

GEOLOGICAL AND MINERALOGICAL CHARACTERIZATION OF SOME ZEOLITIZED TUFFS FROM NW^{RN} TRANSYLVANIA, ROMANIA

Bedelean H.¹, Codrea V.¹, and Barbu O.¹

¹*Babeş Bolyai University Cluj Napoca, Faculty of Biology and Geology, Department of Geology,
Kogălniceanu st., 400084 Cluj Napoca, Romania, hbedelean@yahoo.com,
vcodrea@bioge.ubbcluj.ro, obarbu@bioge.ubbcluj.ro*

Abstract

Zeolites are the most common products of transformation of silicic volcanic glass in the NW-rn part of Transylvania (Romania). Representative samples of volcanic tuffs from Măciş (Cluj county) were investigated by using optical (polarized light) microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), and wet chemical analyses. The volcanic tuff are vitreous with an acid composition. Vitreous matrix and glass shards are replaced by zeolite minerals, mainly clinoptilolite and trace amounts of opal-CT and mordenite. X-ray diffraction semi-quantitative analysis indicated that clinoptilolite represent between 60 % and 70 % of the crystalline fraction of the tuff. The clinoptilolite content of the Măciş tuff deposits is one of the richest in Romania. According to the present status in the zeolite market in Europe, this deposit could have industrial potential in the construction industry and in environmental applications.

Key words: *zeolite, clinoptilolite, opal-CT, diagenesis, tuff, Badenian.*

Περίληψη

Οι ζεόλιθοι αποτελούν τα πιο κοινά παράγωγα μετασχηματισμού της πυριτικής ηφαιστειακής ύελου στο βορειοδυτικό τμήμα της Τρανσυλβανίας (Ρουμανία). Αντιπροσωπευτικά δείγματα ηφαιστειακών τόφφων από την περιοχή Μάτσιş (Νομός Cluj) εξετάστηκαν με τη χρήση οπτικού πολωτικού μικροσκοπίου και ηλεκτρονικού μικροσκοπίου σαρώσεως (SEM), όπως επίσης με διάθλαση ακτίνων Χ (XRD), και υγρές χημικές αναλύσεις. Οι ηφαιστειακοί τόφφοι είναι υαλώδεις με όξινη σύνθεση. Η υαλώδης κύρια μάζα, όπως και τα υαλώδη θραύσματα αντικαθίστανται από ζεολιθικά ορυκτά, κυρίως κλινοπτιλόλιθο, ίχνη οπάλιου-CT και μορντενίτη. Η ημιποσοτική ανάλυση διάθλασης ακτίνων Χ κατέδειξε ότι, ο κλινοπτιλόλιθος αντιπροσωπεύει το 60 - 70 % του υαλώδους κλάσματος των τόφφων; ποσοστό ιδιαίτερα υψηλό. Σύμφωνα με τα σημερινά δεδομένα, όσον αφορά το εμπόριο ζεόλιθων στην Ευρώπη, η απόθεση στην περιοχή Μάτσιş δύναται να αποτελέσει εκμεταλλεύσιμο προϊόν στη βιομηχανική παραγωγή, αλλά και σε περιβαλλοντικές εφαρμογές.

Λέξεις κλειδιά: *ζεόλιθος, κλινοπτιλόλιθος, οπάλιος-CT, διαγένεση, ηφαιστειακός τόφφος, Βαδένιο.*

1. Introduction

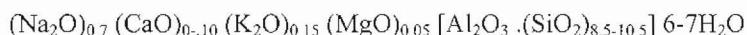
Zeolites are a group of hydrated aluminosilicates of the alkali or alkaline earth metals (sodium, potassium, calcium, magnesium). Zeolites - both natural and synthetic, may be used as ionic or molecular filters due to their particular crystal structure of a tectosilicate-type, characterised by pores with larger sizes than those of the ions (molecules) that pass through (Harben 2002).

Many types of rocks may contain small amounts of zeolites but the main rock-type containing such minerals is the zeolitized volcanic tuff. The volcanoclastic deposits contain large amounts of zeolites, which result from the transformation of volcanic glass and primary aluminosilicate minerals (Hay and Sheppard 2001).

