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# HYDROTHERMAL ALTERATIONS AND ORE MINERALIZATION OF SOME GOLD-POLYMETALLIC DEPOSITS IN EASTERN RHODOPES, BULGARIA

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**ABSTRACT**

Zones of hydrothermally altered rocks in Eastern Rhodopes are mapped in different scales. Investigated area includes Madjarovo, Zvezdel-Pchelojad and Popsko ore fields. The most widespread hydrothermal minerals are distinguished and grouped in several associations according to their temporal relationships. The composition of some associations - propylitic, argillic, chlorite-sericite-carbonatic, quartz-adularian and that of late vein minerals, - is studied in detail. It is displayed that their distribution is controlled by NW and submeridional fault zones. Parallel analysis of data on both ore and hydrothermal mineralizations confirms the suggestion that ore mineralizations of different composition are related to different zones of hydrothermal alteration. This dependence is responsible for the upward gradual displacement of pyrite-chalcopyrite mineralization by sphalerite-galenite and further by sulphosalt one. Summarising all these regularities, different levels of erosion in different parts of Eastern Rhodopes are suggested.

## INTRODUCTION

Investigations of hydrothermal alterations are necessary in order to solve various problems concerning hydrothermal ore deposits. These alterations are studied in detail (Radonova, 1960, 1973; Atanasov, 1962, 1965; Velinov et al., 1977, 1987, 1988; Nokov et al., 1981, 1993; Breskovska et al., 1984-1, 1984-2, 1993; Mavroudchiev et al., 1965, 1973; Gergelchev, 1971, 1978 etc.). However, spatial outlining of hydrothermally altered zones has not been produced purposefully. The authors made an attempt in mapping of such zones. The applied methodology includes studying of the mineral composition and morphology of the zones, their areal distribution, spatial and temporal relationships of hydrothermal minerals. The principles of the methodology have been elaborated by E.V.Pluschev, V.V.Shatov et al. (1981, 1985 etc.), from VSEGEI, St.- Petersburg, Russia.

## GEOLOGICAL SETTING

In the discussed area, the basement is composed by high-rank metamorphites, including gneiss-granites, various gneisses and amphibolites, gneiss-schists, schists and serpentinized ultrabasic rocks. It is overlain by paleogenic volcano-sedimentary complex, represented by conglomerates, sandstones, lime-stones, intermediate and acid volcanites and their tuffs. Hypabyssal gabbro-

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monzonitic intrusions and dikes of various composition penetrate them. Submeridional or NE overthrusts and high-angle faults are the main tectonic structures. Ore deposits are represented by gold-polymetallic veins (Madjarovo, Popsko and Zvezdel-Pchelojad ore fields), some of them with predominant antimonite (ore occurrence Chernichevo), and stratiform gold-silver deposits (Sedefche).

## MAIN HYDROTHERMAL MINERALS

The authors described only the temporarily closest to the ore deposition stages of hydrothermal activity. According to all former researchers, these are the processes following hypabyssal magmatism.

The most widespread hydrothermal minerals in the area are: epidotes, amphiboles (represented by actinolite-tremolite), biotite, sericite, hydromica (according to X-ray structural analysis - hydromuscovite 1M+2M1 and illite 1M + traces of 2M2), chlorite, clay minerals (mostly kaolinite 1T, less frequently - two types of smectite, Ca- and Na-montmorillonite), quartz, chalcedony, albite, K-feldspaths (high-temperature members of the group), adularia, barite, carbonates (calcite, dolomite, siderite). Most of the minerals are present in several generations. They form poly- and monomineral auto- or pseudomorphous aggregates.

## ASSOCIATIONS OF HYDROTHERMAL MINERALS AND THEIR DISTRIBUTION

Associations of hydrothermal minerals are distinguished in dependence of two criteria: statistically stable co-existence, fixed in different points of the area and simultaneous deposition of the minerals proved by petrographic data. Among the associations which have been established, there are five latest and closest to the ore deposition: propylitic, chlorite-sericite-carbonatic, argillic, quartz-adularian and one of late vein minerals. Their distribution is controlled by regional tectonic fractures. Besides, the border between the basement and the paleogenic volcano-sedimentary complex is probably of great significance, too.

