THE MINERALOGY AND DISTRIBUTION OF ZEOLITIC TUFFS IN THE MARAMURES BASIN, ROMANIA

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Abstract—The Maramures Basin, in the Carpathian mountain belt of northern Romania on the border with the Ukraine, belongs to the eastern part of the Pannonian Basin. In the study area, extensional tectonic movements during the Miocene were coeval with silicic and intermediate volcanism in the inner part of the Eastern Carpathians. Throughout this region, explosive events have resulted in the deposition of pyroclastic flows and ash-fall deposits interbedded with marine sediments.

Several tuff units of Badenian (15–13.6 Ma) age occurring throughout the area are extensively zeolitized. These rocks occur as massive homogeneous beds, white to pale greenish-blue, and are commonly extensively jointed. In the Bârsana-Calinesti area and along the Morii Valley, two conspicuous tuff units that can be traced over many km are separated by a calcareous sandstone bed. Most tuffs have a vitroclastic texture in which former glass shards are pseudomorphed by clay minerals and clinoptilolite. Opal-CT commonly occurs as clumps of radiating rods that produce a spherical morphology. Also, rare celadonite is found in the lower greenish tuffs. Pyrogenic crystal fragments are quartz, plagioclase and biotite. Folded muscovite plates and fragments of basement rocks are dominant among the lithic clasts. Above the Bârsana Formation, a second series of white zeolitized tuff, the Ocna Sugatag Formation, is represented by at least two different units overlying an evaporite salt deposit. A large outcrop of a massive white tuff at this locality contains abundant fine-grained clinoptilolite and cation-exchange capacity values of >160 meq/100 g. Clinoptilolite-Ca is also present in the Sighetu tuff unit in the northern part of the Maramures Basin where a distinctive horizon contains plant remains preserved in spherical concretions. Plant material and algal limestones in the same succession strongly suggest that the marine depositional environment was close inshore, and shallow- rather than deep-water conditions are inferred. A mineralogically similar, unaltered, volcanic tuff found in the Coaş area suggests that the precursor glass was rhyolitic (72–74% SiO_2) with a high-K calc-alkaline affinity. We conclude that pervasive zeolitization is due to the interaction between seawater and vitroclasts at an early stage after deposition.

Key Words—Clinoptilolite, Eastern Carpathians, Maramures Basin, Romania, Zeolitic Tuffs.

INTRODUCTION

The Carpathian Mountains in Romania form a sinuous belt comprising northeastern, eastern and southern chains. An inner volcanic arc contains two major volcanic areas located in the northeastern and eastern chains. Inside the volcanic arc, two large Neogene sedimentary basins, the Transylvanian Basin and the Pannonian Basin, are separated by the Bihar Complex (Apuseni Mountains). To the north of the Transylvanian Basin, the much smaller Maramures Basin is situated on the Ukraine border. This basin is filled with a Miocene molasse containing sedimentary sequences and interbedded volcanic rocks, resting on Paleogene flysch that overlies a basement of metamorphic rocks. The volcan-

ism occurred in two distinct phases (Fulop and Kovacs, 1996). The first volcanic phase is of Badenian–Sarmatian (Middle Miocene) age and is calc-alkaline. This phase is characterized by explosive eruptions that generated large quantities of ash deposited as air-fall tuffs and pyroclastic flows of dacitic to rhyolitic composition. The second phase of Sarmatian–Pannonian (Upper Miocene–Lower Pliocene) age is represented by a paroxysmal episode of volcanic activity that generated large quantities of andesitic lavas.

Zeolites in altered volcanic tuffs in Romania were discovered by Neacşu (1969). Bedelean and Stoici (1984) summarized the main zeolite occurrences in Romania, and recent studies on zeolitic tuffs are included in Mârza (1991), Mârza and Meszáros (1991), and Bárbat and Marton (1989).

Following a preliminary study (Damian *et al.*, 1991), the present study aims to investigate the geological distribution, petrography, and mineralogy of the

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Neogene zeolitic tuffs in the Maramures Basin and their zeolite crystal chemistry.

METHODS

Samples were collected during two periods of field-work, in July 2000 and 2001. Thin-sections were prepared at the Laboratoire de Pétrologie Magmatique (Marseille, France). Rock samples were also ground and powdered for both whole-rock chemical analyses and cation exchange capacity (CEC) measurements. Whole-rock chemical analyses were obtained with an inductively-coupled plasma (ICP) source spectrometer at Centre Européen de Recherche et d'Enseignement en Geosciences de l'Environnement (CEREGE), Aix-

