

Review



# **Secondary Sulfate Minerals from Thallium Mineralized Areas: Their Formation and Environmental Significance**

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**Abstract:** Thallium is a highly toxic metal and is predominantly hosted by sulfides associated with low-temperature hydrothermal mineralization. Weathering and oxidation of sulfides generate acid drainage with a high concentration of thallium, posing a threat to surrounding environments. Thallium may also be incorporated into secondary sulfate minerals, which act as temporary storage for thallium. We present a state-of-the-art review on the formation mechanism of the secondary sulfate minerals from thallium mineralized areas and the varied roles these sulfate minerals play in Tl mobility. Up to 89 independent thallium minerals and four unnamed thallium minerals have been documented. These thallium minerals are dominated by Tl sulfosalts and limited to several sites. Occurrence, crystal chemistry, and Tl content of the secondary sulfate minerals indicate that Tl predominantly occurs as Tl(I) in K-bearing sulfate. Lanmuchangite acts as a transient source and sink of Tl for its water-soluble feature, whereas dorallcharite, Tl-voltaite, and Tl-jarosite act as the long term source and sink of Tl in the surface environments. Acid and/or ferric iron derived from the dissolution of sulfate minerals may increase the pyrite oxidation process and Tl release from Tl-bearing sulfides in the long term.

**Keywords:** thallium; pyrite; acid mine drainage; secondary sulfate minerals; environmental significance

# 1. Introduction

Thallium (Tl) is a typical heavy metal element with high toxicity and is listed as a priority pollutant by the United States Environmental Protection Agency (USEPA). Human exposure to Tl leads to acute toxicity or chronic toxicity dependent upon uptake dosage. Kidneys, lungs, heart, and nerve damage have been reported by acute toxicity of Tl [1]. Eighty-seven chronic Tl poisoning cases occurred in the 1960s in a Chinese valley with hair loss, loss of appetite, and pain in the lower extremities as typical symptoms [2]. In recent years, occasional Tl pollution events have been reported in China and Italy [3]. It is suggested that mining and processing of Tl-bearing sulfide ores has become a predominant source of Tl pollution in ecosystems [4–6].

Despite its extreme biotoxicity, Tl is currently still utilized in some high-tech fields (e.g., semiconductors, superconductors, and optical fibers, etc.) in an irreplaceable way [7]. The global Tl deposits widely occur and can be categorized into three types according to their genesis. The first type is associated with Carlin-type gold deposits, distributed in Carlin gold deposits in Nevada, the USA, and Lanmuchang Hg-Tl-Au deposit in Guizhou Province, China. The second type is associated with As and Sb mineralization, and is distributed in North Macedonia, Switzerland, and France [8–12]. The third one is related to Zn-Pb mineralization, such as in Lanping Zn-Pb deposit. Thallium mineralization in the deposits is formed in low-temperature conditions, and Tl is mainly hosted by sulfide minerals, e.g., lorandite, carlinite, and pyrite [13–17]. To date, 63 thallium sulfide or



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). sulfosalt minerals have been documented in the literature. Moreover, scarce thallium selenide minerals were also reported [18].

In spite of the occurrence of diverse independent Tl minerals, the ubiquitous pyrite in hydrothermal deposits has also been reported to exhibit strikingly high Tl content at several sites in China and Spain [19–24], especially in independent Tl deposits (e.g., Lanmuchang and Xiangquan in China) [21,23], as well as in numerous Tl-bearing deposits (e.g., Yunfu and Jinding in China, McArthur River in Australia, and Bathurst Mining Camp in Canada) [25–28] where pyrite is the most important ore mineral. Unfortunately, oxidation and dissolution of these Tl sulfide minerals, particularly pyrite, will generate acid mine drainage (AMD) and mobilize large amounts of sequestered heavy metals. Thus, it raises concern about potential Tl exposure risk in the Tl mineralization areas.

Microbial-mediated sulfide minerals oxidation is responsible for the generation of AMD, which is characterized by low pH value and high load of sulfate and trace metals. As it more abundantly occurs and has a higher S/metal molar ratio than other sulfides, pyrite acts as the predominant AMD producer. Metals liberated by sulfide oxidation and dissolution may keep soluble in the AMD or precipitate locally as sulfate minerals (hereafter referring to secondary sulfate minerals). The formation and dissolution of the secondary sulfate minerals exert an important impact on the storage and transport of Tl and other heavy metals following weathering and oxidation of sulfide minerals. In addition, the composition of the secondary sulfate minerals could provide information about the formation condition and water-rock reaction process [29].

This paper aims to summarize the thallium deposits and minerals and crystal chemistry, field occurrence, formation, and environmental significance of secondary sulfate minerals associated to Tl mineralization areas. The solubility and Tl content of the secondary sulfate minerals are the important aspects for the sequestration and migration of Tl in supergene environments, which is essentially constrained by the crystal chemistry of the metal sulfate that results from AMD reaction with gangue minerals in various mineralized backgrounds. Therefore, Tl cycling constrained by secondary sulfate minerals will contribute new insights into the control of Tl pollution derived from Tl sulfide mining and processing.

