

## NATIVE GOLD AND TELLURIDE MINERALS FROM A DEEP SUPERGENE ZONE IN THE AU-CU DEPOSIT CHELOPECH

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**ABSTRACT.** In the present study, a new data for mineral composition of Western sector in ore bodies in block 149, found about 700 m below the surface, are shortly discussed. In polished sections of the ore bodies are observed and analyzed with  $\mu$ -laser "Raman" spectroscopy a native gold and tellurium minerals (hessite and altaite), established in association with pyrite, chalcopyrite, bornite and anglesite. Their typical features and relationships are described. This complex mineralization is likely due to the later deep supergene processes, associated with open fault structures that have changed the character of mineralization in the deeper parts of the deposit. The analyses of the results obtained by present work will complement previous studies of the typical mineralogical and chemical zoning of this type of epithermal deposits.

**Key words:** „Raman”  $\mu$ -spectroscopy, ore minerals, deep supergene processes, Chelopech deposit

### САМОРОДНО ЗЛАТО И ТЕЛУРОВИ МИНЕРАЛИ ОТ ДЪЛБОЧИННА СУПЕРГЕННА ЗОНА В АУ-СU НАХОДИЩЕ ЧЕЛОПЕЧ

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**РЕЗЮМЕ.** В настоящата работа се съобщават нови данни за минералния състав на участък "Западен", в рудни тела на блок 149, установени на около 700 m под съвременната повърхност. В полирани препарати от рудните тела са наблюдавани и анализирани с  $\mu$ -лазерна „Раман” спектроскопия самородно злато и телурови минерали (хесит и алтаит), установени в асоциация с пирит, халкопирит, борнит и англезит. Описани са техни характерни особености и взаимоотношения. Това комплексно орудяване вероятно се дължи на по-късни дълбочинни супергенни процеси, свързани с отворени разломни структури, които са променили характера на минерализацията в по-дълбоките участъци на находището. Анализът на резултатите от настоящия труд ще допълни предишни изследвания на типичната минерална и химична зоналност за този вид епитермални находища.

**Ключови думи:** „Раман” микро-спектроскопия, рудни минерали, дълбочинни супергенни процеси, находище Чelopeч

### Introduction

The native gold, hessite and altaite are rare ore minerals in the Au-Cu deposit Chelopech. The main reason for the significant lack of sufficient identification of telluride minerals is their mode of occurrence, i.e. as minute phases, often less than 10  $\mu$ m in size and frequently characterized by complex intergrowths. Optical and electron microscopy, and electron-microprobe analyses are the most used techniques for chemical and physical identification of telluride minerals. It is difficult to identify the telluride minerals during petrographic investigation owing to their small sizes and the similarity of the optical properties of many minerals. Furthermore, where the telluride minerals are only a few micrometers in size, the electron microprobe generally provides only semi-quantitative analyses due interferences from surrounding minerals. The small size of telluride mineral grains does also not allow identification with standard X-ray diffraction (XRD) methods.

The author of present study proposes Raman  $\mu$ -spectroscopy as a convenient alternative/complimentary method.

The laser Raman  $\mu$ -spectroscopy is a non-destructive and structurally sensitive technique that can be easily used to identify very small mineral phases less than 10  $\mu$ m in size with different orientations, such as the telluride minerals. The aim of this study is to provide the Raman spectra obtained on telluride minerals (hessite and altaite), described in the ternary systems Pb-Ag-Te, from a deep supergene weathering zone in the Chelopech deposit (Fig. 1).

