Rom. J. Mineralogy, vol. 80, p. 11-20, Bucureşti, 2000

ZEOLITE FORMATION IN THE LOWER MIOCENE TUFFS, NORTH-WESTERN TRANSYLVANIA, ROMANIA

I. SEGHEDI, A. SZAKÁCS, I. VANGHELIE, C. COSTEA

Institutul Geologic al României, str. Caransebeş nr. 1, RO-79678 Bucureşti 32

Key words: Rhyolites. Clinoptilolite. Opal-CT. Mordenite. Diagenesis. Transylvanian Basin.

Abstract: Zeolites are common alteration products of silicic, mostly vitric, Badenian (Lower Miocene) tufts in the northwestern part of the Transylvanian Basin. This study of 50 samples from sections at Tărpiu, Vale, Bobâlna, Aluniş and Şoimeni showed that reworked fallout tuffs and ash-flow tuffs had been extensively altered to a mineral assemblage dominated by zeolites. The relative abundance of zeolites and associated minerals were determined by X-ray powder diffraction. Selected samples were also studied by SEM and optical methods to ascertain the genesis and paragenetic relationships of the minerals. Zeolitic tuffs consist mostly of clinoptilolite (40-90 %) and opal-CT. Trace amounts of fibrous mordenite and phillipsite were detected by SEM. The common paragenetic sequence is volcanic glass-clinoptilolite-mordenite. Opal-CT crystallized at the same time as clinoptilolite or later. The origin of the zeolites and associated minerals in these deposits is shown to be diagenetic. Hydrolysis of the silicic glass brought about by saline alkaline pore water, trapped during marine sedimentation of the pyroclastic material and subsequent burial accompanied by increase of temperature (up to 80^0C), was followed by formation of zeolites at the expence of glass and zeolite and opal-CT precipitation in pore spaces.

Introduction

This investigation deals with the diagenetic history of an important bedded tuft sequence deposited mainly in the Badenian (Lower Miocene) time over a large area, mostly in the Transylvanian Basin. The stratigraphic position of the tuff sequence within the Miocene sedimentary rocks provides an excellent marker horizon. Drilling has shown that this tuff complex occurs throughout the whole Transylvanian Basin with outcrops along the southeastern, western and northern margins. It is also widespread in other parts of the region, as intramountain basins of the Apuseni Mountains, or external border of the Carpathian bend (Fig. 1). The present investigation is restricted to its classical occurrence area, where the tuff sequence crops out between the towns of Cluj-Napoca and Dej. In this area it is known in the literature as the "Dej Tuff" (Posepny, 1867). Evidence of zeolites, mainly clinoptilolite, in the Dej Tufts was reported by Popescu et al., (1975) and later confirmed by Popescu and Asvadurov (1978). Mordenite was recorded by Istrate (1980) and later by Bedelean and Avram (1991). Other investigations recording the presence of zeolites in the study area include those by Bedelean (1982), Ghergari et al., (1991), Răcătăianu et al., (1991) and Bărbat et al., (1991).

General geology

In the Transylvanian Basin the Lower Miocene sedimentary strata, which followed the epicontinental-continental Eocene-Oligocene sedimentation, form a discontinuous post-tectonic cover sequence over the Upper Cretaceous-Paleogene deposits (Săndulescu, 1984). The Dej Tuff Complex, some 20-100 m thick, occurs near to the top of the Lower Miocene succession (Popescu et al., 1995). During the Early Miocene the Transylvanian Basin underwent progressive tectonic subsidence. The whole complex comprises 4 to 5 major volcaniclastic cycles, each including reworked ash-flow and fallout tuffs at the base, fallout tuffs and reworked tuffs in the middle part, and tuffites interbedded with psamitic to siltic sediments in the upper

