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1 Thallium long-term fate from rock-deposit to soil: the
2 Jas Roux sulfosalt natural analogue

3 *Jérôme Rose^{a,*}; Perrine Chaurand^a; Cédric Dentant^{b,c}; Bernard Angeletti^a; Daniel Borschneck^a;*
4 *Isabelle Kieffer^d; Olivier Proux^d; Richard Bonet^b; Mélanie Auffan^a; Clément Levard^a; Till Fehlaue^a;*
5 *Blanche Collin^a; Emmanuel Doelsch^{a,e,f}*

6 ^aCNRS, Aix Marseille Univ, IRD, INRAE, CEREGE, 13545 Aix-en-Provence, France

7 ^bEcrins National Park, 05000 Gap, France

8 ^cUniv. Grenoble Alpes, CNRS, Sciences-Po Grenoble, Pacte, Grenoble, 38000, France

9 ^dUniv. Grenoble Alpes, UAR CNRS 832, OSUG, 38041 Grenoble, France

10 ^eCIRAD, UPR Recyclage et Risque, 34398 Montpellier, France

11 ^fRecyclage et Risque, Univ. Montpellier, CIRAD, 34398 Montpellier, France

12 *Corresponding author: rose@cerege.fr

13 KEYWORDS: high-tech metal, oxidation, national park, critical element, speciation, XAS.

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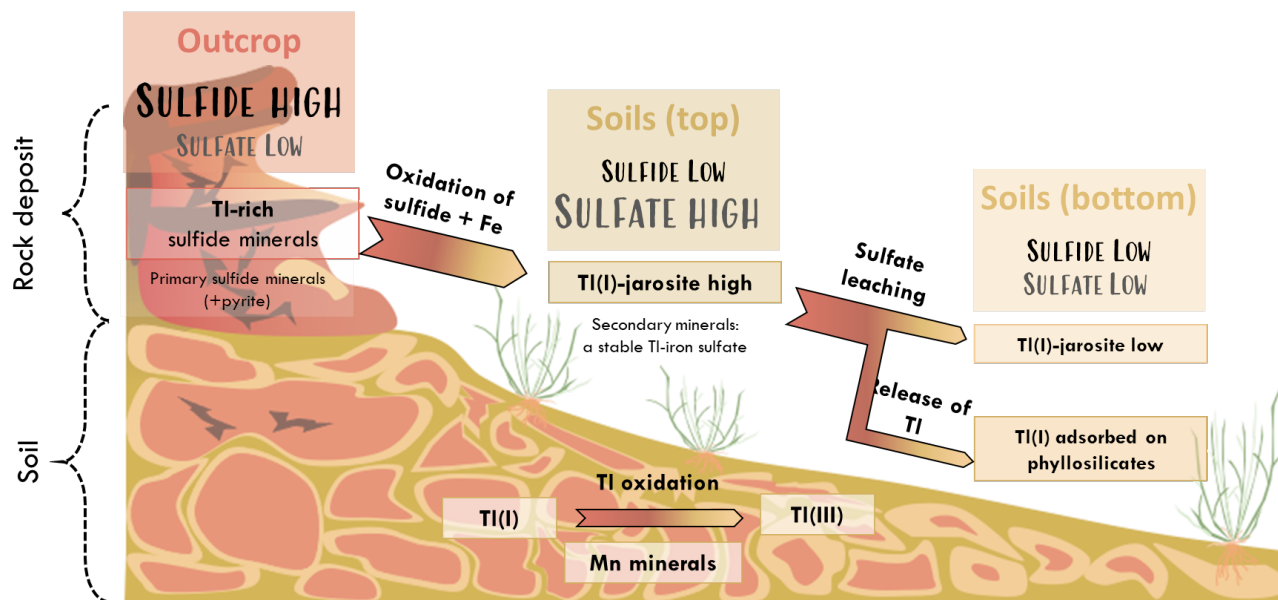
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Jas Roux: a sulfosalt natural analogue



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22 ABSTRACT

23 Inorganic contaminant release resulting from mining activities can impact surrounding ecosystems.
 24 Ores formed by primary sulfide minerals produce sulfuric acid after mineral oxidation which is the
 25 driving force of metal release. Yet secondary metal sulfates may form and play a crucial role in
 26 controlling the metal fate. In the case of thallium (Tl), it has been shown that in natural Tl-rich sulfide
 27 deposits and those found in mining areas, Tl can be trapped by Tl-jarosite (Tl-rich iron sulfate) and
 28 dorallcharite ($TlFe_3(SO_4)_2(OH)_6$). Our Tl speciation characterization results have generated novel
 29 insight into the long-term behavior of this metal derived from a unique natural hotspot—the Jas Roux
 30 site (France). The biogeochemical cycle of the soil ecosystems of Jas Roux dates back almost 15000
 31 years ago and has now reached a steady state. A chemical gradient was found in soils across the
 32 toposequence underlying the Jas Roux outcrop. X-ray absorption spectroscopy revealed that Tl was
 33 mainly present in secondary minerals at the top of the studied zone. Oxidative dissolution of Tl-rich

34 sulfide minerals and pyrite accounts for the presence of Tl-jarosite in soils, either by direct formation
35 in soils or by gravity erosion from the outcrop. The Tl-jarosite quantity was found to decrease from
36 the top to the bottom of the toposequence, probably due to sulfate leaching. Released Tl likely adsorbed
37 on phyllosicates such as illite or muscovite and a fraction of Tl was found to have oxidized into Tl(III)
38 along the toposequence.

39

40 INTRODUCTION

41 Human activities, especially mining, lead to the release of many inorganic environmental
42 contaminants. Globally, the highest tonnages of common metals such as lead, copper and zinc derive
43 from ores containing primary sulfide minerals. These ores are accompanied by iron sulfide minerals
44 (marcasite FeS_2 , pyrite FeS_2 and pyrrhotite Fe_{1-x}S) which produce sulfuric acid by oxidation and
45 hydrolysis. When leached, this acid subsequently triggers the release of metals and metalloids from
46 extracted ores and mine wastes. However, in this acidic environment, secondary metal sulfates may
47 form after sulfide oxidation, which can play a crucial role in affecting the storage and transport of
48 released metals¹.

49 Thallium (Tl) is a low-abundance element (average crustal abundance $<0.8 \text{ mg.kg}^{-1}$ ²) with an
50 average concentration of 0.29 mg.kg^{-1} in French soils³. In soil and rock, Tl can be hosted by many
51 different minerals. Almost hundred Tl-bearing minerals are known⁴. However, Tl generally occurs in
52 three main types of minerals, namely sulfide minerals, secondary sulfate minerals and silicate minerals
53 such as feldspars or phyllosilicates through the isomorphic substitution of K^+ ^{3,5,6}. Natural Tl-rich
54 deposits are rare. Only a few have been identified at different sites, including Allchar (Macedonia)⁷,
55 Lengnabach quarry (Switzerland)^{5,8}, Skrikerum (Sweden), Lanmuchang (China)^{9,10} and Jas Roux
56 (France)¹¹. In the latter deposits, Tl is mainly associated with sulfide minerals and its mobility is driven
57 by oxidative dissolution processes⁴.

58 Due to its specific electronic properties, Tl is used in different modern high technology applications,
59 such as semiconductors, superconductors, fiber optics and thermoelectric conversion¹²⁻¹⁷. However, Tl
60 is just as toxic to mammals as mercury, for instance¹⁸⁻²⁰. Thallium can occur under two oxidation states,
61 with Tl(I) being thermodynamically more stable than Tl(III) and relatively less toxic. Tl(I) is more
62 mobile than Tl(III) in surface ecosystems ^{10,20}. Tl(I) was long considered to be the only form occurring

63 in the critical zone, yet low Tl(III) amounts were subsequently found in rivers, waste waters, soils and
64 plant tissues^{5,21–25}.