Marseille. The CEC measurements were made by the ammonium acetate saturation method using the ammonia electrode technique, following the Kitsopoulos (1999) procedure. Powdered tuff samples of the 150–425 µm size-fraction were used for CEC measurement instead of the <125 µm size-fraction for better reproducibility. Whole-rock samples were X-rayed using a PW 1730 Philips diffractometer for routine zeolite structural characterization and thermal stability at the Department of Earth Sciences, University of Cambridge, UK. Seven whole-rock samples collected during the July 2000 fieldwork were selected on the basis of zeolite crystal size and prepared for microprobe analyses. Clinoptilolite chemistry was determined using a CAMECA SX100 microprobe at the Université des
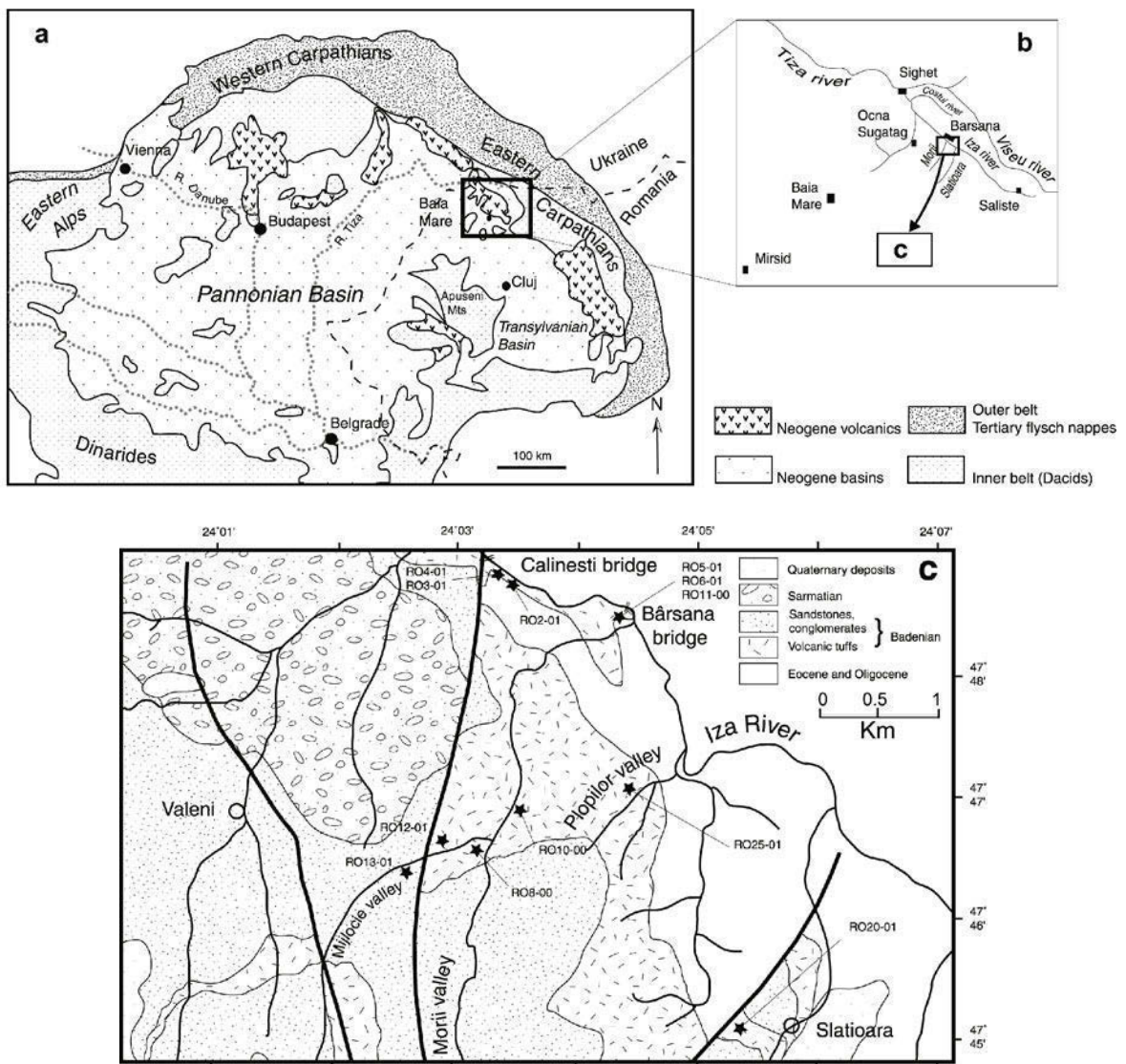

Figure 1. (a) Generalized geologic and terrane map of the Carpatho-Pannonian region showing the Maramures basin (box). (b) Map showing the location of the study area. (c) Geologic map of the study area. Stars indicate sample locations.

Sciences et Techniques du Languedoc, Montpellier, France, operating at an accelerating voltage of 20 kV, a beam current of 10 nA and a spot size of 7 μm. A total of 47 high-quality analyses of zeolite crystals was obtained on four whole-rock samples (RO2-00, RO8-00; RO10-00; RO11-00). A JEOL 6320F scanning electron microscope (SEM) equipped with a TRACOR energy-dispersive (ED) spectrometer was used to obtain complementary semi-quantitative chemical data and images of the authigenic minerals.

Clay mineral identification was carried out at Centre de Recherche sur les Mécanismes de la Croissance Cristalline (CRMC2), Luminy Campus, Marseille, using a Philips Xpert-pro diffractometer with monochromatic CuKα radiation. Measurements were carried out on oriented, air-dried, ethylene glycol-saturated and heated (550ºC) samples. Energy-dispersive spectrometer (EDS) analyses were performed on individual clay particles identified from transmission electron microscope (TEM) observations.

