Review

A review of Te and Se systematics in hydrothermal pyrite from precious metal deposits: Insights into ore-forming processes

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ABSTRACT

Pyrite is one of the most common minerals in many precious and base metal hydrothermal ore deposits and is an important host to a range of trace elements including Au and Co and the semi-metals As, Se, Sb, Te and Bi. As such, in many hydrothermal ore deposits, where pyrite is the dominant sulphide phase, it can represent a major repository for these elements. Furthermore, the concentrations and ratios of Au, As and Co in pyrite have been used to infer key ore-forming processes. However, the mechanisms controlling the distribution of Te and Se in pyrite are less well understood. Here we compare the Te and Se contents of pyrite from a global dataset of Carlin-type, orogenic Au, and porphyry-epithermal deposits to investigate: (1) the potential of pyrite to be a major repository for these elements; and (2) whether Te and Se provide insights into key ore-forming processes. Pyrite from Carlin-type, low-sulphidation and alkaline igneous rock-hosted epithermal systems is enriched in Te (and Se) compared to pyrite from high-sulphidation epithermal and porphyry Cu deposits. Orogenic Au pyrite is characterised by intermediate Te and Se contents. There is an upper solubility limit for Te as a function of As in pyrite, similar to that established for Au by Reich et al. (2005); and this can be used to identify Te present as telluride inclusions, which are common in some epithermal-porphyry and orogenic Au deposits. Physicochemical fluid parameters, such as pH, redox and temperature, as well as crystal-chemistry control the incorporation and concentration of Se and Te in pyrite. Neutral to alkaline fluids have the ability to effectively mobilise and transport Te. Fluid boiling in porphyry-epithermal systems, as well as wall rock sulphidation and oxidation in Carlin-type (and orogenic Au) deposits can effectively precipitate Te in association with pyrite and Au. In contrast, Se concentrations in pyrite apparently vary systematically in response to changes in fluid temperature, irrespective of pH and fO2. Hence, we propose that the Se contents of pyrite may be used as a new geo-thermometer for hydrothermal ore deposits. Furthermore, the comparison of bulk ore and pyrite chemistry indicates that pyrite represents the major host for Te and Se in Carlin-type and some epithermal systems, and thus pyrite can be considered to be of economic interest as a potential source for these elements.

1. Introduction

Pyrite is the most abundant sulphide mineral in the Earth’s upper crust and represents a major mineral in most hydrothermal ore deposits (Rickard and Luther, 2007; Cook et al., 2009a; Deditius et al., 2014; Keith et al., 2016a). Pyrite is stable under various physicochemical fluid conditions and its refractory behaviour to post-depositional metamorphism compared to other sulphides (Craig and Vokes, 1993; Fleet et al., 1993; Craig et al., 1998; Agangi et al., 2013) and its near-ubiquity makes it suitable for micro-analytical studies to reconstruct ore-forming processes through space and time (Agangi et al., 2013; Reich et al., 2013; Wohlgemuth-Ueberwasser et al., 2015; Keith et al., 2016b). Previous investigations have highlighted that pyrite represents an important sink for many trace metals including Co, Ni, Cu, As, Se, Mo, Ag, Sb, Te, Pb, Bi, Au and PGE (e.g., Large et al., 2009; Maslennikov et al., 2009; King et al., 2014; Smith et al., 2014; Tanner et al., 2016). Most of these studies have focused on As and associated trace metals, such Ag, Sb, Au and Pb (e.g., Reich et al., 2005, 2013; Large et al., 2009; Deditius et al., 2009a, 2014; Keith et al., 2016a), but thus far very few investigations have included Te and Se (Huston et al., 1995; Wohlgemuth-Ueberwasser et al., 2015; Keith et al., 2016b). Hence, much less is known about the processes that control the incorporation of Te and Se into pyrite – adjacent group 16 elements that might be expected to show some similarities in geochemical behaviour.

Hydrothermal processes responsible for ore deposition vary between different deposit-types and can significantly fractionate trace elements.
elements in hydrothermal systems between the vapour, liquid and solid phase (Cline et al., 2005; Goldfarb et al., 2005; Seedorff et al., 2005; Simmons et al., 2005). Different deposit-types thus have variable but characteristic trace element enrichments (Cook et al., 2009b). Tellurium and Au, for example, have been identified as elements of economic interest in Carlin-type and episodal systems. Due to its ubiquity and ability to concentrate trace elements, pyrite may represent an economically important host for these metals (Reich et al., 2005; Kesler et al., 2007). Hence, the future supply of a range of trace elements, such as Te and Se (essential for the manufacture of photovoltaic cells in the solar energy industry) may be resolved by the processing of minerals including pyrite (e.g., Hofstra and Cline, 2000; Reich et al., 2013; Deditius et al., 2014). If not recovered, both elements have potential eco-toxicological impacts (Lussier et al., 2003; Perkins, 2011) if sent to tailings and waste, or volatilised during pyro-metallurgical processing, and may require specialised treatment and handling if abundant. Both elements can have impacts (e.g. passivation) on metallurgical processing and the recovery of more valuable elements (Spry et al., 2004; Adams, 2005) and systems and processes need to accommodate the concentration of trace elements in ore feeds. Thus, understanding the behaviour of Te and Se during mineralisation processes and subsequent concentration of trace elements in ore feeds. This study is the first investigation into the chemistry of Te and Se in pyrite from a range of the most economically important hydrothermal precious metal deposits: Carlin-type, orogenic Au, and porphyry-epithermal deposits.

2. Research background

2.1. Pyrite chemistry as a proxy for ore-forming conditions

Several studies have shown that pyrite chemistry can provide a proxy for ore-forming processes in hydrothermal systems (Large et al., 2009; Reich et al., 2013; Deditius et al., 2014; Keith et al., 2016a). It is important to note that the composition of pyrite has been shown to be representative for the signature of the mineralisation fluids in many hydrothermal systems, such as porphyry-epithermal deposits (Deditius et al., 2014) and volcanic-hosted massive sulphide deposits (Keith et al., 2016b). Variations in the trace element composition of pyrite have been interpreted to be caused by changes in physicochemical fluid parameters, such as temperature, pH, redox and the availability of complex-forming ligands (Huston et al., 1995; Deditius et al., 2014; Revan et al., 2014; Keith et al., 2016a), as well as fluid-wall rock interaction and phase separation (Wohlgemuth-Ueberwasser et al., 2015; Keith et al., 2016a,b). Thus, pyrite chemistry is a robust indicator of fluid composition. Furthermore, the results of Wohlgemuth-Ueberwasser et al. (2015) suggest a systematic relationship between pyrite chemistry and the composition of the metal source. However, when using pyrite chemistry to reconstruct processes of ore formation it is important to take the crystal-chemical properties of pyrite into account due to their fundamental control on the trace element incorporation (Chouinard et al., 2005).

