Detailed scientific report

Syn- and epigenetic hydrothermal processes in Jurassic submarine magmatic rocks of Neotethyan origin (NE-Hungary, N-Italy)
(project identification no.: OTKA PD 112580)

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1. Background, previous results

The Szarvaskő Unit is a part of the Bükk Unit, within the Pelso Composite Unit of the Alpine Carpathian Pannonian Terrane (ALCAPA). The approximately 25 km^2-large area of the Szarvaskő Unit, with predominantly basaltic and gabbroic rocks, is interpreted to be a part of the nappe system of the Bükk Unit (Csontos, 2000; Haas & Kovács, 2001; Kovács *et al.*, 2008). The Szarvaskő Unit is a Jurassic incomplete ophiolite sequence associated with deep-sea sediments. It is part of the Neotethyan realm, with geological correlation to Dinaridic occurrences. Its magmatic sequence is quite uncommon in comparison to well-known ophiolites, as the mantle section and the sheeted dikes are absent. Its magmatic rocks are hosted by an accretionary mélange series in a form of up to several kilometre large blocks (Szentpéteri, 1953; Balla, 1984). The petrochemical data for the mafic-ultramafic rocks of the Szarvaskő Unit show significant differences from MORB composition and a back-arc-basin or a marginal sea setting has been suggested as the environment of their formation (Kubovics *et al*., 1990; Downes *et al*., 1990; Harangi *et al*., 1996; Aigner-Torres & Koller, 1999). The pillow basalt blocks of the Szarvaskő Unit show the results of a quite limited seawater-rock hydrothermal interaction. However, cross-cutting veins occur as results of an early Alpine, very low-grade metamorphism (Árkai, 1983, 2001; Péntek *et al.*, 2006; Kiss *et al*., 2011, 2012, 2016).

Ophiolitic units representing the Piedmont-Ligurian basin of the Neotethyan Ocean are found in the Northern Apennines. These non-metamorphosed oceanic crust fragments are forming the Liguride Nappe, divided into two different units. The Internal Ligurides, forming the uppermost nappe, are deriving from a proximal rifting zone, while the External Ligurides below are representing a more distal position. The Eastern Ligurian Ophiolites show an incomplete ophiolitic sequence, in which the sheeted dyke complex and the transition zone are missing or absent. Petrological, geochemical and structural features suggest, that these ophiolites formed during early stages of oceanic crust formation, as marginal basin type, subduction related ophiolites (see e.g. Abbate et al., 1980 and Piccardo et al., 2002 and the references cited therein). Several Fe-Cu-Zn sulphide deposits are found in these non-metamorphosed ophiolitic units, interpreted as Cyprus-type VMS deposits. These occurrences contain more, than 65% of the Italian ophiolite-hosted Cu reserves (Zaccarini and Garuti, 2008). Comprehensive modern studies addressed mainly the mineralogical, mineral chemical and geochemical aspects of the ore deposit formation (see e.g. Garuti and Zaccarini, 2005, Zaccarini and Garuti, 2008, Garuti *et al.*, 2008, 2009, 2011) and only a few data is available about the evolution of the hydrothermal system (B. Kiss, 2015).

2. Research methods

Besides studying archive samples, detailed fieldwork was carried out in NE Hungary and in N Italy. Altogether 6 locations were visited and studied in details in and around the village of Szarvaskő (Két-víz-hegye SE, Várhill, Akasztó-hegy SE, Keselyű-hegy NE, Malomhegy SW, Hegyeskő NE), while 8 locations were involved in the project from the N Apennines (Boccassuolo, Reppia, Campegli, Vigonzano, Monte Loreto, Casali, Bargone, Corchia). Additionally, for comparison purposes, archive samples from 2 Dinaridic locations (Albania) were also studied.

Transmitted/reflected light polarising microscopy study, X-Ray powder diffraction method, scanning electron microscope coupled with energy dispersive spectroscopy (SEM-EDS) and cathodoluminescence (SEM-CL) measurements, fluid inclusion study coupled with Raman

spectroscopy, electron microprobe (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses, whole rock geochemical analyses, stable isotope as well as noble gas isotope geochemical analyses were carried out on representative samples from all study locations. More, than 100 polished thin- and block sections (for polarising microscopy, SEM-EDS and EPMA) as well as more, than 50 double polished thick sections (for fluid inclusion microthermometry, Raman spectroscopy, SEM-CL and LA-ICP-MS) were prepared. Additionally, approximately 60 other preparations (powders for XRD and geochemical analyses, separates for stable isotope and noble gas isotope studies) were also made. Using the above mentioned methods, a rather unique and extensive research database was formed from the studied Jurassic ophiolite related hydrothermal systems, containing, among many others, for example 664 mineral chemistry analyses (of which 516 EPMA, 64 LA-ICP-MS and 84 SEM-EDS) and 990 fluid inclusion microthermometry measurement data.

