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UPPER CRETACEOUS HYDROTHERMAL CHIMNEY FRAGMENTS FROM THE EASTERN PONTIDE BELT, NE TURKEY: IMPLICATIONS FOR PONTIDE VMS DEPOSITS

Изучены трубы «черных курильщиков», обнаруженные в колчеданных месторождениях позднемелового возраста в западной части Понтид. Присутствие минерализованных фрагментов труб в колчеданных месторождениях западной части Понтид и содержания рассеянных элементов в них представляют собой значимые данные для понимания физико-химических условий и истории отложения колчеданной минерализации на океаническом дне.

Introduction

The fossil hydrothermal chimney fragments which have been documented to date in the volcanogenic massive sulfide (VMS) districts are quite limited and specific to very few districts (Urals, Cyprus and Japan). The relics of paleo-sulfide chimney fragments were first described in the Kuroko type VMS deposits of Japan, by Scott [1981]. Later, well preserved paleo-sulfide chimneys were described in the VMS deposits in Urals [Herrington et al., 1998; Maslennikov, 1991, 1999, 2006], Cyprus [Qudin and Constantinou, 1984] and recently in the eastern Pontide VMS deposits [Maslennikov et al., 2009; Revan, 2010]. The fossil chimney fragments in these regions were revealed in clastic sulfide ores. The Late Cretaceous VMS deposits in the eastern Pontides can be added to these limited chimney-bearing VMS districts with their well preserved chimney relics. The purpose of this study is to describe mineralogical and geochemical characteristics of paeo-hydrothermal chimneys of the Pontide VMS deposits and from this to make some interpretations on the environment in which the VMS deposits formed.

Geology of Pontide VMS deposits

The bimodal-felsic VMS deposits are located on the eastern Pontide belt which forms mountain range 500 km long by 100 km wide that lie in the eastern coast of Black Sea. The basement of the eastern Pontides is formed by the Paleozoic metamorphics and the granitoidic rocks that intersect these metamorphics. A thick volcano-sedimentary sequence ranging in ages from Paleozoic to Quaternary overlies these basement rocks. The Late Cretaceous volcanic rocks, in which the massive sulfide deposits occurred, lie along the eastern Black Sea coast. It is generally agreed that the Late Cretaceous to Paleocene volcanic rocks derived from a north-trending subduction zone which is closed today. The eastern Pontide belt is defined as one of the well preserved paleo-island arc samples formed on the ocean floor that has subducted to the north during the Senonian [Şengör and Yılmaz, 1981, Okay and Şahintürk, 1997].

The majority of the VMS deposits in the district relate to circular structures and fault-controlled subsidences (?) which developed on island-arc setting. These structural-controlled VMS deposits formed proximal to rhyolitic/dacitic domes. All known VMS deposits in the eastern Pontide belt occur in dacitic/rhyolitic rocks, not too thick (300–500 meters) and which comprise of lavas, hyaloclastites and sub-volcanic intrusions. They are overlain by a sequence comprising of dacite, andesite, basalt and volcano-sedimentary unit. Some of these are either deep marine cherts or chemical sediments ("exhalites" or "halmyrolytites"). The ore deposits are commonly located at the uppermost contact of the dacitic/rhyolitic pile or within the lowermost part of the overlying sequences [Revan, 2010].

Characteristics of paleo-hydrothermal vent chimneys

All of the fragments of paleo-hydrothermal chimneys in massive sulfide deposits (Cayeli, Killik, Lahanos, K?z?lkaya and Kutlular) are found in the clastic sulfide ores. The major constituents of clastic sulfide ores which includes chimney fragments compose mainly of pyrite, chalcopyrite, sphalerite, galena and bornite.The diameters of the well-preserved chimney fragments range from a few millimeters to ~6 cm, with one reaching ~10 cm. The well preserved chimney fragments typically have distinct concentric zones (Fig. 1). Numerous examples of what appeared to be chimney wall fragments have porous and laminated textures and some of which are displaying a thin alteration rim, indicative of oxidizing conditions on the sea floor. Chimney fragments are associated with vent-related fauna.

The presence of a zoning mostly consist of three layers from exterior to interior is clearly observed in chimney samples (Fig. 2). The zones of the chimney samples mainly comprise of sulfide and sulfate minerals. However, each zone is characterized with the predominant mineral abundance. Table 1 lists the minerals that were found in the chimney samples of the VMS deposits in the eastern Pontides. By using microprobe, some rare minerals such as kawazulite (Bi_2Te_2Se) mixed with chalcopyrite matrix, hessite (Ag_2Te) and wittichenite (Cu_3BiS_3) were detected (Fig. 3).

