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A Review of the Distribution of Critical and Strategic Mineral Raw Materials in the Vein-Type Mineralizations of Vertiskos Unit, Northern Greece †

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Abstract: Supply risk and economic importance are the key aspects controlling the metals classified as critical. Several of the critical metals are also classified as rare based on their restricted geological availability. In Europe, numerous mineralizations have been reported as being enriched in critical, strategic, and rare metals, and could potentially facilitate the production of these metals as by-products. Within this context, this paper reviews the critical and rare metals incorporated in the vein-type mineralization hosted in the Vertiskos unit in Greece. Several Cenozoic polymetallic mineralizations hosted in quartz veins and metamorphic rocks, which are enriched in Cu–As–Pb–Bi–Ag–Au–Te or in Sb-W are being reported in the region. The polymetallic mineral assemblages are characterized by base metal sulfides—Bi-sulfosalts, Bi-sulfotellurides, and tellurides—associated with Au and Ag. On the contrary, Bi-Te mineral phases are lacking or are completely absent from the Sb-W mineralization. The highest critical metals enrichments are reported from Kolchiko and include Bi (995 ppm), Co (320 ppm) and W (844 ppm). Gold is up to 28.3 ppm in Koronouda, while Ag reaches up to 2433 ppm in Laodikino.

Keywords: bulk geochemistry; critical metals; vein-type mineralization; polymetallic mineralization; gold; bismuth; cobalt; Vertiskos unit; Serbo-Macedonian massif; Greece

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1. Introduction

Critical mineral raw materials are essential for high-tech industries and the development of the low-carbon society [1]. They are characterized by supply risk, economic importance, and, frequently, are restricted in terms of their geological availability; thus, their exploration and exploitation are of a high priority [1]. The European Commission 2023 Critical and Strategic Raw Materials list includes the following critical and strategic metals and metalloids: Al, Sb, As, Be, Bi, Co, Ga, Ge, Hf, Li, Mg, Mn, Nb, Ni, Cu, Sc, Ta, W, V, the groups of heavy (HREE; including also yttrium) and light (LREE) rare earth elements and the platinum group metals (PGM) [2]. In addition, rare metals (e.g., Ag, Au, Cd, Hg, etc.) are of specific significance. Previous publications have revealed new mineralogical and geochemical data on the base, precious, and critical metals incorporated in the Oligocene–Miocene magmatic–hydrothermal mineralization hosted in the Vertiskos unit (e.g., [3–8]) (Figure 1). This contribution to the literature constitutes a review of the critical, strategic, and rare metals hosted in the vein-type mineralization of the Vertiskos unit, as the future exploration and exploitation of the metals found in this region could facilitate the production of critical metals (e.g., Bi, Co, Te) as by-products of the main commodities produced (e.g., Cu, Au).