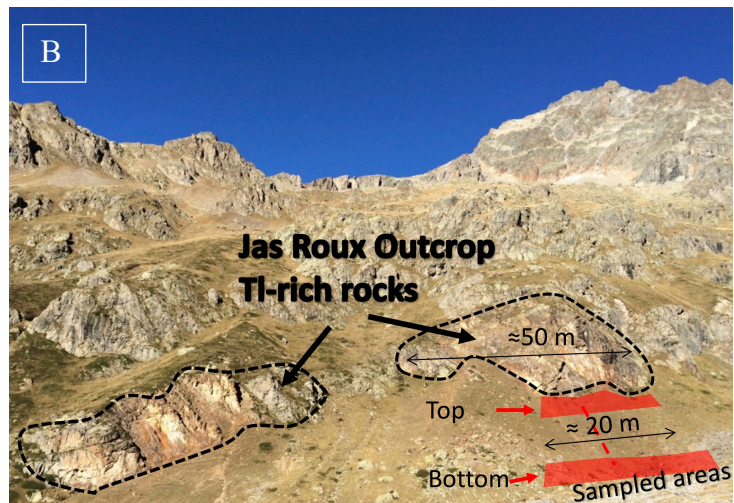
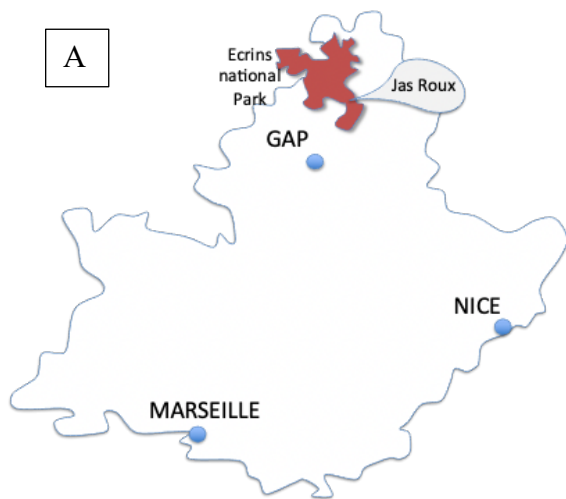
65 In the vicinity of Tl sulfide ores and/or mines, secondary Tl-sulfate phases can precipitate and control
66 Tl(I) free ions in solution. Two main Tl(I)-sulfate minerals have been found, namely lanmuchangite
67 ($\text{TlAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) and dorallcharite ($\text{TlFe}_3(\text{SO}_4)_2(\text{OH})_6$). While lanmuchangite is only stable at
68 acidic conditions, dorallcharite—a jarosite analogue in which K^+ has been fully replaced by Tl(I)
69 (jarosite = $\text{KFe}_3^{3+}(\text{SO}_4)_2(\text{OH})_6$)—is less soluble at > 5.5 pH²⁶. Dorallcharite and Tl(I)-jarosite could
70 therefore act as a trap for Tl since it has been identified in various Tl-rich sulfide deposits, namely
71 Lanmuchang, Allchar and Tuscany^{7,27}, and in Tl polluted areas^{28,29}. However, do dorallcharite and Tl-
72 jarosite remain stable during soil weathering by meteoric water? Besides sulfate minerals, Tl can be
73 hosted by other minerals: silicates in which Tl substitutes K, or Mn oxide minerals via Tl(I) oxidation
74 to Tl(III). Do those Tl-bearing phases also occur after long-term evolution of soils in the vicinity of Tl
75 sulfide-rich or polluted sites?

76 Voegelin et al⁵ reported Tl speciation in a natural soil developed from mineralized carbonate rock
77 (Erzmatt site). In addition to the presence of Tl-jarosite, the study revealed for the first time the
78 important role of Tl(I) associated with illite and Tl(III) associated with manganese minerals in
79 quantifying Tl bioavailability. As the initial source term no longer exists, it is difficult to assess the
80 evolution of Tl-bearing minerals from the supposed parent sulfide minerals and their long-term
81 transformation in soils.

82 Assessing the long-term fate of Tl in soil whether contaminated or pristine might be crucial to better
83 remediate and predict Tl transfer from geogenic environments into living organisms and the food
84 chain. Natural analogues provide an excellent opportunity to study the long-term fate and complex
85 geochemical cycling of Tl.

86 The Jas Roux site is located in Ecrins National Park in La Chapelle-en-Valgaudemar valley, France
87 (Figure 1A), and is a unique unimpacted site with detectable amounts of Tl¹¹. The rock deposit is hosted
88 by a Triassic sedimentary series of the Morges syncline^{11,30}. It has been investigated by Mantiene³⁰,
89 Johan and Mantiene¹¹ and Favreau et al³¹. The geological setting and mineralogical composition were
90 extensively studied. The rock deposit exhibits a unique mineralogy, including pyrite (FeS), stibnite
91 (Sb₂S₃), sphalerite (ZnS), realgar (AsS), other Ag, Pb-rich sulfide minerals such as jasrouxite³², along
92 with rare Tl minerals like pierrotite (TlSb₃As₂S₈), routhierite (Tl(Cu,Ag)(Hg,Zn)₂(As,Sb)₂S₆) and
93 chabourneite ((Tl, Pb)₂₃(Sb,As)₉₁S₁₄₇)^{33,34}. Some parts of the deposit exhibit alteration facies (Figure
94 S1), and oxidized sulfate minerals have been detected. For instance, jarosite was found, while
95 dorallcharite was identified as a Tl-rich secondary mineral^{30,31}. These minerals occur in a small outcrop
96 structured with five blocks separated by NW-SE oriented faults at 2170 to 2300 m elevation. The
97 deposit covers less than 10000 m², with a 45° slope that is subject to heavy erosion, causing the fall of
98 rock debris which ends up downstream. This process leads to the transfer of Tl from upstream to
99 downstream soils, as shown by Fehlauer et al³⁵. The current functioning of the Jas Roux soil ecosystem
100 is the result of long-term processes. The final exhumation of the South-East part of the Pelvoux
101 crystalline massif occurred in the late Miocene³⁶, but the current ecosystem is a result of the
102 colonization by living organisms after the last glacial maximum. Based on ¹⁰Be dating, it was estimated
103 that the glacial retreat in Gioberney valley, close to Jas Roux, occurred 15 ± 1 ky³⁷.

104 Although the chemical composition of soils at the top of the toposequence has been determined, soil
105 evolution from the top to the bottom of the toposequence and the Tl speciation pattern have yet to be
106 clarified.



107

Figure 1: A) Location of the site, B) the Jas Roux deposit with the sampling zones at the top and bottom of the slope below the Tl-rich outcrop.

108 The main aim of this study was to address the fate of Tl in soils developed below the Jas Roux
 109 outcrop. The working hypothesis was that a Tl concentration gradient from the top to the bottom of
 110 the toposequence is associated with a significant change in Tl speciation. The specific objectives were
 111 to determine: i) under which form Tl is transferred from the rocky outcrop to the soil below, ii) whether
 112 stable Tl minerals such as Tl-jarosite are formed in Jas Roux soils to serve as a Tl trap throughout the
 113 toposequence, and iii) whether Tl(III) can be formed in soils beneath the rocky outcrop.

114

115

116 1) MATERIALS AND METHODS

117 **1) Soil samples**

118 The Jas Roux site in Ecrins National Park is protected and sampling is forbidden. A waiver was
119 granted by the National Park to allow for a limited number of soil samples under their supervision.

120 The selected area below the outcrop (Figure 1B) was sampled from the top to the bottom of the
121 toposequence. The developed soil was just a few tens of centimeters thick. The upper soil horizons
122 contained many rock fragments from the outcrop. Furthermore, it is hard to sample soils remote from
123 plants because of the substantial vegetation cover. We sampled soils in the vicinity of three plant
124 species so as to assess their potential impact on the physicochemical soil properties. The top 10 cm
125 soil layer was sampled near the identified plants, i.e. fescue, saxifrage and bedstraw. Soil samples were
126 divided in two sets for chemical and X-ray based analysis (see below).

