Zeolitization of a phonolitic pyroclastic ash flow by ground water

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ABSTRACT: The complex mineralogical zonation of the Nettetal zeolite deposit, Laach volcanic area, Germany, can be considered to be the result of zeolitization of phonolitic glass by temporally changing ground-water levels. Judging from field and experimental data, formation of chabazite, phillipsite, analcime and K-feldspar probably took place in the fringe water zone above varying paleo-ground-water tables. Small-scale mineralogical differences between matrix and pumice clasts are the result of differences in grain size between the precursor glass and the first authigenic mineral formed, chabazite, and hence their different reactivity.

1 INTRODUCTION

The economically most important type of zeolite deposits usually form by alteration of glassy volcanic material in a sedimentary environment (Hay 1977). Two major settings of the hydrologic system in this environment can be distinguished: 1) formation of zeolites in the closed system of saline, alkaline lakes, and 2) zeolitization by the action of ground water in open hydrologic systems. One of the most prominent occurrences of the second type in Europe is the famous Neapolitan Yellow Tuff. The trachytic glass of these deposits is altered mainly to phillipsite and chabazite, but a pronounced mineralogical zonation is not reported (Gennaro et al. 1990).

In contrast to these, the Nettetal zeolite deposit, also of the second type, in the Laach volcanic area, Germany, is mineralogically highly diverse. A field and experimental approach was chosen to shed light on its origin and to obtain insight into the formation of zeolite deposits in open hydrologic systems in general.

2 GEOLOGY AND MINERALOGY

The ca. 11,000 year old Laach volcanic eruption produced about 5 km^3 of phonolitic material, exclusively as pyroclastics. In addition to fallout pumice deposits, two major pyroclastic ash flows were deposited, and one of these is partly zeolitized. The zeolitized flow is situated ca. 5 km SE of the volcanic vent, extends subparallel to the Nettetal and has a thickness of up to 35 m; ash flows with a thickness greater than 10 m cover an area of ca. 8 km^2 (Bogaard & Schmincke 1984).

The Nettetal ash flow is composed predominantly of fine-grained, phonolitic glass shards and contains clasts of phonolitic pumice (up to 10 cm in diameter), basalt, schist, and quartz pebbles, as well as igneous minerals, such as sanidine, pyroxene, hornblende, biotite, and hauyne. Jandausch (1980) distinguished 15 different individual flows, which were deposited within a few days. The composition of the glassy components, either shards or pumice clasts, is identical within the whole ash flow and resembles that of the under- and overlying fallout pumice deposits: SiO_2 58.9, TiO_2 0.18, Al_2O_3 21.7, Fe_2O_3 2.2, MnO 0.31, MgO 0.15, CaO 0.94, Na_2O 9.3, K_2O 6.3 wt% (normalized to 100 wt% on a volatile-free basis, SEM-EDX measurement).