### Propylitic association

In the studied area, it is represented by epidote, chlorite, zeolites, carbonate, specularite, leucoxene. The association is fixed as up to several kilometres wide and over 10 km long strips on the map (fig.1). They are observed in metamorphites as well as in volcanites and have predominantly submeridional and NE direction coinciding with that of the most widespread regional faults in Eastern Rhodopes. The metasomatic column of the association is displayed below (the typical column for propylitisation, proposed by V.Jarikov (1959), is on the right). In this case, alteration is developed in amphibolites. It is absolutely identical in other basic rocks. In more acid environment (gneisses, intermediate and acid tuffs), the difference is in the absence of newly formed amphibole, zeolites and clay minerals.

| | |
|---|---|
| 0. Amphibolite | 0. Andesite |
| 1. Chl+Car+Amf+Bt+Ab+Pl+Gr+Kaol' | 1. Q+KFsp+Ab+Ser+Ep+Chl+Cc |
| 2. Ep+Chl+Car+Amf+Bt+Ab+Pl+Kaol' | 2. Q+Ab+Ser+Ep+Chl+Cc |
| 3. Ep+Chl+Car+Amf+Bt+Ab+Zeol' | 3. Q+Ab+Ep+Chl+Cc |
| 4. Ep+Chl+Spc+Car+Amf+Zeol' | 4. Q+Ab+Ep+Chl |
| 5. Q+Ep+Chl+Spc+Car | 5. Q+Ep+Chl |
| 6. Q+Ep+Chl+Car | 6. Q+Ep |
| 7. Q+Ep | 7. Q |

The substantial similarity of both columns allowed to identify the association as low-temperature propylitic one.

**Argillic association**

It includes quartz, clay minerals, hydromica, sericite, carbonates, rarely barite. This association occupies strips of variable, up to several tens of kilometres length and up to several km width. They occur along almost all known faults (fig. 1), forming circular or oval halos of variable size around their intersections . Similar spots frame all known ore fields. The metasomatic column of this association has the following form (the typical column for argillic alteration (Kazitsin, 1972) is on the right):

| (andesito-dacite) | (granite) |
|---|---|
| 0. Q+KFsp+Pl+Bt+Amf | 0. Q+KFsp+Pl+Bt+Amf |
| 1. Ser+Ab+Chl+Bt+Pl+Amf | 1. Q+KFsp+Pl+Chl+Cc |
| 2. Q+Ser+Ab+Chl+Car+Bt+Pl | 2. Q+KFsp+Ab+Chl+Mnt+(Cc) |
| 3. Q+HSer+Ser+Ab+Chl+Car | 3. Q+KFsp+HSer+(Mnt) |
| 4. Q+Kaol'+HSer+Ser+Car | 4. Q+Kaol+HSer |
| 5. Q+Kaol+HSer | 5. Q+Kaol |
| 6. Q+Kaol | 6. Q |
| 7. Q | |

It is obvious that both columns are almost identical and the association can be defined as argillic. Within it, sericitic, hydrosericitic, kaolinitic and silica subzones are distinguished. The lat-

