Trace element concentrations in porphyry copper deposits from Metaliferi Mountains, Romania: A reconnaissance study

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ABSTRACT

There are fifteen Miocene intrusions with porphyry copper mineralization in the Metaliferi Mountains, Romania; most are associated with epithermal Au–Ag ($\pm$ Te, Bi, Se, Ge) vein systems. The investigation of fifty samples from six deposits (Roşia Poieni, Bucium–Tarniţa, Colnic, Rovina, Valea Morii and Bolcana) indicated bulk rock mean values of 0.16–0.88 ppm Au, <50 ppm Mo, 0.02–0.35 ppm Re, 0.06–0.6 ppm In, 1.3–3.3 ppm Ag, 0.23–1.17 ppm Bi, 3.2–5.5 ppm Se, 2.4–3.3 ppm Ge, and 2.6–18 ppm Te. Trace element analyses by electron microprobe suggest that part of the Au, Ag, As, Te and Se may occur as fine-particle inclusions hosted within common sulfide minerals (pyrite, chalcopyrite and bornite). Measured concentrations range from below the minimum limit of detection to as much as 1430 ppm Au, 530 ppm Ag, 1920 ppm Te, 10,500 ppm As and 2620 ppm Se in pyrite, 970 ppm Au, 1180 ppm Ag, 1000 ppm Te, 410 ppm As and 420 ppm Se in chalcopyrite, and 920 ppm Au, 4830 ppm Ag, 1470 ppm Te, 4230 ppm Se and 1540 ppm Bi in bornite. Gold is concentrated preferentially in pyrite, while silver is consistently high (>1000 ppm) in bornite. In the porphyry-type mineralization, galena forms microinclusions in pyrite, chalcopyrite and bornite, and contains up to 3750 ppm Ag, 17,380 ppm Se, 1570 ppm Ge and 780 ppm Te. Galena and pyrite from the epithermal mineralization in the Măgura–Bolcana–Troiţa system contain concentrations of Ag and Se ten times lower than in the same minerals from the porphyry copper mineralization. The present data show that Te is a significant trace element in the potassic zone of the investigated porphyry systems. The data also shows that this does not correlate with the presence or absence of ophiolitic basement, or with variation in the chemistry of the host intrusions. Tellurium enrichment in porphyry-type deposits of the Metaliferi Mountains supports their genetic relationship with the spatially associated epithermal systems.

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1. Introduction

Copper, Au and Mo are the principal commodities in porphyry-style ores, but other metals, notably Ag and platinum group elements (PGEs), may be recoverable from some porphyry Cu (–Au, –Ag) deposits. Elements such as In, Re, Sn, W, Bi, Zn, Te, Se and Ge can also be present in porphyry Cu–(Mo–W–Sn) systems at elevated concentrations (Berger et al., 2008; Sinclair, 2007) and can potentially be extracted as by-products (Ayres et al., 2002). Although data for porphyry systems is limited, these trace elements are commonly concentrated within the common sulfides, notably gold within pyrite (e.g., Cook and Chryssoulis, 1990; Deditius et al., 2011; Reich et al., 2005, 2013a), silver in chalcocite or bornite (e.g., Cook et al., 2011; Reich et al., 2013b), indium in sphalerite (e.g., Cook et al., 2009a) or rhenium in molybdenite (e.g., Aminzadeh et al., 2011; Ciobanu et al., 2013; Golden et al., 2013).

The Metaliferi Mountains (South Apuseni Mountains) in Romania (Fig. 1) host a dense concentration of ore deposits related to Miocene calc-alkaline magmatism (Ghiţulescu and Socolescu, 1941; Ianovici et al., 1976; Roşu et al., 2001, 2004; Neubauer et al., 2005). Mineralization occurs as veins (Au–Ag $\pm$ Te and base metal), epithermal breccia pipes and replacement bodies, and in several subjacent porphyry Cu-type systems. Some of these deposits are ranked as large or very large (Borcoş et al., 1998; Milu et al., 2004; Udubaşa and Udubaşa, 2004; Vlad and Orlandea, 2004; Tămaş et al., 2006). The largest of these, the Roşia Poieni porphyry Cu deposit contains 431 Mt ore at 0.55% Cu and 0.25 g/t Au (Kouzmanov et al., 2005b). According to Vlad and Orlandea (2004), historical gold production in the district totals 630 t at Roşia Montană, 380 t at Barza–Brad, 330 t at Baia de Arieş and 250 t at Stănija; all these deposits are of epithermal type. The Săcărâmb epithermal deposit produced ca. 30 t Au, 55 t Ag and 60 t Te (Udubaşa and Udubaşa, 2004).

The results of substantial research have been published on individual porphyry Cu deposits. These include accounts of the systems at Roşia

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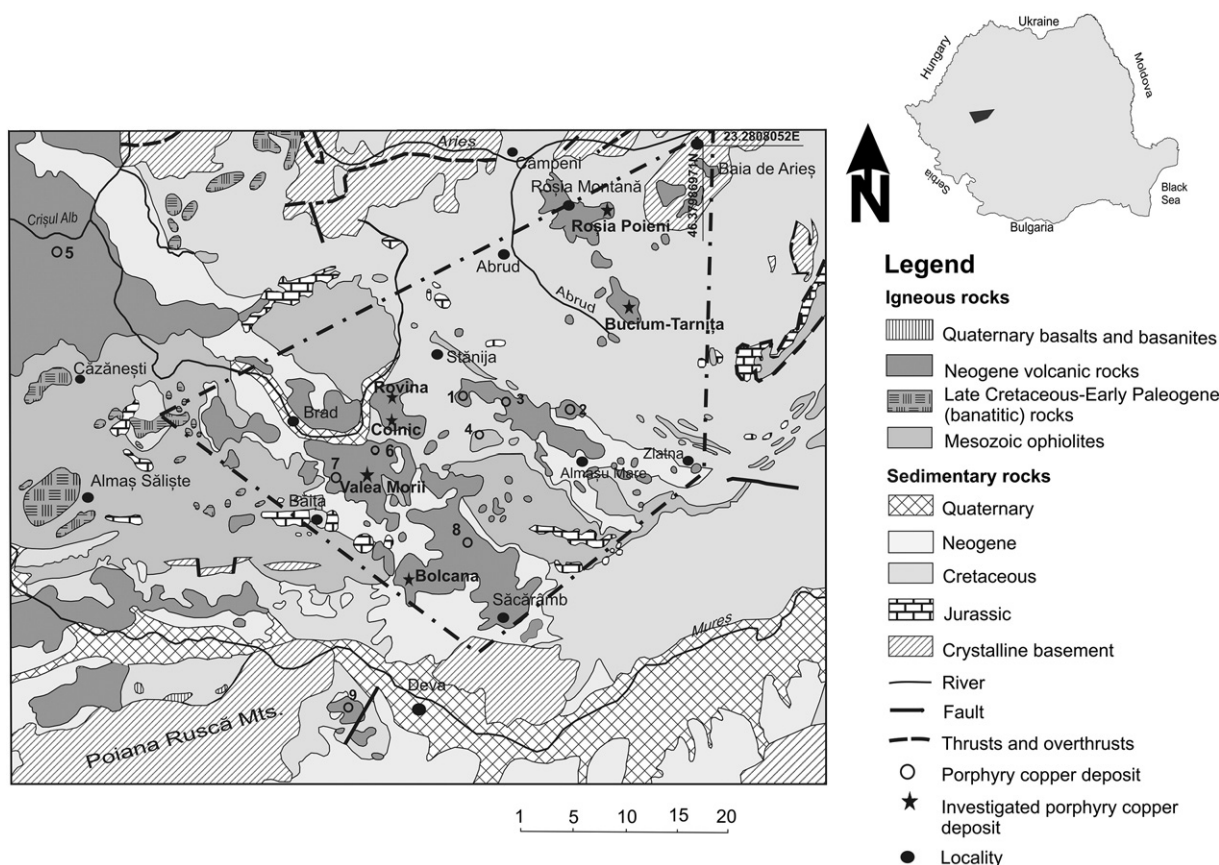*E-mail address:* mihaela.cioaca@igr.ro (M.E. Cioacă).

Fig. 1. Location of the porphyry copper deposits in the "Golden Quadrangle" — Metaliferi Mountains (modified after Cioflica et al., 1973). 1. Valea Tisei, 2. Trâmpoiele, 3. Muncăceasca, 4. Măgura Poienii, 5. Tălagiu, 6. Cireşata, 7. Musariu, 8. Voia, 9. Deva.

Poieni (André-Mayer and Sausse, 2012; Iatan, 2009; Kouzmanov et al., 2005c, 2010; Milu et al., 2004; Popescu et al., 2006); Valea Morii (André-Mayer et al., 2001; Borcoş et al., 1978), Bolcana (Cardon et al., 2005, 2008; Cioacă, 2008, 2011; Cioacă et al., 2010; Milu et al., 2003; Popescu and Cioacă, 2006), Rovina, Colnic and Cireşata (Halga et al., 2010). Attention has also been given to several of the larger epithermal deposits, including Roşia Montană (Bailly et al., 2005; Kouzmanov et al., 2005c; Tămaş et al., 2006, 2014), Săcărâmb (Alderton and Fallick, 2000; Ciobanu et al., 2008; Cook and Ciobanu, 2005; Popescu et al., 2010, 2013), and Larga (Cook and Ciobanu, 2004, 2005). These articles and a number of regional studies (Berbeleac, 1985; Borcoş et al., 1998; Boştinescu, 1984; Harris et al., 2013; Marcoux et al., 2002; Neubauer et al., 2005; Popescu and Neacşu, 2007; Roşu et al., 2001, 2004; Udubaşa and Udubaşa, 2004; Udubaşa et al., 2001; Vlad and Orlandea, 2004) have documented the spatial and genetic relationships between the porphyry Cu deposits and epithermal mineralization.

Remarkably few publications (Cheşu, 1983; Cioacă et al., 2010; Cook and Ciobanu, 2004) deal, however, with the trace element geochemistry of the porphyry copper deposits in the Metaliferi Mountains. Considering this, the research reported here is, in many respects, a reconnaissance study, aimed at identifying geochemical features and trends that can serve as premises for more detailed investigation. We provide new trace element geochemical data on bulk rock samples and on sulfide grains from mineralization in six porphyry deposits that were accessible for sampling: Roşia Poieni, Bucium–Tarniţa, Colnic, Rovina, Valea Morii and Bolcana. Our aim is to establish any similarities or differences between these deposits regarding the distribution of the trace elements of potential economic interest, and to document the role of the main sulfide minerals in concentration of trace elements. We also provide trace element concentrations in sulfides from the Măgura–Bolcana–Troiţa epithermal system and compare them with the trace element contents in porphyry-type mineralization. This comparison is used to show that the well-documented trace element signature of the epithermal assemblages (enrichment in Au, Ag and Te) can also be recognized in higher temperature assemblages within the porphyry type mineralization, thus further supporting a genetic relationship between the two styles of mineralization.

2. Geological setting

Miocene (14–7 Ma) volcanic-hydrothermal activity in the Metaliferi Mountains was controlled by the regional geodynamic evolution of the Carpathian orogen and Pannonian basin during the Cenozoic. This evolution comprised subduction and collision of the European and Moesian plates with the Intracarpathian Alcapa and Tisia blocks, resulting in a subsequent extensional regime, driven by the translation and clockwise rotation of Tisia block (Neubauer et al., 2005; Roşu et al., 2004). Rotation of the Tisia block in excess of 60° at 14–12 Ma produced deep transtensional faults and NW–SE-trending graben-like pull-apart basins, which favored a rapid magma ascent, generating numerous volcanic–subvolcanic systems. Although the geochemical studies indicate that Miocene magmas from the Metaliferi Mountains have a "subduction signature", they were generated by decompressional melting of a heterogeneous source situated at the crust–lithosphere mantle boundary (Neubauer et al., 2005; Roşu et al., 2001, 2004; Seghedi et al., 2007). Variable and higher Nb and Nb/Y ratio in younger rocks (10–7 Ma) suggest the generation of the magma by a mixing of asthenospheric melts (Roşu et al., 2001, 2004). Petrochemical studies indicate a normal calc-alkaline character for the early magmatic products (14–12 Ma), and an adakite-like calc-alkaline signature for the younger (12–7 Ma) rocks (Roşu et al., 2004). This magmatism generated amphibole andesites with pyroxene ± biotite (particularly well represented

in the Zarand–Brad–Zlatna and Roşia Montană–Bucium zones), and high potassium quartz–amphibole andesites with biotite ± pyroxene, which cover large areas in the Deva–Săcărâmb–Hărţăgani and Baia de Arieş–Roşia Montană zones. Small bodies of trachyandesites, microdiorites and basaltic andesites represent the latest products of the Miocene volcanism (10.5–7 Ma) and occur in the Săcărâmb–Hărţăgani and Roşia Montană–Bucium zones (Roşu et al., 2004).

The Miocene metallogeny in the Metaliferi Mountains is characterized by the extensive generation of hydrothermal deposits and mineral occurrences within a relatively small area (ca. 900 km^2), suggestively named the "Golden Quadrilateral" (Ghiţulescu and Socolescu, 1941). The formation of these deposits is related to Miocene magmatism (14–7 Ma; Roşu et al., 2004; Neubauer et al., 2005), which generated volcanic and subvolcanic complexes. Mineral deposits are distributed along four NW–SE-trending alignments considered as metallogenetic districts (Boştinescu, 1984; Ianovici et al., 1976; Vlad and Orlandea, 2004): Brad–Săcărâmb, Almaş–Stănija; Roşia Montană–Bucium; and Baia de Arieş. A fifth district, Bulza–Tisa, is located south of the Golden Quadrilateral, along the E–W-trending Mureş Valley alignment. According to Boştinescu (1984) and Halga et al. (2010), porphyry deposits in the Metaliferi Mountains (Fig. 1) can be classified as: Cu–Mo (Au) type (Deva, Roşia Poieni); Cu–Au type (Valea Morii, Bolcana, Rovina, Voia, Tălagiu, Larga, Trâmpoiele, Valea Tisei, Bucium–Tarniţa); and Au–Cu type (Colnic, Cireşata). Most of these deposits are associated with small subvolcanic bodies within volcanic–subvolcanic systems showing a concentric metallogenetic zoning (Berbeleac, 1985; Borcoş et al., 1998; Cardon et al., 2005; Popescu and Neacşu, 2007). In these systems, the porphyry mineralization occupies the cores of the host subvolcanic bodies, while base metal (Pb–Zn–Cu ± Au, Ag) and Au–Ag epithermal veins occur peripherally, superimposed on the porphyry type deposits, and/or related with andesitic stocks emplaced around the subvolcanic bodies. The spatial overlapping and the so-called "ring-zoning" distribution of copper, polymetallic and Au–Ag deposits is explained by Popescu and Neacşu (2007) as a result of the polystadial evolution of individual caldera systems. Cogenetic relationships between porphyry and epithermal mineralization are evidenced by petrographic and geochemical data, the two mineralization types representing distinct sequences of the same metallogenetic process, which generated mineral accumulations over a vertical extent of ca. 1500 to 2000 m in the case of telescoped porphyry and epithermal systems (Borcoş et al., 1998).

All porphyry Cu deposits are located within large volcanic complexes, emplaced in extensional duplex structures developed during the late Badenian to Sarmatian, a result of strike-slip tectonics (Drew, 2003). The location of the mineralized structures at the intersections of fault systems with different trends (E–W and NW–SE, occasionally WNW–ESE), the superposition of vein meshes on the porphyry copper structures and the geometry of deposits outline the control of tensional strain on the mineralization (Drew, 2003; Neubauer et al., 2005). These structural conditions favored rapid flush upwards of high temperature fluids from porphyry systems into kin veins, causing the destabilization of metal complexes and precipitation of epithermal mineralization (Cook and Ciobanu, 2004; Cook et al., 2009c). Several mechanisms for metal precipitation have been proposed, including pressure variation, multistage boiling or vapor-phase release during magmatic brecciation (Cook et al., 2009c).