According to Hay and Sheppard (2001), zeolites in tuffaceous rocks are formed as a result of the dissolution-precipitation process that affects volcanic glass and pass through an intermediate phase (gel-like material). The reaction of glass may be a complex, multi-stage process, thermodynamically controlled and it depends on the chemical composition of the fluids.

Zeolites are the most common products of transformation of silicic volcanic glass in the NW-rn part of Transylvania, Romania (Bedelean and Stoici 1984).

The sedimentary zeolitized rocks from Romania are represented by Tertiary volcanic tuffs dominated by the presence of clinoptilolite that represents between 30 and 90 % of the rock mass (Cosma 1984). Clinoptilolite is a hydrated aluminosilicate, member of the heulandite group and is one of the more useful natural zeolites. Clinoptilolite is characterised by a lamellar-prismatic habit and the chemical composition given by the formula:



In Romania, the main rock-type containing natural zeolites is the zeolitized volcanic tuff of Badenian-Sarmatian age. In general, the sedimentary units that host zeolite-rich rocks are located in the post-tectonic Carpathian depressions, which functioned as sedimentary basins during Tertiary. Large deposits of zeolitized volcanic tuffs were known since a long time and they were partly exploited for several purposes, mainly as construction materials (Colella *et al.* 2001). In the last decades, new fields of usage such as agriculture and environmental protection (adsorption and ion-exchange processes), special cements, concrete and synthetic silicate melts brought a new insight into the research of these minerals and their applications. All these application fields have triggered the research and usage for new zeolitic occurrences all over the world (and in Romania, too).

Some studies on zeolites in Romania have focused on economically-important deposits of zeolitized volcanic tuffs at Mirșid (Sălaj County), Slănic Prahova (Prahova County) etc (Stamatakis *et al.* 2000).

The aim of the paper is to identify, describe and characterize zeolitized volcanic tuffs from new occurrences from Transylvania (Romania), from geological and mineralogical point of view.

2. Geological setting

Transylvanian Depression is located in the north-western part of Romania. It is a well-defined structural unit, being the most extensive molasse filled depression of Tertiary age in Romania. The Badenian deposits have a transgressive character and they cover the largest areas in the basin (Fig. 1).

The Neogene volcanism started in Romania with large volume explosive eruptions of acidic magma in Lower/Middle Badenian time (15 Ma ago), giving rise to some volcanic tuff levels in Transylvanian Depression, its surroundings and in the external part of the Carpathians Mts.

Within the dominant siliciclastic Neogene rocks, volcanic ash layers represent important stratigraphic index levels for the Badenian, Sarmatian and Pannonian intervals. Eight volcanic tuff

levels were well defined stratigraphically (Mârza and Meszaros 1991). In the Transylvanian Depression, the main zeolite-bearing pyroclastic formation is included within the “Dej Tuff Complex” (Badenian). Its thickness is variable (up to 200 m), having outcrops almost continuously for hundreds of kilometers and consists of sequences of reworked volcanoclastic sand, coarse to fine tuffs and tuffites (Mârza 1965).

The Dej Tuff is a fall-out tuff of a regional extension with a acid composition, that represents the first stage of the Neogene volcanic activity (Styrian phase). The upper limit of Badenian is marked by another fall-out tuff of a dacitic composition, i.e., Borșa-Apahida Tuff. The Sarmatian and Pannonian deposits include thin layers of tuffs (50-60 cm), with a low content of zeolites (Mârza and Meszaros 1991).

3. Materials and Methods

Representative bulk rock samples of the zeolitized volcanic tuffs layers were collected from Măcicaș area (Cluj county) (Figs 1a, b). The pyroclastic rocks belong to the Dej Tuff Complex, of a Lower Badenian age. The main petrographical component of this complex is represented by white and grey volcanic tuff that is interbedded with claystone, marlstone and fine-grained sandstones (Mârza *et al.* 1991b). The intensive alteration processes that affected these tuffs, locally led to the formation of economically valuable accumulations (Bedelean and Stoici 1984).