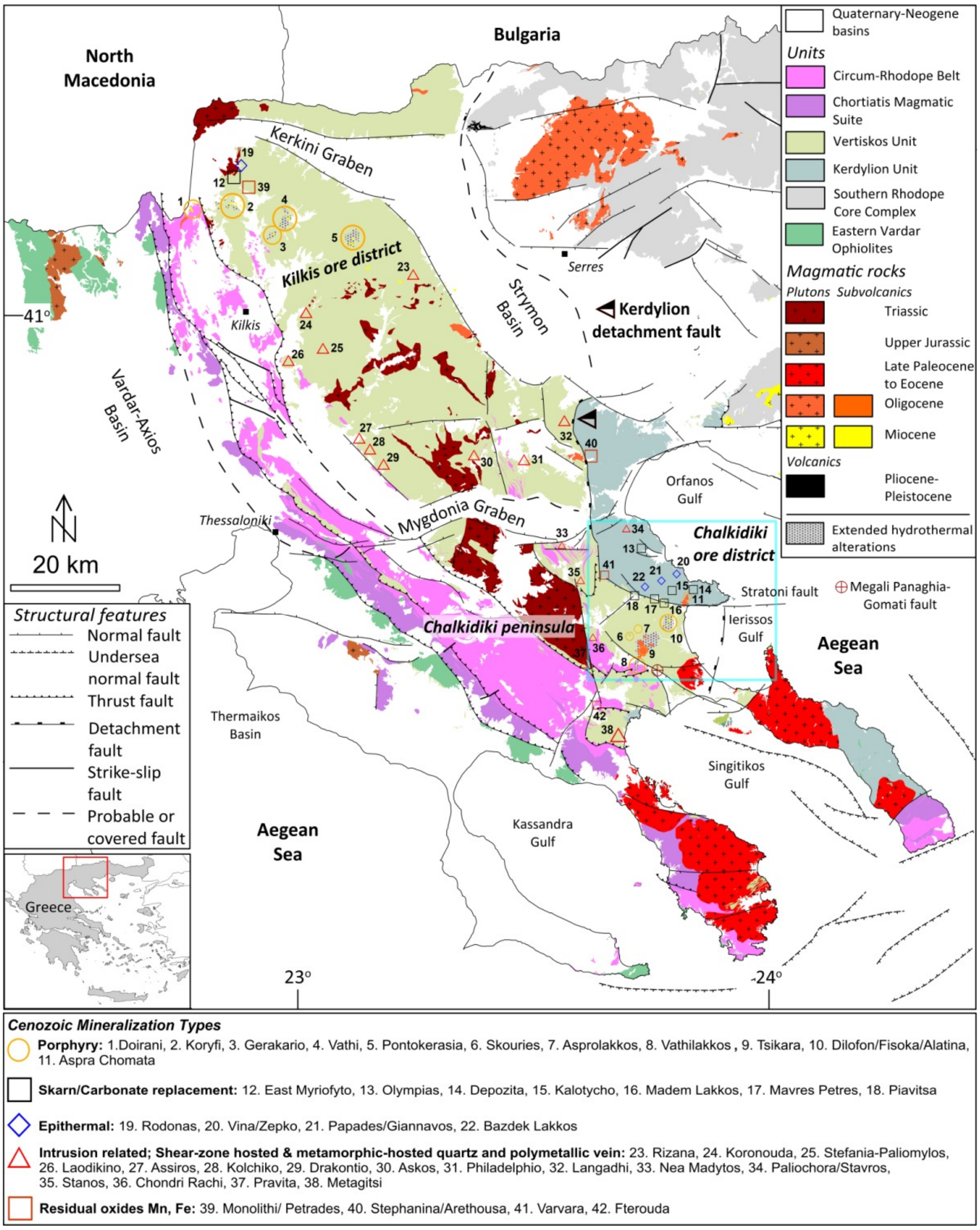

Figure 1. Cenozoic magmatism, structural setting, and mineralization types at the Vertiskos unit and the adjacent Kerdylion unit in Northern Greece (adapted from [9–11] and the references therein).

2. Geological Setting

The Ordovician–Silurian Vertiskos unit is a NW-trending polytectonic and polymetamorphosed geotectonic and basement zone stretching from the Greek–North Macedonian border to the Chalkidiki peninsula that hosts several Cenozoic deposits and prospects [6–8] (Figure 1). Basement rocks include gneiss, schist, amphibolite, metagabbro, and pegmatoids [12]. The Cenozoic igneous evolution of the region incorporates I-type plutonic, sub-volcanic, and volcanic rocks with Late Paleocene to Pliocene ages characterized by calc-alkaline, high-K calc-alkaline, and shoshonitic affinities [6].

This magmatism was accommodated in a post-collisional setting, while the magmatic–hydrothermal processes were structurally controlled by the Kerdylion and Strymon detachment faults and transtensional to transpressional tectonics (i.e., ENE–WSW-and eastward-trending shears; E–W-, NW–SE-, and NE–SW-trending normal to oblique faults and N–Strending strike-slip faults) [6–9,12] (Figure 1). The interplay of magmatism and structural settings resulted in the formation of several mineralization types, mainly between Oligocene and Miocene [4–6]. Several porphyry, skarn/carbonate replacement, epithermal, and intrusion-related mineralization types, as well as Fe-Mn- residual oxide deposits, are documented and largely grouped in the Kilkis ore district of the Vertiskos unit and the Chalkidiki ore district of the Permo-Carboniferous to Late Jurassic Kerdylion unit [6,7,9] (Figure 1).