Petrography, alteration and mineralization of all porphyry type deposits from the Metaliferi Mountains are consistent with Hollister's (1978) dioritic model, polyascendent subtype (Borcoş et al., 1998). This considers that the potassic alteration zones are well developed in the inner parts of the intrusions; argillic/phyllic zones are located at the peripheries, whereas the pervasive propylitic alteration affected mainly the surrounding andesitic rocks (Borcoş et al., 1998; Boştinescu, 1984; Milu et al., 2003, 2004). One characteristic feature of the Miocene mineralization from the Gold Quadrangle is the widespread occurrence of Au-, Ag- and Au–Ag-tellurides. More than 20 occurrences of telluride

mineralization are known in the Metaliferi Mountains (Cook and Ciobanu, 2005). Deposits such as Faţa Băii, Săcărâmb and Baia de Arieş are type localities for native tellurium and telluride species such as krennerite, muthmanite, nagyágite, petzite, stutzite, museumite, sylvanite and tellurite (Papp, 2004). Although the tellurides are most commonly observed in Au–Ag epithermal veins, the Pb-bearing Bi–telluride rucklidgeite was identified by Cook and Ciobanu (2004) in the porphyry Cu-type mineralization at Trâmpoiele, part of the Larga–Faţa Băii–Trâmpoiele porphyry–epithermal system, which shows a vertical zonation of trace element mineralogy in which Au–tellurides and native tellurium occur at shallow levels and Bi–Pb and Pb–tellurides at depth (Cook and Ciobanu, 2004).

3. Deposit background

Out of the six investigated porphyry copper deposits, four are located in the Brad–Săcărâmb District (Rovina, Colnic, Valea Morii and Bolcana), in the western part of the Golden Quadrilateral, while the other two (Roşia Poieni and Bucium–Tarniţa) are located in the eastern part of the quadrilateral, in the Roşia Montană–Bucium district (Fig. 1). The main geological characteristics of the investigated deposits are summarized in Table 1.

3.1. Country and host rocks

The subvolcanic bodies that host the deposits from the Brad–Săcărâmb district (Rovina, Colnic, Valea Morii and Bolcana) intruded Miocene amphibole andesites, which cover Late Cretaceous flysch sediments and ophiolite sequences of Late Triassic to Early Jurassic age (André-Mayer et al., 2001; Berbeleac, 1985; Boştinescu, 1984; Milu et al., 2003). At Bolcana, the host subvolcanic body also intruded the Băiţa rhyolites (Cretaceous) and Paleocene sedimentary rocks (Milu et al., 2003). At Roşia Poieni and Bucium deposits, the Neogene (Sarmatian) andesites intruded by the mineralized subvolcanic bodies lay on a Tertiary and Cretaceous sedimentary sequence and pre-Mesozoic metamorphic basement (Boştinescu, 1984; Milu et al., 2004).

All six investigated deposits are hosted by relatively small porphyry stocks whose petrography varies from amphibole ± pyroxene quartz andesite and quartz diorite at Valea Morii (André-Mayer et al., 2001; Borcoş et al., 1978) to amphibole-bearing andesite and microdiorite/diorite in the other deposits (Table 1; Boştinescu, 1984; Halga et al., 2010; Milu et al., 2003, 2004; Vlad, 1983). A gradual transition from andesite at shallow levels to microdiorite and diorite at depth is common (Boştinescu, 1984). Post-mineralization barren dykes cross the mineralized subvolcanic bodies at Colnic (Halga et al., 2010) and Valea Morii (Borcoş and Berbeleac, 1983). Incipient breccia pipe is recognized at Bolcana (Boştinescu, 1984). A phreato-magmatic breccia is reported at Rovina (Boştinescu, 1984; Halga et al., 2010). Injections of tuffitic material were mentioned at Bolcana and Roşia Poieni (Boştinescu, 1984).

3.2. Alteration

The studied deposits contain zones affected by potassic, phyllic, propylitic and argillic alterations. The potassic zones comprise the inner and deeper parts of the intrusions. The mineral assemblage is dominated by biotite, potassic feldspar and quartz, accompanied by epidote, actinolite, chlorite, anhydrite and carbonates (Berbeleac, 1985; Halga et al., 2010; Milu et al., 2003, 2004; Vlad, 1983), which induces a brownish to gray-greenish color of the rocks. Biotite occurs either as tiny crystals in the groundmass or as replacements of the hornblende and plagioclase phenocrysts (Milu et al., 2003, 2004). The alkaline feldspars replace the plagioclase crystals or occur as rounded to irregular grains in the groundmass (Borcoş et al., 1978; Ionescu et al., 1975; Milu et al., 2003, 2004). Veinlets filled with quartz ± alkaline feldspar ± biotite ± apatite ± carbonate ± magnetite ± sulfides are widespread (Borcoş et al., 1978; Ionescu et al., 1975; Milu et al., 2003, 2004)

Table 1
Geological characteristics of studied deposits and associated veins systems.

Ore deposit	Metallogenetic unit	Host rocks	Hydrothermal alteration	Ore minerals	Geochemical signature	Sizes and tonnages	Age	References
Roșia Poieni	Baia de Arieș–Bucium District	Microdiorite, amphibole-bearing andesite	Potassic, phyllic, propylitic, advanced argillic	Porphyry Cu type: py, cpy, mt, mo ± hem, bn, tet, sp, gal, en, dg, cv. Hydrothermal veins: tet–tenn, en, sp, gal, cpy, py, mar, hess, tbi, gdf, ge, arg–can.	• Cu, Fe ± Au, Mo, Co, Pb, Ga, Sn;	431 Mt (0.55% Cu, 0.25 g/t Au)	9.42 ± 0.14 Ma (U–Pb single zircon)	Borcoș et al. (1984), Che u (1983), Iatan (2009), Kouzmanov et al. (2005c), Milu et al. (2004).
Bucium–Tarnița	Baia de Arieș–Bucium District	Microdiorite, amphibole-bearing andesite	Potassic, phyllic, propylitic, argillic	Porphyry Cu type: cpy, py, mt, pyrr, mo, au. Hydrothermal veins: py, sp, tellurides, gal, bn, cpy, cz, cv, en, lz, tet, mar, au, ge, arg–can.	• Cu, Au, Fe ± Mo; • Cu, Au, Ag, Pb, Zn, Ge, Se, Te, Mn, Ti, Sn, Ni, Co ± Cd, Ga, Sb, Bi, As, In	250 m × 250 m; 335 Mt @ 0.50% Cu and 0.36 g/t	14.80–14.60 Ma (K–Ar on whole rock)	Berbeleac (1985), Borcoș et al. (1984), Che u. (1983), Kouzmanov et al. (2005b), Ro u et al. (2004), Vlad (1983).
Rovina–Remetea	Brad–Săcărâmb District	Microdiorite, amphibole–pyroxene-bearing quartz–andesite	Potassic, magnetite–chlorite–epidote alteration, argillic	Porphyry Cu type: mt, py, cpy, mo, au. Hydrothermal veins py, cpy, sp, au, ge.	• Cu, Au, Ag, Mo, Zn, Sn; • Au, Ag ± Pb, Zn, Cu, Mn, Ti, B, Sn, Co	350 m × 600 m; 0.1–1.0 g/t Au and 0.05–0.70% Cu		Borcoș et al. (1984), Che u. (1983), Halga et al. (2010), Vlad (1983).
Colnic	Brad–Săcărâmb District	Amphibole bearing diorite	Potassic, magnetite–chlorite–epidote alteration, phyllic	Porphyry Cu type: cpy, py, mt, pyrr, mo	Cu, Au	600 m × 400 m 0.3–1.3 g/t Au and 0.05–0.18% Cu		Bo tinescu (1984), Halga et al. (2010).
Valea Morii	Brad–Săcărâmb District	Quartz–diorite, amphiboles–pyroxene-bearing microdiorite	Potassic, propylitic phyllic, argillic	Porphyry Cu type: cpy, py, mt, bn, ru, sp, gal, au. Hydrothermal veins (LS): py, mar, sp, gal, bourn, cpy, tet, emp, au.	• Cu ± Fe, Zn, Pb, Au, Ag ± As, Ga, Sn, Ge, Mo, Mn, V, Se, Sr; • Au, Ag ± Pb, Zn, Cu, As, Cd, Mn, Sn, Ti, Te, Ni, Co, V.	250 m × 330 m 0.26% Cu, 0.49 ppm Au	>11 Ma	André-Mayer et al. (2001), Berbeleac (1985), Borcoș et al. (1984), Harris et al. (2013).
Bolcana	Brad–Săcărâmb District	Microdiorite, amphibole-bearing andesite	Potassic, propylitic phyllic, argillic	Porphyry Cu type: cpy, py, mt, hem, bn, au ± cv, ch, tet, sp, gal, pyrr, mol; Hydrothermal veins: py, sf, gal, cpy, tet–tenn, bn, ch, sb, hess, bourn, sell, mar, aspy, pyrr, au, ge	• Cu, Au ± Pb, Zn, Mo, Ag, Co, Ni, V, Ti, Cd, Sb; • Pb, Zn, Au Ag, Cu, Sb, Cd, Mn, Ga	750 m × 450 m max. extention; 0.2% Cu and 0.3 g/t Au	10.9 ± 1.9 Ma (Re–Os on pyrite)	Borcoș et al. (1984), Cardon et al. (2008), Che u (1983), Cioacă (2008).

Abbreviations: au = gold, arg–can = argyrodite–canfieldite, aspy = arsenopyrite, bn = bornite, bourn = bournonite, cpy = chalcopyrite, ch = chalcocite cv = covellite, dg = digenite, emp = emplectite, en = enargite, gal = galena, ge = germanite, gfd = goldfieldite, hem = hematite, hess = hessite, mt = magnetite, mace = magnetite–chlorite–epidote, mar = marcasite, mol = molybdenite, py = pyrite, pyrr = pyrrhotite, rod = rhodochrosite, ru = rutile, sb = stibnite, sp = sphalerite, sell = selligmanite, tell = undifined tellurides, tet = tetrahedrite, tenn = tennantite, tbi = tellurobismuthite.

sometimes exhibiting a violet coloration (Borcoş et al., 1978; Kouzmanov et al., 2010).

Propylitic alteration is commonly developed in andesitic rocks surrounding the mineralized subvolcanic bodies, but can also be present as relict alteration in the phyllic or/and argillic zones. It contains the assemblage chlorite–epidote–actinolite–sericite–carbonate formed on both plagioclase and mafic minerals (Borcoş et al., 1978; Milu et al., 2003, 2004). At Valea Morii, propylitic alteration is superimposed onto potassic alteration in the central zone of the intrusion, but is also present in the outer zone, affecting the primary magmatic minerals (Borcoş et al., 1978). A chlorite-dominated propylitization is mentioned in the axial zone of the Bucium–Tarniţa deposit (Boştinescu, 1984), but also at Colnic and Rovina, overlapping the potassic zones of the deposits (Halga et al., 2010).

The upper zone of the deposits is affected by phyllic and argillic alteration (Boştinescu, 1984). The phyllic and argillic alterations also occur as haloes to the epithermal veins which cut the porphyry mineralization (André-Mayer et al., 2001; Borcoş et al., 1978; Cioacă, 2008; Milu et al., 2003; Petrulian et al., 1978).

Phyllic alteration consists of the formation of sericite, quartz, pyrite, chlorite, anhydrite and clay minerals ± alunite that overprint the previous types of alteration (potassic, propylitic) in the marginal and/or upper zones of the deposits and was described at Roşia Poieni, Bolcana and Colnic (Boştinescu, 1984; Halga et al., 2010; Milu et al., 2003, 2004).

Argillic alteration affects the upper part of the porphyritic body and the volcanic country rocks from Valea Morii, Rovina, Bucium–Tarniţa (Vlad, 1983), Bolcana (intermediate argillic alteration, Milu et al., 2003) and Roşia Poieni (advanced argillic alteration, Milu et al., 2004). It consists of kaolinite, smectite, mixed-layer minerals and carbonate (Milu et al., 2003, 2004).

Overlapping of the alteration zones has been recognized in most deposits (Borcoş et al., 1998; Boştinescu, 1984; Milu et al., 2003, 2004).

3.3. Mineralization

Copper mineralization extends vertically across at least several hundred meters: 350–550 m at Colnic and Rovina (Halga et al., 2010), and more than 800 m at Roşia Poieni (Milu et al., 2004), Bolcana (Cioacă, 2011) and Valea Morii (Borcoş et al., 1978). Mineralization is broadly coincident with the potassic alteration zone and consists of chalcopyrite–pyrite–magnetite ± native gold + molybdenite either finely disseminated or forming stockwork veinlets. Hypogene bornite was found in the potassic zones at Roşia Poieni, Bolcana, Bucium–Tarniţa and Valea Morii (Borcoş et al., 1978; Boştinescu, 1984; Cioacă et al., 2010; Milu et al., 2003, 2004). Chalcopyrite replacing magnetite, pyrite or bornite is mentioned at Roşia Poieni and Valea Morii (Borcoş et al., 1978; Petrulian et al., 1978). Gold grains appear as small inclusions in both chalcopyrite (Borcoş et al., 1978; Cioacă et al., 2010; Milu et al., 2003, 2004) and pyrite (this study). Galena occurs as microinclusions in pyrite, chalcopyrite and bornite at Colnic, Bolcana and Valea Morii (this study) or as tiny grains in the silicatic matrix of the host rocks, at Bolcana and Roşia Poieni (this study). The presence of pyrrhotite was mentioned at Bucium–Tarniţa, Rovina and Colnic (Borcoş et al., 1984; Halga et al., 2010; Vlad, 1983). Rutile occurs at Valea Morii (Borcoş et al., 1978). In the phyllic and argillic zones, pyrite is the main sulfide, forming impregnations and vein fillings in association with quartz. Tetrahedrite–tennantite, sphalerite, galena and digenite also occur in the phyllic alteration at Roşia Poieni, whereas enargite/luzonite and chalcocite are present in the advanced argillic zone in association with pyrite and marcasite (Milu et al., 2004).

Supergene alteration is developed at the surface of Valea Morii, Bolcana and Roşia Poieni (Borcoş et al., 1978; Milu et al., 2003, 2004). At Bolcana and Valea Morii, a supergene enrichment zone was also developed, where secondary Cu-minerals (covellite, chalcocite, bornite) have partially/totally replaced chalcopyrite and pyrite (Borcoş et al., 1978; Cioacă, 2008). Supergene bornite from Bolcana can contain

inclusions of native gold (>97‰ Au; Cioacă et al., 2010). The zonality of the mineralization is reflected also in the spatial distribution of Cu, Au and Mo, with the higher concentration of Cu and Au in the potassic zone (0.3–0.6% Cu), where there is a positive correlation between these elements (Borcoş et al., 1998). A tendency for Mo to be concentrated towards the periphery and at depth was reported from Roşia Poieni, without any correlation with Cu and Au (Borcoş et al., 1998; Milu et al., 2004).

Late mineralized epithermal vein systems crosscut porphyry-type mineralization in all deposits, and extend into the country rocks (Table 1). Deposition of epithermal vein mineralization mostly took place at low- or intermediate-sulfidation conditions, rarely generating high sulfidation veins (Vlad and Orlandea, 2004). Low-sulfidation epithermal veins (sphalerite, galena, pyrite, tennantite–tetrahedrite, chalcopyrite, marcasite and gold) are present at Valea Morii and Bolcana (Table 1), with quartz–calcite gangue and argillic–sericitic halo (André-Mayer et al., 2001; Borcoş et al., 1978; Cioacă, 2008; Milu et al., 2003). High-sulfidation epithermal veins, containing pyrite, sphalerite, galena, chalcopyrite, tetrahedrite–tennantite, enargite, luzonite and covellite crosscut the Roşia Poieni and Bucium–Tarniţa porphyry Cu deposits (Borcoş et al., 1984; Kouzmanov et al., 2005c, 2010; Milu et al., 2004). Tellurium and germanium-bearing minerals have been recognized in both low- and high-sulfidation veins (Table 1; Cheşu, 1983; Cioacă, 2008; Iatan, 2009).