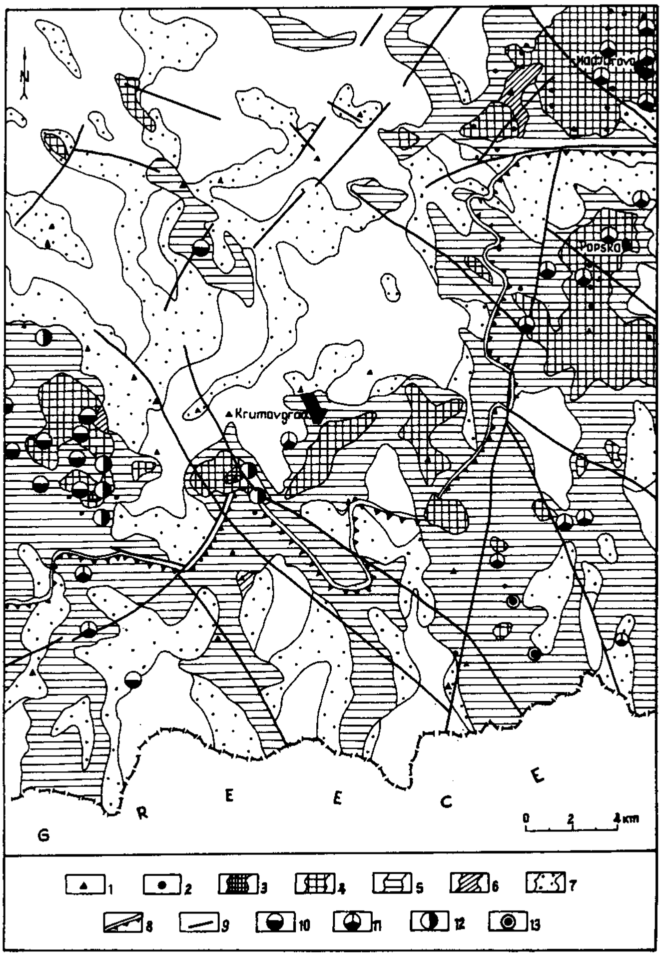


**Fig. 1:** Scheme of the distribution of associations of hydrothermal minerals (geology by Z. Ivanov, D. Kozhoukharov and Iv. Boyanov). 1 - association of late vein minerals; 2- quartz-adularian association; 3-5 - argillic association: 3 - silica subzone, 4 - clay-hydromica subzone, 5 - sericitic subzone; 6- chlorite-sericite-carbonatic association; 7 - propylitic association; 8 - border between the volcano-sedimentary complex and the basement (triangles pointed to basement); 9 - faults; 10-13 - ore deposits and occurrences: 10 - gold, 11 - gold-polymetallic, 12 - polymetallic, 13 - antimonitic.

ter is morphologically represented by veins (deposits in Madjarovo, Zvezdel-Pchelojad and Popsko ore fields, ore occurrences Chernichevo, Tintjava etc.) or lenses and seams (deposit Sedefche, ore occurrence Sarnak). The composition of the association depends partly on host rocks. In metamorphosed basic rocks (amphibolites), only montmorillonitic argillites are fixed, where chlorite and partly carbonate predominate in the external zones of the metasomatic column. In intermediate volcanites, hydromica is usually more abundant than clay minerals. In carbonate rocks, quartz plus one or several generations of carbonate are present, accompanied in some cases by sericite, hydrosericite and barite. In ultrabasic rocks, talc, carbonate and quartz occur.

**Chlorite-sericite-carbonatic association**

It includes chlorite, sericite, carbonate and quartz. The ratios of the minerals are variable. This association is not widespread. It occurs mainly in Madjarovo and Zvezdel-Pchelojad ore fields, forming small irregular halos. As a rule, they are present in basic and intermediate rocks or follow contacts of the two former associations. Metasomatites of similar composition have been described earlier in the mentioned ore fields (Radonova, 1960, 1973; Kasulova-Stankova, 1991 etc.)

**Quartz-adularian association**

It includes the last generation of quartz, adularia, chalcedony and carbonate. These minerals form veins and veinlets mostly in intensively argillized rocks or fill cavities in previously deposed hydrothermal minerals. The association is distributed unevenly in the area (fig.1) and is observed mainly at known ore deposits and occurrences. It is studied in detail by other researchers (Velinov et al., 1977, 1987,; Nokov, Malinov, ,1993 etc.), who suggested it to be formed during the late alkaline stage closely related to the acid leaching one, which is responsible for argillic alteration.

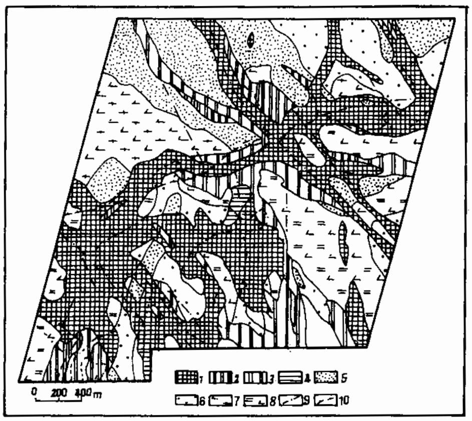


**Fig. 2:** Map of the metasomatic zonation in the northern part of the Popsko ore field
1-3 argillic association: 1 - kaolinitic subzone, 2 - hydrosericitic subzone, 3 - sericitic subzone; 4 - chlorite-sericite-carbonatic association; 5-6 - propylitic association: 5 - epidotic subzone, 6 - chloritic subzone; 7 - amphibolites, muscovite gneisses; 8 - gneiss-schists.

