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Geomaterials (Ore deposits)

# Te-Rich argyrodite occurrence in Roşia Montană ore deposit, Apuseni Mountains, Romania

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## Abstract

A new argyrodite occurrence has been discovered in the Roşia Montană ore deposit located in the South Apuseni Mountains, Romania. Argyrodite is associated with common base metal sulfides and sulfosalts (galena, sphalerite, chalcopyrite, tetrahedrite ± alabandite, pyrite, and marcasite), tellurides (hessite, altaite, sylvanite) and rare electrum grains in the Ag-rich Cărnicele vein hosted by an extracratereal phreatomagmatic breccia within the Cărnicele massif. SEM and EPMA analyses revealed that this argyrodite is Te-rich and a mean  $\text{Ag}_{8,04}\text{Ge}_{0,9}\text{Te}_{2,07}\text{S}_{3,77}$  formula was calculated. This phase could be the germaniferous equivalent of the previously-described Te-rich canfieldite. **To cite this article:** L. Bailly et al., C. R. Geoscience 337 (2005).

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## Résumé

**Occurrence d'argyrodite à tellure dans le gisement de Roşia Montană, monts Apuseni, Roumanie.** Une nouvelle occurrence d'argyrodite vient d'être découverte dans le gisement de Roşia Montană, situé dans les monts Apuseni du Sud, en Roumanie. Elle est rencontrée dans des assemblages à galène, sphalérite, tétraédrite ± alabandite, pyrite, marcasite, hessite, altaite, sylvanite et électrum, dans une veine riche en argent, la veine Cărnicele, encaissée dans une brèche phreatomagmatique extracratérielle du massif de Cărnicele. La formule structurale moyenne de ce minéral est  $\text{Ag}_{8,04}\text{Ge}_{0,9}\text{Te}_{2,07}\text{S}_{3,77}$ . Il pourrait correspondre à l'équivalent germanifère de la canfieldite riche en Te. **Pour citer cet article:** L. Bailly et al., C. R. Geoscience 337 (2005).

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**Keywords:** Roşia Montană; Romania; Argyrodite; Tellurium; Epithermal mineralization

**Mots-clés:** Roşia Montană; Roumanie; Argyrodite; Tellure; Minéralisation épithermale

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## Version française abrégée

### 1. Introduction

Le germanium intervient dans la fabrication de nombreux matériaux de haute technologie : composants électroniques, fibres optiques, optique infrarouge [11]. Les principaux types de gisements exploités ont été répertoriés [3]. Des teneurs anormales en Ge ont été jadis détectées dans des concentrés de pyrite du gisement épithermal à Au–Ag de Roşia Montană (monts Apuseni, Roumanie [1]). Des études microscopiques, au MEB et à la microsonde électronique ont été réalisées sur plusieurs échantillons de la veine Cârnicel, afin d'identifier les phases porteuses ainsi que leur distribution et d'évaluer le potentiel de récupération de Ge.

### 2. Géologie et minéralogie

Le gisement de Roşia Montană (Fig. 1) est lié au volcanisme d'âge Néogène présent tout au long de la chaîne Carpatho-Balkanique [15]. Dans cette région, le socle cristallin est présent sous forme de fragments dans différentes colonnes de brèches [27]. Des flyschs d'âge Crétacé supérieur et une formation volcano-sédimentaire d'âge Néogène (Badenien–Sarmatien) couvrent l'essentiel de la zone étudiée [5, 6]. Les roches volcaniques néogènes sont représentées par la dacite de Cetate (dômes de Cetate et de Cârnic) et des pyroclastites avant la mise en place d'andésites stériles [4,6,8,14].

