BOILING ASSEMBLAGES IN THE KUPEL OCCURRENCE, KRUMOVGRAD GOLDFIELD, SE BULGARIA

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1. Introduction

❖ Indicators of boiling

- Exploration of active geothermal fields and epithermal deposits has revealed the formation of both vein adularia and platy calcite as originated from fluid becoming more alkaline due to the loss of acid volatiles during boiling of hydrothermal fluid.

- Boiling has been evidenced by the presence of coexisting liquid- and vapour-rich fluid inclusions in both minerals.

- These outcomes have made adularia and platy calcite to be mineral indicators of boiling . They remain the only indicators of boiling when suitable fluid inclusions are lacking.

In this presentation

- Boiling is evidenced only by the presence of both vein adularia and platy calcite.

- The present fluid inclusions were not investigated under optical microscope because they are very small in size.

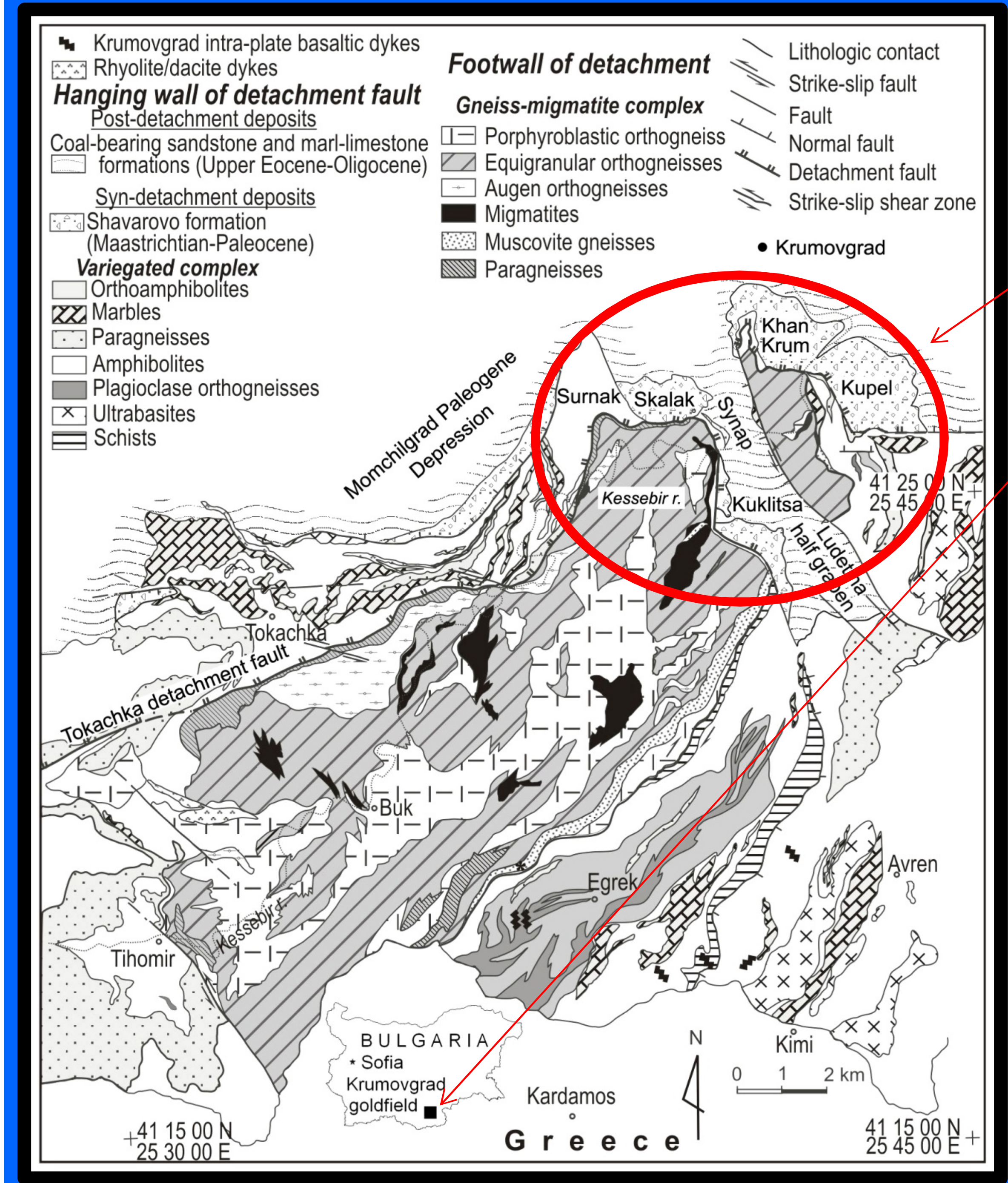
- Data come from the Kupel occurrence, low-sulfidation Krumovgrad goldfield, Eastern Rhodope Mountain , SE Bulgaria.

- Comparison with the next, well studied Khan Krum (known also as Ada Tepe) deposit is made as well.

The low-sulfidation Krumovgrad goldfield is located in the eastern part of the Rhodope tectonic zone and metallogenic province .

The Kupel occurrence is situated at c. 2 km to the SE of the Khan Krum deposit and has similar geological setting – hosted by supradetachment terrigenous rocks of the Shavar Formation (Maastrichtian-Paleocene) which are presented by breccias, breccia-conglomerates and sandstones originated from various metamorphic rocks.

Movements along a regional low-angle detachment fault (Tokachka detachment) has implemented exhumation of deep metamorphic rocks from the core of Kessebir-Kardamos metamorphic dome.