**Association of late vein minerals**

It includes the latest generations of clay minerals, chlorite, carbonates and zeolites. They form fine late veinlets which cross all the rest hydrothermal products. The association is not studied enough because of its rare presence.

**Relationships of the associations**

These relationships are visible on large-scale maps. For instance, such a map of the northern part of Popsko ore field is displayed on fig.2.

The host rocks are predominantly biotite-muscovite gneiss-schists with rare amphibolitic bodies in the south and mostly amphibolites in the north. They are parted by an overthrust fixed northward from the

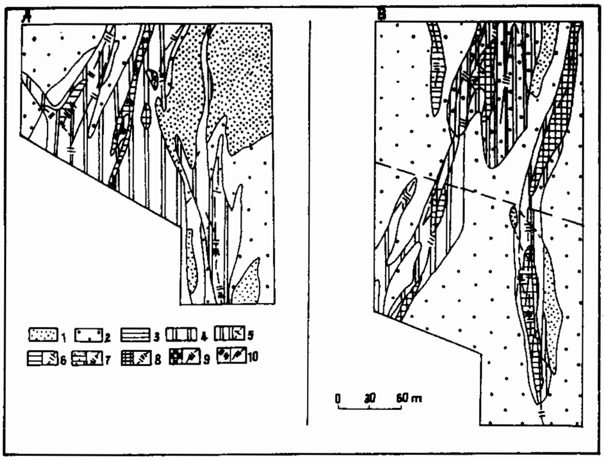

**Fig. 3:** Schematic map of the metasomatic zonation at zone 3 of the Popsko ore field, horizon "700m" (A) and horizon "650m" (B).
1-2 - propylitic association: 1 - epidotic subzone, 2 - chloritic subzone; 3 - chlorite-sericite-carbonatic association; 4-10 - argillic association: 4 - sericitic subzone, 5 - the same with late chalcedony, 6 - hydrosericitic subzone, 7 - the same with late chalcedony; 8 - kaolinitic subzone, 9 - the same with late chalcedony, 10 - late adularia.

village Popsko (Z. Ivanov et al., unpublished). The argillic strips occur along the overthrust and high-angle faults. In the argillites, different positions of the hydrosericitic subzone are fixed. In the northern part of the map, it is more perypheric than the kaolinitic one, while in the southern part it is closer to the centre and displaces kaolinites entirely in the very deposit Popsko. Chlorite-sericite-carbonatic association presents quite rarely, usually related to marginal areas between argillic and propylitic zones. The association of late vein minerals is represented mostly by chlorite and carbonate. In the southernmost part of the area, adularia also occurs.

Hydrothermal alterations near known deposits and ore occurrences were studied better. In the first example, two schemes of the metasomatic zonation along horizons "700m" (fig. 3,A) and "650m" (fig. 3,B) of the Popsko deposit are represented. The host rocks are biotite-muscovite gneiss-schists and rare bodies of amphibolites and aplitoid gneisses. Propylites are widespread and argillites overprint them most noticeably where argillic halos narrow significantly. The comparison of both schemes shows that the overprint occurs mainly in the deeper parts and that the halos are drop-like in section. In the argillic zone, kaolinitic subzone usually occupies the central parts, while upwards it is displaced by hydrosericitic one. The association of late vein minerals is represented here mostly by quartz, chalcedony, adularia and carbonate. It overprints the upper parts of argillites, in some cases - propylites. It is much more widespread in the north from the E-W fault, which is probably caused by subsidence of the northern block. Chlorite - sericite - carbonatic association was fixed predominantly in the deeper horizon.

The second example (fig.4) represents the distribution of metasomatites along a cross section in the northern part of deposit Sedefche (Zvezdel-Pchelojad ore field). The major zonation is also controlled by a fault, but the environment - organogenic limestones overlain by tuffs, tuffites and tuffaceous limestones, provides the involving of the entire high-permeable horizon in metasomatic activity. It is important, that besides kaolinite central subzone, a silica cap occurs uppermost. Propylitic and chlorite - sericite -carbonatic associations are not fixed at all. Late minerals, represented by quartz - chalcedony, adularia, kaolinite, chlorite and barite, are widespread. Adularia predominates at relatively deep horizons.

