

Zeolites in the Smrekovec volcaniclastic rocks, northern Slovenia

Zeoliti v vulkanoklastičnih kamninah smrekovskega podgorja (severna Slovenija)

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Abstract

Volcaniclastics from the Upper Oligocene Smrekovec volcanic complex comprise autoclastic deposits, locally resedimented hyaloclastite deposits, pyroclastic deposits, volcaniclastic debris flow and turbidite ash flow deposits and reworked turbidite ash flow deposits. Particularly coarser-grained rocks underwent changes in mineralogy characterised by the development of zeolites and related new-formed silicate minerals: albite, quartz, chlorite, interlayered chlorite/smectite, prehnite, pumpellyite and sphene. Among zeolites, laumontite is the most widespread mineral; it primarily occurs in veins and as interstitial cement but may also replace volcanic glass, pyrogenetic plagioclases and fine-grained matrix. Other zeolites – heulandite, heulandite-clinoptilolite, analcime, stilbite, yugawaralite and thomsonite are less abundant, and are more localised in occurrence. The formation of zeolites and other new-formed silicate minerals is related to hydrothermal conditions generated by emplacement of high-level intrusive bodies into soft, water-saturated sediments.

Kratka vsebina

Med vulkanoklastiti smrekovskega podgorja najdemo avtoklastične kamnine, lokalno presedimentirane hialoklastite, piroklastite, vulkanoklastične debrite in turbidite ter lokalno presedimentirane vulkanoklastične turbidite. Zeoliti in drugi avtogeni minerali: albit, kremen, klorit, glineni minerali z zmesno strukturo vrste klorit/montmorillonit, prehnit, pumpellyit in sfen so nastali predvsem v bolj debelozrnatih kamninah. Med zeoliti je najbolj razprostranjen laumontit, ki se najpogosteje pojavlja kot žilni mineral ali porni cement, ponekod pa lahko nadomešča tudi prvotne sestavine kamnine – vulkansko steklo, pirogene plagioklaze ali drobnnozrnato tufsko osnovo. Drugi zeoliti, heulandit, trdne raztopine heulandita in klinoptilolita, analcim, stilbit, yugawaralit in thomsonit so v vulkanoklastičnih kamninah smrekovskega podgorja zastopani mnogo redkeje. Nastanek zeolitov je vezan na delovanje hidrotermalnih raztopin, ki so nastale s pregrevanjem pornih vod v vulkanoklastičnih sedimentih tedaj, ko je vanje intrudirala andezitna magma.

Introduction

Volcaniclastic material is particularly susceptible to alteration processes. Being formed at much higher temperatures than that of the depositional medium, it is generally not in equilibrium with its low-temperature sedimentary environment. In response to essentially different chemical and physical conditions on the Earth's surface, volcaniclastic constituents undergo the changes in mineralogy, characterised by reactions of hydration. These changes are particularly pronounced in aqueous environments.

Volcaniclastic sediments may be deposited in environments with high chemical gradient of reacting solutions, in areas of high-temperature gradients and/or hydrothermal activity, and in subsiding sedimentary basins. Herein, volcaniclastic material is subjected to physical and chemical conditions departing further from those that prevailed during deposition and early stage diagenesis. As a result, many of the initially stable minerals become unstable or metastable, whereas the stability conditions of many of other secondary minerals are still far from being attained. The mineral reactions taking place are a response to this instability and tend to establish or re-establish equilibrium between various phases and between the phases and the environment.

The most pronounced new-formed minerals in volcaniclastic rocks are zeolites (Steiner, 1953; Coombs et al., 1959; Kossovskaya & Shutov, 1961; Otalora, 1964; Iijima & Utada, 1966; 1972; Iijima, 1978; 1980; 1984; 1988; Kostov, 1969; Seki et al., 1969; Hay & Iijima, 1968a, 1968b; Utada, 1973; 1988; Hay, 1980). Most common zeolite species are clinoptilolite, heulandite, analcime, phillipsite, chabasite, mordenite, erionite, laumontite and wairakite, somewhat rarer in occurrence are yugawaralite, stilbite, natrolite, gonnardite, thomsonite, harmotome and levynite (Gottardi & Galli, 1985). They form in volcanic rocks in varying geologic environments and due to diverse processes: weathering, percolating of meteoric water, in saline-alkaline lake deposits, by deep sea halmyrolysis, upon burial diagenesis, and by contact metamorphism and hydrothermal alteration (Iijima, 1984; Utada, 1987).

Zeolites form by weathering upon surface conditions in alkali soils of semiarid areas by interaction of volcaniclastic constituents with alkaline soil water. Hay (1970, 1978) has described the alteration of trachytic glass being replaced by phillipsite, chabasite and analcime.

Another environment favourable for the zeolite formation is the so-called open hydrologic system. Meteoric water percolating through a tuff reacts with volcanic glass to increase in pH and alkalinity until zeolites precipitate in interstitial pores and voids of dissolved glass shards. Zeolites and other new-formed minerals are distributed in vertical zones consisting of surface soil, fresh tuff or slightly altered opal- and montmorillonite-cemented tuff, and zeolitic tuff. This type of zeolitization was described for the first time in volcaniclastics of alkali-basaltic composition from Hawaii by Hay and Iijima (1968a, b) and Iijima and Harada (1968). The open system alteration was also recognised in the Pliocene alkali basaltic volcaniclastic rocks at Grad, NE Slovenia (Kralj, 1995). Common zeolites encountered in this type of environment are phillipsite, chabasite and analcime; gonnardite and natrolite may also occur. In tuffs of rhyolitic composition clinoptilolite and abundant smectites form by interaction of silicic glass with percolating ground water (Iijima, 1984).

Alkaline saline lakes are closed hydrologic system where zeolites form by interaction of volcanic glass and alkaline brines (Hay, 1966; 1978; Sheppard, 1973; Surdam & Sheppard, 1978; Sheppard & Gude, 1968; 1969). Typical zeolites produced in lake deposits of mafic composition are phillipsite, chabasite and erionite. In volcanoclastic sediments of silicic composition, clinoptilolite and mordenite occur. Zonation of new-formed minerals is horizontal, extending from the lake-margins to the lake-centre.

Halmyrolysis includes the reactions of volcanic glass from ash layers of younger geologic age, deposited on the bottom of the World's Oceans (Iijima, 1978; Kastner & Stonecipher, 1978; Honnorez, 1978). In mafic tuffs and pelagic brown clay, encountered in the Pacific and Indian Oceans, phillipsite is the dominant authigenic mineral. Clinoptilolite is more abundant in altered silicic tuff, pelagic clay and siliceous oozes in the region of Atlantic Ocean and marginal seas.

Diverse species of zeolites form upon burial diagenesis of volcanoclastic rocks in widespread geosynclinal systems (Combs et al., 1959; Kossovskaya & Shutov, 1961; Iijima & Utda, 1966; Boles & Combs, 1975; 1977; Boles, 1989). During early diagenesis clinoptilolite and mordenite form in silicic glass; upon progressive burial earlier developed zeolites alter further to analcime and/or heulandite and finally to albite and laumontite.

Zeolitization in hydrothermally active environments is rather complex. According to Utda (1987) it can be subdivided into four main types - Kuroko, Iceland, Okinobe and Yellowstone, characterised by different zeolite zoning, the zone morphology and extension, the temperature of zeolite formation and the chemistry of reacting solutions. Some authors, i. e. Iijima (1984), also categorise contact metamorphism among hydrothermal occurrences.

The development of zeolites and other new-formed hydrous silicates in a hydrothermally active environment is strongly controlled by the temperature and chemistry of reacting solutions. Chemical composition, porosity and permeability of the host rock may also be important in zeolitization processes. In volcanoclastic sediments and rocks of mafic composition, heulandite, stilbite, mordenite, laumontite, wairakite and yugawaralite are the most significant zeolites (Kristmannsdottir & Tomasson, 1978; Steiner, 1953; Utda, 1987). In tuffs of silicic composition, clinoptilolite, mordenite and analcime develop (Utda, 1988; Honda & Muffler, 1970).

