Maslennikov, V.V., Maslennikova, S.P., Large, R.R., Danyushevsky, L.V. Study of trace element zonation in vent chimneys from the Silurian Yaman-Kasy volcanic-hosted massive sulfide deposits (the southern Urals, Russia) using laser ablation inductively coupled plasma mass spectrometry (LA-ICP MS) // Econ. Geology, 2009. Vol. 104. P. 1111–1141.

Maslennikov, V.V., Ayupova, N.R., Herrington, R.J., Danyushevsky, L.V., Large, R.R. Ferruginous and manganiferous haloesaround the massive sulphide deposits of the Urals // Ore Geology Reviews, 2012. Vol. 47. P. 5–41.

Okay, A.İ., Şahintürk, Ö. Geology of the eastern Pontides. *In*: Robinson A.G. (ed.) Regional and Petroleum Geology of the Black Sea and Surrounding Regions // American Association of Petroleum Geologist Memoirs, 1997. Vol. 68. P. 291–311.

Qudin, E., Constantinou, G. Black smoker chimney fragments in Cyprus sulphide deposits // Nature, 1984. Vol. 308. P. 349–353.

Revan, M.K. Determination of the typical properties of volcanogenic massive sulfide deposits in the eastern black sea region // Unpub. Ph.D. thesis. Ankara, Hacettepe Univ., 2010. 320 p. [in Turkish].

Scott, S.D. Small chimneys from Japanese Kuroko deposits // In: Seminars on seafloor hydrothermal systems (eds. R.Goldie, T.J. Botrill). Geosci. Can., 1981. Vol. 8. P. 103–104.

Spiess, F.N., Mcdonald, K.C., Atwater, T., Ballard, R., et al. East Pacific Rise: Hot springs and geophysical experiments // Science, 1980. Vol. 207. P. 1421–1433.

Şengör, A.M.C., Yılmaz, Y. Tethyan evolution of Turkey: A plate tectonic approach // Tectonophysics, 1981. Vol. 75. P. 181–241.

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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.

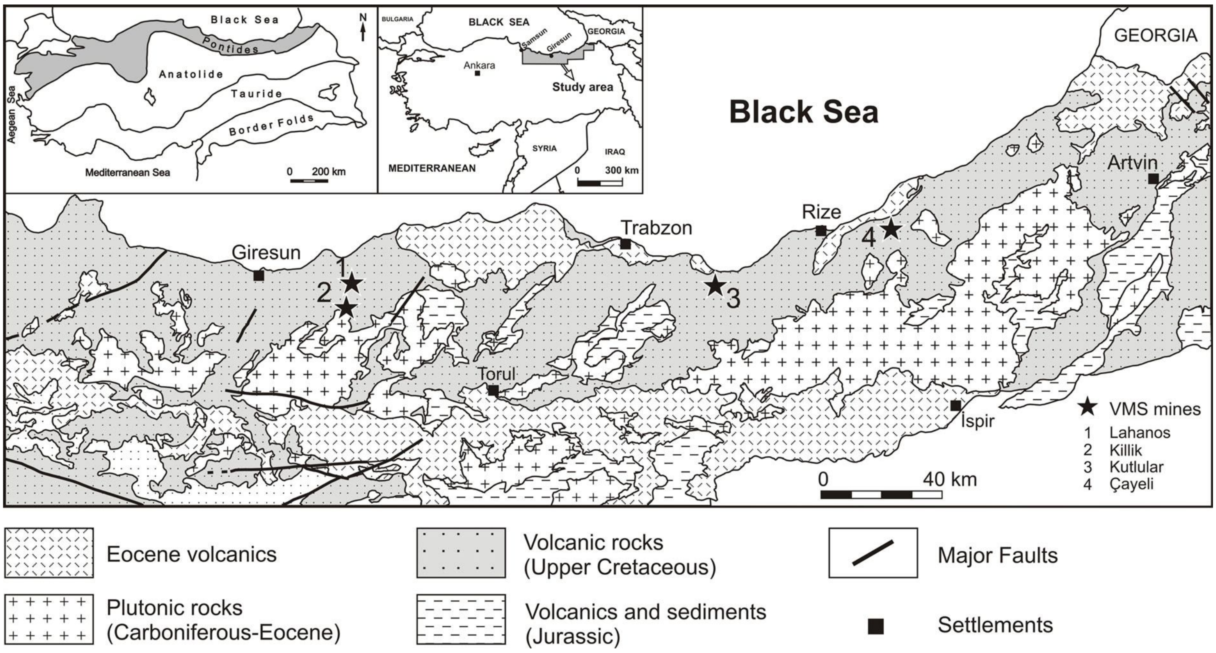

Fig. 1. Site location and simplified regional geologic maps of fossil fauna-bearing VMS deposits in the eastern Black Sea region.

