ZEOLITES IN ALKALINE ROCKS OF THE KAISERSTUHL VOLCANIC COMPLEX, SW GERMANY – NEW MICROPROBE INVESTIGATION AND THE RELATIONSHIP OF ZEOLITE MINERALOGY TO THE HOST ROCK

TOBIAS WEISENBERGER*1 & SIMON SPÜRGIN2

(7 figures, 3 tables and 2 plates)

1 Mineralogisch-Geochemisches Institut, Albert-Ludwigs-Universität Freiburg, Albertstr. 23b, 79104 Freiburg, E-mail: tobias.weisenberger@minpet.uni-freiburg.de, * corresponding author
2 Hans G. Hauri Mineralstoffwerk, Bergstr. 114, 79268 Bötzingen, E-mail: spuergin@gmx.de

ABSTRACT. Low-grade zeolite facies mineralisation in the Kaiserstuhl volcanic complex results from alteration of alkaline volcanic rocks. Nine different zeolite species are known from the volcanic complex: analcime, chabazite-Ca, faujasite-Na, faujasite-Mg, natrolite, offretite, phillipsite-K, phillipsite-Ca and thomsonite. Their occurrence as well as their chemical composition depends on the chemical composition of the host rock, local hydrological features and porosity of the rock. New chemical analyses are presented, in order to give chemical compositions of Kaiserstuhl zeolite species, which were never analysed before, e.g. thomsonite from the Strümpfekopf-Totenkopf area, as well as a re-evaluation of zeolite species from classic localities. New microprobe analyses of barrel-shaped offretite from the Limberg area clearly show that the postulated epitaxial intergrowth of offretite and erionite does not occur.

Textural and chemical observations require that the elements for zeolite formation derived from the hydration and palagonitisation of basaltic glass, and alteration of primary phases (e.g. sodalite, leucite). The zeolite species depends on the primary mineralogy and chemical composition of the host rock: Analcime occurs as pseudomorphs after leucite, which is a rock forming mineral in most lavas and tuffs of tephritic composition, and natrolite is derived from hydrothermal alteration of sodalite-group minerals in phonolitic intrusions.

KEYWORDS: Kaiserstuhl, zeolite, faujasite, offretite, phillipsite, chabazite, thomsonite, natrolite

RESUME. Les zéolites dans les roches alcalines du complexe volcanique de Kaiserstuhl, Sud-Ouest Allemagne – Nouvelles données minéralogiques et géochimiques et leur relation aux roches hôtes

La minéralisation dans le faciès zéolites du complexe volcanique de Kaiserstuhl résulte de l’altération de roches volcaniques alcalines. Neuf espèces de zéolites sont communes dans le complexe volcanique: analcime, chabasite-Ca, faujasite-Na, faujasite-Mg, natrolite, offretite, phillipsite-K, phillipsite-Ca et thomsonite. Leur présence ainsi que leur composition chimique dépendent de la composition de la roche hôte, des caractéristiques hydrologiques locales et de la porosité de la roche. De nouvelles analyses sont présentées (e.g. thomsonite de la région de Strümpekofkopf-Totenkopf) ainsi qu’une réévaluation des différentes espèces de zéolites.

Les observations texturales et chimiques suggèrent que les éléments nécessaires à la formation des zéolites dérivent de l’hydratation et de la palagonitisation de verre basaltique, ainsi que de l’altération de phases primaires (e.g. sodalite, leucite). La présence des différentes espèces de zéolites dépend de la minéralogie et de la composition de la roche hôte: l’analcime remplace la leucite dans la plupart des laves et tufs tephritiques et la natrolite est un minéral d’altération des minéraux du groupe de la sodalite dans les intrusions phonolitiques. De nouvelles données géochimiques des offretites de Limberg montrent que l’enchevêtrement épitaxial d’offretite et d’erionite n’est pas présent.

MOTS-CLES. Kaiserstuhl, zéolite, faujasite, offretite, phillipsite, chabazite, thomsonite, natrolite

ZUSAMMENFASSUNG. Zeolithe in Alkaligesteinen des Kaiserstuhls, SW Deutschland – Neue chemische Untersuchungen und die Beziehung der Zeolithmineralogie zu den Umgebungsgesteinen.


Neue geochemische Analysen werden präsentiert, mit dem Hintergrund der Neu evaluierung der verschiedenen Zeolithspezies klassischer Lokalitäten und der erstmaligen chemischen Beschreibung von Thomsonit aus dem Gebiet Strumpfekofkopf-Totenkopf. Für die tonnenförmigen Offretitkrystalle vom Limberg zeigen die hier präsentierten Ergebnisse
1. Introduction

Zeolites are among the most common products of chemical interaction between groundwater and the earth’s crust during diagenesis and low-grade metamorphism. Natural zeolites commonly form by reactions of aqueous solutions with volcanic rocks, and volcanogenic sediments. Zeolite minerals occur in low temperature (<250°C), low pressure (<200 MPa), water saturated or fluid rich environments. The copious amounts of silica, aluminium, and alkali and alkaline-earth cations necessary for the formation of most zeolites are commonly derived from dissolution of volcanic glass and from the alteration of feldspar and feldspathoids. The zeolite mineralogy of low-grade volcanic rocks is a sensitive indicator for the thermobarometric evolution of oceanic and continental crust (e.g. Neuhoff et al., 2000; Weisenberger & Selbekk, 2008).

Since the early days of its geological and mineralogical exploration, the Kaiserstuhl volcanic complex (KVC) is very famous for its wealth in zeolites. Gmelin & Hessel (1825) first noticed phillipsite from the Limberg-Lützelberg Complex near Sasbach, where this mineral occurs in a highly vesiculated volcanic rock. Further on Eisenlohr (1829) described the zeolites chabazite and stilbite (during that time the name stilbite was used for phillipsite) from the KVC. Only a few years later Blum (1837) mentioned “harmotome” (phillipsite), which is associated with “apophyllite”. By analysing this mineral mistaken for “apophyllite”, Damour (1842) discovered a new member of the zeolite family which was named faujasite.

Julius Schill (1853/54a, 1853/54b) observed on a sample from the Eichberg leucitophyre, that leucite, which was found to occur in most of the Kaiserstuhl volcanic rocks (namely in those of tephritic composition), is replaced by analcime. Fibrous natrolite from the Fohberg phonolite was already described by Knop (1892). Nowadays this rock is known for its excellent qualities in concrete industry, which are directly related to the high density and low permeability.

Figure 1: Simplified geological map. A Geology of the Upper Rhine Graben area. B = Basel; F = Frankfurt; FR = Freiburg; H = Heidelberg; HVF = Hegau volcanic field; K = Karlsruhe; S = Strasbourg; KVC = Kaiserstuhl volcanic complex; UVF = Urach volcanic field. B The Kaiserstuhl Volcanic Complex (after Wimmenauer, 1962 and Sigmund, 1996). C Outline of Germany.

SCHLÜSSELWÖRTER. Kaiserstuhl, Zeolith, Faujasit, Offretit, Phillipisit, Chabasit, Thomsonit, Natrolith
content of zeolites (Hauri, 2006). Rinaldi et al. (1975) presented a study including microprobe analyses of zeolites from the Kaiserstuhl area, which are unique until now. Additionally they first described the appearance of offretite in the KVC. By accident Schelckten (1990) found, for the first time in the KVC, thomsonite in a highly vesiculated tephrite at the Strümpfekopf-Totenkopf locality.