Krumovgrad goldfield

Figure 1. Geological map of the Kessebir-Kardamos metamorphic dome (courtesy of P. Marchev) with added deposits and occurrences in the Krumovgrad goldfield as well the position of latter within Bulgarian territory.

Krumovgrad goldfield includes:

- Khan Krum deposit (or Ada Tepe) with measured reserves,
- Surnak and Kuklitsa deposits with measured reserves,
- and Skalak, Synap and Kupel occurrences.

2. Results and Discussion

- Gold mineralization in the Kupel occurrence is hosted by grey fine-grained arkosic sandstones of grains smaller than 1 mm.

Gold (electrum) is observed mainly under microscope in:

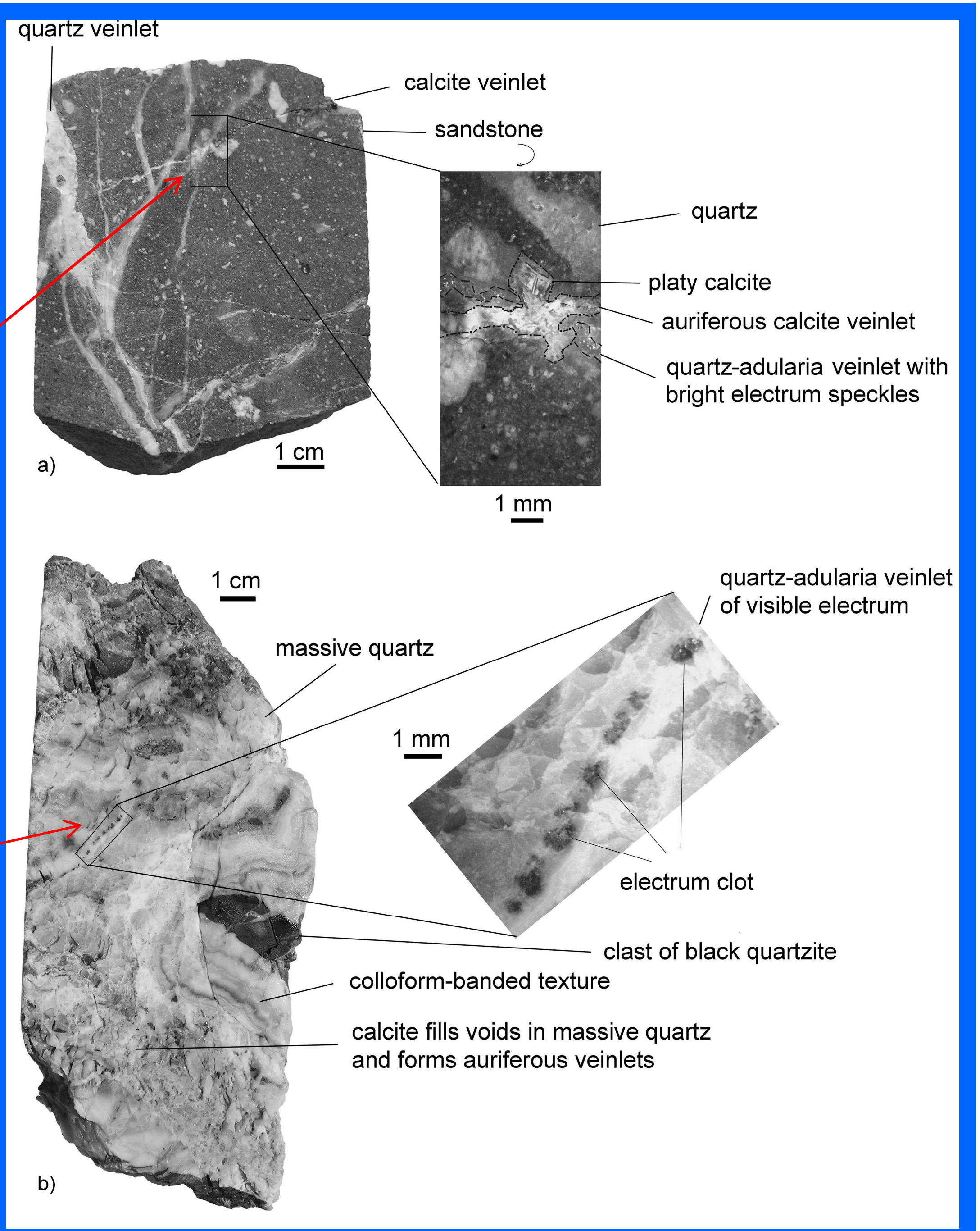
- quartz-adularia or calcite veinlets;
- areas of dense cracking
- or disseminated in massive hydrothermal quartz.
- On rare occasions gold is visible by naked eye.

Auriferous veinlets cross-cut the sandstones and have similar dimensions: centimeter-scale length and thickness to a few millimeters.