The glassy components of the ash are partly or totally zeolitized in three distinct layers (A, B, C, Fig. 1). These horizontal layers can be observed at a nearly constant level in an area of at least one km^2 in the "Trass" pit Meurin. Newly formed minerals are chabazite, phillipsite, and analcime, as well as K-feldspar. The succession of mineral formation determined from textural observations is chabazite → phillipsite/analcime → K-feldspar. Zeolitization leads to a significant increase of compressive strength of the otherwise very friable material. The most interesting features of the deposit are the intercalation of zeolitized layers with fresh, totally unaltered ash layers and the different alteration of fine-grained matrix and pumice clasts, despite similar chemistry of the precursor glass (Fig. 1).
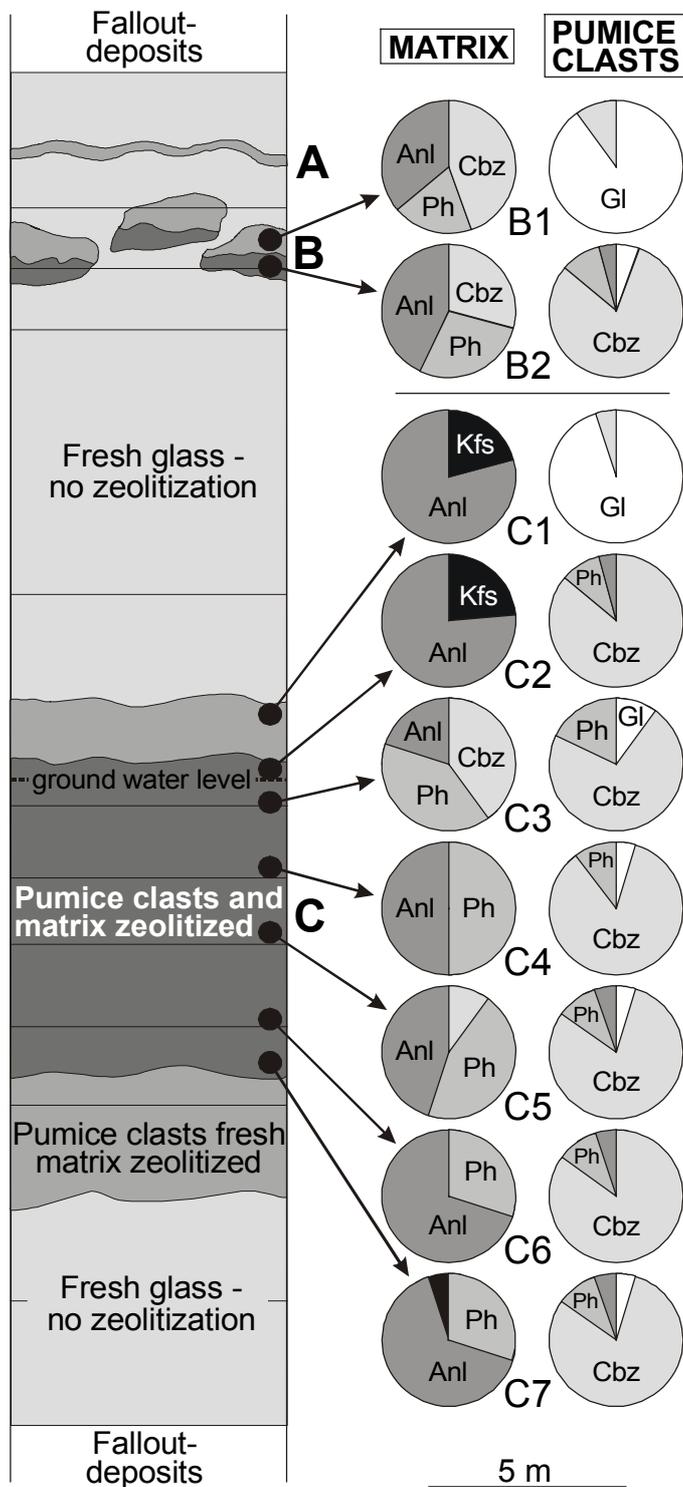
Figure 1. Simplified cross section through the partly zeolitized phonolitic ash flow of the Nettetal as exposed in the "Trass" pit Meurin. Gl = glass, Cbz = chabazite, Ph = phillipsite, Anl = analcime, Kfs = K-feldspar. Mineral content was determined semiquantitatively with XRD and SEM images on polished sections. Cross section below ground-water level was derived from core drillings (Jandausch 1980).

The grain size of newly formed zeolites in the matrix of all zones is 5-15 µm, whereas K-feldspar reaches only 3 µm. Chabazite in the pumice clasts is generally much larger, with phacolitic aggregates usually 30-50 µm in diameter.

