

**RECONSTRUCTION OF TECTONIC  
EVOLUTION AND FLUID MIGRATION  
HISTORY IN THE BODA CLAYSTONE  
FORMATION**

THESES OF THE PhD DISSERTATION

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## **I. INTRODUCTION, AIMS**

During my PhD research, I studied the Late Permian Boda Claystone Formation (BCF) located in the Western Mecsek. The geometrical properties of the rock body, its low porosity and permeability (FEDOR et al. 2008) reveal the outstanding isolating abilities of the formation. According to a national geological survey (KONRÁD & HÁMOS 2006), the BCF is the most suitable formation in Hungary for receiving a deep repository for high-level radioactive waste. However, these rock types, despite the favourable petrophysical properties of the matrix, can often afford significant fluid flow along their structural inhomogeneities. Thus, it is important to know the structural evolution of the formation and the history of paleofluid migration, which can help to assess the isolation properties of the rock body. Consequently, the main objective of my PhD research was to understand and reconstruct the tectonic phases and fluid migration events affecting the BCF. My further aim was to develop a complex methodology suitable for exploring structural, textural, mineralogical, and geochemical relationships that carry information on structural evolution and paleofluid migration. To observe as many structural elements and their mutual relations as possible, the BAF-2 well was chosen to develop the methodology, since this

notable depth profile explores the BCF in the largest thickness (~905 m). My further goal was to investigate whether it is possible to spatially extend the observations made in the BAF-2 well within the formation. To this end, the entire core material of two additional wells (BAT-4 and Delta-3) was reviewed and sampled, as well as the petrographic characteristics of the selected samples were described.

## **II. METHODS**

To solve the outlined environmental geological problem and to achieve the goals of my research, a wide range of analytical methods were applied on mineral veins which may reveal the conditions of the structural development and paleofluid migration of the formation.

The petrographic description of the samples was performed on 30  $\mu\text{m}$  thick polished thin section with an Olympus BX41 type polarizing microscope. The images were taken using Olympus DP73 and UC30 digital cameras.

The minerals were identified by Raman spectroscopy performed with a Thermo Scientific DXR Raman microscope equipped with a 532-nm wavelength Nd:YAG laser. A laser power of 10 mW and pinhole confocal aperture of 25  $\mu\text{m}$  were

used for each measurement. Raman spectra were evaluated based on the RRUFF database (<http://rruff.info>).

Micro X-ray fluorescence mapping was performed on a Horiba Jobin Yvon XGT-5000 X-ray fluorescent spectrometer equipped with Rh X-ray source operating at 30 kV and 0.5 mA.

Cathodoluminescence (CL) microscopy was performed with a Reliotron VII CL instrument mounted on an Olympus BX43 microscope. The operation parameters were 7 kV and 0.7 mA, respectively.

Fluid inclusion (FI) petrography and microthermometry were carried out in doubly polished thin sections of 80–100- $\mu\text{m}$  thickness using a Linkam MDS600 heating-freezing stage mounted on an Olympus BX41 microscope. The heating-freezing stage was calibrated at  $-56.6\text{ }^{\circ}\text{C}$ ,  $0.0\text{ }^{\circ}\text{C}$  and  $374.0\text{ }^{\circ}\text{C}$  using synthetic FIs. Detailed petrographic description of FIs was carried out following the criteria of GOLDSTEIN & REYNOLDS (1994). Homogenisation temperatures ( $T_h$ ) were measured applying stepwise ( $2\text{ }^{\circ}\text{C}$ ) heating, checking all studied inclusions between steps. The final ice melting temperatures [ $T_m$  (Ice)] were determined in the presence of the vapour phase. Both  $T_h$  and  $T_m$  (Ice) values were determined using the cycling technique of GOLDSTEIN & REYNOLDS (1994). Salinities were calculated from  $T_m$  (Ice) data using the empirical equation of BODNAR (1993) and are reported as the mass per cent of NaCl

equivalent. Artificial stretching of one-phase FIs was performed by stepwise heating up to 290 °C. Eutectic temperatures ( $T_e$ ) were not determined due to limited inclusion sizes. The area per cent of vapour phases in FIs was determined by analysing 2D microscopic images with ImageJ 1.53g software. Consequently, these values cannot be regarded as proper volume fraction ( $\phi_v$ ) equivalents. Polarisation and CL microscopy, Raman spectroscopy, X-ray fluorescence mapping, as well as FI microthermometry were carried out at the Department of Mineralogy, Geochemistry and Petrology, University of Szeged.