Geologic features of VMS deposits

A large number of bimodal felsic VMS deposits and prospects are located in the northeastern part of the Pontide belt. The basement rocks of the Pontides consist of Devonian to Carboniferous metamorphic rocks such as gneiss and schist, and Paleozoic intrusive granitic rocks. The predominantly volcanic rocks with various age overlie the basement rocks. The coastal area of the eastern Black Sea is overwhelmingly composed of Upper Cretaceous to Paleocene volcanic and volcaniclastic rocks. Upper Cretaceous volcano-sedimentary sequences host volcanogenic massive sulfides, whereas Eocene volcanics host vein type deposits in the district.

Pontide VMS deposits are formed within volcanic-dominated sequences in deep seawater setting and hosted in a thick dacitic/rhylolite succession containing lavas, hyaloclastites and sub-intrusions. These deposits are commonly overlain by andesite, basalt, dacite and volcano-sedimentary sequence and located at the top contact of the dacitic/rhyolite successions or within the lower part of overlying sequence. Associated sediments are composed of deep seawater cherts, some of which are chemical sediments/exhalites and fossiliferous mudstones [Revan, 2010]. All the known VMS type deposit are hosted by Upper Cretaceous K?z?lkaya formation which is characterized by predominant dacitic volcanics.

Sample descriptions

All of the fossil fauna fragments described in massive sulfide deposits (Cayeli, Killik, Lahanos and Kutlular) are found in the clastic (brecciated) sulfide ores together with black smoker chimney fragments. The dimentions of the fossil tube worm traces defined in the Lahanos, Killik, Kutlular and Cayeli deposits reach up to 25 mm in diameter and 8 cm long (Fig. 2). The well preserved fossil fragments typically have distinct mineralogical zoning. Fossil tube worms were usually replaced by opaque and gang mineral (mostly barite) from the exterior to the interior while inside of which are filled with sulfide clasts such as pyrite, sphalerite, chalcopyrite and galena.

Mineralized fossil tubes are abundant in Lahanos mine and were preserved in a brecciated sulfide matrix consisting mainly of pyrite and sphalerite. In a sample from Lahanos, much of tube worm is infilled with barite (Fig. 3, Fig. 5a). Another sample contains only barite in the outer sections while the inner sides contain sulfide minerals (pyrite, chalcopyrite, covellite, sphalerite) as well as barite.

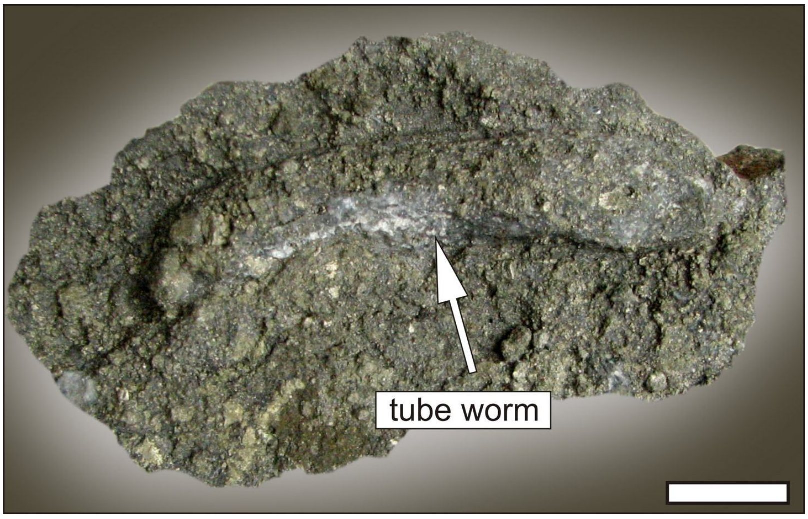

Fig. 2. A well preserved form of tube fossil in the eastern Pontide belt. Sample from the Killik deposit with clastic sulfide ore. Scale bar is 2 cm.

