THE COLORADOITE OCCURRENCE OF THE MUSARIU (METALIFERI MOUNTAINS) TELLURIUM AND TELLURIDE VEIN MINERALIZATION AND ITS POSITION IN THE DEPOSITIONAL SEQUENCE

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Abstract. Coloradoite is present in the tellurium and telluride veins of the now closed Musariu gold mine, appearing in small quantities, but constantly besides Au,Ag – tellurides and native tellurium. The textural position and accompanying minerals indicate its precipitation from the epithermal solutions towards the final stages of the mineralizing process, in cavity fillings and replacement aggregates cross-cutting older telluride assemblages, together with empressite and Ag-tellurides abnormally rich in Te.

Key words: coloradoite, telluride veins, Ag-tellurides, Musariu, Golden Quadrilateral.

Résumé. La coloradoïte est présente dans les filons à tellure et tellurures de la mine d'or actuellement abandonnée de Musariu, apparaissant en petites quantités, mais constamment, à coté du tellure natif et des tellurures d'or et d'argent. La position texturelle et les minéraux accompagnantes indiquent sa précipitation des solutions épithermales vers les stages finales du processus de minéralisation, dans remplissages des cavités et agrégats de remplacement coupant en travers ensembles des tellurures déposés auparavant, associée avec empressite et tellurures d'argent anormalement riches en Te.

Mots-clés: Coloradoïte, Filons à tellurures, Tellurures d'argent, Musariu, Quadrilatère aurifère.

INTRODUCTION

The Golden Quadrilateral in the Metaliferi Mountains (South Apuseni Mountains) represents one of the richest gold provinces worldwide, concentrating on an area of about 900 km^2 as many as 64 gold deposits and prospects. The mineralization, related to Miocene andesitic subvolcanic bodies, consists of epithermal veins and stockworks, partly accompanied by Cu-Au-(Mo) porphyry systems. Tellurium and Au-Ag telluride occurrences are typical, being scattered in about one third of the mineralized areas. It is in this province that the element tellurium was discovered, as are also sited type localities of 12 tellurium minerals, out of which 2 freshly found in this century, museumite (Bindi & Cipriani, 2004) and alburnite (Tămaş *et al*., 2014).

The Musariu deposit distinguishes itself by remarkable native gold, tellurium and telluride veins, displaying complex assemblages and evolution. The tellurium mineralization is dominated by abundant native tellurium and sylvanite deposition, the vein material often consisting of coarse-grained cleavable masses reaching several centimetres in width. Berbeleac (1980) and Berbeleac & David (1982) described an assemblage containing a large number of dominantly Au-Ag tellurides, associated with altaite and frohbergite, while Ciobanu *et al*. (2007) reported Bi-tellurides such as rucklidgeite and tellurobismuthite. In the material collected from the mine before its closing in 2006, we identified a previously overlooked phase, present in small quantities but relatively widespread in the vein aggregate, namely coloradoite (HgTe).

Despite numerous occurrences worldwide in Au-Ag-Te vein deposits, coloradoite is so far considered a rare mineral in Romania. The very few accounts of its presence refer to material collected long ago from Stănija (Popescu & Constantinescu, 1992), where coloradoite replaces krennerite along its grain boundaries with sylvanite, Săcărîmb (Bindi & Cipriani, 2004) – mentioned without description, and as rare blebs associated with tetradymite (Cook *et al.*, 2005) in the same deposit. Recently it was also identified at Măgura (Cioacă, Munteanu & Costin, *oral comm., 2014*) in a base-metal and subordinate Ag-tellurides assemblage.

IDENTIFICATION AND TEXTURAL SETTING

Coloradoite is cubic hexoctahedral, distinguishing itself under the microscope from most of the accompanying Au-Ag tellurides by its lower reflectivity, a darker grey colour with purplish hues in contrast to associated tellurides, and isotropy. It resembles, however, quite closely petzite (Ag_3AuTe_2) in reflectivity and isotropic character, the two phases being hardly distinguishable under the microscope without chemical etching, a circumstance which might have lead to misidentification of coloradoite as petzite in many instances. In BSE images coloradoite has a high scattering power, matched only by altaite, which is also the most reflective phase of the assemblage, thus enabling detection of coloradoite with ease. A combined optical and microprobe study of the Musariu material allowed identification of coloradoite in several textural settings, indicating its crystallization during later stages in the deposition sequence.

