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

(TARANTULA)

D2.1 Preliminary directory of W, Nb and Ta occurrences (v1)

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS AND ACRONYMS

BRGM	Bureau of Recherches Gèologiques et Minières
GIS	Geographic Information System
GKR	Generic Model of 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

Refractory metals are essential to achieve the energy transition. However, they are almost exclusively imported when there is strong geological potential in Europe. The rational exploitation of this potential is therefore a necessity for European industries, the crisis linked to COVID-19 having painfully recalled it.

Going back to the past to identify these potential tungsten resources is easy. Indeed, by the end of the First World War, a significant research effort had been undertaken for this metal and very many companies qualified today as SMEs had undertaken its exploitation.

Finding tungsten today involves first identifying known deposits and occurrences in order to determine their potential in the light of the latest knowledge acquired in metallogeny and mineral processing. The dumps and tailings to be reprocessed will therefore be primarily those of these former tungsten mines.

Niobium and Tantalum have only had real industrial applications for a few years, and for a long time the needs were met by the extraction of an ore generally concentrated in placers, columbo-tantalite. Thus, there are very few known old underground mines of Nb-Ta in Europe. If we exclude the Nordic countries, where geology favours the presence of alkaline complexes and therefore the discovery of specific Nb-Ta deposits, the search for potential resources goes through the recognition of deposits already exploited for other substances, but containing various proportions of Nb-Ta not valued by the ore treatment then used.

Thus, country by Country, we are establishing an exhaustive inventory of old mines and more recent discoveries for tungsten, but also for tin, titanium and Rare Earths whose deposits occasionally contain economic concentrations of Niobium and / or in Tantalum.

This study details the models of deposits concerned and the mineralogical guides which make it possible to select among them those whose potential could be the most interesting.

The results are provided, together with the present report, in the form of Excel tables and kmz files at the end of this deliverable (Complementary information)

1. INTRODUCTION

Europe has been the subject of intense mining activity since the 19th century, and today we can identify more than 3500 sites having known a form of exploitation or exploration of these metals.

The twentieth century saw the almost systematic closure of all the holdings concerning them. These metals, essential to the rise of high technology and the energy transition are now imported.

In addition, awareness of environmental problems has been accompanied by extreme distrust among the public with regard to mining, which is considered to be eminently polluting and a remnant of days gone by. The ignorance of this activity reinforces this feeling and it must be taken into account that almost all the remaining mines having closed in the 1980s, there is today in our territories no witness of this activity under the age of 40 years.

If today we can regret the inconsistency of certain radical positions (these critical metals being essential to the advent of an eco-responsible society but we do not want to extract them from the ground), the fact remains that a reflection must be carried out on how to obtain them while minimizing the environmental impact to achieve them.

In addition, the repeatedly repeated discourse on new technologies and the strict application of environmental regulations is struggling to receive public acceptance, which cannot refer to recent examples of this activity in our territories.

Recycling provides a partial answer to the problem of supply, however it mainly applies to the final products of the industry, and the recovery of waste from the old mining activity has hardly been addressed.

The experience of public meetings which accompanied the demand for mining titles in France in the period 2011 - 2016, shows that a large part of public opinion would not be unfavourable to the resumption of extraction on an old site, if prior restoration of previous pollution was carried out. Indeed, a society capable of restoring an environment contaminated by an old exploitation is therefore, by definition, capable of extracting the ore without contaminating its environment if it wishes to do so. Thus, at the territorial level, the social acceptability of a mining activity would seem to be closely linked to the ability to reprocess old mine wastes.

TARANTULA intends to draw up an exhaustive inventory of the sites which can be the subject of a reprocessing of mining discharges from former operations within the framework of a virtuous activity allowing:

- The recovery of metals essential to our industries and today "wasted"
- Environmental restoration of formerly polluted sites
- The dissemination of a positive image of the extraction of these metals

The historical data of former operations do not reflect their current mining potential, the economic and technological parameters having changed very drastically since their closure.

2. TASKS DESCRIPTION AND PRELIMINARY RESULTS

This preliminary report explains the five stages of the method used to identify refractory metal resources in Europe.

The first step is to establish which models of deposits are likely to supply these metals. Indeed, it should be noted that Nb and Ta can be contained in deposits exploited for other substances, but also that all the deposits containing these substances are not likely to contain Nb or Ta; this probability depends very largely on the metallogenic model.

The second step consists in establishing a mineralogical filter which makes it possible to select from the candidates selected during the first stage, 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 third step is concerned with the economics of the treatment to be applied. The refractory metals contained in mine tailings can represent too low an economic stake to justify reprocessing. It is therefore important to anticipate what other resources could be jointly valued in order to make the economy possible.

The fourth 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.

The fifth step consisted in bringing together within a single IT structure, the GKR, a maximum of deposits and occurrences likely to be of interest for refractory metals. Thus, 3749 targets out of more than 68,000 have been previously listed. However, the corresponding files, coming from a wide variety of sources, must be checked and updated and harmonized.

2.1 GEOLOGY OF THE W, NB, AND TA DEPOSITS

Tungsten, tin, niobium and tantalum are closely associated in the deposits. An excellent synthesis of their geology is summarized in the book "Geology of Mineral Resources" whose definitions we will summarize here (Annex p.41).

The metallogenic (gitological) model is an essential element in anticipating the mining potential of a deposit. Indeed, this model can make it possible, to a certain extent, to anticipate the size of the deposits, the nature of their content, the probable type of exploitation and the environmental problems associated with their exploration and later their exploitation.

The main difficulty in establishing them comes from the frequent confusion with the type of deposit which associates metal content with a mineral body morphology. Thus, the types of deposit can be identical, but belong to different models and therefore present different mining potentials (Table 1).

TABLE 1. Refractory metal deposits

Métallogenic model	Type of deposit	Main ore	Valuable
Granite pegmatites	Pegmatite	Sn, Nb, Ta, Li, Be	
W-Sn Cupolas	Quartz vein W (Vein Field)	W	Au
	Quartz vein Sn-W (Vein Field)	W, Sn	Au, Nb, Ta
	Greisen	Sn, W, Nb, Ta, Li	
	Breccia Pipes	W, Sn, Nb, Ta	
	Stokscheider pegmatite	Sn, W	
Skarns W	Skarns	W	Au, Ag, Cu, Mo
	Mantos	W	Au, Ag, Cu, Mo
Carbonatites	Stratiform	REE, Nb, Ta	
Nepheline syenites	Magmatic intrusion	REE, Nb, Ta	
Peralkaline granites	Magmatic intrusion	REE, Nb, Ta, U	Sn, Zr, Be, Pb, Zn
Peralkaline pegmatites	Pegmatites	REE, Nb, Ta, U	
Placers Sn-Ti	Placer	S, Ti	Nb, Ta

2.2 MINERALOGY OF THE W, NB, AND TA DEPOSITS

2.2.1 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.

2.2.2 MINERALOGICAL APPROACH OF POTENTIALS IN W, NB AND TA

Establishing Europe’s refractory metal potential requires detailed knowledge of the mineralogy of these metals. We will classify these minerals 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.

As mentioned in the Executive Summry, Excel files related to these minerals and their categorization is shown in chapter Complementary Information at the end of this document.

2.2.2.1 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 4.1). 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 present in the gangue and whose recovery could improve or simply authorize the economy of the reprocessing: gold, copper, silver, molybdenum… (Chapter 2.1).

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. This 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.

2.2.2.2 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.

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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 4.3.1

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 4.3.1, we will classify Nb-Ta minerals into the 4 categories already listed (see chapter 2.2.2)

2.3 RECOVERY OF METALS FROM REFRACTORY METAL DEPOSITS

2.3.1 NEED FOR FULL RECOVERY OF METALS

The ore mined by the miner generally does not only contain refractory metals; its gangue is likely to contain useful substances, which an adapted line of treatment would be able to develop. The full recovery of minerals is therefore probably an inevitable development in European mining. The reasons are many:

- Europe, which imports almost all of its high-tech metals, cannot afford to waste the resources it absolutely needs.
- Far from penalizing the economy of a project, a full recovery of the ore can on the contrary improve it.
- Full recovery can drastically reduce the environmental impact of mining wastes.
- The gangues of treatment residues, cleaned of their metallic content, could sometimes find industrial applications.
- The social acceptability of a mining project in Europe can no longer be obtained if the stakeholders of the territory involved believe that future exploitation can be considered as a waste of non-renewable resources, even a looting of heritage; resources that would otherwise contaminate the environment.

Although not systematic, there is therefore a close relationship between recoverable metals and contaminants.

Gangues have only very rarely been systematically and comprehensively analyzed by mining operations, focused on the elements directly involved in their production system. The recovery of metals was rather the business of the foundries, which could (or could not!) pay them to the miner in the formula for the sale of concentrates. The metals remaining in the gangue actually escaped this recovery.

2.3.2 MINERALOGICAL APPROACH TO THE RECOVERABLE METALS

It was not until the early 1980s that the analytical technique by ICP gave access to a multi-elemental analysis of rocks and ores. Imperfect at the start of its application, it is now mature and allows the overall composition of an ore to be obtained at an acceptable price. Likewise, recent developments in LIPS and XRF techniques have brought great flexibility for the rapid detection of recoverable metals in rocks.

These techniques do not exist during the carrying out of the old mining works and the exploitation of the old mines, the overall composition of the ores and their gangues remained very little known. This is all the more accentuated since the majority of metals sought today were of no interest at the time.

In addition, the international community of mineralogists which includes several tens of thousands of amateurs, often enlightened, has found with NICTs the means necessary to share their passion with professionals of distribution on the Internet. Online databases, such as the excellent Mindat.org[1], provide often very comprehensive mineralogical descriptions of former mine sites, favourite targets for mineral collectors.

The identification of the geological models of the indices and deposits corresponding to the old mining works and the old mines, supplemented by a fine analysis of the mineralogical composition of the rocks and ores contained, is a fundamental step to estimate the actualized potential of these targets.

The comparison between the refractory metal ores already exploited and the metal content which could be recoverable today therefore sheds new light on this former mining activity. The refractory metal deposits could therefore also contain the metals presented below, the valuation of which should be studied.

The metals listed below (Table 2) must meet with sufficient frequency and be able to reach a significant proportion in the overall composition of the ore to be able to be valued. In our approach, we will therefore focus mainly on ore minerals and potential ore minerals.

It is also important to note that a mineral capable of providing a recoverable metal may also contain contaminants which would create environmental problems if they were not recovered. The details of all these possibilities are stored in the GKR System. The potential and hazard assessments specific to each occurrence will be based on this information.

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[1] https://www.mindat.org/

Thus, the mineralogical study of indices is an essential background task for the estimation of exploitable potentials in refractory metals.

TABLE 2. Potentially recoverable metals in the W, Nb, and Ta deposits

Metal	N	Ore minerals	N	Potential ore minerals	N
Gold	43	Gold, Electrum …	15	*Arsenopyrite*	
Silver	208	*In progress*	27	*In progress*	4
Molybdenum	49	*In progress*	2	*In progress*	
Lithium	129	*In progress*	7	*In progress*	
REE	210	*In progress*	47	*In progress*	
Uranium	264	*In progress*	24	*In progress*	
Copper	666	*In progress*	43	*In progress*	
Zinc	343	*In progress*	11	*In progress*	

This list is not exhaustive, and the number of mineral species associated with each category will be revised as the WP2 progresses.

2.4 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 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.

Table 3 lists the main contaminants that could be associated with critical metal deposits.

This list is not exhaustive, and the number of mineral species associated with each category will be revised as the WP2 progresses.

TABLE 3. Potential contaminants in the W, Nb, and Ta deposits

Metal	N	Ore minerals	n	Potential ore minerals	n
Arsenic	601	*In progress*	7	*In progress*	
Uranium	264	*In progress*	24	*In progress*	
Mercury	102	*In progress*	3	*In progress*	
Copper	663	*In progress*	43	*In progress*	
Lead	540	*In progress*	18	*In progress*	
Zinc	343	*In progress*	11	*In progress*	
Cadmium	23	*In progress*	1	*In progress*	
Antimony	291	*In progress*	13	*In progress*	
Bismuth	236	*In progress*	6	*In progress*	
Thallium	61	*In progress*	0	*In progress*	0

2.5 EUROPEAN RESOURCES OF REFRACTORY METALS

Tungsten, like tin, tantalum and gold is sometimes exploited in conflict zones and in particular in the Democratic Republic of Congo by armed groups. This source of income has led the United Nations, the OECD, the United States government and the European Union to various initiatives aimed at drying up this source of funding.

United Nations calls for production and export statistics, OECD released "Due diligence guide for responsible supply chains for conflict and high-risk minerals" in the United States, the "Dodd-Frank Wall Street reform and consumer protection act" aims to control the origin of raw materials. European regulations were published in the Official Journal of the EU on May 17, 2017, to take effect on January 1, 2021 and only concerns large companies that import minimum tonnage.

2.5.1 HARMONIZATION OF DATABASES

Europe has experienced centuries of mining activity, but it is only recently that the criticality of refractory metals has become evident.

The geological services of the countries have established mining inventories listing the known deposits and indices in their respective territories. In total, more than 68,000 records were identified and stored in a data integration system, the GKR.

The exploitation of this large amount of information, however, requires an extensive harmonization phase. Indeed, if harmonization exists today in part on significant deposits, it remains very approximate in terms of occurrences, which are however the potential source of new discoveries.

The work carried out during this first year enabled:

2.5.1.1 INDEXING BY ONTOLOGIES

Indexing by ontologies of the terms used in all the files collected in the public databases. The information collected can thus be manipulated without the limitations linked to the language of their original entry and by using semantic clusters allowing queries based on terms not used by the authors of the files. Thus, the same search using the same criteria can be applied to all 68,000 selected files.

2.5.1.2 HARMONIZATION OF VOCABULARY

The use of a vocabulary common to all the records of deposit and occurrences is necessary (Table 4). It should be noted that there is a blurring between the terms used to describe the mining activity and the geological objects which concern it. The GKR will use the vocabulary above for geology and mining operations.

TABLE 4. Relation between Geology and Mining operation

GEOLOGY		Mining Operation
Province	Scale = 100 km. A mineralized province generally corresponds to a geological formation enclosing numerous mineral deposits that can be grouped into districts	Reconnaissance
District	Scale = 10 km. A mineralized district generally corresponds to a geological event generating numerous mineral deposits that can be grouped into fields.	Prospecting
Vein field	Scale =1-10 km. Grouping of deposits generally associated with the same mineralizing phenomenon. Can give rise to many operation sometimes grouped under the name of a single mine.	General exploration
Mineral deposit	A significant concentration, sometimes large, of ore or industrial minerals. The level of knowledge does not make it possible to define whether the economic conditions are favourable for exploitation in the short or medium term	Old mine Exploration
Ore deposit	A mineral concentration that is economically exploitable under the conditions existing at the start of the operation.	Mine (active/dormant) Detailed exploration
Ore body	Part of a deposit that can be exploited selectively. The ore bodies of the same deposit may have different morphologies.	Mining
Occurrence	A visible indication that mineralization exists, whether in the form of an outcrop or a mineralized boulder.	Old mining works Outcrop

2.5.1.3 SELECTION OF POTENTIAL RESOURCES IN W, NB AND TA

We have made a preliminary selection, country by country, of the targets used to assess their potential in refractory metals. Provisionally, we will keep 3750 records in total as specified in table 3. These numbers are provisional and will change as the project progresses, duplicates having been eliminated and new deposits or occurrences added, mainly by detailed mineralogical studies of deposits of other resources.

From this preliminary selection we chose 3 European countries to test the methodological approach which will be extended to all the countries of the community. These countries are:

- **Portugal**, which is a good example for the exploitation of granite domes and whose geology presents strong analogies with that of Spain and France.
- **Austria,** which offers a good example of the geology in central Europe with the exploitation of scheelite skarn.

- **Greenland**, which presents a geological context representative of the Archean basement and offers possibilities of deposits in the models associated with peralkaline magmatism.

The Table 5 allows to follow the progress of the achievement of the deliverables of WP2, country by country.

TABLE 5. Progress in the analysis of refractory metal potentials

Countries (rec.)	Tasks	
Austria (1,288)	☑ Final selection made	☑ Mineralogy update
• First selection (60)	☑ Elimination of duplicates	☐ EU Harmonization
• Final selection (54)	☑ Adding records	☑ Excel table (preliminary)
	☑ Vocabulary update	☑ .kmz file (preliminary)
Czech Republic (484)	☐ Final selection made	☐ Mineralogy update
• First selection (51)	☐ Elimination of duplicates	☐ EU Harmonization
• Final selection	☐ Adding records	☑ Excel table (preliminary)
	☐ Vocabulary update	☐ .kmz file (preliminary)
Denmark (221)	☑ Final selection made	☑ Mineralogy update
• First selection (7)	☑ Elimination of duplicates	☐ EU Harmonization
• Final selection (92)	☑ Adding records	☑ Excel table (preliminary)
	☑ Vocabulary update	☑ .kmz file (preliminary)
Finland (482)	☐ Final selection made	☐ Mineralogy update
• First selection (35)	☐ Elimination of duplicates	☐ EU Harmonization
• Final selection	☐ Adding records	☑ Excel table (preliminary)
	☐ Vocabulary update	☐ .kmz file (preliminary)
France (46,296)	☐ Final selection made	☐ Mineralogy update
• First selection (1,483)	☐ Elimination of duplicates	☐ EU Harmonization
• Final selection	☐ Adding records	☑ Excel table (preliminary)
	☐ Vocabulary update	☐ .kmz file (preliminary)
Germany (1162)	☐ Final selection made	☐ Mineralogy update
• First selection (73)	☐ Elimination of duplicates	☐ EU Harmonization
• Final selection	☐ Adding records	☑ Excel table (preliminary)
	☐ Vocabulary update	☐ .kmz file (preliminary)
Greece (509)	☑ Final selection made	☑ Mineralogy update
• First selection (4)	☑ Elimination of duplicates	☐ EU Harmonization
• Final selection	☑ Adding records	☑ Excel table (preliminary)
	☑ Vocabulary update	☑ .kmz file (preliminary)
Hungary (417)	☐ Final selection made	☐ Mineralogy update
• First selection (1)	☐ Elimination of duplicates	☐ EU Harmonization
• Final selection	☐ Adding records	☑ Excel table (preliminary)
	☐ Vocabulary update	☐ .kmz file (preliminary)
Ireland (224)	☑ Final selection made	☑ Mineralogy update
• First selection (6)	☑ Elimination of duplicates	☐ EU Harmonization
• Final selection (10)	☑ Adding records	☑ Excel table (preliminary)
	☑ Vocabulary update	☑ .kmz file (preliminary)
Italy (977)	☑ Final selection made	☑ Mineralogy update
• First selection (47)	☑ Elimination of duplicates	☐ EU Harmonization
• Final selection (94)	☑ Adding records	☑ Excel table (preliminary)

	☑ Vocabulary update	☑ .kmz file (preliminary)
Netherlands (76) • First selection (2) • Final selection	☐ Final selection made ☐ Elimination of duplicates ☐ Adding records ☐ Vocabulary update	☐ Mineralogy update ☐ EU Harmonization ☑ Excel table (preliminary) ☐ .kmz file (preliminary)
Poland (453) • First selection (9) • Final selection	☐ Final selection made ☐ Elimination of duplicates ☐ Adding records ☐ Vocabulary update	☐ Mineralogy update ☐ EU Harmonization ☑ Excel table (preliminary) ☐ .kmz file (preliminary)
Portugal (2,629) • First selection (802) • Final selection (778)	☑ Final selection made ☑ Elimination of duplicates ☑ Adding records ☑ Vocabulary update	☑ Mineralogy update ☐ EU Harmonization ☑ Excel table (preliminary) ☑ .kmz file (preliminary)
Romania (459) • First selection (17) • Final selection	☐ Final selection made ☐ Elimination of duplicates ☐ Adding records ☐ Vocabulary update	☐ Mineralogy update ☐ EU Harmonization ☑ Excel table (preliminary) ☐ .kmz file (preliminary)
Slovakia (280) • First selection (21) • Final selection	☐ Final selection made ☐ Elimination of duplicates ☐ Adding records ☐ Vocabulary update	☐ Mineralogy update ☐ EU Harmonization ☐ Excel table ☐ .kmz file (preliminary)
Sweden (710) • First selection (48) • Final selection	☐ Final selection made ☐ Elimination of duplicates ☐ Adding records ☐ Vocabulary update	☐ Mineralogy update ☐ EU Harmonization ☑ Excel table (preliminary) ☐ .kmz file (preliminary)
United Kingdom (1,227) • First selection (164) • Final selection (356)	☑ Final selection made ☑ Elimination of duplicates ☑ Adding records ☑ Vocabulary update	☑ Mineralogy update ☐ EU Harmonization ☑ Excel table (preliminary) ☑ .kmz file (preliminary)

2.5.1.4 ELIMINATION OF DUPLICATES

We tested the elimination of duplicates for Portugal, Spain, UK, Greece, Italia, Austria and Denmark (Greenland). These duplicates come either from errors in the published databases, or from an incorrect use of the terms described in Table 4. The correction of these entries, subsequently imposes a search and the elimination of the duplicates caused according to the criteria specified in Table 6

TABLE 6. Main types of duplicates

Nature of the duplicate	Symptom	Remediation
True double	• Match the same target • Same name or not • Coordinates may be different	• Merge records • Fix coordinates
Homonymy	Another target with the same name already exists • Could be near the other one • Could exploit another commodity	• Keep the record • Establish hierarchy with the mine inside the GKR • Check/Fix coordinates
Confusion between mine and deposit	• could have the same name • could have the same coordinates	• Merge records • Fix coordinates
Several mines operating the same deposit	• could create false duplicate with other mines in the same Vein field • Possible confusion with “true” duplicate	• Keep the record • Modify the name if needed • Establish hierarchy with the mine inside the GKR • Check/Fix coordinates
Confusion between deposit and district having the same name	A mine and/or a deposit has the same name as a district in the same region	• Keep the record • Change the name of the district by adding “District” after the name.
Confusion between occurrence and deposit or mine	A record for the occurrence was made before the construction of the mine	• If the occurrence corresponds exactly to the mine site: merging records for the benefit of the mine. • If the occurrence is distant from the mine or deposit: Keep the record by changing the name.