The intrusion-related mineralization includes polymetallic assemblages hosted in quartz veins and/or metamorphic rocks that are enriched in Cu–As–Pb–Bi–Ag–Au–Te or in Sb–W [6,10,11]. Significant polymetallic mineralizations are located across the Vertiskos unit at Laodikino, Koronouda, Stefania–Paliomylos, Kolchiko, Drakontio, and Stanos, while the Sb-W mineralization can be found at Rizana and Philadelphio (Figure 1).

3. Major Cenozoic Vein-Type Mineralization and Critical Metal Distribution at the Vertiskos Unit

The polymetallic mineralization is characterized by base metal sulfides, mainly chalcopyrite, arsenopyrite, and pyrite. In addition, a variety of Bi-sulfosalts, Bi-sulfotellurides, and tellurides associated with Au and Ag can be found [13,14] (Table 1).

Table 1. Overview of the typology, alteration, and textural characteristics of the hypogene mineralization hosted in major vein-type deposits found at the Vertiskos unit (data compiled from [5–11,13,14]).

Locality	Mineralization Style	Host Rock	Alteration Style	Metallic Assemblage	Gangue and Alteration Assemblage
Drakontio	Polymetallic quartz veins	Mica schist	Silicification	Cpy + Py + Gn + Sph + Bm + Au ± Aik ± Emp ± Mtd	Qtz
Kolchiko	Polymetallic massive veins	Mica schist	Sericitization	Apy + Py + Cpy + Gn + Po ± Gab ± Bi ± Au ± Ttn ± Ilm ± Rt ± Urn	Ser + Qz + Chl
	Polymetallic quartz veins			Py + Cpy + Apy + Gn + Sph + Po ± Bi ± Hes ± Tb	
	Quartz-pyrite veins			Py ± Cpy	
Koronouda	Polymetallic quartz veins	Two-mica gneiss + pegmatoids	Silicification	Cpy + Py + Sph + Po + Gn ± Pn ± Apy ± Cob ± Ttr ± Fb ± Bm ± Tb ± Hes ± Aik ± Ptz ± Syv ± Pils ± Js-B ± Hes ± Au	Qtz
Laodikino	Polymetallic massive veins	Two-mica gneiss + chlorite-muscovite schist	Sericitization + chloritization	Apy + Py + Cpy + Sph ± Ttr ± Gn ± Po ± Mag ± Ilm ± Rt ± Cob ± Alt ± Aik ± Pils ± Elc ± Bi	Qz + Ser + Chl + Cal + Brt
	Polymetallic quartz veins			Py + Cpy + Ttr + Sph + Gn	
Philadelphio	Massive stibnite and quartz–stibnite veins	Two-mica gneiss + amphibolite + schist	Silicification + chloritization	Stb + Apy + Cpy + Py ± Ccsb ± See ± Kem ± Mrc ± Po ± Sph ± Ttr ± Sbc ± Zkn ± Wf	Qtz
Rizana	Massive stibnite and quartz–stibnite veins	Two-mica gneiss + augen gneiss	Silicification + Sericitization	Stb + Bth + Sph + Py + Cpy + Sb ± Wf ± Gn ± Ttr ± Mrc ± Po ± Apy ± Rlg ± As ± Au	Qtz + Brt + Ank + Ser
Stanos	Polymetallic massive veins	Orthogneiss + amphibolite + metagabbro + schist	Chloritization + Sericitization + Potassic	Stage I: Py + Apy + Po ± Mol ± Sph	Stage I: Qtz + Bt + Ms + Chl
				Stage II: Cpy + Sph ± Mol ± Bn ± Bm ± Aik ± Lil ± Gus ± Js-A ± Js-B ± Mtd ± Hes ± Cos ± Pek ± Gld ± Krp ± Szb ± Paa ± Gus ± Ik ± Bi ± Elc	Stage II: Bt + Ms + Chl + Sd + Ap + Mnz + Xtm
Stefania–Paliomylos	Polymetallic quartz veins	Two-mica gneiss + pegmatoids	Silicification	Py + Cpy + Sph + Po + Gn ± Apn ± Aik ± Js-B ± Bm ± Gdf ± Cob ± Pils ± Hes ± Au	Qtz