2.2. Te chemistry

Tellurium occurs in various oxidation states from −II to +VI in aqueous solutions including Te\(^{2−}\), Te\(^{4+}\), Te\((s)\), TeO\(_2\)\(^{2−}\) and TeO\(_4\)\(^{2−}\) (Koelbl, 1995; Brugger et al., 2012; Grundler et al., 2013). Despite the low crustal abundance of Te (5 ppb, Wedepohl, 1995), it can occur in high concentrations (ten to thousands of ppm) in association with Au in many ore deposits, which makes it an element of geochemical and potential economic interest (Kelley et al., 1998; Pals and Spyr, 2003; Giobanu et al., 2006; Sung et al., 2009). The most common Te-bearing minerals in nature are tellurides and native Te (Cook et al., 2009b; Giobanu et al., 2012). However, high Te contents have also been identified in As- and Au-rich pyrite (Chouinard et al., 2005; King et al., 2014) that usually occurs in Carlin-type, low-sulphidation episodal and some orogenic Au deposits (Kesler et al., 2007; Cook et al., 2009a; Deditius et al., 2014). Chouinard et al. (2005) explained the association of As, Te and Au in pyrite by their preferential incorporation on the (1 1 0) surfaces in the cubic crystal system. Experimental studies accompanied by mineral stability calculations indicate that Te is highly soluble in hydrothermal fluids at neutral to alkaline pH, low salinity and high temperature and oxygen fugacity (\(\text{O}_2\)), whereas Te solubility significantly decreases under more reduced conditions leading to Te deposition (Cooke and McPhail, 2001; Cook et al., 2009b; Grundler et al., 2013; Gao et al., 2017).

2.3. Se chemistry

Selenium, like other Group 16 elements in the periodic table, such as S and Se, also occurs in several oxidation states (−II, 0, +IV, +VI; Yamamoto, 1976; Koeb, 1995; Schirmer et al., 2014). Selenide minerals are rare in nature compared to tellurides (Simon et al., 1997), despite the significantly higher crustal abundance of Se (130 ppb; Rudnick and Gao, 2003) compared to Te (5 ppb, Wedepohl, 1995). Consequently, in hypogeous mineralisation most Se is hosted by other minerals, such as pyrite, galena and chalcopyrite (Yamamoto et al., 1984; Huston et al., 1995; Williams et al., 2015; Wohlgemuth-Ueberwasser et al., 2015). Selenium is a common trace element analysed in hydrothermal pyrite and Se variations have been commonly attributed to changes in fluid temperature (Aucclair et al., 1987; Huston et al., 1995; Maslennikov et al., 2009; Revan et al., 2014; Keith et al., 2016a,b). However, other studies have pointed out that Se in pyrite may vary as a function of the pH and the redox conditions of the ore-forming fluids (Yamamoto et al., 1984; Huston et al., 1995). Thermodynamic modelling calculations by Huston et al. (1995) and Layton-Matthews et al. (2008) suggest that the Se content of pyrite is directly related to \(\text{ESe}/\text{S}\) ratio of the parental fluid phase. It is worth mentioning that the incorporation of Se, compared to As, Te and Au, is less controlled by the crystal-chemical properties of pyrite (Chouinard et al., 2005).

3. Geological overview: deposit-types and ore mineralisation

This section summarises the key magmatic and hydrothermal data, such as host rock and physicochemical fluid composition (Table 1) and highlights the most important features of metal precipitation in the different deposit-types investigated in this study (Table 2). Further details can be found in the electronic supplementary material (Table A1).

3.1. Carlin-type deposits

The Carlin-type deposits of Nevada have been used as the type locality for Carlin-style Au mineralisation (e.g., Cline et al., 2005). However, similar deposits have been identified in Canada, China and Sweden (Table 2; Garnier et al., 2007; Su et al., 2008; Large et al., 2011). Gold mineralisation in Carlin-type systems is generally accompanied by pyrite precipitation, which represents the primary host for economic Au either in solid solution or as sub-micron sized Au\(^{0}\) inclusions (Emsbo et al., 2003; Cline et al., 2005; Reich et al., 2005). Two principal sources for the ore-forming fluids have been suggested including a meteoric and a magmatic fluid component with variable proportions between different deposits (Cline and Hofstra, 2000; Cline et al., 2005). Carlin-type ore-fluids are characterised by low fluid temperatures (< 240 °C), low \(\text{O}_2\) low salinities and near-neutral pH caused by fluid neutralisation due to the interaction with the carbonate fluid neutralisation due to the interaction with the carbonate.
host rocks (Table 1; Cline and Hofstra, 2000; Cline et al., 2005; Muntean et al., 2011). Metal deposition is generally attributed to sulphidation of Fe in the carbonate wall rocks causing pyrite precipitation accompanied by precious metal mineralization (Cline and Hofstra, 2000; Embs et al., 2003; Cline et al., 2005). Phase separation, i.e. fluid boiling, has been observed in some Carlin-type systems but never in association with the main stage of ore formation excluding it as a principle process for ore mineralisation (Cline and Hofstra, 2000).

### 3.2. Orogenic Au deposits

Orogenic Au deposits form during the late stage of orogeny and are typically hosted by rocks of greenschist to amphibolite metamorphic grade that may be spatially related to granitoid intrusions (Table 1). Arsenopyrite and pyrite represent the most abundant sulphide minerals that occur in association with the Au mineralisation, which formed from low salinity, CO₂-bearing, reduced and near-neutral pH fluids that show a wide range in fluid temperatures from about 200 to 500 °C (Table 1; Goldfarb et al., 2005; Cook et al., 2009b). Fluid-rock interaction accompanied by host rock sulphidation and pressure fluctuation due to crack and seal causing fluid phase separation represent the most important mechanisms for metal precipitation (Sibson et al., 1988; Loucks and Mavrogenes, 1999; Goldfarb et al., 2005; Gao et al., 2017). The chemical and isotopic composition of low temperature orogenic Au fluids, as well as host rock sulphidation as a common precipitation process indicate that some orogenic Au deposits, such as Sunrise Dam (Table 2; Sung et al., 2009) and Dongping (Table 2; Hart et al., 2002; Gao et al., 2017), probably formed under conditions similar to Carlin-type systems (Ridley and Diamond, 2000; Cline et al., 2005; Goldfarb et al., 2005).