The source of metals for porphyry deposits of the Golden Quadrilateral is magmatic, as indicated by the Pb and S isotopic signatures of the mineralization (André-Mayer et al., 2001; Marcoux et al., 2002). Stable and radiogenic isotopic data (S, O, H and Pb) of epithermal deposits also indicate a predominant magmatic source for metals and hydrothermal fluids (Alderton and Fallick, 2000; André-Mayer et al., 2001; Marcoux et al., 2002). Fluid inclusion data are available for Valea Morii, Roşia Poieni and Bolcana (André-Mayer et al., 2001; Cioacă, 2011; Pettke et al., 2001; Pintea, 2001) and indicate early high temperature fluids (350 °C to >700 °C) and pressures in excess of 400 bars. The coexistence of low salinity vapors and brine inclusions (40–70 wt.% NaCl equiv.), containing halite, sylvite, anhydrite, hematite and chalcopyrite as daughter crystals, is characteristic of all deposits (André-Mayer et al., 2001; Cioacă, 2011; Pettke et al., 2001; Pintea, 2001). The tendency for enrichment of Cu, As, Sb and As in the volatile phase relative to brine inclusions from the porphyry-stage boiling assemblage at Roşia Poieni (Pettke et al., 2001) supports a genetic relationship between porphyry and epithermal mineralization.

The epithermal deposits are characterized by low-salinity aqueous inclusions with homogenization temperatures in the range 202 °C to 278 °C at Valea Morii (André-Mayer et al., 2001), 300 °C to 450 °C at Bolcana (Cioacă, 2011) and 250 °C to 340 °C at Roşia Poieni (Kouzmanov et al., 2010). Boiling may have been involved at some deposits, e.g., at Valea Morii (André-Mayer et al., 2001) but is absent in others, e.g., at Bolcana (Cioacă, 2011).

4. Samples and analytical methods

Fifty bulk rock samples from the six porphyry copper deposits were analyzed for trace elements. The bulk samples (1–2 kg each) were taken from open pits (Valea Morii, Roşia Poieni), outcrops (Colnic), and from mine dumps (Bucium–Tarnita, Rovina). Samples from Bolcana were collected from an open pit (argillic alteration zone), +150 adit, and from a mine dump. Most samples were taken from the potassic zones of the intrusions, as these characterize the early stage of mineralization. Our aim was to investigate the rocks affected by pervasive alteration and mineralization. Therefore, only rocks devoid of veinlets thicker than 1 mm across were sampled. When the samples contained thicker veins, these and their alteration haloes were handpicked and removed during crushing. All fifty whole rock samples were investigated with the optical microscope (at least one thin section and one polished section of each

sample) for the study of the ore and gangue minerals and for the identification of the alteration type.

Concentrations of trace elements other than gold were determined by inductively-coupled plasma mass-spectrometry (ICP-MS) using a Bruker Aurora M90 instrument, Guizhou Tuopu Resource and Environmental Analysis Center, China, using the method of Qi et al. (2000) for sample preparation. About 0.05 g of powdered sample was placed in a PTFE bomb, and 1 ml of HF and 1 ml of HNO$_3$ were added. The sealed bombs were then placed in an electric oven and heated to 190 °C for about 36 h. After cooling, the bombs were placed on a hot plate to evaporate to dryness. 500 ng of Rh was added as an internal standard, and then 2 ml of HNO$_3$ and 4 ml of water were added. The bomb was again sealed and placed in an electric oven at 140 °C for about 5 h to dissolve the residue. After cooling, the final dilute factor is about 3000 for ICP-MS measurements. The sensitivity of the instrument was adjusted to 300,000 cps for 1 ng ml^{-1} ^{115}In and 100,000 cps for 1 ng ml^{-1} of ^{232}Th. Medium attenuation (about 50 times) was used in the scan settings for the elements with relatively high concentration (for example, Cu). The accuracies for reference materials, AMH-1 (andesite, Thompson et al., 2000) and OU-6 (slate, Potts and Kane, 2005) of the ICP-MS analyses are estimated to be better than ±5% (relative) for most elements.

Gold concentrations in whole-rock samples were obtained using atomic absorption spectroscopy (AAS), with pre-concentration by fire assay method at the Geological Analyses Laboratory of Prospectiuni S.A., Bucharest. The minimum detection limit for Au is 0.01 ppm.

Fifteen samples of porphyry mineralization which showed relatively high trace element values were also investigated with respect to the trace element concentration of individual sulfide minerals by electron probe microanalysis (EPMA). This microprobe investigation was focused on porous pyrite (see mineralogical and textural descriptions below), which is clearly not related to vein-type mineralization. Chalcopyrite and bornite were also analyzed. Galena was identified as microinclusions in the pyrite, chalcopyrite and bornite from four porphyry deposits (Colnic, Valea Morii, Roşia Poieni and Bolcana) and was also analyzed. For the purpose of comparing between the porphyry and epithermal mineralization types, pyrite and galena from eight samples of vein-type epithermal ore from the Măgura–Bolcana–Troiţa system were investigated. EPMA data were acquired on a Jeol JXA 8230 Superprobe (Rhodes University, South Africa). Four WD spectrometers were used to identify and then measure concentrations of major and minor (>0.01 and <0.1 wt.%) elements in specific minerals. Analytical conditions were: acceleration voltage 15 kV; probe current 20 nA; beam size 1 μm; and count times 10 s (peak) and 5 s (upper and lower backgrounds). ZAF correction method was used for quantification. For trace element analysis, the accelerating voltage was kept at 15 kV, but a higher beam current (200 nA) was employed. Count times were 100 s (peak) and 50 s (lower and upper backgrounds). Only large, sensitive diffracting crystals were used (TAPL, PETL and LiFL). Standards (St), diffracting crystals, characteristic X-rays measured, peak (Pk) positions, lower (bk-) and upper (bk+) backgrounds, standard deviation 1 sigma (SD) and detection limits (DL) are detailed in Appendix 1. A second set of measurements have been done with the count time for peak increased to 200 s to lower the detection limits for Ag, Au, Te and As to 10 ppm, 30 ppm, 20 ppm and 10 ppm, respectively.

5. Mineral assemblages and textural relations

The main minerals and types of alteration in the investigated samples are summarized in Table 2. Magmatic textures are preserved in samples from the potassic alteration zones. The plagioclase phenocrysts show twinning and zoning, frequently having completely altered cores (Fig. 2A). The mafic phenocrysts are completely replaced by secondary hydrous silicates. The groundmass contains biotite flakes and rounded grains of potassium feldspar and quartz. The feldspars commonly show various degrees of sericitization. Accessory zircon, apatite and

barite occur in the groundmass but locally can occur at much higher concentrations (Fig. 2B). In samples from the phyllic alteration zones, magmatic textures are mostly obliterated by the development of a sericite mass.

The ore minerals in the studied samples occur as disseminated or clustered grains (Figs. 2A, E and 3A, B, D, E) in the groundmass of the host rocks, in the altered mafic minerals and plagioclase phenocrysts (Fig. 2A) or as veinlet fillings (Fig. 3A–D). Among the ore minerals from the potassic zone, chalcopyrite and magnetite are dominant in most deposits, followed by pyrite. The size of the sulfide grains generally varies in the range 100–500 μm, seldom larger. Magnetite can occur as isolated grains or as clusters of many crystals that may be contiguous or scattered (Fig. 2C, D). Magnetite veinlets, <1 mm across, commonly with quartz selvages, are widespread in the samples from Roşia Poieni, Valea Morii, Bolcana, and Rovina (Fig. 3D). These are mostly sulfide-free, but sometimes contain subordinated pyrite, chalcopyrite or bornite (Fig. 3D). The magnetite is sometimes transformed into hematite. Chalcopyrite commonly occurs as tiny crystals interstitial to silicates or as veinlet fillings but can also form larger grains adjacent to the magnetite and pyrite. Chalcopyrite is frequently included in magnetite and pyrite (Figs. 2C, D and 4B) in all deposits. Chalcopyrite with inclusions of pyrite (at Bolcana and Valea Morii), or magnetite (at Roşia Poieni), is relatively rare and is restricted to the largest chalcopyrite grains (Fig. 2D). In sericite-altered samples from Colnic and Bolcana, chalcopyrite is totally or partially substituted by bornite and covellite.

Pyrite forms euhedral to subeuhedral crystals, which can be clustered (especially at Colnic and Rovina, Figs. 3B and 4A). In quartz veinlets, pyrite is often anhedral, interstitial to quartz (Fig. 3B). Pyrite can grow adjacent to magnetite and chalcopyrite, and, occasionally, fills fractures in magnetite. Pyrite and, less frequently, magnetite exhibit porous skeletal structures (Figs. 2D; 3B–D and 4A–H), engulfing silicate grains (mostly plagioclase). Porous pyrite occurs in all studied intrusions but is most characteristic and widespread at Colnic and Rovina, where pyrite is the main sulfide. At Roşia Poieni, porous pyrite occurs only in the samples with phyllic alteration. Some porous pyrite grains can contain microinclusions of galena (at Colnic, Valea Morii and Bolcana) and electrum (at Colnic) (Fig. 4E–H). In one sample from Bolcana, we also observed tiny grains of galena disseminated within the host rock (Fig. 4G).

Hypogene bornite was found in association with chalcopyrite at Roşia Poieni and at Bolcana, more rarely at Valea Morii (Table 2). At Bolcana, bornite can occur as inclusions in magnetite or as distinct grains in the groundmass of the host rock, but also as rare crystals in veinlets with magnetite filling (Fig. 3D). At Roşia Poieni, the bornite is partially replaced by covellite. We observed molybdenite in samples from Rovina and Bolcana as 50–100 μm-sized grains, sometimes euhedral, in the rock groundmass (Fig. 2F). Sphalerite was found in the samples from Bolcana and Colnic (Fig. 2E). Gold is present as small inclusions (up to 10–20 μm) in chalcopyrite (Rovina), quartz and chalcopyrite (Bolcana) and in pyrite at Colnic (Fig. 4E, F).

Samples of epithermal mineralization contain varied mineral assemblages. When sphalerite is the dominant metallic mineral, galena, tetrahedrite–tennantite and chalcopyrite form small polymineral aggregates interstitial to sphalerite grains. Sphalerite can contain chalcopyrite disease. Galena can form large grains, which encapsulate sphalerite and pyrite. Pyrite occurs as round to subeuhedral grains together with sphalerite, tennantite–tetrahedrite, galena and chalcopyrite in a polymineral mass. In one polished section from the Măgura vein, we found grains of hessite together with subordinate empressite, petzite, sylvanite, cervelleite, electrum and coloradoite.

6. Results

6.1. Trace elements in bulk rock samples

Mean trace element concentrations in the investigated samples are given in Table 3, separated by alteration type. Individual data are

Table 2
Description of the samples.

Deposits	Sample	Alteration type	Mineralization	Location
Ro ia Poieni	RP01	Potassic	mt, cpy, bn(cv)	Open pit — bottom
	RP02	Potassic	mt, cpy, bn(cv)	Open pit — bottom
	RP03	Potassic	mt, cpy, bn(cv)	Open pit — bottom
	RP04	Potassic	mt	Open pit — bottom
	RP05	Potassic	mt, cpy, bn(cv)	Open pit — bottom
	RP06	Potassic	mt, bn (cv)	Open pit — bottom
	RP07	Sericitization	py, cpy	Open pit — bottom
	RP08	Sericitization	mt (hem), cpy, py	Open pit — bottom
	RP09	Potassic, incipient sericitization	mt, cpy, py	Open pit — bottom
	RP10	Potassic, incipient sericitization	mt, cpy, bn(cv)	Open pit — bottom
Bucium–Tarni a	BI01	Potassic, silicification	py, cpy, mt	Mine dump, Napoleon adit
	BI04	Potassic, cloritization, incipient sericitization	cpy, mt, py	Mine dump, Napoleon adit
	BI05	Potassic, incipient sericitization	cpy, mt, py	Mine dump, Napoleon adit
	BI07	Potassic	mt, cpy, py	Mine dump, Napoleon adit
	BI08	Potassic	mt (hem), cpy, py	Mine dump, Napoleon adit
	BI16	Potassic, partial sericitization	cpy, mt, py	Mine dump, adit +880
	BI17	Potassic, cloritization, partial sericitization	cpy, mt, py	Mine dump, adit +880
	BI30	Sericitization, cloritization	py, cpy	Mine dump, adit +980
	BI32	Sericitization, cloritization	py, cpy	Mine dump, adit +980
	BI33	Sericitization, cloritization	py, cpy	Mine dump, adit +980
	BI34	Potassic, cloritization	mt, py, cp	Mine dump, adit +980
Rovina	ROV02	Potassic, biotitization	mt, cpy, py	Mine dump
	ROV03	Potassic, partial sericitization	mt, cpy, mol	Mine dump
	ROV05	Potassic, partial sericitization	cpy, py, mt	Mine dump
	ROV09	Sericitization	py	Mine dump
	ROV12	Potassic	cpy, mt, py	Mine dump
	ROV14	Potassic, biotitization	py, mt	Mine dump
	ROV16	Potassic	py, mt, cpy	Mine dump
	ROV17	Potassic, partial sericitization	py, cpy, mt, mo	Mine dump
	ROV18	Potassic	py, cpy, mt	Mine dump
Colnic	COL01	Potassic	cpy(cv), py, mt, sp	Outcrop
	COL02	Potassic	py, cpy, au	Outcrop
	COL04	Potassic	py, cpy(cv), mt, gal, au	Outcrop
	COL06	Potassic	cpy(cv), py, mt	Outcrop
	COL08	Potassic	py, mt, cpy, bn, au	Outcrop
	COL10	Potassic	mt, py, cpy(cv), au	Outcrop
	COL13	Sericitization	py, cp(cv)	Outcrop
	COL17	Sericitization, silicification	py	Outcrop
Valea Morii	ARS01	Potassic	cpy, mt, py	Open pit — bottom
	ARS02	Potassic	mt (hem), cpy, bn	Open pit — bottom
	ARS03	Potassic	cpy, mt, py	Open pit — bottom
	ARS07	Sericitization	mt, cpy, bn	Open pit — bottom
	ARS13	Potassic	cpy, mt	Open pit — bottom
	ARS16	Potassic, cloritization, partial sericitization	mt, cpy, bn	Open pit — bottom
	ARS17	Potassic, cloritization, partial sericitization	cpy, mt, py	Open pit — bottom
Bolcana	BO-C2	Argillic alteration, silicification	py	Open pit
	BO-150	Potassic	cpy, py, mt(hem), mol	+150 adit
	BO-150-3	Potassic	cpy, mt, py, au	+150 adit
	BO-F21	Potassic–propylitic	mt	Mine dump
	BO-F3-02	Potassic–propylitic	mt, py, cpy (bn), bn, gal	Mine dump
	M1278		mt, py, ccp	

Abbreviations: au = gold, bn = bornite, cpy = chalcopyrite, cv = covellite, gal = galena, hem = hematite, mt = magnetite, mol = molybdenite, py = pyrite, sp = sphalerite.

given as electronic supplementary material. Comparing the mean values from the potassic zone of each deposit, Colnic displays the highest Au contents (average 0.81 g/t). Of the five values above 1 g/t Au in Appendix 2, three are from Colnic. The samples from Valea Morii have the lowest Au content (average 0.24 g/t), while the other deposits have values between 0.37 g/t (Rovina) and 0.54 g/t (Bolcana). In phyllic or argillic alterated samples, Au is lower than the mean value for the corresponding potassic zone for each deposit, except in the case of Colnic (1.1 ppm Au) and Ro ia Poieni (0.67 ppm Au). Average Cu contents vary from <0.1% in the potassic zone at Rovina to ca. 0.34% at Bucium. Phyllic alterated samples have lower Cu contents in each deposit, except for samples from Valea Morii and Bolcana. The mean Ag concentrations in the potassic alterated samples range between 0.79 ppm (Rovina) and 2.80 ppm (Colnic and Bolcana). Samples from Valea Morii, Roșia Poieni and Bucium–Tarnița and Bolcana contain concentrations between 1.22 ppm and 1.72 ppm Ag. Comparing the mean concentrations of Ag in the potassic zone with Ag from sericitized samples, a tendency for Ag enrichment is evidenced at Rovina, Colnic and

Bucium–Tarni a. Molybdenum shows the highest mean concentrations (>15 ppm) at Roșia Poieni and Colnic, where the most elevated mean values come from the phyllic alteration zones (42 ppm, and 79 ppm, respectively) (Table 3). In samples from Valea Morii, Bolcana, Rovina and Bucium–Tarnița, mean Mo contents are <10 ppm in both potassic and phyllic/argillic samples. The average Re contents of the bulk rock samples in the investigated deposits vary between 0.02 ppm (Bolcana) and 0.36 ppm (Roșia Poieni). The highest Re values were obtained from samples with higher Mo contents.