The degree of zeolitization of pumice clasts decreases toward the contacts with the fresh ash over a
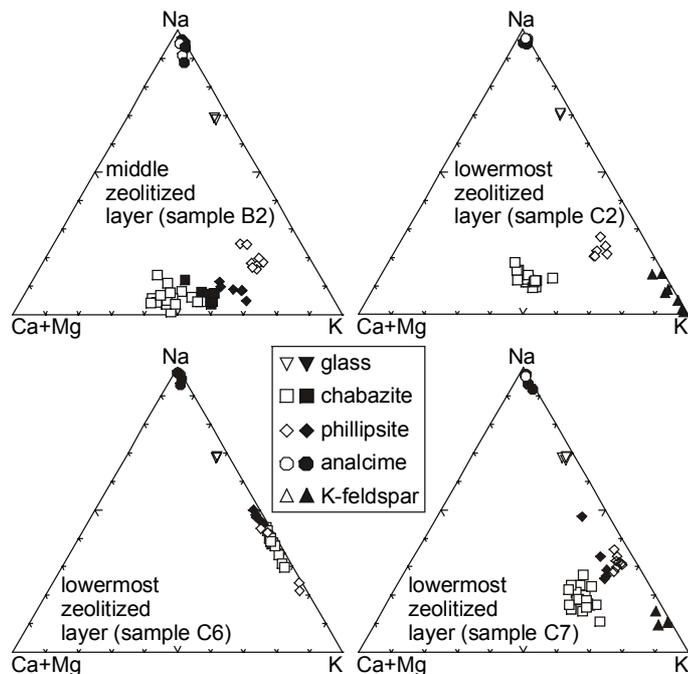

Figure 2. Chemical composition of glass, zeolites and K-feldspar within the middle and lowermost zeolitized layer. Open symbols: pumice clasts; filled symbols: matrix. The analyses were obtained with SEM-EDX on polished sections.

distance of 0.5-2 m (Fig. 1), whereas the boundary between fresh and zeolitized matrix is relatively sharp within 1-2 cm. The first three cm of the matrix at the top of the uppermost zeolitized layer (A) consist predominantly of chabazite, whereas the remaining part has the same mineralogical composition as the matrix of the middle layer (B).

No evidence of leached glass surfaces was observed. For example, neither surfaces of glass shards in unaltered zones between zeolitized layers nor small glass relics within nearly totally chabazitized pumice clasts show any sign of Na-loss.

The molar Si/Al ratio of zeolites (2.3-2.7) is close to that of the glass (Si/Al = 2.3) or slightly higher throughout the deposit. The content of exchangeable cations, however, differs in most cases from that of the glass (Fig. 2). Chabazite above the ground-water table is invariably Ca,K-rich, phillipsite is K-rich and analcime has a composition near the Na-end-member throughout the deposit. The composition of chabazite below the present ground-water table is highly variable, ranging from Ca-rich to very Ca-poor (Fig. 2).

The zeolitized parts of the Nettetal ash flow are mined as a pozzolanic additive ("Rheinischer Trass").

3 EXPERIMENTAL SETUP

Experimental zeolitization of phonolitic glass was carried out in unstirred 70 ml Teflon-coated stainless-steel vessels. Starting material was pre-

pared from the overlying fallout pumice deposit. The glass from the fallout pumice deposit has been proven to have the same chemical composition as the glass in the pyroclastic flow.

Experiments can be divided into two major groups. The first group was designed to investigate the influence of solution chemistry and temperature with a given solid/liquid ratio and grain size (Fig. 3A,B). Samples of 0.5 g of ground pumice (<63 μm) were reacted with 25 ml solution (0.01 m NaOH, 0.005 m NaOH + 0.005 m NaCl, 0.005 m NaOH + 0.005 m KOH, distilled water) for eight to 400 days at 100, 150 and 200° C. Very dilute solutions were used in order to simulate ground-water compositions as closely as possible.

The second group of experiments was designed to explore reaction progress with different solid/liquid ratios and different grain sizes of starting material at otherwise constant conditions (Fig. 3C,D). Samples of 0.5, 1.0 and 2.0 g of ground pumice (<63 μm), as well as samples of 2.0 g pumice with a grain size of 0.2-1 mm and single pumice fragments of ca. 2 g in weight were reacted with 25 ml distilled water at 200° C for eight to 80 days.

Experiments were also carried out to simulate zeolitization in a slightly open system at 200° C with distilled water (Fig. 3E). For this purpose, the solution was replaced after 8 days by fresh distilled water.

The possibility of direct formation of Ca,K-rich chabazite was investigated with experiments using 0.005 m Ca(OH)$_2$ solution at 200° C (Fig. 3F).

Cation exchange experiments were performed on the synthetic Na,K-rich chabazite with the tap water of Graz (90 ppm Ca^{2+}) in batch mode.

Reaction products from experiments were semi-quantitatively determined with XRD.