Geological setting of the Smrekovec volcanoclastics

The Smrekovec mountains, located in northern Slovenia (fig. 1) are characterised by a widespread occurrence of coherent volcanic rocks and volcanoclastic deposits. The complex encompasses an area of approx. 15 sq. km and includes three major mountain peaks, Komen, Krnes and Smrekovec, reaching 1684 m, 1613 m and 1577 m respectively. The basement consists mainly of Mesozoic carbonates encountered as tectonically uplifted blocks on the NW and SE margins of the Smrekovec volcanic complex. A NW-SE trending fault of the peri-Adriatic lineament zone separates this complex from the Karavanke tonalite (Mišč, 1983). The Smrekovec volcanic complex represents a part of a wider volcanic belt, named the "Smrekovec series", extending along a distance of about 100 km towards the southeast (Mišč, 1978; Mišč

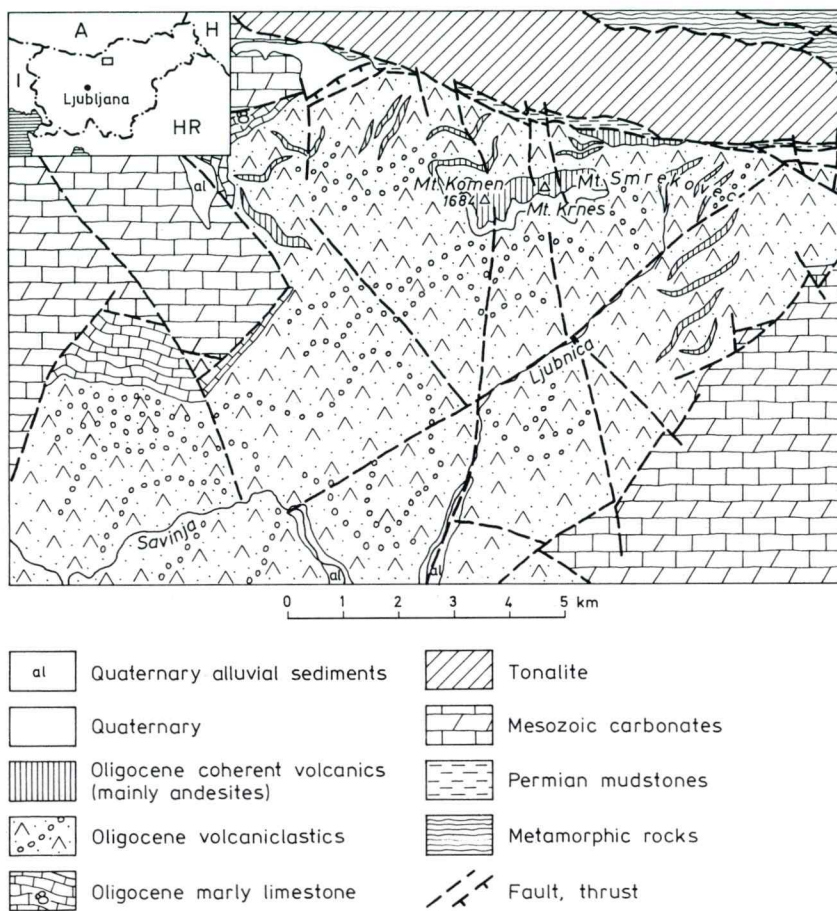


Fig. 1. The Smrekovec volcanic complex: geological sketch map (after Mioč, 1983)

Sl. 1. Poenostavljena geološka karta smrekovskega podgorja (po Mioču, 1983)

et al., 1986). The Smrekovec volcanics are of Upper Oligocene stratigraphic age, as determined on the basis of foraminifera fauna, found in the locally underlying marine marls and siltstones (Rijavec, 1966).

The present rather complicated situation in northern and north-eastern Slovenia is associated with global tectonic processes of Late Cretaceous to Tertiary subduction and collision of the continental African and oceanic European plates and their segmented parts, Apulia and the Pannonian fragment (Oberhauser, 1980; Royden, 1988; Dercourt et al., 1986). In early Miocene, the Pannonian fragment separated from Apulia and began to escape eastward from the collision zone in Eastern Alps. Due to the mentioned eastward escapement, an extension of the Pannonian fragment began, being followed by subsidence, and consequently, the formation of a back-arc basin - the Pannonian basin.

It remains undefined whether the Smrekovec volcanism is related to an active continental margin or to one of the collision combinations: island arc - active continental margin - passive continental margin (Gill, 1981). However, chemical composition of the Smrekovec intermediate volcanics is not very characteristic of orogene andesites (Kralj, 1997). It indicates that tholeiitic magma very possibly underwent a differentiation due to crystal fractionation. Consequently, basalts, basaltic andesites, acid andesites, dacites and finally rhyodacites evolved in time, forming a volcanic suite. The Smrekovec volcanism may be related to local extension and leakage at the plate boundary, as it is the case in central California (Dickinson & Snyder, 1979a, b).

Smrekovec volcanic activity built a complex of submarine stratovolcano(es) with a significantly elevated relief composed of lavas, high-level intrusive bodies, autoclastic deposits, pyroclastic deposits and syn-eruptive resedimented volcanoclastic deposits (Kralj, 1997). The early stage of volcanic activity was dominantly non-explosive. Basalts and basaltic andesites were emplaced as submarine lavas or high-level intrusive bodies. The style of fragmentation was mainly autoclastic, related to chill and quench processes. The late-stage volcanic activity is characterised not only by non-explosive volcanism of acidic andesitic to rhyodacitic composition, but also by explosions, either combined hydrovolcanic and magmatic, or solely hydrovolcanic. Juvenile material, chiefly pumice and glass shards, became relatively abundant. Explosive volcanic activity was probably instrumental in generation of volcanoclastic debris flows and turbidite ash flows. Their deposits are recently the most widespread throughout the Smrekovec volcanic complex.

Lithofacieses of volcanoclastic deposits were subdivided into four main groups (Kralj, 1997):

1. lithofacieses of autoclastic deposits and resedimented hyaloclastite deposits comprising sublithofacieses of hyaloclastite breccia, hyaloclastites, peperitic breccia, and peperites;
2. lithofacieses of assumed pyroclastic deposits;
3. lithofacieses of volcanic debris flow and turbidity ash flow deposits comprising sublithofacieses of polymict volcanoclastic breccia, volcanoclastic tuff-breccia, horizontally stratified coarse-grained tuffs, horizontally laminated and vaguely laminated fine-grained tuffs, and massive fine-grained tuffs;
4. lithofacieses of reworked turbidite ash deposits which comprise sublithofacieses of massive tuffaceous sandstone, through-cross stratified tuffaceous sandstone and massive tuffaceous sandstone.

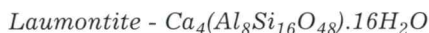
Zeolites and accompanying secondary minerals in the Smrekovec volcanics

Some of the volcanoclastic, autoclastic and coherent volcanic rocks have undergone the changes in mineralogy, characterised by the development of zeolites and other new-formed minerals: interlayered chlorite/smectite, albite, quartz, prehnite, pumpellyite, epidote, sphene, apophyllite, alkali feldspars and amphiboles (Kovič & Krošl - Kuščer, 1986; Kovič, 1988). They are abundantly developed on the contacts of high-level intrusive bodies with the enclosing sediments or in their vicinity. Particularly zeolitization was strongly controlled by porosity and permeability of sediments and is more pronounced in the coarser-grained volcanoclastics. This can easily be recognised in interbedded coarser- and finer-grained volcanoclastic rocks from the same profile: in coarser-grained varieties, laumontite, prehnite and pumpel-

lyite developed, whereas interbedded, well-sealed fine-grained volcaniclastics do not contain either laumontite or prehnite and pumpellyite.

Rock composition controlled the kind of zeolite developed, although to some extent only. Laumontite occurs in the rocks of various composition, from basaltic to rhyodacitic. It replaces the primary constituents (volcanic glass, fine-grained matrix or plagioclases) or infills interstitial space, voids or fissure systems. On the other hand, clinoptilolite and heulandite occur mainly in hyaloclastites of acid andesitic to dacitic composition replacing volcanic glass and infilling vesicles and the rock pore space. Analcime and thomsonite developed in some complexly altered rocks of basaltic to basaltic andesitic composition. Herein, analcime replaces formerly developed laumontite, and albitised plagioclases. Yugawaralite and stilbite are characteristic vein minerals, and do not seem to be influenced by the host rock composition.

Studies of zeolites and accompanying new-formed minerals in the Smrekovec volcanics are based on X-ray diffraction (determination of mineral composition of 94 powdered samples, and determination of cell parameters for 3 analcimes), petrographic investigation under the microscope (86 thin sections), elemental analysis by scanning electron microscope and energy dispersive X-ray spectrometry (30 zeolites and accompanying new-formed minerals), and combined chemical analysis - wet, atomic absorption spectrometry and emission spectrometry with inductively coupled plasma source (4 zeolite bearing rocks and 3 separated analcimes).