Coloradoite occurs in four main settings, namely (1) vuggy cavities completely enclosed in compact tellurium masses, (2) in polygranular replacement aggregates substituting earlier stützite (3) in anastomosed veinlets of silver tellurides, mostly empressite, cross-cutting fractured aggregates of coarse-grained native tellurium and sylvanite and (4) open veinlets lined-up by drusy quartz outside the massive tellurium and telluride aggregates.

The compact aggregates built dominantly of native tellurium often contain small pockets of drusy quartz, completely surrounded from all sides. The voids between the individual idiomorphic quartz crystal are partly filled by mineral phases intergrown in random proportions or coating each other. Coloradoite was identified in a composite grain together with tellurium. The other phases appearing in this setting are stützite, sylvanite and a sulfoantimonide identified as skinnerite, as well as subordinate sphalerite, galena and chalcopyrite. The contour of the filled cavities is outlined by sylvanite containing small pyrite inclusions and stand-alone idiomorphic quartz, passing towards the host native tellurium. Precious metal tellurides are represented only by sylvanite, appearing slightly pink and less reflective in most orientations as compared to tellurium, and showing conspicuous bireflection, polysynthetic lamellar twinning and strong anisotropy, in contrast with both tellurium and stützite. The latter is greyish, devoid of observable bireflection and showing a weak anisotropy, sometimes in complementary bluish to reddish brown hues. Skinnerite is slightly anisotropic and has reddish inner reflections. The diagnostic is supported by its anisotropy and the analysed M:N:S ratio approaching 3:1:3, typical of skinnerite (ideally Cu_3SbS_3), unlike both tetrahedrite and enargite group minerals which contain relatively more S (M:N:S ratios of 3:1:3.25 and 3:1:4 respectively).

In other totally or partly sealed voids, coloradoite occurs together with empressite, while the surroundings of the cavity are represented by sylvanite including subhedral tellurium grains. Empressite is distinguished by its very strong bireflectance, being less reflective in the darker setting than sylvanite, in brown-grey shades. The anisotropy of empressite is very strong, from bright white to reddish brown and (indigo and cobalt) blue, and it is untwinned. Coloradoite appears even darker than empressite and isotropic, with a distinct purple shade. Complex inclusion relationships may appear among the minerals of the assemblage, as for instance sylvanite included in coloradoite including at its turn tellurium blebs. Coloradoite and empressite appear in the inner part of the voids or coating the host phases.

Coloradoite also appears inside the coarse-grained aggregates making up the bulk of the telluride veins. Some of the large tellurium grains, and much more often sylvanite overgrowing and corroding it, contain subhedral, partly digested stützite inclusions, distinguished by their grey colour, lack of conspicuous bireflectance and weaker anisotropy (Fig. 1). In rare occasions the stützite inclusions are partly or totally decomposed in a polygranular aggregate consisting of other silver tellurides and coloradoite. In Fig. 1 the upper tip of the stützite inclusion in the lower left corner of the picture is transformed to a slightly brownish mineral in comparison with the (conspicuously darker) neutral grey of stützite, associated with small coloradoite grains. The optical properties of the neoformed silver telluride are strikingly similar to those of empressite, yet the chemical composition is characterized by excess tellurium (Săbău *et al*., 2014). For instance, the grain in Fig. 1 has a composition which can be approximated to Ag_2Te_3, the Ag equivalent of the mineral montbrayite. This composition appears surprising, because experimental results (Karakaya *et al*. 1966, and refs therein) have shown that no stable silver tellurides exist towards the Te-rich part of the Ag-Te system beyond stützite; even empressite of composition AgTe failed to be synthetized, implying the metastable status of this mineral. While empressite has been nevertheless firmly established as a distinct mineral species (Bindi *et al*., 2004), it seems also probable that other metastable phases with Te layers stacked between empressite-like sheets along the (010) plane occur naturally, which would be the case here.