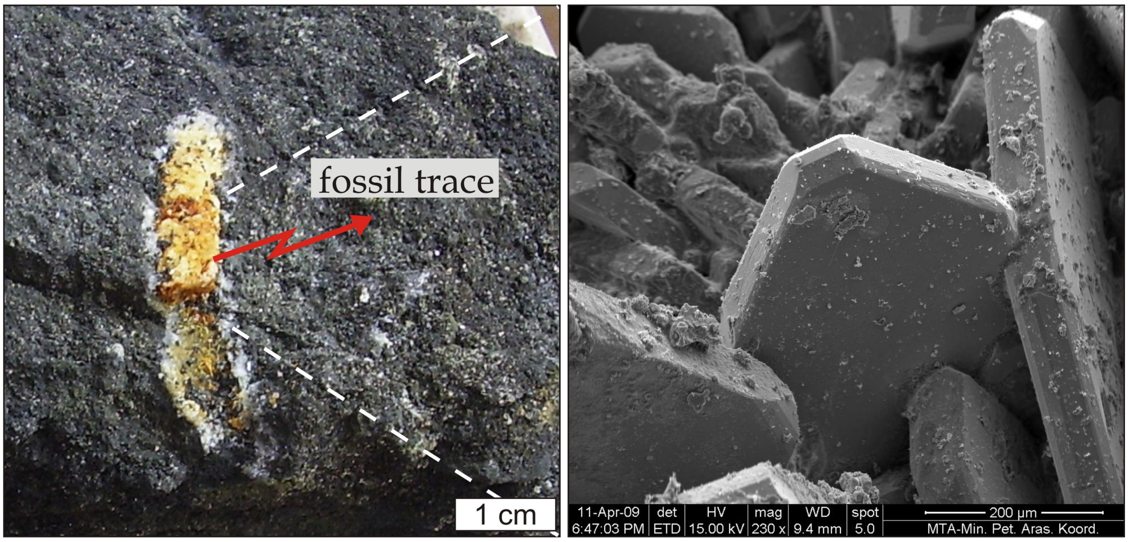

Fig. 3. SEM image of barite minerals from fossil tube worm replaced by sulfate and sulfide minerals. Sample is from clastic sulfide ore zone of Lahanos deposit.

In some samples from Lahanos mine, the existence of secondary minerals such as goethite [FeO(OH)], serpierite [$Ca(Cu,Zn)_4(SO4)_2(OH)_6.3(H_2O)$], native sulfur [S] and jarosite [$KFe_3(SO4)_2(OH)_6$] and dolomite [$CaMg(CO_3)$] in amounts that cannot be differentiated by microscope, has been detected by Raman Spectrometry.

In Killik mine, some tube walls are formed of predominantly silica and have infillings of barite and silica (Fig. 4, Fig. 5b). The restricted number of samples which appeared to be fossil fauna fragments were preserved in clastic sulfide ore of Kutlular and Cayeli deposits.

Discussion

Modern hydrothermal vent fields leading to massive sulfide accumulations are favorable sites for unusual vent faunas that depend on the vent fluid for their energy [Tunnicliffe et al. 1998]. In this complex environment, hydrosulfiric conditions which are inconvenient for the survival of many other organisms are dominant. The organisms that survive in such a environment have such special living conditions that is almost impossible for them to maintain their lives in other environments. Some of the unique fauna that survive in such a environment are tube worms which live in a symbiotic relationship with bacteria. The possible ancient analogues represented by tubular worm relics of this unique fauna living at present-day sea floor hydrothermal vents were discovered for the first time in the Sibay

