech metals (Nb-Ta but also, Li and Rare Earths) could be part of this gangue.

2.1.2 MINERALOGICAL APPROACH OF POTENTIALS IN W, NB AND TA

2.1.2.1 MINERALOGY OF TUNGSTEN AND TIN

Tin and tungsten will only be recovered by processing their respective ore minerals, that is to say that they will not be recoverable in the ores of other metals.

This does not mean that they will not be present and valued in deposits of other metals, but in this case, it will always be the same minerals which will have to be separated in different production lines. For example, the copper-zinc deposits of massive sulphides in the Iberian pyritic belt can contain cassiterite and produce tin (Neves Corvo, Portugal).

For these metals, the mineralogical approach will consist in detecting the presence of their ore minerals (cassiterite, wolframite ...) within the ore contained in deposits that may not correspond to tin or tungsten mines.

Scheelite and wolframite (including of course ferberite and hübnerite) are the only exploited and these ore minerals do not integrate Nb or Ta in their crystal structure; if we look for Ta or Nb in tungsten ores, we will have to look at the other mineral species that will be contained in the gangue of these ores.

If there are 77 minerals identified today as integrating W in their chemical formula and 200 minerals integrating Sn, these generally rare or very rare minerals are not particularly useful for the search for potential sources in W, Sn, Nb and Ta. The scheelite, the wolframite, the cassiterite, easy to detect and well represented in the deposits, thus constitute the best markers of these deposits.

Consequently, the detailed study of rare minerals containing tin or tungsten will not be decisive in estimating the recoverable potential of these metals. Their usefulness will however remain indirect, because by making it possible to specify the diagnosis of the metallogenic model, they will provide indications on the potential volume of the deposits and deposits considered.

In our study, we will therefore not detail exhaustively the mineralogy of these metals

TUNGSTEN

The nature of the ore will be dictated by the metallogenic model of the deposit (Annex **¡Error! No se encuentra el origen de la referencia.**). Schematically we will distinguish:

- **Wolframite** in W-Sn quartz vein which constituted the majority of artisanal work at the start of the 20th century. This type of deposit will therefore often be a mixed tin-tungsten ore, likely to contain Nb-Ta in substitution for Sn in cassiterite.
- **Scheelite** skarns and skarnoids, whose gangue composition will reflect the rocks transformed by contact metamorphism.
- Pegmatitic ores, which will contain a high proportion of quartz, feldspar and micas.

The fragility of the minerals does not allow easy concentration in the placers, and their development in alluvial concentrations will therefore be exceptional.

Valuing mining waste from operations by extracting Nb-Ta should focus on:

- The rate of recovery from cassiterite; the subsequent metallurgical treatment will then be carried out in the majority of cases on the concentrate obtained.

- Research and recovery of minerals (in particular columbo-tantalite) present in the gangue.
- The search for other metals also existing in the gangue and whose recovery could improve or simply authorize the economy of the reprocessing: gold, copper, silver, molybdenum… (Chapter **¡Error! No se encuentra el origen de la referencia.**).

TIN

Only **cassiterite** appears to be mineable as a tin ore in Europe, teallite ($PbSnS_2$) being mined only in Bolivian mines. The Tantalum integrated into its crystal structure will be valued during the metallurgical treatment.

Cassiterite is the hardest mineral of the heavy minerals and the heaviest of the hard minerals. These characteristic favours its concentration in the placers (alluvial or maritime) which are today in the world an important source of supply.

In Europe, primary ores will be close to tungsten ores with which they will be intimately associated in the granite W-Sn Cupolas.

- Cassiterite into quartz veins constituted the majority of artisanal work until the early twentieth century; also pegmatitic ores, which will contain a high proportion of quartz, feldspar and micas (former mine of Abbaretz, France).
- Alluvium / eluvion type placers developed near or on granite domes. These placers have given rise in the Iberian Peninsula to numerous small artisanal exploitations of cassiterite and or ilmenite, minerals which can each integrate Nb-Ta in their composition.

The recovery of tin mining wastes will therefore be equivalent to that of tungsten mines. However, the metallogenic model of these deposits does not make it possible to consider recovering gold if tungsten is not as present.

2.1.2.2 MINERALOGY OF NIOBIUM AND TANTALUM

These metals offer the particularity of being able to integrate into the tin and titanium ores by substitution in cassiterite, ilmenite or rutile, which can even form a mineral species with these groups (ilmenorutile). In addition, they are generally substitutable with each other, and combine in the vast majority of minerals.

Thus, the Niobium and Tantalum ores will present a greater variety than those of tin or tungsten, an in-depth study of their mineralogy is important for the estimation of European potential. This mineralogy is complex, comprising 300 minerals, a mineralogical synthesis of which is presented in Annex 4.1.1

Explaining the importance of these minerals requires clarification on the concept of the rarity of a mineral, a rarity that should be distinguished from its abundance within a deposit. A mineral can be very rare, since it is observed in very few sites worldwide, or even on only one site. Within these sites, these rare minerals can form a significant part of the rock containing them, and then become a potential ore mineral if a mineralurgical and / or metallurgical treatment then allows the extraction of the metal.

In addition, the Nb-Ta ore minerals all allow very many substitutions and they correspond in fact to families of minerals whose rarity can be significant: the pyrochlore exploited at Araxá in Brazil is in fact a bariopyrochlore. It follows a blur in the reading of the mineralogical databases, the descriptions of the mineralogy of the deposits not always specifying whether reference was made to the mineral species or to the families of minerals in an undifferentiated way.

This subtlety is of great importance, because some species can integrate recoverable metals other than Nb or Ta, such as Lithium or rare earths, but also penalizing metals such as Uranium or Thorium.

In Annex 4.1.1, we will classify Nb-Ta minerals into the 4 categories already listed (see chapter 2.2.1)

2.2 MINERALOGY OF METALLIFEROUS SITES

2.2.1 METHOD USED

For each site, we will carry out a bibliographic search on its mineralogy. Old mining exploration reports are very often succinct and poorly documented. Sometimes, mineralogical data are completely absent or they correspond to simple “field” observations. Some sites, well known to mineralogists, can present lists of several hundred minerals. These sites generally correspond to occurrences associated with alkaline or hyperalkaline volcanic deposits and mainly concern niobium and tantalum deposits.

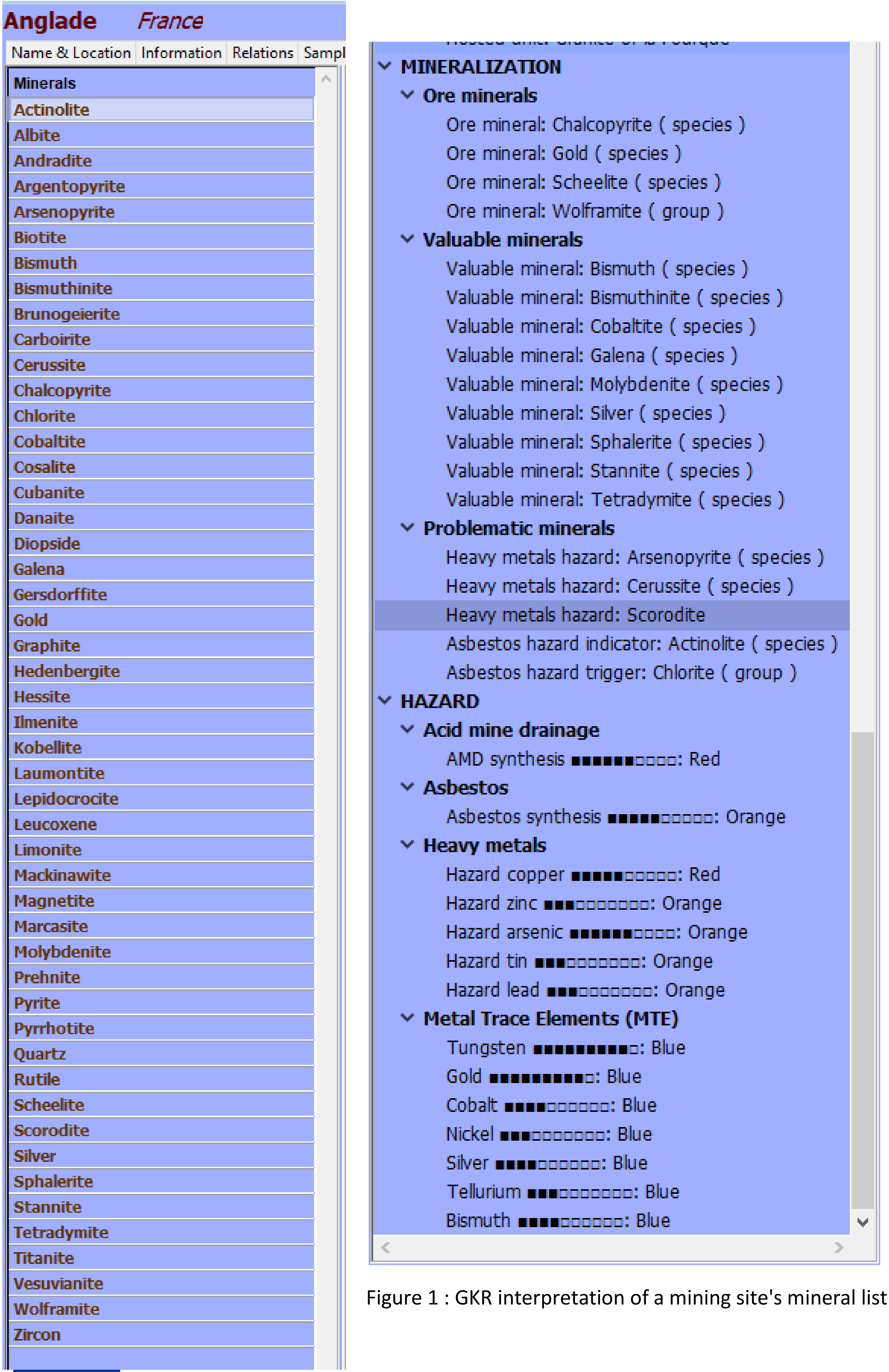
In total, more than 43,000 minerals were entered manually during this work.

The minerals from each site are then classified into 4 categories:

- Ore minerals: These are the minerals conventionally used for the production of metal. These minerals are widely represented and can constitute a significant proportion of the ore.
- Potential ore minerals: These are minerals that often accompany ore minerals. They may be only weakly represented in the deposits, but sometimes they can reach significant proportions in the ore (the rock) and become the main ore mineral of the deposit. Their characterization is particularly important because their presence is an essential element to establish the potential of recoverable metals in wastes.
- Tracers: These are generally rare minerals. Being able to contain a high proportion of the sought metals, they are however not observed in sufficient proportions to influence the economic characterization of the deposit. They are of interest by indicating refractory metals within a rock, metals which have the possibility of also being expressed either in other mineral species (which may not have been recognized) or as substitutions in host mineral species.
- Metallogenic indicators: These are mineralogical rarities whose extreme rarity as well as the minute proportions in the parageneses do not allow use, even to indicate a potential for possible economic mineralization. Their usefulness lies only in their possible specificity with metallogenic sub-models. We will report them in our work without, however, including them in the mining potential selection procedures.

The GKR system incorporates the complete list of minerals, for which the above classification, chemical composition and surface alterability are also known by the system.

The example below (Figure 1) presents the interpretation(right) by the GKR automatic interpretation method of the list of minerals present in the Salau tungsten deposit (left).



Anglade *France*

Minerals

- Actinolite
- Albite
- Andradite
- Argentopyrite
- Arsenopyrite
- Biotite
- Bismuth
- Bismuthinite
- Brunogeierite
- Carboirite
- Cerussite
- Chalcopyrite
- Chlorite
- Cobaltite
- Cosalite
- Cubanite
- Danaite
- Diopside
- Galena
- Gersdorffite
- Gold
- Graphite
- Hedenbergite
- Hessite
- Ilmenite
- Kobellite
- Laumontite
- Lepidocrocite
- Leucoxene
- Limonite
- Mackinawite
- Magnetite
- Marcasite
- Molybdenite
- Prehnite
- Pyrite
- Pyrrhotite
- Quartz
- Rutile
- Scheelite
- Scorodite
- Silver
- Sphalerite
- Stannite
- Tetradymite
- Titanite
- Vesuvianite
- Wolframite
- Zircon

- MINERALIZATION
  - Ore minerals
    - Ore mineral: Chalcopyrite (species)
    - Ore mineral: Gold (species)
    - Ore mineral: Scheelite (species)
    - Ore mineral: Wolframite (group)
  - Valuable minerals
    - Valuable mineral: Bismuth (species)
    - Valuable mineral: Bismuthinite (species)
    - Valuable mineral: Cobaltite (species)
    - Valuable mineral: Galena (species)
    - Valuable mineral: Molybdenite (species)
    - Valuable mineral: Silver (species)
    - Valuable mineral: Sphalerite (species)
    - Valuable mineral: Stannite (species)
    - Valuable mineral: Tetradymite (species)
  - Problematic minerals
    - Heavy metals hazard: Arsenopyrite (species)
    - Heavy metals hazard: Cerussite (species)
    - Heavy metals hazard: Scorodite
    - Asbestos hazard indicator: Actinolite (species)
    - Asbestos hazard trigger: Chlorite (group)
- HAZARD
  - Acid mine drainage
    - AMD synthesis ■■■■■■□□□□: Red
  - Asbestos
    - Asbestos synthesis ■■■■■□□□□□: Orange
  - Heavy metals
    - Hazard copper ■■■■■□□□□□: Red
    - Hazard zinc ■■■□□□□□□□: Orange
    - Hazard arsenic ■■■■■■□□□□: Orange
    - Hazard tin ■■■□□□□□□□: Orange
    - Hazard lead ■■■□□□□□□□: Orange
  - Metal Trace Elements (MTE)
    - Tungsten ■■■■■■■■■□: Blue
    - Gold ■■■■■■■■■□: Blue
    - Cobalt ■■■■□□□□□□: Blue
    - Nickel ■■■□□□□□□□: Blue
    - Silver ■■■■□□□□□□: Blue
    - Tellurium ■■■□□□□□□□: Blue
    - Bismuth ■■■■□□□□□□: Blue

Figure 1 : GKR interpretation of a mining site's mineral list

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The minerals on this list are cited in the various studies undertaken on the site. It is not a systematic reflection of the composition of the latter, but rather that of the quality of the observations made by the various authors. The minerals described have sometimes been identified by direct observation in the field, without laboratory study, and their diagnosis may have been approximate.

A specific tooltip is displayed in the interactive map provided with this job. It is accessible by clicking on the following icon ◈

In the "Minerals" balloon, each mineral is indicated by a colored chip:

- ● Mined or exploitable minerals (the GKR does not prejudge the quality of the mineral processing used).
- ● Potential minerals (excluding substances listed as exploited / exploitable on the site).
- ● Valuable minerals if appropriate processing were possible.
- ● Minerals that can be considered as indicators of the nature of a deposit and participating in the diagnosis of the deposit model.
- ● Gangue minerals.
- ● Minerals that can be considered mineralogical rarities.

Radioactive minerals will be indicated by a specific chip respecting the color code above: ☢

The name of each mineral has a link to the “Mindat.org” database.

2.2.1.1 SECTION “MINERALIZATION”

The "Mineralization" section details the minerals of maximum interest for the site. This interest is specified in 3 chapters:

- Ore minerals: exploited or exploitable minerals. in the example presented, gold was not exploited in the Salau deposit whose ore grades around 3g/t. It is therefore listed by the system in the ore minerals chapter.
- Valuable minerals: The minerals listed in this chapter are susceptible to valorization. As the proportions of each mineral are generally not known for the sites, it is not possible to estimate the economic interest of this potential valorization. On the other hand, the user will be able to use this information to estimate the possibilities of mineralurgical treatment if of interest.

- Problematic minerals: certain minerals may present an environmental hazard during exploitation or exploration (heavy metals, radioactivity, asbestos, etc.). They will be listed in this chapter.

2.2.1.2 SECTION "HAZARD"

The hazard section uses both mineralogical data and data from the definitions established in Task 2.2. The mineralogical composition is interpreted in the context of the metallogenic model and/or that of the deposit type. This interpretation also takes into account the extent of the work on the site. It specifies:

- Acid mine drainage: the system specifies the intensity of the phenomenon (gauge) and the probability of its existence (color which will be sent in the tooltips of the interactive Google Earth map).
- Asbestos: Asbestos can be directly observed if described in the list of asbestos minerals. Not generally part of standard mineralogical descriptions of deposits, we can however estimate the probability of its presence by identifying indicator minerals, such as amphiboles, and the simultaneous absence of minerals signalling the existence of hydrothermalism favourable to its appearance.

  The intensity of the "asbestos" phenomenon and its probability are also indicated by a gauge and a colour system included in the tooltips of the interactive map.
- Radioactivity: not present in the Salau deposit. The intensity of the hazard depends on the mineralogy and the importance of the work and the volume of mining waste left in-situ.
- Heavy metals: heavy metal hazard (according to the EU definition) directly dependent on the minerals contained, the importance of the work and/or the waste, the intensity of the AMD deduced from the metallogenic model and the type of deposit.
- Metal Trace Elements: other elements not included in the list of heavy metals. They therefore do not constitute a significant hazard a priori but they can have a strong impact on the geochemical interpretations of exploration campaigns.

2.3 ENVIRONMENTAL IMPACT OF THE W, NB, AND TA DEPOSITS

The ores of W, Sn, Nb or Ta contain in their paragenesis minerals having heavy metals in various proportions. These minerals were generally not recovered in the old mines because the complete recovery of metals from a specific ore was not economical. They therefore end up in mining wastes, in which they are a potential, often proven source of contamination of surface water.

The minerals which present a significant hazard are those susceptible to dissolution by surface water: generally, they will be sulphides. However, minerals soluble in sulfuric acid are also capable of releasing their heavy metal content if they are associated with abundant sulfides (mainly pyrite and / or pyrrhotite), which will generate this acid in surface waters.

The "heavy metals" hazard will, however, be limited to minerals capable of a relatively high abundance in the ore, of the order of %. In detail, however, we must take into account:

- The nature of the mining waste: dumps or tailings (which generally present a higher risk).
- The solubility of the minerals present (direct or in sulfuric acid)
- The distribution of minerals in the rocks constituting the dumps: soluble minerals, but included in a solid non-cracked quartz, will be protected from dissolution phenomena.
- The presence of carbonates in the ore or the gangue; these carbonates having the particularity of buffering in situ the sulfuric acid released by AMD (acid mine drainage).

So, we can admit that only a part of the minerals having an environmental hazard for heavy metals will be taken into account. The rare minerals, very often present in accessory minerals in the exploited mineralization, will therefore intervene very little in these phenomena of surface water contamination.

Automatic procedures analyse the potential hazards associated with the various occurrences and deposits. Several parameters are taken into account:

- the nature of the metals exploited or exploitable;
- the type of deposit and the metallogenic model;
- the presence of contaminating minerals and the estimation of their possible abundance in the ore or gangue;
- the importance of existing mining works;
- the presence/volume of mining waste.

Each parameter listed above is weighted by the assumed reliability of its assessment. The hazards detected are taken into account by the score of the occurrence or deposit.

A specific Google Earth tooltip is attached to each metallogenic site. Each hazard is thus evaluated: AMD, heavy metals, radioactivity, asbestos. The tooltip also explains the metallic trace elements associated with the occurrence or deposit. Although not considered contaminants, these elements can constitute the geochemical signature of the mineralization and provide a guide for exploration.

Table 1 lists the main contaminants that could be associated with critical metal deposits.

TABLE 1. Potential contaminants in the W, Nb, and Ta deposits

Metal	Skarns W	Veins W-Sn W – Nb - Ta	Pegmatites Nb - Ta	Peralkaline deposits Nb - Ta
Antimony		*		
Arsenic	*	****	*	*
Cadmium	**	**	*	
Copper	***	***	*	
Lead	*	**		
Nickel		*	**	*
Uranium		*	***	****
Zinc	**	***	*	
Asbestos	***			
AMD	****	**	*	

The table above reflects the generally observed trends. In the detail of each deposit, the nature and proportion of the various contaminants may vary. The user will refer to the tooltips of the interactive map to assess the situation of each metalliferous site.

3. CONCLUSIONS

During Task 2.2 an exhaustive mineralogy of all mining exploration work concerning tungsten, niobium and tantalum undertaken in Europe since the beginning of the twentieth century was established.

This approach sheds new light on Europe's mining potential for these metals. Numerous metalliferous sites, exploited or only explored in an old economic and industrial context, thus reveal themselves as potential targets for a resumption of mining activity, until now neglected for decades.

The integration of mineralogical data into the deposit models listed during task 2.2 allows a hierarchy of potential hundreds of targets that could bring domestic production of tungsten, niobium and tantalum to Europe.

This classification not only examines the economic interest of the main metal which characterizes the deposits, but it also takes into account:

- the recoverable metals also contained in the deposits in order to guide future choices of mineralurgical techniques to obtain full valorization of the metalliferous content of the deposit;
- the hazards that stakeholders in the exploration or exploitation of deposits will have to face;
- the potential resources constituted by mining waste from former operations.

The dissemination of the results in the form of an interactive Google Earth map provides all mining exploration/exploitation stakeholders with a common platform from which the necessary social and societal consensus can be established.

4. ANNEXES

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4.1 MINERALOGY OF REFRACTORY METALS DEPOSITS

The minerals listed in the following paragraphs will be reported in the balloons of the KMZ file (See Appendices: "Europe_W-Nb-Ta_WP2-D2.kmz"). They will specify the assumptions made relating to recoverable potentials and environmental hazards.

4.1.1 MINERALOGY OF NIOBIUM AND TANTALUM (REE)

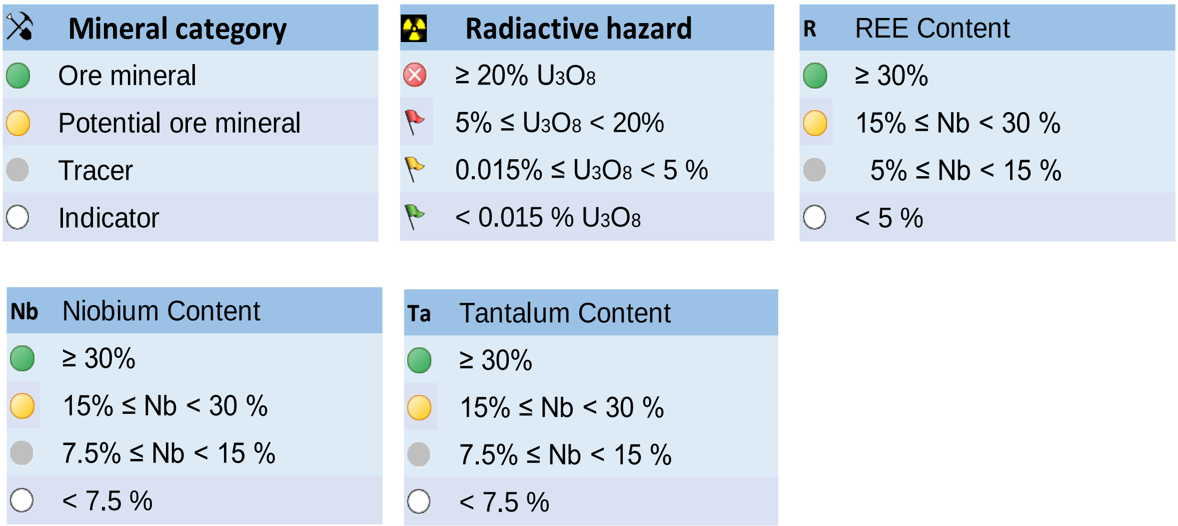
The detailed mineralogy of Niobium and Tantalum includes 300 minerals. These minerals may contain varying proportions of recoverable or penalizing metals depending on the case. In particular, very variable uranium, lithium and rare earth content will be noted.