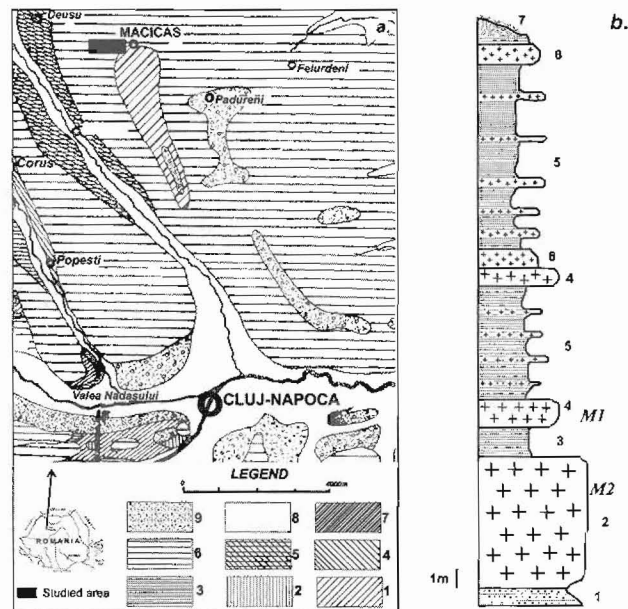


Figure 1 - a. Geological sketch of the Măcicaș area, Cluj county (modified after Meszaros and Nicorici 1976). 1- Moigrad Formation+Dâncu Formation (Rupelian); 2- Gruia Sandstone+Var Sandstone (Rupelian); 3- Cuzăplac Formation+Cubleșu Formation (Egerian); 4- Coruș Formation+Chechiș Formation (Eggenburgian); 5- Hida Formation (Ottangian); 6- Badenian (with Dej Tuff Complex); 7- Sarmatian; 8- Alluvium; 9- Terraces of the Someșul Mic River.

b. Lithologic profile of the tuffs from Măcicaș, Cluj county. 1- Yellowish-gray yellowish coarse to medium granular sandstones; 2- Macroporous volcanic tuff, coarse granulation, white-yellowish color (sample M2); 3- Clays; 4- Volcanic tuff with a medium porosity (sample M1), yellow-greenish; 5- Grayish clays with interlayers of tuff and tuffaceous sandstones; 6- Microporous, fine granulation, white-greenish volcanic tuff; 7- Yellowish clays, soil cover

The bulk rock samples were collected from the stratigraphically lower tuff level (sample M2, macroporous tuff) and the median level (sample M1, medium porous tuff). Representative samples from Măciçaş were investigated by using optical (polarized light) microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), and wet chemical analyses.

The petrographic analysis was performed by optical microscope (Zeiss AxioLab) on thin sections. The microscopic investigation was focused on the identification of the different mineralogical phases, on their quantification, and on the structural description of the material. The micromorphological features of zeolite tuffs were examined on silver-coated, fresh surfaces of the selected samples with a JEOL JSM 5510LV scanning electron microscope (SEM). The chemical analyses of bulk rocks were performed at CEROC Cluj-Napoca using usual analytical methods for silicate materials (wet chemistry). The identification of the minerals is completed by X-ray diffraction on random powders, by using a Siemens Bruker unit with Cu K α anticathode. The diffractograms were recorded from 10° to 70° 2 θ . The analytic conditions are 40 A, 40 kV, step of 2 degrees. A semi-quantitative X-ray diffraction method to determine mineral composition was used.

4. Results

4.1. Petrographic investigations

In all the studied occurrences, zeolitized volcanic tuffs are interbedded with clayey or marly rocks (Fig. 1b). In general the limits are sharp, even, and rarely irregular. Often a gradual lamination and stratification is noticeable within the tuff layers. The material is an ash tuff, the microclasts of glass shards (vitroclasts) and crystals have different granulation from fine (<0.06 mm) to coarse (0.5-2 mm) (Mărza *et al.* 1991a). In the same profile, the textures vary from microporous (the pores visible only at the microscope) to macroporous (the pores visible with the naked eye). The tuffs are white-greyish in colour and build-up a normally graded sequence. Some local colour changes can be mentioned: grey-greenish in the basal part, grey and grey-yellowish, sometimes reddish in the upper part (due to the weathering processes).

Field observations and macroscopic study of the samples revealed a rock sequence with a thickness of about 30 m (Fig. 1b).