Les échantillons ont été prélevés dans la veine Cârnicel, riche en Ag (environ 1 kg/t Ag et 5 g/t Au). Cette veine est caractérisée par une alternance de rubans de minéraux de gangue (rhodochrosite–rhodonite–quartz) et de rubans minéralisés. La minéralisation se compose de galène, de sphalérite, de chalcopryrite, de tétraédrite, de pyrite et d'alabandite. Cet assemblage contient également d'abondants tellures (hessite  $\pm$  altaïte, argyrodite, sylvanite) et de rares grains d'électrum. La roche encaissante est une brèche phréatomagmatique extracratérielle composée de fragments de dacite, de roches sédimentaires et cristallines dans une matrice silto-argileuse.

### 3. Argyrodite

En section polie, l'argyrodite montre une association fréquente avec la hessite (Fig. 2). Sa couleur est grise, avec une arrière-teinte bleutée, qui contraste avec l'argyrodite de référence. Les analyses réalisées à la microsonde électronique permettent de calculer une formule chimique moyenne proche de  $\text{Ag}_{8,04}\text{Ge}_{0,9}\text{S}_{3,77}\text{Te}_{2,07}$  (Tableau 1). Une solution solide entre argyrodite et canfieldite existe [30] et de nombreuses occurrences de canfieldites riches en Te ont été décrites [10,13,16–19,25,31] (Tableau 2). Dans le diagramme de la Fig. 3, les points d'analyses de l'argyrodite sont groupés autour d'une composition théorique proche de  $\text{Ag}_8\text{GeTe}_2\text{S}_4$  (Fig. 3), mais plusieurs analyses montrent des rapports S/Te supérieurs à 2 et suggèrent la possibilité d'une solution solide entre  $\text{Ag}_8\text{GeS}_6$  et  $\text{Ag}_8\text{GeTe}_6$ , équivalent synthétique de l'argyrodite [7].

### 4. Discussion

Longtemps suspectée [1,27], la présence et la nature chimique du porteur de Ge à Roşia Montană sont clairement établies. Il semble qu'il s'agisse de la première description d'argyrodite riche en Te, alors que l'existence de canfieldite à tellure est établie. Les analyses à la microsonde sur sphalérite et tétraédrite, porteurs potentiels de Ge [2,12], ne montrent pas de teneurs significatives en Ge. De nombreux gisements situés dans la chaîne Carpatho-Balkanique contiennent des minéraux germanifères, en Bulgarie [22,28] et en Serbie [9]. Il s'agit de dépôts épithermaux de type acide. L'argyrodite a été identifiée dans un seul épithermal neutre, Wolyu, en Corée [32]. La présence d'alabandite, de sphalérite dépourvue de fer et de minéraux de germanium dans la veine Cârnicel suggère des conditions de fugacité en soufre intermédiaires entre celles rencontrées dans les gisements épithermaux acides et neutres [3,23]. En Roumanie, des minéraux germanifères sont également décrits dans d'autres gisements des monts Apuseni [1,24,29] et dans la région de Baia Mare [1,20,21,26]. Les dépôts épithermaux apparaissent comme des hôtes potentiellement intéressants pour le germanium et doivent être évalués en termes de récupération.

## 1. Introduction

Germanium (Ge) is a high-technology metal largely used in electronic applications, infrared instruments, as well as optic fibres [11]. The more currently cited sources of Ge include sulfide ore deposits, iron oxide deposits, oxidized sulfide ore deposits, pegmatites, greisens and skarns, coal and lignified wood [3]. The epithermal ore deposits in which various Ge-bearing minerals have been frequently reported have only a minor commercial importance.

In 1962, metallurgical tests conducted on ore concentrates from the Roşia Montană Au–Ag epithermal ore deposit (South Apuseni Mountains, Romania) have revealed the presence of anomalous Ge contents in pyrite concentrates [1]. Recent mineralogical tests combined with SEM microscopy and EPMA analyses performed on samples collected from the Ag-rich Cărniceş vein allowed us to study the distribution, the mineralogical expression and consequently the potential of recovery of Ge.

