

Postmetamorphic palaeofluid evolution of the Baksa Gneiss Complex

*A Baksai gneisz komplexum posztmetamorf paleofluidum
evolúciója*

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Summary of the dissertation

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Introduction

Palaeohydrological investigation of basement crystalline rocks, especially Variscan crystalline basement complexes have become very important in the latest decades both from basic and applied geological research points of view. Hydrodynamic importance of crystalline basement rocks is inherent in the advanced state of their secondary porosity and special characteristics of their flow permeability. The significant role of fracture porosity of crystalline rocks is obvious in case of several applied geological problems exploration for geothermal energy, in case of deep rock burial site as place for radioactive waste disposal or fluid mining, such as fractured hydrocarbon reservoirs.

The structure, geometrical and cementation features of the fracture system, essentially determines the fluid-retention capacity and fluid conductivity of the crystalline rocks. On the one hand, fracture-filling minerals cause decrease of the porosity and permeability of rocks; on the other hand, they possess essential information about the physicochemical conditions of cementation processes. From this perspective, fracture-filling mineral grains play a pivotal role by capturing fluid inclusions. These inclusions can preserve the fluid located in the fracture during crystal growth, and allow scientists to determine the original composition and entrapment conditions of the fluid.

The wall rock alteration activity of such fluids has a significant role in different geological processes. Considerable secondary porosity may develop if metasomatic alteration is associated with leaching, and the locally increased porosity can play a pivotal role in the hydrological behaviour of otherwise low permeability crystalline rocks. Another important aspect is that hydrothermal metasomatism can be frequently associated with formation of mineral deposits. Ore mineral depositions in some cases containing sulphide minerals (pyrite, chalcopyrite, pyrrhotite, and sphalerite) iron oxides (hematite, magnetite), or in other cases precious metal minerals can occur during hydrothermal metasomatism that mainly relates to magmatic intrusions.

In the dissertation, the complex mineralogical and paleohydrological analysis and possible interpretation of the post-metamorphic fracture cementation of the Baksa Complex (BC) will be presented in detail. I try to distinguish the different fracture filling types occurring in the rock body and determine a relative formation sequence of the distinguished types. By detailed petrographic investigation of fracture filling mineral phases I try to determine the exact cementation sequence of the analyzed veins and make paragenetic mineral succession of the different vein types. I make an attempt to determine the physicochemical conditions of cementation of veins by using detailed mineral chemical and fluid inclusion analysis of the different mineral phases of the veins. By the help of microthermometric and Raman spectroscopic investigations I try to make a model of P - T - X evolution of paleofluids which migrated in the veins. Summarizing the results I make an attempt to sketch a detailed model for post-metamorphic paleofluid evolution that occurred in the fracture system of the BC.

Samples and analytical methods

The high core recovery of the Baksa-2 drill underlies the detailed macroscopic examinations made on individual drill cores to identify the different vein types. For this purpose 31 core sample were chosen. Standard ($\sim 30 \mu\text{m}$) thin sections were made from the most representative samples in order to make accurate microscopic identification of the vein filling minerals to expose the geometrical features of the veins and determine the relative sequence of formation of fracture filling minerals.

To reveal the intracrystalline textures including growth zonation or chemical heterogeneities in single grains, as well as to detect the textural relationship between different minerals cathodoluminescence (CL) microscopy and scanning electron microscopy (SEM) were used. The cathodoluminescence images were made at the Geochemical Institute of MTA using a Reliotron cold

cathode cathodoluminescence instrument mounted on a Nikon Eclipse E600 optical microscope. The applied beam current was 0.3-0.8 mA and 8-9 kV electron energy. Secondary electron (SE) and backscattered electron (BSE) images were made by using a Hitachi S4700 scanning electron microscope at the Institute of Environmental Sciences of University of Szeged. The beam conditions of this instrument were 25 kV and 10 μ A during measurements.

Informative chemical microanalyses were made by EDS of the SEM but most of the quantitative analyses of minerals were made in the Eugen F. Stumpfl electron microprobe laboratory at the Montanuniversität Leoben by using JEOL JXA 8200 Superprobe electron microprobe equipment. The instrument works with five WDS and can measure each element from boron to uranium. High resolution digital X-ray mapping can be made with using both WDS and EDS. All analytical modes are fully automatic. Analyses were carried out at 10 nA beam current and 15 kV accelerating voltage. The beam diameter was 1 μ m but 5 μ m during feldspar analyses. Accumulation time was 10 s for the peaks and 4 s for the backgrounds. Detection limit was 0.1-0.02 % in case of Si, Al, Ti, Fe, Mg, Ca, Na, K, Mn, S, Co, Ni, As, Cu, Zn, Cd, and Cr, while 0.2-0.07 % in case of Ba.

Stable isotope geochemistry analyses were made at the Geochemical Institute of MTA using a Finnigan delta plus XP mass spectrometer in He carrier gas. Sampling was made by micro-drilling of crack filling calcite obtaining 0.1-0.3 mg calcite powder. These samples were reacted with purified phosphoric acid producing CO₂ gas which was analyzed by the mass spectrometer. $\delta^{13}\text{C}$ (vs. V-PDB) and $\delta^{18}\text{O}$ (vs. V-SMOW) isotopic values of each sample are averages of replicate analyses. Precision of the measurements was $\pm 0.1-0.2\%$ in both cases of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.