2.5.2 ORE AND DEPOSITS

2.5.2.1 TUNGSTEN

Seventy-seven minerals can incorporate tungsten into their crystal lattice, but only two of them are exploited and will be considered as ore minerals:

- Scheelite ($CaWO_4$) which represents 70% of the world's tungsten reserves.
- Wolframite $(Fe, Mn)WO_4$, a continuous solid solution between ferberite ($FeWO_4$), and hübnerite ($MnWO_4$), which represents the remaining 30% of the world's tungsten reserves.

As explained in Annex 4.1, tin, molybdenum, niobium and / or tantalum are often associated with tungsten in ores.

The tungsten ores are dense and brittle, the scheelite also being fluorescent under ultraviolet radiation. Only scheelite can be concentrated by flotation; wolframite, paramagnetic, being mainly concentrated by magnetic methods.

Grinding must be done with care to avoid the formation of too much fine particles due to the brittleness of the ore. A first concentration uses gravimetric methods (dense medium, spirals, shaking tables ...) followed, depending on the nature of the ore in a flotation or magnetic separation.

The content of merchant ore is between 60 and 75% of WO_3.

In 2018, world mining production amounted to 82,000 t, of which 67,000 t produced by China and 2,430 t produced by the European Union (Austria, Portugal, Spain).

- **In Austria**, a scheelite ore is mined underground and concentrated by flotation in **Mittersill**, in the province of Salzburg, by the company Wolfram Bergbau und Hütten, controlled since 2009 by the Swedish group Sandvik.
- **In Portugal**, the **Panasqueira** underground mine is operated by Beralt Tin and Wolfram, a subsidiary of the Canadian company Almonty Industries which bought it in January 2016 from the Japanese group Sojitz Corp.

  Ferberite ore, found in quartz veins, contains cassiterite, chalcopyrite and silver. The deposit has been mined since 1896. Between 1947 and 2014, 31 million t of ore produced 111,123 t of tungsten concentrate, 5,383 t of 72% tin Sn concentrate and 31,702 t of copper concentrate containing 28% Cu.

  This deposit currently offers the largest stockpile of dumps and tailings relating to W, Sn in Europe.

- **In Spain, in the province of Salamanca**, the open-pit scheelite mine at **Los Santos** is operated by Almonty Industries. In 2016, the extraction of 519,803 t of ore containing 0.35% WO3, with a recovery rate of 60.2% produced 931 t of WO3. Proven and probable reserves are 3.582 million t of ore containing 0.23% of WO3. In the same province, the **Barruecopardo** open pit mine shows proven and probable reserves of 8.69 million t of ore containing 0.30% of WO3.

  In Extremadura, the **La Parrilla** open-pit tungsten-tin mine, owned by the company W Resources, has proven and probable reserves of 30 Mt of ore containing 0.1% WO3 and 116 ppm Sn.

- **In the United Kingdom**, the Drakelands open pit wolframite mine opened in 2015 by Wolf Minerals, produced 1,123 t of WO3 in concentrates and 194 t of tin in 2016. Reserves are 32.2 million t ore containing 0.17% WO3 and 0.03% Sn. In 2018, the mine was closed.
- **In France**, there is no longer any mining, but during the 20th century, 13 deposits were exploited with a total production of 25,771 t of WO3. The most important were those of Salau (09), with 12,415 t, Puy les Vignes (87), with 3,970 t, Echassières (03), with 3,900 t, Leucamp (15), with 1,700 t, Enguialès (12), with 1,300 t. The Salau mine (09), in operation between 1971 and 1986, was operated by the Société Minière d'Anglade (SMA).

  The resources estimated by the BRGM amount to 83,122 t of WO3; the main ones being located at Fumade (81), with 14,300 t, Coat-an-Noz (22), with 11,000 t, Montredon-Luitré (35), with 1,500 t.

  A new estimate of the resources of the Salau deposit was undertaken by the E-Mines Company from 2015. Studies conclude that there is a very significant mining potential on this site which can exceed 50,000 tonnes of high-grade WO_3 (> 0.6% WO_3). The bankruptcy of the Apollo subsidiary in France and the questioning of the validity of the mining title that preceded it suspended the exploration work on this project.

2.5.2.2 TIN

Tin has been known since Antiquity since it is used in bronze, the first alloy produced which characterizes a prehistoric era.

Cassiterite (SnO_2) is practically the only mineral actually mined. Primary deposits are closely associated with those of W (see Annex p.44) and their ore represents 60% of world production; 90% of them are mined underground and 10% open pit.

The rest of the production comes from alluvial deposits (placers), formed after physical and chemical alteration of the primary rocks, transport and storage.

Cassiterite can fix up to 4% tantalum in substitution in its crystal structure; deposits from Thailand, Malaysia, Indonesia and Brazil are of this type.

During metallurgical operations to reduce the ore, tantalum is found in the slag. This source represents around 67,000 tonnes / year of Ta, or around 10% of world consumption.

2.5.2.3 NIOBIUM AND TANTALUM

Tantalum is often associated with niobium in its deposits, the two elements having similar chemical properties. However, there are niobium mines in which tantalum is not recovered and vice versa tantalum mines in which niobium is not exploited.

The main ore minerals are oxides with:

- The family of pyrochlores, whose composition varies between that of the pyrochlore proper $(Na, Ca)_2Nb_2O_6(OH, F)$ and that of the microlite $(Na,Ca)_2Ta_2O_6(OH,F)$. Pyrochlore, mainly exploited in Brazil and Canada, is the main source of niobium, with more than 99% of the world total. The rest comes from columbite in Central Africa and slag from the processing of tin ores, in Malaysia and Thailand.

  World reserves were more than 9.1 million t of niobium contained in 2018, divided between Brazil and Canada.

  The niobium concentrates sold, in the form of pyrochlore, have a content of 54% to 60% of Nb_2O_5.

- The family of columbo-tantalites, called coltan in Central Africa and whose exploitation is often artisanal and in the Democratic Republic of Congo, carried out by armed groups. Columbo-tantalite forms a solid solution between the columbite group $(Fe,Mn)Nb_2O_6$ and the tantalite group $(Fe,Mn)Ta_2O_6$ (Figure 1). Tantalite now accounts for 60% of world tantalum production.

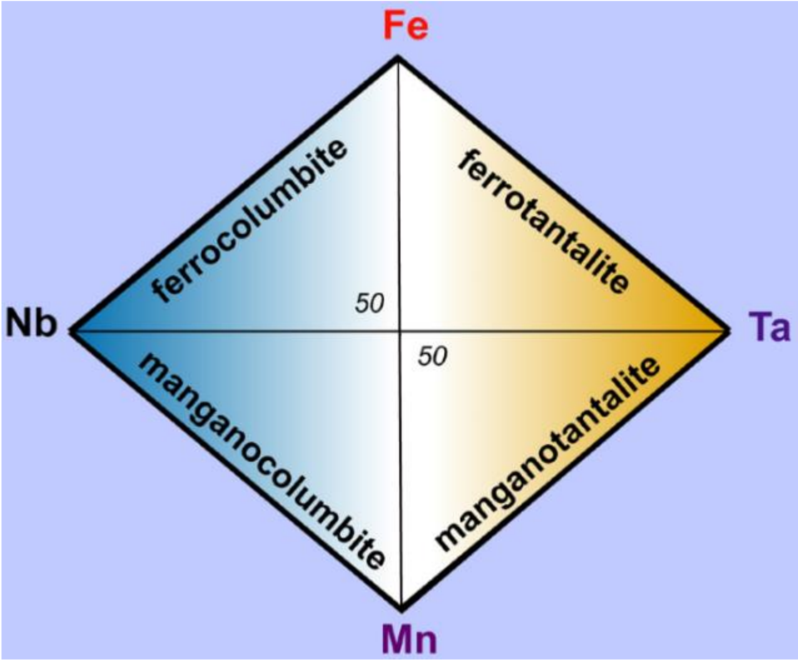

Figure 1: Compositions of minerals in the columbite and tantalite groups

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

- Wodginite: $(Ta,Nb,Sn,Mn,Fe)_4O_8$.

The contents of the niobium and tantalum ores are expressed respectively in Nb_2O_5 and Ta_2O_5; The Nb_2O_5 contents are between 0.6% in Canada and 2.5% in Brazil, for the Araxá (bariopyrochlore) deposit.

Niobium and tantalum are often found in tin and titanium ores, replacing tin in cassiterite and titanium in rutile and ilmenite. In cassiterite, tantalum can replace up to 4% of tin; this source represented in 2014 around 15% of world production.

Depending on the nature of the deposits (see Annex p.53), niobium and tantalum will also be associated with rare earths or lithium.

The minerals often contain radioactive uranium and thorium. When the radioactivity of marketed products reaches 10 Bq / g, this must be declared and precautions taken. This radioactivity corresponds to a content of 0.13% of ThO_2 and 0.048% of U_3O_8.

2.5.3 EVALUATE EUROPEAN POTENTIALS IN W, NB AND TA: METHODE

All of the exploited European tin-tungsten deposits are linked to felsic magmatism, in the form of granite domes and scheelite skarns.

The need for niobium and tantalum has emerged with the high-tech industry. These metals were therefore not the target of historical productions focused on tin (since prehistoric times) or tungsten (early 20th century).

The approach we will develop here is to examine the production potential of these critical and strategic metals based on existing information on their deposits and their exploitation.

From the gathering of metals to the exploitation of giant hyper-mechanized mines managed by artificial intelligence, the mining industry has evolved considerably, far from the images often conveyed by the media little interested in the question. In our approach, we will therefore distinguish mining activity by period, each of which reflects technological advances and specific economic needs.

2.5.3.1 HISTORICAL WORKS

We will classify in this group the mining works from the Roman era to the mid-nineteenth century. These are generally small works, although some exploitations have been maintained for centuries and have therefore been able to reach significant sizes over their lifespan. The metals exploited were few: iron, gold, silver, copper, lead, tin, antimony.

The exploitation, not mechanized, was interested in rather rich ores which can be extracted by hand and susceptible to recovery by known metallurgy.

Today, these exploitations will be considered as occurrences to be re-examined in the light of current knowledge because the deposits involved could turn out to be deposits that are still (almost) intact.

Due to the sorting which was carried out directly on the cutting face by the miner, these operations have in fact produced very few waste dumps and treatment residues capable of recovery. However, an environmental impact will be associated with them and its importance will depend on the importance of the works and the mineralogy of the ore.

2.5.3.2 OLD MINING WORKS

We will classify in this group the exploitations and the mining researches before 1950. The mining techniques are mechanized, but the powers involved remain low and impose rather modest returns.

In this way, production will focus on rich minerals and the extraction of dumps will be reduced to a minimum.

The tungsten mines, which experienced strong development with the discovery of the qualities of W, often developed on small geological structures such as veins and pegmatites associated with granite domes, will often be developed by small companies, which we could qualify of SMEs today. Generally, these operations will only extract a few hundred tonnes of metal, sometimes less. The high grades required for the ore and the low production therefore imply volumes of dumps and rejects of modest size. In general, they will not have sufficient volume to justify today an in-situ recovery.

On the other hand, the selection criteria which prevailed at the time of the decision to bring into operation could indicate the existence of potentially exploitable deposits.

It is more than likely that strong social pressure will impose environmental restoration of these former mine tailings before any exploration / exploitation of the deposit. Their recycling will probably be an obligation to obtain the social operating permit (SLO).

ENVIRONMENTAL IMPACT OF OLD MINING WORKS

During this period, the extraction of tungsten and tin, then considered as "small metals", fell under the SME. The "heavy" mining industry then only concerned coal and iron in Europe. We are therefore witnessing a multitude of small operations, often artisanal, especially located in Southern Europe (Variscan basement). Rock mining mainly targeted veins outcropping with tungsten (quartz - wolframite) and / or tin (quartz-cassiérite), easily recognizable in areas with low vegetation cover. The grouping of these veins in mineralized fields (see Annex p.44) has led to a multiplicity of small works distributed over small areas which can generate relatively diffuse pollution of the environment.

The dispersion of these piles of dumps is therefore an essential element in controlling the quality of surface water. Their density on reduced surfaces is in theory likely to have a greater impact than that which would be caused by a single pile having the same volume of rejections.

A simple pile of dumps of 50 x 20 m of surface and a thickness of 3 m (that is to say approximately 7500 tons), which we will qualify as “small”, even “very small” compared to the dumps of the current mines, and which would contain approximately 1% of arsenopyrite (which is little for the majority of mineralization) is still likely to release 35 tonnes of arsenic.

It should also be noted that environmental precautions, which are now absolutely essential, were not a concern. Generally, the waste was left in the open air without any form of protection.

Fortunately, the W-Sn mineralizations are mainly composed of oxides and the ores and their gangues are little subject to major phenomena of sulfuric acid production by weathering (acid mine drainage); the arsenopyrite crystals, included in quartz, are not easily damaged and the arsenic will not be widely diffused in the end.

During the same period, numerous small alluvial mines for tin and titanium also developed in the context of granite domes. As these operations do not meet sulphides by definition, their current environmental impact can be considered as completely negligible.

2.5.3.3 OLD MINES

The 1990s saw the closure of almost all metal mines in Europe. This closure had already reached tungsten mines in the 1980s, following dumping of Chinese tungsten; China remains by far the largest producer with 85% of world production.

The period 1950 - 2000 saw the advent of the modern mine. The evolution of equipment and technologies was continuous and it continues this trend today with an increasingly present digital activity.

As the technologies used allow for the effect of scale, mining operations have seen their size increase exponentially, limited only by their geology. It is largely this race for gigantism that has fueled a phenomenon of rejection of this activity in European public opinion and exacerbated the NIMBY effect.

New techniques allowing the exploitation of lower and lower grades, the volumes of dumps and treatment discharges underwent a considerable increase in volume.

It was this period that initiated the opening of open pits, always larger and presenting stripping rates that can reach or exceed 10: 10 tonnes of “waste rock” removed for the extraction of a ton of ore, itself often containing less than 1% of the exploited substance.

During this same period, the valued metals saw the number increase very significantly. From under 15 at its inception, it is today almost all of the metals listed in the periodic table of the elements that today find use, mainly in the high-tech industries. The dumps and treatment waste from these old mines, especially those that had activity at the start of the period, are therefore likely to contain appreciable quantities of these critical substances.

In the context of an imposed circular economy, knowledge of this potential is therefore essential. Its estimation is a complex operation, because the new metals sought (including Nb and Ta) were not a priori analyzed at the time of the feasibility, then of the exploitation of these mines. As the management of the dumps does not foresee their existence, the enriched parts of these dumps can be masked by recoveries of products from other totally sterile sectors of the mine. In addition, in many cases, mine tailings undergo significant transformations by the action of meteoric weathering, in particular during acid mine drainage (transformation of sulphides into sulfuric acid) and their surface part does not lend themselves to a representative sample.

Assessing the potential of these stocks therefore represents a cumbersome operation, the more important the greater the volume concerned. The purpose of this work is to provide guides allowing a first approach to select releases that are interesting enough to justify such estimation work.

ENVIRONMENTAL IMPACT OF OLD MINES

This is where the problem lies!

The effective taking into account of the preservation of the natural environment is a recent operation, which we will rather relate to the 21st century. Discards from old mines are often stored by applying (sometimes not!) Protective measures which today are deemed to be largely insufficient.

Underground mines, especially the older ones, generated less waste due to the high selectivity applied during extraction. These dumps generally contain a lot of “poor ore” according to current criteria and correspond above all to the rocks containing mineralization disseminated in the vicinity of the “rich” ores which were only exploited. For example, in the last years preceding its closure in 1986, the Salau tungsten mine in France practiced a cut-off grade (grade below which mineralization is no longer considered as an ore) of 0.9% WO3, which today corresponds to 3 times the average grade of a working mine.

Thus, it will be considered that the oldest mines are likely to provide waste presenting the best potential in terms of content, but that their volume will often be relatively small. Of course, these remarks remain general and the estimate made on a case-by-case basis.

The Salau mine, which closed in 1986, still left a stockpile of at least 500,000 t of dumps and tailings of at least 900,000 t in the open air. Although the recovery rate of tungsten (82%) may still appear excellent today, due to the initial richness of the ore these tailing contain more than 0.3% of WO3; this grade now corresponds to the operating grades of many tungsten mines.

From the point of view of the composition of the ore, we will distinguish the ores made up of wolframite (and / or cassiterite) quartz, almost devoid of sulphides, scheelite skarns which in some cases, as in Salau, can contain significant quantities of iron sulfides. In both cases, the risks of chemical contamination of surface water are relatively reduced compared to mines of base metals such as copper, lead or zinc. Indeed, the wolframite ores, containing almost no sulphides, will only present very weak acid mine drainage, while the sulfuric acid released by the sulphide ores contained in the skarns will be neutralized by the carbonates which compose them.

2.5.3.4 DORMANT MINES

They will be cited here for the record. These are mines which have ceased to operate but retain infrastructure maintenance with the possibility of resumption of activity. In the context of our study, only the Drakeland mine can be classified in this category.

The study of mine releases can be an important element in planning a reopening. However, in the case of mines such as Drakeland, which were opened very recently and closed immediately, the resumption of discharges can in no case be a decisive criterion given the low volume produced.

2.5.3.5 ACTIVE TUNGSTEN MINES

These mines are few in Europe and they can be classified into two categories:

- Mines already having a long period of activity
    - Panasqueira (Portugal)
    - Mittersill (Austria)
    - Kaolins de Beauvoir, a subsidiary of Imerys, produces 55 t / year of tin-tantalum-niobum concentrates in Echassières (03), by-products of a kaolin operation. The content of the concentrates is approximately 10% of Ta2O5.
- Recently opened mines

- These mines are opening or have recently opened under new environmental regulations. The reprocessing of dumps and old residues is part of their exploitation strategy:
  - Barruecopardo (Spain, old existing mining works)
  - Los Santos (Spain, old existing mining works)
  - La Parrilla (Spain, old existing mining works)

2.5.3.6 THE MINES OF THE FUTURE

By definition, one would think that there would not be any problems with the recovery of waste for these future mines since their exploitation remains to come. The main objective would therefore be the full recovery of the metallic content of their ores with maximum recovery. The new technologies, tested and developed within the framework of the TARANTULA project, fit well into this approach.

However, the following observations should also be taken into account:

- 75% of the mines were explored by 2 to 5 companies before their discovery. In Europe, this research work, including non-mechanized artisanal operations, will be classified as old work.
- There are no longer any “virgin” areas of exploration in Europe.
- The highest likelihood of discovering a new mine is to assess the potential for occurrences, the vast majority of which corresponds to former mining work. Current examples are the recently opened mines in Spain of Barruecopardo and Los Santos, or in the process of opening of La Parrilla.