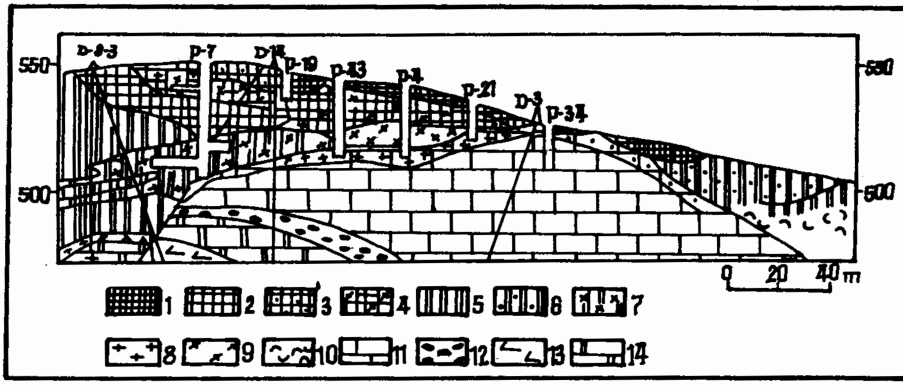


**Fig. 4:** Metasomatic zonation of deposit Sedefche (schematic cross section). 1-7 - argillic association: 1 - silica subzone, 2 - kaolinitic subzone, 3 - the same with late chalcedony, 4 - the same with late adularia, 5 - hydrosericitic subzone, 6 - the same with late chalcedony, 7 - the same with late adularia; 8 - argillic association developed in limestones; 9 - intensive limonitization; 10 - andesitic tuffs; 11 - limestones; 12 - conglomerates, sandstones; 13 - amphibolites; 14 - marbles.

**ORE MINERALIZATION**

According to the data on ore mineralization in the area, obtained by the authors and previous researchers (Atanasov, 1965; Breskovska et al., 1984-1, 1984-2; Breskovska, Tarkian, 1993; Gergelchev, Krusteva, 1978; Iliev, 1982; Mladenova, 1984, 1989; Dimitrov (ed.), 1988; Kasulova-Stankova, 1991), the following associations of ore minerals are distinguished:

1. Quartz-hematitic. It is the earliest one, represented by quartz associated with chlorite, in some cases epidote and sericite.
2. Quartz-pyrite-chalcopyritic. Represented by pyrite - I and chalcopyrite - I, accompanied by quartz identical to that of chlorite-sericite-carbonatic and argillic associations.
3. Quartz-sulphidic. Includes sphalerite, galena, chalcopyrite - II and quartz in association with kaolinite, hydrosericite and carbonate.
4. Quartz-chalcedony-sulphosalt. Includes tetrahedrite, argentite, native gold, proustite, polybasite-pearceite, stromeyerite?, matildite (shapbahite?), schirmerite?. This association is undoubtedly in closest connection with quartz, adularia and carbonate.
5. Pyrite-arsenopyritic. The latest one, represented by marcasite, arsenopyrite and pyrite. It is connected with the late vein minerals - last generations of kaolinite, carbonate and chlorite.

The two last examples of concrete deposits prove these relationships. At the demonstrated part of horizon "700m" (fig. 3,A) of deposit Popsko, mainly ore minerals from the quartz-sulphidic association are present, while those from the quartz-chalcedony-sulphosalt one have been quite rarely fixed. At horizon "700", the relationships of the ore minerals are opposite (Kasulova-Stankova, 1991). On the other hand, at deposit Sedefche only quartz-chalcedony-sulphosalt and pyrite-arsenopyritic association are observed. Other ore minerals are absent (Mladenova, 1984, 1989; Dimitrov (ed.), 1988).

