

1 **Textural and trace element evolution of pyrite during greenschist facies metamorphic**
2 **recrystallization in the southern Apuan Alps (Tuscany, Italy): initiation of Tl-rich**
3 **sulfosalt melt formation**

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9
10 **Abstract**

11
12 Several small pyrite ± baryte ± iron oxide orebodies (Buca della Vena, Canale della Radice,
13 Fornovolasco, Monte Arsiccio and Pollone) are hosted in the metamorphic rocks of the southern Apuan
14 Alps, northern Tuscany, Italy. These deposits are exceptionally Tl-rich, expressed in part by
15 assemblages comprising rare Tl-sulfosalts. Using a variety of techniques including laser ablation
16 inductively-coupled plasma mass spectrometry (LA-ICP-MS) on fifty-four samples, the textural and
17 trace element evolution of pyrite during greenschist facies metamorphism has been described. Five
18 generations of pyrite have been recognised (py1-py5). Py1 and py2 (framboidal and colloform pyrite,
19 respectively) likely crystallized in the sedimentary package, incorporating trace elements from
20 surrounding water and sediments, as well as from circulating low-temperature hydrothermal fluids. Py3
21 forms fine-grained disseminations often aligned with the metamorphic fabric and likely formed during
22 the earliest stages of deformation associated with metamorphism. Py4 forms coarse, euhedral,
23 inclusion-rich aggregates and likely formed as previous pyrite generations began to recrystallize. Py5
24 is typically coarse, relatively 'clean' and often euhedral. It is interpreted to be the end-product of pyrite
25 recrystallization, with grain size increasing and micro-inclusions being expelled late on the prograde
26 path, then granoblastic annealed textures forming during retrograde cooling. Pyrite (especially primary

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27 pyrites; py1 and py2) is particularly rich in As (up to 17,400 ppm), Sb (up to 5,100 ppm) and Tl (up to
28 4,200 ppm), while Ni, Pb and Mn may be present above 1,000 ppm, and Hg, Co, Cu, Zn, Mo, Bi and
29 Ag may all be present above 100 ppm. Some trace elements, particularly As, Ni and Co, are commonly
30 zoned in late metamorphic pyrite overgrowths. The incorporation of many trace elements into pyrite
31 seems to have been facilitated by the presence of Sb in a similar way that As generally facilitates Au
32 incorporation. Concentrations of most trace elements decrease from py3 to py4 at Fornovolasco and
33 Monte Arsiccio, while in the other deposits the opposite trend is observed. This is interpreted to be due
34 to differing availabilities of elements in the environment of recrystallizing pyrite on the prograde path.
35 Concentrations of most trace elements drop significantly from py4 to py5, where complete
36 recrystallization of pyrite liberates a large proportion of As, Sb, Tl, Pb, Hg, Cu, Zn, Ag and Mn, likely
37 during retrograde cooling and annealing. The release of these elements from pyrite during metamorphic
38 recrystallization has directly facilitated the formation of late-stage sulfosalts, especially at Monte
39 Arsiccio, where textural evidence suggests sulfosalt assemblages intimately associated with py5 were
40 mobilised as melts during greenschist facies metamorphism. At Monte Arsiccio, around 75 % of Tl
41 hosted in early recrystallized pyrite is released upon complete recrystallization. As such, mass balance
42 calculations show that all Tl contained in Tl-sulfosalts could be supplied from locally recrystallizing
43 pyrite, and that in total, more than 250 tons of Tl could potentially have been liberated from the pyrite
44 orebody at Monte Arsiccio during metamorphism. This study highlights the significant quantities of Tl
45 and other metals that may be hosted in pyrite, and also the potential role that metamorphic
46 recrystallization may play in mobilising and (re)-concentrating (or indeed dispersing) metals in a pyrite-
47 dominant ore system.

48

49 **Key words**

50 Pyrite evolution; recrystallization; trace element; thallium; sulfosalt; low-temperature melt

51

52 **1. Introduction**

53

54 The southern Apuan Alps, northern Tuscany, Italy, host a number of small pyrite ± baryte ±
55 iron oxide orebodies that have been exploited since at least the Middle Ages, with mining activity
56 ceasing at the end of the 20th century. Although of little current economic significance, these deposits
57 have been persistently studied from a mineralogical perspective for over two centuries since they host
58 many rare and well crystallized mineral species. More than 270 different minerals have been identified
59 so far in this area, approximately 100 belonging to the sulfide and sulfosalt classes. Significantly, among
60 the 32 new mineral species that have been described for the first time from the hydrothermal ores of the
61 Apuan Alps, 21 are sulfosalts.

62 Amongst the new discoveries are a number of Tl-sulfosalts that have been identified from the
63 Sant'Olga tunnel at the Monte Arsiccio mine, e.g., boscardinite (Orlandi et al., 2012), protochabournéite
64 (Orlandi et al., 2013) and arsiccioite (Biagioni et al., 2014). Assemblages of Tl-Hg-As-Sb-(Ag,Cu)-Pb
65 sulfosalts from Monte Arsiccio have also been recognised to have been mobilised as melts during
66 regional greenschist facies metamorphism; amongst the lowest temperature sulfide melts documented
67 on Earth (Biagioni et al., 2013). Such occurrences reflect the recently recognised anomalous Tl-rich
68 nature of Monte Arsiccio and the other Apuan Alps pyrite ores. Indeed, analyses of pyrite ores have
69 revealed up to 1,100 µg/g Tl, as well as high levels of As and Sb, indicating that pyrite is likely the
70 primary mineralogical host of Tl in Apuan Alps pyrite ± baryte ± iron oxide ores (D'Orazio et al., 2017).

71 Pyrite is the most common sulfide mineral and is ubiquitous in many hydrothermal ore deposits.
72 Its ability to host a wide variety of trace elements and its refractory nature, which frequently records
73 and preserves the physiochemical changes occurring during ore deposit evolution, makes it a valuable
74 study target (e.g., Large et al., 2009; Hazarika et al., 2013; Reich et al., 2013; 2016; Franchini et al.,
75 2015). A large body of research has focussed on the role of pyrite in concentrating Au during ore deposit
76 evolution, leading to, for example, recognition of the difference between Au occurring in solid solution
77 or as micro- to nano-inclusions of Au bearing phases (e.g., Cook and Chryssoulis, 1990; Fleet and
78 Mumin, 1997; Ciobanu et al., 2012), an understanding of the role of As as a catalyst for Au
79 incorporation (Reich et al., 2005; Deditius et al., 2014) and the speciation of Au and As in pyrite (e.g.,
80 Simon et al., 1999a; Savage et al., 2000; Deditius et al., 2008).

81 Although it has been interpreted that the geochemistry and textures of the Apuan Alps pyrite
82 orebodies are related to multiple processes, including original syn-sedimentary textures overprinted by
83 features relating to metamorphic remobilisation and recrystallization (e.g., Cortecci et al., 1992;
84 Costagliola et al., 1998), this study presents the first detailed textural and *in situ* geochemical
85 investigation of the evolution of pyrite in the Apuan Alps. Moreover, the relationship between pyrite
86 and Tl-rich sulfosalt melt formation under greenschist facies metamorphism is shown for the first time.
87 The implication is that pyrite may play a significant role in the redistribution of Tl and other trace metals
88 during metamorphic recrystallization. Although pyrite has been shown to play an important role in the
89 mobilisation of Au during regional metamorphism (e.g., Large et al., 2007; 2012; Cook et al., 2009a;
90 Kampmann et al., 2018), its role with respect to other metals has been less well documented until now.

91

92 **2. Geological Setting of the Apuan Alps Pyrite Deposits**

93

94 The Apuan Alps represent a tectonic window where the most complete succession of northern
95 Apennine units is exposed. Several tectonic units were stacked during the Tertiary Apennine Orogeny
96 and the Apuan Alps tectonic window allows the study of the lowermost ones, i.e., the Apuane and
97 Massa units (e.g., Fellin et al., 2007 and references therein). These units were affected by regional
98 metamorphism under greenschist facies conditions in late Oligocene – early Miocene, with best peak
99 estimates at 350-450 °C and 0.3-0.4 GPa (e.g., Franceschelli et al., 2004; Fellin et al., 2007). Carmignani
100 and Kligfield (1990) proposed the occurrence of two main deformation phases, i.e. a main shortening
101 event (D1) at 27 Ma followed by an extensional phase (D2) between 14 and 12 Ma (Kligfield et al.,
102 1986; Carmignani and Kligfield, 1990).

103 Several types of ore deposit are hosted in the metamorphic units of the southern Apuan Alps
104 (e.g., Lattanzi et al., 1994). Pyrite ± baryte ± iron oxide ores are one of the most important and they
105 were exploited in several mines. From south-west to north-east, the main mining sites were the Pollone
106 mine, close to the village of Valdicastello Carducci (Benvenuti et al., 1990; Martarelli et al., 1995;
107 Costagliola et al., 1998; Biagioni et al., 2016); Monte Arsiccio mine, near Sant'Anna di Stazzema
108 (Costagliola et al., 1990); Canale della Radice, close to the small hamlets of Mulina di Stazzema and

109 Farnocchia (Carmignani et al., 1976; Garofalo, 1990); Buca della Vena mine, near the village of
110 Cardoso (Benvenuti et al., 1986); and Fornovolasco (Carmignani et al., 1976; Cioffi, 1991).

111 These deposits are distributed within a ~10 km long belt along a NE-SW orientation in the
112 southern Apuan Alps massif (Figure 1). As summarised in D’Orazio et al. (2017), these orebodies share
113 multiple similarities:

- 114 • they have lens-shaped morphologies, are stratiform and mostly conformable and they are
115 located at the boundary between a Paleozoic phyllitic complex and the Triassic
116 metadolostone belonging to the Grezzoni Formation;
- 117 • they have simple primary mineralogies: pyrite, baryte, hematite, magnetite;
- 118 • they typically display mineralogical zoning, with pyrite ± baryte mainly located within the
119 phyllitic rocks at the orebody footwall, and iron oxide ± baryte mainly occurring near the
120 contact with hanging wall metadolostone;
- 121 • the host Paleozoic phyllitic complex is characterized by the widespread occurrence of
122 tourmalinite rocks. Tourmalinite is also common in the Pb–Ag–Zn deposits from the
123 Bottino–Gallena area, approximately 2.5 km NW of Monte Arsiccio;
- 124 • they are spatially associated to Permian metarhyolite rocks (Vezzoni et al., in review);
- 125 • the orebodies show evidence of metamorphic deformation and recrystallization at various
126 scales. Late-stage discordant bodies are likely the products of metamorphic remobilization
127 from the main stratiform ores (e.g., Cortecchi et al. 1992).

128 There has been significant debate in the literature over the genesis of the Apuan Alps pyrite ±
129 baryte ± iron oxide deposits. Carmignani et al. (1972; 1976) proposed that they were carbonate
130 replacement ores formed from fluids associated with a supposed Tertiary granitic intrusion. However,
131 no evidence of such magmatism has been observed. Most authors have considered the deposits as
132 sedimentary exhalative in origin, forming before substantial reworking during the Tertiary Apennine
133 Orogeny. Bergmann (1969), suggested the ores were originally Permian-Triassic, Orberger et al. (1986)
134 supported a Silurian-Devonian date, while Lattanzi et al. (1994) favoured a Middle-Late Triassic age.

135 However, all these models are weakened by the lack of knowledge about the actual stratigraphic setting
136 of the phyllitic complex hosting the orebodies.

