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Constraints on the solid solubility of Hg, Tl and Cd in arsenian pyrite

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Abstract

Arsenic-rich (arsenian) pyrite can contain up to tens of thousands of parts per million (ppm) of toxic heavy metals such as Hg, Tl and Cd, although few data are available on their solid solubility behaviour. When a compilation of Hg, Tl and Cd analyses from different environments are plotted along with As in a *M*(Hg, Tl, and Cd)-As log-log space, the resulting wedge-shaped distribution of datapoints suggests that the solid solubility of the aforementioned metals is strongly dependent on the As concentration of pyrite. The solid solubility limits of Hg in arsenian pyrite – i.e., the upper limit of the wedge-shaped zone in compositional space – are similar to the one previously defined for Au by Reich et al. (2005) ($C_{Hg,Au}= 0.02C_{As} + 4\ x10^{-5}$), whereas the solubility limit of Tl in arsenian pyrite is approximated by a ratio of Tl/As = 1. In contrast, and despite a wedge-shaped distribution of Cd-As datapoints for pyrite in Cd-As log-log space, the majority of Cd analyses reflect the presence of mineral particles of Cd-rich sphalerite and/or CdS. Based on these data, we show that arsenian pyrite with *M*/As ratios above the solubility limit of Hg and Tl contain nanoparticles of HgS, and multimetallic Tl-Hg mineral nanoparticles. These results indicate that the

uptake of Hg and Tl in pyrite is strongly dependent on As contents, as it has been previously documented for metals such as Au and Cu. Cadmium, on the other hand, follows a different behaviour and its incorporation into the pyrite structure is most likely limited by the precipitation of Cd-rich nanoparticulate sphalerite. The distribution of metal concentrations below the solubility limit suggests that hydrothermal fluids from which pyrite precipitate are dominantly undersaturated with respect to species of Hg and Tl, favouring the incorporation of these metals into the pyrite structure as solid solution. In contrast, the formation of metallic aggregates of Hg and Tl or mineral nanoparticles in the pyrite matrix occur when Hg and Tl locally oversaturate with respect to their solid phases at constant temperature. This process can be kinetically enhanced by high-to-medium temperature metamorphism and thermal processing or combustion, which demonstrates a retrograde solubility for these metals in pyrite.

Keywords: mercury, thallium, cadmium, arsenic, pyrite, nanoparticles

Introduction

Pyrite (FeS_2) is the most common sulphide in the upper crust and can host from a few parts per million (ppm) up to weight percent (wt. %) levels of heavy metals and metalloids such as As, Hg, Tl and Cd (Rickard and Luther 2007; Deditius et al. 2008; Lefticariu et al. 2011, Keith et al. 2016). Mineral processing of gold-bearing arsenian pyrite and combustion of pyrite-bearing coal result in the liberation of these toxic elements into the environment posing significant threats to the biosphere (Ikramuddin et al. 1986; Wang et al. 2010; Kolker 2012). For example, 810 Mt/year of Hg are released into the atmosphere as a result of coal combustion (Pirrone et al. 2010), and industrial processing is responsible for the mobilization of 2000-5000 t/year of Tl (Kazantzis 2000; John Peter and Viraraghavan 2005). Furthermore, recent studies have estimated the emission of 4.7 t/year of Cd from sulphide ore mining and 10 t/year in air from basic non-ferrous metals manufacture in Australia (Kyle et al. 2011). In the particular case of As, there are numerous studies

reporting natural and anthropogenic contamination of water and soil, and its effects on human health (Plant et al. 2014). Among the numerous toxicological effects of As and heavy metals (Tl, Hg and Cd) on biota, carcinogenic and brain dysfunction effects are considered some of the most important for human life (Kyle et al. 2011 and references therein).

In arsenian (As-rich) pyrite, previous studies have revealed that Hg and Tl tend to accumulate in zones where precious metals such as Au are concentrated, particularly, in low-temperature (<200 ºC) sedimentary environments, and Carlin-type and epithermal Au deposits (Cline 2001; Emsbo et al. 2003; Reich et al. 2005; Barker et al. 2009; Deditius et al. 2011; Large et al. 2014). In contrast, it is known that Cd partitions into sphalerite (ZnS) and/or Cd-sulphides under higher-temperature magmatic-hydrothermal conditions and submarine hydrothermal vents (Cook et al. 2009; Pass 2010; Lockington et al. 2014; Revan et al. 2014; Keith et al. 2016). Metal incorporation into pyrite is complex and studies have shown that both speciation (structurally-bound vs. nanoparticulate) and concentration (ppm to weight % levels) are controlled by the incorporation of As into the structure (Reich et al. 2005; Deditius et al. 2014). For example, transmission electron microscopy (TEM) observations have revealed that metals like Au (and associated Hg) in pyrite are commonly hosted as nanoparticles (NPs) or are incorporated into solid solution, particularly in the As-rich growth bands and sectors (Palenik et al. 2004; Deditius et al. 2011). The coupled geochemical behaviour between metals and arsenic (e.g., Au vs. As) is clearly exemplified by the solid solubility model proposed by Reich et al. (2005) for Carlin-type and epithermal Au deposits where the Au content of pyrite is a function of As content. Using micro-analytical (EMPA, SIMS) and spectroscopic analyses (synchrotron XANES), the aforementioned authors showed that when Au-As datapoints are plotted on an Au vs. As log-log space, an As-dependent Au solubility curve defines two fields where Au is present as native Au nanoparticles (above the solubility curve) or as solid solution Au^{+1} (below the solubility curve). Recently, this solubility limit was extended to all types of ore deposits containing pyrite (Deditius et al. 2014), and recent studies have reported a significant relation between As and metals such as Ag and Cu, to name a few (Reich et al. 2010,

2013).

Despite these advances, to the best to our knowledge there is no detailed information on the behaviour of Hg, Tl and Cd in pyrite, and their potential dependence on the contained As of the pyrite mineral host. In one of the very few studies documenting this particular association, Zhou et al. (2005) report elevated concentrations of Tl (up to 3.5 wt. %) in pyrite from the Xiangquan deposit in China that correlate with high concentrations of As (up to 2.6 wt. %) and Hg (up to 400 ppm). In this Tl deposit, thallium occurs mainly in As and Hg-rich pyrite with minor amounts of lorandite ($TlAsS_2$) and hutchinsonite ($TlFeS_2$), strongly suggesting a complex incorporation of these metals in pyrite. Furthermore, experimental evidence suggests that sorption of Cd and other soft Lewis acids in the natural environment suppresses FeS_2 oxidation, and may retard the release of acidity and trace metals to the environment (Bostick et al. 2000). However, the particular role of As during Hg, Tl and Cd uptake and release remains obscure. This significant gap in understanding of the geochemical behaviour of Hg, Tl and Cd in arsenian pyrite encouraged us to test the hypothesis that these metals have solid solubility behaviour in arsenian pyrite that is similar to that of Au.