GEOLOGICAL SETTING

In the study area, extensional tectonic movements during the Miocene led to silicic and intermediate volcanism in the inner part of the eastern Carpathians. Throughout this region, explosive events resulted in the deposition of pyroclastic flows and ash-fall deposits that are interbedded with marine sediments. The top of the succession contains coal-rich lacustrine detrital sediments of Pontian age (6 Ma). Due to thick forest cover and subsequent burial by andesitic volcanics, the eruption centers are not well exposed, but the widespread nature of the pyroclastic rocks is evident from good outcrops in river valleys.

In the Bârsana-Calinesti area (Figure 1) and along the Morii Valley, two conspicuous tuff units, thought to be Upper Badenian (13.6 Ma) in age, overlie the Transcarpathian flysch formation. The tuffs, which are extensively zeolitized and separated by a calcareous sandstone unit, can be traced over many km. The tuffs occur as massive, homogeneous beds, 70–100 m thick, and white to pale greenish-blue in color. Because of complex jointing and lack of obvious bedding, the structures in the tuffs do not show any regional pattern.

The Bârsana Tuff Formation at Ocna Sugatag, 10 km WSW of Bârsana, underlies an evaporite salt formation that has diapirically intruded conglomerate, marl and calcareous sandstone. Above this formation, a second series of white zeolitic tuffs, the Ocna Sugatag Tuff Formation, is represented by at least two different units at three locations. White, fine-grained tuffs occur in a quarry ~1 km southwest of the village and also at the western edge of the village. A pumiceous tuff unit, having the appearance of a pyroclastic flow, occurs in the vicinity of sink holes caused by the collapse of the roof of an abandoned salt mine on the outskirts of the village.

PETROGRAPHIC DETAILS

Nearly thirty samples of tuffs from the Maramures Basin were studied both optically (Table 1) and by SEM and compared with zeolitic tuffs from localities outside the area. All tuffs from the study area are extensively zeolitized and they generally have a vitroclastic texture. Pyrogenic crystal fragments include quartz, plagioclase and biotite. Folded muscovite plates and small clasts of quartzite and muscovite-schist from the basement are dominant among the lithic fragments. The tuffs commonly contain abundant tabular clinoptilolite crystals formed by the pseudomorphic replacement of the vitroclasts. Opal-CT lepispheres (Figure 2) commonly coexist with and postdate clinoptilolite. A fibrous mineral is occasionally seen to postdate both clinoptilolite and opal-CT. It occurs as individual thin (<0.5 μm wide) fibers and clusters. The low abundance makes its identification by X-ray diffraction (XRD) and SEM uncertain, although its fibrous habit suggests this mineral is mordenite. Celadonite grains occur together with smectites in the greenish tuffs of Sighetu and Bârsana. Celadonite, identified by microprobe analyses, occurs as clusters of radiating needles (~2 μm in diameter). The green grains and other clay minerals were identified to be mixtures of Al-smectite and celadonite (Figure 3). A selection of transmission electron microscope (TEM) analyses is reported in Table 2.

The textures of zeolitized glass shards as viewed by SEM are similar to that of the Beli-Plast zeolitic tuff of the southeastern Rhodopes Mountains, Bulgaria (Leggo et al., 2001). The outstanding textural feature includes an outer clay coating from which clinoptilolite grew inwards in the form of a radial zone of tightly packed, oriented plates, from which large idiomorphic forms project into an internal void. Detailed study suggests that the clinoptilolite bears an epitaxial growth relationship with the clay outer coating (Leggo et al., 2001). Important differences, however, do exist between the Maramures examples and those of the Bulgarian zeolitic tuffs. The Beli-Plast shards, ranging 0.1–0.5 mm in length, are larger than those of Maramures. The Maramures shards commonly average 0.1 mm in length, with an outer clay coating ~1 μm thick compared with a 5 μm coating on the former, and they do not have a well defined radial zone of clinoptilolite plates.

A distinctive zeolitic tuff horizon crops out in the Sighetu area (Figure 1), where plant fossils occur in spherical concretions. Petrographic examination has shown the concretions to be composed of fine-grained volcanic ash supporting subangular quartz grains, muscovite plates, celadonite and occasional feldspar crystals. At this locality, perfectly preserved leaves of *Ligustram vulgare* L. are carbonized within individual concretions. Microscopic examination of algal limestones from Remecioara, 20 km south of Baia Mare

Table 1. Petrophysical characteristics of the studied samples.

