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On the age of the Dej Tuff, Transylvanian Basin (Romania)

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Abstract: The Dej Tuff is an important stratigraphic marker in the Transylvanian Basin. However, its Early Badenian age is known only on biostratigraphical grounds so far. A number of radiometric dating techniques including K-Ar, Ar-Ar and fission-track have been used in order to constrain more precisely its age, allowing the calibration of the Transylvanian Basin’s evolutionary models. Although individual dating methods could not provide a unique, reliable and accurate radiometric age, comparison and evaluation of multiple methods gives 14.8–15.1 Ma as the most likely formation age of the Dej Tuff.

Key words: Badenian, Transylvanian Basin, radiometric dating, tephrochronology, explosive volcanism, rhyolite tuff.

Introduction

Acidic tuffs are widely recognized throughout the Middle- and Upper Miocene in the eastern part of the Carpathian-Pannonian area, especially in and around the Transylvanian Basin (Mârza & Mészáros 1991). Only within the Badenian deposits of the Transylvanian Basin, at least three different widespread acidic tuffs have been recognized and described (Răileanu 1959; Mârza & Mészáros 1991). The Dej Tuff (Pošepny 1867) is the most prominent of them, and it is the only one predating the intermediate calc-alkaline volcanism of the Eastern Carpathians and the Apuseni Mts.

This easily recognizable lithological unit consisting of alternations of numerous reworked tuff layers and fine-grained siliciclastic sediments is also known as the upper part of the “Dej Tuff Complex” (Moisescu & Popescu 1967) or as the Dej Formation (Popescu 1970). However, its most frequently used denomination in Romania and the neighbouring countries is the Dej Tuff, the term introduced by Pošepny in 1867, after the north-western Transylvanian town of Dej, where it was first time described in detail.

Although the Early Badenian age of the Dej Tuff is widely accepted, based on planktonic foraminifera (e.g. Popescu 1970; Mészáros & Şuraru 1991; Popescu & Cioflica 1973), and calcareous nannoplankton (e.g. Mészáros & Filipescu 1991; Mészáros et al. 1991; Mészáros & Şuraru 1991; Mărunţeanu et al. 2000), its precise age is still not well constrained on the grounds of radiometric dating. Since the Dej Tuff is widely dispersed throughout the whole Transylvanian Basin and its closer or broader surroundings, its value as a regional marker horizon would be significantly increased by the application of more accurate dating techniques. Calibration of basin evolution models is impossible without precisely defined and dated marker horizons within the sedimentary sequences of the basin fill. This paper aims to constrain the age of the Dej Tuff based on data obtained with various radiometric dating methods, such as K-Ar, Ar-Ar and fission-track (FT) supplementing the updated biostratigraphic age constraints.

General features of the Dej Tuff

Occurrence

The Dej Tuff represents one of the most prominent felsic (acidic) tuff “layers” of the whole Carpathian-Pannonian region. Its classical outcrop area is the northwestern and northern border of the Transylvanian Basin. It is also exposed along the southeastern border of the Silvania and Baia Mare basins, which are small marginal sub-basins belonging to the great Pannonian Basin System. The lithological and chronostratigraphic equivalents of the Dej Tuff are known under various names, namely Perşani Tuff at the southeastern margin of the Transylvanian Basin (Rado et al. 1980); Slănic Tuff along the outer Carpathian bend (Murgeanu et al. 1968) and Govora Tuff at the southern tip of the Southern Carpathians. Furthermore, drillhole and subsurface data strongly suggest that the Dej Tuff forms an almost continuous lithostratigraphic unit inside the Transylvanian Basin (Mârza et al. 1991; Krézsek & Filipescu 2005; Krézsek & Bally 2006), frequently used as a marker horizon in early gas exploration works (e.g. Ciupagea et al. 1970). Taking into account the geographical distribution of all these “tuffs”, and their litho- and biostratigraphic as well as petrographic features, it is apparent that they form a well-defined unique lithological enti-

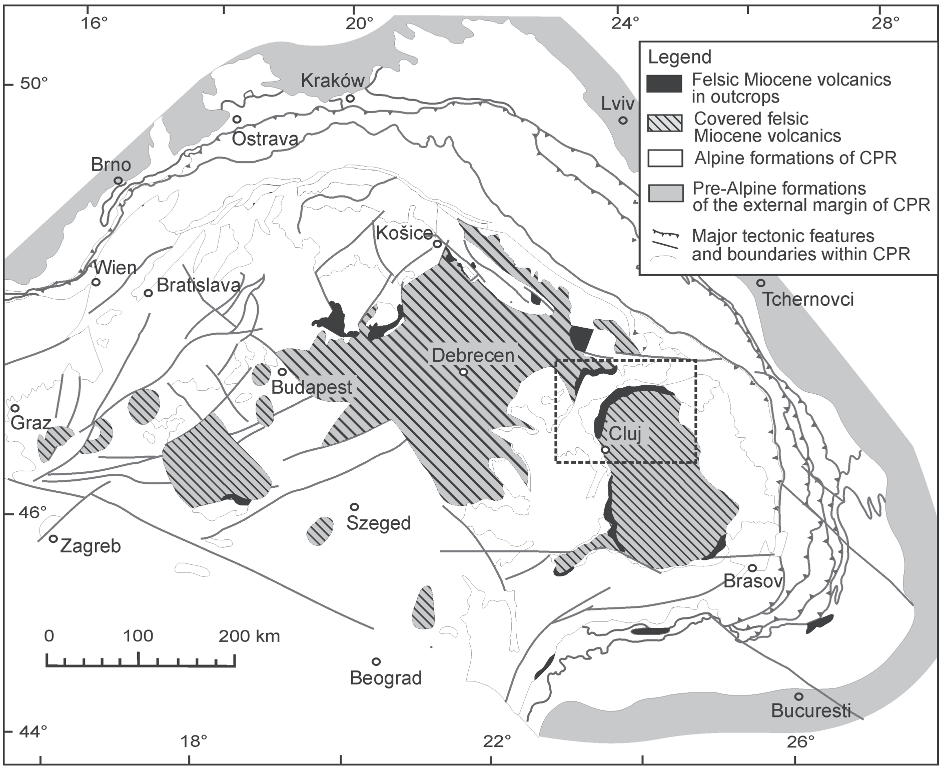

Fig. 1. Occurrence of felsic Miocene tuffs in the Pannonian-Carpathian region in outcrops (black) and in drillings, covered by younger sediments (hatched). The dotted-line frame shows the area of Fig. 3. The main tectonic elements (thrusts and faults) are shown.

ty over an area of at least 15,000 km^2 in the eastern part of the Carpathian-Pannonian region (Fig. 1).

Stratigraphy

The ca. 2000 m thick Badenian sedimentary pile of the Transylvanian Basin (Krézsek & Filipescu 2005) consists of (see Fig. 2; Krézsek & Filipescu 2005; Filipescu 2001 and references therein):

1) the Lower Badenian (*Praeorbulina glomerosa* Biozone) Ciceu-Giurgeşti Formation composed of conglomerates and/or gravels, covered by an alternation of sandy marls and thin tuff layers;

2) alternation of tuffs and marls (=Dej Tuff of Pošepny 1867) covering the previous unit, and correlated to the *Orbulina suturalis/Globorotalia bykovae* and *Globoturborotalita druryi/Globigerinopsis grilli* Biozones (Lower–Middle Badenian);

3) the Middle Badenian evaporites: gypsum in the western border of the basin (Cheia Formation) and salt (Ocna Dejului Formation) in its middle part;

4) the Upper Badenian (*Velapertina* Biozone) deep-marine siliciclastics (Pietroasa Formation).