Under these conditions, the new mine will have to be concerned with the fate of the old mining wastes which could result from previous operations or works.

From the exploration stage, this need is likely to be imposed by the neighbouring communities.

This prerequisite is requested by the stakeholders of the territory affected by the project to study the feasibility of a new exploitation of the Salau deposit. Because of the volume and the content represented by the tailings, the TARANTULA project is particularly interested in the techniques which would allow the valuation of this stock.

2.5.4 POTENTIAL IN REFRACTORY METALS FROM EUROPEAN COUNTRIES

The progression of the WP2 work program can be understood from the Table 5

The mining potential and / or reprocessing of wastes is estimated country by country using the same evaluation criteria with a view to harmonizing data on a European scale. For this we have established for each of them:

- A list as exhaustive as possible of all known occurrences, mineral deposits and ore deposits for these metals. The data sources have been filtered to eliminate as much as possible the duplicates and errors that appeared during their integration. The geographic coordinates have been corrected, where possible, using Google Earth which today offers ground accuracy that did not exist when the source data was created.
- Exploration works, historical works, old mining works have been grouped in the occurrence rank. The size of the deposits mined in the traditional way for tin and tungsten do not allow today to anticipate the existence of a deposit without the resumption of exploration work.
- Old mines or positive exploration work will be classified as deposits. For the most part, these mines closed after Chinese dumping in the 1980s and the deposits, then exploited with much higher cut-off grades than today, are very likely not to be exhausted.
- Study of the ore and gangue parageneses to determine:
    - Recoverable metals
    - Potential contaminants (heavy metals, arsenic, radioactivity, etc.)

Occurrences and deposits are examined according to the metals contained, the potential for recoverable metals, but also in relation to the environmental hazard which would be attached to the reopening of old works or the reprocessing of wastes.

The document provided is intended as a guide for institutions wishing to promote the enhancement of their mining heritage. The information provided may allow a prior assessment of the economic and environmental risk incurred.

For each country, the results are provided in the form of an electronic annex which includes:

- A database in Excel format presenting the main characteristics of the indices and deposits (georeferenced WGS 84).
- A .kmz file (Google Earth) which allows users who do not have a G.I.S. to easily access a very precise geographic location of all the referenced sites.

It will be recalled that the opening of such files requires the download of the free application "Google Earth" to the user's computer. Internet access is required. Once this prerequisite is executed, the opening of a .kmz file is automatic by a simple double-click on its icon. Different .kmz files can be integrated into the same consultation session.

As it was mentioned in the Executive Summary, this information (Excel and .kmz files) is available in Complementary Information at the end of this document

3. CONCLUSIONS

In the twelfth month of the Tarantula project, WP2 was able to establish the methodology which will be continued until its conclusion.

In its current configuration, the GKR makes it possible to integrate and harmonize the records of deposits and occurrences published by the geological services of the countries of the European Community.

The information will be supplemented by the mineralogical descriptions posted on Mindat.org and other on-line databases. Crossing the data thus obtained makes it possible to specify the metallogenic models and to refine the potential in refractory metals of a large majority of the occurrences listed.

A first test was carried out on 8 countries with complementary geological characteristics: Portugal, Spain, UK, Ireland, Greece, Italia, Austria and Denmark (Greenland).

The first conclusions concern the geological potential:

- Greenland and Sweden offer the best potential for opening mines for the selective exploitation of Nb and Ta. The Precambrian basement of these countries indeed presents a geology compatible with the presence of peralkaline complexes which are today the only true primary source for these metals. However, this geology is not particularly favorable for the discovery of significant tungsten deposits.
- On the contrary, Portugal, Spain and France have a very significant potential for tungsten, either in W-Sn cupolas, or in scheelite skarns. This observation can be extended to the countries of central Europe.
- A very large majority of the old mining works, which today correspond to a large part of the occurrences listed were associated with vein mineralization (W-Sn cupolas and greisens). A detailed study of these occurrences in Portugal shows that approximately 10% of these latter are likely to contain Nb-Ta in their mineralization. However, there is probably no hope of discovery for deposits that would be developed or reopened for the sole exploitation of Nb and Ta.

At the current stage of the study, it is too early to optimize the algorithms that will establish the hierarchy of occurrences and deposits at European level.

The main deliverables for this study will be provided for each country in the form of two complementary folders:

- Excel folders, which will provide a preliminary table of the approx. 3500 deposits and indices that will be the subject of this study (Europe_W-Nb-Ta_v1.xls).

- kmz files (Google Earth) which will allow precise location of each of the occurrences after making the necessary corrections in the raw data excel files extracted from the GKR. The main information relating to these occurrences will be summarized in a balloon attached to the coordinates of the points.

The standards of these two types of files make it possible to envisage the integration of information into any computer system, database or GIS.

As it was mentioned in the Executive Summary, this information (Excel and .kmz files) is available in chapter Complementary Information at the end of this document. The standards of these two types of files make possible to envisage the integration of information in any computer system: database or GIS. In addition, these files are also directly usable by any user, their universality allowing wide dissemination.

4. ANNEXES

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

4.1 GEOLOGY OF THE W, SN, NB, AND TA DEPOSITS[2]

4.1.1 RARE-METAL GRANITE PEGMATITE

Pegmatite is a coarse-grained silicated igneous rock that forms at the end of volatile-rich (H_20, $C0_2$, F, Cl, B) magma crystallization. It occurs most commonly in association with felsic magmatism, and more rarely with mafic magmatism, whereupon the term pegmatoid is used. In this report we shall only consider the former, commonly referred to as granite pegmatite

Pegmatite is composed mainly of quartz, feldspar (microcline and albite in its cleavelandite facies) and mica, with many accessory minerals commonly of economic value. The main accessory minerals are beryl (Be), cassiterite (Sn), molybdenite (Mo), spodumene, petalite, lepidolite and amblygonite (Li), columbite, pyrochlore and tantalite (Nb, Ta), pollucite (Cs), as well as various uranium, thorium and rare-earth (allanite, monazite...) minerals, and several phosphates. These metals occupy a prominent place in the field of advanced technologies, be it the metallurgy of light metals (Be, Li, lighter than water), resistant metals (tantalum, unalterable and radiation opaque) or the energy sector (niobium superconductors, lithium batteries). Thus pegmatite assumes an economic importance for these metals, as well as for cesium, rubidium and gallium.

However, although beryllium was once extracted from pegmatite which provided very large beryl crystals (7 metres weighing 18 tonnes from Albany, Maine, United States, and a crystal record of 18 metres long and weighing 470 tonnes from Malakialina, Madagascar), this metal is now mainly provided by the bertrandite of the Spor Mountain volcanic deposit. Pegmatite is also worked for its main components, i.e. feldspar for ceramics, mica for insulation and quartz for its piezo-electric characteristics. Finally, pegmatite may contain several kinds of gemstone, especially the valuable varieties of beryl (blue-green aquamarine, pink morganite, yellow heliodor, and more rarely emerald), topaz and tourmaline.

In Europe, the ceramic industry has required the exploitation of many pegmatites. Numerous quarries, often of modest size, bear witness to this activity. These sites have focused the attention of amateur and / or professional mineralogists whose publications are a source of valuable data for their reinterpretation in terms of potential resources in Nb-Ta or Li.

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[2] Geology of Mineral Resources, by Michel Jebrak & Eric Marcoux. Geological Association of Canada, c/o Departement of Earth Sciences, Room ER4063, Alexander Murray Building, Memorial University of Newfoundland, St. John’s, NL A1B 3X5 CANADA

There are four main types of felsic pegmatite according to its depth of formation:

- abyssal pegmatite (> 11 km) comprising mobilizates and anatectic leucosomes hosted by sillimanite and kyanite schist in amphibolite- or granulite-facies rock, and rich in Ca, Ba, Sr, Mg, Fe, although generally of no economic interest;
- deep muscovite pegmatite (7 to 11 km) conformable to the foliation, rarely mineralized, but which can produce feldspar and muscovite. It was once considered as resulting from a high-pressure metamorphism, hosted by almandine garnet and kyanite schist; it can contain concentrations of Th, U, Nb, Ta, Zr or Ti;
- medium-depth, low-pressure, rare-element pegmatite (3.5 to 7 km) with rare earths and a lithophile element mineralization (Li, Rb, Cs, Be, Ta, Sn...), hosted by cordierite-andalusite schist and associated with allochthonous granite. Grades are commonly quite low, of the order of 0.02% Ta_20_5, 0.05% BeO and Li_2O;
- miarolitic gem pegmatite associated with epizonal to subvolcanic domes (1.5 to 3.5 km) in weakly metamorphosed areas; it contains pure quartz for piezo-electric use, locally precious beryl, topaz and, in places, optical-quality fluorite.

The deposits are almost all related to medium-depth rare-element pegmatite that geochemistry enables one to split into two groups; the one with Nb, Y and F (NYF, or rare-earth pegmatite) with alkaline affinities, and the second with Li, Cs and Ta (LCT) associated with Type S intrusions.

The morphology of the pegmatite bodies depends on many factors: the depth of installation, the structural context, and the competence of the surrounding. In Europe, they form small veins (often less than a hundred meters).

Pegmatite emplacement is controlled by fracture zones and generally results from hydraulic fracturing. Pegmatite is commonly more abundant in competent country rock cut by major faults that can be marked by sedimentary breaks or grabens. Deep pegmatite can occupy saddle zones, conformable with the country rock, tension cracks or pressure shadows.

At the regional level, pegmatite commonly shows a zoning with increasingly differentiated facies away from the pluton (Figure 2)INTRODUCTION. The zoning is better defined in the vertical sense rather than horizontally. Thus, a general sequence drawn up from the centre outwards gives associations with;

- (2) plagioclase – microcline;
- (3) microcline – albite;
- (4) lithium-rubidium mineralization;

- (5) albite-spodumene, sometimes mineralized in Be, Ta, Sn;
- (6) beryl quartz, cassiterite and wolframite.

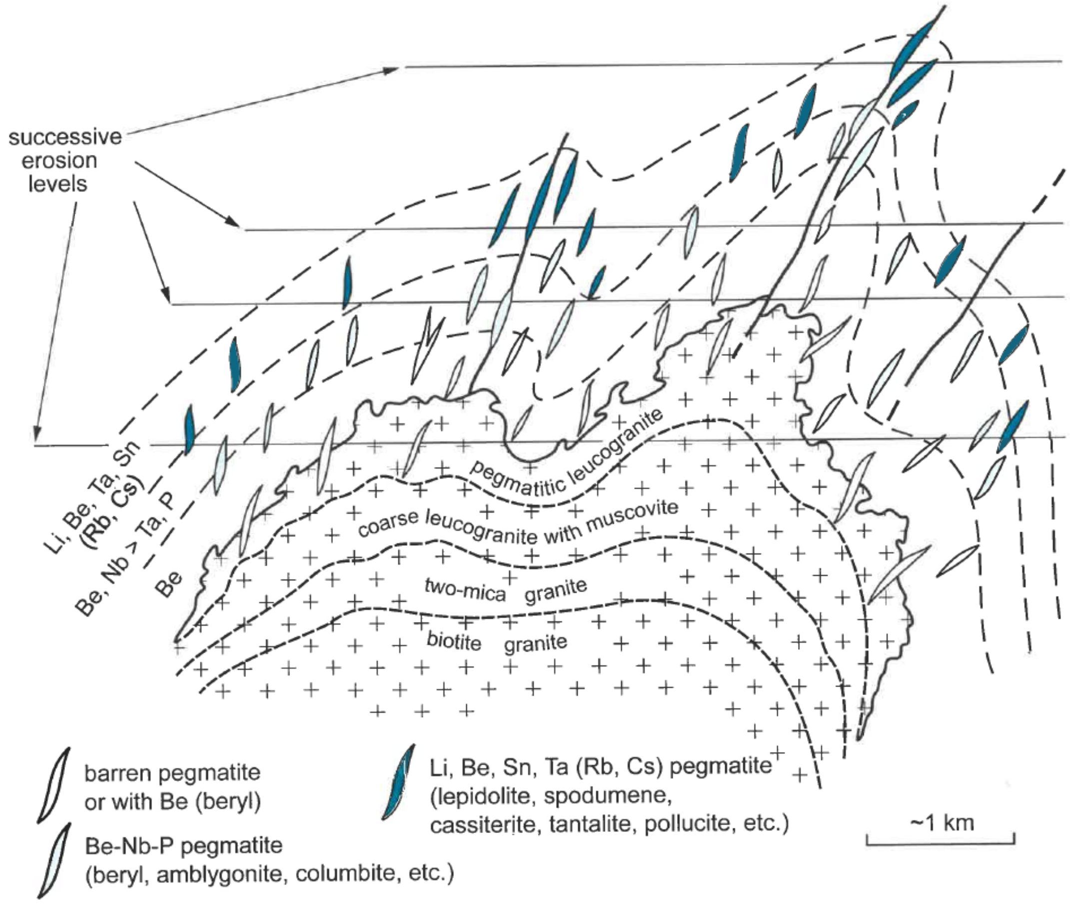

Figure 2: Idealized perigranitic zoning of pegmatite veins around a granite (veins not to scale). Note the concentric arrangement of the pegmatite veins around the irregular roof of the batholith and the strong influence of the level of erosion on the composition of the outcropping veins (from Cerny et al., 20053).

At the local level, one uses zoning, paragenetic criteria, mineral typomorphism: thus blue apatite indicates Be, Nb-Ta mineralization; green columnar spodumene is restricted to lithium pegmatite; tourmaline is black in the barren areas (schorl), blue-green in the areas albitized with Sn-Nb-Ta (indicolite variety of elbaite), and pink (rubellite variety of elbaite) in pegmatite with Li, Cs, Rb. Other elements, such as Li, Be, Sn in muscovite and cesium in potassium feldspar, can provide indications on the metal potential.

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[3] Cerny P. et Ercy T.S. , 2005. The classification of granite pegmatites revisited. Canadian Mineralogist 43:2005-2026

4.1.2 TIN AND TUNGSTEN PORPHYRIES AND CUPOLAS

Tin and tungsten porphyries and cupolas are found at the top of late- to post-orogenic plutons emplaced at a shallow depth (2-4 km, sometimes more).They are the trace of fossil hydrothermal systems centred on late, highly fractionated, granite intrusions (**Figure 3**). They occur in three types of geodynamic context:

- Zones of continent-continent hypercollision where they are associated with highly differentiated late-orogenic S-type two-mica leucogranite with a marked crustal character rich in hydroxyl minerals (muscovite) and enriched in lithophile elements such as Nb, Ta, Li, Be, P, F.

  The size of the cupolas varies from 1-5 Mt at 1% Sn to 15-80 Mt at 0.2-0.3% Sn, and an association with wolframite-bearing quartz veins (0.3 to 1.5% WO) is common.

  The Erzgebirge Altenberg (Germany) and Cinovec-Zinnwald (Czech Republic) deposits of Central Europe (known since Agricola, 1556), the historical deposits of Cornwall (England), and the Panasqueira (Portugal) and Montbelleux (Armorican Massif France) deposits are classic examples of this type of mineralization.

  In France, very large potential reserves of Li, Sn,Ta (and possibly Be) also exist in the Beauvoir-Echassieres albite-lepidolite-topaz granite cupola of the French Massif Central (Cuney and Autran, 1987[4]).

- Zones of continental collision producing crusta! overthickening with tin porphyries. The mineralization comes from very shallow subvolcanic peraluminous intrusions (Sillitoe et al., 1975) containing numerous tin minerals (dominant cassiterite, stannite, mawsonite, cylindrite...), quartz, pyrite and marcasite, etc. Such deposits are known in the Andes, mainly in Bolivia (Oruro, Llallagua, Cerro Rico de Potosi, and Chorolque), commonly at the site of inner continental arcs. Their very large size (100 to 1000 Mt at 0.2% Sn) makes them veritable tin porphyries.

  Absent in Europe, we will not describe them more precisely in this work and we will refer to the work of M. Jebrak and E. Marcoux.

- Continental rifts with annular anorogenic Sn-W-Be-Zn-bearing alkaline granite, locally with a rapakivi texture, found particularly in the Proterozoic of Brazil (Rondonia and Itu) and the Mesozoic of Nigeria (Younger granite). They have produced more than 0.5 Mt of tin in Amazonia. The granite is highly fractionated, rich in fluorine, and

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[4] Cuney, M et Autran, A., 1987. Le forage scientifique d'Echassières (Allier). Une clé pour la compréhension des mécanismes magmatiques et hydrothermaux associés aux granites à métaux rares. Géologie de la France 2-3 :1-35.

peraluminous with alkali feldspar, riebeckite, hastingsite, biotite, topaz, muscovite and zinnwaldite. The style of mineralization varies from stockworks, rarely skarns, to cupolas with greisen.

Also absent in Europe, we refer to the work of M. Jebrak and E. Marcoux.

GEOLOGY OF THE CUPOLAS

Mineralized cupolas form the apex of complex intrusion systems, in places porphyritic at the top of large batholiths of peraluminous felsic granitoid and locally of quartz gabbro (Indonesia). The intrusions are multiphase, with enrichment in incompatible elements in the youngest and smallest intrusions originating from fractions of a solidifying magma chamber.

The country rock is commonly sedimentary and weakly metamorphosed.

The upper contact of the intrusions is commonly marked by a stockscheider (German word meaning separation between two granitic units) or unidirectional solidification textures (UST), a few metres thick. This is indicated by arcuate and feathery pegmatitic feldspar, and quartz growing from the roof of the pluton.

The mineralization is associated with zones of tourmaline-rich aplite and topaz granite. The morphologies are varied: stockworks, simple and narrow veins (a few ten of centimetres thick), narrow vein systems, breccias, chimneys (Puy-lesVignes, France; Correas), disseminations in greisens, skarn-replacement with sulphides.

The morphology depends on local conditions of permeability and the ratio between the fluid pressure Pf generated by the magma and the lithostatic pressure Pl (**Figure 3**):

- A low Pl allows the formation of thick veins. The vein fields can have varied structures: parallel, two directional, vertical or horizontal, divergent above an apex (Enguiales, France), subhorizontal (Panasqueira, Portugal).They can extend vertically over hundreds of metres and horizontally for more than a kilometre.
- A high Pl and Pf balance one another, giving rise to extended fracturing with laminate veins and stockworks.
- A very high Pf in depth or in an area of low permeability near the surface, leads to an explosive rupture with the formation of hydraulic breccia and pipes.
- A high Pl and a low Pf results in the trapping of fluids in the intergranular space of the magma crystals, which can give rise to marginal pegmatite, few veins and a disseminated mineralization associated with an extended greisenization (Montebras, France; Lagares, Portugal).

These varied morphologies are due to the passage of a radial or concentric tectonism at the top of an active intrusion for the earliest deposits, and to a regional stress-related tectonism for the later deposits.

The observed alterations can include early potassic alteration with dominant muscovite (greisen), or boron alteration with black tourmaline taken up by albite, sericite and clays. Greisen is a metasomatic rock with dominant muscovite and quartz, locally with zinnwaldite, lepidolite, beryl and lithium phlogopite, which marks a potassium and lithium metasomatism at the top of the system. It corresponds to an alteration of potassium feldspar or plagioclase to muscovite at a pressure of the order of 1 to 2 Kbar and a temperature ranging from 500 to 600 °C. These alteration suites can be taken up by the percolation of meteoric water, a superposition that causes the formation of kaolinite, the raw material of the china clay of Cornwall and Brittany.

Zoning at cupola scale is commonly very marked with tin-tungsten at the core, then tungsten-bismuth, and finally copper commonly preceding lead-zinc (Figure 3). Other minerals are less common: argentiferous sulphosalts, stibnite, molybdenite, gold. Finally, it is rare that the tin and tungsten are equivalent in terms of their economic volumes in a deposit; one often finds deposits of tin or tungsten, but rarely mixed deposits.