The most frequent way of occurrence of coloradoite is along veinlets crosscutting the coarse-grained tellurium and sylvanite aggregates, disposed randomly and frequently interconnecting, usually completely filled-up, but sometimes also preserving open spaces and cracks (Fig. 2). The composition of the veinlets is dominated by silver tellurides, besides which coloradoite appears frequently, together with micronic quartz and some tellurium. The silver tellurides are remarkable as they display a pseudo-graphic to pseudo-diablastic structure given by worm-like cavities pervading the otherwise optically homogeneous crystals. The cavities may affect monocrystals entirely or be only confined to certain zones, usually around grain boundaries and outer shells, but may also be randomly set. This type of intergrowths was first reported by Berbeleac (1980) in the Musariu ore, similar structures having been described by Kelly & Goddard (1969) in mosaic-textured empressite associated with coloradoite, which is an environment strikingly similar to that discussed here. Kelly & Goddard (1969) describe them in the telluride ores of Boulder County as “minute graphic voids of unknown origin” and notice also similarily spongy skeletal crystals of sylvanite grown in open vugs. The authors have also noticed that some of the “hessite” druses from Boteș in museum collections have the same type of spongy crystals.

The optical properties of the silver tellurides in the late veinlets correspond perfectly to those of empressite, yet the chemical composition is frequently richer in Te, compositions like Ag_2Te_3 or even $AgTe_2$ being often recorded besides “normal” empressite. Stoichiometric empressite compositions are more frequent in homogeneous grains with no worm-like cavities, while those affected by cavities have as a rule Te-richer compositions. The cavities may extend only on parts of the optically continuous monocrystal, but optical zonality denoting growth zoning may also separate filled from spongy domains as in the zoned crystal in the aggregate on the middle right side of Fig. 2.

Another textural setting in which coloradoite was identified is in veinlets which are satellite to the massive tellurium and sylvanite vein filling. Attached to the coating of drusy quartz in open fissures, coloradoite appears in association with other tellurides (altaite, Ag-tellurides), native tellurium and rare sulfides (Fig. 3). The phases are often intergrown; Ag-tellurides are represented by both empressite and Te-rich tellurides, undistinguishable by optical means and providing no noticeable mass contrast in BSE images. Compact crystals are empressite, while the aggregates hosting vermicular holes may display a marked Te enrichment. Nevertheless, similar hollow aggregates in mutual contact may show clearly different compositions, ranging from empressite to $AgTe_2$. A more detailed investigation of the abnormal silver tellurides from Musariu is in progress. Coloradoite appears intergrowh with Ag-tellurides and altaite, mantling native tellurium (Fig. 3).

MINERAL CHEMISTRY

The chemical composition of the mineral phases was investigated with a Cameca SX 100 microprobe operating at the Institute of Mineralogy and Crystal Chemistry in Stuttgart. The samples were analysed for 13 elements after an EDS and WDS investigation of the phases present in the assemblage. The operating conditions were an accellerating potential of 20 kV and a beam current of 10 nA, using a set of standards containing besides natural sphalerite, chalcopyrite and hematite, elemental Au and synthetic sulfides, selenides, antimonides and tellurides. Peak and backgound positions were optimized using the Virtual WDS application (Reed, 2002).

Analytical values were cut off at 1σ level and recalculated to structural formulae on specific normalization bases corresponding to the total number of element per formula unit, with the exception of stützite, which was recalculated to 3 atoms of Te (and substituents) p.f.u., according to the general formula $Ag_{5-x}Te_3$, when the Ag/Te ratio was smaller than 1.66. The compositions of representative minerals discussed in text is given in Table 1.

The analytical values correspond fairly to the theoretical stoichiometry of the phases while delivering good totals, also outlining the abnormal Ag-telluride compositions which are strikingly distinct from the empressite analyses determined on the same sample during the same measuring session.

As a general characteristic, low amplitude isomorphic substitutions of Te by Se are recorded especially in sylvanite and Te-rich Ag-tellurides. Coloradoite contains Bi and Pb as detectable microelements, while Cu, Hg and Sb may reach higher values in stützite than in the other phases. Skinnerite analyses yielded low totals, related probably to S underestimation, while Fe and Zn were found to be most abundant metals after Cu as in fahlores, unlike in most published skinnerite analyses which concentrate Ag. Yet the Cu/(Zn+Fe) *p.f.u.* ratio is notably higher (7.6) than that typical of fahlores (5).