127 Fresh soils were dried for 48 h at 40°C and then sieved at 2 mm to recover the fine fraction according
128 to the NF-ISO-11464 standard. A portion of the sieved soils was ground very finely in a Mixer Mill
129 MM-400 (Retsch®) with ZrO₂ beads in 25 mL bowls. The grinding time was 150 s at 20 Hz frequency.
130 A first set of ground soils were stored at -80°C prior to XAS analysis, while a second set was set aside
131 for chemical analysis. The total chemical element content was determined for each sample (0.1 g) after
132 soil digestion. Digestion is achieved by adding 1.5 mL HNO₃ to 0.1 g of powder in Teflon beakers. 3
133 mL HCl and 0.5 mL HF were then added according to the NF-X31-147 standard. The last digestion
134 step was carried out in a microwave oven (MLS-UltraWave Thermo-Scientific). The sieved soils were
135 deposited on scotch tape on an XRF sample holder before micro-XRF analysis.

136 **2) Soil pH**

137 The soil pH was determined according to the NF-ISO-10390:1994 standard³⁸. The measurements
138 were carried out in a 5 mL soil suspension obtained with 1 g of 2 mm sieved soil and ultrapure water

139 (18.2 M Ω ·cm). The suspension was stirred for 5 min at 80 rpm on an IKA® 10-digital Roller Shaker
140 then left to settle for 2 h. A multimeter (Hanna Instruments HI-2550) was used for pH measurement.

141 **3) *In situ* chemical analysis for sample preselection:**

142 A handheld X-ray fluorescence spectroscope (XRF-Bruker Tracer®) was used on-site for fast non-
143 destructive analysis directly on the soil so as to directly determine the metal plume below the deposit
144 while optimizing the selected sample number (Figure S2).

145 **4) Chemical analysis**

146 The major elements (Mg, Al, Si, K, Ca, Fe) were analyzed using the inductively coupled plasma
147 atomic emission spectrometry (ICP-AES) method (ICP-Perkin-Elmer 4300 DV). Digested samples
148 were introduced with the fast autosampler ESI SC-4 DX-FAST. Inductively coupled plasma mass
149 spectrometry (ICP-MS) was used (Perkin-Elmer Nexion 300x quadrupole) to quantify minor and trace
150 elements (V, Mn, Zn, As, Sr, Ag, Sb, Cs, Ba, Tl, Pb). Soil samples were diluted prior to analysis to
151 avoid saturation of the instrument. Multi-element standards CCS4, CCS5 and CCS6 (Inorganic
152 Ventures, USA) diluted in 2% HNO₃ were used to obtain the ICP-MS calibration curves.

153 **5) Statistical analysis**

154 Statistical significance of differences between elemental concentrations of soils on top and the
155 bottom of the toposequence were assessed using the Mann-Whitney U-test. The tests were performed
156 using the Real-Statistics-Resource-Pack software package (Copyright (2013–2020) Charles Zaiontz.
157 www.real-statistics.com). Statistical significance was set at $p < 0.05$ for all tests.

158 **6) Mineralogical analysis**

159 Soil mineralogy was determined by X-ray diffraction (XRD) using an X'Pert-Pro PANalytical X-ray
160 diffractometer equipped with a cobalt anode ($\lambda = 1.79 \text{ \AA}$) and operating at 40 kV and 40 mA.

161 **7) Hyperspectral chemical mapping by X-ray fluorescence microscopy**

162 Hyperspectral chemical mapping was performed by X-ray fluorescence microscopy (micro-XRF)
163 with a micro-XRF (XGT-7000 Horiba) equipped with an Rh X-ray source (50 kV, 1 mA). This enabled
164 characterization of the spatial distribution of elements from Na to U and the identification of element
165 co-localizations. 10 and 100 μm X-ray spot sizes were used for soil samples. By combining K
166 ($11 < Z < 43$) and L ($Z > 43$) X-ray emission lines, all elements with $Z > 11$ could be detected with a
167 sensitivity ranging from about 50 mg/kg to a few % mass.

168 The Fiji version of ImageJ software was used for chemical image analysis³⁹. The co-localization
169 procedure was performed with the Coloc2-plugin (https://imagej.net/Coloc_2) based on the pixel
170 intensity correlation. Coloc2 calculates a variety of co-localization parameters such as the Pearson
171 coefficient and the Manders correlation. The background of each element channel was removed. The
172 Coloc2-plugin was implemented with bisection threshold regression on the entire image (128 x 128
173 px) or on selected regions of interest (ROI).

174 **8) X-ray absorption spectroscopy for Tl speciation analysis**

175 Thallium L_3 -edge XAS spectra were obtained on the FAME beamline (ESRF Synchrotron,
176 Grenoble, France) using a Si(220) monochromator. Freeze-dried or frozen-hydrated (-80°C) samples
177 were powdered at -80°C and analyzed at 8-10 K to avoid sample beam damage. Measurements were
178 performed in fluorescence mode with a 30-element Ge solid-state detector (SSD). A Gallium foil filter
179 was used to avoid detector saturation due to the X-ray fluorescence of the matrix mainly due to As
180 concentrations 10 times higher than the Tl concentration. On this beamline and using an SSD, XAS
181 spectra can be measured with a sensitivity range from about 10 mg/kg to a few % mass⁴⁰. Each final
182 spectrum was the average of at least five scans of different zones of the same sample, and the standard
183 deviation of these scans was used to assess the XAS signal variability. Energy calibration was
184 performed using a metallic Se reference foil recorded simultaneously with the samples for which the

185 K-edge was at the same energy level as the Tl L_3 edge. The absorption edge was defined at 12658 eV.
186 Data reduction was performed using Athena software⁴¹ and the MAX package⁴². Spectra were scanned
187 from 12600 to 13200 eV. This energy range was limited by the presence of other elements such as Pb
188 (L_3 edge at 13035 eV). XAS analysis was thus limited to the study of the X-ray absorption near edge
189 structure (XANES) and the lower energy zone of extended X-ray absorption fine structures (EXAFS),
190 thereby providing information on the valence state, the site geometry of Tl, as well as the nature of the
191 ligands.

192 Seventeen XAS spectra composed the spectral library of reference compounds (Table S1) used for
193 principal component analysis (PCA) and linear combination fitting (LCF). PCA is a multivariate
194 analysis technique that can be used to determine the lower number of independent components
195 (principal components) needed to reproduce the experimental spectra dataset. The LCF sensitivity
196 using reference compounds ranged from 5 to 20%⁴³. PCA analysis of the soil spectra revealed that the
197 variance could be explained by a maximum of three components (Figure S3). A maximum of three
198 spectra from the reference database could therefore be used to fit the Jas Roux sample spectra via LCF.
199 During the fitting, the weight of each reference compound was restricted to between 0 and 1 without
200 forcing the sum to equal 100%.

201 One reference compound was used at the start of the fitting procedures and additional compounds
202 were added only if the fit residue was improved by >30% and was higher than the spectrum variability
203 calculated from the different scans per sample. One example is outlined in Figure S5. The relative
204 goodness-of-fit between the data and the model was represented by the residual factor (R-factor).