# 2. Thallium Ore Deposits and Tl Minerals

## 2.1. Thallium Ore Deposits

Thallium deposits occur in diverse geological environments and countries (Figure 1). Carlin-type gold deposit, characterized by Au–Tl–As–Hg–Sb geochemical signature, was first reported containing high Tl concentrations in mineralized rocks. Thallium has been proposed as a more useful indicating element than gold in finding this type of gold deposit [8]. Carlin-type gold deposits have become chief gold sources and are mainly distributed in Nevada State in the USA and southwest China [30]. Thallium in the ores is mainly hosted by independent thallium minerals (e.g., lorandite, carlinite, galkhaite, and hutchinsonite) or incorporated into pyrite, orpiment, or other sulfides [19]. Lanmuchang Hg–Tl–Au deposit in southwest China is the first reported independent Tl deposit in the world [31]. The additional small size of Carlin-type deposits are also found in Canada, the Republic of North Macedonia, Russia, Southern Tienshan Belt (including Uzbekistan, Tajikistan, Kyrgyzstan, and China), Indonesia, and Malaysia [6,30,32–34]. Given the widespread distribution of the Carlin-type gold deposits, Tl mineralization areas associated with gold, antimony, and mercury are supposed to become the global important Tl ore deposit occurrences.

The metamorphic-hosted deposits represent the second important thallium occurrence documented in the literature. Typical deposits include Apuan Alps; Tuscany in Italy [35], Lengenbach in Switzerland; and Yunfu in Guangdong, China [12,36]. This type of Tl deposit shares the elemental assemblage of Tl–Hg–As–Sb–Pb–Zn in ore geochemistry. The primary Tl-bearing phases are pyrite and the complex sulfosalt due to the metamorphic remobilization of Tl [37]. Both Apuan Alps and Lengenbach are well known for the Tl-bearing sulfosalts and sulfides [37,38].

Mississippi Valley Type zinc-lead deposits have emerged as a new type of Tl-bearing sulfide deposit reported in Yunnan Lanping and Anhui Xiangquan of China [19,22]. The mineralized wall rock is carbonate rock (e.g., Xiangquan) or gypsum-bearing sandstone (e.g., Lanping). Zn–Pb–Tl–Ba–Sr characterizes the element assemblage, with pyrite being the prevailing Tl-bearing mineral, and less common, lorandite and raguinite [39,40]. Skrikerum Cu–Ag–Tl–(Au) selenide deposit from SE Sweden is the only thallium selenide deposit in which thallium is mainly hosted by bukovite (Cu<sub>4</sub>Tl<sub>2</sub>Se<sub>4</sub>) and crookesite (Cu<sub>7</sub>(Tl,Ag)Se<sub>4</sub>) in calcite-selenide veins [18].



Figure 1. Tl-(bearing) deposits occurrence in the world (modified from [6,7]).

Despite the fact that Tl-(bearing) deposits are increasingly discovered in various mineralized geological settings around the world, little research has been conducted to date focusing on Tl mineralization. Apparently, almost all Tl-(bearing) deposits are associated with lowtemperature hydrothermal fluids, and Tl is predominantly hosted in sulfide phases. It signifies that in hydrothermal systems Tl shows a higher affinity for sulfur compared to potassium. To the best of our knowledge, weakly acidic Tl-rich polymetallic ore fluids originated from the deep crust are considered to be the prerequisite for Tl mineralization [41,42]. Both theoretical calculations [43] and simulation experiments [44] support that the temperature decrease, especially the effective neutralization of acidity by the host rock, are crucial factors for Tl precipitation from ore fluids, and field observations have also revealed extensively developed argillization from neutralizing acidic fluids in the Lanmuchang-independent Tl deposit [45] as well as Tl mineralisation in the Allchar Au-As-Sb-Tl deposit in North Macedonia occurring at the distal end of the hydrothermal system [46].

#### 2.2. Thallium Minerals

Owing to the same charge (+1) and similar ionic radii between Tl and K (1.70 Å for Tl<sup>+</sup> and 1.64 Å for K<sup>+</sup>), Tl can be incorporated into K-bearing silicate minerals by isomorphic substitution for potassium. It is evidenced by the elevated concentration of Tl in mica and K-feldspar over 20 ppm compared to 0.7 ppm of the crust abundance [47]. However, Tl also appears to have sulfur affinity for similar-sized Ag<sup>+</sup> and Pb<sup>2+</sup> in sulfides and sulfosalts [48]. As such, Tl can form independent sulfide or sulfosalt minerals with Pb, Zn, Cu, As, Sb, Fe, Hg, and Au in various hydrothermal processes [15].

# 2.2.1. Thallium Sulfide

Thallium sulfide mineral carlinite was first found in the Carlin gold deposit in Nevada, the USA and is named for its locality Carlin [49]. Although Tl could present as Tl(I)

and Tl(III), carlinite (Tl<sup>+1</sup><sub>2</sub>S) is the only reported thallium sulfide mineral that occurs in Carlin gold deposit and Buus Fe–As–Tl mineralized occurrence in the Swiss Jura Mountains [49,50].