3. Scientific results of the project

Hydrothermal processes happening in submarine basaltic environments are widely studied in case of the mid-oceanic ridges as well as their hydrothermal fluid source is also in the centre of interest (see e.g. Pirajno, 2009, and the references therein). Geological evidences indicate generally evolved seawater origin, though there is a continuous debate regarding the mode of modification: fluid-rock interaction in the oceanic crust and/or admixture of magmatic fluid and/or phase separation may also play role. Understanding these processes bears high importance, as they can contribute significantly to the metal content of the deposit. However, studies on VMS deposits have shown, that finding reliable evidences of the fluid source can be a challenge (see e.g. Pirajno, 2009, Bodnar et al. 2014 and the references cited therein). In addition, information on the processes happening at non typical mid-oceanic ridge environments, as well as the epigenetic processes, which have effects on those basalts, are generally incomplete. As it is shown in the above sections, neither the Hungarian, nor the Italian localities were studied in details from the aspects of the syn- and epigenetic hydrothermal processes. Therefore, the present research project efficiently complete the scientific knowledge on these kinds of unique systems as well as could contribute to the geological knowledge on the studied regions.

Based on detailed investigation of the localities in the Hungarian and in the Italian incomplete ophiolitic sequences, different steps of syn- and epigenetic hydrothermal processes were distinguished. In case of the Hungarian locations, firstly a local submarine hydrothermal process happened, immediately after eruption. Physico-chemical data of this process and detailed volcanic facies analyses revealed distal formation in the submarine lava flow. During spreading, this was followed by a superimposing, bigger scaled fluid circulation system, resulting also a weak sulphide ore mineralisation (similar to VMS systems). Still at ridge setting/spreading, a peculiar Ca-metasomatic (rodingitisation *s.l.*) process with grossular-bearing mineral assemblage has overwritten the above

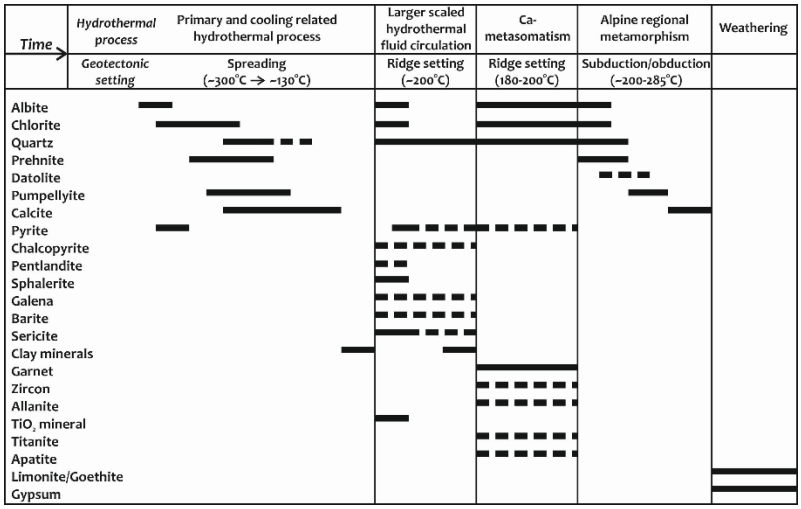

Figure 1: The hydrothermal mineral precipitation series observed in the Szarvaskő Unit, linked to the different steps of hydrothermal alteration as well as tectonic processes.

mentioned alteration parageneses. Finally, epigenetic veins formed during the Alpine regional metamorphism, during the subduction/obduction stage (Figure 1.). To sum up, the observed hydrothermal minerals represent several different steps of the geotectonic evolution of the Szarvaső Unit. Hence, studying the superimposing alteration mineral assemblages can be a useful tool for reconstructing the tectonic history of an ophiolitic complex. Determination of the development of the larger scaled, ore bearing hydrothermal circulation as well as the unique Ca-metasomatism is completely new scientific information from the studied regions. In addition, during our studies, the physical-chemical conditions (P, V, T, x) of the (ore) mineral formation were carefully determined, which is also clearly new scientific result. All relevant information are published in B. Kiss *et al.* (2018).