### 3.3. Porphyry-epithermal deposits

Porphyry and epithermal mineralisation are controlled by cooling and condensation of magmatic vapours, fluid boiling and mixing of magmatic and meteoric fluids (Cooke and McPhail, 2001; Seedorff et al., 2005; Simmons et al., 2005), which is in contrast to the described ore precipitation mechanisms in Carlin-type (Cline and Hofstra, 2000; Embs et al., 2003; Cline et al., 2005) and orogenic Au systems (Sibson et al., 1988; Loucks and Mavrogenes, 1999; Goldfarb et al., 2005). Deditius et al. (2014) stressed that metals are fractionated between porphyry and epithermal systems. Gold, for example, generally stays in solution in the deeper porphyry environment and precipitates at shallower crustal levels under epithermal conditions (< 1.5 km, < 300 °C; Simmons et al., 2005), which explains the lower Au grades in porphyry compared to epithermal systems (Deditius et al., 2014). The Rosia Poieni deposit (Table 2) represents an example where a porphyry system has been overprinted by a later high-sulphidation epithermal vein network highlighting the close relationship between porphyry and epithermal systems (Kouzmanov et al., 2010). High temperature fluids that reach up to 300 °C in high-sulphidation epithermal systems are mainly of magmatic origin and therefore oxidised and more acidic compared to shallower low temperature (< 200 °C) fluids in low-sulphidation epithermal systems that are reduced and near neutral in pH due to host rock buffering and a higher meteoric fluid component (Table 1; White and Hedenquist, 1996; Einaudi et al., 2003; Sillitoe and Hedenquist, 2003; Simmons et al., 2005). These differences lead to systematic variations in the composition of high- and low-sulphidation epithermal deposits, such as higher Cu contents, higher abundances of sulphosalts and a higher Au/Ag ratio in high- compared to low-sulphidation systems (Einaudi et al., 2003).

A notable sub-class within the epithermal deposits are those hosted within alkaline igneous rocks. These systems are commonly described as having alteration assemblages similar to calc-alkaline-hosted low-sulphidation systems, but with a greater magmatic component in the fluids, higher temperatures, and a notably higher Te abundance (Jensen et al., 2003).
were analysed by ICP-MS and ICP-OES (Table 2). Elements investigated and proton microprobe analysis. In addition, pyrite crystal separates by-product Te in the future (Green, 2009).

Studies have suggested that these deposits may be useful as sources of (Papua New Guinea), Cripple Creek (USA) and Emperor (Fiji). Previous in pyrite can be found in the electronic supplementary material (A2).

The results presented in this study are based on previously published data of pyrite and arsenian pyrite (n = 3283) and arsenopyrite deposits, Table 3). The minimum detection limit for each element with respect to the analytical technique can be found in Table 4. For detailed information about the analytical techniques we refer to the source references as listed in Table 2.

The data set was supplemented by bulk ore data from the OSNACA data base (http://www.cet.edu.au/) and previously published and unpublished Te and Se bulk ore data from Carlin-type (Emso et al., 2003), orogenic Au (Koneev et al., 2005), epithermal (Kwak, 1990; Mueller et al., 2002; Dye, 2015) and porphyry Cu deposits (Gioacă et al., 2014).

4. Methods

The results presented in this study are based on previously published data of pyrite and arsenopyrite (n = 3283) and arsenopyrite (n = 61), to complete the range in As contents, from different hydrothermal precious metal deposits (Table 2). Analyses were carried out by electron microprobe analysis (EPMA), Laser Ablation ICP-MS (LA-ICP-MS) and to a lesser extent by secondary-ion mass spectrometry (SIMS) and proton microprobe analysis. In addition, pyrite crystal separates were analysed by ICP-MS and ICP-OES (Table 2). Elements investigated in this study include: Fe, S, V, Cr, Ni, Cu, Zn, As, Se, Mo, Te and Au (Table 3). Details of other trace elements, such as Co, Cd, Sb, Pb and Bi in pyrite can be found in the electronic supplementary material (A2).

The data set includes pyrite analyses of both Te and Se but also some analyses where only Se or Te were reported (e.g., low-sulphidation epithermal deposits, Table 3). The minimum detection limit for each element with respect to the analytical technique can be found in Table 4. For detailed information about the analytical techniques we refer to the source references as listed in Table 2.

and Barton, 2000; Kelley and Spry, 2016). This sub-class includes some of the world’s largest epithermal Au-Te deposits, such as Porgera (Papua New Guinea), Cripple Creek (USA) and Emperor (Fiji). Previous studies have suggested that these deposits may be useful as sources of by-product Te in the future (Green, 2009).

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on these chemical variations two compositional end-members can be defined in the As-Fe-S system, namely pyrite (FeS₂) and arsenopyrite (FeAsS₂, Fig. 1). Arsenic-rich pyrite with As contents between the two end-members is usually called arsenian pyrite (Fe(As, S)₂ or FeAsS₂) and characteristically shows ppm to wt.% levels of As (Reich et al., 2005; Qian et al., 2013; Deditius et al., 2014). Alternatively, As may be concentrated into liquid nano-inclusions hosted in pyrite (Deditius et al., 2009b). Deditius et al. (2014) presented a method to distinguish between different types of As substitution into pyrite, based on the composition of pyrite and arsenopyrite in the ternary As-Fe-S system (Fig. 1). Pyrite that plots on a line parallel to the As-S join mainly incorporates As⁺ due to isovalent S substitution in pyrite, based on the composition of pyrite and arsenopyrite in the ternary As-Fe-S system (Fig. 1). Hence, As-S substitution apparently occurs in pyrite along the Fe-S join in the As-Fe-S system are most likely related to the incorporation of trace elements substituting for Fe and S (Deditius et al., 2014).