CONCLUSIONS

Coloradoite is present in the Musariu native tellurium and telluride mineralization, as a mineral phase rather frequent than abundant. Its deposition corresponds to the late stages of the mineralizing sequence, appearing either from residual fluids entrapped amidst earlier vein mineral aggregates, or from freely flowing hydrothermal solutions, deposited on younger fractures cross-cutting the older tellurium and sylvanite vein filling, bordering it or participating in replacement assemblages. It is typically associated with Ag-poor silver tellurides with various compositions, from empressite to tellurium rich compounds not reported so far to our knowledge. The relatively low abundance of coloradoite and its properties which do not allow optical distinction from petzite may have contributed to the low number of coloradoite occurrences reported from the Golden Quadrilateral, as well as from the Romanian territory in general.

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Table 1

Point ID	6MA_2-7	9M_1-8	9M_6-1	4M_5	9MA_1-1	9M_1A-1	9M_11-5	9M_11-4	9M_1A-2	9MA_4-1	9M_1-7	6MA_2-10	9M_1-10	6MA_2-4	9M_11-3
Mineral		coloradoite		sylvanite			stützite		empressite		Ag_2Te_3	$AgTe_2$		tellurium	skinnerite
S				0.02		0.01	0.01	0.09		0.02	0.01	0.01		0.02	21.20
Fe				0.02	0.04	0.02		0.06		0.11					3.18
Cu				0.04			0.08	1.31				0.05		0.03	38.48
Zn					0.29			0.04		0.28					1.50
As															1.27
Se	0.03	0.08	0.05	0.08	0.06	0.05	0.03	0.03	0.06	0.04	0.10	0.10	0.13	0.21	
Ag	0.06	0.22	0.09	13.05	13.26	56.30	56.01	56.61	44.74	45.33	37.15	30.08	30.06		0.16
Sb				0.13	0.15		0.04	0.22		0.10	0.04	0.09	0.14	0.23	29.23
Te	39.49	38.81	39.20	61.74	62.52	41.48	41.29	41.01	54.90	53.31	63.26	69.84	70.98	98.41	0.07
Au	0.06			23.52	22.61	0.09								0.13	
Hg	60.40	59.80	58.67			1.18	0.83		0.48						
Pb	0.10	0.15													0.83
Bi	0.16	0.13													
Sum	100.3	99.19	98.01	98.6	98.93	99.13	98.29	99.37	100.18	99.19	100.56	100.17	101.31	99.03	95.92
NF*		2		6		7.863	7.856	8	2		5	3	3	1	7
S				0.005		0.003	0.003	0.026		0.001	0.002	0.001		0.001	2.875
Te	1.010	1.003	1.022	3.988	4.001	2.991	2.993	2.943	1.015	0.987	2.944	1.980	1.992	0.992	0.002
Se	0.001	0.003	0.002	0.008	0.006	0.006	0.004	0.003	0.002	0.001	0.008	0.005	0.006	0.003	
Σ	**1.011**	**1.006**	**1.024**	**4.001**	**4.007**	**3.000**	**3.000**	**2.972**	**1.017**	**0.989**	**2.954**	**1.986**	**1.998**	**0.996**	**2.877**
Bi	0.002	0.002													
Sb				0.009	0.010		0.003	0.017		0.002	0.002	0.003	0.004	0.002	1.044
As															0.074
Au	0.001			0.984	0.937	0.004								0.001	**Σ = 1.118**
Ag	0.002	0.007	0.003	0.998	1.004	4.802	4.803	4.806	0.977	0.994	2.044	1.008	0.998		0.006
Hg	0.982	0.983	0.973	0.000		0.054	0.038		0.006						
Fe				0.003	0.006	0.003		0.010		0.005					0.248
Cu				0.005			0.012	0.189				0.003		0.001	2.633
Zn					0.036			0.006		0.010					0.100
Pb	0.002	0.002													0.017
Σ	**0.989**	**0.994**	**0.976**	**1.999**	**1.993**	**4.863**	**4.856**	**5.028**	**0.983**	**1.011**	**2.046**	**1.014**	**1.002**	**0.004**	**3.004**