### Materials and methods

Studies are performed on 10 polished sections, prepared from 20 representative samples for conducting the mineralogical studies of ore bodies of block № 149 from sector "West" in the gold-copper deposit Chelopech. Polished sections are observed through microscope for polarizing light Meiji 9430 supplied by photo camera Meidji DK 1000. Reflected light microscopy is used for establishing the optical and textural characteristics of ore minerals. Raman spectra

were collected using a LABRAM (ISA Jobin-Yvon) instrument at room temperature in the Laboratory of fluid inclusions of the University of Leoben, Austria. A frequency-doubled 100 mW Nd-YAG laser with an excitation wavelength of 532.068 nm was used. The laser power at the sample surface is about 1 to 2 mW. Measurements were carried out with an LMPlanFI 100x/0.8 (Olympus) objective lens. Additional neutral filters with variable optical densities were used to decrease the laser power to prevent damage or transformation of the samples. The subsequent interpretation and analysis of spectral data is accomplished with the software product Crystal Sleuth, which provides an opportunity to compare the obtained spectra with the database RRUFF. The database RRUFF is internet based, freely accessible and maintain a full range of high quality spectral data from well characterized minerals (Downs, 2006).

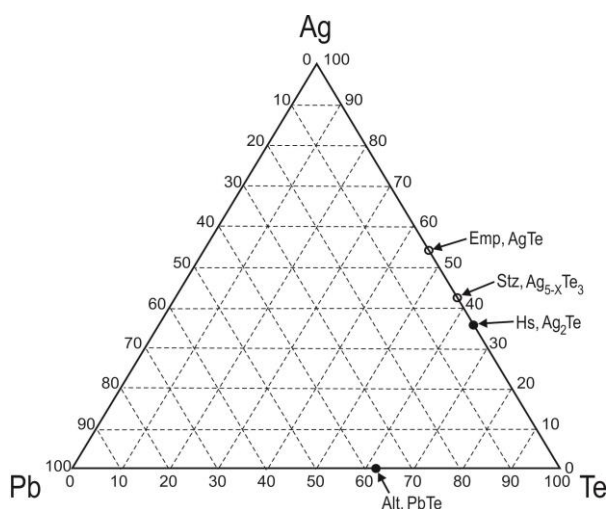


Fig. 1. Compositional diagram (atomic proportions) of the ternary system Ag-Pb-Te for mineral compositions analyzed in the present study (Hs – hessite; Alt – altaite) and other silver tellurides (Stz – stützite; Emp – empressite) from the Elatsite-Chelopech ore field.

## Geology

The genesis of the Au-Cu Chelopech deposit (Bulgaria), the major ore producing epithermal deposit in this area, is related to intermediate Late Cretaceous volcanism, which extruded in the northern part of the Central Srednogorie metallogenic zone.