A database in the form of an Excel Folder (See Appendices: Mineralogy_Nb-Ta.xls) presents the details of this mineralogy. It indicates the content of recoverable metals of each mineral, its rarity, its abundance, its characterization as ore mineral, typology...

As it was mentioned in the Executive Summary, this information (Excel and .kmz files) is available in the appendices of the report. The categories mentioned in the paragraph 2.1.2 also appear for each mineral, the radioactive hazard of which will be specified.

Due to the size of the document, the information has been displayed in different tabs.

The following caption appear in the "Short - EN" tab (



⚒	Mineral category
🟢	Ore mineral
🟡	Potential ore mineral
●	Tracer
○	Indicator

☢	Radiactive hazard
⊗	≥ 20% U_3O_8
🚩	5% ≤ U_3O_8 < 20%
⚑	0.015% ≤ U_3O_8 < 5 %
⚑	< 0.015 % U_3O_8

R	REE Content
🟢	≥ 30%
🟡	15% ≤ Nb < 30 %
●	5% ≤ Nb < 15 %
○	< 5 %

Nb	Niobium Content
🟢	≥ 30%
🟡	15% ≤ Nb < 30 %
●	7.5% ≤ Nb < 15 %
○	< 7.5 %

Ta	Tantalum Content
🟢	≥ 30%
🟡	15% ≤ Nb < 30 %
●	7.5% ≤ Nb < 15 %
○	< 7.5 %

Figure 2)

Figure 2. Caption in the "Short – EN" tab

4.1.2 MINERALOGY OF OTHER METALS INVOLVED IN REFRACTORY METAL DEPOSITS

It will be noted that certain metals which can be recovered, will also correspond to contaminants if they were kept in wastes. The mineralogical study of the deposits therefore provides the basic elements for estimating the potential for recoverable metals contained in the wastes, but also the nature of the environmental problems which will have to be resolved in the event of restoration or recovery for reprocessing.

4.1.2.1 GOLD

The presence of gold in tungsten deposits has been known since the beginning of the exploitation of tungsten. However, the beginning of the historic exploitation of tungsten coincided with a low value of the precious metal, and many exploitations, even important, did not value it. This is the case of the Salau mine, operated between 1975 and 1986, the ore of which contains gold grades that are currently economical. Salau has a million tonnes of tailings containing about 0.3% WO_3 and probably 1 to 3 g / t of gold (E-Mines is responsible for this estimate).

Gold is probably the easiest metal to recover from refractory metal deposits. Its high density and inalterability today allow it to be concentrated by inexpensive techniques such as centrifugation by Falcon or Knelson processes.

The Au-Ag-Te diagram (Figure 3) includes native elements and most common tellurides.

Gold ores are rare, the latter being almost always in the form of native metal, alloyed with more or less important contents of silver (electrum). We will recall here the other gold ores, mainly tellurides, which are often rare and which could therefore have gone unnoticed.

In total, around forty minerals incorporate gold into their crystal lattice.

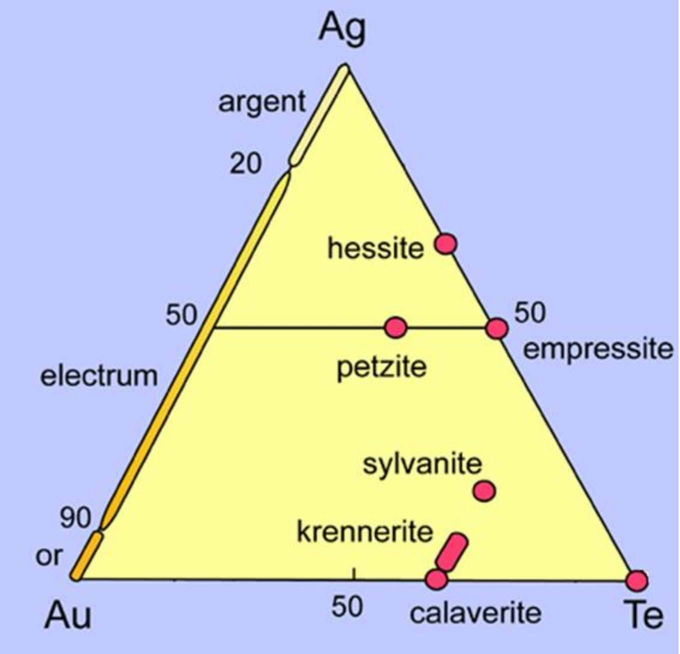


FIGURE 3. Diagram Au-Ag-Te

It is generally accepted that gold can contain up to 10% silver, and silver up to 20% gold without these variations in composition generating variety names. The intermediate term, the electrum, covers all the intermediate compositions even if the majority of the electrums contain between 20 and 50% of Ag.

Gold arsenopyrite

Gold can replace iron in the crystal structure of arsenopyrite (up to 1.6%), which mineral can then constitute a real gold ore. Gold arsenopyrite has a characteristic needle-like habitus and strong chemical zoning of crystals in which a high proportion of antimony also replaces arsenic.

4.1.2.2 SILVER

Silver is not a common accompanying metal of refractory metal deposits; it will therefore not really be a recoverable metal for the vast majority of these deposits. However, it can be found in certain skarns or into certain parageneses in Pb-Zn deposits, and as such we will include it in the list of recoverable metals.

4.1.2.3 MOLYBDENUM

Molybdenite is the most common of the molybdenum minerals and the only ore of this metal. Molybdenite is a common primary sulfide of high-temperature hydrothermal deposits (copper porphyries, skarns, pneumatolytic veins) and granite pegmatites. It is lead gray with a metallic luster and perfect easy lamellar cleavage lamellar along {0001}.

The sulfur can be replaced by **selenium** in significant amounts (up to 25 %)

Molybdenite is found in high-temperature hydrothermal deposits (copper porphyries, pneumatolytic veins, pyrometasomatic bodies, etc.) as well as disseminations in some granite, aplite and pegmatites. It is generally exploited with copper deposits, more rarely with tungsten deposits.

4.1.2.4 RARE EARTHS

Rare earths are commonly associated with Nb-Ta deposits and there are many minerals that can be considered both Nb-Ta ores and REE ores (see Appendices).

Rare earths represent the group of lanthanides (elements with atomic numbers between 57 and 71, from lanthanum to lutetium) to which we add, due to similar chemical properties (same column of the periodic table), yttrium (Y) and scandium (Sc).

Despite their name, rare earth elements are not rare and the minerals which contain them are found in numerous deposits, and therefore with the deposits of W, Nb and Ta.

Bastnaesite – (REE)FCO_3

Primary ore	
Common mineral	*Fluorocarbonate*
Ore mineral	REE
Hazard	U, Th

Bastnaesite was initially a cerium carbonate. However, the cerium is commonly replaced by other rare earths (lanthanum, neodymium, praseodymium, etc.) and by yttrium in such large amounts that it can even become minority.
These major substitutions led most mineralogists to consider bastnaesite as a group composed of several minerals that had previously been considered as varieties: bastnaesite-(La), bastnaesite-(Y), bastnaesite-(Ce), depending on the dominant element. In addition to these substitutions, the bastnaesites also commonly contain calcium, and also thorium or uranium, responsible for the metamict state of certain crystals.

Bastnaesite-(Ce) is a typical mineral of nepheline syenites and soda granites, in particular their pegmatites, and is also found in skarns in contact with these same rocks. More rarely, it occurs in hydrothermal metasomatic deposits in a dolomitic environment (Luzenac, France). Although common in alluvium, bastnaesite is easily weathered in outcrop, evolving ti the various rare earth compounds such as lanthanite.
Basnaesite (as a group) is an important rare earth ore. It is notably worked in two gigantic deposits: Bayan Obo (Inner Mongolia, China) and Mountain Pass (California).

Monazite – (REE, Th)PO_4

Primary ore	
Common mineral	*Phosphate*
Ore mineral	Th, REE
Hazard	U, Th

Monazite is a primary phosphate of granite and particularly its pegmatites (where crystals in excess of 100 kilos have been discovered), also present in nepheline syenite and carbonatite, as well as in certain high-temperature vein deposits (Sn, W, Mo veins). It is also abundant in charnockite complexes of ancient shields as well as in placers and paleoplacers.

In monazite with the ideal formula $CePO_4$, the cerium is commonly replaced by lanthanum or neodymium, which leads to the individualization of three minerals depending on the dominant rare earth: monazite-(Ce), monazite-(Nd) and monazite-(La). In addition to these common replacements, other rare earths can enter the lattice, as well as radioactive elements like thorium or uranium, making the monazite commonly metamict.

Monazite is mined as a rare-earth ore and was, in the recent past, the main ore for thorium: concentrations of this element can be as much as 32% ThO_2, with 4% U_3O_8 (chelarite variety derived from charnockite and concentrated in the coastal placers of Travancore, in India).
Monazite is mainly obtained from large placers (Florida, Georgia, India, etc.), where it is associated with zircon and ilmenite, and from large alkaline complexes (Mountain Pass, California; Bayan Obo, China).

Xenotime – (Y, REE, Th, U)PO_4

Primary ore	
Common mineral	*Phosphate*
Ore mineral	REE
Hazard	U, Th

Xenotime is a relatively rare mineral.
It is found mainly as an accessory mineral in granite, and as larger crystals in pegmatites, where it is difficult to distinguish from zircon.
It shows the same tetragonal prisms terminated by two pyramids, and has the same brown, yellow-brown or reddish color as zircon. More rarely, it is found in alkaline granite and alpine fissures: the deposits are thus comparable to those of monazite.

Its chemical composition changes, with a significant amount of the yttrium being replaced by rare earths (lanthanum, neodymium, etc.), thorium, uranium or zirconium. Despite the presence of radioactive elements, xenotime is not metamict. Unaffected by weathering, it can concentrate as important, and locally exploitable, placers.

Xenotime-(Y) is a common accessory mineral mainly in granite, alkaline syenite and associated pegmatites. It is also found disseminated in gneiss and more rarely in metamorphic limestone or alpine fissures. It is fairly rare in alluvium despite high local concentrations.

Loparite – $(Na,Ce,Sr)(Ce,Th)(Ti,Nb)_2O_6$

Primary ore	
Common mineral	*Oxide*
Potential ore mineral	REE, Nb
Hazard	Th

Loparite is a relatively rare REE mineral.
It is found mainly in Pegmatites from ultra-alkaline agpaitic and miaskitic rocks display even greater mineral diversity than granite pegmatites. Much of this mineralogical diversity results from the unusual concentration of Be, Ti, Y, Zr, Nb, and rare earth elements in these alkali-rich, silica-poor rocks.

Loparite is a rare earth niobiotitanate found in Russia, in the Kola Peninsula. The ore exploited contains 28 to 30% rare earth oxides, 35 to 38% titanium dioxide, 7.5 to 8% niobium oxide, 0.5 to 0.8% tantalum oxide. The concentrates obtained contain approximately 32% rare earths, especially ceric.

Lujavrite – $(Na,Ce,Sr)(Ce,Th)(Ti,Nb)_2O_6$

Primary ore	
Common mineral	*hyperalkaline rock*
Potential ore mineral	REE, Nb
Hazard	Th

Lujavrite is not a mineral. It is a variety of nepheline syenite, a silicoaluminate rock not containing quartz, which has been enriched in various elements including rare earths. This rock is present in the Kvanefjeld deposit, in southern Greenland, whose exploitation is currently being prepared. Proven and probable reserves are 108 million t of ore containing 2,600 ppm of Zn, 362 ppm of U_3O_8 and 14,300 ppm of REE oxides. The planned production is 12,420 t/year of calcium fluoride, 6,060 t/year of zinc concentrate, 454 t/year of U_3O_8, 19,000 t/year of La and Ce oxide as well as 4,300 t/year of year of Nd oxide, 1,400 t/year of Pr oxide, 30 t/year of Eu oxide, 45 t/year of Tb oxide, 270 t/year of Dy oxide. The rare earth concentrates produced, containing 20 to 25% REE oxide, must be processed in China to separate the REE.

4.1.2.5 URANIUM

Uranium is one of the metals conventionally associated with refractory metal deposits; some ores are also de facto Nb-Ta ores. Particular attention will be paid to the uranium hazard due to the possible double contamination, chemical and radioactive.

We will detail here the 24 most common minerals, among the very many species (more than 250) which incorporate it in their crystal structure. Because of its toxicity, all of its species will be sought in the parageneses of refractory metal deposits in order to estimate the potential hazard.

By frequency and abundance, we will retain:

Uraninite - UO_2

Primary ore	
Very common mineral	*Oxyde*
Ore mineral	U
Hazard	U

Uraninite is the natural oxide of uranium, but a certain confusion exists between the terms "uraninite" and "pitchblende".

International mineralogical nomenclature recommends the term "uraninite" for designating the natural oxide of all facies of tetravalent uranium. However, based on Dana's (1861) nomenclature, the term "uraninite" is still too frequently reserved in the literature for the clearly crystalline facies, with the term "pitchblende" being used for the collomorph uranium oxide facies.

Uraninite is rarely euhedral, as cubes or cubo-octahedrons, generally of less than a millimeter, but capable of exceeding 10 cm on its edges (pegmatites of the Cordoba region, Spain). This crystalline variety is mainly found in pegmatites, more rarely in hydrothermal veins; it is common, but microscopic, in certain granite.

Uraninite is much ore common in its collomorph facies ("pitchblende"), and then forms aggregates of spherulites that can be more than 20 cm in diameter, forming masses with a mammillated appearance. Although euhedral uraninite is mainly magmatic, "pitchblende" is an uraninite facies of hydrothermal origin, as in many veins and detrital sedimentary rocks.

Regardless of the facies, uraninite is black with a submetallic to resinous luster and a conchoidal fracture. It is characterized by a high density (varying from 7.5 to more than 10, depending on the oxidation state of the uranium), and a very high radioactivity.
From the chemical point of view, the relationship of the uraninite structure with thorianite explains the presence of a solid solution between these two minerals. It has been proven that this was continued artificially.

Easily weathered in outcrop, uraninite epigenizes or alters to an impressive suite of yellow to orange (rarely black) powdery minerals collectively designated as "gummite".

They were discovered in pegmatites from Spain (Fuente Ovejuna and Hornachuelos, Andalusia) and South Africa (Bokseputs, Northern Cape).

Pitchblende is an infinitely more common facies than uraninite in most uranium deposits. Much more abundant than well-crystallized uraninite, pitchblende is by far the most important ore of uranium.

Pitchblende - UO_2

Primary ore	
Very common mineral	*Oxyde*
Ore mineral	U
Hazard	U

Pitchblende is the collomorph variety of uraninite, and commonly forms spherulites or aggregates of spherulites whose dimensions can exceed 20 cm in diameter, forming masses with a mammillated appearance.

Pitchblende is thus the most widespread variety of uraninite. It is of hydrothermal origin, common in many uraniferous veins and clastic sedimentary rocks; it is by far the most important ore of uranium.

It is known that vein pitchblende results from a leaching of uraninite grains disseminated in the granite, with the resulting uranium-rich fluids accumulating in the fractures where they precipitate the pitchblende.

Pitchblende is black with a submetallic to resinous luster and a conchoidal fracture. It is characterized by a high density (varying according to the degree of the uranium's oxidation: from 7.5 to more than 10) and obviously by a very high radioactivity.

Highly alterable in outcrop, pitchblende epigenizes or alters to an impressive suite of yellow to orange, rarely black, powdery minerals collectively described under the name "gummite". Pitchblende is a facies that is almost invariably present in most uranium deposits.

Gummites

Secondary ore	
Very common mineral	
Potential Ore Mineral	U
Hazard	U

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Like garnierite, limonite and bauxite, gummite is not a mineral but an assemblage of minerals. The term "gummite" in fact designates secondary cryptocrystalline minerals of uranium, generally powdery, formed under a hot or temperate climate from the oxidation of uraninite (commonly in its concretionary facies of pitchblende).

It consists mainly oxides and silicates of uranium associated with various metals. Almost all gummites preserve the characteristic structures of uraninite and especially of the pitchblende that they epigenize.

"Yellow gummite", which is the most common, is composed largely of uranophane (or uranotile), and "orangey gummite" (which can be red) is mainly curite (lead uranate), billietite (barium uranate) or ianthinite. "Black gummite" corresponds to weathered rocks colored black by small amounts of residual UO_2, surviving from the transformation to UO_3 during oxidation of the pitchblende.

Gummites make up a not insignificant part of the uranium ore in the shallow parts of deposits.

Autunite - $Ca(UO_2)_2(PO_4)_2 \cdot 11H_2O$

Secondary ore	Autunite group
Very common mineral	*Uranyl-phosphate (Figure 18)*
Ore mineral	U
Hazard	U

Autunite is, with the "gummites", the most widespread weathering product of uraninite. It is the most common of the uranium supergene minerals, abundant in the surficial oxidized zones of uranium deposits; it is also present, although more rarely, in uraninite-bearing pegmatite veins and in certain hydrothermal veins.

Autunite forms thin crystals deposits lamellar with a square or octagonal section, commonly grouped into subparallel or fan-shaped aggregates. The mineral commonly forms micaceous scaly masses, flakes, incrustations with a lamellate surface, or microcrystalline coatings. Autunite has a luminous green-yellow color passing to lemon yellow to sulfur yellow through dehydration and transformation to meta-autunite. With more intense alteration, it passes to yolk-yellow phosphuranyllite. Autunite reacts to ultraviolet rays with a very characteristic intense yellowish green fluorescence.

Autunite is a secondary mineral derived from the weathering of uraninite and is present in oxidized zone of all uraniferous environments: in the first place, the uranium deposits of all types, but also the uranium-bearing pegmatites and granites.

Torbernite - $Cu(UO_2)_2(PO_4)_2 \cdot 12H_2O$

Secondary ore	Autunite group
Very common mineral	*Uranyl-phosphate (Figure 18)*
Ore mineral	U
Hazard	U

Torbernite (also called chalcolite) is a very common secondary mineral in the surficial oxidized zone of uranium deposits; it is rarer in uraniferous pegmatites. It is the most common oxidation mineral of uraninite when this is associated with copper sulfides.

Torbernite belongs to the autunite group, differing from autunite by the presence of copper instead of calcium, the metal being the cause of the mineral's greener color. This chemical difference explains why torbernite does not fluoresce under ultraviolet light, unlike many minerals of the autunite group.

Torbernite occurs as variably thick square tablets with a perfect micaceous cleavage on {001}, more rarely as tetrahedral octahedrons; it can form crystals mixed with autunite. It has a magnificent emerald green to dark green color and is transparent when fresh; but torbernite dehydrates easily in air to the less hydrated phase, metatorbernite, resulting in opacification of the crystals and their exfoliation along the perfect cleavage {001}. Torbernite is a major ore of uranium.

Sabugalite- $HAl(UO_2)_4(PO_4)_4 \cdot 16H_2O$

Secondary ore	Autunite group
Common mineral	*Uranyl-phosphate (Figure 18)*
Potential Ore Mineral	U
Hazard	U

Sabugalite is a hydrated uranium phosphate of the autunite group.

The crystals are elongate lamellar laths with fibrillose ends, commonly joined into bundles or trellises, or forming thick incrustations. They barely reach 10 mm. It is straw yellow to lemon yellow, fluorescing yellow-green under ultraviolet light.

Sabugalite is rarer than autunite, with which it is commonly associated in the oxide zone of uranium deposits, forming thick incrustations at the periphery of zones of this mineral.

Sabugalite can, as in its type locality near Sabugal (Portugal), form an ore of uranium. It is also found in the vanadium and uranium mines of Ciudad Rodrigo and Pedro Alvaro, in the Province of Salamanca (Spain). Elsewhere it is more discreet, although fairly common in the pitchblende veins of Limousin, notably at Margnac and Pény (Haute-Vienne, France), which yielded the most beautiful crystals known.

Uranophane - $Ca(UO_2)_2(SiO_3OH)_2 \bullet 5H_2O$

Secondary ore	Uranophane group
Common mineral	*Silicate*
Ore mineral	U
Hazard	U

Uranophane or **uranotile** is a hydrated secondary uranium – calcium silicate. It is common in the oxidized zone of uraniferous deposits where it derives from the weathering of uraninite (and notably its collomorph facies, pitchblende).

Uranophane (sometimes called uranophane-alpha in opposition to its monoclinic dimorph uranophane-beta) is the main mineral phase of "yellow gummite", a common term for all the secondary uranium minerals and composed mainly of uranium silicates.

Uranophane forms fine acicular crystals, a few millimeters at the most, grouped into bundles, crests or "urchins", or as earthy to finely fibrous masses, locally very voluminous. These masses commonly retain the banded and concretionary structure of the pitchblende that the alpha-uranophane is replacing. The color, normally yellow to lemon yellow or greenish, becomes pale yellowish white in the earthy masses.

This mineral, like the other uranium silicates, is soluble in acids with a gaseous release of radon. Clear crystals are rare.

As the main constituent of yellow gummite, alpha-uranophane (or alpha-uranotile) is an important ore for uranium.

Curite - $Pb_3(UO_2)_8O_8(OH)_6 \cdot 3H_2O$

Secondary ore	
Common mineral	*Uranyl-hydroxide*
Potential Ore Mineral	U
Hazard	U, Pb

Curite is one of the seven currently known mixed lead – uranium oxides. These are secondary minerals present in the oxidation zone of uranium deposits where they derive from the alteration of pitchblende.

Curite is, with fourmarierite, one of the main "orange gummites", easily recognizable in the alteration rings of pitchblende.

Curite forms acicular crystals no larger than 5 mm, with a strong adamantine luster, or occurs as microcrystals, powdery coatings, or compact cryptocrystalline masses. It is orange to orangey red. It can totally pseudomorph uraninite crystals.

Coffinite - $U(SiO_4) \cdot nH_2O$

Primary ore	Zircon group
Common mineral	*Silicate*
Ore mineral	U
Hazard	U

Coffinite is a hydrated uranium silicate that appears to be isostructural with zircon.
This important uranium ore was for a long time unnoticed because of its occurrence as minute patches and black unattractive coatings. Macroscopic crystals (a few millimeters), squat to elongate, are exceptional. Coffinite generally occurs as very fine crystals (<20 µm), as collomorph, botryoidal or radial-fibrous incrustations, and as powdery aggregates, invariably black.

Coffinite is subject to metamictization and commonly decomposes to uraninite and quartz in Precambrian deposits.

It is a primary uranium mineral that is particularly abundant in the large sedimentary uranium deposits of the Colorado "roll" type, where the ore impregnates detrital beds rich in organic matter, uraninite, pyrite and commonly vanadium minerals. These Permian to Eocene deposits are dispersed over four states, being particularly important in the Grants area (New Mexico).

Coffinite is abundant in France's pitchblende veins at La Rabasse (Hérault), where it forms original radial aggregates around nickel arsenide cores, and in Germany's polymetallic uranium-bearing veins of Saxony (Marienberg, Johanngeorgenstadt, Schneeberg). Extremely rare millimeter-size crystals are found in the uranium deposits of Kovary (Poland) and Príbram (Czech Republic).

Carnotite - $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$

Secondary ore	Carnotite group
Common mineral	*Uranyl-vanadate (Figure 19)*
Ore mineral	*U*
Potential Ore Mineral	V
Hazard	U, V

Carnotite is a fairly common secondary in the oxidized zone of uranium deposits in a sedimentary context (Uravan region, Colorado and Utah).

It is hydrated potassium-uranium vanadate that generally forms a crystalline powder or unconsolidated microcrystalline aggregates with lemon yellow to amberish yellow color. More rarely, it forms flattened crystals, associated as divergent aggregates.

Carnotite is the main uranium ore of the sedimentary deposits in Colorado (Uravan, Placerville, Paradox, etc. In Arizona, carnotite is also very abundant in the Monument Valley mines, where it is worked as a twofold uranium and vanadium ore.