In this study we present an overview of the spatial distribution of zeolite localities in the KVC. A chemical investigation of the Kaiserstuhl zeolite species – for some of them the first chemical survey at all – is presented in order to demonstrate variabilities between different localities, which can be expressed as function of the chemistry of different distinctive types of alkaline host rocks, i.e. phonolite, basanite, tephrite and leucitite. An approach is done to explain the zeolite occurrence in the KVC.

2. Geological setting

The Miocene Kaiserstuhl Volcanic Complex (KVC) is located in the central-southern segment of the Upper Rhine Graben, SW Germany (Fig. 1A), which is part of the European Cenozoic Rift System. The KVC is the only larger volcanic edifice in the Upper Rhine Graben, where alkaline and carbonatitic rocks erupted along deep-rooting faults in a disrupted crustal segment (Bourgeois et al., 2007) at the intersection of two prominent fault zones (Hüttner, 1996; Schreiner, 1996).

Numerous highly silica-undersaturated alkaline dykes and dikes of smaller volume than the KVC are found locally in the graben and along its shoulders, i.e. in the crystalline complexes of the Black Forest, Vosges and Odins Forest, as well as in adjacent Mesozoic – early Cenozoic sediment blocks. They belong to the Cenozoic volcanic province of Central Europe, which formed in the course of the Alpine continent-continent collision (cf. Wedepohl et al., 1994). These graben volcanics and subvolcanics, olivine-melilitites and olivine-nephelinites, are the unfractored products of low-percentage partial mantle melts (Keller, 2001). Geochemical data prove magmatism in the area of the present Upper Rhine Graben since the Campanian (81 Ma, Lippolt et al., 1974).

2.1. The Kaiserstuhl Volcanic Complex (KVC)

The KVC, an eroded volcanic complex with a morphologically height of 270 m compared to the surrounding alluvial plain, covers an area of 16x12 km northwest of the city of Freiburg (Fig. 1A). A N-S oriented prevolcanic horst structure in the eastern Kaiserstuhl, mainly comprising Paleogene marls, sandstones and limestones, is partly overlain by effusive and explosive volcanics, and penetrated by subvolcanic intrusions (Fig. 1B). The surface rocks of the KVC erupted from various volcanic centres and formed a complex stratocone or a volcanic field (cf. Keller, 2001). Eccentric vents are found in the SW (Münsterberg/Breisach) and NW (Limberg/Sasbach) of the Kaiserstuhl.

According to their outcrop and petrographical characteristics, the volcanic rocks belong to different groups: A) Lava flows, generally porphyric with vitreous matrix; predominantly tephrites. B) Pyroclastic rocks, e.g. ash-/lapillituffs, agglomerates; mainly tephrites, minor phonolite and rare carbonatite (Keller, 1981). C) Porphyric dyke rocks with essexitic, phonolitic or carbonatitic affinity, also intermediate compositions and highly evolved rocks; most prominent in the inner KVC and radially oriented towards the centre. D) Subvolcanic intrusives of larger dimensions, fine- to medium grained; especially essexite, phonolite and carbonatite. E) Volcanic breccias, occurring both at surface intercalated in pyroclastics, and as intrusion-related diatreme breccias of subvolcanic niveau.

The magmatic rocks of the KVC, an alkaline rock-carbonatite complex, are supposed to be derived from two different parental magmas (Keller, 1984, 2001; Schleicher & Keller, 1991). A primary olivine nephelinite magma, exposed at the Limberg-Lützelberg Complex near Sasbach, resembles those found at several places in the Upper Rhine Graben. Its derivates are slightly fractionated basanites (“limburgites”, see 5.1.), melilite-bearing rocks (“bergalite”) and carbonatites.

The second primary magma is a hypothetical, initially fractionated K-basanite, which is influenced by crustal contamination. It is not exposed in the KVC. Fractionation of this second source material led to two petrographically distinctive rock “families”. The essexitic family (Wimmenauer, 1957, 1959a; Kim, 1985) comprises leucite- and olivine-tephrites and phonolitic tephrites, which form the major part of the KVC. Continued fractionation is responsible for the formation of the phonolitic family (Wimmenauer, 1962), e.g. phonolites, syenites and evolved leucocratic dykes. The alternating deposition of tephritic and phonolitic tuff beds indicates simultaneous activity of these magma systems (Wimmenauer, 1962).

Volcanism in the KVC lasted from 19.0-15.3 Ma. Activity started with the eruption of olivine nephelinites (19.0 ± 1.6 Ma, whole-rock K-Ar age; Baranyi et al., 1976), followed by the deposition of mainly tephritic rocks (18.2 – 16.5 Ma) and the emplacement of various subvolcanic intrusions and dykes during the volcanic main phase between 18.4 and 15.3 Ma (compiled in Wimmenauer, 2003). Some of the youngest surface volcanics forming the parasitic Limberg-Lützelberg Complex were deposited at 16.2 ± 0.2 Ma (Kraml et al., 2006).

2.2. Field description

Our zeolite samples come from five localities (Fig. 1B), where specimens of different rock types in different appearance, containing varying zeolite paragenesis, were sampled: 1) a vesicular limburgite lava from the Limberg near Sasbach, 2) a vesicular tephritic lava from Eichert near Sasbach, 3) a tephritic rock from the Strümpfekopf-Totenkopf area 4) fissures in the large intrusive phonolite
of the Fohberg near Bötzingen, and 5) a leucitophyre dyke from Strümpfekopf near Bickensohl.

2.2.1. Limberg quarry

The Limberg belongs to the Limberg-Lützelberg-Complex, a parasitic volcano in the NW corner of the KVC (Fig. 1B). It is composed of a succession of lavas (named \( \lambda_1-\lambda_5 \), Soellner, 1914) and agglomerates of tephrite, nephelinite and basanite (“limburgite”) and intercalated tuffs (t1-t7) of tephritic and phonolitic affiliation (Lorent, 1933; Wimmenauer, 1957, 2003), which probably erupted from a strombolian-type vent on the southern Limberg. The related lava flows are the most voluminous ones known in the KVC; the mantle-xenolith bearing olivine nephelinite flow forming the Lützelberg reaches a length of 1.4 km and a maximum thickness of 50 m. Synvolcanic extensional deformation formed the 150 m wide, NW-SE striking Limberg Graben (Wimmenauer, 2003), which is filled with Burdigalian (Tobien, 1958) marls and sandstones of the Limberg Formation (Jörg, 1951). These sediments are overlain by the younger tuff t7 (16.2 ± 0.2 Ma, Kraml et al., 2006) and the lava flow units \( \lambda_4 \) and \( \lambda_5 \).

Our limburgite was sampled in the old quarry I, NE of the Limberg Graben. The quarry wall consists of two superimposed, clearly distinguishable lava flow units (\( \lambda_4 \) and \( \lambda_5 \)), which are separated by a yellowish band of tuffite (t7) (Pl. 1). The limburgite flows are identical in their petrographic and geochemical characteristics. They consist of a massive, partly crystallised main zone, which becomes increasingly vesicular towards the more vitreous, scoriaceous top. Based on this transition, several successive lava flows are distinguishable in flow unit \( \lambda_5 \), which shows a repeated change of massive and porous zones in vertical direction (Lorent, 1933).