The Dej Tuff was re-interpreted and re-named several times due to its lithological heterogeneity and the presence of some minor tuff layers within the conglomerates below it, causing nomenclatural confusions. Moisescu & Popescu (1967) grouped the above mentioned first three lithological entities into the "Dej Tuff Complex", and named the Dej Tuff as the "Dej Tuff level" within, whilst Popescu (1970) noticed the lithological heterogeneity and therefore proposed the "Dej Beds" (=Dej Formation) name for it, and described it as such.

It is beyond the scope of this article to fully discuss the nomenclature problems one may encounter in the relevant literature. We will use the original name Dej Tuff (Pošepny 1867) for the lithostratigraphic entity composed by the alternation of tuffs and marls, because it should be considered as a valid name, being in accordance with the International Stratigraphic Guide (see Salvador 1994).

Lithology

The Dej Tuff is actually extremely variable in thickness (from a few meters to 116 m) and composition. In the outcropping area (north-western Transylvanian Basin) a large number of tuff layers alternate with siliciclastic deposits consisting of non-volcanic or mixed material, mostly marls. Three types of lithofacies have been recognized. They alternate in a rather regular manner (Szakács 2000): (1) meters thick coarse, sand to pebble-sized, volcaniclastic deposits, including coarse lapilli tuff, (2) meters thick massive to stratified and/or graded tuff layers, and (3) centimeter to decimeter thick, coarse- to medium-grained tuff layers alternating with fossiliferous marls. They represent (1) subaqueous debris flow deposits and redeposited pyroclastic flow deposits, (2) high-density turbidites and (3) low-density turbidites, respectively. The erosional base is often visible at the bottom of type 1) deposits, which commonly show lenticular morphology and cannot be correlated over even short distances. One may easily recognize Bouma sequences within the tuff layers deposited from low-density turbidites. Lithofacies types commonly succeed each other according to the above order, from bottom to top, in characteristic facies associations. Such facies associations may be repeated 3 to 6 times.

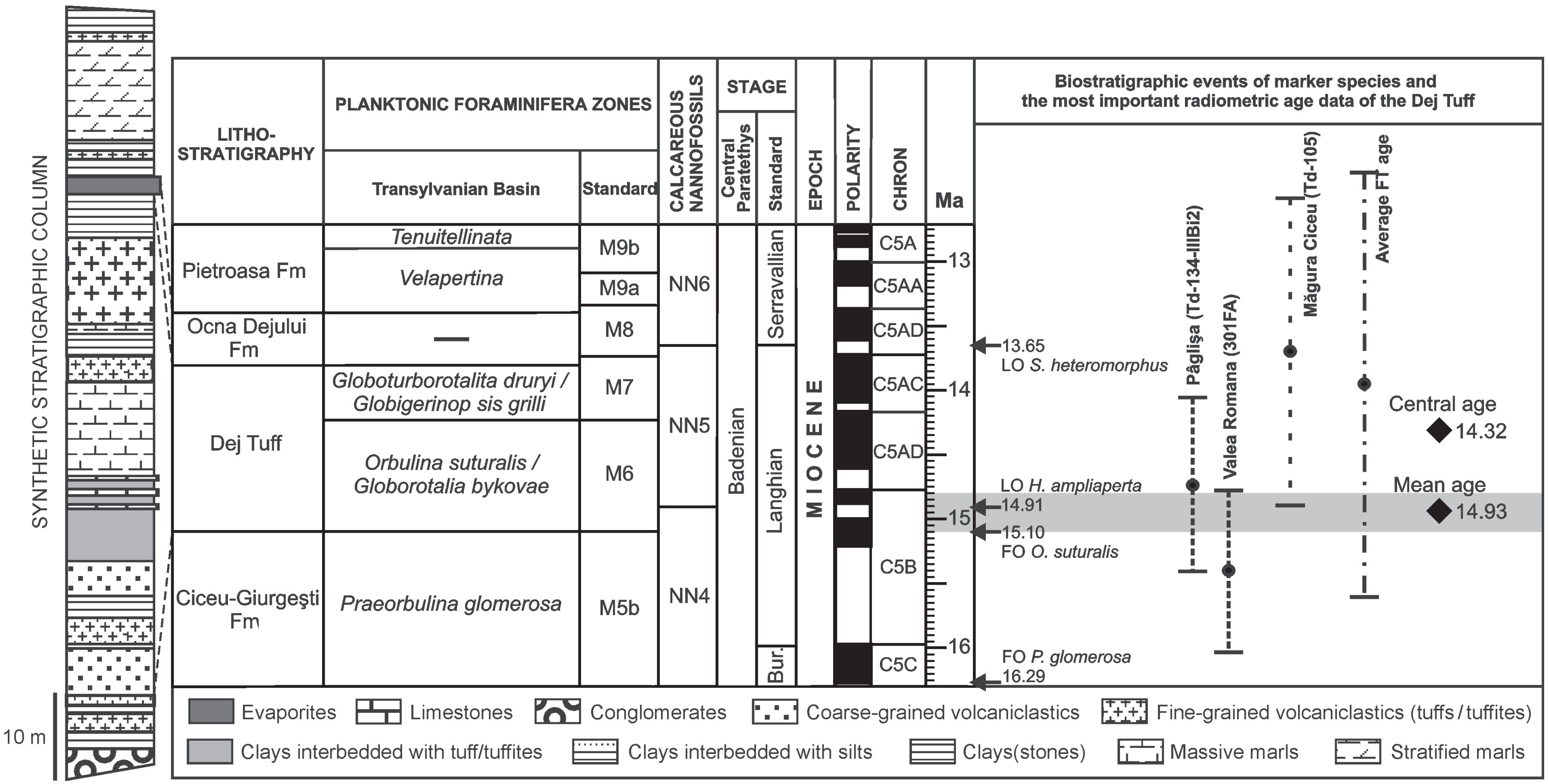

Fig. 2. Detailed correlation of the stratigraphic position of the Dej Tuff within the Badenian succession of Miocene sediments in the north-western Transylvanian Basin with a summary of the radiometric age data for the Dej Tuff. The light grey band shows the most likely time interval of its genesis. Lithostratigraphy based on Filipescu (2001). Biozonation of planktonic foraminfera in the Transylvanian Basin after Filipescu & Silye (2008), Popescu (1975), and Popescu & Gheţa (1984), the later drawn here according to the recalibration of Krézsek & Filipescu (2005), standard zonation after Wade et al. (2011). Calcareous nannoplankton zones after Martini (1971). Standard chronostratigraphy based on Lourens et al. (2004a), and regional chronostratigraphy according to Rögl et al. (2008). Ages of magnetic chrons are from Lourens et al. (2004a,b) with corrections according to Hüsing et al. (2010). Data on biostratigrahic events from Lourens et al. (2004b), and Berggren et al. (1995).

These lithofacial features strongly suggest that the great bulk of the Dej Tuff tephra has been reworked and redeposited into a marine basin shortly after primary deposition (Szakács 2000).

Primary pyroclastic flow deposits are found in a single occurrence area (Măgura Ciceu Hill) as slightly welded ignimbrites deposited in an underwater environment (Mârza & Mirea 1991; Seghedi & Szakács 1991).

Petrography and mineralogy

Since it is widely redeposited, the Dej Tuff contains clasts of both volcanic and non-volcanic origin in variable amounts. Components of magmatic origin include vitric clasts, crystal clasts and lithic clasts of which the first two are juvenile. Coarse, lapilli-sized vitric clasts are pumice, while ash-sized vitric clasts are both pumice and glass shards. Except for a few outcrops, these clasts are strongly transformed, being replaced by an assemblage of mostly zeolite minerals. Massive, non-altered glass fragments (obsidian) are present in accessory amounts. Slightly flattened pumice clasts are characteristically present in the primary pyroclastic flow deposits at Măgura Ciceu. Crystal clasts of juvenile origin include quartz, plagioclase and biotite as the most common components. Biotite is ubiquitous but it is frequently overprinted by subaqueous alteration. K-feldspar and amphibole are also present in part of the deposits, while the presence of clinopyroxene characterizes certain levels of the sequence in a few outcrops. Zircon, apatite, allanite and Fe-Ti oxides are common accessory minerals.