Carnotite is an important ore for uranium, radium and vanadium.

Parsonsite - $Pb_2(UO_2)(PO_4)_2$

Secondary ore	
Rare mineral	*Uranyl-phosphate (Figure 18)*
Potential Ore Mineral	U
Hazard	U, Pb

Parsonsite is a hydrated uranium – lead phosphate. It is a rare secondary mineral found in the surficial zone of uranium deposits.
It occurs as elongate to acicular prismatic crystals. They are millimeter size, pale yellow to yellow-brown, possibly green-brown (or chocolate brown at Shinkolobwe), grouped as radiate aggregates or in bundles. Parsonsite is commonly associated with phosphuranylite, renardite and torbernite.

Initially considered as very rare, parsonsite was discovered in abundance in the pitchblende veins at Forez, near Lachaux and at Grury (Puy-de-Dôme, France), where it forms most of the ore. The most beautiful samples known come from these small deposits.
Parsonsite is also found in the pegmatites at Ruggles, near Grafton Center (New Hampshire), and Wölsendorf (Bavaria, Germany).

Tyuyamunite - $Ca(UO_2)_2(VO_4)_2 \cdot 5\text{-}8H_2O$

Secondary ore	
Rare mineral	*Uranyl-vanadate (Figure 19)*
Potential Ore Mineral	U, V
Hazard	U, Pb

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Tyuyamunite is a fairly widespread secondary uranium mineral from the oxidized zone of uranium deposits where it is associated notably with carnotite and metatyuyamunite, two other uranium – vanadium minerals.

Tyuyamunite forms impregnations, masses and powdery coatings, possibly small waxy yellow to lemon yellow lamellar crystals, elongate along [100] and flattened on {001}, with commonly curved faces. It also occurs as crystalline aggregates with a radiate and fan-shaped structure.

Tyuyamunite is the calcic analog of carnotite; this particularity explains why it is reported, and in places common, in most carnotite-bearing uranium deposits, notably in the United States (Colorado, New Mexico, Arizona, etc.). The Laguna deposit, near Grants (New Mexico) has notably yielded good crystallized specimens.

The best site for crystals, however, is the deposit where it was discovered, Tyuya-Muyun, in Uzbekistan, where the mineral was sufficiently abundant to form a good uranium ore.
With the loss of a few molecules of water (zeolitic water weakly bound within the lattice), tyuyamunite dehydrates to metatyuyamunite. Tyuyamunite is a locally important ore for uranium and vanadium.

Bétafite, Euxynite –(Y), Pyrochlore- see Appendix

Nb-Ta ores	
Common minerals	
Ore mineral	U, REE, Nb, Ta
Hazard	U, Pb

4.1.2.6 COPPER

Certain deposits of refractory metals, in particular the skarns, can contain appreciable quantities of copper. As chalcopyrite is a particularly abundant sulfide present in most hydrothermal mineralization, we will look for the possibility of copper contamination. The impact of copper-containing minerals will be limited by focusing only on the main copper ores likely to be encountered in refractory metal deposits. As with lead and zinc, copper was not valued on tin-tungsten operations, so it will be found in the wastes of old operations. In certain cases, it could contribute to the economy of reprocessing wastes.

Chalcopyrite – $CuFeS_2$

Primary ore	
Very common mineral	*Sulfide (Figure 5)*
Ore mineral	Cu
Hazard	Cu

Chalcopyrite is a very common primary sulfide, found in all types of copper deposit: hydrothermal veins of all temperatures and all origins, copper porphyries (commonly with bornite and molybdenite), massive polymetallic sulfides (with pyrite, sphalerite, galena, gray copper, etc.), magmatic segregations in basic and layered ultrabasic rocks (commonly accompanied by nickel sulfides such as pentlandite, millerite, etc.), stratiform deposits in a sedimentary context (kupferschiefer), etc.

Chalcopyrite is the main copper ore, concentrated in considerable amounts in all the above deposits, forming finely granular compact masses, possibly mamillated, in company with many other minerals.

It is easy to recognize by its bronze yellow color, its iridescent copper red and purplish blue tarnish, indicating the appearance of an oxidizing film of bornite.

Azurite – $Cu_3(CO_3)_2(OH)_2$

Secondary ore	
Very common mineral	*Anhydrous carbonates (Figure 9)*
Potential Ore Mineral	Cu
Hazard	Cu

Azurite is a very sought after mineral by collectors for the magnificent pronounced blue color and beauty of its crystals.
It is a common secondary carbonate of the oxidized zone of copper deposits, where it is associated with other secondary copper minerals, notably malachite, which is much more abundant.

The crystals are commonly very well formed and large. The show varied facies, commonly tabular or elongate, more rarely short prismatic or pseudorhombohedral. In the last case the crystals are grouped as nodular aggregates bristling with triangular crystalline tips. The faces are commonly slightly wavy and striated. Rosette-shaped aggregates of prismatic crystals are rarer.

Azurite is less commonly massive, concretionary or stalactitic with a columnar or coarsely radial structure, or as coatings or amorphous masses. The crystal color is azure to a superb midnight blue (light blue for the powdery coatings), with a vitreous, almost adamantine luster. They can be pseudomorphosed by malachite.

Although mainly sought for collections when it is well crystallized, massive azurite can constitute an appreciable copper ore in the surficial part of certain deposits.

Malachite – $Cu_2(CO_3)(OH)_2$

Secondary ore	
Very common mineral	*Anhydrous carbonates (Figure 9)*
Ore mineral	Cu
Hazard	Cu

Malachite is the most common of the secondary copper minerals. It forms in the surficial oxidized zone of deposits, accompanied by a suite of other secondary copper minerals, notably azurite which it can completely pseudomorph. Pseudomorphs of barite or cuprite are not uncommon.

This characteristic green mineral results from the supergene alteration of primary copper minerals, mainly chalcopyrite, under conditions of neutral to basic pH and in the presence of carbon dioxide.

Translucent, with a vitreous to matt luster (adamantine for the crystals), malachite is pale green to yellow-green (thin incrustations), dark green (crystals), pure green to darkish green (concretionary masses). It has a high density (more than 4).

The most common form of malachite is the stalactiform fibrous concretionary facies with a concentric banding of carried greens resulting form the more or less intense compaction of the acicular crystals composing the different bands; the surface is smooth, undulating to mammillated, possibly bristling with crystals. Visible crystals are rare, small and elongate, generally forming radial-fibrous groups; twinning is common. The centimeter-size squat prismatic crystals are almost invariably pseudomorphs of azurite crystals.

Malachite is worked as copper ore.

Bornite – Cu_5FeS_4

Primary and secondary ore	
Very common mineral	*Sulfide (Figure 5)*
Ore mineral	Cu
Hazard	Cu

Primary **bornite** is found associated with basic rocks, high-temperature hydrothermal veins, and skarn-type metasomatic deposits. Secondary bornite occurs as an alteration product in the cementation zone of many copper deposits, where it can be the dominant copper mineral. Bornite generally forms compact, possibly granular, masses. It has a metallic luster, and a bronze to brilliant pinkish brown color when fresh, but tarnishes rapidly to red, copper red, purple-blue or purplish, with a pronounced iridescence.

Crystals can be pseudoquadratic with a cubic configuration, octahedral or dodecahedral with striated curved faces, but are very rare and generally millimeter size, although individuals of 8 cm have been found.

Bornite is one of the main copper ores, along with chalcopyrite and chalcocite.

Chalcocite – Cu_2S

Primary and secondary ore	
Very common mineral	*Sulfide (Figure 5)*
Ore mineral	Cu
Hazard	Cu

Chalcocite is a common mineral that is typical of hydrothermal veins as well as of the oxidized zones and cementation of copper deposits (copper porphyries, acid epithermal deposits, sedimentary "red bed" type deposits and "kupferschiefer" type deposits). Chalcocite can thus be primary or secondary, and thus formed at the expense of other copper sulfides, such as chalcopyrite or bornite. In addition to the suite of copper minerals that generally accompany it, it is commonly associated with primary and secondary lead, zinc and iron minerals.

A black-gray mineral, blackening on exposure to air, with a metallic luster, it forms beautiful pseudohexagonal tabular prismatic crystals, commonly twinned (including cruciform twins), as well as finely granular to compact masses. Chalcocite is also found pseudomorphing fossil wood and as incrustations on roots.

Chalcocite is an important copper ore, commonly dominant in the cementation zones of the major deposits.

Covellite – CuS

Primary and secondary ore	
Very common mineral	*Sulfide (Figure 5)*
Ore mineral	Cu
Hazard	Cu

A primary or secondary sulfide, **covellite** is common in most hydrothermal copper deposits. It is generally secondary, arising from the alteration of chalcopyrite: it is found, in abundance, as foliate masses in the cementation zone in the company of many other copper minerals (cuprite, digenite, chalcocite, malachite, native copper, etc.), as well as alteration coatings on most of the other copper sulfides. More rarely, covellite occurs as primary mineral in volcanic fumaroles (Vesuvius, Italy) or epithermal gold deposits.

Covellite is lamellar and flexible, of a characteristic indigo blue with a brass yellow or purplish red iridescence. It is not very hard (1.5 to 2), and is systematically associated with pyrite, chalcopyrite or bornite.

Crystals are rare and appear to be specific to primary covellite. The occur as small hexagonal tablets grouped into hexagonal lamellar aggregates, possibly assembled into rosettes. Covellite is a valuable alternative copper ore which locally forms large masses.

Tennantite-Tetraedrite series (fahlore) – $Cu_6(Cu_4X_2)As_4S_{12}S$ to $Cu_6(Cu_4X_2)Sb_4S_{13}$

Primary ore	
Common mineral	*Sulfosalt (Figure 15)*
Ore mineral	**Ag**, Cu
Hazard	As, Cu, Sb, Hg, Bi

Fahlore is a common gray to iron-black sulfosalt with the general formula $X_{12}Y_4S_{13}$, where X is mainly Cu or Ag, with Y being As or Sb. It forms two complete isomorphous solid solutions passing from an antimoniferous end-member (tetrahedrite, the most common fahlore) to an arseniferous end-member (tennantite, the least common) and to an argentiferous end-member (freibergite, relatively rare). The complex crystal structure is based on a three-dimensional frame made up of CuS4 tetrahedrons. This leaves large cavities that receive varied metallic ions. There are also many substitutions, the most common being the replacement of Ag+ by Cu+. This replacement can be major to the point where Ag exceeds Cu in the number of atoms and the silver content can be as high as 48%: this is freibergite (which some authors nevertheless consider as an argentiferous variety of tetrahedrite). This richness in silver, added to the frequency of fahlore, makes this group of sulfosalts the main reservoir of silver on the planet, way ahead of the silver sulfides, which are richer in silver but less abundant. Fahlore is also a notable ore for copper. Cu2+ is also commonly replaced by Zn2+ or Fe2+, and Sb or As by Hg (in amounts exceeding 10% in the schwatzite variety) or Bi (goldfieldite variety), which makes for chemically complex minerals.

Fahlore is common in most hydrothermal deposits (polymetallic and gold veins, massive sulfides, sedimentary deposits, etc.). The crystals take on an isometric form, commonly displaying tetrahedrons and interpenetration twins. The most remarkable specimens (centimeter-size tetrahedrons measuring up to 25 cm) have been extracted from polymetallic veins and gold and silver veins. Their easy alteration to blue and green carbonates (azurite and malachite) makes them easily identifiable

Fahlore includes two complete isomorphous solid solutions passing from an antimoniferous end-member (tetrahedrite, the most common gray copper) to an arseniferous end-member (tennantite, the least common) and to an argentiferous end-member (freibergite, relatively rare).

Cuprite – Cu_2O

Secondary ore	
Very common mineral	*Oxide (Figure 4)*
Ore mineral	Cu
Hazard	Cu

Cuprite is a common oxide in the surficial parts of copper deposits, mainly the cementation zone where it is often found with native copper and other copper oxide minerals (malachite, azurite, chrysocolla, etc.). Normally massive and earthy, cuprite is nevertheless commonly crystallized; the crystals take on an octahedral form, and to a lesser extent an dodecahedral or cubic form, and can develop an acicular facies through elongation along [001] (chalcotrichite variety). Cuprite is blood red and translucent with the small crystals, and dark red to black and opaque with the large crystals, and has an adamantine to submetallic luster. Pseudomorphs in malachite are common and spectacular, those in azurite are rarer: they arise from carbonatization following oxidation of the Cu+ ions to Cu2+.

Cuprite is a notable copper ore in the upper parts of deposits.

Digénite – Cu_9S_5

Secondary and primary ore	
Common mineral	*Sulfide (Figure 5)*
Potential Ore Mineral	Cu
Hazard	Cu

Digenite is a copper sulfide mainly of secondary origin. It derives from the alteration of chalcocite, chalcopyrite and bornite, and systematically accompanies secondary covellite in oxidation and cementation zones of copper deposits.

Primary digenite is much rarer, found in basic intrusions and pegmatites.

Digenite is mainly massive, rarely as cubo-octahedrons of up to 3 cm. It is blue-black to black.

Renierite – $(Cu^{1+},Zn)_{11}Fe_4(Ge^{4+},As^{5+})_2S_{16}$

Primary ore	Germanite group
Rare mineral	*Sulfide*
Ore mineral	Ge
Hazard	Cu, Zn, As

Renierite is a complex **germanium** sulfide with a slightly orange bronze color. Although rare, it is the commonest of the germanium minerals, commonly accepting some zinc and gallium in its lattice.

Renierite generally occurs as microscopic grains of up to a millimeter disseminated in other sulfides, or as masses in germanium-rich deposits. Renierite is an important ore of germanium.

Stannite – Cu_2FeSnS_4

Primary ore	
Common mineral	*Sulfide*
Potential Ore Mineral	Sn, Cu
Hazard	Cu, Sn

Stannite is the commonest of the tin sulfides.

It is a fairly common hydrothermal mineral found in pneumatolytic and high-temperature hydrothermal deposits, as well as in the Andean telescoped deposits.

Stannite is steel gray with a greenish hue and a metallic luster. It generally occurs as granular masses, generally alongside chalcopyrite, cassiterite and arsenopyrite.

Stannite is a potential ore for tin.

4.1.2.7 ZINC

Refractory metal deposits generally do not contain much zinc. However, since sphalerite is a particularly abundant sulphide and present in most hydrothermal mineralizations, we will look for the risk of zinc contamination. Minimize the impact of zinc-containing minerals by focusing only on the main zinc ores. As with lead, zinc was not valued on tin-tungsten operations, so it will be found in the discharges of old operations.

Sphalérite – ZnS

Primary ore	
Common mineral	*Sulfide*
Ore mineral	Zn
Potential Ore Mineral	Sn, Ge, In, Cd
Hazard	Zn, Hg, Cd, Sb

This zinc sulfide, previously known as "blende", is one of the four most abundant sulfides in the Earth's crust, after pyrite and with galena and chalcopyrite.

It the main ore of zinc, found in most hydrothermal environments (veins, skarns, sedimentary deposits, massive sulfides, etc.) where it forms large, even gigantic, masses.

Sphalerite has a strong adamantine luster, close to that of diamond, and forms crystals of various shapes, all derived from the cube, in places highly complex and with a spheroidal appearance. Its colors are very varied, depending on the amount of minor and trace elements, notably iron: colorless, brown (the most common), red, green (sphalerite with manganese), yellow to black ("marmatite" variety with a high iron content). Its alteration is the source of many secondary minerals such as smithsonite and hemimorphite; the term "calamine", now restricted to hemimorphite, once designated all the secondary zinc minerals.

Sphalerite is associated with a large number of minerals, mainly sulfides, foremost of which are pyrite, galena, chalcopyrite and the gray coppers. It is found in varied quartz, calcite, siderite, barite or fluorite gangues.

Wurtzite – (Zn,Fe)S

Primary ore	
Common mineral	*Sulfide*
Ore mineral	Zn
Hazard	Zn, ?

Wurtzite is the hexagonal polymorph of sphalerite and, like this mineral, is of hydrothermal origin. It is, however, less widespread than sphalerite and is found mainly in the hydrothermal veins and telescoped deposits of the Andes.

Wurtzite has several polytypes, polytype 2H being the most common. As with sphalerite, iron or manganese replaces zinc locally in large amounts.

Smithsonite – $ZnCO_3$

Secondary ore	
Common mineral	*Anhydrous carbonates (Figure 10)*
Ore mineral	Zn
Potential Ore Mineral	Cu
Hazard	Zn, Cu, Cd, Hg,

Smithsonite is one of the commonest zinc oxide minerals and is particularly in carbonate environments.

Smithsonite generally forms concretionary or stalactitic, locally radial-fibrous, masses with a surface that is mammillated or spiked with small crystals. The masses are commonly colored reddish brown by goethite, and contain cavities which gives them an uncharacteristic appearance which does not help their identification. The high density (more than 4.2) is nevertheless a good criterion.

Pure smithsonite is naturally colorless, but partial substitution of the zinc by a number of metals (up to 20% iron, up to 9% manganese, up to 6% copper, etc.) brings about strong color variations; it can thus be tinted brown to yellow-brown by iron, blue to blue-green and green by copper, more rarely pink by cobalt; micro-inclusions of greenockite color it yellow.

Crystals are rare, most commonly rhombohedral or scalenohedral. Unalterable, smithsonite projects from the top of zinc deposits and is thus an excellent exploration guide. It is still a locally important zinc ore in the shallow oxidized zone of the deposits.

It should be mentioned here that the old mining term "calamine" designated indifferently zinc carbonates and zinc silicates indifferently. International mineralogical nomenclature recommends reserving this term only for hemimorphite.

Typology:
Smithsonite forms in the oxidized zone of zinc deposits, particularly in carbonate environments where it can form substitution bodies. It is a very occasional secondary mineral in pegmatites.

Hydrozincite – $Zn_5(CO_3)_2(OH)_6$

Secondary ore	
Common mineral	*Anhydrous carbonates (Figure 9)*
Ore mineral	Zn
Hazard	Zn ?

The TARANTULA project has received funding from the European Union's EU Framework Program for Research and Innovation Horizon 2020 under Grant Agreement No 821159 - https://h2020-tarantula.eu

Hydrozincite is a hydrated carbonate that forms under arid conditions in the oxidized zone of zinc deposits. Hydrozincite rarely forms small colorless and transparent acicular to lamellar crystals, rarely larger than 1 mm, lining geodes and fissures in karstic cavities. It generally occurs as concretionary incrustations with a fibrous texture, as earthy or chalky masses having a stalactitic, pisolitic or reniform aspect.

It is snow white, gray, yellowish, and may be colored brownish or reddish by iron oxides. Hydrozincite is very abundant and mined in the Comillas deposit, near Santander (Spain), which has also yielded some beautiful millimeter-size crystals.

4.1.2.8 ARSENIC

Arsenic is present in the vast majority of mineralisation. Its most common form, capable of representing several percent in mineralization, is arsenopyrite.

Arsenopyrite ($FeAsS$)

Primary ore	**Arsenopyrite group**
Very common mineral	*Sulfide (Figure 8)*
Ore mineral	As
Potential Ore Mineral	Au, Co
Hazard	As, Sb

Arsenopyrite, previously called "mispickel", is a common mineral in hydrothermals deposits, particularly in high-temperature hydrothermal gold veins (gold-bearing "shear-zones" of Canada, France and West Africa), and tin-tungsten veins (Europe), as well as in pyrometasomatic deposits (notably skarns). It is less common in massive sulfide deposits. This presence probably affirms that arsenopyrite is the most abundant sulfide after the four "majors": pyrite, galena, sphalerite and chalcopyrite.

Arsenopyrite commonly occurs as prismatic crystals, elongate or short, forming pseudo-orthorhombic octahedrons, which can be centimeter size with striated faces. It also occurs as massive granular aggregates with lozenge-shaped sections and possibly a radiate texture. Auriferous arsenopyrite, very rare, has a particular habit that is highly acicular derived from the integration of gold atoms in its lattice: the gold content can be as much as 1.6%, which makes it a valuable gold ore (deposits in Ghana and at Châtelet, Creuse, France). IN this case, the gold is present in ionic form, and thus invisible under the microscope.

Arsenopyrite is a silver white to light steel gray mineral, with ablack or black-gray streak, which gives off a characteristic odor of garlic when hit with a hammer. It weathers easily to green scorodite. It commonly contains cobalt (variety variety danaite: up to 12% Co). It accompanies most of the metallic sulfides in a generally quartzose gangue.

Typology:

Arsenopyrite is found in high- and medium-temperature hydrothermal deposits, mainly veins and pyrometasomatic deposits. It is found more rarely disseminated in metamorphic rocks, basic rocks and pegmatites.

Scorodite - $Fe^{3+}AsO_4 \cdot 2H_2O$

Secondary ore	Variscite group
Very common mineral	*Hydrated arsenate (Figure 13)*
Potential Ore Mineral	As
Hazard	As

Scorodite is the most common of the arsenopyrite and löllingite alteration products.

It is found in the oxidized zone of arsenic deposits as light-green cryptocrystalline incrustations with an earthy or banded appearance.

Crystals are rare, dipyramidal {111}, elongate along [010] or flattened on {001}, generally millimeter size, but exceptionally larger than a centimeter. Bluish green to bottle green or greenish brown in natural light, some crystals become blue to violet in artificial light (alexandrite effect).

The replacement of iron by aluminum being very weak (less than 6% Al_2O_3), the solid solution toward mansfieldite is thus very limited.

At Gold Hill and Tintic (Utah), scorodite was sufficiently abundant to be worked as arsenic ore.

Scorodite is a very local ore for arsenic.

Adamite - $Zn_2(AsO_4)(OH)$

Secondary ore	Olivenite group
Common mineral	*Anhydrous arsenate (Figure 12)*
Potential Ore Mineral	Co, Zn
Hazard	As

Adamite is a common arsenate in the oxidized zones of arsenic-rich zinc deposits, where it accompanies olivenite, smithsonite, malachite and other secondary zinc and copper minerals. It is the first of the zinc arsenates to form under both acid and basic conditions. The replacement of zinc by copper gives rise to a complete (albeit imperfect) solid solution with olivenite.

Adamite generally forms radiating aggregates or spherulitic incrustations with a mammillated surface, but it is occurs as commonly elongate prismatic crystals. Its color is varied: generally yellow to brownish-yellow or light-blue to green, it is brilliant green in the cupriferous variety (cuproadamite), and pink to purple in the cobaltiferous (cobalto-adamite) or manganiferous variety.

Glaucodot – $(Co_{0.5},Fe_{0.5})AsS$

Primary ore	Arsenopyrite group
Rare mineral	*Sulfide (Figure 8)*
Potential Ore Mineral	Co
Hazard	As

Glaucodot (Arsenopyrite Group, dimorph: alloclasite) is a rare mineral present in high-temperature hydrothermal deposits with iron and cobalt, possibly copper. Its structure is similar to that of, however, it does not form a continuous series: the iron content of glaucodot ceiling at 22%.

Glaucodot forms prismatic crystals, elongate along [001] and more rarely along [010], striated along [001], and no larger than 2 cm; rarer are pseudo-orthorhombic octahedrons or lamellar aggregates. Cruciform twinning is fairly common.

Tin white with a pinkish hue and a metallic luster, glaucodot accompanies pyrite, arsenopyrite and the classic suite of cobalt and nickel minerals (nickeline, alloclasite, safflorite).

Löllingite - $FeAs_2$

Primary ore	Löllingite group
Uncommon mineral	*Arsenide (Figure 11)*
Hazard	As

Löllingite is an uncommon iron arsenide. It is mainly found in high temperature hydrothermal deposits, often in connection with granitic intrusions: gold veins, stanno-wolframifers, or polymetallics - notably the old Ni-Co-Bi-Ag-U- formations, sometimes pegmatites and skarns.