# 2.2.2. Thallium Sulfosalt

Thallium sulfosalts represent the most abundant thallium minerals mainly found in hydrothermal deposits due to their complex structure, structure diversity, and the prevalence of isomorphism substitution among cations (e.g., As, Sb, Pb, Hg, Ag). Sulfo-arsenite and sulfo-antimonide dominate 63 known thallium sulfosalts. Thallium sulfosalt mineralogy and crystal chemistry have been well-reviewed [51–54]. According to their structure types, seven archetypes (SnS, PbS, sphalerite, Tl-rich structures, structures of combination of two archetypes, chain structures, and layer structures with thallium-rich layers) have been categorized, and detailed crystal structures and crystal-chemical generalizations have been made [54]. Tuscany in Italy and Lengenbach in Switzerland are two classic localities for these rare thallium sulfosalt minerals [35,55]. Metamorphic overprint upon previous hydrothermal deposits is responsible for the complex thallium mineralization [55,56].

Lorandite (TlAsS<sub>2</sub>) is the most common thallium sulfosalt mineral in Tajikistan, Russia, Iran, Switzerland, North Macedonia, and China in various mineralized backgrounds [57,58]. However, Allchar in Macedonia and Lanmuchang in China are two prominent concentrated localities [31,57]. Unlike common links with Hg, As, and Sb mineralization, lorandite in Fengshan of Eastern China is closely associated with Cu–Au skarn mineralization with high Tl concentrations (up to 2016 ppm) in gold ore [58].

## 2.2.3. Thallium Telluride and Selenides

Very rare thallium tellurides and selenides are documented in some sites. Honeaite  $(Au_3TITe_2)$  is the only reported natural thallium-bearing gold telluride [59]. These minerals are found in Karonie gold deposit, Eastern Goldfields province, Western Australia. Native gold and tellurobismuthite are common paragenetic minerals [60]. Electron-microprobe data on 17 grains of honeaite give an average Tl concentration of 19.46% [60]. Bukovite  $(Cu_4Tl_2Se_4)$ , crookesite  $(Cu_7(Tl,Ag)Se_4)$ , and Sabatierite  $(Cu_6TlSe_4)$  are three reported thallium selenides, which together with Tl tellurides, are formed in the low temperature and slightly oxidized conditions [18].

## 2.2.4. Other Thallium Minerals

Thallium halides and primary sulfates are both limited to the fumaroles. Lafossaite (Tl(Cl, Br)), Nataliyamalikite (TlI), thallium-enriched flinteite (K,Tl)<sub>2</sub>ZnCl<sub>4</sub> (27.7 wt.% Tl), saltonseaite (K,Tl)<sub>3</sub>NaMnCl<sub>6</sub> (3.5 wt.% Tl), chrysothallite K<sub>6</sub>Cu<sub>6</sub>Tl<sup>3+</sup>Cl<sub>17</sub>(OH)<sub>4</sub>·H<sub>2</sub>O, kalithallite K<sub>3</sub>Tl<sup>3+</sup>Cl<sub>6</sub>·2H<sub>2</sub>O, karpovite Tl<sub>2</sub>VO(SO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O), evdokimovite Tl<sub>4</sub>(VO)<sub>3</sub>(SO<sub>4</sub>)<sub>5</sub>(H<sub>2</sub>O)<sub>5</sub>, and markhininite TlBi(SO<sub>4</sub>)<sub>2</sub> have been discovered in the fumaroles [61–63]. It is noteworthy that chrysothallite and kalithallite are two of the three known natural minerals of Tl<sup>3+</sup> (the third is avicennite Tl<sub>2</sub>O<sub>3</sub>), containing not only thallium but also potassium in different structural sites. Occurrences of these thallic minerals imply that there may be other mechanisms responsible for the oxidation of Tl<sup>+</sup> to Tl<sup>3+</sup> in addition to the avicennite typically associated with manganese oxides [64,65]. However, the mechanisms for oxidation have not been elucidated yet.

Pd thallide (Pd<sub>3</sub>Tl) and two new Pd thallide phases were documented in the magmatic PGE deposit of Russia and South Africa. These Pd thallide phases occur as composite grains or intergrowths of sub-millimeter size. Post magmatic-hydrothermal fluid reaction with PGE minerals is responsible for forming these unusual PGE thallide minerals [63,66].

In addition to the above-mentioned Tl minerals, other Tl minerals occur much rarer. All reported 89 thallium minerals and their chemical formula are given in Table 1. Taken together, thallium sulfosalts and monovalent thallium minerals dominate.

# 3. Secondary Sulfate Mineralogy in Tl Mineralization Areas

The oxidation/weathering of pyrite (FeS<sub>2</sub>) and other sulfide minerals introduces a high metal (e.g., Fe, Mn, Tl, Cu, Ni) concentration and sulfate into the surrounding environment. However, the formation of secondary sulfate could critically mediate the metal releasing process due to incorporating metal and sulfate into the secondary minerals. Many of the secondary sulfate minerals are soluble in the aqueous media; they represent the transient sink for sulfate, acidity, and metals [67]. Crystal chemistry exerts the primary control for the solubility of and incorporation of metal into the minerals.