Coupled geochemistry of Hg, Tl, Cd and As in pyrite

A compilation of previously published electron microprobe analyzer (EMPA), secondary ion mass spectrometry (SIMS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), proton-induced X-ray emission (PIXE), instrumental neutron activation analysis (INAA) data was used to constrain elemental relations between Hg, Tl, Cd and As in pyrite (Table 1). Data was compiled for pyrite from a variety of environments including porphyry Cu, epithermal and orogenic Au, volcanogenic massive sulphide (VMS), Witwatersrand and Carlin-type Au deposits, and pyrite-bearing metamorphic rocks, sedimentary sequences and coal beds. This work provides a compilation of pyrite analyses obtained by methods that combine low detection limits (ppm levels) such as SIMS, LA-ICP-MS and PIXE, with high spatial resolution techniques (EMPA).

Concentrations of Hg, Tl, and Cd in pyrite in these environments vary from below the

105 detection to ~15,000 ppm. With the exception of pyrite from the Mt. Polley porphyry Cu-Ag-Au
106 deposit, more than 99% of the metals' analyses in arsenian pyrite plot below the *M*/As = 1; where *M*
107 = Hg, Tl and Cd (Fig. 1A-C). In all three cases, the distribution of the data points approximates the
108 wedge-shaped zone interpreted as the solid solubility limit for Au in arsenian pyrite (Reich et al.
109 2005; Deditius et al. 2014). The highest content of Hg and Tl was measured in pyrite from Carlin-
110 type, epithermal and coal deposits, while the highest concentrations of Cd (up to ~1000 ppm) occur
111 in pyrite from porphyry Cu deposits, VMS deposits, and sedimentary environments (Figs. 1A-B).
112 No data for Cd is available for pyrite from Carlin-type deposits.

113 Mercury. Figure 1A displays a positive trend of increasing Hg and As contents in pyrite. The
114 lowest content of Hg, ~0.01-10 ppm, was reported for pyrite from porphyry (Cu-Au-Mo) deposits,
115 sedimentary pyrite, and orogenic Au deposits (Pass 2010; Franchini et al. 2015; Marin-Carbonne et
116 al. 2014; Paleonova et al. 2015). In contrast, the highest amounts of Hg were found in pyrite from
117 Carlin-type and epithermal Au deposits (Cline 2001; Emsbo et al. 2003; Deditius et al. 2011).
118 Except for a few outliers, almost all the data plot below the Hg/As = 1 limit (Fig. 1A). As a
119 reference, the As-dependent solubility limit of Au is shown. EMPA data of Hg-rich (500-1,900 ppm)
120 arsenian pyrite from the Lone Tree Au deposit in Nevada plot above the solubility limit defined by
121 Reich et al. (2005) ("nanoparticle field", NP), and close to the ratio Hg/As = 1 that marks the upper
122 limit of the datapoint cloud (Fig. 1A, black triangles, circled and labelled "NP"). High-resolution
123 TEM observations of the high-Hg pyrite revealed the presence of HgS nanoparticles (NPs)
124 (Deditius et al. 2011). Therefore, analytical data are indicative of the occurrence of Hg-bearing NPs
125 when Hg and As concentrations exceed the solubility limit in pyrite by Reich et al. (2005), or Hg/As
126 ratios approach unity (Fig. 1A). A similar behaviour was observed for Hg-bearing metamorphic
127 pyrite, where Hg partitions into the low-temperature melt (< 420^{o}C, greenschist facies) and
128 recrystallizes as complex Tl-Hg-As-Sb-(Ag,Cu)-Pb sulfosalts in pyrite samples from Alpi Apuane
129 (Biagioni et al. 2013). These analyses also plot above the solubility limit (in the NPs field), close to
130 Hg/As = 1 (Fig. 1A, open squares, circled and labelled "NP").

In contrast, high Hg and As contents of pyrite in the Deep Star Carlin-type deposit in Nevada plot below the solubility defined by Reich et al. (2005), and at Hg/As ratios lower than 1 (Hg: 900-14,300 ppm, As: >50,000 ppm As, Fig. 1A). TEM observations and XANES analyses of these anomalously Hg-As-rich pyrite samples show no evidence of Hg-bearing NPs (Reich et al. 2005). Therefore, Hg-As datapoints plotting below the solubility limit are interpreted to contain structurally bound or solid solution Hg (Fig. 1A, oval, labelled "SS").

Our analysis shows, as a first approximation, that the As-dependent solubility limit of Au in Figure 1A is a good proxy to evaluate the speciation of Hg in pyrite, i.e., Hg is incorporated in solid solution at lower Hg/As ratios, while its incorporation is favoured as NPs at high Hg/As ratios. A similar behaviour/feature of solid solubility for Hg and Au in pyrite is expected, considering the ability of these two metals to form alloys and amalgams even at the nanoscale (Schopf et al. 2015). However, it is important to mention that this behaviour is observed in the higher range of concentrations of As and Hg, i.e., > 1000 ppm and >100 ppm, respectively (Fig. 1A). Unfortunately, no nano-analytical and spectroscopic information of Hg and As in pyrite is available for samples characterized by lower amounts of these elements (i.e., <100 ppm for both Hg and As).

