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Neotethyan rifting-related ore occurrences: study of an accretionary mélange complex (Darnó Unit, NE Hungary)

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Abstract: The geology of the NE Hungarian Darnó Unit is rather complicated, as it is composed mostly of a Jurassic accretionary mélange complex, according to the most recent investigations. The magmatic and sedimentary rock blocks of the mélange represent products of different evolutionary stages of the Neotethys; including Permian and Triassic sedimentary rocks of marine rifting related origin, Triassic pillow basalt of advanced rifting related origin and Jurassic pillow basalt originated in back-arc-basin environment. This small unit contains a copper-gold occurrence in the Permian marly-clayey limestone, an iron enrichment in the Triassic sedimentary succession, a copper-silver ore occurrence in Triassic pillow basalts and a copper ore indication, occurring both in the Triassic and Jurassic pillow basalts. The present study deals with the Cu(-Ag) occurrence in the Triassic basalt and the Fe occurrence in the Triassic sedimentary succession. The former shows significant similarities with the Michigan-type mineralizations, while the latter has typical characteristics of the Fe-SEDEX deposits. All the above localities fit well into the new geological model of the investigated area. The mineralizations represent the different evolutionary stages of the Neotethyan rifting and an epigenetic, Alpine metamorphism-related process and their recent, spatially close position is the result of the accretionary mélange formation. Thus, the Darnó Unit represents a perfect natural laboratory for studying and understanding the characteristic features of several different rifting related ore forming processes.

Keywords: hydrothermal processes, submarine basalt, pelagic sedimentary rocks, Michigan-type copper, SEDEX iron, fluid inclusion study, EPMA analyses.

Introduction

Understanding and interpretation of the complex geology of the NE Hungarian Darnó Unit (Fig. 1.) was constantly changing according to the prevailing structural theories until the past decade. According to the recent investigations, it is composed mostly of a Jurassic accretionary mélange complex, with a great variety of rock types in complex geological structures. The magmatic and sedimentary rock blocks of the mélange represent products of different evolutionary stages of the Neotethys; including Permian and Triassic marine sedimentary rocks of rifting related origin, Triassic pillow basalt of advanced rifting related origin and Jurassic pillow basalt of back-arc-basin opening related origin (see e.g. Aigner-Torres & Koller 1999; Dimitrijević et al. 2003; Haas & Kovács 2001; Harangi et al. 1996; Kovács et al. 2008; Kiss et al. 2010, 2012). Several ore indications occur in this small (about 10 km^2) structural unit, though until recent times, they were poorly investigated, due to the uncertainties about the geological background.

A copper-(Au) occurrence in the Permian marly-clayey limestone, an iron enrichment in a sedimentary succession, a copper-(Ag) mineralization in pillow basalt series and an epigenetic copper ore indication, occurring both in the Triassic and Jurassic pillow basalt series were also recognized in this unit (Papp 1938; Mezősi & Grasselly 1949; Kiss 1958; Baksa et al. 1981), besides a few ore mineralogical specialities (e.g. Co minerals in a drillcore sample, É. Hartai pers. comm.). Two of the mineralizations were recently studied in details (Kiss & Zaccarini 2013; Molnár et al. 2015), while the copper-(Ag) occurrence in the pillow basalt series and the iron occurrence in the sedimentary succession have not been investigated with state-of-the-art methodology. Therefore, the relationship of the different ore occurrences, as well as their association with the complex geology of the region was never studied before. Hence, this study has double aims; one is the detailed characterization of previously neglected occurrences, while the other is their placement into the regional geological context.

Geological background

Regional and local geology

The ca. 10 km^2 area of the Darnó Hill is found in NE Hungary, about 15 km to the NW from the city of Eger (Fig. 1). The hill forms a part of the Darnó Unit, which is interpreted as a part of the Bükk Unit, within the Pelso Unit of the ALCAPA Block (ALpine, CArpathian, PAnnonian; Csontos 1995; Schmid et al. 2008). The Bükk Unit is composed of four nappes, of which the Darnó Unit, containing Triassic

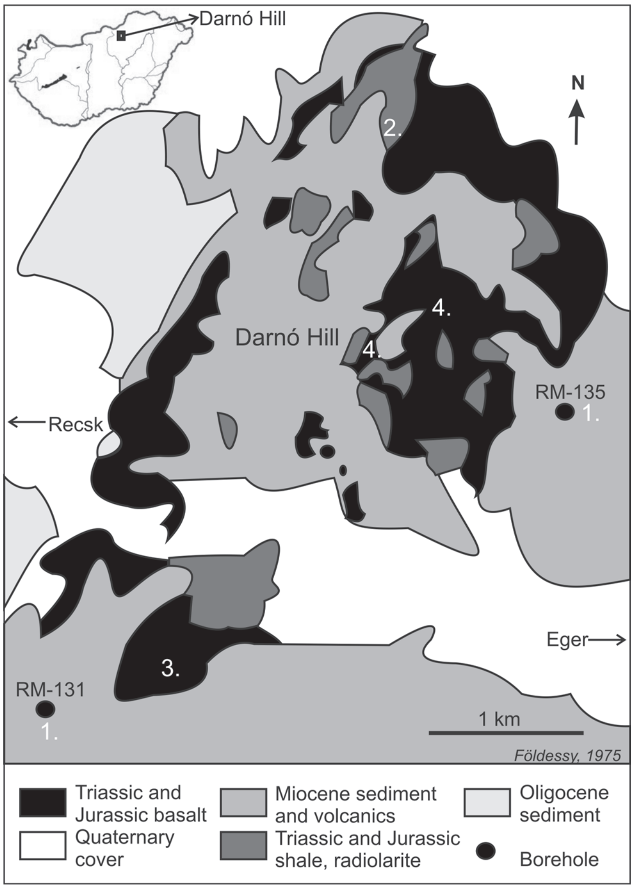


Fig. 1. Simplified geological map of the studied area (based on Földessy 1975) and its location in Hungary. The numbers refer to the studied locations, the ore occurrences observed on the Darnó Hill (**1** — copper and gold ore occurrence in the Permian marly-clayey limestone; **2** — iron ore occurrence in the Triassic sedimentary succession; **3** — copper and silver ore occurrence in the Triassic pillow basalt series; **4** — copper ore indication in both the Triassic and the Jurassic pillow basalt series).

and Jurassic submarine basalts as well as sedimentary rocks, is located in the uppermost position. Below it, the Szarvaskő Unit is made up by a Jurassic incomplete ophiolitic sequence and related sediments. The Mónosbél Unit is found below the Szarvaskő Unit and is composed of Jurassic, redeposited slope sediments, while the lowermost positioned Bükk Parautochthon contains Paleozoic to Jurassic formations. Based on the recent tectonic models, the Bükk Unit can be correlated with the NW Dinarides, thus its magmatic rocks can be interpreted as dismembered fragments of the Dinaridic Ophiolites, which suffered 300–400 km displacement along the Mid-Hungarian Lineament (Aigner-Torres & Koller 1999; Csontos 1995, 1999; Dimitrijević et al. 2003; Haas & Kovács 2001; Harangi et al. 1996; Kovács et al. 2008; Kiss et al. 2010, 2012).