Löllingite can form elongated and striated, bipyramid prismatic crystals, but usually occurs in flabelliform fracture masses, bacillary aggregates, or fibroradiated nodules. Its shine is metallic, its silver white color tarnishing fairly quickly in light steel gray. Like arsenopyrite, it easily deteriorates to scorodite on outcrops.

Réalgar- As_4S_4

Primary ore	
Common mineral	*Sulfide (Figure 8)*
Ore mineral	As
Hazard	As

Realgar is, with orpiment, the most common of the arsenic sulfides.

It occurs in low-temperature hydrothermal deposits, mainly in epithermal deposits, directly related to recent volcanism, and in certain fumarole deposits. It is generally associated with orpiment, cinnabar or stibnite.

A priori, this mineral will therefore not be encountered in refractory metal deposits

Realgar is transparent to translucent yellow-orange to orange red and has an adamantine to resinous luster. The mineral is sectile and has perfect cleavage along {010}. It is highly photosensitive: the crystals crack when exposed to light and alter to a yellow arsenolite – orpiment powder. Realgar form prismatic to acicular crystals striated along [001], granular masses, local concretionary crusts (fumarole deposits).

Realgar was a major arsenic ore that was intensely mined. Now arsenic is mainly recovered from arsenopyrite, a common mineral in many gold mines.

Orpiment- As_2S_3

Primary ore	
Common mineral	*Sulfide (Figure 7)*
Ore mineral	As
Hazard	As

Orpiment is an arsenic sulfide, slightly rarer than realgar with which it is commonly found in deposits.

It occurs in low-temperature hydrothermal deposits, mainly epithermal, directly dependent on recent volcanism, as well as in fumarole deposits. Other than realgar, it is commonly associated with pyrite, cinnabar and stibnite.

Like the realgar, this mineral will therefore probably not be encountered in refractory metal deposits.

Transparent to translucent, orpiment is lemon yellow to orange-yellow, passing to brownish in the large crystals, with a perfect flaky cleavage along {001}, and a resinous luster. It gives of a strong characteristic smell of sulfur.

Orpiment generally occurs as foliaceous, fibrous or columnar aggregates (as much as 35 cm in section) with a flabellate fracture, and commonly as short prismatic crystals showing shiny, vertically striated and possibly deformed, {010} faces.

Orpiment is the end weathering/alteration product of arsenic sulfides, and is thus stable in outcrop; it nevertheless tends to tarnish and form powdery heaps.

Orpiment was an important ore for arsenic.

4.1.2.9 ANTIMONY

Interpretation of the detailed mineralogy of this metal is in progress

Antimony is not a metal likely to be found in abundance in refractory metal deposits. However, due to the toxicity of this heavy metal, it is advisable to search in the ores and gangues of these deposits for the presence of the main antimony ores in order to assess the environmental hazard.

Stibnite- Sb_2S_3

Primary ore	Stibnite group
Common mineral	*Sulfide (Figure 7)*
Ore mineral	Sb
Hazard	Sb, As

Stibnite is the commonest of the antimony minerals and also the main antimony ore. It is a mineral of hydrothermal deposits that forms over a wide range of temperatures.

With a metallic luster, and a lead gray color and dust, it has a subconchoidal fracture and an excellent cleavage along (010). Crystals are common: elongate to acicular prismatic along [001] with a great richness of terminal faces, the prism faces being striated or fluted parallel to the elongation. Flexible, it melts in a candle flame, whilst coloring it blue-gray.

In outcrop, stibnite weathers easily to white to yellowish oxides, possibly as pseudomorphs (the antimony "ochers": stibiconite, cervantite, etc.), commonly accompanied by red spotty coatings of kermesite.

Berthierite- $FeSb_2S_4$

Primary ore	Berthierite group

Common mineral	*Sulfide*
Potential Ore Mineral	Sb
Hazard	Sb, As

Berthierite is an antimony and iron sulfide that occurs in low- and medium-temperature hydrothermal veins, commonly in association with quartz, barite and stibnite.

Free crystals are elongate, commonly acicular, striated longitudinally along [001]: they are, however, exceptional and do not exceed 1 cm. Berthierite generally forms masses that are fibrous (more common than with stibnite), feathery or radiate with a radius as much as 6 cm, or granular.

Fresh berthierite is steel gray in color similar to stibnite, but is iridescent and tarnishes rapidly on exposure to air to give a bronze patina that darkens with time.

Berthierite oxidizes easily in outcrop to form a mixture of iron and antimony oxides ("chocolate" oxides) that generally retain the fibrous configuration of the replaced mineral.

Berthierite is a less interesting antimony ore than stibnite because of its lower grade in this metal (57% as against 72%) and the fact that it is more difficult to roast.

4.1.2.10 MERCURY

Interpretation of the detailed mineralogy of this metal is in progress

Mercury is one of the heavy metals to be systematically sought in mine tailings because of its toxicity. It is, however, unlikely to encounter significant quantities of mercury ore minerals (cinnabar or calomel) in wastes from refractory metal mines whose models do not correspond to those favouring its concentration.

However, this metal has the characteristic of entering as an impurity in sphalerite. Thus, a potential mercury hazard can be attached to rocks containing the faith of sphalerite.

Cinnabar- HgS

Primary ore	
Common mineral	*Sulfide*
Ore mineral	Hg
Hazard	Hg

Cinnabar is a sulfide of low-temperature hydrothermal deposits related to recent volcanism, also present in volcanic fumaroles (Monte Amiata, Italy).

It generally occurs as granular masses with a visible cleavage. Its color is crimson to vermilion red that tarnishes brownish red then black-gray, and it has an adamantine luster, with a scarlet streak. At Almaden (Spain), it sweats fine droplets of native mercury.

Crystals (pseudohexagonal rhombohedral and thick tablets flattened along {0001}) larger than 1 cm are rare.

Almaden (Spain), the largest mercury mine in the world, has only yielded rare small crystals hardly bigger than 10 mm.

Cinnabar is the only mercury ore currently mined in less than 10 mines worldwide.

Calomel - $([Hg^{1+}]_2)Cl_2$

Secondary ore	
Rare mineral	*Chloride (Figure 21)*
Potential Ore Mineral	Hg
Hazard	Hg

Calomel is a rare chloride found in the surficial oxidized zone of mercury deposits, notably in desert regions. It results from the alteration of cinnabar in a chloride-rich environment, such as provided by outcropping evaporites or salt-laden air (if the deposit is close to the sea). Other than cinnabar, calomel is almost invariably accompanied by eglestonite, another mercury chloride.

Crystals are rare, commonly complex, with many faces, generally square and tabular on {001} or elongate prismatic along [001].

The mineral is grayish or yellowish gray, tending to black when exposed to light, with a strong adamantine luster. Not very hard (1 to 2), it is very dense (more than 7), plastic and highly sectile. It fluoresces in a characteristic brick red.

4.1.2.11 LEAD

Lead is extremely common in a large number of deposits. Not valued in refractory metal mines, it will a priori meet in the latter's releases.

Although galena is the only ore exploited today, the old mining works having mainly exploited the superficial parts of the deposits, it will also be necessary to focus on secondary ores of lead.

A lead hazard can therefore be attached to the deposits that contain the ores of this metal.

Galena - PbS

Primary ore	Galena group
Very Common mineral	*Sulfide (Figure 6 Figure 7)*
Ore mineral	Pb
Potential Ore Mineral	Ag
Hazard	Pb, Bi

Galena is the most common of the lead minerals and one of the most abundant sulfides in nature, after pyrite, and with sphalerite and chalcopyrite. It is also practically the only ore of lead mined today.

Galena has a cubic structure identical to that of NaCl. It normally forms cubic, cubo-octahedral or octahedral crystals with up to 1 m sides, more rarely it forms tabular crystals flattened along {001}, reticulate or dendritic masses, skeletal crystals; also occurs s cleavable, coarsely or finely granular masses with the three orthogonal cleavage directions imparting a characteristic "staircase" aspect, or exceptionally as fibrous and feathery aggregates.

It has a metallic luster, is lead gray with slightly bluish glint, and a high density (7.6). Its lattice can admit atoms of silver, bismuth, etc., which can make a workable ore of silver.

Galena deposits are innumerable: low- and medium-temperature hydrothermal lead-zinc-silver veins, volcano-sedimentary and sedimentary deposits, skarn-type metasomatic deposits, hydrothermal replacement in limestone, etc. Galena is also found in pneumatolytic veins and exceptionally in pegmatites.

Cerussite - $PbCO_3$

Secondary ore	Aragonite group
Very Common mineral	*Anhydrous carbonates (Figure 10)*
Ore mineral	Pb
Hazard	Pb

Cerussite is the most common of the lead carbonate minerals present in the oxidized zone of lead deposits. It results from the alteration of galena, commonly with an intermediate passage via anglesite, unstable in the presence of CO_3 ions. Its development is greater with a carbonate country rock and an arid climate.

Crystals are common and can be very large (several kilos). They are elongate, commonly flattened, prismatic, pseudohexagonal, and also pseudoisoscelohedral. They are commonly twinned, forming spectacular reticulate assemblages with angles of 60° and 120°, or more rarely heart-shaped twins. Cerussite also forms compact or earthy masses, and skeletal laths that can be stalactitic.

Transparent as crystals, also opaque as a mass, cerussite has a characteristic high density (more than 6.5). Pure, it is colorless with an adamantine luster, but it is commonly blackened by inclusions of galena, or colored gray, yellow, green, blue or red by metal oxides.

Cerussite is locally an important lead ore, notably in calcareous rocks where all the surficial part of the deposits may have been altered to a cerussite - anglesite assemblage.

Anglésite - $PbSO_4$

Secondary ore	**Baryte group**
Very Common mineral	*Anhydrous sulphate (Figure 15)*
Ore mineral	Pb
Hazard	Pb

Anglesite is a secondary mineral from the oxidized zone of lead deposits and forms under acid conditions. With diminishing acidity of the environment, it disappears to the benefit of cerussite.

Formed through the weathering of galena, which may persist at the core the masses, anglesite is associated with other lead and zinc oxides (smithsonite, cerussite, hemimorphite) as well as sulfides (galena, sphalerite, etc.).

The crystals are generally squat to elongate, but never acicular, reminiscent of barite; they are commonly tabular and flattened along the cleavage. Anglesite is also massive, concretionary, stalactitic or nodular. With a high density (more than 6.3), it is transparent to translucent, with an adamantine, almost metallic, luster. It is colorless, grayish white, and possibly yellow, green, blue; it may even be black from the presence of fine inclusions of galena.

Pyromorphite, Campylite - $Pb_5(PO_4)_3Cl$

Secondary ore	**Apatite group**
Common mineral	*Anhydrous phosphate (Figure 17)*
Potential Ore Mineral	Pb
Hazard	Pb

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Pyromorphite is a common secondary mineral of the oxidized zone of lead deposits, the phosphorus necessary for its formation coming from the apatite of the surrounding rocks.

It belongs to the apatite group and is the phosphorus end-member of the pyromorphite-mimetite-vanadinite series. Other elements are commonly present as traces: calcium, chrome (terms extending to the mimetite member), possibly radium (Grury, Saône-et-Loire, France). The color of pyromorphite is varied: yellow, brown, or green, possibly highly luminous. It generally crystallizes as hexagonal prisms, commonly cavernous, commonly more or less elongate, locally evolving to an acicular facies. The acicular crystals are commonly combined into radiate groups, locally forming tight bands or mammillated incrustations.

Due to its magnificent colors, pyromorphite is highly valued by collectors.

Mimétite – $Pb_5(AsO_4)_3Cl$

Secondary ore	Apatite group
Common mineral	*Anhydrous arsenates (Figure 12)*
Ore mineral	
Potential Ore Mineral	
Hazard	As, Pb

Mimetite belongs to the apatite group and is the arsenic end member of the mimetite - pyromorphite – vanadinite series. Very similar in appearance to pyromorphite, which is at the origin of its name, it is much rarer than the latter with which it forms a continuous series.

Like pyromorphite, mimetite is found in the oxidized zones of lead deposits. When pure, mimetite is colorless to yellowish with an almost adamantine luster. That is a very rare case, the crystals being much more commonly yellow, orange-yellow to orange-red with a resinous luster, possibly green. The crystals are prismatic capped by a pyramid, or form hexagonal casks with curved edges (campylite facies), or the mineral occurs as reniform to globular masses.

Vanadinite – $Pb_5(VO_4)_3Cl$

Secondary ore	Apatite group
Common mineral	*Vanadates (Figure 22)*
Hazard	As, V, Pb

Vanadinite structurally belongs to the apatite group in which it forms a partial series with mimetite and a very limited series with pyromorphite. The 'endlichite' variety is defined when the V/As atomic ration is close to 1.

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This oxidation mineral is found mainly in the gossans of lead deposits, associated with other minerals of vanadium (mottramite, descloizite, etc.) and lead (cerussite, anglesite, etc.). The vanadium derives from the oxidation of vanadium-bearing sulfides or of the country rock through silicate leaching.

The most common habit of vanadinite is the short terminated prism, with a hexagonal outline, locally hollow; commonly the crystals form prisms that are very flattened on {0001} giving the appearance of thick lamellae. Fibrous or globular facies are rare. Its bright red to orange-red color can pass to brown in the varieties with arsenic substitution (endlichite variety).

Semseyite – $Pb_9Sb_8S_{21}$

Primary ore	Apatite group
Common mineral	*Sulfosalt (Figure 7)*
Potential Ore Mineral	Ag, Sb, Pb
Hazard	Pb, Sb

Semseyite is a lead – antimony sulfosalt common in medium-temperature hydrothermal veins. It is found, like boulangerite, jamesonite, zinkenite and plagionite, in dominantly stibnite veins invaded by plumbiferous fluids, and in galena - sphalerite veins infiltrated by antimoniferous fluids. It is associated mainly with galena, sphalerite, and other sulfosalts such as bournonite, zinkenite and jamesonite.

Gray to black in color, it forms lamellar crystals, elongate along [010] and flattened on {001}, possibly twisted, commonly joined into radiate aggregates. Semseyite weathers easily in outcrop to give mixed antimony and lead oxides.

Semseyite is locally worked as antimony or lead. At Rode (Ally, Haute-Loire, France), for example, it was an important ore of lead (and silver due to its association with many silver sulfosalts).

Wulfénite – $Pb(MoO_4)$

Secondary ore	Scheelite group
Common mineral	*Molybdate (Figure 20)*
Potential Ore Mineral	Mo, W
Hazard	Pb

Due to its bright orange to red color, wulfenite is one of the most remarkable of the secondary lead minerals.

Formed mainly in an arid or semi-arid climate, it is a fairly rare lead molybdate with an atomic structure identical to that of scheelite and powellite. The molybdenum can be partly replaced by tungsten (more than 20% WO_3 in the chillagite variety), and part of the lead by calcium. It forms an isomorphous series with stolzite (lead tungstate).

Wulfenite invariably occurs as clear crystals, the facies being closely dependent on the acidity (pH) and oxidizing character (Eh of the environment of crystallization: thin square tablets, denoting a low Eh and high pH, are the most common; elongate tetragonal octahedrons, indicating high Eh and pH, are rarer; finally, for low Eh and pH, it forms thick crystals with a dominant (001) face associated with pyramids (not very common).

The color is generally yellow, orange to orange-red, becoming bright red in the presence of chrome (1 to 3%: Iranian deposits at Anarak). It is exceptionally colorless or grayish. Its luster is very bright due to its high refractive index (2.4), which is the highest of all the lead minerals lead.

Bournonite – $PbCuSbS_3$

Primary ore	**Bournonite group**
Common mineral	*Sulfosalt (Figure 6)*
Potential Ore Mineral	Mo, W
Hazard	Pb

Bournonite is a fairly common sulfantimonide in medium- and low-temperature hydrothermal veins. It commonly accompanies galena, pyrite, sphalerite, tetrahedrite, chalcopyrite, fluorite and barite, among others.

It occurs as flattened pseudoquadratic crystals, commonly implanted on the side with the striated prism faces, as short to tabular prismatic crystals with grooved faces as much as 11 cm, and as compact, possibly granular, masses.

Bournonite is in particular famous for its characteristic cruciform twinning, poetically denominated as "wheel ore" or "cogwheel ore". It has a commonly bright metallic luster and a steel gray color tensing to iron black or darkish lead gray.

Highly alterable in outcrop, bournonite commonly gives rise to a suite of variously colored copper, lead and antimony oxides.

Boulangerite, Plumosite – $Pb_5Sb_4S_{11}$

Primary ore	
Common mineral	*Sulfosalt (Figure 7)*
Hazard	Pb, Sb

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Boulangerite is a common sulfosalt in medium-temperature hydrothermal lead-antimony veins: it is found, like jamesonite, semseyite, zinkenite and plagionite, in dominantly stibnite veins invaded by lead-bearing fluids or in sphalerite - galena veins infiltrated by antimony-bearing fluids.

Well-formed crystals are very rare; they are prismatic and deeply striated longitudinally along [001], possibly acicular. Boulangerite almost invariably forms capillary fibers or fibrous masses, commonly asbestiform ("plumosite" variety). It alters easily in outcrop to give mixtures of antimony oxides and varied lead oxides.

Its color is black-gray to bluish lead gray, and its luster is metallic.

Exceptional samples of the plumosite variety were discovered around 1940 at Príbram (Czech Republic): they are acicular crystals of as much as 30 cm, and the most beautiful specimens in the world.

4.1.2.12 CADMIUM

Like mercury, cadmium is one of the heavy metals to be systematically sought in mine tailings because of its toxicity. It is, however, unlikely to encounter significant quantities of greenockite, the only true Cadnium ore, in wastes from refractory metal mines whose models do not correspond to those favouring its concentration.

However, this metal has the characteristic of entering as an impurity in sphalerite, which can thus become a potential mineral for this metal. Thus, a potential cadmium hazard can be attached to rocks containing the faith of sphalerite having or not trace minerals (93 minerals) of the presence of cadmium.

Greenockite – CdS

Primary ore	Wurtzite group
Common mineral	*Sulphide*
Ore mineral	Cd
Hazard	Cd

Greenockite is a relatively common hydrothermal mineral present in zinc-rich hydrothermal veins containing cadmium, as well as in the cavities of certain basic rocks.

It is the most common of the cadmium minerals. It generally forms powdery lemon-yellow coatings or earthy incrustations on sphalerite and contiguous minerals; it has an adamantine to resinous luster. Crystals are very rare; they are hemimorph pyramidal with a conic or tabular termination, and scarcely exceed 1 cm.

4.1.2.13 BISMUTH

In ores, bismuth occurs in the **native** state, combined with sulphur in the form of **bismuthinite**, Bi_2S_3, or complex sulphides with lead and copper, combined with oxygen in the form of **bismite**, Bi_2O_3, or combined with tellurium and selenium.

Bismuth is mainly, at 90-95%, co-produced during the metallurgies of lead and tungsten, but also, to a lesser extent, by those of copper, tin, silver and gold. In China and Vietnam, bismuth is often co-produced with tungsten, with ore contents of 0.006% Bi in China and 0.10% in Vietnam.

In Vietnam, the Nui Phao open-cast mine had a production of 20,000 t of WO_3 contained in ammonium paratungstate, 9,200 t of Cu contained in copper concentrates and 2,000 t of Bi in 2021.

Bismuth – Bi

Primary ore	
Common mineral	*Native*
Ore mineral	Bi
Hazard	

Native bismuth is a fairly common mineral in high-temperature hydrothermal veins linked to granitic intrusions. Bismuth is found in hydrothermal quartz veins associated with silver, gold, cobalt, nickel, uranium or tin minerals. It is rare in cassiterite- and topaz-bearing granitic pegmatites as wall as in alluvium. It is commonly associated with many minerals: arsenopyrite and löllingite, wolframite, cassiterite, gold, bismuth sulfides, more rarely nickeline and rammelsbergite or silver sulfides (Erzgebirge deposits).

Bismuth is pinkish white with a bright metallic luster, but tarnishes rapidly to a dirty brown, or alters to bismutite (the carbonate) or bismite (the oxide).

It generally occurs as arborescent, reticulate or shapeless masses with cleavages, and as dendritic, skeletal or arborescent aggregates (Schneeberg and Johanngeorgenstadt, Saxony, Germany).

Masses of 150 kg have been obtained from Kingsgate (Australia), and from large strips of the Bolivian tin mines (Oruro, Llallagua, Tazna, etc.) and Madagascan tin mines (Ampangabé), whilst Meymac and Puy-les-Vignes (W deposit, Limousin, France) have yielded smaller masses of up to 250 g.

Bismuthinite – Bi_2S_3

Primary ore	
Common mineral	*Sulphide*
Tracer mineral	Bi
Hazard	

Bismuthinite is an accessory mineral of high-temperature hydrothermal mineralization associated with granitoid intrusions, notably tin and tungsten deposits, and is also found in pegmatites (Madagascar), gold-bearing veins (Salsigne, France), and fluorite – siderite veins. It commonly accompanies native bismuth, arsenopyrite, cassiterite and wolframite.

Fairly rare as finely striated squat to acicular prismatic crystals, reminiscent of stibnite, bismuthinite generally occurs as lamellar aggregates, foliated, fibrous or granular cleavable masses, also similar to stibnite.
It is lead-gray to tin white mineral that commonly tarnishes to yellow or to a surface iridescence, and which alters easily to bismutite in outcrop.

The best samples come from the Bolivian tin province: Tazna (perfect crystals of 8 cm), Llallagua, Huanuni. Other outstanding samples come from Cornwall (England), Ehrenfriedersdorf (Saxony, acicular crystals of 10 cm), Spind (Norway), as well as from the Madagascan pegmatites that enclose large decimeter-size crystals commonly highly altered to bismutite and bismite. In France, centimeter-size blades come from Meymac (Corrèze).

Bismite – Bi_2O_3

Primary ore	
Rare mineral	*Oxide*
Tracer mineral	Bi
Hazard	

Bismite is a rare bismuth oxide that forms yellow to yellow-gray and grayish green, earthy to powdery, possibly compact, masses; the crystals are microscopic.

Bismite forms in the weathering zone of bismuth-bearing deposits.

It is a high-density mineral (more than 8) that derives from the oxidation of bismuth minerals in the surficial zone of high-temperature veins. In collection samples, it is commonly confused with the bismuth carbonate, bismutite.
The best specimens come from the pegmatites of Madagascar (Ampangabé, Fefena), but bismite is much more common in the tin, lead, silver and bismuth veins of Bolivia (Oruro, Llallagua, Colavi, etc.). It is found in the polymetallic silver veins at Schneeberg (Saxony,

Germany) and the Californian pegmatites of Pala and Rincon.
In France, it has been collected in the oxidized zone of the Maymac bismuth vein (Corrèze).

Bismutite – $(BiO)_2CO_3$

Primary ore	
Common mineral	*Carbonate*
Potential ore mineral	Bi
Hazard	

Bismutite is the usual mineral resulting from the supergene alteration of native bismuth and bismuthinite.
It is found in the oxidized zone of bismuth-bearing hydrothermal deposits, notably the epithermal gold deposits and the polymetallic "Ni-Co-Bi-Ag-U" type veins, and possibly in pegmatites.
Crystals are very rare; bismutite mainly forms medium- to dark-gray or olive-brown, rarely white to pale-yellow, powdery masses or spheroidal aggregates with an earthy fracture. Its identification is possible by the fact that it effervesces in cold acids and by its high density (8.1 to 8.3).
The most spectacular specimens of bismutite come from the Ampangabé pegmatites (Madagascar): they are pseudomorphs of bismuthinite crystals weighing several kilos. The Pilgrim's Rest deposit (South Africa) has yielded beautiful 5-mm crystals joined into tufted aggregates. Good samples have been found at Johanngeorgenstadt (Germany) and Beresovsk (Urals, Russia), as well as in many American deposits.
In France, bismutite exists in the surficial part of the Meymac bismuth veins (Corrèze).