Arsenic occurs in several oxidation states (−I, +II, +III, +V) and can therefore substitute into the pyrite lattice as either a cation or anion (Reich et al., 2005; Qian et al., 2013; Deditius et al., 2014). Alternatively, As may be concentrated into liquid nano-inclusions hosted in pyrite (Deditius et al., 2009b). Deditius et al. (2014) presented a method to distinguish between different types of As substitution into pyrite, based on the composition of pyrite and arsenopyrite in the ternary As-Fe-S system (Fig. 1). Pyrite that plots on a line parallel to the As-S join mainly incorporates As⁺ due to isovalent S substitution in tetrahedral sites (Fig. 1). Hence, As-S substitution apparently occurs in pyrite and arsenopyrite from Carlin-type, low-sulphidation epitaxial, alkaline rock-hosted epitaxial and orogenic Au ores and a distinct Fe-S/pyrite/arsenic-pyrite join along the Fe-S join in the As-Fe-S system are most likely related to the incorporation of trace elements substituting for Fe and S (Deditius et al., 2014). Across all deposit-types Te and Se concentrations in pyrite vary from 0.02 ppm (the minimum detection limit for both elements) to 20,800 ppm and 4250 ppm, respectively (Fig. 2, Table 3). Carlin-type pyrite generally shows the highest average concentrations of Se (1000 ppm, Table 3) and Te (570 ppm, Table 3). In contrast, the lowest average concentrations of Se (6 ppm, Table 3) and Te (26 ppm, Table 3) were observed in porphyry Cu pyrite. Epithermal pyrite is characterised...
by highly variable Te and Se concentrations ranging from 0.1 to 7940 ppm and 0.4 to 2150 ppm, respectively (Table 3). Hence, epithermal pyrite overlaps with Carlin-type and porphyry Cu pyrite in terms of its Te and Se content (Fig. 2). It is worth noting that pyrite from alkaline rock-hosted epithermal systems shows the highest Te concentrations (up to 7940 ppm) compared to high- and low-sulphidation epithermal pyrite (Table 3). Orogenic Au pyrite has intermediate Te and Se contents but characteristically shows a significant Te variation over a small range of Se (Fig. 2). Unpaired data for Te reaches major element levels of up to 20,800 ppm (Table 3) in a few pyrite crystals from the Chinese Huangtuliang and Dongping Au deposits, which has been explained by the occurrence of telluride inclusions (Cook et al., 2009a; Ciobanu et al., 2012). In contrast, Se in orogenic Au pyrite generally occurs in trace amounts with concentrations below 200 ppm (Fig. 2, Table 3).

6. Discussion

6.1. Te and Se incorporation into hydrothermal pyrite

Previous studies have suggested that Te and Se in pyrite can be either structurally bound in the lattice due to S substitution (Huston et al., 1995; Chouinard et al., 2005; Kesler et al., 2007) or hosted as micron to sub-micron sized inclusions (Emsbo et al., 2003; Pals et al., 2003; Cook et al., 2009a; Tanner et al., 2016).

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Table 4

<table>
<thead>
<tr>
<th>Analytical techniques</th>
<th>Fe (wt.%)</th>
<th>S (wt.%)</th>
<th>V (ppm)</th>
<th>Cr (ppm)</th>
<th>Ni (ppm)</th>
<th>Cu (ppm)</th>
<th>Zn (ppm)</th>
<th>As (ppm)</th>
<th>Se (ppm)</th>
<th>Mo (ppm)</th>
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References to the analytical techniques as listed in Table 2.
6.1.1. Te incorporation

It has been shown that As-rich pyrite is usually enriched in trace elements compared to As-poor pyrite. For example, Ag, Cd, Sb, Au, Hg, Tl and Pb in pyrite form a triangular wedge-shaped zone with As in a log–log diagram. Concentrations of these elements that plot outside the wedge-shaped zone with respect to their As content are interpreted to reflect micro- or nano-particle inclusions in pyrite (Reich et al., 2005, 2013; Deditius et al., 2014; Keith et al., 2016a). Interestingly, most of the Te data also form a triangular wedge-shaped zone (Fig. 3A) with As in a log–log plot similar to the elements listed above. Chouinard et al. (2005) proposed that the association of Te and As is controlled by the crystal-chemical properties of pyrite due to their preferential incorporation on the (1 1 0) surfaces in the cubic crystal system. However, some orogenic Au (Dongping and Huangtuliang, Table 2) and a few high-sulphidation epithermal (Bawone and Binebase, Table 2) As-poor pyrites show elevated Te concentrations and therefore plot outside the wedge-shaped zone (Fig. 3A) suggesting that those pyrites host telluride inclusions.