The secondary sulfate minerals in thallium deposits, including thallium sulfate and Fe- and Al-hydroxysulfate minerals, have been documented in the literature [19,68–70]. As oxidation/weathering of pyrite releases large amounts of Fe<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> into the AMD, the melanterite group dominates the secondary sulfate with less occurrence of monovalent metal sulfates (e.g., lanmuchangite and alum), other divalent metal sulfates (e.g., gypsum and epsomite), and trivalent metal sulfates (e.g., alunogen and coquimbite).

Table 1. Independent thallium minerals.

Mineral (Ref.)	Chemical Formula	Mineral (Ref.)	Chemical Formula
Argentobaumhauerite [71]	(Ag,Tl) <sub>1.5</sub> Pb <sub>22</sub> As <sub>33.5</sub> S <sub>72</sub>	Jentschite [72]	TlPbAs <sub>2</sub> SbS <sub>6</sub>
Arsiccioite [73]	AgHg <sub>2</sub> TlAs <sub>2</sub> S <sub>6</sub>	Kalithallite [74]	K <sub>3</sub> Tl <sup>3+</sup> Cl <sub>6</sub> ·2H <sub>2</sub> O
Auerbakhite [75]	$MnTl_2As_2S_5$	Karpovite [76]	$Tl_2VO(SO_4)_2(H_2O)$
Avicennite [77]	$Tl_2O_3$	Lafossaite [63]	Tl(Cl,Br)
Bernardite [78]	Tl(As,Sb) <sub>5</sub> S <sub>8</sub>	Lanmuchangite [68]	$TIAI(SO_4)_2 \cdot 12H_2O$
Biagioniite [79]	$Tl_2SbS_2$	Lorándite [80]	TlAsS <sub>2</sub>
Boscardinite [81]	$TlPb_4(Sb_7As_2)S_{18}$	Markhininite [82]	$TlBi(SO_4)_2$
Bukovite [83]	$Cu_4Tl_2Se_4$	Nataliyamalikite [61]	TlI
Carlinite [49]	Tl <sub>2</sub> S	Parapierrotite [84]	Tl(Sb,As) <sub>5</sub> S <sub>8</sub>
Chabournéite [85]	Tl <sub>4</sub> Pb <sub>2</sub> (Sb,As) <sub>20</sub> S <sub>34</sub>	Perlialite [86]	K <sub>3</sub> TlAl <sub>3</sub> Si <sub>4</sub> O <sub>18</sub> ·5H <sub>2</sub> O
Chalcothallite [83]	$Tl_2(Cu,Fe)_6SbS_4$	Philrothite [87]	$TlAs_3S_5$
Christite [88]	TlHgAsS <sub>3</sub>	Picotpaulite [89]	TlFe <sub>2</sub> S <sub>3</sub>
Chrysothallite [74]	$K_6Cu_6Tl^{3+}Cl_{17}(OH)_4 \cdot H_2O$	Pierrotite [90]	$Tl_2(Sb,As)_{10}S_{16}$
Criddleite [91]	$TlAg_2Au_3Sb_{10}S_{10}$	Pokhodyashinite [92]	Cu <sub>2</sub> Tl <sub>3</sub> Sb <sub>5</sub> As <sub>2</sub> S <sub>13</sub>
Crookesite [93]	Cu <sub>7</sub> (Tl,Ag)Se <sub>4</sub>	Protochabournéite [94]	Tl <sub>2</sub> Pb(Sb,As) <sub>10</sub> S <sub>17</sub>
Cuprostibite [95]	Cu <sub>2</sub> (Sb,Tl)	Raberite [96]	$Tl_5Ag_4As_6SbS_{15}$
Dalnegroite [97]	$Tl_4Pb_2Sb_8As_{12}S_{34}$	Raguinite [98]	TlFeS <sub>2</sub>
Dekatriasartorite [99]	TlPb <sub>58</sub> As <sub>97</sub> S <sub>204</sub>	Ralphcannonite [100]	AgZn <sub>2</sub> TlAs <sub>2</sub> S <sub>6</sub>
Dorallcharite [101]	$TlFe_3(SO_4)_2(OH)_6$	Rathite [102]	$Ag_2Pb_{12-x}Tl_{x/2}As_{18+x/2}S_{40}$
Drechslerite [103]	$Tl_4(Sb_{4-x}As_x)S_8$	Rayite [104]	$(Ag,Tl)_2Pb_8Sb_8S_{21}$
Écrinsite [105]	AgTl <sub>3</sub> Pb <sub>4</sub> As <sub>11</sub> Sb <sub>9</sub> S <sub>36</sub>	Rebulite [106]	$Tl_5Sb_5As_8S_{22}$
Edenharterite [107]	TlPbAs <sub>3</sub> S <sub>6</sub>	Richardsollyite [108]	TlPbAsS <sub>3</sub>