Thallium. Figure 1B shows that Tl-As data of pyrite from different environments form a similar wedge-shaped zone, limited above by a line of approximate slope Tl/As=1. Pyrite from Carlin-type and coal deposits contain the highest amount of Tl, while the concentrations of Tl in pyrite from porphyry Cu and orogenic Au deposits are generally below 1 ppm. This can be attributed to the volatile nature of Tl and its strong affinity towards organic matter. A recent review of the composition of sedimentary pyrite by Large et al. (2014) revealed a broad range of Tl concentrations varying from 0.1 ppm – 10,000 ppm. The majority of these analyses plot below a Tl/As ratio of 1 (Fig. 1B). Similarly to Hg, Tl-bearing NPs in pyrite were observed in metamorphic settings, suggesting that metamorphism induced the mobilization of multimetallic melts (Bagnioni et al. 2013). These representative Tl-As analyses plot homogenously above the indicated Tl/As = 1, over range of As concentrations from 10's to 10,000's ppm. Unfortunately, there is no

157 nanostructural or spectroscopic data that would help constrain the speciation and/or its structural
158 position of Tl in arsenian pyrite. However, Kouzmanov et al. (2010) did not notice any Tl particles
159 (or other metallic nanonuggets) during LA-ICP-MS profiling of pyrite from the Rosia Poeni
160 porphyry Cu deposit. Therefore, acknowledging the fact that it is not straightforward to establish
161 precise Tl-As solubility relations with the available data, we suggest that the upper limit ratio Tl/As
162 = 1 may represent, as a first approximation, the solid solubility limit of Tl in arsenian pyrite (i.e.,
163 analyses plotting below Tl/As ratios of 1 represent Tl in solid solution, while datapoints plotting
164 above this limit are most likely related to the presence of Tl-bearing nanoinclusions).

165 Cadmium. Similarly to Hg and Tl, the majority of Cd data points cluster in a wedge-shaped
166 zone and plot below the *M*/As ratio of 1 (Fig. 1C). The amount of Cd in pyrite varies significantly
167 between the different types of ore deposits. The highest contents of Cd, > 5 ppm, have been
168 reported for pyrite from porphyry Cu deposits, hydrothermal vents in mid-ocean ridges, and
169 volcanic precipitates (Yudovskaya et al. 2006; Pass 2010; Revan et al. 2014; Keith et al. 2016),
170 while the lowest amounts (below ppm-levels) have been found in As-poor pyrite from epithermal
171 Au deposits (Franchini et al. 2015) (Fig. 1B). Most of the datapoints come from sedimentary
172 settings, where variable Cd concentrations spread from ppb- up to thousands of ppm-levels (Large
173 et al. 2014) (Fig. 1C). Unfortunately, there is no data available to constraint the structural behaviour
174 of Cd in arsenian pyrite or predict the presence of Cd NPs vs. solid solution incorporation.
175 However, it has been suggested that Cd partitions into sulphide nano- and/or micro-particles and
176 crystallizes as CdS and/or Cd-rich sphalerite in pyrite under wide range of temperatures (from 250-
177 650 ^{o}C) conditions (Hannington et al. 1988, 1991; Genna and Gaboury 2015; Keith et al. 2016).

178 Therefore, it is likely that higher concentrations of Cd contents in pyrite from porphyry Cu
179 deposits, hydrothermal vents (VMS) and volcanic precipitates (Fig. 1C) represent inclusions of Cd-
180 sulfides and or sphalerite, as previously reported (Hannington et al. 1988, 1991; Genna and
181 Gaboury 2015; Keith et al. 2016). The datapoints representing Cd in sphalerite NPs plot in the field
182 of nanoparticles and solid solution, Thus, it is likely the wedge-shaped distribution of the Cd data

183 points in the Cd-As log-log space below the Cd/As = 1 ratio does not indicate a solubility limit,
184 despite its position to be similar to the one for Au, Hg, and Tl (Fig. 1C).
185
186 **Intrinsic controls on the solubility limit of Hg, Tl, and Cd in arsenian pyrite**
187 Our compilation and review of the available data on the behaviour of Hg, Tl and Cd in
188 arsenian pyrite has revealed the presence of similar compositional features previously reported for
189 Au (e.g., Reich et al. 2005; Deditius et al. 2014). Perhaps the most noticeable first-order feature
190 observed is the wedge-shaped pattern that arises when Hg, Cd and Tl concentrations are plotted
191 against As. These wedge-shaped zones are limited above by a solubility limit in compositional log-
192 log space, which can be approximated either by the solubility relation found for Au by Reich et al.
193 (2005) (for Hg, Cd and Au: $C_{Hg,Cd,Au} = 0.02C_{As} + 4 \times 10^{-5}$, see curve in Figure 1**)** or, for the particular
194 case of Tl, by a Tl/As ratio of ~1 (Fig. 1B). While these relationships suggest some common and
195 fundamental mechanisms controlling the uptake as Au, Hg, and Tl into arsenian pyrite, the
196 behaviour of Cd seem to be controlled by the precipitation of mineral nanoparticles of sphalerite
197 and/or Cd-sulphides and is more likely related to fluid-mineral interaction. The described features
198 are relevant to explore the mechanisms of incorporation of Hg, Tl and Cd into pyrite, but may also
199 have a similar impact when evaluating the release of such metals from the arsenian pyrite matrix.
200 It has been documented that the incorporation of anionic (As^{1-}, Simon et al. 1999; Abraitis et
201 al. 2004) or cationic (As^{3+}, Deditius et al. 2008) arsenic species into the pyrite structure facilitates
202 substitution of other metals, most noticeable Au. Similar behaviour reported here for the heavy
203 metals Hg and Tl in arsenian pyrite may be related to the relatively small differences in their crystal
204 radii with respect to Au. Substitutional mechanisms discussions are commonly limited to the formal
205 charges, which should be treated with caution considering the covalent type of bonding in
206 sulphides, i.e., Au^{+} and Au^{3+} (0.157 and 0.099 nm, respectively), Hg^{+} and Hg^{2+} (0.133 and 0.116
207 nm, respectively), Tl^{+} and Tl^{3+} (0.164 and 0.1025 nm, respectively), (data after Shannon 1976, for
208 octahedral coordination).