In case of the Italian locations, several different mineralogical and geochemical research methods were utilised in order to better and more safely model syngenetic hydrothermal process, i.e. the fluid source and evolution in VMS deposits. Fluid inclusion study of gangue minerals coupled with SEM-CL and LA-ICP-MS study provide valuable information on the variability of fluid characteristics during the entire hydrothermal process. This combined study of quartz revealed the superposition of multiple hydrothermal events and dynamically changeable formation conditions at both locations, resulting in several quartz generations (some also coeval with ore mineral formation) and a late calcite formation process (B. Kiss *et al.*, 2019a). The observed wide homogenisation temperature ranges (~60-360 °C) are also the results of this variability (Figure 2.). The salinity results (~3-9 NaCl equiv. wt%) are within the typical range of VMS deposits (Figure 2.), and Raman spectroscopy have revealed methane content at each locations. Compositional data, however, cannot be interpreted alone, as several seawater modifying processes (e.g. fluid-rock interaction, phase separation, magmatic fluid admixture) can cause the observed variability. Hence, well established interpretation is possible only with involvement of other research methods, such as stable and noble gas isotopic studies. Oxygen isotopic composition of late calcite ($\delta^{18}O$=15.0-22.7‰) is in good agreement with low temperature alteration zones of VMS deposits (Ridley, 2012), though some lower $\delta^{13}C_{PDB}$ values (up to $\delta^{13}C_{PDB}$ -6.9 ‰) are uncommon. The calculated isotopic composition of the fluid in equilibrium with calcite stays around the typical VMS range (Figure 3A), though the mode of seawater modification is still ambiguous. δD and R/Ra values of quartz hosted fluid inclusions, however, clearly exclude the significant magmatic component at the studied locations (δD from -47 to -39‰ and R/Ra up to 0.17). In addition, the noble gas isotopic composition of quartz and sulphides hosted fluid inclusions verify the importance of seawater-rock interaction due to long lasting circulation in the oceanic crust (Figure 3B) (B. Kiss *et al.*, 2019b). Reliable determination of the fluid source as well as precise reconstruction of the dynamically variable formation conditions (P, V, T, x) and superposition of the hydrothermal events are both new scientific results from the study regions. In addition, the afore mentioned combined methodology is unique in the field of VMS deposit studies, therefore bears of high importance.

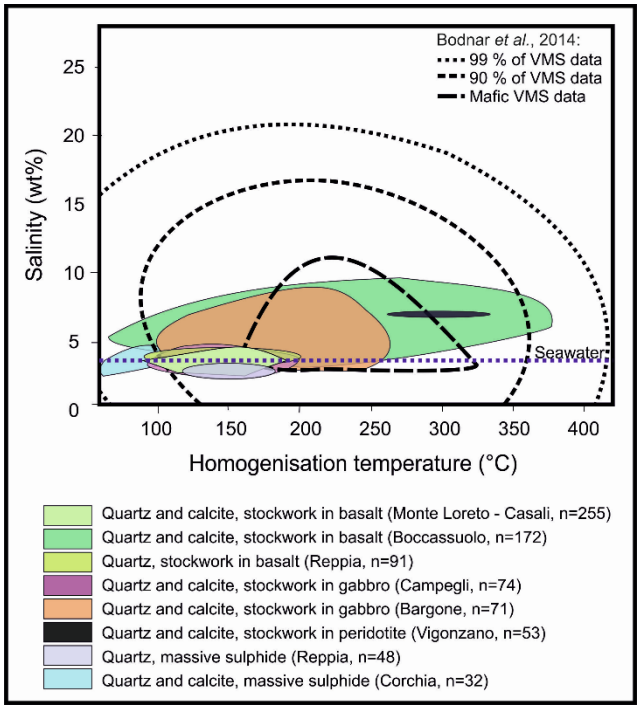

Figure 2: Fluid inclusion homogenisation temperature vs. salinity diagram of the studied Italian locations