Petrochemistry

Whole-rock major element analyses on a few selected samples recalculated on a volatile-free basis as well as microprobe analyses on unaltered massive glass fragments revealed the basically rhyolitic composition of the Dej Tuff (Szakács 2000), which is in contrast with the traditionally (e.g. Koch 1900; Vancea 1960) considered dacitic composition. The trace element distribution clearly shows the subduction signature of the generating magma. Interaction with crustal material is pointed out by Sr and Nd isotopic ratios. Mineral chemistry indicates the origin of the rhyolitic magma through differentiation processes from more mafic melts in zoned magma chambers (Szakács 2000).

Dating the Dej Tuff

Summary of biostratigraphic age data

The Dej Tuff is very poor in its macrofossil record. Chira (1991) listed a number of 17 bivalves and 1 gastropod species from the collection of the Paleontology-Stratigraphy Museum of the Babeş-Bolyai University (Cluj-Napoca, Romania) originating from the Dej Tuff. Due to their scarcity and their stratigraphic distribution, these fossils are almost useless for biostratigraphic dating of their host deposits.

In contrast, the thin marls, or the marly tuffs, or sometimes the tuff layers themselves contain calcareous nannoplankton, planktonic foraminifera, and even ostracods.

The calcareous nannoplankton assemblages recovered from the Dej Tuff were unanimously assigned to the NN5 *Sphenolithus heteromorphus* Zone (Martini 1971) proving the Early Badenian age of the tuff (e.g. Mészáros et al. 1991; Mészáros & Filipescu 1991; Mészáros & Şuraru 1991; Mărunţeanu et al. 1999; Vulc & Silye 2005). The planktonic foraminiferal assemblages of the Dej Tuff were assigned in classical studies (e.g. Mészáros et al. 1991; Mészáros & Şuraru 1991) to the *Orbulina suturalis/Globorotalia bykovae* Biozone, which was later re-interpreted by Popescu & Gheţa (1987), Popescu (2000) and re-calibrated by Krézsek & Filipescu (2005). Therefore it corresponds, in the current biozonations in use, to the *Orbulina suturalis/Globorotalia bykovae* and *Globoturborotalita druryi/Globigerinopsis grilli* Biozones and are correlated to the M6, and partly to the M7, zones of Wade et al. (2011). This also suggests a mostly Early Badenian biostratigraphic age for the Dej Tuff. The Early Badenian age of the Dej Tuff was also confirmed, based on ostracods recovered in the southern Baia Mare Basin, by Wanek & Clichici (1991).

However, the first occurrence (FO) of *Orbulina suturalis* is 15.10 Ma (Berggren et al. 1995), which is earlier than the last occurrence (LO) of *Helicosphaera ampliaperta* dated to 14.91 Ma (Lourens et al. 2004a,b), which suggest some correlation problems at the base of the Dej Tuff (see also in Chira & Bălc 2002), or simply the base of the Dej Tuff must be correlated with the topmost part of NN4.

The biostratigrahic age of the Dej Tuff can be further constrained based on the LO of *Sphenolithus heteromorphus* dated to 13.65 Ma (Lourens et al. 2004a,b), and on the FO of *Orbulina suturalis* dated to 15.10 Ma (Berggren et al. 1995; Wade et al. 2011). Although, the regional biostratigraphic markers do not allow a more accurate location within this 1.45 Myr interval, this interval can be further reduced to 1.29 Myr based on the beginning of the deposition of the Badenian salt, dated to 13.81 ± 0.08 Ma (de Leeuw et al. 2010). The Badenian salt as a lithostratigraphic unit is regionally distributed in the Central Paratethys and it covers the Dej Tuff in the Transylvanian Basin.

Radiometric dating

Due to the inherent difficulties in obtaining accurate radiometric ages, a number of different dating techniques have been used, their results then compared and evaluated. Tuff samples were collected from different occurrences in order to meet the requirements of these methodologies. Sampling localities are shown in Fig. 3.

K-Ar dating

Methodology: Measurement of K-Ar ages was performed in the Institute of Nuclear Research of Hungarian Academy of Sciences (ATOMKI), Debrecen. Part of each sample was pulverized for K determination. An argon extraction line and a mass spectrometer, both designed and built in the ATOMKI, were used for argon measurement. The rock was degassed by high frequency induction heating, the usual getter materials (titanium sponge, getter pills of SAES St707 type and cold traps) were used for cleaning and transporting Ar. The ^{38}Ar

