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# AN OVERVIEW OF MINERALS TOXICITY

Written by RDG, 2014

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# 1. INTRODUCTION

## 1.1. Why discuss the toxicity of minerals?

Just like optical properties (how the mineral affects light), we can also look at biological activity (how the mineral affects living organisms) as another intrinsic property of a mineral. As such, toxic, medicinal or nutritive properties of minerals make another scientifically meaningful topic to discuss: when mineralogy meets biology!

Furthermore, the question of mineral toxicity is recurrent amongst beginner collectors, and this amateur study will try to approach it on the basis of concrete toxicological data.

However, in order to avoid any overreacting to this article, let's immediately make it clear that, with only a little bit of common sense, building a mineral collection remains quite a safe hobby!

## 1.2. A few basic notions of toxicology:

### 1.2.1. Dose:

An important principle of toxicology is that almost any chemical substance can be harmful if the dose (i.e. the administered amount) is high enough. Which is commonly translated as "the dose makes the poison". While toxicity largely depends on the dose, other important factors to be taken into consideration include the dose-time relationship (as frequency and duration of exposure), and the route of exposure (i.e. oral, dermal, inhalation).

### 1.2.2. Bioavailability:

Bioavailability refers to the extent to which an administered dose will reach the systemic circulation (thereby accessing the site of action). Hydrophobicity, pKa, and solubility of the compound will influence its bioavailability.

### 1.2.3. Toxicity class, Acute toxicity, and Median lethal dose:

The Toxicity Class of a compound is a classification system based on acute toxicity.

Acute toxicity represents the toxic potential of a compound on the short-term. That is its capacity to produce harmful effects relatively soon after oral or cutaneous administration (as a single dose), or after a 4 hours exposure to the compound in air. 'Relatively soon' is usually defined as minutes, hours (up to 24h), or days (up to about two weeks), but rarely more.

The acute toxicity of a compound is represented by its Median Lethal Dose, which is the dose that kills 50% of the tested animals (most often rats or mice). It is written LD50 for oral or cutaneous exposure (as mg/kg of body weight), and written LC50 for inhalation (as mg/m<sup>3</sup> of air for solids, or as ppm for gases).

So, comparing the median lethal dose of chemicals in animals gives a relative ranking of the acute toxicity of each, but it's only an approximative ranking considering that the median lethal dose is a single value which does not indicate the shape of the dose-response curve. Also keep in mind that the tested animals might possibly be more/less sensitive to the compound than humans.

It's important to understand that the median lethal dose only addresses short-term toxicity, while the full range of toxicity testing for a chemical should also include subacute/subchronic toxicity, chronic toxicity, carcinogenic, and reproductive (mutagenic, teratogenic) toxicity.

Let's also define two more terms:

The Lowest published Lethal Dose (LDLo, LCLo) is the lowest dosage known to have resulted in fatality in a particular animal species.

The Lowest published Toxic Dose (TDLo, TCLo) is the lowest dosage, administered over any given period of time, known to have resulted in any kind of toxic effects (other than death) in a particular animal species.

As an example, salt (sodium chloride) oral LD50 in rat is 3000mg/kg, and oral LDLo in man is about 1000mg/kg (for a 70kg man, that would represent ingestion of 70g of salt). For comparison, it is several hundreds times less toxic than sodium cyanide (oral LD50 in rat 6.44mg/kg).

So, here is the simplified acute toxicity rating system that will be used in this study:

Highly toxic: oral LD50 in rat/mouse less than 50mg/kg

Toxic: oral LD50 in rat/mouse between 50 and 100mg/kg

Moderately toxic: oral LD50 in rat/mouse between 100 and 500mg/kg

Low toxicity: oral LD50 in rat/mouse more than 500mg/kg

Please note that for the purpose of this study, the addition of a 50-100mg/kg category (which isn't found in the official classification system) does make sense, considering that this study will mostly deal with very dense metals/metalloids compounds (so that a toxic quantity might represent a very small volume of the material).

Online LD50 database: <https://chem.nlm.nih.gov/chemidplus/chemidheavy.jsp>

Another source of toxicological data is the Material Safety Data Sheet (MSDS) which is a document providing safety procedures for handling or working with a given chemical. MSDS can be accessed online, notably from chemical suppliers websites: <https://www.alfa.com/>  
<https://www.acros.com/> <https://www.sigmaaldrich.com/>

#### **1.2.4. Chronic toxicity:**

While acute toxicity refers to short-term effects from a single exposure, chronic toxicity addresses delayed effects produced by prolonged or repeated lower level exposures. Chronic toxicity results from poison accumulation in the body (cumulative poison), or from cumulative effects. Which can result in very serious health condition.

#### **1.2.5. Carcinogenic, Mutagenic, Reprotoxic:**

Some compounds show carcinogenic (causes cancer), mutagenic (causes genetic mutations) or reprotoxic (damages the reproductive process) potential, which is a serious concern in case of prolonged/repeated exposures.

### **1.3. Risk assessment:**

Objectively, minerals toxicity is mostly an occupational (i.e. professional) issue: people in the mining industry and stone industry (miners, ore smelters, quarry-workers, stone cutters, stone carvers..) are very exposed and need to observe strict safety precautions in regard of prolonged/repeated exposures to powdered minerals, airborne dust, and contaminated waters/sludges. Thus chronic toxicity through oral, dermal, and especially inhalation route has to be taken in consideration (along with possible carcinogenic, mutagenic and reprotoxic effects).

However, the context of exposure is quite different for mineral collectors who are mostly dealing with solid mineral pieces, which they will handle only occasionally, thus accidental absorption is way more unlikely than for miners.

In the home, let's also consider the risk to young children (who often put things in their mouth).

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## 2. TOXICITY OF MINERALS

### 2.1. Radiotoxicity (minerals that are harmful due to emitted radiations):

Radium, Uranium and/or Thorium containing minerals are radioactive (for instance let's mention radium barite, uraninite, thorianite, etc...). Let's also note that some rare-earth elements minerals can be radioactive (due to some of the REE being replaced by thorium, or more rarely uranium).

See <http://www.webmineral.com/> for case by case estimation of radioactivity (any mineral rated as strongly radioactive or very strongly radioactive definitely requires some caution).

Radioactivity can have carcinogenic, mutagenic, and reprotoxic effects. For the mineral collector, there would be three different concerns from storing radioactive specimens:

- direct radioactivity from the mineral samples themselves: prolonged/repeated exposures at close distance are hazardous, the annual exposure limit for the general public being set at 1mSv/year (on top of local background noise).

- fine radioactive volatile dust which separates from the samples and may become airborne: ingestion and inhalation hazard (the main concern here is inhalation which is more harmful).

- radioactive radon gas that emanates from the samples (and airborne radon daughters): inhalation hazard. Radon gas is invisible, odorless and much heavier than air (thus, it tends to accumulate in low and poorly ventilated areas). The health hazard from radon is mostly related to inhalation of its airborne radioactive decay products (known as 'radon daughters', or 'radon progeny'), especially the short-lived ones.

Additional warning about abandoned (thus unventilated) underground uranium mines: accumulation of radioactive airborne dust and radon (to potentially dangerous levels). Let's note that this may also apply to some mines which were not mined for uranium while actually containing significant amounts of uranium ore. Recommended reads:

[https://www.academia.edu/21052256/Radon\\_Levels\\_in\\_Abandoned\\_Metalliferous\\_Mines\\_Devon\\_Southwest\\_England](https://www.academia.edu/21052256/Radon_Levels_in_Abandoned_Metalliferous_Mines_Devon_Southwest_England)

<https://www.cdc.gov/niosh/docs/88-101/88-101.pdf?id=10.26616/NIOSH PUB88101>

### 2.2. Physical toxicants (minerals that are harmful due to their physical nature):

#### 2.2.1. Coal (and graphite):

Inhalation of coal or graphite dust over a long period of time can lead to a lung disease known as Coal workers' pneumoconiosis. This is a miner's disease and it's obviously not a concern to mineral collectors.

#### 2.2.2. Asbestos (fibrous amphibole group and serpentine group minerals Crocidolite, Amosite, Tremolite, Actinolite, Anthophyllite, and Chrysotile):

Prolonged/repeated inhalation of microscopic airborne fibers from those minerals can lead to asbestosis and cancer (mesothelioma and lung cancer), exposures are cumulative.

Let's note that miners working in a serpentinite, talc or vermiculite quarry might be exposed, as those can be associated to asbestos.

Other minerals which can occur in fibrous asbestiform habit and which are known or suspected to cause mesothelioma include Erionite, Magnesio-riebeckite, Fluoro-edenite, Winchite, Richterite, Antigorite, Nematite, Palygorskite, and to a lesser extent Sepiolite.

However, in the case of brief occasional exposure to low concentrations of asbestos fibers, the

probability of any future health issue can be expected to be very low. Which means that while asbestos is a serious occupational concern, on the other hand, without storing large quantities, mineral collectors should be rather safe.