Fluid inclusions were studied in 75-150 μ m double polished thick sections prepared from the vein materials. Microthermometric measurements were carried out with a Linkam THMSG 600 heating-freezing stage operating over a

temperature range from -190 to 600 °C at the University of Szeged. Synthetic fluid inclusions were used for the calibration at -56.6, 0.0 and 374.0 °C. The accuracy of the data is approximately ± 0.2 °C under freezing and ± 0.5 °C under heating conditions. LMPlanFI 100X objective lens (Olympus) were used to analyze the inclusions.

Raman spectroscopic analysis of the fluid inclusions was carried out at the Department of Mineralogy and Petrology at the Montanuniversität Leoben (Austria), using a Jobin Yvon LABRAM confocal Raman microspectroscope, which uses a frequency doubled Nd-YAG 100 mW capacity laser. Each sample was irradiated using a laser light with a 532.2 nm (green) wavelength. Calibration of the spectrometer was made by synthetic silicon chip, polyethylene, calcite, and a natural diamond crystal. The spectral resolution of the instruments was 4 cm^{-1} , while the spatial resolution was a few μm^3 . The acquisition time was 100 s with 20 s accumulation periods in each spectrum.

Whole rock chemical analyses of the wall-rocks were carried out at the University of Szeged by using a Horiba Jobin Yvon XGT 5000 X-ray fluorescence spectrometer. Beam diameter was 100 μm and acceleration voltage was 30 kV in each case. Natural standards were used for standardization of each measured element.

New scientific results

- (1) Ca-Al-silicate dominant vein system with $di \rightarrow ep \rightarrow sph \rightarrow ab \pm kfp \rightarrow chl1 \pm prh \pm adu \rightarrow chl2 \rightarrow chl \rightarrow pyr \rightarrow call \rightarrow cal2 \rightarrow cal$ paragenetic sequence can be observed in the rock body of the Baksa Gneiss Complex.
- (2) Ca-Al-silicate veins were formed by the effect of postmagmatic originated hydrothermal fluid according to considerable trace elements content and characteristic Co/Ni ratio (~1-5) of pyrite. Crystallization of individual minerals in the veins occurred from low salinity (0.2-3% wNaCl eq.) pure aqueous-electrolite solution according to microthermometry results of D_1 inclusion of diopside and E_1 inclusions of epidote.
- (3) The P-T window which is obtained by intersection of calculated formation temperature of chl1 and isochors of E_1 fluid inclusions confirms that formation of chl1 and epidote phases occurred at <200 MPa pressure conditions. Considering the fact that aplite dykes – which are regarded as magmatic heat source of the hydrothermal fluid circulation – might have cooled down to the ambient rock temperature (~150 °C based on thermometry results of chl3) very rapidly so constant pressure conditions (~100 MPa) can be assumed during cooling.
- (4) On the study area ~39 °C/km regional palaeogradient can be estimated based on nearly constant (~100 MPa) pressure conditions. Based on the obtained closely constant pressure, trapping temperature of the D_1 inclusions in diopside is $T_t \sim 354-480$ °C, while $T_t \sim 236-475$ °C interval is presumable in case of E_1 inclusions in epidote. Vein filling mineralization occurred in cooling hydrothermal fluid regime from ~480 °C down to ~150 °C.
- (5) Symmetrical metasomatic bands can be observed along Ca-Al-silicate dominant veins and these bands can be divided to four distinct metasomatic zones based on their characteristic mineral paragenesis: 1) $ab + ttn \pm ep$; 2) $ep + chl + ttn + ab \pm ser$; 3) $chl + ep + ser + rt \pm ttn$; 4) $ser \pm chl$. In the

metasomatic column, which is defined by the four zones the basic rocks suffered significant loss of K, Mg, Fe, and Mn, while gained in Ca content.

- (6) Primary fluid inclusions of epidotes precipitated in secondary cavities in the metasomatic column contain a fluid type identical with that are originated from the Ca-Al-silicate dominant veins. Fluid migrated in the vein system penetrated into the wall rock along secondary pore systems metasomatizing the wall rock leading to form an alteration rock type which belongs to propylite metasomatic family. The absence of quartz from the alteration mineral paragenesis of the metasomatic column indicates higher temperature (~360-410°C) propylitization.
- (7) Considering microthermometry results of C1 fluid inclusions of cal1 (low T_h : 75-124 °C; high salinity: 17.5-22.6% wCaCl₂ eq.) and calculated $\delta^{18}\text{O}$ values (-4 to -12.9‰) of fluid from which cal1 phase precipitated meaning that formation of this carbonate phase occurred due to an exotic originated basinal brines or descending meteoric water that infiltrated through evaporite bodies.
- (8) Quartz-carbonate veins of the BC can be characterized by *qtz*→*dol*±*cal1*→*cal2* vein filling mineral sequence. Fluid inclusions of *qtz* host captured highly saline fluid exhibiting 20-26% wNaCl, 1.5-6% wCaCl₂ salt composition and contain minor amount of CH₄ and N₂ in the vapour phase. Pressure-temperature range of crystallization of quartz phase is presumable $P \sim 20\text{-}100$ MPa, and $T \sim 80\text{-}180$ °C intervals obtained from intersection of isochors of primary fluid inclusions and lithostatic and hydrostatic thermobaric gradients (assumed thermal gradient is ~ 35 °C/km).

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