*NF - normalizing factor

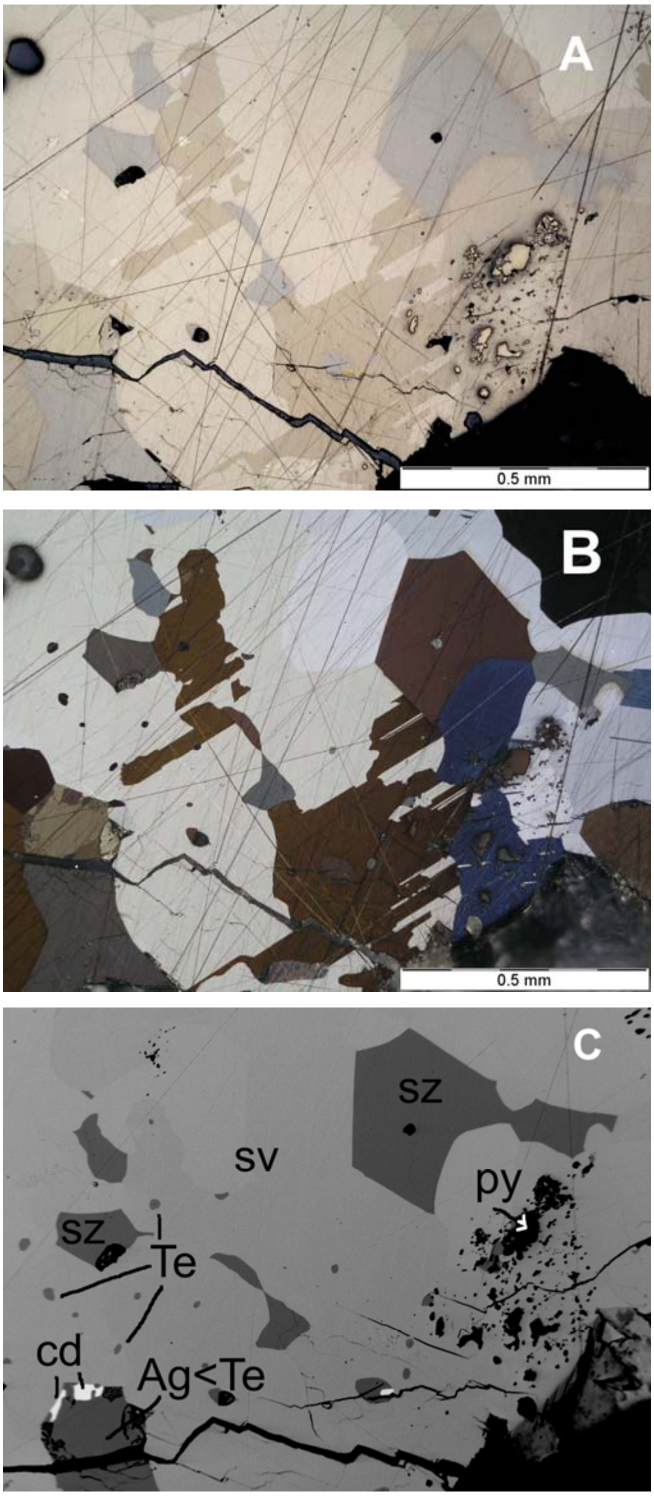

Fig. 1 – Corroded stützite (sz) inclusions and tellurium (Te) droplets hosted in twinned sylvanite (sv). Stützite in the lower left corner partly replaced by a Te-rich silver telluride associated with coloradoite (cd). Strong bireflection (A) and anisotropy (B) of the secondary telluride, contrasting with those of the stützite precursor. A –microphotograph, reflected polarized light; B – the same field under crossed polarizers; C – BSE-image showing the mass contrasts among the phases. Silver telluride of composition Ag_2Te_3 (Ag<Te) indistinguishable from stützite, but displaying completely different optical properties (A, B) py – pyrite.