### **2.2.3. Crystalline silica** (tridymite, cristobalite, quartz):

Prolonged/repeated inhalation of crystalline silica dust can lead to silicosis, and lung cancer.

Of course, silicosis can result from chronic inhalation of dust from any rock containing or contaminated with substantial amounts of free silica (see link below).

However, some brief or casual exposure to low concentrations of crystalline silica won't result in silicosis. So, while it isn't a concern to mineral collectors, silicosis still remains a serious concern for miners, quarry-workers, stone cutters/carvers, and also gemcutters.

Highly recommended read for workers of the mining and stone industry: Encyclopaedia of Occupational Health and Safety, Volume 3, Part 62.2 to 62.7

<https://books.google.fr/books?>

[id=nDhpLa1rl44C&pg=PT65&lpg=PT65&dq=encyclopaedia+occupational+health+safety+minerals&source=bl&ots=zMSiWTCykV&sig=I8DGwjxDbnY5NNaFpfhEAHFJcw&hl=en&sa=X&ei=3ywnVMTyKYnjatH1gPgP&ved=0CCMQ6AEwAA#v=onepage&q=encyclopaedia%20occupational%20health%20safety%20minerals&f=false](https://books.google.fr/books?id=nDhpLa1rl44C&pg=PT65&lpg=PT65&dq=encyclopaedia+occupational+health+safety+minerals&source=bl&ots=zMSiWTCykV&sig=I8DGwjxDbnY5NNaFpfhEAHFJcw&hl=en&sa=X&ei=3ywnVMTyKYnjatH1gPgP&ved=0CCMQ6AEwAA#v=onepage&q=encyclopaedia%20occupational%20health%20safety%20minerals&f=false)

## **2.3. Chemical toxicants** (minerals that are harmful due to their chemical nature):

### **2.3.1. Acute toxicity of elements and their inorganic compounds:**

Acute toxicity can be a concern to mineral collectors, but mainly by oral route (as accidental ingestion of a toxic quantity). Indeed, mineral collectors aren't supposed to be dealing with powdered materials thus acute inhalation toxicity shouldn't be a major concern, and significant dermal absorption could be expected to be rather unlikely just from occasional handling of a solid piece. So, concerning acute toxicity, this study will essentially focus on oral route of exposure.

As a preliminary step, let's establish a rough ranking of the acute toxicity potential by oral route of different chemical elements by investigating the oral LD50 value in rats or mouse of "simple" inorganic salts of each element (elemental form, chlorides, oxides, sulfides, sulfates, nitrates, hydroxides, carbonates, salts with sodium...which of course don't necessarily have any natural counterpart).

Elements investigated: Ag, Al, As, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cu, F, Fe, Ga, Gd, Ge, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Sb, Sc, Se, Si, Sn, Sr, Ta, Te, Ti, Th, Tl, U, V, W, Y, Zn, Zr.

Most of these are well documented through LD50 databases (although for a few ones, such as Os, only two or three salts were documented), still it is possible to get an approximative idea of their respective acute toxicity potential in inorganic form:

-Mercury, selenium, arsenic, phosphorus (but low toxicity as phosphate group), thallium, tellurium, vanadium, and chromium(VI). Some of their inorganic compounds are highly toxic, with oral LD50 in rat/mouse that is less than 50mg/kg.

-Then come fluorine, cadmium, and beryllium. Some of their inorganic compounds are toxic, with oral LD50 in rat/mouse that is between 50 and 100mg/kg

-And then come cobalt, nickel, barium, and copper. Some of their inorganic compounds have an oral LD50 in rat/mouse that is between 100 and 150mg/kg

-Concerning uranium and thorium salts, there isn't much LD50 data available. The benchmark for uranyl toxicity is uranyl acetate with oral LD50 in rat/mouse between 200 and 250mg/kg, which would qualify as moderate acute toxicity by oral route (which is also consistent with uranyl nitrate

data: oral LD100 in mouse 350mg/kg). Some soluble thorium compounds are also considered to exhibit moderate acute toxicity by oral route (although soluble thorium nitrate actually shows lesser acute toxicity, with oral LD50 in mouse 1760mg/kg).

-Concerning the other elements that were investigated: their inorganic compounds usually show moderate to low acute toxicity potential with oral LD50 in rat/mouse mostly higher than 200mg/kg (and even way higher than 500mg/kg for many of these), which means that immediate poisoning from a single exposure is unlikely to occur accidentally (as that would require higher doses).

As a side note, let's mention that many inorganic compounds showing significant acute toxicity by oral route (i.e. oral LD50 less than 150mg/kg) will also show significant acute toxicity by inhalation route. Besides, there were few inorganic compounds showing significant acute toxicity by dermal route (which was mainly encountered amongst mercury II compounds, water-soluble thallium salts, and some fluorides). Anyway, as already explained, these are not our main exposure concerns here.

So, this initial sorting shows us that some elements have more significant acute toxicity potential by oral route than others (i.e. mainly those potentially forming compounds with oral LD50 under 150mg/kg). However, the mere presence of potentially toxic elements doesn't necessarily impart a mineral with any significant toxicity. Indeed, the toxicity of minerals showing a significant content of these elements will largely depend on their bioavailability, and in a general way, acute toxicity by oral route should be investigated amongst minerals that have decent solubility in either water, hydrochloric acid, alcohol, or aqueous sodium bicarbonate (as those would dissolve in gastric acid or intestinal base).

Solubility data for quite a few minerals can be found here:

<https://www.mindat.org/article.php/553/Solubility+Data+on+646+Common+and+Not+So+Common+Minerals>

Solubility data also available from: <https://www.mineralatlas.eu/index.php?lang=en&language=english>

Starting from that point, acute toxicity of minerals by oral route will be investigated (case by case) in the next chapter.

### **2.3.2. Chronic toxicity of elements and their inorganic compounds:**

Most elements which have significant acute toxicity potential (see previous paragraph) also have the potential for significant chronic toxicity in case of prolonged/repeated exposures by oral, inhalation or, in some cases, dermal route.

However, that is also the case for some elements which inorganic compounds only rank as moderate to low acute toxicity, notably inorganic compounds of lead and antimony. Chronic exposure to uranium and thorium inorganic compounds also represents a serious hazard, as they show both some chemical toxicity (especially uranium which is nephrotoxic) and radiotoxicity.

Let's add that for some elements, prolonged/repeated exposures might also be associated with carcinogenic, mutagenic or reproductive toxicity (Hg, As, Be, Cd, Cr(VI), Ni, Co, Sb, V, Pb, U, Th). Prolonged/repeated exposures is a serious occupational concern (notably in the mining industry), but such context of exposure doesn't apply to mineral collectors.

### **2.3.3. Acute and chronic toxicity in organic compounds:**

For completeness sake, it should probably be mentioned that while this study is focusing on inorganic (i.e. mineral) compounds, toxicity of organic compounds is a rather different matter.

Indeed, some organic lead or tin compounds are way more toxic than inorganic lead or tin compounds, many organophosphates are also very toxic compared to the relatively low toxicity of inorganic phosphates, while at the opposite organic arsenic tends to be a bit less toxic than inorganic arsenic. Let's also mention the toxicity of antimony potassium tartrate. Of course I didn't bother to investigate toxicity of elements in organic form as, unless chemically processing the inorganic compounds into organic ones, that is not a concern.

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## 3.ACUTE TOXICITY OF MINERALS BY ORAL ROUTE

This chapter will investigate the acute toxicity of minerals by oral route, case by case, on the basis of their oral LD50. For comparison purposes, a few minerals of lesser toxicity will also be mentioned, which should allow some perspective.