Mean Te concentrations range from 1.9 to 11 ppm in potassic zones, and between 0.44 and 34 ppm in phyllic alterated samples (Table 3). The lowest values (<5 ppm) were obtained from Valea Morii, Rovina and from the potassic zone of Bolcana and Bucium–Tarnița. The sample with the highest Te content (105 ppm) comes from sericitized sample of Roșia Poieni deposit. Selenium records the highest mean value (5.8 ppm) in the potassic zone at Bucium–Tarnița and is ca. 3–4 ppm in the other deposits. Our data indicate concentrations of ca. 2–3 ppm Ge in all the samples investigated. Bismuth has a mean concentration
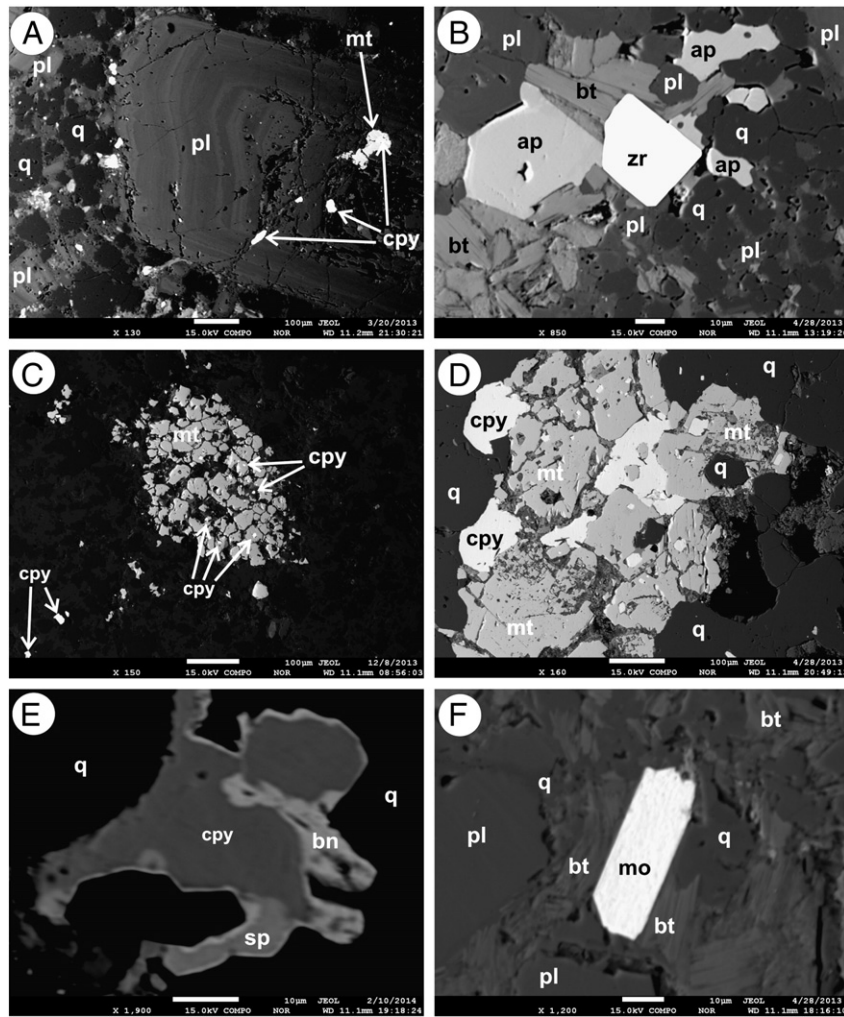
Fig. 2. Back-scatter electron image showing petrographic aspects of the investigated samples. A. Zoned plagioclase phenocryst (pl) with several chalcopyrite grains in its altered core (Colnic; sample COL06). B. Zircon and apatite-rich mineral assemblage in the potassic zone at Rovina (sample ROV17). C. Aggregate of magnetite grains in a groundmass of potassium feldspar and quartz grains; some magnetite grains contain chalcopyrite inclusions (Valea Morii; sample ARS06). D. Aggregate of magnetite and chalcopyrite grains; in its central part, smaller grains of each mineral are included in larger grains of the other mineral (Roşia Poieni; sample RP02). E. Interstitial sulfide grain (chalcopyrite + bornite + sphalerite) in quartz veinlet from Colnic (sample COL01). F. Molybdenite grain in potassic alteration zone from Rovina (sample ROV17). Other abbreviations: ap = apatite, bt = biotite, cpy = chalcopyrite, mo = molybdenite, mt = magnetite, q = quartz, sp = sphalerite, zr = zircon.

between 0.14 ppm at Bucium–Tarniţa and 1.17 ppm at Roşia Poieni and Colnic. Indium contents vary between 0.37 and 0.6 ppm at Bolcana and Colnic, 0.2 and 0.3 ppm at Valea Morii and Bucium–Tarniţa, and 0.06 and 0.07 ppm at Rovina and Roşia Poieni. Other trace elements, such as Sn and W, are present in low to very low concentrations, with minor range of variation between deposits (Table 3). The distribution of trace elements in bulk rock samples is illustrated in Figs. 5 and 6. Overall, the samples from Colnic show higher Zn, Cd and Ag contents than the other samples, while Se is highest at Bucium and in several samples from Rovina and Roşia Poieni (the sericitized zone). Indium has higher contents at Bolcana, Colnic, Bucium–Tarniţa and Valea Morii than those from Roşia Poieni and Rovina. Tungsten is higher at Valea Morii, Colnic and in the sericitic zone from Roşia Poieni. Bismuth is highest at Roşia Poieni, Colnic and in some samples from Bolcana.

There is a good agreement between the bulk rock analyses and the mineral assemblages present in the investigated samples. The samples with the highest Pb concentrations contain galena, either as inclusions (sample COL04 in Fig. 4E) or as separate grains (sample ARS06 in Fig. 4F). Samples with the most elevated Zn and Au values contain sphalerite in chalcopyrite (e.g., sample COL01, Fig. 2E) and electrum included in pyrite (sample COL04, Fig. 4E), respectively.

The Spearman correlation coefficients of Cu, Au and Mo with other elements were calculated for samples from potassic zones (Table 4). There is a good to strong correspondence of Cu with Au, Te, In and Bi for samples from the potassic alteration zones of most deposits. Tellurium, In and Bi also show a strong correspondence with Au. There is a good correlation between Au and Ag at Rovina and Valea Morii, and between Au and Se at Roşia Poieni.

6.2. Trace elements in sulfide minerals

Measured concentrations are given as supplementary electronic material and display a broad range, from below minimum detection limit to hundreds or thousands of ppm. Table 5 shows the average values of the trace elements in pyrite, chalcopyrite, bornite and galena.

6.2.1. Pyrite

Arsenic exceeds 1 wt.% in one spot, but commonly varies between 100 and 4000 ppm. Gold, Te, Se and Ag show measured values up to 1430 ppm, 1920 ppm, 2620 ppm and 530 ppm, respectively (Electronic Appendix 3). Germanium and indium contents are commonly <10 ppm; most measured In concentrations are only slightly above
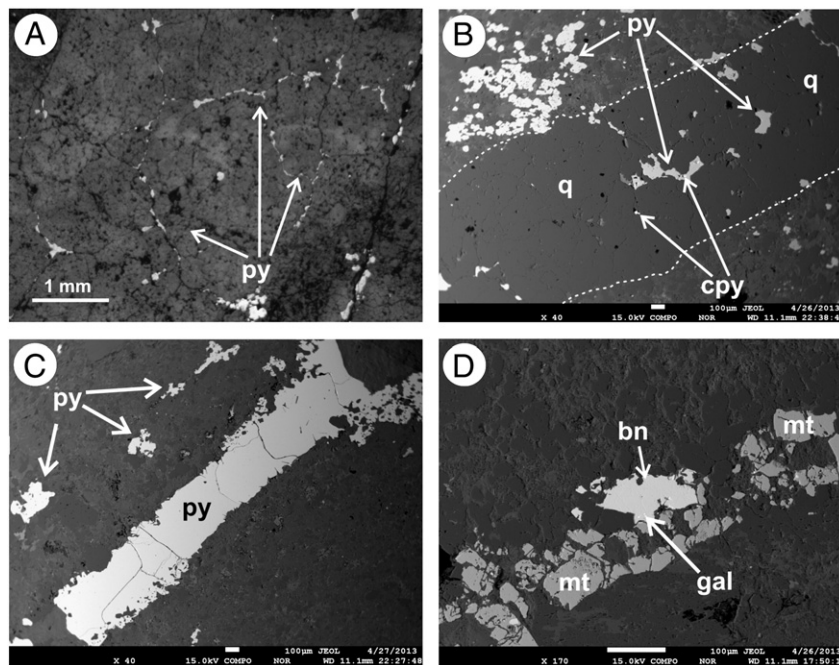
Fig. 3. Back-scatter electron images showing veining and its relationship with mineralization. A. Pyrite partially filling stockwork veinlets at Colnic (sample COL04). B. Interstitial pyrite in quartz veinlet and porous pyrite cluster outside the veinlet (Colnic; sample COL06). C. Veinlet with pyrite filling at Rovina (sample ROV17). Pyrite is compact within the veinlet and porous towards the host rock. D. Bornite with galena inclusions on a magnetite veinlet from Bolcana (sample BO-F3-02). Abbreviations: bn = bornite, cpy = chalcopyrite, gal = galena, mt = magnetite, py = pyrite, q = quartz.

the minimum detection limit. The highest mean concentrations of Ag, Au and Te in pyrite were obtained at Colnic (69 ppm, 256 ppm and 174 ppm, respectively). Pyrite has the highest Au contents at Colnic, in agreement with bulk rock analysis, suggesting that Au is contained mostly in pyrite. Pyrite from Colnic also has the highest contents of Co, but lowest Cu. Pyrite from Bucium has the highest contents of Se and Ni. Overall, Ag, Au, Te and Se concentrations in pyrite are one order of magnitude higher in the porphyry mineralization than in the epithermal ore (Table 5).

6.2.2. Chalcopyrite

The contents of Ag, Au, Te and Se show highest measured values of 1180 ppm, 970 ppm, 1000 ppm and 420 ppm, respectively (Electronic Appendix 3). Indium was detected in just a few samples, with values close to 10 ppm. Ge is constantly below 10 ppm. Chalcopyrite from Rovina and Valea Morii shows mean Ag contents higher than the other deposits. Chalcopyrite from Rovina shows higher mean Te than in the other deposits. Silver is clearly higher in chalcopyrite than in pyrite (by one order of magnitude) in all deposits; As is consistently lower.

6.2.3. Bornite

In samples from Roşia Poieni and Bolcana, bornite yielded measured values of up to 4830 ppm Ag, 920 ppm Au, 1470 ppm Te, 290 ppm As, 4230 ppm Se, 1540 ppm Bi and 210 ppm Sb (Electronic Appendix 3). Indium and Ge concentrations are below minimum detection limits in all measured grains. Silver in bornite is one order of magnitude higher than in chalcopyrite, and two orders of magnitude higher than in pyrite. If the average values are considered, Au content in bornite from Roşia Poieni (412 ppm) is higher than in any sulfide mineral from the other deposits (Table 5).

The fine grains of *galena* that occur as inclusions in porous pyrite from Colnic, Bolcana and Valea Morii contain up to 3700 ppm Ag, 27,190 ppm Se, 1500 ppm Ge, 780 ppm Te and <100 ppm Sb (Electronic Appendix 3). Galena in samples from epithermal mineralization shows Ag contents one order of magnitude lower than those from the galena in the porphyry mineralization (Table 5). Except in one sample, Se contents are <10 ppm in galena from the epithermal mineralization. Germanium

and tellurium contents in galena show no differences between the porphyry and epithermal mineralization (Electronic Appendix 3).

One grain of *electrum* included in pyrite at Colnic (Fig. 4E, F) contained 81.73% Au, 15.23% Ag, 0.13% Te, 1.15% Fe, <319 ppm Cu, <1440 ppm Hg, <294 ppm As, and <114 ppm Se.

7. Discussion

7.1. Trace element concentration in bulk rock samples

Whole rock data for samples from all studied deposits indicate substantial enrichment of Au, Ag and Te relative to the Earth's crust. The average Mo values <0.005% are typical for porphyry Cu–Au deposits (Singer et al., 2008). The higher Mo values in some samples from Roşia Poieni (324 ppm) and Rovina (83 ppm), as well as the strong correlation between Mo and Re overall, suggest the occurrence of molybdenite as a distinct sulfide phase, in agreement with microscope observations (Fig. 2F).

Samples from the potassic zone at Roşia Poieni display concentrations of Sr, Ba, La, Th, U and Be higher than those of the other deposits (Fig. 5A–F). Almost all samples from the other deposits, irrespective of dominant alteration type, have geochemical signatures that are similar to samples from the phyllic zone at Roşia Poieni (Figs. 5 and 6). The latter display higher Mo, Te, Se, Sn, Pb and Ge than samples from the potassic zone at Roşia Poieni. The geochemical similarities between the samples from most investigated deposits and the samples from the sericitic zone at Roşia Poieni probably reflect a phyllic overprinting of the potassic alteration. At Roşia Poieni, the potassic zone is exposed to deeper levels, below the portions overprinted by phyllic alteration, thus preserving primary features of the potassic alteration. It is conceivable that, in their deeper parts, the other intrusions contain rocks with geochemistry comparable to that exhibited by the potassic zone at Roşia Poieni.