Ellisite [109]	$Tl_3AsS_3$	Rohaite [83]	$TlCu_5SbS_2$
Erniggliite [110]	$Tl_2SnAs_2S_6$	Routhierite [111]	TlCuHg <sub>2</sub> As <sub>2</sub> S <sub>6</sub>
Enneasartorite [112]	Tl <sub>6</sub> Pb <sub>32</sub> As <sub>70</sub> S <sub>140</sub>	Sabatierite [113]	Cu <sub>6</sub> TlSe <sub>4</sub>
Evdokimovite [114]	Tl <sub>4</sub> (VO) <sub>3</sub> (SO <sub>4</sub> ) <sub>5</sub> (H <sub>2</sub> O) <sub>5</sub>	Saltonseaite [115]	(K,Tl) <sub>3</sub> NaMnCl <sub>6</sub>
Fangite [116]	$Tl_3AsS_4$	Sicherite [117]	$TlAg_2(As,Sb)_3S_6$
Ferrostalderite [118]	CuFe <sub>2</sub> TlAs <sub>2</sub> S <sub>6</sub>	Simonite [119]	TlHgAs <sub>3</sub> S <sub>6</sub>
Ferrovorontsovite [120]	(Fe <sub>5</sub> Cu)TlAs <sub>4</sub> S <sub>12</sub>	Spaltiite [121]	$Tl_2Cu_2As_2S_5$
Flinteite [122]	$(K,Tl)_2ZnCl_4$	Stalderite [123]	TlCu(Zn,Fe,Hg) <sub>2</sub> As <sub>2</sub> S <sub>6</sub>
Gabrielite [124]	$Tl_2AgCu_2As_3S_7$	Steropesite [125]	Tl <sub>3</sub> BiCl <sub>6</sub>
Gladkovskyite [126]	MnTlAs <sub>3</sub> S <sub>6</sub>	Thalcusite [83]	$Tl_2Cu_3FeS_4$
Galkhaite [120]	Tl(Hg,Cu,Zn) <sub>6</sub> (As,Sb) <sub>4</sub> S <sub>12</sub>	Thalfenisite [127]	Tl <sub>6</sub> (Fe,Ni,Cu) <sub>25</sub> S <sub>26</sub> Cl
Gillulyite [116]	$Tl_2(As,Sb)_8S_{13}$	Thalliomelane [103]	$TlMn^{4+}_{7.5}Cu^{2+}_{0.5}O_{16}$
Gungerite [128]	$TlAs_5Sb_4S_{13}$	Thalliumpharmacosiderite [121]	$TlFe_4[(AsO_4)_3(OH)_4] \cdot 4H_2O$
Hatchite [129]	AgTlPbAs <sub>2</sub> S <sub>5</sub>	Thunderbayite [130]	TlAg <sub>3</sub> Au <sub>3</sub> Sb <sub>7</sub> S <sub>6</sub>
Hendekasartorite [112]	$Tl_2Pb_{48}As_{82}S_{172}$	Tsygankoite [131]	$Mn_8Tl_8Hg_2(Sb_{21}Pb_2Tl)S_{48}$
Hephaistosite [62]	TlPb <sub>2</sub> Cl <sub>5</sub>	Twinnite [132]	$Pb_{0.8}Tl_{0.1}Sb_{1.3}As_{0.8}S_4$
Heptasartorite [112]	$Tl_7Pb_{22}As_{55}S_{108}$	Vaughanite [133]	TlHgSb <sub>4</sub> S <sub>7</sub>
Honeaite [60]	Au <sub>3</sub> TlTe <sub>2</sub>	Voltaite [35]	$(K,Tl)_2Fe_8Al(SO_4)_{12}\cdot 18H_2O$
Hutchinsonite [134]	$(Pb,Tl)_2As_5S_9$	Vorontsovite [120]	(Hg5Cu)TlAs4S12
Imhofite [135]	$Tl_{5.8}As_{15.4}S_{26}$	Vrbaite [136]	$Hg_3Tl_4As_8Sb_2S_{20}$
Incomsartorite [137]	$Tl_6Pb_{144}As_{246}S_{516}$	Wallisite [138]	CuPbTlAs <sub>2</sub> S <sub>5</sub>
Jarosite [64]	$(Tl,K)Fe_3(SO_4)_2(OH)_6$	Weissbergite [139]	TlSbS <sub>2</sub>
Jankovicite [140]	$Tl_5Sb_9(As,Sb)_4S_{22}$		

#### 3.1. Secondary Thallium and Potassium Sulfate

The mineralogy of thallium sulfate in secondary environments of mining areas is constrained to very few species. Two Tl<sup>+</sup>-oxysalts, namely dorallcharite [101] and lanmuchangite [68], are the reported secondary sulfate minerals, with thallium occurring as a monovalent ion in the two minerals. Potassium sulfate minerals (e.g., voltaite) have elevated Tl contents due to the substitution of K by Tl [141]. The chemical formula, unit cell parameter, and crystal system for these two minerals and the other three thallium sulfate minerals are given in Table 2.