### 3.1. MERCURY:

- Montroydite:  $\text{HgO}$ , with 92.6% Hg (by weight), sol.HCl, light sensitive (oral LD50 mouse 16mg/kg, rat 18mg/kg, highly toxic. Additional note: significant skin absorption, dermal LD50 rat 315mg/kg)
- Schuetteite:  $\text{Hg}_3(\text{SO}_4)_2$ , with 82.5% Hg, sol.HCl, very slightly sol.H<sub>2</sub>O (oral LD50 unavailable, but as an HCl soluble mercury II compound it is highly toxic, as stated in the MSDS. Additional note: significant skin absorption)
- Coccinite:  $\text{HgI}_2$ , with 44.1% Hg, moderately sol. warm alcohol, slightly sol. in oils, volatile at ambient temperature, light sensitive, rare and microscopic (oral LD50 mouse 17mg/kg, rat 18mg/kg, highly toxic. Also highly toxic by skin contact, with dermal LD50 in rat 75 mg/kg!)
- Chursinite and Kuznetsovite:  $\text{Hg}_2(\text{AsO}_4)$  and  $\text{Hg}_3(\text{AsO}_4)\text{Cl}$ , with 74.3%Hg 13.9%As and 77.5%Hg 9.7%As, respectively. Toxicological data unavailable, but as mercury(I,II) arsenates, these two would possibly qualify as toxic (if not highly toxic), however these are so rare and microscopic species that they are barely worth mentioning.
- Some other HCl soluble mercury(II) minerals (for instance terlinguaite, kleinite) might possibly show serious acute toxicity (with skin absorption also likely), but this couldn't be confirmed as there isn't any available toxicological data for such compounds. Let's note that, in a general way, Hg(II) compounds are usually more soluble and thus more toxic than Hg(I) analogue compounds.
- Moschelite:  $\text{Hg}_2\text{I}_2$ , with 61.3% Hg, sol.HCl, light sensitive (turns greenish,  $\text{HgI}_2$  and Hg being formed), rare and microscopic (oral LD50 mouse 110mg/kg, which would qualify as moderate acute toxicity by oral route, but the MSDS rather gives it as toxic if ingested, inhaled, and with skin absorption)
- Calomel:  $\text{Hg}_2\text{Cl}_2$ , with 85% Hg, moderately sol.alcohol, slightly sol.HCl, insol.H<sub>2</sub>O (oral LD50 mouse 180mg/kg, rat 210mg/kg, moderately toxic)
- Native mercury: Hg (100% Hg), insol.HCl and insol.H<sub>2</sub>O, evaporates at room temperature, vapours being invisible and odorless (liquid mercury shows low acute toxicity by oral route and dermal route, but vapours are highly toxic if inhaled. LCLo by inhalation in rabbit is 29mg/m<sup>3</sup>/30H)
- Cinnabar (and metacinnabar):  $\text{HgS}$ , with 86.2% Hg, insol.HCl and insol.H<sub>2</sub>O (very poor gastrointestinal absorption thus low acute toxicity by oral route). However, while cinnabar itself shows low acute toxicity, beware that native mercury (which vapours are highly toxic by inhalation) might be present in some cinnabar samples (especially massive samples). Also note that heating cinnabar can release mercury vapours.

### 3.2. SELENIUM:

- Native selenium: Se (100% Se), insol.HCl, insol.H<sub>2</sub>O (oral LD50 rat 6700mg/kg, very low acute toxicity by oral route)
- Downeyite:  $\text{SeO}_2$ , with 71.2% Se, sol.H<sub>2</sub>O, hygroscopic, rare and microscopic (oral LD50 mouse 23.3mg/kg, rat 68.1mg/kg, highly toxic)
- Nestolaite:  $\text{CaSeO}_3 \cdot \text{H}_2\text{O}$ , with 42.7% Se, sol.dilute HCl, insol.H<sub>2</sub>O, rare and microscopic (oral LD50 unavailable, but the MSDS gives it as highly toxic by ingestion and inhalation)

- Cobaltomenite:  $\text{CoSeO}_3 \cdot 2\text{H}_2\text{O}$ , with 35.6% Se, sol.HCl (oral LD50 unavailable, but the MSDS gives it as toxic by ingestion and inhalation)
- Chalcomenite and Clinochalcomenite:  $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ , with 34.9% Se, sol.HCl (oral LD50 unavailable, but the MSDS gives it as toxic by ingestion and inhalation)
- let's note that some other soluble selenite minerals (for instance softite, mandarinoite, molybdomenite, ahlfeldite, zincomenite) might possibly show significant acute toxicity, but this couldn't be confirmed as there isn't any available toxicological data for such compounds, anyway these are rare and microscopic species.
- selenium sulfides and selenides: There isn't any available LD50 data for such compounds, but their acute toxicity by oral route probably ranges from moderate to low (most are insoluble, but a few HCl soluble ones might possibly show some more significant toxicity).

### 3.3. ARSENIC:

- Native arsenic: As (100% As), moderately sol.HCl (oral LD50 mouse 145mg/kg, rat 763mg/kg, moderately toxic)
  - Arsenolite and Claudetite:  $\text{As}_2\text{O}_3$  (cubic and monoclinic respectively), with 75.7% As, sol.HCl, slightly sol.H<sub>2</sub>O (oral LD50 rat 14.6mg/kg, mouse 31.5mg/kg, oral LDLo in human 1.429mg/kg, highly toxic. Accordingly to the LDLo, ingestion of a 3.5 to 4mm edged octahedron could be fatal to an adult!)
  - Stibioclaudeite:  $\text{AsSbO}_3$ , with 30.6% As (toxicological data unavailable, but being chemically closely related to claudetite, it might possibly qualify as toxic or highly toxic)
  - Orpiment:  $\text{As}_2\text{S}_3$ , with 60.9% As, sol.alkalies, insol.HCl, insol.H<sub>2</sub>O (oral LD50 rat 185mg/kg, mouse 254mg/kg, moderately toxic)
- However, while orpiment itself is only moderately toxic, beware that arsenolite (highly toxic) might be present as a decomposition product in some oxidized orpiment samples (especially powdery/crumblly massive samples).
- Realgar:  $\text{As}_4\text{S}_4$ , with 70% As, insol.HCl, insol.H<sub>2</sub>O (oral LD50 in mouse reported to be 3200mg/kg, which would suggest low acute toxicity by oral route)
  - arsenic sulfides and arsenides: most are poorly soluble and these usually range from moderately toxic to low acute toxicity by oral route. Still, they can be toxic in case of prolonged/repeated exposure by inhalation or ingestion.
  - Weilite, Pharmacolite and Haidingerite:  $\text{Ca}(\text{HAsO}_4)$ , with 41.6% As (weilite), sol.HCl (oral LD50 in rabbit 50mg/kg, rat/mouse data unavailable, toxic)
  - Raueenthalite and Phaunouxite:  $\text{Ca}_3(\text{AsO}_4)_2 \cdot 10\text{H}_2\text{O}$ , with 25.9% As (raueenthalite), sol.HCl (oral LD50 rat 20mg/kg, oral LD50 mouse 794mg/kg, oral LDLo rabbit 50mg/kg, toxic, as confirmed by the MSDS)
  - Schultenite:  $\text{Pb}(\text{HAsO}_4)$ , with 21.6% As, sol.HCl (oral LD50 rat 80mg/kg, rabbit 125mg/kg, mouse 1000mg/kg, toxic)
  - Reinerite:  $\text{Zn}_3(\text{AsO}_3)_2$ , with 33.9% As, sol.dilute HCl (oral LD50 in mouse 144mg/kg, in rat 271mg/kg, moderately toxic)
  - Hornesite:  $\text{Mg}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ , with 30.3% As, sol.HCl (oral LD50 in mouse 315mg/kg, oral LDLo rabbit 80mg/kg, oral LDLo rat 280mg/kg, moderately toxic)
  - Lammerite, Rollandite and Babanekite:  $\text{Cu}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ , with 27.7% As (rollandite), sol.HCl (oral LD50 mouse 167mg/kg, rat 1501mg/kg, moderately toxic)
  - Castellarite:  $\text{Mn}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ , with 29.1% As, slightly sol.dilute HCl (oral LD50 in mouse 194mg/kg, in rat 791mg/kg, moderately toxic)
  - other soluble arsenites and arsenates: oral LD50 values unavailable, but a few ones might possibly be toxic (i.e. oral LD50 below 100mg/kg), although most would probably only qualify as moderately toxic. Let's note that arsenic(III) compounds are usually more toxic than arsenic(V) analogue compounds.

### 3.4. PHOSPHORUS:

Low acute toxicity as inorganic phosphate group, but some phosphides can be toxic. However, the only phosphide mineral worth mentioning would be Schreibersite:  $(\text{Fe,Ni})_3\text{P}$ , with 15.4% P, insol.H<sub>2</sub>O and insol.HCl (oral LD50 unavailable, but insoluble thus acute toxicity by oral route is probably low).

Then, there is the questionable case of native phosphorus (P<sub>4</sub>), which was once suspected in a meteorite sample, but never proven (hypothetically, if it had been occurring in its white form allotrope then it would qualify as highly toxic: oral LD50 rat 3.03mg/kg, mouse 4.82mg/kg).

### 3.5. THALLIUM:

soluble thallium minerals are very rare and mostly microscopic, let's still mention:

-Avicennite:  $\text{Tl}_2\text{O}_3$ , with 89.5% Tl, sol.HCl (oral LD50 rat 44mg/kg, highly toxic)

-Lafossaite:  $\text{Tl}(\text{Cl,Br})$ , with 81.4% Tl, slightly sol.H<sub>2</sub>O (oral LD50 unavailable, but quite probably highly toxic considering that  $\text{TlCl}$  oral LD50 in mouse is 24mg/kg. Additional note: while known from some water-soluble thallium salts, skin absorption isn't mentioned in the MSDS for thallium chloride or bromide)

-other rare (and microscopic) thallium minerals which may possibly qualify as toxic or highly toxic include Steropesite  $\text{Tl}_3\text{BiCl}_6$ , Lanmuchangite  $\text{TlAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , Dorallcharite  $\text{TlFe}_3(\text{SO}_4)_2(\text{OH})_6$ , Carlinite  $\text{Tl}_2\text{S}$  (for those showing significant water-solubility, let's note that they might possibly show some skin absorption).