- In the base of the tuffs' succession, yellowish to yellow-reddish coarse to medium granular sandstones occur.
- The volcanoclastic sequence begins with a compact, macroporous tuff (6 m thickness), microclasts have a coarse granulation (0,5-2 mm), with conchoidal fracture and vacuolar texture, white-yellowish in colour. This level has been occasionally mined as raw material for buildings.
- Bluish clays, 1.5 m in thickness, separating the macroporus tuff from the medium porous one.
- A level of ash tuff with medium porosity and conchoidal fracture, yellow-greenish in colour, 1-1.5 m thickness.
- Greyish clays with centimetre interlayers of tuffs, tuffaceous sandstones, marls, 5-6 m thickness.
- Volcanic tuff level with a medium porosity, 0.8-1 m thickness, yellow-brownish colour.
- Microporous white-greenish tuff, with a fine granulation of the microclasts (<0.06 mm), in the upper part of the profile, 0.8-1 m thickness.
- 5 m of clays interlayered with tuffs.
- In the upper part of the succession a 0.5-1 m thickness brownish volcanic tuff is present.
- On its top, a yellowish clay level and the soil cover are present.

Bulk rock samples were collected from the medium porous tuff level (labelled M1) and the macroporous tuff level (labelled M2), due to their relative homogeneous composition and structure.

The optical microscopy observations on the samples collected from Măciș area are presented in Table 1. The studied samples were compared with zeolitized tuffs from other occurrences (Mirșid, Sălaj County - the most important and the only currently active quarry in northern Romania, and Pâglișă – Cluj county).

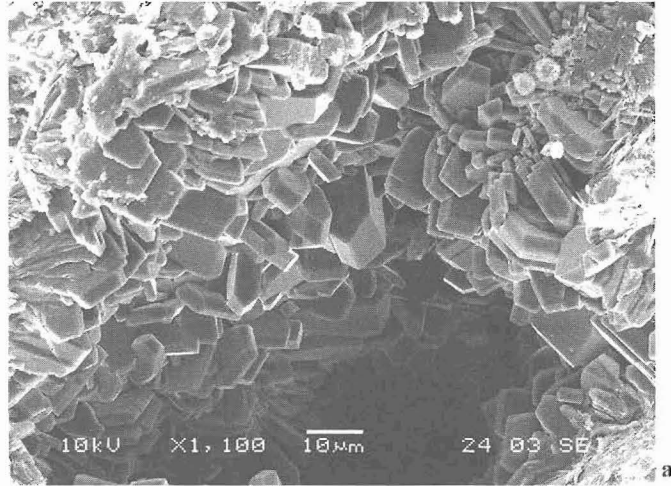


Figure 2a - SEM images of the tuff sample M1 - Clinoptilolite euhedral tabular crystals. Opal-CT lepispheres rarely occur [upper, right]

All the tuffs from all the layers cropping out in the study area have mostly a vitric texture and contain 70-80 % altered vitreous matrix and also abundant altered glass shards. Among the pyrogenic crystals (10-15 %), K-feldspars and acid plagioclases dominate, but quartz, micas, amphiboles and opaque minerals - Fe-oxides and sulphides are also present. Lithic fragments are present in subordinate amounts (2-3 %), being mainly of metamorphic origin. The green color of the tuff is due probably to the presence of celadonite (as in other tuff occurrences from Transylvania) (Mârza 1965).

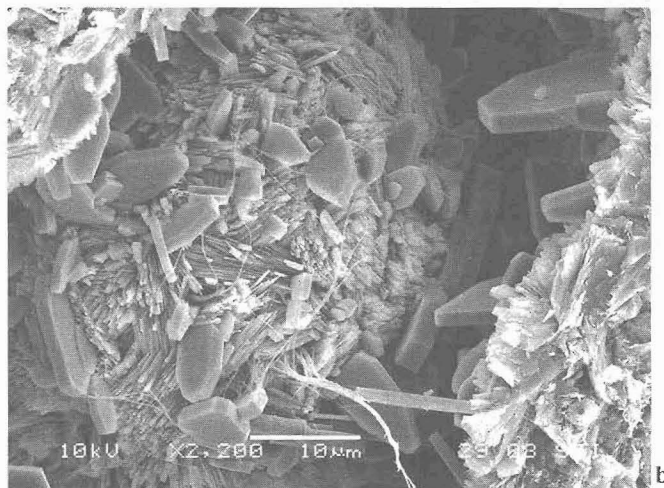


Figure 2b - SEM images of the tuff sample M2. Tabular clinoptilolite crystals with minor fibrous crystal (most likely mordenite)

Scanning electronic microscopy (SEM) revealed that the vitreous matrix and glass shards are extensively diagenetically altered in Măciçaş samples (Figs 2a, b) as in Pâglişa samples (Fig. 3a, b).

