Volcanic agents of zeolitization in the Eastern Rhodopes: V/S of volcanic glass particles

Вулкански фактори на зеолитизацията в Източни Родопи: V/S на стъклените вулканокласти

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Zeolites are polygenic minerals forming in large number of geological setting and, therefore, there is a large number of agents causing and favoring zeolite formation. But when the focus is on larger and economically potential zeolite occurrences only, there are just 2 main preconditions for intensive zeolite formation: large volume of metastable glass and additional water. There are several naturally occurring materials that can transform into zeolites but volcanic glass is the most important zeolite precursor. Unfortunately, the original volcanic features of the precursor material are often overlooked when zeolitization processes are discussed and, traditionally, more attention is paid on the hydrology of the associated water systems. We do agree that the environmental agents such as presence and chemistry of ambient water are also of crucial significance. Moreover, the initial volcanic features could be of less importance or can be significantly obscured in certain geological settings. However, in some of the zeolitized pyroclastic deposits, as in the Eastern Rhodopes, the original volcanic features are well preserved, they directly correspond to deposits quality and their consideration can significantly contribute the study of zeolitization. And many researchers worldwide have come to similar conclusions (Lenzi, Passaglia, 1974; Aleksiev, Djourova, 1975; De'Gennaro et al., 1999; Hall, 2000, etc.).

All processes related to generation, distribution and deposition of the zeolite precursor material can be inferred as volcanic agents having an effect on zeolitization. The most important volcanic agent is glass, respectively, magma composition. Besides being the source of the chemical compounds needed for zeolites and accompanying glass-replacing phases to grow, magma composition is related or directly defines the volumes of erupted glass, eruption styles, degrees of fragmentation, transportation modes, clast morphologies, etc. The aim of this note is to outline the impact of size and morphology of glass particles on zeolitization and quality of zeolite deposits, hosted by Eastern Rhodopes Paleogene volcaniclastics.

The largest zeolite (mainly clinoptilolite) deposits in Eastern Rhodopes associate with acid pyroclastic rocks. Broadly speaking, their grain-size is a function of eruption style and intensity, degree of fragmentation and mode of transportation. The effect of grain-size on zeolitization was noticed long ago (Hay, 1966; Kirov et al., 1976). But volcanic glass fragments have peculiar morphology that is also important agent controlling distribution of glass-alteration products (Fig. 1A). The parameter combining grain size and shape is known as surface-area-to-volume ratio (or conversely V/S, as defined by Vlahov, 2013) and it is an important factor for the reactivity of solid materials. Thus, on the basis of V/S of the common volcanic glass particles, 3 edge cases of their alteration can be distinguished.

1. The alteration of particles having low V/S, due to small volume (finest ash shards), is very sensitive to the environmental conditions. Distal fine-grained ash layers can be converted to bentonite. In the clinoptilolitized composite sections, still away from the sources, fine-grained layers can be zeolitized but the clinoptilolite is also very fine-grained and poorly crystalline. And when the conditions are favorable, such fine-grained varieties faster (than coarser-grained) can become feldspar-dominated (Kirov et al., 1976). The finest ash particles have highest reactivity so whatever the grade and type of their alteration they get totally consumed and no traces of their outlines can be observed. All left behind is very fine-grained aggregate of different secondary minerals.

2. Particles with low V/S, but when it is due to large surface area (pumice), would preferentially transform to phyllosilicates. Formation of clay cover on glass particles is common for the zeolite deposits in the Eastern Rhodopes. In pumice clay fills in the open bubbles and when the bubble walls are thin (as in the resulting from eruptive shearing tube pumice) then

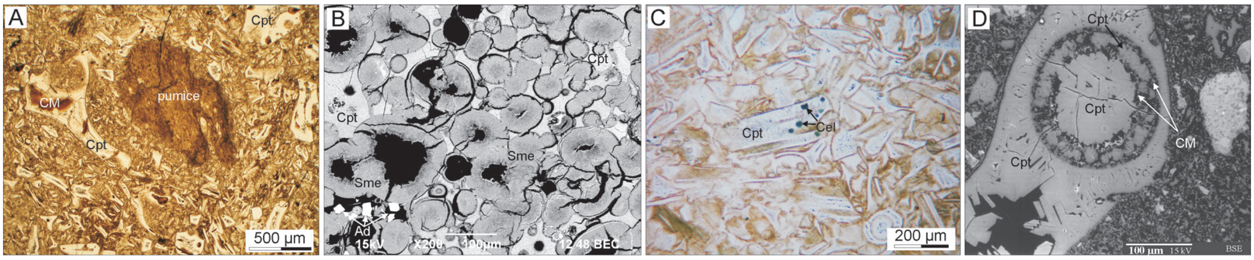

Fig. 1. Microphotographs (A, C, plane-polarized light) and SEM images (B, D) of altered pyroclastics from E. Rhodopes: *1A*, zeolitized shards and argillized pumice in zeolitized acid tuff (Sheinovets caldera); *1B*, smectite fills in pumice bubbles, clinoptilolite replaces bubble walls (Propast-Dobrovolets bentonite deposit, Kardzhali); *1C*, zeolitized shards, the largest contain celadonite grains (Beli Plast deposit); *1D*, zonal arrangement of clinoptilolite and clays in a shard (Plazishte village)
CM, clay minerals; Cpt, clinoptilolite; Ad, adularia; Sme, smectite; Cel, celadonite

no zeolite formation could even initiate. Such pumice fragments have low V/S and the larger is the pumice the lower its V/S becomes. This explains why the larger pumice fragments tend to host only or enriched in clays secondary association even when the whole rock and smaller pumice fragments are zeolitized (Fig. 1A). Rarely, the bubble walls are thicker and, respectively, V/S gets relatively higher. If such pumice fragments are present in zeolitized acid rocks they are zeolitized too. Curiously, in bentonite (even when resulting from alteration of intermediate in composition magma) these pumice fragments also tend to be zeolitized while clays remain restricted in the bubbles only (Fig. 1B).

3. High values of V/S of volcanic glass particles (coarser shards and perlitic clasts) strongly favor zeolite formation (Fig. 1). It is not accidental that all zeolite deposits in Eastern Rhodopes are hosted by enriched in ash shards pyroclastic varieties. But when V/S is very high (large and relatively isometric particles) other phases also appear together or after zeolite formation. In the Eastern Rhodopes these minerals are mainly bright green Fe-rich phyllosilicates occurring in the central parts of the zeolitized shards and giving nice, but sometimes undesired, greenish color of the rocks (Fig. 1C). Rarely, single glass particle replacement process can produce zonal patterns parallel to outer clast surface (Fig. 1D). Therefore, the alteration of glass particles having high V/S is not only a pseudomorphic process but it also could be an example of small-scale closed-system process, fully controlled by glass composition.

In reality, sorting defines which of these trends in glass alteration will prevail. In poorly sorted pyroclastic deposits (commonly flow in origin), composed by different clasts embedded in finer-grained matrix, all the described alteration scenarios can be observed together (Fig. 1). In well sorted varieties (most often fall in origin) they can even lead to formation of different mineral occurrences (zeolite, bentonite, and feldspar) that can be closely associated, as it is in the area of Eastern Rhodopes. But sorting is mainly related to modes of tephra dispersal. They in turns depend on eruption characteristics and even on meteorological condition during eruptions. Therefore, the alteration of each single volcaniclastic section results from complex and unique interaction of many volcanic and environmental agents. And V/S of volcanic glass particles is just one of the parameters that should be considered but it could be very helpful in revealing of existed mysteries in distribution of the glass-replacing products.

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