The origin of the Triassic and Jurassic magmatic rocks of the region was a question of debate in the past few decades. Uncertainty had been caused partly by contradictory petrological and geochemical evidences and partly by the scarcity of good outcrops in the Darnó Hill. In the case of the Triassic magmatites, origin was related to rifting and MOR events and geology correlated with the Inner-Western Carpathian (Meliata) and Northwestern Dinaridic units (see e.g. Balla et al. 1980; Downes et al. 1990; Dosztály & Józsa 1992; Harangi et al. 1996). While the Jurassic magmatites, however, were referred to back arc basin or marginal sea opening and correlated with the Dinaridic Ophiolite Zone as well as with the Vardar Zone (see e.g. Downes et al. 1990; Harangi et al. 1996; Aigner-Torres & Koller 1999). Extended research with up to date methodology has taken place in the region from the 2000s. According to the latest models, the Triassic submarine rocks are of Neotethyan advanced rifting origin. The formation of the Jurassic submarine succession is related most likely to marginal basin opening, while their common occurrence in the Darnó Unit is interpreted as a result of accretionary mélange formation during the evolution of the Neotethys (Kovács et al. 2008, 2010; Kiss et al. 2008, 2010, 2012; Haas et al. 2011).

Ore indications of the Darnó Hill

The unresolved geology of the Darnó Hill also led to the insecure interpretation of the genesis of the mineralizations. The afore mentioned deposits were already described and partly interpreted by a number of researchers (Papp 1938; Mezősi & Grasselly 1949; Kiss 1958; Baksa et al. 1981; Kiss & Zaccarini 2013; Molnár et al. 2015 and the references cited therein).

Native copper found south of the hill drew attention to the region in the middle of the 19^{th} century. Discovery was followed by the preparation of a 76 m long adit. The ore was found in calcite-laumontite veins of the basalt, but mining was never successful due to the irregular occurrence of the native copper grains and aggregates (Haidinger 1850; Lőw 1925; Papp 1938; Mezősi & Grasselly 1949). Kiss (1958) ruled out the earlier proposed Keweenawan-type origin of the ore and related the ore formation to epigenetic alteration processes. According to his study, the above mentioned quartz-prehnite-chalcopyrite veins found on the central part of the Darnó Hill represent the deeper, while the calcite-laumontite-native copper veins represent the shallower, more altered parts of the same hydrothermal vein system. In this study, Kiss (1958) also shed light on the hematite-bearing iron ore occurrence developed in continuum on the host, red radiolarite, found on the northern slopes of the hill and concluded on its exhalative origin. Recent studies by Kiss et al. (2013) proved the presence of weakly mineralized Kupferschiefer-type occurrence in the Permian marly-clayey limestone, while Molnár et al. (2015) ascertained epigenetic origin, related to the low-grade Alpine metamorphism, for the quartz-prehnite-chalcopyrite veins found in both the Triassic and Jurassic basalt blocks. The present research brings some novelty regarding the formation of the calcite-laumontite-native copper veins and the quartz-hematite occurrence. Therefore, this study contributes to our mineralogical, petrographical and ore geological knowledge on these localities, as well as to the better understanding of the connection between the ore occurrences and the local geology and draws the possible metallogenical conclusions.

Methods

Outcrops on the northern part of the Darnó Hill, and the ore exposed in an old adit on the southern part of the hill, were studied in detail. Sampling paid attention on the gangue and ore minerals as well as on their host rock and its alteration. Stereomicroscopic observations were carried out with an SM Lab2 type equipment, while polarized microscopic observations on polished standard thin and block sections were done using a Zeiss Axioplan microscope working with transmitted and reflected light. Fluid inclusion petrography was carried out on double polished, 100 μm thick sections with an Olympus-BH2 type microscope, while microthermometry measurements were performed with a Linkam FT-IR 600 type heating-freezing stage mounted on an Olympus-BX51 type microscope, providing magnification up to 1000×. Calibration of the stage was done by synthetic CO_2 and H_2O inclusions, allowing an accuracy of 0.1 °C below and 1 °C above 0 °C. The X-Ray Powder Diffraction (XRD) method was used to determine the clay minerals on oriented, air dried and ethylene glycol solvation samples, using a Siemens D-5000 type, Bragg–Brentano geometric diffractometer emission (Θ–Θ working method, Cu Kα (λ=0.154178 nm), secondary graphite crystal monochromator and scintillation detector). The interpretation of the data was done using EVA software. A PC controlled thermoanalytical instrument was used to determine the clay mineral and zeolite content more precisely. MOM Derivatograph Q 1500 D was used, with a heating rate of 10 °C/min, until 1000 °C, the sample was put in a corundum crucible. All of these measurements were completed at the Department of Mineralogy, Eötvös Loránd University. Raman spectroscopy analyses were performed on fluid inclusions in calcite at the Eötvös Loránd University Faculty of Science Research Instrument Core Facility, using a Horiba Yvon Jobin LabRAM HR 800 edge filter based confocal dispersive Raman spectrometer, with 800 mm focal length, coupled with an Olympus BXFM type microscope. During the 2×5 min long measurements, 784 nm emission of a frequency doubled Nd:YAG laser, 600 grooves/mm grating, 50 μm confocal aperture and 50× and 100× long working distance objectives were used. ICP OES analyses was carried out on a Jobin Yvon Ultima 2C type spectrometer, equipped with a monochromator at the Geological and Geophysical Institute of Hungary. Lithium borate was used to fuse the samples, while the detection limits are shown in Table 2. SEM+EDS analyses of the Cu-oxide bearing veins was carried out at the Department of Petrology and Geochemistry (Eötvös Loránd University) with an Amray 1830 scanning electron microscope, equipped with an EDAX PV9800 energy dispersive detector, operating at 20 kV accelerating voltage, 10 nA beam current and 50 nm beam diameter. Electron microprobe analyses of the native Cu were carried out at the University of Miskolc using a Jeol JXA-8600, equipped with a wavelength dispersive detector, operated at 20 kV accelerating voltage, 20 nA beam current and 1 μm beam diameter. The detection limits were the following for the studied elements: 0.049 wt. % for Cu, 0.277 wt. % for As and 0.085 wt. % for Sb. Electron microprobe analyses of hematite was performed at the Eugen F. Stumpfl Microprobe Laboratory (University of Leoben) using a Jeol Superprobe JXA-8200, equipped with a wavelength dispersive detector, operated at 15 kV accelerating voltage, 10 nA beam current, ~1 μm beam diameter. The counting time was 15 sec for the peaks and 5-5 sec for the background (except in the case of the Zn, where 20 sec and 10 sec were used, respectively). The detection limits are shown in Table 1. Determination of some fine-grained minerals found at the studied localities was also carried out with the above mentioned instruments in EDS mode. Calibration of both instruments was carried out with the help of natural and synthetic standards.