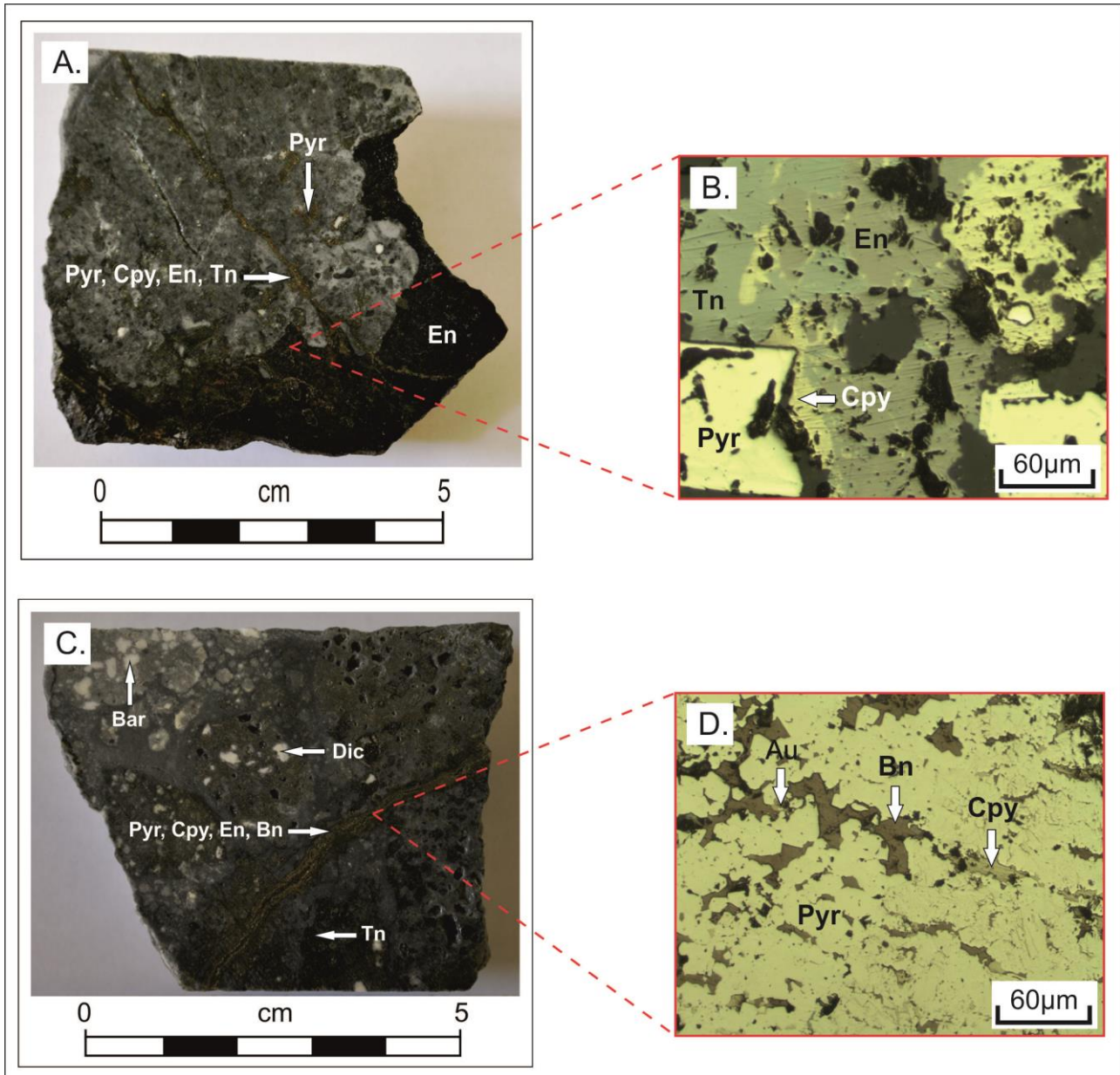
The high permeability of volcanic breccias and volcanites of the Vozdol member of the Chelopech Formation in the area of the deposit is predestined the penetration of the hydrothermal fluids in them and the formation of massive, layered, lenticular and disseminated type of ores with textures of replacement. The ore mineralization in the Chelopech deposit replaces the effusive rock minerals, forming massive bodies, veins and disseminated ores, embedded in the central part of the Chelopech volcano, built of volcanic breccias and volcanites (Kovachev et al., 1992). In areas with the highest degree of cracking and faulting in the deposit, a stockwork and lenticular ore bodies are formed mainly, which together with the vein-disseminated type of ore mineralization are the most common among volcanic breccias and volcanites. In the development of so-called secondary mineralized breccias (Chambefort, 2005)

are formed massive type of ore bodies, whose matrix consists of ore minerals and phenocrysts of the host rocks.

A massive ore (enargite-tennantite-chalcopryrite) mineralization, developed on an earlier massive pyrite was found in block №149, level 225 at the ore sector "West" of the Chelopech deposit (Fig. 2, A, B). This development of Cu-As-S mineralization over an earlier massive-sulphide ore is typical for the main economic ore, found in the central parts of the ore bodies in the form of massive aggregates in the deposit. Rarely with that mineralization is established a native gold as well (Fig. 2, D).

