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Middle Miocene zeolite-bearing turbidites, Abrămuț Basin (Pannonian Basin), NW Romania

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Detailed lithostratigraphic data from a borehole in the Abrămuț Basin, located in the northwestern part of Romania, has revealed the presence of turbiditic deposits containing several layers with tuff/tuffaceous materials in the Lower Badenian. The age of these deposits is determined by the presence of the foraminifera *Praeorbulina glomerosa* and *Orbulina suturalis*. Detailed quantitative and qualitative X-ray diffraction data (XRD) on 10 different tuff layers situated at depths between 2450 and 2640 m show a mineralogical association comprising analcime, quartz, volcanic glass, smectite, mica, calcite, K-feldspar, glass and minor quantity of chlorite and albite. The presence of analcime suggests that the albite isograd for the interval studied has been never reached and the maximum temperatures have been lower than *c*. 125°C since the Early Badenian.

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Key words: Early Badenian, foraminifera, borehole, tuffs, zeolite facies, XRD, Abrămuț Basin.

INTRODUCTION

Previous mineralogical studies from the northwestern Basin (Seghedi Transylvania et al., 2000)Coștui-Maramureș Basin (Damian et al., 2007 and reference therein) have shown that the zeolites found in tuffs of Badenian age consist mainly of clinoptilolite (40-90%) with minor amounts of mordenite or phillipsite. These tuffs have a similar stratigraphic position to other volcanic tuffs from the Transylvania Basin (Dej Tuff, Ciupagea et al., 1970), the Maramureş Basin (e.g., Cochemé et al., 2003), the Gutâi Mts. (Szakács and Seghedi, 1996; Kovács et al., 1997; Kovács and Fülop, 2003), the Apuseni Mts. (Seghedi et al., 2004), the Beregovo and northern Trans-Tisza regions (Pécskay et al., 2006), the Slănic Tuff in the foreland of the Eastern Carpathians (Mărunțeanu, 1999), and the Styrian Basin (Bojar et al., 2004; Handler et al., 2006).

The Abrămuț Basin is situated in northwestern Romania and corresponds with the Derecske Basin from the Hungarian sector of the Pannonian Basin (Fig. 1). In the boreholes, several levels of tuffs were recorded. In order to compare them with the previously known occurrences, micro-faunal and mineralogical (qualitative and quantitative) investigations were performed for the borehole interval analysed.

GEOLOGICAL SETTING

The lithostratigraphy of the Abrămuț Basin is based on subsurface geological data, represented by geophysical logs, cores and cuttings (Fig. 2). The oldest deposits drilled are polymictic conglomerates, probably of late Karpatian age. These deposits are interpreted to represent the onset of the extension in the northeastern part of the Pannonian Basin (Tulucan, 1999; Boroşi, 2004; Tiliţ *et al.*, 2007; Răbăgia, 2010). The Lower Badenian is represented by sandstones and marls with intercalations of tuff and tuffaceous sandstone in the uppermost part of the succession. The Early Badenian age is indicated by a foraminifera assemblage with *Praeorbulina glomerosa* and *Orbulina suturalis* (Boroşi, 2004; Barbu *et al.*, 2008). The Middle Badenian, characterized by the *Globigerina*



Fig. 1A - geographic location of the study area; B - regional distribution of the Badenian tuffs (after Pecskay et al., 2006)

decoraperta–Globigerina druryi foraminifera assemblage, has not been recognized in the Abrămuţ boreholes. The Upper Badenian consists of siliciclastic deposits (sandstones, marls/shales with a few tuffaceous sandstone intercalations) with *Bulimina–Bolivina* and *Velapertina* micropalaeontological associations. Locally, on the basin margins the siliciclastic deposits are replaced by fossiliferous limestones, characterised by the *Lithothamnium–Borelis* and *Amphistegina* association. There are similar calcareous facies outcrops east of the Abrămuț Basin in the northeastern section of the Plopiş Mountains (e.g., Plopiş and Tuşa localities).