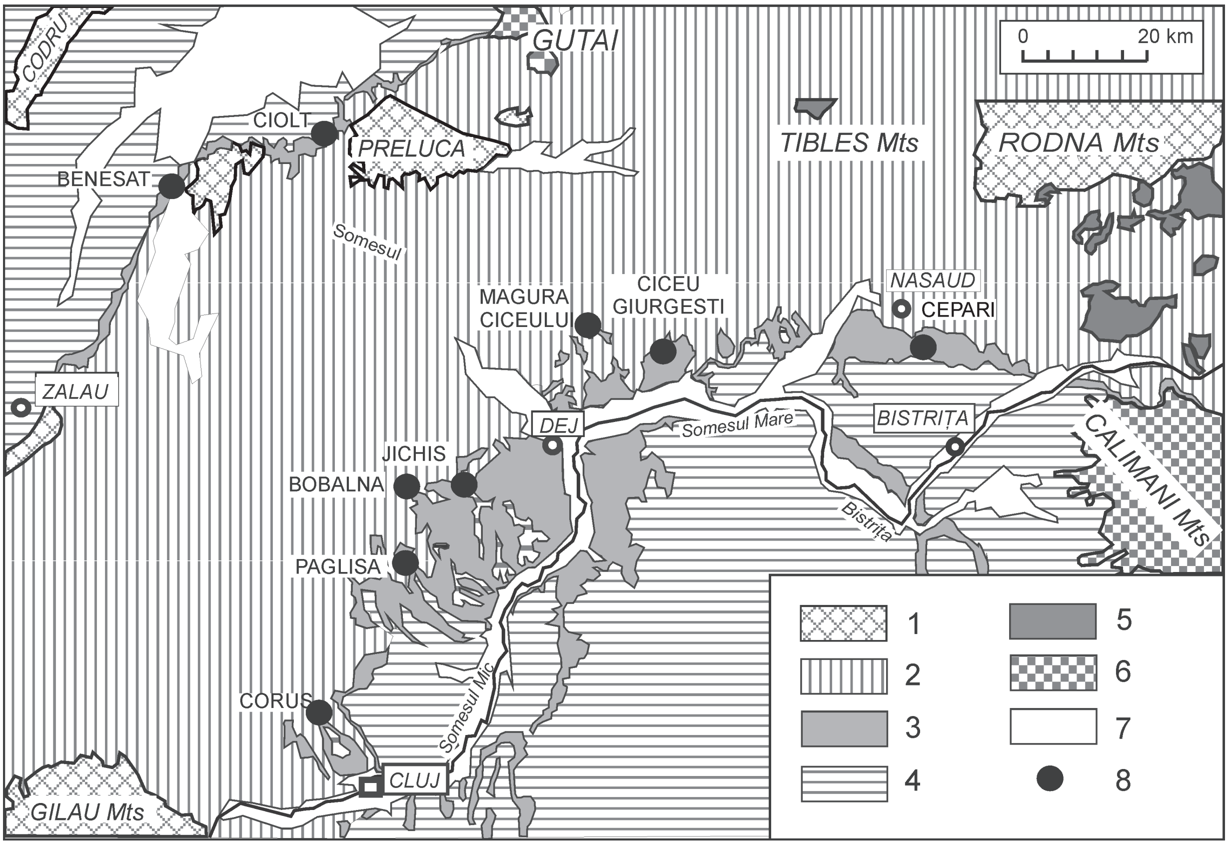

Fig. 3. Sample locations of the Dej Tuff used for radiometric dating in the north-western Transylvanian Basin. **1** — Metamorphic basement rocks on the basin margin, **2** — Pre-Lower Badenian sedimentary fill of the Transylvanian Basin, **3** — Lower Badenian sedimentary rocks including the Dej Tuff, **4** — Post-Lower Badenian sedimentary fill of the Transylvanian Basin, **5** — Neogene intrusive magmatic rocks, **6** — Neogene volcanic rocks, **7** — Pleistocene-Holocene deposits, **8** — Sampling localities. Open square and open circles mark major cities and towns.

spike was introduced to the system from a gas-pipette before the degassing was started. The purified Ar was directly introduced into the mass spectrometer. The mass spectrometer was a 90° magnetic sector type of 150 mm radius and was operated in the static regime. Recording and evaluation of the Ar spectrum was controlled by a microcomputer. Potassium was determined by flame photometry with a Li internal standard and Na buffer.

The interlaboratory standards Asia 1/65, HD-B1, LP-6 and GL-0 as well as atmospheric Ar were used for controlling and calibration of analyses. Details of the instruments, the applied methods and results of calibration have been described in more detail elsewhere (Odin et al. 1982; Balogh 1985). K-Ar ages were calculated using the constants proposed by Steiger & Jäger (1977).

Results

Precise radiometric dating of the Dej Tuff samples is challenging, because these rocks are the products of distal facies, mainly fallout tephra, often reworked by various processes.

Three different occurrences of the Dej Tuff (Figs. 3, 4) have been sampled and studied by conventional K-Ar and incremental ^{40}Ar-^{39}Ar dating. K-Ar analytical data are summarized in Table 1. Whole-rock samples enclosing accidental lithoclasts may not be completely outgassed of its pre-existing radiogenic argon, even at high temperatures, therefore only monomineral fractions separated from the rhyolite tuffs have been dated. Since the outcropping rhyolite tuffs usually lack separable high K, fresh biotite, we paid attention to sampling

Table 1: K-Ar dating of Dej Tuff samples.

Lab #	Sample #	Locality	Dated fraction	K (%)	^{40}Ar$_{rad}$/g (mcm3g)	^{40}Ar rad (%)	K-Ar age (Ma)	Obs.
4698	TD105	Măgura Ciceu	biotite	6.00	2.757×10^{-6}	18.1	11.78 ± 0.94	Ar loss, minimum age
4700	TD134-I-Bi1	Pâglișa	biotite	2.48	1.233×10^{-6}	23.3	12.76 ± 0.83	altered, minimum age
4699	TD134-I-Bi2	Pâglișa	biotite	2.48	1.109×10^{-6}	13.0	11.47 ± 1.24	altered, minimum age
4701	TD134-III-Bi1	Pâglișa	biotite	3.78	1.698×10^{-6}	23.5	11.52 ± 0.68	altered, minimum age
4702	TD134-III-Bi2	Pâglișa	biotite	5.14	2.958×10^{-6}	41.6	14.74 ± 0.67	treated
4056	301FA	V. Română	biotite	6.26	3.765×10^{-6}	56.0	15.40 ± 0.63	W Gutâi Mts

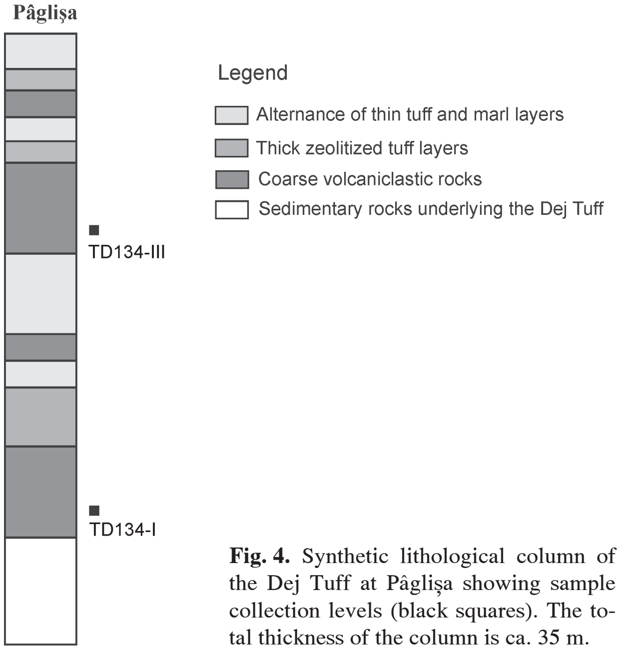

Fig. 4. Synthetic lithological column of the Dej Tuff at Pâglişa showing sample collection levels (black squares). The total thickness of the column is ca. 35 m.

the most suitable samples. For instance, samples were collected from two different levels of the Pâglişa occurrence, and measurements were performed on two biotite separates from each sample (Table 1, Fig. 4). Mineral separation has been made on the basis of microscopic inspection of thin-sections. Strongly altered rock specimens were eliminated. All samples were first crushed and sieved. Biotite and feldspar crystals were separated from the 250–315 μm grain-size fraction. Magnetic separator and heavy liquids were used for obtaining mineral concentrates. For the sake of improving the purity of the mineral fractions, additional hand-picking was used under a binocular microscope.

Nevertheless, there is a spread in the measured ages which is uncorrelated with biostratigraphic ages in some instances. Consequently, some K-Ar ages can be considered as "apparent ages", but others are in accordance with the geological data.

Evidence for the role of syn- and/or post-depositional changes was found in the variety of biotite chemistry (see the K concentrations in Table 1). As a consequence, low K contents (less than 4 %) and substantial atmospheric Ar concentrations (about 80 %) of the biotites result in low $^{40}Ar_{rad}/^{40}Ar_{tot}$ ratios. This hampers the precision of K-Ar age determinations. According to our experience, after cleaning biotite in methyl alcohol (no. 4702) the atmospheric Ar content decreased and the K concentration increased. We suppose that this simple treatment partially removed the very fine-grained clay minerals which are presumably located at the grain boundaries of biotite. For the sake of detecting possible $^{40}Ar_{rad}$ loss, or the presence of excess Ar, plagioclase mineral fractions (no. 4701 and no. 4699) were also measured by conventional K-Ar dating.

In spite of the highly consistent K-Ar ages obtained on biotites no. 4701, no. 4699 and no. 4698 (11.5 Ma–11.8 Ma) we do not consider them as formation ages, rather we assume that they are the consequence of some rejuvenation processes resulting in secondary effects. However, it is worth mentioning that a similar age (11.9 ± 0.7 Ma) has been determined on biotite separated from the Călineşti Tuff, exposed in the Oaş Mts, NW Romania (Pécskay et al. 1995a). Thus, this age can reflect a geological event, which has strongly affected the rocks under investigation. Fischer & Steiger (1988) studied the influence of lithification on K-Ar ages. They observed that decrease of the K-Ar ages occurs with the degree of lithification and is presumably correlated with it. Grant et al. (1984) arrived at similar conclusions. They suggest that diagenetic events should have caused substantial chemical change leading to loss of previously accumulated $^{40}Ar_{rad}$, hence rejuvenated K-Ar ages.