Scanning electron microscopy coupled with energy-dispersive X-ray spectrometry was performed using a Hitachi S-4700 field emission scanning electron microscope and a Bruker (Röntec) QX2 energy-dispersive X-ray fluorescence spectrometer at the Faculty of Science and Informatics, University of Szeged. The operating parameters were 15–20 kV and 10  $\mu$ A.

Vein-forming and host rock calcite samples, as well as sulphate and separated vein-filling sulphide samples were analysed for carbon ( $n=22$ ), oxygen ( $n=22$ ) and sulphur isotope ratios ( $n=8$ ) at the Isotope Climatology and Environmental Research Centre (ICER), Institute for Nuclear Research (ATOMKI), Hungarian Academy of Sciences (MTA) by a

Thermo Finnigan DELTA<sup>plus</sup>XP Isotope Ratio Mass Spectrometer using a Fisons NA1500 NCS Elemental Analyser for the carbon and sulphur measurements, and a Thermal Combustion/Elemental Analyser interface for the oxygen measurements. The results are expressed as  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$  relative to V-PDB, V-SMOW and V-CDT standards, where  $\delta(\text{‰}) = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$  and  $R = {}^{13}\text{C}/{}^{12}\text{C}$  for  $\delta^{13}\text{C}$ ,  ${}^{18}\text{O}/{}^{16}\text{O}$  for  $\delta^{18}\text{O}$  and  ${}^{34}\text{S}/{}^{32}\text{S}$  for  $\delta^{34}\text{S}$ . The standard deviation of stable isotope measurements is 0.08, 0.1 and 0.4 or better for  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$ , respectively.

### III. RESULTS

In my PhD research, I examined rock samples from BAF-2, BAT-4 and Delta-3 wells. After reviewing the total core material of the wells, 56 core samples were collected from the BAF-2 well, 21 from the BAT-4 well, and 11 from the Delta-3 well. Petrographic observations were performed on samples from all three wells, while geochemical studies were performed on the core material of the BAF-2 well.

1. In the rock material of the BAF-2 well 4 mineral vein generations were identified with different geometries: braided veins rich in wall rock inclusions and cone-a-cone structures

(*Vein<sub>CIC</sub>*), straight veins (*Vein<sub>STR</sub>*), en-echelon vein systems (*Vein<sub>ECH</sub>*), and breccia-like fracture fillings (*Vein<sub>BR</sub>*). The relative age of the vein generations can be determined by their intersection relations. The oldest is the *Vein<sub>CIC</sub>* generation followed by the *Vein<sub>STR</sub>*, the *Vein<sub>ECH</sub>* and the *Vein<sub>BR</sub>* veins (HRABOVSKI et al. 2022).

**2.** Based on the microstructures (inclusion trails, inclusion bands, cone-in-cone structures) and wall rock inclusion geometries appearing in the *Vein<sub>CIC</sub>* generation, the formation of the veins was continuous. In this sense, the development of the veins did not occur through the classical crack-sealing mechanism (RAMSAY 1980), but as a result of the pressure exerted by the growing crystals. This is evidenced by (a) the curved geometry of the wall rock inclusions, (b) the gradual decrease in the interlimb angle of the wall rock inclusions from the vein walls towards the vein centres, (c) the solid inclusions partially detached from the vein walls, and (d) the significantly different size of the adjacent clasts. The diffuse wall rock inclusion boundaries, cone-in-cone microstructures, authigenic albite around the wall rock inclusions, and the small solid inclusions in albite grains suggest that the ductile-style deformation of solid inclusions and thus the formation of the *Vein<sub>CIC</sub>* veins took place in low-cohesion sediment during non-tectonic, early diagenetic processes.

Based on the relative position of the lithoclasts appearing on both sides of some *Vein<sub>CIC</sub>* veins and the orientation of the microstructures, the observed veins were initially Mode I type, tensional fractures. However, the formation of the microstructure and texture of the *Vein<sub>CIC</sub>* veins is not compatible, based on which the primary texture has already been transformed, the current mineral filling of the samples is of secondary origin thus, it does not carry information about the conditions of vein formation. This is supported by the fact that continuous vein growth is associated with the formation of fibrous crystals (BONS et al. 2012), suggesting that *Vein<sub>CIC</sub>* veins may have originally been cemented by an early fibrous mineral that is no longer present in these structural elements. This hypothetical fibrous mineral could be replaced by the observed minerals during diagenetic, hydrothermal processes, preserving the original microstructures (HRABOVSKI et al. 2020).