209 The incorporation of Hg and Tl depends on the presence of other substitutions in the pyrite
210 structure. Therefore, changes in the semi-conducting behaviour of pyrite surfaces during crystal
211 growth may have a significant impact on metal uptake, i.e., As and Sb promote *p*-type conductivity,
212 while the presence of divalent metals such as Co and/or Ni in the structure induces *n*-type
213 conductivity (Pearce et al. 2006 and references therein). Substitution of As for S in the tetrahedral
214 position generates a hole in the Fe *d*-like valence band, which makes As an acceptor capable of
215 accommodating one electron from the valence band, and as a consequence, a charge carrier. Such
216 contrasting As vs. Co/Ni-rich areas may occur within a single crystal of pyrite. In addition, the
217 increase in As contents in pyrite expands the unit cell and creates structural distortion. Therefore, a
218 combination of the electrical and crystal-chemical properties of As may generate favourable
219 conditions promoting the incorporation of heavy metals in pyrite in natural environments (Lehner et
220 al. 2006, 2012). In the case of synthetic materials, it has been reported that *p*-type conductivity
221 promotes high solid solubility of Au in semiconductors matrices such as silicon (O'Shaugnessy et
222 al. 1974). Because *p*-type conductivity occurs in phosphorous-doped synthetic pyrite (Blenk et al.
223 1993), it is very likely that the effects on metal behaviour are similar. In particular, phosphorous-
224 bearing pyrite crystals have complex morphologies such as combinations of {111}, {110} and
225 {100} forms that have also been observed in natural As and Au-rich hydrothermal pyrites
226 (Chouinard et al. 2005). However, the influence of As on pyrite morphology remains ambiguous, as
227 some authors report enhanced development of the {111} face (Sunagawa and Takahashi 1955),
228 while others document higher contents of As in |hk0| sectors (Chouinard et al. 2005).

229 The other important factor that may regulate the amount of impurities in the pyrite structure
230 is the size of the single crystals, which can be as small as 8 nm (Deditius et al. 2008). Material
231 science provides evidence for nanoparticulate semiconductors that experience self-purification
232 resulting in the expulsion of the non-stoichiometric impurities/dopants towards the grain boundaries
233 (Erwin et al. 2005 and references therein). This feature is consistent with the occurrence of
234 "invisible" (i.e., refractory) Tl in hydrothermal coarse-grained pyrite from Xiangquan thallium

deposit (China), which contains up to 35,000 ppm. In contrast, the amounts of Tl, Hg and Cd in the colloidal form of pyrite in this deposit were below 9,300 ppm; 400 and 230 ppm, respectively (Zhou et al. 2005). Such behaviour is mainly controlled by the surface morphology, shape of the nanocrystals, and surfactants in the solution. While in synthetic systems the diffusion of the trace element (Mn) in semiconductors (CdSe) around temperature of 300 $^{\circ}$C is negligible, 1-3 Å in short time (1h) (Jamil and Shaw 1994), the equilibration and homogeneous distribution of the trace element within individual nanoparticles can be achieved over the geological time scale (Reich et al., 2006; Deditius et al. 2008; González-Jiménez et al., 2015). Moreover, it was found that the formation of trace element-rich semiconducting NPs - with homogeneously distributed doping element - is possible when the trace element is adsorbed on the growing surface of the nanocrystal (Erwin et al. 2005). Consequently, the rate of kinetically controlled growth of pyrite must exceed the rate of equilibration and removal of the impurities to accommodate Au, Hg and Tl in the crystal structure. This kinetically controlled formation of pyrite under lower temperature conditions (e.g., collomorphic pyrite, Huston et al. 1995; Abraitis et al. 2004), promotes distortion of the pyrite structure and incorporation of higher quantities of large metals. This is envisaged by a positive correlation between Tl (up to about 8,000 ppm) and As in porous pyrite associated with the (As,Sb)-growth zones, which have been interpreted to be a result of precipitation from hydrothermal fluids originating from multiple sources (Ingham et al. 2014). It is likely that the presence of As-promoting distortion and surface modification enables incorporation of the large cations, Au, Hg, and Tl, via stoichiometric or nonstoichiometric substitutions involving the formation of vacancies (Chouinard et al. 2005; Deditius et al. 2008), or nanoscale phase decomposition such as polycrystalline pyrite nano-aggregates (Palenik et al. 2004).

Role of fluid composition and temperature

Firstly, the chemical composition of the fluid is one of the main factors that control metal uptake during pyrite growth. For example, the presence of Hg-rich growth zoning on pyrite in

Carlin-type and epithermal Au deposits is indicative that the deposition of Hg is restricted by its availability in the fluid, similar to Au (Barker et al. 2009). In sedimentary environments, pyrite is a natural sink for Hg during coal formation, where recrystallized pyrite can incorporate up to 7600 ppb of Hg (Hannington et al. 1991; Lefticariu et al. 2011). In both examples, the mechanism of Hg incorporation would involve the breakdown of aqueous Hg complexes and the adsorption of Hg species onto the growing pyrite surfaces. It is likely that this process is enhanced by local fluid oxidation (Chouinard et al. 2005; Barker et al. 2009) and the presence of As in the mineralizing fluid (see previous section).

Chemisorption of metal species onto pyrite surfaces can result in a highly efficient mechanism for sequestering metals from mineralizing fluids. Erhardt et al. (2000) reported partial oxidation of pyrite surfaces during adsorption of Hg^{2+} with the formation of inner surface complexes. This mechanism is supported by XPS and XAS studies of Hg incorporation into pyrite, which revealed formation of surface complexes between S(-I) and Hg(II) (Behra et al. 2001), and Hg-Cl complexes on the pyrite surface (Bower et al. 2008). No native Hg or Hg-sulphides were found in these studies. Unlike Hg (or Tl), the relatively small amounts of Cd present in pyrite may be a result of the decreasing efficiency of Cd uptake with increasing concentration in the pyrite surface (Parkman et al. 1999). The lack of separation between the datapoints representing nanoparticulate Cd-rich sphalerite and Cd in solid solution in pyrite (Fig. 1C) suggests that Cd incorporation into pyrite is not controlled by solid state solubility rules. In contrast, it is suggested that sphalerite NPs form at the pyrite-fluid interface due to rapid precipitation from the Cl-depleted fluids, which become supersaturated with respect to (Zn,Cd)-sulphides (Reich et al. 2013; Keith et al. 2016). In addition, Bostick et al. (2000) proposed reconstruction and disproportionation of pyrite surface that resulted in the mixture of native sulphur, Fe-hydroxides and CdS, supporting preferential formation of particulate sulphides rather than incorporation into the structure as solid solution (Fig. 1C).