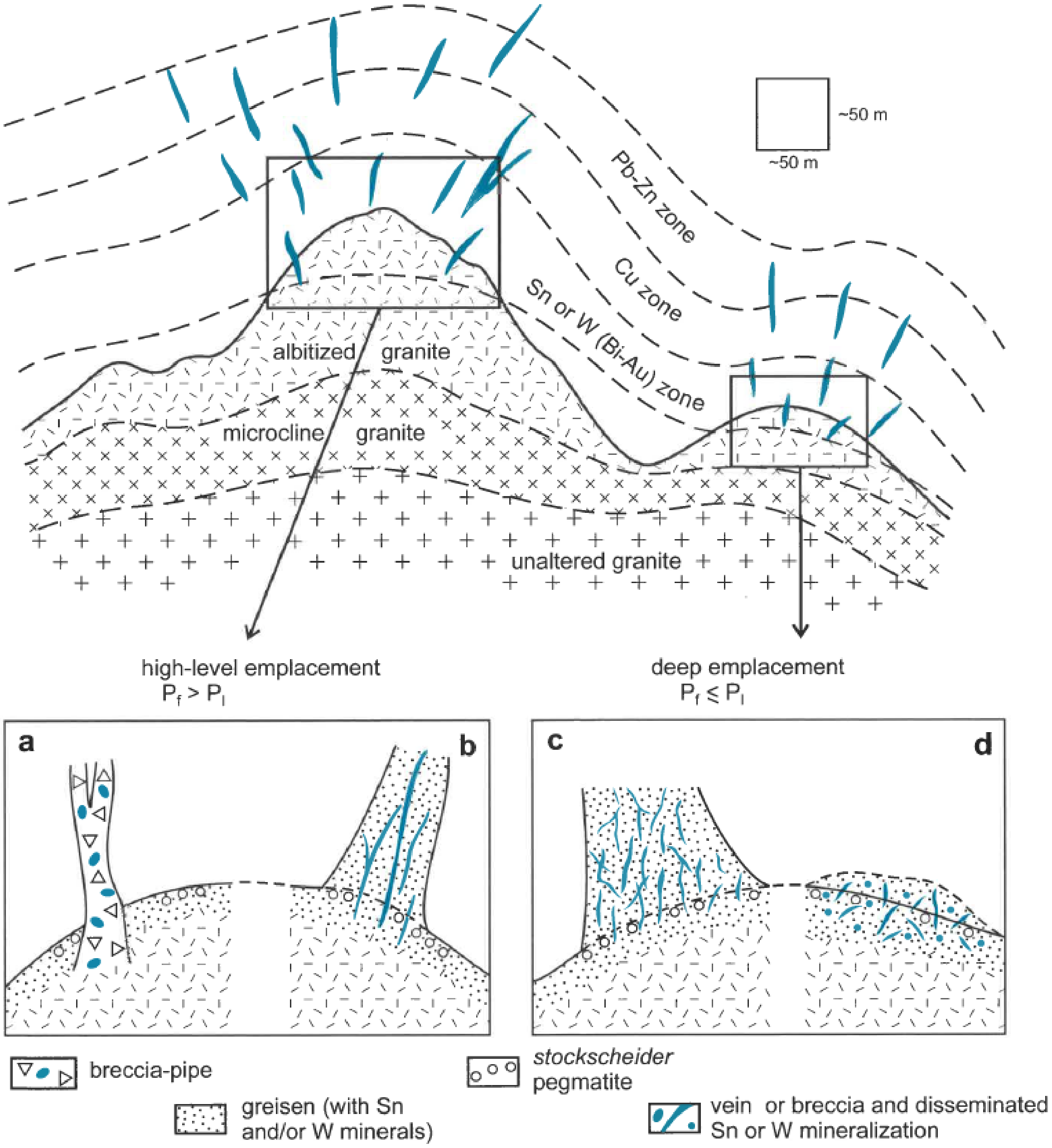


Figure 3: W-Sn cupolas. Top: idealized cross-section of a W-Sn granite cupola showing zoning of the mineralized veins. Bottom: morphology of the mineralization as a function of the ratio between fluid pressure (Pf) and lithostatic pressure (Pl). **a)** Pf >> Pl (very high fluid overpressure) causes explosions with the formation of breccia conduits and pipes; **b)** Pf > Pl causes the formation of fissures giving thick veins; **c)** Pf = Pl (balanced pressures) causes fissuring in the structure and the formation of stockworks and complex veins; **d)** Pf < Pl (high lithostatic pressure) maintains the fluids within the cupola, giving rise to intense greisenization and disseminated W-Sn mineralization.

4.1.3 SKARNS AND SKARNOIDS

Contact metamorphism is accompanied by metasomatic or replacement processes in the vicinity of an intrusion, belonging to two main types: skarns and mantos. The skarns are in the immediate vicinity of the intrusion, while the mantos (Spanish word meaning cover, alluding to its frequently stratiform appearance) can be located up to several kilometers from the intrusion.

Metasomatosis, also called allochemical metamorphism, consists of a slow transfer of elements (Si, Al, Fe, Mn ...) by fluids impregnated in rocks which causes mineral transformations which can lead to deposits. These displacements are carried out thanks to hydrothermal circulations in porous environment, without open fracture. Fluid circulation and adjoining metasomatic transformations are then controlled by the lithology of the surrounding, both by its porosity and permeability, and by its ability to react with fluids.

The deposits developed by these metasomatic processes meet in a metamorphic environment. Skarns, mantos, and distal gold replacements of the Carlin type in particular are linked to contact metamorphism, or thermometamorphism. The action of high temperature magmatic fluids is manifested by the arrival of volatile elements (fluorine, chlorine, boron) and metals of magmatic origin (tungsten, molybdenum, and copper, gold ...). These deposits are related to the placement of plutons in sedimentary rocks and often associated with differentiated tin-tungsten granite domes.

Skarns are among the most widespread types of deposits on the planet and they constitute important deposits of tungsten, lead-zinc, copper or gold, but tin is also mined in the form of malayaite ($CaSnSiO_5$) or cassiterite, beryllium in the form of beryl, boron in the form of datolite and danburite, iron in the form of magnetite, or molybdenite and wollastonite.

The vast majority of skarns develop in contact with or near a magmatic intrusion. They result from diffusion phenomena generally at high temperature associated with granitic to dioritic intrusions of orogenic belts. The composition and texture of the protolite will largely control that of the resulting skarn, which explains the great variety of facies of these deposits.

The majority of authors propose a pragmatic classification based on the dominant economic metal. The characteristics of the different skarns are summarized below:

- iron skarns;
- copper skarns;
- zinciferous skarns;
- tungsten skarns which appear in depth, within vast metamorphic halos with skarnoids and corneas, in connection with calc-alkaline plutons dependent on vast batholiths;

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

- tin skarns which are formed in connection with very siliceous granites, following a partial fusion of the continental crust; their strong fluorine activity develops an original retrograde alteration of the greisen type which sees the crystallization of topaz, fluorite, tourmaline, muscovite and quartz;
- the rarer molybdenum skarns (Azegour, Morocco; Little Boulder Creek, Idaho) and sometimes grouped with tungsten skarns which they come close to by the paragenesis rich in scheelite, but differ in their association with leucocratic granites.
- Boron skarns.

GEOLOGICAL CONTEXT

Skarns are commonly associated with small intrusions (a few km^2) containing host-rock pendants and having a sharp contact with a slightly tectonized carbonate host rock (**Figure 4**). Locally, the granite can be located above the carbonates. A distinction is made between exoskarn, which corresponds to mineralization replacing the host in contact with or in the immediate vicinity of the intrusion, and endoskarn, to replace the intrusion; the latter is rarer and less mineralized. A strong diffusion of calcium in the intrusive is marked by the disappearance of the feldspar and a replacement by an assembly with clinopyroxene, plagioclase, titanite and quartz.

MORPHOLOGY

The morphology of the skarns is a consequence of the depth of installation of the intrusions. The halo of thermometamorphism is less extensive and of lower intensity in copper skarns linked to porphyry intrusions placed at relatively shallow depth, than in ***batholites placed more deeply and commonly associated with tungsten skarns***. However, the extent of superficial skarns may be greater in the event of high fracturing intensity.

The morphology is a function of the respective importance of stratigraphic and structural controls, as well as the shape of the pluton. The skarns consist of very irregular mono-mineral beds, generally concordant but often locally discordant on the bedding (Figure 4).

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

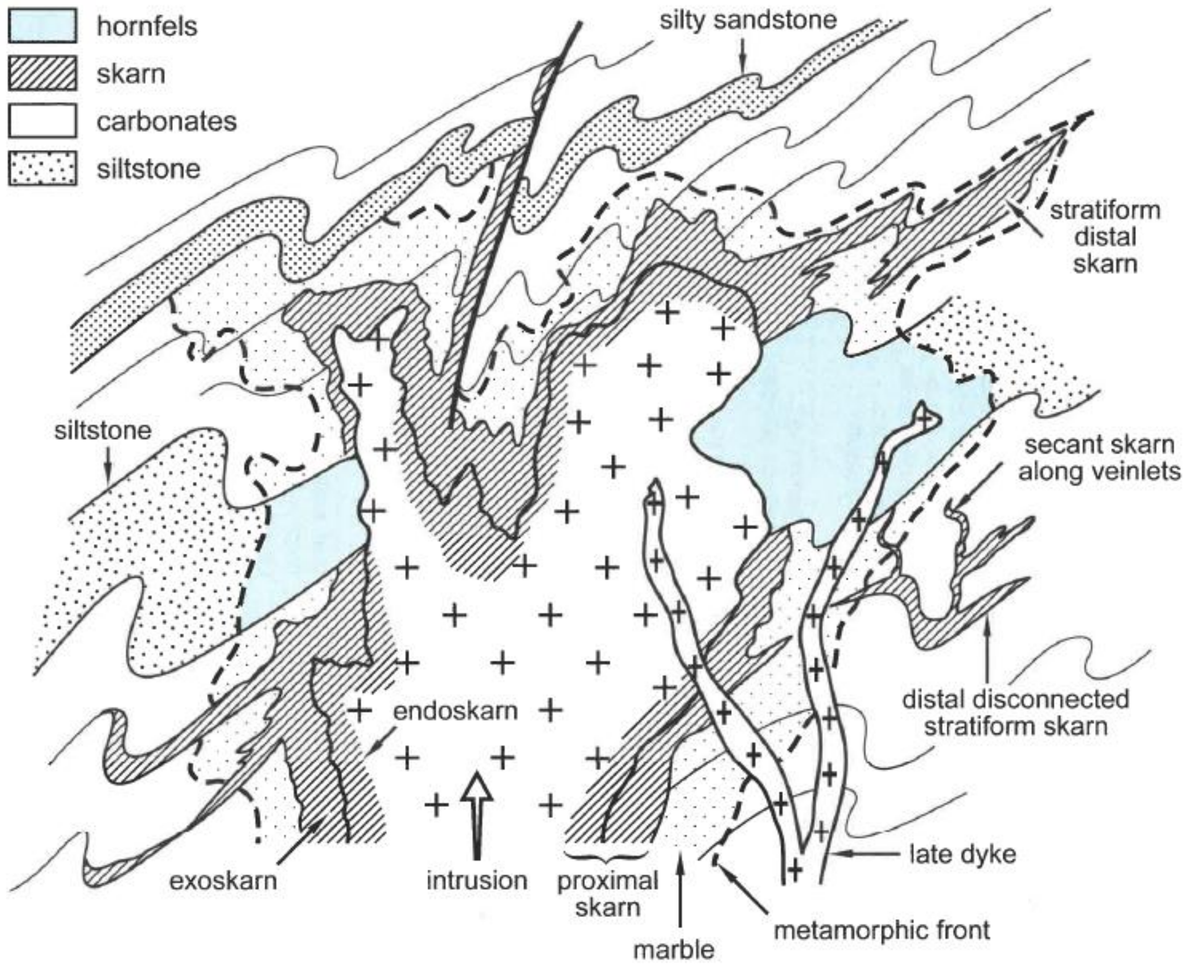


Figure 4: Idealized contact metamorphic aureole around an intrusion. Skarns are developed in the carbonate layers of the country rock and can spread quite far from the intrusion if there is fluid diffusion. Disconnected distal. Skarns are equivalent to the mantos. Hornfels occurs in the silico-aluminous levels.

FORMATION

Skarns show a clear zoning, in places with a greisen or a tourmalinization of the intrusion, commonly manifested at the initial stage and termed prograde (Figure 5).

The mineralogy of the metasomatic reaction zones, dominated by calcium silicates, is however highly variable; it depends on the lithological nature of the intrusion and the country rock, as well as on the temperature and degree of oxidation of the solutions.

This mineralogy evolves during the second stage of skarn formation, termed retrograde, with the appearance of hydrated minerals and sulphides. The changes do not generally significantly upset the zoning.

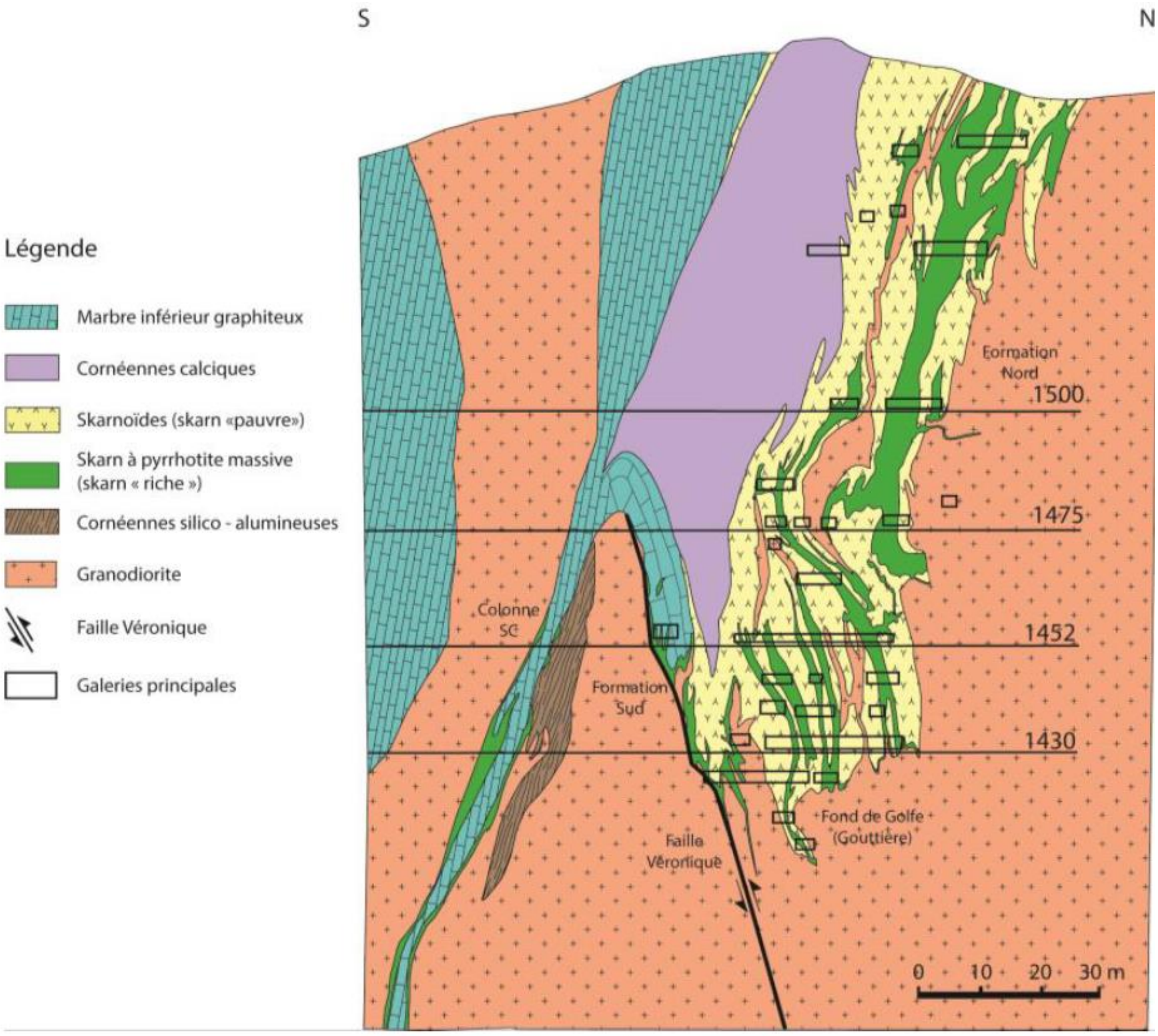


Figure 5: N-S section in the upper part of the Salau mine (France)

The deposits show a multiphase emplacement with three major stages that, in general, widely overlap:

- **A thermometamorphic** stage corresponding to the emplacement of the intrusion and the dehydration of the country rock with expulsion of the fluids. It is an isochemical process that transforms limestone to marble.
- **A prograde metasomatic stage** corresponding to an early metasomatism with the introduction of iron, manganese and aluminium at high temperature (600 to 500 "C) by the magmatic fluids released from the pluton. Typical anhydrous metamorphic silicates appear at this stage through reaction with the country rock: pyroxene (diopside-hedenbergite), garnet (andradite-grossular), clinozoisite, titanite, wollastonite, vesuvianite, as well as calcite and biotite. It is a diffusion process where element transfers are limited.

- In the case of tungsten skarns, fine deposits of disseminated low-grade scheelite (0.01% $W0_3$) may appear as of this episode. The episode is poor in copper and sulphides. Endoskarns form through the input of calcium from the country rock.
- **A retrograde hydrothermal** stage with the system being invaded by lower temperature fluids (450-300 "C). This fluid influx causes partial hydrolysis of the prograde-stage minerals and intrusive rock, leading to the appearance of many hydrated minerals, including amphiboles (actinolite, hornblende and tremolite), epidote, talc, chlorites, possibly sericite and montmorillonite clays, in addition to quartz and calcite.
- It is also the essential stage of sulphide deposition where the ore can be enriched to a mineable grade.

Stockworks and episodes of brecciation may accompany the emplacement of the sulphides.

The final paragenesis of the skarns therefore consists of preserved prograde minerals and later retrograde minerals. One thus finds hornblende-pyroxene skarns with, depending on their metal specificity, pyrrhotite, pyrite, chalcopyrite, or magnetite, possibly cubanite and scheelite, associated with actinolite and chlorite, and garnet-wollastonite skarns with sulphides (bornite, chalcopyrite, sphalerite, galena, tennantite) associated with dominant epidote. Lead-zinc sulphides can form veins, chimneys or peripheral layers (mantos).

Nature of the mineralization is closely associated with that of the magma and tin-tungsten deposits are linked with ilmenite granite.

4.1.4 DEPOSITS ASSOCIATED WITH ALKALINE PLUTONISM

Alkaline magmatism is rare since it represents only 5% of igneous rock, but it involves nearly 50% of the rock names, which gives an idea of the complexity of the assemblages distinguished by petrologists. The associated granite belongs to the A-type granite family: A as in Alkaline, but also as in Abnormal, Anorogenic and Aluminous.

In this work, we will quickly summarize the main characteristics of these deposits, which many responsible for the main productions of Nb, Ta known, however are limited in Europe to a few deposits in the Scandinavian shield and Greenland.

The alkaline series includes many rock types ranging from ultramafic to felsic; the most widelyaccepted definition corresponds to rock containing feldspathoids and/or pyroxenes and alkaline amphiboles. Peralkaline rock is characterized by an agpaitic ([N a + K]/ Al) index greater than 1.

Alkaline magmatism can occur in two extensional geotectonic contexts that allow direct passage to the surface without contamination; one at rift level and the other behind subduction zones.

It is especially abundant at the continental or oceanic rift level, associated in particular with hot spots caused by mantle plumes. The recent volcanism of the French Massif Central is an example.

The alkaline magmatism also appears behind the subduction zones, both in continental and oceanic context. The alkaline magmas can appear very far from the subduction zone, in connection with a deep rupture of the subducted plate.