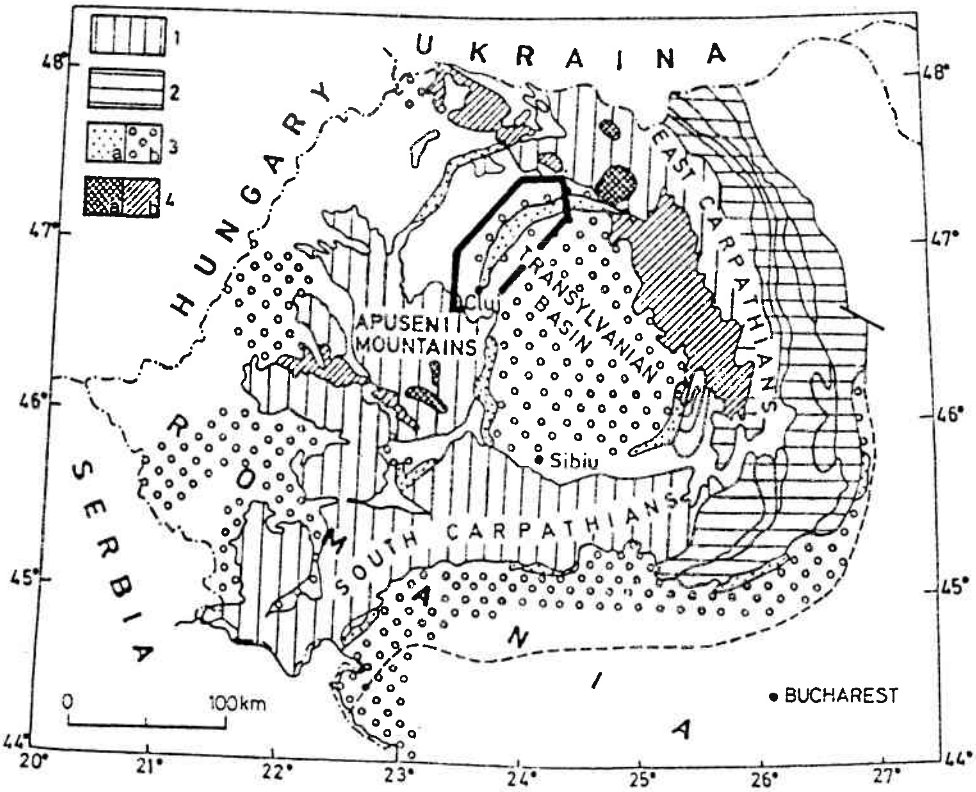

Fig. 1 - Location and distribution of Neogene igneous rocks in Romania 1: Inner Carpathian Units; 2: Outer Carpathian Units; 3: Acid caic-alkaline volcanism: a) cropping out, b) buried; 4: Intermediate cab-alkaline magmatism: a) intrusive, b) stratovolcanic. The frame shows the study area.

part. As a whole, the complex has a rhyolitic character (Seghedi and Szakacs, 1991). Stratigraphically, the Dej Tuff Complex is constrained to Langhian (Lower Badenian) (Popescu, 1970), but a K-Ar age determination, obtained on biotite from the basal level of the complex, gave 18.0±0.5 Ma (Berggren and Popescu, unpublished data). The volcanic source area is still unknown.

Sampling and methods of study

Samples were collected along the western outcrops of the Transylvanian Basin, between Ciceu-Giurgeşti and Cluj-Napoca (Fig. 2). Generalized lithological columns of the Bobalna Hill and Aluniş are shown in Figure 3 with the sampled intervals. Material was collected wherever an obvious change in lithology was observed. Stratigraphic sections were measured at all the locations (Ciceu-Giurgeşti, Tirulul Hill-Dej, Rapa Dracului, Aluniş, Paglişa, Şoimeni and Coruş) with a complex sampling for petrographical observations. 50 samples were examined from all the studied profiles. Their mineral composition (Table 1) was determined by X-ray powder diffraction technique (XRD) after heat treatment at 550°C, using a Dron-3 instrument and Ni-filtered CuKα radiation. S[illegible] electron microscopy (SEM) was carried out with a REMMA 202 instrument.

Petrography and mineralogy

Macroscopic and microscopic features

Two main volcaniclastic rock types have been found: reworked pyroclastics and tuffites. The first ones are grouped in secondary ash-flow tuffs and second fall-out tuffs. The color of these rocks is white, light green or green. The last color characterizes zeolite-rich vitroclastic tuffs. The rocks are indurate, having conchoidal fractures. The tuffs generally are fine-grained, well-graded, showing parallel bedding stratification. The reworked ash-flow tuffs are massive and richer in crystals.