Aïkinite – $PbCuBiS_3$

Primary ore	
Uncommon mineral	*Sulphide*
Tracer mineral	Bi
Hazard	

Aikinite is an uncommon sulfide of Cu-Bi-Pb in high-temperature hydrothermal veins and gold-bearing veins. Lead gray to steel gray in color, it forms fluted acicular crystals or rods set in quartz, as much as 3 cm in size, that may be grouped into radiate aggregates. More rarely aikinite forms compact masses where it mixes with other sulfides and sulfosalts (galena, chalcopyrite, enargite, etc.).
The best crystals in the world come from the Beresovsk gold veins (Urals, Russia) where they form exceptional centimeter-size tufts. Good samples are also reported from the Sunnyside gold mine (Colorado, United States) as well as in many other mines in Colorado, Arizona

(Bisbee) and Nevada.
In France it is found in the small La Gardette gold lode (Isère).

Cosalite – $Pb_2Bi_2S_5$

Primary ore	
Common mineral	*Sulfosalt*
Potential ore mineral	Bi
Hazard	

Cosalite is a relatively common mineral in medium-temperature Pb-Bi-Cu-bearing hydrothermal veins and in contact metamorphic deposits.
It can occur as commonly fibrous to acicular and capillary prismatic crystals, with elongation along [001], but is generally massive, forming fibrous or feathery aggregates with a radiate texture. It is lead gray to steel gray with a metallic luster. On weathering it commonly becomes covered with a thin green skin of malachite.
Beautiful crystals come from the Nordmark deposit (Sweden). Good samples are also reported in several American mines of Arizona (Magma), California (Darwin), and Colorado (Red Mountain), as well as in the Transylvanian gold deposits of Romania (Cavnic, Moravita).

Emplectite – $CuBiS_2$

Primary ore	Chalcostibite Group
Rare mineral	*Sulfosalt*
Tracer mineral	Bi
Hazard	

Emplectite is a rare copper – bismuth sulphide from from high- and medium-temperature hydrothermal metalliferous veins where it is associated with other minerals of these two metals, notably wittichenite. It forms elongate to acicular prismatic crystals, striated parallel to [001], normally not very spectacular. Its luster is metallic, its colour greyish to tin white, becoming bronze through oxidation. Pseudomorphs in mixite are common. Good centimetre-size crystals have been discovered in France (Faymont, Vosges, as free crystals in quartz geodes), and in the Erzgebirge mountains (Pechtelsgrün, Johanngeorgenstadt, Germany, and Horní Slavkov, Czech Republic, as needles in quartz – barite geodes).

Joséite – Bi_4TeS_2

Primary ore	Chalcostibite Group
Rare mineral	*Sulphides*
Tracer mineral	Bi, Te
Hazard	

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Joséite (sometimes called joséite-A) is a fairly rare bismuth sulfo-telluride, silver-white in colour, tarnishing with iridescence, which comes in sheets or flexible plates with a metallic luster, sometimes of good size (5 cm). Not to be confused with joséite-B, similar in composition but richer in tellurium.

Joséite is a hydrothermal mineral mainly distributed in high temperature veins, pegmatites and bismuth-rich skarns. It is also an alluvial mineral.

Joséite is known in San José (Brazil), its type locality, in several English sites (Carrock Fell, Coniston, etc.), Australian (Kingsgate pegmatite, Maldon), Canadian (Glacier Gulch, Windpass mine, etc.), Czech (Smolotely), Uzbeks (Kosh-Bulak), and Russians (Sokhoi Log deposit), in particular. Alluvial joséite occurs in the Clear Creek and Highet Creek placers in the Canadian Yukon.

Mixite – $BiCu_6(AsO_4)_3(OH)_6 \cdot 3H_2O$

Primary ore	Mixite Group
Common mineral	*Arsenate*
Tracer mineral	Bi, Te
Hazard	As

Mixite is a fairly common bismuth – copper arsenate that forms millimeter-size striated acicular crystals, commonly grouped into clusters, rosettes, or incrustations. More rarely it forms small reniform masses with a fibrous texture. Its magnificent green to blue-green color is a good distinctive criterion.
It is an alteration mineral of the oxidized zone of copper and bismuth deposits.
Mixite is a common (locally abundant) mineral in the Tintic mining district (Utah), where the Mammoth Mine and its neighboring Boss Tweed Mine have yielded the most beautiful specimens known. It forms good crystals at Durango (Mexico), and was abundant in the surficial part of the Wittichen copper veins (Black Forest, Germany).

In France fibrous crystals of 15 mm come from the Roches Mine at Val d'Ajol (Vosges), and smaller specimens are found at Cap Garonne (Var).

Tetradymite – Bi_2Te_2S

Primary ore	Tetradymite Group
Common mineral	*Tellurides*
Ore mineral	Te
Hazard	

Tetradymite is the most common of the tellurides.

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The mineral is found mainly in low- to high-temperature gold veins, with the most classic deposits being those of Transylvania (Moravita and Sacarimb, Romania) and Colorado (Gold Hill). Here tetradymite is associated with different tellurides (hessite, altaite, petzite, etc.), native bismuth and native gold.

The mineral is steel gray, tarnishing grayish or iridescent, and had a metallic luster. It also has a perfect cleavage and splits into flexible lamellae. Crystals are rarely well formed: they are acute rhombohedrons with striated faces, reminiscent of hexagonal prisms, with common twinning associating four individuals. More commonly, tetradymite occurs as small foliate or lamellar masses. The Zubkov (or Schubkau) gold deposit, near Banska Stiavnica (Slovakia) has yielded the most beautiful crystals, of up to a centimeter, on a gangue of altered trachyte. The gold deposits of California (Carson Hill) and Colorado have also supplied beautiful crystals.

Witttichenite – Cu_3BiS_3

Primary ore	**Tetradymite Group**
Rare mineral	*Tellurides*
Tracer mineral	Bi
Hazard	

Wittichenite is a fairly rare sulfide of hydrothermal copper – bismuth veins.

Wittichenite crystals, prismatic or thick tabular, possibly acicular, are rare, the mineral generally occurring as microscopic steel-gray to tin-white patches with a metallic luster, although tarnishing to lead gray to brass yellow on exposure to air.

Millimeter-size crystals are found in the veins of the Wittichen district (Germany), its type locality, principally associated with emplectite. It is a mineral found in small amounts in many deposits in America (Butte, Bisbee), Peru (Colquijirca), Canada (Cobalt), etc. It is also reported in the Mangualde pegmatite (Portugal).

4.1.2.14 THALLIUM

Thallium minerals are rare species. We will list them here due to the very high toxicity of this metal

Crookesite – $(Cu,Tl,Ag)_2Se$

Primary ore	**Tetradymite Group**
Rare mineral	*Selenides*
Tracer mineral	Se
Hazard	Tl

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Crookesite is a rare selenide of hydrothermal copper veins.

Lorandite – $TlAsS_2$

Primary ore	Tetradymite Group
Very rare mineral	*Sulphides*
Tracer mineral	Tl
Hazard	Tl

Lorandite is an arsenic –thallium sulfide.

It is a very rare mineral of hydrothermal mercury and arsenic veins associated with the volcanism of young belts or with hydrothermally altered rocks (low-temperature hydrothermal deposits).

The crystals are short and squat, red to dark red, and have an adamantine luster. They are no larger than 10 mm.

Lorandite is found in less than 20 deposits worldwide; Allchar (Macedonia) and Lengenbach, near Binn (Switzerland), having provided the best specimens..

Hutchinsonite – $TlPbAs_5S_9$

Primary ore	Tetradymite Group
Very rare mineral	*Sulphides*
Tracer mineral	Tl
Hazard	Tl

Hutchinsonite is a very rare mineral, present in hydrothermal veins and in the hydrothermally altered dolomites at Lengenbach (Switzerland).

It forms rare prismatic to acicular pseudo-orthorhombic crystals possibly up to 1 cm in size, or radiate aggregates. Generally, it occurs as foliate or fibrous masses with a micaceous cleavage. It is scarlet to cherry red, tending to brown with the large crystals.

Hutchinsonite is found in less than 10 deposits worldwide; the most beautiful crystals are from Lengenbach (Switzerland), and in particular from the La Libertad mine (Peru).

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4.1.3 MINERALOGICAL CLASSES OF SIGNIFICANT MINERALS FROM RARE METAL DEPOSITS

Here we will present the diagrams illustrating the relationships between the various minerals mentioned in the previous chapter inside their mineralogical class. These diagrams illustrate the main combinations and or substitutions of metals that define the composition of a mineral.

4.1.3.1 OXIDES (CU-PB-ZN)

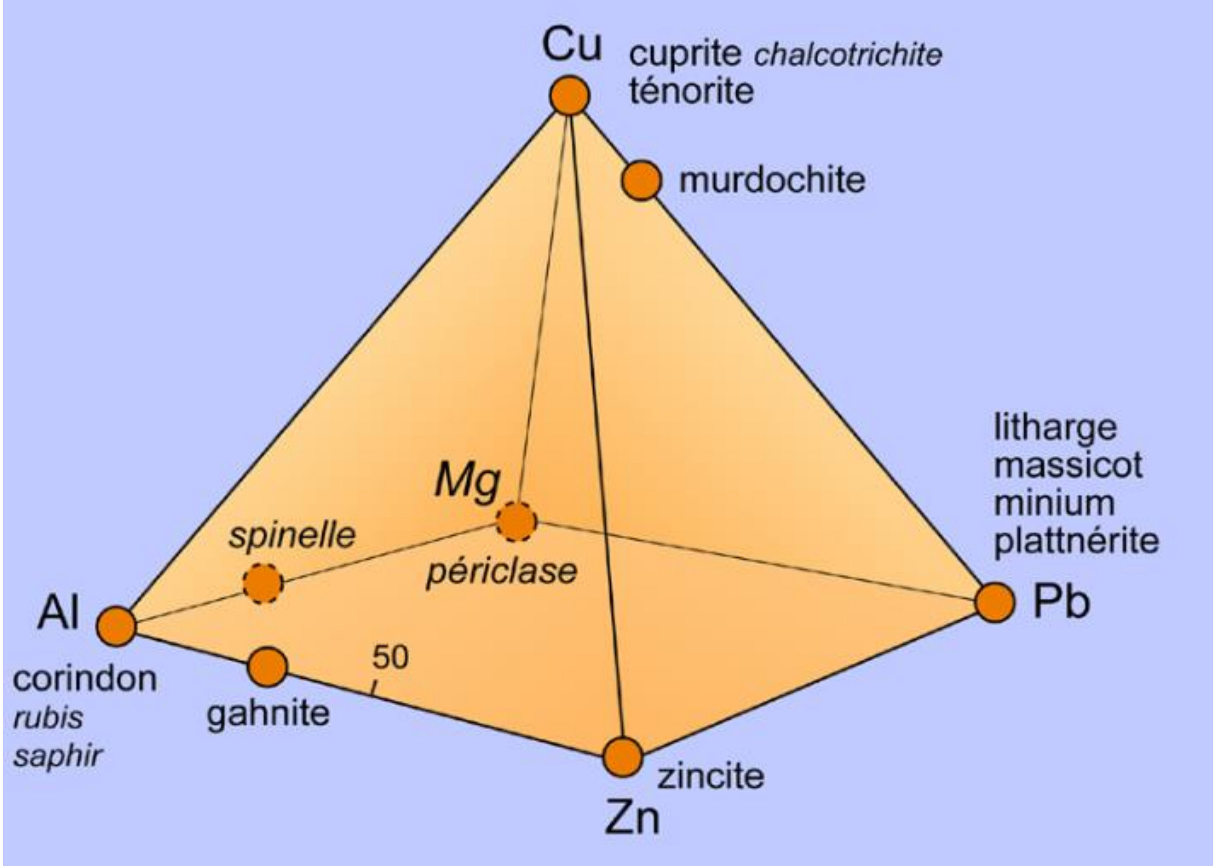

Figure 4: Composition of main base metal oxides

4.1.3.2 SULFIDES (CU)

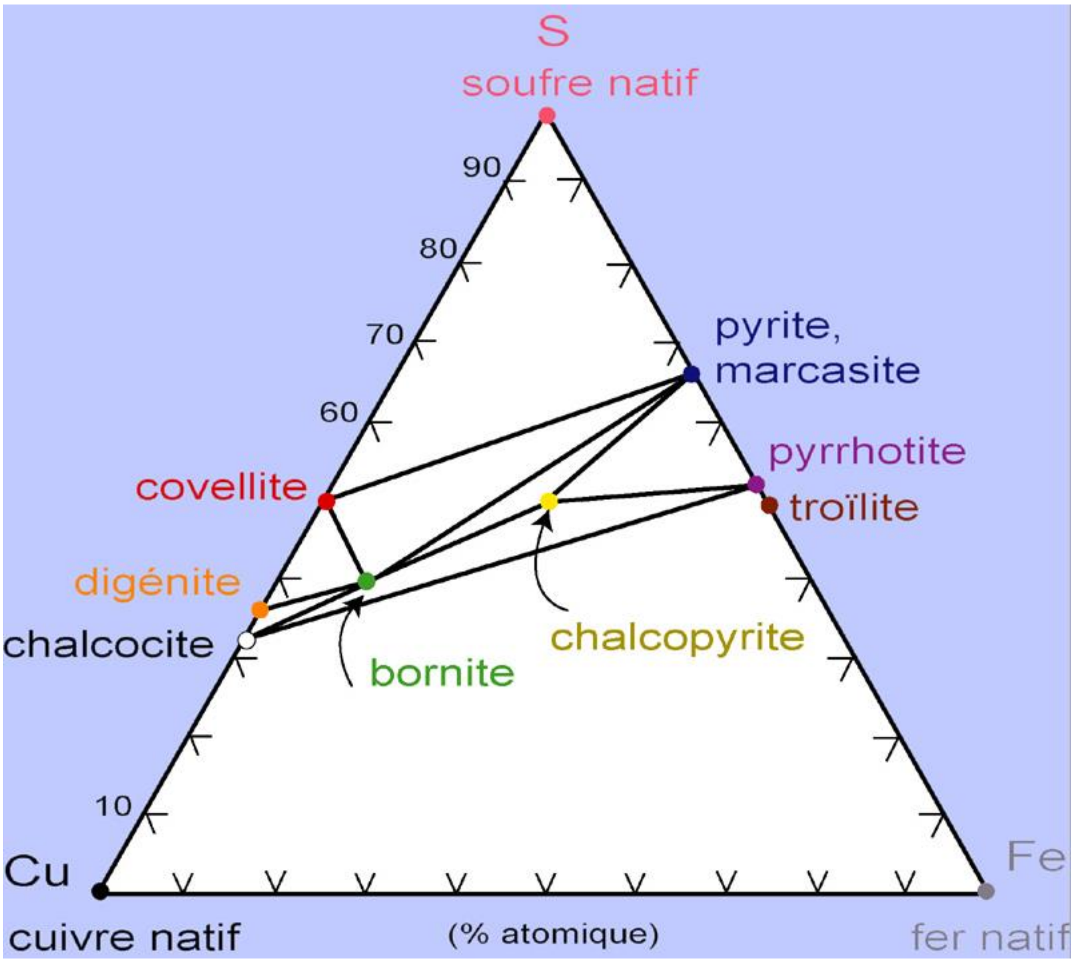

Figure 5: Position of the main copper sulphides in the Cu-Fe-S diagram

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4.1.3.3 MAIN SULFIDES AND SULFOSALTS IN THE SYSTEM PB-SB-CU

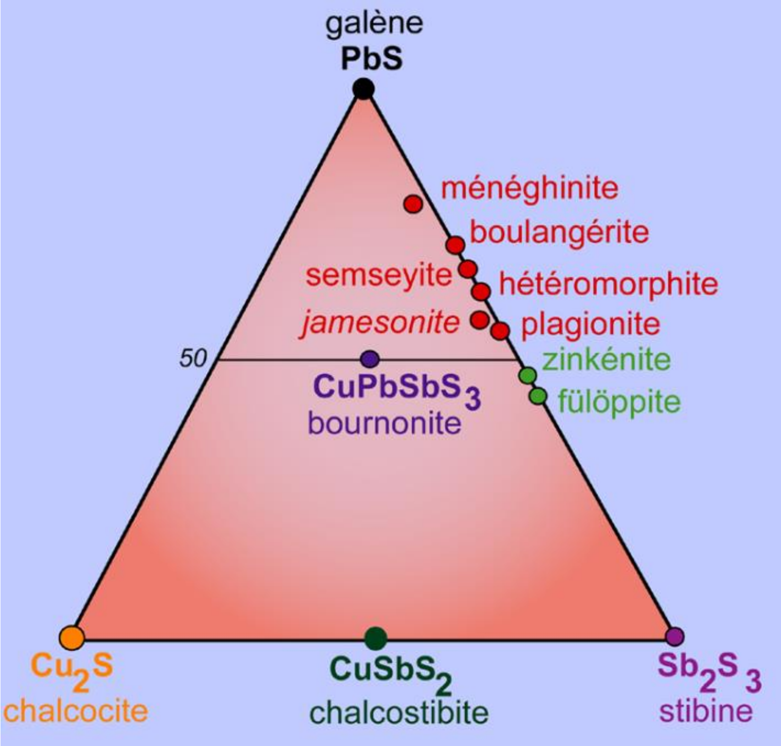

Figure 6: Diagram illustrating the position of the main sulphides and sulfosalts in the Pb - Sb - Cu system. The jamesonite (containing iron) in its chemical composition does not allow to register it rigorously in this diagram.

4.1.3.4 MAIN SULFIDES AND SULFOSALTS IN THE SYSTEM PB-SB-AS

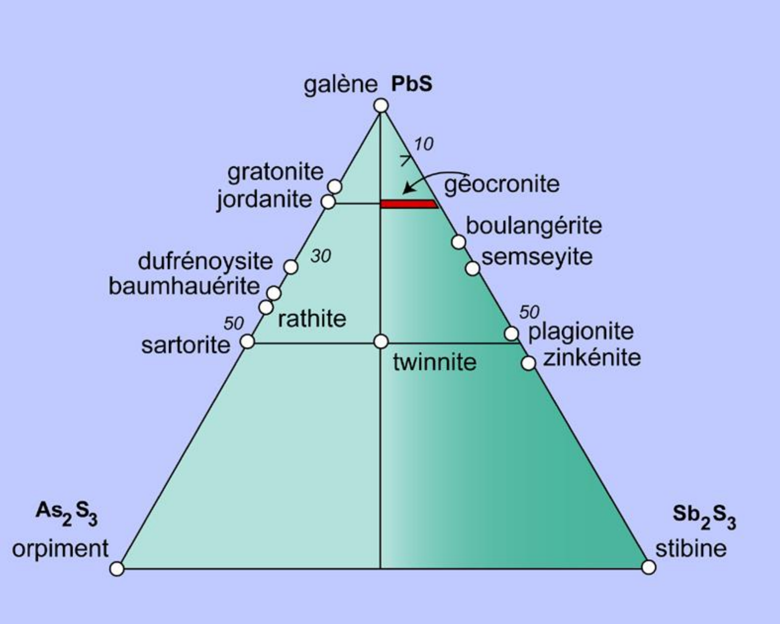

Figure 7: Diagram illustrating the position of the main sulphides and sulfosalts in the Pb - Sb - As system. The colored band reflects the variable composition of the geocronite.

4.1.3.5 MAIN SULFOSALTS, SULFOANTIMONIIDES AND SULFOARSENIDES OF NI - CO –FE

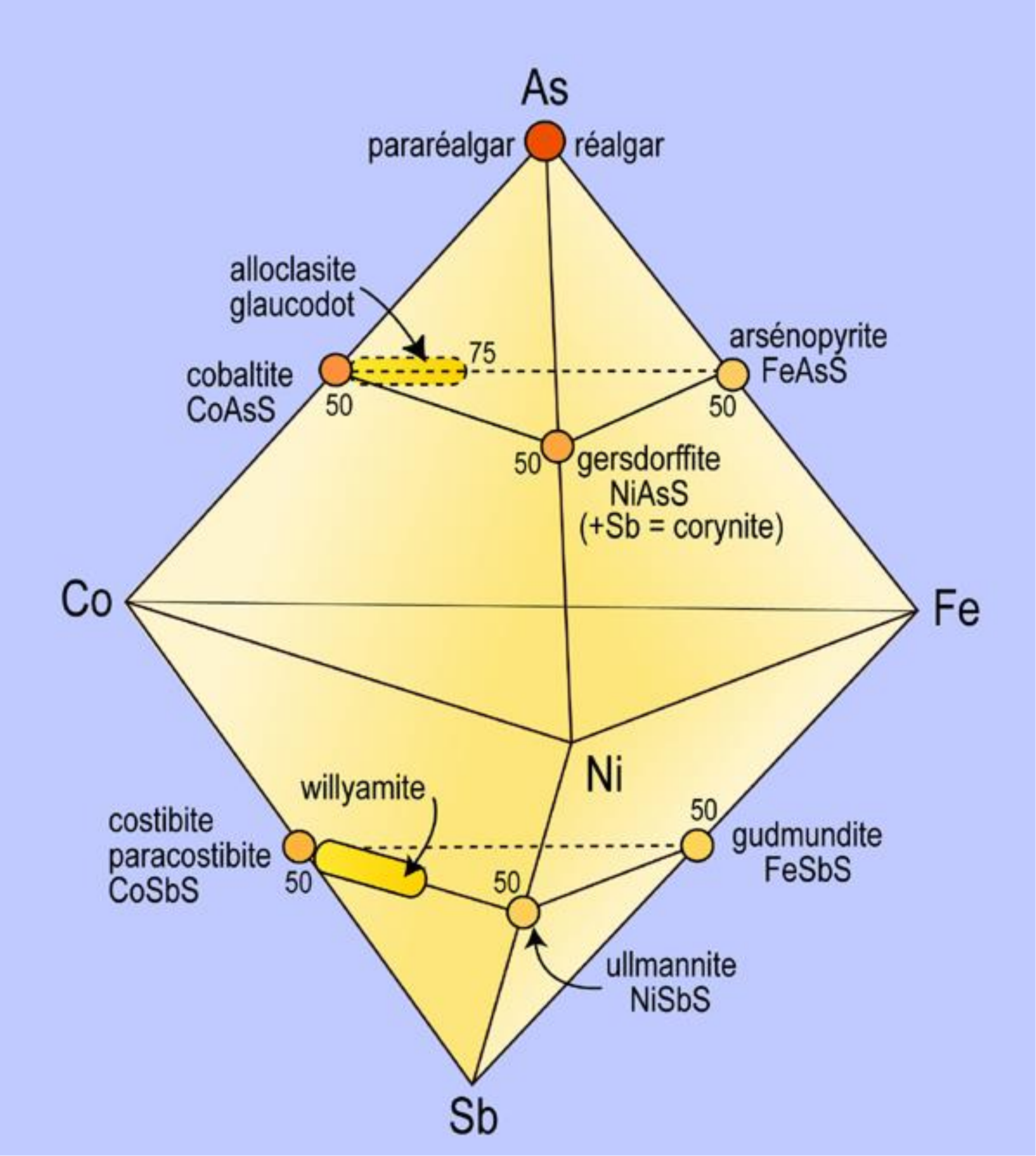

Figure 8: Compositions of the main sulfosalts, sulfantimonites and sulfoarsenides of Ni - Co -Fe (atomic %)

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4.1.3.6 ANHYDROUS CARBONATES

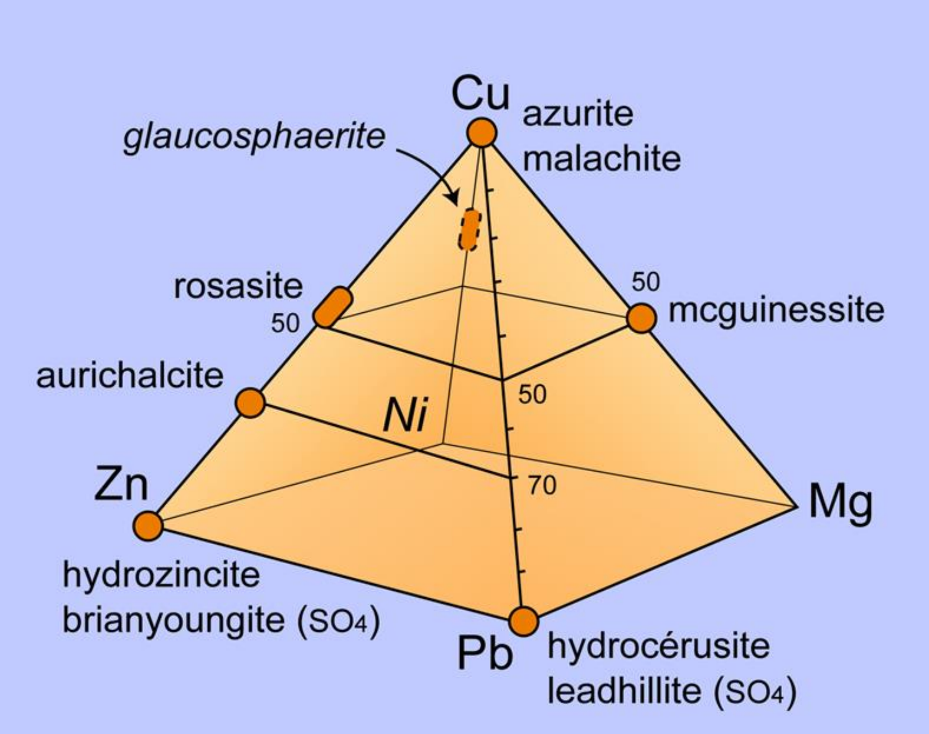

Figure 9: Composition of the most common hydroxylated carbonates of Cu, Zn, Pb, Mg and Ni (atomic %); parentheses indicate that complexes (SO4) also enter the structure of the carbonates concerned.