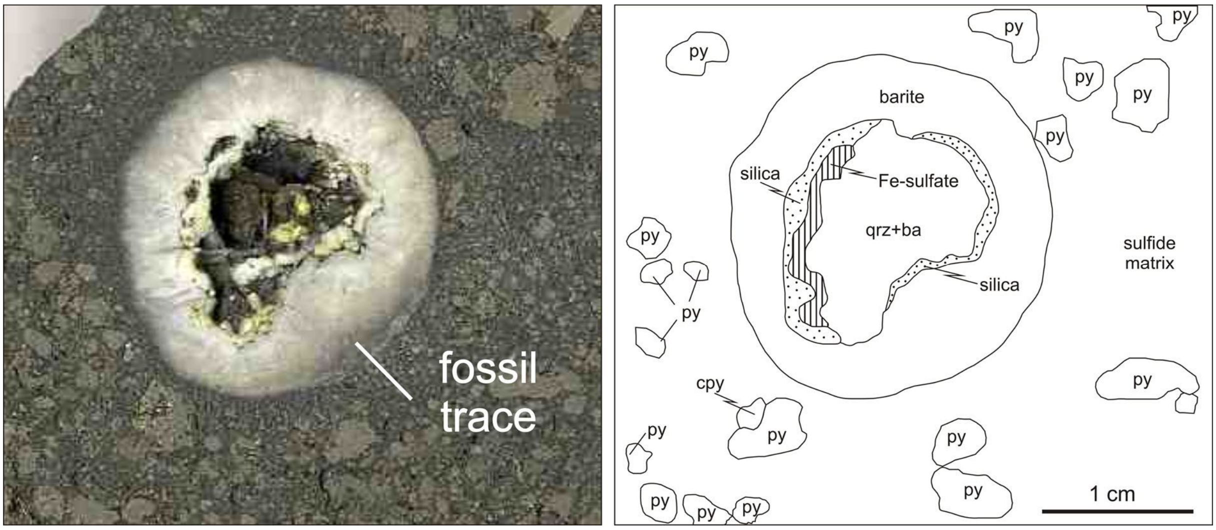

Fig. 4. A tube worm relic, having infillings of barite and silica in clastic sulfide ore of Killik deposit (py – pyrite; cpy – chalcopyrite; qrz – quartz; ba – barite).

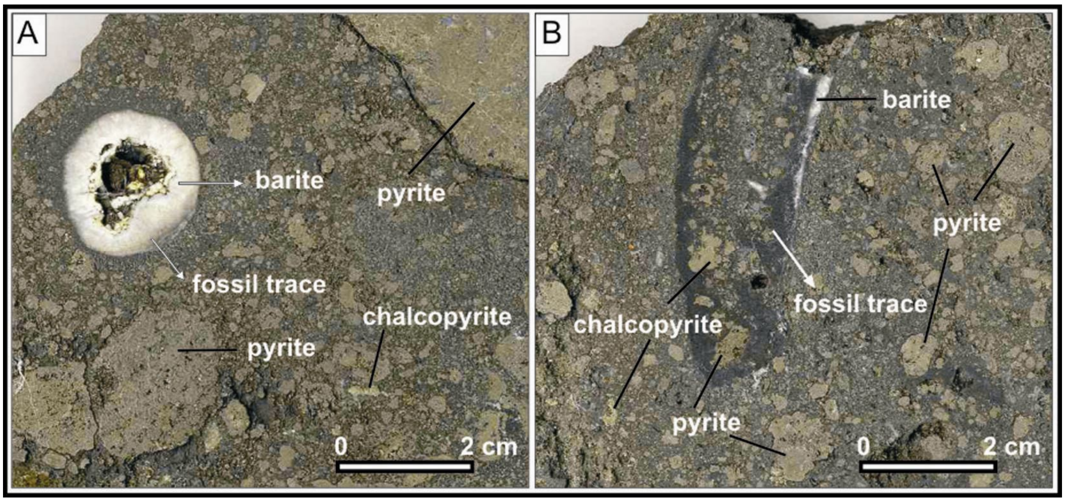

Fig. 5. Photographs representative of the various tube worm traces. Fossil tube worm trace replaced by the various sulfide minerals within the clastic sulfide ore of Killik deposit (A) and Lahanos mine (B).

deposit by Ivanov [1947]. Later, the similar fossil findings were defined in VMS deposits of Oman, Cyprus, Ireland, Alaska and Urals [Haymon et al., 1984; Qudin and Constantinou, 1984; Banks, 1985; Moore et al. 1986; Maslennikov, 1991; Kuznetzov et al., 1993; Zaykov et al., 1995]. Traces of fossil tube worms are also present in Late Cretaceous Pontide VMS deposits. The fossil fauna fragments described in Pontide deposits are well-preserved in comparision to similar ones in the other massive sulfide districts and associated with hydrothermal sulfide chimney fragments.

The fossil tube worms are diagnostic of sea-floor sulfide accumulation and their existence in sulfide ore bodies suggest that Pontide VMS deposits are remnants of Cretaceous sea-floor hydrothermal vent fields. The fossil fauna findings have not received systematic treatment because there are only 4 known fossilliferous VMS deposits in Pontide belt. The massive sulfide deposits probably host diverse fossil vent assembledge. Thus, much more detailed studies should be done in the belt.

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References

Banks, D.A. A fossil hydrothermal worm assemblage from the Tynagh lead-zinc deposit in Ireland // Nature, 1985. Vol. 313. P. 128–131.

Haymon, R.M., Koski, R.A., Sinclair, C. Fossils of hydrothermal vent forms discovered in Cretaceous sulfide ores of The Semail ophiolite, Oman // Science, 1984. Vol. 223. P. 1407–1409.

Ivanov, S.N. Study experience of geology and mineralogy of the Sibay massive sulphide deposit // Akademia Nauk SSSR, Uralskiy Filial, 1947. Vol. 2. P. 1–109 [in Russian].