4 EXPERIMENTAL RESULTS

Chabazite, phillipsite, analcime and K-feldspar formed in the dilute solutions independent of Na,K concentration, Na/K ratio and (OH)$^-$/Cl$^-$ ratio in the temperature range of 100°-200° C. Generally, the succession of experimental mineral formation, which is independent of solution composition, grain size, and temperature, was chabazite/phillipsite → phillipsite + analcime → analcime + K-feldspar (Fig. 3A,B). However, chabazite and phillipsite re-present metastable transition phases with respect to analcime and K-feldspar at all investigated experi-mental conditions. Increasing temperature and alkali concentration of solutions speeded up the alteration process, as well as the formation of analcime and K-feldspar.

A high solid/liquid ratio speeded up the beginning of zeolite formation, but slowed down the con-version of phillipsite to analcime and K-feldspar (Fig. 3C,D). Charges with an increased grain size of 0.2-0.8 mm did not show a slower reaction rate than charges with starting material of <63 μm. Experi-mental zeolitization of 2 g pumice fragments began at their surfaces, with the same reaction sequence as for ground material. The 2 g pumice fragments were totally transformed to phillipsite and analcime within
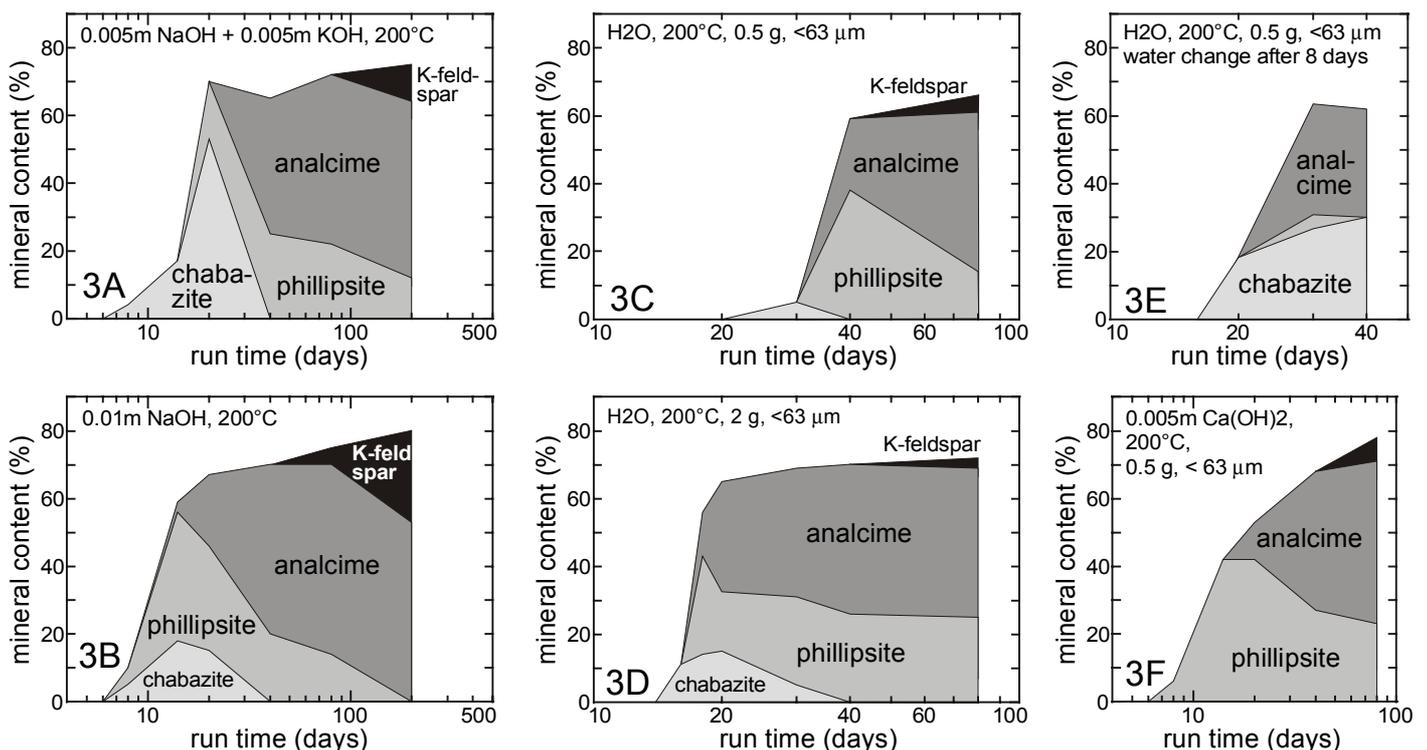

Figure 3. Mineral content versus time for exemplary experimental run conditions. For further explanation see text.