**DISCUSSIONS**

As a result of parallel analysis of the distribution of ore and hydrothermal

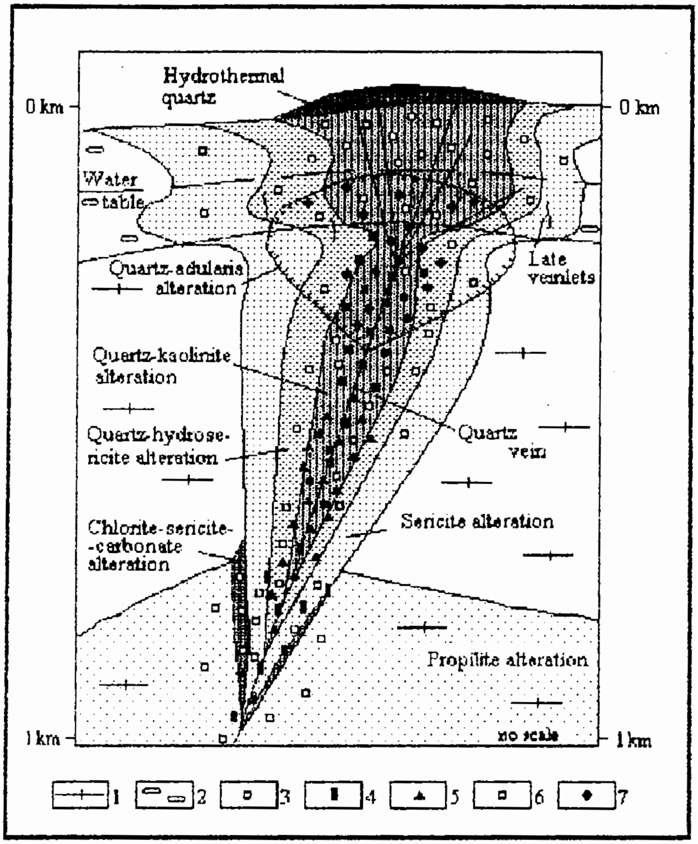


**Fig. 5:** Occurrence model for veins and strata bound gold-polymetallic deposits. 1 - basement; 2 - pyroclastic and sedimentary rocks; 3-7; ore mineralization: 3 - pyrite, 4 - chalcopyrite, 5 - sphalerite, 6 - galena, 7 - sulphosalts.

mineralizations, a generalised model of their connections is suggested (fig.5). A schematic section of basement and paleogenic sheet, cut by high-angle fault, is represented. The fault crops out at the palaeo-surface, providing a channel for hydrothermal solutions. Hydrothermal alterations are present as narrow zones along the faults in the basement, while, in the high-permeable layers of the paleogenic sheet, they form much wider subhorizontal zones.

The main characteristics of the spatial distribution of hydrothermal alterations and ore mineralization are formulated as follows:

1. Quartz-hematite-chloritic is the earliest and deepest association of ore minerals. As for hydrothermal minerals, chlorite-quartz, chlorite-sericite-quartz or chlorite-epidote-quartz are the earliest and deepest ones, forming the quartz-epidotic subzones of propylites adjacent to chlorite-sericite-carbonatic and argillic zones.

2. Quartz-pyrite-chalcopyritic association is younger. It is followed by quartz-sulphidic one, so that both associations coexist in a common temporal and spatial (vertical) zonality. The same relationships are observed for chlorite-sericite-carbonatic and argillic associations of hydrothermal minerals, which accompany the former ones.

3. Quartz-chalcedony-sulphosalt is the fourth association. It is later and, according to the petrographic data and the character of the spatial distribution, undoubtedly connected with the quartz-adularian association.

The suggested model displays a similarity of the distribution of the zones to the metasomatic zonation fixed at deposits of acid- sulphate type (Hayba et al., 1985; Heald et al., 1987). On the other hand, adularia is present here, which is typical for epithermal deposits of sericite-adularian type. The similarity to "low-sulphadation systems" (Mitchel & Leach, 1991; Mitchel & Csongredi, unpublished) is also substantial, although some differences are fixed. Probably, the model demonstrates a compound type. The quoted authors do not deny its existence.

The character of the regional metasomatic zonation suggests a general southward dipping of the erosion level from the Madjarovo ore field to the Popsko one where ore occurrence Tintjava is the most eroded. Further south, the erosion level ascends gradually to the occurrences Chatal Cheshma and Chernichevo. The tendency is obviously the same in the Greek part of the region. This conclusion is probably important for prognosis of ore mineralizations, especially gold ones, as well as estimation of the known ore manifestations.

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