Secondly, the temperature of pyrite formation or subsequent metamorphism is a key factor

287 controlling the metal budget of pyrite in geologic environments. The identification of particulate Hg
288 and Tl in pyrite in low-temperature metamorphic rocks Bagioni et al. (2013) demonstrates that low-
289 temperature recrystallization processes involving trace element-rich pyrite are one of the most
290 important factors controlling the post-entrapment mobilization of these metals (Fig. 1). The
291 temperature of mobilization depends on the association of metals; i.e., the larger the numbers of
292 metals, characterized by low-temperature melting, chemically connected in the structure of the
293 hosting sulphide the lower the melting temperature of the sulphide domain (Tomkins et al. 2007);
294 the melting temperatures of Tl-Au, Hg-Au, and Bi-Au systems are as low as 147 ^{o}C, 39 ^{o}C, and 241
295 ^{o}C respectively (Okamoto and Massalski 1987).

296 The in-situ thermal stability experiments by Reich et al. (2006) are one of the very few
297 studies that document the effect of temperature on metal nanoparticle stability in pyrite. In this
298 study, native Au NPs of ~10 nm begin to dissolve in the As-rich pyrite matrix and diffusively
299 growth at the expense of smaller ones at temperatures close to 400 ºC. Therefore, it is likely that
300 Hg, Tl, and Cd may be liberated much easier from the structure of a distorted, nanoparticulate, As-
301 rich pyrite matrix. However, it is expected that these metals will behave differently within
302 multimetallic NPs with the increase of temperature as envisaged by separation of Pt and Au,
303 diffusion of Au through the Ag_2S, and its Ostwald ripening-based recrystallization on the surface of
304 Ag_2S (Yang and Ying 2010). Alternatively, the aggregates of separate mineral NPs will form alloys
305 with the temperature increase (Bonifacio et al. 2015). For example, given the paucity of information
306 on the occurrence of Tl NPs in well-investigated pyrite samples suggests that Tl preferentially
307 dissolves into the pyrite matrix (see Fig 1B), rather than forming separate domains of Tl-sulfides.
308 This might be related to the possible higher oxidation state of Tl^{3+} in collomorphic pyrite (Huston et
309 al. 1995). In addition, the decrease in the Fe content in pyrite will promote formation of "liquid-
310 like" As-Fe-S NPs entrapped in the arsenian pyrite structure (Deditius et al. 2009), which in turn
311 may sequester migrating/diffusing metals. The separation of metallic nanodomains is also supported
312 by positive correlation between Cd and Zn in pyrite from paleo-chimneys, which suggests that Cd is

incorporated by micro-inclusions of sphalerite (Revan et al. 2014; Genna and Gaboury 2015; Keith et al. 2016). In additional, under hydrothermal conditions >344 ^{o}C HgS (metacinnabar) precipitates from Hg^{2+}-aqueous solutions rich in S(-II), while cinnabar is forming below the indicated temperature (Barnes and Seward 1997).

Consequently, the behaviour of Hg, Tl and Cd in arsenian pyrite is an outcome of primary intrinsic factors, in the studied case, the presence of As-rich pyrite surface and extrinsic features of the environment in which pyrite forms. These include: (i) "fluid"-control, i.e., chemical composition of the hydrothermal fluid; which also impacts the surface morphology and thus controls chemisorption and processes of "solid solution" incorporation, and (ii) a temperature control that influences stability of the matrix, formation and stability of NPs.

Geochemical implications and future studies

Based on the aforementioned discussion, we propose a conceptual model that describes the behaviour of Hg, Tl and Au in the metal-As-T space (Fig. 2). Figure 2 shows that the two fields NPs and solid solution are separated by bowl-like solubility surface with the crest of solubility limit after Reich et al. (2005) projected from the As-Au space. Note that this solubility limit crest may shift up- and downwards along the solubility plane with the changes in the temperature (Fig. 2). The increase in temperature is likely to cause metal mobilization from pyrite during recrystallization and high-temperature alteration under metamorphic conditions reported for orogenic Au deposits (Sung et al. 2009). On the contrary, cooling will promote formation of metallic mineral NPs in case of As-poor pyrite across all geological environments as discussed in detail by Deditius et al. (2014).

The recognition of solid solubility limits for Hg, and Tl, and the presence of micro-to-nanoparticulate Cd in pyrite provide new insights into the environmental sequestration of Hg, Tl and Cd. Until now, the geochemical behaviour of Hg and Tl in pyrite was exclusively linked with the presence mineral particles and/or (non) stoichiometric structural substitutions. We suggest that the uptake of Hg, and Tl into arsenian pyrite is strongly tied to presence of As, and that the

339 occurrence of these metals as nanoparticles vs. solid solution in pyrite may be predicted if the solid
340 solubility limits are precisely determined using a combination of experimental, analytical and
341 spectroscopic data. The distribution of most of the analyses below the solubility limit suggests that
342 Hg and Tl are preferentially incorporated as structurally-bound species in pyrite, probably through
343 chemisorption processes in aqueous solutions that are mostly undersaturated with respect to their
344 native metals species or mineral NPs (Figs. 1 and 2). Furthermore, the restricted occurrence of Hg,
345 and Tl nanoparticles in arsenian pyrite, as predicted by the solid solubility limits, is most likely the
346 result of local over-saturation of aqueous solutions and/or post-entrapment modifications resulting
347 from changes in temperature during diagenesis or metamorphism. The documented lack of a
348 solubility limit for Cd in arsenian pyrite can be extended to other elements, e.g., Pb, Ag, Te and Sb,
349 which have been detected in significant concentrations in pyrite but predominantly occur as micro-
350 to-nanoscale inclusions in porous zones (Pačevski et al. 2012).

351 Considering the scarce nanostructural and largely non-systematic information available for
352 hazardous metals in pyrite, future studies aiming to elucidate the geochemical cycle of these
353 elements should incorporate a combination of experimental approach and studies of representative
354 natural samples involving: i) determination of the major and trace element composition using a
355 combination of EMPA, SIMS and/or LA-ICP-MS, ii) preliminary tests to target NPs (e.g., FE-SEM
356 observations, and depth profiling using SIMS or LA-ICP-MS), iii) sampling prospective areas of
357 pyrite using focused-ion beam (FIB), iv) TEM studies to detect, image and resolve the crystal-
358 chemistry of NPs, vi) synchrotron-based XANES and EXAFS studies to determine the oxidation
359 state and/or speciation of trace elements.