Small vugs in the sampled lava flows are normally spheroidal, whereas larger ones, reaching a size of 10 cm, are of irregular shape. The size of pores increases with height in each lava flow.

2.2.2. Eichert quarry and Strümpfekopf-Totenkopf area

Both the old quarry on the NW flank of Eichert mountain near Sasbach and the area between the tops of Strümpfekopf and Totenkopf in the central Kaisersuhl are located in the tephrites, which form a complex stratovolcano of alternating lava flows and pyroclastic deposits (Fig. 1B) (Wimmenauer, 1957, 1959a). Samples were taken from a vesicular part of a phonolitic tephrite lava flow with typical phenocrysts of titanian augite (Eichert), and from a grey, porphyric tephrite of unclear affiliation (lava or pyroclastite) in the Strümpfekopf-Totenkopf area, where thomsonite occurs in round, regular vugs up to 20 mm in diameter.

2.2.3. Fohberg quarry

The ca. 600 x 450 m large Fohberg phonolite in the southeastern Kaisersuhl (Fig. 1B) is a shallow subvolcanic stock which intruded in Oligocene marls of the Pechelbronn Formation. Whole-rock K-Ar geochronology yields an age of 15.6 Ma (Lippolt et al., 1963). The main primary magmatic minerals are a sodalite-group mineral, sanidine, aegirine-augite, wollastonite and titanian andradite (“melanite”) (Wimmenauer, 1962; Albrecht, 1981). Fresh portions of the rock show a porphyric texture with phenocrysts (≤ 3 mm) of the mentioned minerals in a greenish-grey matrix. The phonolite stock is cut by a younger dyke of porphyric, black essesite (Pl. 2).

Alteration decomposed virtually all sodalite-group minerals to zeolites, which makes natrolite the major rock-forming mineral in the Fohberg phonolite (about 45 vol-%; Albrecht, 1981). Fibrous natrolite aggregates, and occasionally massive calcite, form pseudomorphs after the euhedral sodalite-group mineral and therefore hinder the exact identification of the precursor mineral. The mineralization of secondary phases is most substantial along joints and fissures, where massive portions of calcite, natrolite, or both, may be formed. The majority of these joints is the result of subsolidus post-magmatic cooling, whereas some are related to regional tectonics (Stober, 1955). Open fissures are commonly overgrown with euhedral needles or radial aggregates of natrolite, or calcite of variable shape (cf. Marzi, 1983). Rare members belonging to the fissure assemblage are reported by Wimmenauer (1959b), Beyer (1960) and Marzi (1983): hyalite/opal, apophyllite, chabazite, fluorspar, celestine, pectolite, strontianite, barite and clay minerals.

Active mining of the Fohberg phonolite in the village of Bötzingen permits accessibility to a large portion of the intrusive body, and continuously provides excellent natrolite specimen.

2.2.4. Strümpfekopf locality

A vertical dipping, NE-SW striking leucitophyre (phonolitic leucite) dyke is found in the vineyards of Strümpfekopf NE the village of Bickensohl (Fig. 1B). It cuts an intrusive essesite, whose age was determined to 16.3 Ma by Lippolt et al. (1963). After Spürgin et al. (2008) it contains abundant (25.5 vol-% of the bulk rock) leucite phenocrysts (0.2-10 mm) in a greenish-grey vitreous matrix (57.6 vol-%) (Fig. 2). Other phenocryst species are aegirine-augite, sanidine, titanian andradite and apatite. All leucite is completely transformed to fine-grained, pseudomorphic aggregates of analcime. As discussed by Spürgin et al. (2008), analcime formed as alteration product in the solidified rock.

The presence of analcime in rock-forming quantities, replacing primary magmatic leucite, is a common feature in many Kaisersuhl volcanics, i.e. in the leucite-tephrites. On the other hand, the presence of magmatic analcime in the KVC is not testified.

3. Analytical methods

X-ray diffraction (XRD) and electron microprobe (EMP) analyses were performed at the Mineralogical-Geochemical Institute, University of Freiburg, Germany. Quantitative EMP mineral analyses were done using a CAMECA SX 100 equipped with five WD spectrometers.
and one ED detector with an internal PAP-correction program (Pouchou & Pichior, 1991). Major and minor elements in zeolites were determined at 15 kV accelerating voltage and a defocused electron beam of 20 \( \mu \text{m} \) in diameter, with a current of 10 nA and a counting time of 20 s. In all cases Na and K were counted first to minimise loss during the measuring procedure. Since zeolites lose water when heated, the crystals were mounted in epoxy resin to minimise loss of water due to the electron bombardment. Natural and synthetic standards were used for calibration.

Identification of zeolites and other secondary minerals was obtained by a BRUKER AXS D8 Advance powder diffractometer (XRD) combined with DIFFRACplus v5.0 software for evaluation.

The morphology of mineral species was studied with a Zeiss DSM 960 scanning electron microscope (SEM) at the Institute of Crystallography, University of Freiburg. Before carbon-coating, the samples were carefully dried at room temperature in order to generate a high-vacuum in the sample chamber. Secondary electrons (SE) were detected using 20 kV, 16 nA.

4. Characterisation of zeolites

4.1. Spatial distribution of zeolite species in the Kaiserstuhl

Zeolites occur widespread in the volcanic rocks of the KVC (Table 1). Altogether nine different zeolite species are known to occur in the volcanic complex: analcime, chabazite-Ca, faujasite-Na, faujasite-Mg, natrolite, offretite, phillipsite-K, phillipsite-Ca and thomsonite.

The occurrence of different zeolite species and their frequency in the rock is not homogeneous, even in a single lithological unit. The spatial distribution of some species is directly controlled by local characteristics, whereas others are typical for a given rock type. It is conspicuous that analcime and phillipsite occur in most parts of the KVC, whereas chabazite, faujasite, natrolite, offretite and thomsonite occur only locally (e.g. Fohberg, Limberg).

![Figure 2: Thin section from the leucitophyre dyke at Strümpfekopf showing analcime as replacement product formed by the reaction: leucite + Na\(^{+}\) + H\(_2\)O = analcime + K\(^{+}\). The replacement reaction from leucite to analcime involves a 10% molar-volume increase, which produces the cracking around the analcime aggregate.](image)