The alteration features are detectable under large magnifications (optical microscopy) and by scanning electronic microscopy. These alterations are attributed to the diagenesis of the volcanic glass (vitreous matrix and glass shards) to zeolite minerals, opal-CT and probably montmorillonite that replaces zeolite minerals. Zeolites are present as tabular clinoptilolite crystals, micron- and submicron-sized crystals, or as larger crystals in the pores or voids. The zeolite crystals are about 2-10 microns in size, rarely they reach 40-50 microns.



Figure 3a - SEM images tuff samples from Pâglişa area (located close to the studied area, for comparison). - Euhedral clinoptilolite crystals with minor opal-CT lepispheres and fibrous zeolite (mordenite?)

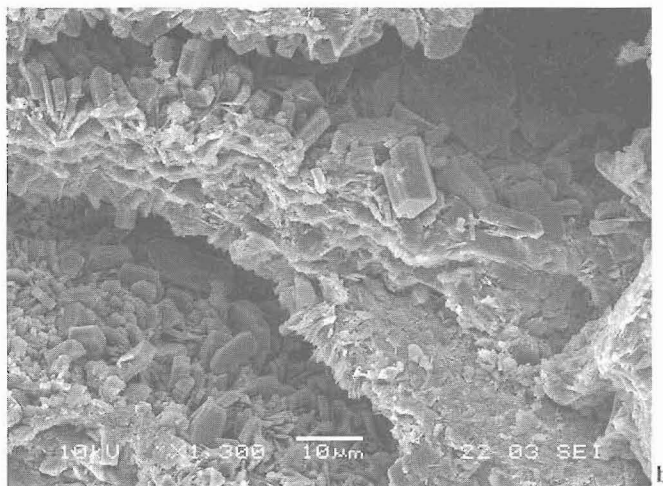


Figure 3b - Glass shards showing pseudomorphic replacements by euhedral tabular clinoptilolite crystals (Pâglişa area)

Opal-CT forms thin bladed crystals, which aggregate locally into small lepispheres and commonly coexist with clinoptilolite. Some clusters of a fibrous mineral are present with clinoptilolite and opal-CT. There is no specific evidence in the XRD pattern, probably due to low quantities, but its fibrous habit suggests that is most likely mordenite.

Table 1 - Mineralogical composition of some Zeolitized Volcanic Tuffs from the NWrn part of Transylvania (Romania). Q=quartz; Fp=feldspar; M=micas; Hb=hornblende; Lim=limonite; Cal=Calcite; M1= medium porous tuff (median level); M2 = macroporous tuff (lower level), P = Pâglișa, Mirs = Mirșid

	Crystals				Lithic fragments	Volcanic glass (secondary minerals)
	Q	Fp	M	Other		
M1	2-4 %	4-5 %	5-6 %	Cal, Lim	<1 %	~85 % (70 % zeolite)
M2	7-10 %	16-20 %	1 %	Hb, Lim	3 %	~72 % (60 % zeolite)
P	8-10	12-15	3-4	Cal, Lim	<1	39-77 % (54-69 % zeolite)
Mirs	2-5	3-6	2-3	Cal, Lim	1	10-84 % (20-80 % zeolite)

4.2. X-ray diffraction

The X-ray diffraction measurements performed on random powder of the whole material indicated the massive presence of clinoptilolite as the main zeolite species (Fig. 4). The semi-quantitative estimation from the X-ray diffractograms indicate that zeolites represent between 60 % and 70 % of the crystallized fractions of the tuff. The amount of zeolite is slightly higher in the macroporous tuff from the lower level than that in the medium porous tuff from the medium level. According to the microscopic observations, the other minerals identified are quartz, feldspar, probably clay minerals.