Fable 2. Crystal chemist	y for thallium	sulfate minerals	[68,76,82	,101,114].
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Mineral	Chemical Formula	Crystal System	Unit-Cell Parameters
Lanmuchangite	TlAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	Isometric	$a = 12.212 \text{ Å}, V = 1871 \text{ Å}^3$
Dorallcharite	$TlFe_3(SO_4)_2(OH)_6$	Trigonal	a = 7.3301, c = 17.6631 Å, $V = 821.73$ Å <sup>3</sup> ,
Evdokimovite	$Tl_4(VO)_3(SO_4)_5 \cdot (H_2O)_5$	Monoclinic	$a = 6.2958, b = 10.110, c = 39.426$ Å, $V = 2509.4$ Å <sup>3</sup> , $\beta = 90.347^{\circ}$
Karpovite	$Tl_2VO(SO_4)_2(H_2O)$	Monoclinic	$a = 4.6524, b = 11.0757, c = 9.3876$ Å, $V = 478.60$ Å <sup>3</sup> , $\beta = 98.353^{\circ}$
Markhininite	TlBi(SO <sub>4</sub> ) <sub>2</sub>	Triclinic	$a = 7.378, b = 10.657, c = 10.657 \text{ Å}, V = 680.2 \text{ Å}^3, \alpha = 61.31, \\ \beta = 70.964, \gamma = 70.964^{\circ}$

Dorallcharite (TlFe<sup>3+</sup><sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) is the Tl-analog of jarosite; it was initially found in Allchar of North Macedonian and thereafter in France [142] and Switzerland [49]. The crystal structure for dorallcharite is presented in Figure 2. Dorallcharite occurs associated with gypsum, rosselrite (MgHAsO<sub>4</sub>·7H<sub>2</sub>O), thalliumpharmacosiderite (TlFe<sub>4</sub>[(AsO<sub>4</sub>)<sub>3</sub> (OH)<sub>4</sub>]·4H<sub>2</sub>O), and amorphous Fe and Mn sulfate and/or arsenate at Allchar [101]. The mean concentration of Tl and K from 25 microprobe measurements is 23% and 1.23%, respectively [143]. It is formed following Tl removal from sulfide oxidation and subsequently retained by the sulfate [101]. Given that Tl<sup>+</sup> substitutes K<sup>+</sup> in jarosite, a complete solid-solution series exists between jarosite and dorallcharite [101].



Figure 2. Crystal structure of dorallcharite.

Lanmuchangite (TlAl(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O) is the Tl-analog of alunite. It is only reported in its type locality, China [68], which is associated with melanterite, pickeringite, alum, jarosite, gypsum, native sulfur, arsenolite, and some unknown minerals in the oxidized zone of the Lanmuchang Hg-Tl deposit [68]. It belongs to the alum group with the general formula  $X^+Al^{3+}(SO_4)_2 \cdot 12H_2O$  in which X site is occupied by Na, K, NH<sub>4</sub>, and Tl. The crystal structure of the mineral is given in Figure 3. Biagioni et al. [35] documented Tlbearing alum (K) from the Apuan Alps in Italy and argued that the substitution of Al<sup>3+</sup>



by  $Fe^{3+}$  and  $K^+$  by both  $NH_4^+$  and  $Tl^+$  are responsible for the nonlinear variation of the unit-crystal parameter from Alum(K) to lanmuchangite.

Figure 3. Crystal structure of Lanmuchangite.

Thallium voltaite ((K,Tl)Fe<sup>2+</sup><sub>5</sub>Fe<sup>3+</sup><sub>3</sub>Al(SO<sub>4</sub>)<sub>12</sub>·18H<sub>2</sub>O) is reported in the oxidized zone of thallium deposits (e.g., Tuscany of Italy), which was first named as a new Tl<sup>3+</sup>-K mineral monsmedite and was later discredited [35]. The study suggests that the unit-cell parameter (a = 27.2587 Å and a = 27.2635 Å for Romania and Italy, respectively) of Tl voltaite is slightly larger than that of synthetic K<sub>2</sub>Fe<sup>2+</sup><sub>5</sub>Fe<sup>3+</sup><sub>3</sub>Al(SO<sub>4</sub>)<sub>12</sub>·18H<sub>2</sub>O (a = 27.234 Å) [35,144]. It is reported that Tl voltaite is chemically zoned with Tl more enriched in the rims (Tl<sub>2</sub>O 3.30%) than in the core (Tl<sub>2</sub>O 2.88%) of the voltaite as revealed by electron microprobe analyses [35]. The Tl voltaite closely occurs with more than 15 secondary sulfate minerals. The K site replacement by Tl in the voltaite from Apuan Alps has been confirmed by quantitative EXAFS and single-crystal X-ray diffraction refinement [35].