## 2. Geology and ore mineralogy

The Roşia Montană (RM) world-class epithermal Au–Ag deposit (reserves: 217 Mt of ore @ 1.5 g/t Au and 7.5 g/t Ag), situated in the northern part of the southern Apuseni Mountains (Fig. 1), is related to Neogene volcanism that outcrops all along the Carpatho-Balkan belt [15]. In the RM area (Fig. 1) the crystalline basement occurs only as fragments within various breccia pipe structures [27]. The sedimentary rocks in the area are represented by Upper Cretaceous flysch and Neogene rocks (Badenian and Sarmatian) [5,6]. The Neogene sedimentary rocks occur as narrow sequences within a volcano-sedimentary formation. The volcanic rocks are represented by Cetate dacite (Cetate and Cărniceş domes), to which is related the RM ore genesis and dacite pyroclastics – the so-called volcano-sedimentary formation. The volcanic activity continues with barren andesitic lava flows and pyroclastics (Rotunda type) [4,6,8,14].

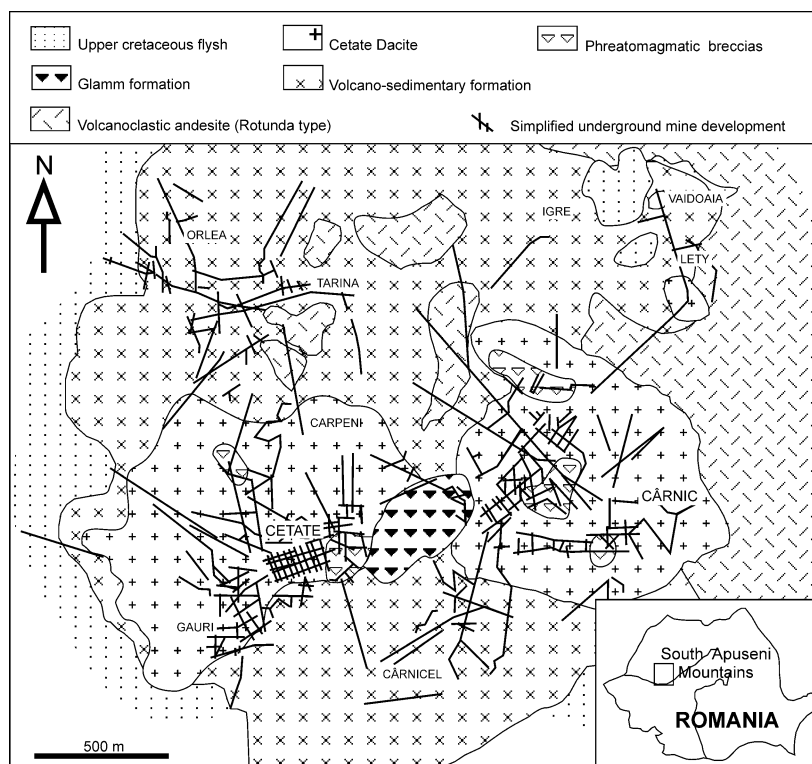


Fig. 1. Simplified geological map of the Roşia Montană ore deposit (modified from [6]).

Fig. 1. Carte géologique simplifiée du gisement de Roşia Montană (modifiée d'après [6]).

The studied samples were collected in the Ag-rich, north–south Cârnicel vein (around 1 kg/t Ag and 5 g/t Au) characterised by a well marked banded structure with alternating bands of ore minerals and gangue minerals (rhodonite/rhodochrosite–quartz). The ore assemblage is mainly composed of dominant galena, Fe-free and Mn-rich sphalerite (3.4 to 6.3 wt% Mn), argentiferous tetrahedrite – mean composition:  $(\text{Cu}_{9.47}\text{Ag}_{0.39}\text{Zn}_{1.58}\text{Mn}_{0.3})(\text{As}_{0.63}\text{Sb}_{3.6})\text{S}_{12.92}$  – associated with minor amounts of chalcopyrite, pyrite, marcasite, and rare alabandite. Besides common base metal sulfides, the ore assemblage is completed by abundant hessite, argyrodite, rare altaite and electrum grains ( $\text{Ag}_{0.23}\text{Au}_{0.76}$ ), and sylvanite (at the interface between hessite and electrum). The host rock of Cârnicel vein is an extracratereal phreatomagmatic breccia (vent breccia) composed of sub-angular to sub-rounded rock fragments (dacite, sedimentary and crystalline rocks) held together in a coarse-to-silty–clayey matrix. The

dominant rock fragments are adularised dacite and dacitic ground mass.