The most reliable K-Ar ages (14.74 ± 067 Ma and 15.40 ± 0.63 Ma) have been determined on the biotites (no. 4036 and no. 4702, respectively) with the highest K content and with the highest radiogenic Ar percentage. Consequently, the eruption of the Dej Tuff cannot have occurred earlier than the Early Badenian or later than the Middle Badenian. Similar ages were reported for some rhyolite tuffs within the Pannonian Basin (Pécskay et al. 1995b).

On the basis of lithostratigraphic data it is possible to distinguish various tuff sequences (Szakács 2000) with similar radiometric ages, but the time interval of the volcanic activity that produced these volcanic products cannot be clearly defined because the experimental error surely overlaps with the life span of the volcanism.

Ar-Ar dating

Methodology: Biotite separated from sample TD-105, showing the highest K content and the least signs of alteration of all Dej Tuff samples, has been chosen for Ar-Ar dating after it was dated previously by the K-Ar method.

The sample was irradiated in the 229/3 position (out of the centre of the core) of the nuclear reactor of the Atomic Energy Research Institute of Physics, Budapest, along with interlaboratory standard biotite LP-6. Samples were wrapped in Al foil and placed in a cylindrical container made of 0.5 mm thick Cd. The Cd container was sealed hermethically in an Al canister. The distribution of the integrated fast neutron flux was monitored by Ni foils placed beside the samples. The irradiation parameter was $J = 1.277 \times 10^{-3}$ for the sample.

Ar extraction was performed in a resistance heated molybdenum furnace. The temperature was controlled by a Pt–PtRd thermocouple. The furnace was connected to the Ar purification line used for K-Ar dating. The sample was heated for 50 minutes at each temperature step. Procedural system blanks (atmospheric composition) were measured before degassing for different temperature steps, they were increasing from 10^{-9} cm^3 STP to 10^{-8} cm^3 STP at 1400 °C. The particularities of the experimental method used in this work are described by Balogh & Simonits (1998).

Evaluation of Ar-Ar age spectrum

A disturbed age spectrum has been obtained (Table 2, Fig. 5). The ages gradually increase with increasing temperature, and the spectrum obtained is similar to a diffusive loss profile. The oldest age of 13.7 ± 1.2 Ma at the highest tem-

Table 2: Ar-Ar dating (sample Td-105).

Step	^{39}Ar (% cumulative)	Temperature (ºC)	Age (Ma)
1	30.5	400	7.04±0.57
2	48.5	645	9.70±1.00
3	84.5	860	12.7±0.50
4	100	990	13.7±1.20

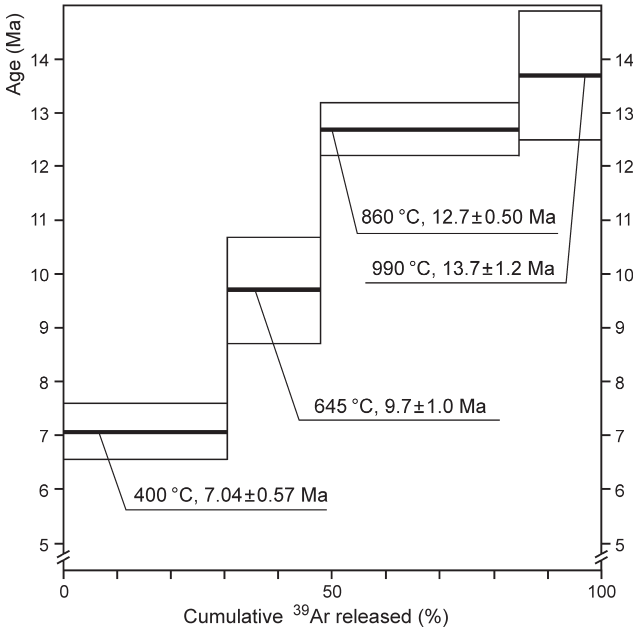

Fig. 5. Ar-Ar spectrum of sample TD-105.

perature gives a lower limit for the time of volcanic activity producing the dated sample-rock and the lowest age of 7.04 ± 0.54 Ma is the oldest age limit of the age of the main secondary post-depositional event, most likely a fluid interaction effect, that released part of the radiogenic argon from sites near the grain-boundary of biotite and from the phase boundaries between elementary crystallites (subcrystals) within the biotite grains.

Few Ar-Ar ages are available for Miocene tuffs in the Carpathian-Pannonian Basin. An Ar-Ar age on biotite from the ignimbrite at Ipolytarnóc has been published by Hámor et al. (1987).

This spectrum is also disturbed and shows the irregularities characteristic for heterogeneous samples which are composed of micrometer-sized mineral phases differing in age and mineral composition. Unpublished results from altered biotites from the rhyolite tuffs at Ipolytarnóc show that higher K concentration is not a convincing argument against loss of $^{40}Ar_{rad}$. For example, a zero age has been measured in biotite of 4.3 % K concentration.

Few Ar-Ar ages are available for Miocene rhyolite tuffs, exposed in the Carpathian Pannonian Basin. Ar-Ar fusion ages obtained from biotite and plagioclase have been published by Hámor et al. (1987) and Pálfy et al. (2007). Middle Badenian tuff outcropping in South Poland gave 13.81 ± 0.08 Ma (de Leeuw et al. 2010), and a highly similar age has been determined for the Bochnia tuffites (13.76 Ma, Bukowski et al. 2010).

FT dating

Since both K-Ar and Ar-Ar dating failed to result in accurate age determination of the Dej Tuff, we attempted to use the FT method on zircon grains. Seven samples have been measured, five of them from outcrops in the north-western Transylvanian Basin and two from the south-eastern margin of the Silvania Basin (marginal sub-basin of the great Pannonian Basin) (Fig. 3, Table 3).

Methodology: The analyses were done in the Mineral Separation Laboratory and Fission Track Laboratory of the Free University of Amsterdam on 7 samples from 7 different outcrops (Vlad 1998). The external detector method has been used on a number of single zircon grains. Monomineral zircon grain separates of > 80 % purity have been obtained from each sample by crushing, pulverizing, sieving, separation using heavy liquids and final magnetic separation. Zircon grains were embedded in Teflon. Grinding of mounted grains was done with carbide abrasive papers with adhesive-backing and a HANDIMET grinder. Smooth surfaces of the grains resulted from polishing with a 6 micrometers diamond polishing compound (METADI II) and with a diamond grain-size of 1 micrometer. A Buchler POLIMET machine (6 micrometers) and a KENT MK 2A machine (1 micrometer), both with polishing cloth disks with activated adhesive were used. Eutectic melt of KOH + NaOH was used for etching. The mounts were covered with a flake of low-uranium mus-

Table 3: Fission-track dating of the Dej Tuff using zircon grains.

Sample	Sample locality	FT age* (Ma)	Central age** (Ma)	Mean age** (Ma)	n	Obs.***
North-western	**Transylvanian Basin**					
CEP1	Cepari	13.79 ± 1.92	13.82	13.95	15	H
CG1	Ciceu-Giurgeşti	14.34 ± 1.92	14.39	14.80	16	H
TD-137-3	Coruş	13.94 ± 1.58	13.95	14.34	20	H
TD-142	Jichişul de Sus	15.11 ± 1.50	15.41	16.05	25	NH
TD-144-2B	Bobâlna	14.86 ± 1.74	15.14	15.78	26	NH
	Average	**14.41 ± 1.73**	**14.54**	**14.98**		
Silvania Basin						
TD-148-2C	Benesat	13.32 ± 1.56	14.40	15.65	20	NH
TD-149-5D	Ciolt	12.31 ± 1.38	13.10	13.96	30	NH
	General average	**13.95 ± 1.66**	**14.32**	**14.93**		

* — Calculated acc. to the Berekening external detection method, ** — Calculated according to the radial projection method, *** — Population homogeneity; H — homogeneous, NH — not homogeneous, n — number of zircon grains measured.

covite and were irradiated in a nuclear reactor. A standard of known age and a glass dosimeter with known uranium concentration was included in the sample package during irradiation. For age calculation the zeta approach was used, according to the formula developed by Price & Walker (1963) and Naeser (1967).