Pyrite oxidation and subsequent Tl release and K substitution by Tl in various ratios in the secondary K sulfate are responsible for the formation of dorallcharite, lanmuchangite, voltaite, and other K sulfate minerals, as evidenced the elevated content of Tl in alum(-K)  $(KAl(SO_4)_2 \cdot 12H_2O)$ , goldichite  $(KFe^{3+}(SO_4)_2 \cdot 4(H_2O))$ , jarosite  $(KFe^{3+}(SO_4)_2 \cdot (OH)_6)$  and krausite  $(KFe^{3+}(SO_4)_2 \cdot (H_2O))$  in Apuan Alps [69] and Lanmuchang [145]. It is expected that some K sulfate minerals from Apuan Alps, in which Tl contents have not been analyzed, such as giacovazzoite  $(K_5Fe^{3+}_{3}O(SO_4)_6 \cdot 10H_2O)$ , Magnanelliite  $(K_3Fe^{3+}_2(SO_4)_4(OH)(H_2O)_2)$ , and scordariite  $(K_8(Fe^{3+}_{0.67}\Box_{0.33})[Fe^{3+}_{3}O(SO_4)_6]_2 \cdot 14H_2O)$ , should contain high Tl concentrations.

# 3.2. Secondary Iron Sulfate

Secondary iron sulfates including ferrous sulfate melanterite  $(Fe^{2+}(SO_4)\cdot(H_2O)_7)$ and halotrichite  $(Fe^{2+}Al_2(SO_4)_4\cdot22H_2O)$ , mixing ferrous and ferric sulfate römerite  $(Fe^{2+}Fe^{3+}_2(SO_4)_4\cdot14H_2O)$ , and ferric sulfate fibroferrite  $(Fe^{3+}(SO_4)(OH)\cdot5H_2O)$  are found in the oxidized zone of thallium deposit [68,69]. Melanterite is the most common secondary sulfate mineral formed in the earliest period of pyrite oxidation [29]. Partial oxidation of ferrous iron in the solution under acid conditions leads to the formation of romerite and fibroferrite. Due to the significant ionic radius difference between iron and thallium, only a trace amount of Tl is incorporated into iron-sulfate minerals [69]. All reported four iron-sulfate minerals are more soluble than jarosite and schwertmannite  $(Fe_8O_8(OH)_6SO_4 \cdot nH_2O)$  [29].

# 3.3. Secondary Calcium, Magnesium, Aluminum Sulfate

Gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), anhydrite (CaSO<sub>4</sub>), alunogen (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·17(H<sub>2</sub>O)), coquimbite (AlFe<sup>3+</sup><sub>3</sub>(SO<sub>4</sub>)<sub>6</sub>(H<sub>2</sub>O)12·6(H<sub>2</sub>O)), khademite (Al(SO<sub>4</sub>)F·5(H<sub>2</sub>O)), pickeringite (MgAl<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>·22H<sub>2</sub>O), and magnesiocopiapite (MgFe<sup>3+</sup><sub>4</sub>(SO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>14</sub>·6H<sub>2</sub>O) are reported secondary calcium, aluminum, and magnesium sulfate in thallium deposit [68,69]. All these sulfate minerals have high solubility, especially in acid solutions [29]. Crystal chemical difference between Tl and Ca, Mg, and Al inhibits Tl from entering the crystal lattice of these minerals.

## 4. Environmental Significance of the Secondary Sulfate Minerals

Precipitation and dissolution of the secondary sulfate mineral in the alternating wetdry climate in mining areas can store or release acid and/or toxic elements. Owing to the varied Tl concentration, crystal structure and composition, and solubility, the secondary sulfate minerals play different roles in the environment.

### 4.1. Tl Sulfate

Natural Tl sulfate mineral lanmuchangite is readily soluble in water [68] and remains stable only in acidic conditions [16]; therefore, lanmuchangite serves as a transient Tl source and sink in the Tl-bearing mining environment. A high concentration of Tl appeared in rims of the voltaite at Alpuan mine, which suggests that Tl is enriched in the sulfide oxidation in K-poor environments [69]. Unfortunately, no literature is documented for Tl behavior during voltaite dissolution.

Tl-jarosite, which is transformed to dorallcharite when Tl completely substitutes K in the jarosite crystal lattice, represents common Tl sulfate in the Tl mining areas. In contrast to lanmuchangite, jarosite is relatively insoluble in water [67]. Moreover, jarosite and most other sulfate minerals are formed in acid conditions [146]. Therefore, Tl-jarosite plays a pivotal role in the storage of acid and Tl following sulfide weathering and oxidation and serves as a long-term sink for Tl and acid, notably in acid mine drainage and acid soil. Interestingly, the sites where these Tl sulfate minerals are documented, namely Allchar, Lanmuchang, and Tuscany, are Tl-rich deposits and notorious Tl-polluted areas [6]. Thus, occurrence of Tl sulfate minerals implies Tl-rich geological settings and abundant Tl release from oxidation of Tl-bearing sulfide minerals.