### 3. Argyrodite

Argyrodite mainly occurs as anhedral to subhedral grains up to 100  $\mu\text{m}$  in size included in hessite (Fig. 2a), but reverse assemblages are also observed (Fig. 2b). In most cases, argyrodite is intimately associated with hessite wires (Fig. 2c). Its reflection colour is grey, with a strong bluish tint that differs from the violet tint of Te-free argyrodite. No reflection pleochroism or internal reflection has been observed. A weak anisotropism is detected in air with slightly uncrossed nicols.

Representative EPMA analyses of argyrodite are listed in Table 1. Beside Ag, Ge, Te and S, traces of Fe, Cu, Zn, Pb and Mn are locally detected, but are prob-

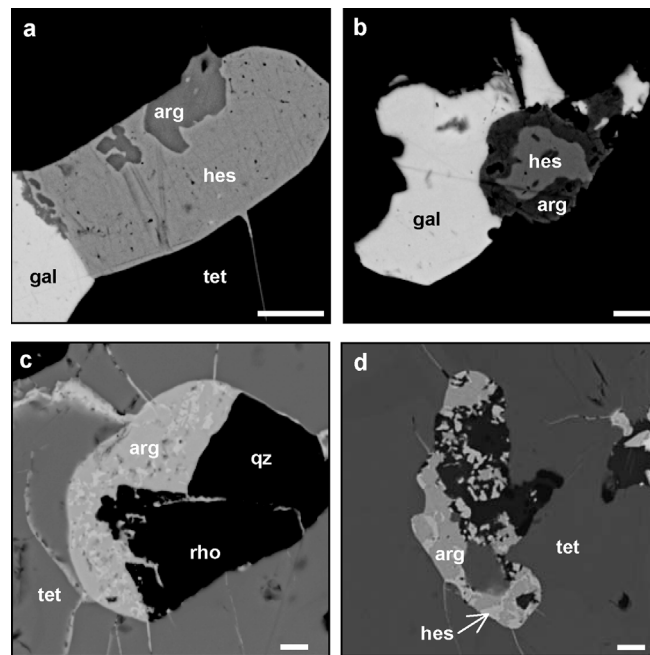


Fig. 2. SEM microphotographs of argyrodite bearing assemblages of the Cârnicel vein. (a) Subhedral argyrodite crystals included in hessite (sample RM 611B). (b) Hessite (light grey) included in argyrodite (sample LPC 42 122). (c) Argyrodite rich in hessite wires in tetrahedrite (sample LPC 42 122). (d) Argyrodite, hessite associated with chalcopyrite (in black) in tetrahedrite (sample RM 611B). **gal**: galena; **hes**: hessite; **arg**: argyrodite; **tet**: tetrahedrite; **qz**: quartz; **rho**: rhodochrosite. Scale bar: 5  $\mu\text{m}$ .

Fig. 2. Photographies MEB des assemblages à argyrodite de la veine Cârnicel. (a) Cristaux subautomorphes d'argyrodite en inclusion dans la hessite (éch. : RM 611B). (b) Hessite en inclusion dans l'argyrodite (éch. : LPC 42 122). (c) Argyrodite riche en inclusions de hessite dans la tétraédrite (éch. : LPC 42 122). (d) Argyrodite, hessite et chalcopyrite (en noir) dans la tétraédrite (éch. : RM 611B). **gal** : galène ; **hes** : hessite ; **arg** : argyrodite ; **tet** : tétraédrite ; **qz** : quartz ; **rho** : rhodochrosite. Barre d'échelle : 5  $\mu\text{m}$ .