The Sarmatian *s.s.* (*sensu* Rögl, 1998; Suess, 1866) comprises marls and calcareous sandstones. The Lower Sarmatian *s.s.* deposits contain a microfauna with the foraminfera *Anomalinoides badenensis, Elphidium reginum* and *Varidentella reussi*, and the Upper Sarmatian *s.s.* contains the foraminifera *Porosononion aragviensis* and *Elphidium antoninum* and the mysid statolith *Paramysis mihaii* (Boroşi, 2004).

The rare, poor faunal assemblages made it difficult to identify the Lower Pannonian. We presume that the Lower Pannonian only exists in the deepest (western) part of the Abramut Basin. The Upper Pannonian is formed by shales and marls and includes a typical fauna with *Congeria banatica* and *Cyprideis sublitoralis*. The Pontian is developed in a similar lithofacies, but comprises *Congeria digitifera*, *Congeria partschi*, *Paradacna abichi*, *Bacunella dorsoarcuata* and *Pontoniella acuminate* (Boroşi, 2004).

The Pliocene (Dacian–Romanian) consists of gravels, sands and shales interbedded with coals. The Pliocene age is



Fig. 2. General stratigraphy of the Abrămuț Basin

confirmed by the presence of *Melanopsis decolata*, *Valvata subcarinata*, *Limnocardium decorum*, *Candona lactea* and *Candona* sp. (Boroși, 2004)

The aim of this paper is to discuss the origin, timing of deposition and characteristics of the Lower Badenian tuffs and tuffaceous sandstone intercalations in the deep part of the Abrămuț Basin on the basis of cutting samples from one borehole (Fig. 3).

MATERIAL AND METHODS

MICROPALAEONTOLOGICAL DETERMINATIONS

The micropalaeontological analysis was performed on four cutting samples collected from one Abrămuţ borehole. The first three micropalaeontological samples are from cuttings of the 1st, 2nd, 6th tuff layers which were also used for mineralogical determinations. The fourth micropalaeontological sample is positioned below the 7th tuff cutting sample (Fig. 3). The micropalaeontological samples were prepared using H_2O_2 . The microfossil taxa of each sample were identified in the 125–600 µm fractions.

MINERALOGICAL DETERMINATIONS

Qualitative and quantitative mineralogical analysis was performed on 10 cutting samples collected from one borehole. X-ray diffraction patterns were measured on a *Bruker AXS D8* diffractometer equipped with a one-dimensional strip-detector (lynx-eye) using a Cu-k α radiation (40 kV, 40 mA, sample rotation). Quantification was performed as described by Eberl (2003) with synthetic Al₂O₃ as internal standard. Pure minerals and glass were used as internal reference spectra. One gram of sample was mixed with 0.25 g Al₂O₃, milled with ethanol in a McCrone micronizing mill, dried at 60°C in a compartment drier, and loaded in acrylic glass (PMMA) sample holders for powder-XRD measurements. The measuring conditions were: step-size 0.02°, 2 sec/step (equivalent to 304 sec/steps with a conventional point-detector). Calculations were done with *Rockjock 11* software (Eberl, 2003).

RESULTS

BIOSTRATIGRAPHY

For the borehole interval studied (2450 to 2580 m; Fig. 3), micropalaeontological analysis of the samples indicate the presence of Praeorbulina glomerosa circularis, Orbulina suturalis, Globigerina bulloides, Globigerina praebulloides, Globigerina angustiumbilicata, Globigerina falconensis, Globigerina bolli, Globigerinoides trilobus, Globoquadrina dehiscens, Orbulina bilobata, Cibicidoides pseudoungerianus, Pullenia bulloides, Heterolepa dutemplei, Melonis pompilioides and Sphaeroidina bulloides. The co-occurrence of the biomarkers Praeorbulina glomerosa circularis and Orbulina suturalis indicates an Early Badenian age (Upper Lagenid Zone; Rögl et al., 2002, 2008) and corresponds to the Middle Langhian M6 Zone of Berggren et al. (1995). In absolute ages, this co-occurrence spans a short time interval between 15.1 Ma (First Occurrence - FO O. suturalis) and 14.8 Ma (Last Occurrence - LO Praeorbulina glomerosa; comp. Berggren et al., 1995, Rögl et al., 2002; Kováč et al., 2004).