137 Few data are available on pyrite textures and geochemistry. Minguzzi and Talluri (1951) gave
138 some geochemical data on a sample of microcrystalline pyrite from the Monte Arsiccio mine, finding
139 Ni higher than Co and detecting high contents of Sb and Ag. Martarelli et al. (1995) gave geochemical
140 data of pyrite from the Pollone mine, indicating Pb as the most abundant trace element and Co/Ni ratios
141 ranging between 0.5 and 1.5, suggesting a sedimentary origin and a subsequent hydrothermal
142 recrystallization for pyrite ores. Similarly, Natale (1974), Benvenuti et al. (1986; 1990) and Costagliola
143 et al. (1990) recognised two pyrite generations in the Apuan Alps ores. The first generation consisted
144 of equant and anhedral crystals approximately 1–5 μm in size. This generation graded to second
145 generation pyrite characterized by cubic or pyritohedral crystals, 10–500 μm in size, with strongly
146 zoned and anhedral cores of low crystallinity, surrounded by wide homogeneous crystalline rims.
147 Framboidal pyrite aggregates were also recognised.

148

149 **3. Sample Suite and Methodology**

150

151 In total, fifty-four samples were collected for this study, almost all from abandoned pyrite \pm
152 baryte \pm iron oxide mines in the southern Apuan Alps. Eight samples came from Buca della Vena,
153 eleven from Canale della Radice, thirteen from Fornovolasco, fourteen from Monte Arsiccio, six from
154 Pollone and two from Sennari, a small occurrence of pyrite cropping out on the road from Sant'Anna
155 di Stazzema to Case Sennari. Samples were collected that showed a wide variety of pyrite textures.
156 Each hand specimen was cut and mounted in epoxy resin as a 1-inch block and polished to 0.3 μm . The
157 mineralogy and texture of each sample is summarised in Table 1 and was determined by reflected light
158 optical microscopy, micro-Raman spectroscopy, using a Jobin-Yvon Horiba XploRA Plus apparatus
159 with a solid-state laser ($\lambda = 532 \text{ nm}$), and scanning electron microscopy (SEM), using a Philips XL30
160 equipped with an EDAX DX4 energy-dispersive spectrometer.

161 Laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) spot analysis and
162 mapping was carried out using an ASI M-50-LR 193 nm Excimer laser attached to an Agilent 7700cx

163 Quadrupole inductively-coupled mass spectrometer (Adelaide Microscopy, University of Adelaide).
164 The sample was ablated in an atmosphere of ultra-high purity (UHP) He (0.7 L/min), and the resulting
165 aerosol was mixed with Ar (0.93 L/min) after leaving the ablation cell. The aerosol mix passed through
166 a pulse-homogenizing device (squid) preceding direct introduction into the torch. Throughout each LA-
167 ICP-MS session, the ICP-MS was calibrated regularly to ensure maximum sensitivity on the isotopes
168 of interest and minimal production of unwanted molecular species.

169 Before each LA-ICP-MS session, the laser beam energy output was adjusted to maintain a
170 fluence of 3 J/cm³ at the sample surface. The spot size was also varied between 19 and 29 μm depending
171 on the size of pyrite grain analysed. Laser repetition rate was maintained at 5 Hz. The total acquisition
172 time for each individual spot analysis was 70 s; 30 s of background measurement followed by 40 s of
173 sample ablation. A 20 s delay time was allowed after each spot analysis to ensure the ablation cell was
174 sufficiently washed-out and the gases had stabilized. The laser fired 5 pulses prior to this delay to clean
175 the sample surface.

176 During spot analysis and mapping the following suite of isotopes were measured: ²⁷Al, ²⁹Si,
177 ⁴³Ca, ⁴⁹Ti, ⁵³Cr, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co, ⁶⁰Ni, ⁶⁵Cu, ⁶⁶Zn, ⁶⁹Ga, ⁷¹Ga, ⁷⁵As, ⁷⁷Se, ⁹⁵Mo, ¹⁰⁷Ag, ¹¹¹Cd, ¹¹⁵In, ¹¹⁸Sn,
178 ¹²¹Sb, ¹²⁵Te, ¹³⁷Ba, ¹⁸²W, ¹⁹⁷Au, ²⁰²Hg, ²⁰⁵Tl, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb and ²⁰⁹Bi. During spot analysis, the dwell
179 time for most elements was set at 0.02 s, while Se, Au and Tl were set at 0.04 s, Co, Ni, Cu and Zn were
180 set at 0.01 s and Al, Si, Ca, Mn, Fe and Ba were set at 0.005 s. Aluminium, Si, Ca and Ba counts were
181 monitored to ensure gangue phases were not analysed; these elements were not quantified. During
182 mapping, the dwell time for most elements was 0.01 s, while Ti, Cr, Mn, Co, Ni, Cu, Zn, As, Ba, Pb
183 and Bi were set at 0.005 s and Al, Si, Ca and Fe were set at 0.002 s.

184 Two 51-μm analyses were made on the STDGL3 standard (Belousov et al., 2015) every 20
185 unknown analyses. Since STDGL3 does not contain Hg, concentrations of this element were determined
186 by making one 74-μm analysis on the MASS-1 sulfide reference material (formerly PS-1; Wilson et al.,
187 2002) every 80 unknown analyses. Using the standard analyses, instrument drift was monitored and a
188 linear drift correction was applied. All spot data calculations were carried out using Iolite (Paton et al.,
189 2011), an open source software package for ICP-MS data processing developed by the Melbourne
190 Isotope Group as an add-in for the data analysis program Igor by WaveMetrics. Iron was used as the

191 internal standard assuming stoichiometric pyrite. The potential error introduced from using the
192 stoichiometric value of Fe compared to the actual Fe value determined, for example, by electron
193 microprobe, has been shown to be within LA-ICP-MS instrumental error (George, 2017).

194 For elements hosted in solid solution in a mineral, LA-ICP-MS time-resolved down-hole
195 ablation profiles will appear smooth, whereas sub-surface inclusions usually show as peaks on such
196 profiles if they are sufficiently large (e.g., Cook et al., 2009b; George et al., 2015; 2018). Using Iolite,
197 the LA-ICP-MS down-hole ablation profile for each element in each analysis was carefully checked for
198 peaks that may indicate an inclusion was accidentally ablated. If an inclusion was recognized, the
199 analysis was discarded. In special cases where an inclusion was only ablated towards the end of a spot
200 analysis, the selected time interval for integration excluded the section of the downhole ablation profile
201 in which the inclusion was recognized. Analyses that were below the minimum detection limit (MDL)
202 for a given element were treated MDL/2 since this normally allows for a closer estimation of the actual
203 mean. In cases where all analyses of a certain element in a pyrite type were below the MDL, these
204 analyses were ignored and no mean was calculated.

205 While LA-ICP-MS spot analysis is generally adequate to establish trace element variation in a
206 sample (e.g., Cook et al., 2016), LA-ICP-MS mapping is desirable to truly quantify variation, especially
207 where systematic zonation is present. Twelve LA-ICP-MS element maps were made on areas of coarse
208 pyrite to give a visual representation of elemental distributions and concentrations. Mapping was
209 achieved by ablating multiple parallel adjacent trenches in a grid across the sample surface. A square
210 laser shape was used and the spot size was varied between 11 and 32 μm to provide adequate spatial
211 resolution for each map. The spacing between adjacent trenches was also modified to match the spot
212 size. Similarly, the laser beam scan speed was set to $X \mu\text{m/s}$, where X = the laser spot size. The repetition
213 rate was maintained at 10 Hz. A 10 s background measurement was acquired before the ablation of each
214 trench, followed by a 20 s delay after ablation. Each trench was cleaned prior to ablation by passing the
215 laser over the sample at a repetition rate such that each point on the map surface was cleaned with 4
216 laser pulses. Two 51- μm spot analyses were made on the STDGL3 standard at 10 Hz before and after
217 each map.

218 All LA-ICP-MS trace element maps were processed with Iolite. A linear drift correction was
219 applied to the unknown trench analyses based on the STDGL3 analyses acquired before and after a
220 mapping run. The average background intensity for each element was then subtracted from its
221 corresponding trench acquisition, and the resulting time-resolved linear intensities were compiled into
222 a two-dimensional image for each element. Iron was used as the internal standard to produce
223 quantitative maps.

224

225 **4. Results**

226

227 **4.1 Pyrite Textural Analysis**

228

229 Five different pyrite types (py1 – py5) have been recognized in samples from the Apuan Alps.
230 Py1 (Figure 2A) consists of very fine ($\sim 20\ \mu\text{m}$) framboids and are only preserved in two samples
231 (CDR4A and ARS17M). Py2 (preserved in samples FOR19, ARS9A and ARS9B) forms very coarse
232 colloform bands more than 2 mm thick and typically more than 5 mm in extent (Figure 2B and C). Py3
233 (Figure 2D) is slightly coarser than py1 ($\sim 100\ \mu\text{m}$) and is often disseminated in host rock and/or
234 aligned with the main metamorphic fabric. Habits vary from irregular shapes to euhedral crystals.
235 Importantly, py3 does not form aggregates. Py4 (Figure 2E and F) is between approximately 50 to 300
236 μm in size, is usually anhedral and forms aggregates (sometimes aggregates are elongated into bands)
237 characterized by abundant micro-inclusions. Py5 (Figure 3A, B and C) grains are usually more than 50
238 μm in size and are larger than 1 mm on occasions. They are well defined often rounded grains or with
239 euhedral boundaries. Py5 frequently forms relatively un-deformed granoblastic aggregates and is
240 occasionally aligned in bands. It contains far fewer micro-inclusions than py4. It is worth noting that
241 py4 and py5 represent endmembers on a textural continuum rather than wholly different pyrite types;
242 transitional textures are common (Figure 3D, E and F). Interestingly, the abundance of preserved pyrite
243 increases from py1 to py5 across the sample suite, i.e., py1 is the least preserved pyrite type while py5
244 is the most abundant type present in the Apuan Alps.

245 Much research has focussed on the formation mechanisms of both colloform and framboidal
246 pyrite types, both of which are considered primary precipitate textures (Barrie et al., 2009). Colloform
247 pyrite seems to be able to crystallize in a variety of different settings, and may form through biogenetic
248 aided processes, or inorganic processes (e.g., Gao et al., 2016 and references therein). Although
249 colloform pyrite is frequently formed in a sedimentary environment (e.g., Gao et al., 2017), it may also
250 crystallise from hydrothermal processes in the shallow subsurface (Gao et al., 2016). In studying growth
251 controls in colloform pyrite, Barrie et al. (2009) concluded on the basis of sulphur isotope data that
252 colloform pyrite from Ezuri, Japan, grew from purely hydrothermal sulfur. On the other hand, colloform
253 pyrite from Greens Creek, Alaska, formed from a bacteriogenic sulfur source. It was inferred that in the
254 VMS-SEDEX setting of the Greens Creek deposits, that colloform pyrite precipitation occurred as
255 metals ascended and mixed with sulfur near the paleo-seafloor (Barrie et al., 2009). Such a setting is
256 not unlike the inferred setting of the Apuan Alps pyrite ores (D’Orazio et al., 2017).