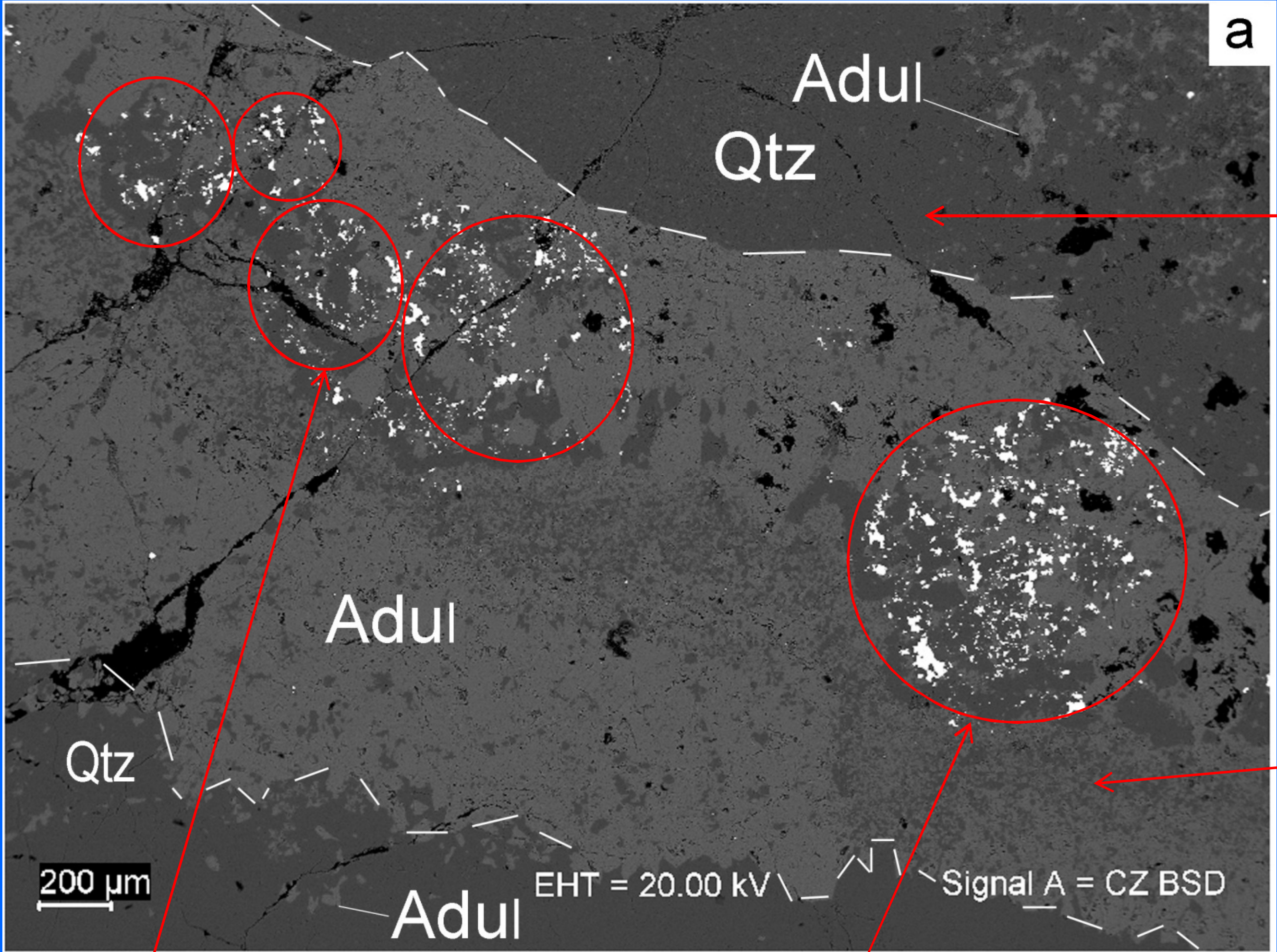
2.1. Boiling assemblages

1) Auriferous veinlet of calcite composition intersects quartz-adularia veinlet

2) Auriferous veinlet of quartz-adularia composition



Auriferous quartz-adularia veinlet