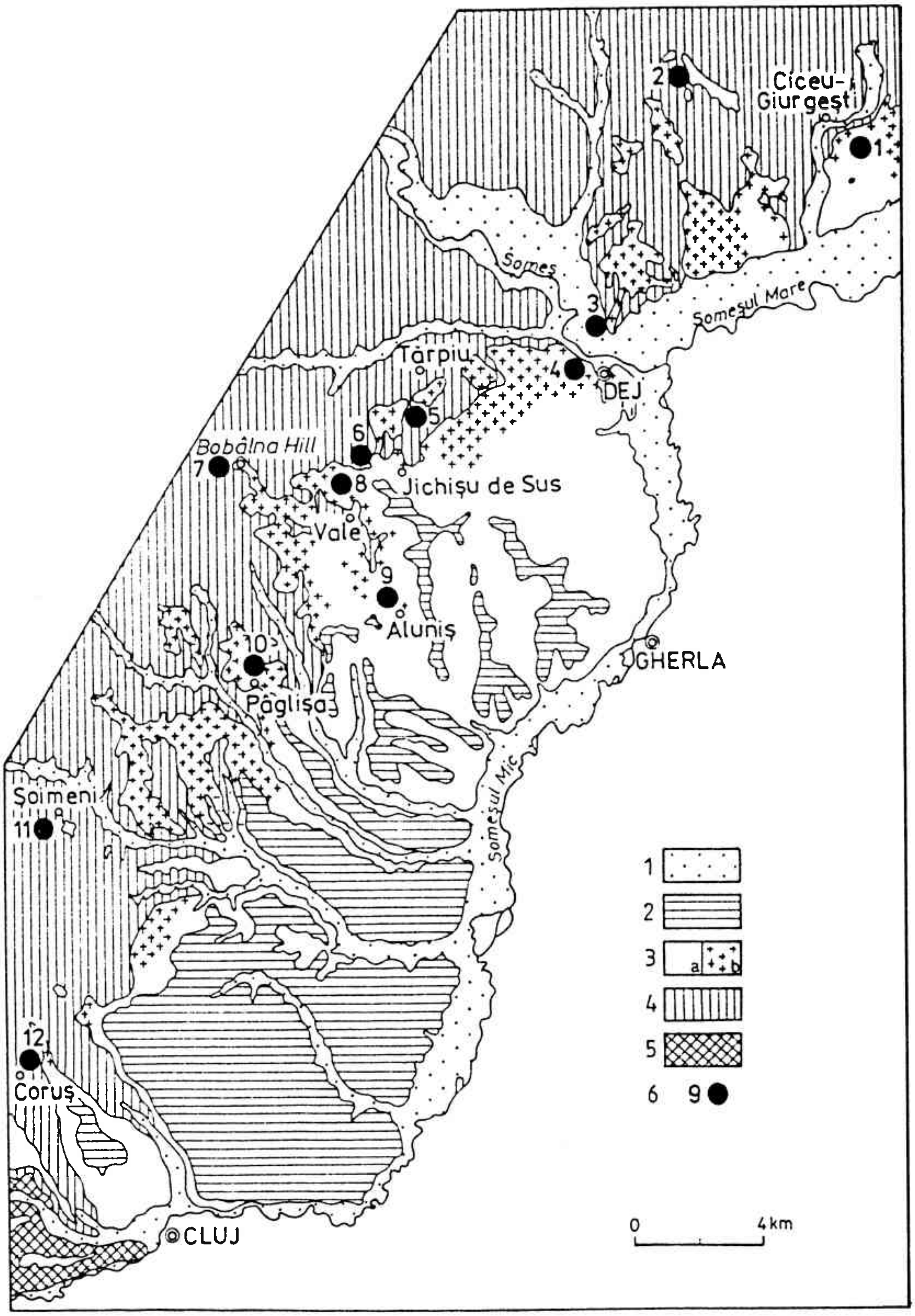

Fig. 2 - General geological sketch of the northwestern border of the Transylvanian Basin showing the area of investigation. 1: Quaternary deposits; 2: Sarmatian strata; 3: Badenian: a) Dej strata, b) Mireş strata; 4: Lower Miocene strata; 5: Paleogene strata; 6: Location of the sections.