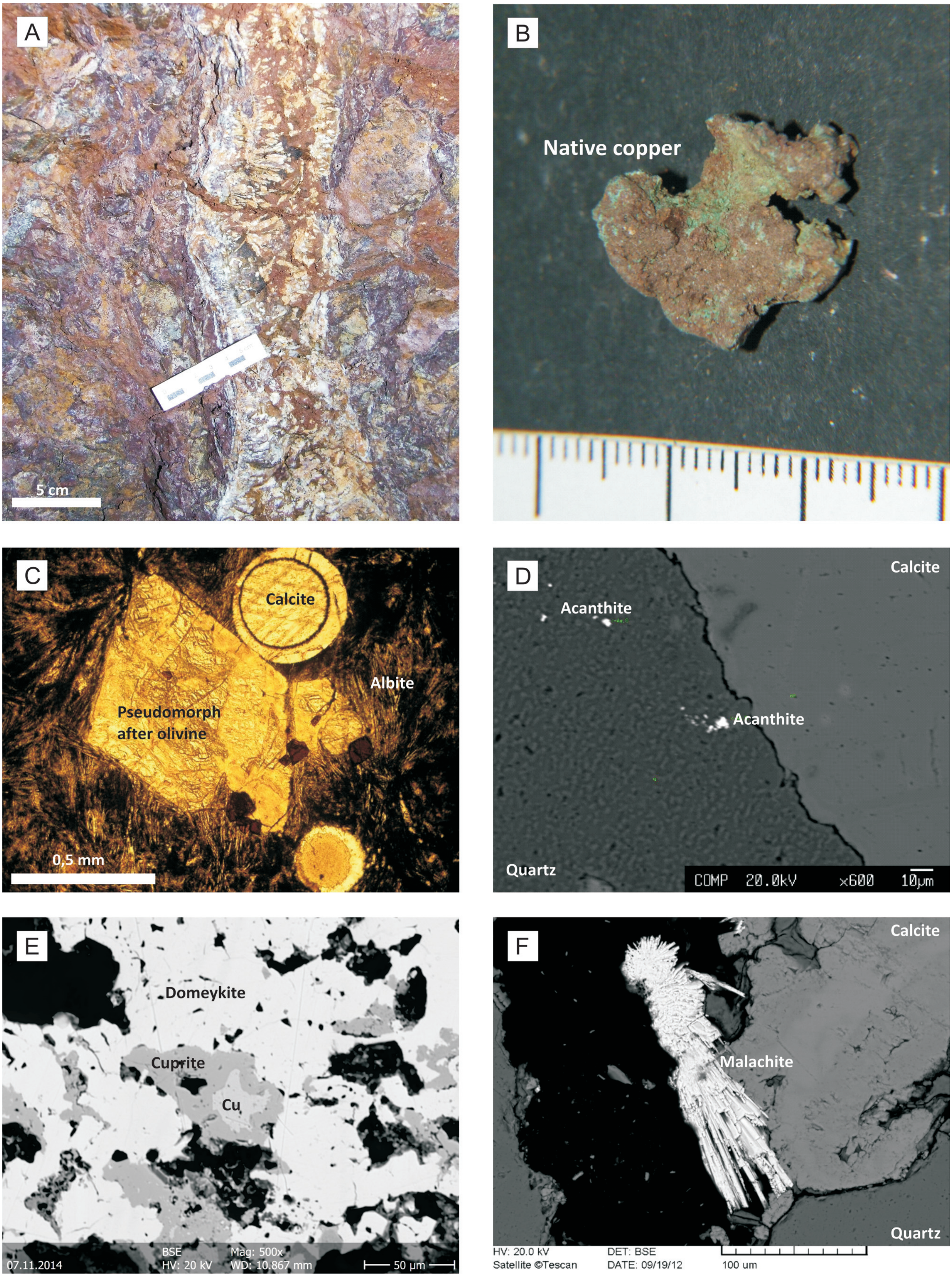
Results

The native copper bearing calcite-laumontite veins

Though several natural pillow basalt outcrops were studied in the valley of the Báj Brook (southern part of the Darnó Hill), the calcite-laumontite veins were found only in the old shaft and the adjacent, partly collapsed adit. The shaft is about 8 m deep and the connecting N-S running adit is about 15 m long, ending in a room, from which E–W running, ca. 10-10 metres long crosscuts (collapsed at the ends) are found. The NNW–SSE trending, 10–20 cm thick, nearly vertical dipping veins are traceable in the wall of the shaft, on the roof of the N–S adit and on the wall of the room (Fig. 2A). Coarse grained laumontite is placed along the walls of the vein, together with calcite and finer grained quartz. Coarse grained calcite and quartz with fine grained laumontite is found in the middle of the veins. Native copper (Fig. 2B) is most commonly found in this coarse grained calcite, while secondary Cu minerals are abundant in every part of the vein as well as in the host rock. The host rock is red, amygdaloidal, strongly altered pillow basalt with abundant jig-saw-fit and epigenetic veinlets and a high amount of inter-pillow hyaloclastite breccia. The younging direction of the pillows shows the effects of later tectonic movements.

Based on the microscopic observations, the host basalt is composed of glassy, microcrystalline, strongly hematitized ground mass (up to 50–70 %). Skeletal euhedral crystals of plagioclase (up to 30–40 %) and disseminated calcite, quartz, chlorite and clay minerals filled 0.2–1.2 mm sized pseudomorphs after olivine (Fig. 2C) occur in the rock. The size of the plagioclase crystals is up to 0.3 mm, the crystals are partly altered to clay minerals and their position highlights the sphaerolitic-variolitic texture of the basalt. The rock is rich in 0.15–0.7 mm sized calcite and rarely greenish smectite filled amygdales and cooling cracks. Jig-saw-fit veins, filled up by calcite, quartz and greenish smectite with a thickness up to 1.5 mm are present in places. The contact of the host rock and the 10–20 cm thick calcite-laumontite (epigenetic) veins is sharp, marked with strong hematitization and the presence of 1–3 mm thick auxiliary veins.