360

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618

619 **Figure captions**

620 **Figure 1.** Concentrations of Hg, Tl, and Cd as a function of As concentration in pyrite (in ppm; log-
621 log scale). Grey solid line depicts the solubility limit of Au in pyrite as a function of As content after
622 Reich et al. (2005). Distribution of the analyses in metal-As log-log space as a function of the type
623 of ore deposit. (A) Solubility limit of Hg in arsenian pyrite compared to the solubility of Au in
624 arsenian pyrite. (B) Solubility limit of Tl in arsenian pyrite compared to the solubility of Au in

625 arsenian pyrite. (C) Concentration of Cd vs. As in arsenian pyrite compared to the solubility of Au
626 in arsenian pyrite. Note the thick, black, dashed line outlining the data points that represent Cd-rich
627 sphalerite inclusions in pyrite from VMS deposits and hydrothermal vents. The summary of
628 literature data is provided in Table 1.

629 **Figure 2.** Solubility of metals (Au, Hg, Tl) in arsenian pyrite in As-metal-T (log-log-^{o}C) space.
630 Note the shift of the solubility limit along the solubility place as a function of changing temperature.

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Figure 1

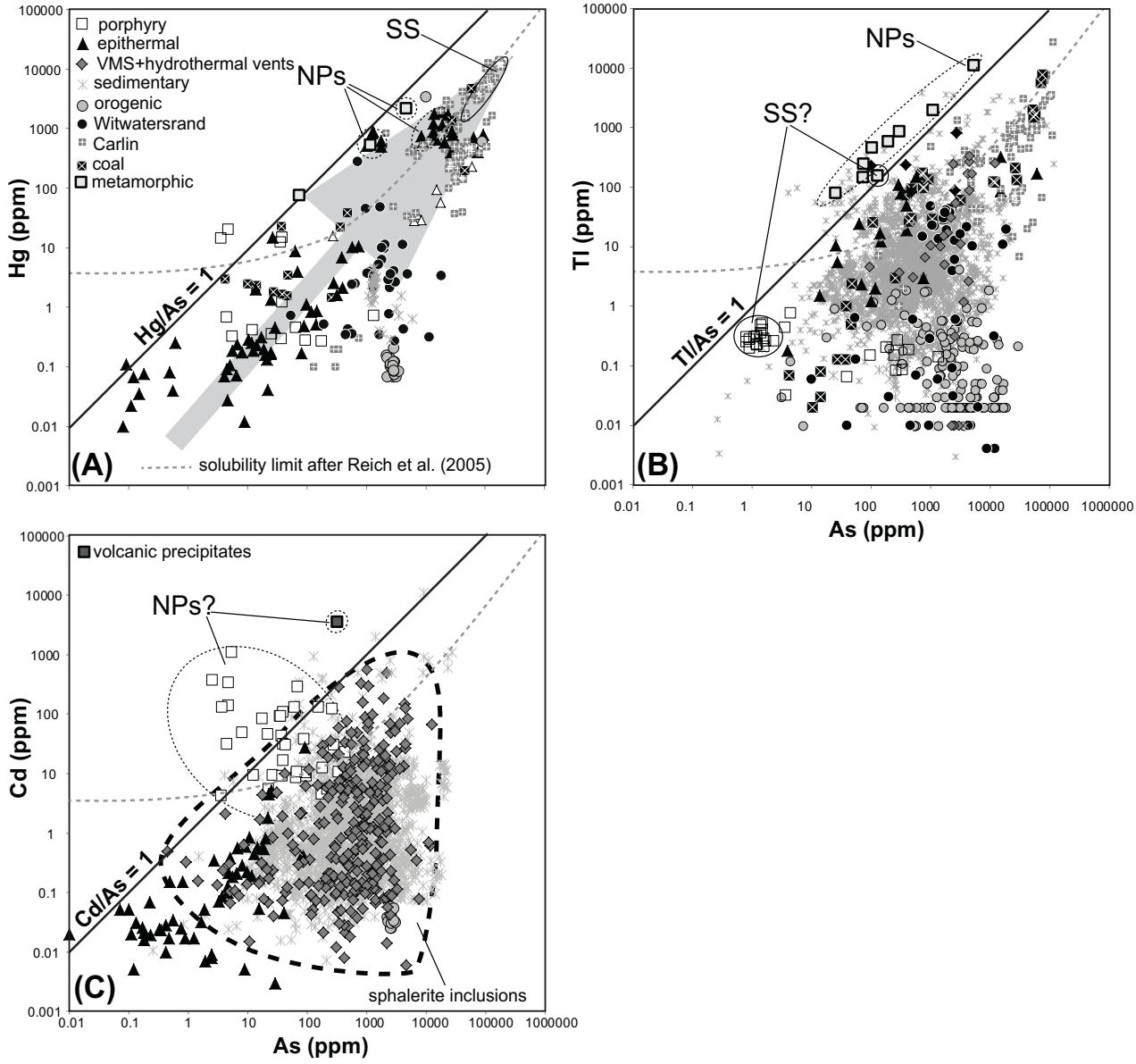

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Figure 2

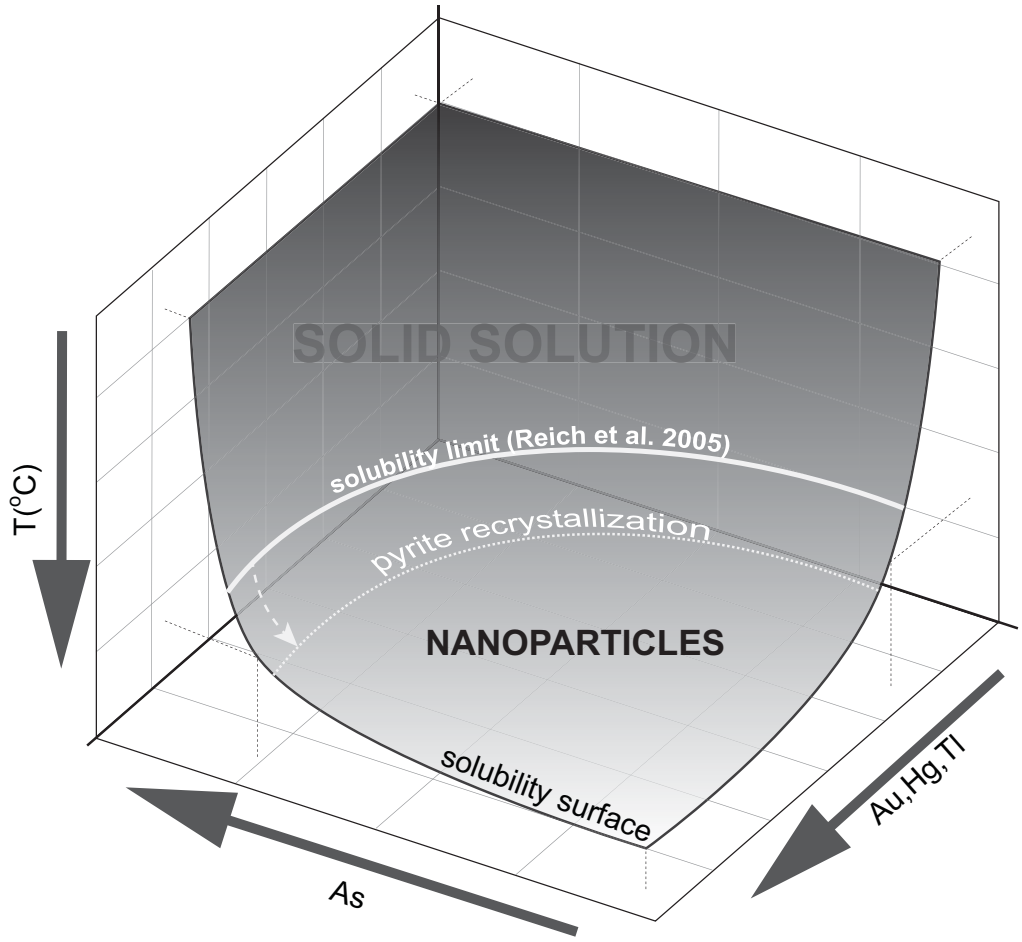

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Table 1. List of the discussed deposits.

REFERENCE	TYPE OF ORE DEPOSIT	ELEMENTS			LOCALITY, MINERAL ASSEMBLAGE (MA)*, INCLUSIONS (INCL)	ANALYTICAL METHODS
		Hg	Tl	Cd		
Scott et al. (2009)	Sedimentary	--	X	--	Fosterville (Victoria, Australia); MA: py, gn, INCL: N/D	LA-ICP-MS
Hoffman et al. (2009)			X		Belingwe Greenstone Belt (Zimbabwe); South Africa; MA* and INCL** - N/D ***	HR-ICP-MS
Berner et al. (2013)		--	X	X	Posidonia Shale (Germany); MA: N/D; INCL: - sph	IC P-MS
Ingham et al. (2014)		--	X	--	roll-front Beverly North uranium deposits (South Australia); MA: py, sph, Se; INCL: Se,	LA-ICP-MS
Large et al. (2014)		--	X	X	Black shale (numerous localities); MA and INCL: N/D	LA-ICP-MS
Marin-Carbonne et al. (2014)		X	X	--	Carbonaceous shales, Bubi Greenstone Belt (Zimbabwe); MA: N/D; INCL: cpy	EMPA, LA-ICP-MS
Palenova et al.(2015)		X	X	X	Kopylovsky and Kavkaz (black shale) (Russia); MA: py, Au, po, cpy, gn, sph,mar, pn, vio, mil, gers, ulm, cob, asp, mo; INCL: Au, cpy, po, gn,	EMPA, LA-ICP-MS
Staedman et al. (2015)		--	X	--	Golden Mile (black shales) (Australia); MA: py, cpy, cas, sph, po, asp, ull; INCL: sph, cpy, ten, Au, Au-tellurides	LA-ICP-MS
Zhang et al. (2002)	Coal	X	X	--	SW Guizhou province (China); MA and INCL: N/D	ICP-MS
Ding et al. (2001)		X	--	--	SW Guizhou Province (China); MA: py, asp, rlg: INCL: N/D	EMPA, INAA