Alkaline magmatism frequently presents an enrichment in incompatible elements such as zirconium, niobium, uranium, yttrium, and rare earths. It is thus at the origin of a large number of mineralisations which appear at different structural levels, and even sometimes in the vicinity of the surface in the form of a diatreme. We can recognize several types of mineralization at Nb-Ta:

- mineralization associated with lamprophyres and carbonatites (Nb-Ta, rare earths; exceptionally Fe, Sr, Ti, Mo, Ta, U, Cu, Zn, vermiculite and platinoids);
- the mineralizations associated with the nepheline and carbonatite syenite massifs: these are mainly very refractory minerals such as zircon, high-tech metal minerals (niobium-tantalum, rare earths, thorium-uranium), or apatite (mainly fluorapatite) usable in the phosphate industry;
- hydrothermalism associated with granites and pegmatites from more advanced alkaline systems is also responsible for various mineralizations. The alkaline pegmatites produced iron, rare metals (Ba, F, Ce, rare earths, Y, Zr, Nb), and the differentiated granites from the annular complexes of Nb, Ta and Sn;

4.1.4.1 RARE EARTH, NIOBIUM AND TANTALUM CARBONATITES

Around 500 carbonatites are currently known worldwide (including 34% in Africa), and around 25 deposits are active. We can distinguish two sub-groups:

- primary carbonatites which produce rare earths, niobium-tantalum (pyrochlore, columbite). Carbonatites of this type are in use at Mountain Pass (California, United States), St Honoré (Quebec), and Araxa (Brazil). The latter is particularly rich with a 3% Nb_2O_5 ore. Bayan Obo (Inner Mongolia, China) or Palabora (South Africa) are also associated with this type;
- hydrothermalized carbonatites, used for fluorite, result from a reaction between magma and groundwater, such as the Amba Dongar (India) and Okorusu (Namibia) deposits.

Carbonatite bodies are often located in fault zones or at the heart of alkaline complexes with dominant nepheline syenites: they therefore generally occupy volcanic devices of the diatreme-maar type, and sometimes form veins. Their surface appearance is roughly circular to elliptical, but their general morphology is that of pipes or dykes. They frequently contain pyrochlore, colombite, tantalite, bastnaesite, apatite and alkaline feldspar.

The mineralization generally occupies a crescent at the periphery of the pipes and can constitute powerful tabular bodies of 50 m. The carbonatites are often surrounded by a halo of alteration, or fenitization, which obscures the contacts and can extend up to 4 km around the intrusion. Fenitization is a desilicification accompanied by the development of alkaline minerals (aegyrine, riébeckite), and alkaline feldspar (microcline). The composition of the fenites also depends on the nature of the host rocks. The zoning of the alterations shows a potassium metasomatism at the top, and more sodic alterations in depth. Fluorite appears late and replaces carbonates.

A tropical supergene alteration can play an important role, allowing a residual enrichment. This type is well known in Araxa (Brazil), where the primary niobium mineralization becomes a loose and enriched ore, exploitable in the quarry in its altered surface part, making this deposit the first world producer of niobium.

4.1.4.2 ALKALINE COMPLEXES

Differentiated alkaline magmatism is represented by plutons, often zoned, called alkaline complexes, set up in an anorogenic context. There are two main types, quite commonly associated within a complex:

- nepheline syenites with zirconium and niobium, respectively in the form of zircon and pyrochlore, or with sodalite, rich in rare earths, uranium and thorium. They frequently contain deposits of rare metals (Zr, Nb, Ta, Y, Be, rare earths), such as Arendal in Norway or Ilimaussaq in Greenland.
- hyperalcaline granites and their pegmatites, of variable nature. The term "hyperalcalin" indicates a (Na + K) / Al ratio greater than 1.

These complexes are locally mined for Zr, Nb, Ta, Sn, sometimes uranium, and even gold, linked to late alkaline intrusions from the Archean greenstone belts.

NEPHELINE SYENITES

Nepheline syenites are usually small intrusive massifs, frequently circular in appearance, and often intersected by late carbonatite dykes. The nepheline syenites of Ilimaussaq (Greenland), also show a fenitization (hydrothermal alteration inducing a desilicification of the rock) associated with the concentrations of zirconium, yttrium and rare earths.

These are highly undersaturated, granular magmatic rocks made up of alkaline feldspars (usually perthitic microcline and albite) constituting nearly 70% of the rock, feldspathoids (nepheline, more rarely sodalite, analcime or haüyne) 20%, biotite, amphibole and alkaline pyroxenes (riébeckite and aegyrine respectively), and an impressive procession of accessory minerals including zircon, titanite, fluorine, pyrochlore, corundum, bastneasite, l apatite, etc.

They may exceptionally contain large quantities of phosphate in the form of apatite ("urtite" from Khibiny, Russia). Magmatic phosphates represent 14% of world production.

PERALKALINE GRANITES

These granites can be aligned along large crustal structures in extension (1600 km in Nigeria) and seem in connection with the horsts of the Precambrian basement. The massifs are in the form of annular complexes or massive bodies with a felsic heart and a more mafic margin. The magmatic sequence extends from alkaline gabbros to riebeckite-biotite granites with an albite granite border.

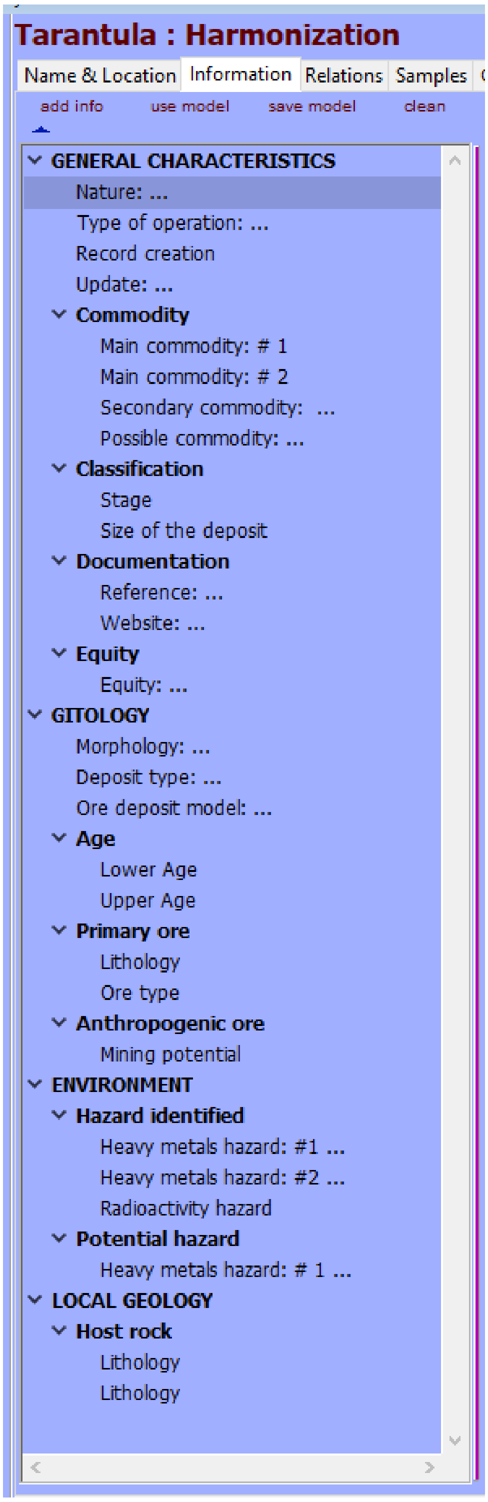
The peralkaline granites with rare elements are characterized by a very low phosphorus content, a large abundance of fluorine, rare earths, yttrium, zirconium and niobium, as well as high contents of thorium, tin, beryllium, rubidium and uranium. The paragenesis is mainly with albite, riébeckite, zircon, aegyrine, arfvedsonite, and niobium minerals (columbite, tantalite).

Economically, in addition to tin, exploited as cassiterite almost exclusively in alluviums and eluvions, peralkaline granites also produced Pb, Zn, U, Nb, Th and rare earths.

Alkaline mineralization forms at the magmatic stage and are often reconcentrated at the hydrothermal stage in the associated pegmatites.

4.2 HARMONIZATION OF VOCABULARY

As the GKR is a generic information system (Figure 6), each record can use different labels, and the number of items entered in a file is not limited.



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  - Type of operation: ...
  - Record creation
  - Update: ...
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    - Main commodity: # 1
    - Main commodity: # 2
    - Secondary commodity: ...
    - Possible commodity: ...
  - Classification
    - Stage
    - Size of the deposit
  - Documentation
    - Reference: ...
    - Website: ...
  - Equity
    - Equity: ...
- GITOLOGY
  - Morphology: ...
  - Deposit type: ...
  - Ore deposit model: ...
  - Age
    - Lower Age
    - Upper Age
  - Primary ore
    - Lithology
    - Ore type
  - Anthropogenic ore
    - Mining potential
- ENVIRONMENT
  - Hazard identified
    - Heavy metals hazard: #1 ...
    - Heavy metals hazard: #2 ...
    - Radioactivity hazard
  - Potential hazard
    - Heavy metals hazard: # 1 ...
- LOCAL GEOLOGY
  - Host rock
    - Lithology
    - Lithology

FIGURE 6. main labels in the GKR

To carry out our study and establish comparisons between deposits and the occurrences of refractory metals in Europe, it is however essential that each record has a minimum of common criteria with all the other records. We will only detail here these main labels, a GKR sheet can contain several dozen more. Each label can be repeated several times if multiple entries are required, the GKR then having the necessary instructions to prioritize the various options.

Nature

The values entered in "Nature" will include at least one of the values listed in chapter 2.5.1.2; it can then be more detailed by additional indications, for example an occurrence can be supplemented by the value "outcrop".

Type of operation

To be able to estimate a mining potential, it is essential to clearly distinguish the nature of the mineralization (occurrence, mineral deposit, ore deposit...) and the activity associated with it (mine, mining work, ...). A giant deposit may not be exploited and a giant mine may be completely depleted. Mining potential must therefore take these two parameters into account.

Mine: the term is quite blur, and it is often used for very different operations. It will often be confused with "exploitation", the meaning of which is more restrictive. In the GKR we will consider that the mine is the industrial operation which carries out the exploitation of a mining site. Depending on its size, a parallel will be drawn with the nature of the mineralization.

We should avoid any legal reference to the mining regime defined by the countries (notion of mine and quarry in France for example). The technique used for exploitation will be explained in an "exploitation" label.

Modern mine in operation: the parallel is established with the notion of ore deposit. However, it should be noted that a giant deposit can be exploited by several mines belonging to different companies. On the mine site, there may be several operations that would be interested in different mineral bodies. The most classic example is that of the surface part of the deposit exploited in a quarry while the deep part is exploited by a well located at a distance from the quarry.

Former medium / large mine: we will always refer to the notion of mineral deposit. Note that the closure of the mine does not mean that the deposit is depleted. In addition, there will necessarily be associated tailings which could be examined in the light of new economic and / or technical parameters.

Artisanal mine: we will associate it by default with the notion of occurrence; the geologist's opinion may, however, extend this notion to that of mineral deposit depending on the number and quality of other evidences that would be found in its immediate environment.

Exploitation: Large deposits are often exploited by the same mining company from several sites close to each other. The concept of mine will refer to all of its sites which will generally centralize the processing of ores on only one of them.

For example, the Panasqueira mine (Portugal) does not correspond to a single site, but it brings together several exploited sites which will be defined as operations:

- Panasqueira and Barroca Grande
- Corga Seca, Alvoroso, Veia Branca and Giestal
- Lomba da Cevada
- Ledges and Seladinho
- Fonte das Lameiras
- Vale das Freiras and Vale da Ermida
- Cabeço do Pião

Each operation, if significant, is the subject of a specific record, hierarchically linked to that of the mine which corresponds to it. In many cases, this operation will have its own name, separate from that of the mine. This peculiarity is the cause of numerous duplicates within the databases because the operations will be difficult to distinguish from the mines (separate coordinates, distinct names, different mining techniques, commodities exploited close but not necessarily identical in the event of zoning in the deposits …). Comprehensive work to establish the mining potential of a region should therefore ensure that this distinction is made. If necessary, we will create for each farm whose name is not known, a record bearing the name of the mine (Mine) which contains it followed by an index (Mine # 1, Mine # 2 ...)

In the case of giant deposits, the discussion could relate to the parallel to be established between the notion of mine and that of ore deposit. In some cases, the parallel would rather be to establish with the notion of mineralized field.

The values entered in "Type of operation" will include at least one of the values listed in chapter 2.5.1.2 ; it can then be more detailed by additional indications or use of ontologies, for example "quarry" will be understood as a mine or a mining works according to its size.

Mining Works: mining or exploration work will be systematically linked to the notion of Occurrence. Depending on their nature, they will have a different weight in the definition of mineral deposit or ore deposit that they can induce in a mining expertise. We can distinguish (non-exhaustive list)

- o Very small artisanal exploitations (recent or old)
- o Small exploration works (recent or old)
- o Outcrops, drillings or trenches
- o Boulders
- o Geochemical or geophysical anomalies

Main commodity

Commodity having defined the notion of deposit and mine. The extraction is managed by the exploitation of these commodities.

Secondary commodity

Commodity enhanced by the formula for selling merchant concentrates containing the main commodities. Are often considered as an operating bonus but do not define the selection of the ore.

Possible commodity

Commodities not valued by mining, but which could participate in the economy of the deposit if new recovery technologies could be implemented. In the old mines, could correspond to metals not exploited or sought during the period of life of these old mines. Niobium and Tantalum are examples of these commodities.

Morphology

This is the geometry of the deposit detailed at the level of the mineralized bodies. We will distinguish veins, layers, clusters... Several morphologies can coexist within the same deposit or deposit. In the event of operation, they will define the method of operation. However, the morphology alone is insufficient to characterize the deposit.

Deposit type

The type of deposit provides important precision in relation to the morphology. In general, it will correspond to the association of a morphology with a mineralized content, for example: a vein of fluorite, a layer of sulphides, a copper stockwork...

In many cases, the type of deposit is confused with the metallogenic model. However, it does not provide information on the genesis of the deposit, and therefore on the fundamental characteristics of the ore or the criteria that would allow its efficient exploration/exploitation and/or the environmental impact of it. Several types of deposits can coexist within the same deposit and be generated by the same metallogenic model

Metallogenic model

The metallogenic model explains the genesis of the deposit. The deposits belonging to the same model have very similar characteristics, which makes it possible to anticipate their mining potential and the environmental constraints which could be induced by their exploitation (themselves deductible from paragenesis of the gangue and the ore). Knowledge of this model is an essential parameter to guide the exploration and later the development of a deposit. Knowledge of the model is also an important element in anticipating the environmental hazards associated with their exploitation or even their exploration.

4.3 MINERALOGY OF REFRACTORY METALS DEPOSITS

The minerals listed in the following paragraphs will be reported in the balloons of the KMZ file (See Complementary Information at the end of this document). They will specify the assumptions made relating to recoverable potentials and environmental hazards.

4.3.1 MINERALOGY OF NIOBIUM AND TANTALUM

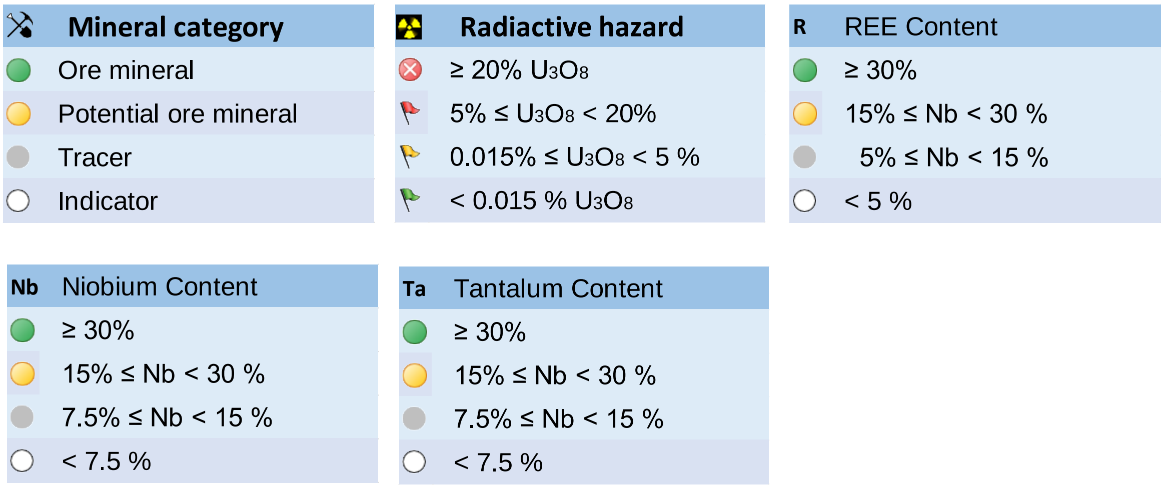
The detailed mineralogy of Niobium and Tantalum includes 300 minerals. These minerals may contain varying proportions of recoverable or penalizing metals depending on the case. In particular, very variable uranium, lithium and rare earth content will be noted.

A database in the form of an Excel Folder (See Complementary Information at the end of this document) 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, Excel and .kmz files are available in Complementary Information at the end of this document. The categories mentioned in the paragraph 2.2.2 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 7)

Figure 7. Caption in the “Short – EN” tab

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4.3.2 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.

4.3.2.1 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.

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.

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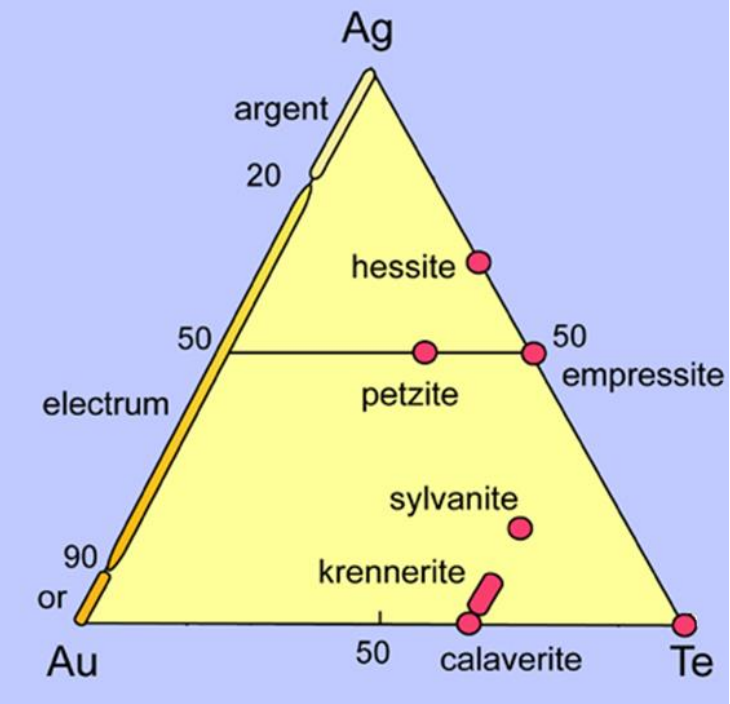

FIGURE 8. Diagram Au-Ag-Te

The Au-Ag-Te diagram (Figure 8) includes native elements and most common tellurides. 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 electums 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.

4.3.2.2 SILVER

Interpretation of the detailed mineralogy of this metal is in progress

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.

4.3.2.3 MOLYBDENUM

Interpretation of the detailed mineralogy of this metal is in progress

4.3.2.4 LITHIUM

Interpretation of the detailed mineralogy of this metal is in progress

4.3.2.5 RARE EARTHS

Interpretation of the detailed mineralogy of this metal is in progress

4.3.2.6 URANIUM

Interpretation of the detailed mineralogy of this metal is in progress

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.

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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

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 23)*
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 23)*
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.

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

Secondary ore	Autunite group
Common mineral	*Uranyl-phosphate (Figure 23)*
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 24)*
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 23)*
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 24)*
Potential Ore Mineral	U, V
Hazard	U, Pb

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 Chapter : 4.3.1

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

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4.3.2.7 COPPER

Interpretation of the detailed mineralogy of this metal is in progress

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 10)*
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 mammillated, 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 14)*
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.

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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 14)*
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 10)*
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 10)*
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 10)*
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 19)*
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 CuS_4 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. Cu^{2+} is also commonly replaced by Zn^{2+} or Fe^{2+}, 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) make 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 9)*
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 Cu^{2+}.

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

Digénite – Cu_9S_5

Secondary and primary ore	
Common mineral	*Sulfide (Figure 10)*
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

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.

4.3.2.8 ZINC

Interpretation of the detailed mineralogy of this metal is in progress

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 15)*
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.

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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 14)*
Ore mineral	Zn
Hazard	Zn ?

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.

4.3.2.9 ARSENIC

Interpretation of the detailed mineralogy of this metal is in progress

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

Arsenopyrite (FeAsS)

Primary ore	Arsenopyrite group
Very common mineral	*Sulfide (Figure 13)*
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 18)*
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 17)*
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 13)*
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 16)*
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 13)*
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.

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<u>Orpiment-</u> As_2S_3

Primary ore	
Common mineral	*Sulfide (Figure 12)*
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.