LA-ICP MS analysis

Two chimney samples collected from Cayeli ore body were analysed for their geochemical signatures. Each sample was analysed from the chimney interior to its exterior wall. Systematic trace element distribution across chimney zones is notable. As the result of the analysis performed using LA-ICP-MS, the chimney samples may be broadly divided into to three zones from external to internal considering the changes in the element values.

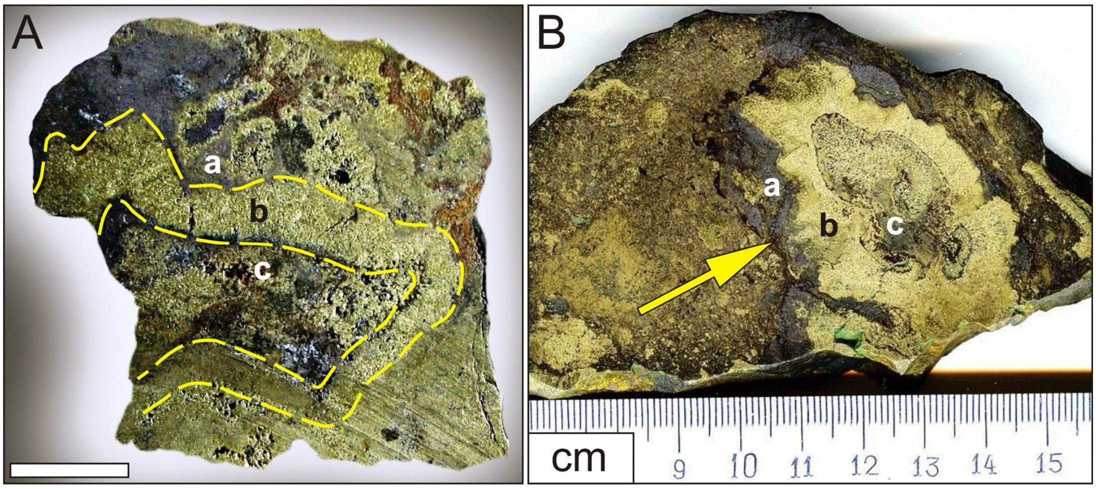

Fig.1. Photographs of paleo-chimney fragments. (A) The mineralogical zoning in the chimney sample of Killik mine. (B) Well preserved chimney from Lahanos mine. a – outer wall: b – inner zone: c – central zone. The scale bar is 2.0 cm.

Table.

The mineral associations in sulfides of chimney zones from the eastern Pontide VMS deposits

Mineral	Analytical Method			Deposit				
	TS	PS	MP	Cayeli	Kutlular	Lahanos	Killik	Kızılkaya
Barite ($BaSO_4$)	X	X		√	√	√	√	√
Bornite (Cu_5FeS_4),		X		√		√		√
Chalcopyrite ($FeCuS_2$)		X		√	√	√	√	√
Covellite (CuS)		X		√			√	√
Chalcocite (Cu_2S)				√				
Electrume		X						√
Fahlore		X					√	
Galena (PbS),		X		√	√	√	√	√
Gold (Au)		X		√	√	√		√
Hessite (Ag_2Te)		X	X			√		
Kawazulite $Bi_2(TeSeS)_3$			X			√		
Marcasite (FeS_2)		X		√			√	√
Pyrite (FeS_2)		X		√	√	√	√	√
Pyrrhotite (FeS)		X						√
Quartz (SiO_2)	X			√	√	√		√
Silver-sulfosalt		X					√	
Sphalerite (ZnS)		X		√	√	√	√	√
Tellurobismuthite (Bi_2Te_3)		X	X			√		
Tetrahedrite		X				√		
Tennantite		X		√		√		√
Wittichenite (Cu_3BiS_3)		X	X			√		

Analytical method being used to detect minerals are indicated. TS: thin section, PS: polished section, MP: microprobe.