Table 1

Electron probe microanalyses of Te-bearing argyrodite. L: sample LPC 42 112, R: sample RM611A. \*: assuming the total number of atoms to be 15. nd: not determined

Tableau 1

Composition chimique de l'argyrodite riche en tellure (analyses à la microsonde électronique). L : échantillon LPC 42 112, R : échantillon RM611A. \* : Nombre total d'atomes estimé de 15. nd : non déterminé

N°	94	104	110	15	19	4	5	105	14	16	32	42	11	6	43	9	8
Sample	R	R	R	L	L	R	R	R	L	L	L	L	R	R	L	R	R
Weight percent																	
Ag	66.70	66.85	65.19	65.78	65.24	65.03	65.15	66.95	65.69	65.18	65.36	66.22	65.95	63.62	63.65	63.97	64.62
Cu	0.00	0.00	0.43	0.54	0.00	0.35	0.63	0.00	0.43	0.00	0.76	0.00	0.32	0.49	0.00	0.87	0.22
Fe	0.25	0.00	0.00	0.00	0.00	0.24	0.00	0.00	0.00	0.00	0.25	0.00	0.00	0.61	0.00	0.20	0.50
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35	0.00	0.26	0.00
Mn	0.27	0.00	0.00	0.00	0.38	nd	nd	0.00	0.00	0.28	0.00	0.00	nd	nd	0.00	nd	nd
Ge	4.66	4.93	4.94	4.89	5.18	5.37	5.05	5.12	5.13	4.96	4.57	5.16	5.38	4.89	4.58	4.62	4.47
Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.20	0.47	0.00	0.19
S	9.76	9.87	9.73	9.39	9.52	9.14	8.89	9.74	9.69	9.50	9.14	9.67	8.46	8.52	9.06	7.72	7.50
Te	18.38	18.89	18.92	19.03	19.09	19.12	19.22	19.36	19.43	19.63	20.09	20.13	20.29	20.68	20.69	22.21	23.33
T	100.02	100.55	99.21	99.62	99.42	99.26	98.94	101.16	100.35	99.54	100.17	101.18	100.65	99.37	98.46	99.84	100.82
Chemical formula*																	
Ag	8.07	8.06	7.95	8.04	7.96	8.05	8.13	8.05	7.94	7.99	7.98	7.96	8.20	7.96	7.95	8.14	8.23
Cu	0.00	0.00	0.09	0.11	0.00	0.07	0.13	0.00	0.09	0.00	0.16	0.00	0.07	0.10	0.00	0.19	0.05
Fe	0.06	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.15	0.00	0.05	0.12
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.05	0.00
Mn	0.06	0.00	0.00	0.00	0.09	—	—	0.00	0.00	0.07	0.00	0.00	—	—	—	—	—
Ge	0.84	0.88	0.89	0.89	0.94	0.99	0.94	0.91	0.92	0.90	0.83	0.92	0.99	0.91	0.85	0.87	0.85
Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.03	0.00	0.01
S	3.97	4.00	3.99	3.86	3.91	3.80	3.73	3.94	3.94	3.91	3.76	3.91	3.54	3.59	3.81	3.30	3.21
Te	1.88	1.92	1.95	1.97	1.97	2.00	2.03	1.97	1.99	2.03	2.07	2.04	2.13	2.19	2.19	2.39	2.51

Table 2

Electron-probe microanalyses of Te-bearing canfieldites. \*: Assuming the total number of atoms to be 15

Tableau 2

Analyses à la microsonde électronique de canfieldites riches en tellure. \*: Nombre total d'atomes estimé de 15