205 **9) Sensitivity of the XAS reference compound database to the Tl speciation**

206 The sensitivity of XAS in differentiating a high variety of Tl-species was investigated. The details
207 are given in the Supporting Information. In summary, the spectra of the 17 reference compounds
208 (Figure 4A & B) enabled us to distinguish Tl(I) and Tl(III) compounds via the position of the main

209 absorption line (Figure 4A), as well as a pre-edge feature at 12658.8 eV in the case of Tl(III). The
210 spectra of all Tl(I)-reference compounds also differed in terms of their oscillation amplitudes (high
211 amplitude for Tl(I)-jarosite, Tl_2SO_4 and Tl^+ adsorbed on illite and low for the others (Figure 4B)) and
212 the slight differences in their white line positions. The spectrum of Tl(I) adsorbed on illite exhibited a
213 positive oscillation at 12720 eV (Figure 4B), while the oscillations were negative for the others.
214

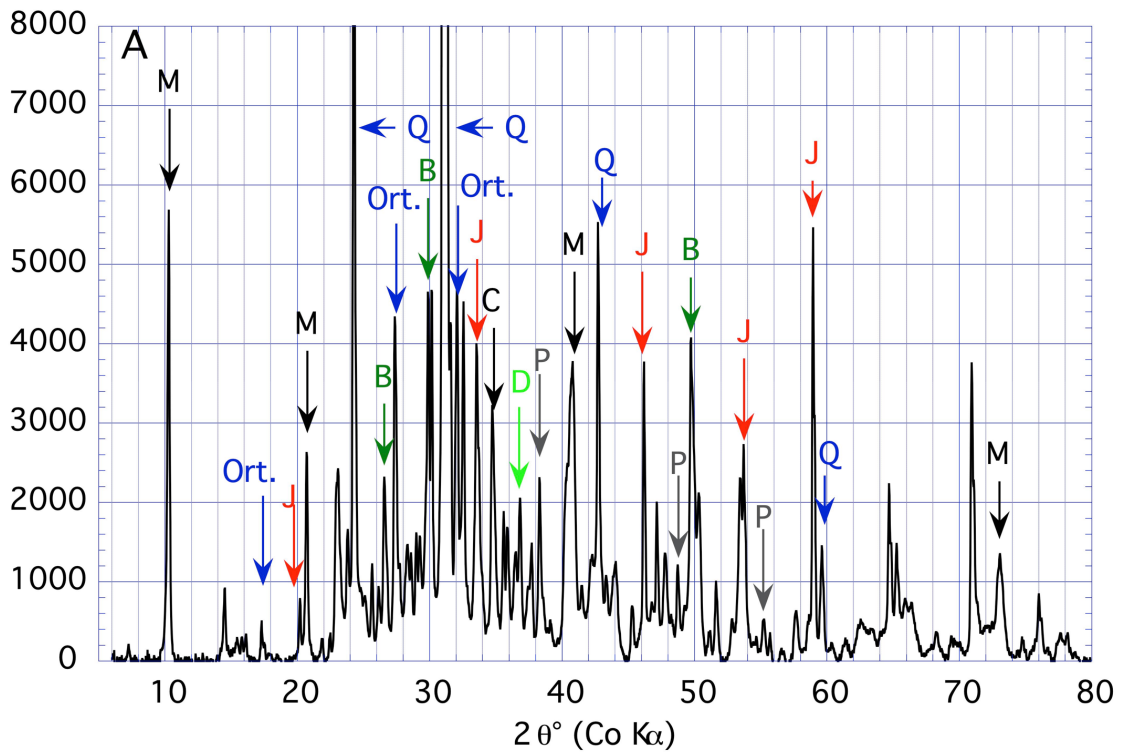
215 2) RESULTS AND DISCUSSION

216 1) Physicochemical gradient in the soil toposequence below the outcrop

217 The XRD soil mineralogical analysis findings at the top of the toposequence (Figure 2A) indicated the
218 presence of abundant non-site-specific silicate minerals such as muscovite, orthoclase and quartz, as
219 well as carbonate minerals such as calcite and dolomite. XRD also revealed the original features of the
220 site, including the presence of soilborne barite (barium sulfate), jarosite (iron sulfate) and pyrite (iron
221 sulfide) while confirming the results of Fehlauser et al.³⁵ concerning the top of the toposequence. Iron
222 sulfides were highly abundant in the Jas Roux deposit¹¹ and were found to have been transferred to the
223 soil below the outcrop. Jarosite was detected in soils. Its presence in the soil samples could be
224 explained by pyrite oxidation in the soils or gravity erosion from the outcrop. Mineralogical analysis
225 of soils sampled at the bottom of the toposequence revealed a similar mineral assembly pattern (Figure
226 2B). The presence of primary sulfide mineral confirmed the transfer of minerals via falling rocky debris
227 due to mechanical erosion. At this stage, XRD only provided qualitative information regarding the
228 presence of mineral phases—no quantitative information was obtained for comparison. Other
229 parameters such as the pH and chemical composition revealed differences between soils at the top and
230 bottom of the toposequence.

231 The soil pH at the top of the toposequence was 6.5 ± 0.20 ($n=5$), which was similar to the values
232 reported by Fehlauser et al.³⁵ (6.8 ± 0.3 ($n=10$)), while the pH was lower at the bottom (5.6 ± 0.18 ; $n=5$).
233 There could have been many possible causes for the lower pH at the bottom, but they could not be
234 determined at this stage. For example, sulfide oxidation undoubtedly causes soil acidification, yet the
235 presence of carbonate minerals such as calcite could partially offset this phenomenon. The decreased
236 calcite content at the bottom (XRD and decreased Ca level (Table 1) could thus explain why the pH
237 was significantly more acidic. Other phenomena, such as micro-organism activity, could also partly
238 contribute to the pH variation from the top to the bottom of the toposequence.)

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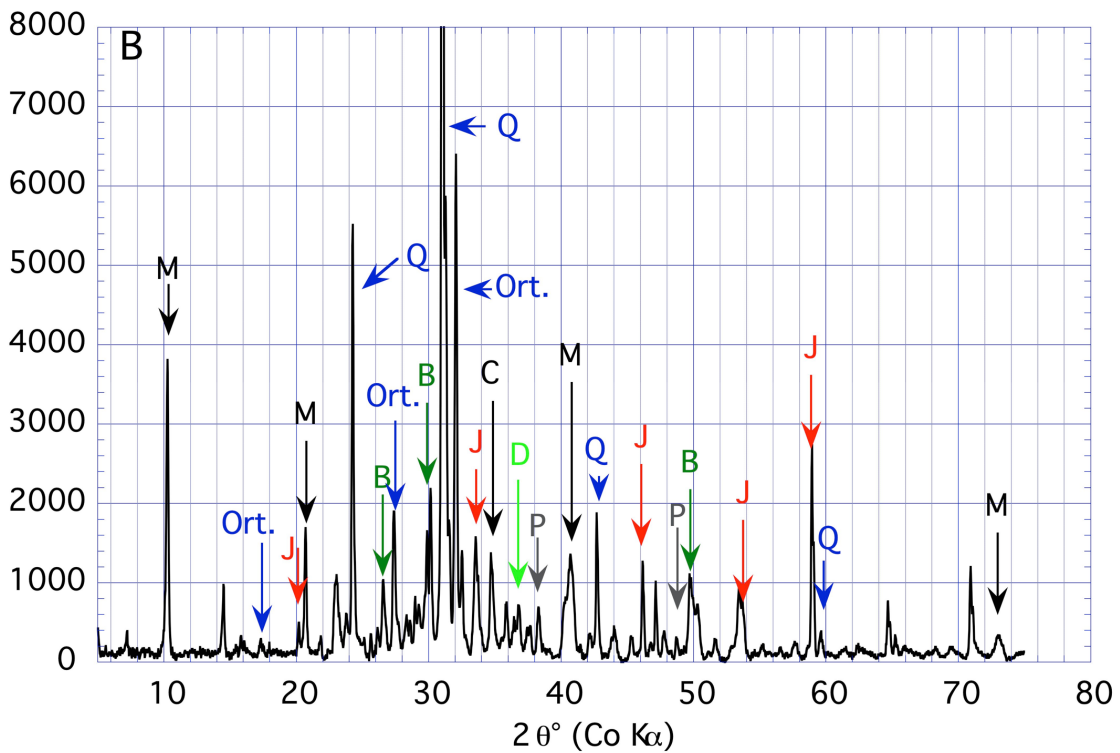