For comparison purposes, analyses of some Dinaridic (Albanian) samples were also involved in the present project. This work allowed to better understand the deeper parts of the VMS related hydrothermal systems and helped to find reliable tracers of (magmatic) fluid source. We have found, that mineral chemistry of pyrite, chalcopyrite and epidote are useful tracers of the processes happening in the stockwork zone. We have also proven, that the above mentioned combined mineralogical, petrological, geochemical method (which was efficiently used at the Italian locations) is able to supply trustworthy model of the VMS fluid source. Therefore, this comparison contributed efficiently to develop a reliable model of the entire hydrothermal process (Lovász *et al.*, 2018, B. Kiss *et al.*, 2019b)

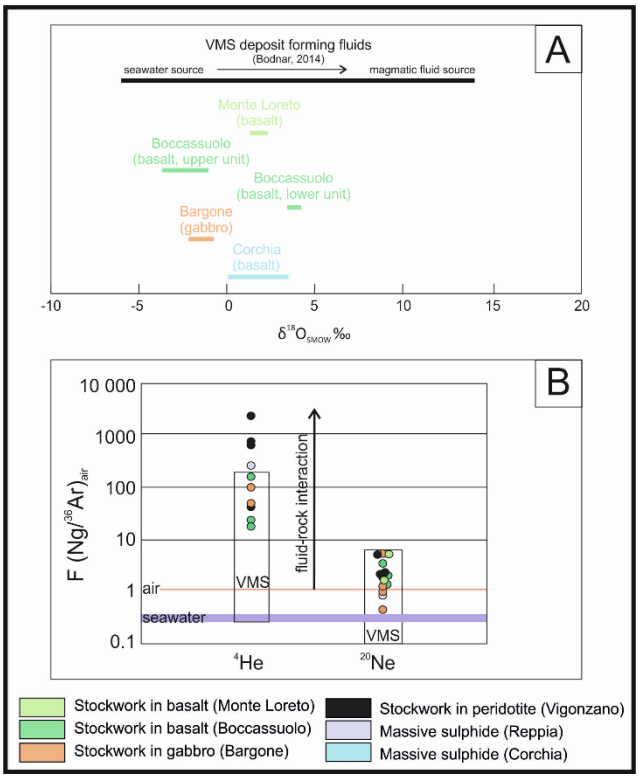

Figure 3: Stable isotopic composition of VMS calcite forming fluids (A) and noble gas isotope ratios of quartz and sulphides hosted fluid inclusions (B) (air, seawater and VMS compositions are after Kendrick and Burnard, 2013).

To sum up, as a result of all afore mentioned analyses, well constrained models of the syn- and epigenetic hydrothermal fluid-rock interaction processes were created. The physical-chemical conditions of the hydrothermal mineral formation were determined at each study locations. The obtained project results completed well the earlier studies as well as a high amount of new scientific data is now available. Studying the submarine hydrothermal processes at the well preserved Italian locations gives us a lot of useful experience in this field, thus help a lot in understanding some processes at the strongly tectonised Hungarian sites.

4. Participation at conferences, scientific meetings

Altogether 13 presentations (either oral or poster) appeared at different national and international conferences (+1 already accepted), related to this project. The following conferences and scientific meetings were attended:

- January 2015: 10th Winter Mineralogical School (Balatonfüred, Hungary)
- May 2015: 5th Mineral Sciences in the Carpathians Conference (Veszprém, Hungary)
- June 2015: 23rd European Current Research on Fluid Inclusions (Leeds, UK)
- September 2015: MinPet 2015 (Leoben, Austria)
- September 2016: 2nd European Mineralogical Conference (Rimini, Italy)
- January 2017: 12th Winter Mineralogical School (Veszprém, Hungary)
- June 2017: 24th European Current Research on Fluid Inclusions (Nancy, France)
- September 2017: 8th Petrological-Geochemical Assembly of the Hungarian Geological Society (Szihalom, Hungary)
- September 2018: 21st International Congress of the Carpathian Balkan Geological Association (Salzburg, Austria)
- May 2019: 9th Petros Conference (Bratislava, Slovakia)
- June 2019: 25th European Current Research on Fluid Inclusions (Budapest, Hungary) (2 presentations)

- August 2019: Goldschmidt 2019 congress (Barcelona, Spain)
- October 2019: accepted presentation for the SEG 2019 congress (Santiago, Chile)

5. Utilisation of the project results

The project results related to submarine hydrothermal (ore forming) processes can be incorporated into a larger scaled, generalised model. This model can be successfully utilised in future research/exploration projects conducted at regions characterised by similar geology. Thus, the results may have some economic/practical use –indirectly– in the future.

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