DEPOSITIONAL ENVIRONMENT

In the Abrămuț area, for the interval studied, which represents the uppermost Lower Badenian, geophysical logs, cores and cut-

Stage (Foram. Zone)	Depth [m]	Lithology	Gamma Ray [API]	Samples	Micropalaeontological associations			
Lower Badenian (M6, Upper Lagenid Zone; Rögl <i>et al.</i> , 2008)	-2400		$ = \frac{1}{2} \frac$		Praeorbulina glomerosa circularis Orbulina suturalis Globigerina bulloides Globigerina praebulloides Globigerina falconensis Globigerina falconensis Cibicidoides pseudoungerianus Heterolepa dutemplei Melonis pompilioides			
				Å Å	 tuff sample micropalaeontological sample tuffaceous sandstone tuff 			
	-2680		Mar Vad W hand		marl sandstone			

Fig. 3. Detailed lithostratigraphy and Gamma Ray log of the studied borehole interval

ting information were used to determine the lithology. In a previous study, Boroşi (2004) interpreted the marls, tuffs, tuffaceous sandstones and sandstones as turbidite deposits (Fig. 3).

Species of the benthic foraminifera genus *Cibicides* can be used to estimate the depositional palaeodepths. Recent and Miocene faunas with *Cibicides dutemplei*, *C. ungerianus* and *C. pseudoungerianus* are found at shallower water depths (0–500 m) than are those with *C. kullenbergi*, *C. pachyderma*, *C. wuellerstorfi*, *C. bradyi*, *C. robertsonianus* and *C. italicus* (around 1000 m depth; e.g., Hohenegger, 2005; van Hinsbergen *et al.*, 2005 and references inside).

In the present case, the benthic foraminiferal assemblages are dominated by *Orbulina suturalis* and *Praeorbulina glomerosa* and contain the palaeodepth markers *Cibicides pseudoungerianus* (100–500 m), and *Uvigerina* spp. (200–1000 m; van Hinsbergen *et al.*, 2005). The co-occurrence of these palaeodepth markers species and the presence of deeper-dwelling planktonic foraminiferal taxa such as *Globigerina bulloides* (>50 m; upwelling zone) indicate a palaeowater depth between 200 and 500 m.

MINERALOGY OF THE TUFF LAYERS

XRD data show that the mineralogical composition of the tuff layers consists of quartz, analcime $(Na_xAl_xSi_{3-x}O_6 [(3-x)/2] H_2O)$, volcanic glass, glass and minor amounts of smectite, calcite mica, K-feldspar, albite and chlorite (Table 1 and Fig. 4).

DISCUSSION

Zeolites occur when temperatures and fluid pressures are below 250°C and 2 kbar respectively (Liou, 1971; Cho et al., 1987, Cho, 1991). The burial-depth zonation of zeolites has been described by Coombs et al. (1959). The type of zeolite formed, mainly depends on the temperature, the type of fluid and the composition of the source rock. Among the largest volumes of zeolites are formed in sedimentary rocks deposited along convergent continental margins and associated with volcanic arcs (Utada, 2001). A classical zeolite suite formed during burial metamorphism of volcaniclastic rocks was described by Ijima and Ogihara (1995), who estimated the boundary between unaltered glass (zone I) to alkali-clinoptilolite/mordenite (zone II) at 44°C; the next boundary to analcime, heulandite (zone III) was placed at 84°C, followed at 123°C by the boundary to albite (zone IV; Fig. 5). The temperature boundary between the zeolite zones may be different when saline alkaline fluids are present in the section (Ijima, 2001). In this case, the temperature values are lower – between 21 to $34^{\circ}C$ at the boundary between zone I and II, and between 37 to 51°C at the boundary between zones II and III. Neuhoff

et al. (2004) plotted compositional and thermodynamic data for analcime with thermo-barometric isograds. The authors discuss the stability of analcime with various chemical compositions in the system analcime–quartz–albite–H₂O. Their experimental data agree well with evidence from boreholes in Japan, as described for example by Ijima (2001). Both data sources demonstrate that Liou (1971) overestimated the upper temperature of stability for analcime.