### 3.6. TELLURIUM:

-Native tellurium: Te (100% Te), insol.HCl, insol.H<sub>2</sub>O (oral LD50 in both rat and mouse higher than 5000mg/kg, very low acute toxicity by oral route)

-Tellurite and Paratellurite:  $\text{TeO}_2$ , with 80% Te, sol.concentrated HCl, slightly sol.diluted HCl (oral LD50 in rat reported to be higher than 5000mg/kg, which would suggest very low acute toxicity by oral route, surprisingly considering the relative solubility of this Te(IV) compound)

-Teineite, Graemite, Millsite and Balyakinite:  $\text{Cu}(\text{TeO}_3)_2 \cdot 2\text{H}_2\text{O}$ , with 46.4% Te (teineite), sol.HCl (oral LD50 unavailable, as a soluble tellurite it might possibly show some significant toxicity, but this couldn't be confirmed as there isn't any available toxicological data for this compound)

-let's note that some other soluble tellurite and tellurate minerals (for instance emmonsite?) might possibly qualify as toxic or moderately toxic, but this couldn't be confirmed as there isn't any available toxicological data for such compounds.

-tellurium sulfides and tellurides: There isn't any available LD50 data for such compounds, but their acute toxicity by oral route probably ranges from moderate to low.

### 3.7. VANADIUM:

-Metamunirite and Munirite:  $\text{NaVO}_3$ , with 41.8% V (metamunirite), sol.H<sub>2</sub>O (oral LD50 mouse 74.6mg/kg, rat 98mg/kg, toxic)

-Metarossite, Rossite, Calciodelrioite:  $\text{Ca}(\text{VO}_3)_2 \cdot 2\text{H}_2\text{O}$ , with 37.2% V (metarossite), sol.H<sub>2</sub>O (oral LD50 unavailable, but MSDS data tends to suggest that it is toxic)

-Shcherbinaite and 'Alaite':  $\text{V}_2\text{O}_5$ , with 56% V (shcherbinaite), sol.HCl, slightly sol.H<sub>2</sub>O (oral LD50 64mg/kg in mouse and 86mg/kg in rat, toxic. Additional note: skin absorption, dermal LD50 rabbit 200mg/kg)

-Karelianite:  $\text{V}_2\text{O}_3$ , with 68% V, slightly sol.H<sub>2</sub>O (oral LD50 mouse 130mg/kg, rat 566mg/kg, moderately toxic. Additional note: skin absorption)

-Minasragrite (and Anorthominasragrite, Orthominasragrite, Bobjonesite, Stanleyite, Pauflerite):  $(\text{VO})(\text{SO}_4) \cdot 5\text{H}_2\text{O}$ , with 20.1% V (minasragrite), sol.H<sub>2</sub>O (oral LD50 rat 448mg/kg, mouse 467mg/kg, moderately toxic)

-Vanadinite:  $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ , with 10.8% V and 73.2% Pb, sol.HCl (oral LD50 data unavailable, but acute toxicity by oral route is probably moderate or, more likely, low. Still, prolonged/repeated

exposures by inhalation or ingestion might possibly be an issue).

### 3.8. CHROMIUM:

chromium(VI) compounds, such as chromates, can be toxic, let's mention:

-Lopezite:  $K_2(Cr_2O_7)$ , often synthetic, with 35.4% Cr, sol.H<sub>2</sub>O (oral LD50 rat 25mg/kg, mouse 190mg/kg, toxic. The MSDS gives it as toxic if ingested, and very toxic if inhaled. Additional note: skin absorption, dermal LD50 rabbit below 200mg/kg)

-Tarapacaite:  $K_2CrO_4$  (may be synthesized), with 26.8% Cr, sol.H<sub>2</sub>O (oral LD50 mouse 180mg/kg, rat data unavailable, but let's still qualify it as toxic)

-Chromatite:  $Ca(CrO_4)$ , with 33.3% Cr, sol.HCl (oral LD50 rat 327mg/kg, moderately toxic)

-Crocoite:  $Pb(CrO_4)$ , with 16.1% Cr and 64.1% Pb, slightly sol.HCl (oral LD50 mouse 12000mg/kg, very low acute toxicity by oral route. The MSDS still mentions that prolonged/repeated exposures by inhalation or ingestion might be an issue.)

-let's note that chromium(III) compounds are usually low acute toxicity by oral route.

As an example, Chrome alum (artificial crystals):  $KCr(SO_4)_2$ , with 18.4% Cr(III), sol.H<sub>2</sub>O (oral LD50 rat 3530mg/kg, low acute toxicity by oral route)

### 3.9. FLUORINE:

-Villiaumite: NaF (may be synthesized), with 45.3% F, sol.H<sub>2</sub>O (oral LD50 rat 52mg/kg, mouse 57mg/kg, toxic)

-Cryptohalite and Bararite:  $(NH_4)_2[SiF_6]$ , with 64% F, sol.H<sub>2</sub>O (oral LD50 mouse 70mg/kg, oral LDLo rat 100mg/kg, toxic. Additional note: skin absorption)

-Malladrite:  $Na_2[SiF_6]$ , with 60.6% F, slightly sol. cold H<sub>2</sub>O, moderately sol. hot H<sub>2</sub>O (oral LD50 mouse 70mg/kg, rat 125mg/kg, toxic. Additional note: skin absorption)

-Hieratite and Demartinite:  $K_2[SiF_6]$ , with 51.8% F, slightly sol. cold H<sub>2</sub>O (oral LD50 mouse 70mg/kg, rat 156mg/kg, toxic. Additional note: skin absorption)

-Griceite: LiF (may be synthesized), with 73.2% F, sol.HCl, slightly sol.H<sub>2</sub>O (oral LD50 143mg/kg in rat, MSDS gives it as toxic if ingested)

-Carobbiite: KF (may be synthesized), with 32.7% F, sol.H<sub>2</sub>O (oral LD50 rat 245mg/kg, however the MSDS still gives it as toxic if ingested, inhaled, and with skin absorption)

-Frankdicksonite:  $BaF_2$  (may be synthesized), with 21.7% F, slightly sol.H<sub>2</sub>O, sol.HCl (oral LD50 rat 250mg/kg, moderately toxic)

-let's note that some other soluble fluoride minerals (for instance water-insoluble heklaite?) might possibly show some toxicity, but this couldn't be confirmed as there isn't any available toxicological data for such compounds.

-Sellaite:  $MgF_2$  (may be synthesized), with 61% F, very slightly sol.H<sub>2</sub>O (oral LD50 rat 2330mg/kg, low acute toxicity by oral route)

-Cryolite:  $Na_3[AlF_6]$ , with 54.3% F, very slightly sol.H<sub>2</sub>O, very slightly sol.HCl (oral LD50 rat higher than 5000mg/kg, very low acute toxicity by oral route. The MSDS still mentions that it is toxic in case of prolonged/repeated exposures by inhalation or ingestion)

-Fluorite:  $CaF_2$ , with 48.7% F, slightly sol. hot HCl (oral LD50 rat 4250mg/kg, low acute toxicity by oral route. Still, prolonged/repeated exposures by inhalation or ingestion might be an issue)

-Fluorapatite:  $Ca_5(PO_4)_3F$ , with 3.8% F, sol.HCl (oral LD50 unavailable, but most probably low acute toxicity by oral route, as confirmed by the MSDS)

-Water soluble tetrafluoroborates minerals Avogadrite, Barberiite and Ferruccite: probably moderate to low acute toxicity by oral route (according to the MSDS for sodium, potassium and ammonium tetrafluoroborates, which only give those as corrosive/irritants).

### 3.10. CADMIUM:

- Monteponite:  $\text{CdO}$ , with 87.5% Cd, sol.HCl (oral LD50 mouse 72mg/kg, rat 72mg/kg, toxic. The MSDS gives it as toxic if ingested, and very toxic if inhaled)
- Voudourisite, Drobecite and Lazaridisite:  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ , with 49.6% Cd (voudourisite), sol.H<sub>2</sub>O (LD50 oral mouse 88mg/kg, rat 280mg/kg, toxic. The MSDS gives it as toxic if ingested and very toxic if inhaled)
- Otavite:  $\text{CdCO}_3$ , with 65.2% Cd, sol.HCl (oral LD50 mouse 310, rat 438, moderately toxic)
- Greenockite and Hawleyite:  $\text{CdS}$ , with 77.8% Cd, moderately sol.concentrated HCl (oral LD50 mouse 1166mg/kg, rat 7080mg/kg, low acute toxicity by oral route. The MSDS still mentions that it is toxic in case of prolonged/repeated exposures by inhalation or ingestion)

### 3.11. BERYLLIUM:

Some soluble laboratory beryllium salts show oral LD50 in rat/mouse between 80 and 100mg/kg, however there isn't any available LD50 data for beryllium minerals. Let's still mention:

- Behoite and Clinobehoite:  $\text{Be}(\text{OH})_2$ , with 21% Be, sol.HCl (the MSDS gives it as toxic if ingested, and very toxic if inhaled)
- Bromellite:  $\text{BeO}$  (may be synthesized), with 36% Be, moderately sol.HCl (the MSDS gives it as toxic if ingested, and very toxic if inhaled)
- let's note that some other HCl soluble beryllium minerals might possibly qualify as toxic or moderately toxic (for instance, moraesite and glucine?) but this couldn't be confirmed as there isn't any available toxicological data for such compounds.