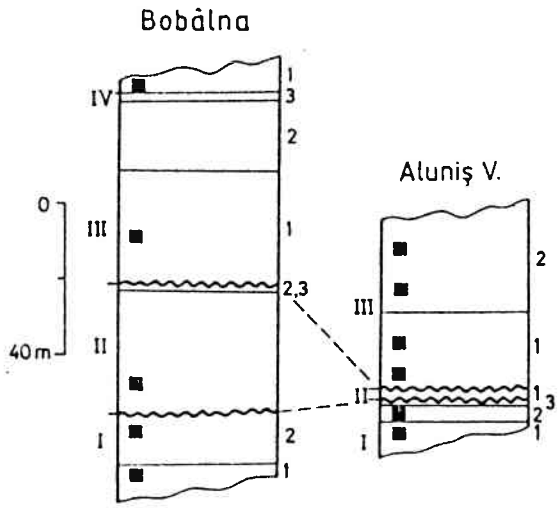

Fig. 3 - Generalised lithologic columns of the Dej Tuff sequences from Bobâlna Hill and Aluniş; sections show the sampling intervals. I, II, III and IV indicate the major volcaniclastic sequences: 1: ash-flow tuffs; 2: fallout tuffs; 3: interbedded fallout tuffs, epiclastic rocks and sedimentary strata.

In thin section, the main petrographic components include vitroclasts, crystaloclasts and lithoclasts. Based on the relative amount of these components, the rocks can be defined as vitroclastic and/or crystaloclastic tuffs, and crystal-vitric/vitric-crystal tuffs The lithoclastic component is less abundant, particularly found at the base of the main reworked ash-flow tuffs. The vitric component consists of glass, shards, pumice and massive glass fragments. The crystaloclasts are mostly quartz, plagioclase, biotite, green amphibole, alkali-feldspar and accessory pyroxene, allanite and opaque minerals (titano-magnetite, ilmenite).

Secondary minerals

Thin-section petrography, XRD and SEM data show that the vitric matrix of the tuffs was partially or entirely altered to zeolites and cristobalite (opal-CT) (Table 1). Other minerals, such as quartz and plagioclase, represent primary constituents. Rhyolitic glass in the samples from the locality of Coruş is mostly unaltered, although interstitial calcite is locally abundant In the altered samples the growth of euhedral secondary minerals was observed within interstitial voids between the shards.

Clinoptilolite

This mineral is the main secondary product in all the studied sections occurring in a wide range of euhedral forms, including blades, laths, plates with the characteristic coffin shape, and blocky crystals. The crystals are about 1-30 microns long (Fig. 4). The shards are pseudomorphosed and the larger crystals have grown perpendicular to the shards, filling the interstitial cavities (Fig. 4). The XRD pattern of clinoptilolite is very similar to that of heulandite (Mumpton, 1960), but after thermal treatment at 550 ^{0}C heulandite breaks down, whereas clinoptilolite is unaffected. The 8.95 Å and 3.95 Å peaks are unequivocal (Fig. 5).

Opal-CT lepispheres

Diagenetic silica, known previously as low-cristobalite, is frequently present besides clinoptilolite in the studied sections. Silica lepispheres are microspheroidal bodies of bladed crystals, consisting of more or less disordered cristobalite and trydimite, randomly intergrown, being defined as opal-CT by Oehler (1975) (Figs. 6, 7). Opal-CT crystallized at the same time as clinoptilolite, or later. In Figure 5 the sharp peak at 4.05 Å is due to opal-C and not opal-CT (Jones and Segnit, 1971). As a result of the heat treatment the very broad reflection of Opal-CT around 4.3, 4.1 and 3.9 Å has been converted to the low-cristobalite-like peak in this difractogram.

Mordenite

This mineral, found only in vitric fallout tuffs at Tărpiu, Aluniş and Vale, was detected by SEM. It occurs as randomly distributed fibers on clinoptilolite and opal-CT, but never as a direct alteration product of the volcanic glass (Fig. 6).

Table
Mineral associations and relative frequency of mineral species of selected Dej Tuff samples determined by XRD analyses.