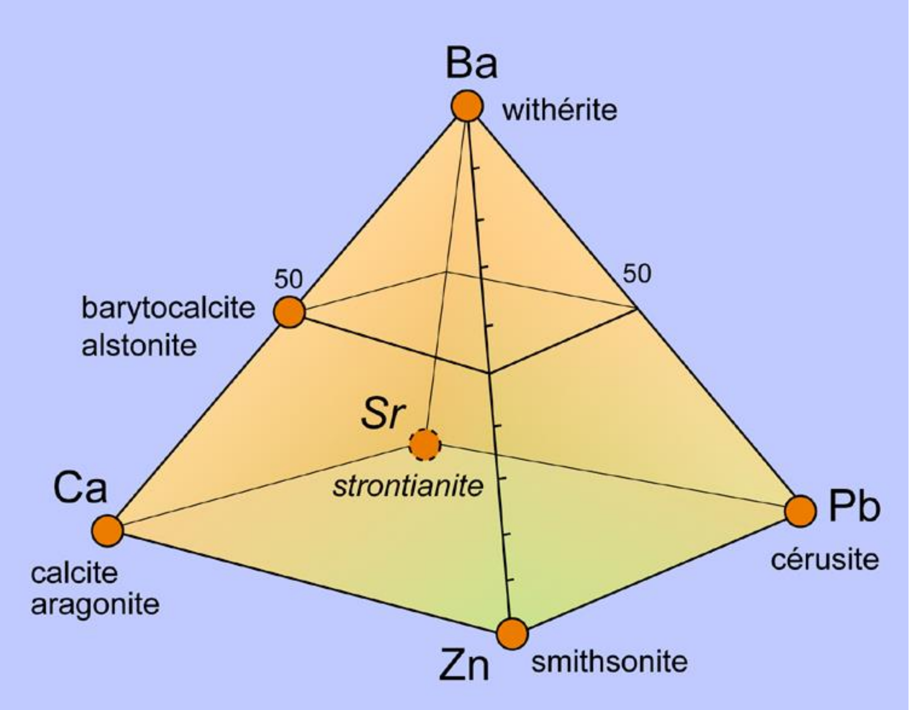

Figure 10: Composition of the most common anhydrous carbonates of Ca, Ba, Pb, Zn and Sr (atomic %).

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4.1.3.7 MAIN ARSENIDES OF CO-NI-FE

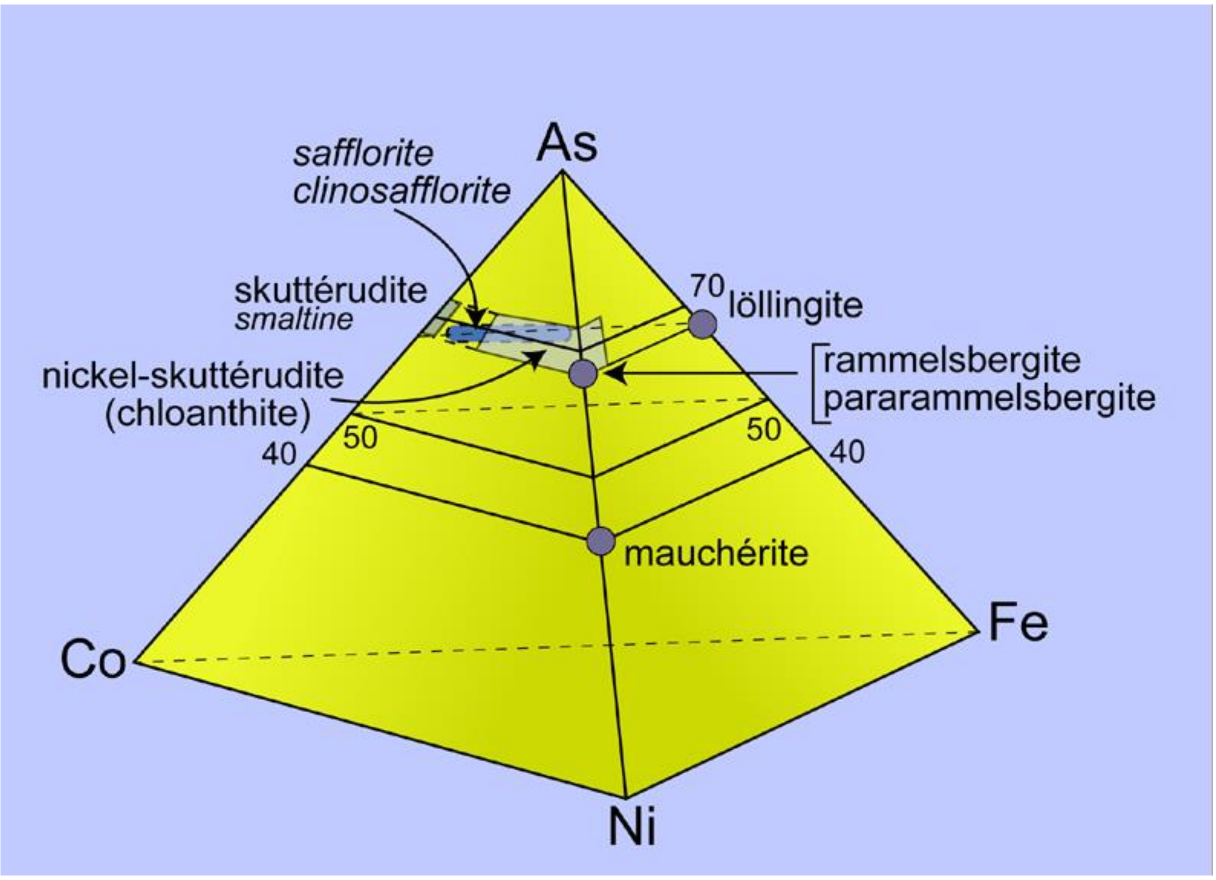

Figure 11: Main arsenides of Co, Ni and Fe in a ternary diagram (atomic %). The surfaces occupied on the front of the diagram by the fields of skutterudite and nickel-skutererudite result from the presence of 2 to 3 atoms of arsenic in the formula of these minerals. Safflorite and clinosafflorite occupy the dotted field on the back of the diagram.

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4.1.3.8 MAIN ANHYDROUS ARSENATES

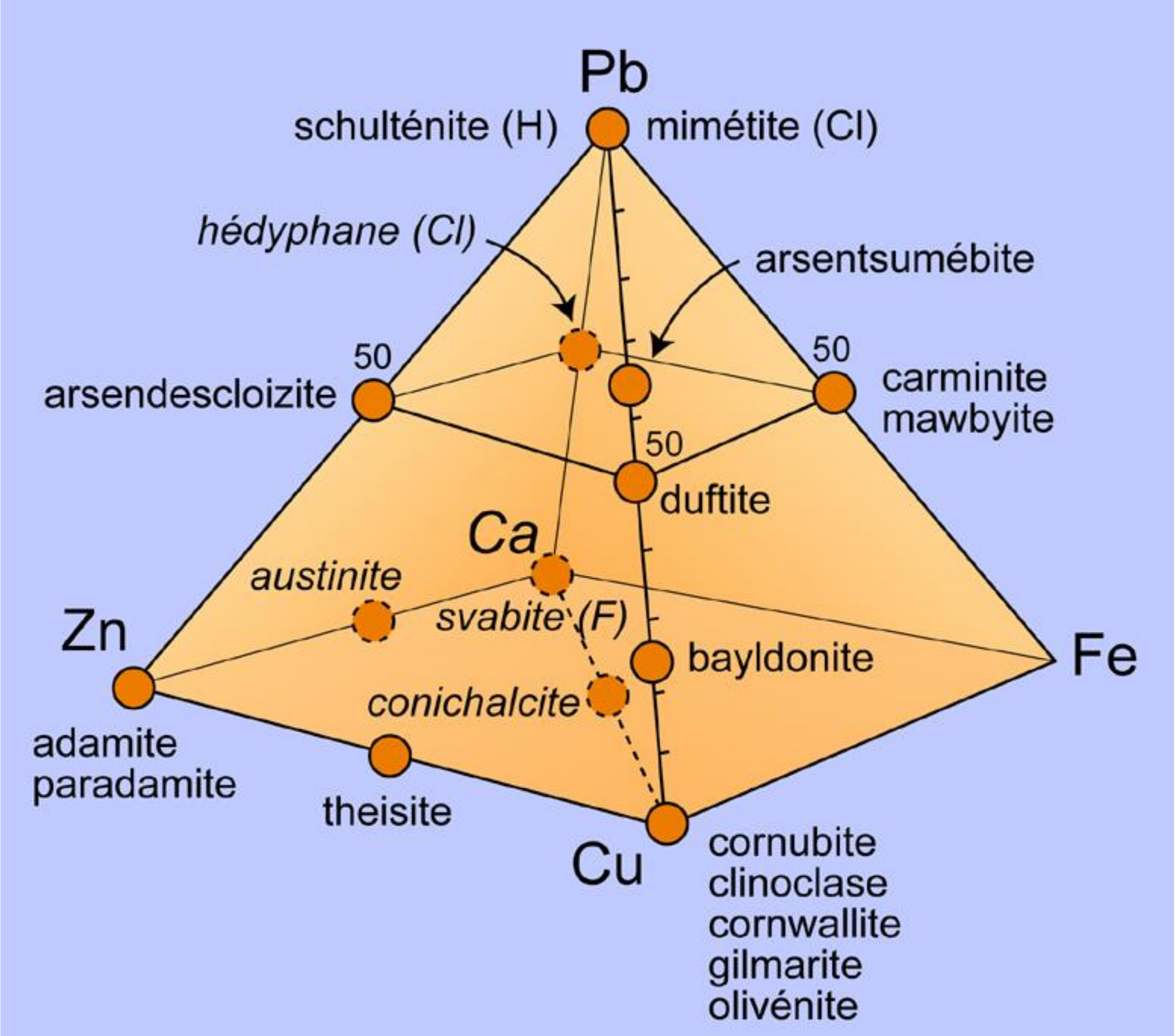

Figure 12: Composition of the main anhydrous arsenates of the Zn - Cu - Fe - Pb - Ca system (atomic%); in brackets the other elements entering into the structure of certain minerals

4.1.3.9 MAIN HYDRATED ARSENATES

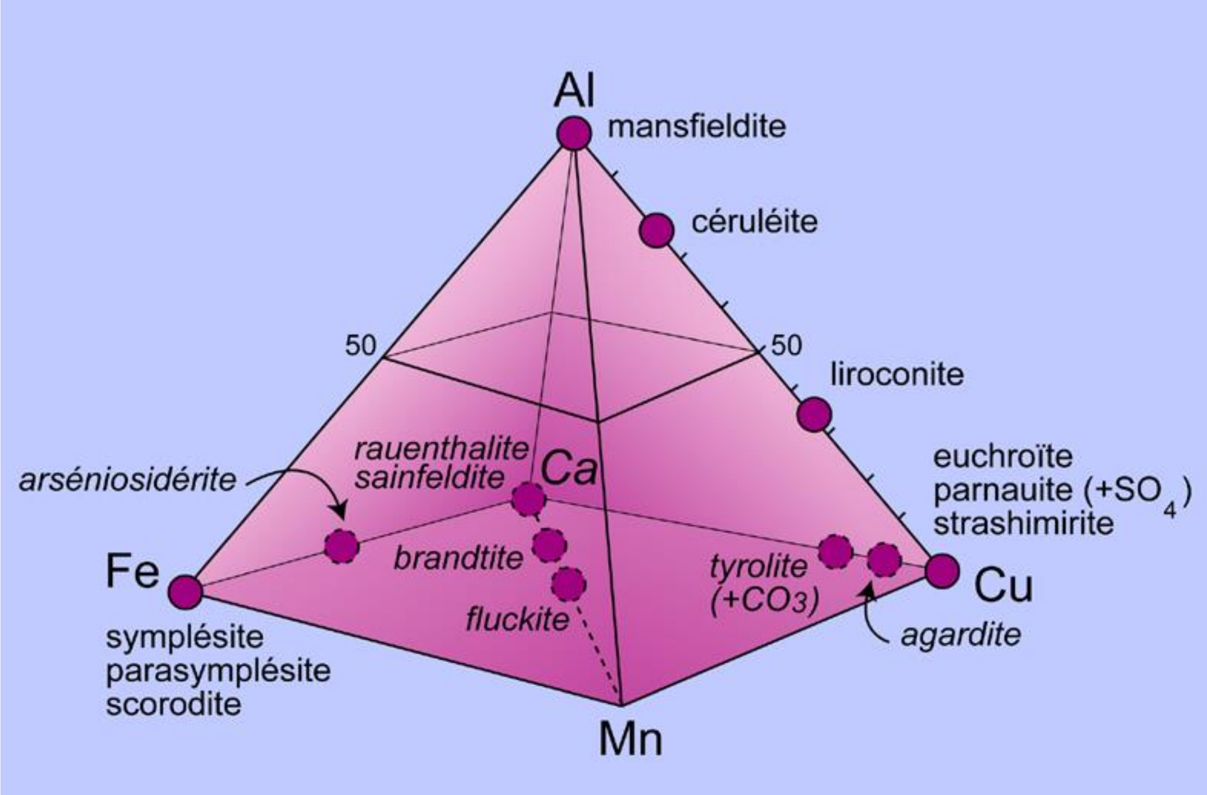

Figure 13: Compositions of the main hydrated arsenates of the Al - Cu - Ca - Fe - Mn system (atomic %); the groupings in parentheses also integrate the structure of the minerals indicated

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4.1.3.10 SULFOSALT

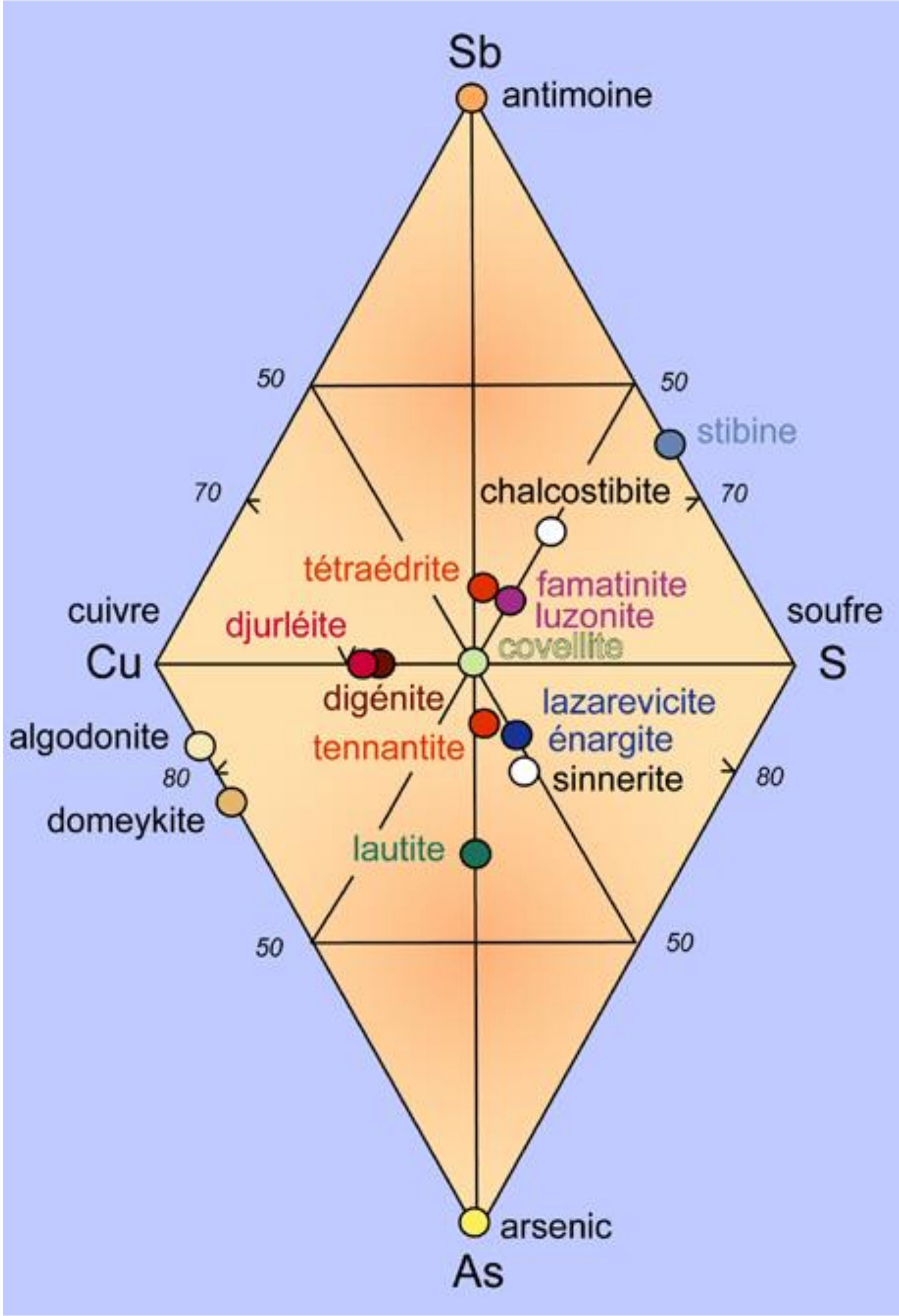

Figure 14: Compositions of the main native elements, sulfides, arsenides and sulfosalts of the Cu - Sb - S and Cu - As - S systems (atomic%); the solid tetrahedrite - tennantite solution is not shown in this diagram; the composition of chalcocite is very close to that of djurleite

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4.1.3.11 MAIN ANHYDROUS SULFATES

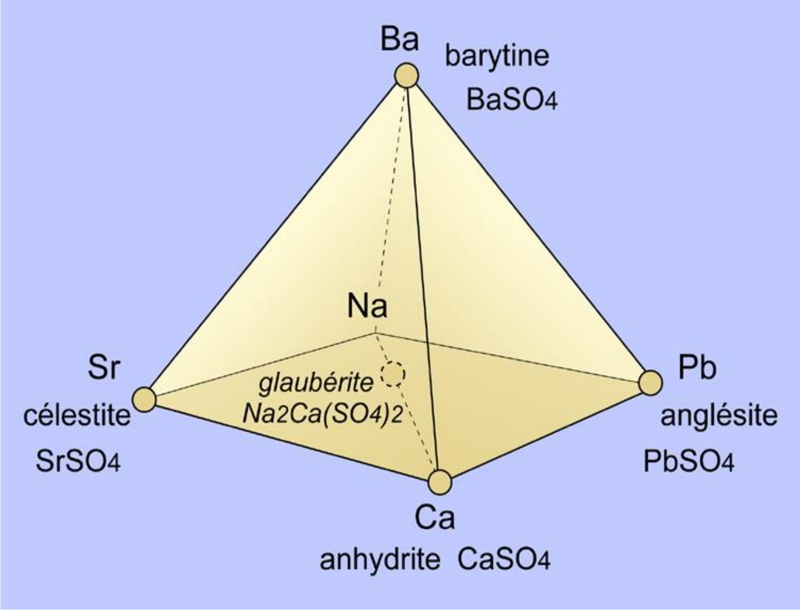

Figure 15 : Composition of the most communs anhydrous sulfates

4.1.3.12 ANHYDROUS ARSENATE (PB-ZN-CU-FE-CA)

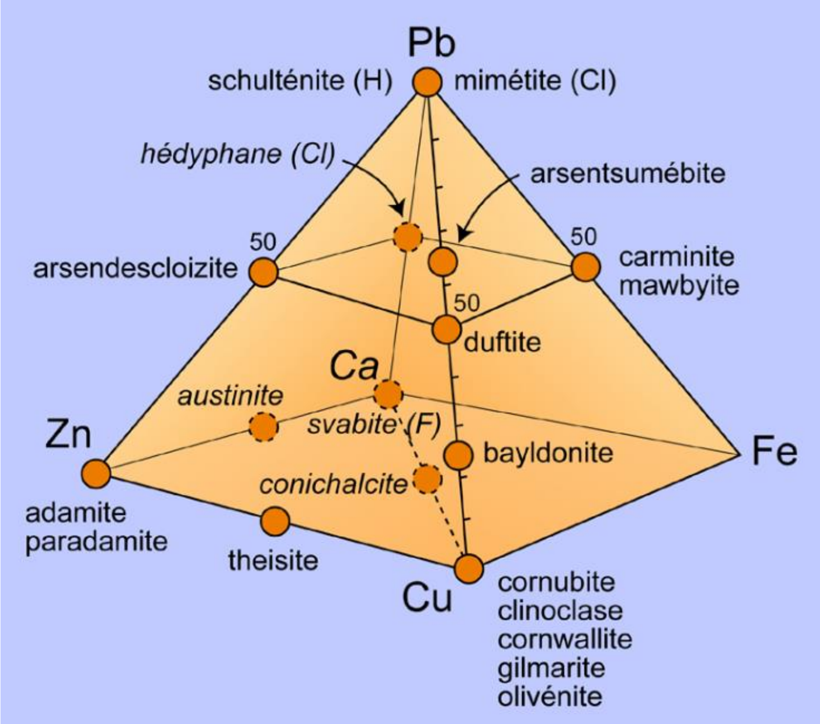

Figure 16: Composition of the main anhydrous arsenates of the Zn - Cu - Fe - Pb - Ca system (atomic %); in brackets the other elements entering into the structure of certain minerals.