The formation of high-sulphidation epithermal deposits is a result of fluids (containing gases such as SO<sub>2</sub>, HF, HCl), penetrating directly from the hot magma. These fluids are highly acidic (pH 2-3) and after their interaction with the host rocks, dissolve most of the rock forming minerals, leaving mainly quartz. As a result of this process the host rocks become cavernous – so called "vuggy quartz" texture (Fig. 2, D). Rich in gold and copper fluids, which rise from the magma, penetrate the created permeable medium and unload the metals within porous and cavernous ("vuggy quartz") areas. The factors such as the host rocks and tectonics have influenced the ore-forming processes and character of the mineralization in the Chelopech deposit. A later depth supergene processes, associated with an open fault structures, change the character of the mineralization as extracting and redeposition a large amount of chemical elements, as a result of which are formed a complex ores rich in copper, gold, silver, tellurium, bismuth, lead and zinc. The typical ore minerals for these deep supergene areas of the deposit are bornite, often replacing pyrite and chalcopryrite (Fig. 2, D), native gold, hessite, altaite, nagyagite, tetradyomite and others telluride minerals like stützite and empressite. The telluride assemblages are commonly deposited in a later mineralization stage, at specific physicochemical conditions: relatively high oxidation potential and rather low temperature of formation (250-200-170°C) (Bonev et al., 2005). According to Tokmakchieva (2008) these minerals are formed of systems concentrated with tellurium, gold and silver under subsolid bringing processes under temperatures lower than 210°C. Gold and other noble metals precipitate at sharp pressure decrease, solution salt decrease and their temperature.

The impact of the deep supergenesis on the ore-forming processes in the Chelopech deposit is mentioned by the author in earlier publications, related to the study of anglesite from the deposit (Petrov, 2014). Under certain conditions due to the deep supergene weathering, minerals such anglesite and cerussite could be discovered within the deeper parts of the deposits, containing Pb-Zn mineralization. These minerals belong to the fourth stage of mineralization in the Chelopech deposit: quartz - carbonate – barite stage and probably are formed as a result of the interaction of cool and with nearly neutral pH magmatic fluids with the host rocks. The native gold, hessite and altaite, presented in this work, are established in the same polished sections, where the secondary minerals anglesite and cerussite are observed, analyzed and reported by the author in Petrov (2014).



**Fig. 2. Massive, vein and cavernous ("vuggy quartz") textures.**

- A. A drill core sample № DH15CS2 (veins filled with pyrite (Pyr), chalcopyrite (Cpy), enargite (En) and tennantite (Tn), cut by massive enargite);
- B. Mineral association in polished section of the marked area, observed in reflected light, parallel nicols (chalcopyrite (Cpy) aggregates among enargite (En) and tennantite (Tn) matrix; a well-formed pyrite (Pyr) crystals and gangue minerals);
- C. A drill core sample № DH15CS4 (pyrite (Pyr) – chalcopyrite (Cpy) – enargite (En) – tennantite (Tn) – bornite (Bn) vein mineralization, also dickite (Dic) and barite (Bar) as gangue minerals among typical cavernous quartzite);
- D. A micro-photo of a polished section, observed in reflected light, parallel nicols (bornite (Bn), chalcopyrite (Cpy) and native gold (Au) in pyrite (Pyr) matrix).