Kuznetzov, A.P., Maslennikov, V.V., Zaikov, V.V., Sobetskii, V.A. Fosil fauna in the sulfide hydrothermal hills from the middle Devonian paleo-ocean of the Ural area // Doklady Akademii Nauk SSSR, 1988. Vol. 303. no. 6. P. 1477–1489 [in Russian].

Kuznetzov, A.P., Maslennikov, V.V., Zaikov, V.V. The near hydrothermal fauna of the Silurian paleoocean in the South Ural // Izvestia Akademii Nauk SSSR. Seria Biologicheskaya, 1993. no. 4. P. 525–534 [in Russian].

Little, C.T.S., Herrington R.J., Maslennikov, V.V., Morris, N.J., Zaykov, V.V. Silurian high temperature hydrothermal vent community from the Southern Urals, Russia // Nature, 1997. Vol. 385, no.9. P. 146–148.

Maslennikov, V.V. Lithological control of copper massive sulfide ores (after the example of Sibai and Oktyabrskoye deposits, Ural). Sverdlovsk, UB AN USSR, 1991. 139 p. [in Russian].

Moore, D.M., Young, L.E., Modene, J.S., Plahuta, J.T. Geological setting and genesis of the Red Dog zinc-lead-silver deposit, western Brooks Range, Alaska // Economic Geology, 1986. Vol. 81. P. 1696–1727.

Qudin, E., Constantinou, G. Black smoker chimney fragments in Cyprus sulphide deposits // Nature, 1984. Vol. 308. P. 349–353.

Revan, M.K. Determination of the typical properties of volcanogenic massive sulfide deposits in the eastern black sea region // Unpub. Ph.D. thesis. Ankara, Hacettepe Univ., 2010. 320 p [in Turkish].

Tunnicliffe, V., McArthur, A.G., McHugh, D. A biogeographical perspective of the deep-sea hydrothermal vent fauna // Advances in Marine Biology, 1998. Vol. 34. P. 353–442.

Zaykov, V.V., Shadlun, T.N., Maslennikov, V.V., Bortnikov, N.S. Yaman-Kasy sulfide deposits – ancient "black smoker" of Urals paleoocean // Geology of ore deposits, 1995. Vol. 37. P. 511–529.

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MAGNETIC FIELD EFFECT ON FRACTIONATION OF CARBON ISOTOPES IN THE REACTION OF $Ca(OH)_2$ WITH AIR CARBON DIOXIDE

Проведена серия экспериментов по изучению влияния магнитного поля на изотопный состав углерода в карбонате кальция, образующемся при взаимодействии $Ca(OH)_2$ с углекислотой воздуха. Изучение изотопного состава углерода образцов $CaCO_3$, синтезированных в магнитном поле и вне поля, показало, что под воздействием магнитного поля происходит обогащение карбоната кальция изотопом ^{13}C. Различия в величинах $\delta^{13}C$ достигает 14 ‰, PDB. Область максимального обогащения тяжелым изотопом углерода располагается там, где магнитное поле имеет максимальную напряженность. Вне зависимости от величины напряженности магнитного поля все изученные образцы имеют существенно облегченный изотопный состав по сравнению с изотопным составом углерода в углекислом газе атмосферы.

The nuclear spin (magnetic) isotope effect was discovered by A.L. Buchachenko and coworkers in 1976 [Buchachenko et al, 1976]. In the present work, we revealed for the first time the magnetic field effect on the carbon isotope composition in the course of formation of an inorganic compound, calcite $CaCO_3$. The experiments on studying the magnetic field effect on the carbon isotope fractionation during formation of calcite were carried out by the following scheme.

$$CaCO_3 \rightarrow CaO+CO_2\uparrow \rightarrow CaO+H_2O \rightarrow Ca(OH)_2 + CO_2(air) \rightarrow CaCO_3.$$

In all experiments, two plates with calcium hydroxide were used simultaneously. One of them was placed in the magnetic field, another, control one, was out of the field. The plates were disposed perpendicular to Earth's magnetic field.

In the first run, the plate with $Ca(OH)_2$ was placed in the field of a permanent magnet, which was located on the edge of the plate. The isotopic compositions at different distances from the magnet were determined in 500 h. The $\delta^{13}C$values at distances equal to 0.5, 1, and 2 cm from the magnet were –22, –26, and –27‰, respectively. The isotopic composition of $Ca(OH)_2$ on the control plate was $\delta^{13}C$ = – 26.65‰, PDB. A similar result was obtained when $Ca(OH)_2$ was applied to a steel plate not exposed to the magnetic field.