Thermodynamic modeling shows a wide stability field for dorallcharite [69]. Dorallcharite and Tl-jarosite are susceptible to significantly incongruent dissolution to release Tl and form iron hydroxides or schwertmannite under circumneutral pH conditions as described by the following reaction [147–149]:

$$(Tl_{x}K_{1-x})Fe_{3}(SO_{4})_{2}(OH)_{6} + 2H_{2}O = 3Fe(OH)_{3} + xTl^{+} + (1-x)K^{+} + 2SO_{4}^{2-} + 3H^{+}$$
(1)

The dissolution is also enhanced by microbial reduction of structural Fe and S. Dissimilatory iron-reducing bacteria (DIRB) (e.g., *Shewanella putrefaciens* CN32, *Geobacter metalloproteins*) have been proved using iron oxides as an electron acceptor for respiration. Jarosite enhanced reductive dissolution and iron oxides formation by *Shewanella putrefaciens* CN32, and *Shewanella oneidensis* MR-1 have been well recognized under anaerobic and neutral pH conditions [69,150]. Sulfate-reducing bacteria (SRB) can use sulfate as a terminal electron acceptor, and reductive-dissolution of jarosite by SRB has also been argued in anaerobic conditions [151–153]. Aqueous Tl data, adsorption experiments, and thermodynamic modeling demonstrate Tl did not have strong affinity for the iron oxides [147–149,154]. Taken together, Tl-jarosite and dorallcharite dissolution will increase Tl mobility and bioavailability driven by biotic and abiotic processes.

## 4.2. Calcium, Magnesium, Alumina, and Iron Sulfate

The pyrite's predominance in sulfides and Tl-hosted phases of Tl ore bodies, pyrite oxidation, and the subsequent sulfate mineral formation play a significant role in Tl release from primary Tl-hosted phases. It is commonly accepted that abiotic pyrite oxidation proceeds as the following simplified reactions [155]:

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
 (2)

$$Fe^{2+} + 1/4O_2 + H^+ \to Fe^{3+} + 1/2H_2O$$
 (3)

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$
(4)

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$
 (5)

Soluble minerals (e.g., gypsum, alum (without K), melanterite, halotrichite, römerite, and fibroferrite) may precipitate at the surface of mineralized rocks during dry periods [156]. These sulfate minerals are highly impossible to act as a temporary or long-term storage for Tl for the crystal chemistry reason as evidenced by trace amounts of Tl in these minerals mentioned in Sections 3.2 and 3.3. Besides, we argued that redox cycling between ferrous and ferric iron in Equations (3) and (5) might impact the Tl release from Tl-bearing sulfide oxidation. It is well known that ferrous iron oxidizes to ferric iron in Equation (3) during pyrite oxidation and is a rate-limiting step [155]. Moreover, the ferrous iron that oxidizes to ferric iron is also pH dependent. Under the circumneutral pH conditions, the ferric iron tends to hydrolyze to ferrihydrite, which causes the removal of ferric iron from the aqueous system. Since the rate of pyrite oxidation involving  $Fe^{3+}$  is significantly higher than that of O<sub>2</sub>, as suggested by reaction Equation (2), the O<sub>2</sub>-dominated pyrite oxidation will proceed at a relatively lower rate. At the low pH conditions resulting from the secondary sulfate dissolution during the wet periods, ferric iron oxidizing pyrite in Equation (5) is preferred to Equation (4). Thus, Equations (3) and (5) construct a closed iron cycling to prompt the pyrite oxidation approach to a steady state.

The ferrous iron oxidation rate in Equation (3) becomes very slow at lower pH values, and dissolution and adding of ferric iron sulfate minerals (e.g., fibroferrite) may compensate for the lower rate. Despite the effectiveness of microbial catalysis for pyrite oxidation process, abiotic pyrite oxidation at depth is argued at the global scale owing to the pore limit for the access of bacteria [157]. Therefore, precipitation and dissolution of soluble iron-sulfate minerals probably sustains long-term pyrite oxidation and associated Tl release in areas impacted by Tl mining and processing.

#### 5. Conclusions

Tl is a highly toxic heavy metal that is strictly regulated by many countries but has an irreplaceable role in several high-tech fields, and is mainly introduced into the environment unintentionally by the mining, mineral processing, and metallurgy related to Tl-(bearing) deposits. The numerous discoveries of new Tl minerals and Tl-bearing deposits in recent years suggest that the risk of Tl exposure is much higher than documented, and the potential Tl pollution associated with the mining activities has attracted considerable attention. Although up to 89 Tl minerals have been reported, hydrothermal pyrite is the predominant Tl-bearing phase in most Tl-(bearing) deposits. Pyrite oxidation not only generates acid but also releases Tl into the environment. Thallium and other metal sulfate minerals formed during the dry season play varied roles in Tl mobility and scavenging due to different crystal chemistry signatures. Furthermore, secondary sulfate minerals dissolution and ferric iron adding can accelerate the pyrite oxidation and Tl release from pyrite and other Tl-bearing sulfides.

More in-depth knowledge is needed about the behavior of Tl release during Tl sulfide minerals oxidation and constrained factors under different natural conditions. Besides, the roles that the secondary sulfate minerals play on Tl uptake by plants should be further investigated in future works. These efforts could enable us to control Tl pollution and reclaim Tl-polluted lands.

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