257 Similarly, pyrite framboids may also form in a variety of environments. Sediments and
258 sedimentary rocks are the most common setting (e.g., Sweeney and Kaplan, 1973; Hallbauer, 1986;
259 Perry and Pedersen, 1993; Large et al., 2007; Pitcairn et al., 2010; Wacey et al., 2015), but framboids
260 may also crystallize as a result of hydrothermal processes (e.g., Sassano and Schrijver, 1989; England
261 and Ostwald, 1993). Formation of framboidal pyrite has been frequently linked to microbial activity
262 (Large et al., 2001; MacLean et al., 2008) but pyrite framboids have also been synthesised in the
263 laboratory without organic influence (Sweeney and Kaplan, 1973; Ohfuji and Rickard, 2005). Their
264 formation requires a nucleation rate significantly higher than crystal growth rate. This is linked to very
265 high degrees of supersaturation as a result of the addition of elemental S and/or O₂, or by increasing Eh
266 or temperature (Ohfuji and Rickard, 2005).

267 In light of the geological setting of the Apuan Alps and commonly inferred crystallization
268 mechanisms for framboidal and colloform pyrite, both py1 and py2 are interpreted to be of primary
269 origin, growing in the sedimentary package near the water interface as is typical for these pyrite types.
270 This is in agreement with a number of S isotope studies that support a biogenetic source for S due to
271 microbial reduction of marine sulfate in shallow water sediments (e.g., Cortecchi et al., 1985; Orberger
272 et al., 1986; Martarelli et al., 1995). As such, pyrite generations 1 and 2 will be referred to as ‘primary

273 pyrite'. Since py3 is frequently aligned with the metamorphic fabric, it likely crystallized in the initial
274 stages of metamorphism during early deformation. It is very difficult to completely rule out the
275 possibility that py3 formed in the primary environment or during diagenesis in bedding aligned layers
276 that were later overprinted with a parallel metamorphic fabric, however this interpretation seems less
277 likely. Py4 is interpreted to have formed during metamorphism later than py3. It likely represents the
278 early stages of recrystallization of earlier pyrite generations. The aggregates typical of this pyrite
279 generation probably formed as py3 grains began to coalesce, trapping micro-inclusions within. Py5 is
280 interpreted to have formed late during metamorphism and is considered the end-product of pyrite
281 recrystallization. During the formation of this generation, pyrite habits became more euhedral, trapped
282 micro-inclusions were expelled and grain sizes coarsened on the prograde path to peak metamorphic
283 conditions, then characteristic granoblastic annealed textures would have formed during cooling on the
284 retrograde path. A very similar textural evolution for pyrite was interpreted by Large et al. (2007) for
285 the Sukhoi Log gold deposit, eastern Siberia. Similar to the Apuan Alps, primary pyrite at Sukhoi Log
286 included pyritic framboids which formed in the sedimentary environment in carbonaceous sediments.
287 Late diagenetic to earliest deformation pyrite formed inclusion-rich aggregates, and syn- to late-
288 deformation pyrite was coarser, more euhedral and relatively inclusion-free.

289 Pyrrhotite and arsenopyrite are sometimes present in samples from the Apuan Alps (especially
290 at Fornovolasco and Monte Arsiccio) and typically occur as replacement products of pyrite (Figure 4A
291 and B). Although pyrite replacement reactions seem to have been unimportant in the Apuan Alps
292 orebodies, at least some evidence of pyrite alteration can be seen in many samples. In most cases,
293 alteration is evidenced by the destruction of euhedral pyrite shapes, and possibly also an increase in
294 pyrite porosity (although porosity is also due to incomplete prograde recrystallization).

295 Other common sulfides include sphalerite, galena and chalcopyrite, although these are
296 infrequently present above trace level. Various sulfosalts are also observed in samples from the Apuan
297 Alps (see Table 1). Tetrahedrite has been recognised in samples from Buca della Vena, Canale della
298 Radice and Fornovolasco, while jamesonite has been observed at Fornovolasco and Monte Arsiccio.
299 Ag-Pb sulfosalts are frequently observed in Pollone samples, in agreement with the relatively common
300 occurrence of complex sulfosalts (e.g., sterryite; Moëlo et al., 2011). By far the most sulfosalt-rich

301 samples come from the Sant’Olga tunnel at Monte Arsiccio. These samples contain complex
302 assemblages of rare As ± Sb ± Ag ± Tl ± Hg ± Cu ± Pb sulfosalts (including ferdowsiite, laffittite,
303 aktashite, arsiccioite-routhierite solid solution members and other Tl-Sb sulfosalts) closely associated
304 with py5 (Figure 4C and D).

305

306 **4.2 Trace Element Trends Between Deposits**

307

308 One of the advantages of using the LA-ICP-MS technique to collect trace element data is that
309 any unintentionally analysed micro-inclusions in the host mineral will show up as peaks on the time-
310 resolved down-hole ablation profile, assuming the inclusion is sufficiently large as is not one of many
311 homogeneously distributed inclusions (Cook et al., 2016). The practice of checking for inclusions on
312 down-hole ablation profiles has proven reliable in filtering out inclusion-influenced LA-ICP-MS data
313 in a variety of sulfides and sulfosalts, e.g., sphalerite, galena, chalcopyrite and tetrahedrite-tennantite
314 (Cook et al., 2009b; George et al., 2015; 2016; 2017; 2018). The same data-filtering process has been
315 undertaken here, thus all data may be assumed to reflect trace elements in solid solution. The only
316 exception was py1 from CDR4A, where fine-grained framboids were intergrown with matrix minerals.
317 While LA-ICP-MS down-hole ablation profiles were still smooth, these analyses may be understood to
318 be somewhat bulk.

319 LA-ICP-MS data for 20 trace elements measured in Apuan Alps pyrite is summarised in Table
320 2. Appendix A is the complete LA-ICP-MS dataset, while Appendix B displays the MDL and error for
321 these trace elements in each pyrite generation in each deposit. Figures 5 and 6 show cumulative plots
322 of the pyrite trace element data. These plots reveal the mean concentration and data spread for each
323 trace element in each deposit, showing that, in general, Canale, della Radice and Fornovolasco are
324 deposits most enriched in As, Sb, Tl, Hg, Cu and Bi. The distribution of many trace elements was found
325 to frequently display zonation within individual pyrite grains. Most typically, this zoning revealed
326 distinct pyrite generations, where, for example, a py4 core was overgrown with a py5 rim. In some
327 cases, however, trace element zoning was observed in pyrite belonging to a single generation. In such

328 cases, this zonation accounted for much of the data spread in a given pyrite generation in a single
329 deposit.

330 *Arsenic* was the most abundant trace element measured in Apuan Alps pyrite in this study.
331 Concentrations were highest in py4 from FOR21 (17,441 ppm); one spot recorded over 5 wt. % As.
332 Py4 from sample FOR23 also contained pyrite with just over 1 wt. % As and a number of other
333 individual spot analyses on Fornovolasco pyrite likewise reached above 10,000 ppm As. Because of
334 this, the mean As concentration in Fornovolasco pyrite was significantly higher than at Canale della
335 Radice, the next most As-rich pyrite. While As concentrations were lowest in py5 from BDV2 (41
336 ppm), overall, Sennari pyrite was most depleted in As. Mean As concentrations at Buca della Vena,
337 Monte Arsiccio and Pollone all approximated 1,000 ppm. At Buca della Vena, Canale della Radice and
338 Fornovolasco, the As concentrations spread over approximately 3 orders of magnitude, while Monte
339 Arsiccio, Pollone and Sennari data spread over only 2 orders of magnitude.

340 *Antimony* was the next most abundant trace element in pyrite from the Apuan Alps. Py4 in
341 ARS5B contained 5,090 ppm Sb, the most of any sample. However, the highest single spot
342 measurement of Sb came from py4 in FOR21 where almost 1.3 wt. % Sb was recorded. The
343 concentration of Sb at all deposits except Fornovolasco spread over more than 5 orders of magnitude,
344 meaning some pyrite was heavily depleted in Sb. Significantly, the lowest Sb values, those < 1 ppm, all
345 came from py5 in samples from Buca della Vena, Canale della Radice, Monte Arsiccio and Pollone.
346 Overall, Fornovolasco and Sennari pyrite hosted the most Sb, while pyrite from Buca della Vena and
347 Pollone was most depleted.

348 Py1 from sample CDR4A contained 4,244 ppm *thallium*, the most of any pyrite here. A number
349 of additional samples also hosted levels of Tl over 2,500 ppm, including py4 from CDR4B and ARS5B,
350 and all py2 (i.e., from FOR19, ARS9A and ARS9B). The levels of Tl in pyrite measured here are
351 amongst the highest of any reported in the literature, especially for pyrite that is neither from a Carlin-
352 type deposit, or associated with coal (Deditius and Reich, 2016). Every deposit showed a very large
353 spread in Tl concentrations; each over approximately 6 orders of magnitude. Similar to Sb, the vast
354 majority of Tl measurements below 1 ppm came from py5. In general, Pollone pyrite was most depleted

355 in Tl, and Canale della Radice, Fornovolasco, Monte Arsiccio and Sennari pyrite all averaged ~1,000
356 ppm Tl.

357 In this study, the most *mercury* was hosted in py4 from CDR3B (166 ppm); one spot on this
358 pyrite returned over 670 ppm Hg. Py4 from BDV3, ARS5B and SEN1B, and py5 from CDR4B, FOR22
359 and FOR24 also concentrated over 100 ppm Hg each. Data at Canale della Radice and Fornovolasco
360 spread over more than 3 orders of magnitude, while values from the other deposits varied over less than
361 3 orders of magnitude. Sennari pyrite hosted the most Hg, while Pollone pyrite was most depleted.

362 *Lead* concentrations reached 1,357 ppm in py3 from FOR8. Interestingly, this sample came
363 from outside the orebody at Fornovolasco, indicating metal enrichment was not necessarily constrained
364 to individual orebodies. No other pyrite generation in any sample contained more than 1,000 ppm Pb.
365 With the exception of py3 from BDV7, only py5 hosted less than 1 ppm Pb. At each deposit, data
366 typically spread over approximately 5 orders of magnitude. Pyrite from Fornovolasco was most
367 enriched in Pb, while Canale della Radice pyrite was most depleted. Pyrite in other deposits on average
368 hosted approximately 100 ppm Pb.

369 *Nickel* concentrations in pyrite were systematically higher than *cobalt*. Only py3 from FOR8
370 was more enriched in Co than Ni; 63 ppm compared to 29. Concentrations of Ni in pyrite reached 1,816
371 ppm (in py3 from CDR4B) while the highest concentration of Co was 155 ppm (py5 from BDV2). The
372 only other pyrite generations that hosted more than 100 ppm Co were py1 and py3 from CDR4A and
373 CDR4B, respectively. The only pyrite generations with Ni concentrations over 1,000 ppm came from
374 Canale della Radice. As such, this pyrite was most enriched in Ni on average, followed by pyrite from
375 Buca della Vena. Pyrite from Buca della Vena and Canale della Radice contained the most Co, while
376 Monte Arsiccio pyrite was most depleted. Data for Ni was generally less spread than for Co, typically
377 around 3 orders of magnitude compared to 4.

378 The maximum concentration of *copper* in Apuan Alps pyrite was 322 ppm (py4 in FOR21),
379 compared to 281 ppm (py1 in CDR4A) for *zinc*. Across the sample suite, only py5 hosted less than 1
380 ppm of either Cu or Zn. Overall, Canale della Radice and Fornovolasco pyrite was most enriched in Cu,
381 while Pollone and Sennari pyrite was most depleted. Pollone pyrite was also most depleted in Zn;
382 concentrations of Zn were highest in pyrite from Canale della Radice and Monte Arsiccio. Zinc values

383 usually spread over approximately 2 orders of magnitude, while Cu values sometimes spread over 4
384 orders of magnitude.