Figure 2: X-ray diffractograms of the soil at: A) the top and B) the bottom of the selected areas below the outcrop (Q=quartz, Ort=orthoclase, M=muscovite, B=barite P=pyrite J=jarosite, C=calcite, D=dolomite). Intensity: arbitrary unit

241 The chemical composition (Table 1) of the soils determined by ICP-AES and ICP-MS also, for the
242 first time, highlighted significant quantitative changes in major and minor elements along the
243 toposequence. While Mg, Al, Si, K, Ca, V, Mn and Cs concentrations did not statistically vary, the Fe,
244 Zn, As, Sr, Ag, Sb, Ba, Tl and Pb concentrations markedly decreased as function of the distance from
245 the source (outcrop). Note that the presence of different plant species did not affect the soil chemical
246 composition at the top or bottom of the toposequence. The decreased Fe concentration from 86
247 $005 \pm 26\,385 \text{ mg.kg}^{-1}$ at the top to $42\,400 \pm 8\,720 \text{ mg.kg}^{-1}$ at the bottom, and the decreased Ba
248 concentration from $53\,020 \pm 23\,190 \text{ mg.kg}^{-1}$ at the top to $24\,080 \pm 22\,090 \text{ mg.kg}^{-1}$ at the bottom indicated
249 a lower amount of primary minerals (pyrite and barite) from the outcrop source at the bottom of the
250 toposequence

251 In the case of Tl, a significant decrease of the concentration of this element was documented for the
252 first time in soils from the top ($565 \pm 195 \text{ mg.kg}^{-1}$) to the bottom ($182 \pm 49 \text{ mg.kg}^{-1}$) of the toposequence.
253 This decrease could have been related to the reduction in the amount of primary minerals from the
254 source, as suggested by the decreased Fe and Ba concentrations, but it could also have been related to
255 higher weathering and leaching of soil minerals and to ongoing Tl chemical and mineralogical
256 transformation. The soil Tl concentration range was high compared to the average crustal abundance
257 ($< 0.8 \text{ mg.kg}^{-1}$). These chemical analyses confirmed the results obtained by Fehlauser et al.³⁵ at the top
258 of the toposequence. Compared to other natural analogue sites, the Tl concentration was lower than at
259 the Erzmetz site, where it reached up 6000 mg.kg^{-1} ⁵, and lower than in soils below the abandoned
260 Allchar mine, where it reached $20\,000 \text{ mg.kg}^{-1}$ for an average of 660 mg.kg^{-1} in 134 soils⁷.

261

262

263

264

Table 1: Chemical composition (\pm standard deviation) of soils at the top and bottom of the study zone below the outcrop. (* significant differences between top and bottom)

265

mg.kg ⁻¹	Soils at the top) (n=14)	Soils at the bottom (n=6)
Mg	11 940 \pm 16 550	6 070 \pm 3 570
Al	32 929 \pm 8 784	33 941 \pm 4 549
Si	132 339 \pm 24 451	118 043 \pm 22 279
K	33 445 \pm 3 380	30 140 \pm 7 510
Ca	140 130 \pm 185 201	36 542 \pm 76 029
V	100 \pm 14	94.4 \pm 20
Mn	2 250 \pm 1 140	2 410 \pm 645
Fe*	*86 005 \pm 26 385	42 400 \pm 8 720
Zn*	*832 \pm 327	422 \pm 59
As*	*3 810 \pm 1 670	816 \pm 243
Sr*	*949 \pm 550	390 \pm 311
Ag*	*20 \pm 13	4.2 \pm 1.4
Sb*	*2 160 \pm 1 000	361 \pm 168
Cs	14.4 \pm 5.0	14.5 \pm 2.9
Ba*	*53 020 \pm 23 190	24 080 \pm 22 090
Tl*	*565 \pm 195 (max 702)	182 \pm 49 (max 280)
Pb*	*385 \pm 190	137 \pm 19

266

267 2) Qualitative identification of Tl-bearing minerals in soils

268 Although jarosite was a clear Tl-bearing phase candidate, XRD failed to identify minerals containing
 269 Tl in soils. This suggests that Tl-minerals were present in scant amounts, with an ill-ordered structure
 270 or, as we assumed, that Tl speciation was more complex (i.e. Tl(I) substitution in minerals). Figure 3
 271 presents a micro-XRF chemical image of a 2.56x2.56 mm² zone of one soil from the top zone, which
 272 illustrates the co-localization of Tl with other elements and possible Tl-bearing phases.

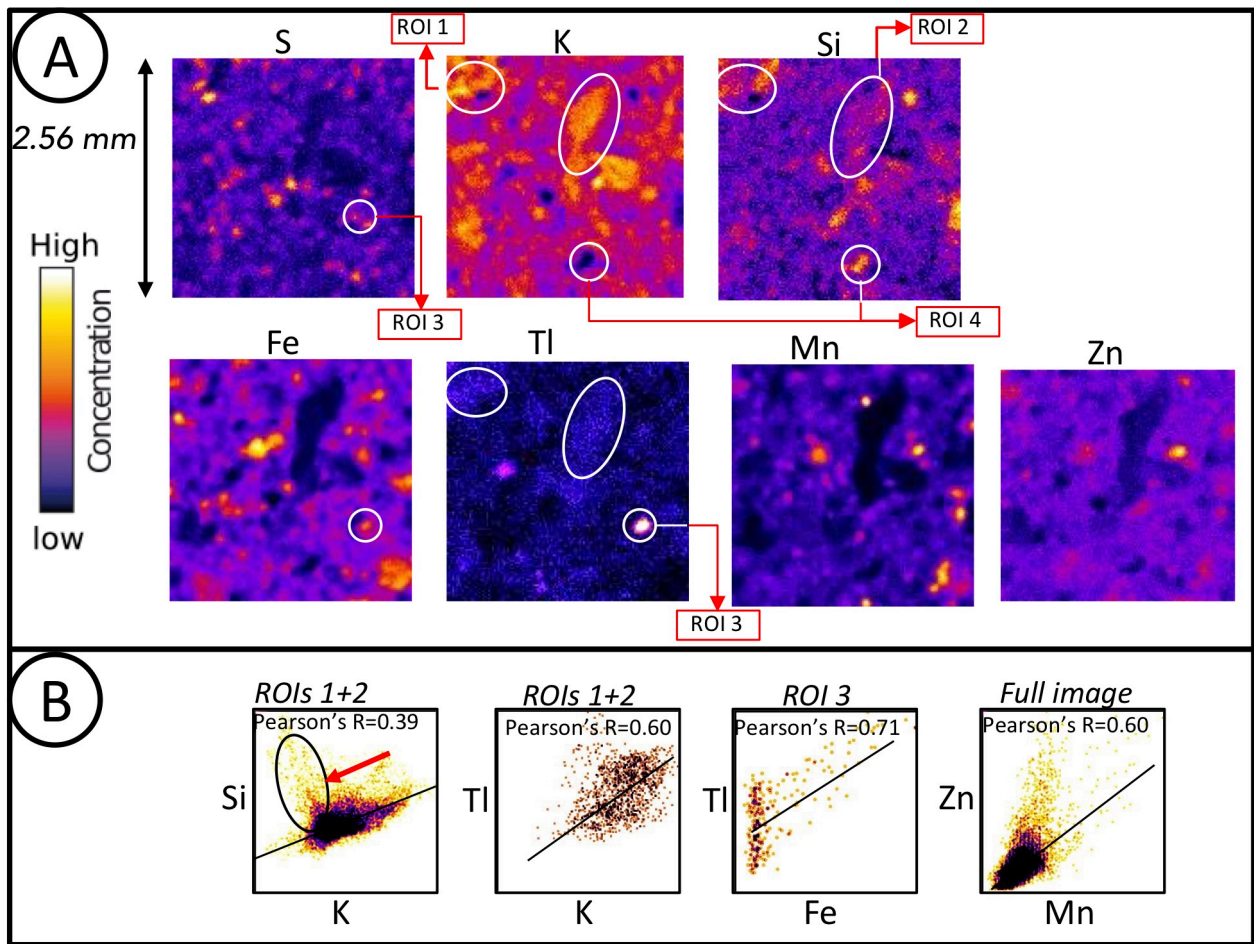


Figure 3: A) micro-XRF elemental maps of a soil from the top of the toposequence. The map size is $2.56 \times 2.56 \text{ mm}^2$ ($20 \mu\text{m}$ pixel size). Several element colocalization zones (regions of interest [ROI]) are highlighted: ROI 1&2 for K, Si and Tl, ROI 3 for S, Fe and Tl, ROI 4 for Si. B) 2D intensity diagram with co-localization Pearson's coefficient obtained using the Coloc2-plugin on selected ROIs and the full image for the Zn-Mn 2D diagram.