According to Reich et al. (2005) high Au/As ratios (> 0.02, Table 3) in pyrite imply that Au is hosted as Au0 sub-micron inclusions. Those pyrites plot above the Au solubility line, which defines the upper concentration limit for Au solid solution in pyrite as function of the As content (Fig. 4). Hence, Au- and Te-rich but As-poor pyrite from the Dongping and Huangtuliang orogenic Au deposits (Figs. 3A and 4) most likely hosts Au-telluride inclusions. Cook et al. (2009a) confirm that the high Te and Au concentrations identified in As-poor pyrite from Dongping and Huangtuliang are related to Au-telluride inclusions, namely calaverite (AuTe2). Deditius and Reich (2016) pointed out that the Au solubility line can also be used to identify Hg and Tl inclusions in pyrite in a log (Hg, Tl)-log (As) diagram due to the similar covalent radii of Hg (132 pm), Tl (145 pm) and Au (136 pm). Importantly, the covalent radius of Te (138 pm) is very similar to that of Au (136 pm) indicating that the Au solubility line may also be used for Te in the same way as for Hg and Tl. The positive correlation of Te and Au in pyrite (R² = 0.55, Fig. 5A) supports this conclusion and suggests that the incorporation of these elements is controlled by a similar process and that they are closely associated in the pyrite structure (Pals and Spry, 2003; Kesler et al., 2007). Pals et al. (2003) identified Au-telluride inclusions (calaverite, krennerite, sylvanite and petzite) by LA-ICP-MS time-resolved depth profiles in pyrite (39PY53) from the alkaline rock-hosted Emperor epithermal deposit, which also plots above the Au solubility line in the Te-As (Fig. 3A) and Au-As system (Fig. 4). Similarly, it has been shown that Au-telluride inclusions in low-sulphidation epithermal pyrite are common (Pals and Spry, 2003; Pals et al., 2003; Kesler et al., 2007), which correlates with the position of many alkaline-hosted epithermal pyrites above the solubility line in the
log (Au, Te)-log (As) diagrams (Figs. 3A and 4). Hence, it is reasonable to propose that Au-telluride inclusions in pyrite may be identified based on the combined use of the Au solubility line by Reich et al. (2005) in the Te-As (Fig. 3A) and Au-As (Fig. 4) systems, as previously reported for Hg and Tl by Deditius and Reich (2016). This conclusion is supported by the positive correlation of Au and Te in pyrite (R² = 0.55) and in particular by the Te/Au ratio of the regression line, which is close to one (Fig. 5A). In addition, pyrite (39PP53) from Emperor that hosts Au-telluride inclusions plots into the compositional range of calaverite (AuTe₂), krennerite (Au₃AgTe₅), sylvanite (Ag₂AuTe₄) and petzite (Ag₃AuTe₂, Fig. 5A), which also intersects the data set of the Dongping Bawone deposits show Te concentrations above (Fig. 3A) but Au concentrations below the Au solubility line (Ahmed et al., 2003). However, pyrite from Binebase and Bawone differs from the compositional range defined by Au-Cu tellurides, such as kostovite (AuCuTe₄) in the high-sulphidation system of Mount Kasigh (Fiji). High-sulphidation epithermal systems are generally enriched in Cu compared to their low-sulphidation counterparts (Einaudi et al., 2003). However, pyrite from Binebase and Bawone differs from the compositional range defined by Au-Cu tellurides, such as kostovite (AuCuTe₄), bezsmertnovite ((Au₄Ag)₃(Cu,Te)₄), bilimbiskite (Au₉Cu₂PbTe₅) and bogdanovite ([(Au, Te, Pb)(Cu, Fe)]₄) indicating that the high Te/Au ratios and the positive Cu-Te correlation (Fig. 6B) cannot be explained by Cu-rich telluride inclusions. Hence, Te is hosted in pyrite as a telluride phase not considered here or in its native form, which is reasonable to conclude because native Te is stable in association with pyrite in acidic and oxidised high-sulphidation epithermal fluids (Naden and Henney, 1995; Cook et al., 2009b). Alternatively, Te may be hosted by complex Cu-bearing sulfosalts, such as goldfieldite (Cu₁₀Te₃S₁₃) that typically occur in high-sulphidation epithermal systems (Naden and Henney, 1995; Berger et al., 2014).

In contrast, As-rich Carlin-type pyrite mainly plots inside the wedge-shaped zone and below the Te solubility line in the Te-As system (Fig. 3A) implying that Te most likely occurs in solid solution. The different covalent radii of As (1.19 pm) and S (1.05 pm) suggest that the high amounts of As incorporated into Carlin-type pyrite by substituting the smaller S atom (Fig. 1) expand the unit cell causing structural distortion, which facilitates the incorporation of heavier and larger elements, such as Te (138 pm) in solid solution. Furthermore, Reich et al. (2005) pointed out that Carlin-type pyrite incorporates high amounts of As, Au and other trace elements in solid solution due to extra vacancies and lattice defects caused by rapid crystal growth under non-equilibrium conditions at low temperatures (< 250 °C). Due to the close association of Te with As and Au in pyrite (Figs. 3A and 5A), we propose that the incorporation of Te in solid solution into Carlin-type pyrite (Fig. 3A) is also facilitated by non-equilibrium conditions.

6.1.2. Se incorporation

No systematic correlation exists between Au and Se in pyrite (Fig. 5B; Kesler et al., 2007) indicating that Au-Se inclusions in pyrite are absent, rare or of minor importance for the Se distribution in hydrothermal pyrite on a larger scale. However, more detailed observations on distinct deposit-types (e.g., Carlin) or on an individual deposit revealed that Se systematically varies with other trace elements on a smaller scale (electronic supplementary material A2). For example, Carlin-type pyrite displays a positive correlation between Se and other trace elements (Fig. 7) including V (R² = 0.69), Cr (R² = 0.85), Ni (R² = 0.59), Cu (R² = 0.55), Zn (R² = 0.75) and Mo (R² = 0.85) and characteristically shows elevated Se concentrations reaching 4250 ppm (Table 3) probably indicating selenide inclusions of Ni, Cu, Zn and Mo with a composition similar to mäkinenite (NiSe), bellidoite (Cu₄Se), tyrrellite (Cu₉(Co, Ni)₂Se₄), stilleite (ZnSe) and drysdallite (MoSe₂, Fig. 7C–F). In contrast, there are no known minerals that contain Se and V or Cr. Alternatively, the presence of these elements in pyrite may distort the lattice facilitating the incorporation of Se in solid solution. However, another possibility to take into account is an inverse mechanism where the incorporation of Se facilitates the incorporation of other trace elements such as those listed above. Similar correlations between Se and other trace elements have been observed for high-(electronic supplementary material, Table A2.2) and low-sulphidation (Table A2.3) epithermal pyrites also reaching Se concentrations of up to 1900 and 2150 ppm, respectively. Kouzmanov et al. (2010) identified Au-Ag selenide inclusions in pyrite from the Rosia Poieni high-sulphidation epithermal system. In contrast, orogenic Au and porphyry Cu pyrites are depleted in Se compared to the other deposit-types (Fig. 2, Table 3) and Se generally lacks any systematic variation with other trace elements (Tables A2.4–A2.5). Hence, selenides seem to be of minor importance in these deposits and Se most likely occurs in solid solution in the corresponding pyrites due to isovalent S substitution.

![Fig. 6. Concentrations of Te vs. (A) Au and (B) Cu in pyrite from the Bawone and Binebase high-sulphidation epithermal deposits. Note the positive correlation between Te and the other trace elements possibly indicating Au-Cu telluride inclusions. The dark grey line represents the best fit regression line for the presented data set. The black solid lines represent the compositional range of common Cu-Au-tellurides based on their Te/Au and Te/Cu ratio: bogdanovite (−0.2 and −0.9), bezsmertnovite (−0.1 and −1.1), biliimbiskite (−0.4 and −2.2) and kostovite (−2.5 and −9.7). Further diagrams and correlation coefficients (R²) between Te and other trace elements in the different deposits can be found in the electronic supplementary material A2. (Figures in colour can be found in the web version of this article.)](image-url)
(Chouinard et al., 2005; Reich et al., 2013). Moreover, Se forms no wedge-shaped zone with As in a log (Se)-log (As) diagram (Fig. 3B) opposed to Te (Fig. 3A) suggesting an As independent incorporation of Se into pyrite.