Analytical results and interpretation

Fission tracks have been counted on a variable number (15 to 30) of zircon grains in each sample. The analytical results are given in Table 3. The mean ages, obtained using the radial projection method, range from 13.96 to 16.05 Ma, with an average of 14.93 Ma. This value is consistent, within analytical error, with the K-Ar age of the Valea Romană sample (15.4 ± 0.63 Ma) and the 134-III-Bi2 Pâglişa sample (14.74 ± 0.67 Ma). Moreover, it is also consistent, within analytical error, with the FO of *Orbulina suturalis* dated to 15.10 Ma (Berggren et al. 1995), whilst the calculated central ages (14.54 Ma, and 14.32 Ma), fit well within the 13.65 Ma and 15.10 time interval constrained according to the LO of *Sphenolithus heteromorphus*, and the FO of *Orbulina suturalis*.

Discussion and conclusions

Different radiometric methods have been used in order to accurately determine the age of the Dej Tuff. Although all methods applied yielded results which are generally consistent with Early Badenian dating of the Dej Tuff on biostratigraphic grounds, none of them is able alone to constrain its age to higher accuracy.

Monomineral samples have been measured by K-Ar and Ar-Ar methods. Although biotite is the most suitable mineral for this kind of dating, the biotite in the Dej Tuff is altered by fluid interaction during burial and diagenesis, thus showing argon loss and recording events which are younger than the eruption and emplacement of tephra. Thus, K-Ar dating resulted in minimum ages for most of the samples. However, one sample (TD-134-III-bi2, Table 1), which has been specially treated for measurement, yielded an age (14.74 ± 0.67 Ma) close to the eruption age of the Dej Tuff. Such an age partially overlaps with the age (15.40 ± 0.63 Ma) obtained for the rhyolitic ignimbrites in the western Gutai Mts (sample 301FA, Table 1) which can be regarded as the proximal facies of the Dej Tuff (Szakács & Fülöp 2002).

A minimum age (13.7 ± 1.2 Ma) has also been obtained by applying the Ar-Ar method to one sample. Although it is not interpretable alone, the minimum age obtained using this method is consistent with the K-Ar ages. There is a limited overlap of the Ar-Ar age, including error-bars, with the age of the most reliable K-Ar age of the Pâglişa samples.

One sample (TD105) has been measured by both the K-Ar and Ar-Ar methods. The K-Ar age of the sample (11.78 ± 0.94 Ma, Table 1) is well within its Ar-Ar age spectrum (7.04–13.7 Ma). We consider that the K-Ar age represents a post-depositional event related to the burial history of the tuff sequence, while the Ar-Ar spectrum step at 13.7 ± 1.2 Ma (Fig. 5) is interpretable as the minimum formation age.

On the basis of the Ar-Ar step degassing spectra (Fig. 5) it can be stated that the biotite was affected by extensive alteration during post-depositional processes. The alteration products often do not retain $^{40}Ar_{rad}$ quantitatively. As a consequence, the K-Ar age of the same biotite mineral fraction cannot be regarded as a real geological age, since it has been rejuvenated.

FT ages obtained on zircon grains show a higher dispersion, but the average mean age value (14.93 Ma) is close, within analytical error, to the most reliable K-Ar ages, as well as to the biostratigraphic age constraints based on dated FO or LO of biostratigraphic marker species.

A summary of radiometric ages, together with their error bars, obtained during this study, along with the summary of current biostratigraphic constraints, is presented in Fig. 2. It is obvious that most of the age values — and their related error-bars — obtained with different radiometric dating methods overlap in two domains, at 14.75–15 Ma and at 11.4–12 Ma. The clustering of data in the 14.75–15 Ma age domain reflects, in our opinion, the formation age of the Dej Tuff as a whole, as it was previously suggested by Szakács et al. (2000). Practically the same age (i.e. 15.1 ± 0.5 Ma) has been obtained recently on zircon crystals from the Dej Tuff by Nicolescu & Mârza (2010) by using the higher-resolution (U-Th)/He dating method. Since reworking of loose volcanic material occurs shortly after eruption and primary deposition, "formation age" includes both the eruption and reworking processes. Furthermore, these age data show no clues concerning the number of eruptive and related secondary deposition events, although a succession of three eruptions has been inferred from compositional sequences (Szakács 2000). The whole story would have occurred within a time interval of a few hundred thousand years, well within the analytical error bars. Thus, eruption sequentiality is not resolvable with the currently used radiometric dating methods.

The radiometric ages around 15 Ma correspond to the Middle Langhian age, or early Middle Miocene on the standard stratigraphic scale of Lourens et al. (2004a), and can be correlated to the Early Badenian regional age (e.g. Rögl et al. 2008).

It is worth mentioning, that about half of the K-Ar ages obtained for the Dej Tuff are clustered in the 11.4–12 Ma time interval. Moreover, the K-Ar age (11.9 ± 0.7 Ma, Pécskay et al. 1995a) of the Călineşti Tuff in the Oaş Mts (NW from the Tansylvanian Basin), considered Badenian on biostratigraphic grounds, also fall into this time interval. This fact probably bears some geological meaning. We interpret these ages as reflecting a post-depositional event in the thermal history of the sedimentary pile including the Dej Tuff. Sanders (1998) inferred a ca. 3.5 ± 0.5 km burial depth and a corresponding temperature of ca. 80 ± 10 °C for one Dej Tuff sample from Cepari, based on apatite FT data. These burial temperatures are not high enough to "reset" the K-Ar isotopic clock. However, a long time exposure to these temperatures can result in a partial loss of radiogenic argon by diffusion, hence younger analytical ages are obtained.

Processes related to long-term fluid-mineral contact and pore-fluid expulsion may also have resulted in Ar loss, which in turn "rejuvenated" the rocks. Certain tectonic events may trigger such processes. The last major convergence and deformation event occurred ca. 11 Ma ago in the Outer Carpathians (Săndulescu et al. 1981; Săndulescu 1988) with a likely echo in the "back-arc" realm, such as the Transylvanian Basin. Thus, the "rejuvenation" of the Dej Tuff around 11.5 to 12 Ma may be related to a major tectonic event in the Carpathians.

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References

Balogh K. 1985: K/Ar dating of Neogene volcanic activity in Hungary: Experimental technique, experiences and methods of chronologic studies. *ATOMKI Report D/1*, 277–288.

Balogh K. & Simonits A. 1998: Improvements in experimental techniques of conventional K/Ar and Ar/Ar geochronological methods. *Rapid. Comm. Mass. Spectrom.* 12, 22, 1769–1770.

Berggren W.A., Kent D.V., Swisher C.C. III & Aubry M.-P. 1995: A revised Cenozoic geochronology and chronostratigraphy. In: Berggren W.A., Kent D.V., Aubry M.-P. & Hardenbol J. (Eds.): Geochronology, time scales and global stratigraphic correlations: A unied temporal framework for an historical geology. *SEPM Spec. Publ.,* Tulsa 54, 129–212.

Bukovski K., de Leeuw A., Gonera M., Kuiper K.F., Krzywiec P. & Peryt D. 2010: Badenian tuffite levels within the Carpathian orogenic front (Gdów-Bochnia area, Southern Poland): radio-isotopic dating and stratigraphic position. *Geol. Quart.* 54, 4, 449–464.