Sample number	Location	Original rock type	Mineralogy	Frequency
TD-143-1	Tărpiu (5)	Tuff	clinoptilolite quartz	++++ +
TD-144-2a	Bobâlna (7)	Ignimbrite	clinoptilolite quartz	+++ +
TD-144-2a	Bobâlna (7)	Ignimbrite	clinoptilolite quartz cristobalite	++++ ++ +
TD-144-6	Bobâlna (7)	Ignimbrite	clinoptilolite quartz opal-CT	+++ + +
TD-145-1A	Bobâlna (7)	Ignimbrite	clinoptilolite quartz	+++ +++
TD-154-4A	Bobâlna (7)	Ignimbrite	clinoptilolite quartz plagioclase	+++ +++ +++
TD-141-6B	Vale (8)	Coarse tuff	clinoptilolite	++++
TD-139	Aluniş (9)	Medium tuff	clinoptilolite plagioclase opal-CT	+++ +++ +
TD-139-1A	Aluniş (9)	Fine tuff	clinoptilolite quartz	++++ ++
TD-139-1B	Aluniş (9)	Fine tuff	clinoptilolite quartz opal-CT	+++ + +++
TD-139-4	Aluniş (9)	Fine tuff	clinoptilolite quartz	++++ +
TD-139-5C	Aluniş (9)	Fine tuff	clinoptilolite quartz	++++ +
TD-139-3A	Aluniş (9)	Fine tuff	clinoptilolite quartz	++++ ++
TD-140-3	Aluniş (9)	Fine tuff	clinoptilolite	++++
TD-140-6	Aluniş (9)	Fine tuff	clinoptilolite	++++
TD-134-4-2	Pâglişa (10)	Fine tuff	clinoptilolite	++++
TD-145-4-2	Şoimeni(11)	Fine tuff	clinoptilolite quartz	++++ +
TD-137-1	Coruş (12)	Tuffite	amorfous material quartz calcite plagioclase kaolinite	+++ + + + +
TD-137-0	Coruş (12)	Tuffite	calcite amorfous material quartz plagioclase	++++ ++ + +

Frequency symbols: ++++ - very abundant
+++ - abundant
++ - small amount
+ - sporadic