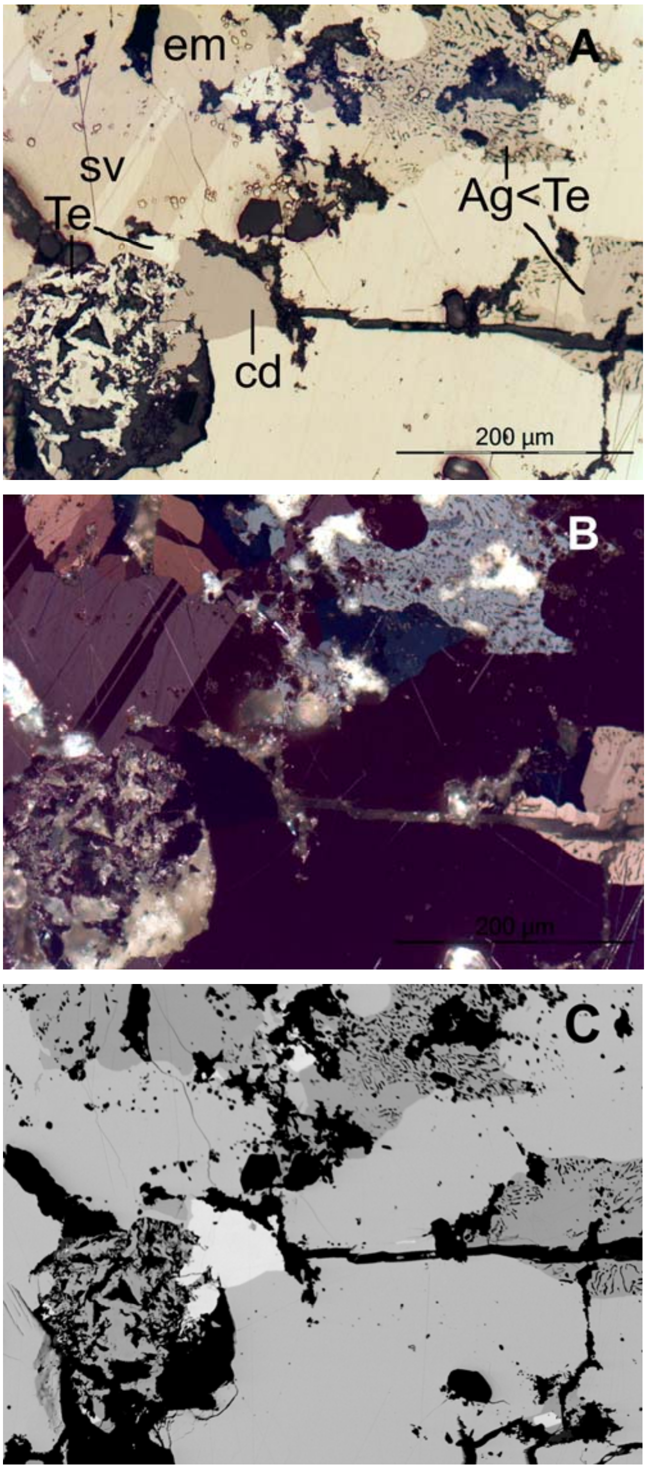

Fig. 2 – Coloradoite, pyrite and silver tellurides deposited and insinuated along partly filled interconnected cracks cross-cutting native tellurium and sylvanite. Strongly anisotropic silver tellurides range in composition from empressite (em) to Te-richer phases and display unusual pseudo-symplectitic aspects. Some of the crystals have optical growth zoning (A, B), middle-right of the picture. A –microphotograph, reflected polarized light; B – the same field under crossed polarizers; C – BSE-image showing bright coloradoite and darker silver tellurides contrasting with the middle-grey sylvanite host. Tellurium and silver tellurides have about the same scattering power.