The good correlations between Cu and Au, Ag, Te, In and Bi in the potassic alteration zones from most of the studied deposits (Table 4) may be an effect of the common magmatic source of all these elements. The relatively high concentration of Te, Mo, Re and Se in samples with intense phyllic alteration (Bucium–Tarniţa, Rovina, Roşia Poieni
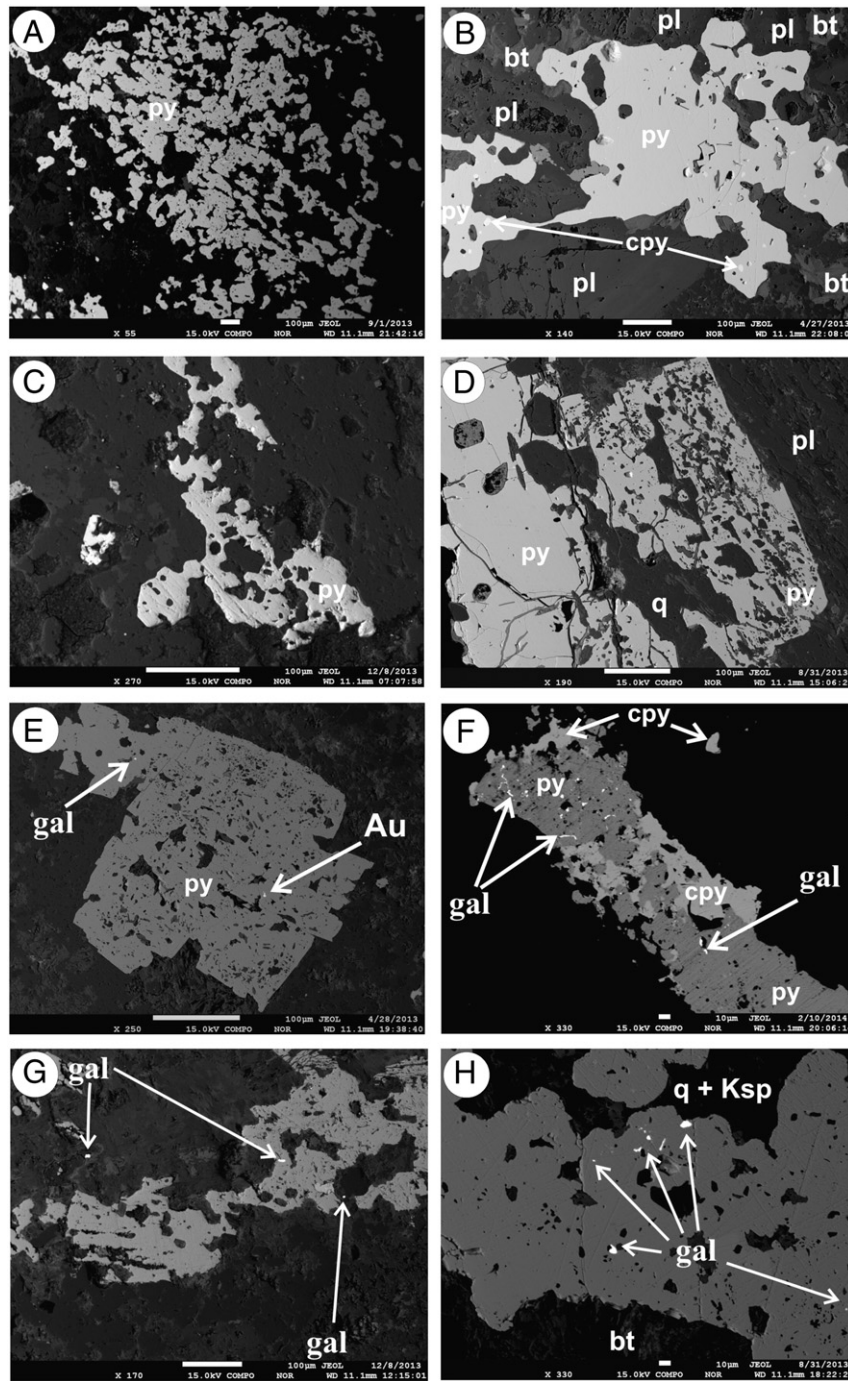
Fig. 4. Back-scatter electron images showing porous/poikilitic pyrite. A. Cluster of porous pyrite (Colnic; sample COL06). B. Skeletal porous pyrite with chalcopyrite inclusions (Rovina; sample ROV17). C. Porous skeletal pyrite from the phyllic alteration zone at Roşia Poieni (sample RP09). D. Compact pyrite on a veinlet (left) and porous pyrite (right) (Colnic; sample COL04). The clustered pyrite as that in picture A probably represents a precursor of the porous pyrite in image D. E. Porous pyrite grain with galena and electrum inclusions in a fine-grained matrix of quartz, potassium feldspar and biotite (Colnic, sample COL04). F. Pyrite with galena inclusions and associated chalcopyrite (Valea Morii; sample ARS03). G. Galena as inclusions in porous pyrite and as tiny grains in the silicate rock (Bolcana; sample M1278). H. Porous pyrite with multiple galena inclusions (Colnic; sample COL04). Abbreviations: Au = electrum, bt = biotite, cpy = chalcopyrite, gal = galena, Ksp = potassium feldspar, pl = plagioclase, py = pyrite; q = quartz.

and Valea Morii) suggests enrichment in these elements during sericitization of the host rocks, whereas the lower Cu contents in the same samples could be a result of partial mobilization of the Cu and its transport to shallower depths.

7.2. Mineral compositions

Our results show a wide variation of trace element concentrations in the same sulfide minerals, even in the same sample. Such variations, apparently not correlated with any visible inclusions, are similar with those reported from hydrothermal sulfides in other deposits (e.g., Deditius et al., 2011; Reich et al., 2013a). Non-uniform Au distribution in pyrite from various hydrothermal environments is widely reported in the literature (e.g., Barker et al., 2009; Benzaazoua et al., 2007; Cook and Chryssoulis, 1990; Cook et al., 2009a, 2011, 2013; Deditius et al., 2011; Reich et al., 2005, 2013a), often as a consequence of heterogeneous distribution at the grain-scale, and commonly related to compositional zoning with respect to As. Because the capacity of the

Table 3
Bulk rock contents of selected trace elements (mean values) in the investigated porphyry copper deposits from Metaliferi Mountains, Romania.

Element	Roşia Poieni		Bucium–Tarniţa		Rovina		Colnic		Valea Morii		Bolcana	
	Potassic zone (n = 8)	Phillic zone (n = 2)	Potassic zone (n = 8)	Phillic zone (n = 3)	Potassic zone (n = 8)	Phillic zone (n = 1)	Potassic zone (n = 6)	Phillic zone (n = 2)	Potassic zone (n = 6)	Phillic zone (n = 1)	Potassic zone (n = 4)	Argillic zone (n = 1)
Cu	2541	1805	3410	2640	883	544	1550	1227	1684	1940	1826	8020
Au	0.40	0.67	0.53	0.41	0.37	0.20	0.81	1.1	0.24	0.16	0.54	0.51
Zn	142	139	127	298	65.3	150	478.5	137	110	120	271	45.90
Pb	44.23	113	13.20	43.4	6.9	16.20	40.32	29.90	13.39	10.20	17.43	49.20
Ge	2.07	3.76	3.22	3.51	2.47	1.77	3.04	2.54	2.72	2.68	2.56	2.07
Se	4.10	5.50	5.89	4.78	4.13	6.43	2.95	4.69	3.28	3.07	2.96	4.05
Mo	15.4	42	9.05	8.55	5.21	6.44	21.52	79	6.54	8.46	3.54	4.01
Ag	1.58	0.95	1.72	2.77	0.79	0.94	2.80	5.03	1.22	1.08	2.79	1.58
In	0.07	0.10	0.27	0.12	0.06	0.07	0.54	0.62	0.28	0.25	0.37	1.56
Sb	0.30	0.10	0.17	1.01	0.27	0.25	0.25	0.53	0.65	1.09	0.56	46.93
Bi	1.17	0.70	0.14	0.09	0.24	0.21	1.17	1.17	0.31	0.59	0.57	0.68
Te	10.60	0.44	3.94	12.79	4.35	5.67	11.03	34	1.93	1.42	2.44	9.68
W	1.45	2.60	1.04	1.23	1.45	1.79	2.16	3.24	2.99	2.34	1.01	1.14
Re	0.36	0.29	0.09	0.07	0.14	0.11	0.14	0.71	0.03	0.04	0.02	0.03

Abbreviations: n – number of samples.

host sulfide to accommodate elements with large atomic radii in their lattice is limited by the mineral structure, at higher concentrations, a significant proportion of the trace elements may be present as inclusions (Ciobanu et al., 2008, 2009, 2012; Cook and Chryssoulis, 1990; Cook et al., 2011, 2013; Deditius et al., 2011; Reich et al., 2005, 2006, 2013a, b), often in the size range of fine particles (100 to 2500 nm) or nanoparticles (<100 nm). In our samples, Au is concentrated preferentially in pyrite, reaching concentrations of >30 ppm in more than half the analytical spots. The importance of pyrite as a carrier of Au and other trace elements (Ni, Co, As, Te) is acknowledged in a wide range of hydrothermal deposits, including porphyry Cu-type systems (Cook and Chryssoulis, 1990; Reich et al., 2005, 2013a). The incorporation of Au into pyrite lattice (as Au^{1+}) is favored by the presence of As, which replaces sulfur (Cook and Chryssoulis, 1990; Reich et al., 2005). On the diagram of Au solubility in pyrite as a function of As content, introduced by Reich et al. (2005), almost all our measured values plot in the field of pyrite with Au inclusions (Fig. 7). This is nonetheless the distribution of the measurements with Au in excess of 30 ppm (74 measurements out of 148). It is conceivable that in the other measured points, Au is below the nugget limit determined by Reich et al. (2005) and should therefore be trapped in the pyrite lattice.

As shown in Table 5, the Ag contents in bornite (average 1500 ppm) are much higher than in chalcopyrite (average ~180 ppm) or pyrite (average ~40 ppm). The preferential concentration of Ag in bornite was documented by Cook et al. (2011), who concluded that bornite may be a main collector of Ag in hydrothermal systems, especially in chalcocite-free assemblages. Preferential concentration of Ag in chalcopyrite and bornite was also reported from Mantos Blancos, Chile (Reich et al., 2013b).

7.3. Significance of porous pyrite

The mineralization from the investigated deposits contains porous pyrite, sometimes clustered (Fig. 4). Porous pyrite was previously mentioned at Roşia Poieni by Petrulian et al. (1978) in the peripheral zones of the mineralization. Comparable porous pyrite has been commonly reported from clastic sedimentary accumulations that underwent only diagenesis or weak metamorphism (e.g., Koglin et al., 2010; Ulrich et al., 2011), or were subjected to low-temperature hydrothermal processes (e.g., Ingham et al., 2014). Only rarely has porous pyrite been described from porphyry or epithermal deposits (Reich et al., 2013a; Winderbaum et al., 2012). It may be thus inferred that some of the disseminated pyrite crystals in the deposits studied here likely (re)crystallized at relatively low temperatures, possibly associated with late-stage alteration. A late generation of porous pyrite is mentioned by Cook et al. (2011) from intermediate-sulfidation mineralization at the Radka mine, Panagyurishte district, Bulgaria, in a sulfide assemblage precipitated at ca. 250 °C. In this context, it is worth noting that, at Roşia Poieni, porous pyrite occurs in the samples from the phyllic alteration zone. It thus grew at lower temperature than the main mineralization, which is associated with the potassic alteration. The low formation temperature would be consistent with the incapacity of the hydrothermal solutions to decompose and completely replace the silicate minerals during pyrite precipitation. When compared with the much more 'compact' structure of most pyrite crystals in veinlets (Figs. 3E and 4B), it appears that precipitation of porous pyrite in the mass of the rock took place with inadequate supply of mineralizing solutions, at low fluid/rocks ratios. Precipitation was relatively quick, as the thermodynamic and chemical conditions of the rock prevailed over those of the hydrothermal solutions in veinlets. The sulfide crystals grew, sometimes even the euhedral shapes were outlined, but chemical homogenization was not achieved.

On the other hand, porous pyrite can be viewed as a result of pyrite growth under non-equilibrium conditions, where a kinetic control on trace element incorporation is dominant compared with the entrapment in the crystallographic lattice of the sulfide (Deditius et al., 2008). Rapid precipitation of pyrite seems to favor incorporation of
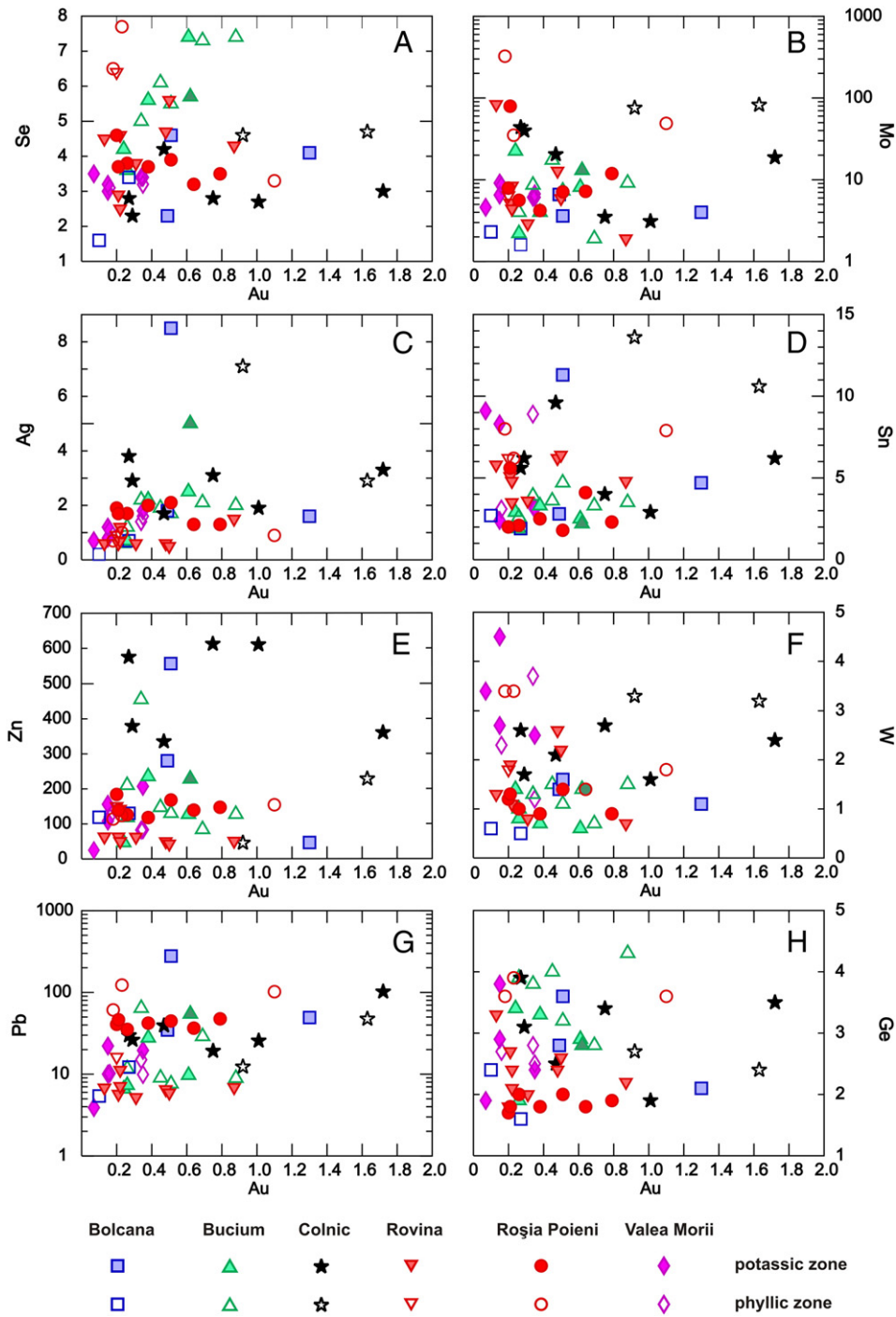
Fig. 5. Diagrams illustrating the geochemistry of the bulk rock samples, showing the differences between deposits (values in ppm). A. Se concentrations are higher at Bucium and in the sericitic zone from Roșia Poieni; B. At Roșia Poieni and Colnic, Mo contents in the sericite zones are more elevated than in the potassic zone; C. The samples from Colnic are generally richer in Ag contents than those from other deposits. D. At Roșia Poieni and Colnic, Sn is higher in the sericitic zone than in the potassic zone. E. Colnic exhibits higher Zn contents than the other deposits. F. The samples from Valea Morii show the highest W contents. G. The samples from Roșia Poieni show Pb contents higher than in the other deposits, with most elevated values in the sericitic zone. H. Ge concentrations are highest at Bucium–Tarnița and lowest in the potassic zone from Roșia Poieni.

trace elements (Huston et al., 1995) and this is consistent with the presence of inclusions of other metallic phases in porous pyrite.