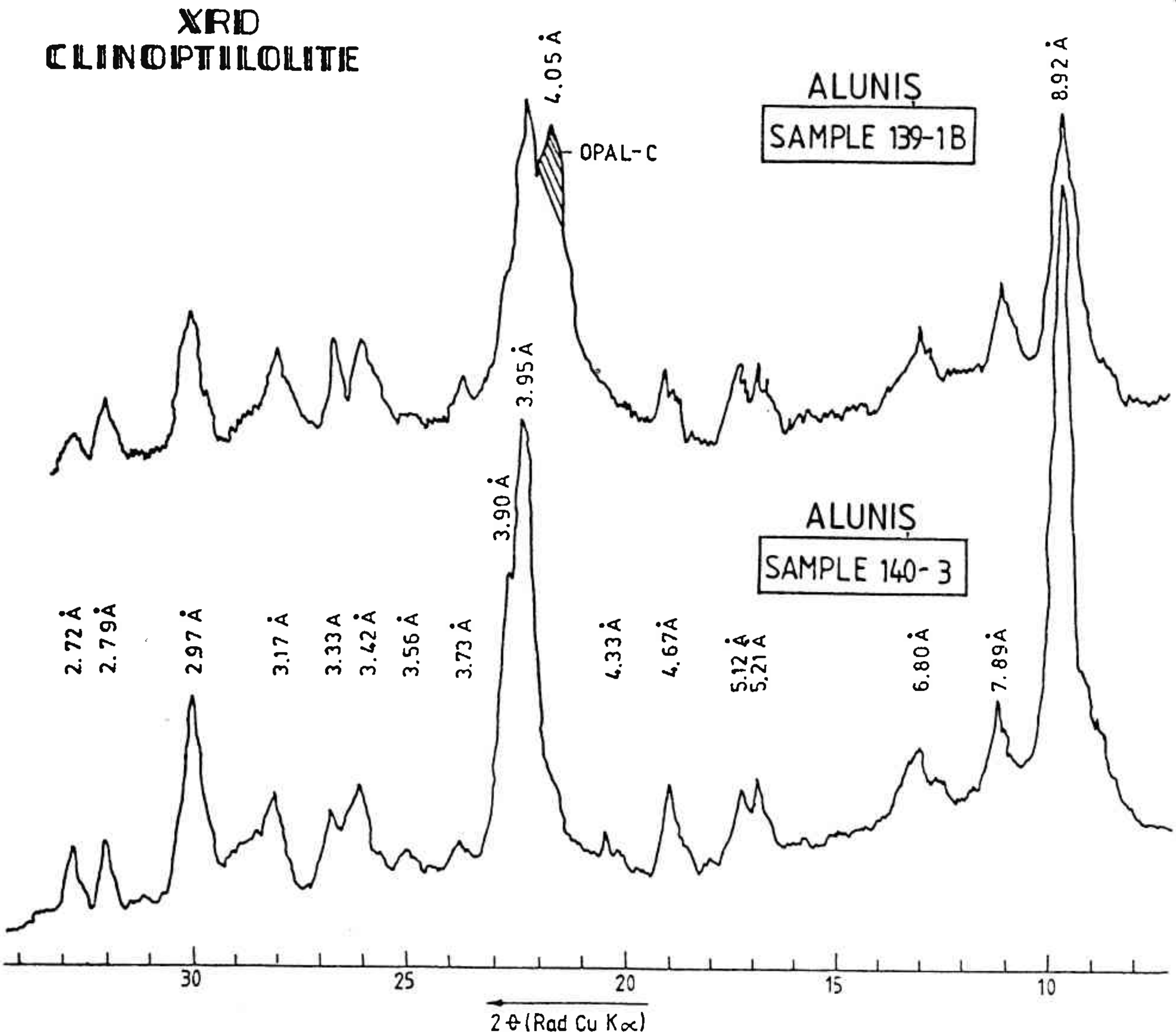

Fig. 4 - X-ray powder diffraction diagrams for clinoptilolite (sample 140-3) and clinoptilolite associated with opal-C (sample 139-18) from Aluniş, after heat treatment at 550°C.

Phillipsite

Phillipsite occurs only at Tărpiu as a secondary alteration product of clinoptilolite associated with opal-CT. It was detected by SEM and appears as laths of prismatic crystals (Fig. 7).

Carbonate minerals

Calcite is the most abundant secondary mineral in the tuffs at Coruş. Its formation seems to have inhibited the development of zeolites so the glass shards are practically unaltered.

Paragenesis of secondary minerals

The paragenetic relations are closely connected with the amount of volcanic glass in the deposit. No evidence was found that zeolites replaced other minerals. The main observed parageneses are: (1) ctinoptilolite; (2) clinoptilolite - opal-CT; (3) clinoptilolite - opal-CT - mordenite.