385 The highest concentration of *manganese* was 1,116 ppm, measured in py4 from BDV4. No
386 other pyrite generation in any sample hosted more than 500 ppm Mn. Overall, Mn concentrations were
387 highest in pyrite from Buca della Vena, Canale della Radice and Monte Arsiccio, each averaged
388 approximately 100 ppm Mn. *Molybdenum* concentrations reached 118 ppm in py4 from CDR2B, and
389 in general, Canale della Radice and Sennari pyrite was most rich in Mo. Compared to other deposits,
390 Pollone pyrite was depleted in both Mn and Mo. Data for both elements sometimes spread over as much
391 as 4 orders of magnitude in a given deposit.

392 *Bismuth* concentrations reached as high as 621 ppm in py3 from FOR8, again indicating metal
393 enrichment outside the Fornovolasco orebody. Concentrations only exceeded 10 ppm in pyrite
394 generations from 7 other samples. Data for Bi spread over a maximum of 6 orders of magnitude at
395 Fornovolasco, and down to as little as 2 orders of magnitude at both Pollone and Sennari. In general,
396 data for *silver* was less spread as it only varied over 2 or 3 orders of magnitude in a given deposit. The
397 highest amount of Ag was measured in py4 from POLS2 (115 ppm), while on average Monte Arsiccio
398 and Pollone pyrite was most enriched in Ag. In general, concentrations of Bi were highest in pyrite
399 from Canale della Radice and Fornovolasco.

400 *Selenium* and *tellurium* concentrations reached as high as 64 ppm and 67 ppm in py3 from
401 ARS17M and py1 from CDR4A, respectively. It was only in samples CDR4A and CDR4B that Te
402 concentrations in pyrite exceeded 10 ppm, and as such, Canale della Radice pyrite hosted on average
403 more Te than any other deposit here by almost an order of magnitude. Selenium concentrations were
404 generally higher than Te such that pyrite from all deposits except Pollone and Sennari averaged around
405 10 ppm Se. Concentration data for both elements spread over as much as 2 orders of magnitude. The
406 only exception was Te at Canale della Radice which varied over 3 orders of magnitude.

407 The most *tungsten* was measured in py3 from CDR4B (5.9 ppm) while py4 from FOR15
408 contained the most *cadmium* (3.7 ppm). The average concentration of W and Cd in pyrite from any
409 given deposit was always approximately equal to or less than 1 ppm. *Tin* concentrations were only

410 higher than 1 ppm in py1 from CDR4A where 5.2 ppm was measured. The most *gold* and *indium*
411 measured was 0.51 ppm and 0.09 ppm in py4 from FOR21 and py5 from FOR18, respectively.

412

413 **4.3 Trace Element Trends Between Pyrite Generations**

414

415 Figures 7 and 8 show the trace element composition of the different pyrite generations from the
416 Apuan Alps orebodies. *Arsenic* levels in primary pyrite varied from above 1,000 ppm to almost 4,000
417 ppm across the sample suite. In samples from Fornovolasco and Monte Arsiccio, the concentration of
418 As in primary pyrite was always higher than in py4 or py5 from the same sample, whereas at Canale
419 della Radice, py1 hosted less As than both py4 and py5. Similarly, at Fornovolasco and Monte Arsiccio
420 py3 hosted more As than py4, but at Buca della Vena, Canale della Radice and Pollone, the opposite
421 was true. In all deposits except Canale della Radice, As levels in py5 were almost always lower than in
422 py4 from the same sample, usually by around half an order of magnitude.

423 Similar trends were observed for *antimony*. Primary pyrite contained up to ~2,500 ppm Sb, and
424 always dropped to coexisting py4 or py5. Py3 at Fornovolasco and Monte Arsiccio contained more Sb
425 than coexisting py4. However, at Buca della Vena, Canale della Radice and Pollone, py3 was depleted
426 in Sb compared to py4 from the same sample. At Buca della Vena and Pollone, this depletion was more
427 than two orders of magnitude. Although exceptions were present, in every deposit py5 was typically
428 depleted in Sb compared to py4 from the same sample. This depletion was commonly more than an
429 order of magnitude at Buca della Vena, Monte Arsiccio and Pollone.

430 All primary pyrite was enriched in *thallium* by up to half an order of magnitude compared to
431 coexisting py4 or py5, always hosting above 2,500 ppm Tl. Py3 at Buca della Vena, Canale della Radice
432 and Pollone contained less *thallium* than py4 from the same sample; the greatest difference was in POL1
433 where py3 contained 0.1 ppm Tl compared to 973 ppm Tl in py4. However, at Fornovolasco and Monte
434 Arsiccio, py3 hosted more Tl than py4. In all samples except FOR22 and FOR23, py5 was depleted in
435 Tl compared to py4. This depletion was commonly more than an order of magnitude, and was
436 sometimes multiple orders of magnitude, for example, in samples from Monte Arsiccio.

437 In every deposit, the concentration of *mercury* in primary pyrite was higher than in coexisting
438 py4 or py5. In all deposits except Buca della Vena, py3 hosted more Hg than py4 from the same sample.
439 Consistent Hg depletion by usually less than an order of magnitude was observed in py5 compared to
440 coexisting py4 in all samples except those from Fornovolasco, CDR4B and ARS3. At Fornovolasco,
441 py5 contained less Hg than py4 in 4 out of 7 samples, though concentrations between the two pyrite
442 generations were very similar.

443 All primary pyrite, except py2 from FOR19, was more enriched in Pb in comparison to
444 coexisting py4 or py5. Py3 from Buca della Vena and Pollone contained less *lead* than coexisting py4,
445 whereas py3 in all other deposits was enriched in Pb compared to py4. In all samples except for FOR22,
446 FOR24 and ARS3, py5 was depleted in Pb compared to coexisting py4, frequently by around an order
447 of magnitude and sometimes by up to 3 orders of magnitude, for example, in samples BDV4 and
448 ARS17M.

449 *Cobalt* and *nickel* trends between pyrite types were very similar in all deposits. At Monte
450 Arsiccio, primary pyrite was significantly depleted in Co and Ni compared to py5, whereas at Canale
451 della Radice and Fornovolasco, primary pyrite was enriched in both elements in comparison to
452 coexisting py4 or py5. At Buca della Vena, Canale della Radice and Pollone, py3 was enriched in both
453 Co and Ni compared to py4 from the same sample. At Fornovolasco and Monte Arsiccio, the opposite
454 was true (except in FOR25 where the concentration of Ni in py3 and py4 was approximately equal).
455 The concentration of Co and Ni in py5 compared to py4 from the same sample varied significantly
456 across the sample suite. At Buca della Vena, Co and Ni were enriched in py5 in comparison to py4.
457 Overall trends of depletion from py4 to py5 were observed at Canale della Radice and Sennari for both
458 elements, and at Fornovolasco for Co.

459 Except at Fornovolasco, *copper* and *zinc* were significantly enriched in primary pyrite
460 compared to py4 or py5 from the same sample. Concentrations of Cu and Zn in py3 from Buca della
461 Vena, Canale della Radice and Pollone were less than (or, in the case of Cu in CDR4B, roughly equal
462 to) coexisting py4. At Fornovolasco and Monte Arsiccio, py3 was enriched in Cu and Zn relative to
463 py4. In all deposits, the concentration of Cu and Zn in py4 was higher than in py5 from the same sample,
464 often by more than an order of magnitude. The only exceptions to this trend were samples CDR4A,

465 FOR22, FOR24 and ARS3, where only slight enrichment of either Cu or Zn was observed from py4 to
466 py5.

467 All primary pyrite was enriched in both *manganese* and *molybdenum* compared to either py4
468 or py5 from the same sample (the only exception being Mo in CDR4A). Py3 at Buca della Vena, Canale
469 della Radice and Pollone was depleted in both elements in comparison to coexisting py4; the opposite
470 was true at Fornovolasco and Monte Arsiccio. With the exception of samples CDR4A for Mn and
471 CDR2A, FOR22, FOR24 for Mo, all other samples showed depletion, or occasional equivalency, of
472 both elements from py4 to py5.

473 The concentration of *silver* and *bismuth* in all primary pyrite was higher than, or sometimes
474 approximately equal to, quantities in coexisting py4 or py5. At Buca della Vena and Pollone, py3 was
475 depleted in both elements compared to py4. Conversely, Canale della Radice, Fornovolasco and Monte
476 Arsiccio py3 contained greater, or equivalent, amounts of Ag and Bi compared to coexisting py4. In all
477 samples except FOR23 and FOR24, the concentration of Ag and Bi in py4 was greater than, or
478 essentially equivalent to, concentrations in py5 from the same sample.

479

480 **5. Discussion**

481

482 **5.1 Element Correlations**

483

484 Figures 9, 10 and 11 show the correlations between various trace element pairs in pyrite from
485 the Apuan Alps. Two different types of correlation are noted; (1) approximately linear correlations
486 (Figure 9), and (2) wedge-shaped correlations (Figures 10 and 11). Linear correlations may imply a
487 mutual dependence between the incorporation of two trace elements, whereas wedge-shaped
488 correlations possibly suggest the incorporation of one trace element depends, to some degree, on the
489 presence of another.

490 Cobalt and Ni display a general mutual dependence on each other such that pyrite enriched in
491 one element is also enriched in the other (Figure 9A). However, Ni concentrations are consistently
492 higher than Co so that almost all data plots below the $Co = Ni$ line, i.e., all pyrite has a Co:Ni ratio < 1

493 (this is also true when both elements are plotted as ppm rather than as mol. %). It has long been proposed
494 that the Co:Ni ratio of pyrite can be useful in discriminating between different pyrite formation
495 environments (e.g., Loftus-Hills and Solomon, 1967; Bralía et al., 1979). This approach has been used
496 extensively in the literature for differentiating between volcanic, magmatic, hydrothermal and
497 sedimentary pyrites (e.g., Brill, 1989; Subba Rao and Naqvi, 1997; Serranti et al., 2002; Monteiro et
498 al., 2008; Wang et al., 2015; Reich et al., 2016). Since all pyrite from the Apuan Alps has Co:Ni ratios
499 < 1 [contrary to Martarelli et al. (1995) who documented some pyrites from Pollone with Co > Ni], this
500 represents strong evidence that this pyrite has a strong sedimentary fingerprint, as can be inferred from
501 the occasionally preserved primary textures and S isotope data.

502 Strong positive correlations are observed in the Mo vs. Zn, Zn vs. Mn, and Mo vs. Mn plots
503 (Figure 9B, C to D). These plots imply a three-way correlation between Mn, Zn and Mo. Since the data
504 on each graph plots with an approximate slope of 1, a substitution of the type $4\text{Fe}^{2+} \leftrightarrow \text{Mn}^{2+} + \text{Zn}^{2+} +$
505 $\text{Mo}^{4+} + \square$ could be envisaged for these elements, assuming the presence of Mo^{4+} , as is generally the
506 case for sulfides (e.g., molybdenite; Stein et al., 2003). Vacancies are commonly interpreted to form as
507 a result of a number of substitutions in pyrite (e.g., Simon et al., 1999a; Deditius et al., 2008).
508 Alternatively, since such a concomitant substitution would be unusual, these correlations may simply
509 indicate that Mn, Zn and Mo behaved geochemically alike within the formation environment of the
510 Apuan Alps such that these elements were similarly enriched or depleted within pyrite.