80 days, but only subordinate amounts of chabazite formed as a transition phase.

The formation of large amounts of chabazite, as observed in pumice clasts, is favored by low temperatures (100° C) or by an increase of the K/Na ratio in the system. The increase of the K/Na ratio can be achieved either by addition of K by the KOH + NaOH bearing solution (Fig. 3B) or by removing some Na from the system in the experiments simulating a slightly open system (Fig. 3E). With the 0.005 m $Ca(OH)_2$ solution, chabazite did not appear as experimental product, but large amounts of phillipsite formed instead (Fig. 3F).

The cation exchange experiments on synthetic, Na,K-rich chabazite revealed that the Na of these chabazites is exchangeable at a faster rate than K, thereby approaching the K,Ca-rich composition of the natural chabazites. Nearly complete exchange of Na by Ca was achieved within five days with the tap water of Graz at ca. 20° C (5 x 1 l water, 0.1 g chabazite). The K-content decreased only slightly during this kind of exchange experiment.

5 DISCUSSION AND CONCLUSIONS

One of the most striking features of the Nettetal zeolite deposit is the occurrence of zeolitization in three distinct layers. Assuming zeolitization by ground water, the zeolitized parts of the deposit could represent former capillary fringes immediately above the ground-water table. Support for this hypothesis comes from the fact that the lowermost part of the flow, which has been in contact with ground water for 11,000 years, is free of alteration. In the saturated but stagnant fringe water zone, a fluid composition suitable for quick zeolitization may build up very rapidly because of the high solid/liquid ratio, which also speeds up zeolite formation in experiments. In lower zones of the ground-water column where flow velocity is high, the system is always flushed with fresh water preventing favorable conditions for zeolite formation. The zeolitized zones can, therefore, be considered as paleo-ground-water tables. The succession of the levels of active zeolitization and also of the level of the capillary fringe is A → B → lowermost part of C → more or less continuously propagating to the uppermost part of C. The sequence of changes in the ground-water table can be correlated with an immediate rise in the receiving river level caused by deposition of the pyroclastic material, followed by stepwise erosion of this soft sediments and later sedimentation in the receiving river, leading to a rise of the ground-water table to the present level. The different stages of zeolitization in different layers within the deposit possibly indicate that the ground-water table remained at distinct levels for varying times, as-suming the same temperature and composition of the solution. The zone immediately above the present ground-water level (C1,2) represents the most advanced stage of alteration within the deposit.

The exclusively chabazite-dominated, altered pumice clasts record the first stage of zeolitization at retarding conditions throughout the deposit. This retardation may be caused by the slightly lower reaction velocity of the clasts compared to the fine-grained matrix. Experimentally, large amounts of chabazite form at high temperatures only with an increase in the K/Na-ratio. But at a low temperature (100° C), large amounts of chabazite occur as a transition phase even with a decrease of the K/Na-ratio. Consequently, the low temperature conditions of natural zeolitization do not require element transport to form large amounts of chabazite. The large grain size of the chabazites in pumice clasts makes them also less susceptible to further reaction. This is in contrast to the fine-grained chabazites in the matrix which react quickly to form phillipsite, analcime and K-feldspar. The alteration may start also in the matrix with massive chabazite formation, judging from the occurrence of nearly pure chabazite in the very uppermost zeolitized matrix.

A direct formation of Ca,K-rich chabazite seems unlikely in the light of the experimental results, but is easily established by cation exchange. The source of Ca in the natural chabazites is not clear. Temporally, the exchange must postdate the formation of analcime otherwise this Na-dominated mineral could not form.

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