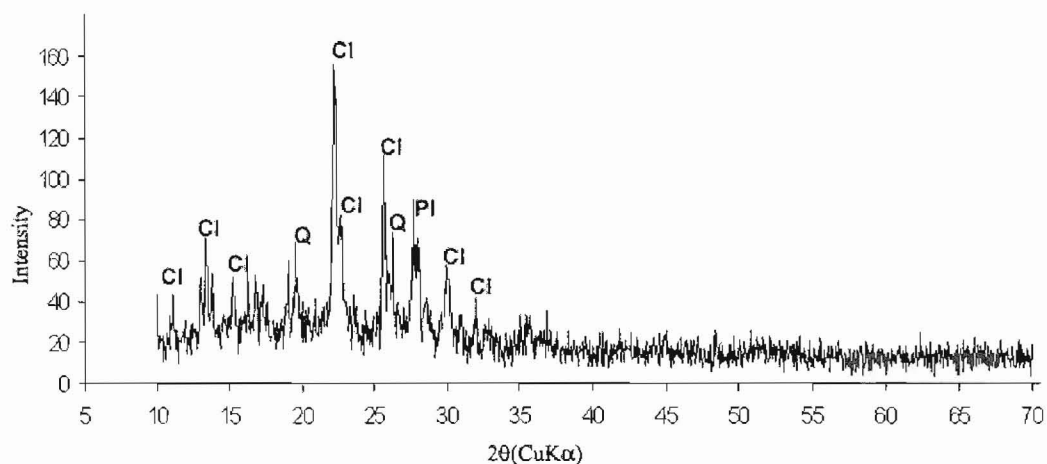


Figure 4 - Powder X-ray diffractogram of sample M2, volcanic tuff from Măcițaș, Cluj County. Cl = clinoptilolite, Pl=plagioclase; Q = quartz;

4.3. Whole-rock chemistry

The bulk chemical analyses performed on tuff samples are presented in Table 2. The high amounts of secondary and hydrated materials (zeolite and probably smectitic clay minerals) is indicated by the high values of the L.O.I (11.86 and 12.14). Considering an average 15 % L.O.I for zeolites (of which clinoptilolite is dominant) the amount of this mineral in the two analysed samples could be higher than those estimated by XRD.

Since the tuffs consist mainly of altered volcanic glass, their original chemical composition should reflect the chemistry of the volcanic eruptive rocks from which they were derived. The bulk chemistry indicates that the zeolitized volcanic tuffs from Măciçaş were derived from a precursor rock of acid composition. The differences between the K₂O and Na₂O values in the samples are due to the different locations of the outcrops and the corresponding variations in the diagenetic processes.

Table 2 - Chemical composition of some Zeolitized Volcanic Tuffs from the NW^{rn} part of Transylvania (Romania) (analyses performed at CEROC Cluj-Napoca, 2004)

Oxides% Occurrence	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	L.O.I.	Total
Măciçaş 2	63.92	0.35	14.53	1.71	5.46	0.23	1.00	0.88	11.86	99.94
Măciçaş I	63.84	0.42	14.38	1.77	5.21	0.37	1.04	0.84	12.14	100.01
Pâglişa	62.04	0.14	14.07	1.61	5.72	0.96	0.35	0.86	14.23	99.98
Mirşid	65.34	0.29	13.94	1.31	3.98	0.41	0.28	2.06	12.30	99.91

4.4. Specific area

The measured specific area is 27.40 m²/g for the medium porous volcanic tuff (Măciçaş M1) in the median part of the succession from Măciçaş, and respectively 21.42 m²/g for the macroporous tuff sample (Măciçaş M2).

5. Discussions and Conclusions

The volcanic tuffs studied were formed by consolidation of pyroclastic products of acidic composition in a marine basin (Meszaros and Filipescu 1991). Optical microscopy and XRD data indicate an almost complete alteration of volcanic glass to a series of authigenic minerals, mainly clinoptilolite, and secondarily to opal-CT, and probably montmorillonite and mordenite.

The zeolitized volcanoclastic rocks have been derived from pyroclastic falls related to an acid-intermediate, calc-alkaline Neogene volcanism. An open hydrological system must have prevailed in the NW^m part of Transylvania during the alteration of the volcanoclastic materials.

The thickness of the entire formation in the investigated area suggests shallow burial conditions, therefore the temperature and pressure during diagenesis must have been relatively low. Discrete illite and mixed layer illite/smectite, which commonly indicate formation in argillaceous sequences at elevated temperatures, are absent (Kassoli-Fournaraki *et al.* 2000)

The pH must have been <9 because there is no evidence of the presence of aluminous zeolites (erionite, phillipsite) and/or authigenic K-feldspar, but ≥8, values necessary for the crystallization of clinoptilolite and/or montmorillonite (smectite, which is probably present in low amounts) (Sheppard 1991).