Abbreviations: Aik = aikinite, Alt = altaite, Apn = argentopentlandite, Apy = arsenopyrite, As = native arsenic, Au = native gold, Bi = native bismuth, Bm = bismuthinite, Bn = bornite, Bth = berthierite, Ccsb = chalcostibite, Cob = cobaltite, Cos = cosalite, Cpy = chalcopyrite, Elc = electrum, Emp = emplectite, Fb = freibergite, Gab = galenobismuthinite, Gdf = gersdorffite, Gld = gladite, Gn = galena, Gus = gustavite, Hes = hessite, Ik = ikunolite, Ilm = ilmenite, Js-A = joseite-A, Js-B = joseite-B, Kem = kermesite, Krp = krupkaite, Lil = lillianite, Mag = magnetite, Mol = molybdenite, Mrc = marcasite, Mnz = monazite, Mtd = matildite, Paa = paarite, Pek = pekoite, Pils = pilsenite, Po = pyrrhotite, Pn = pentlandite, Ptz = petzite, Py = pyrite, Rlg = realgar, Sb = native antimony, Sbc = stibiconite, Sd = siderite, See = seelite, Stb = stibnite, Sph = sphalerite, Syv = sylvanite, Szb = salzburgite, Tb = tellurobismuthite, Ttn = titanite, Ttr = tetrahedrite, Rt = rutile, Urn = uraninite, Wf = wolframite, Xtm = xenotime, Zkn = zinkenite.

Based on ore assemblages, mineral chemistry, and fluid inclusion studies, two stages of magmatic–hydrothermal activity are mainly documented: an early, higher-temperature stage rich in Fe-As with arsenopyrite- and pyrite-dominated polymetallic massive veins and a later, lower-temperature stage related to the polymetallic quartz veins enriched in Bi-sulfosalts and tellurides. Aikinite, hessite, bismuthinite, joseite-B, and pilsenite are the more common Bi and/or Te mineral phases occurring in the polymetallic vein mineralization [6,13,14] (Table 1). On the contrary, Bi-sulfosalts, Bi-sulfotellurides, and tellurides are lacking from the intrusion-related vein mineralizations related to Sb-W enrichment (i.e., Rizana and Philadelphio [11]) (Table 1).

At Laodikino, chalcopyrite hosts pilsenite (Bi_4Te_3) and native gold inclusions, galena incorporates altaite, and tetrahedrite contains up to 7185 ppm of Ag (Figure 2a,b). At Kolchiko, native bismuth is commonly hosted in galena (Figure 2c,d). In the quartz veins at Koronouda, hessite, pilsenite, tellurobismuthite, and Bi_4Te_2S (Joseite-B) coexist with native gold, while the gold content after bulk geochemistry is up to 28.3 ppm [7]. At Drakontio, the presence of native gold (Au < 22.5 ppm; bulk geochemistry) is correlated with the occurrence of matildite, emplectite, and aikinite [7]. Argentopentlandite is found in the quartz veins at Stefania–Paliomylos and Koronouda [7]. At Stanos, mineral phases of the bismuthinite–aikinite and lillianite–gustavite series, along with minerals of the Bi-Te-S-Se system (cf., Voudouris et al. [14]), represent a complex assemblage of Bi-sulfosalts, Bi-sulfotellurides, and tellurides [13]. On the contrary, Bi-sulfosalts, Bi-sulfotellurides, and tellurides are lacking from the intrusion-related vein-type mineralizations enriched in Sb-W (i.e., Rizana and Philadelphio, [9]). In these mineralizations, Sb and W oxides and hydroxides are mainly found as minor mineral phases due to supergene processes (Table 1).