6.2. Effect of coexisting phases: bulk ore vs. pyrite chemistry

The combined use of bulk ore and pyrite chemistry (Fig. 2) provides important information on the control of bulk ore Te and Se by pyrite and coexisting phases. Carlin-type pyrite is generally enriched in Te and Se compared to the bulk ores implying that pyrite is the main host for these elements in Carlin-type ores (Fig. 2; Kesler et al., 2007). In contrast, a compositional overlap exists between orogenic Au pyrite and the corresponding bulk ores indicating that Te and Se in pyrite may represent the bulk ore composition. Orogenic Au deposits also host pyrite that is depleted in Te but similar in Se compared to the bulk ore implying that Te is incorporated into another mineral phase that occurs in association with pyrite. Some epithermal pyrites show Te and Se contents higher than the bulk ore, as characteristically shown for Carlin-type systems, or are enriched in Se but depleted in Te compared to the bulk ore. This suggests that epithermal pyrites represent the main hosts for both elements or only for Se, whereas most Te is hosted by mineral phases other than pyrite. Porphyry Cu pyrite shows a much larger range in Te and Se than the corresponding bulk ores suggesting a complex history of pyrite precipitation (Reich et al., 2013), where pyrite can either represent the main host for these elements or is depleted in them due to the competitive incorporation by other mineral phases.

Pyrite from low-sulphidation and alkaline-rock hosted epithermal systems is generally enriched in As and tends to show higher Te contents compared to pyrite from high-sulphidation deposits (Fig. 3A, Table 3). The lower As contents of pyrite in high-sulphidation epithermal and porphyry Cu systems correlate with the occurrence of other common As-rich phases, such as realgar (AsS), and sulphosalts including enargite (Cu₃AsS₄), luzonite (Cu₃AsS₄) and tennantite ((Cu, Ag, Zn, Fe)₃As₄S₁₃; Einaudi et al., 2003), which probably host most of the As in the bulk ores. However, As seems to be an essential component in pyrite to incorporate high amounts of Te, and hence it is likely that Te is hosted in another mineral phase in high-sulphidation epithermal and porphyry Cu systems (cf. Section 6.1.1) or is depleted in them due to the competitive incorporation by other mineral phases.

Pyrite from low-sulphidation and alkaline-rock hosted epithermal systems is generally enriched in As and tends to show higher Te contents compared to pyrite from high-sulphidation deposits (Fig. 3A, Table 3). The lower As contents of pyrite in high-sulphidation epithermal and porphyry Cu systems correlate with the occurrence of other common As-rich phases, such as realgar (AsS), and sulphosalts including enargite (Cu₃AsS₄), luzonite (Cu₃AsS₄) and tennantite ((Cu, Ag, Zn, Fe)₃As₄S₁₃; Einaudi et al., 2003), which probably host most of the As in the bulk ores. However, As seems to be an essential component in pyrite to incorporate high amounts of Te, and hence it is likely that Te is hosted in another mineral phase in high-sulphidation epithermal and porphyry Cu systems (cf. Section 6.1.1) or is depleted in the ore-forming fluids. Selenides are very rare in contrast to telluride minerals (Simon et al., 1997), which makes them less important for the Se distribution in the bulk ores. Only porphyry Cu pyrite shows Se concentrations lower than the bulk ores (Fig. 2) indicating that most of the
Se is hosted by a mineral phase other than pyrite or occurs as free selenides. For example, it has been shown that chalcopyrite and galena can potentially incorporate Se in high concentrations reaching 1500 (Wohlgemuth-Uberwasser et al., 2015) and 1900 ppm (Williams et al., 2015), respectively.

6.3. Redox- and pH-controlled Te and Se incorporation into pyrite

The speciation of As in pyrite has been used to compare the redox conditions of ore-forming fluids between different deposit-types, which is based on the redox sensitivity of As indicated by its occurrence in several oxidation states (−I, +II, +III, +V; Reich et al., 2005; Qian et al., 2013; Deditius et al., 2014). Carlin-type, low-sulphidation epithermal and orogenic Au systems are all characterised by reduced ore fluids (Table 1; Cline et al., 2005; Goldfarb et al., 2005; Simmons et al., 2005; Deditius et al., 2008), which coincides with the formation of As−-pyrite in these systems (Fig. 1). According to Einaudi et al. (2003), high-sulphidation epithermal fluids characteristically show higher fO2 compared to their low-sulphidation counterparts, which explains the occurrence of As2+/3+ -pyrite in these systems (Fig. 1).

Importantly, Te is typically enriched in As−-pyrite from Carlin-type and low-sulphidation epithermal systems, including those hosted in alkaline igneous rocks (Fig. 3A; Kesler et al., 2007). Previous studies pointed out that Te is less soluble in reduced hydrothermal fluids and that the reduction of Te4+ results in the precipitation of Te (Cooke and McPhail, 2001; Grundler et al., 2013). Surprisingly, As-poor pyrite from the Dongping and Huangtuliang orogenic Au deposits also shows high Te contents (Fig. 3A; Cook et al., 2009a) probably reflecting an As-poor but Te-rich ore-forming fluid. Gao et al. (2017) stressed that the pyrite and telluride precipitation in the Dongping orogenic Au deposit was caused by a decrease in fO2 similar to the deposit-types described above. Hence, we conclude that the incorporation of Te in pyrite is highly sensitive to redox changes in the parental fluids and high Te contents in pyrite are related to low fluid fO2 (2013). Pointed out that Te is highly soluble in neutral to alkaline fluids (e.g., Cripple Creek, Emperor, Table 2) and some orogenic Au deposits (Table 1; Goldfarb et al., 2005; Seedorff et al., 2005; Simmons et al., 2005). However, the high Te contents in pyrite from these systems require an efficient precipitation process, which is therefore mainly pH independent. Consequently, high pH fluids may effectively mobilise Te from the source rocks and transport it to the site of deposition but the precipitation of Te is mainly controlled by redox changes in the parental fluid phase. In contrast, Se shows no systematic variation between As−-pyrite from Carlin-type, low-sulphidation epithermal and alkaline-hosted epithermal systems compared to As2+/3+ -pyrite from high-sulphidation epithermal deposits (Fig. 3B) suggesting that Se in pyrite is not primarily controlled by fO2 and fluid pH (Maslennikov et al., 2009; Revan et al., 2014; Keith et al., 2016a,b).