| Sample | Location | Rock type/description | Shards | | Mineralogical composition | | CEC (meq/100g) |
			size (μm)	central void	authigenic min.	pyrogenic min*/lithics	
RO2-00	Sighetu	gray-green vitroclastic tuff; strong compaction	50/150	no	clay min., zeol., celadon.	q, pl, bi/mu, carbonates	27
RO21-01						q, pl, bi, op/mu	50
RO3-01	Iza river, Barsana	yellow-green coarse pumice tuff	250/2500	+	clay min., zeol., celadon.	q, pl, bi/mu	182
RO4-01			60	+			196
RO6-01		fine, green vitroclastic tuff	150	small		q, pl, /mu	69
RO11-00			200/600	+		q, pl, bi/mu	
RO2-01			120	+		q, pl, bi/mu	
RO5-01		green, reworked tuff	150/200	+	clay min., zeol.	q, bi, pl/mu	37
RO8-00/	Morii valley	gray/green vitroclastic tuff; crystal-rich	250	+	clay min., zeol., celadon., calcite	q, pl./mu, microfossils	115
RO10-00							
RO12-01	Valea Mijlocie	light green, fine vitroclastic tuff	150	+	v. small zeol., celadon.	q, pl, /mu	69
RO13-01		fine reworked tuff; stratified	100	rare	v. small zeol., calcite		158
RO4-00-pl/	Ocna Sugatag	white to light green, fine reworked tuff	50/200	+	clay min., zeol., opal CT	q, pl, /mu	85 / 87
RO14-01							
RO15-01		gray ignimbrite, coarse grained	100/200	+	zeol., celadon., opal CT, adul.	q, zoned pl, /mu	99
RO5-00-pl/		green, fine vitroclastic tuff	100	+	clay min., v. small zeol., celadon., rare opal CT	q, pl, bi, op/mu	126 / 167
RO16-01							
RO25-01	Plopilor valley	green, fine vitroclastic tuff	100/150	no	zeol., celadon.	q, pl, bi/mu, microfossils	94
RO20-01	Slatioara	white, fine vitroclastic tuff	200	+	clay min., zeol., opal CT	q, pl, /mu	68
RO26-01	Mirsid quarry	white vitroclastic tuff	100/120	+	clay min., v. small zeol.	q, pl, bi/mu, microfossils	147
RO31-01	Paglisa quarry	green vitroclastic tuff	up to 120	+	clay min., zeol.	q, pl, bi, amphibole/mu	171
RO14-00	Coas	yellow-white, coarse and crystal-rich pumice tuff; stratified	up to 750	unaltered glass	clay min.	q, zoned pl, bi	

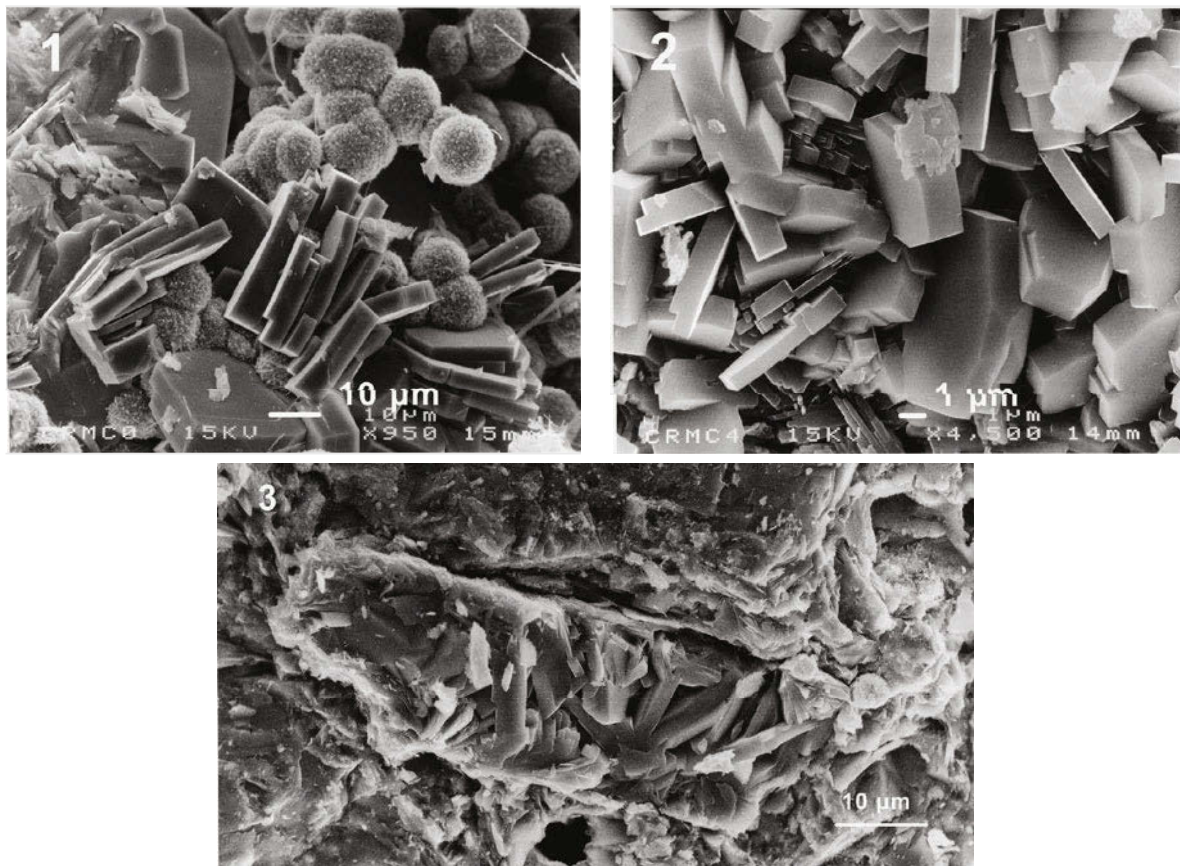*q: quartz; pl: plagioclase; bi: biotite; op: opaque minerals; mu: muscovite