Laumontite is the most widespread new-formed zeolite in the Smrekovec volcanics. Very commonly, it can be encountered in veinlet systems (plate 1, fig. 1). It also infills vesicles of volcanic lithic fragments (plate 2, fig. 1, 2) and interstitial pore space (plate 2, fig. 3). Replacements of the primary constituents - pyrogenetic plagioclases (plate 2, fig. 4) or volcanic glass (plate 3, fig. 1, 2) are somewhat less abundant. In general, the amount of laumontite rarely exceeds 20 wt.% of the whole rock, even in the most extensively altered volcanics. The average laumontite content, determined by X-ray diffraction method in 48 of the laumontite-bearing rock samples, ranged between 5 and 15 wt.%. The accompanying new-formed minerals determined are quartz, albite, chlorite and interlayered chlorite/smectite, written in the order of descending abundance. The amounts of prehnite, sphene, pumpellyite, epidote or apophyllite were beyond the X-ray detection limits; these minerals can only be recognised under the microscope.

Laumontite crystals are very seldom transparent in a hand specimen (plate 1, fig. 1); most commonly they are earthy whitish. Crystal size ranges from some 10 μm up to 2 mm; the largest crystals formed in veins. Elemental analysis of ten laumontite samples by scanning electron microscope and energy dispersive X-ray spectrometry (SEM-EDX) revealed that laumontite may also contain small amounts (approx. up to 2 wt.%) of K_2O (fig. 2) besides calcium; sodium has not been detected in any of the examined samples.

Laumontite commonly replaces volcanic glass along with albite and quartz as accompanying new-formed minerals (plate 3, fig. 1, 2). Intergrowths of laumontite, albite and quartz are sometimes very fine-grained, detectable by X-ray diffraction only, although sometimes they may be recognised under the microscope, too. Replacements of volcanic glass by laumontite are often observed in hyaloclasts of autobrecci-

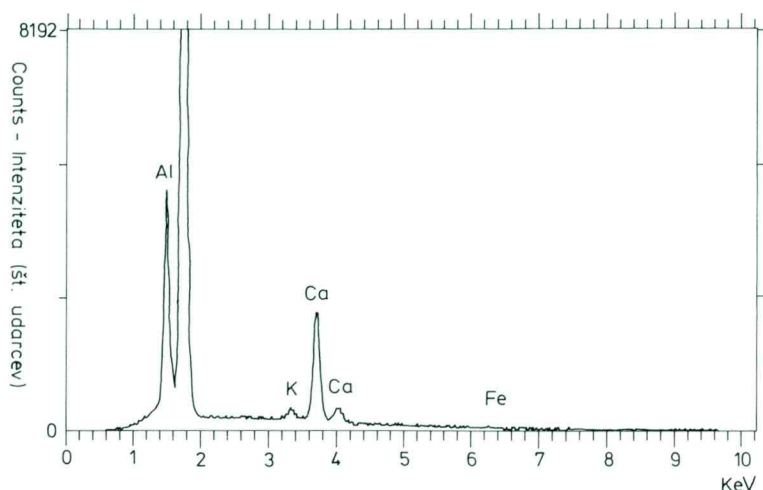


Fig. 2. Energy dispersive X-ray spectrum (EDX) yielding the major elements of laumontite (sample Sm 29, northern slopes of Smrekovec)

Sl. 2. Energijsko disperzijski spekter rentgenskih žarkov (EDX), na katerem so prikazane glavne prvine laumontita (vzorec Sm 29, severno pobočje Smrekovca)

ated lavas, high-level intrusive bodies and peperitic breccias. Rapid heat transfer from the emplaced high-level intrusive body into soft volcanoclastic sediments caused sudden increase in temperature of the enclosing sediments and their pore waters. Consequently, local hydrothermal conditions arised affecting predominantly marginal parts of the high-level intrusive body and the hyaloclasts of peperitic breccias. The laumontite-albite-quartz mineral assemblage commonly replaces spherical areas of hydrated volcanic glass produced by perlitic cracks (plate 3, fig. 1, 2).

Laumontite from the Smrekovec volcanics can also replace pyrogenetic plagioclases and alkali feldspars, although the majority of plagioclases is albitised. According to C o o m b s et al. (1959), laumontite replaces the anorthite component in plagioclases whereas the albite component alters to fine-grained aggregates of albite. Some of alkali feldspars are altered to laumontite and secondary alkali feldspars. The two new-formed minerals are not intimately intergrown but replace crystal grains in the form of irregular patches, attaining a few tenths of mm in length.

Microfissures developed in the Smrekovec volcanics are often infilled solely by laumontite (table 1) although veinlets containing besides laumontite also one or two other zeolites - i.e. analcime (plate 3, fig. 3, 4), stilbite, yugawaralite, or yugawaralite and analcime, can also be encountered. On the other hand, the prehnite association with laumontite is rather common, not only in veins, but also in interstitial infillings of volcanoclastic and autoclastic rocks (plate 1, fig. 3, 4; plate 2, fig. 3). Laumontite postdates and also replaces prehnite. This is a very exceptional relationship between the two minerals, since in burial environments where prehnite replaces laumontite, the situation is opposite (B o l e s & C o o m b s, 1975; 1977, T h o m p s o n, 1971). According to the activity diagram of phase relations for laumontite, heulandite and prehnite (B o l e s & C o o m b s, 1977), heulandite alters either to laumontite or

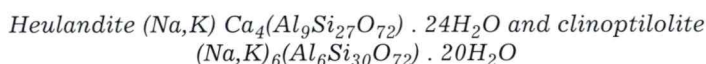
Table 1. X-ray powder pattern of laumontite

Tabela 1. Zapis rentgenske difrakcije vprašenega vzorca iz laumontitne žilice

d (Å)	I/I ₀	d (Å)	I/I ₀
9.42	100	2.882	13
6.88	30	2.803	6
6.22	4	2.649	3
5.06	5	2.579	11
4.73	23	2.539	5
4.50	9	2.466	7
4.17	63	2.445	16
3.782	3	2.366	17
3.675	19	2.274	6
3.517	36	2.220	5
3.411	3	2.155	14
3.367	4	2.092	3
3.276	28	2.036	2
3.204	14	1.961	9
3.156	22	1.890	2
3.047	23	1.852	5
2.952	2		

Sample (GN 38v) from a laumontite veinlet. Northern slopes of Komen;
 Philips diffractometer, Ni filtered CuK α radiation ($\lambda = 1.54051$), slits 1°,
 0.1 mm, 1°, scanning speed 1°/min

prehnite when the activity of hydrous silica $a_{\text{H}_4\text{SiO}_4(\text{aq})}$ decreases. Both reactions are strongly controlled by the activity ratio $a_{\text{Ca}^{2+}}/(a_{\text{H}^+})^2$. The reaction from laumontite to prehnite occurs unlikely in the presence of waters saturated with quartz, since silica is, along with water and the H^+ ions the reaction byproduct (Boles & Combs, 1977). Instability of prehnite and its conversion to laumontite evidenced in the Smrekovec volcanoclastic rocks could therefore be related to the decreased ratio $a_{\text{Ca}^{2+}}/(a_{\text{H}^+})^2$ in reacting solutions; additional favourable conditions might be the increased activity of hydrous silica $a_{\text{H}_4\text{SiO}_4(\text{aq})}$ and the decreased temperature of reacting solutions.



Heulandite and clinoptilolite form a continuous solid solution series along the join between the stoichiometric formulae given above (Mumpton, 1960; Gottardi & Galli, 1985). Heulandite, clinoptilolite and numerous members of the heulandite-clinoptilolite solid solution series altogether belong to the heulandite group; for this reason, the name heulandite may sometimes refer to the whole genus. For proper distinction of heulandite and clinoptilolite at least the thermal test of Mumpton (1960) must be applied.

Heulandite is very common in hydrothermally altered basic volcanics as vesicle and fissure filling. Sedimentary occurrences of heulandite with proper evidence are

rare. On the contrary, clinoptilolite is a very rare hydrothermal mineral and has been shown to be the main constituent of many sediments, and is hence much more abundant in the Earth's crust than heulandite (Gottardi & Galli, 1985).