Two types of calcite occur in the veins, filling up to 70 vol. % of it. The 1–10 mm sized subhedral grains formed earlier, or together with euhedral coarse grained laumontite, while the 0.1–0.6 mm sized anhedral grains formed later,


A
5 cm
B
Native copper
C
Calcite
Albite
Pseudomorph
after olivine
0,5 mm
D
Calcite
Acanthite
Acanthite
Quartz
COMP 20.0kV ×600 10μm
E
Domeykite
Cuprite
Cu
07.11.2014
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HV: 20 kV
Mag: 500x
WD: 10.867 mm
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F
Calcite
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together and even after the zeolite and quartz formation. Up to 10 % of the veins is filled up by quartz, forming subhedral, 1–2 mm sized grains as well as later, fine grained anhedral crystals. Laumontite (up to 20 %) is generally strongly altered (to clay minerals and limonite), but phillipsite (up to 5 %) is more fresh and forms anhedral and subhedral grains up to 0.8 mm. Barite forms fine grained disseminated crystals occurring together with calcite and zeolites. Fine grained, disseminated hematite is a common opaque mineral, but up to 10 µm sized native silver in zeolite, Ag_sS (acanthite, based on optical characteristics) as inclusions within the quartz and as small grains among the quartz and calcite crystals and clay minerals, as well as galena in calcite and together with native copper were also identified by SEM+EDS. Up to 3 cm sized native copper aggregates were found in calcite, while copper oxides and carbonates, formed obviously as its alteration products, were observed disseminated together with all the veinfilling minerals. The native copper is composed almost exclusively of Cu (97.60–98.89 wt. %), no traceable As or Sb content was observed. Domeykite forms up to 50 µm grains, rimming the native copper aggregates (Fig. 2D, E, F).

More precise identification of the clay minerals was performed with derivatography and XRD analyses. The results supported the presence of laumontite and phillispite as well as revealing the occurrence of a dioctahedral, Ca and Al-bearing smectite, i.e. beidellite and montmorillonite.

Fluid inclusion study was carried out in order to determine the minimum formation temperature as well as the salinity of the mineral forming fluid. Both the coarser grained calcite and the finer grained anhedral calcite and quartz contain a high amount of secondary fluid inclusion planes, which makes the observations difficult. Only the early, coarse grained, subhedral calcite contains measurable primary fluid inclusions, occurring generally close to the rim of the crystals. The coarser grained quartz was not sufficiently transparent to identify the inclusions. The observed, generally 4–7 µm sized (rarely up to 15 µm) primary fluid inclusions were found independently from the secondary planes and they were characterized by a constant phase ratio of 5–10 area % vapour phase and 95–90 area % liquid phase, indicating a homogenous entrapment from a homogenous parent fluid. The phenomenon of metastability often hindered the observation of the final melting temperature, thus, the calculation of the salinity. The homogenization temperature (i.e. minimum formation temperature) was Th(LV-L)=81±14 °C (n=33), while the calculated salinity was 0.5±0.24 NaCl equiv. wt. % (n=11) (Fig. 3). Based on eutectic temperature observed at −21.8 °C and totally frozen inclusions at −45 °C, the thermodynamics of the system were modelled as a binary NaCl-H_2O system. No traceable gas content was found in the vapour phase of the inclusions by Raman spectroscopy observations.

The quartz-hematite occurrence

This mineralization was found in natural outcrops on the northeastern slopes of the Darnó Hill. Besides the quartz-hematite bearing samples, blocks of red radiolarite and red basalt (together with pinkish limestone) were identified in the vicinity. Due to the bad exposure and the mélange nature of the studied formation, the connection with the basalt cannot be clarified based on the surface mapping. The studied rock is composed of up to 5 mm sized grains of quartz and fine

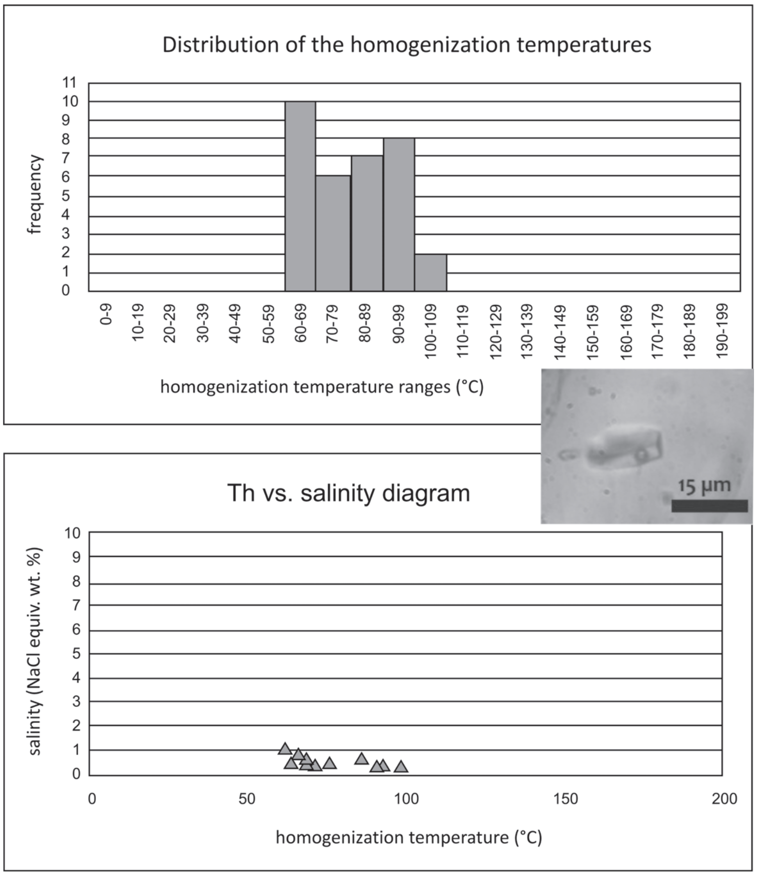

Fig. 3. Results of the fluid inclusion study performed on primary fluid inclusions of calcite of the Cu-Ag bearing samples (Báj Brook, S Darnó Hill).

Fig. 2. Textural features of the studied Cu-Ag bearing samples (Báj Brook, S Darnó Hill). **A** — texture of a vein, found at the end of the adit. The host basalt is strongly altered. **B** — native copper, found in one of the veins. **C** — typical textural features of the host basalt, with calcite filled amygdales, calcite and clay minerals filled pseudomorph after olivine and sphaerolitic-variolitic plagioclase (microphotograph, 1N). **D** — acanthite grains in quartz (BSE image). **E** — domeykite is surrounding the partly altered (to cuprite) native copper grain (BSE image). **F** — late, cavity filling malachite (BSE image).

grained hematite. The latter may form up to 4–5 mm sized patches, composed of 0.05-0.1 mm sized specular hematite flakes (Fig. 4A). A continuous change is observable from this quartz-hematite rock through hematitized siliceous sediment to the red radiolarite. Both rocks may be cut by later quartz veins.

Based on the microscopic observations, the host siliceous sediment is composed of fine grained quartz (up to 80 %) and hematite (<3 %) and up to 20 % bioclasts (0.1–0.2 mm recrystallized radiolarians and similar sized siliceous sponge spicules). This rock contains quartz filled cavities of 1–3 cm in diameter and it is cut and at some places even slightly brecciated by later quartz veins, which are 1–5 mm thick and contain exclusively up to 2 mm sized quartz crystals.