273

274 The K and Si co-localization pattern (ROIs 1&2, Figure 3A) was consistent with the presence of
 275 muscovite, a phyllosilicate mineral identified by XRD. The Pearson's coefficient (Figure 3B) was a
 276 bit low and may have been due to the noise level on the Si image and the presence of an Si-rich zone
 277 not correlated with K such as quartz revealed by XRD (e.g. ROI 4, Figure 3A). The Tl elemental map
 278 suggests a relatively high XRF intensity associated with the muscovite zones (K and Si co-
 279 localization). The Tl-K intensity diagram of the K-rich ROIs 1&3 and the high Pearson's coefficient
 280 confirmed the co-localization of Tl with muscovite (Figure 3B). It has been shown that Tl can be
 281 adsorbed to illite⁶, a phyllosilicate mineral very similar to muscovite. Besides, the Tl elemental map
 282 revealed a highly heterogeneous distribution and a hotspot in a Fe- and S-rich zone (ROI 3). This could

283 have been related to the presence of iron sulfide or iron sulfate minerals since XRF is not sensitive to
284 the redox state of elements. Although Tl-Fe sulfide minerals are known to exist (picotpaulite (TlFe_2S_3),
285 raguinite (TlFeS), etc.), none of them were identified at the Jas Roux deposit. However, using an
286 electron microprobe, Johan and Mantiene¹¹ found that pyrite contained 0.07% Tl. Jarosite may also
287 contain Tl. The formation of dorallcharite ($\text{TlFe}_3(\text{SO}_4)_2(\text{OH})_6$) was confirmed by Favreau et al³¹ in
288 altered zones of the outcrop, and Tl-rich jarosite formed via the substitution of K by Tl⁴⁴⁻⁴⁶ has been
289 reported. This may also be the case in soils at the Jas Roux site, as confirmed below.

290 Similarities in the Mn and Zn maps were confirmed by the 2D intensity diagram and the high Pearson
291 coefficient. The high correlation could be attributed to the presence of phyllosulfate minerals such
292 as birnessite (δMnO_2) or chalcophanite ($\text{ZnMn}_3\text{O}_7 \cdot 3\text{H}_2\text{O}$). Even if not detected via XRD, such minerals
293 are ubiquitous in soils⁴⁷ and can control the redox state of other metals and metalloids⁴⁸ such as Fe and
294 Tl as proposed below.

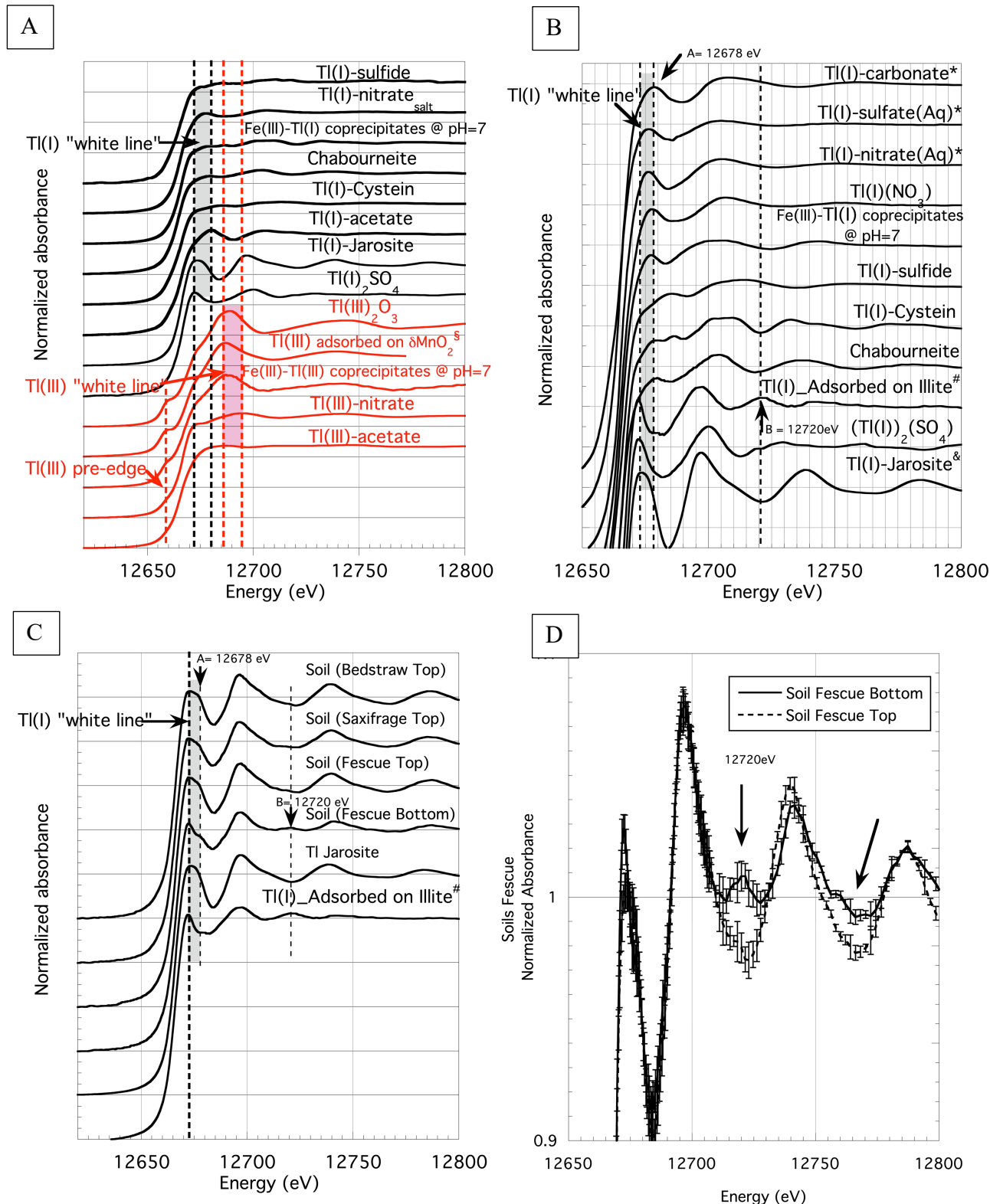
295 Micro-XRF only provided qualitative information due to the high spatial heterogeneity, and the
296 previous chemical map is only presented to suggest possible Tl-bearing phases. The following XAS
297 analyses further identified and quantified the Tl bearing phases and speciation.

298 **3) Tl(I) -jarosite/dorallcharite as major soilborne Tl-bearing minerals**

299 XAS spectra of the soil samples all exhibited a white line at 12672.5 eV, in the Tl(I) energy range
300 (Figure 4C). A feature/shoulder at 12678 eV (arrow A, Figure 4C) was also specific to the soil spectra.
301 The spectra of the three soils at the top of the toposequence appeared to be very similar, whereas
302 significant differences were noted in soils at the bottom, as shown in Figure 4C and 4D, especially at
303 12720eV.