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4.1.3.13 MAIN ANHYDROUS PHOSPHATES (CU-PB)

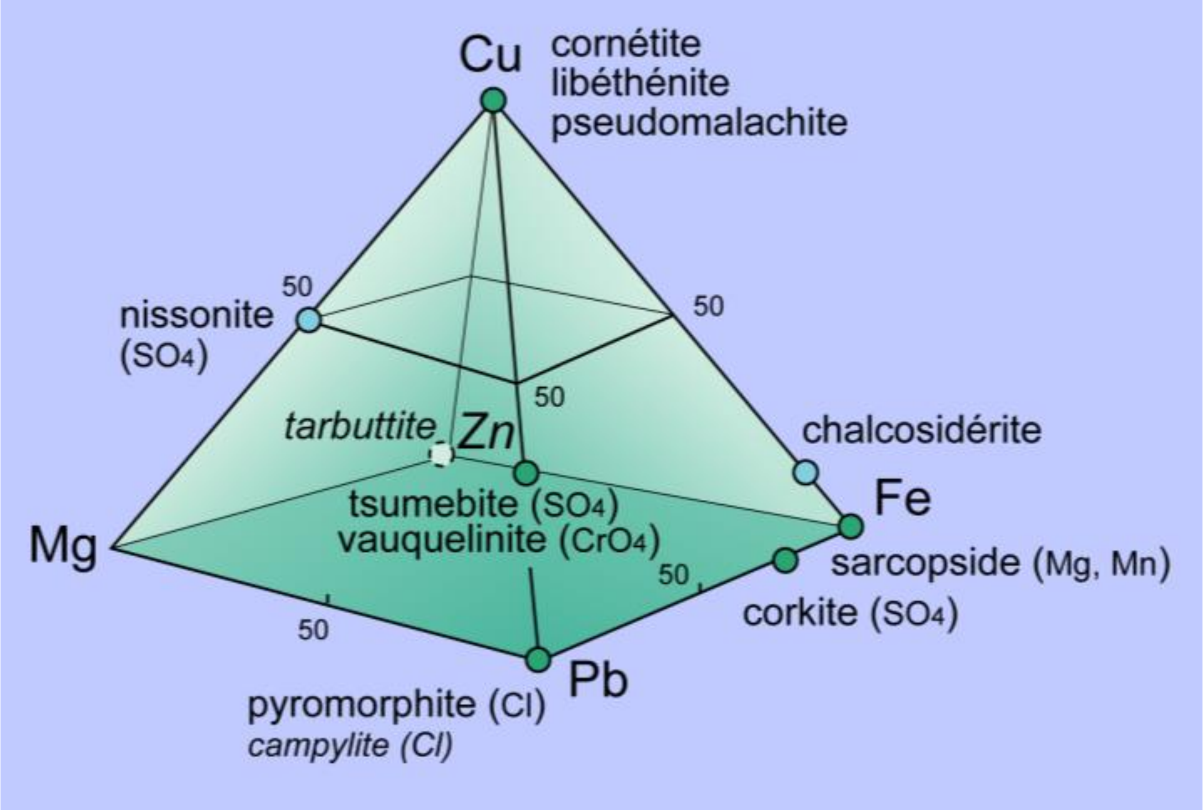

Figure 17: Composition of the main phosphates in the Cu - Mg - Pb - Fe - Zn system (atomic%); the elements and groupings in brackets integrate the structure of the minerals concerned; blue dots are hydrated phosphates

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4.1.3.14 URANYL-PHOSPHATES

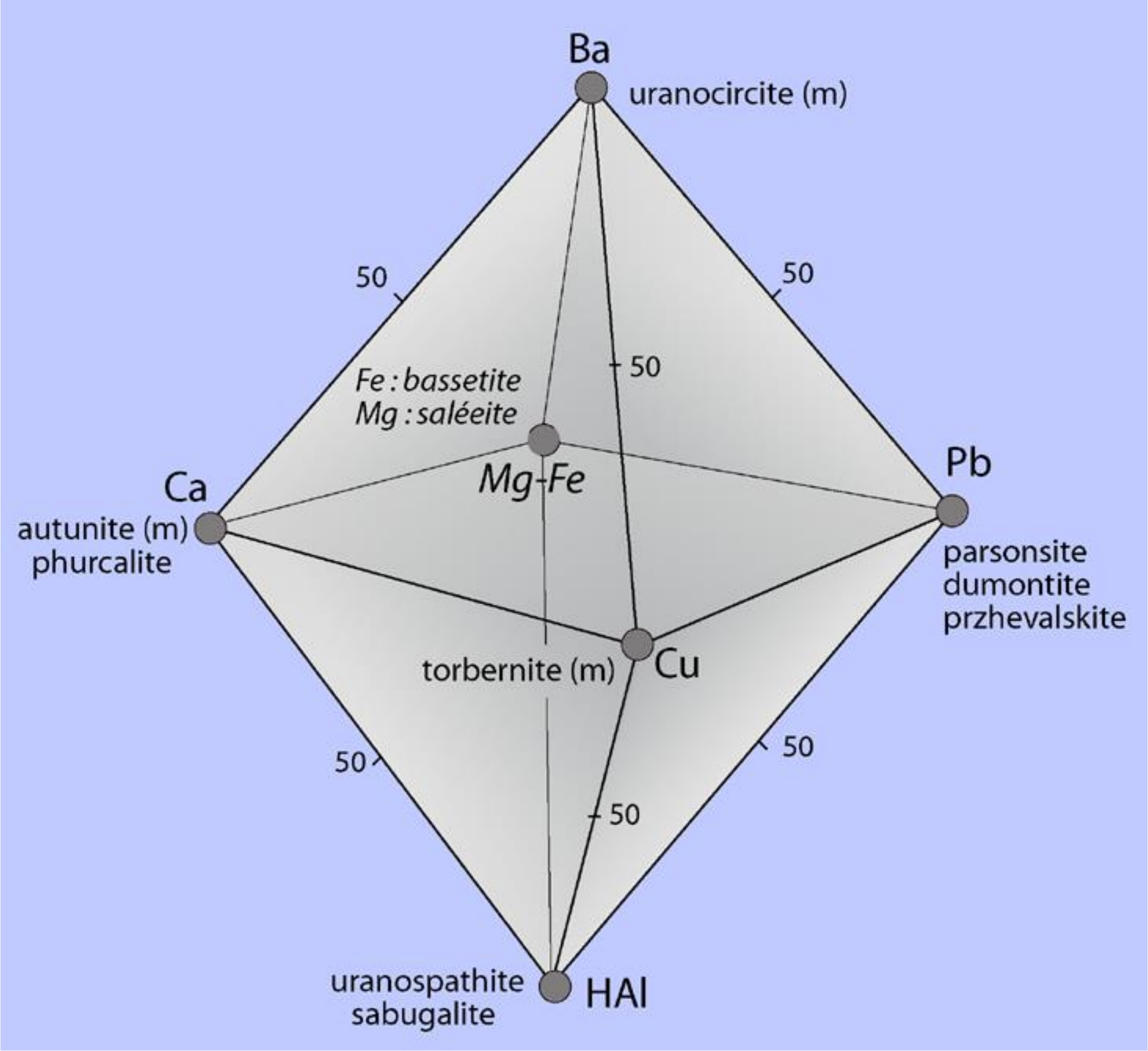

Figure 18: Main hydrated phosphates combining uranium and other elements (atomic %). The "m" indicates the existence at the same location of a meta form of the mineral, generally less hydrated.

4.1.3.15 URANYL-VANADATES

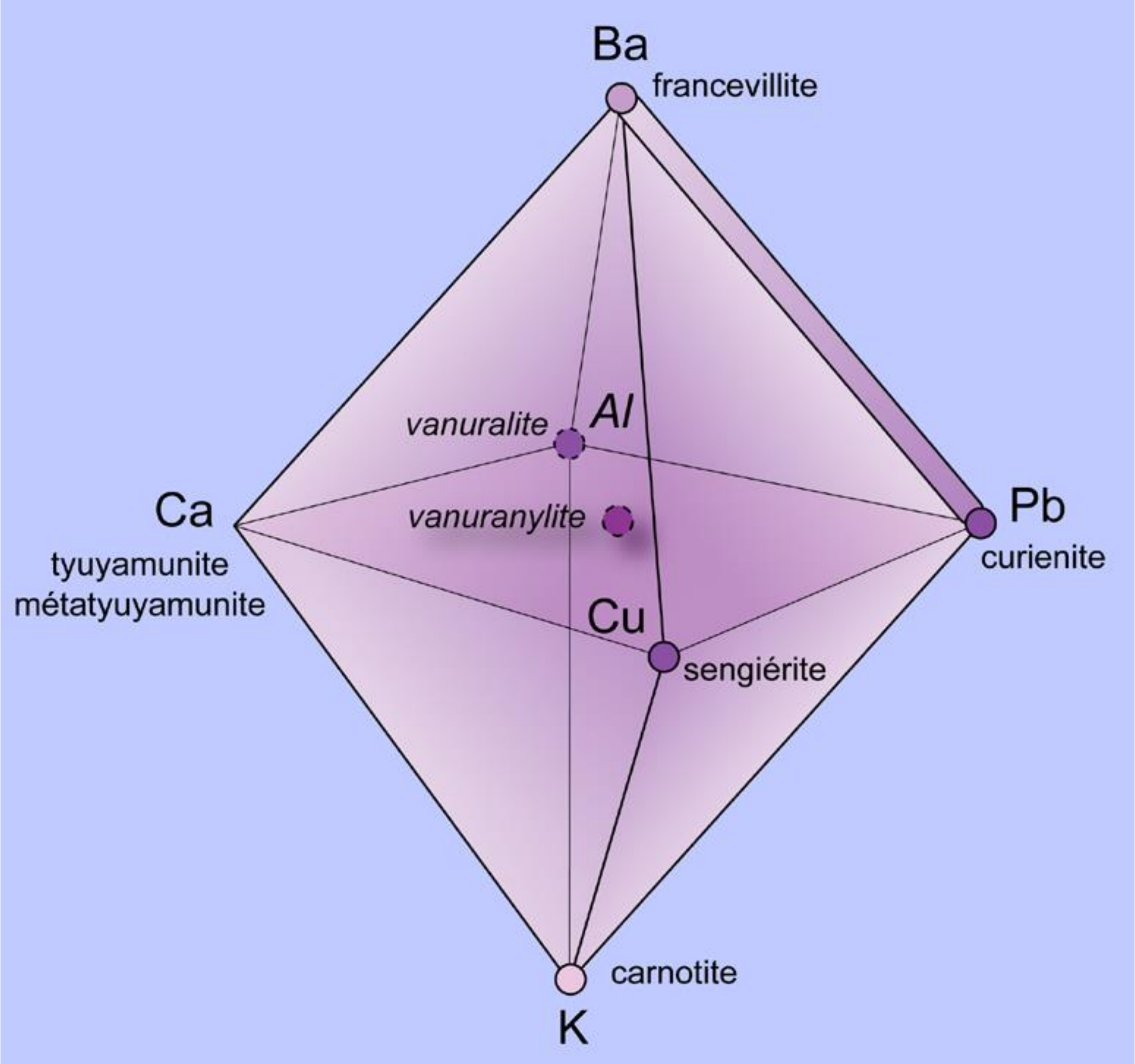

Figure 19 : Composition of the main uranyl-vanadates

4.1.3.16 TUNGSTATES AND MOLYBDATES (PB-CA)

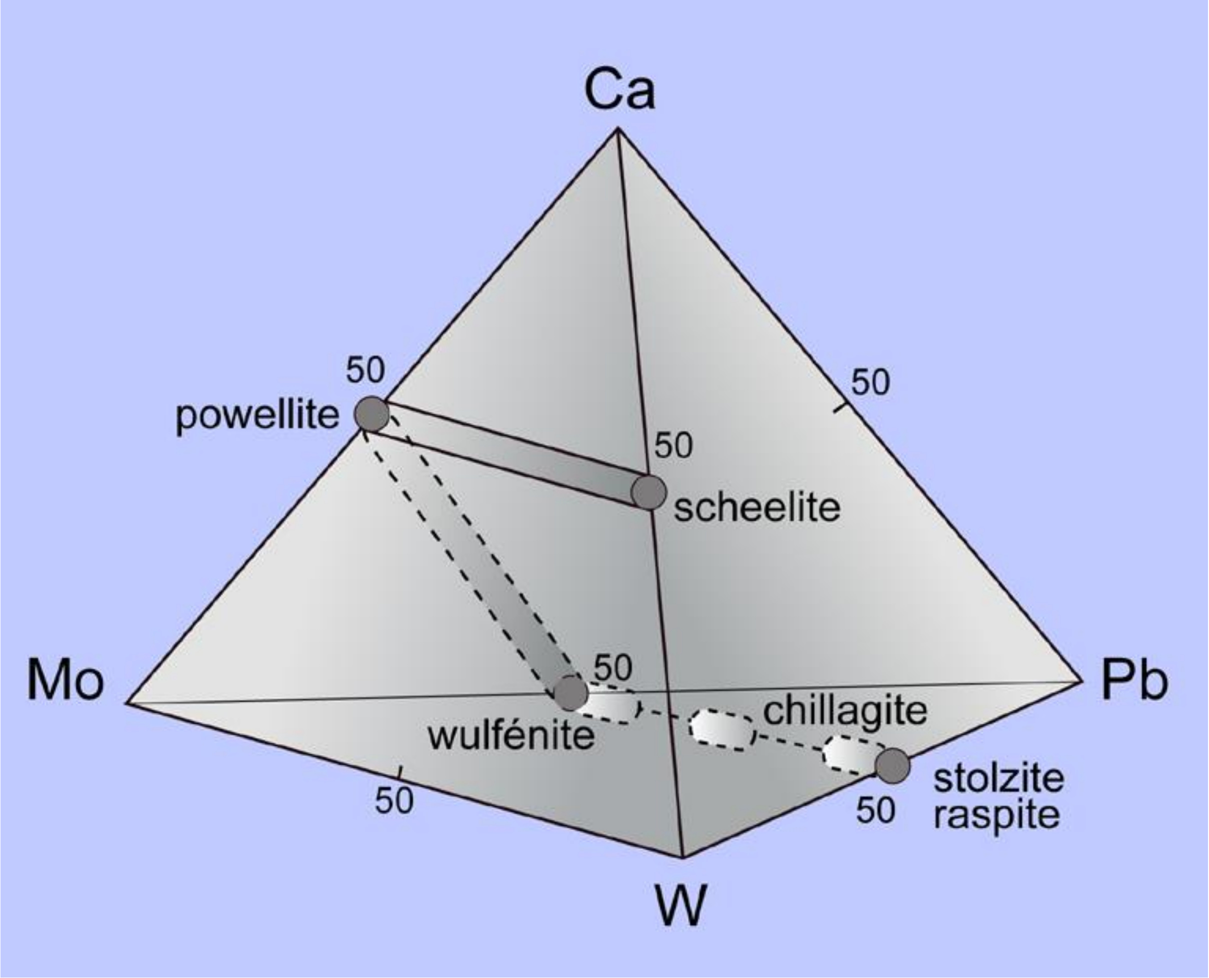

Figure 20: main tungstates and molybdates of Pb and Ca (atomic %)

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4.1.3.17 CHLORIDES

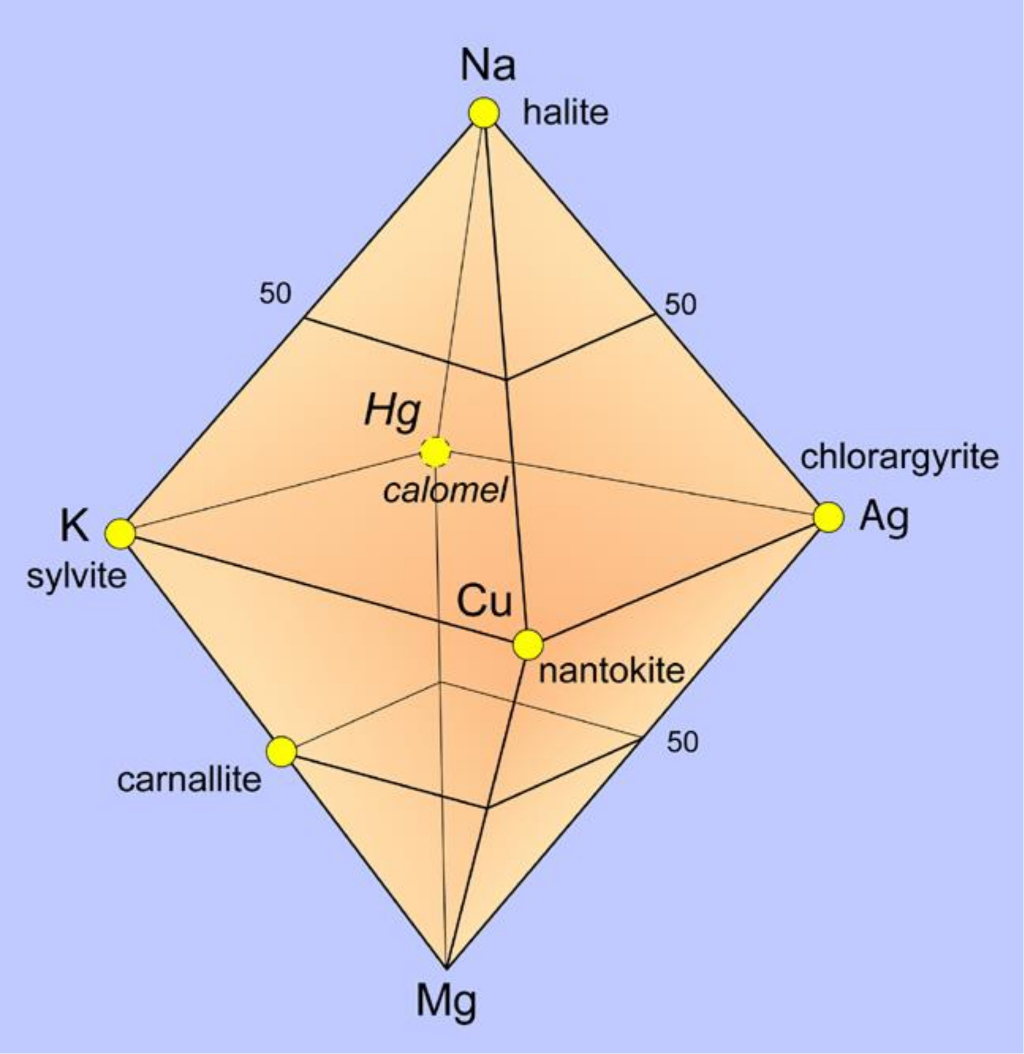

Figure 21 : Composition of the most commun chlorides

4.1.3.18 PB-ZN-FE-CU VANADATES

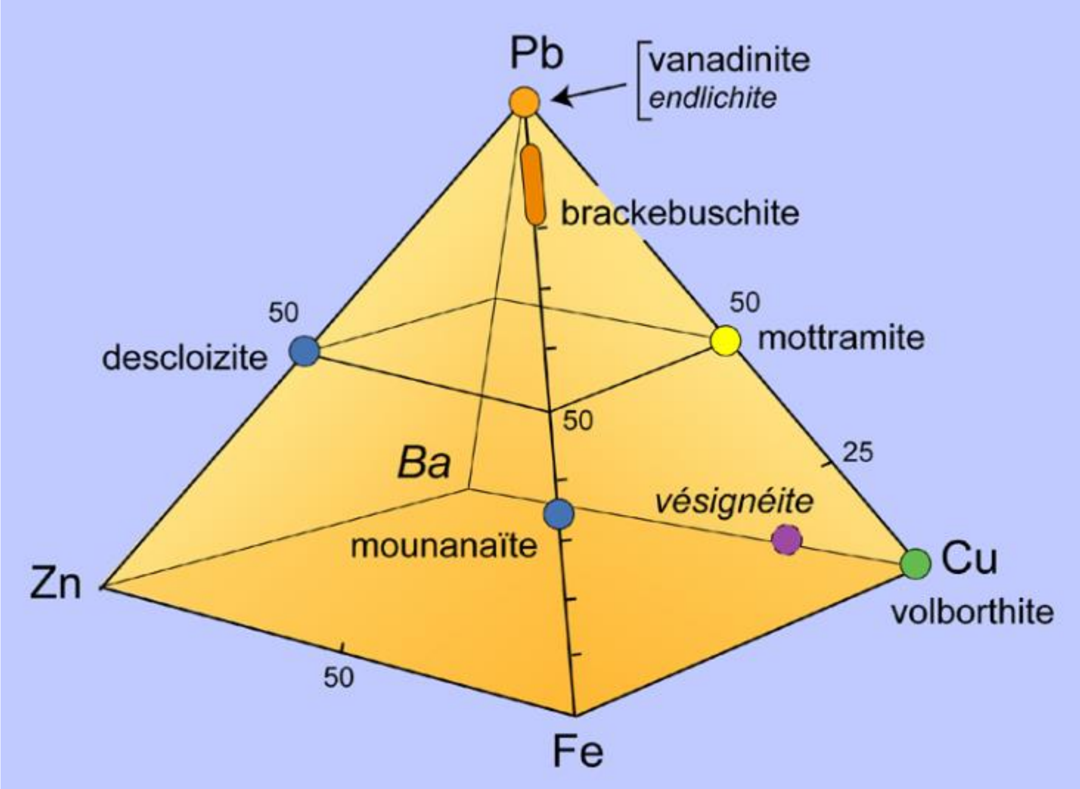

Figure 22: Composition of the most common vanadates of the Pb - Zn - Fe - Cu - Ba system (atomic %)

4.2 HAZARD ASSESSMENT METHOD

Anticipation of the hazards attached to mining exploration or exploitation is today a determining component of the SLO. Here we will develop the approach used to determine the hazards that could be induced by the exploration or exploitation of the metalliferous sites pointed out on the interactive map.

4.2.1 ACID MINE DRAINAGE (AMD)

Acid mine drainage is a common phenomenon in mining operations, whether these operations are active, old or very old.

4.2.1.1 SULPHIDES IN METAL DEPOSITS

The vast majority of metal mines exploit sulphides (minerals combining sulfur with a metal) which constitute the ore. For example, galena (lead sulphide) is the main ore of lead, chalcopyrite (copper sulphide) is the main ore of copper, blende (zinc sulphide) or sphalerite is that of zinc, etc.

If for the mineralogist the term “ore” is used to designate the minerals that are exploited, for the miner this term ore designates the rock which contains these minerals.

This confusion of terms can often lead to misunderstandings during technical discussions. Regarding acid mine drainage, we will use the term “ore” in the miner’s sense: the exploited rock.

Metal ores very often contain significant quantities of iron sulphides (pyrite, pyrrhotite or marcasite), which have no economic value but which can constitute the majority of the ore exploited. Thus, a copper ore contained in certain types of deposits, such as sulphide masses, can be made up of lenses and layers of massive pyrite which can represent several tens, or even hundreds of millions of tons.

4.2.1.2 OXIDATION OF SULPHIDES

When a sulphide oxidizes, it produces sulfuric acid which in turn can dissolve other minerals that otherwise would have remained stable. Oxidized sulphides therefore release metals or metalloids into the environment in a form which can sometimes be assimilated into the food chain and therefore cause cascading contamination.

Not all sulphides have the same sensitivity to oxidation. For example, galena is not very sensitive if it is the only sulphide present in the ore; but it is more easily oxidized if sulfuric acid released by other more sensitive sulphides is found in its environment.

On the other hand, pyrite (FeS_2) or pyrrhotite (FeS) are extremely easy to oxidize, and these minerals are almost always present in ores in significant quantities. We therefore see that the oxidation of a metalliferous ore can depend greatly on the sulphides exploited, but above all also on the iron sulphides which accompany them.

Oxidation of a sulphide does not occur when immersed in water. This is also why mining processing residues are often stored in basins under a layer of water to avoid the process.

To oxidize, a sulphide must therefore be in contact with air in a humid environment.