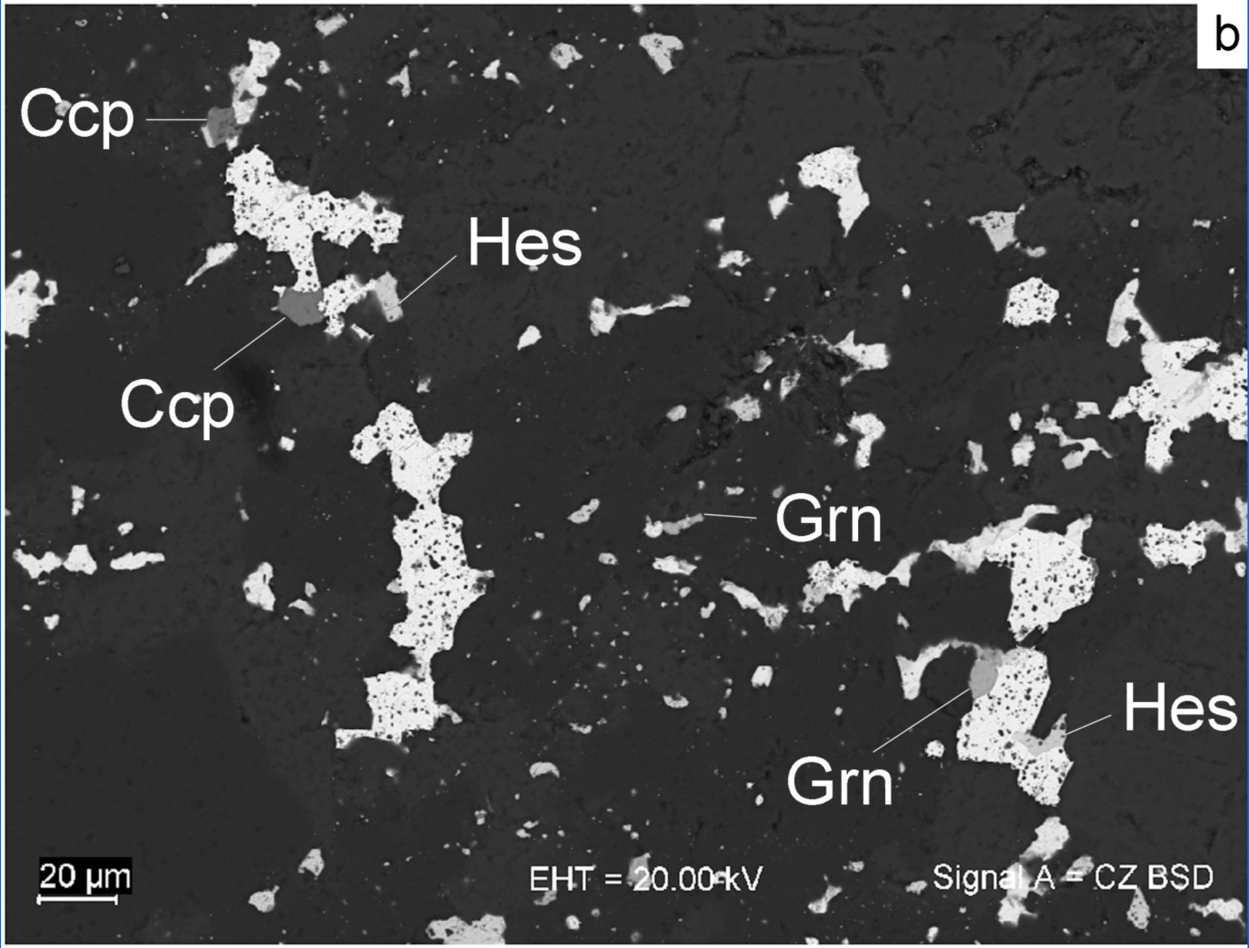


In the host hydrothermal quartz : Adul<<Qtz.

In the veinlets: Adularia>>Qtz; Adularia abundance reach and even exceed 90 vol. % at places.

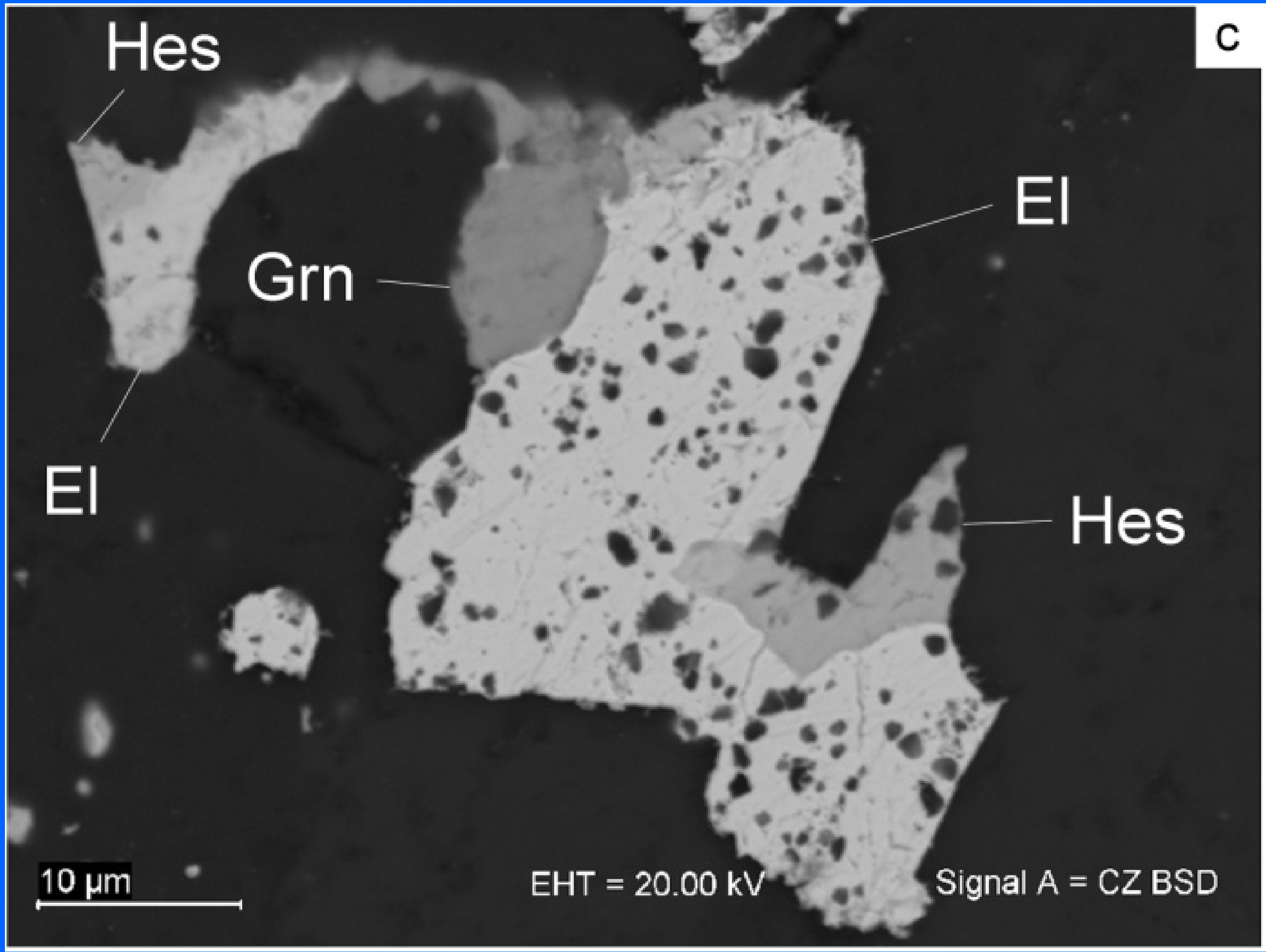
Globular electrum aggregates in quartz-adularia matrix