Chira C. 1991: Mollusc fauna from the Badenian-Sarmatian deposits in the Transylvanian Basin correlated to volcanic tuffs. In: Mârza I. (Ed.): The volcanic tuffs from the Transylvanian Basin, Romania. *Geol. Formations Transylvania, Romania,* University of Cluj-Napoca, Cluj-Napoca 3, 117–123.

Chira C. & Bălc R. 2002: Miocene calcareous nannofossils from Dej-Reteag-Ciceu area (Transylvanian Basin, Romania). Biostratigraphical importance and Paleogeographical data. In: Olaru L. (Ed.): 3rd Romanian National Symposium of Palaeontology. *Acta Palaeontologica Romaniae,* Vasiliana '98, Iaşi, 3, 53–65.

Ciupagea D., Pauca M. & Ichim T. 1970: Geology of the Transylvanian Depression in Romanian. *Acad. R.S.R*, Bucharest, 1–256 (in Romanian).

de Leeuw A., Bukowski K., Krijgsman W. & Kuiper K.F. 2010: Age of the Badenian salinity crisis; impact of Miocene climate variability on the circum-Mediterranean region. *Geology* 38, 8, 715–718.

Filipescu S. 2001: Cenozoic Lithostratigraphic Units in Transylvania. In: Bucur I.I., Filipescu S. & Săsăran E. (Eds.): Algae and carbonate platforms in western part of Romania. 4th Regional Meeting of IFAA Cluj-Napoca 2001 — Field Trip Guidebook. *Cluj University Press*, 75–92.

Filipescu S. & Silye L. 2008: New Paratethyan biozones of planktonic foraminifera described from the Middle Miocene of the Transylvanian Basin (Romania). *Geol. Carpathica* 59, 6, 537–544.

Fischer H. & Steiger R.H. 1988: The influence of sediment lithification on K-Ar ages and chemical zoning of glauconites. *Schweiz. Mineral. Petrogr. Mitt.* 68, 2, 203–214.

Grant N.K., Laskowski T.E. & Foland K.A. 1984: Rb-Sr and K-Ar ages of Paleozoic glauconites from Ohio-Indiana and Missouri, U.S.A. *Isot. Geosci.* 2, 3, 217–239.

Hámor G., Ravasz-Baranyai L., Halmai J., Balogh K. & Árva-Sós E. 1987: Dating of Miocene acid and intermediate volcanic activity in Hungary. *Magy. Áll. Földt. Intéz. Évk.* (*Ann. Hungar. Geol. Inst.*) 70, 149–154.

Hüsing S.K., Cascella A., Hilgen F.J., Krijgsman W., Kuiper K.F., Turco E. & Wilson D. 2010: Astrochronology of the Mediterranean Langhian between 15.29 and 14.17 Ma. *Earth. Planet. Sci. Lett.* 290, 3–4, 254–269.

Koch A. 1900: Az erdélyrészi medencze harmadkori képződményei. II. Neogén csoport. [Tertiary formations of the Transylvanian Basin. II Neogene group.] *Magy. Földt. Társulat*, Budapest, 1–329 (in Hungarian).

Krézsek C. & Bally A.W. 2006: The Transylvanian Basin (Romania) and its relation to the Carpathian fold and thrust belt: Insights in gravitational salt tectonics. *Mar. Petrol. Geol.* 23, 4, 405–442.

Krézsek Cs. & Filipescu S. 2005: Middle to late Miocene sequence stratigraphy of the Transylvanian Basin (Romania). *Tectonophysics* 410, 1–4, 437–463.

Lourens L., Hilgen F., Shackleton N.J., Laskar J. & Wilson D. 2004a: The Neogene Period. In: Gradstein F.M., Ogg J.G. & Smith A.G. (Eds.): A geologic time scale 2004. *Cambridge University Press*, Cambridge, UK, 409–440.

Lourens L., Hilgen F., Shackleton N.J., Laskar J. & Wilson D. 2004b: Appendix 2. Orbital tuning calibrations and conversions for the Neogene Period. In: Gradstein F.M., Ogg J.G. & Smith A.G. (Eds.): A geologic time scale 2004. *Cambridge University Press*, Cambridge, UK, 469–471.

Martini E. 1971: Standard Tertiary and Quaternary calcareous nannoplankton zonation. In: Farinacci A. (Ed.): Proceedings of the 2nd International Conference on Planktonic Microfossils. *Ed. Tecnosci*, Roma 2, 739–785.

Mărunţeanu M., Crihan M. & Chira C. 2000: Badenian nannofossil zonation — the Carpathian Area, Romania. In: Bucur I.I. & Filipescu S. (Eds.). *Acta Palaeontologica Romaniae*, Presa Universitară Clujeană, Cluj-Napoca 2, 261–267.

Mârza I. & Mészáros N. 1991: Les tufs volcanique de Transylvanie: historique, valeur théorique et pratique dans le développement de la géologie Transilvaine. In: Mârza I. (Ed.): The volcanic tuffs from the Transylvanian Basin, Romania. *Geol. Formations Transylvania, Romania,* University of Cluj-Napoca, Cluj-Napoca 3, 11–21.

Mârza I. & Mirea O. 1991: Le Massif eruptif de Ciceu (Dej) — Considerations petrographiques et volcanologiques. In: Mârza I. (Ed.): The volcanic tuffs from the Transylvanian Basin, Romania. *Geol. Formations Transylvania, Romania,* University of Cluj-Napoca, Cluj-Napoca 3, 147–157.

Mârza I., Niţă P. & Niţă S. 1991: Considérations sur la répartition et les sources volcaniques des principaux horizons de tufs de la Dépression de Transylvanie, sur le base des données de forage. In: Mârza I. (Ed.): The volcanic tuffs from the Transylvanian Basin, Romania. *Geol. Formations Transylvania, Romania,* University of Cluj-Napoca, Cluj-Napoca 3, 191–199.

Mészáros N. & Filipescu S. 1991: Le nannoplancton du compexe du Tuf de Dej (Ripa Dracului). In: Mârza I. (Ed.): The volcanic tuffs from the Transylvanian Basin, Romania. *Geol. Formations Transylvania, Romania,* University of Cluj-Napoca, Cluj-Napoca 3, 79–81.

Mészáros N. & Șuraru N. 1991: Le nannoplancton et les foraminifères du Complexe du Tuf de Dej de la région Þoimeni-Pâglița. In: Mârza I. (Ed.): The volcanic tuffs from the Transylvanian Basin, Romania. *Geol. Formations Transylvania, Romania,* University of Cluj-Napoca, Cluj-Napoca 3, 83–88.

Mészáros N., Nicorici E. & Ianoliu C. 1991: Le nannoplancton et la microfaune du complexe du Tuf de Dej de la region Cluj-Napoca. In: Mârza I. (Ed.): The volcanic tuffs from the Transylvanian Basin, Romania. *Geol. Formations Transylvania, Romania,* University of Cluj-Napoca, Cluj-Napoca 3, 73–78.

Moisescu V. & Popescu G. 1967: Studiul stratigraphic al formațiunilor paleogene și miocene din regiunea Chinteni-Baciu-Sânpaul (nord-vestul Transilvaniei). [Stratigraphic study of the Paleogene and Miocene formations in the Chinteni-Baciu-Sânpaul region (north-western Transylvania)] *St. Cerc. Geol. Geofiz. Geogr., Geol.* 12, 1, 211–224 (in Romanian).