### 3.12. COBALT:

- 'Albrittonite':  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (may be synthesized), with 24.8-35.5% Co, discredited species now regarded as only existing artificially, sol.H<sub>2</sub>O, sol.alcohol (oral LD50 guinea pig 55mg/kg, mouse 80mg/kg, rat 80mg/kg, which would qualify as toxic, although other sources give higher LD50 values such as oral LD50 rat 418mg/kg, which would rather qualify as moderately toxic).
- Cobaltkieserite and Bieberite:  $\text{CoSO}_4 \cdot \text{H}_2\text{O}$  (may be synthesized), with 34.1% Co (cobaltkieserite), sol.H<sub>2</sub>O (oral LD50 rat 424mg/kg, mouse 584mg/kg, moderately toxic)
- Pakhomovskiyite:  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ , with 34.6% Co, sol.HCl (oral LD50 rat 387mg/kg, moderately toxic)
- Sphero-cobaltite:  $\text{CoCO}_3$ , with 49.6% Co, slowly sol.cold HCl, sol.hot HCl (oral LD50 rat 640mg/kg, low acute toxicity by oral route)
- Heterogenite:  $\text{CoO}(\text{OH})$ , with 64.1% Co, sol.HCl (oral LD50 unavailable, but probably moderate to low acute toxicity by oral route)

### 3.13. NICKEL:

- Retgersite and Morenosite:  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (may be synthesized), with 22.3% Ni (retgersite), sol.H<sub>2</sub>O, sparingly sol.alcohol (oral LD50 rat 264mg/kg, moderately toxic)
- Nickelbischofite:  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (may be synthesized), with 24.7% Ni, sol.H<sub>2</sub>O, sol.alcohol (oral LD50 rat 105mg/kg, the MSDS gives it as toxic if ingested or inhaled)
- Zaratite:  $\text{Ni}_3(\text{CO}_3)(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ , with 46.8% Ni, sol.HCl (oral LD50 rat 840mg/kg, low acute toxicity by oral route)

### 3.14. BARIUM:

- Witherite:  $\text{BaCO}_3$ , with 69.6% Ba, sol.HCl (oral LD50 mouse 200mg/kg, rat 418mg/kg, moderately toxic)
- Nitrobarite:  $\text{Ba}(\text{NO}_3)_2$ , with 52.6% Ba, sol.H<sub>2</sub>O (oral LD50 mouse 266mg/kg, rat 355mg/kg, moderately toxic)
- Baryte:  $\text{BaSO}_4$ , with 58.8% Ba, insol.H<sub>2</sub>O, insol.HCl (oral LD50 mouse and rat higher than 3000mg/kg, low acute toxicity by oral route. The MSDS doesn't mention any hazard)

### 3.15. COPPER:

- Native copper: Cu (100% Cu), very slowly sol.HCl (oral LD50 mouse higher than 5000mg/kg, very low acute toxicity by oral route)
- Chalcocyanite, Chalcantite, Boothite and Bonattite:  $\text{CuSO}_4$ , natural or synthetic, with 39.8% Cu (chalcocyanite), sol.H<sub>2</sub>O (oral LD50 rat 300mg/kg, mouse 369mg/kg, moderately toxic). Let's also mention water-soluble Kröhnkite  $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  which may show similar toxicity.
- Nantokite: CuCl (may be synthesized), with 64.2% Cu, sol.H<sub>2</sub>O, sol.concentrated HCl (oral LD50 rat 140mg/kg, mouse 347mg/kg, moderately toxic)
- Eriochalcite and Tolbachite:  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (may be synthesized), with 37.3% Cu (eriochalcite), sol.H<sub>2</sub>O, sol.ethanol (oral LD50 mouse 209 mg/kg, rat 290mg/kg, moderately toxic)
- Hoganite:  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (may be synthesized), with 31.8% Cu, sol.H<sub>2</sub>O, sol.alcohol (oral LD50 mouse 196mg/kg, rat 501mg/kg, moderately toxic)
- Malachite:  $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ , with 57.5% Cu, sol.HCl (oral LD50 rabbit 159mg/kg, rat 1350mg/kg, moderately toxic. However note that prolonged/repeated exposure by inhalation or ingestion can result in chronic copper poisoning, which could also be expected from other soluble copper minerals such as Azurite)
- Cuprite: Cu<sub>2</sub>O, with 88.8% Cu, sol.HCl (oral LD50 rat 470mg/kg, moderately toxic)
- Tenorite: CuO, with 79.9% Cu, sol.HCl (oral LD50 unavailable, but probably moderate to low acute toxicity by oral route)
- Chalcopyrite and Chalcocite are insoluble copper sulfides thus expected to show very low acute toxicity by oral route.

### 3.16. RADIUM:

-Radian barite (aka radiobarite):  $(\text{Ba,Ra})\text{SO}_4$ , which is the only existing radium mineral, is insoluble in water and rather insoluble in HCl, the radium content might be about 0.01% bw (although some specimens might show higher content). Acute oral toxicological data unavailable. Level of radioactivity in radian barite may vary greatly depending on sample origin, however the 'hottest' specimens might be extremely radioactive and should be considered very dangerous in case of ingestion, inhalation, or from any prolonged skin contact. Indeed, in a worst-case scenario, the article 'Here be dragons' (by Alysson Rowan) gives an estimated specific dose as high as 5.02799 mSv/hr for a 100g sample at 1m distance. And webmineral.com gives an estimated exposure of 44452.81mRem/hr (that is 444.5281mSv/hr) if a 100g sample was to be held in the hand for one hour. Moreover, let's note that the 'hottest' samples of radian barite should also be expected to evolve lots of radon gas (and radon daughters).

This being said, the 'hottest' radian barite samples are mostly recovered from industrial activities (i.e. as scaly precipitates on oil industry equipment). Anyway, one might use a dosimeter to check how 'hot' a radian barite specimen actually is.

### 3.17. URANIUM and THORIUM:

There are many HCl soluble uranium minerals (for instance Ianthinite, Becquerelite, Rutherfordine, Uranopilite, etc...), and even a few water soluble ones (Shumwayite, Grimselite and Andersonite for instance). Based on established oral LD50 of a few soluble laboratory uranyl salts (200 to 250mg/kg in rat and mouse), some soluble minerals might also be expected to show moderate acute toxicity by oral route.

There are also a few HCl soluble thorium minerals, and some soluble thorium minerals might possibly also show moderate acute toxicity by oral route.

However, while uranium/thorium minerals can be expected to show moderate to low acute toxicity by oral route (depending on the species), they should be considered hazardous in case of ingestion and especially inhalation, as they combine both some chemical toxicity (mostly for uranium) and radiotoxicity.

### **3.18. LEAD:**

Oral LD50 mostly higher than 500mg/kg for anglesite (PbSO<sub>4</sub>), galena (PbS), litharge (PbO), minium (Pb<sub>3</sub>O<sub>4</sub>), cerussite (PbCO<sub>3</sub>), cotunnite (PbCl<sub>2</sub>). However, while lead minerals tend to show rather low acute toxicity by oral route, those can still be seriously toxic in case of prolonged/repeated exposures by inhalation or ingestion.

### **3.19. ANTIMONY:**

Oral LD50 higher than 500mg/kg for native antimony (Sb), stibnite (Sb<sub>2</sub>S<sub>3</sub>), valentinite and senarmontite (Sb<sub>2</sub>O<sub>3</sub>). Antimony minerals tend to show rather low acute toxicity by oral route. Still, prolonged/repeated exposures by inhalation or ingestion might cause some toxicity.

### **3.20. MANGANESE:**

Manganese minerals may show moderate (for instance water soluble Scacchite MnCl<sub>2</sub>, oral LD50 rat 250mg/kg) to low acute toxicity by oral route (for instance HCl soluble pyrolusite MnO<sub>2</sub>). Let's still note that prolonged/repeated exposures by ingestion and especially inhalation may cause neurotoxicity (manganism).

So, while I might have missed a few significantly toxic minerals due to lack of any available LD50 data (possibly amongst arsenites and arsenates for instance), we can see that there are actually few toxic (LD50 less than 100mg/kg) or highly toxic (LD50 less than 50mg/kg) minerals, and most of these are rare (and often microscopic) species. Still, such minerals deserve some caution as accidental absorption could be a possibility, especially considering that these are rather dense minerals so that a toxic dose might be the size of a pea or less.