In the Smrekovec volcanics heulandite replaces volcanic glass of acid andesitic composition, being accompanied by cristobalite/quartz and montmorillonite; it also infills pore space in the same rock. Heulandite has not been encountered as vesicle and fissure filling in the rocks of more basic composition; therein, laumontite is the predominant zeolite.

Common hostrocks of heulandite are resedimented hyaloclastites (plate 4, figs. 1, 3, 4) which also contain pumice lapilli and glassy, fine-grained matrix of similar composition. Plagioclases are fresh. The new-formed minerals are very fine-grained and can not be recognised under the microscope. Heulandite crystals sometimes attain up to some hundred μm (plate 3, fig. 1); smectite/montmorillonite occurs in globular aggregates having a few hundred μm in diameter (plate 3, fig. 1). Heulandite and cristobalite or microcrystalline quartz are intimately intergrown when replacing volcanic glass. Besides heulandite, very small amounts of analcime may locally occur. According to Mumpston (1960) clinoptilolite remains stable after being heated for twelve hours at 600°C , whereas the heulandite lattice collapses. X-ray diffraction patterns of four thermally treated samples have confirmed the presence of heulandite; in one of the samples solid solution heulandite-clinoptilolite with predominating heulandite component has been determined (figs. 3a, 3b).

Resedimented hyaloclastites with pumice lapilli occur in the form of scarce, small and isolated erosional remnants on the top of the mountain range from Komen to Smrekovec. They are also to be found along the southern and northern slopes of Komen, Krnes and Smrekovec, dipping outward from the top of Komen towards the southeast and northwest, respectively. In general, the hyaloclastites contain heulandite, heulandite-clinoptilolite, smectite and quartz. Locally, they can be found altered to laumontite, albite, quartz, interlayered chlorite/smectite and traces of analcime. The laumontite-albite-quartz-chlorite/smectite-(analcime) mineral assemblage occurring in the same rock layer as the heulandite-cristobalite/quartz-smectite could indicate the presence of the progressive zeolite reaction pattern: silicic andesitic/dacitic glass $\rightarrow$ clinoptilolite-cristobalite/quartz-smectite $\rightarrow$ (mordenite)-heulandite-analcime-cristobalite/quartz-smectite $\rightarrow$ laumontite-albite-quartz-interlayered chlorite/smectite. However, the relationship between laumontite and heulandite seems to be more complicated. In heulandite-bearing hyaloclastites, laumontite locally occurs in very small amounts being developed as the replacement of volcanic glass in larger hyaloclasts or as interstitial cement. Herein, laumontite was found to be partially replaced by clinoptilolite-heulandite (plate 4, fig. 2). Microscopic observation and X-ray analysis indicate the transformation can be either direct or related to prior alteration of laumontite to kaolinite or montmorillonite. The occurrence indicates that a post-hydrothermal process, diagenesis or halmyrolysis, must be superimposed on the earlier alteration.



Besides some subordinate occurrences of analcime developed during the progressive alteration of silicic andesitic or dacitic glass to heulandite, smectite and cristoba-

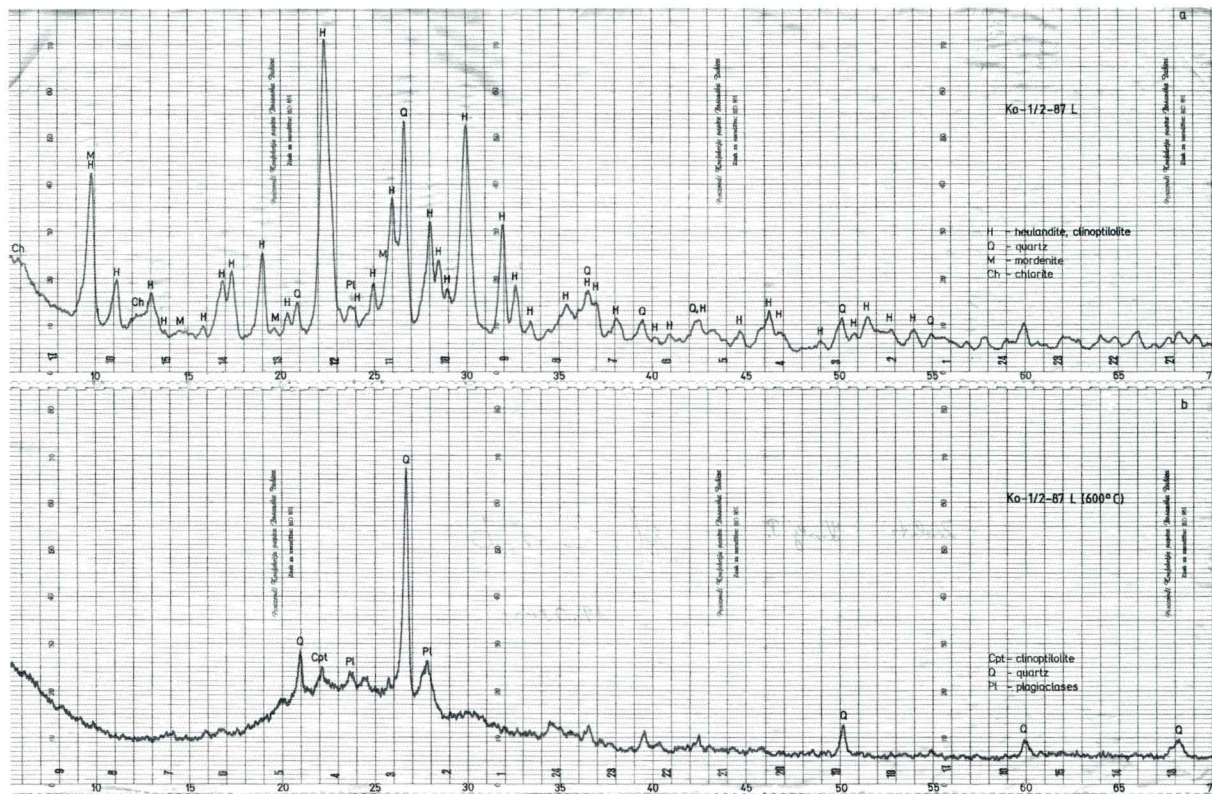


Fig. 3a. X-ray diffraction pattern of heulandite-clinoptilolite (sample Ko 1/2-87 L) before thermal treatment

Fig. 3b. X-ray diffraction pattern of heulandite-clinoptilolite (sample Ko 1/2-87 L) after being heated at 600°C for 12 hours. The heulandite lattice collapsed whereas clinoptilolite persisted. Analyst M. Mišič

Sl. 3a. Difraktogram trdne raztopine heulandita in klinoptilolita (vzorec Ko 1/2-87 L) pred termično obdelavo

Sl. 3b. Difraktogram trdne raztopine heulandita in klinoptilolita (vzorec Ko 1/2-87 L) po segrevanju na 600°C v trajanju 12 ur. Struktura heulandita se je porušila, struktura klinoptilolita pa se je ohranila tudi po segrevanju. Analitik M. Mišič

lite, analcime may also show very exceptional style of formation. In the northern slopes of Smrekovec, extensively altered autoclastic and volcanoclastic rocks occur containing up to 60% of analcime (plate 1, fig. 2). Herein, analcime replaces formerly developed laumontite and albitised plagioclases, and is accompanied by interlayered smectite/chlorite.

A complex alteration history leading to analcime development can be observed in a 50 metres thick profile in the northern slopes of Smrekovec. The early stage of alteration is characterised by an intrusion of basaltic andesite into volcanoclastic sediments. Andesite marginal parts were autobrecciated and autoclasts partially admixed to the enclosing sediments. A plagioclase-rich dyke of similar composition cuts the andesite. By contact metamorphism and hydrothermal activity related to the andesite emplacement laumontite extensively developed in the layer of autoclastic andesite along with albite, quartz, interlayered chlorite/smectite and traces of sphene. Small amounts of prehnite and pumpellyite also occur in this autoclastic layer that was situated immediately above the source of heat. Herein, pumpellyite may replace plagioclases along with albite and prehnite (plate 5, fig. 1, 2) or infills vesicles in autoclasts (plate 5, fig. 4). The laumontite-albite-quartz-chlorite/smectite mineral assemblage is developed above the andesite intrusive body for over 120 metres, up to the top of Smrekovec. However, the laumontite content in the section is fairly variable, but is generally much lower in volcanoclastic rocks (5-20 wt.%) than in the autoclastic layer where it may attain up to 50 wt.%. Interstratified fine-grained volcanoclastic rocks, even if situated in close vicinity of the intrusive andesite, contain only traces of zeolites, whereas plagioclases are completely albitised and the matrix replaced by interlayered chlorite/smectite.