304 Qualitatively the XAS spectra of the four soils highly resembled that of Tl-jarosite and differed
305 markedly from Tl sulfide primary minerals such as chabourneite or TlS.

306



307

308

309 **Figure 4:** XAS spectra of: A) comparison between Tl¹⁺ (black curves) and Tl³⁺ (red curves) reference
 310 compounds; B) full list of Tl¹⁺ reference compounds for comparison; C) soil samples. Reference spectra
 311 from §⁴⁹, *⁵⁰, #⁶, &⁵ D) comparison of XAS spectra of bottom samples, including the variability level
 312 (error bars).

313 LCF was used to estimate the amount of Tl(I)-jarosite, but this technique, although efficient, has
 314 some limitations. Beyond the intrinsic sensitivity of the technique, i.e. ± 5 to 20%⁴³ in some cases, it

315 was impossible to choose among several fits because no significant differences in their residues were
316 noted. In the case of saxifrage and fescue soils, two fits were not distinguishable and are therefore just
317 presented as potential results. We found that Tl(I)-jarosite accounted for $93\% \pm 10\%$, $86-89\% \pm 10\%$
318 and $67-82\% \pm 10\%$ of Tl speciation (Figures 5 & 6, Table S2) in the soil in the vicinity of bedstraw,
319 saxifrage and fescue plants, respectively, at the top of the toposequence. Tl-jarosite was previously
320 detected in the most altered zones of the outcrop³¹ and our results corroborated its presence in soils
321 underlying the deposit. Other authors detected jarosite in soils with pH ranging from 6.2 to 7.2⁵, which
322 is similar to the pH of the soils sampled at Jas Roux. Thermodynamic constants suggest that
323 dorallcharite and/or Tl-jarosite are more stable at $\text{pH} > 5.5$ compared to other Tl sulfate minerals such
324 as lanmuchangite²⁶. The very high fraction of Tl found to be entrapped in Tl-jarosite therefore suggests
325 that in the vicinity of the sulfide deposit primary Tl-sulfide mineral oxidation would lead to the
326 formation of stable Tl-sulfate, in agreement with previous findings.

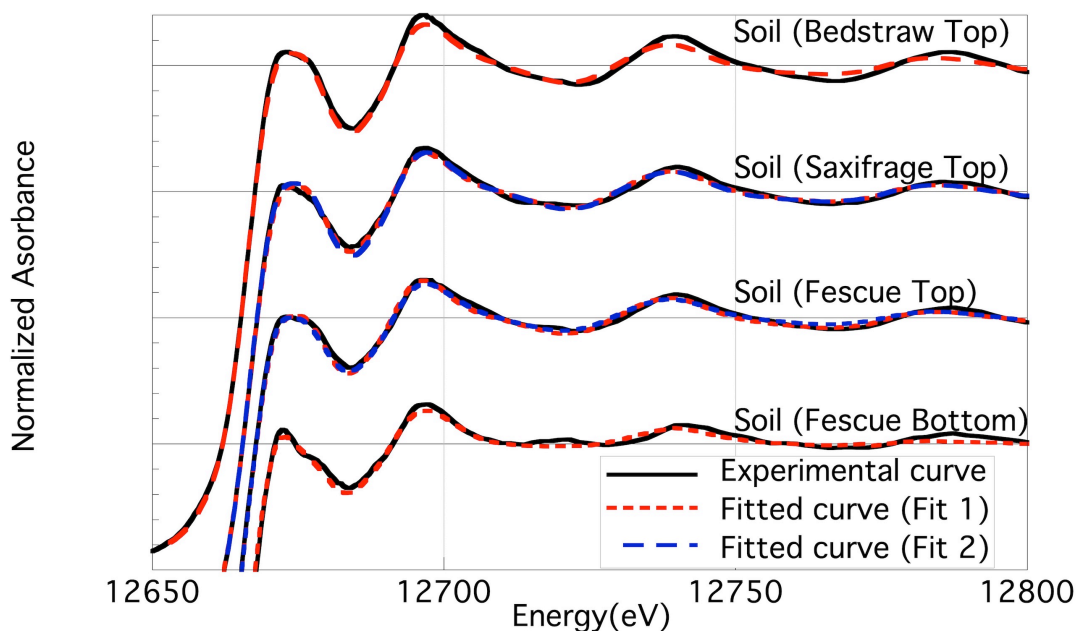
327 **4) Evidence of Tl(I) oxidation in Jas Roux soils**

328 For the fit of the soil in the vicinity of bedstraw plants at the top of the sequence, the use of a second
329 reference compound (7% of Tl(III) /Fe(III) coprecipitated at $\text{pH}=7$) decreased the residue by 40%
330 (Table S2) and the fit improvement was significantly higher than the variability of the soil XAS spectra
331 in the zone 12680-12700 eV (Figure S4). This strongly suggests the presence of Tl(III).

332 For the two other soils collected at the top (soils near fescue and saxifrage plants), the presence of
333 Tl-jarosite was $> 67\%$, thereby highlighting that possible other phases could exist, such as Tl_2O_3 and/or
334 $\text{Tl(I)(NO}_3\text{)}$ solid salt. Adding a second reference compound to Tl-jarosite decreased the residue.
335 However, the mathematical solutions were not unique since the absolute differences between the two
336 calculated spectra using two reference compounds, i.e. Fits 1 and 2 (Figures 5 & 6), were lower than
337 the XAS signal variability. In topsoil in the vicinity of saxifrage plants, the two indistinguishable fits
338 includes Tl(III) reference compounds, thereby strongly suggesting the presence of this element. The

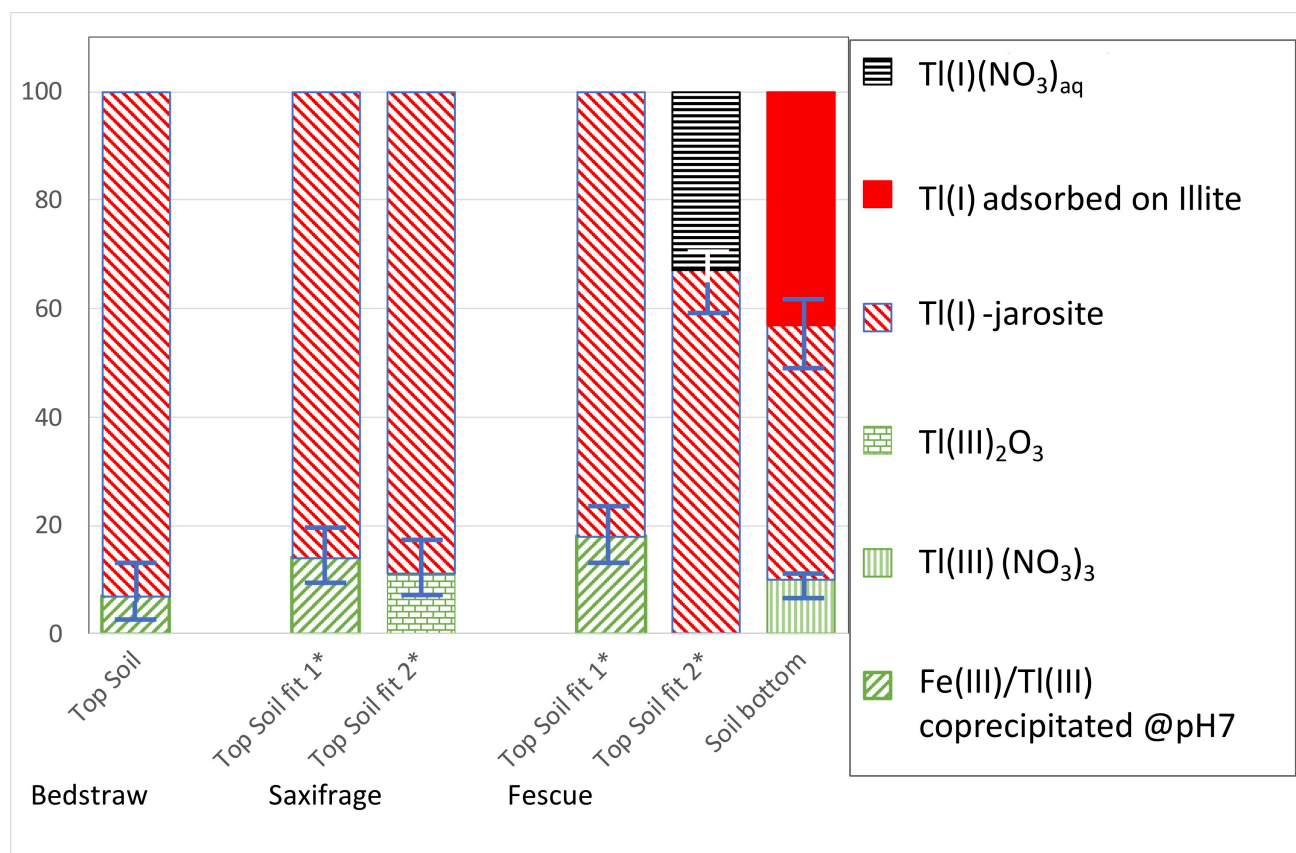
339 Tl(III) presence could not be confirmed for the fescue soil since only one of the two indistinguishable
340 fits included one Tl(III) reference compound (Table S2). For the soil at the bottom, the fit using three
341 reference compounds (Tl-jarosite 47%, Tl adsorbed on illite 43% and Tl(III)(NO₃)₃ 10%) also
342 suggested the presence of Tl(III) (Figure 6).