511 A notable positive correlation is also observed between Pb and Cu (Figure 9E), where the slope
512 of data closely approximates 1. This could indicate a coupled substitution between the two elements;
513 conceivably $2\text{Fe}^{2+} \leftrightarrow \text{Pb}^{2+} + \text{Cu}^{2+}$, however, Cu is normally monovalent in sulfides and divalent Cu is
514 very rare (Pearce et al., 2006). It would be difficult to argue for oxidised copper without other
515 independent evidence. Therefore, the correlation between Pb and Cu seems best explained by
516 geochemical affinity. The positive correlation between Au and Bi (Figure 9F) can also best be explained
517 by the strong geochemical affinity between the two elements that has been recognised in a variety of
518 deposits (e.g., Hale, 1981; Nurmi and Sorjonen-Ward, 1993; Thompson et al., 1999; Meinert, 2000;
519 Voudouris, 2005). This affinity is commonly attributed to the scavenging of Au by Bi-melts (Ciobanu
520 et al., 2009; 2010), but has also been linked to hydrothermal processes (e.g., Skirrow and Walshe, 2002).

521 The strongest positive correlation present is between Tl and Sb (Figure 9G). Most of the data
522 plots on or just below the Tl = Sb line. Such a strong correlation seems best explained by a coupled
523 substitution between the two elements in the pyrite structure, i.e., $2\text{Fe}^{2+} \leftrightarrow \text{Tl}^+ + \text{Sb}^{3+}$. Such a
524 substitution was also supported by D’Orazio et al. (2017). Recently, the presence of monovalent Tl and
525 trivalent Sb in the structure of Tl-Sb-As-rich pyrite from the Apuan Alps has been confirmed by X-ray
526 absorption spectroscopy (XAS) by George et al. (in prep.). When other typically monovalent cations
527 are considered (Cu^+ and Ag^+), the correlation with Sb becomes even stronger and closer approximates
528 the line $(\text{Tl} + \text{Cu} + \text{Ag}) = \text{Sb}$ (Figure 9H). This indicates that monovalent Cu and Ag are likely also
529 incorporated in a coupled substitution with Sb i.e., $2\text{Fe}^{2+} \leftrightarrow (\text{Cu}, \text{Ag})^+ + \text{Sb}^{3+}$. This correlation provides
530 strong evidence that the Tl, Cu, Ag and Sb measured here is present within the pyrite structure, even
531 though these elements are often attributed to micro-inclusions of other minerals in studies of
532 sedimentary pyrite (e.g., Large et al., 2014). Even concentrations of Tl in the thousands of ppm may be
533 hosted in solid solution in pyrite, in agreement with Deditius and Reich (2016).

534 It is interesting to note that when As is considered as a trivalent cation possible of participating
535 in the above coupled substitution, all indication of the strong 1-to-1 correlation with monovalent ions
536 disappears (Figure 9I). This seems to imply that As is generally substituted into the lattice of pyrite
537 without any accompanying monovalent cation, likely as As^- for S^- , creating As-S dimers. This is the
538 most common oxidation state of As in pyrite in deposits that are not strongly oxidised, e.g., high-
539 sulphidation epithermal and porphyry deposits (Simon et al., 1999a; 1999b; Savage et al., 2000; Reich
540 et al., 2005; 2013; Deditius et al., 2008; Qian et al., 2013). However, closer examination of Figure 9I
541 reveals two distinct groups of data, an upper and a lower group. This may indicate two distinct types of
542 As are present in pyrite from the Apuan Alps, As^- and As^{3+} . Indeed, XAS data shows that As is present
543 in Apuan Alps pyrite in both oxidation states (George et al., in prep.), possibly indicating two different
544 sources for As; one reduced and one oxidised. This is similar to pyrite documented by Deditius et al.
545 (2008). The same two data groups are present in Figure 9J when Sb is plotted against As. In this case,
546 the lower data group most likely corresponds to As^{3+} since the presence of trivalent As in pyrite would
547 restrict the incorporation of trivalent Sb, due to the excess positive charge this would entail, therefore

548 creating Sb-depleted pyrite. The upper data group in Figure 9J would correspond to As⁻ since anionic
549 As would not impede Sb³⁺ incorporation, therefore permitting the formation of Sb-enriched pyrite.

550 Figure 10 displays plots of various trace elements against Sb. Interestingly, each shows a
551 wedged-shaped distribution similar to that of Reich et al. (2005) for Au vs. As. In the aforementioned
552 study, concentrations of Au plotting below the 'wedge' may be expected to occur in solid solution,
553 whereas those plotting above the 'wedge' form nanoparticles or larger inclusions of visible Au. This
554 implies that Au nanoparticle nucleation is controlled by the concentration of As in the pyrite lattice, and
555 thus the Au saturation limit is defined by the line $C_{Au} = 0.02 \times C_{As} + 4 \times 10^{-5}$ (where C_{Au} and C_{As} are
556 the mol. % concentrations of Au and As in pyrite, respectively). This saturation limit has been extended
557 to all types of ores containing pyrite (Deditius et al., 2014). Deditius et al. (2009) and Deditius and
558 Reich (2016) also showed that when other elements such as Ag, Te, Hg, Sb, Pb, Tl and Cd are plotted
559 against As, similar wedged-shaped distributions are formed, implying that the concentration of such
560 elements in pyrite is strongly dependant on the As content (see also Keith et al., 2018). Deditius and
561 Reich (2016) showed that while the upper solubility limit for Hg in pyrite is approximately the same as
562 for Au, the saturation limit of Tl is more closely approximated by the Tl = As line; i.e., Tl:As = 1. Pyrite
563 with Hg and Tl concentrations greater than their given solubility limits contain nanoparticles of HgS
564 and other Tl-Hg minerals. Cook et al. (2009a) suggested that elements such as Bi, Pb and Te may also
565 play a role as catalysts for Au incorporation in a similar way to As. Similar relationships have also been
566 noted in other minerals, for example, a wedge-shaped trend on a Au vs. Ag plot has been interpreted as
567 Ag controlling the incorporation of Au in Bi-tellurides and sulfosalts (Ciobanu et al., 2009).

568 The analogous wedge-shaped patterns on the plots here (Figure 10) indicate that, similar to As,
569 Sb may also underpin the uptake of various trace elements into the pyrite structure. On the Cu vs. Sb,
570 Te vs. Sb, Pb vs. Sb and Bi vs. Sb plots (Figure 10B, E, G and H), some selected LA-ICP-MS spots
571 have been plotted that, on the basis of down-hole ablation profiles, have clearly analysed inclusions of
572 Cu-, Te-, Pb- and Bi-bearing phases, respectively. Since each of these points plot above their respective
573 wedge-shaped data trends, this gives supporting evidence that each element plotted against Sb in Figure
574 10 likely has an upper solubility limit controlled by the presence of Sb in the pyrite lattice. Above this
575 limit, an element may form micro- to nano-inclusions of a discrete mineral, and below this limit the

576 element is likely present in solid solution. At first approximation, the elements Pb and Bi seem to have
577 an upper limit defined by $X = \text{Sb}$ (where $X = \text{Pb}$ or Bi), i.e., an X:Sb ratio of 1. Nevertheless, from a
578 crystal-chemical point of view, it does seem strange that trivalent Sb would control the incorporation
579 of Bi, therefore the correlation on Figure 10H may be due to geochemical coupling. The solubility limit
580 of Mn may be represented by a Mn:Sb ratio of approximately 10. The elements Cu, Zn, Ag, Te and Hg
581 display more curved shaped trends when plotted against Sb in log-log space such that their upper
582 saturation limits are better approximated by a line of the form given by Reich et al. (2005). For Cu, Zn
583 and Hg, a first approximation of such a line is $C_{\text{Cu,Zn,Hg}} = C_{\text{Sb}} + 10^{-4}$, for Ag the line would be $C_{\text{Ag}} = 0.3$
584 $\times C_{\text{Sb}} + 0.3 \times 10^{-4}$, and for Te, $C_{\text{Te}} = 0.1 \times C_{\text{Sb}} + 0.3 \times 10^{-4}$ (where C_{Sb} , C_{Ag} and C_{Te} , etc., are the mol. %
585 concentrations of Sb, Ag and Te in pyrite, respectively).

586 This data seems to show that Sb (and, by extension, possibly As) may control the incorporation
587 of a much wider range of elements in the pyrite structure than previously recognised, e.g., also Mn, Cu,
588 Zn and potentially Bi. The interpretation that Sb may behave similar to As in controlling the uptake of
589 trace elements into pyrite seems somewhat intuitive, since As and Sb are geochemically similar group
590 15 metalloids. Many authors have proposed mechanisms by which Au incorporation into pyrite is
591 enhanced by As. For example, Au may be substituted by chemisorption onto As-enriched, Fe-depleted
592 pyrite surfaces (Fleet and Mumin, 1997). The presence of As may also alter the semiconducting
593 properties of pyrite from *n*-type to *p*-type, which could enhance Au incorporation (Maddox et al., 1998;
594 Rickard and Luther, 2007). Pokrovski et al. (2002) suggested that As in pyrite could form local reducing
595 environments favouring Au deposition through Au-sulfide complex destabilisation. Since Au
596 incorporation in pyrite seems to be analogously controlled by either As^- or As^{3+} (e.g., Simon et al.,
597 1999b; Palenik et al., 2004; Deditius et al., 2008; 2014), the presence of Sb^{3+} in pyrite may also aid the
598 incorporation of trace elements through similar processes to As.

599 It is interesting to note that As does not correlate well with most trace elements that form wedge-
600 shaped trends when plotted against Sb. The only elements that seem to correlate with As are Zn and Au
601 where wedge-shaped trends are observed (Figure 11A and B). Thus, it seems that Sb- and As-facilitated
602 incorporation of trace elements into pyrite may act, at least generally, independently of each other. It is
603 unclear why, in the particular case of the Apuan Alps, Sb has played the facilitator role for trace element

604 incorporation at the expense of As, especially when one considers the abundance of As present in Apuan
605 Alps pyrite. Any potential correlations between As^{3+} and other trace elements may be diluted by the
606 presence of As^- , however, as mentioned, Au incorporation in pyrite seems to be analogously controlled
607 by either As^- or As^{3+} (e.g., Simon et al., 1999b; Palenik et al., 2004; Deditius et al., 2008; 2014)

608 The only other element correlations of note occur between Te and Co, and Te and Ni (Figure
609 11C and D). Since Co and Ni correlate strongly with each other (Figure 9A) it is to be expected that if
610 Te correlates with one of these elements, it would also correlate with the other. Therefore, the wedge-
611 shaped trends observed on the Te vs. Co and Te vs. Ni plots could be interpreted as Te incorporation
612 being aided by the presence of Co and Ni in pyrite, or simply as a result of one of these elements.