<table>
<thead>
<tr>
<th>Locality</th>
<th>Zeolites</th>
<th>Host rock</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bergwald/Silberbrunnen</td>
<td>phillipsite, chabazite</td>
<td>tephrite</td>
<td>Fricke, 1971</td>
</tr>
<tr>
<td>Burrisboden/Oberbergen</td>
<td>phillipsite, chabazite</td>
<td>tephrite</td>
<td>Fricke, 1971</td>
</tr>
<tr>
<td>Burgberg/Burkheim</td>
<td>phillipsite, chabazite</td>
<td>tephrite</td>
<td>Fricke, 1971</td>
</tr>
<tr>
<td>Büchsenberg/Niederrotweil</td>
<td>phillipsite, chabazite</td>
<td>tephrite</td>
<td>Fricke, 1971</td>
</tr>
<tr>
<td>Eichert/Sasbach</td>
<td>chabazite</td>
<td>tephrite</td>
<td>Fricke, 1971; this study</td>
</tr>
<tr>
<td>Endhalden/Bötzingen</td>
<td>analcime, natrolite,</td>
<td>phonolite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>chabazite</td>
<td></td>
<td>Fricke, 1988</td>
</tr>
<tr>
<td>Föhrenberg/Ihringen</td>
<td>phillipsite, chabazite</td>
<td>tephrite</td>
<td>Fricke, 1971</td>
</tr>
<tr>
<td>Fohberg/Bötzingen(^a)</td>
<td>natrolite, chabazite,</td>
<td>phonolite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>mesolite</td>
<td></td>
<td>Fricke, 1971; Beyer, 1960;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Albrecht, 1981; Marzi, 1983;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fricke, 1988; this study</td>
</tr>
<tr>
<td>Horberg/Oberbergen</td>
<td>chabazite</td>
<td>tephrite</td>
<td>Fricke, 1971</td>
</tr>
<tr>
<td>Kirchberg/Niederrotweil</td>
<td>natrolite, chabazite</td>
<td>phonolite</td>
<td>Fricke, 1988</td>
</tr>
<tr>
<td>Liliental/Ihringen</td>
<td>phillipsite, chabazite</td>
<td>tephrite</td>
<td>Fricke, 1971; Lorent, 1933;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rinaldi et al., 1975;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hentschel, 1976; Betz, 2005;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>this study</td>
</tr>
<tr>
<td>Limberg/Sasbach</td>
<td>phillipsite, faujasite,</td>
<td>limburgite</td>
<td></td>
</tr>
<tr>
<td></td>
<td>offretite, chabazite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mondhalde/Oberbergen</td>
<td>phillipsite</td>
<td>mondhaldeite</td>
<td>Fricke, 1971</td>
</tr>
<tr>
<td>Neunlinden</td>
<td>phillipsite, chabazite</td>
<td>tephrite</td>
<td>Fricke, 1971</td>
</tr>
<tr>
<td>Nord/Oberbergen</td>
<td>chabazite</td>
<td>gauheit</td>
<td>Fricke, 1971</td>
</tr>
</tbody>
</table>
| Sauwasen/Ihringen         | phillipsite, chabazite    | tephrite  | Fricke, 1971; Spielberg/Oberbergen
| Spielberg/Oberbergen      | phillipsite               | tephrite  | Fricke, 1971                   |
| Strümpfekopf-Totenkopf\(^a\) | thomsonite             | tephrite  | Schelcken, 1990; this study    |
| Bickensohl                | analcime                  | leucitophyre| Spürgin et al., 2008;          |
| Strümpfekopf\(^b\)        |                           |           | this study                     |

\(^{a}\) thomsonite (Beyer, 1960), ferrierite and scolecite (Albrecht, 1981) are mentioned in the literature, but only based on poor chemical analyses and no sufficient structural analyses were presented to proof the occurrence of these zeolite species

\(^{b}\) the Strümpfekopf locality was chosen as example. Analcime occurs in most of the tepritic lavas as pseudomorphs after primary leucite.
The local distribution of different zeolite species is controlled by the chemical composition of the host rocks and local distinct hydrological regimes. It is additionally depending on the porosity of the host rock, which controls the ratio of fluid/rock interaction.

In the following we present descriptions of the zeolite appearance, occurrences, and their textural relations as well as new chemical data of each zeolite species.

4.2. Analcime

Analcime (Na$_{16}$[Al$_{16}$Si$_{32}$O$_{96}$] •16H$_2$O, Passagli & Sheppard, 2001) is the most widespread zeolite in the Kaiserstuhl area and usually occurs as a macroscopically rock-forming mineral phase replacing primary leucite phenocrysts (e.g. Kim, 1985; Spürgin et al., 2008) in most of the Kaiserstuhl rocks. The secondarily formed, fine-grained analcime aggregates show the typical leucite habit of deltoid-icositetrahedron with well developed {211} faces (Fig. 2).

The analcime pseudomorphs are milky white to grey apparently from cracking of crystals (Fig 2), which is caused by nearly 10% volume increase during the conversion of leucite to analcime (Putnis et al., 2007).

Geochemical analyses of analcime phenocrysts from the Strümpfekopf leucitophyre dyke in the centre of the KVC (Figs 1B and 2) are presented in Table 2. Analcime has very minor amounts of cations other than Na. Sodium is the main extra-framework cation with amounts up to 14.413 apfu and up to 0.740 apfu Ca.

4.3. Chabazite-Ca

Chabazite ([Ca$_{0.5}$NaK]$_4$[Al$_4$Si$_8$O$_{24}$] •12H$_2$O) appears, together with phillipsite, in numerous tephritic lavas and tuffs in the KVC. Additionally it occurs rarely within the Fohberg phonolitic intrusion (Fig. 1B; Pl. 2), associated with natrolite (Table 1).

Table 2: Representative zeolite analyses of the KVC

<table>
<thead>
<tr>
<th>Sample no:</th>
<th>AnalK</th>
<th>PCEK1</th>
<th>NBK1</th>
<th>FLK2</th>
<th>PCEK1</th>
<th>FLK3</th>
<th>TSK1</th>
<th>TSK1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot no:</td>
<td>2</td>
<td>1</td>
<td>7</td>
<td>9</td>
<td>14</td>
<td>18</td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td>Mineral:</td>
<td>Strümpfekopf</td>
<td>Eichert</td>
<td>Fohberg</td>
<td>Limberg</td>
<td>Eichert</td>
<td>Limberg</td>
<td>Strümpfekopf</td>
<td>Tetenkopf</td>
</tr>
<tr>
<td></td>
<td>wt.%</td>
<td>wt.%</td>
<td>wt.%</td>
<td>wt.%</td>
<td>wt.%</td>
<td>wt.%</td>
<td>wt.%</td>
<td>wt.%</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>53.74</td>
<td>57.19</td>
<td>47.89</td>
<td>52.99</td>
<td>51.02</td>
<td>55.54</td>
<td>53.96</td>
<td>38.35</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>23.14</td>
<td>18.57</td>
<td>26.77</td>
<td>19.36</td>
<td>20.30</td>
<td>19.76</td>
<td>20.68</td>
<td>18.0</td>
</tr>
<tr>
<td>FeO</td>
<td>0.23</td>
<td>0.004</td>
<td>0.030</td>
<td>0.028</td>
<td>0.037</td>
<td>0.067</td>
<td>0.000</td>
<td>0.023</td>
</tr>
<tr>
<td>MgO</td>
<td>0.00</td>
<td>1.59</td>
<td>0.00</td>
<td>2.57</td>
<td>0.03</td>
<td>0.42</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>CaO</td>
<td>0.55</td>
<td>6.44</td>
<td>0.02</td>
<td>3.69</td>
<td>6.36</td>
<td>4.51</td>
<td>8.90</td>
<td>12.82</td>
</tr>
<tr>
<td>SrO</td>
<td>0.06</td>
<td>0.65</td>
<td>0.00</td>
<td>1.34</td>
<td>0.10</td>
<td>0.95</td>
<td>0.00</td>
<td>0.84</td>
</tr>
<tr>
<td>BaO</td>
<td>0.00</td>
<td>0.00</td>
<td>0.06</td>
<td>0.32</td>
<td>1.19</td>
<td>0.18</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>12.51</td>
<td>0.08</td>
<td>15.63</td>
<td>0.10</td>
<td>0.49</td>
<td>1.23</td>
<td>0.32</td>
<td>3.92</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.26</td>
<td>2.31</td>
<td>0.01</td>
<td>3.29</td>
<td>5.46</td>
<td>6.32</td>
<td>3.94</td>
<td>0.74</td>
</tr>
<tr>
<td>Total*</td>
<td>90.53</td>
<td>86.91</td>
<td>90.34</td>
<td>83.45</td>
<td>84.15</td>
<td>89.99</td>
<td>88.07</td>
<td>85.29</td>
</tr>
</tbody>
</table>