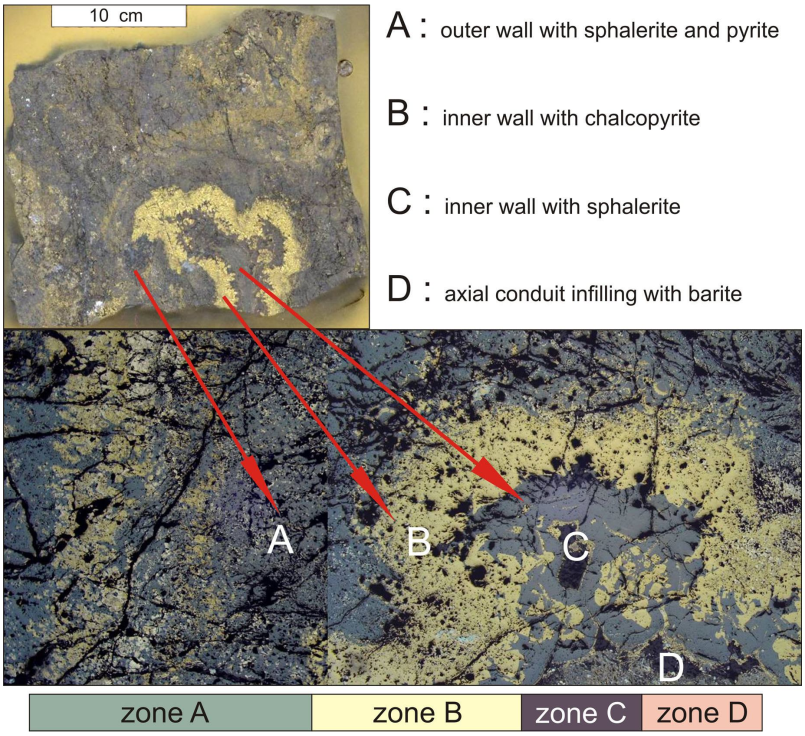

Fig.2. The mineralogical zoning in the chimney sample collected from Cayeli mine and their mineralogical contents (above). Close-up of the chimney walls shown above throught ore microscopy (below). See Fig. 1B for location of this chimney fragment.

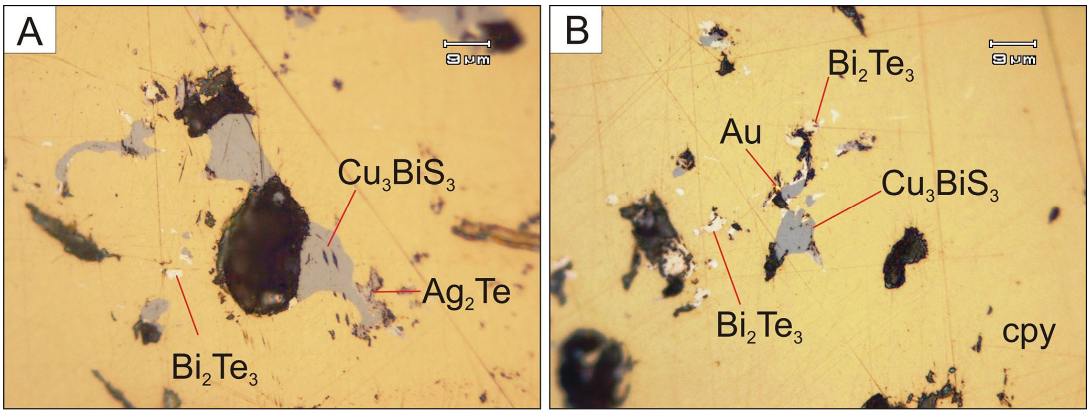

Fig.3. The rare minerals identified in the mineralized hydrothermal chimneys in Lahanos massive sulfide deposit. (A) Wittichenite (grey Cu_3BiS_3) – hessite (brown-grey Ag_2Te) in the inner zone. (B) Gold-wittichenite-tellurobismuthite (Bi_2Te_3) in chalcopyrite in the inner zone.

Some elements such as Ni, Co, Ag, Au, Mn, As, V and U are concentrated in the outer chimney wall (zone A). Co, Mn, Ag, V and U elements decrease through the zone B to the central zone C and Co, Ni and U elements remarkably decrease in the zone C. The high values of Sn (up to 760 ppm), Se (up to 407 ppm) and Te (up to 434 ppm) in the Zone B draw attention, especially where Cu concentrations exceed ~ 8 %. Gold is found in all chimney zones but has its highest concentrations (25 ppm) in zone A of chalcopyrite.

Se, Sn and Te elements enrich more than the other elements in the chalcopyrites in all zones. Average Se contents up to 39 ppm are present in the zone A, up to 236 ppm in the zone B, up to 188 ppm in the zone C. Average Te values up to 347 ppm are present in the zone A, up to 45 ppm in the zone B and up to 44 ppm in the zone C. When average Sn values are considered, it reaches up to 16 ppm in the zone A, to 48 ppm in the zone B and to 30 ppm in the zone C.