The hydrothermal quartz-hematite samples are composed of 5–20 % hematite, 5–20 % prehnite and up to 90 % quartz (Fig. 4B, C). The distribution of the different minerals is inhomogenous. The quartz forms anhedral to subhedral, generally 0.1–0.3 mm sized grains, though bigger crystals up to 5 mm may occur in cavities, too. The subhedral quartz may be characterized with growth zones, in which hematite inclusions may also occur. The anhedral to subhedral hematite forms up to 0.1 mm sized grains, often forming crystal aggregates. This hematite is often surrounded by anhedral prehnite grains of up to 0.05 mm size and eu- to subhedral elongated pumpellyite crystals of up to 0.05 mm size, both occurring together with the quartz. The SEM+EDS observations revealed the rare presence of Fe-Ti-oxides and Mn-oxides in the studied sections and the occurrence of 5–10 μm thin barite veinlets. The EPMA analyses of the hematite grains show that besides the 99.52–101.42 mass % Fe_2O_3, it contains generally 0.018–0.077 mass % MgO, 0.688–3.583 mass % Al_2O_3, 0.058–0.361 mass % MnO and 0.046–0.192 mass % V_2O_3, while rare measurements of Cr_2O_3 up to 0.050 mass %, ZnO up to 0.155 mass % and TiO_2 up to 0.199 mass % were also determined (Table 1).

In contrast with the findings of Kiss (1958), who described rocks with up to 87 mass % Fe_2O_3 content from the area, the whole rock ICP OES analyses of the studied samples revealed, that they contain 8.95–11.4 mass % Fe_2O_3 and 87.8–90.2 mass % SiO_2. Traces of Al_2O_3, MnO, CaO, Na_2O, SrO and a total metal content of 190–235 ppm (Co, Cr, Cu, Ni, Pb, V and Zn) were also observed (Table 2). The Fe_2O_3-SiO_2 (hematite-quartz) ratio was also proven by the XRD study.

Fluid inclusion study was carried out in order to determine the minimum formation temperature and the composition of the hydrothermal fluid. Quartz syngenetic with the hematite flakes indicated by the tiny hematite inclusions in its growth zones was examined. The crystals contain several secondary generations, but among those planes, rarely independent primary inclusions as well as primary inclusions in 3D clouds occur with a size of 4–10 μm. The growth zones of the quartz generally contain ~1 μm sized fluid inclusions, too, but in rare cases measurable sized (up to 10 μm) primary inclusions also occurred. All primary inclusions were trapped homogenously from a homogenous parent fluid, which is represented by a constant phase ratio of 5–10 area % vapour and 95–90 area % liquid phase. The phenomenon of metastability often hindered the observation of final melting temperatures, thus, only a few salinity data are available. The measured homogenization temperature was Th(LV-L)=70–155 °C (n=6) while the calculated salinity (based on the final mel-

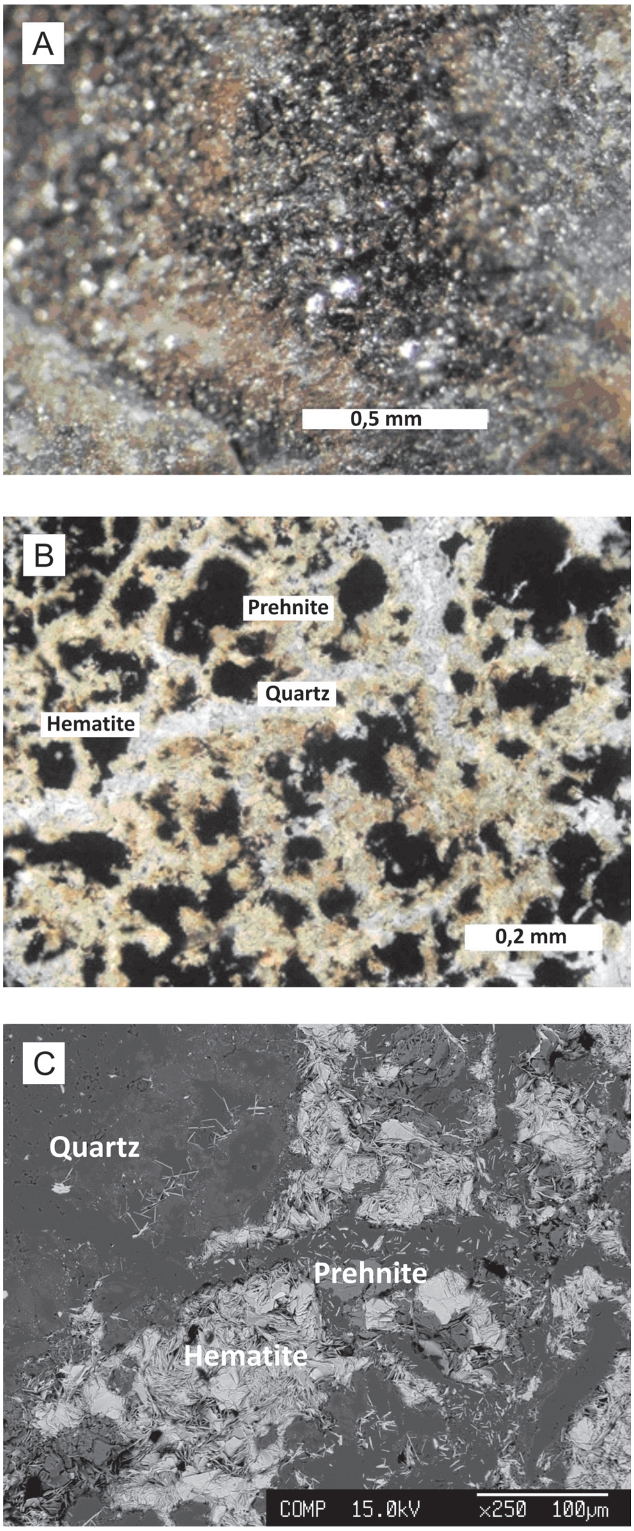

Fig. 4. Textural features of the studied Fe bearing samples (NE Darnó Hill). **A** — hematite flakes with quartz and prehnite. **B** — textural relation of the hematite, quartz and prehnite (microphotograph, 1N). **C** — inhomogenous distribution of the hematite flakes and the quartz, prehnite grains (BSE image).