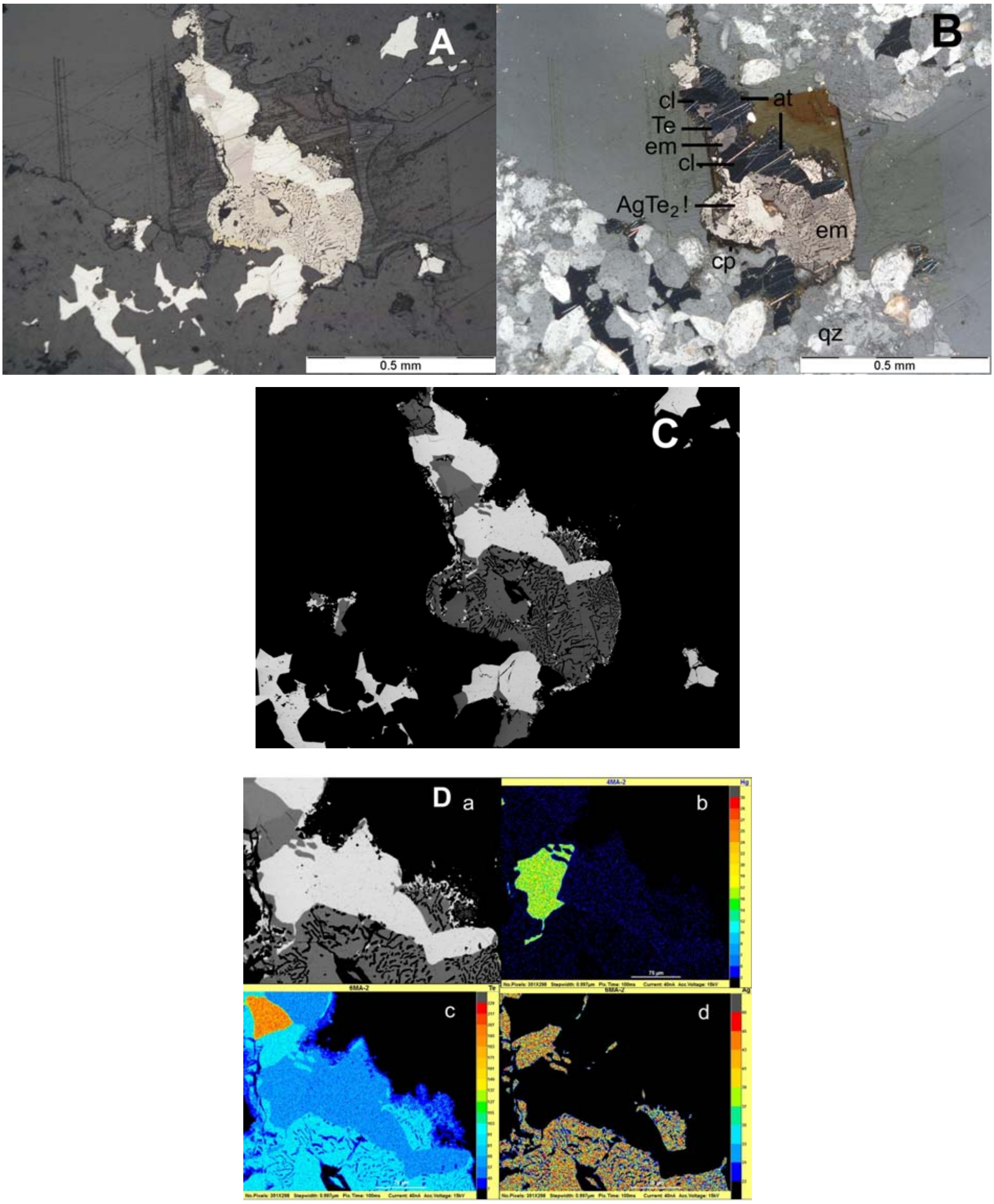

Fig. 3 – Coloradoite deposited in open quartz vugs, associated with altaite (at), tellurium, empressite and Te-rich silver telluride. Silver tellurides are partly permeated by worm-like void channels imparting a pseudo-symplectitic structure, and variable compositions for similar aspects – the aggregate in the centre of the image consists of both empressite and $AgTe_2$ telluride. A – microphotograph, reflected polarized light; B – the same field under crossed polarizers, cp – chalcopyrite; C – BSE-image; D – detail of the BSE image (a) with element distribution maps of the same field for Hg (b), Te (c) and Ag (d).

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