In the Abrămuț Basin section, the mean geothermal gradient is 4.5° C/100 m (Fig. 5). The geothermal gradient was calculated using the following formula:

$$GT = [T^{o}_{formation} - T^{o}_{surface}/d] \times 100$$

where: $T^{o}_{formation}$ – temperature measured in borehole, $T^{o}_{surface}$ – average temperature at surface, d – depth where temperature formation was measured in metres.

Table 1

	Sample name										
Mineral	H2450	H2500	H2510	H2520	H2530	H2546	H2570	H2600	H2640		
	weight [%]										
quartz	29	33	33	32	36	36	32	31	33		
albite	1	1	1	1	1	2	1	1	1		
K-feldspar	3	5	9	6	8	10	4	7	5		
calcite	7	1	<1	2	2	2	1	<1	1		
analcime	1	35	33	36	27	18	38	38	36		
glass	33	18	18	17	21	24	18	16	18		
smectite	15	2	2	3	3	4	3	2	4		
mica	10	5	4	3	2	4	2	5	2		
chlorite	1	<1	<1	<1	<1	<1	<1	<1	<1		

Qualitative and quantitative mineralogical composition of samples



Fig. 4A – XRD spectra of the tuff sample situated at 2520 m depth, mineral abbreviations according to Kretz (1983), corundum was used as internal standard; B, C – tuff thin sections (crossed light) with glass (extinction with cross lights), feldspar and quartz



Fig. 5. Stability interval of zeolites for: A – burial diagenesis (after Ijima and Ohigara, 1995); B – burial diagenesis and saline alkaline pore-fluid diagenesis (Ijima, 2001)

The temperature was measured in the borehole for the depth interval between 2500 to 2720 m, and varies from 120 to 134°C, respectively. The average surface temperature is 10°C. The thermal gradient is reflected by a high heat flow value of 90 mW/m² (Demetrescu, 1978, 1982; Tari *et al.*, 1999; Lenkey *et al.*, 2002; Ádám *et al.*, 2003; Fig. 6).

The fluids have a neutral to slightly alkaline pH, with salinities varying between 9–21 g/l, and contain Na⁺, Ca²⁺, Cl⁻ and CO_3^{2-} (courtesy OMV-Petrom). Major components of the tuffs are quartz, analcime and glass. In the section presented in this study, the only zeolite detected by XRD is analcime. The clay mineral content is minor and low proportions of muscovite and chlorite are also present. The mineralogical association determined, which contains only a minor amount of albite, implies that, in the present case at a maximum depth of 2640 m, the maximum temperature has never exceeded c. 125°C since Miocene times, which is the upper temperature boundary between analcime and albite, in the absence of fluids after Ijima and Ogihara (1995; Fig. 5). Based on both the previously known data concerning the stability zone of analcime in similar deposits and the data acquired for this borehole, the Abrămut section did not reach the analcime-albite transition.

CONCLUSIONS

The interval studied belongs to the uppermost Lower Badenian (Upper Lagenid Zone), was deposited in the upper



Fig. 6. Pannonian Basin heat flow map (Ádám et al., 2003)

bathyal zone and contains several intercalations of volcanoclastic material. Mineralogical quantitative and qualitative investigations show the presence of analcime with only minor amounts of albite. The results strongly suggest that, for the interval investigated, temperatures never exceeded c. 125° and the albite isograd was never reached.

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