Anhydrous formula unit composition

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.114</td>
<td>0.001</td>
<td>0.013</td>
<td>0.006</td>
<td>0.007</td>
<td>0.011</td>
<td>0.000</td>
<td>0.010</td>
</tr>
<tr>
<td>Mg</td>
<td>0.000</td>
<td>0.358</td>
<td>0.000</td>
<td>0.912</td>
<td>0.010</td>
<td>0.128</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Ca</td>
<td>0.350</td>
<td>1.045</td>
<td>0.009</td>
<td>0.941</td>
<td>1.463</td>
<td>0.979</td>
<td>1.944</td>
<td>7.408</td>
</tr>
<tr>
<td>Sr</td>
<td>0.021</td>
<td>0.057</td>
<td>0.000</td>
<td>0.186</td>
<td>0.013</td>
<td>0.112</td>
<td>0.000</td>
<td>0.262</td>
</tr>
<tr>
<td>Ba</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.006</td>
<td>0.027</td>
<td>0.094</td>
<td>0.015</td>
<td>-</td>
</tr>
<tr>
<td>Na</td>
<td>14.413</td>
<td>0.023</td>
<td>15.312</td>
<td>0.046</td>
<td>0.203</td>
<td>0.482</td>
<td>0.126</td>
<td>4.094</td>
</tr>
<tr>
<td>K</td>
<td>0.197</td>
<td>0.446</td>
<td>0.006</td>
<td>1.001</td>
<td>1.496</td>
<td>1.636</td>
<td>1.025</td>
<td>-</td>
</tr>
<tr>
<td>O</td>
<td>96</td>
<td>24</td>
<td>80</td>
<td>36</td>
<td>32</td>
<td>32</td>
<td>80</td>
<td>384</td>
</tr>
<tr>
<td>E%</td>
<td>5.56</td>
<td>-2.21</td>
<td>3.95</td>
<td>5.88</td>
<td>8.81</td>
<td>-0.45</td>
<td>-2.03</td>
<td>-0.88</td>
</tr>
<tr>
<td>T$_{Si}$</td>
<td>0.663</td>
<td>0.723</td>
<td>0.603</td>
<td>0.699</td>
<td>0.681</td>
<td>0.705</td>
<td>0.689</td>
<td>0.518</td>
</tr>
</tbody>
</table>

* adapted from Rinaldi et al., 1975

* total includes traces of TiO$_2$ and MnO

E% - a measure of charge balance, = 100[(Al+Fe$^{3+}$)-(Na+K)-2(Mg+Ca+Sr+Ba)]/[(Na+K)+(2(Mg+Ca+Sr+Ba)]

T$_{Si}$ = Si/(Si+Al)
Chabazite forms triclinic white to clear, rarely yellowish brown crystals, often with rhomboid faces. Crystals are often twinned, penetrating each other with corners projecting from the faces. Crystal grain size ranges from 0.1 to 1 mm, but usually smaller crystals predominate. A detailed observation of the mineral succession shows that chabazite formed as one of the latest secondary minerals, overgrowing phillipsite as earlier formed zeolite species.

Chabazite crystals from Eichert (Fig. 1B), grown on top of phillipsite, were analysed to evaluate their chemical composition (Table 2). The average composition evaluated from 10 microprobe analyses is \([\text{Ca}_{0.916}\text{Sr}_{0.078}\text{Mg}_{0.390}\text{Na}_{0.029}]^{+} [\text{Al}_{3.327}\text{Si}_{8.714}\text{O}_{24}] \cdot 12\text{H}_{2}\text{O}\). Calcium is the dominant extra-framework cation (up to 1.045 apfu). Additional K and Mg is present in the triclinic chabazite structure with maximum values of 0.519 and 0.426 respectively, whereas Na and Sr occur only in traces. No chemical zoning is visible and the composition of chabazite varies only in a small range, as is shown in the extra-framework cation distribution diagram (Fig. 3), and in the T_{Si} ratio (Si/Si+Al), where T_{Si} shows an average value of 0.710 and ranges from 0.723 to 0.736 (Fig. 4).

4.4. Faujasite

Faujasite ([NaCa_{0.5}Mg_{0.5}K]^{+} [\text{Al}_{x}\text{Si}_{12-x}\text{O}_{24}] \cdot 16\text{H}_{2}\text{O}) is a rare zeolite, described only from a few places outside the KVC, where it occurs in cavities of basaltic lavas and pyroclastic rocks, and in hydrothermally altered granitic and metamorphic rocks (Parker, 1922). Faujasite was first described as new mineral by Damour (1842) from the Limberg (Fig. 1), which is therefore the type locality for this zeolite. Coombs et al. (1998) defined three faujasite species, faujasite-Na, faujasite-Ca and faujasite-Mg.

In the KVC, faujasite is only found in the old quarries of the Limberg area, where it occurs in a highly vesiculated “limburgite” (olivine-augite basanite) as minor secondary mineral, associated with offretite, phillipsite, chabazite, aragonite, calcite, dolomite, montmorillonite and hylite. Faujasite occurs as clear well-shaped octahedra up to 3 mm in diameter, but crystal sizes between 0.1 and 0.3 mm are most common (Fig. 5A). Twinning on {111} by the spinel law is common. Faujasite forms directly on the vesicle wall without being preceded by clays. It is occasionally associated with phillipsite, which forms radiating thin spherules, and offretite. Faujasite octahedra are commonly covered with a blue-grey, amorphous hydrated aluminosilicate.

Rinaldi et al. (1975) observed that the chemical composition of faujasite crystals varies to a large extent, even when occurring in the same amygdale, showing a wide range of extra-framework cation contents: sodium ranges from 7 to 15, Ca from 4 to 15, Mg from 8 to 15 and K from 0.6 to 9.7 apfu (Figs 3 and 4). Except one single analysis faujasite from the Limberg area can be classified as faujasite-Na (Coombs et al., 1998). The Limberg area is also the type locality for faujasite-Mg which was classified based on a single microprobe analyse, made on an old museum sample (Rinaldi et al., 1975).