4.3.2.10 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 12)*
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.

4.3.2.11 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 26)*
Potential Ore Mineral	Hg
Hazard	Hg

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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.

4.3.2.12 LEAD

Interpretation of the detailed mineralogy of this metal is in progress

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 11 Figure 12)*
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 15)*
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 20)*
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 22)*
Potential Ore Mineral	Pb
Hazard	Pb

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 17)*
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 27)*
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.

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 12)*
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 25)*
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 11)*
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 12)*
Hazard	Pb, Sb

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.

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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.

4.3.2.13 CADMIUM

Interpretation of the detailed mineralogy of this metal is in progress

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.

4.3.2.14 BISMUTH

Interpretation of the detailed mineralogy of this metal is in progress

4.3.2.15 THALLIUM

Interpretation of the detailed mineralogy of this metal is in progress

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4.3.3 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.

4.3.3.1 OXIDES (CU-PB-ZN)

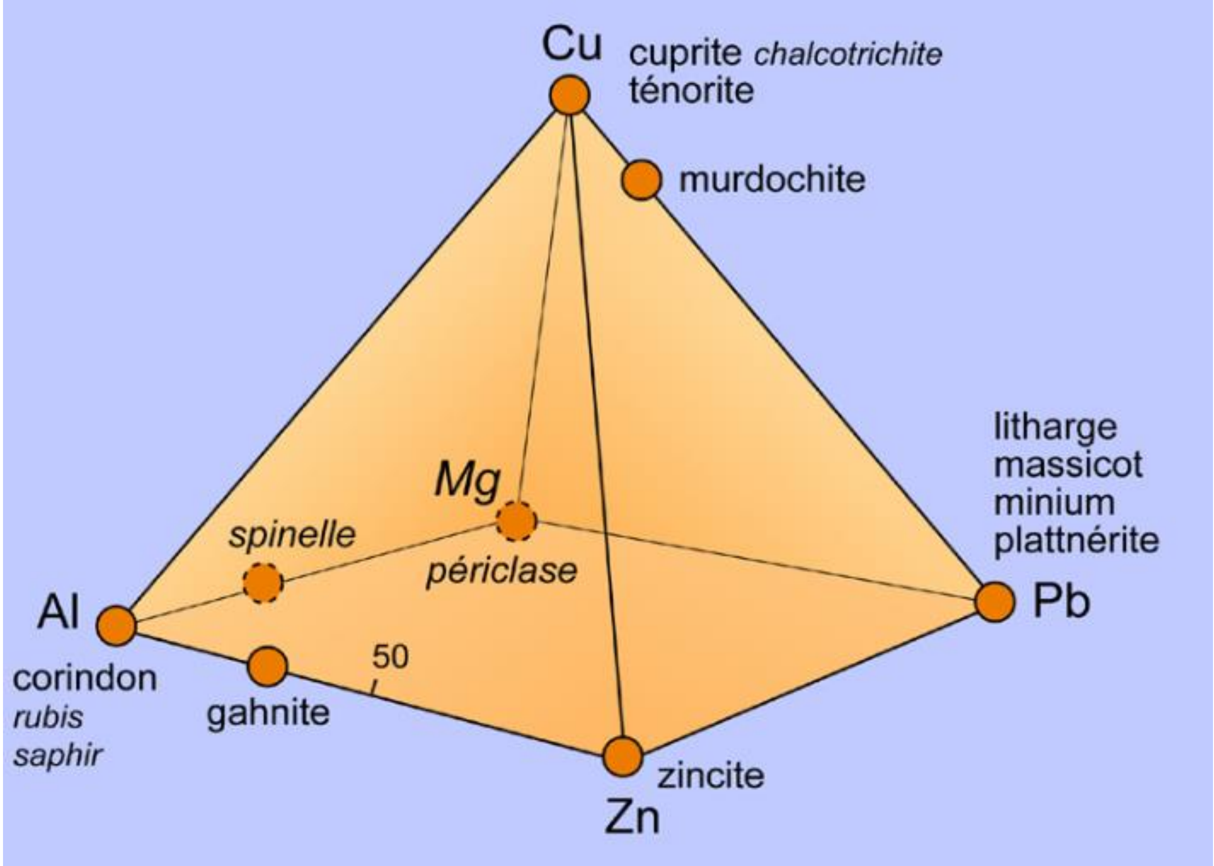

Figure 9: Composition of main base metal oxides

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4.3.3.2 SULFIDES (CU)

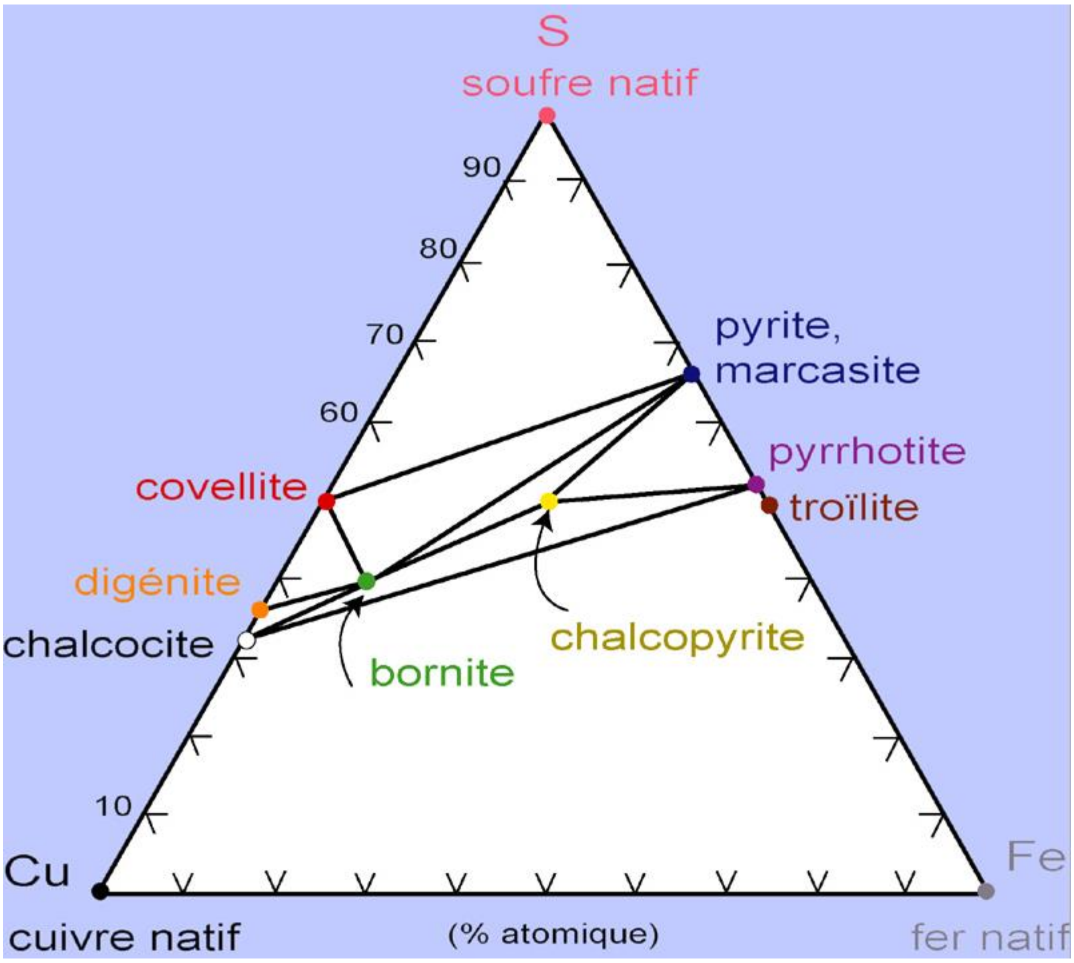

Figure 10: Position of the main copper sulphides in the Cu-Fe-S diagram

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

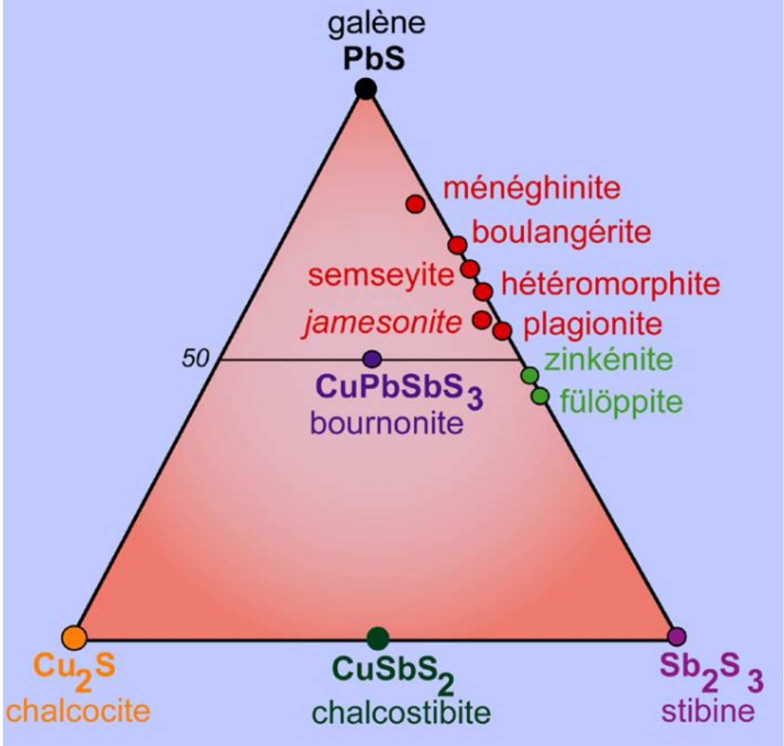

Figure 11: Diagram illustrating the position of the main sulphides and sulfosalts in the Pb - Sb - Cu system. The jamesonite (containing iron) in its chemical composition does not allow to register it rigorously in this diagram.

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

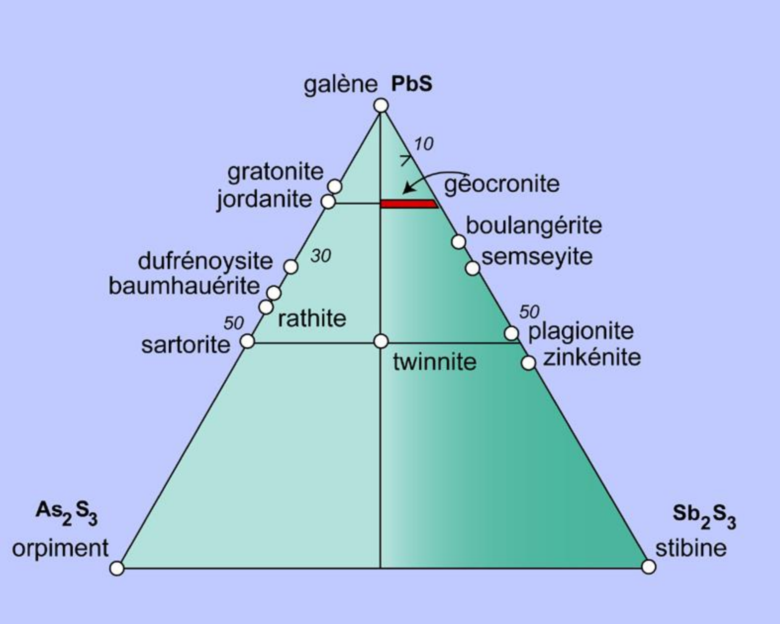

Figure 12: Diagram illustrating the position of the main sulphides and sulfosalts in the Pb - Sb - As system. The colored band reflects the variable composition of the geocronite.

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

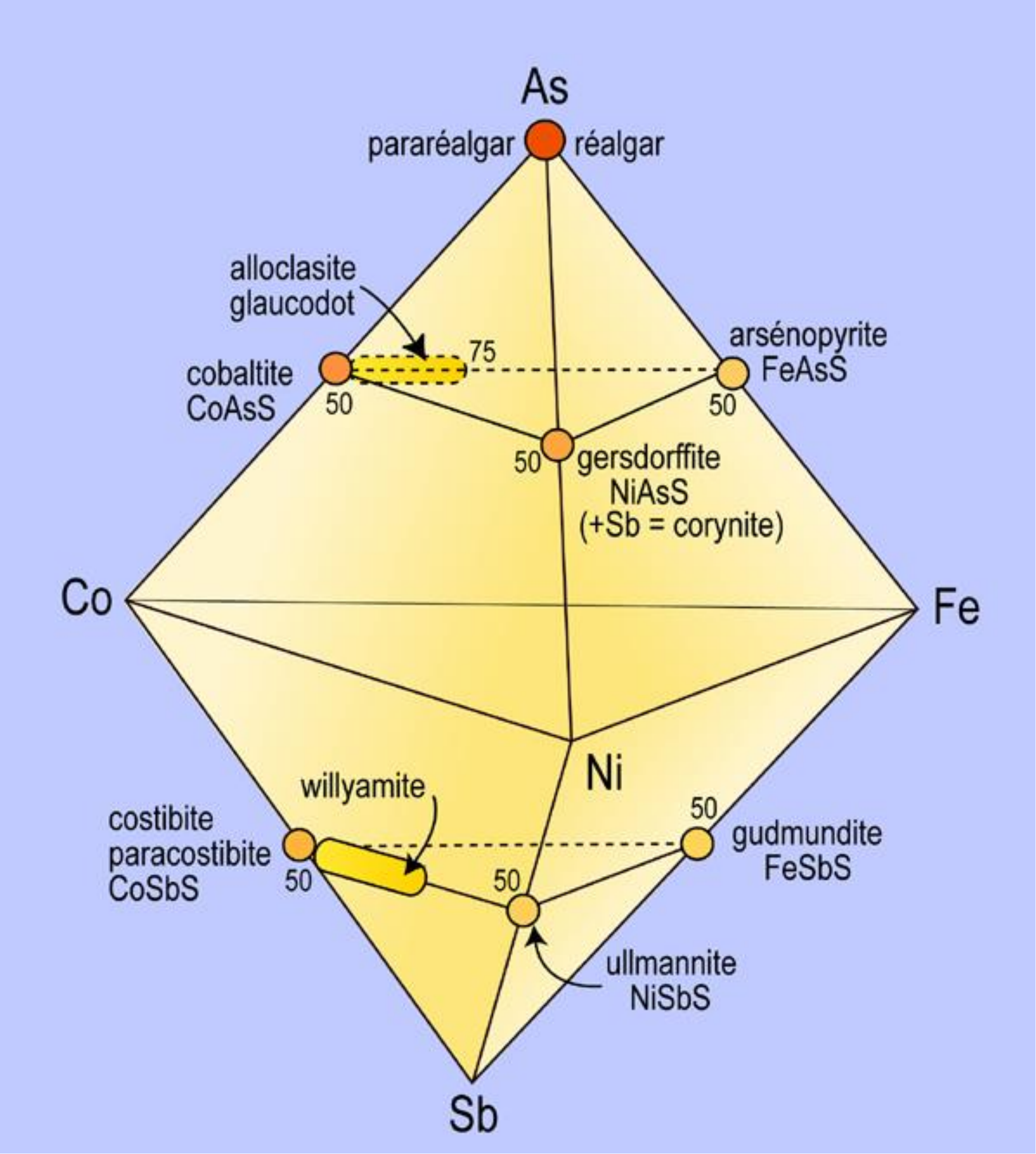

Figure 13: Compositions of the main sulfosalts, sulfantimonites and sulfoarsenides of Ni - Co -Fe (atomic %)

4.3.3.6 ANHYDROUS CARBONATES

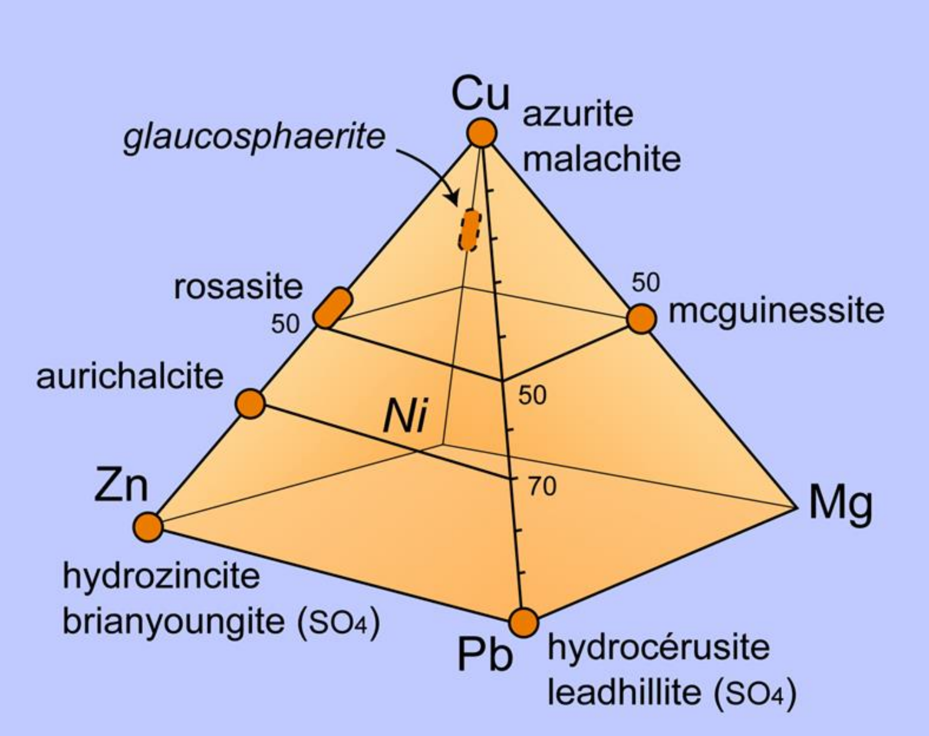

Figure 14: Composition of the most common hydroxylated carbonates of Cu, Zn, Pb, Mg and Ni (atomic %); parentheses indicate that complexes (SO4) also enter the structure of the carbonates concerned.

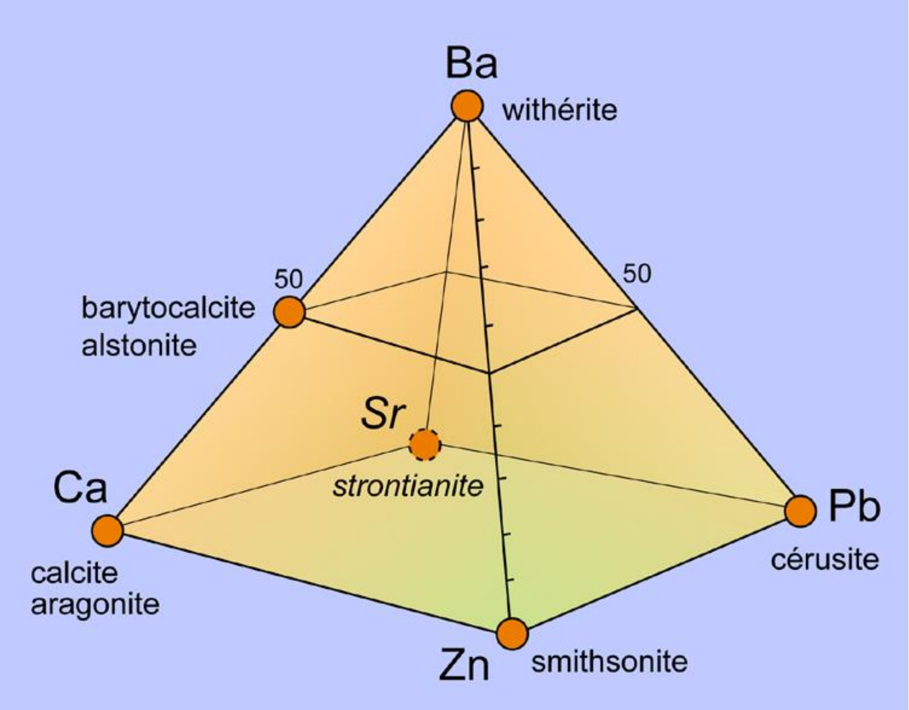

Figure 15: Composition of the most common anhydrous carbonates of Ca, Ba, Pb, Zn and Sr (atomic %).