613

614 **5.2 Metallogenesis of the Apuan Alps Pyrite Ores**

615

616 Based on textural analysis, pyrite Co:Ni ratios and S isotope studies (e.g., Cortecci et al., 1985;
617 Orberger et al., 1986; Martarelli et al., 1995), primary Apuan Alps pyrite shows a strong sedimentary
618 fingerprint, likely forming near the sediment-water interface. As such, this pyrite would have
619 incorporated trace elements contained in surrounding water and sediments. In these environments,
620 pyrite may form through microbial reduction of marine sulfate (Large et al., 2014), the interpreted
621 source of S for Apuan Alps pyrite (e.g., Cortecci et al., 1985; Orberger et al., 1986; Martarelli et al.,
622 1995). Through absorption from seawater and sediment pore-waters, studies have shown that As, Hg,
623 Mo, Co, Cu, Mn, Ni, Pb, Zn and Ag are commonly incorporated into this pyrite at this time (Huerta-
624 Diaz and Morse, 1992; Morse and Arakaki, 1993; Large et al., 2007; 2009; Mukherjee and Large, 2017).
625 Similarly, Tl is often strongly adsorbed on Fe-Mn oxy-hydroxides and clays that are abundant in marine
626 sediments, and during pore-water reduction Tl may desorb to partition to crystallizing pyrite (e.g.,
627 Turner et al., 2010; Nielsen et al., 2011). Thus, the sedimentary environment of py1 and py2 may have
628 contributed to their enrichment of As, Tl, Hg, Cu, Mn, Ni, Pb, Zn and Ag (Figure 12).

629 As noted by D'Orazio et al. (2017), the strong Tl, Hg, Sb and As signature of Apuan Alps pyrite
630 is typical of various hydrothermal deposits, most notably, stratiform basin-hosted sulfide deposits (e.g.,
631 Meggen, North-Rhine Westfalia, Germany; Krebs, 1981) and Carlin-type deposits (e.g., Carlin,

632 Nevada, USA; Radtke, 1985). This elemental association characterizes low-temperature ($< \sim 300$ °C)
633 hydrothermal fluids including those derived from evolved continental crust within intracontinental
634 marine basins (Leach et al., 2005; Wilkinson, 2014). Hydrothermal deposits related to transitional arcs
635 and intracontinental back-arc basins are also richer in these elements compared to similar ores in oceanic
636 crust, for example, at mid-ocean ridges with or without hot spot interaction, and intraoceanic back-arc
637 basins (Hannington et al., 2005; Wilkinson, 2014)

638 Based on their stratabound and lens-like morphologies within the Paleozoic metasedimentary-
639 metavolcanic sequence, their mineralogical zonation and association with tourmalinites, D’Orazio et al.
640 (2017) inferred that the pyrite \pm baryte \pm iron oxide ores of the Apuan Alps are likely intracontinental
641 stratiform basin-hosted sulfide deposits. Indeed, Benvenuti et al. (1989) suggested a pre-metamorphic,
642 likely sedimentary-exhalative, origin for the tourmalinite bodies from the Bottino deposit. Such an
643 interpretation is consistent with the elemental transition from Bottino type (Pb, Zn, Ag, Cu) ores, which
644 may have formed from higher-temperature hydrothermal fluids proximal to a central feeder vent, to
645 distal pyrite \pm baryte \pm iron oxide type ores. In the distal zones, hydrothermal fluids would be cooler
646 and more enriched in Tl, Hg, Sb and As, leading to the strong enrichment of these elements in pyrite
647 (Figure 12). No evidence in this study contradicts such an interpretation, even if the sedimentary
648 influence on pyrite trace element content in distal zones has been highlighted. Indeed, Mukherjee and
649 Large (2017) describe enrichment of Tl and As in sedimentary pyrite due to interactions with exhalative
650 hydrothermal fluids. A dual trace element source for pyrite forming in a similar setting was also
651 interpreted by Gadd et al. (2016), with Tl, As and Sb (as well as Zn, Pb, Mn and Ag) originating in
652 SEDEX-forming hydrothermal fluids, and Co, Ni, Cu, Mo and Bi traced to seawater at the sediment
653 water interface.

654 In a recent study, Vezzoni et al. (in review) reported new dating of the Fornovolasco
655 Metarhyolite, a porphyritic tourmaline-bearing rock spatially associated with tourmalinite bodies and
656 pyrite ores in the southern Apuan Alps. Uranium-Pb dating suggests a Permian crystallization age,
657 linking this meta-volcanic rock to post-Variscan magmatism. These new data agree with those presented
658 in D’Orazio et al. (2017) which, through Pb isotope signatures, links pyrite, galena and Pb-sulfosalts
659 from ore deposits in the southern Apuan Alps to Paleozoic ores and Variscan magmatic rocks of

660 Sardinia (see also Boni and Koepfel, 1985; Ludwig et al., 1989; Boni et al., 1992; Lattanzi et al., 1992;
661 Dini et al., 2005). Thus, Permian magmatism in the southern Apuan Alps may have played a similar
662 role to the Variscan magmatic rocks of Sardinia in instigating a Paleozoic metallogenic event (Lattanzi
663 et al., 1994). Upwelling magma under a post-Variscan crustal thinning regime may have been the heat
664 source causing the development of circulating hydrothermal fluids in the basement of an
665 intracontinental marine basin. Fluids circulating within the sedimentary package, especially if acidic,
666 would have readily leached Tl hosted in K-bearing silicates and could re-deposit Tl upon cooling to
667 below 150 °C and/or neutralization (Li, 1996; Chen and Zou, 2000; Xiong, 2007).

668

669 **5.3 Pyrite Trace Element Evolution**

670

671 Primary pyrite generations 1 and 2 are amongst the richest in Sb, Tl and Hg (Figure 7B, C and
672 Figure 8A), likely owing to the contribution of these elements from circulating low-temperature
673 hydrothermal fluids in the host sedimentary package. As discussed, the presence of Sb in such fluids
674 appears to have been instrumental in facilitating the incorporation of many other elements. Colloform
675 pyrite typically displays complex trace element zonation patterns (Figure 13). These patterns could
676 indicate changing physiochemical conditions at the pyrite growth interface over time, or a complex
677 interplay between differing trace element contributions from hydrothermal and sedimentary sources.

678 Since metamorphic pyrite generations maintain sedimentary Co:Ni ratios, they likely grew from
679 precursor primary pyrite types rather than as completely separate pyrites. Comparing trace element
680 concentrations in py1 and py3 in CDR4 samples (CDR4A and CDR4B; Figure 7B), a depletion of Tl,
681 Zn, Ag and Mn is apparent. This may indicate that the initial formation of metamorphic pyrite at the
682 expense of py1 may have caused the release of such elements from pyrite (Figure 12). However, due to
683 the rarity of pyrite generations 1 or 2 being preserved alongside py3, it is difficult to make confident
684 interpretations relating to this stage of pyrite evolution.

685 Clearer trends are observed comparing trace element concentrations in py3 and py4 from the
686 Apuan Alps. At Fornovolasco and Monte Arsiccio, py3 is generally enriched in As, Sb, Tl, Hg, Zn and
687 Mn compared to py4 (Figures 7C, 8A and 14). However, at Buca della Vena, Canale della Radice and

688 Pollone, py3 is typically depleted in As, Sb, Tl, Mn, Cu and Zn compared to py4 (Figure 7A, B and
689 Figure 8B). The opposite is generally true for Co and Ni. This clearly indicates that the trace element
690 evolution of pyrite during early- to mid-metamorphism was not uniform across all deposits.

691 Metamorphic recrystallization typically increases the grain size of pyrite as the movement of
692 Fe and S allows for nucleation or growth on pre-existing surfaces (Craig and Vokes, 1993). Similarly,
693 during prograde metamorphism, higher T could favour the expansion of pyrite lattice, likely allowing
694 easier incorporation of larger trace cations (e.g., Sb, Tl, Mn and Cu). Therefore, if such cations are
695 present in the system as pyrite is progressively recrystallizing, one might expect enrichment of pyrite
696 in trace elements during this stage. Indeed, the concentration of a number of trace elements has been
697 shown to increase in chalcopyrite as crystallization temperature increases, especially during
698 metamorphic recrystallization (George et al., 2018). Alternatively, if additional Fe and S are present in
699 the environment of recrystallizing pyrite without other trace elements, then they could contribute to new
700 nucleation or growth on pre-existing surfaces, effectively diluting the already present trace elements
701 within the structure of pyrite and lowering the overall concentration of such elements in pyrite. Thus,
702 the enrichment or depletion of various trace elements in pyrite during progressive recrystallization may
703 simply be a function of the availability of Fe, S and trace elements present in each individual orebody
704 during prograde metamorphism.

705 Another interpretation may be offered to explain the different trace element trends between py3
706 and py4, although only if py3 is indeed a pre-metamorphic pyrite generation that became aligned with
707 the metamorphic fabric during deformation. The occurrence of tourmalinite clasts and pyrite-bearing
708 quartz veins within the Triassic Verrucano Formation (e.g., Cavarretta et al., 1992; Pieruccioni et al., in
709 press) indicates the erosion of mineralized areas during the extensional regime developed in the Early
710 Mesozoic. Thus, if the southern Apuan Alps orebodies were close to the surface in the Mesozoic, then
711 supergene processes associated with downward moving meteoric waters may have affected some of the
712 pyrite ores, i.e., possibly Buca della Vena, Canale della Radice and Pollone only. This process would
713 have caused the oxidation of pyrite, leading to the formation of sulfuric acid or sulfate, freeing metals
714 to move downward and form new pyrite enriched in elements such as As, Sb, Tl, Mn, Cu and Zn. Pyrite
715 frequently plays an important role in the supergene enrichment of porphyry Cu deposits (Reich et al.,

716 2013). The observation of pyrite enrichment between py3 and py4 at Pollone is only made from one
717 sample (POL1), and therefore is only tentative. Nevertheless, Pollone is likely a stratigraphically deep
718 system, and does not have an oxidised portion associated with the pyrite ore, distinct from the Buca
719 della Vena and Canale della Radice orebodies. Given this, and the fact that py3 is more likely a
720 metamorphic pyrite generation, the interpretation described in the previous paragraph is preferred.

721 The most obvious trend noticed in Figures 7 and 8 is the clear depletion of almost all trace
722 elements from early recrystallized pyrite (py4), to late recrystallized pyrite (py5). This depletion is also
723 apparent in LA-ICP-MS maps (Figures 14, 15 and 16). Thus, it seems as though the complete
724 recrystallization of pyrite not only led to the expulsion of trapped micro-inclusions, but also the
725 expulsion of As, Sb, Tl, Pb, Hg, Cu, Zn, Ag and Mn from the pyrite lattice (Figure 12). Given that
726 progressive recrystallization has increased the concentration of various trace elements in py4 compared
727 to py3 from some deposits, the mechanism for pyrite depletion in late recrystallized pyrite must be
728 distinct. Additionally, this mechanism has uniformly affected all pyrite from all deposits. Late
729 recrystallized pyrite frequently forms relatively undeformed granoblastic aggregates with annealed
730 textures that likely formed during retrograde cooling after D2. Therefore, it seems most likely that the
731 main release of trace elements from pyrite actually occurred during retrograde cooling, as it favours a
732 contraction of pyrite lattice and could promote the expulsion of larger cations.

733 On the contrary, Co, Ni, and As are sometimes retained, sometimes even enriched, in the pyrite
734 structure during recrystallization, analogous to observations made by Large et al. (2007). For example,
735 Co and Ni are enriched in py5 compared to py4 at Buca della Vena (Figures 7A and 15), while py5
736 from Canale della Radice contains slightly more As than py4 (Figures 7B and 16). These elements
737 commonly show complex zoning patterns in py5 rims overgrowing py4 (Figures 14 and 15). Similar
738 late metamorphic pyrite from Kundarkocha, India, also displayed oscillatory zoning with respect to Co
739 and As (Hazarika et al., 2013). Other trace elements may also be zoned within py5 rims; zonation in
740 py4 is less common. The strong affinity of Co, Ni and As for the pyrite lattice seems to be the best
741 explanation for their preservation, even incorporation in pyrite during the late recrystallization stage,
742 despite most other elements being expelled at this time (e.g., Deditius et al., 2008; 2014; Large et al.,
743 2014).