Based on mineralogical (XRD and SEM) analyses, the studied volcanic tuffs from Măciçaş contain exclusively the zeolite clinoptilolite (heulandite group). As shown in Figure 2, glass shards have been leached and the former molds are partly filled by clinoptilolite crystals. This suggests that the processes of zeolitization involved direct dissolution of glass and precipitation of clinoptilolite. There is no evidence for the clinoptilolite precipitation being preceded by the initial alteration of the glass to a clay mineral, as proposed for the zeolitization of volcanic glass in other sedimentary zeolite deposits by Leggo *et al.* (2001). The opal-CT represents, probably, the silica that was left over after the formation of zeolite from the glass shards, which being of acid composition, are silica rich (> 60 % SiO₂).

5.1. Conclusions

The zeolitized volcanic tuffs from Măciçaș (Cluj county) are mainly represented by acid vitric tuffs.

Zeolites formed as a result of the reaction between water and rock components, especially volcanic glass. The marine genetic conditions point to pH values between 8 and 9 and salinity values close to those normal marine ones. The resulted zeolitic species were dependent on temperature, pressure and the variable chemical parameters: Si:Al ratio, Ca²⁺, Na⁺ and K⁺ ratios and the pressure-dependent H₂O (P_{H_2O}) and CO₂ (P_{CO_2}) activities (Bedelean and Stoici 1984).

It was estimated that the Miocene rocks overburden that overlies the Dej Tuff Complex was 3.5 ± 0.5 km thick, thus the burial conditions lead to temperatures within the tuff complex of $80^\circ \pm 10^\circ$ C (Sanders 1998 in Seghedi *et al.* 2000). This temperature range is consistent with the thermodynamic stability field of clinoptilolite, as defined by studies on present-day counterparts (Iijima, 1986). Still, no effects of burial metamorphism could be evidenced in the studied occurrences.

Devitrification of volcanic glass and zeolite formation represented ubiquitous anadiagenetic processes in the parts of the rock where originally glass masses or vitroclasts were present, both in the tuff levels and the marly interlayers, where the reworked volcanic glass underwent zeolitization and some times carbonation processes. The amount of zeolites is directly correlated to the original amount of volcanic glass. Thus, the zeolite-richest levels are represented by the vitric tuffs, and respectively the medium- and fine-grained vitric-crystal ones. The main zeolite phase identified by optical microscopy and X-ray diffraction is clinoptilolite.

The poly-sequential character of the pyroclastic formation, as well as the presence of heat flows in other proximal areas plead for a not very far volcanic source, similar to the situation of other structures in the region.

Zeolite rocks are currently mined in the nearby located Zalău area for applications in the construct industry, animal food additives and raw materials in cement and ceramics industries.

This zeolite tuff formation studied is a significant deposit with economic potential. Two main zeolite-bearing layers, a coarse grained, macroporous zeolitized tuff and a tuff with a medium porosity, appears significant industrial potential. The content of clinoptilolite in the two zeolite-rich layers is 60-70 %, making the Măciçaș deposit one of the richest among the zeolite formations from Romania. Taking into account the significant volume of zeolitized rock, the possibility of mining in open pits, the simple processing procedure and the diverse fields of possible usage, the Măciçaș deposit could represent an important economic source.

6. Acknowledgments

Thanks are expressed by the authors to prof. Stamatakis M.G. (NKUA Greece) for reviewing of a version of the manuscript.

7. References

- Bedelean, I., and Stoici, S., 1984. *Zeoliți*. Ed. Tehnică, București, 227p.
- Colella, C., de'Gennaro, M., and Aiello, R., 2001. Use of zeolitic tuff in building industry. In D.L. Bish and D.W. Ming (eds), *Reviews in Mineralogy and Geochemistry, Natural Zeolites, Occurrence, Properties, Applications*, vol 45, 551-588pp.
- Cosma, R., 1982. *Caracteristici calitative, zone de perspectiva si posibilitati de valorificare a tufurilor vulcanice din Romania*, Mine, Petrol si Gaze, 33/1, 27-30.