4.5. Natrolite

Natrolite (Na_{2} [\text{Al}_{2}\text{Si}_{3}\text{O}_{10}] \cdot 2\text{H}_{2}\text{O}) has a high economic impact in the Kaiserstuhl area, but it occurs only in a few outcrops (Table 1). Natrolite is a secondary mineral within igneous rocks of phonolitic composition, formed during cooling of the intrusive bodies under subsolidus conditions. It occurs either as rock forming mineral and as vein filling mineral. In the latter case, natrolite forms long, thin needles elongated along the c-axis as well as radial aggregates, and compact masses. The colour varies from colourless to white, and light yellowish to light redbrown. Individual crystals have a size up to 10 mm in length, but smaller needles (<1mm) are more common. Natrolite is
overgrown by following mineral phases: apophyllite, fluorite, calcite, analcime, chabazite and hyalite.

Chemical analyses were obtained on natrolite crystals from the Fohberg quarry, which were precipitated as euhedral crystals in a vein, approximately 1 cm in width. Sodium is the main extra-framework cation (Table 2; Fig. 3). Other cations, like Ca, K, Sr and Ba, occur only in traces. The average T\textsubscript{Si} ratio is 0.606 (Fig. 4).

4.6. Offretite

Barrel-shaped offretite (Ca\textsubscript{K}Mg\textsubscript{Al\textsubscript{5}Si\textsubscript{13}O\textsubscript{36}} \cdot 16H\textsubscript{2}O) forms simple hexagonal prisms up to 0.3 mm and 0.1 mm in diameter (Figs 5B and 6). The crystals are colourless and flared pinhead-like groups of epitaxial offretite occur in vesicles in the limburgite lavas (Rinaldi, 1976). Offretite appears to have grown as first zeolite species, followed by an amorphous hydrous alumosilicate, which is, again, followed by the other secondary minerals.

The average composition of offretite is (K\textsubscript{0.979}Mg\textsubscript{0.94}Ca\textsubscript{0.084}Mg\textsubscript{0.06}Al\textsubscript{0.01})\textsubscript{0.989}Mg\textsubscript{0.01}O\textsubscript{4}\textsubscript{.5}.

Figure 5: Scanning electron microscopy images showing the morphology of zeolite species from the Limberg quarry I. A Faujasite cube covered with a thin amorphous film, associated with later formed ball-shaped phillipsite aggregates. B Barrel-shaped offretite in parageneses with later formed ball-shaped phillipsite aggregates.

Figure 6: Backscattered electron and element distribution images of offretite in a limburgite vesicle, collected in the Limberg quarry I. A BSE image. B Mg-distribution image shows a slight zoning, decreasing from core to rim. C K-distribution image shows no zoning. D Ca-distribution image shows no zoning. E Al-distribution image shows a slight zoning, decreasing outwards. F Si-distribution image shows a slight zoning, increasing to the rim.
Besides the rock-forming zeolite species analcime, phillipsite ([KNaCa$_{0.5}$Ba$_{0.5}$]$_{32}$[Al$_{4.984$Si$_{11.002$}O$_{32}$] $_{•}12$H$_2$O) is by far the most abundant zeolite in amygdales of the KVC (Table 1). Phillipsite occurs in most tephritic lavas and tuffs as cavity filling zeolite and additionally appears in most of the tuff-breccias as secondary mineral forming the matrix cement (Wimmenauer, 1957). Phillipsite forms transparent, colourless pseudo-orthorhombic twinned (Morvenite and Stempel) prismatic crystals, commonly elongated along the a-axis. Individual crystals are small; usually not larger than 1-2 mm in length. Furthermore phillipsite often forms radial aggregates, with diameters up to 3 mm, and mushroom-like tuffs. A detailed observation of the mineral precipitation chronology shows that phillipsite crystallised after offretite and faujasite and that phillipsite crystallised after offretite and faujasite and the observation of the mineral precipitation chronology shows that phillipsite crystallised after offretite and faujasite and before the younger species chabazite and calcite (Betz 2005).

Phillipsite crystals from three different localities (Limberg/Sasbach, Eichert/Sasbach and Strümpfekopf-Totenkopf/Bickensohl) were analysed to evaluate the chemical composition in this zeolite, hosted in different rocks and in parageneses with different secondary cations, with approximately equal concentrations (Fig. 3). As Passaglia et al. (1998) reported, Sr occurs only as minor cation up to 0.186 apfu, what is in disagreement to analyses of Rinaldi et al. (1975), who reported Sr contents up to 0.9 apfu for offretite from the limberg locality. Sodium occurs only in traces. The average T$_{Si}$ ratio is 0.702 and ranges from 0.692 to 0.719 (Fig. 4). Element distribution images (Fig. 6) showing only slight chemical variations.

4.7. Phillipsite-K/Phillipsite-Ca

The extra-framework cations vary in a wide range as reflected by the Si/Al ratio: 0.689, 0.690 and 0.702, respectively. The dominant extra-framework cation in phillipsite from Strümpfekopf-Totenkopf is Ca (Fig. 3), whereas a Ca-K substitution can be observed (Fig. 3).

Average chemical compositions for phillipsite samples from Limberg, Eichert and Strümpfekopf-Totenkopf are:

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Si/Al</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Sr</th>
<th>Al</th>
<th>Si</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$<em>{7.395}$Na$</em>{4.074}$Sr$<em>{0.227}$Al$</em>{4.984}$Si$<em>{11.002}$O$</em>{32}$ • 12H$_2$O</td>
<td>0.689</td>
<td>0.690</td>
<td>0.702</td>
<td>0.689</td>
<td>0.690</td>
<td>0.702</td>
<td>0.689</td>
<td>0.690</td>
<td>0.702</td>
</tr>
</tbody>
</table>

Phillipsite in all samples is dominated by Ca and K, whereas a Ca-K substitution can be observed (Fig. 3). The extra-framework cation in phillipsite from Eichert is classified as phillipsite-Ca (Coombs et al., 1998).

Sodium reaches concentrations up to 0.222 apfu. Phillipsite from the Limberg area is dominated by potassium, with higher contents of Na, up to 0.595 apfu (Fig. 3). Conspicuous are the relatively high amounts of Ba and Mg, up to 0.117 and 0.125, respectively. A barium enrichment is also observed in phillipsite from the other two localities, but there it is less pronounced. Phillipsite from the Limberg area is classified as phillipsite-K (Coombs et al., 1998).

4.8. Thomsonite

Thomsonite (Ca$_n$Na$_m$Al$_4$Si$_5$O$_{20}$ • 6H$_2$O) is very rare in the KVC. It is known only from one locality in the centre of the KVC, the Strümpfekopf-Totenkopf locality in the vineyards between Bickensohl and Totenkopf (Fig. 1). It occurs together with phillipsite and is formed as early zeolite species in cavities of fragile tephritic rocks (Schelken 1990). Colourless, transparent to whitish yellowish thomsonite forms either euhedral block- to needlelike prisms with the forms {100}, {010} and {001}, or irregular crystal aggregates, as well as spherical or fan-shaped aggregates. Crystal size can be up to 6 mm, but is commonly less than 1 mm.

The Strümpfekopf-Totenkopf thomsonite is chemically homogeneous with a composition of (Ca$_{7.395}$Na$_{4.074}$Sr$_{0.227}$Al$_{4.984}$Si$_{11.002}$O$_{32}$ • 24H$_2$O). Calcium and sodium are the only significant extra-framework cations, except Sr, whose concentration reaches 0.296 apfu. The T$_{Si}$ ratio varies between 0.514 and 0.534, with an average of 0.520 (Fig. 4).