744 The overall depletion of trace elements in late recrystallized pyrite from the Pollone mine was
745 proposed previously by Martarelli et al. (1995) and seems to be somewhat common to pyrite from
746 metamorphosed, recrystallized pyrite deposits. For example, Large et al. (2007) described trace
747 elements, especially Au, being liberated from diagenetic pyrite during recrystallization associated with
748 deformation. Similar behaviour has also been described during pyrite recrystallization by other authors
749 (e.g., Huston et al., 1995; Cook et al., 2009a; Hazarika et al., 2013; Kampmann et al., 2018) and during
750 recrystallization of base metal sulfides (e.g., Lockington et al., 2014; George et al., 2015; 2016; 2018).
751 In most previous studies, the content of trace elements in recrystallized pyrite seems to decline
752 progressively with degree of recrystallization. However, this study has shown that this simple rule may
753 not hold in all circumstances, as some trace elements may become enriched in pyrite during
754 metamorphism related recrystallization.

755 The different trace element patterns in recrystallized pyrite documented here may be somewhat
756 due to the fact that this study has sought to focus only on those trace elements hosted in the structure of
757 pyrite, rather than on those within micro- to nano-inclusions. Given that pyrite recrystallization clearly
758 leads to the expulsion of inclusions, those trace elements contained in such inclusions are effectively
759 depleted in pyrite during recrystallization. Thus, the progressive depletion of trace elements in pyrite
760 with degree of recrystallization noted by some previous authors may be due to the fact that their
761 microanalysis has, either intentionally or unintentionally, analysed micro- to nano-inclusions in pyrite
762 that are the actual hosts of trace elements. However, when one considers only those elements hosted in
763 solid solution in pyrite, then a more nuanced picture emerges. The availability of elements in the
764 environment of recrystallizing pyrite controls its enrichment or depletion on the prograde path, while
765 the main release of trace elements from pyrite occurs during retrograde cooling and pyrite annealing.

766

767 **5.4 Mobilisation of Sulfosalt Melts**

768

769 A number of studies have focussed on the potential of pyrite to host significant concentrations
770 of Au that may be released during metamorphic recrystallization, remobilised and subsequently re-
771 concentrated as visible Au and/or Au-tellurides (e.g., Large et al., 2007; Cook et al., 2009a; Kampmann

772 et al., 2018), or in new pyrite generations in orogenic Au deposits (e.g., Large et al., 2012). However,
773 far less attention has been given to the potential role of pyrite as a source of other metals that may
774 become mobilized and enriched, or indeed dispersed, during metamorphic recrystallization (e.g., Cook
775 et al., 1998).

776 During metamorphism of the Apuan Alps pyrite ores, the release of trace elements from pyrite,
777 particularly As, Sb, Tl, Pb, Hg, Cu and Ag, seems to have directly facilitated the formation of sulfosalt
778 assemblages enriched in these metals. Sulfosalts are typically hosted in late-stage extension veins and
779 along grain boundaries of the baryte and pyrite orebodies (Biagioni et al., 2013; 2016). At Monte
780 Arsiccio, Biagioni et al. (2013) recognised strong evidence that these sulfosalts were largely mobilized
781 and emplaced as melts based on, (1) high concentrations of low melting point chalcophile elements
782 (LMCE), (2) drop-like internal textures, (3) low interfacial angles between sulfosalts and matrix
783 minerals and (4) sulfosalt migration along matrix grain boundaries.

784 Low melting point chalcophile elements, Ag, As, Bi, Hg, Se, Sb, Sn, Tl, and Te (Frost et al.,
785 2002), have liquid phase fields at low temperatures. For example, a large liquid phase field exists at 315
786 °C within the Sb_2S_3 - Tl_2S - As_2S_3 pseudoternary system (Sobott, 1984). Melts are present in many other
787 Tl-bearing systems to temperatures below 300 °C (Moh, 1991). The more elements present in the
788 system, the lower the melting temperature will be. As such, the general increase in melting point
789 temperature caused by increasing pressure in many systems is assumed to be negated, or even
790 overwhelmed, by the addition of minor elemental components (e.g., Frost et al., 2002). Thus, at
791 temperatures associated with even greenschist facies metamorphism (e.g., 350-450 °C peak
792 metamorphism associated with the Apennine Orogeny), concentrations of LMCE may be expected to
793 melt (e.g., Tomkins et al., 2007). Because such melts have high densities, yet quite low viscosities, they
794 are easily mobilized and concentrated under a variety of stresses (e.g., Flaschen et al., 1960; Tomkins
795 et al., 2007). Despite this, sulfide melts in deposits metamorphosed at greenschist conditions are rare,
796 with the only other reported occurrences being Lengenbach, Switzerland (Hofmann, 1994), and in the
797 Highiş Massif, Romania (Ciobanu et al., 2006). Thus, the Apuan Alps sulfosalt melts are amongst the
798 lowest temperature sulphide melts reported.

799 This study contributes to the body of evidence supporting the interpretation that some of the
800 sulfosalts associated with the Apuan Alps pyrite orebodies, especially those at Monte Arsiccio, were
801 mobilised and concentrated as melts during greenschist facies metamorphism. Figure 17 shows various
802 sulfosalt assemblages from Monte Arsiccio. These are usually associated with late recrystallized pyrite
803 and situated at baryte grain boundaries. The finest grained sulfosalts occur as melt blebs that form planar
804 distributions seemingly along baryte cleavage. Figure 17A shows such blebs of arsiccioite-routhierite
805 solid solution members extending beneath the baryte sample surface. Accumulation of such tiny melts
806 form characteristic sulfosalt pockets interstitial to baryte grains (Figure 17B). These pockets typically
807 pinch out at low angles along grain boundaries and frequently consist of multiple sulfosalt phases
808 (Figure 17B, C and D). Often, internal textures appear drop-like, and commonly one sulfosalt forms a
809 selvage around another (Figure 17D). On occasions, sulfosalt melts appear to have accumulated and
810 become interconnected along baryte grain boundaries (Figure 17E). Such melt networks would have
811 allowed some local mobilisation of melts, which seem to have pooled in structurally controlled sites
812 (Figure 17F).

813 Although inferred in past studies (e.g., Biagioni et al., 2013), this work has, for the first time,
814 highlighted the direct influence pyrite may have in forming late stage sulfosalt melts through
815 recrystallization related trace element release. The intimate association of As ± Sb ± Ag ± Tl ± Hg ±
816 Cu ± Pb sulfosalts with late recrystallized pyrite provides strong evidence that sulfosalt melts were
817 formed from As, Sb, Tl, Pb, Hg, Cu and Ag released from pyrite during recrystallization. Based on LA-
818 ICP-MS data, early recrystallized pyrite at Monte Arsiccio on average hosts approximately 1,000 ppm
819 Tl in ore zones containing sulfosalt melts. Around 75 % of this Tl is released from pyrite upon complete
820 recrystallization. Modestly assuming that in the mixed pyrite-baryte ore only a third is pyrite by volume,
821 then a 10 × 10 × 10 cm package of ore would produce more than enough Tl during recrystallization for
822 a sulfosalt grain 1 cm³ in size comprising 20 wt. % Tl (common Tl-sulphosalts from Monte Arsiccio
823 protochabournéite/chabournéite, arsiccioite and routhierite all contain approximately 20 wt. % Tl).
824 Since all pools of mixed sulfosalt melt observed are smaller than 1 cm³, it is reasonable to conclude that
825 all Tl-sulfosalts could have formed from local melt drainage networks in the immediate package of
826 pyrite-baryte ore.

827 The main orebody at Monte Arsiccio is approximately lenticular, extending around 120 m NW-
828 SE, 90 m NE-SW with maximum thickness of 80 m (Costagliola et al., 1990). If one assumes an average
829 orebody thickness of 40 m, Monte Arsiccio may have contained around 340,000 m³ of ore. The deposit
830 is zoned, from dominantly pyrite in the lowermost section, to pyrite-baryte and finally to baryte-iron
831 oxides at the top. Yet for simplicity, if one were to divide the ore into two zones, pyrite-baryte and
832 baryte-iron oxides, with 50:50 pyrite:baryte and baryte:iron oxide ratios, one could hypothesize pyrite
833 makes up 25 % of the total ore by volume. Based on the assumptions above, the pyrite in the Monte
834 Arsiccio orebody could potentially release 350 tons of Tl upon recrystallization. Even assuming a much
835 more modest 700 ppm Tl in pyrite prior to metamorphism (the mean quantity of Tl hosted in all pyrite
836 generations in all ore zones), recrystallization of pyrite could still potentially liberate almost 250 tons
837 of Tl, the quantity contained in the worlds sole Tl-only deposit (Xiangquan, China; Zhou et al., 2005).

838 If all possible liberated Tl accumulated in Tl-sulfosalts, this would represent a total sulfosalt
839 volume of $5 \times 6 \times 6 \text{ m}^3$. It seems improbable that such a large volume of Tl-sulfosalts existed at Monte
840 Arsiccio. Therefore, it is likely, since Tl is highly soluble especially in acidic fluids (Xiong, 2007), that
841 some Tl was transported out of the deposit by acidic metamorphic fluids while only a small proportion
842 of Tl accumulated as melts under the greenschist facies metamorphic conditions. Upon fluid cooling
843 and neutralization, Tl would be re-deposited, perhaps replacing K in micas and other silicates forming
844 a halo around the deposit. Since carbonaceous rocks have strong neutralization potential, the overlying
845 Grezzoni Formation metadolostone would be ideal for destabilizing Tl⁺ in acidic fluids (Xiong, 2007).

846 Nevertheless, it is possible that significant accumulations of sulfosalts remain undiscovered in
847 parts of Monte Arsiccio, since collapses in the mine have rendered most of the orebody inaccessible.
848 Regardless, this study clearly highlights the significant amounts of Tl and other metals that may be
849 hosted in pyrite, and also the potential metamorphic recrystallization may have on redistributing metals
850 in a sulfide ore system. Sulfosalt melt accumulation and mobilisation seems to be an effective way of
851 concentrating metals in structurally controlled sites, while metals dissolved in fluids may be more
852 effectively transferred from the orebody and dispersed in surrounding host rocks.

853

854 **6. Conclusions**

855

856 • Five generations of pyrite have been observed in samples from the Apuan Alps pyrite ± baryte
857 ± iron oxide ores. Py1 consists of very fine framboids while py2 forms very coarse colloform
858 bands. Both are interpreted to have crystallized in the sedimentary package, incorporating trace
859 elements from surrounding water and sediments, as well as from circulating low-temperature
860 hydrothermal fluids in an intracontinental basin. Py3 forms fine grained disseminations often
861 aligned with the metamorphic fabric and is considered to have grown in the earliest stages of
862 deformation related to metamorphism. Py4 forms coarse, euhedral aggregates characterized by
863 abundant micro-inclusions and likely formed as earlier pyrite generations began to recrystallize.
864 Py5 is typically coarse, relatively 'clean' and often euhedral. It is interpreted to be the end-
865 product of pyrite recrystallization, with grain size increasing and micro-inclusions being
866 expelled late on the prograde path, then granoblastic annealed textures forming during
867 retrograde cooling.

868 • Apuan Alps pyrite (especially py1 and py2) is particularly rich in As (up to 17,400 ppm), Sb
869 (up to 5,100 ppm) and Tl (up to 4,200), while Ni, Pb and Mn may be present above 1,000 ppm,
870 and Hg, Co, Cu, Zn, Mo, Bi and Ag may all be present above 100 ppm.