The distribution of galena inclusions in pyrite is not uniform. Such disparity could be interpreted as the effect of a shift in fluid composition, from a metal-rich fluid, which precipitated inclusion-bearing pyrite, to a relatively metal-depleted one that precipitated inclusion-free pyrite. Changes in the physical conditions, such as loss of volatiles from the system, which induce rapid precipitation of porous trace element-rich pyrite, have been invoked to explain concentric Pb-rich zones in pyrite

from the Čoka Marin deposit, Bor ore district, Serbia (Pačevski et al., 2012). The galena inclusions in the porous pyrite from the deposits studied here are not homogeneously distributed within the host grain, but are instead grouped in small areas, which often have an eccentric position (Fig. 4H). This patchy distribution of the inclusion-rich areas suggests pyrite formation via recrystallization of a pre-existing aggregate of finer-grained pyrite, as opposed to the growth of concentric trace element-rich zones like in the case at Čoka Marin. Such a recrystallization is consistent with the shape of the silicate-rich zones
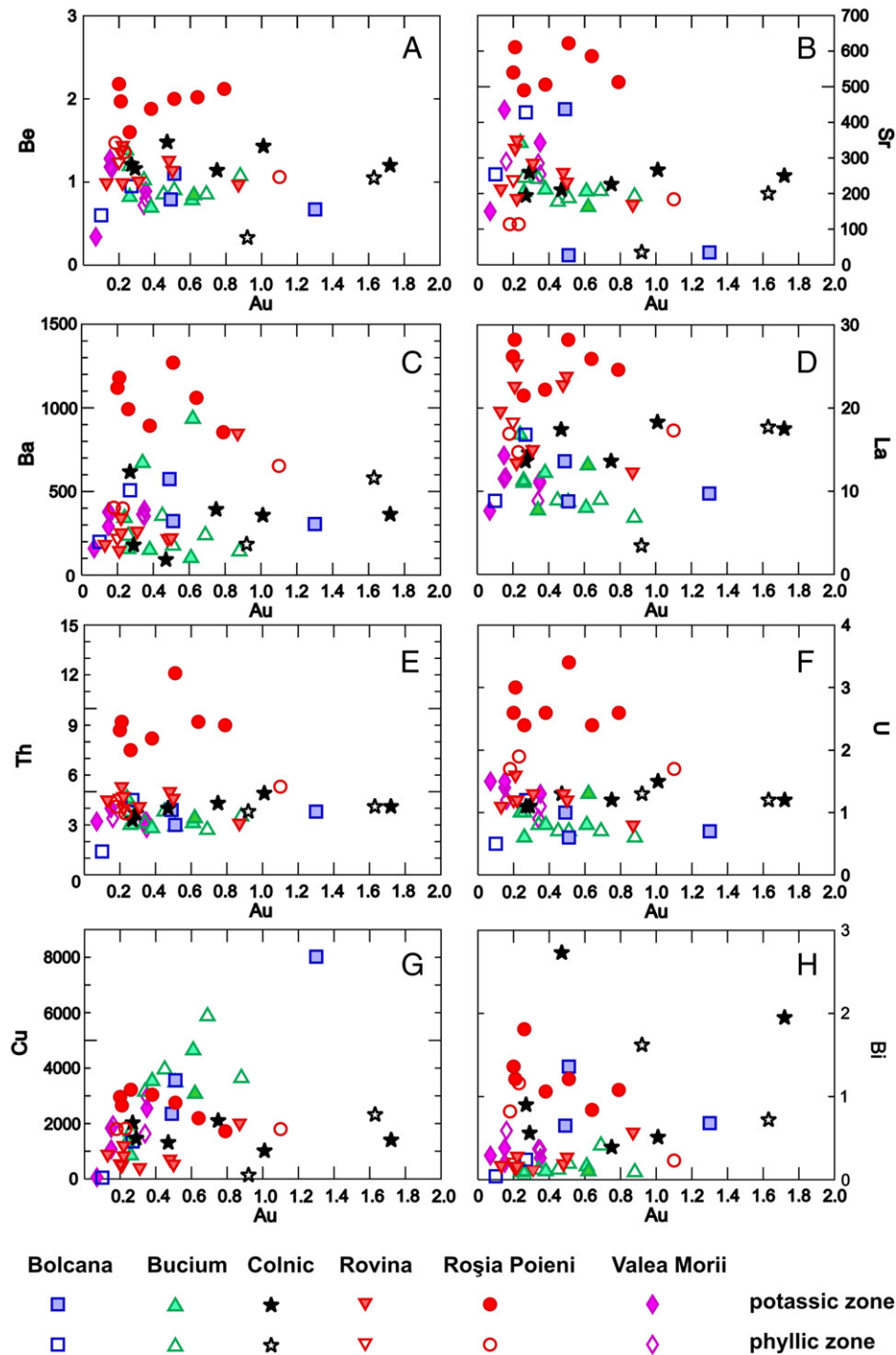
Fig. 6. Elemental diagrams for bulk rock samples. Diagrams A to F illustrate the greater concentrations of Be, Ba, Sr, La, Th and U in the potassic zone from Roşia Poieni than in all other investigated deposits, which plot together with the samples from the sericitic zone from Roşia Poieni. G. Cu vs. Au, showing the relatively high Cu concentrations at Bucium–Tarniţa. H. Bi vs. Au, showing higher Bi concentrations at Roşia Poieni (potassic zone), but also elevated values in some samples from Colnic.

included in the porous pyrite, which also suggests aggregation of several smaller crystals within a larger grain (Fig. 4B, D, E).

7.4. Porphyry–epithermal correspondence

A genetic relationship between porphyry copper mineralization and the epithermal veins, as well as a magmatic origin of metals for both types of mineralization, are supported by isotopic and geochemical data (André-Mayer et al., 2001; Cardon et al., 2005; Kouzmanov et al., 2010; Marcoux et al., 2002; Roşu et al., 2004). This relationship can be

further supported by our data for the porphyry type mineralization. The Miocene metallogenesis from the Metaliferi Mountains is characterized by an enrichment in Au, Ag and Te, which has been well documented for the epithermal mineralization (Alderton and Fallick, 2000; Bailly et al., 2005; Ciobanu et al., 2008; Cook and Ciobanu, 2004, 2005; Kouzmanov et al., 2005c; Papp, 2004; Popescu et al., 2010, 2013; Tămaş et al., 2006, 2014; Udubaşa and Udubaşa, 2004; Udubaşa et al., 2001). An important question would be whether Te, Au, Ag and other elements that are enriched in the epithermal mineralization are also at high concentrations in the porphyry-type mineralization compared to

Table 4
Spearman correlation coefficients (r) of trace elements with copper, molybdenum and gold in potassic zone of the porphyry copper deposits from Metaliferi Mountains.

	Au					Ag					Te					In					Se					Bi				
	RP	BI	ROV	COL	ARS	RP	BI	ROV	COL	ARS	RP	BI	ROV	COL	ARS	RP	BI	ROV	COL	ARS	RP	BI	ROV	COL	ARS	RP	BI	ROV	COL	ARS
Cu	0.75	0.86	0.76	0.70	0.90	0.70	0.55	0.96	0.58	0.76	0.62	0.74	0.80	0.80	0.29	0.82	0.88	0.78	0.92	0.85	0.50	−0.26	0.68	0.04	−0.16	0.84	0.84	0.77	0.78	0.79
Mo	–	–	0.40	–	0.42	0.06	−0.26	0.07	−0.23	−0.47	0.14	−0.40	0.05	−0.22	−0.3	−0.47	−0.33	0.16	−0.20	−0.63	−0.29	−0.01	−0.01	−0.10	−0.11	−0.40	−0.33	0.24	−0.18	−0.47
Au	–	0.45	0.42	0.32	0.42	0.39	0.29	0.77	0.14	0.84	0.57	0.84	0.71	0.77	0.56	0.81	0.95	0.90	0.80	0.92	0.79	−0.44	0.57	0.40	−0.02	0.79	0.91	0.93	0.79	0.86

Abbreviations: RP — Roşia Poieni, BI — Bucium-Tarniţa, ROV — Rovina-Remetea, COL — Colnic, ARS — Valea Morii, BO — Bolcana.

the porphyry systems from other parts of the world, especially to those showing enrichment in Au and Te. An extended overview on Au–Te–Ag–Se deposits is given by Cook et al. (2009c). Ciobanu et al. (2006) also discuss on the importance of alternative models for Te-enriched signatures in the absence of a dedicated Te-rich source. Tellurium-enriched epithermal–porphyry systems are commonly related to alkaline or calc-alkaline magmatism and are mostly generated at conditions of intermediate- or low-sulfidation (e.g., Ciobanu et al., 2006; Cook and Ciobanu, 2005; Jensen and Barton, 2000; Spry et al., 1996; Vourdouris et al., 2006). The Golden Quadrilateral is not a typical 'alkaline magmatism'-related province in the sense of Au–telluride deposits from the Pacific Rim (Jensen and Barton, 2000), but calc-alkaline in character. Mineralization is largely of intermediate- to low-sulfidation type (Vlad and Orlandea, 2004). The presence of Te-bearing epithermal systems spatially related to porphyry deposits was reported from other parts of the Alpine–Balkan–Carpathian–Dinaride region, notably from Pagoni Rachi–Kirki and St. Barbara–St. Demetrios, Greece (Vourdouris et al., 2006, 2013), and from the Elatsite and Radka deposits, Bulgaria (Kouzmanov et al., 2005a). Cu-rich and Mo-rich porphyry deposits with associated telluride-rich epithermal mineralization occur in North America, at Galore Creek, Allard Stock and Golden Sunlight (Jensen and Barton, 2000; Spry et al., 1996) but also at Nakodka, Russia (Nagornaya et al., 2012).

The PGE-enriched Elatsite porphyry Cu–Au deposit (0.33% Cu, 0.96 ppm Au, 0.19 ppm Ag) is part of the Late Cretaceous Banatitic Magmatic and Metallogenetic Belt (Ciobanu et al., 2002). Many of the Au–Ag deposits in this belt display a pronounced Bi–Te–(Se) signature (Ciobanu et al., 2009; Cook et al., 2011). The Elatsite deposit is hosted by a quartz–monzonitic to quartz–monzodioritic intrusion; the porphyry mineralization contains tellurides and selenides in both potassic and sericitic alteration zones (Tarkian et al., 2003). Bulk rock analyses indicate contents of <1 ppm Te and Se and 7–740 ppm Bi in the sericitic zone, but 2.2–3.8 ppm Te, 39–291 ppm Se and 240–800 ppm Bi in the potassic zone, where the mineralization is dominated by a magnetite–bornite–chalcopyrite assemblage (Tarkian et al., 2003). Bornite from Elatsite contains ca. 0.05 ppm Au, 131 ppm Ag, 424 ppm Bi, 27.4 ppm Te and 277 ppm Se (Cook et al., 2011). Pagoni Rachi is a porphyry Cu–Mo ± Re ± Au deposit related to an Oligocene calc-alkaline hornblende–biotite-bearing granodiorite–tonalite porphyry stock (Vourdouris et al., 2013). The porphyry mineralization has average contents of 0.18 ppm Au, 1.6 ppm Ag, 1.6 ppm Bi, 8.2 ppm Se, and 1.4 ppm Te, whereas the associated epithermal veins contain an average of 0.05 ppm Au, 35 ppm Ag, 67 ppm Bi, 16.5 ppm Se, 7.4 ppm Te, and 1.3 ppm In. The Skouries deposit (Greece), hosted in porphyritic monzonites (Kroll et al., 2002), has average grades of 2.7 ppm Au, 1.5 ppm Te, 6–25 ppm Se, 2–3 ppm Mo and 186 ppb (Pt + Pd), while values of 22 ppm Au and 18.5 ppm Te were found in chalcopyrite concentrate with 21% Cu (Economu-Eliopoulos and Eliopoulos, 2000). Pyrite from Skouries contains 0.5 ppm Au, while bornite and chalcopyrite contain 1.7 ppm Au and 0.1 ppm Au, respectively (Kesler et al., 2002). At Batu Hijau (Indonesia), pyrite, bornite and chalcopyrite in the porphyry copper mineralization contain 0.2 ppm Au, up to 8 ppm Au and up to 0.3 ppm Au, respectively (Arif and Baker, 2004; Kesler et al., 2002), while Ag can reach 617 ppm in bornite and 130 ppm on chalcopyrite (Arif and Baker, 2004).

Compared with the deposits mentioned above, our bulk rock samples contain lower concentrations of Bi and Se (<10 ppm Se and <5 ppm Bi) but higher Te, with values of 14–20 ppm at Bolcana, Colnic and Roşia Poieni (comparable with the chalcopyrite concentrate from Skouries). This suggests a distinct Te-rich character of the Miocene porphyry mineralization from the Metaliferi Mountains, which is a point of similarity with the epithermal mineralization. Sulfides in the studied deposits (Table 5) show concentrations of Au, Ag and Te contents higher than in the same minerals from the other Au-rich porphyry Cu deposits for which data on trace elements in sulfides is available (e.g., Batu Hijau, Kingking, Skouries, Elatsite). The higher trace element content in

Table 5
Mean values of the EPMA trace element contents in pyrite, chalcopyrite, bornite and galena from the investigated deposits. The mean values were calculated considering each content below detection limit as being 0. Therefore, the values in the table can be considered as minimal estimates of the average contents. All samples without the mention "epith" were taken from the porphyry mineralization.

Mineral/deposit	Ag ppm	Au ppm	Te ppm	Co ppm	Ni ppm	As ppm	Se ppm	Cu ppm	Sb ppm	Bi ppm	Ge ppm
Py porph. (148)	40	168	89	647	36	575	98	867	79	nm	<10
Py epith. BO (27)	5	30	10	1266	89	445	0.7	1236	nm	nm	<10
Py ARS (32)	17	79	15	495	4	926	130	1304	nm	nm	<10
Py BI (8)	10	19	21	1666	189	834	706	1268	nm	nm	<10
Py COL (41)	69	256	174	1950	50	502	45	338	75	nm	<10
Py BO (21)	6	46	6	414	23	512	3	1100	nm	nm	<10
Py ROV (37)	42	166	88	677	38	578	102	873	88	nm	<10
Py RP phyllic (9)	<10	20	<20	394	751	50	21	1172	nm	nm	<10
Cpy ARS (18)	220	178	141	243	<30	101	57	nm	112	nm	<10
Cpy BI (12)	83	<200	4	249	<30	3	19	nm	nm	nm	<10
Cpy BO (11)	129	108	51	248	<30	75	35	nm	120	nm	<10
Cpy COL (19)	151	283	185	nm	nm	168	49	nm	106	nm	<10
Cpy ROV (17)	277	141	306	nm	nm	145	60	nm	56	nm	<10
Cpy RP (2)	125	<200	<200	nm	nm	<20	250	nm	<30	nm	<10
Bn BO (16)	1510	116	335	nm	nm	102	464	nm	94	636	<10
Bn RP (6)	1477	412	247	nm	nm	45	165	nm	140	720	<10
Gal COL (11)	2497	<30	89	nm	nm	nm	1991	nm	<30	nm	779
Gal ARS (3)	1563	<30	77	nm	nm	nm	19,827	nm	<30	nm	517
Gal BO (3)	2760	<30	487	nm	nm	nm	11,200	nm	nm	nm	903
Gal RP phyllic (3)	297	<30	<20	nm	nm	nm	<10	nm	<30	nm	<10
Gal epith. (15)	575	<30	160	nm	nm	nm	2052	nm	1057	nm	874

Abbreviations: ARS = Valea Morii; BI = Bucium–Tarniţa; Bn = bornite; BO = Bolcana; COL = Colnic; Cpy = chalcopyrite; epith = epithermal; Gal = galena; porph = porphyry; py = pyrite; ROV = Rovina; RP = Roşia Poieni.

sulfides might be the effect of less sulfides by volume in the deposits from the Metaliferi Mountains.

In our samples, inclusions of galena in the porous pyrite contain more than 1000 ppm Ag (up to 3750 ppm), while Se can exceed 1.5%. This contrasts with the larger crystallized galena from the epithermal mineralization in the Măgura–Bolcana–Troiţa system, where the Ag contents are an order of magnitude lower (up to 520 ppm), and Se contents are commonly <10 ppm. Our unpublished data reveals the same relative depletion in Ag and Se within galena from epithermal mineralization at Săcărâmb. A somehow similar situation was described at Mantos Blancos, Chile (Reich et al., 2013b) where smaller chalcopyrite grains are significantly richer in trace elements than the large chalcopyrite grains. At this stage of the research we can only speculate that some small grains of porous pyrite incorporated Pb, Au, Ag, Te, Se and Ge during their rapid precipitation. After crystallization, Au and Ag were expelled as electrum, while the remaining Ag together with Pb, Te, Se, and Ge was separated as galena microinclusions. A slower growth rate

Fig. 7. Plot of Au against As (ppm) in pyrite from the investigated porphyry deposits. For comparison, several values from the Măgura epithermal mineralization (related to Bolcana porphyry system) were added. The dashed line, representing the boundary between gold substituted in the pyrite lattice (Au+) and gold present as inclusions (probably Au0), is drawn after Reich et al. (2013a).

in the case of the epithermal minerals could have induced a relative depletion of trace elements in sulfides, as it allowed better crystallographic and chemical equilibration, with the expulsion of a greater proportion of trace elements. The occurrence of altaite (PbTe) microinclusions in galena from Bolcana epithermal veins (Cioacă, 2008) is probably the result of Te expulsion from the lattice of the sulfide. The presence of other minerals that can accommodate Ag in their lattice can induce its depletion in galena. Tetrahedrite is a better Ag carrier than galena. In epithermal tetrahedrite from Bolcana, minerals of the tetrahedrite–tennantite series have high Ag contents, and vary depending on the position of veins relative to the subvolcanic body (3–4 wt.% Ag in veins crosscutting the subvolcano, and 5–6 wt.% Ag in veins outside the intrusive body; Cioacă, 2008). The preferential Ag concentration in electrum can also be an explanation for the lower Ag in the epithermal galena. The analyzed electrum inclusion from Colnic shares a chemical composition with gold inclusions in the chalcopyrite from Bolcana porphyry mineralization (15–21% Ag and 0.01–0.21% Te; Cioacă et al., 2010). In contrast, electrum from the epithermal deposits in the Gold Quadrangle (Roşia Montană, Musariu, Trestia, Măgura, Săcărâmb, Muncăceasca–Stănija) has a broad compositional variability, and is generally richer in Ag than electrum from porphyry mineralization, with contents that exceed 40% Ag in some samples from Roşia Montană (Brana, 1958; Neacşu et al., 2009; Pop et al., 2011).