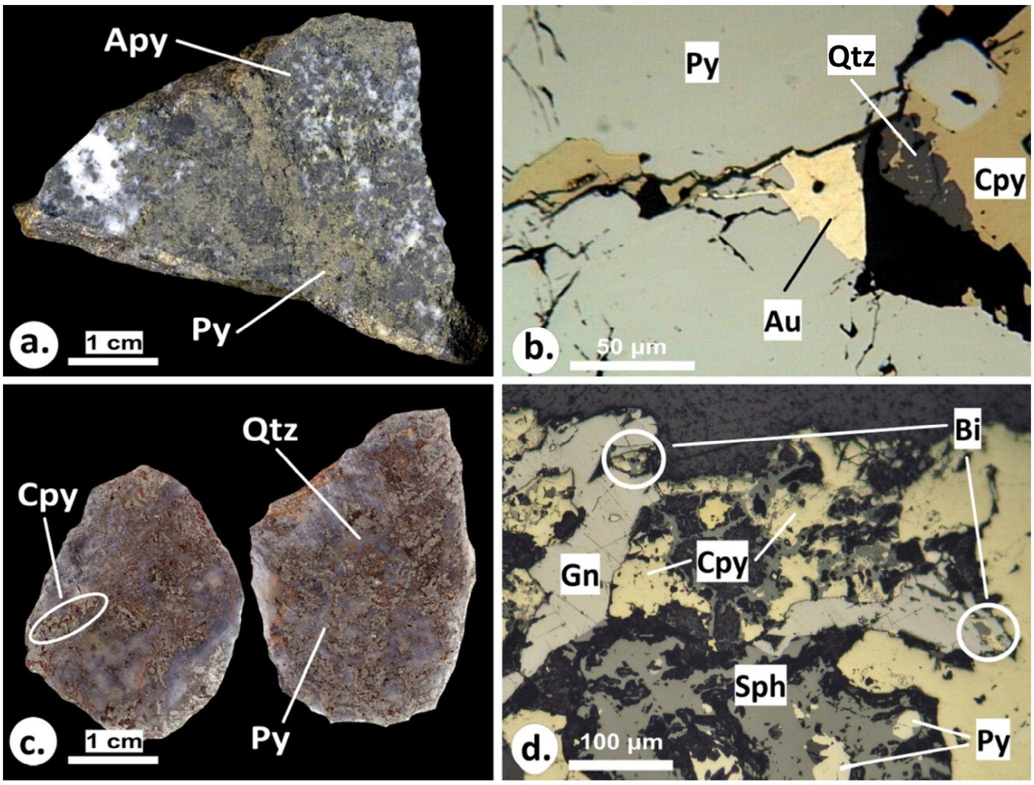

Figure 2. Photographs of hand-collected specimens from the polymetallic massive veins at Laodikino (**a**) and from the polymetallic quartz veins at Kolchiko (**c**). Photomicrographs (plane-reflected light: **b**,**d**) of the hypogene mineralization in these veins: (**a**) Massive pyrite (Py) and arsenopyrite (Apy); (**b**) native gold (Au) associated with pyrite (Py), as well as chalcopyrite (Cpy) from a polymetallic massive vein; (**c**) pyrite (Py) and chalcopyrite (Cpy) in quartz (Qtz); (**d**) pyrite (Py), sphalerite (Sph), chalcopyrite (Cpy), and galena (Gn) with inclusions of native bismuth (Bi) in a polymetallic quartz vein.

Based on the published bulk geochemical data, the vein-type mineralization is enriched in Cu–As–Pb–Bi–Ag–Au–Te, with Au up to 28.3 ppm at Koronouda; Ag up to 2433 ppm at

Laodikino; and Bi, W, and Co up to <995 ppm, <844 ppm, and <320 ppm, respectively, at Kolchiko [11]. Other enrichments include Cd (<247 ppm), Hg (<187 ppm), Se (<59 ppm), and V (<10 ppm) at Laodikino, as well as Te (<3 ppm) at Kolchiko [11]. Antimony is up to 7 wt.% in the polymetallic quartz veins from Laodikino and is mainly hosted in tetrahedrite. The Sb-W-enriched vein-type mineralizations (i.e., at Rizana and Philadelphio) are depleted in other critical metals [11]. The stibnite mineralization at Rizana mainly comprises W (<45 ppm), Co (<33 ppm), and V (<23 ppm) [11].