Table 1: Results of the EPMA analyses of the studied hematite grains (NE Darnó Hill)

	MgO	Al_2O_3	Cr_2O_3	MnO	ZnO	TiO_2	V_2O_3	Fe_2O_3	Total
Detection limit	0.0189	0.0169	0.0361	0.0444	0.0624	0.0455	0.0374	0.0434	
1	0.048	3.583	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.109	101.135	104.875
2	0.035	0.838	0.05	0.058	0.07	b.d.l.	0.12	101.521	102.692
3	0.021	1.136	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.162	99.588	100.907
4	0.031	1.026	b.d.l.	0.106	b.d.l.	b.d.l.	0.071	99.420	100.654
5	b.d.l.	0.688	b.d.l.	0.361	0.148	0.083	0.072	101.991	103.343
6	0.028	1.119	b.d.l.	0.119	b.d.l.	0.108	0.056	100.187	101.617
7	0.049	1.126	b.d.l.	0.222	0.089	0.074	0.046	100.514	102.120
8	b.d.l.	0.746	b.d.l.	0.19	0.155	0.151	0.033	100.418	101.693
9	0.027	0.979	b.d.l.	0.147	b.d.l.	0.199	0.04	99.869	101.261
10	0.077	0.077	b.d.l.	0.335	b.d.l.	b.d.l.	b.d.l.	100.746	101.235
11	b.d.l.	0.831	b.d.l.	0.197	b.d.l.	0.125	0.072	100.764	101.989
12	0.018	0.843	b.d.l.	0.268	b.d.l.	0.076	0.087	100.490	101.782
13	1.767	0.254	b.d.l.	1.721	0.202	23.477	0.236	71.187	98.844

Results are given in mass %. **b.d.l.** — below detection limit.

Table 2: Results of the ICP OES analyses of the quartz-hematite samples (NE Darnó Hill)

	Detection limit	Sample 1	Sample 2
SiO_2	0.05	87.8	90.2
TiO_2	0.02	b.d.l.	b.d.l.
Al_2O_3	0.1	0.159	0.159
Fe_2O_3	0.03	11.415	8.955
MnO	0.003	0.021	0.015
CaO	0.03	0.088	0.175
MgO	0.15	b.d.l.	b.d.l.
Na_2O	0.03	b.d.l.	0.100
K_2O	0.2	b.d.l.	b.d.l.
P_2O_5	0.15	b.d.l.	b.d.l.
SO_3	0.15	b.d.l.	b.d.l.
BaO	0.005	b.d.l.	b.d.l.
SrO	0.0002	0.0003	0.0003
^-H_2O	0.01	0.05	0.05
LOI	0.01	0.33	0.27
Co	0.5	40.4	88.2
Cr	0.5	18.1	12.0
Cu	0.5	16.9	8.6
Ni	1.0	19.8	15.9
Pb	1.5	5.0	b.d.l.
V	2.5	97.4	12.8
Zn	0.25	37.2	51.8

Results are given in mass % for the major and minor elements (above the thick line) and in ppm for the trace elements (below the thick line). **b.d.l.** — below detection limit.

ting temperature of ice) was 3.87–4.34 NaCl equiv. wt. % (n=2). Though no eutectic temperature was observed, the system was modelled in a NaCl-H_2O system, as all the inclusions were totally frozen by −45 °C.

Discussion

The native copper bearing calcite-laumontite veins

In the early study of Haidinger (1850), diorite was identified as the host rock of this occurrence. However, a later study by Lőw (1925) has found, that the veins occur in diabase, though the age was still not determined. Modern research by Kiss et al. (2010) revealed that both Triassic and Jurassic basaltic occurrences are known on the surface in the Darnó Hill and collected their distinguishing features. Comparing the typical textural features written above, with the typical characteristics described by Kiss et al. (2010), the host rock is most likely a Triassic basalt of rifting-related origin. Kiss et al. (2012) have also shown, that this basalt bears a within-plate basalt geochemical signature and formed in shallow-marine conditions.

The observed mineral paragenesis (calcite, laumontite, phillipsite, quartz, barite, native copper and silver, acanthite, domeykite and galena and their alteration products) is not the typical mineral assemblage of volcanogenic massive sulphide deposits formed by submarine hydrothermal processes (see e.g. Shanks & Thurston 2012). Furthermore, the measured fluid characteristics are significantly different from those found in the primary hydrothermal minerals of the Darnó Unit (Kiss et al. 2008, 2012; Fig. 5). These features draw attention to the fact, that the studied mineralization was most likely not related to the primary submarine processes. The occurrence of domeykite and some other mineralogical and textural features corroborates origin from some kind of hydrothermal processes (Ramdohr 1969).The alteration characteristics of the host rock (e.g. intensive hematitization) suggest an oxidative and slightly acidic environment for the beginning of the ore forming processes. This allows Cu, Ag and Pb to form chlorocomplexes, which means that they are collected from the host basalt, dissolved in a hydrothermal fluid. The mineral precipitation sequence of the veins (Fig. 6) shows that the conditions became more and more reducing. This allowed the precipitation of native copper and silver and the early gangue minerals. Later, reaching neutral pH and redox conditions, the precipitation of sulphides and arsenides could happen, together with gangue minerals (Fig. 7). Cooling of the hydrothermal fluid resulted in the precipitation of late calcite and phillipsite (forms generally between 65–85 °C), followed by the formation of different alteration products (clay minerals, Cu-oxides, Fe-oxides, -hydroxides and Cu-carbonates) (Barton & Skinner 1967; Brown 2006; Hanor 2000; Deer & Howie 2004; Pirajno 2009).

The epigenetic mineral paragenesis is characteristic of the zeolite facies metamorphism, which happens generally at 200–270 °C temperature and 150–250 MPa pressure (Ivanov & Gurevich 1975). Using this approximation, pressure correction on the fluid inclusion microthermometry data suggests formation temperature of 140–200 °C (Fig. 8). This is in good agreement with the presence of acanthite, which forms below 173 °C (Ramdohr 1969) and laumontite, which forms generally between 90–190 °C (Deer & Howie 2004). Although these metamorphic-hydrothermal conditions are presumed, no gas content was identified by Raman spectroscopy and the observed low salinity values assume the possibility of mixing with meteoric water.

Similar typical Cu, Ag and As bearing mineral assemblage in red amygdaloidal basalt was described by several authors (e.g. Butler & Burbank 1929; Heinrich 1976; Lefebure & Church 1996; Brown 2006; Bornhorst & Barron 2011 and the references cited therein) on the Keweenaw Peninsula, Michigan, USA. There the mineralization is related to rifting related subaerial to shallow marine basalt, which suffered sub-greenschist (typically zeolite) facies metamorphism. According to the genetic model of Brown (2006), the basaltic Michigan-type copper ore formation is related to the evolution of an epigenetic, mixed metamorphic and meteoric hydrothermal fluid, which steadily accomodates its original oxidative and acidic characteristics to neutralizing conditions. Although originally Precambrian deposits were classified as Michigan-type, nowadays Phanerozoic examples are also known (e.g. in Central-Iran, Nezafati et al. 2005).