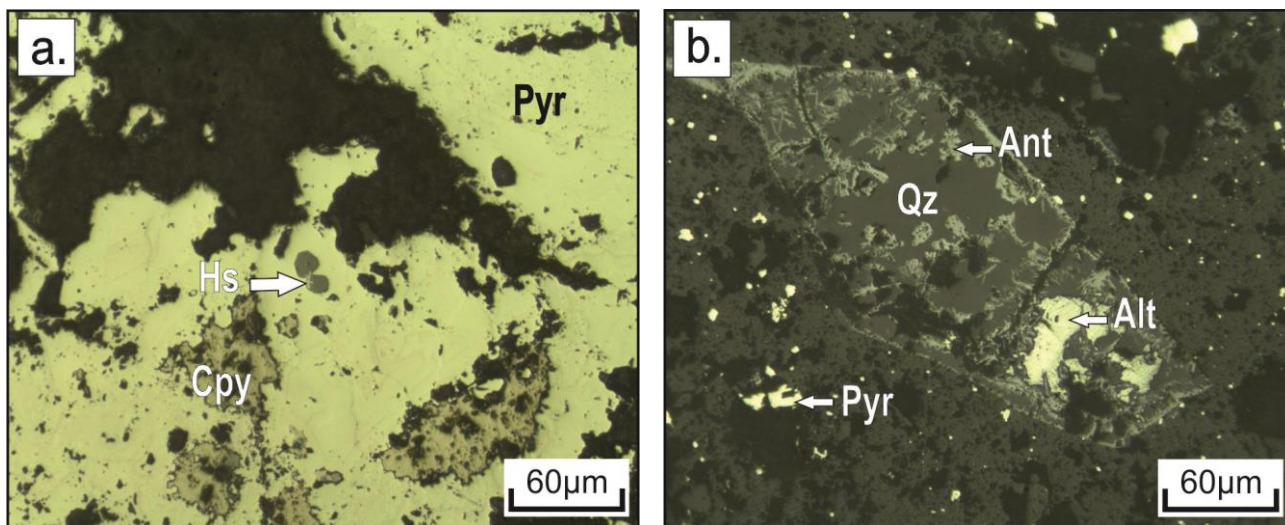
## Results and discussions

The ore mineralization in the Chelopech deposit is characterized by a rich geochemical variety, typical for the high-sulphidation epithermal Au-Cu deposits. The main economic elements Cu, Au and Ag have a strong correlation relationship with higher contents of As due to the large presence of sulphosalts such as tennantite, enargite, luzonite and famatinite, as well as high content of S, which main carrier is pyrite. The correlations between elements in ores from the Chelopech deposit are reported in Petrov and Popov (2015). Despite relatively inert behavior of Ti during the hydrothermal processes, the chemical element shows a tendency to slight enrichment in the areas with advance argillic alteration, in

which are located the ore bodies as well. This often presence of Ti is due to the extraction of some petrogenic components from the host rocks, during the hydrothermal alteration (Hikov, 2001). Using an ore microscope and the Raman  $\mu$ -spectral analysis, reported in Petrov (2016), is confirmed the replacement of the apatite by a mixture of quartz and  $\text{TiO}_2$  (anatase), during the advance argillic alteration of ore hosting rocks. In a deep supergene conditions, the bornite replaces chalcopyrite and pyrite in association with native gold (Fig. 2, D) and hessite (Fig 3, a). These later deep supergene processes have led to the formation of inclusions of altaite (Fig. 3, b), among quartz-anatase-pyrite mineral association, typical for the studied ore sector.

The native gold is established as very fine (3 - 5 $\mu$ m) irregular grains together with bornite and chalcopyrite among pyrite matrix (Fig. 2, D). In previous mineralogical studies (Petrov et al., 2013) of the same ore sector of the deposit a native gold is found as fine (10-50  $\mu$ m) inclusions among enargite or in association with pyrite and baryte. The shape of gold

inclusions is irregular or elongated along the micro fractures in matrix from enargite or barite. Chemical composition of the native gold shows low content of Ag (up to 7.45 wt. %) and sustainable content of copper within 2.89 to 7.93 wt.% (Petrov et al., 2013).



**Fig. 3. Micro-photos of ore minerals in polished sections from the Western sector of the gold-copper deposit Chelovech (reflected light):**

- A massive pyrite (Pyr), corroded by chalcopyrite (Cpy) and gangue minerals (black) is observed. Among the pyritic matrix a mineral inclusion of hessite (Hs) in quartz grain (dark grey) is established.
- Inclusions of altaite (Alt) in idiomorphic gangue mineral (apatite?), fully corroded by quartz (Qz) and anatase (Ant), together with fine single grains of pyrite (Pyr), among gangue mineral mass are established.