4. Discussion and Conclusions

At the Vertiskos unit, the vein-type mineralization was formed during the regional Cenozoic magmatic and structural evolution from magmatic–hydrothermal fluids at mesothermal to low to intermediate sulfidation epithermal conditions [7,13] (Figure 3). Locally, they are restricted in extended shear zones at the transition between ductile and brittle deformation, demonstrating retrograde greenschist facies metamorphism [7,11,13]. Bismuth- and Te-bearing melts are thought to be scavengers of gold in the polymetallic vein-type mineralization [6,14]. The various Bi-sulfosalts, Bi-sulfotellurides, and tellurides that are incorporated in these mineralizations in close relation with native gold support the Au scavenger character of the initial polymetallic melts [6,14].

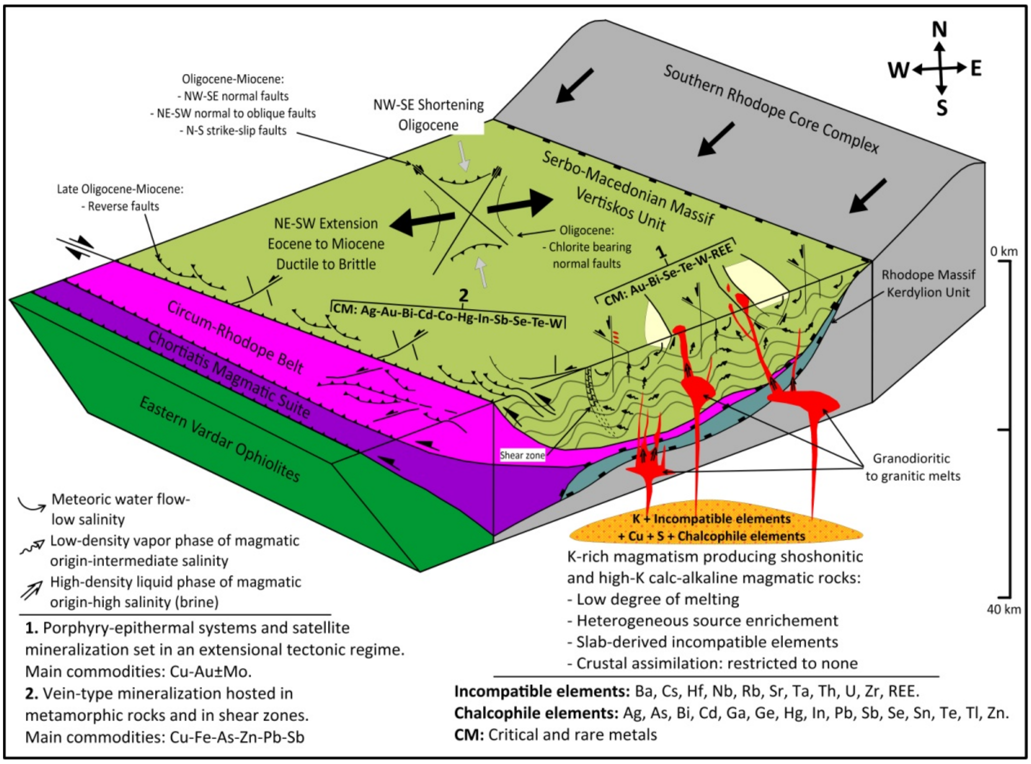

Figure 3. Schematic model showing the magmatic–hydrothermal mineralizing processes and tectonic settings at the Vertiskos unit during Cenozoic. Specific enrichments in critical and rare metals are highlighted for the porphyry–epithermal and the vein-type mineralization (modified after [13]).

The schematic model of the vein-type mineralization and the porphyry–epithermal systems found at the Vertiskos unit is shown in Figure 3. The vein-type mineralizations are hosted in metamorphic rocks and in shear zones and were formed under transpressional to transtensional tectonic settings mainly along the border between Vertiskos unit and the Circum–Rhodope belt. On the contrary, the porphyry–epithermal systems were formed in an extensional setting. Critical and rare metals are variably associated with this mineralization. Nevertheless, enrichments in Bi, Te, and Au can be found in both mineralization groups. For the vein-type mineralization, this may be an indication for concealed proximal and/or distal magmatic intrusions and magmatic–hydrothermal mineralizing processes set along or near shear zones [6,11,13,14].

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