However, let's put things into perspective by outlining that most soluble minerals containing potentially toxic elements are only showing moderate (LD50 from 100 to 500mg/kg) to low (LD50 higher than 500mg/kg) acute toxicity by oral route. Which means that the toxic dose will represent a significant volume of the material, thus it is very unlikely that a mineral collector would ever accidentally poison himself just from handling the specimen.

Now, let's spare a thought for these unfortunate rodents :-)

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## 4.SAFETY CONSIDERATIONS

The following safety considerations are mainly addressed to mineral collectors, and do not deal with the case of prolonged/repeated exposures to powdered minerals (which would require more constraining safety measures)

### 4.1. Basic warnings:

So, I've been thinking of which minerals would deserve a warning (although some of these might actually be so microscopic species that owning a toxic quantity would be very unlikely), and what would be the most appropriate way to formulate such safety precautions, case by case. Please keep in mind that this list is not exhaustive.

MINERAL: Coccinite

WARNING: Contains mercury in bioavailable form. Highly toxic if ingested, or if inhalation of dust, and also by skin contact. Volatile at ambient temperature. Never lick, ingest or sniff, avoid skin contact, thus wear disposable nitrile gloves for handling, and always wash hands immediately after handling, do not generate dust by grinding or sawing. Keep in an airtight box and away from heat.

MINERAL: Montroydite, Schuetteite

WARNING: Contains mercury in bioavailable form. Highly toxic if ingested, or if inhalation of dust, and also by skin contact. Never lick or ingest and always wash hands immediately after handling, do not generate dust by grinding or sawing, avoid prolonged skin contact.

MINERAL: Terlinguaite, Kleinite, Moschelite

WARNING: Contains mercury in bioavailable form. Never lick or ingest and always wash hands immediately after handling, do not generate dust by grinding or sawing, avoid prolonged skin contact.

MINERAL: Chursinite, Kuznetsovite

WARNING: Contains mercury and arsenic in bioavailable form. Never lick or ingest and always wash hands immediately after handling, do not generate dust by grinding or sawing, avoid prolonged skin contact.

MINERAL: Nestolaite

WARNING: Contains selenium in bioavailable form. Highly toxic if ingested, or if inhalation of dust. Never lick or ingest and always wash hands after handling, do not generate dust by grinding or sawing.

MINERAL: Downeyite

WARNING: Contains selenium in bioavailable form. Water soluble mineral. Highly toxic if ingested, or if inhalation of dust. Never lick or ingest and always wash hands immediately after handling, do not generate dust by grinding or sawing.

MINERAL: Arsenolite, Claudetite

WARNING: Contains arsenic in bioavailable form. Water soluble mineral. Highly toxic if ingested, or if inhalation of dust. Never lick or ingest and always wash hands immediately after handling, do not generate dust by grinding or sawing.

MINERAL: Avicennite

WARNING: Contains thallium in bioavailable form. Highly toxic if ingested, or if inhalation of dust. Never lick or ingest and always wash hands after handling, do not generate dust by grinding or sawing.

MINERAL: Lafossaite

WARNING: Contains thallium in bioavailable form. Water soluble mineral. Highly toxic if ingested, or if inhalation of dust. Never lick or ingest and always wash hands immediately after handling, do not generate dust by grinding or sawing.

MINERAL: Steropesite, Lanmuchangite, Dorallcharite, Carlinite

WARNING: Contains thallium in bioavailable form. Never lick or ingest and always wash hands immediately after handling, do not generate dust by grinding or sawing.

MINERAL: Cobaltomenite, Chalcomenite, Clinochalcomenite

WARNING: Contains selenium in bioavailable form. Toxic if ingested, or if inhalation of dust. Never lick or ingest and always wash hands after handling, do not generate dust by grinding or sawing.

MINERAL: Sofiite, Mandarinoite, Molybdomenite, Ahlfeldite, Zincomenite

WARNING: Contains selenium in bioavailable form. Never lick or ingest and always wash hands after handling, do not generate dust by grinding or sawing.

MINERAL: Weillite, Pharmacolite, Haidingerite, Rauenthalite, Phaunouxite, Schultenite, Stibioclaudetite (as well as a few more arsenite/arsenate species)

WARNING: Contains arsenic in bioavailable form. Toxic if ingested, or if inhalation of dust. Never lick or ingest and always wash hands after handling, do not generate dust by grinding or sawing.

MINERAL: Metamunirite, Munirite, Metarossite, Rossite, Calciodelrioite

WARNING: Contains vanadium in bioavailable form. Water soluble mineral. Toxic if ingested, or if inhalation of dust. Never lick or ingest and always wash hands after handling, do not generate dust by grinding or sawing.

MINERAL: Shcherbinaite, 'Alaite'

WARNING: Contains vanadium in bioavailable form. Water soluble mineral. Toxic if ingested, or if inhalation of dust. Never lick or ingest and always wash hands immediately after handling, do not generate dust by grinding or sawing.

MINERAL: Lopezite, Tarapacaite

WARNING: Contains hexavalent chromium in bioavailable form. Water soluble mineral. Toxic if ingested, and very toxic if inhalation of dust. Never lick or ingest and always wash hands immediately after handling, do not generate dust by grinding or sawing.

MINERAL: Villiaumite

WARNING: Contains fluorine in bioavailable form. Water soluble mineral. Toxic if ingested, or if inhalation of dust. Never lick or ingest and always wash hands immediately after handling, do not generate dust by grinding or sawing.

MINERAL: Cryptohalite, Bararite, Malladrite, Hieratite, Demartinite, Carobbiite

WARNING: Contains fluorine in bioavailable form. Water soluble mineral. Toxic if ingested, or if inhalation of dust, and also by skin contact. Never lick or ingest and always wash hands immediately after handling, do not generate dust by grinding or sawing, avoid prolonged skin contact.

MINERAL: Griceite

WARNING: Contains fluorine in bioavailable form. Toxic if ingested, or if inhalation of dust. Never lick or ingest and always wash hands after handling, do not generate dust by grinding or sawing.

MINERAL: Monteponite

WARNING: Contains cadmium in bioavailable form. Toxic if ingested, and very toxic if inhalation of dust. Never lick or ingest and always wash hands after handling, do not generate dust by grinding or sawing.

MINERAL: Voudourisite, Drobecite, Lazaridisite

WARNING: Contains cadmium in bioavailable form. Water soluble mineral. Toxic if ingested, and very toxic if inhalation of dust. Never lick or ingest and always wash hands after handling, do not generate dust by grinding or sawing.

MINERAL: Behoite, Clinobehoite, Bromellite

WARNING: Contains beryllium in bioavailable form. Toxic if ingested, and very toxic if inhalation of dust. Never lick or ingest and always wash hands after handling, do not generate dust by grinding or sawing.

MINERAL: Native Mercury

WARNING: Evaporates at ambient temperature and its vapours are highly toxic if inhaled, thus keep in an airtight box and away from heat. Never lick or ingest and always wash hands after handling, avoid generating dust by grinding or sawing the associated matrix.

MINERAL: Radian barite

WARNING: Contains radium. Some specimens might be dangerously radioactive. Never lick, ingest or sniff. Minimize manipulations, wear disposable nitrile gloves, and always wash hands immediately after handling. Never generate dust by grinding or sawing so to avoid inhalation/ingestion of dust. Avoid long exposures at close distance, thus do not store in rooms where you spend most of your time (not in bedroom). Radioactive minerals evolve radioactive radon gas and should thus be stored in well-ventilated area (not in a confined basement). Keep away from food/kitchen. Keep radioactive minerals in limited quantities (and radian barite in very limited quantity).

MINERAL: Radioactive minerals (see <http://www.webmineral.com/> for case by case estimation of radioactivity, any mineral rated as strongly radioactive or very strongly radioactive definitely requires some precautions)

SAFETY PRECAUTIONS: Contains significant quantity of uranium and/or thorium. Radioactive mineral. Do not lick or ingest. Avoid frequent or prolonged manipulations of radioactive minerals, and always wash hands after handling. Do not generate dust by grinding or sawing so to avoid inhalation/ingestion of dust. Avoid long exposures at close distance, thus do not store in rooms where you spend most of your time (not in bedroom). Radioactive minerals evolve radioactive radon gas and should thus be stored in well-ventilated area (not in a confined basement). Keep away from food/kitchen. Keep radioactive minerals in limited quantities.

MINERAL: Teineite, Graemite, Millsite, Balyakinite, Emmonsite

SAFETY PRECAUTIONS: Contains tellurium in bioavailable form. Do not lick or ingest and wash hands after handling, do not generate dust by grinding or sawing so to avoid inhalation/ingestion of dust.

MINERAL: Orpiment

SAFETY PRECAUTIONS: Contains arsenic in bioavailable form. Do not lick or ingest and wash hands after handling, do not generate dust by grinding or sawing so to avoid inhalation/ingestion of dust. Beware that arsenolite (highly toxic) might be present in some orpiment samples (especially powdery/crumblly massive samples).