7.5. Economic considerations

As shown above, almost all porphyry-type deposits in the Metaliferi Mountains are of Cu–Au or Au–Cu type. At Bucium–Tarniţa, Colnic and Bolcana, Ag has higher grade than the average of ca. 1.7 ppm, indicated for porphyry Cu–Au deposits by Cox and Singer (1988), which suggests relative Ag enrichment of the three deposits. The Te contents in the investigated deposits (2.16–18.12 ppm Te) are higher than those indicated by Ayres et al. (2002) and may potentially reach economic concentrations in some copper ores (1.5–3 ppm Te). Cheşu (1983) reported a content of 500 ppm Te in the Cu concentrate from Bucium–Tarniţa. Comparing this value with the average contents in our bulk rock samples from Bucium–Tarniţa (6.35 ppm Te), an enrichment factor of 78 times in copper concentrate would result. If this ratio were applicable to the other deposits, the potential Te contents in Cu concentrates could be ~1500 ppm at Roşia Poieni; ~350 ppm at Rovina; ~1300 ppm
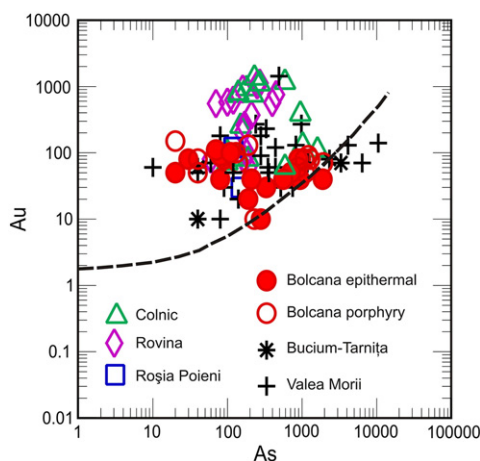
at Colnic; ~100 ppm at Valea Morii; and ~1100 ppm at Bolcana. Given the economic significance of such potentially high concentrations, further work should be undertaken to provide a better estimate of the Te resources in the porphyry systems from the Metaliferi Mountains.

There are also indications for Se and Ge enrichment in Miocene mineralization from the Metaliferi Mountains. The Ge-bearing minerals (argyrodite and alburnite) described in the epithermal mineralization at Roşia Montană (Bailly et al., 2005; Tămaş et al., 2006, 2014) and the germanite and/or argyrodite mentioned in the epithermal veins related to the Roşia Poieni, Bucium–Tarniţa, Bolcana and Rovina porphyry Cu deposits (Borcoş et al., 1984; Cheşu, 1983) suggest the possibility of a widespread Ge enrichment. High Ge concentrations in Cu-sulfides were reported by Cheşu (1983) from epithermal mineralization at Bucium (432 ppm Ge in chalcopyrite and 2900–4700 ppm in enargite). Anomalous enrichment of Ge in sphalerite was also reported from epithermal mineralization at Măgura, Săcărâmb and Roşia Montană (Cook et al., 2009b). In our samples, Ge concentrations in pyrite and Cu–(Fe)–sulfides are typically <10 ppm. Nevertheless, the high Ge contents in galena inclusions within porous pyrite from the porphyry mineralization (up to 1570 ppm Ge) support the relatively high Ge contents of the mineralizing fluids. The Ge from the epithermal galena, with values similar or even higher (up to 1690 ppm Ge) than those in the porphyry mineralization, may suggest Ge precipitation mainly as impurities in galena rather than as discrete minerals. In the latter case, a depletion of Ge in the epithermal galena would be expected.

The Se contents in the investigated deposits (3.20–5.50 ppm Se) are comparable with the value of 4 ppm Se indicated by Ayres et al. (2002) as potentially economic when considered as a by-product of Cu extraction. A content of 500 ppm Se in the copper concentrate at Deva (Cheşu., 1983) and the presence of the Pb–selenide clausthalite at Trâmpoiele (Cook and Ciobanu, 2004) point to a potential Se-rich signature in some Miocene porphyry deposits of the Metaliferi Mountains. In this context, the bulk rock Se concentrations in porphyry mineralization from Bucium–Tarniţa (average 5.6 ppm Se in bulk rocks and ca. 700 ppm in pyrite), higher than in the other deposits, might be an indication of a local Se enrichment worthy of more extensive research.

8. Conclusions

Investigation of samples from six porphyry deposits reveals several characteristics that can be significant for the metallogenesis of the entire Miocene province in the Metaliferi Mountains.

1. All investigated deposits show Au enrichment to various degrees (highest at Colnic, lowest at Valea Morii) and local geochemical variation (e.g., Colnic is richest in Zn, Cd, In and Ag, Roşia Poieni has the highest U and Bi contents, Bucium–Tarniţa is richest in Se).
2. Results indicate a preferential concentration of Au in porous pyrite, probably because of its rapid crystallization. Silver is preferentially concentrated in bornite (up to 0.5% Ag). The broad variations of Au, Ag, Te and Se concentrations in the sulfides suggest their presence as both lattice-bound and as included nanoparticles.
3. The Au–Te rich character of the epithermal deposits is also recognized in the porphyry mineralization, a feature most obviously at Bolcana, Colnic and Roşia Poieni. The similar trace element signatures of the mineralization in the porphyry and epithermal systems confirm their genetic relationship.
4. Germanium enrichment, indicated by previous studies, is reflected in our results by the composition of galena, which contains up to 1500 ppm Ge.
5. Several trace elements show lower concentrations in the sulfides from the epithermal deposits than in the porphyry mineralization. This tendency is most obvious for galena, which is much richer in Ag ± Se in the porphyry mineralization than in the epithermal veins.
6. Our results do not indicate significant differences in the trace element contents between porphyry deposits underlain by different types of country rocks (e.g., metamorphic basement at Roşia Poieni, ophiolitic basement at Valea Morii, Rovina, Colnic and Bolcana).

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.oregeorev.2014.04.016.

References

Alderton, D.H.M., Fallick, A.E., 2000. The nature and genesis of gold–silver–tellurium mineralization in the Metaliferi Mountains of Western Romania. Econ. Geol. 95, 495–516.

Aminzadeh, B., Shahabpour, J., Maghami, M., 2011. Variation of rhenium contents in molybdenites from the Sar Cheshmeh porphyry Cu–Mo deposit in Iran. Resour. Geol. 61, 290–295.

André-Mayer, A.S., Sausse, J., 2012. Fissural permeability in the Roşia Poieni copper deposit: influence on ore repartition at the open pit scale. Rom. J. Earth Sci. 85 (1), 35–41.

André-Mayer, A.S., Leroy, J.L., Marcoux, E., Lerouge, C., 2001. Inclusions fluides et isotopes du soufre du gisement Cu–Au de Valea Morii (Monts Apuseni, Roumanie): un télescopage porphyre–épithermal neutre. Earth Planet. Sci. Lett. 333, 121–128.

Arif, J., Baker, T., 2004. Gold paragenesis and chemistry at Batu Hijau, Indonesia: implications for gold-rich porphyry copper deposits. Mineral. Deposita 39, 523–535.

Ayres, R.U., Ayres, L., Råde, I., 2002. The Life Cycle of Copper, Its Co-products and By-products. http://pubs.iied.org/pdfs/G00740.pdf (Last access 18.02.2014).

Bailly, L., Tămaş, C.G., Minuţ, A., 2005. Te-rich argyrodite occurrence in Roşia Montană ore deposit, Apuseni Mountains, Romania. C. R. Geosci. 337, 755–762.

Barker, S.L.L., Hickey, K.A., Cline, J.S., Dipple, G.M., Kilburn, M.R., Vaughan, J.R., Longo, A.A., 2009. Uncloaking invisible gold: use of NanoSIMS to evaluate gold, trace elements, and sulfur isotopes in pyrite from Carlin-type gold deposits. Econ. Geol. 104, 897–904.

Benzaazoua, M., Marion, P., Robaut, F., Pinto, A., 2007. Gold-bearing arsenopyrite and pyrite in refractory ores: analytical refinements and new understanding of gold mineralogy. Mineral. Mag. 71, 123–142.

Berbeleac, I., 1985. Gold Ore Deposits. Editura Tehnică, Bucureşti (315 pp. in Romanian).

Berger, B.R., Ayuso, R.A., Wynn, J.C., Seal, R., 2008. Preliminary model of porphyry copper deposits. USGS Open-file Report (http://pubs.usgs.gov/of/2008/1321/pdf/OF081321_508.pdf. Last access 18.02.2014).

Borco , M., Berbeleac, I., 1983. Tertiary metallogeny zoning in the porphyry copper deposits from Valea Morii and Musariu (Brad area, Metaliferi Mountains). Ann. Inst. Géol. Géophys. 61, 159–168.

Borcoş, M., Berbeleac, I., Gheorghiţă, I., Bratosin, I., Colios, E., Zămircă, E., Anastase, S., Verdeş, G., Stănescu, I., 1978. Geochemical remarks on the Valea Morii-porphyry copper deposit (the Metaliferi Mountains). Dări Seamă Şedinţelor LXIV, 17–36.

Borcoş, M., Krautner, H.G., Udubaşa, G., Săndulescu, M., Năstăseanu, S., Biţoianu, C., 1984. Map of the mineral resources, Explanatory Note2nd edition. Institute of Geology and Geophysics, Bucharest.

Borcoş, M., Vlad, S., Udubaşa, G., Găbudeanu, B., 1998. Qualitative and quantitative metallogenetic analysis of the ore genetic units in Romania. Rom. J. Miner. Depos. 78, 1–160.

Boştinescu, S., 1984. Porphyry copper systems in the South Apuseni Mountains — Romania. An. Inst. Geol. Geofiz. LXIV, 163–175.

Brana, V., 1958. Metalliferous Deposits of the Subsoil of Romania. Editura Ştiinţifică, Bucharest (261 pp. in Romanian).

Cardon, O., André-Mayer, A.-S., Sausse, J., Milu, V., Chauvet, A., Leroy, J.L., Lespinasse, M., Udubaşa, S., 2005. Connexion porphyre cuprifère–épithermaux de type low-sulfidation: analyse structurale et représentation 3D du secteur de Bolcana, monts Apuseni, Roumanie. C. R. Geosci. 337, 824–831.

Cardon, O., Reisberg, L., André-Mayer, A.S., Leroy, J.L., Sausse, J., Milu, V., Zimmermann, C., 2008. Re–Os systematics of pyrite from the Bolcana porphyry copper deposit, Apuseni Mountains, Romania. Econ. Geol. 103, 1695–1702.

Cheşu, M., 1983. Minor Elements in Non-ferrous Ores from Romania. Editura Tehnică, Bucureşti (in Romanian).

Cioacă, M.E., 2008. Study of the Cu and Au "porphyry" type mineralization from Bolcana, Metaliferi Mts. Unpublished PhD thesis, University of Bucharest. (in Romanian).

Cioacă, M.E., 2011. Fluid evolution in the Bolcana ore deposit, Metaliferi Mountains (Romania). Carpath. J. Earth Environ. Sci. 6, 215–224.

Cioacă, M.E., Popescu, C.G., Munteanu, C.G., 2010. Contribution to the gold geochemistry from the porphyry Cu–Au mineralization of Bolcana deposit, Metaliferi Mts. Rom. J. Miner. Depos. 84, 48–50.

Ciobanu, C.L., Cook, N.J., Stein, H., 2002. Regional setting and geochronology of the Late Cretaceous banatitic magmatic and metallogenic belt. Mineral. Deposita 37, 541–567.

Ciobanu, C.L., Cook, N.J., Spry, P.G., 2006. Preface-special issue: telluride and selenides minerals in gold deposits — how and why? Mineral. Petrol. 87, 163–169.

Ciobanu, C.L., Cook, N.J., Pring, A., Damian, G., Căpraru, N., 2008. Another look at nagyagite from the type locality, Săcărâmb, Romania: replacement, chemical variation and petrogenetic implications. Mineral. Petrol. 93, 273–307.

Ciobanu, C.L., Cook, N.J., Pring, A., Brugger, J., Danushevsky, L., Shimizu, M., 2009. "Invisible gold" in bismuth chalcogenides. Geochim. Cosmochim. Acta 73, 1970–1999.

Ciobanu, C.L., Cook, N.J., Utsunomiya, S., Kogawa, M., Green, L., Gilbert, S., Wade, B., 2012. Gold–telluride nanoparticles revealed in arsenic-free pyrite. Am. Mineral. 97, 1515–1518.

Ciobanu, C.L., Cook, N.J., Kelson, C.R., Guerin, R., Kalleske, N., Danyushevsky, L., 2013. Trace element heterogeneity in molybdenite fingerprints stages of mineralization. Chem. Geol. 347, 175–189.

Cioflica, G., Savu, H., Borcoş, M., Ştefan, A., Istrate, G., 1973. Geological map of Apuseni Mountains with the distribution of the ore deposits, according with the geological map of Romania, scale 1:200,000. In: Alpine Volcanism and Metallogenesis in the Apuseni Mountains, Guidebook no 13, Symposium Volcanism and metallogenesis, Published by the Geological Institute of Romania. Bucharest

Cook, N.J., Chryssoulis, S.L., 1990. Concentrations of "invisible gold" in common sulfides. Can. Mineral. 28, 1–16.

Cook, N.J., Ciobanu, C.L., 2004. Bismuth tellurides and sulphosalts from the Larga hydrothermal system, Metaliferi Mts., Romania: paragenesis and genetic significance. Mineral. Mag. 68, 301–321.

Cook, N.J., Ciobanu, C.L., 2005. Tellurides in Au deposits: implications for modelling. In: Mao, J.W., Bierlein, F.B. (Eds.), Mineral deposit research: meeting the global challenge. Proceedings of the Eighth Biennial SGA Meeting Beijing, China, 18–21 August 2005, pp. 1387–1390.

Cook, N.J., Ciobanu, C.L., Pring, A., Skinner, W., Danyushevsky, L., Shimizu, M., Saini-Eidukat, B., Melcher, F., 2009a. Trace and minor elements in sphalerite: a LA-ICP-MS study. Geochim. Cosmochim. Acta 73, 4761–4791.

Cook, N.J., Ciobanu, C.L., Mao, J., 2009b. Textural controls on gold distribution in As-free pyrite from the Dongping, Huangtuliang and Hougou gold deposits, North China Craton (Hebei Province, China). Chem. Geol. 264, 101–121.

Cook, N.J., Ciobanu, C.L., Spry, P.G., Vourdouris, P., the participants of IGCP-486, 2009c. Understanding gold–(silver)–telluride–(selenide) mineral deposits. Episodes 32, 249–263.

Cook, N.J., Ciobanu, C.L., Danyushevsky, L.V., Gilbert, S., 2011. Minor and trace elements in bornite and associated Cu–(Fe)–sulfides: LA-ICP-MS study. Geochim. Cosmochim. Acta 75, 6473–6496.

Cook, N.J., Ciobanu, C.L., Meria, D., Silcock, D., Wade, B., 2013. Arsenopyrite–pyrite association in an orogenic gold ore: tracing mineralization history from textures and trace elements. Econ. Geol. 108, 1273–1283.

Cox, D.P., Singer, D.A., 1988. Distribution of gold in porphyry copper deposits. US Geological Survey Open-file Report.