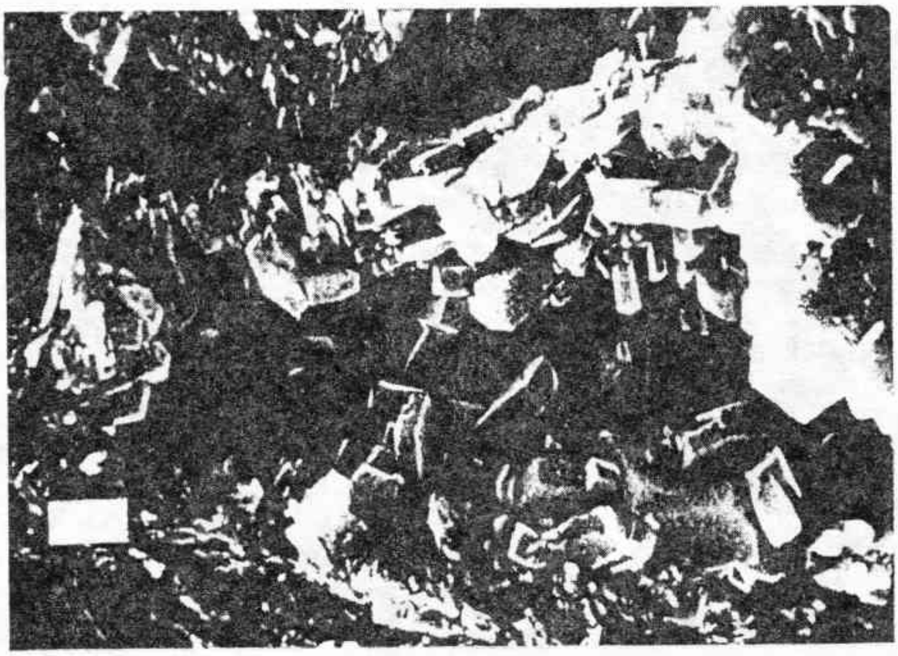

Fig. 5 – Scanning electron micrograph showing relationships between blade- and lath-shaped clinoptilolite filling voids between diagenized glass shards; Pâglişa occurrence; scale bar is 7 μm long.

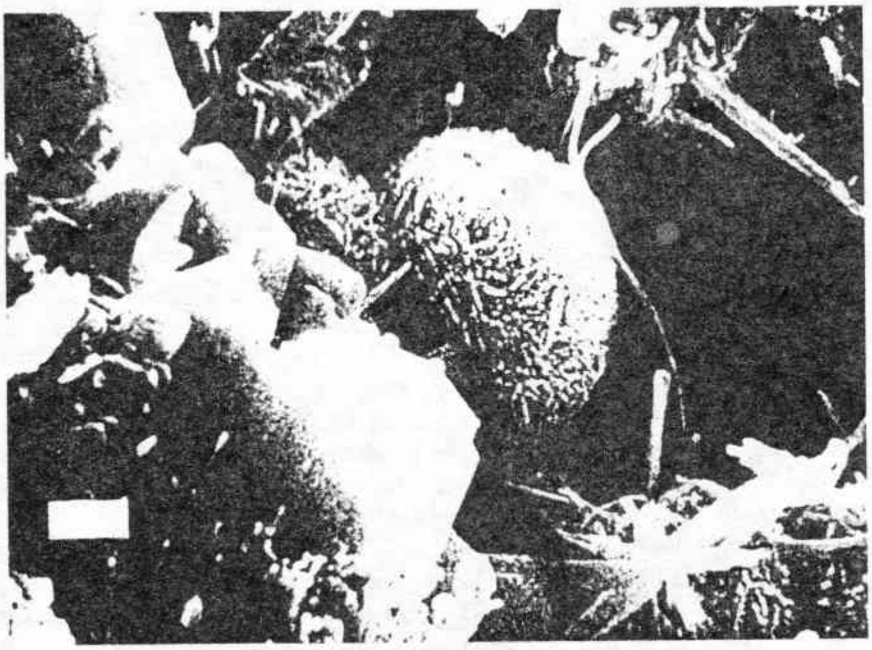

Fig. 6 – Scanning electron micrograph of opal-CT lepispheres, fibmus mordenite and clinoptilolite blades from Aluniş: scale bar is 0.5 μm long.