This high-level intrusive body of basaltic andesitic composition is interrupted by another andesite body - probably a feeder dyke - which is of acidic andesitic composition. Analcime is closely related to this late-stage intrusion and predominantly follows previous alteration replacing laumontite. It is very localised in occurrence; at a distance of some 10 metres laterally from the intrusion, analcime becomes very scarce - often below the X-ray detection limit. Herein, incomplete replacements of laumontite by analcime are commonly encountered (plate 3, fig. 3, 4). Closer to the intrusion, analcime becomes more pronounced, replacing not only laumontite but also albitised plagioclases (plate 1, fig. 2). Analcime is particularly abundant in autoclastic rocks that previously underwent extensive laumontite alteration. The replacement of laumontite by analcime is accompanied by crystallisation of alkali feldspars (plate 5, fig. 3). The presence of alkali feldspars was confirmed by elemental analysis of seven analcime-rich samples by scanning electron microscope and energy dispersive X-ray spectrometry (fig. 4). As already mentioned, laumontite may also contain, besides calcium, small amounts (approx. up to 2 wt.%) of K_2O (fig. 2); during the reaction from laumontite to analcime, potassium might have been fixed by crystallisation of alkali feldspars. Together with alkali feldspars, up to 200 mµ sized exsolutions of thomsonite sometimes occur.

Chemical analyses of four analcime- or laumontite-bearing rocks important for interpretation of analcime occurrence in the Smrekovec volcanoclastics is shown in table 2. The rock samples no. 3 (Sm 34/51) and no. 4 (Sm 34/II) are texturally alike and also, similarly extensively altered. The only conspicuous difference is in the type of zeolite developed: the rock sample no. 3 contains analcime, and the rock sample no. 4, laumontite. It is very interesting that no obvious distinction between the abundances of major elements can be observed, although at least the difference in the sodium

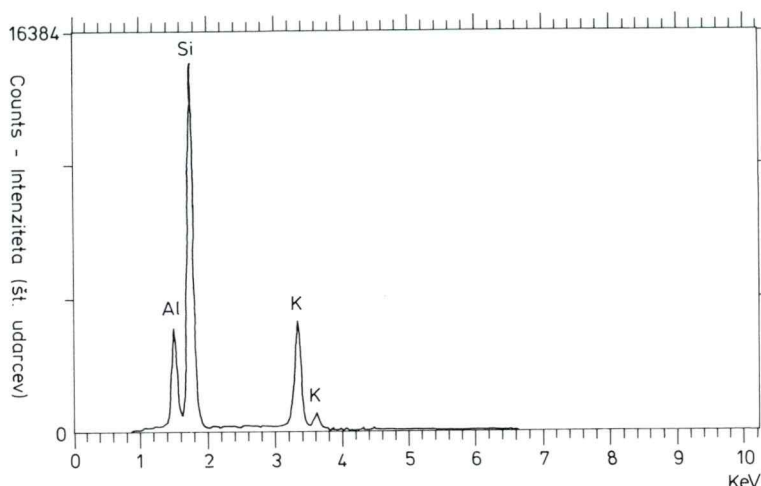


Fig. 4. Energy dispersive x-ray spectrum (EDX) yielding the major elements of alkali feldspar exsolutions in analcime (sample Sm 34 c)

Sl. 4. Energijsko disperzijski spekter rentgenskih žarkov (EDX), na katerem so prikazane glavne prvine alkalnega glinenca, ki je kristaliziral med nadomeščanjem laumontita po analcimu (vzorec Sm 34 c)

and calcium contents would be expected. The rocks could have undergone some ion exchange processes in interlayered smectite/chlorite clay minerals after crystallisation of zeolites.

Analcime has been separated almost completely from the bulk samples of extensively altered rocks by the use of heavy liquids. Three relatively pure analcime samples containing no other minerals detectable by X-ray diffraction were obtained. The analcime samples were investigated by the means of X-ray diffraction method (tables 3, 4, 5) and combined wet chemical analysis, atomic absorption spectrometry and optical emission spectrometry with inductively coupled plasma source (table 6). The results have shown that analcimes are cubic, low-silica and calcian varieties. No solid solution with wairakite (Aoki & Minato, 1980; Harada & Sudo, 1976) can be assumed.

The analcime occurrence bears evidence of a very complex alteration history of the Smrekovec volcanoclastic rocks. Analcime is superimposed on the earlier, laumontite yielding alteration, and is related to the late-stage emplacement of an acid andesite body - probably a feeder dyke. Experimental work on hydrothermal alteration of the Smrekovec volcanics (table 1, sample no. 1) performed by Barth-Wirsching (pers. comm.) indicates laumontite alters to analcime in closed or open system at the temperatures of above 150°C by action of sodium-bearing reacting solutions. Hydrothermal fluids responsible for the laumontite to analcime transformation could have been magmatic in origin but it is also possible that marine water from the sea-bottom became superheated when penetrating along the fissures opening the pathway of the ascending magma.

Table 2. Chemical composition of four analcime- or laumontite- bearing rocks
 Tabela 2. Kemična sestava štirih vzorcev kamenin, ki vsebujejo analcim ali laumontit

Element (wt. %)	Sample			
	1	2	3	4
SiO ₂	49.6	56.4	46.1	50.8
TiO ₂	0.88	0.9	0.7	0.9
Al ₂ O ₃	16.9	16.1	19.9	17.9
Fe ₂ O ₃	3.3	5.0	3.8	4.5
FeO	4.3	2.1	3.8	3.7
MnO	0.14	0.09	0.15	0.15
MgO	5.48	3.5	7.5	5.4
CaO	8.44	5.5	6.5	6.5
Na ₂ O	3.64	4.0	3.8	3.5
K ₂ O	0.19	1.0	1.1	1.5
P ₂ O ₅	0.13	0.18	0.05	0.05
L.O.I.	5.70	4.7	6.6	5.0
sum.	99.18	99.56	100.0	99.90

1. Ko-3, altered basaltic rock from northern slopes of Komen. Mineral composition, determined by X-ray diffraction method: laumontite (20-25%), albite (15-20%), interlayered chlorite/smectite (50-65%), quartz (<5%), K-feldspars in traces. Optically observer traces of prehnite and sphene
2. Sm 31a, altered coarse-grained volcanoclastic rock, northern slopes of Smrekovec. Mineral composition, determined by X-ray diffraction method: albite (35%), interlayered chlorite/smectite (20-30%), laumontite (20-30%), quartz (15-16%)
3. Sm 34/51, altered volcanoclastic rock, northern slopes of Smrekovec. Mineral composition determined by X-ray diffraction method: analcime (40-45%), interlayered chlorite/smectite (45-50%), quartz (<5%), albite in traces
4. Sm 34/II, altered autoclastic rock, northern slopes of Smrekovec. Mineral composition, determined by X-ray diffraction method: albite (35%), laumontite (20-25%), interlayered chlorite/smectite (35-45%), quartz (<5%)

Sample (Ko-3) was analysed in X-RAL Activation Services Inc., Ann Arbor, Michigan. Samples Sm 31a, Sm 34/51 and Sm 34/II were analysed in National Chemical Institute (KIBK), Ljubljana

Stilbite $\text{NaCa}_4(\text{Al}_9\text{Si}_{27}\text{O}_{72}) \cdot 30\text{H}_2\text{O}$ and *yugawaralite* $\text{Ca}_2\text{Al}_2\text{Si}_{12}\text{O}_{32} \cdot 8\text{H}_2\text{O}$

Stilbite and yugawaralite are typical hydrothermal zeolites (Gottardi & Galli, 1985). In the Smrekovec volcanics both stilbite (fig. 5a) and yugawaralite (fig. 5b) occur only as vein minerals, being always accompanied by laumontite. Stilbite commonly crystallises at lower temperatures than laumontite (Iijima, 1984; Boles & Combs, 1975; Liou, 1971a). Yugawaralite develops at higher temperatures than laumontite and in comparison with wairakite at lower pressures (Liou, 1971b).