343 Although not confirmed for all of the soil samples, Tl(III) was likely present in the soils below the
344 deposit. Jia et al.⁵¹ suggested the possible oxidation of Tl(I) to Tl(III) by MnO₂ in soils, as noted in
345 synthetic systems. Indeed, Bidoglio et al. observed surface precipitation of Tl₂O₃ resulting from Tl(I)
346 adsorption on δ-MnO₂(s) and oxidation at the mineral surface. In a soil fraction from the Erzmatt site
347 (Switzerland), Voegelin et al.⁵ observed that up to 80% of Tl was absorbed as Tl(III) on birnessite and
348 Tl₂O₃. The presence of Tl(III) in the soils below the Jas Roux deposit might be explained by the
349 presence of Mn minerals, as revealed by the micro-XRF map (Figure 3), thereby causing Tl oxidation.



350 **Figure 5:** XAS spectra of the soils. Dotted lines represent reconstructed spectra using LCF (red = fit 1, blue = fit 2).

351



352 **Figure 6:** Quantitative analysis of XAS data using LCF. *= fits with similar statistical significance levels.

353 **5) TI(I)- silicate as a possible consequence of a TI-jarosite decrease at the bottom of the**
 354 **toposequence.**

355 One of the main interests of the Jas Roux site is that the TI content in soils decreased from the top
 356 to the bottom of the toposequence. With distance from the source along the toposequence, oxidation
 357 of primary sulfide minerals may no longer be the only mechanism and other geochemical
 358 transformations may take place. This could therefore enhance the overall understanding of the long-
 359 term transfer and transformation of TI at polluted sites.

360 The XAS spectrum fit obtained for soil at the bottom of the toposequence, suggested that TI(I)-
 361 jarosite was main component (47%±10%), but its amount was significantly lower than that noted in
 362 soils at the top. This difference could be explained by partial dissolution of TI(I)-jarosite and the
 363 formation of other secondary minerals such as FeOOH amorphous phases. Released TI may either
 364 coprecipitate with FeOOH or adsorb at the surface of phyllosilicates such as muscovite or illite. The
 365 XAS fit of the spectrum favored the second hypothesis (Figure 6), with 43% (±10%) of TI being

366 adsorbed on phyllosilicate. The presence of Tl adsorbed on phyllosilicate was also noted in soils
367 sampled at the Erzmatt site⁵.

368 **6) Tl long-term transfer and transformation in soils**

369 Our results provide valuable information indicating possible long-term Tl speciation changes in
370 polluted areas. The unique feature of the Jas Roux site is that soils can be sampled at various distances
371 from the Tl source in the outcrop. The soilborne primary sulfide and secondary sulphate contents were
372 found to decrease with the distance from the outcrop. Indeed, the amount of sulfide minerals decreased
373 from the top to the bottom of the toposequence, as suggested by the decrease in Fe (a major pyrite
374 component), Zn (the main component of sphalerite) and also Pb and Ag (which were present in the
375 form of sulfosalts in the outcrop). Note also that secondary sulfate mineral contents might have been
376 lower at the bottom, as suggested by the decrease in Ba, which was mainly present in the form of Ba-
377 sulfate minerals. Moreover, the Tl speciation pattern evolved from Tl-jarosite being a major
378 component of soils at the top of the toposequence to a mix of Tl-jarosite and Tl adsorbed on
379 phyllosilicate at the bottom. Tl(III) was also detected but there was no clearcut specific top-down
380 evolution pattern.

381

382 **CONCLUSION**

383 The Tl speciation pattern in soils underlying the Jas Roux deposit was assessed for the first time.
384 The results revealed that the Tl and Ba concentrations in the soils was high compared average soil
385 values, as described by Kabata-Pendias². A chemical gradient was found in soils from the top to the
386 bottom of the studied zones below the Jas Roux outcrop. Using XAS, Tl was mainly found at the top
387 of the toposequence in secondary minerals formed by oxidation and dissolution of Tl-rich sulfide
388 minerals and reprecipitation of Tl(I)-jarosite, i.e. a stable Tl iron sulfate. The Tl(I)-jarosite content
389 decreased at the bottom of the toposequence, with the possible release of Tl(I) and its adsorption at the

390 phyllosilicate surface. Although Tl(I)-jarosite was dominant, a decrease of sulfate at the bottom of the
391 toposequence might have led to Tl-jarosite dissolution, a pattern that has not yet been clearly
392 documented at contaminated sites. Tl adsorption on phyllosilicate that we identified at the Jas Roux
393 site may represent another possible means of long-term Tl retention in soils. Note also that a fraction
394 of Tl (7-18%) could exist in its Tl(III) oxidized form. Mn minerals may be involved in Tl oxidation,
395 although there was no clear evidence of this at the Jas Roux site.

396
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402 chabourneite compounds and expertise on the Jas Roux site. The Jas Roux site is located in Ecrins
403 National Park. Sample collection is strictly forbidden, except in cases of special waivers, which must
404 be authorized in advance by the park administration. Any offender is liable to serious penalties.

405 **CORRESPONDING AUTHOR**

406 Jérôme Rose

407 CEREGE, CNRS, Aix-Marseille Univ, IRD, INRAE

408 Avenue Louis Philibert, BP-80, 13545 Aix-en-Provence, cedex 4, France

409 rose@cerege.fr

410 **Author Contributions**

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580 **Supporting information**

581 Table S1 lists all the reference compounds used in XAS analysis. Table S2 details the quantitative
582 parameters used in EXAFS spectra modeling, illustrated in figure 6. Figure S1 shows the rock outcrop
583 and its various oxidized and slightly weathered zones. Figure S2 shows X-ray fluorescence spectra
584 acquired on site using a portable spectrometer, illustrating the differences between the weathered zones
585 of the outcrop and the underlying soils. Figure S3 shows the results of the statistical analysis of the
586 spectra, which indicates the number of spectra that can be used in the linear combination analysis.
587 Figure S4 shows the difference between two XAS models and the signal-to-noise level.