Deditius, A., Utsunomiya, S., Renock, D., Ewing, R.C., Ramana, C.V., Becker, U., Kesler, S.E., 2008. A proposed new type of arsenian pyrite: composition, nanostructure and geochemical significance. Geochim. Cosmochim. Acta 72, 2919–2933.

Deditius, A., Utsunomiya, S., Reich, M., Kesler, S.E., Ewing, R.C., Hough, R., Walshe, J., 2011. Trace metal nanoparticles in pyrite. Ore Geol. Rev. 42, 32–46.

Drew, L.J., 2003. Model of the porphyry copper and polymetallic vein family of deposits—applications in Slovakia, Hungary, and Romania. Int. Geol. Rev. 45, 143–156.

Economu-Eliopoulos, M., Eliopoulos, D.G., 2000. Palladium, platinum and gold concentration in porphyry copper systems of Greece and their genetic significance. Ore Geol. Rev. 16, 59–70.

Ghiţulescu, T.P., Socolescu, M., 1941. Étude géologique et minière des Monts Metallilifères (Quadrilatère aurifère et régions environnantes). An. Inst. Geol. 21, 181–464.

Golden, J., McMillan, M., Downs, R.T., Hytdad, G., Goldstein, I., Stein, H.J., Zimmerman, A., Sverjensky, D.A., Armstrong, J.T., Hazen, R.M., 2013. Rhenium variations in molybdenite (MoS$_2$): evidence for progressive subsurface oxidation. Earth Planet. Sci. Lett. 366, 1–5.

Halga, S., Ruff, R., Stefanini, B., Nicolici, A., 2010. The Rovina Valley Project, Apuseni Mts., Romania. Gold copper porphyry discoveries in a historic mining district. Rom. J. Miner. Depos. 84, 12–15.

Harris, C., Pettke, T., Heinrich, C.A., Roşu, E., Woodland, S., Fry, B., 2013. Tethyan mantle metasomatism creates subduction geochemical signatures in non-arc Cu–Au–Te mineralizing magmas, Apuseni Mountains (Romania). Earth Planet. Sci. Lett. 366, 122–136.

Hollister, V.F., 1978. Geology of the Porphyry Copper Deposits of the Western Hemisphere. AIME, New York (219 pp.).

Huston, D.L., Sie, S.H., Suter, G.F., Cooke, D., Both, R.A., 1995. Trace elements in sulfide minerals from Eastern Australian volcanic-hosted massive sulfide deposits: part I. Proton microprobe analyses of pyrite, chalcopyrite and sphalerite and part II. Selenium levels in pyrite: comparison with (δ^{34}S) values and implications for the source of sulfur in volcanogenic hydrothermal system. Econ. Geol. 90, 1167–1196.

Ianovici, V., Borcoş, M., Bleahu, M., Patrulius, D., Lupu, M., Dimitrescu, R., Savu, H., 1976. Geology of Apuseni Mountains. Editura Academiei Republicii Socialiste, România (603 pp. in Romanian).

Iatan, L., 2009. A new occurrence of tellurium-bearing minerals in the Metaliferi Mountains: Roşia Poieni porphyry copper deposit. Rom. J. Mineral. 84, 78–79.

Ingham, E.S., Cook, N.J., Cliff, J., Ciobanu, C.L., Huddleston, A., 2014. A combined chemical, isotopic and microstructural study of pyrite from roll-front uranium deposits, Lake Eyre Basin, South Australia. Geochim. Cosmochim. Acta 125, 440–465.

Ionescu, O., Soare, C., Gheorghiu, M., 1975. Contributions to the knowledge of the Roşia–Poieni copper deposit. Hypogene alterations. Stud. Cercet. Geol. Geofiz. Geogr. 20, 159–170 (Bucharest in Romanian).

Jensen, E.P., Barton, M.D., 2000. Gold deposits related to alkaline magmatism. Rev. Econ. Geol. 13, 279–314.

Kesler, S.E., Chryssoulis, S.L., Simon, G., 2002. Gold in porphyry copper deposits: its abundance and fate. Ore Geol. Rev. 21, 103–124.

Koglin, N., Frimmel, H.E., Lawrie Minter, W.E., Brätz, H., 2010. Trace-element characteristics of different pyrite types in Mesoarchean to Palaeoproterozoic placer deposits. Mineral. Deposita 45, 259–280.

Kouzmanov, K., Bogdanov, K., Ramboz, C., 2005a. Te- and Bi bearing assemblage in the Elashita and Radka epithermal deposits, Central Srednogorie, Bulgaria: mineralogy and genetic features. Geochem. Mineral. Petrol. 43, 108–112.

Kouzmanov, K., Ivascanu, P., O'Connor, G., 2005b. Porphyry Cu–Au and epithermal Au–Ag deposits in the southern Apuseni Mountains, Romania. South Apuseni Mountains district: lat. 46 degrees 03 ′N, long. 22 degrees 58 ′E. Ore Geol. Rev. 27, 46–47.

Kouzmanov, K., Von Quadt, A., Peytcheva, I., Harris, c., Heinrich, C., Roşu, E., O'Connor, G., 2005c. Roşia Poieni porphyry Cu–Au and Roşia Montană epithermal Au–Ag deposits, Apuseni Mts., Romania: timing of magmatism and related mineralisation. Geochem. Mineral. Petrol. 43, 113–117.

Kouzmanov, K., Pettke, T., Heinrich, C.A., 2010. Direct analysis of ore-precipitating fluids: combined IR microscopy and LA-OCP-MS study of fluid inclusions in opaque ore minerals. Econ. Geol. 105, 351–373.

Kroll, T., Müller, D., Seifert, T., Herzig, P.M., Schneider, A., 2002. Petrology and geochemistry of the shoshonite-hosted Skouries porphyry Cu–Au deposit, Chalkidiki, Greece. Mineral. Deposita 37, 137–144.

Marcoux, E., Grancea, L., Lupulescu, M., Milesi, J.-P., 2002. Lead isotope signatures of epithermal and porphyry-type ore deposits from the Romanian Carpathian Mountains. Mineral. Deposita 37, 173–184.

Milu, V., Leroy, J.L., Piantone, P., 2003. The Bolcana Cu–Au ore deposit (Metaliferi Mts., Romania) first data on the alteration and related mineralization. C. R. Geosci. 335, 671–680.

Milu, V., Milesi, J.-P., Leroy, J.L., 2004. Roşia Poieni copper deposit, Apuseni Mountains, România: advanced argillic overprint of a porphyry system. Mineral. Deposita 39, 173–188.

Nagornaya, E.V., Baksheev, I.A., Bryzgalov, I.A., Yapaskurt, V.O., 2012. Minerals of the Au–Ag–Pb–Te–Se–S system of porphyry–copper–molybdenum deposits from the Nakhodka ore field, Chukchi Peninsula, Russia. Mosc. Univ. Geol. Bull. 67, 233–239.

Neacşu, A., Popescu, Gh.C., Constantinescu, B., Vasilescu, A., Ceccato, D., 2009. The geochemical signature of native gold from Roşia Montană and Musariu ore deposits Metaliferi Mts. (Romania); Preliminary data. Carpath. J. Earth Environ. Sci. 4 (1), 49–59.

Neubauer, F., Lips, A., Kouzmanov, K., Lexa, J., Ivăşcanu, P., 2005. Subduction, slab detachment and mineralization: the Neogene in the Apuseni Mountains and Carpathians. Ore Geol. Rev. 27, 13–44.

Pačevski, A., Moritz, R., Kouzmanov, K., Marquard, K., Živković, P., Cvetković, L., 2012. Texture and composition of Pb-bearing pyrite from the Čoka Marin polymetallic deposit, Serbia, controlled by nanoscale inclusions. Can. Mineral. 50, 1–20.

Papp, G., 2004. History of minerals, rocks and fossil resins discovered in the Carpathian region. Studia Naturalia, 15. Hungarian Natural History Museum, Budapest (216 pp.).

Petrulian, N., Steclaci, L., Jude, R., Popescu, R., Cioran, A., 1978. Contributions to the knowledge of the mineralogy and geochemistry of the copper mineralization from Roşia–Poieni (Metaliferi Mountains) (in Romanian). Stud. Cercet. Geol. Geofiz. Geogr. 23, 3–17 (Bucharest).

Pettke, T., Werner, E.H., MacIntosh, I., Heinrich, C.A., 2001. The porphyry to epithermal link: preliminary fluid chemical results from Roşia Poieni, Romania, and Famatina, Argentina. Rom. J. Miner. Depos. 79, 81–82.

Pintea, I., 2001. Melt and fluid inclusions study in the Neogene porphyry Cu–Au (Mo) from Metaliferi Mountains. Rom. J. Miner. Depos. 79 (2), 28–29 (Field Guidebook).

Pop, D., Ionescu, C., Forray, F., Tămaş, C.G., Benea, M., 2011. "Transylvanian gold" of the hydrothermal origin: an EMPA study in an archeological provenancing perspective. Eur. J. Mineral. 23, 911–923.

Popescu, Gh.C., Cioacă, M., 2006. Preliminary data concerning the Cu, Au, Ag distribution in the Bolcana ore deposit, Metaliferi Mts., Romania. Acta Mineral. Petrogr. 5, 95 (Abstracts series).

Popescu, Gh.C., Neacşu, A., 2007. Relationship between gold and copper metallogenesis in the Metaliferi Mts. Analele Ştiinţifice ale Univ. "Al. I. Cuza". Geologie LIII, 71–78.

Popescu, Gh.C., Neacşu, A., Ilinca, Gh., Topa, D., Bilal, E., 2006. Mineralogical features of enargite — Cu3AsS4 — from Roşia Poieni. Rom. J. Miner. Depos. 82, 217–220.

Popescu, Gh.C., Neacşu, A., Cioacă, M., Filipescu, D., 2010. The selenium and Se-minerals in the Săcărâmb ore deposits — Metaliferi Mountains., Romania. Rom. J. Miner. Depos. 84, 127–130.

Popescu, Gh.C., Neacşu, A., Cioacă, M., Buia, G., 2013. Tellurium, selenium and cadmium resources in the waste dumps of Săcărâmb area (Apuseni Mountains), Romania. Carpath. J. Earth Environ. Sci. 8 (3), 199–206.

Potts, P.J., Kane, J.S., 2005. International association of geoanalysts certificate of analysis: certified reference material OU-6 (Penrhyn slate). Geostand. Geoanal. Res. 29, 233–236.

Qi, L., Jing, H., Gregoire, D.C., 2000. Determination of trace elements in granites by inductively coupled plasma mass spectrometry. Talanta 51, 507–513.

Reich, M., Kesler, S.E., Utsunomiya, S., Palenik, C.S., Chryssoulis, S.L., Ewing, R.C., 2005. Solubility of gold in arsenian pyrite. Geochim. Cosmochim. Acta 69, 2781–2796.

Reich, M., Utsunomiya, S., Kesler, S.E., Wang, L.M., Ewing, R.C., Becker, U., 2006. Thermal behavior of metal nanoparticles in geologic materials. Geology 34, 1033–1036.

Reich, M., Deditius, A., Chryssoulis, S., Li, J.-W., Ma, C.-Q., Parada, M.A., Barra, F., Mittermayr, F., 2013a. Pyrite as a record of hydrothermal fluid evolution in porphyry copper system: a SIMS/EMPA trace element study. Geochim. Cosmochim. Acta 104, 42–62.

Reich, M., Palacios, C., Barra, F., Chryssoulis, S., 2013b. "Invisible" silver in chalcopyrite and bornite from the Mantos Blancos Cu deposit, northern Chile. Eur. J. Mineral. 25, 453–460.

Roşu, E., Szakacs, A., Downes, H., Seghedi, I., Pecskay, Z., Panaiotu, C., 2001. The origin of Neogene calc-alkaline and alkaline magmas in the Apuseni Mountains, Romania: the adakite connection. Rom. J. Miner. Depos. 79 (2), 3–23.

Roşu, E., Szakacs, A., Downes, H., Seghedi, I., Peckskay, Z., 2004. Timing of Miocene–Quaternary magmatism and metallogeny in the South Apuseni Mountains, Romania. Rom. J. Miner. Depos. 81, 33–38.

Seghedi, I., Bojar, A.V., Downes, H., Roşu, E., Tonarini, S., Mason, P., 2007. Generation of normal and adakite-like calc-alkaline magmas in a non-subductional environment: an Sr–O–H isotopic study of the Apuseni Mountains Neogene magmatic province, Romania. Chem. Geol. 245, 70–88.

Sinclair, W.D., 2007. Porphyry deposits. In: Goodfellow, W.D. (Ed.), Geological Association of Canada, Mineral Deposits Division, Special Publication, pp. 223–243.

Singer, A.D., Berger, I.V., Moring, C.B., 2008. Porphyry copper deposits of the world: database and grade and tonnage models, 2008. US Geological Survey Open-file Report 2008-1155.

Spry, P.G., Paredes, M.M., Foster, F., Truckle, J.S., Chadwick, T.H., 1996. Evidence for a genetic link between gold–silver telluride and porphyry molybdenum mineralization at the Golden Sunlight deposit, Whitehall, Montana: fluid inclusion and stable isotope studies. Econ. Geol. 91, 507–526.

Tămaş, C., Bailly, L., Ghergari, L., O'Connor, G., Minuţ, A., 2006. New occurrences of tellurides and argyrodite in Roşia Montană, Apuseni Mts., Romania, and their metallogenetic significance. Can. Mineral. 44, 367–383.

Tămaş, C.G., Grobety, B., Bailly, L., Bernhardt, H.-J., Minuţ, A., 2014. Alburnite, $Ag_8GeTe_2S_4$, a new mineral species from the Roşia Montană Au–Ag epithermal deposit, Apuseni Mountains, Romania. Am. Mineral. 99, 57–64.

Tarkian, M., Hünken, U., Tokmakchieva, M., Bogdanov, K., 2003. Precious-metal distribution and fluid inclusion petrography of the Elatsite porphyry copper deposit, Bulgaria. Mineral. Deposita 38, 261–281.

Thompson, M., Potts, P.J., Kane, J.S., Wilson, S., 2000. GeoPT5. An international proficiency test for analytical geochemistry laboratories—report on round 5 (August 1999). Geostand. Geoanal. Res. 24, E1–E28.

Udubaşa, G., Udubaşa, S.S., 2004. Au–Ag telluride deposits in the Metaliferi Mts.: effects of local geology or of a "hydrothermal ichor". Rom. J. Miner. Depos. 81, 39–46.

Udubaşa, G., Roşu, E., Seghedi, I., 2001. The "Golden Quadrangle" in the Metaliferi Mts., Romania: what does this really mean? Rom. J. Miner. Depos. 79 (2), 24–35.

Ulrich, T., Long, D.G.F., Kamber, B.S., Whitehouse, M.J., 2011. In situ trace element and sulfur isotope analysis of pyrite in a Paleoproterozoic gold placer deposit, Pardo and Clement Townships, Ontario, Canada. Econ. Geol. 106, 667–686.

Vlad, S.N., 1983. Geology of Porphyry Copper Deposits. Editura Academiei, Bucharest (in Romanian).

Vlad, S.N., Orlandea, E., 2004. Metallogeny of the gold quadrilateral: style and characteristics of epithermal–subvolcanic mineralized structures, South Apuseni Mts., Romania. Stud. Univ. Babeş–Bolyai Geol. XLIX (1), 15–31.

Vourdouris, P., Tarkian, M., Arikas, K., 2006. Mineralogy of telluride-bearing epithermal ores in the Kassiteres–Sappes area, western Thrace, Greece. Mineral. Petrol. 87, 31–52.

Vourdouris, P., Melfos, V., Spry, P.G., Kaltal, T., Schleicher, H., Moritz, R., Ortelli, M., 2013. The Pagoni Rachi/Kirki Cu–Mo ± Re ± Au deposit, Northern Greece: mineralogical and fluid inclusion constraints on the evolution of a telescoped porphyry–epithermal system. Can. Mineral. 51, 253–284.

Winderbaum, L., Ciobanu, C.L., Cook, N.J., Paul, M., Metcalfe, A., Gilbert, S., 2012. Multivariate analysis of an LA-ICP-MS trace element dataset for pyrite. Math. Geosci. 44, 823–842.