The newly identified in the Au-Cu deposit Chelovech hessite (Ag<sub>2</sub>Te) is a rare ore mineral. In plane-polarized incident light the hessite is grey with slightly brownish tint, scratches, while in crossed nicols it shows a dark orange and bluish distinct anisotropy. It is found as very fine (up to 10  $\mu$ m) inclusions in quartz, in association with pyrite, chalcopyrite, bornite, and gangue minerals quartz, barite, dickite, anhydrite and kaolinite (Fig. 3, a). The mineral probably is deposited in a later mineralization stage, and its spatial and structural relationships give grounds to be assigned to the galena-sphalerite mineral association in the ore deposit. The hessite in the Elatsite deposit, part of the same Elatsite-Chelovech ore field, where the studied deposit is located, occur as fine (1-30  $\mu$ m) inclusions, or as exolutions in bornite and chalcopyrite, or at their grain boundaries, associated with native gold, native Te, stützite, sylvanite, empressite, merenskyite, or clausthalite (Petrunov et al., 1992; Tarkian et al., 2003; Bogdanov et al., 2005).

It is presented on Figure 4. A., B. and Table 1 the obtained spectrum of hessite from the Chelovech deposit, compared with those of database RRUFF (№ R070445, the Klondike mine, USA). The positions of the typical peaks in the "Raman" waves in the spectrum of the mineral are marked by numbers. According to the RRUFF database, hessite from the Klondike mine, the positions of the "Raman" spectra's peaks are indicated at 345 and 381  $\text{cm}^{-1}$  (Fig. 4, B, Table 1). Apopei et al. (2014) reported the Raman spectrum of hessite with two strong

peaks at 119  $\text{cm}^{-1}$  and 138  $\text{cm}^{-1}$ , which are not recognizable on the Raman spectra in the present work. The data received in the present study differ from the compared spectrum in the range of 1-2  $\text{cm}^{-1}$  (Fig. 4, A, B). The very small size of the mineral aggregates do not allows a correct electron microprobe analysis. According to the published data (Apopei et al., 2014) the content of Ag and Te in hessite is from 57.35 wt.% to 60.61 wt.%, and from 35.77 wt.% to 38.35 wt.%, respectively.

Altaite (PbTe) is also very rare established mineral in the western sector of the deposit and it belongs to the pyrite-chalcopyrite mineral association. It is found as fine grains up to 20-30  $\mu$ m among idiomorphic gangue mineral (apatite), fully corroded by quartz (Qz) and anatase (Ant) (Fig. 3, b). In some cases the altaite displays triangular cleavage breakouts and it is difficult to separate from galena only by its optical properties. The mineral has tin white color with a grayish-green hue and high metallic luster. It is reported as irregular inclusions in coarse nagyagite, associated with hessite, native gold, and hedleyite in similar to the present study vuggy quartz host rocks at the Hedley Monarch Mine, Canada (Thompson, 1949).

According to Vymazalova et al. (2014) the synthetic phase PbTe (altaite) is "Raman" inactive, and does not reveal a spectrum in the range of 80 to 1600  $\text{cm}^{-1}$ . This is confirmed by the received "Raman" spectra of natural altaite in the present study (Fig. 4, C) and those of RRUFF database №R060939, Mattagami mine, Quebec, Canada (Fig. 4, D).