In veins, yugawaralite and laumontite may also be accompanied by analcime. One of the veinlets containing yugawaralite, laumontite and analcime occurs in a fine-grained tuff which does not contain zeolites but is located in the vicinity of analcime-rich rocks. Immediately above the contact with tuff, a few mm thick layer of fine-grained laumontite and yugawaralite occurs. Above this layer, cubic crystals of anal-

Table 3. X-ray diffraction pattern of analcime (sample N 34 1/4 L)
 Tabela 3. Zapis rentgenske difrakcije vprašenega vzorca analcima, izdvojenega iz kamenine v težki tekočini (vzorec N 34 1/4 L)

d (Å)	I/I ₀	d (Å)	I/I ₀
6.82	5	1.87	7
5.59	46	1.83	1
4.84	10	1.74	14
3.66	6	1.71	4
3.42	100	1.68	5
3.23	2	1.66	2
2.92	44	1.60	2
2.79	5	1.59	5
2.69	13	1.50	2
2.50	13	1.48	3
2.42	6	1.46	2
2.28	1	1.45	2
2.22	8	1.41	5
2.16	2	1.41	3
2.12	1	1.39	2
1.94	1	1.37	3
1.90	11	1.36	6

Sample N 34 1/4 L, separated from altered volcanoclastic rock from northern slopes of Smrekovec; Philips diffractometer, Ni filtered CuK α radiation ($\lambda = 1.54051$), slits 1°, 0.1 mm, 1°, scanning speed 1°/min; cubic cell parameter $a = 13.1950$

cime developed; the analcime crystals are of approx. equal size of 2-3 mm. On the analcime crystals, fine-grained laumontite occurs. The described succession of vein zeolites indicates that laumontite crystallised before and after the analcime. Analcime, occurring between the layers of calcic zeolites seems to crystallise during short episode of sodium-yielding hydrothermal activity.

Zeolite formation in the Smrekovec volcanoclastic rocks

The occurrence of zeolites and other new-formed minerals in the Smrekovec volcanoclastics is rather complex. The most common zeolite is laumontite; heulandite, heulandite-clinoptilolite, analcime, yugawaralite, stilbite and thomsonite are subordinate and more localised in occurrence. The accompanying new-formed minerals are quartz, albite, chlorite, interlayered chlorite/montmorillonite, prehnite, pumpellyite, sphene, epidote, zoisite and apophyllite.

Laumontite is a common zeolite in different environments. Upon burial and contact metamorphism, it forms from a zeolite precursor - most frequently heulandite, but also mordenite or clinoptilolite (Coombs et al., 1959; Boles & Coombs, 1975; 1977; Iijima & Utda, 1966; Utda, 1973). On the other hand, hydrothermal genesis of laumontite, attributed to those crystals filling veins and fractures with no obvious reaction of the mineralising fluid with the wallrock, is also rather

Table 4. X-ray diffraction pattern of analcime (sample Sm 34/31)

Tabela 4. Zapis rentgenske difrakcije vprašenega vzorca analcima, izdvojenega iz kamenine v težki tekočini (vzorec Sm 34/31)

d (Å)	I/I ₀	d (Å)	I/I ₀
6.83	3	1.90	10
5.58	43	1.87	6
4.84	11	1.83	2
3.66	6	1.74	13
3.42	100	1.71	6
3.22	5	1.69	5
2.92	39	1.66	2
2.79	5	1.61	2
2.69	13	1.59	5
2.50	11	1.49	2
2.42	7	1.47	3
2.29	1	1.46	1
2.22	7	1.45	1
2.17	2	1.41	5
2.12	2	1.41	3
2.02	2	1.38	1
1.94	1	1.37	2
		1.35	6

Sample Sm 34/31, separated from altered volcanoclastic rock from northern slopes of Smrekovec; Philips diffractometer, Ni filtered CuK_α radiation ($\lambda = 1.54051$), slits 1°, 0.1 mm, 1°, scanning speed 1°/min; cubic cell parameter 13.7143

common (G o t t a r d i & G a l l i, 1985). For comparison of the laumontite occurrence in the Smrekovec volcanoclastics, the alteration upon contact metamorphism, encountered in Neogene sediments of Japan is particularly interesting. The following text is a very brief summary of the comprehensive work of U t a d a (1973).

Neogene sediments surrounding volcano-plutonic masses underwent complex changes in mineralogy related to contact metamorphic, diagenetic and hydrothermal alteration. According to the assemblages of new-formed minerals eight alteration zones were recognised. Higher-grade zones are completely metamorphic and comprise: the hornblende-plagioclase zone, the actinolite-plagioclase-chlorite zone, the prehnite-epidote-plagioclase-chlorite zone, and the chlorite-epidote-plagioclase-quartz zone. Lower-grade alteration zones comprising abundant zeolites are the following: the laumontite-chlorite-plagioclase-quartz zone, the analcime-heulandite-chlorite-montmorillonite-quartz zone, the mordenite-montmorillonite-opal/quartz or the clinoptilolite-mordenite-montmorillonite-opal zone, and the zone of altered volcanic glass, montmorillonite and opal. The laumontite-bearing zone commonly spreads in the outer areas apart from the intrusive mass but sometimes it also immediately surrounds intrusive bodies of small sizes. Laumontite replaces plagioclase phenocrysts, fine-grained matrix and groundmass of various rocks, and is interspersed with other new-formed minerals. It also occurs in druses and as a vein mineral. The original rock texture is relatively well preserved.

Table 5. X-ray diffraction pattern of analcime (sample Sm 34/60 L)
 Tabela 5. Zapis rentgenske difrakcije vprašenega vzorca analcima, izdvojenega iz kamenine v težki tekočini (vzorec Sm 34/60 L)

d (Å)	I/I ₀	d (Å)	I/I ₀
6.83	3	1.87	8
5.59	48	1.83	1
4.84	11	1.74	14
3.66	7	1.71	5
3.43	100	1.69	6
3.22	4	1.66	2
2.06	2	1.62	3
2.92	47	1.60	4
2.79	6	1.49	3
2.69	14	1.48	3
2.50	14	1.46	1
2.42	7	1.45	2
2.28	2	1.44	2
2.22	9	1.41	5
2.17	2	1.39	1
2.12	2	1.38	1
2.02	2	1.37	2
1.90	11	1.36	7

Sample Sm 34/60 L, separated from altered volcanoclastic rock from northern slopes of Smrekovec; Philips diffractometer; Ni filtered CuK α radiation ($\lambda = 1.54051$), slits 1°, 0.1 mm, 1°, scanning speed 1°/min; cubic cell parameter 13.7231

In the Smrekovec volcanoclastics laumontite is the most widespread zeolite, developed as interstitial filling, a vein mineral or replacement of volcanic glass and plagioclases. The average laumontite content in altered volcanoclastic rocks rarely exceeds 20 wt.% of the bulk composition. The replacements of volcanic glass and pyrogenetic plagioclases are more localised in occurrence and related to the proximity of high-level intrusive bodies. The degree of zeolitisation is also strongly dependent on porosity and permeability of the host-rock; this relationship is the most obvious in the sections, composed of interbedded coarse-grained rocks containing abundant zeolites, and fine-grained tuffs which lack of zeolites, except for fissure fillings.

Laumontite and other zeolites show no obvious zonal arrangement. Away from extensively altered rocks encountered in close vicinity of high-level intrusive bodies, laumontite-cemented volcanoclastics grade into the rocks in which zeolites do not occur any more, not even as vein minerals. The only occurrence which could indicate the presence of two possible zones with defined progressive reaction pattern, is related to resedimented hyaloclastites spreading from the top of Komen towards the south-east and north-west. The hyaloclastites are generally altered to heulandite, heulandite-clinoptilolite, quartz and montmorillonite. Locally, laumontite, albite, quartz and interlayered chlorite/montmorillonite are encountered in the same type of rocks; due to extensive erosion of hyaloclastites it is uncertain whether the two alteration patterns occur in exactly the same layer. In heulandite-bearing rocks, scarce remains