Paragenesis of auriferous quartz-adularia veinlets:



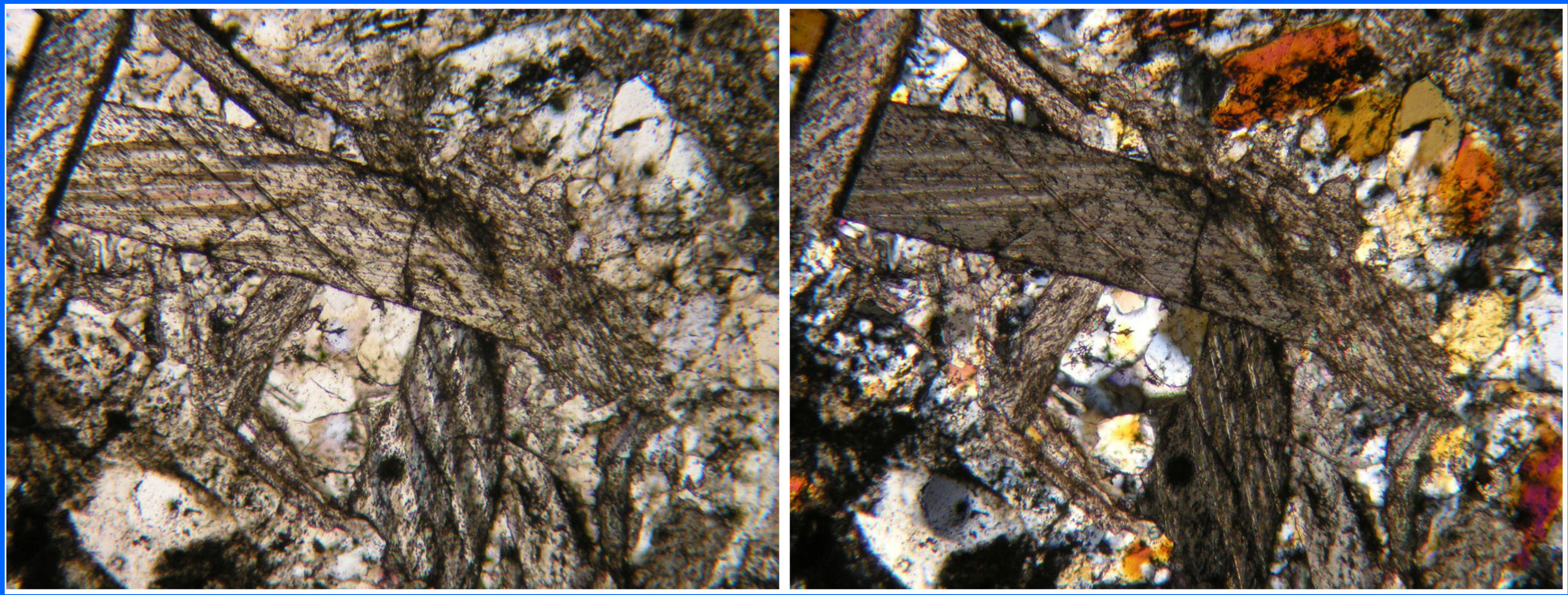
Electrum (white grains) is intergrown with chalcopyrite (Ccp), hessite (Hes) and greenockite (Grn). Detail from the previous slide.

Electrum displays highly porous texture.



Electrum (El) intergrown with hessite (Hes) and greenockite (Grn).