Zhou et al. (2008)		--	X	--	Xiangquan (Hexian, China); MA: N/D; INCL: Tl-bearing grains	ICP-MS
Hower et al. (2009)		X	X	--	Manchester coal bed, Clay County, (Kentucky, USA); MA: py, mar, claus; INCL:	Micro-PIXE
Cline (2001)	Carlin-type	X	X	--	Getchell, Nevada (USA); MA: py, cpy, asp, gn, sph, mar, stb, rlg; INCL: N/D	EMPA, SIMS
Emsbo et al. (2003)		X	X	--	Meikle, (USA); MA: Au, py, (As,Au)-py, mc, asp, tetr, sph, stb, HgTe, AgTe; INCL: N/D	EMPA, SIMS
Reich et al. (2005)		X	--	--	Deep Star, (Nevada, USA); MA and INCL: N/D	EMPA, SIMS
Su et al. (2012)		X	--	--	Shuiyindong, (Guiuzhou, China); MA: py, asp, mar, orp, rlg, stb; INCL: asp, Au,	EMPA
Barker et al. (2009)		X	X	--	West Banshee, Turquoise Ridge, (Nevada, USA); MA: py, asp, orp, rea; INCL: N/D	EMPA, SIMS
Deditius et al. (2011)		X	--	--	Deep Star (Nevada, USA); MA: N/D; INCL: (Ag,Pb)-sulfides, Au, Ag Screamer (Nevada, USA); MA: N/D; INCL: cin Lone Tree (Nevada, USA): MA: N/D; INCL: (Au,Ag,As,Ni)-sulphide, (Fe,As,Ag,Ni)-sulphide, (Fe,As,Sb,Pb,Ni,Au)-sulphide	EMPA, SIMS
Large et al. (2009)		--	X	--	Rodeo, Meikle, Gold Quarry (Nevada, USA); MA: py, marc; INCL - N/D	LA-ICP-MS
Scott et al. (2009)		--	X	--	Goldstrike, Gold Quarry, (Nevada, USA); MA: py, mar; INCL: N/D	LA-ICP-MS
Gryffin et al. (1991)	Epithermal	X	X	--	North Arm (Queensland, Australia); MA: py, mar, sph, cpy, Ag, Au, naum, frei, asp; INCL: mar, Au, Ag, cpy, sph, gn, po, mo.	PIXE
Cepedal et al. (2008)		X	--	--	El Valle (Spain); MA: py, po, marc, asp, tetr, and, gud, cpy, cov, gn, sph, gr; INCL: asp,	EMPA
Reich et al. (2005)		X	--	--	Porgera (Papua New Guinea); ; MA and INCL: N/D	EMPA, SIMS
Okrush et al. (2007)		X	--	--	Wilhelmine mine, (Bavaria, Germany); MA: py, enarg, ten, cpy, bor, dig, dju; INCL: N/D	EMPA
Deditius et al. (2011)		X	--	--	Pueblo Viejo (Dominican Republic); MA: py, enar; INCL: (Pb,Bi,Sb,Ag,Te)-sulphide; Au, Ag, Au-telluride; Ag-Sb. Porgera (Papua New Guinea); MA: N/D; INCL: gn, (Pb,Ag,Sb)-sulphides	EMPA, SIMS
Scher et al. (2013)		X	X	X	Kawah Ijen volcano, Java (Indonesia); MA: N/D; INCL: mo, bis, gn, sph.	LA-ICP-MS
Franchini et al. (2015)		X	--	X	Agua Rica Cu (Mo-Au) (Argentina) (high-sulfidation epithermal part); MA: py, mo, mar, sph, en, kur, cv; INCL: cpy, bn, po,	LA-ICP-MS
Kozmanov et al. (2010)	Porphyry	--	X	--	High-sulphidation epithermal veins overprinting porphyry Cu, Rosia Poieni (Romania); MA-py,en, mo, col, Au-Ag-Bi tellurides, ten, cpy, bn, dig, cov, Te; INCL: cpy, en, bn, cov, Ag-Au tellurides or selenides.	EMPA, LA-ICP-MS
Pass et al. (2010)		X	X	X	Mt. Polley, (British Columbia, Canada); MA: py, cpy, bor; INCL: cpy, gn, sph, Au, telluride; Pt-,Pd-bearing minerals	LA-ICP-MS
Large et al. (2007)	Orogenic gold	--	X	--	Sukhoi Log (Russia); MA: py, asp, po, Au, Au-tellurides; INCL: Au, asp, po, sph, cpy, gn	LA-ICP-MS