In the case of the studied Darnó Hill occurrence, not only the ore and gangue mineral paragenesis shares similarities with the above mentioned deposit type, but also the tectonic setting (rifting related, shallow marine conditions), the observed metamorphic facies (zeolite), the formation temperature (within the typical range of 150–250 °C) and the evolution of the hydrothermal fluid are also analogous. Therefore, based on the

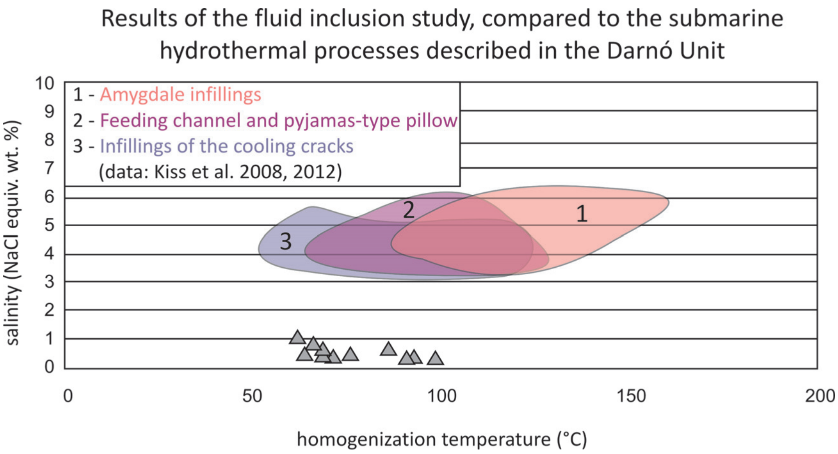

Fig. 5. Results of the fluid inclusion study of the calcite-laumontite veins (Báj Brook, S Darnó Hill), compared to the submarine hydrothermal processes described in the Darnó Unit by earlier studies (Kiss et al. 2008, 2012). The observed characteristics are significantly different.

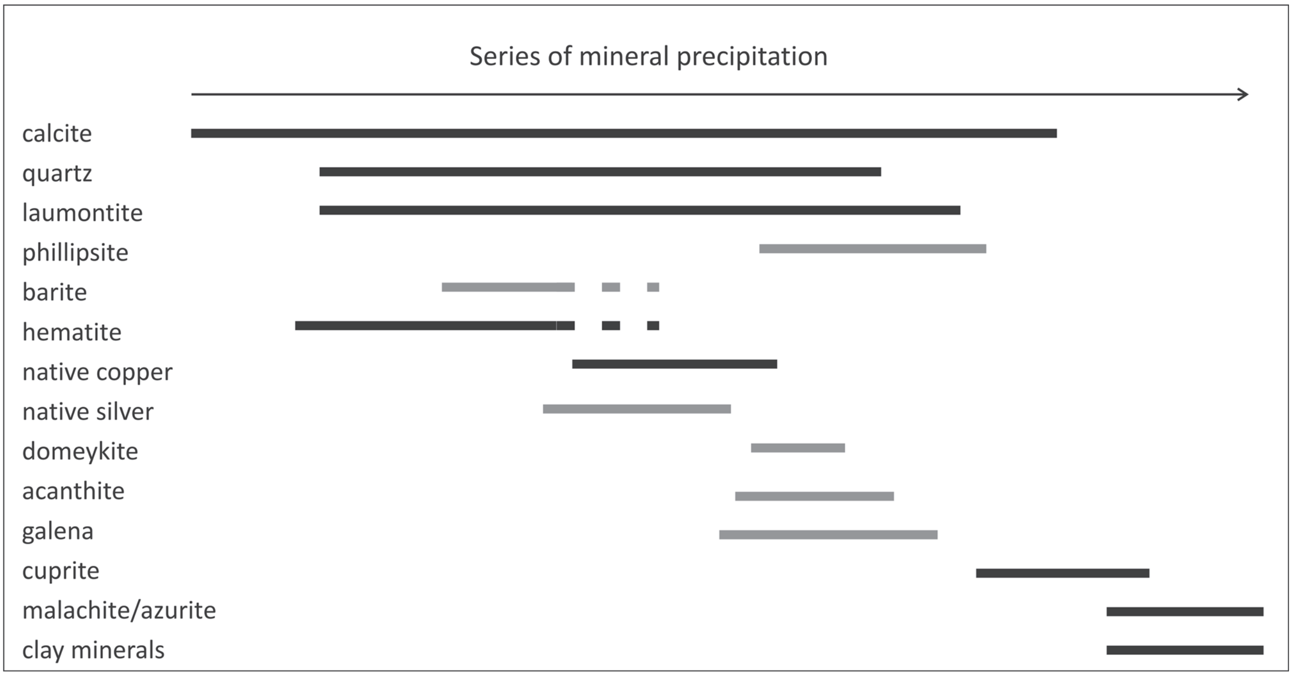

Fig. 6. The observed mineral precipitation sequence in the studied Cu-Ag occurrence (Báj Brook, S Darnó Hill). Newly described minerals from the area are marked with grey columns.

present research, a genesis similar to the Michigan-type ore formation is suggested for this native copper occurrence of the Darnó Unit, as opposed to former opinions (Kiss 1958). This finding fits well into the geology of the rocks found in the studied mélange.

The quartz-hematite occurrence

The host rock of the quartz-hematite occurrence is most likely the Ladinian chert and radiolarite, as suggested by Kiss (1958). The studied samples also support this finding, as a continuous change from the hematite-bearing chert to the quartz-hematite rock was observed in the different samples.

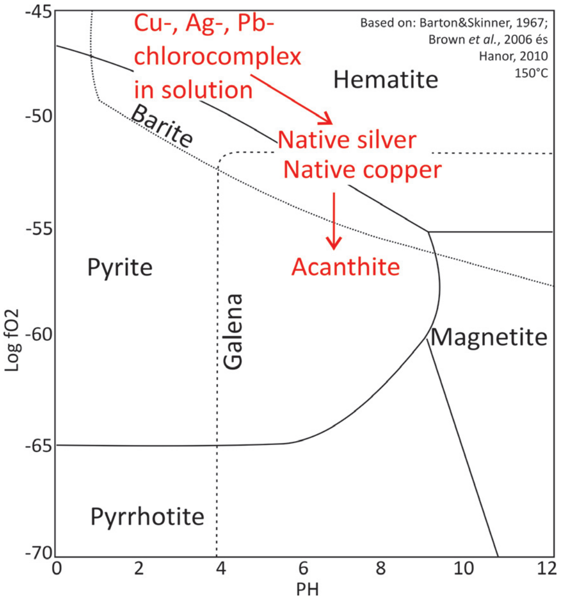

Fig. 7. The change in the redox and pH conditions during the evolution of the hydrothermal fluid, as mirrored by the precipitation sequence and the stability field of the studied minerals (Báj Brook, S Darnó Hill).

The textural features of the samples, as well as their chemical composition and fluid inclusion data suggest that these rocks were not formed during submarine sedimentary processes (e.g. bacterial precipitation). According to Bonatti et al. (1971, 1972), low Mn and Ni+Co+Cu+Cr contents (<1 mass %) are not typical during submarine sedimentary conditions, but can be characteristic in exhalative processes. In our case, 0.015–0.021 mass % MnO and low, 95–125 ppm Ni+Co+Cu+Cr support the origin by an exhalative process. The minimum formation temperature (70–155 °C) also suggests a hydrothermal origin and the flake-like (specular) shape of hematite also supports this assumption. The precipitation series is established by the microscopic observations. The hematite was followed by prehnite and quartz, both occurring as simultaneous and later minerals. Pumpellyite and barite formed only as late minerals.