871 • LA-ICP-MS element correlations strongly suggest that Tl, Sb, Cu and Ag are incorporated into
872 the pyrite lattice via coupled substitutions with trivalent Sb. Similarly, wedge-shaped trends
873 formed when Mn, Cu, Zn, Ag, Te, Hg, Pb and Bi are plotted against Sb indicate that the
874 concentrations of these elements in pyrite are strongly controlled by the presence of Sb such
875 that each element likely has an upper solubility limit that depends on the concentration of Sb in
876 pyrite. Above this limit, an element may form micro- to nano-inclusions of a discrete mineral,
877 and below this limit the element is likely present in solid solution.

878 • At Buca della Vena, Canale della Radice and Pollone, the concentration of As, Sb, Tl, Mn, Cu
879 and Zn in py4 is significantly higher than in co-existing py3. On the contrary, at Fornovolasco
880 and Monte Arsiccio py3 is generally enriched in As, Sb, Tl, Hg, Zn and Mn compared to py4.
881 Therefore, the trace element evolution of pyrite during early- to mid-metamorphism was not

882 uniform across all deposits and is likely controlled by the availability of elements in the
883 environment of recrystallizing pyrite on the prograde path.

884 • Concentrations of most trace elements decrease significantly from py4 to py5. Thus, complete
885 recrystallization of pyrite liberates significant concentrations of As, Sb, Tl, Pb, Hg, Cu, Zn, Ag
886 and Mn, interpreted to have occurred primarily during retrograde cooling and annealing.
887 However, Co, Ni, and As are sometimes retained, sometimes even enriched, in pyrite during
888 recrystallization.

889 • In the Apuan Alps pyrite ores, especially Monte Arsiccio, the release of trace elements from
890 pyrite during metamorphic recrystallization has directly facilitated the formation of late-stage
891 sulfosalts. At Monte Arsiccio, textural evidence suggests that As ± Sb ± Ag ± Tl ± Hg ± Cu ±
892 Pb sulfosalts intimately associated with late recrystallized pyrite were mobilised as sulfosalt
893 melts during greenschist facies metamorphism. These melts are amongst the lowest temperature
894 sulfide melts documented on Earth.

895 • Mass balance calculations show that all Tl contained in Tl-sulfosalts at Monte Arsiccio could
896 be supplied via local recrystallization of pyrite. In total, more than 250 tons of Tl could
897 potentially have been liberated from pyrite during metamorphism at Monte Arsiccio. Thus,
898 pyrite may host significant quantities of Tl and other metals in hydrothermal ore deposits, and
899 metamorphic recrystallization plays an important role in the redistribution of metals in such
900 systems. Evidence suggests that while redistribution has enriched the content of metals in some
901 late-stage metamorphic structural sites, much of Tl seems to have been lost from the orebody
902 and dispersed within the surrounding rock package.

903

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905

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910

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912

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1223

1224 **Figure captions**

1225

1226 Figure 1

1227

1228 Simplified geological map of the southern Apuan Alps. Figure modified from D’Orazio et al. (2017).

1229

1230 Figure 2

1231

1232 Reflected light photographs illustrating different pyrite types from the Apuan Alps. (A) Very fine framboidal
1233 pyrite (py1) < 20 µm in size from Canale della Radice. (B and C) Coarse colloform pyrite (py2) from Monte
1234 Arsiccio and Fornovolasco, respectively. (D) Fine (<~100 µm) disseminated pyrite (py3) of various habits from
1235 Pollone. (E and F) Coarse aggregates of anhedral pyrite (py4) with abundant micro-inclusions from Fornovolasco.

1236

1237 Figure 3

1238

1239 Reflected light photographs illustrating different pyrite types from the Apuan Alps. (A, B and C) Coarse (>~50
1240 µm) pyrite (py5) from Pollone, Monte Arsiccio and Canale della Radice, respectively. Note the fewer contained
1241 micro-inclusions than py4, the euhedral habits in (B) and the large grain size (up to 1 mm) in (C). (D, E and F)
1242 Pyrites showing transitional pyrite textures. (D) Py4 containing abundant micro inclusions grading to 'clean' py5
1243 with more euhedral habits from Monte Arsiccio. (E) Py4 cores overgrown with py5 rim from Fornovolasco. (F)
1244 Bands of fine py3 becoming inclusion rich py4 and eventually grading to 'cleaner' py5 from Fornovolasco.

1245

1246 Figure 4

1247

1248 Reflected light photographs illustrating different minerals associated with pyrite from the Apuan Alps. (A and B)
1249 Pyrrhotite (Po) and arsenopyrite (Apy) forming as replacement products of pyrite at Fornovolasco, respectively.
1250 (C and D) Coarse Tl-Sb sulfosalts (Tl-Sbss) associated with py5 from the Sant'Olga tunnel at Monte Arsiccio. Re
1251 = realgar.

1252

1253 Figure 5

1254

1255 Cumulative plots showing the mean concentration (horizontal line) and data spread for As, Sb, Tl, Hg, Pb, Ni, Co,
1256 Cu, Zn and Mn in pyrite from Buca della Vena, Canale della Radice, Fornovolasco, Monte Arsiccio, Pollone and
1257 Sennari. Y axis = concentration (parts per million).

1258

1259 Figure 6

1260

1261 Cumulative plots showing the mean concentration (horizontal line) and data spread for Mo, Bi, Ag, Se, Te, W,
1262 Cd, Sn, In and Au in pyrite from Buca della Vena, Canale della Radice, Fornovolasco, Monte Arsiccio, Pollone
1263 and Sennari. Y axis = concentration (parts per million).

1264

1265 Figure 7

1266

1267 Plots showing the concentration of various trace elements in different pyrite generations from Buca della Vena
1268 (A), Canale della Radice (B) and Fornovolasco (C). Y axis = concentration (parts per million). Different pyrite
1269 generations indicated at the base of each plot. P = primary pyrite (py1 – py2). Specific primary pyrite generation
1270 indicated by number next to each plotted primary pyrite point.

1271

1272 Figure 8

1273

1274 Plots showing the concentration of various trace elements in different pyrite generations from Monte Arsiccio
1275 (A), Pollone (B) and Sennari (C). Y axis = concentration (parts per million). Different pyrite generations indicated
1276 at the base of each plot. P = primary pyrite (py1 – py2). Specific primary pyrite generation indicated by number
1277 next to each plotted primary pyrite point.

1278

1279 Figure 9

1280

1281 Plots showing inter-element correlations in pyrite from the Apuan Alps. (A) Co vs. Ni, (B) Mo vs. Zn, (C) Zn vs.
1282 Mn, (D) Mo vs. Mn, (E) Pb vs. Cu, (F) Au vs. Bi, (G) Tl vs. Sb, (H) Tl + Cu + Ag vs. Sb, (I) Tl + Cu + Ag vs. As
1283 and (J) Sb vs. As. Data plotted as mol. %. Straight line is ideal 1:1 correlation.

1284

1285 Figure 10

1286

1287 Plots showing inter-element correlations in pyrite from the Apuan Alps. (A) Mn vs. Sb, (B) Cu vs. Sb, (C) Zn vs.
1288 Sb, (D) Ag vs. Sb, (E) Te vs. Sb, (F) Hg vs. Sb, (G) Pb vs. Sb and (H) Bi vs. Sb. Data plotted as mol. %. Straight
1289 line is ideal 1:1 correlation. In (B), (C), (D), (E) and (F), approximate upper limit of data is plotted as line of the
1290 form $C_X = m \times C_{Sb} + c$, where C_{Sb} and C_X = the mol. % concentrations of Sb and X in pyrite, respectively. X =

1291 Cu, Zn, Ag, Te or Hg. In (B), (E), (G) and (H), some selected LA-ICP-MS spots have been plotted (black crosses)
1292 that, on the basis of down-hole ablation profiles, have clearly analysed inclusions of Cu, Te, Pb and Bi,
1293 respectively.

1294

1295 Figure 11

1296

1297 Plots showing inter-element correlations in pyrite from the Apuan Alps. (A) Zn vs. As, (B) Au vs. As, (C) Te vs.
1298 Co and (D) Te vs. Ni. Data plotted as mol. %. Straight line is ideal 1:1 correlation.

1299

1300 Figure 12

1301

1302 Schematic diagram showing the textural and trace element evolution of Apuan Alps pyrite during metamorphic
1303 recrystallization.

1304

1305 Figure 13

1306

1307 LA-ICP-MS trace element maps showing the distribution and concentration of As, Sb, Tl, Pb, Hg, Mo, Zn, Mn,
1308 Ag, Co and Ni in colloform pyrite (py2) from Fornovolasco (FOR19). Since the standard STDGL3 does not
1309 contain Hg, the Hg map is qualitative only (displayed as counts-per-second; CPS). All other scales in parts per
1310 million. Note zoning of most elements in different colloform bands.

1311

1312 Figure 14

1313

1314 LA-ICP-MS trace element maps showing the distribution and concentration of As, Sb, Tl, Pb, Hg, Cu, Zn, Mn,
1315 Ag, Co and Ni in py3, py4 and py5 from Monte Arsiccio (ARS17M). Since the standard STDGL3 does not contain
1316 Hg, the Hg map is qualitative only (displayed as counts-per-second; CPS). All other scales in parts per million.
1317 Note zoning of As, Co and Ni in euhedral py5 grains.

1318

1319 Figure 15

1320

1321 LA-ICP-MS trace element maps showing the distribution and concentration of As, Sb, Tl, Pb, Hg, Co and Ni in
1322 py4 and py5 from Buca della Vena (BDV2). Since the standard STDGL3 does not contain Hg, the Hg map is
1323 qualitative only (displayed as counts-per-second; CPS). All other scales in parts per million. Note zoning of Co
1324 and Ni in py5 rims.

1325

1326 Figure 16

1327

1328 LA-ICP-MS trace element maps showing the distribution and concentration of As, Sb, Tl, Pb, Hg, Cu, Zn, Mn,
1329 Ag, Co and Ni in py4 and py5 from Canale della Radice (CDR3B). Since the standard STDGL3 does not contain
1330 Hg, the Hg map is qualitative only (displayed as counts-per-second; CPS). All other scales in parts per million.

1331

1332 Figure 17

1333

1334 Reflected light photographs and SEM images illustrating sulfosalt melt textures from Monte Arsiccio. (A) Fine-
1335 grained arsiccioite-routhierite solid solution members (Ars-Rou) occurring as planer distributions of melt blebs
1336 below the sample surface seemingly along baryte cleavage. Photo taken in crossed-polarized light. (B, C and D)
1337 Characteristic polymineralic sulfosalt pockets interstitial to baryte grains (Fd = ferdowsiite, Tl-Sbss = Tl-Sb
1338 sulfosalt, Ci = cinnabar, La = laffittite). Note how pockets pinch out at low angles along baryte grain boundaries
1339 and how Ars-Rou forms selvage around La in (D). Photo in (B) taken in crossed-polarized light. (E) Sulfosalts
1340 that have accumulated and become somewhat interconnected along baryte grain boundaries. Such accumulations
1341 would allow local mobilisation of melts. Photo taken in plane-polarized light. (F) Coarser accumulation of Tl-
1342 sulfosalts in structurally controlled site adjacent to fracture. Note twinning in Ars-Rou. Photo taken in crossed-
1343 polarized light.