Figure 2. SEM images of glass shards. (1) Sample RO15-01 (Ocna Sugatag) contains clinoptilolite crystals with opal-CT spheres inside an individual shard. (2) Sample RO15-01 (Ocna Sugatag) contains euhedral clinoptilolite showing 'coffin'-shaped morphology. (3) Sample RO11-00 (Morii Valley). The center of the image is occupied by a glass shard showing pseudomorphic replacement by clinoptilolite. A thin coating of clay minerals is on the outer surface. (Scales are represented by the white bars).

occurring in the local Badenian succession, revealed the presence of several species of foraminifera, ostracods, bryozoa and echinoderm fragments, all of which attest to a shallow marine depositional environment.

Figure 3. Phyllosilicate compositional range in $M^+-4Si-3R^{2+}$ coordinates; black dots: sample RO2-01. Open squares: references in Deer *et al.* (1962); Buckley *et al.* (1978).

CHEMISTRY OF WHOLE ROCKS AND MINERALS

Chemical studies focused on rocks and minerals from the Bârsana and Ocna Sugatag formations. Six whole-rock analyses were made on tuffs from the Bârsana and Sighetu areas and three of these samples were analyzed using the electron microprobe. Two samples from Ocna Sugatag were analyzed for whole-rock chemistry, but the zeolites were too small to obtain crystal chemical data. For comparison, tuff samples were collected and analyzed from quarries outside the Maramures Basin at Mirsid (Pop and Kovacs, 1982), 60 km southwest of Baia Mare and Paglişa, 70 km south of Baia Mare. The sampled tuffs from Paglişa show a distinctive pyrogenic mineral assemblage (Table 1) in which both amphibole and biotite are present. In the Coaş area, 15 km south of Baia Mare, a sample of unaltered tuff that was mineralogically (phenocryst assemblage) similar to the Maramures tuffs was collected and the glass analyzed using the microprobe (Table 3).
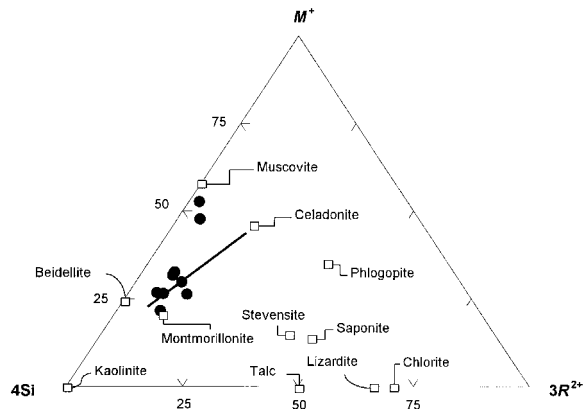
Whole-rock chemistry

In as much as the tuff samples represent altered and hydrated rocks, their chemistry is unlike that of normal

Table 2. Structural formulae ($/O_{10}(OH)_2$) of phyllosilicates from sample RO2-01, based on analytical transmisson electron microscopy analyses.

Sample RO2-01

| Analysis # | Tetrahedral site | | Octahedral site | | | Interlayer site | | |
	^{IV}Si	^{IV}Al	Fe^{3+}	Mg^{2+}	^{VI}Al	Ca^{2+}	Na^+	K^+
6	3.954	0.046	0.809	0.18	0.956	0.012	0.009	0.359
7	3.955	0.045	0.665	0.229	1.066	0.012	0.068	0.304
8	3.878	0.122	0.601	0.321	1.067	0.025	0.091	0.337
9	3.969	0.031	0.387	0.272	1.339	0.013	0.007	0.277
10	3.907	0.093	0.401	0.41	1.216	0.081	0.034	0.225
11	3.248	0.752	0.022	0.082	1.859	0	0.125	0.82
12	3.275	0.725	0.061	0.17	1.835	0	0.056	0.767
16	3.971	0.029	0.635	0.23	1.044	0	0.016	0.519
17	3.929	0.071	0.542	0.226	1.162	0.051	0.136	0.269

igneous rocks. The variation in silica concentrations among the analyzed samples, on a water-free basis, is small (2.7 wt.%). In general, the tuffs are low in Na but higher in Ca and K (Table 4). No systematic chemical variation, either vertically or laterally, within the tuff units was found in this study. Comparison between the composition (major elements) of the zeolitized and unaltered rocks shows that Al_2O_3 and SiO_2 did not migrate significantly (Figure 4). Our data do illustrate a general enrichment of MgO, CaO, K_2O and a decrease in total Fe_2O_3, MnO, Na_2O, P_2O_5. The unaltered glass in

the sample from Coaş is silica rich with a mean concentration of 73.4 SiO_2 wt.%, confirming the rhyolitic nature of the rock. Mean K and Na concentrations are characteristically high, *i.e.* 5.03 K_2O wt.% and 2.10 Na_2O wt.%, whereas the mean CaO concentration is 0.58 wt.%.