MINERAL: Native arsenic

SAFETY PRECAUTIONS: Contains arsenic in bioavailable form. Do not lick or ingest and wash hands after handling, do not generate dust by grinding or sawing so to avoid inhalation/ingestion of dust.

MINERAL: Calomel

SAFETY PRECAUTIONS: Contains mercury in bioavailable form. Do not lick or ingest and wash hands after handling, do not generate dust by grinding or sawing so to avoid inhalation/ingestion of dust.

MINERAL: Quartz

SAFETY PRECAUTIONS: long-term inhalation of quartz dust (or dust from quartz-rich rocks) can lead to silicosis thus avoid dry-sawing and dry-grinding. If regularly exposed to quartz dust, apply dust control measures.

MINERAL: Crocidolite, Amosite, Tremolite, Actinolite, Anthophyllite, Chrysotile, Erionite, Magnesio-riebeckite, Fluoro-edenite, Winchite, Richterite, Antigorite, Nematite, Palygorskite

SAFETY PRECAUTIONS: inhalation of dust (fibers) from the asbestiform variety is hazardous, thus do not generate dust by grinding or sawing, do not lick or ingest, and wash hands after handling.

MINERAL: Retgersite, Morenosite, Nickelbischofite

SAFETY PRECAUTIONS: Contains nickel in bioavailable form. Water soluble mineral. Do not lick or ingest and wash hands after handling, do not generate dust by grinding or sawing so to avoid inhalation/ingestion of dust.

MINERAL: Cobaltkieserite, Bieberite, 'Albrittonite'

SAFETY PRECAUTIONS: Contains cobalt in bioavailable form. Water soluble mineral. Do not lick or ingest and wash hands after handling, do not generate dust by grinding or sawing so to avoid inhalation/ingestion of dust.

MINERAL: Chalcocyanite, Chalcanthite, Boothite, Bonattite, Kröhnkite, Nantokite, Eriochalcite, Tolbachite, Heganite

SAFETY PRECAUTIONS: Contains copper in bioavailable form. Water soluble mineral. Do not lick or ingest and wash hands after handling, do not generate dust by grinding or sawing so to avoid inhalation/ingestion of dust.

MINERAL: Nitrobarite

SAFETY PRECAUTIONS: Contains barium in bioavailable form. Water soluble mineral. Do not lick or ingest and wash hands after handling, do not generate dust by grinding or sawing so to avoid inhalation/ingestion of dust.

MINERAL: Witherite

SAFETY PRECAUTIONS: Contains barium in bioavailable form. Do not lick or ingest and wash hands after handling, do not generate dust by grinding or sawing so to avoid inhalation/ingestion of dust.

MINERAL: Scacchite

SAFETY PRECAUTIONS: Contains manganese in bioavailable form. Water soluble mineral. Do not lick or ingest and wash hands after handling, do not generate dust by grinding or sawing so to avoid inhalation/ingestion of dust.

MINERAL: Malachite, Azurite

SAFETY PRECAUTIONS: Contains copper in bioavailable form. Do not ingest and avoid generating dust by grinding or sawing so to avoid inhalation/ingestion of dust (otherwise, cut it wet and apply dust control measures).

MINERAL: Cinnabar

SAFETY PRECAUTIONS: Do not heat. Avoid dry-grinding and dry-sawing so to avoid inhalation/ingestion of dust, and so to avoid overheating. Beware that native mercury (which vapours are highly toxic by inhalation) might be present in some cinnabar samples (especially massive samples).

## **4.2. Extended safety procedures for handling and storage:**

### **4.2.1. ASBESTIFORM MINERALS:**

- keep out of young children's reach.
- do not lick or ingest or sniff.
- do not generate dust by polishing, grinding or sawing (so to avoid inhalation of dust/fibers)
- do not put your hand to your face (mouth, nose) or eat/drink/smoke during the manipulation of samples.
- after manipulating samples, clean work surface from the dust (using moist disposable paper-towel). Manipulating samples over a large sheet of paper (that will be folded and discarded afterwards) would also help with avoiding dispersion of fibers.
- wash your hands (use soap) immediately after you're done.
- storing specimens inside individual transparent airtight boxes would allow to confine the fibers (then, when you need to manipulate the sample itself, it is suggested to first ventilate the box outdoor).

### **4.2.2. PREVENTING SILICOSIS** (such dust control measures are only necessary for people regularly exposed to crystalline silica dust):

- quartz and quartz rich rocks should be polished/grinded/sawed wet (along with treatment of wastewater).
- do not proceed inside your home (i.e. not in the place where you live)
- proceed in a well-ventilated area (proper indoor ventilation can be supported by air purification systems)
- moistening the workplace (with water hose) will prevent deposited dust from getting airborne.
- regularly clean the workplace (floor, work surface, equipment) so to prevent accumulation of dust (use water hose and wet sweeping).
- wear appropriate respirator when operating the polishing/grinding/sawing machinery
- wear disposable or washable work clothes (washed daily). Change into clean clothes (and if possible shower) before leaving the workplace (this will avoid contaminating your car and home).

If you couldn't shower at the worksite, do it as soon as you get back home.

-avoid eating/drinking/smoking in dusty areas, wash hands and face before eating/drinking/smoking (by the way, let's note that chronic inhalation of crystalline silica dust is potentially even more harmful to smokers).

-prohibit abrasive materials containing more than 1% crystalline silica (substitute less hazardous abrasive materials).

-proceed to periodic air quality monitoring in the workplace (exposure limit for respirable crystalline silica dust is set at 0.05mg/m<sup>3</sup>) and provide periodic medical examinations for all exposed workers.

-recommended read: <https://www.cdc.gov/niosh/docs/96-112/>

#### **4.2.3. MODERATELY TOXIC MINERALS:**

-do not lick or ingest, and keep out of young children's reach.

-wash hands after handling (use soap).

-if the specimen is powdery (for instance some powdery pigment samples), you might place it inside a transparent plastic box (so to confine the dust and allow easy manipulations).

-do not generate dust by polishing, grinding or sawing (so to avoid inhalation/ingestion of dust). If required (i.e. in the context of some professional activity), apply the same safety procedures than for silicosis prevention.

#### **4.2.4. TOXIC AND HIGHLY TOXIC MINERALS:**

-keep away from food/kitchen.

-keep out of young children's reach.

-mention the nature of the hazard on the specimen label.

-never lick or ingest or sniff.

-never generate dust by polishing, grinding or sawing (so to avoid inhalation/ingestion of dust).

-never heat/burn or chemically attack such minerals.

-do not put your hand to your face (mouth, nose, eyes) or eat/drink/smoke during the manipulation of samples.

-don't manipulate with bare hands if you have any cuts or grazes on your hands/fingers.

-avoid prolonged or repeated skin contact with minerals which are known for skin absorption (or wear disposable nitrile gloves).

-for easier manipulations, place water-soluble minerals, and minerals known for skin absorption, and minerals which are volatile at room temperature inside individual airtight boxes made of transparent plastic.

-after manipulating samples, clean work surface from the dust (using disposable paper-towel).

Manipulating samples over a large sheet of paper (that will be folded and discarded afterwards) would also help with avoiding dispersion of dust.

-thoroughly wash your hands (use soap) immediately after you're done (even when you have been wearing gloves).

#### **4.2.5. RADIOACTIVE MINERALS:**

-do not lick or ingest or sniff.

-do not handle more than necessary, avoid frequent or prolonged manipulations. If prolonged manipulation is required, wear disposable gloves (also, for lesser hand exposure, it is advisable to work 'hands off' as much as possible).

[special case: some specimens of radium barite might be extremely radioactive, for manipulating the 'hottest' samples of radium barite (which are mostly from industrial sources, though), wear disposable nitrile gloves and grasp the specimen by means of forceps/tongs, and keep manipulations to an absolute minimum.]

-do not generate dust by polishing, grinding or sawing (so to avoid inhalation/ingestion of dust).

-do not heat/burn or chemically attack such minerals.