Large et al. (2009)					Bendigo (Australia); MA: N/D; INCL: cpy, gn Sukhoi Log (Russia); MA: N/D; INCL: sph, cpy, po, gn, Au Spanish Mt. (Canada); MA: N/D; INCL: cpy, sph, gn	LA-ICP-MS
Wood and Large (2007)		--	X	--	Western Victoria (Australia) – localities in Table 2 therein; MA and INCL: N/D	LA-ICP-MS
Large et al. (2009)		--	X	--	Spanish Mt., (Canada); MA-N/D; INCL: Au, sph, gn, cpy; Sukhoi Log, (Russia); MA: N/D; INCL: Au, sph, cpy, gn, po; Bendigo, (Australia); MA-N/D; INCL: cpy, gn, Pb-Bi-Au tellurides	LA-ICP-MS
Shackleton et al. (2003)		X	--	--	Golden Mile (Australia); MA: py, asp, po, sph, cpy, cv, Au, Te, precious metals tellurides; INCL: Au, clv, syl, kren, ptz.	EMPA
Thomas et al. (2011)		--	X	--	Bendigo, (Australia); MA: py, Au, sph, asp, po, gn; INCL: gn	LA-ICP-MS
Deol et al. (2012)		--	X	--	Bhukja-Jagpura (India); MA: py, asp, po, cpy; INCL: Au,	EMPA, LA-ICP-MS
Cabral et al. (2013)		X	--	X	Antônio Pareira (Brazil); MA: py, asp, po; INCL: N/D	LA-ICP-MS
Li et al. (2014)		--	X	--	Getiaowan-Anba gold deposits, Yangshan gold belt (China); MA: py, MA and INCL: asp, Au, stb, sph, gn, cpy, ten, jam, boul, fam	EMPA, LA-ICP-MS
Duchesne et al. (1983)	Pb-Zn	--	X	--	Pb-Zn deposits (Belgium); MA: py, mar; INCL: hut	SIMS
Revan et al. (2014)	VMS	--	X	X	Pontide orogenic belt (Turkey); MA: py, cpy, sph, gn, bn, Au, Ag, ma, cc, cv, en, Bi, tet, dgn, gersd, INCL: (Au,Ag)-tellurides	LA-ICP-MS
Genna and Gaboury (2015)		--	X	X	Bracemac-McLeod (Canada); MA: py, cpy,gn, sph, INCL: cpy, gn, sph, Ag-Au-Te,	LA-ICP-MS
Agangi et al. (2013)	Witwatersrand	X	--	--	INCL: cpy, gn, Au, sph, po, Au-Ag-Hg alloy,	EMPA, LA-ICP-MS
Yudovskaya et al. (2006)	Volcanic precipitates	--	--	X	Kudryavy volcano (Kurile Islands; Russia); MA: py, gn, sph, cov, cpy, cc, $Pb_4Bi_6S_{13}$, TlCl; INCL: N/D	INAA
Zelenski and Bortnikova (2005)		X	X	X	Mutnovsky volcano, Kamchatka (Russia); MA: py, po, gn, gr, Cd-sulfosalts, TlI; INCL: N/D	EMPA
Biagioni et al. (2013)	Metamorphic	X	X	--	Alpi Apuane (Italy); MA: py, cinnabar, realgar, sph, stb, twinnite, polhemusite, Tl-Hg-As-Sb-Ag-Pb sulfosalts;	EMPA, ICP-MS

*MA - Mineral assemblage – the information is limited to minerals that might contaminate pyrite with Hg, Tl, and Cd. **INCL – inclusions in pyrite; ***N/D – no data;

Mineral abbreviations: and – andorite, ani – anilite, asp – arsenopyrite, bis – bismuthinite, bn – bornite, boul – boulangerite, cas – cassiterite, cc – chalcocite, cal – calaverite, cob – cobaltite, clau – clausthalite, cv – covellite, col – colusite, cpy – chalcopyrite, dig – digenite, dju – djurleite, en – enargite, fam – famatinite, frei – freibergite, gersd – gersdorfite, gn – galena, gr – greenockite, gud – gudmundite, hut – hutchinsonite, ida – idaite, jam – jamesonite, kren - krennerite, kur - kuramite, mar – marcasite, mil – millerite, mo – molybdenite, naum – naumannite, orp – orpiment, pn – pentlandite, po – pyrrhotite, py – pyrite, ptz – petzite, rlg – realgar, sph – sphalerite, spi – spinkopite, stb – stibnite, ten – tennantite, tetr – tetrahedrite, ull - , ulm - , vio - violarite, yar – yarrovite.