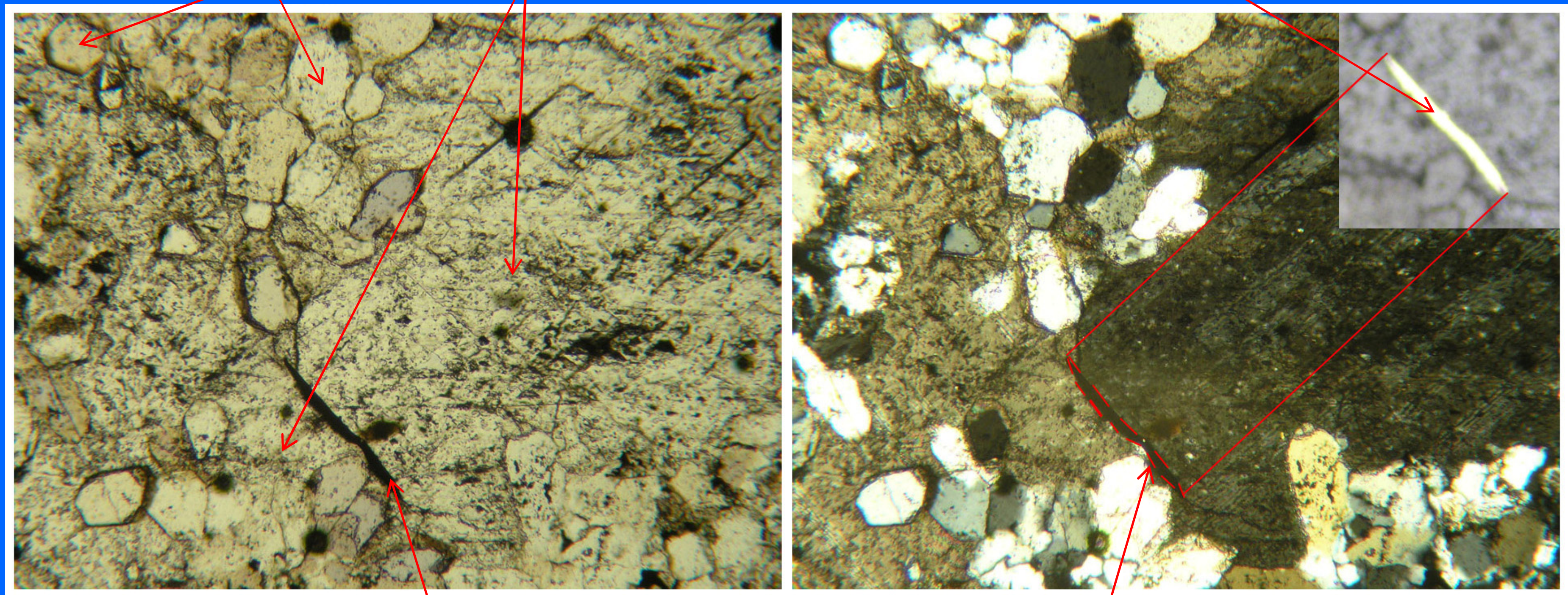
Auriferous calcite veinlets



Auriferous veinlet of bladed calcite intersects hydrothermal quartz. Transmitted light: left – in plane polarized light, right – in cross polarized light.

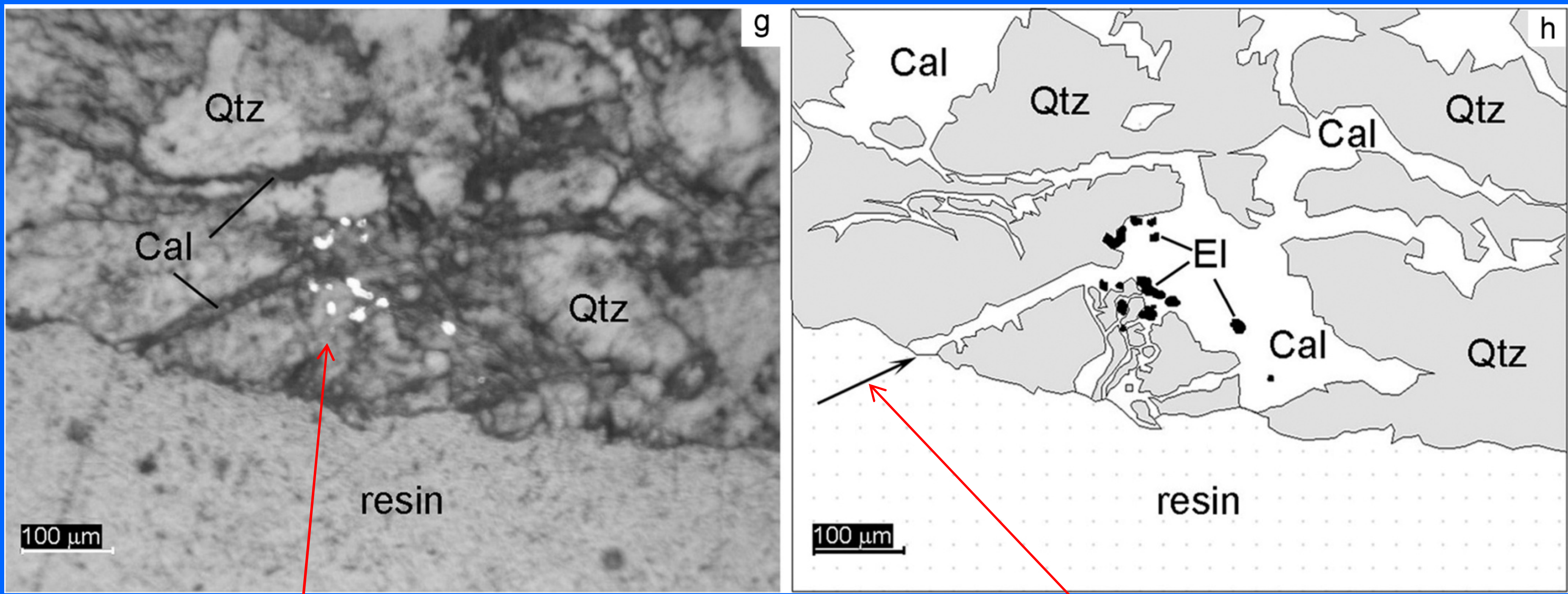
inset – electrum wire (pale yellow) in reflected light

quartz calcite



Electrum wire at a calcite grain boundary, in transmitted light: left in plane polarized light, right in cross polarized light

Effect of throttling:



Electrum (bright) is highly accumulated in areas of sharp thickness expansion after throttle portions, cross polarized reflected light.

Drawing of “g” with inferred flow direction

The previous slide demonstrates that :

- the veinlet geometry has played first-order control on the electrum distribution;
- electrum has been transported by a flowing fluid;
- electrum has been transported in a particulate form;
- electrum deposited due to pressure drop during hydrofracturing;
- electrum particles have been arrested in low velocity (expanded) portions of the ore conduits.

