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## ZEOLITIZATION OF BASALTIC TUFF FROM THE GRACZE QUARRY

### INTRODUCTION

Determination of products and conditions of alteration of basaltic tuff from the Gracze quarry (the Opole Silesia) was the aim of the study. The area is situated in the easternmost part of Central European Volcanic Province (CEVP). The occurrence of basalts is related to the Odra fault zone (Birkenmajer 1974). Volcanic rocks from the main Gracze quarry date to the Oligocene/Miocene (Birkenmajer and Pécskay (2001).

According to Kapuściński and Probierz (1999), the tuff is composed of pyroxene group minerals – augite and diopside (present in all studied samples), magnetite, nepheline, antigorite and clay minerals (illite and montmorillonite). Chabasite series of zeolites (phillipsite, chabasite, analcime) is present. Calcite, iddingsite, Fe-oxides, serpentine and zeolites replace primary olivine. Kapuściński and Probierz (1999) noted that – dark red tuff is more altered than gray and green ones.

### SAMPLING AND ANALYTICAL METHODS

Samples collected in the Gracze quarry from different locations and exploitation levels, represent tuff from the contact with marls (two samples) and tuff emplaced between lava flows. Fine-grain gray tuff, dark red tuff, coarse-grain gray tuff and green breccia-like tuff (with fragments of sedimentary rocks and lapilli), which forms a thin layer on the contact with marls were studied.

Scanning electron microscopy with energy dispersive spectrometry, X-ray diffractometry and optical microscopy were used during investigations.

### RESULTS

The tuff is composed of pyroxene (augite – diopside), nepheline and oxide minerals (magnetite and minor amount of chromite, and probably anatase and Mg, Fe, Al spinel), calcite, serpentine and smectite. Zeolites represent two groups: natrolite type (NAT according to International Zeolite Association classification) noted in one sample and phillipsite type zeolites (PHI according to IZA classification) present in other samples. Chemical composition of zeolite minerals is strongly variable, especially in the content of Fe, K, Mg. Zeolite crystals are present on the pyroxenes and calcite. Halite occasionally overgrows zeolite crystals. NAT phases are present close to basalt/marls contact and PHI dominates in tuff emplaced by lava flows.

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Morphology of zeolite crystals is variable: euhedral prismatic crystals often are overgrown by fibrous branchy zeolite (fig. 1). Both natrolite and phillipsite occur in prismatic (older) and fibrous branchy (younger) forms.

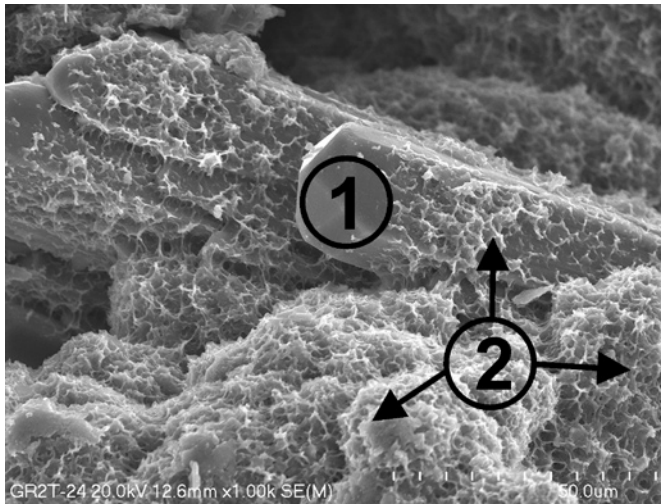


Fig. 1. Euhedral (1) and fibrous branchy form (2) of zeolites.

#### DISCUSSION OF RESULTS AND CONCLUSIONS

Primary (magmatic) components of tuff (pyroxene, nepheline and olivine) are partly transformed into secondary minerals (calcite, Fe oxides and zeolites). Development of zeolites is widespread and voluminosly very significant (up to 40%).

Formation of NAT and PHI phases is related probably more to temperature of crystallization then to availability of Na and Ca. Na zeolites growth (NAT group) at the contact marls/tuffs is probably related to low temperature and relatively high pH conditions. Wirsching (1979, 1981) synthesised NAT phase at  $\sim 150^{\circ}\text{C}$  and pH  $\sim 12.5$ . NAT phase crystallization may be connected with rapid cooling of tuff (after deposition) by fluids from marls. Supply of Na ions was probably related to nepheline decomposition.

It is possible that PHI zeolites grow at higher temperature. Experimental data suggest the temperature range of  $150 - 250^{\circ}\text{C}$  and pH 12-13 (Kawano, Tomita 1997). However, low temperature crystallization of phillipsite (sea floor environment) is also possible (Lee, Lee 1998; Ibrahim, Hall 1996). PHI zeolites could also replace older NAT zeolites during re-heating of tuff related to subsequent stages of volcanic activity. Replacement of Na-zeolites by Ca-zeolites related to increase of temperature was suggested by Thugutt (1899).

It can be supposed that growth of unusual fibrous branchy forms of zeolites was related to the presence of specific template (conf. Collinson 2002; Griffiths, Hemsley 2002) probably of microbial (bacterial?) origin. The role of organic template was point-

ed out by Nesterova et al. (2003) in formation of biomimetic nanocrystalline FeOOH characterised by morphology similar to that of zeolites from studied tuffs.

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