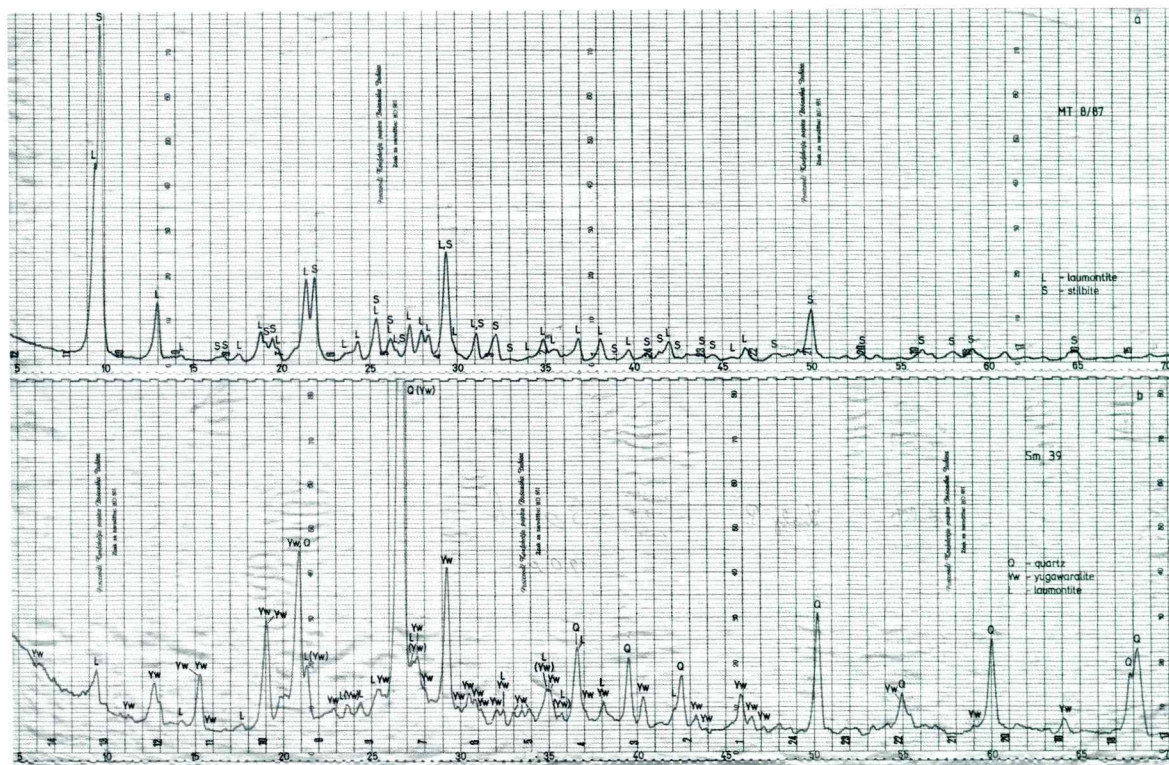


Fig. 5a. X-ray diffraction pattern of stilbite and laumontite from a veinlet in a fine-grained tuff (sample MT-8/87)

Fig. 5b. X-ray diffraction pattern of yugawaralite, laumontite and quartz from a veinlet in a fine-grained tuff (sample Sm 39). Quartz is not an associated vein mineral. Investigations by scanning electron microscopy revealed that quartz originates from siliceous algae living in a creek the sample was taken from

Sl. 5a. Difraktogram stilbita in laumontita iz žilice v drobnnozrnatem tufu (vzorec MT-8/87)

Sl. 5b. Difraktogram yugawaralita, laumontita in kremenja iz žilice v drobnnozrnatem tufu (vzorec Sm 39). Kremen ni paragenetski mineral; raziskave vzorca z vrstičnim elektronskim mikroskopom so pokazale, da izvira kremen iz kremenovih alg, ki naseljujejo dno potoka, ob katerem je bil vzorec odvzet

Table 6. Analcimes: chemical composition, formulae on the basis of 96 oxygens and lattice constants in Å

Tabela 6. Analcimi: kemična sestava, formule na osnovi 96 kisikov ter mrežne konstante v Å

Element (wt. %)	Sample		
	1	2	3
SiO ₂	54.0	53.9	54.1
Al ₂ O ₃	23.1	21.9	21.9
Fe ₂ O ₃	0.6	0.6	0.6
MgO	0.5	0.4	0.4
CaO	2.1	2.3	2.2
Na ₂ O	9.9	10.0	10.5
K ₂ O	0.5	0.5	0.5
H ₂ O ⁻	0.2	0.5	0.2
H ₂ O ⁺	8.7	9.3	9.1
sum.	99.9	99.4	99.5
Si	31.86	32.28	32.33
Al	16.06	15.46	15.45
Fe	0.26	0.27	0.26
Mg	0.65	0.36	0.32
Ca	1.29	1.47	1.31
Na	11.32	11.61	12.61
K	0.38	0.38	0.39
H ₂ O	17.0	18.3	17.9
E %	4.7	0.5	0.6
Si/Al	1.98	2.08	2.09
Si+Al+(Fe ³⁺)	48.12	48.1	48.3
Na+K+2Ca	14.28	14.93	15.17
D	2.582	2.579	2.584
a	13.7195	13.7143	13.7231
b	13.7195	13.7143	13.7231
c	13.7195	13.7143	13.7231
$\gamma=\beta=\alpha$	90.000	90.000	90.000

1. Sample N34 1/4L, separated analcime from volcanoclastic rock from northern slopes of Smrekovec. Chemical formula: (Na+K+2Ca)_{14.28} Al_{16.06} Si_{31.86} O₉₆ · 17 H₂O
2. Sample 34/31 2L, separated analcime from volcanoclastic rock from northern slopes of Smrekovec. Chemical formula: (Na+K+2Ca)_{14.93} Al_{15.46} Si_{32.28} O₉₆ · 18.3 H₂O
3. Sample 34/60 L, separated analcime from volcanoclastic rock from northern slopes of Smrekovec. Chemical formula: (Na+K+2Ca)_{15.17} Al_{15.45} Si_{32.33} O₉₆ · 17.3 H₂O

Chemical analyses were performed in National Chemical Institute (KIBK) in Ljubljana. Cell dimensions were determined in University of Belgrade, Faculty for Mining and Geology, Yugoslavia

of laumontite occur being extensively replaced by clinoptilolite-heulandite. This relationship between the two minerals would hardly justify the progressive reaction pattern and the existence of zonal arrangement of zeolites. It strongly suggests that

other mechanisms - diagenesis or halmyrolysis - must have operated after the hydrothermal stage of alteration.

Yugawaralite is a vein mineral genetically related to crystallisation from hydrothermal fluids. Stilbite is very common hydrothermal zeolite although it can also be encountered in burial environments as is the case in Taringatura Hills, New Zealand (Boles & Combs, 1975; 1977). Analcime in the Smrekovec volcanoclastics is of hydrothermal origin formed during late-stage emplacement of a high-level intrusive body - most probably a feeder dyke.

If the zeolite occurrence in the Smrekovec volcanoclastics is compared with the previously described contact metamorphic alteration, it can be concluded that higher-grade metamorphic zones are missing. Zeolites do not show any obvious zonal arrangement although an enhanced rock alteration in close vicinity of the outcrops of high-level intrusive bodies suggests their emplacement must have been instrumental in the development of laumontite and other zeolites but was probably too small to produce zonation recognisable on larger scale. On the other hand, laumontite and heulandite locally replace volcanic glass indicating the precipitation from hydrothermal fluids could not have been the only mechanism responsible for the zeolite development.

Conclusions

The Smrekovec volcanoclastic rocks underwent alteration characterised by the development of zeolites and related silicate minerals: albite, quartz, chlorite and interlayered chlorite/smectite. Laumontite is the most widespread in occurrence; heulandite, heulandite-clinoptilolite and analcime may locally be abundant whereas stilbite and yugawaralite can be encountered only as vein minerals. Laumontite developed as replacement of the primary constituents - volcanic glass, pyrogenetic plagioclases and a fine-grained matrix, and as abundant interstitial filling and a vein mineral. Heulandite and heulandite-clinoptilolite occur abundantly in resedimented hyaloclastites of acid andesitic to dacitic composition. Herein, they replace volcanic glass and infill vesicles in glassy hyaloclasts or pumice lapilli. Analcime-rich rocks are very localised in occurrence. Herein, analcime replaces previously developed laumontite, and rarely also albitised plagioclases. It formed during the late-stage emplacement of a dyke into already lithified and altered volcanoclastic rocks.

Zeolites developed in the Smrekovec volcanoclastics, their occurrence and association with prehnite and pumpellyite indicate their formation to be closely related to local hydrothermal conditions generated in water-saturated sediments by emplacement of high-level intrusive bodies. These intrusives were obviously too small sources of heat to produce zonation on kilometre scale as encountered in contact metamorphic settings.