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4.3.3.7 MAIN ARSENIDES OF CO-NI-FE

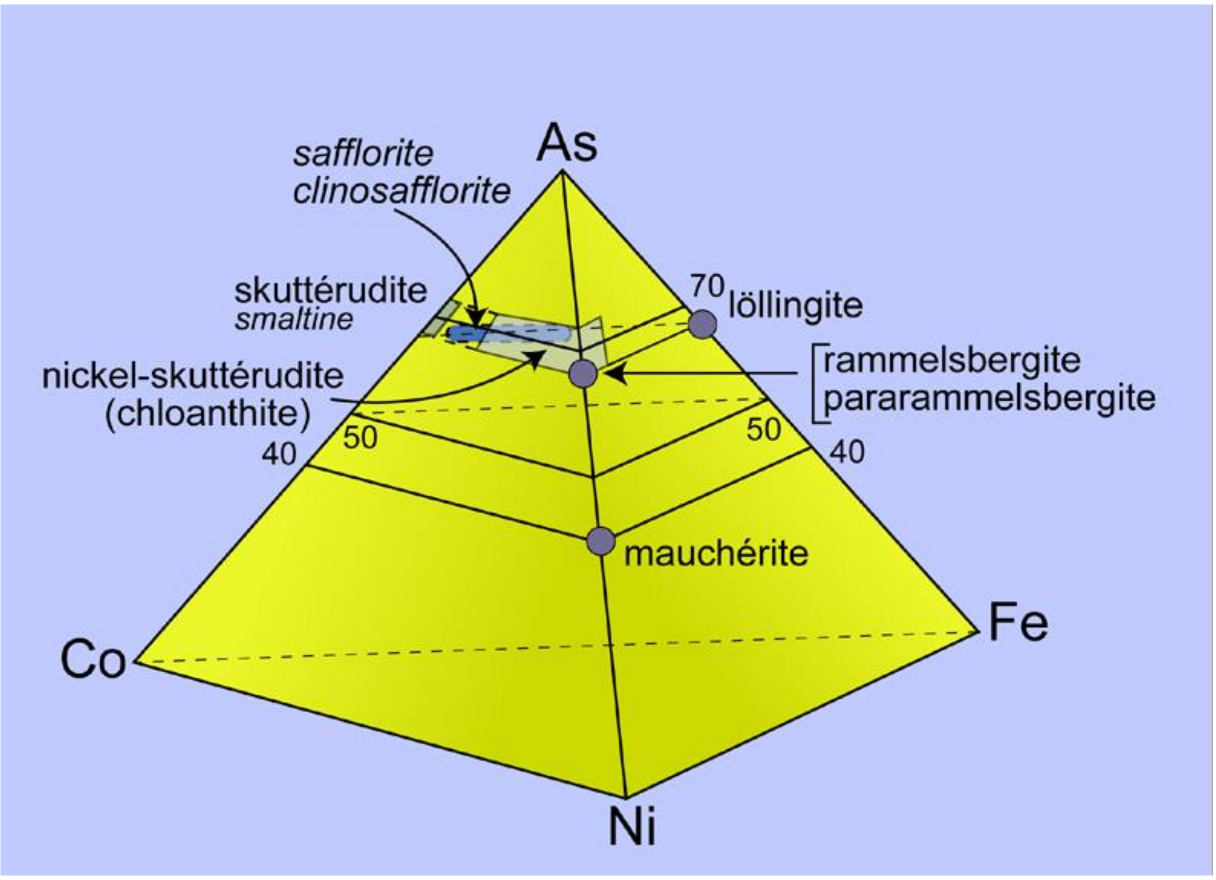

Figure 16: Main arsenides of Co, Ni and Fe in a ternary diagram (atomic %). The surfaces occupied on the front of the diagram by the fields of skutterudite and nickel-skutererudite result from the presence of 2 to 3 atoms of arsenic in the formula of these minerals. Safflorite and clinosafflorite occupy the dotted field on the back of the diagram.

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4.3.3.8 MAIN ANHYDROUS ARSENATES

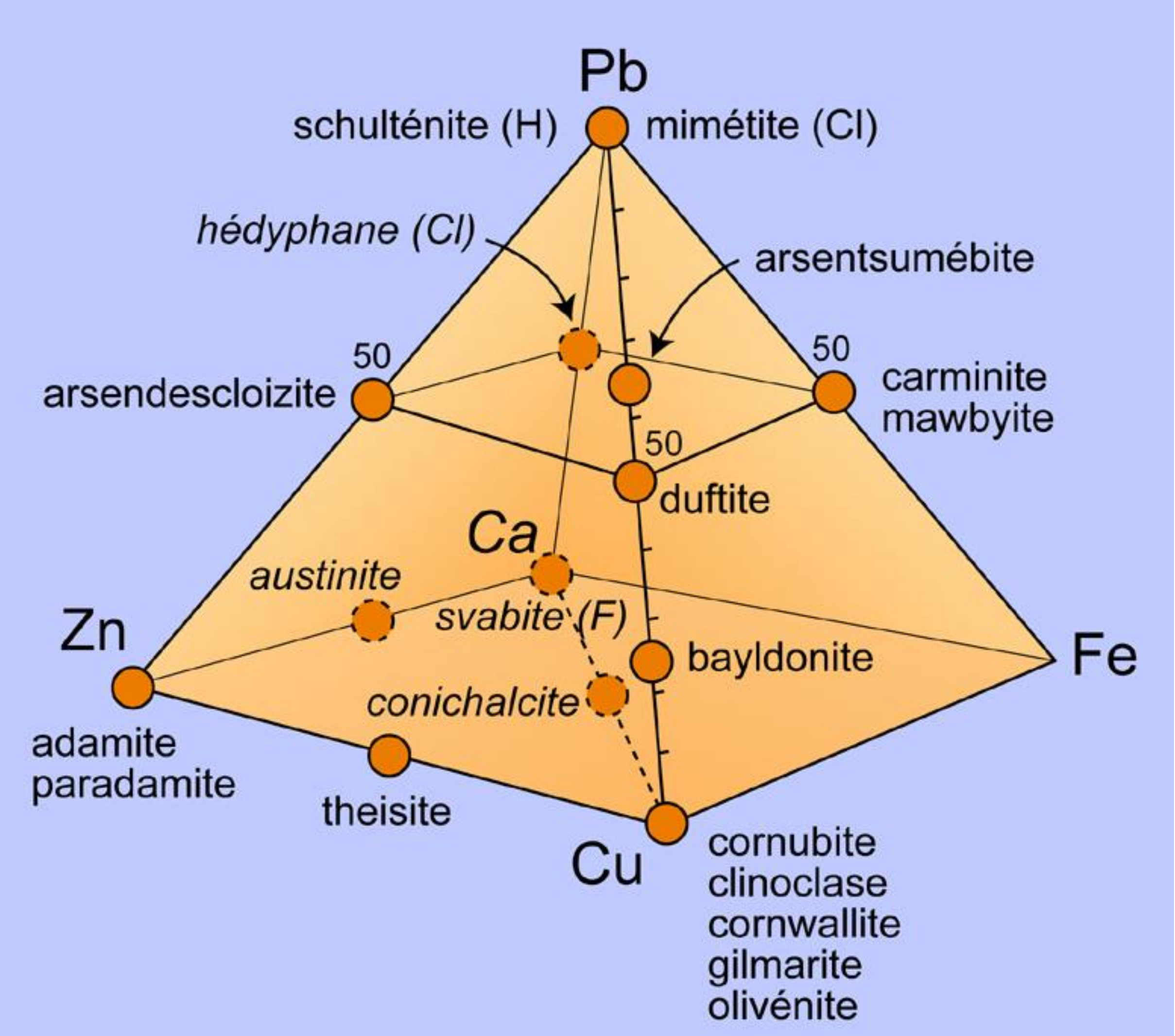

Figure 17: Composition of the main anhydrous arsenates of the Zn - Cu - Fe - Pb - Ca system (atomic%); in brackets the other elements entering into the structure of certain minerals

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4.3.3.9 MAIN HYDRATED ARSENATES

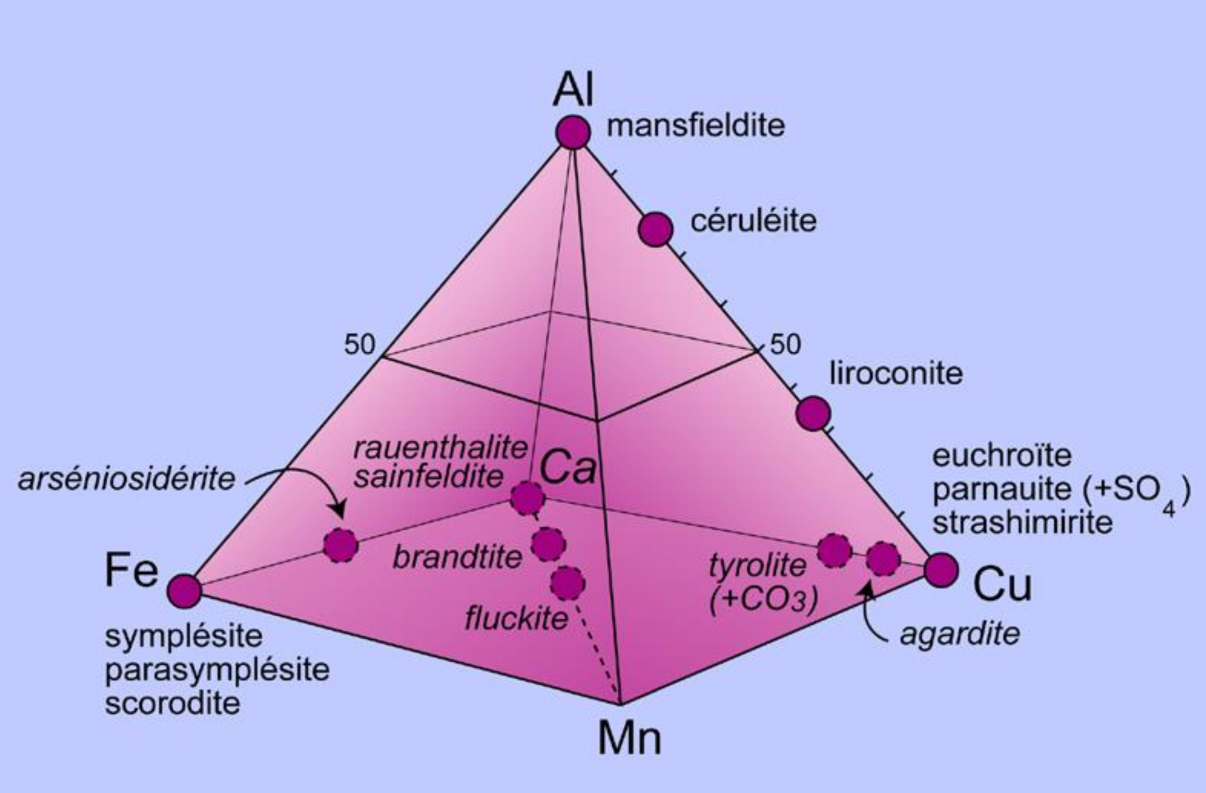

Figure 18: Compositions of the main hydrated arsenates of the Al - Cu - Ca - Fe - Mn system (atomic %); the groupings in parentheses also integrate the structure of the minerals indicated

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4.3.3.10 SULFOSALT

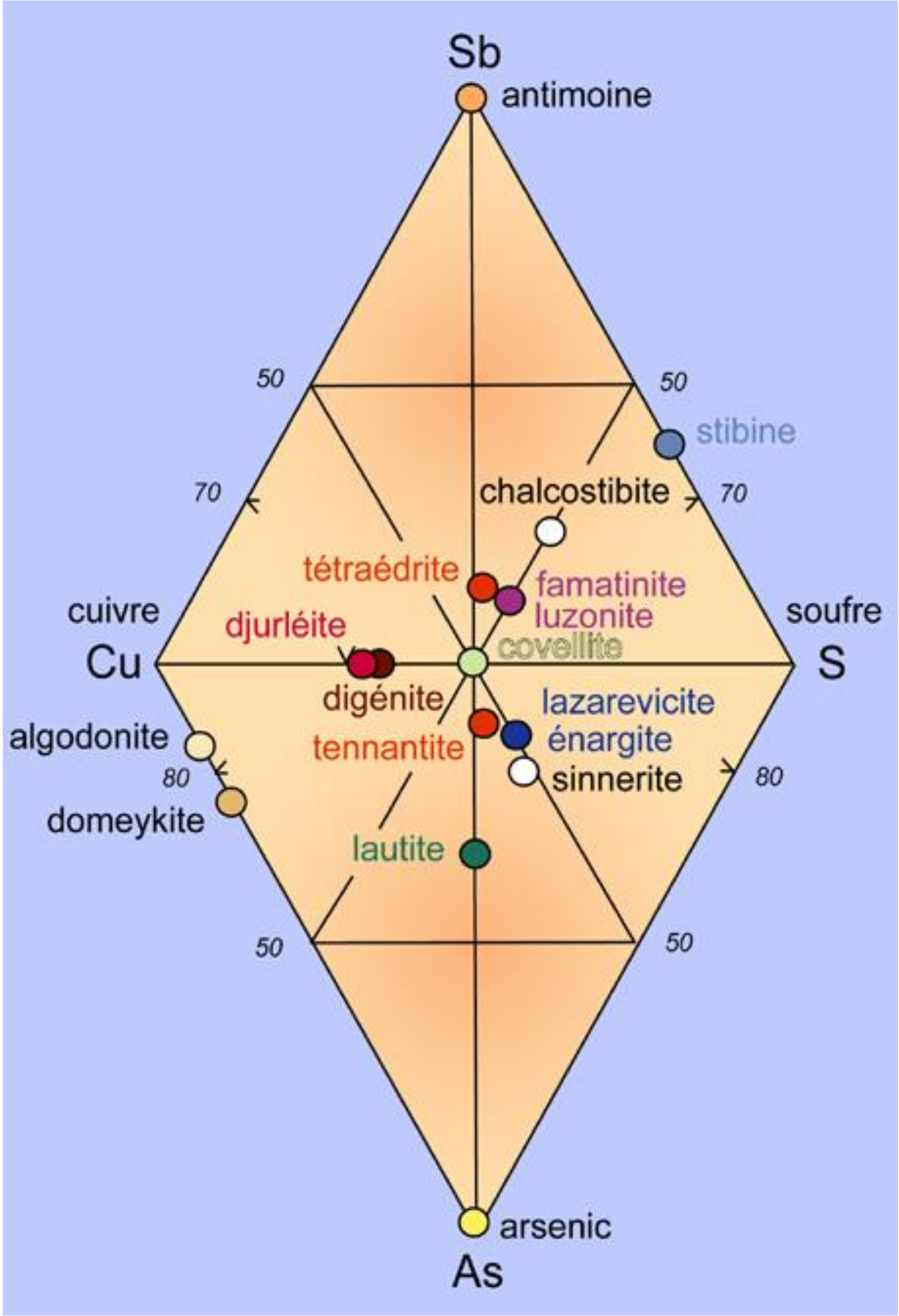

Figure 19: Compositions of the main native elements, sulfides, arsenides and sulfosalts of the Cu - Sb - S and Cu - As - S systems (atomic%); the solid tetrahedrite - tennantite solution is not shown in this diagram; the composition of chalcocite is very close to that of djurleite

4.3.3.11 MAIN ANHYDROUS SULFATES

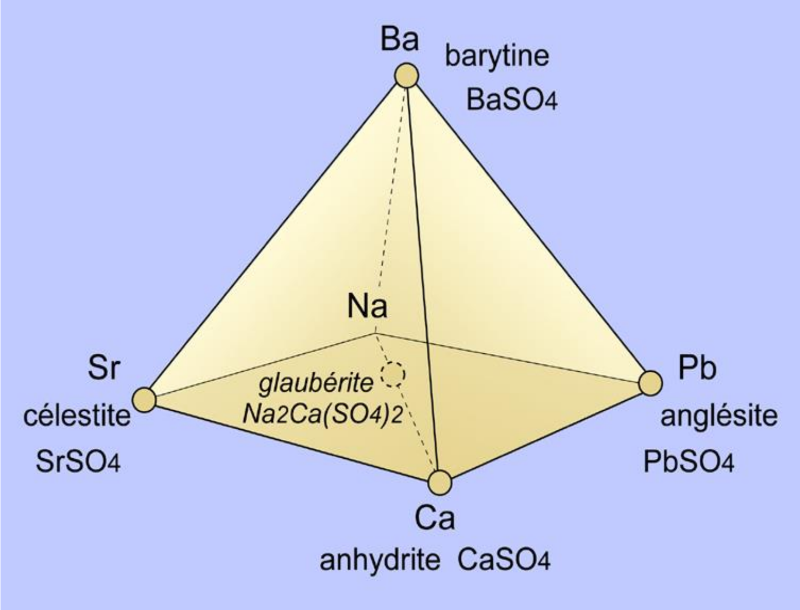

Figure 20 : Composition of the most communs anhydrous sulfates

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

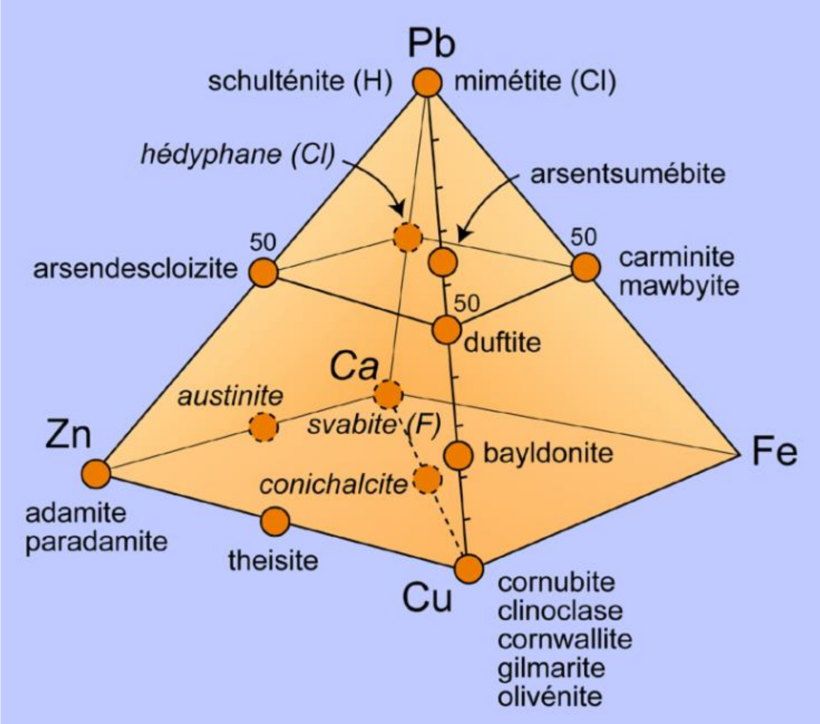

Figure 21: Composition of the main anhydrous arsenates of the Zn - Cu - Fe - Pb - Ca system (atomic %); in brackets the other elements entering into the structure of certain minerals.