4.2.1.3 THE VARIOUS CASES OF AMD

In Task 2.2, we examine four typical situations in which sulfuric acid will be released into the environment, and with it a possible dispersion of heavy metals if they are present in the mineral associations of the ore or gangue.

The natural environment

This is not a AMD phenomenon since human activity is absent. In the absence of work, the superficial part of the metalliferous deposits was oxidized to the lowest level which was reached by the water table (if it exists) or more generally to a depth exposed to both water and water (infiltration and the atmosphere).

In our temperate climates, this “oxidation zone” can reach a depth of around fifty meters, sometimes more in very fractured deposits. The phenomenon is measured here on a “geological” time scale, and equilibrium has generally been achieved a long time ago. Without human intervention, a sulphide deposit will not naturally emit DMA.

Mining works: galleries, sites, wells, etc.

When they are “drowned” these structures are sheltered from the atmosphere. They therefore theoretically do not emit DMA. This situation can exist in plain areas when water pumping is interrupted and the level stabilizes with that of groundwater or surface water tables. However, the most superficial part of the mine is generally exposed, the water level in the old exploitation generally not reaching the surface and varying according to the seasons.

In mountainous areas, where several galleries are staged at various altitudes and are connected by wells or inclined planes, natural drainage of these galleries is maintained. The AMD phenomena which take place on the wall of the structures or within the existing backfilling are then maximum. It will be all the more important as the presence of iron sulphides or as the size of the work increases.

The dumps and stocks of “poor ores”

The digging of ore access galleries and underground infrastructure generates a significant volume of spoil that must be evacuated from the mine. The rocks thus evacuated have no economic value and they will not be sent to the ore processing units. They are stored outside the mine, forming a pile called “dumps”.

Although of no economic value, these dumps can contain significant proportions of iron sulphides. Their particle size is that of the rock fragments directly produced by digging: small size for digging by hand or by purely mechanical means, or larger size if explosives are used. Thus, their specific surface area will vary depending on the mining technique, with old mining works most often generating high specific surface areas.

The proportion of iron sulphides contained depends above all on the model of deposit exploited. Certain deposits form an ore core within a large halo of disseminated mineralization, poor in metals but rich in sulphides, which must be crossed before reaching the exploitable ore zone. These very sulphide rocks are thus found on the dumps.

The higher the specific surface area and the greater the proportion of iron sulphide contained, the higher the resulting AMD will be. The pile of dumps exposed to bad weather may take several tens, or even hundreds of years, to reach a new chemical equilibrium and a low overall level of oxidation.

In the second half of the 20th century, the economy was the main driver of mining activity and the environmental aspects of operations neglected. The miners were perfectly aware that the dumps could contain two types of products: rocks with absolutely no economic value (with or without iron sulphides) and rocks too poor in metals to be economically exploitable (and therefore merit the term ore, at the time of their extraction), but sufficiently “rich” to become exploitable if the price of metals rose. In this case, they could be stored outside on “special” piles: stocks of poor ores.

If this hope of recovery of these stocks had been disappointed during the life of the mine, they remained in place. Today they can be totally confused with classic dumps. From an environmental point of view, however, they present a much greater “heavy metal hazard” because their composition then combines the presence of metals in high concentration with those of sulphides capable of generating the acid causing their dispersion.

Mining tailings

Mining residues come from ore processing. This treatment aims to extract the useful minerals (ore in the mineralogist's sense) from the other minerals (the gangue) which together constitute the ore (in the miner's sense). For economic reasons, it is carried out as close as possible to the operating site when geographical conditions allow it. Thus, tailings are generally stored on or near the mine site.

Generally speaking, useful minerals represent only a small proportion of the minerals contained in ores. More than 90% of the initial tonnage of the processed ore will therefore end up in the residue.

The treatments applied are very diverse in nature (density treatment, magnetic separation treatment, flotation treatment, etc.) but they all have in common that they have to work with very fine particle sizes of between 0.2 and 0.04 mm. These residues therefore have enormous specific surface areas. They can oxidize very quickly and release large quantities of sulfuric acid if they contain sulphides and if they remain exposed to the action of the air. Their storage on operating sites is therefore carried out under water in basins.

For certain ores, the tailings may contain carbonates that are very reactive with sulfuric acid. In this case, the acid formed during the oxidation of the sulphides is immediately neutralized and the DMA is thus reduced, or even almost eliminated.

4.2.1.4 PRELIMINARY ESTIMATE OF THE AMD HAZARD

In the absence of specific analyses and studies, it is difficult to establish for each mining occurrence or deposit the importance of the AMD that may be associated with it. These observations also apply to the estimation of the heavy metal hazard which is one of the main consequences of the DMA.

The descriptions of the ore, when they exist in the bibliography, are of course a valuable indication, but they are generally very incomplete:

- We may only have information on the minerals useful at the time of their exploitation; in particular pyrite or pyrrhotite, the main vectors of AMD, were not among the ores and they were not always described, even present in abundance.
- The relative proportions of the various minerals are not always indicated and it is often difficult to know whether a mineral cited is just an accessory mineral and therefore has no impact on a hazard or, on the contrary, if it is strongly present with the hazards that he can then bring.

Fortunately, an approach to DMA can be carried out using the deposit’s geological model. The deposit model is a real identity card for the deposit. It can specify the relative importance of the minerals contained, that of the accompanying mineralized disseminations, the nature of the metals contained, and the potential size of the deposit.

Thus, by combining observations on the nature of the mining works, the time of their completion, the minerals identified in the ore and the deposit model, we can obtain a preliminary estimate of the AMD hazard.

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4.2.1.5 PROBABILITY OF THE AMD HAZARD

The probability will be indicated in the Google Earth "balloons" by a coloured bullet placed in front of the term "DMA Hazard". We will consider four levels illustrated by the following colours:

- 🔴 **DMA hazard: certain**. Iron sulphides, the main cause of AMD, have been clearly identified as being a major or important constituent of the ore and/or the accompanying rocks. There are mining works.
  The intensity of the AMD is proportional to the size of the mining works weighted by the nature of the deposit model
- 🟡 **DMA hazard: probable**. The sulphides responsible for AMD have been clearly identified but it is difficult to understand their proportions in the ore. Failing this, the deposit model could be established. There are mining works of sufficient size.
  The intensity of the AMD is proportional to the size of the mining works weighted by the nature of the deposit model.
- 🔵 **DMA hazard: possible**. The sulphides responsible for AMD have been clearly identified but it is difficult to understand their proportions in the ore. Failing this, the deposit model could be established. There are small-scale mining works.
  The intensity of the AMD is proportional to the size of the mining works weighted by the nature of the deposit model.
- ● **DMA hazard: potential.** There is no mining work and therefore no DMA. Here we will estimate the AMD that could be generated by exploitation if the evaluated index were to be exploited.
  The intensity of the potential AMD is induced only by the nature of the deposit model

4.2.1.6 INTENSITY OF THE AMD HAZARD

In the Hazard balloons deployed on the interactive map, the intensity of the hazard is expressed graphically; four cases are possible:

- DMA hazard ▭ ▭ ▭: negligible hazard. This type of hazard will be linked to geological models devoid of sulphides or containing sulphides in low proportions and having undergone minor work.
- DMA hazard ▬ ▭ ▭: low hazard. This type of hazard will generally be linked to mining research work: trenches, small galleries of a few tens of meters, small exploration wells, superficial scrapings, etc. The remobilized material has low volumes and its impact on the environment remains very limited; even in the case of deposit models containing a high proportion of sulphides.

This type of hazard will also be linked to medium-sized works carried out on a deposit whose deposit model only involves a small participation of sulphides.

- DMA hazard ▬ ▬ ▭: medium hazard. This type of hazard will be mainly linked to old exploitation works, generally of an artisanal type, of small to medium size and having excavated only a few hundred to a few thousand tonnes of material in deposits rich in sulphides.
  This type of hazard will also be associated with larger works carried out on a deposit whose deposit model only involves a small quantity of sulphides.

- DMA hazard ▬▬▬: strong hazard. This hazard corresponds to deposits belonging to sulphide-rich deposit models. In the case of certain or probable hazards, the operations correspond to medium to large mines.

4.2.2 ASBESTOS

In this work, the estimation of the “asbestos” hazard is carried out on the ore of the occurrence or mineral deposits. It was not carried out on all the rocks present in their environment.

This estimate therefore answers the question: “Will the extraction and/or processing of the ore present an asbestos hazard for which the risk will need to be assessed? ".

It does not answer the question: “Does the construction of the road or that of the infrastructure which would be necessary for the exploitation of a deposit on the site present an “asbestos” risk for the personnel involved? »

Indeed, there is also a purely geological “asbestos hazard” (natural hazard), capable of occurring anywhere as long as the conditions for the formation of asbestos minerals are met. Its evaluation should not be carried out on the basis of mining potential, but on that of hydrothermal phenomena mainly affecting magnesium rocks, whether magmatic (ultrabasic and basic rocks) or sedimentary (dolomites).

Thus, the faults presenting a strong hydrothermal circulation cutting ultramafic massifs or the dolomite formations which often enclose the deposits are sites where an asbestos hazard is potentially present.

We will evaluate the asbestos hazard on the basis of two parameters: its probability of existence and its potential intensity.

4.2.2.1 REMINDER OF DEFINITIONS

The generic term asbestos refers to a series of minerals which, under certain crystallization conditions, present a morphology in very fine and flexuous fibers which we qualify as

asbestiform. The evaluation of the fineness of these fibers and their length is the basis of the regulations on asbestos which we will not detail here. It should be noted, however, that this characterization can only be carried out using very detailed studies, generally carried out using an electron microscope. An expert can, however, make a preliminary diagnosis by simple observation under a magnifying glass, taking into account a large number of geological parameters at the sampling site. However, the definitive diagnosis can only be confirmed by a specialized laboratory.

These asbestiform minerals, referred to in the generic form of asbestos, correspond to mineral species that are often very widespread in nature in their prismatic forms and which should therefore not be confused with asbestos. These asbestiform shapes are sufficiently characteristic to “merit” a specific mineralogical definition, as follows:

- **Chrysotile**, the most common form of industrial asbestos, is actually an asbestiform variety of serpentine.
- **Crocidolite**, rarer, is an asbestiform form of riebeckite or magnesio-riebeckite, amphiboles that are otherwise harmless in their natural state in their other forms.
- **Amosite** is an asbestiform form of amphiboles which form a series between grunerite and cummingtonite.
- **Byssolite** is an asbestiform form of amphiboles generally grouped under the name actinolite and which form a continuous series between tremolite and ferroactinolite.

The toxicology of these four types of asbestos being equivalent, the identification of the mineral species which corresponds to them will not always be provided in the assessments and the generic term “asbestos” will be used to refer to them.

4.2.2.2 PROBABILITY OF AN ASBESTOS HAZARD

The probability will be indicated in the “balloons” of the interactive map by a colored chip placed in front of the term “Asbestos Hazard”. We will consider 3 levels:

- 🔴 **Asbestos hazard: certain.** An asbestiform mineral classified in the asbestos category was observed and identified by a professional mineralogist.

We will add to this category natural fibrous minerals whose toxicity in dust is equivalent: **erionite** (species of zeolite) and **palygorskyte** (species of sepiolite)

- 🟡 **Asbestos hazard: possible.** No asbestiform mineral has been identified but the minerals present contain mineral species likely to develop an asbestiform form if the necessary conditions are met. A good indicator of these necessary (but not sufficient) conditions is the simultaneous existence of minerals which account for suitable hydrothermal circulation in the ore and in its immediate environment.

When the deposits were described, often several decades ago, no particular attention was paid to the asbestiform forms of the minerals, their dangerousness not yet being established. Often, the descriptions mention “amphiboles” without even specifying the mineral species and even more so the morphology of the crystals. Under these conditions, the existence of asbestos will be considered possible if the mineral species association and the indications of the hydrothermal phenomenon necessary for the formation of the fibers are met.

- **Asbestos hazard: slightly possible.** Minerals likely to develop asbestiform facies have been observed, but no asbestos has been described. No mineral indicative of a hydrothermal phenomenon is cited, but very often these gangue minerals are not part of the descriptions provided by the authors of the reports and their absence in the description may be due simply to this omission. For these reasons, a slightly possible hazard persists.

4.2.2.3 INTENSITY OF AN ASBESTOS HAZARD

We will focus exclusively on the hazard induced by human intervention on a deposit during its exploitation or research intended to determine its exploitability. The intensity of the hazard will therefore be directly proportional to the size of the work carried out.

In the interactive map provided, the intensity of the asbestos hazard is expressed graphically, four cases are possible:

- Asbestos hazard ▭ ▭ ▭: negligible hazard. This type of hazard will be linked to prospecting work. If asbestos is released into the environment, it can only be released naturally; for example, the effect of wind on rock outcrops reported as a mining indicator. However, in the event of an assessment of the interest of this index, it will be strongly recommended to take the relevant protective measures, especially since the probability of the presence of asbestos will be high.

- Asbestos hazard ▬ ▭ ▭: low hazard. This type of hazard will generally be linked to mining research work: trenches, small galleries of a few tens of meters, small exploration wells, superficial scrapings, etc. The remobilized material has low volumes and its impact on the environment remains very limited.
- Asbestos hazard ▬ ▬ ▭: medium hazard. This type of hazard will mainly be linked to old mining works, generally of an artisanal type, of small to medium size having excavated only a few hundred to a few thousand tons of material.
- Asbestos hazard ▬ ▬ ▬: strong hazard. This hazard will be mainly linked to mines and quarries in operation or abandoned from the second half of the 20th century. In

fact, these operations were mechanized and they often used significant quantities of material in the form of dumps but also sometimes in mining residues.

4.2.3 THE HEAVY METAL HAZARD

4.2.3.1 HEAVY METAL

This definition, widely used in everyday language, is in fact based on an industrial concept and not on chemistry. Overall, we considered that these were metals which have a high density, greater than 5000 kg/m^3 such as lead, mercury or cadmium. Subsequently, this density was reduced to 4000 kg/m^3.

This definition of heavy metals turned out to be too imprecise to precisely define a chemical element, but its use was widespread enough not to replace it purely and simply with a definition based on chemistry such as MET (Metal Trace Elements), which was however more appropriate.

Europe has therefore retained the following definition for European law: “A heavy metal designates any compound of **antimony**, **arsenic**, **cadmium**, **hexavalent chromium**, **copper**, **lead**, **mercury**, **nickel**, **selenium**, **tellurium**, **thallium** and **tin**, as well as these materials in metallic form, provided that they are classified as dangerous substances.

We will add **uranium** to this list because of its chemical toxicity, comparable to that of lead or cadmium. Furthermore, this element will induce a radioactivity hazard which will be independent of its mineralogy.

4.2.3.2 HEAVY METAL HAZARD ASSESSMENT METHOD

In mineral deposits or ore deposits, metals are incorporated into minerals. With very rare exceptions, these metals are not found in metallic form. Thus, the mining hazard of a metal should not be confused with the hazard induced by an industrial activity of transformation or machining of this same metal.

For example, tin ore is generally made up of a tin oxide: cassiterite (SnO_2). It is a very hard, very dense mineral and completely insoluble in water and weak acids as they may exist in nature. This tin ore will therefore not release tin Sn^{4+} ions into the environment which could be fixed elsewhere in soils and waterways in forms that cannot be incorporated into the supply chain. Cassiterite, although containing a high proportion of tin, will therefore not present a tin hazard.

The sole chemical analysis of the contents of dumps or residues is therefore not sufficient to determine the importance of the “heavy metals” hazard associated with this metal. We still need to know in what form it is found in the dumps, that is to say what minerals contain it. This characterization is defined as mineral speciation.

The presence of MET in dumps or residues therefore does not systematically imply the existence of a heavy metal hazard for the elements considered. The assessment of a heavy metal hazard involves the simultaneous consideration of three fundamental parameters: the existence and importance of the work, the nature of the mineral associations observed, and the impact of the deposit model.

Size of the mining work

The absence of mining works or the relative importance of these is an essential parameter to determine the importance of a hazard. However, this parameter alone is totally insufficient to be able to assess the importance of a heavy metal hazard. Indeed, major works that have been able to generate a large volume of dumps from a very low sulfide deposit can induce a much lower hazard than that generated by mining works, much smaller, but carried out on a very sulfide deposit.

Furthermore, the absence of mining work does not automatically imply the absence of a heavy metal hazard.

The ore from certain deposits can be exposed to the open air by erosion of the land. A chemical equilibrium will have been reached because the oxidation of the sulfides has long since ended and therefore ceased to produce sulfuric acid; there will therefore not be a massive dispersion of heavy metals in this way into the environment.

However, certain ores will have been strongly transformed by this surface alteration, and the heavy metals initially contained in the minerals dissolved by surface oxidation may recombine in minerals, called “secondary”, which will remain in the close environment of the outcropping deposit.

The soils developed above these deposits sometimes contain extremely high levels of heavy metals. For example, above the large fault structures which define certain gold deposits, levels of more than 1% arsenic have been observed in the soils. This phenomenon, completely natural and independent of any human activity, can develop over relatively large areas, sometimes extending over kilometers.

In the absence of mining work, we will therefore speak of a potential hazard, that is to say a hazard which would be likely to occur if a mining operation were carried out, or even in the absence of any mining activity, if the deposit model can cause it naturally (case of arsenic for example).

The existence of mining works and a possible associated AMD will have an amplifying effect on this phenomenon of dispersion of heavy metals. In this case, the more extensive the work, the greater the heavy metal hazard associated with this work will be.

Mineral associations and heavy metal hazard

Metals are contained in minerals. Some minerals are unalterable and will therefore not be able to release their metallic content in a "contaminating" form into the environment. Thus, the chemical analysis of soil alone is not sufficient in itself to determine its level of contamination in terms of toxicity/ecotoxicity. Other minerals, on the contrary, either by dissolution in water or in a weak acid released by AMD, or by direct absorption by an organism, will be able to do so. The assessment of a heavy metal hazard must therefore take into account mineral speciation.

In our approach, we will estimate a "heavy metal hazard" as follows:

- A heavy metal hazard exists in the described site: the mineral which contains this metal has been described or it is symptomatic of a well-identified deposit model.
- This mineral must represent a significant proportion in the ore, sufficient to introduce measurable quantities of heavy metals into the environment.
- This mineral can release the heavy metal in the form of compounds assimilated by living organisms, directly or indirectly, and therefore induce toxicity or ecotoxicity.

The document provided should not be interpreted in terms of health risk which must be established based on the TRV (Toxicological Reference Value) as established in France by INERIS. Therefore, the risk linked to a hazard presented in this study should be the subject of a specific study. The hazard indicated simply allows us to estimate the relevance of carrying out this risk study.

The minerals encountered in the deposits may contain metals other than those cited by Europe in the category of heavy metals. These metals (MET) will also be listed for each site. However, we will consider that they do not a priori induce a heavy metal hazard and they will only be cited for information purposes.

Metallogenic model

In the bibliography attached to the sites carried on the Google Earth document, generally:

- Complete chemical analyzes of the ore are absent.
- Complete mineralogical descriptions are quite rare, very often limited to useful minerals in ores. Sometimes they are completely absent.

However, the assessment of a heavy metal hazard remains possible if we can establish the deposit model of the exploited or simply discovered deposit. Indeed, this model makes it possible to know with a very high level of probability which will be the essential minerals which will constitute the ore. Thus, a “copper VMS” type deposit will always contain a very significant quantity of pyrite and/or pyrrhotite. If the geological criteria for its diagnosis are clearly established, direct observation of these minerals is no longer necessary to obtain certainty of their presence.

A zinc deposit of the “sedimentary exhalative” (SEDEX) type will of course contain zinc and generally one will find in the bibliography the description of its main ore (sphalerite – ZnS). . This deposit will always contain lower proportions of lead (galena - PbS) or copper (chalcopyrite - $CuFeS2$) ores. Furthermore, sphalerite always contains a variable proportion of cadmium, it is even the main source of this heavy metal. It is therefore not necessary to observe cadmium minerals to anticipate a cadmium hazard in the presence of significant quantities of sphalerite.

4.2.3.3 PRELIMINARY ESTIMATE OF THE HEAVY METALS HAZARD

This estimation will be carried out using criteria comparable to those used to estimate the AMD. This estimate will be carried out for each of the heavy metals listed by Europe.

Probability of a heavy metal hazard

The probability will be indicated in the “balloons” of the interactive map by a colored chip placed in front of the term “Hazard…”. We will consider four levels illustrated by the following colors:

- 🔴 **Hazard: certain**. Easily altered minerals rich in heavy metals have been clearly identified as being an important constituent of the ore and/or surrounding rocks of the site. There are mining works. The intensity of the hazard is proportional to the size of the mining works weighted by the nature of the deposit model.
- 🟡 **Hazard: probable.** Easily alterable minerals rich in heavy metals have been identified but it is difficult to understand their proportions in the ore. Failing this, the deposit model could be established. There are mining works of sufficient size. The intensity of the hazard is proportional to the size of the mining works weighted by the nature of the deposit model.
- 🔵 **Hazard: possible.** Easily alterable minerals rich in heavy metals have been identified but it is difficult to understand their proportions in the ore. Failing this, the deposit model could be established. There are small-scale mining works. The intensity of the hazard is proportional to the size of the mining works weighted by the nature of the deposit model.

- Hazard: potential. There is no mining work. Here we will estimate the hazard that could be generated by exploitation if the evaluated index were to be exploited. The intensity of the potential hazard is directly induced by the nature of the deposit model.

Intensity of a heavy metal hazard

In the interactive map provided, the intensity of the hazard is expressed graphically; four cases are possible:

- ▭ ▭ ▭: negligible to very low hazard. This type of hazard will be linked to geological models almost devoid of heavy metal sulfides or containing minerals containing them in small proportions, and having been the subject of small works.

- ▬ ▭ ▭: low hazard. This type of hazard will generally be linked to mining research work: trenches, small galleries of a few tens of meters, small exploration wells, superficial scrapings, etc. The remobilized material has low volumes and its impact on the environment remains very limited; even in the case of deposit models containing a high proportion of heavy metal minerals.
  This type of hazard will also be associated with medium-sized works carried out on a deposit whose deposit model only involves a small presence of heavy metal minerals.

- ▬ ▬ ▭: medium hazard. This type of hazard will mainly be linked to old exploitation works, generally of an artisanal type, of small to medium size having excavated only a few hundred to a few thousand tons of material in deposits rich in sulfides.
  This type of hazard will also be linked to larger works carried out on a deposit whose deposit model only implies a weak presence of minerals rich in heavy metals.

- ▬ ▬ ▬: strong hazard. This hazard corresponds to deposits belonging to deposit models rich in heavy metals. In the case of certain or probable hazards, the operations correspond to medium to large mines.

4.2.4 THE RADIOACTIVITY HAZARD

The radioactivity of ores is induced by the presence of **uranium** or **thorium** in certain minerals. These metals can be constituent elements of minerals, but they can also be part of the composition of minerals, even though they are not part of the usual constituents.

Thus, the radioactivity of an ore or a rock can also be caused by the presence of minerals theoretically devoid of radioactive metals.

These minerals, occasionally or frequently radioactive, can concentrate in ores other than uranium ores and generate a radioactivity hazard in phosphate or rare earth deposits or in certain alluvial or coastal concentrations such as black sands.

This hazard can create a risk in various circumstances:

- In underground operations, there will be a production of radon which will have to be managed by appropriate ventilation.
- In the manufacture of concentrates, it will be necessary to ensure that the mining concentrate of metals other than uranium does not present a radioactive risk during its handling or storage (concentrates of niobium, tantalum, rare earths, zircon, etc.).

The radioactivity hazard will therefore be directly induced by the uranium hazard to which we will also add the hazard induced by the thorium contained in chemically harmless minerals such as zircons which can however have a high thorium content.

Its representation in the “balloons” of the interactive map will be carried out following the same rules as those of heavy metals. We will use the bullet ☢ to define it.