Ref.	[12]	[12]	[13]	[13]	[14]	[14]	[15]	[16]	[17]	[17]	[18]	[18]
Weight percent												
Ag	56.44	58.33	52.52	63.51	63.30	60.90	65.12	61.86	62.78	62.94	67.60	71.22
Cu	3.13	1.74	–	–	–	–	–	–	–	–	–	–
Fe	2.91	1.00	–	–	–	–	–	0.88	–	–	–	–
Zn	0.12	0.04	–	–	–	–	–	–	–	–	–	–
Bi	–	–	–	–	2.00	–	–	–	–	–	–	–
Sn	9.41	10.19	8.86	9.27	9.10	7.80	10.57	9.08	8.62	8.70	7.17	6.36
S	10.74	8.99	8.99	9.34	9.60	8.60	13.95	8.04	9.14	9.25	11.45	11.70
Te	17.10	21.09	19.07	20.04	19.70	17.50	8.69	18.60	20.32	20.13	13.78	10.72
Se	–	–	–	–	0.20	0.50	–	3.48	–	–	–	–
T	99.85	101.38	89.44	102.16	103.90	95.30	98.33	101.94	100.86	101.02	100.00	100.00
Chemical formula*												
Ag	6.68	7.26	7.33	7.92	7.86	8.13	7.57	7.78	7.94	7.94	8.17	8.61
Cu	0.63	0.37	–	–	–	–	–	–	–	–	–	–
Fe	0.67	0.24	–	–	–	–	–	0.21	–	–	–	–
Zn	0.02	0.01	–	–	–	–	–	–	–	–	–	–
Bi	–	–	–	–	0.13	–	–	–	–	–	–	–
Sn	1.01	1.15	1.12	1.05	1.03	0.95	1.12	1.04	0.99	1.00	0.79	0.70
S	4.28	3.76	4.22	3.92	4.01	3.86	5.46	3.40	3.89	3.92	4.66	4.76
Te	1.71	2.22	2.33	2.11	2.07	1.97	0.85	1.98	2.17	2.15	1.41	1.10
Se	–	–	–	–	0.03	0.09	–	0.60	–	–	–	–

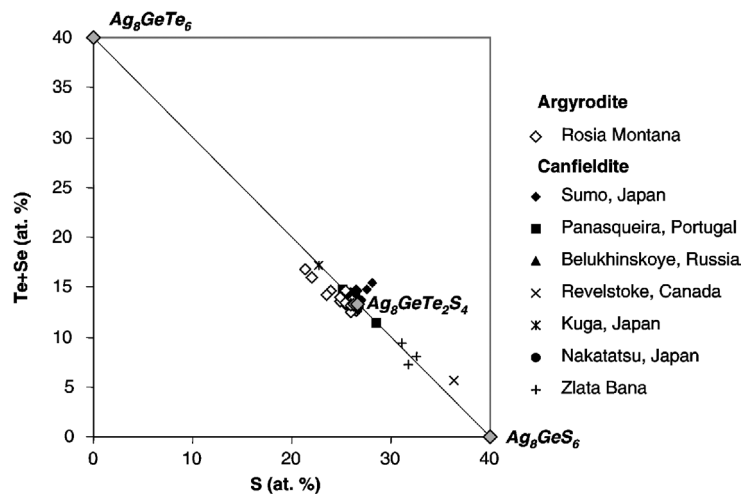


Fig. 3. Te + Se versus S (in atomic %) of the Te-rich argpyrodite from Roșia Montană and analyses of Te-bearing canfieldite from the literature (see Table 2 for references). Synthetic  $\text{Ag}_8\text{GeTe}_6$  and theoretical  $\text{Ag}_8\text{GeTe}_2\text{S}_4$  compositions are also reported.

