

## Fluid inclusions in datolite from siliciclastic peperite in a Jurassic pillow basalt series of a dismembered Dinaric mélangé in NE-Hungary

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The pillow basalt blocks of the Szarvaskő Unit in the SW-Bükk Mountains are parts of an accretionary mélangé which was displaced from the Dinarides to its current position in NE-Hungary by the Mid-Hungarian fault system during the Alp-Carpathian collision (e.g. Haas & Kovács 2001; Dimitrijević et al. 2003). The origin of the basalt is related to a back-arc-basin or marginal sea environment in the Mesozoic Vardar Ocean (e.g. Harangi et al. 1996; Aigner-Torres & Koller 1999).

The Egerbakta quarry in the Szarvaskő Unit exposes a pillow basalt block from a submarine basaltic volcano, in which the so-called peperitic facies *s.l.* (i.e. local admixture of siliciclastic sediments into the pillow sequence) occurs among the closely packed pillows and some pillow fragmented hyaloclastite breccia volcanic facies (Kiss et al. 2011). A quite limited seawater-rock interaction resulted in precipitation of hydrothermal minerals, such as quartz, calcite, chlorite and prehnite. They occur in every volcanic facies, mainly in short veinlets within the pillows, however, the matrix of the pillow fragmented hyaloclastite breccia facies contains the best example of this kind of hydrothermal mineralization. The upheated seawater related origin is proven by fluid inclusion data obtained from calcite, where 4.59 mass% NaCl salinity was detected. These elevated salinities are results of seawater-rock interaction. Formation temperature-pressure conditions of 160 °C and 0.5 kbar were determined by combining results of fluid inclusion microthermometry with chlorite thermometry (Kiss et al. 2011). Another mineral association of prehnite, calcite, quartz and chlorite, as results of the later Alpine low grade metamorphism (Sadek et al. 1996) are confined to veins cross-cutting the basalt pillows.

Occurrence of datolite [ $\text{CaBSiO}_4(\text{OH})$ ] is restricted to cross-cutting veins in the peperitic facies only, together with prehnite and minor chlorite, calcite and albite. The prismatic and more isometric datolite crystals are anhedral to euhedral (in cavities of the veins) and their size can reach up to 7 mm. Close to the walls of the vein crystals are dull, due to the presence of large amount of fluid inclusions, while they are water clear in the cavities of the central parts of the veins. Prehnite formed earlier and also together with datolite, while chlorite precipitated synchronously with it.

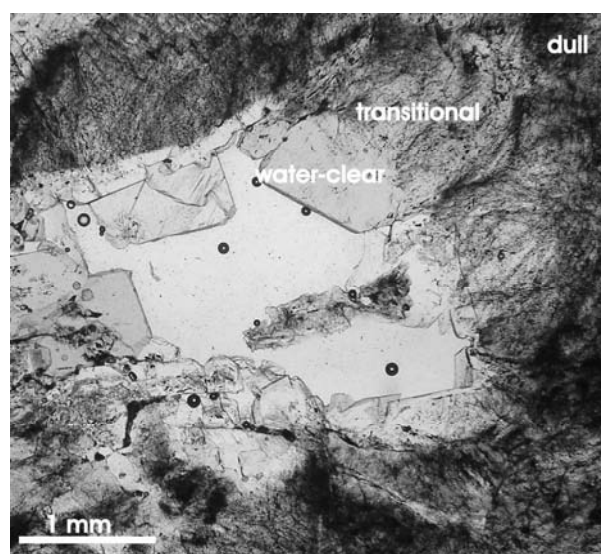


Fig. 1: Different types of datolite around a cavity in a vein.

The electron microprobe analysis revealed that there is no significant compositional difference among the different types of datolites. All of them consist of typical datolite constituents; Ca, B, Si with minor Al (most probably as substitution of Si, as shown by slight negative correlation between Si-Al), K, Na, F and Cl.

The primary fluid inclusions of 5-30 $\mu$ m size in datolite form an: (P1) water-rich  $L_{aq}+V_{CH_4}$  inclusions and (P2) liquid methane-rich  $L_{CH_4}$  inclusions, thus petrography suggests their entrapment from an immiscible fluid system. A minor amount of invisible aqueous phase may occur in the P2 type primary inclusions. The estimated volume fraction of  $V_{CH_4}$  in P1 type inclusions varies between 5 and 20 %. Salinities estimated from the ice melting temperatures are between 0.4 and 1.8 mass% NaCl. Calculations based on the Raman spectra of the aqueous fluid also proved low salinities (around 1.22 mass% NaCl) for P1 inclusions. These low salinities are sensibly lower than values of seawater. This observation confirms that datolite (and the host hydrothermal veins) does not represent a product of seawater-rock interaction. Raman spectroscopy of the P1 inclusions proved the presence of methane in the vapour phase of aqueous inclusions, however, its amount is rather small as it is illustrated by absence of methane peak in the homogenized liquid at the  $T_h$  and by the absence of observable clathrate formation during freezing experiments. A slight decrease of the Raman shift was found in relation to vapour methane in the P2 inclusions confirming the liquid state, but no trace of water was detected even at the  $T_h$  of P1 inclusions. Therefore the thermodynamic behaviour of the P2 inclusions is modelled by properties of pure methane.

Entrapment conditions of P1 and P2 inclusions are obtained by intersections of  $T_h(LV \rightarrow L)$  for P1 inclusions and representative isochors of P2 inclusions. Results indicate increasing temperature and pressure during the crystallization from dull (180-200 °C, 0.5 kbar) through the transitional (200-230 °C, 0.7-0.9 kbar) to the water-clear (~240 °C, 1.1 kbar). Composition of chlorite associated to the transitional datolite also suggests a formation temperature around 220 °C.

Datolite contains at least three generations of secondary inclusions. A group of  $L_{aq}+V_{CH_4}$  inclusions (S1) with uniformly  $v_{vap} \approx 10$  % and an average  $T_h = 162$ °C and 0.9 mass% NaCl salinity. The other two generations of secondary inclusions (S2 and S3) have apparently monophasic  $L_{CH_4}$  composition. Their average  $T_h(LV \rightarrow L)$  is -85.2 °C

(S2) and -94.5 °C (S3). The presence of methane in the vapour phase of S1 and in the liquid phase of S2 and S3 was proven by Raman spectroscopy

The precipitation of datolite took place under conditions of increasing temperature and pressure. This could have happened during the progression of the low-grade Alpine metamorphism, when in the area of the SW-Bükk Mts. a maximum of 270-285 °C at 1.5-2 kbars was (Sadek et al. 1996, Péntek et al. 2006). The source of the boron and the methane was most likely the siliciclastic sediment in the peperitic facies of the submarine basaltic volcano. Methane was also present in fluids circulating in fractures of basalt after the datolite precipitation (S1, S2, S3 inclusions).

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