4.3.3.13 MAIN ANHYDROUS PHOSPHATES (CU-PB)

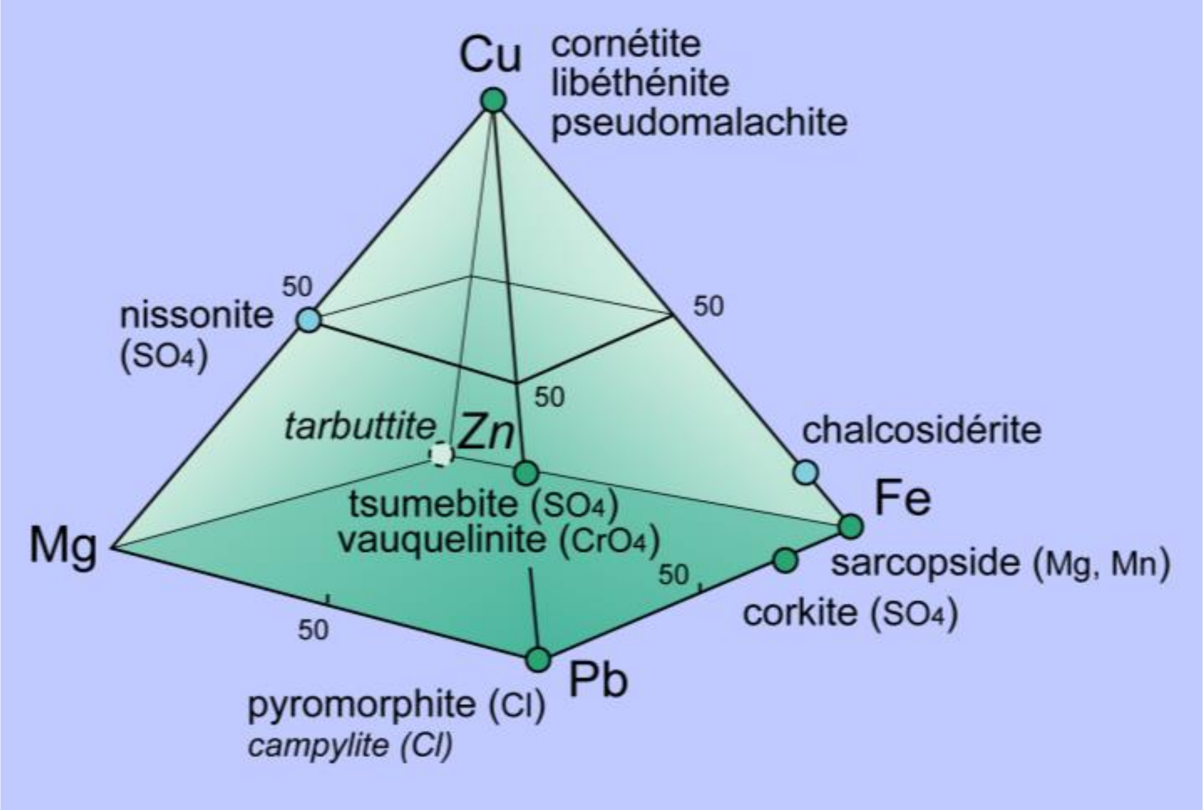

Figure 22: Composition of the main phosphates in the Cu - Mg - Pb - Fe - Zn system (atomic%); the elements and groupings in brackets integrate the structure of the minerals concerned; blue dots are hydrated phosphates

4.3.3.14 URANYL-PHOSPHATES

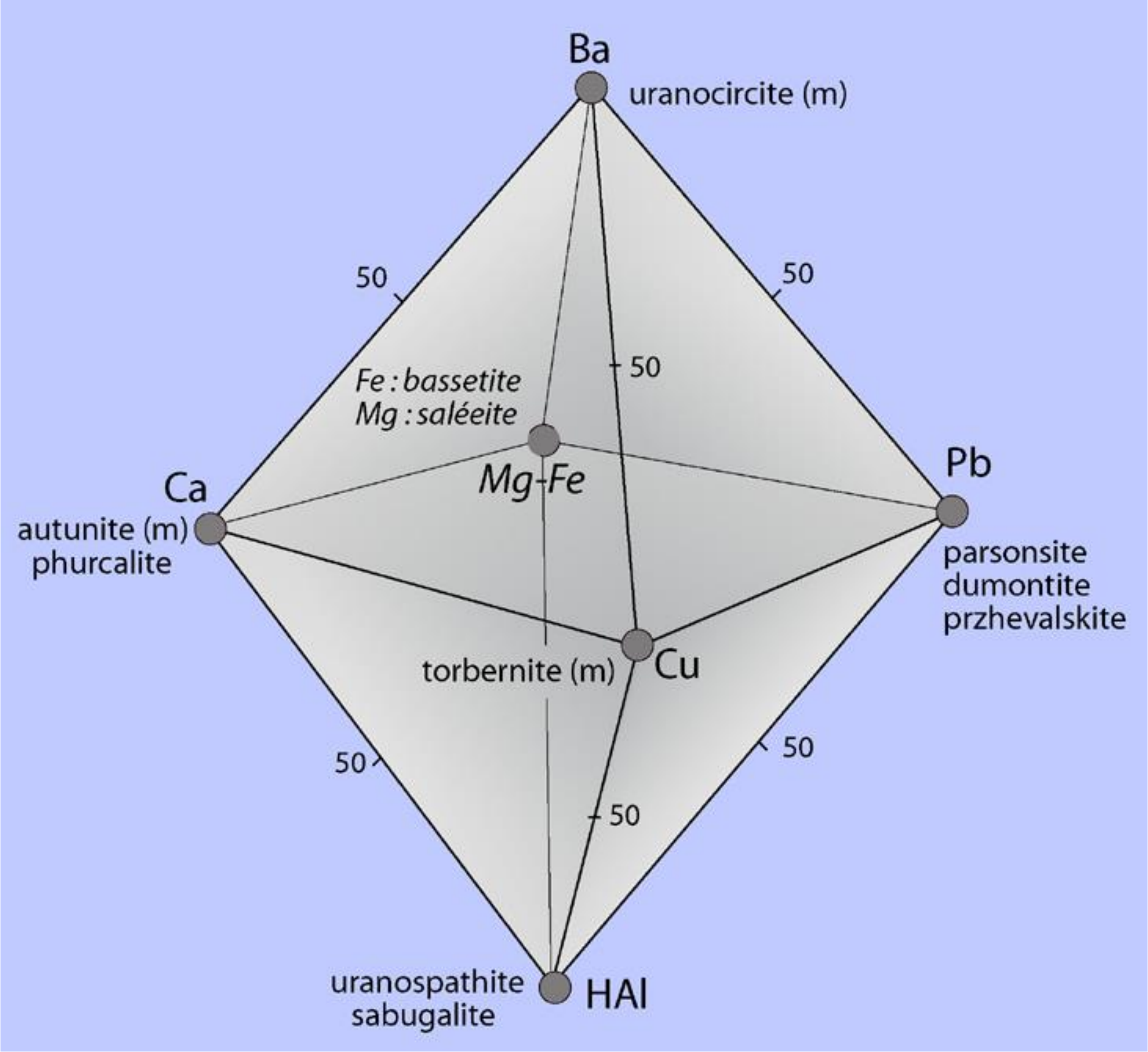

Figure 23: Main hydrated phosphates combining uranium and other elements (atomic %). The "m" indicates the existence at the same location of a meta form of the mineral, generally less hydrated.

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4.3.3.15 URANYL-VANADATES

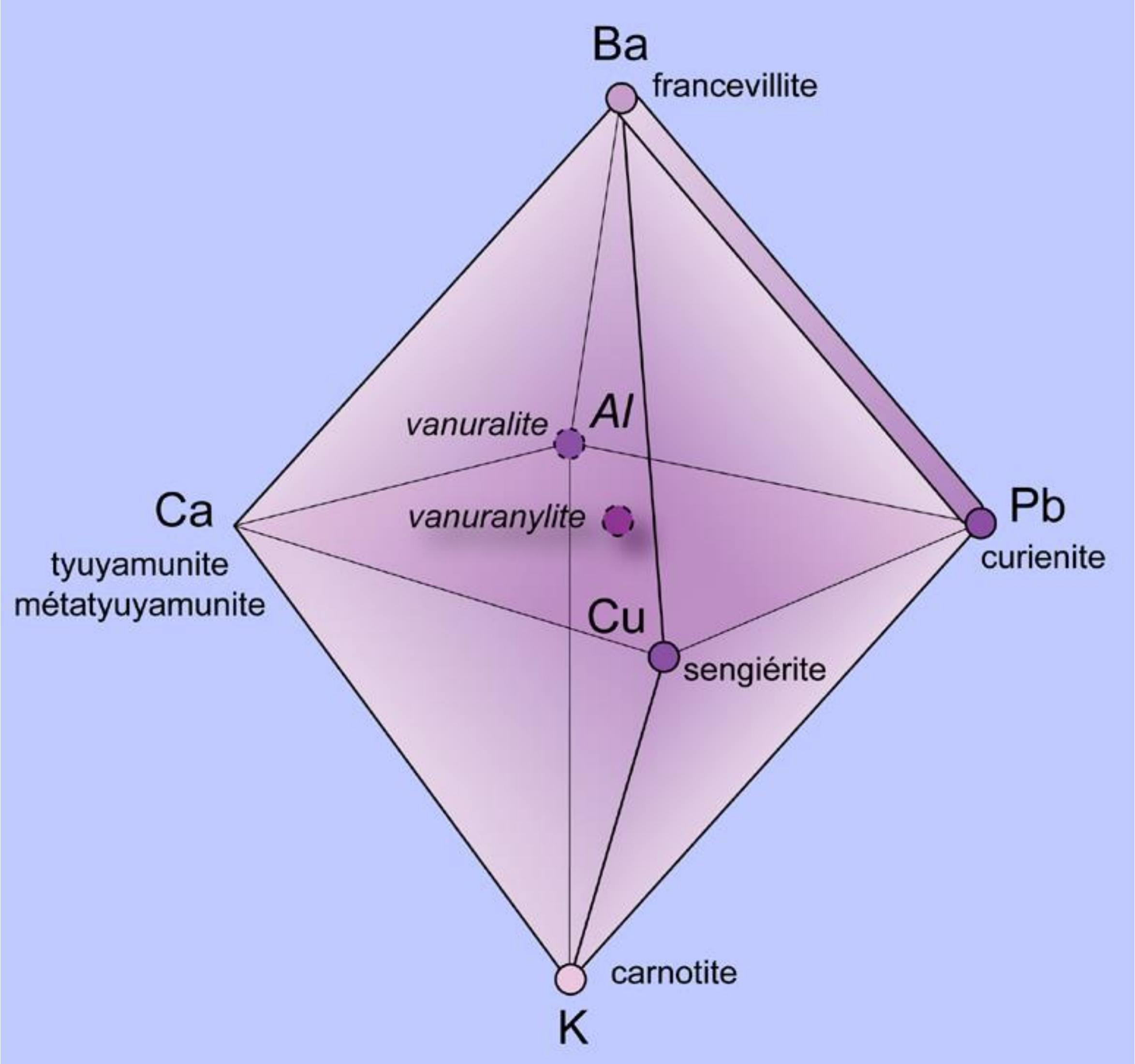

Figure 24 : Composition of the main uranyl-vanadates

4.3.3.16 TUNGSTATES AND MOLYBDATES (PB-CA)

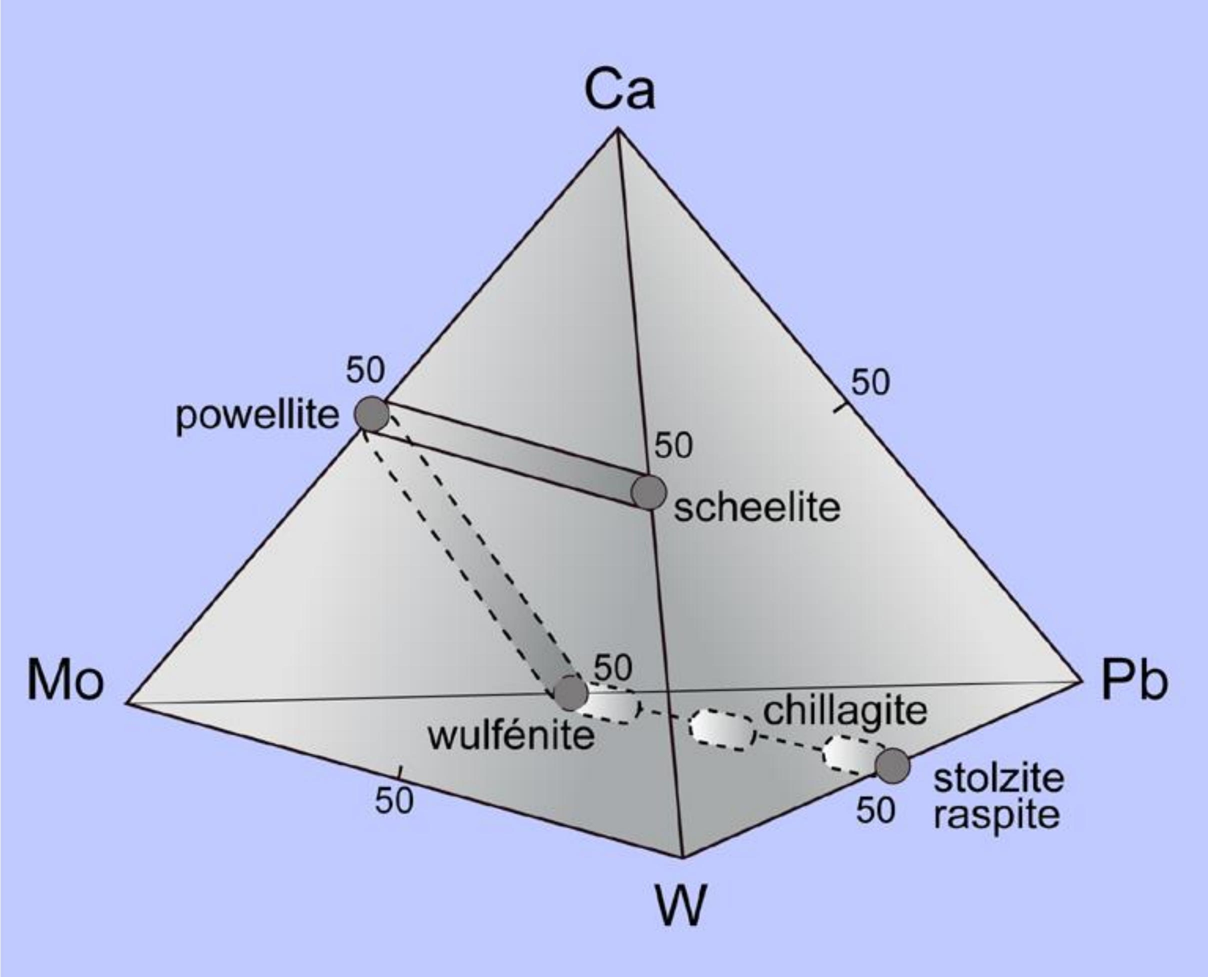

Figure 25: main tungstates and molybdates of Pb and Ca (atomic %)

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4.3.3.17 CHLORIDES

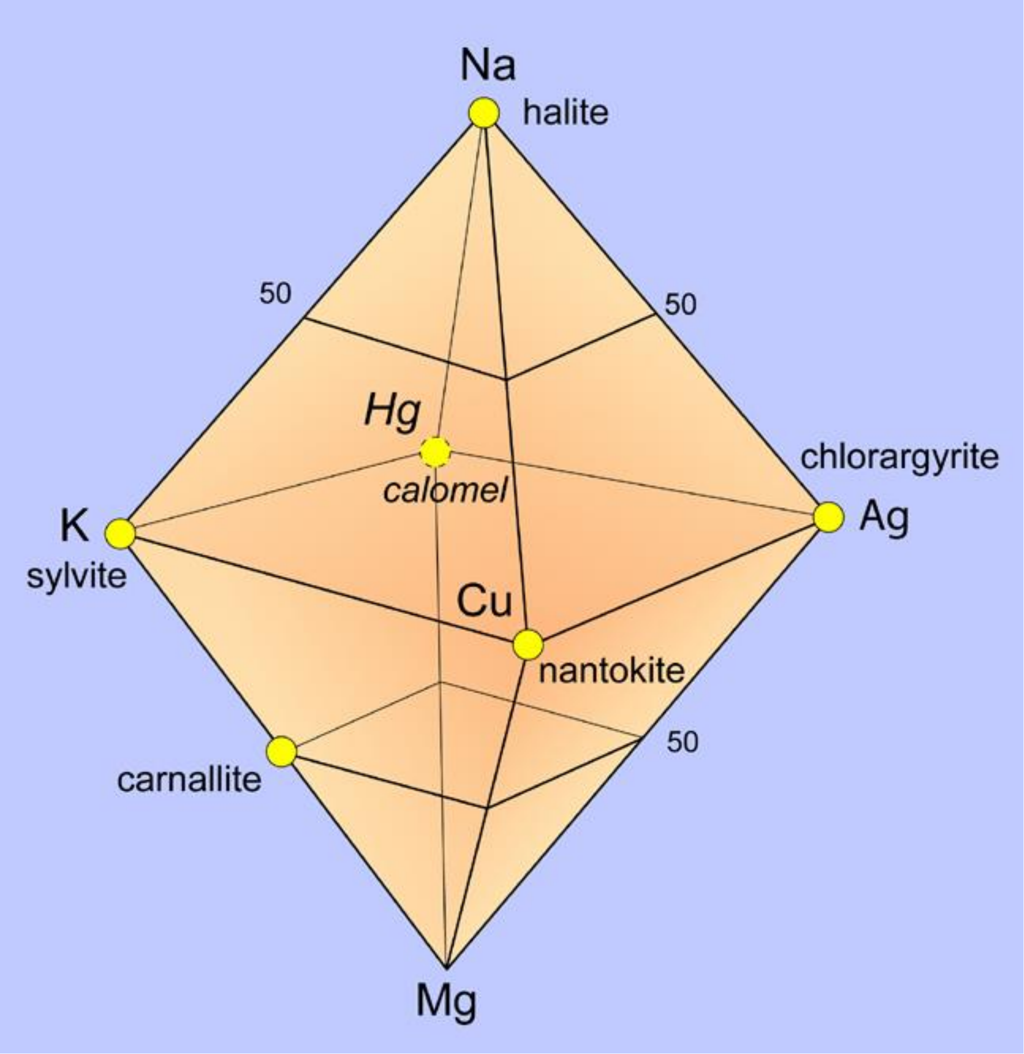

Figure 26 : Composition of the most commun chlorides

4.3.3.18 PB-ZN-FE-CU VANADATES

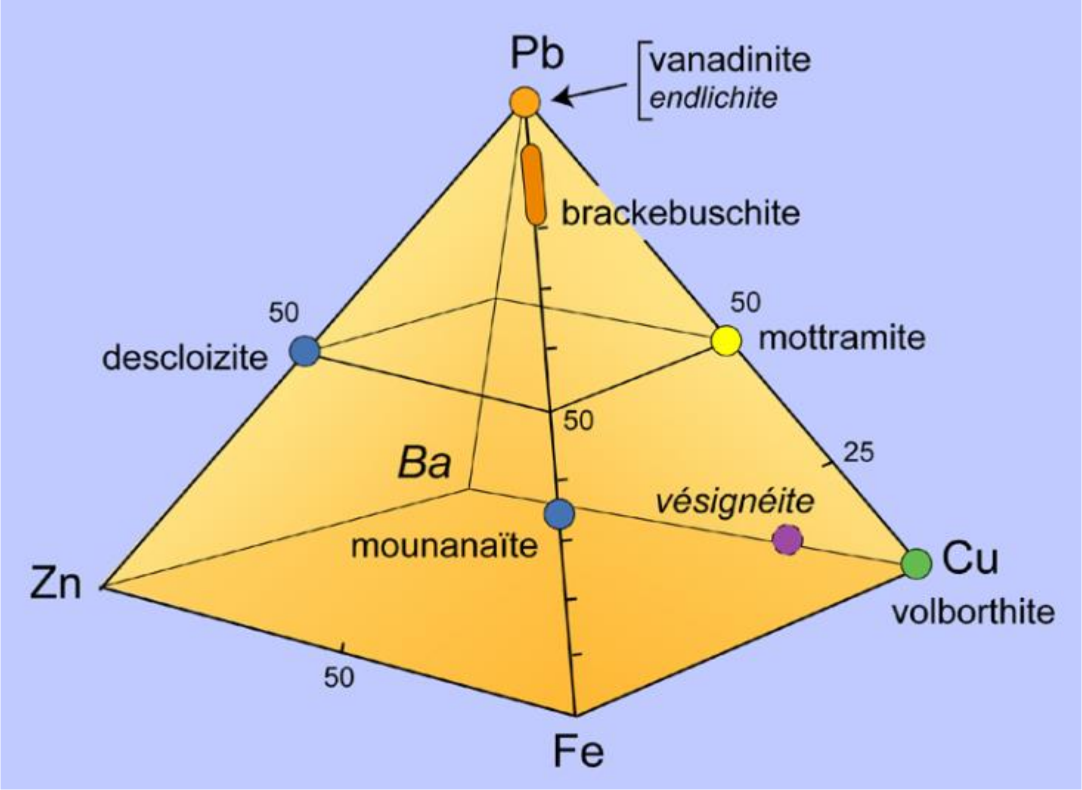

Figure 27: Composition of the most common vanadates of the Pb - Zn - Fe - Cu - Ba system (atomic %)

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5. COMPLEMENTARY INFORMATION

Excel tables:

https://tecnaliaresearchinnovation.box.com/s/mdo77pq0fa6t5j45kcspy1mtfthbhmwb

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kmz files:

https://tecnaliaresearchinnovation.box.com/s/nxrdkkhifgo9yyryu7gvm4hsku0rmhj5

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