Murgeanu G., Dumitrescu I., Mirăuță O., Săndulescu M., Ștefănescu M. & Bandrabur T. 1968: Geological Map of Romania 1:200,000, Sheet Bacau. *Geol. Inst., Bucharest.*

Naeser C.W. 1967: The use of apatite and sphene for fission track age determinations. *Bull. Geol. Soc. Amer.* 78, 12, 1523–1526.

Nicolescu S. & Mârza I. 2010: The Dej Tuff of Transylvania (Romania): how old, what flavour and where from? *Acta Mineralogica-Petrographica. Abstract Series* 6, IMA2010, 20th Genereal Meeting of the International Mineralogical Association, 21–27 August, 2010, Budapest, Hungary, 1–684.

Odin G.S., Adams C.J., Armstrong R.L. et al. 1982: Interlaboratory standards for dating purposes. In: Odin G.S. (Ed.): Numerical dating in stratigraphy. *Wiley and Sons*, Chichester-New York-Brisbane, 123–149.

Pálfy J., Mundil R., Renne P.R., Bernor R.L. & Kordos L. 2007: U-Pb and 40Ar/39Ar dating of the Miocene fossil track site at Ipolytarnóc Hungary and its implications. *Earth Planet. Sci. Lett.* 258, 160–174.

Pécskay Z., Edelstein O., Seghedi I., Szakács A., Kovacs M., Crihan M. & Bernad A. 1995a: K-Ar datings of Neogene-Quaternary calc-alkaline volcanic rocks in Romania. *Acta Vulcanol.* 7, 2, 53–61.

Pécskay Z., Lexa J., Szakács A., Balogh Kad., Seghedi I., Konečný V., Kovacs M., Márton E., Kaličiak M., Széky-Fux V., Poka T., Gyarmati P., Edelstein O., Roșu E. & Žec B. 1995b: Space and time evolution of Neogene-Quaternary volcanism in the Carpathian-Pannonian Region. *Acta Vulcanol.* 7, 2, 15–28.

Popescu G. 1970: Planktonic foraminiferal zonation in the Dej Tuff Complex. *Rev. Roum. Géol. Géophys. Géograph., Ser. Geol.* 14, 2, 189–203.

Popescu G. 1975: Études des foraminifères du Miocène inférieur et moyen du nord-ouest de la Transylvanie. *Mem. Inst. Geol. Geofiz.* 23, 5–121.

Popescu G. & Cioflica G. 1973: Contribuții la microbiostratigrafia miocenului mediu din nordul Transilvaniei. [Contributions to the biostratigraphy of Middle Miocene in northern Transylvania.] *St. Cerc. Geol. Geofiz. Geogr., Geol.* 18, 1, 187–218 (in Romanian).

Popescu G. & Gheța N. 1984: Comparative evolution of the marine Middle Miocene calcareous microfossils from the Carpathian and Pannonian areas. *D.S. Inst. Geol. Geofiz.* 69 (1982), 3, 125–133.

Pošepny F. 1867: Studien aus dem Salinengebiet Siebenbürgens. *Jb. K.-Kön. Geol. Reichsanst.* 17, 4, 475–516.

Price P.B. & Walker R.M. 1963: Fossil tracks of charged particles in mica and the age of minerals. *J. Geophys. Res.* 68, 16, 4847–4862.

Rado G., Țicleanu N., Gheorghian M. & Popescu A. 1980: New data concerning the lito-biostratigraphy of Miocene and Pliocene deposits in the Comănești-Lueta-Mărtiniș region (Harghita county). *St. Cerc. Geol. Geofiz. Geogr., Geol.* 25, 95–108 (in Romanian).

Răileanu G. 1959: Recherches geologiques dans la region Cluj-Apahida-Sic. *D.S. Com. Geol.* 39 (1949–1952), 127–131.

Rögl F., Ćorić S., Harzhauser M., Jimenez-Moreno G., Kroh A., Schultz O., Wessely G. & Zorn I. 2008: The Middle Miocene Badenian stratotype at Baden-Sooss (Lower Austria). *Geol. Carpathica* 59, 5, 367–374.

Salvador A. (Ed.) 1994: International Stratigraphic Guide — A guide to stratigraphic classification, terminology, and procedure. 2nd Edition. International Subcommission on Stratigraphic Classification (ISSC) 1994. *Int. Union Geol. Sci.*; *Geol. Soc. Amer., Inc.*, 1–214.

Sanders C.A.E. 1998: Erosion and tectonics: Competitive forces in a compressional orogen. A fission track study of the Romanian Carpathians. *PhD Thesis*, *Vrije Universiteit*, Amsterdam, 1–204.

Săndulescu M. 1988: Cenozoic tectonic history of the Carpathians. In: Royden L.H. & Horváth F. (Eds.): The Pannonian Basin, a study in basin evolution. *AAPG Mem.* 45, 17–25.

Săndulescu M., Kräutner H.G., Borcos M., Balintoni I., Russo-Săndulescu D. & Micu M. 1981: The structure of the East Carpathians (Moldavia-Maramureş area). Carp.-Balc. Assoc., XII Congr., Guide to Excursions B1. *Inst. Geol. Geophys.*, Bucharest, 1–92.

Seghedi I. & Szakács A. 1991: "The Dej Tuff complex" from Dej-Ciceu area: some petrographical, petrochemical and volcanological aspects. In: Mârza I. (Ed.): The volcanic tuffs from the Transylvanian Basin, Romania. *Geol. Formations Transylvania, Romania,* University of Cluj-Napoca, Cluj-Napoca 3, 135–146.

Steiger R.H. & Jäger E. 1977: Subcommission on geochronology: convention on the use of decay constants in geo- and cosmochronology. *Earth. Planet. Sci. Lett.* 36, 3, 359–362.

Szakács A. 2000: Petrologic and tephrologic study of the Lower Badenian volcanic tuffs in the north-western Transylvanian Basin (in Romanian). *PhD Thesis*, University of Bucharest.

Szakács A. & Fülöp A. 2002: Correlating Badenian rhyolitic pyroclastics of the Western Gutai Mts. with the Dej Tuff Complex. *Rom. J. Mineral Deposits* 80, 117–121.

Szakács A., Vlad D., Andriessen P.A.M., Fülöp A. & Pécskay Z. 2000: Eruptions of the "Dej Tuff": when, where and how many? *Vijesti Hrv. Geol. Društva* 37, 3, PANCARDI 2000 Spec. Issue, Abstract Volume, 1–122.

Vancea A. 1960: Neogene of the Transylvanian Basin. *Editura Academiei RSR*, Bucharest, 1–262 (in Romanian).

Vlad D. 1998: Fission track thermochronology. Possibilities for application in Romania. *Anal. Univ. Bucureşti, Geol.* 47, 21–32.

Vulc A.-M. & Silye L. 2005: Preliminary data on biostratigraphy and palaeoecology of calcareous nannofossils and foraminifera in Cepari quarry (North-Eastern Transylvania, Romania). In: Csíki Z., Grigorescu D. & Lazăr I. (Eds.). *Acta Palaeontologica Romaniae,* Ars Docendi, Bucureşti 5, 493–501.

Wade B.S., Pearson P.N., Berggren W.A. & Pälike H. 2011: Review and revision of Cenozoic tropical planktonic foraminiferal biostratigraphy and calibration to the geomagnetic polarity and astronomical time scale. *Earth. Sci. Rev.* 104, 1–3, 111–142.

Wanek F. & Clichici O. 1991: Age and sedimentation paleoenvironment of the Badenian deposits with cinerite intercalations from Benesat (Eastern border of the Silvania basin). In: Mârza I. (Ed.): The volcanic tuffs from the Transylvanian Basin, Romania. *Geol. Formations Transylvania, Romania,* University of Cluj-Napoca, Cluj-Napoca 3, 51–54.