5. Geochemistry of the host rocks

5.1. “Limburgite”

The name “limburgite”, introduced by Rosenbusch (1872), is a descriptive term for a porphyric magnetite-olivine-augite rock with vitreous matrix. By means of the geochemistry and following the modern nomenclature (e.g. Le Maitre et al., 2002) this term should be replaced by “nepheline basanite”, but nevertheless, the old name is still in use by Kaiserstuhl geologists. Limburgites in the KVC are only slightly fractionated from their parental olivine nephelinitic magma.

Table 3 shows a geochemical analysis of limburgite from Keller et al. (1990). The content of normative nepheline is 6.3 wt.%. Compared to the Fohberg phonolite (see 5.3.) and the leucitophyre (see 5.4) the alkalies are considerably lower (1.20 % K$_2$O, 2.50 % Na$_2$O). The alkali content in the limburgite is Na+K = 2.86 wt.%, the alkaline earth content (Mg+Ca+Sr+Ba) is 15.84 wt.%. The alkalies/alkaline earth ratio (Na+K)/(Mg+Ca+Sr+Ba) = 0.18.
5.2. Tephrite

Tephrites are the most abundant eruptive rock type in the KVC, forming usually thin lava flows and pyroclastic deposits. Their petrography and geochemistry are described in detail by Wimmenauer (1957, 1959) and Kim (1985). They form olivine-free and subordinate olivine-bearing varieties, usually with leucite as primary foid mineral. Table 3 shows the chemical composition of the Eichert tephrite (Kim, 1985). The SiO₂ content is 44.86 wt.%, alkalies total to 3.02 % and alkaline earths to 13.26 %, leading to a ratio of 0.23.

5.3. Fohberg phonolite

An average of geochemical characteristics of the Fohberg phonolite are presented in Table 3 (average of 13 analyses; Albrecht, 1981). Phonolites, syenites and related dyke rocks form an evolved magmatic rock suite in the Kaiserstuhl. With 49.28 wt.% SiO₂, the Fohberg phonolite is strongly silica-deficient which results in 23.1 % normative nepheline according to the CIPW calculations of Albrecht (1981). Alkalies are present in average proportions of 4.86 % (K₂O), 6.81 % (Na₂O) and 195 ppm (Rb), respectively. They are considerably higher compared to the limburgite (see 5.1.). Concentrations in the Fohberg phonolite are alkalies = 9.08 % and alkaline earths = 6.20 %. For this reason, the elemental ratios in the Fohberg phonolite differ distinctly from those in the limburgite, the ratio of alkalies to alkaline earths is higher: (Na+K)/(Mg+Ca+Sr+Ba) = 1.46.

5.4. Leucitophyre

The leucitophyre from Strümpfekopf (Spürgin et al., 2008) represents a highly evolved member of the phonolitic family. Its chemical composition is shown in Table 3 (Spürgin et al., 2008). The alkali concentrations (4.96 %) show a potassium dominance and lead to elemental proportions of Na/K = 0.34. It is noteworthy that the alkali ratio of the matrix can be as high as 1.91 (mean 0.77) due to a much higher Na₂O-content (max. 5.62 %) and a K₂O range similar to the bulk rock (mean 4.66 %). The concentration of Mg+Ca+Sr+Ba is 6.79. The alkalies/alkaline earth ratio, (Na+K)/(Mg+Ca+Sr+Ba) = 0.73, is intermediate between the phonolite on one hand, and the values of limburgite and tephrite on the other hand. Again, the matrix of the leucitophyre shows distinctive discrepancies to the bulk composition. Ca is strongly (mean 1.74 %), Ba slightly (mean 2453 ppm) depleted, whereas Sr is enriched (mean 3898 ppm).

6. Discussion

Zeolites in the KVC formed during different processes. Zeolites are formed either during surface water infiltration succeeding eruptive episodes, either as replacement of primary phases or as precipitation in open space, like in vesicles or veins, or by hydrothermal activity during subsolidus post-magmatic cooling of the shallow intruded phonolite bodies. Soellner (1912) proposed a zeolitisation stage at the end of the volcanomagmatic period. In the following we will discuss genetic connections between zeolites and their host rocks as well as new observations on zeolite species.

6.1. Genetic relations in the Limberg complex

Detailed systematic observations by Betz (2005) of the parageneses of secondary minerals, which were formed during hydrothermal activity in vesicles of the Limberg complex, resulted in the following order (from old to young): montmorillonite, offrettite, phillipsite I, faujasite, amorphous Si/Al oxide films, phillipsite II, chabazite, calcite, dolomite, Fe-oxides and magnesite. Similar temporal observation can be done at the Mont Semiol/France zeolite occurrence, with the exception that mazzite occurs instead of faujasite (Betz, 1982).

Chemical components necessary for zeolite and secondary mineral formation were released directly from the sideromelane glass during the formation of palagonite (Fig. 7). Eggleton & Keller (1982) studied in detail the palagonitisation of limburgitic glass. Element mass transfer during the palagonitisation is summarised in Fig. 7. The mass balance, calculated with data from Eggleton & Keller (1982), shows clearly that chemical elements necessary for zeolite and secondary mineral formation (Mg, Ca, Na, K, Al and Si) were mobile during the palagonitisation processes. Faujasite is most abundant.
near the vitreous top of the lava section (Lorent, 1933), but is present sparingly throughout. A similar observation is done in San Bernardino County/California (Wise, 1982).

The zeolites probably formed in fluids, which penetrated the vesicles sporadically from hand-specimen scale to the scale of the entire quarry face, but the source of the fluid is unknown. Because of the tectonic relations and sediment record during the evolution of a limnic environment in the Limberg complex (Jörg, 1951), locally heated surface water seems to be a likely source, but juvenile hydrothermal fluids, penetrating the whole volcanic Limberg complex, cannot be excluded.

It seems possible that the occurrence of faujasite near the top of the lava flows may be related to the higher content of easily altered volcanic glass in this part, to a higher fluid flow in the more vesicular rocks and may have been influenced by surface water, derived from the limnic environment forming the Limberg Formation (Jörg, 1951; Tobien, 1958).

The high Mg content of all zeolites (Table 2) is consistent with the relative high Mg content of the limburgite rocks (Table 3), pointing to fluids with a local compositional fingerprint. The compositions of the zeolites are clearly distinguishable on the Na, K and Ca+Mg+Sr plot (Fig. 3), which represents a crystal-structural control (Rinaldi et al. 1975) forcing element fractionation between the different zeolite framework geometries.

6.2. Offretite

Observations done earlier (Hentschel, 1976; Rinaldi, 1976) propose that barrel-shaped zeolite individuals are formed by offretite with an epitaxically overgrowth of erionite. Their results are mainly based on optical elongation sign, using the method of Sheppard & Gude (1969). Additionally Rinaldi (1976) reported chemical analyses, which vary continuously from the composition of offretite and erionite. A new method to discriminate between offretite and erionite was published by Passaglia et al. (1998). They clearly show that a discrimination based on the optical elongation sign is not possible, because elongation is related to the Si/Al ratio (Fig. 6). Additionally they clearly revealed that erionite-offretite intergrowths are very uncommon. They conclude that the activity of the Mg cation is a major factor in controlling the crystallization of the mineral species. Our new chemical investigation shows (Figs 3, 4 and 6; Table 2) that erionite does not epitaxially overgrow offretite. Although a slight chemical zoning can be observed, magnesiu contents are still too high to classify it as erionite.