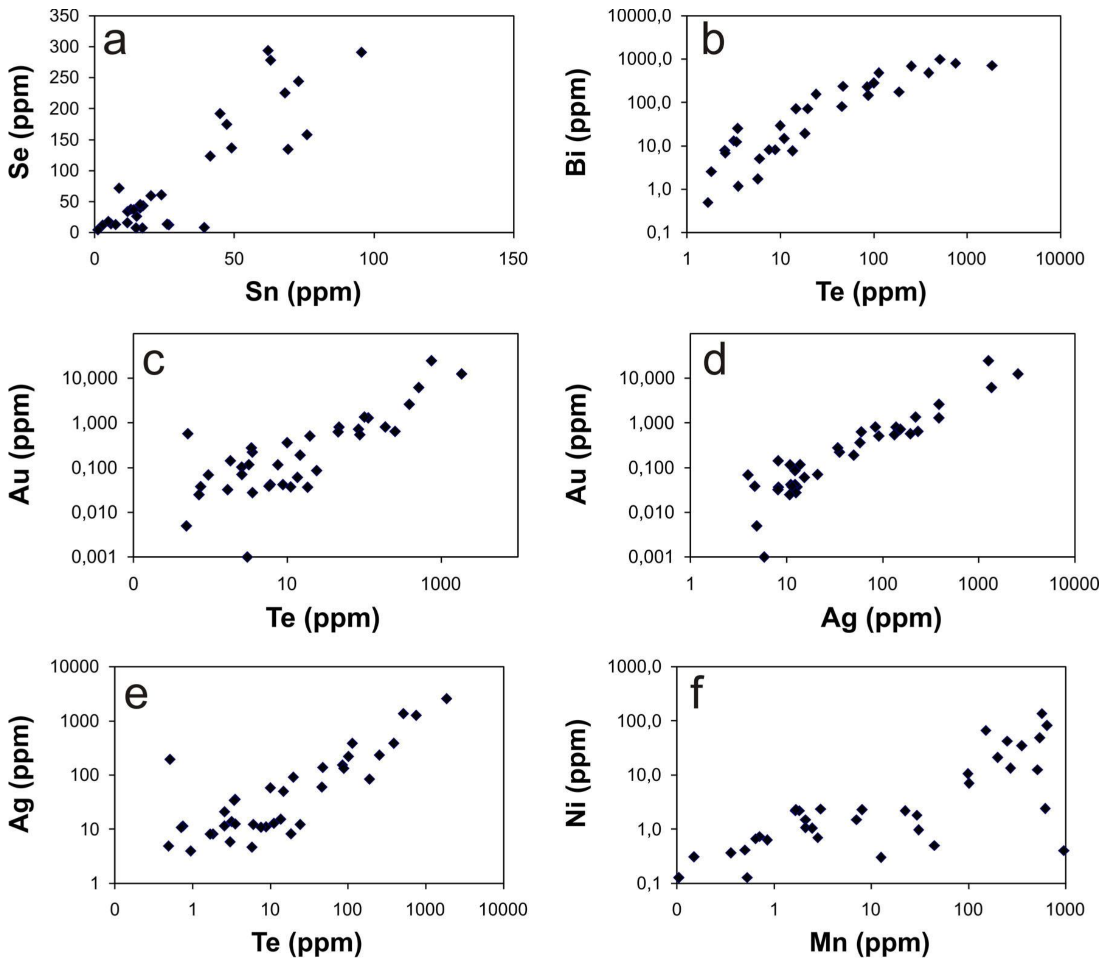

Fig.4. Chalcopyrite LA-ICPMS trace element correlations for Se-Sn, Bi-Te, Au-Te, Au-Ag, Ag-Te and Ni-Mn for the Cayeli chimney samples. Diamonds are analytical data points for chimneys.

Se contents reach up to 407 ppm in chalcopyrite. High level of Se in the inner zones of chimney supports the model of precipitation from a high temperature hydrothermal fluid. Tellurium contents (up to 1840 ppm) are also high in chalcopyrites from all zones, especially in zone A. Tin concentrations are high in chalcopyrite (Fig. 4a) and sphalerite compared with pyrite and reach 760 ppm in zone B. High Sn content is among the typical features of medium to high temperature sulfides from VMS deposits [Hannington et al., 1999].

The maximum Bi values, up to 1000 ppm, are noted in chalcopyrites of zone A. Elevated Bi concentrations also occur in sphalerite (up to 253 ppm) and pyrite (up to 729 ppm) of other zones. Bismuth is usually present in the high-temperature VMS assemblage while Te is typical in medium temperatures and Pb is common in the lower temperature assemblage [Hannington et al., 1999; Halbach et al., 2003]. Despite being characteristic of different temperature association there is a good correlation among these elements (Fig. 4b).