- do not put your hand to your face (mouth, nose, eyes) or eat/drink/smoke during the manipulation of samples.
- don't manipulate with bare hands if you have any cuts or grazes on your hands/fingers.
- after manipulating radioactive samples, clean work surface from the dust (using moist disposable paper-towels and a few drops of dishwashing liquid). Do not manipulate radioactive minerals over porous surfaces (such as unsealed wood). Moreover, manipulating samples over a large sheet of paper (that will be folded and discarded afterwards) would also help with avoiding dispersion of dust (preferably use impermeable paper such as Kraft or Benchkote).
- thoroughly wash your hands (use soap) immediately after you're done (even when you have been wearing gloves).
- store radioactive minerals away from food/kitchen/dining room, and out of young children's reach
- radioactive minerals evolve radioactive radon gas and should thus be stored in well-ventilated area (i.e. not in a confined basement).
- avoid long exposures at close distance, thus do not store radioactive minerals in rooms where you spend most of your time (i.e. not in bedroom, living room, or work office).
- storing samples inside individual airtight boxes made of transparent plastic would allow to confine radioactive dust. Then, when you need to manipulate the sample itself, it is suggested to first open the box in a well-ventilated location (ideally outdoor) and allow to ventilate for a while (ideally for at least an hour). Let's note that micaceous species (autunite, torbernite, uranocircite, zeunerite..) easily release dust.
- unless confined into closed boxes, specimens should be placed in a tray for transport (so to avoid scattering dust along the way).
- mention the radioactive nature of the material on the specimen label.
- conform to exposure limits: the annual radiation exposure limit for the general public is set at 1mSv/year (on top of local background noise). Conforming to exposure limits is a matter of storing limited quantities of radioactive minerals, and evaluating the time of exposure at a given distance.
- Building a radioactive minerals collection will call for more constraining measures (due to the number of specimens):
  - let's first note that tiny specimens (micromounts, thumbnails) are a practical alternative for building a radioactive mineral collection (indeed lesser quantities means less radiations). But use a microscope rather than a small loupe for observing the samples (lesser eye exposure).
  - get a dosimeter so to make sure that you're not exceeding radiation exposure limits (test in the storage room and also in adjacent rooms, since gamma rays can cross walls/floors/ceiling). If approaching the limit, consider some lead shielding.
  - Shielding considerations: the inner lining of the mineral cabinet should be made of either 2.5cm thick plywood or 1cm thick plexiglas (that will absorb most beta particles before they can reach the lead layer, which is important to keep braking radiation low, otherwise the radiation dose on the outside of the cabinet might possibly be higher than without the lead). Then lead sheet (6mm thick) is sandwiched between the inner wood/plexiglass lining and the outer lining of the mineral cabinet. Any wooden surface must be sealed (use some high gloss varnish such as floor or yacht varnish or some hard-surface paint such as is used on cars).
  - for display purpose, one might consider using radiation shielding lead glass for the viewing side of the cabinet (lead equivalencies for 7mm and 14mm thick lead glass are usually about 1.5 and 3mm of lead sheet, respectively).
- Ideally, specimens should be placed at least 10cm from the viewing window.
- a sealed airtight mineral cabinet would advantageously avoid dust and radon build-up in the room and house. Ideally, such sealed cabinet would also feature an outdoor ventilation system (i.e. vented to the outside of the building), so to avoid radon build-up inside the closed cabinet.
- whenever you need to rearrange its contents, a closed mineral cabinet (unless featuring a built-in ventilation system) should first be left open to ventilate for 3 hours before proceeding (so to allow short-lived radon daughters to decay).
- storage room (i.e. the room where you keep the specimens) must be kept clean and very well-

ventilated (i.e. to avoid accumulation of radioactive dust and radon). Besides regularly opening windows, the presence of permanent air vents in the room is suitable (let's note that in the case of a basement, proper ventilation should also be supported by an active forced air extraction set at floor level, considering that radon is much heavier than air and tends to stay down).

- ideally, avoiding porous/fibrous surfaces (such as floor carpeting, upholstered furnitures, unsealed wood, etc.) which tend to catch dust would allow the storage room to be cleaned easily (for instance, consider linoleum/vinyl flooring, etc.)

- also consider setting a radon detector (about 1 meter from the floor) in the storage room. Ideally, radon concentration in the house should be kept under 150 Bq/m<sup>3</sup>.

- never smoke in the storage room (spent smoke collects and concentrate radon daughters).

- pregnant women shouldn't linger in the storage room.

- if trimming of a radioactive mineral sample is required, this should be done in a well-ventilated location, with specimens and tools confined (at all times) inside a thick transparent plastic bag (to avoid dispersion of dust and fragments), set on a sealed (non porous) work surface. Use tools that produce as little dust as possible (i.e. keep hammering to an absolute minimum, do not dry-saw, use a rock trimmer instead). Wear a disposable respirator (featuring HEPA filter, P100 rated) and disposable gloves (ideally, a disposable lab-coat/overall and disposable overshoes are also recommended so to avoid contaminating your clothes with dust). The tools shall be rinsed afterwards, and the bag shall be sealed (use adhesive tape) and placed inside another bag which will also immediately be sealed closed and then discarded (such "double-bagging" process is meant to avoid leaks). Also, clean the work surface (using moist disposable paper-towels and a few drops of dishwashing liquid) and surrounding floor. Finally, wash hands, forearms and face (nevertheless, whenever dust contamination may have occurred, it is actually recommended to put your clothes in the washer, and then have a shower, including shampoo).

- recommended read:

[https://www.academia.edu/31501150/Here\\_be\\_Dragons\\_The\\_Care\\_and\\_Feeding\\_of\\_Radioactive\\_Mineral\\_Species\\_Feb\\_2017\\_](https://www.academia.edu/31501150/Here_be_Dragons_The_Care_and_Feeding_of_Radioactive_Mineral_Species_Feb_2017_)

### **4.3. Hazardous chemical reactions when cleaning minerals with acids**, a few examples:

-when attacked by acids, fluorides or fluorophosphates (for instance fluorite, cryolite, fluorapatite..) will yield hydrofluoric acid in solution (this acid causes severe burns, it is also quite toxic by ingestion as well as skin contact, and with toxic vapours. Also note that HF attacks glass).

-when HCl reacts with strong oxidizing agents (for instance minium, plattnerite, manganese oxides such as pyrolusite, psilomelane, hausmannite, manganite, braunite..), then chlorine (toxic gas) is evolved.

-when sulfide minerals are attacked by strong acids, a toxic gas is evolved (usually hydrogen sulfide from HCl or H<sub>2</sub>SO<sub>4</sub>, or nitrogen dioxide from HNO<sub>3</sub>)

-when attacked by acids, minerals containing toxic elements will yield a toxic solution.

When working with acids, wear appropriate protective gloves and protective goggles. Proceed in a well ventilated area (preferably outdoor), and do not seal the container where the reaction is taking place. Of course keep it out of children reach and label it so to warn people that the content isn't water but acid. Also keep in mind that diluting an acid should be done by progressively adding the acid to the water (not adding the water to the acid).

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## 5.CONCLUSIONS

This study has been reviewing the potential acute to chronic toxicity from exposure to some specific minerals (either as radiotoxicity, physical toxicity or chemical toxicity), however while people in the mining industry and stone industry are very exposed, the context of exposure is obviously quite different for mineral collectors who should be on the safe side as long as some simple safety precautions are observed in the handling and storage of a rather limited number of potentially hazardous species.

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## 6.HAPPIER PERSPECTIVES

Enough with poisons, now what about happiness stone?

Let me share my investigations about Lithium minerals. Most psychoactive substances are organic compounds, but bioavailable inorganic lithium compounds are an exception to the rule. Lithium salts are indeed used in psychiatry, as mood-stabilizer drug (normothymic), primarily in the treatment of bipolar disorder, where they have a role in the treatment of depression and particularly of mania. The most commonly prescribed lithium salt being lithium carbonate (brand names: Eskalith, Teralithe...).

Unlike many other psychoactive drugs, lithium typically produces no obvious psychotropic effects (such as euphoria) in normal individuals at therapeutic concentrations.

The specific biochemical mechanism of lithium action in mania is not fully understood, but upon ingestion, lithium ions ( $\text{Li}^+$ ) become widely distributed in the central nervous system and would be interacting with a number of neurotransmitters and receptors.

However, lithium isn't without side effects, notably renal (kidney) toxicity which may lead to chronic kidney failure (too much lithium can be fatal), and considering that therapeutic dosage is slightly less than the toxic level, blood levels need to be monitored closely during treatment.

As there's no directly bioavailable lithium mineral occurring in industrial quantities, lithium must be extracted from other lithium ores or concentrated from lithium rich waters.

However, there are three rare minerals which, while not available in industrial quantities, are interestingly bioavailable forms of lithium:

-Zabuyelite:  $\text{Li}_2\text{CO}_3$  (that is lithium carbonate), sol.HCl, moderately sol.H<sub>2</sub>O, Li 18.79% bw, but it's a rare and very microscopic mineral.

-Lithiophosphate:  $\text{Li}_3\text{PO}_4$ , sol.HCl, slightly sol.hot H<sub>2</sub>O, Li 17.98% bw, crystals (typically as cleavages) can reach 5cm in size.

-Nalipoite:  $\text{NaLi}_2\text{PO}_4$ , sol.HCl, Li 10.53% bw, crystals rarely reach 1cm in size.

Of course, I'm not suggesting anyone to medicate with minerals as this could result in serious poisoning, but I'm simply sharing my enthusiasm about such minerals which combine my modest interest in pharmacology with my passion for mineralogy.

The medicinal potential of some minerals would indeed make another interesting discussion, well...maybe another time :-)