6.4. Effects of fluid temperature on Te and Se in pyrite

Tellurium shows no systematic variation in pyrite with the temperature of ore deposition (Fig. 8A). Hence, the incorporation of Te into pyrite seems to be temperature independent but highly sensitive to changes in fO2 (cf. Section 6.3). It has been shown that Se in pyrite can be used as a proxy for relative temperature estimations in ore-forming fluids and most studies have suggested that the Se content of pyrite increases with increasing fluid temperature (Auclair et al., 1987; Maslennikov et al., 2009; Revan et al., 2014). In contrast, the numerical simulations by Huston et al. (1995) imply that Se-rich pyrite usually forms from low temperature fluids. The results presented in this study are in agreement with Huston et al. (1995) and display a negative correlation (R2 = 0.40, Fig. 8B) between average Se in pyrite from the different deposits and the mean temperature of ore deposition (1100 °C, Tanner et al., 2016) significantly exceeds typical ore-forming temperatures of high-sulphidation epithermal systems (≤ 300 °C; Simmons et al., 2005). Sulphur isotope geo-thermometry on alunite-pyrite pairs from El Indio revealed similar depositional temperatures of ~700 °C (Jannas et al., 1999). Tanner et al. (2016) explained these high temperatures by the direct precipitation of pyrite from a hot magmatic vapour phase. However, Deyell et al. (2004) argued that these temperatures are unreasonably high and...
that the alunite-pyrite pairs probably indicate a S isotope disequilibrium. Magmatic vapour inclusions displayed average homogenisation temperatures of $\sim 270^\circ$C (Jannas, 1995), which are similar to the temperature estimations (200–300°C) presented by Deyell et al. (2004). Eq. (1) can be used to estimate the average precipitation temperature of pyrite yielding a temperature of 268 °C ± 49 °C for the deposition of early pyrite at El Indio, which is well in the range of typical high-sulphidation epithermal precipitation temperatures (< 300 °C; Simmons et al., 2005). Importantly, the Binebase and Bawone high-sulphidation epithermal deposits are genetically similar to El Indio and pyrite deposition occurred due to magmatic vapour condensation under epithermal conditions at 900–1300 m paleo-depth and temperatures between 250 and 340 °C (King et al., 2014). These independent results confirm that the estimated fluid temperatures of 268 °C ± 49 °C for the deposition of early pyrite at El Indio are in a reasonable range.

Therefore, we conclude that Eq. (1) represents a potential geothermometer to estimate the average precipitation temperature of pyrite in various deposit-types. The presented results further imply that Se in pyrite is apparently related to the temperature of ore deposition (Fig. 8B) irrespective of the $\rhoOH$ and the pH of the ore-forming fluids (cf. Section 6.3). Alternatively, Se in pyrite may vary due changes in the $\Delta$Se/S ratio of the ore-forming fluids (Huston et al., 1995). Hence, in high temperature magmatic-hydrothermal systems (e.g., high-sulphidation epithermal-porphyry deposits) the fluids are either depleted in Se compared to their low temperature counterparts (e.g., low-sulphidation epithermal and Carlin-type deposits) or Se is competitively incorporated by other minerals or forms selendites (e.g., Rosia Poieni, Kouzmanov et al., 2010) that precipitate in association with pyrite.

6.5. Fluid-rock interaction vs. fluid boiling: Effects of ore precipitation processes on Te and Se in pyrite

The different deposit-types investigated in this study are characterised by distinct ore precipitation mechanisms. Carlin-type mineralisation is generally attributed to carbonate-hosted Fe$^{2+}$ sulphidation and oxidation in the surrounding wall rocks causing pyrite precipitation accompanied by precious metal mineralisation (Cline and Hofstra, 2000; Emso et al., 2003; Cline et al., 2005). Loss of Se from the ore fluids due to wall rock sulphidation destabilises the Au-bisulphide complexes causing Au deposition (Cline and Hofstra, 2000; Emso et al., 2003; Cline et al., 2005; Muntean et al., 2011). The oxidation of Fe$^{2+}$ in the wall rocks to Fe$^{3+}$ due to the interaction with the ore-forming fluids results in a $\rhoOH$ decrease in the fluid phase causing efficient Te precipitation (cf. Section 6.3), which can therefore explain the Au-Te association in As$^{+}$-pyrite from Carlin-type systems (Figs. 3–5).

Fluid boiling is one of the most important processes for ore deposition in porphyry-epithermal systems (Cline and McPhail, 2001; Seedorff et al., 2005; Simmons et al., 2005). Deditius et al. (2009a) and Tardani et al. (2017) pointed out that processes such as fluid boiling can fractionate trace elements in hydrothermal fluids causing systematic compositional differences and chemical zonation in precipitated pyrite. Low-sulphidation epithermal and alkaline-hosted epithermal pyrite is enriched in Te compared to high-sulphidation and porphyry Cu pyrite (Figs. 3A and 5A) suggesting different Te concentrations in the parental fluid phase, variable degrees of Te precipitation during fluid boiling and the competitive incorporation of Te in mineral phases other than pyrite (cf. Section 6.2). Thermodynamic modelling calculations by Grundler et al. (2013) revealed that Te can partition into the vapour phase during fluid boiling, which is most efficient from acidic fluids prevalent in high-sulphidation epithermal and porphyry Cu systems (Table 1; Seedorff et al., 2005; Simmons et al., 2005). Similarly, Cooke and McPhail (2001) pointed out that fluid boiling causes metal sulphide precipitation in epithermal-porphyry systems; however, under acidic (high-sulphidation) conditions Te fractionates into the vapour phase and precipitates at shallower crustal levels in Au-rich zones (Cooke and McPhail, 2001) yielding low Te and Au grades in the deeper high-sulphidation epithermal and porphyry environment. In contrast, under neutral to alkaline fluid conditions Te partitions into the liquid phase during fluid boiling (Grundler et al., 2013); the strong affinity of H$_2$S to the vapour phase significantly reduces the S content of the corresponding liquids, which destabilises the Au-bisulphide complexes causing Au deposition (Cooke and McPhail, 2001; Simmons et al., 2005). Importantly, As-rich pyrite associated with Au and Te mineralisation usually forms from hydrothermal fluids with low S contents (Reich et al., 2005) that typically occur in low-sulphidation and alkaline-hosted epithermal systems, as well as in Carlin-type deposits (Figs. 3–5).