High Au and Ag concentrations occur in chalcopyrite and pyrite of zone A. It is observed that there is a positive correlation among Au, Ag and Te (Fig. 4c, 4d, 4e). This may be derived from the presence of hessite (Ag_2Te), electrum and other Ag-Te-Au bearing micro inclusions in chalcopyrites. When plotted of Mn against Ni, these element show positive correlations (Fig. 4f) and infer similar low-temperature and redox conditions [Maslennikov et al., 2009].

Discussion and conclusions

The sulfide chimney fragments exhibit a marked concentric mineral zoning. In the outer zone, main sulfides are pyrite and sphalerite with lesser amount of chalchopyrite. Sulfides within the inner zone consist predominantly of chalchopyrite with lesser pyrite and sphalerite. Axial conduit is commonly filled by barite gangue and with lesser amount of fahlore, sphalerite, chalchopyrite and galena. The chimney fragments are characterized by high metal content. Average Cu, Zn and Fe contents are

25.3 %, 20.7 % and 27.9 % respectively. Au concentrations in the zones of chimneys range from ~1 ppb to 25 ppm. Systematic trace element distribution across chimney zones is also notable. In general, Mn, Co, Ni, Tl, U and V are enriched in the outermost zones of chimneys and decrease towards interior zones. Elements indicative of high temperature conditions include Mo, Se, Sn and Cu and are generally enriched in the inner zones of chimneys.

Hydrothermal vent chimneys provide diagnostic evidence for sulfide accumulation at the sea floor and are of the products of rift (extensional) settings. They also provides strong evidence that VMS deposits formed on a deep-sea floor setting. Considering that present-day massive sulfides are situated near extentional zones [Francheteau et al., 1979; Hekinian et al., 1980; Haymon, 1983; Goldfarb et al., 1983; Qudin and Constantinou, 1984; Hannington et al., 2005] at depths >2500 m [Spiess et al., 1980; Qudin and Constantinou, 1984], it is essential that the depths in which hydrothermal black smoker chimneys formed should also be highly much. The same is true of ancient deposits. From this we may conclude that the VMS deposits of the eastern Pontide belt formed on a highly deep-sea floor and are attributed to extensional settings.

VMS deposits of the eastern Pontide belt are associated with rhyolitic to dacitic domes and show clear evidence of having formed on the seafloor. The presence of chimney fragments, fossil tube worms, sedimentary structures, exhalites and clastic nature of massive ores have provided distinctive evidence in support of a sea-floor origin for VMS deposits. Some chimney fragments display alteration rim indicating sea-floor oxidation. Alteration of these fragments implies that they laid on the sea floor for a long period and subjected to oxidation. Such an oxidation around chimney fragments and post-depositional modifications can be attributed to submarine alteration (halmyrolysis). It is clear that halmyrolitic processes such as oxidation, dissolution, hydration and resedimentation of disintegrated material [Maslennikov et al., 2012] were highly effective on Pontide paleo-oceans floor.

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FOSSIL FAUNA FINDINGS IN THE MASSIVE SULFIDE DEPOSITS OF THE EASTERN PONTIDE BELT, NORTHEAST TURKEY

В колчеданных месторождениях западной части Понтид изучены реликты придонных палеосообществ мелового возраста. Эти червеобразные формы организмов могут рассматриваться как предковые формы необычных придонных сообществ, обнаруженных в современных гидротермальных полях ВТП, Галапагоса и Хуан де Фука.

Introduction

Discovery of the communities living around the hydrothermal sulfur vents on the sea floor drew the interest of the researchers. Some of the most impressive of the unusual organisms are the tube worms which live in a symbiotic relationship with bacteria. Traces of these unique organisms living at present-day sea floor hydrothermal vents are rarely encountered in the massive sulfide paleohydrothermal fields. Since the discovery of hydrothermal venting along spreading centers, much has been learned about vent communites and associated sulfur deposits. But the findings and detailed studies on fossil fauna [Haymon et al. 1984; Banks, 1986; Kuznetzov et al. 1988; Little et al. 1997] are generally lacking. The possible ancient analogues of these fossil fauna living at present-day sea floor hydrothermal vents were described in the massive sulfide deposits in Cyprus, Urals, Oman and Ireland to date. Apart from above-mentioned VMS districs, Late Cretaceous Pontide massive sulfide deposits (Lahanos, Killik, Cayeli and Kutlular) are host to vent fossils (Fig. 1).

In the context of this study, VMS deposits in the eastern Black Sea region are included in massive sulfide districts in which findings of this unique fauna are found. The fossil fauna fragments (possibly fossil vestimentiferan tube worms) in the Pontide deposits are well-preserved in comparision to similar ones in the other massive sulfide districts.