The composition of the hematite grains gives further refinement about the origin. Only a low amount of replacement is allowed in the unit cell of hematite; about 1 mass % of Al_2O_3 and TiO_2 may occur, together with rare V and Cr (Gaines et al. 1997). On the contrary, the studied hematite crystals are richer in trace elements and besides the above mentioned components, ZnO, MgO and MnO were also found. Comparing these results with the ones published by Dupuis & Beaudoin (2011) from several different deposit types, significant similarities with the trace element distribution patterns of the iron oxides from SEDEX deposits can be observed (slight enrichment in Al, Mn, Zn and slight depletion in Ti, V, Mg and Cr) (Fig. 9). This finding supports the submarine exhalative origin, together with the few available fluid inclusion data, which resulted in slightly higher salinity, than the typical seawater (Kennett 1982). This slight enrichment to 3.87–4.34 NaCl equiv. mass % can be the result of the water-rock interaction during the circulation of the hydrothermal fluid.

According to Bonatti et al. (1972) and Boström et al. (1979), the occurrence of Fe-SEDEX is typical in the early stages of rifting, therefore it fits well into the geology of the Darnó Hill. This finding helps in understanding the relationship of the different ore occurrences of the studied mélange.

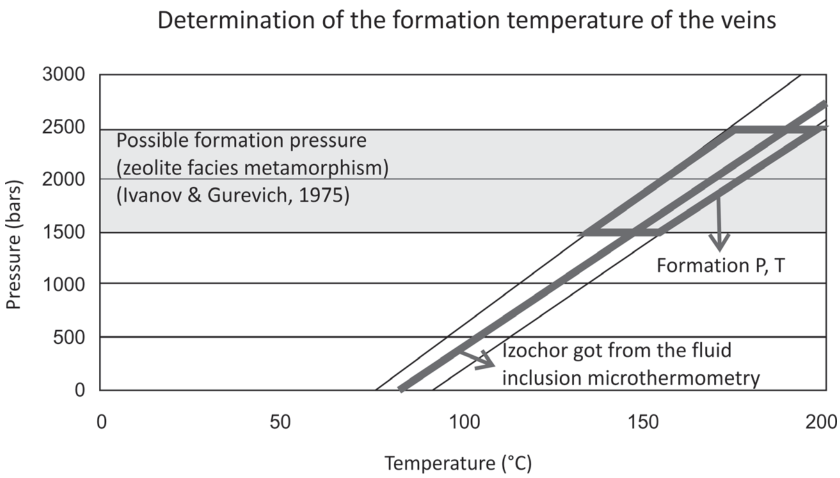

Fig. 8. Pressure correction performed on the fluid inclusion data in order to obtain the real formation conditions of the calcite-laumontite veins (Báj Brook, S Darnó Hill). Standard deviation of the data was also taken into consideration, when the isochores were determined (see the thin lines).

Conclusions

The NE Hungarian Darnó Unit is composed of a Neo-tethyan accretionary mélange complex, containing blocks of different age and origin. Its magmatic and sedimentary rock blocks derive from different evolutionary stages of the Neo-tethys; including Permian and

Triassic marine sedimentary rocks related to early rifting, Triassic pillow basalt related to advanced rifting and Jurassic pillow basalt related to back-arc-basin opening are also present (see e.g. Harangi et al. 1996; Aigner-Torres & Koller 1999; Haas & Kovács 2001; Dimitrijević et al. 2003; Kovács et al. 2008; Kiss et al. 2010, 2012).

Several different ore occurrences were also described from the Darnó Unit and the present study successfully completes the series of modern research in the area (Kiss & Zaccarini 2013; Molnár et al. 2015). The Cu(-Au) bearing occurrence in the Permian marly limestone was found to be similar to the black-shale hosted deposits by Kiss & Zaccarini (2013), which deposit type forms typically related to intracontinental rifting (Vaughan et al. 1989). The recently investigated Fe occurrence in the Triassic marine sedimentary succession is most likely a Fe-SEDEX, which is a characteristic deposit type during early rifting (Bonatti et al. 1972; Boström et al. 1979). The studied Cu(-Ag)-bearing calcite-zeolite-quartz veins are found in Triassic pillow basalt and their genesis is assumed to be related to a process, which is similar to the Michigan-type deposit formation. This deposit type forms generally during epigenetic (though closely related) hydrothermal process, during the advanced rifting stage (Lefebure & Church 1996; Brown 2006; Bornhorst & Barron 2011). Finally, Molnár et al. (2015) found that the origin of the Cu-bearing quartz-prehnite veins, occurring in both Triassic and Jurassic basalt blocks, was related to the Alpine low-grade regional metamorphism, which is obviously a later (Jurassic or younger), regional epigenetic process.

Different types of ore occurrences found on the Darnó Hill are closely related to different evolutionary stages of the Neotethys in space and time. Their recent, spatially close position is the result of the accretionary mélange formation (Dimitrijević et al. 2003), which brought blocks with various origins close to each other. Therefore, the direct economic importance of the studied occurrences is low, as the extent of the isolated ore-bearing blocks in the mélange is not always known. However, the region has a metallogenic importance, as the Darnó Unit is a perfect natural laboratory to understand the rifting-related ore forming processes.

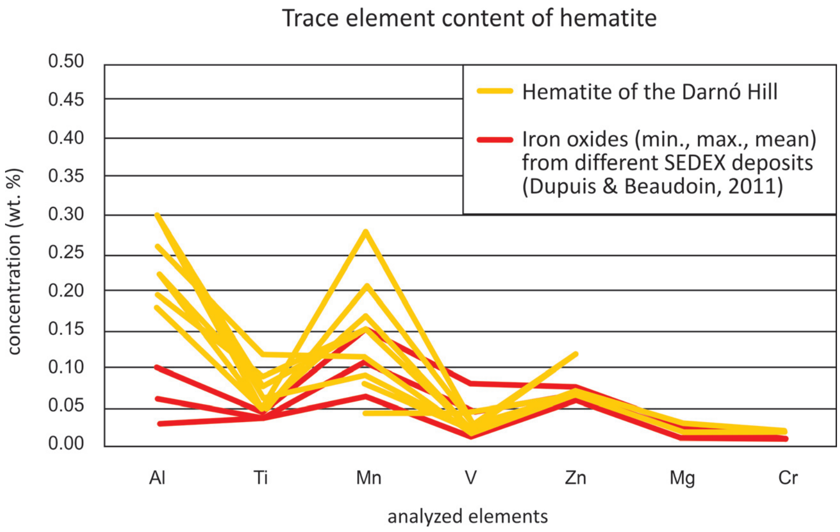

Fig. 9. Trace element composition of the studied hematite grains (NE Darnó Hill), compared to the minimum, maximum and mean values of different SEDEX deposits (Dupuis & Beaudoin 2011). Significant similarities among the patterns can be observed.

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