Zeolite crystal chemistry

Four tuff samples were studied, three from the Bârsana area and one from Sighetu. It was not possible to analyze the clinoptilolite from the Ocna Sugatag tuffs

Table 3. Crystal chemistry: representative EPMA of clinoptilolites and unaltered glass.

Sample #	Morii Quarry RO8-00	Valea Morii RO10-00	Iza River RO11-00	Sighetu RO2-00	Coaş* RO14-00
SiO_2	61.30	64.56	63.90	67.61	73.39 (0.46)
Al_2O_3	10.07	11.09	11.61	12.17	12.42 (0.12)
FeO_{tot}	0.07	0.04	0.14	0.03	0.84 (0.05)
MgO	0.22	0.09	0.38	0.44	0.03 (0.01)
CaO	2.88	1.49	3.42	4.05	0.58 (0.04)
Na_2O	0.83	2.58	1.12	0.60	2.1 (0.16)
K_2O	2.28	3.07	1.47	2.00	5.03 (0.09)
TiO_2	0.04	0.00	0.03	0.00	0.03 (0.02)
Cr_2O_3	0.00	0.00	0.00	0.01	
Total	77.69	82.92	82.07	86.91	94.49 (0.53)
Si	30.18	29.83	29.56	29.39	
Al	5.85	6.04	6.33	6.24	
Fe^{3+}	0.03	0.02	0.06	0.01	
Mg	0.16	0.06	0.26	0.28	
Ca	1.52	0.74	1.70	1.88	
Na	0.79	2.31	1.00	0.50	
K	1.43	1.81	0.87	1.11	
Ti	0.01	0.00	0.01	0.00	
Cr	0.00	0.00	0.00	0.34	
Total	39.97	40.81	39.79	39.75	
Si/Al	5.16	4.94	4.67	4.71	
[†]E%	5.15	5.96	10.21	5.02	

Clinoptilolites: structural formulae calculated on the basis of 72 oxygen atoms.
* Note that the chemical analysis of the Coaş Glass sample was obtained by electron microprobe; the results shown are the mean and standard deviation of eight analyses. FeO_{tot}: total iron as FeO. [†] charge balance.

Table 4. Whole-rock chemistry.

	Calinesti bridge RO4-01	Bârsana bridge RO6-01	Middle Valley RO12-01	Ocna Sugatag RO15-01	Ocna Sugatag RO16-01	Slatioara RO20-01	Sighetu RO21-01	Plopilor RO25-01	Mirşid RO26-01	Paglişa RO31-01	Coaş RO14-00
SiO_2	67.09	66.76	67.72	68.97	68.44	68.28	68.46	66.25	67.21	66.37	71.59
TiO_2	0.18	0.25	0.16	0.13	0.14	0.19	0.15	0.18	0.18	0.13	0.16
Al_2O_3	11.37	10.82	11.16	11.66	11.6	11.06	11.85	11.38	11.21	11.31	11.96
Fe_2O_3	0.34	0.61	0.37	0.35	0.34	0.28	0.38	0.22	0.93	0.68	n. d.
FeO	0.51	0.96	0.33	0.4	0.48	0.3	0.86	0.42	0.18	0.31	n. d.
MnO	0.02	0.01	0.01	0.02	0.01	0.03	0.01	0.01	0.01	0.01	0.02
MgO	0.27	0.74	0.82	0.72	0.61	1.34	0.6	0.44	0.63	0.39	0.38
CaO	0.86	2.82	2.73	2.09	2.08	2.51	2.27	2.38	3.15	2.36	1.69
Na_2O	3.73	1.01	0.33	1.23	1.6	0.18	0.98	1.78	0.44	2.36	1.84
K_2O	2.78	1.96	2.68	2.36	2.39	2.43	2.21	2.12	2.83	1.64	1.36
P_2O_5	0.02	0.03	0.02	0.01	0.01	0.02	0.03	0.01	0.04	0.02	0.05
H_2O^+	8.91	8.74	9.36	9.23	9.07	9.33	8.37	9.82	9.22	10.46	1.03
H_2O^-	2.67	2.75	3.07	2.18	2.25	3.12	2.44	3.23	3.18	3.2	3.13
$t.Fe_2O_3$	0.9	1.67	0.73	0.79	0.87	0.61	1.33	0.68	1.12	1.02	5.76
Total	99.65	99.13	99.49	100.14	99.89	99.68	99.94	98.92	100.33	100.26	98.97
Sr ppm	243	403	173	385	198	342	1009	138	1250	635	
Ba ppm	687	633	710	649	526	816	5585	558	1066	378	

$t.Fe_2O_3$: total iron as Fe_2O_3

because of the small size of the crystals (1 to 2 µm long), but the SEM was used to estimate chemical compositions. Representative electron microprobe analyses of clinoptilolites are shown in Table 3, together with structural formulae and charge balance E% (Passaglia, 1970). From XRD patterns obtained from whole rocks, only one zeolite species, which is of the heulandite–clinoptilolite series, occurs in the Maramures tuffs. These zeolites are classified according to their Si/Al ratio (Boles, 1972; Coombs *et al.*, 1997), as calcic and alkali clinoptilolites. Clinoptilolite in the Bârsana area is alkaline, whereas that from Sighetu is calcic. A further variation is seen in the Bârsana clinoptilolites in as much

as the sample from the lower unit is more sodic than that of the upper unit. The Sighetu sample plots in a region of compositional overlap characterized by an Si/Al ratio of >4 with divalent cations greater than univalent extra-framework cations (Figure 5). Clearly, the exchangeable cations differ from one unit to the other, but the framework has a nearly constant Si/Al ratio.