- Hay, L.R., and Sheppard, A.R., 2001. Occurrence of zeolites in sedimentary rocks: An Overview. In D.L. Bish and D.W. Ming (eds), *Reviews in Mineralogy and Geochemistry, Natural Zeolites, Occurrence, Properties, Applications*, vol 45, 217-234pp.
- Harben, P.W., 2002. *The industrial minerals handybook - 4th Edition: A guide to markets, specifications & prices*, Surrey, U.K., Industrial Minerals Information, 412 p.
- Iijima, A., 1986. Occurrence of natural zeolites, *Nendo Kagaku*, 26, 90-103.
- Kassoli-Fournaraki, A., Stamatakis, M., Hall, A., Filipidis, A., Michailidis, K., Tsirambides, A., and Koutles., Th., 2000. The Ca-rich clinoptilolite deposits of Pentalofos, Thrace, Greece. In C. Colella and F.A. Mumpton (eds), *Natural Zeolites for the Third Millennium*, De Frede Editore, Napoli, Italy, 193-202pp.
- Leggo, P.J., Cocheme, J.J., Demant, A., and Lee, W.T., 2001. The role of argilic alteration in the zeolitization of volcanic glass, *Mineralogical Magazine*, 65 (5), 653-663.
- Mârza, I., 1965. Date noi privind petrografia, originea și culoarea tufului de Dej, *Studii și Cercetări de geologie-geofizica-geografie*, București, , seria Geologie, 10, 1, 237-281.
- Mârza, I., Anastasiu, N., Seghedi, I., Szakacs, Al., Kovacs, M., Ghergari, L., Bedelea, I., Șeclăman, M., Nicolescu, Șt., Ștefănescu, N., and Voiculescu, L., 1991a. On the nomenclature and classification of pyroclastites. In I. Mârza (ed.), *The Volcanic Tuffs from the Transylvanian Basin, Romania. Special volume*, Babes-Bolyai University Cluj-Napoca, 449-464pp.
- Mârza, I., Codoreanu, Fl., Hosu, Al., Plăceanu, M.L., Marian, D., Pop, R., and Tămaș, D., 1991b. Caractérisation pétrographique synthétique des tufs volcaniques de la région Dej-Cluj-Napoca et signification volcanologique. In I. Mârza (ed.), *The Volcanic Tuffs from the Transylvanian Basin, Romania. Special volume*, Babes-Bolyai University Cluj-Napoca, 171-181pp.
- Mârza, I., and Meszaros, N., 1991. Les tuffs volcaniques de Transylvanie: histoire, valeur theoretique et pratique dans le developpment de la geologie Transylvaine. In I. Mârza (ed.), *The Volcanic Tuffs from the Transylvanian Basin, Romania. Special volume*, Babeș-Bolyai University Cluj-Napoca, 11-21pp.
- Meszaros, N., and Nicoricî, E. (coord), 1976. *Pe poteci cu bănuși de piatră*, Ed.Sport-Turism, București, 190p.
- Meszaros, N., and Filipescu S., 1991. Le nannoplancton du Complex du Tuf de Dej (Rîpa Dracului). In I. Mârza (ed.), *The Volcanic Tuffs from the Transylvanian Basin, Romania. Special volume*, Babeș-Bolyai University Cluj-Napoca, 79+81pp.
- Sanders, C., 1998. Tectonics and erosion, competitive forces in a compressive orogen. A fission track study of the Romanian Carpathians, *Ph.D. thesis, Vrije Universiteit Amsterdam*, 204 pp.
- Seghedi, I., Szakacs, A., Vanghelie, I., and Costea, C., 2000. Zeolite formation in the Lower Miocene tuffs, north-western Transylvania, Romania, *Romanian Journal of Mineralogy*, 80, 11-20.
- Sheppard, R.A., 1991. Zeolitic diagenesis of tuffs in the Miocene Chalk Hills Formation, western Snake River Plain, Idaho, *U.S.Geol.Surv.Bull*, 1963, 27pp.
- Stamatakis, M.G., Fragoulis, D., Chaniotakis, E., Bedelea, I., and Csiris, G., 2000. Clinoptilolite-rich tuffs from Greece, Hungary and Romania and their industrial potential as cement additive, *Proceedings V.I., of the 3rd International Congress on Mineral Wealth, Technical Chamber of Greece, Athens*, 451-458.