2.2. Mineral chemistry

- *Adularia*

Adularia from electrum-rich quartz-adularia veinlets has entirely potassic composition without sodium. In this it is identical to adularia from the Khan Krum and Kuklitsa deposits (unpublished data of the first author).

No.	Analysis no.	K_2O	Na_2O	Al_2O_3	SiO_2	Sum
1	15	16.08	bdl	17.96	65.96	100.00
2	17	17.29	bdl	17.72	64.99	100.00
3	21	16.65	bdl	17.74	65.61	100.00

Abbr.: bdl – below detection limit.

Table 2a. Composition of electrum from the Kupel occurrence, wt %. The boiling assemblage consists of quartz-adularia-electrum-chalcopyrite-galena-hessite-greenockite.

No.	Analysis no.	Boiling assemblage	Au	Ag	Sum	Au/Ag
1	1	El-Qtz-Adul-Sul-Tel	77.44	22.56	100.00	3.43
2	2	El-Qtz-Adul-Sul-Tel	76.24	23.76	100.00	3.21
3	3	El-Qtz-Adul-Sul-Tel	77.03	22.97	100.00	3.35
4	4	El-Qtz-Adul-Sul-Tel	76.87	23.13	100.00	3.32
5	5	El-Qtz-Adul-Sul-Tel	76.15	23.85	100.00	3.19
6	6	El-Qtz-Adul-Sul-Tel	76.81	23.19	100.00	3.31
7	7	El-Qtz-Adul-Sul-Tel	76.35	23.65	100.00	3.23
8	8	El-Qtz-Adul-Sul-Tel	75.63	24.37	100.00	3.10
9	9	El-Qtz-Adul-Sul-Tel	76.13	23.87	100.00	3.19
10	10	El-Qtz-Adul-Sul-Tel	76.15	23.85	100.00	3.19
11	11	El-Qtz-Adul-Sul-Tel	76.31	23.69	100.00	3.22
12	12	El-Qtz-Adul-Sul-Tel	77.46	22.54	100.00	3.44

Abbr.: El – electrum, Qtz – quartz, Adul – adularia, Sul – sulfides, Tel – tellurides, Cal - calcite.

Table 2b. Composition of electrum from the Kupel occurrence, wt %. The boiling assemblage consists of electrum and calcite.

No.	Analysis no.	Boiling assemblage	Au	Ag	Sum	Au/Ag
13	13	El-Qtz-Cal	77.00	23.00	100.00	3.35
14	14	El-Qtz-Cal	77.77	22.23	100.00	3.50
15	16	El-Qtz-Cal	77.48	22.52	100.00	3.44
16	18	El-Qtz-Cal	76.41	23.59	100.00	3.24
17	19	El-Qtz-Cal	76.69	23.31	100.00	3.29
18	20	El-Qtz-Cal	76.63	23.37	100.00	3.28
19	30	El-Qtz-Cal	80.60	19.40	100.00	4.15

Abbr.: El – electrum, Qtz – quartz, Cal - calcite.

The Au/Ag ratio of electrum in the Kupel is from 3.10 up to 3.50 (Table 2), whereas in the Khan Krum (outcrops on the summit) this ratio varies from 2.30 up to 3.2 but generally below 3.

This implies different levels of mineralization and/or formation temperature for the Kupel and Khan Krum with deeper level and/or higher temperature for the Kupel occurrence.

- *Hessite*

Hessite is composed of only silver and tellurium. Earlier, hessite associated with petzite (Ag_3AuTe_2), electrum, and galena has been found in the Khan Krum (Ada Tepe) deposit and reported in [9].

- *Greenockite*

Greenockite is found for the first time in the Krumovgrad goldfield in this study. It contains small amounts of Zn and Fe.

- *Galena*

Galena is composed of only lead and sulphur.

Table 3. Representative electron microprobe analyses of minerals intergrown with electrum, wt % (bdl – below detection limit).

Mineral	**Hess**	**Hess**	**Hess**	**Hess**	**Hess**	**Hess**	**Grn**	**Grn**	**Grn**	**Gn**	**Gn**
An. no.	**23**	**24**	**25**	**26**	**29**	**35**	**26**	**27**	**32**	**32**	**35**
Au	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Ag	61.77	61.68	61.86	61.86	61.81	60.97	bdl	bdl	bdl	bdl	bdl
Pb	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	87.26	87.54
Cu	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cd	bdl	bdl	bdl	bdl	bdl	bdl	78.03	81.90	76.36	bdl	bdl
Fe	bdl	bdl	bdl	bdl	bdl	bdl	0.34	bdl	bdl	bdl	bdl
Zn	bdl	bdl	bdl	bdl	bdl	bdl	3.43	bdl	3.50	bdl	bdl
S	bdl	bdl	bdl	bdl	bdl	bdl	20.20	18.10	20.14	12.74	12.46
Te	38.13	38.23	38.06	38.14	38.19	39.03	bdl	bdl	bdl	bdl	bdl
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Abbr.: Hess – hessite, Grn – greenockite, Gn – galena, btl – below detection limit.

2.3. Significance of throttling

High accumulation of electrum after throttle portions has already been described in samples from the next Khan Krum deposit. That picture has been interpreted with a causative sequence of several processes in [52]:

(i) increased boiling in expanded veinlet portions compared to weak boiling or non-boiling conditions in narrow ones;

(ii) flocculation of colloidal solution and retention/arrest of heavy electrum flocs in expanded veinlet portions (low velocity zones) and

(iii) formation of mixed electrum-silicate gel and its further crystallization.