Thermal treatment of the Sighetu samples, according to the methods of Mumpton (1960) and Alietti *et al.* (1977), confirms that clinoptilolite-Ca is present in these tuffs, as after heating for 12 h at 450°C, a great reduction in peak height of the 020 reflection occurred with no shift in the peak position. Some of the Ocna Sugatag and
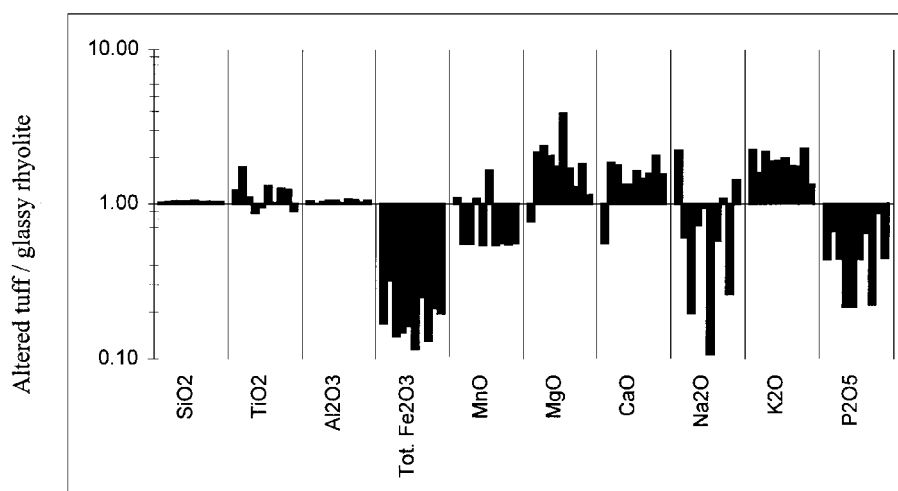

Figure 4. Logarithmic plot showing chemical differences between altered tuffs and a fresh glassy rock, represented by the Coash sample RO14-00.
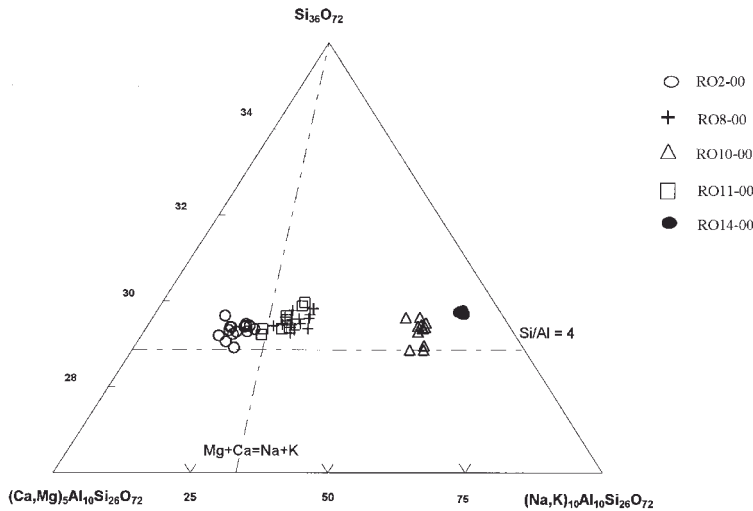
Figure 5. Triangular diagram showing electron microprobe analyses of clinoptilolites and the Coaş glass sample RO14-00.

Bârsana samples also show this effect. According to Bish and Boak (2001), samples plotting in this region of the triangular diagram (Figure 5) may represent mixtures, intergrowths or zoned, or overgrown materials. Because no evidence of zoning, overgrowth, or mixtures was seen, we suspect that intergrowths might explain the observed properties, as suggested by Vaughan *et al.* (1995).