**3.** In contrast to the minerals that form the *Vein<sub>CIC</sub>* generation, the cement minerals of *Vein<sub>STR</sub>*, *Vein<sub>ECH</sub>* and *Vein<sub>BR</sub>* can be nearly as old as the fractures, so they can be treated as carriers of the original physicochemical conditions during the tectonic events. Exceptions are the anhydrite generations (*Anh<sub>EB</sub>*, *Anh<sub>FIB</sub>*), which, based on their textural relations replaced the primary vein-forming minerals. Similarly, the

youngest mineral of *Vein<sub>BR</sub>*, the Cal<sub>EB2B</sub> is of secondary origin, which, based on its petrographic and geochemical properties, were precipitated after the brecciation (HRABOVSKI et al. 2022).

4. Based on the elongated blocky and blocky morphology of the vein-forming crystals, the predominant material transport mechanism for the *Vein<sub>CIC</sub>* and *Vein<sub>STR</sub>* veins was advection (BONS et al. 2012). Based on the fibrous crystal morphology of the *Vein<sub>ECH</sub>* generation and the similar stable isotope ratios of the vein-forming and wall rock carbonate, the material transport process characteristic of *Vein<sub>ECH</sub>* development was diffusion. Many rectangular, perfectly matched wall rock inclusions (in-situ fragmentation structures) appearing in the *Vein<sub>BR</sub>* generation suggests that the vein development was associated with fluid-associated, hydraulic brecciation as a result of mobile hydrofractures (JÉBRAK 1997; BONS 2001; HRABOVSKI et al. 2022).

5. The homogenization temperatures ( $T_h$ ) of primary fluid inclusions in the carbonates (Cal<sub>SHR2</sub>, Cal<sub>EB1A-B-C</sub>) of the *Vein<sub>CIC</sub>* and *Vein<sub>STR</sub>* generations are concentrated in a narrow range, averaging between 108 and 132 °C (min. values: 90, 80, 94 and 84 °C). The  $T_h$  values characteristic of the *Vein<sub>ECH</sub>* (Cal<sub>FIB2</sub>), *Vein<sub>CIC</sub>*, and *Vein<sub>STR</sub>* generations fall in a close range, although the average  $T_h$  values of the *Vein<sub>ECH</sub>* fluid inclusions

range from 99 to 115 °C (min. value: 80 °C). Fluid inclusions of the Cal<sub>EB</sub>2A (*Vein<sub>BR</sub>*) homogenized at elevated temperatures (~140–148 °C, min. value: 130 °C); while most fluid inclusions in the Cal<sub>EB</sub>2B are one-phase (L) and suggest a closure temperature below 50 °C. The  $T_h$  values (43–50 °C) and final ice melting temperatures of fluid inclusions measured in the Cal<sub>EB</sub>2B also suggest near-surface formation conditions (HRABOVSKI et al. 2022).

6. Based on the  $\delta^{18}\text{O}$  values of the vein-forming minerals and the  $T_h$  values of the fluid inclusions, it is probable that the parent fluids of most fracture-filling carbonates (Cal<sub>SHR</sub>2, Cal<sub>EB</sub>1A, Cal<sub>EB</sub>1B, Cal<sub>EB</sub>1C, Cal<sub>FIB</sub>2, Cal<sub>EB</sub>2A) were of similar origin. The saline pore waters representing the parent fluid of these minerals may be derived from a mixture of fossil playa fluids and diagenetic fluids from clay mineral transitions. That is, the parent solutions of the calcite generations of the *Vein<sub>CIC</sub>*, *Vein<sub>STR</sub>*, and *Vein<sub>ECH</sub>* veins were formed as a result of mixing local formational fluids and fluids of diagenetic origin. Since these parent fluids are derived from the BCF, their formation presupposes a long-term, closed geochemical system that supports the outstanding isolation properties of the rock body (HRABOVSKI et al. 2022).

7. In the youngest calcite (Cal<sub>EB</sub>2B) of the *Vein<sub>BR</sub>* generation, the low (<50 °C) homogenization temperatures and

low salinity (0.0–0.4%  $w_{\text{NaCl}_{\text{eq}}}$ ) of the fluid inclusions, as well as the  $\delta^{18}\text{O}$  values of the parent fluid are separated from the other vein-forming calcites. Based on all this, and the blocky, elongate blocky morphology of the crystals, the formation of the Cal<sub>EB</sub>2B occurred after the primary vein development, during the advective transport of meteoric fluids, suggesting the presence of an open geochemical system. Although breccias are not common in the BCF, their open pores indicate that assessing their frequency, spatial location, and fluid conductivity deserves special emphasis in the selection of the appropriate site (HRABOVSKI et al. 2022).

8. Based on structural, textural, and mineralogical features, the BAT–4 and Delta–3 wells display all mineral veins characteristic of the BAF–2 well. In consequence, the parameters of structural and paleofluid evolution observed in the BAF–2 well are also valid for the rock volume of the BCF sampled by the above two wells.

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