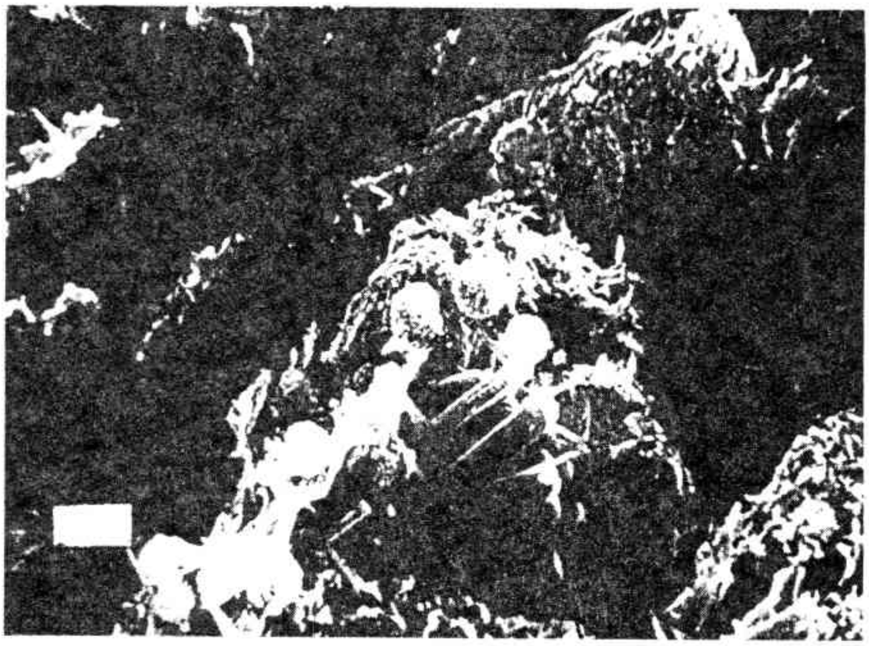

Fig. 7 - Scanning electron micrograph of lath-shaped phillipsite crystals associated with opal-CT lepispheres from Ta rpiu; scale bar is 3 μm long.

Genesis of zeolites and associated minerals

All the evidence provided by these investigations support the view that the described alteration products are authigenic in origin. Hay (1993) has summarized the major factors controlling the formation and distribution of zeolites and other authigenic minerals. These include mineralogical composition, permeability and age of the host rock, temperature variation, pressure and chemistry of the pore waters.

The examined rocks are mainly rhyolitic reworked fallout and ash-flow tuffs, rich in volcanic glass. The primary volcaniclastic deposits were redeposited in a marine environment. In all observed sections the deposits have a similar mineralogical composition and structure, and are more or less equally affected by zeolitization. The roughly constant mineralogical composition of the rocks, in the whole deposit, suggests that no significant mass transfer was involved in the formation of diagenetic minerals. The distribution of any authigenic minerals in the deposits should reflect the chemistry of the pore fluids present during diagenesis. Experimental and theoretical approaches (e.g. Hess, 1966) suggest that the main characteristics of the pore water controlling the dissolution and precipitation of either argillic phases or zeolites are closely related to the relative activity of alkalis and hydrogen. High alkali ions/hydrogen ions ratio and a relative high activity of silica favor the prevailing generation of zeolites as opposed to clay minerals. This situation would characterize generation of the zeolites described here. Such situations are typical of alkaline saline lake or marine environment (Hay, 1978, Iijima, 1978). The presence of alkaline saline water favorizes zeolitization, but additional factors must also be involved. The Dej Tuff Complex was buried during the Miocene under a significant cover of later sediments up to 3.5±0.5 km Sanders, 1998). It seems likely that the deposits suffered enough burial to give rise to significant changes in temperature and pressure, which favored the diagenetic processes. The burial temperature of 80 ^{0}±10 ^{0}C (Sanders, 1998) is in the estimated range for clinoptilolite formation and stability (49-83 ^{0}C) in the present-day diagenesis in various areas worldwide (Iijima, 1986, Ogihara, 1996).

Paleoenvironmental conditions during the Early Miocene times suggest that the secondary minerals in the Dej tuffs were generated through hydrolysis and dissolution of silicic glass by interstitial saline waters in a marine environment. The subsequent burial favored the diagenetic processes during the rise of temperature and pressure. The almost complete zeolitization of the volcanic glass-rich deposits suggests that the pore water, which caused the diagenesis, was of cognate type, trapped in the sediments during or shortly after the underwater deposition of the volcaniclastics. Some mineralogical variation in the different studied profiles could be related to different compositions of the interstitial pore fluids, but also to differences in the composition of the protoliths. The crystallization sequence during tuff diagenesis was probably controlled by growth kinetics allowing the metastable precipitation of clinoptilolite and opal-CT as a result of kinetic barriers (Murata and Larson, 1975), followed in some cases by mordenite or phillipsite generation. The lack of transformation of volcanic glass in the case of the occurrence suggests that there were not favorable conditions for zeolitization. The abundant presence of authigenic calcite in the Coruş tuffs suggests a slightly acidic environment, inherited by pore waters, that precluded the formation of zeolites at the expense of volcanic glass.

We can assume that the amount of zeolites in the diagenetically transformed tuffs closely reflects the amount of primary volcanic glass initially present in the volcaniclastic deposits.

Acknowledgements

The Geological Institute of Romania supported this research. We are grateful to Hilary Downes and Anthony Hall for reviewing and correcting the early version of the manuscript.

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Received: October 2000
Accepted: December 2000