Cation exchange capacity measurements

The CEC values of 18 samples were measured, 16 from the tuffs of the Maramures Basin and two from outside the area (Table 1). RO26-01 is a zeolitic tuff from the Mirsid Quarry, the only currently active quarry in northern Romania, and RO31-01 is a similar rock from a recently abandoned quarry at Pagliṣa. The CEC values range from 27 meq/100 g to 196 meq/100 g. Two tuffs from the Sighetu area have very low values ranging from 27 to 50 meq/100 g, whereas tuffs from the Bârsana area and Ocna Sugatag have larger values. The tuffs in the Bârsana area range from tuffaceous sandstone (37 meq/100 g) to homogeneous vitroclastic tuff (196 meq/100 g). At Ocna Sugatag, the fine-grained rocks from the small quarry, 1 km southwest of the village, have high CEC values (126 and 167 meq/100 g), whereas a pumice flow at the western edge of the village has a lower value (99 meq/100 g). Close to this site, two samples from an abandoned working have similar values (85 and 87 meq/100 g). For comparison, samples from Mirsid and Pagliṣa yield 147 and 171 meq/100 g, respectively. No qualitative consistent relationship was found between petrophysical characteristics and CEC values (see Table 1), mainly because of variable amounts of clay minerals. Other parameters, such as porosity and differences in the size of the original glass shards, may also be important. As no attempt was made to measure the amount of clinoptilolite, smectite and celadonite quantitatively in any of the zeolitic tuffs, it is difficult to reach a

conclusion on the relationship between the whole-rock CEC measurements and that of the individual zeolite and clay phases. An assessment based on the optical petrography suggests that the major ion-exchange properties are due to the presence of the zeolite phase but this qualitative judgement is hindered by the very small crystal size (<10 μm) in most of the rocks.

DISCUSSION AND CONCLUSIONS

Our investigations of the Badenian tuffs, interbedded with the Maramures Basin sediments, show that the tuffs are widespread and that zeolitization is pervasive. The volcanic vent areas remain largely unknown because of a lack of detailed geological mapping and the fact that late andesitic volcanism has obscured the earlier rhyolitic rocks. Moreover, the tuffs are strongly affected by faulting as they were deposited during early basin formation. Thick tuff units with intercalated sediments are recognized all over the Pannonian and Transylvanian basins (Pécskay *et al.*, 1995). The sampled tuffs in the Maramures Basin show a remarkable homogeneity. They have the same pyrogenic mineralogy and their anhydrous chemical composition is close to a rhyolitic glass precursor found in the vicinity at Coaş. Stratification is vague in all units and there is no evidence of strong reworking as the shapes of the glass shards are remarkably well preserved. Pervasive zeolitization of the glass fragments was found in all the sampled units over the basin. Clinoptilolite is the dominant species among the authigenic minerals and opal-CT spherules occur on clinoptilolite in some samples. Clinoptilolite shows a wide variation in exchangeable cations but has only slight variability in the Si/Al ratio.

In the Sighetu area, coalified leaves of *Ligustrum vulgare* L., a shrub common in modern coastal areas, are perfectly preserved in concretions within the alkali-rich

clinoptilolitic tuffs. A shallow marine environment is deduced from the association of foraminifers such as fossil miliolids and globigerines found in the tuffs. Limestone of Badenian age, ~20 km south of the Maramures Basin at Remecioara, contains a spectacular fossil assemblage of red algae, foraminifera, ostracoda and bryozoa which, without doubt, indicate a shallow, marine environment. This evidence, together with the presence of plant fossils in the zeolitic tuffs, suggests that silicic volcanism occurred during an uplift period corresponding to a shallow marine environment that became continental with a general increase in the amount of detrital sediments.

The origin of the zeolites can be inferred from the results above. Petrographic observations show that the clinoptilolite formed *in situ* from volcanic glass, as commonly described (*e.g.* Ghiara *et al.*, 1999) in silicic tuffs. Zeolites do not fill the pore-space between the glass shards in Maramures Basin tuffs. This fact, together with the observed pervasive and complete alteration of the glass, tends to exclude focused hydrothermal alteration. The observed characteristics of the Maramures Basin zeolitization share some similarity with the Rhodopean tuffs in southern Bulgaria (Aleksiev and Djourova, 1975). Both areas contain thick, homogeneous tuff units, similar authigenic zeolite species and replacement textures, and reveal a change from shallow marine to a continental environment, suggesting that a similar process acted on the whole pile. From the inferred environment and observed succession of authigenic minerals in the Maramures tuffs, all clinoptilolites are genetically related to the alteration of the volcanic glass.

The precursor glass of the Maramures tuffs is thought to be rhyolitic, as the Coaş tuff sample has a similar pyrogenic assemblage and the unaltered glass is rhyolitic. It can be argued that zeolitization in the Maramures tuffs is an early alteration process occurring in shallow marine waters. For such porous tuffs (*e.g.* 19% porosity in sample RO8-00 measured by the triple weighing method), the process is favored by (1) an open fluid interaction system and (2) acidic fluids. The acidity arises from magmatic volatiles and water-rock reactions when cations are hydrolyzed (Resing and Sansone, 1999). Moreover, the hydrolysis of the glass surface is thought to happen relatively quickly when it takes place at the temperatures expected in thick beds lacking the appearance of air-fall deposits. In such an environment, smectites crystallize from the glass fragments, forming a clay rim preserving the shape of the shards. Then, the inner part of the shard evolves at a much slower rate in a semi-closed system at increased pH (the water/rock ratio lowers) so that the glass transforms isochemically into high-Si zeolites + opal C-T by a dissolution/precipitation process. There is no evidence that opal-CT crystallized later because opal-CT is restricted to the inner part of the shards and is never found filling the inter-shard porosity.

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