6.3. Natrolite

Natrolite in the Fohberg phonolite stock is commonly occurring as fissure mineral and in the matrix of the rock, where it replaces a member of the sodalite group, probably sodalite (Wimmenauer, 2003), or additional leucite (Albrecht, 1981). The near-endmember composition of natrolite, as well as its vast dominance in the fissure assemblage (beside calcite), implies that decay of other
primarily crystallised phases plays only a subordinate role in the composition of the percolating fluids, which is in agreement with textural observations. Natrolite may also be formed by decomposition of plagioclase or nepheline (Wimmenauer, 1959b), but these minerals are both lacking in the Fohberg phonolite. In the KVC it is generally observed that fissures with macroscopic natrolite crystals occur only in the phonolite stocks (Fig. 1B), which were originally rich in sodalite or hauyne.

The presence of other species crystallographically related to natrolite, namely mesolite and sodalite (Albrecht, 1981; Wimmenauer, 2003), cannot be confirmed by our observations and thus it seems very likely that these minerals do not occur in significant quantity.

6.4. Secondary analcime phenocrysts

The crystal structures of leucite (KAlSiO3) and analcime (NaAlSi2O6·16H2O) are very similar. The origin of analcime phenocrysts has perplexed geologists since the last two centuries (Stamm, 1856; Knight, 1904; Karlsson & Clayton, 1991; Putnis et al., 2007). The question is whether the crystals have grown as primary phase from a melt or whether they have formed as secondary phase as a result of postmagmatic alteration of leucite. However, analcime pseudomorphs after leucite are well known (e.g. Karlsson & Clayton, 1991). The replacement reaction from leucite to analcime includes a 10% molar-volume increase, which makes it difficult to explain the solid-state ion exchange process (Putnis et al., 1994): KAlSiO3 + Na+ + H2O = NaAlSi2O6 + H2O + K+

This transformation can either occur during cooling of the magma or after the host rock has solidified (Karlsson & Clayton, 1991). The replacement reaction from leucite to analcime includes a 10% molar-volume increase, which makes it difficult to explain the solid-state ion exchange process (Putnis et al., 2007). Line et al. (1995) noted the powdery texture of analcime, which may result from the breakup of leucite into smaller analcime crystals or structural cluster units in order to accommodate expansion. Karlsson & Clayton (1991) suggested that the volume increase results in expansion cracks in the vicinity of analcime crystals.

Stamm (1856) first recognised that leucite crystals from the KVC were replaced by secondary analcime. The typical “Schlackenkörzchen” leucite texture, which is formed by small inclusions of pyroxene or glass arranged concentrically close to the crystal margins, is observed in pseudomorph analcime aggregates, which points out the secondary leucite replacement by analcime (Kim, 1985). The high potassium content of the analcime fits quite well with other secondary analcime replacing leucite in alkaline volcanic rocks (e.g. Luhr & Kyser, 1989; Karlsson & Clayton, 1991). As mentioned by Karlsson & Clayton (1991) cracks in the vicinity of the analcime crystals, which are the result of volume increase during replacement, are observed in samples from the Kaiserstuhl area (Fig. 2). Additionally to the leucite replacement, feldspar replacement by other zeolites and clay minerals can be observed, which supports the secondary origin of analcime in the alkaline volcanic rocks of the KVC. Potassium, which is released during the leucite-analcime transformation, remains in the matrix and is not released from the host rock (Spürgin et al., 2008).

7. Conclusion

Zeolite formation in extrusive rocks occurred during interaction of groundwater with rock following the eruptive episode, although the contribution of hydrothermal magmatic fluids cannot be excluded.

Zeolitisisation of subvolcanic phonolite intrusions was driven by fluid circulation during the hydrothermal stage of the magmatic evolution at temperatures below 200°C. Natrolite and minor amount of analcime and chabazite are the result of alteration and replacement of primary phases in the phonolite intrusion. High permeability and porosity of the extrusive rocks permit high fluid flow in the magmatic period, which causes the devitrification of primary volcanic glass and therefore the formation of zeolites, like phillipsite, chabazite, analcime, faujasite and offretite. The subsolidus post-magmatic formation of zeolites is the dominant process in impermeable rocks, while water circulation during magmatic episode is dominant in permeable rock.

Host rock chemistry and mineralogy clearly control the formation of zeolites and other secondary minerals. Analcime derived from cation exchange reaction between a Na-rich fluid and leucite, as well as natrolite, which forms as an alteration product of sodalite-group minerals. Additional to the chemical composition of the host rock, permeability seems to be an important factor for zeolite formation. For the Limberg area we can show that the ions, necessary for zeolite formation, were derived from palagonitisation of primary glass.

The chemical reinvestigation of barrel-shaped offretite from the Limberg area clearly shows that the postulated epitaxial overgrowth of offretite and erionite does not occur, due to the misleading understanding of the species discrimination based on the optical elongation sign.

Continuing research may provide interesting results on the formation of faujasite, which can be easily synthesised but is fairly rare in natural environments. Further detailed investigations of mineralogical and chemical variations in zeolite-bearing assemblages from selected localities are a promising subject, to complete our understanding of zeolite generation in the KVC.
8. Acknowledgments

We are grateful to J. Höth who provided us with high-quality mineral specimen from his collection. Special thanks go to the technicians and staff of the Mineralogical-Geochemical Institute, University of Freiburg: I. Schmidt for her help during sample preparation and for the XRD and XRF analyses; M. Katt for the careful preparation of fragile thin sections; H. Müller-Sigmund for her useful advise during EMP analyses and her patience with us at the electron microscope. Thanks to K. Wilker (Institute of Crystallography, University of Freiburg) for her help on the scanning electron microscope. We are grateful to F. Parat and V. Huber for their comments on the manuscript. We also thank Lieven Machiels and Rune Selbekk for the thorough and constructive reviews and Jean-Clair Duchesne for his editorial efforts and the editorial handling of the paper.

9. References


Plate 1: Zeolite localities around Sasbach. A Limberg quarry I. The quarry wall consists of two superimposed, clearly distinguishable lava flow units (λ₁ and λ₂), which are separated by a yellowish bend of tuffite (t₁). Faujasite and offretite occur especially in the top regions of the lava flow units. B Vesicle rich limburgite from the top of lava flow λ₁ with phillipsite and calcite; coin for scale. C Hand specimen of tephrite from Eichert, showing well distributed vesicles filled with phillipsite, which is overgrown by chabazite. Black grains are titanian-augite. D Phillipsite-K bearing vesicle, Limberg quarry I. E Dolomite crystals covering early grown calcite crystals, Limberg quarry I.
Plate 2: Phonolite quarry, Fohberg, Bötzingen. A Phonolite cut by a later dyke of essexitic composition. The host rock shows numerous small veins, which are filled with secondary minerals. B White natrolite needles covered by light green hyalite. C Profile from the host rock (right) to the secondary vein minerals (left) showing a leaching zoning into the phonolite.