Fig. 3. Te + Se versus S (en % atomique) des argpyrodites à tellure de Roșia Montană et analyses des canfieldites à tellure de la littérature (Tableau 2 pour références). Les composés synthétique  $\text{Ag}_8\text{GeTe}_6$  et théorique  $\text{Ag}_8\text{GeTe}_2\text{S}_4$  ont également été reportés.

ably due to the host sulfides and gangue minerals. Sn and Se are systematically below detection limit. The average chemical formula, assuming the total number

of atoms to be 15, is  $\text{Ag}_{8.04}\text{Ge}_{0.9}\text{S}_{3.77}\text{Te}_{2.07}$ . A solid solution exists between argpyrodite and canfieldite [30], and several studies have reported the existence of Te-

bearing canfieldite [10,13,16–19,25,31] (Table 2). In Fig. 3, Te + Se versus S of Te-bearing argyrodite and Te-(Se)-bearing canfieldite is plotted. The argyrodite analyses are grouped around a hypothetical compound  $\text{Ag}_8\text{GeTe}_2\text{S}_4$ , but several points extend toward more Te-rich compositions (S/Te atomic ratio ranges between 1.28 and 2.11), suggesting a possible solid solution between  $\text{Ag}_8\text{GeS}_6$  and  $\text{Ag}_8\text{GeTe}_6$ , a synthetic equivalent of argyrodite not known in nature [7]. Compared to argyrodite, Te-rich canfieldite is characterized by highly variable S/Te ratio (1.7 to 6.4), whereas significant Se contents are reported. However, the high Te contents of several analyses of argyrodite may be also due to the presence of undetected hessite wires (Fig. 2c).

#### 4. Discussion

After many years of uncertainties [1,27], the existence and the chemical composition of a Ge carrier mineral within Roşia Montană ore deposit are now established. This phase, identified as argyrodite, shows a substitution of S by Te. To our knowledge, this is the first reported occurrence of Te-bearing argyrodite, whereas the existence of Te-bearing canfieldite was reported in several studies [10,13,16–19,25,31]. Sphalerite with Ge contents exceeding 1000 ppm in the Saint-Salvy deposit (Tarn, France [2]) and tetrahedrite are potential hosts for Ge [12]. The Ge content of these two phases, investigated by EPMA, is systematically null or below the detection limit (around 400 ppm in the used analytical conditions). In the absence of whole-rock analyses for Ge, it is not yet possible to conclude about the presence of other Ge-carriers in Roşia Montană.

Germaniferous minerals (germanite, briartite, rhenierite, Ge-rich colusite) are reported in several deposits of the Carpatho-Balkan belt in Radka, Chelopech, Krassen (Panagyurishte district, Bulgaria [22, 28]) as well as in Tilva Ros (Bor district, Serbia [9]). All these deposits are mainly considered as high-sulfidation epithermal type deposits. To our knowledge, argyrodite was only reported in the Korean Wolyu deposit, clearly identified as a low-sulfidation epithermal Au–Ag deposit [32]. The presence of alabandite, Fe-free sphalerite, germaniferous minerals in

the Cârnicel vein strongly suggests intermediate sulfidation conditions [3,23].

The occurrences of germanite, and members of the canfieldite–argyrodite series are also reported in other deposits of the southern Apuseni Mountains: Bucureşti-Rovina and at Băiţa-Crăciuneşti [1]; Bucium<sup>1</sup> [29]; Pârâul lui Avram [24]. In the three former deposits, enargite is also reported. In the Baia Mare region, the occurrence of germanite was briefly reported at Ilba-Handal [1], Baia Sprie [21], Toroiaga [26], and Căvnic [20]. The presence of germanium may be considered as a common signature of several ore deposits of the Carpatho-Balkan belt. Epithermal ore deposits of high- and low-sulfidation type are potentially interesting hosts for Ge and have to be evaluated for its recovery and refining.

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<sup>1</sup> Within Bucium area occur several epithermal and one porphyry copper ore deposits (Bucium-Frasin, Bucium-Rodu, Bucium-Arama, Bucium-Târniţa, etc.). Taking into account the description given by [28], the occurrence of germanite corresponds to Bucium-Arama epithermal deposit.



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