- Effect of throttling displayed above in the picture from the Kuppel occurrence was earlier predicted by numerical simulations which have demonstrated that throttling leads to “cessation of boiling” [53]. These authors have inferred stopping of the gold deposition in throttle portions of ore conduits.

- Even earlier, accumulations of precious and base metals as scales has been found downstream of throttles installed in geothermal production wells in New Zealand for a pressure reduction of the geothermal fluid [54].

- In addition, formation of colloidal solution as a response to boiling has been already proposed in other studies of epithermal deposits and geothermal systems [55-58].

2.4. Boiling and deposition of Au, Ag, Cu, Pb, Cd and Te

The assemblages in the Kupel occurrence besides boiling indicate in addition a saturation of hydrothermal fluid in respect to their minerals and hence high effectiveness of boiling for deposition of Au, Ag, Cu, Pb, Cd, and Te likely through collective loss of H_2, CO_2, H_2S and H_2Te.

Similarly, in [59] it have been concluded that boiling removes Au, Ag, Cu, Pb, Cd and Te from modern geothermal solutions.

In contrast, other elements like Zn, only partially remove during boiling and remain available for transport and deposition in peripheral and shallow portions of an epithermal system [59].

The absence of sphalerite demonstrated in this study is in line with the conclusion in [59] about the behavior of Zn during boiling.

2.5. Possible sources of Te

The presence of Au-Ag tellurides in the precious metal mineralization of Krumovgrad goldfield and their genetic relationship with calc-alkaline to alkaline rocks, well constrained in the literature, **suggest a relationship of the goldfield with underlying shallow calc-alkaline and high-K intrusive rocks.**

Two available contributors of Te exist in the Kessebir-Kardamos dome where the supradetachment terrigenous rocks host the precious metal mineralization:

- Te-bearing magmatic fluids separated from shallow seated and buried plutons of Eocene age and
- leaching of Te from the older metamorphic rocks in the core of the metamorphic dome.

The first possibility is advocated in [9, 13]. The authors of [9] have proposed that volcanism in the Eastern Rhodope has been preceded by an accumulation of magma at greater depths. Lately, it has been suggested that the Eastern Rhodope gold deposits have been related to intrusions of deep-seated mafic magmas [61].

The first author of the present study thinks that such mafic rocks should be parental of both epithermal mineralization and Iran Tepe volcano since the volcanic rocks of the latter bear calc-alkaline and high-K characteristics [34].

The second possibility exists because of the presence of old intrusive rocks of similar high-K characteristics in depth:

- The metamorphic core complexes of the Rhodope Tectonic zone comprise metamorphosed I- and S-granitoids of Palaeozoic to Mesozoic age which have originated from the crust or enriched subcontinental mantle and crust [62].
- The core granitoids fall into the field of high-K calc-alkaline and K-subalkaline rocks [64].

- To constrain the source of Te for the tellurides in the Krumovgrad goldfield a sampling of the Rhodope metamorphic basement and determination of the Te abundances in the different metamorphic rocks are required in future.

3. Materials and Methods

The studied samples comes from borehole cores provided by Dundee Precious Metals Krumovgrad Co. (DPMK).

The methods comprise observations under stereo and optical microscope (in transmitted and reflected light), scanning electron microscope, and electron microprobe analysis.

Mineral composition was defined in polished sections from borehole cores using energy dispersive X-ray microprobe analysis through ZEISS SEM EVO 25 LS-EDAX Tident spectrometer at acceleration voltage of 15 kV, electron beam current of 500 pA and beam diameter of 1 μm for all analyses. The standardless quantification results are performed through automatic background subtraction, matrix correction, and normalization to 100% for all of the elements in the peak identification list. Data in the tables are from individual point analyses with detection limits <0.01 wt %.

4. Conclusions

- 1. Precious metal mineralization in the Kupel occurrence, Krumovgrad goldfield, is presented mainly by electrum and trace hessite, chalcopyrite, galena, and greenockite. It has deposited in a response of multiple boiling episodes resulted from hydrofracturing by overpressurized fluid. The boiling is evidenced by the presence of vein adularia and platy calcite and it demonstrates high effectiveness for deposition of Au, Ag, Cu, Pb, Cd and Te.
- 2. Two types of boiling assemblages and respective two ore stages were identified: (i) earlier, quartz-adularia-electrum-chalcopyrite-galena-hessite-greenockite and (ii) later, calcite-electrum one. The first assemblage displays textural evidence for flocculation of colloidal solution of silicates and electrum like in the next Khan Krum deposit. The second assemblage is specific for the Kupel occurrence and increases its gold potential.

- 3. The higher gold content in electrum from the Kupel occurrence compared to the one from the next Khan Krum deposit as well as the presence of greenockite in the first both suggest deeper level and/or higher formation temperature for the Kupel occurrence.
- 4. The presence of tellurides in the Krumovgrad goldfield and their relationship with calc-alkaline, subalkaline and alkaline rocks worldwide, points to two possible sources:

  (i) underlying shallow calc-alkaline and high-K Eocene intrusive rocks trough magma degassing or

  (ii) metal leaching from host metagranitoid rocks by hot fluids.

  Tellurides points also to a formation temperature in the range of 280-200 °C and origin from neutral to slightly acid, low-salinity fluids.

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Conflicts of Interest: The authors declare no conflict of interest. DPMK has given permission to publish the results.

Thank you for the attention!