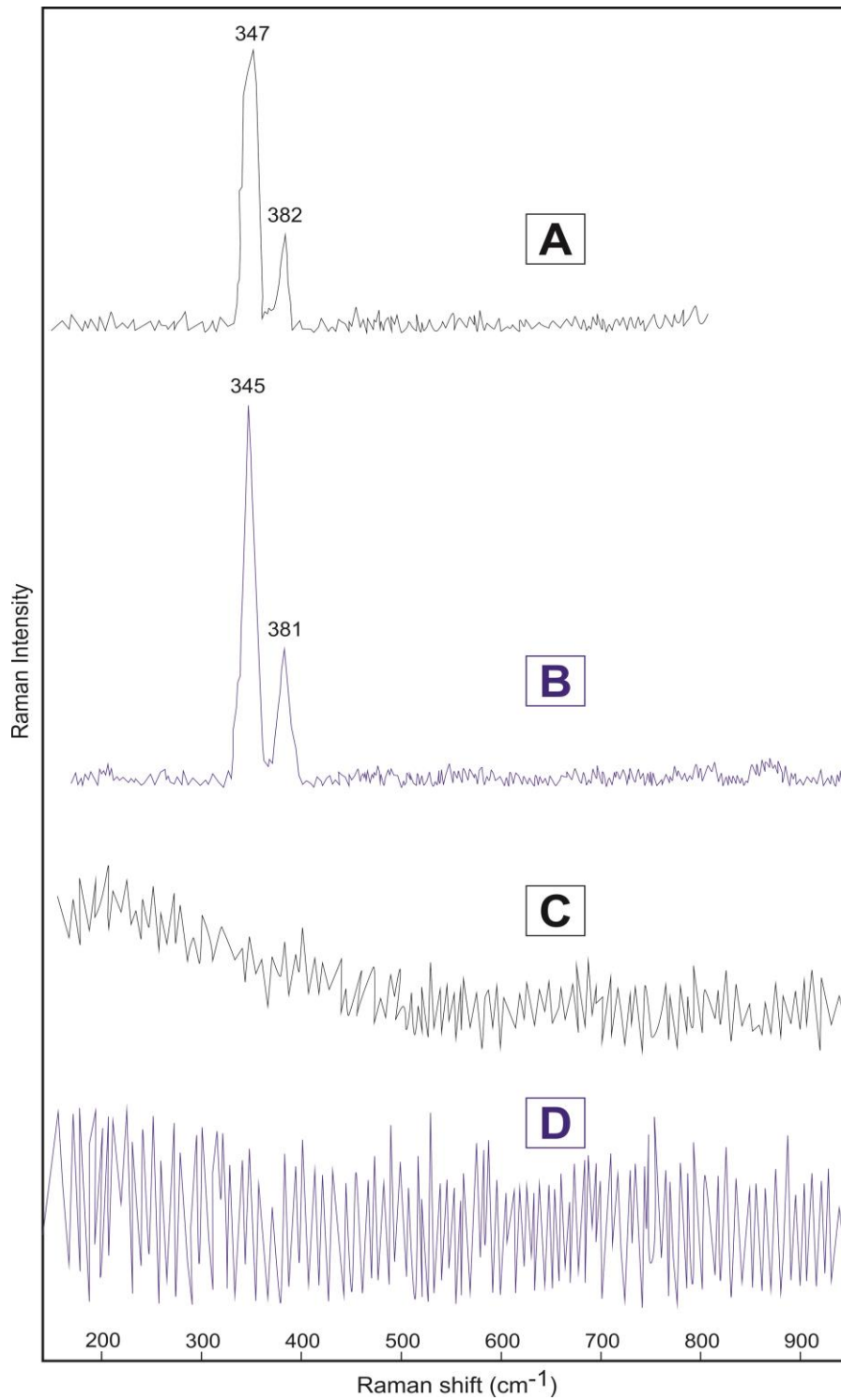


Fig. 4. "Raman" spectra of hessite and altaite from the Chelopech deposit and RRUFF database at 532 nm wave length (A. - hessite; B. – hessite, database RRUFF №R070445; C. – altaite; D. altaite, database RRUFF №060939).

Table 1.  
"Raman"  $\mu$ -spectral wave's peaks of hessite ( $cm^{-1}$ )

Hessite (the Chelopech deposit)	Hessite, RRUFF database №R070445 (the Klondike mine)
347	345
382	381

## Concluding remarks

The established mineral phases of native gold, hessite and altaite in this work, corresponds to deep supergene zone, associated with open fault structures in the Chelopech deposit. These phases are observed as small grains in association with pyrite, chalcopyrite, bornite, anatase, and secondary minerals like anglesite and cerussite.

The results presented in this study confirm that Raman  $\mu$ -spectroscopy as quick and generally non-destructive method can be considered as an innovative technique with a potential to better characterize and identify rare and tiny phases such as telluride minerals. Together with the optical microscopy the laser Raman  $\mu$ -spectroscopy it is a modern powerful diagnostic tool for mineral identification.

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