Tellurium in pyrite from orogenic Au deposits shows a wide variation overlapping with porphyry Cu, epithermal and Carlin-type systems (Fig. 2, Table 3). The high chemical variability of orogenic Au ores has previously been described and assigned to complex variations in fluid composition and metal precipitation through time (Goldfarb et al., 2005). It has been shown that some orogenic Au districts formed by reduced fluids with near-neutral pH and isotopic signatures similar to Carlin-type systems (Ridley and Diamond, 2000; Cline et al., 2005; Goldfarb et al., 2005; Cook et al., 2009; Gao et al., 2017). Goldfarb et al. (2005) pointed out that fluid-rock interaction accompanied by sulphidation of Fe-rich wall rock represent the most important processes for metal sulphide precipitation in orogenic Au systems. The composition of the ore-forming fluids in combination with the precipitation process may explain the high Te and Au contents of some orogenic Au pyrites that are similar to those from low-sulphidation epithermal, alkaline-rock hosted epithermal and Carlin-type deposits (Fig. 5A). However, the low Au and Te contents in other orogenic Au pyrites that overlap with those of high-sulphidation epithermal and porphyry Cu deposits (Fig. 5A) indicate that the precipitation mechanisms in these systems prevent extensive Te deposition associated with pyrite precipitation or that Te is hosted by mineral phase other than pyrite (Fig. 2, Section 6.2).

No systematic variation has been observed for Se in pyrite between the different deposit-types in relation to the mineralisation process (Fig. 3B and 5B). Hence, Se most likely does not fractionate during fluid boiling or wall rock sulphidation in contrast to Te. This suggests that the precipitation of Se and its distribution in pyrite is mainly controlled by fluid temperature (cf. Section 6.3).

6.6. Source rock control on Te and Se in pyrite

The Te and Se contents in the source rocks of hydrothermal systems are still largely unknown. However, it has been shown that alkaline rock-hosted low-sulphidation epithermal deposits, such as Cripple Creek (Colorado) and Emperor (Fiji), are Au- and Te-rich (Naden and Henney, 1995; Jensen and Barton, 2000). Oceanic sediments are Te-rich and melting of these sediments in subduction zones represents a potential source for Te in alkaline magmas and associated low-sulphidation epithermal systems (Jensen and Barton, 2000). Similarly, the results of Loftus-Hill and Solomon (1967) and Schirmer et al. (2014) highlight that oceanic sediments and carbonate-bearing rocks are enriched in Te and Se compared to other rock-types associated with hydrothermal systems. Importantly, pyrite from Carlin-type and alkaline-hosted epithermal systems typically shows the highest average Te contents (Table 3) suggesting a potential source rock control for Te in pyrite. In contrast, Se is not particularly enriched in these pyrites possibly indicating that the distribution of Se in pyrite is less controlled by the source composition, as observed for other trace metals in pyrite (Keith et al., 2016a). We conclude that Te (but not Se) in pyrite is potentially controlled by its concentration in the source rocks. Hence, the high Te contents in Carlin-type and alkaline rock-hosted epithermal pyrite are probably related to a combination of host rock enrichment (Naden and Henney, 1995; Jensen and Barton, 2000; Schirmer et al., 2014) and neutral to alkaline fluid conditions, which are necessary for
the efficient mobilisation and transportation of Te from the source region to the depth of deposition (Grundler et al., 2013; Gao et al., 2017).

6.7. Economic relevance

The bulk ores and significant amounts of the pyrite data show Te/Se ratios (> 0.038) above the average continental crust reference line (Fig. 2, Wedepohl, 1995; Rudnick and Gao, 2003), and therefore represent an important reservoir for Te in the continental crust. It has been shown that As-rich pyrite represents the primary host for Au in Carlin-type deposits, which highlights that trace metals can be enriched in pyrite in economic amounts (Palenik et al., 2004; Large et al., 2009; Deditius et al., 2014). Gold and Te, for example, reach concentrations of up to 8400 and 6600 ppm, respectively, in Carlin-type pyrite (Table 3).

Bulk ore analyses from the Northern Carlin Trend (Nevada) display Au and Te contents of up to 390 and 75 ppm, respectively (Emso et al., 2003). Even higher Au and Te concentrations of up to 550 and 690 ppm, respectively, were observed in mineralised ores from the alkaline rock-hosted Cripple Creek (USA) epithermal deposit and pyrite associated with these ores show Au and Te concentrations reaching 8710 and 7940 ppm, respectively (Dye, 2015). Consequently, Carlin-type and alkaline rock-hosted epithermal pyrite displays similar Te concentrations (Fig. 3A, Table 3) but variable concentrations in the bulk ores. Tellurium is enriched in the Cripple Creek ores compared to those from the Northern Carlin Trend, which can be explained by the common occurrence of free telluride minerals that are associated with Te-rich pyrite (Jensen, 2003; Dye and Smyth, 2012; Dye, 2015). Hence, in Carlin-type systems most Te is hosted by pyrite (Fig. 2, Section 6.2, as is Au (Palenik et al., 2004; Large et al., 2009; Deditius et al., 2014), free-telluride minerals are absent or rare (Emso et al., 2003). However, Emso et al. (2003) present no paired Se-Te data and hence, pyrite that occurs in association with free-telluride minerals is not shown in the Se-Te diagram (Fig. 2). This suggests that alkaline igneous rock-hosted epithermal fluids reach the Te saturation limit during their evolution opposed to many Carlin-type fluids that are Te undersaturated indicated by the lack of telluride minerals in their precipitates (Fig. 3A, Sections 6.1 and 6.2). Pyrite is the most important sink for As in these systems and the positive correlation of Au and Te with As (Fig. 3A, Sections 6.1 and 6.2). Pyrite is therefore enriched in economic amounts (Palenik et al., 2004; Large et al., 2009; Deditius et al., 2014). Hence, in Carlin-type systems most Te is hosted by pyrite (Fig. 2, Section 6.2).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.oregeorev.2017.07.023.

References

Cioacă, M.E., Munteanu, M., Qi, L., Costin, G., 2014. Trace element concentrations in porphyry copper deposits from Metaliferi Mountains, Romania: a reconnaissance