Quartz, interlayered chlorite/smectite and albite are widely developed throughout the Smrekovec volcanic complex, irrespective of finer- or coarser-grained texture of volcanoclastic rocks, their position or zeolite content. For this reason, they could have also developed upon shallow burial diagenesis.

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Zeoliti v vulkanoklastičnih kamninah smrekovškega podgorja

Uvod

Piroklastičen material se je potem, ko je bil odložen na zemljini površini, hitro spreminjal, saj so temperature in tlaki v novem okolju mnogo nižji kot tisti, ki je v njem nastajala magma. Predvsem vulkansko steklo se zelo hitro hidratizira, še posebej, če je bil piroklastični material odložen na jezerskem ali morskem dnu. Reakcijam hidratacije sledijo spremembe v mineralni sestavi tako, da začno kristalizirati glineni minerali, opal, odvisno od danih okoliščin pa tudi zeoliti.

Ker sedimentacijsko okolje ni statično, temveč se nenehno spreminja, se tudi vulkanski material prilagaja novim kemičnim in fizikalnim razmeram. Pri tem je kinetika reakcij navadno počasnejša od hitrosti sprememb v okolju. Zato lahko - sicer v nekaterih danostih tlaka, temperature in kemične sestave delujočih fluidov - nestabilni minerali zelo dolgo obstanejo kot metastabilne faze. Značilni minerali te vrste so prav zeoliti, ki lahko obstajajo kot metastabilni celo več milijonov let.

Če se piroklastični sediment, v katerem so se že pričele spremembe, začne pogrezati ali pa je izpostavljen hidrotermalnemu delovanju, visokemu termičnemu ali kemičnemu gradientu, postanejo prej obstojni avtigeni minerali neobstojni. Namesto njih prične kristalizirati drugi, ki so bolj prilagojeni novim razmeram v okolju. Pri tem lahko nekatere faze dosežejo v danih okoljih termodinamično ravnotežje, druge pa ne, vendar kljub temu lahko obstajajo še naprej kot metastabilne faze. V okolju diagenetice tonjenja se spremembe tlaka, temperature in sestave porčnih raztopin spreminjajo sorazmerno počasi. Zato nastajajo in obstajajo določene združbe zeolitov in drugih avtigenih mineralov v bolj ali manj debelih slojih, imenovanih zone zeolitov (Coombs et al., 1959; Kossovskaya & Shutov, 1961; Iijima & Ueda, 1966; Boles & Coombs, 1975; 1977). V okoljih, kjer se pojavlja hidrotermalno delovanje, pa so nihanja v temperaturi in predvsem v sestavi delujočih fluidov znatna in so zato zone zeolitov le malokje razvite (Iijima, 1984), razen na kontaktih globočnin in sedimentov v geosinklinalnih območjih (Ueda, 1973).

Zeoliti so hidratizirani alumosilikati alkalnih in zemljoalkalnih kovin in so najbolj razširjeni avtigeni minerali v piroklastičnih sedimentih (Ueda, 1987). Nastajajo v številnih geoloških okoljih in zaradi različnih procesov: s površinskim preperevanjem vulkanskega pepela alkalne sestave, v slanih-alkalnih jezerih (zaprti hidrološki sistemi), v odprtih hidroloških sistemih zaradi pronicanja meteornih vod, s halmirolizom vulkanskega stekla na dnu oceanov, pri diageneti tonjenja in v hidrotermalno aktivnih sistemih (Iijima, 1984). Združbe zeolitov, ki pri tem nastajajo, so odvisne od

temperature, tlaka, sestave delujočih raztopin, sestave prikamnine in pogosto tudi njene poroznosti in permeabilnosti.

Geološko okolje smrekovških vulkanoklastitov

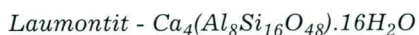
Smrekovško podgorje (sl. 1) grade zgornjeoligocenske vulkanske kamnine, v katerih se pojavljajo zeoliti in drugi avtigeni minerali. Raztezajo se na površini približno petnajst kvadratnih kilometrov in predstavljajo osrednji del obsežnejšega vulkanskega pasu, imenovanega tudi smrekovška serija (Mioč, 1978; 1983; Mioč et al., 1986). Najvišje se vzpenjajo vrhovi Komen (1684), Krnes (1613) in Smrekovec (1577). Zgornjeoligocenska starost predornin je določena na osnovi foraminiferne favne, vsebovane v meljastih sedimentih podlage (Rijavec, 1966).

Vulkanizem je pričel delovati v morskem okolju, kjer je nastal vulkanski masiv z enim ali več stratovulkanov in izrazitim pozitivnim reliefom. Sestava magme se je zaradi frakcijske kristalizacije bazaltne taline s časom spreminjala od bazaltne prek bazaltne andezitne in kisle andezitne do dacitne in tako ustvarila vulkanski diferenciacijski niz.

Smrekovške vulkanoklastične kamnine obsegajo tri glavne zvrsti - avtoklastične kamnine s presedimentiranimi hialoklastiti, vulkanoklastične debrite in turbidite ter lokalno presedimentirane sedimente vulkanoklastičnih turbiditov. Za pojav zeolitizacije so najpomembnejše plitve intruzije magme v vlažne, še nekonsolidirane sedimente, saj so le-te predstavljale glavni izvor toplote, zaradi katere so se porne vode v vlažnih sedimentih segrele in povzročile kristalizacijo zeolitov.

Zeoliti v vulkanoklastičnih smrekovškega podgorja

Zeolite in druge avtogene minerale smo preiskovali z različnimi metodami: z mikroskopijo v presewni polarizirani svetlobi, kjer sem pregledala 86 zbruskov; z rentgensko difrakcijo 94 vprašenih vzorcev, z elektronsko mikroskopijo, kombinirano z energijsko-disperzijskim spektrometrom rentgenskih žarkov (SEM-EDX), kjer smo pregledali 30 vzorcev in s kemično analizo (kombinirana mokra analitska metoda, atomska absorpcijska spektroskopija in emisijska spektroskopija z induktivno sklopljeno plazmo), kjer smo analizirali 4 vzorce kamnine in 3 vzorce separiranega analcima.

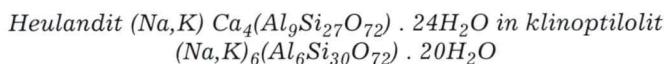


Med zeoliti v vulkanoklastičnih kamninah smrekovškega podgorja je najbolj razširjen laumontit. Pojavlja se kot žilni mineral (tabla 1, sl. 1), zapolnitev votlinic plinskih mehurčkov (tabla 2, sl. 1, 2) ali kot porni cement (tabla 2, sl. 3). Lahko pa nadomešča tudi plagioklaze (tabla 2, sl. 4), vulkansko steklo (tabla 3, sl. 1, 2) in drobnozrnato tufsko osnovo. Kot žilni mineral ali porni cement se pogosto pojavlja sam, včasih pa ga spremljajo tudi stilbit, yugawaralit, analcim (tabla 3, sl. 3, 4) ali prehnit (tabla 1, sl. 3, 4). V kamninah je njegova zastopanost običajno skromna, saj le redkokje presega 20 mas.% celotne kamnine. Najpogostejši minerali, ki v vulkanoklastičnih smrekovškega podgorja spremljajo laumontit, so albit, kremen, klorit in glineni minerali vrste klorit/montmorillonit. V slednjih količinah je pogosto prisoten sfen, pone-

kod pa se pojavljata tudi prehnit in pumpellyit. Prav pojav prehnita z laumontitom je zelo neobičajen, saj v vulkanoklastitih smrekovskega podgorja laumontit ne le da je kristaliziral kasneje kakor prehnit, temveč ga tudi nadomešča (tabla 1, sl. 3, 4). V okolju diagenese tonjenja prehnit nadomešča laumontit. Iz diagrama stabilnosti heulandita, laumontita in prehnita (Boles & Combs, 1977) je mogoče nakazati, da bi morda iz prehnita retrogradno lahko nastajal laumontit ob povišani aktivnosti kremenice $a_{\text{H}_4\text{SiO}_4(\text{aq})}$ in zmanjšanjem razmerju aktivnosti kalcijevih in vodikovih ionov $a_{\text{Ca}^{2+}}/(a_{\text{H}^+})^2$.

Raziskave z vrstičnim elektronskim mikroskopom, kombiniranim z energijsko-disperzijskim spektrometrom rentgenskih žarkov (SEM-EDX) so pokazale, da vsebujejo nekatera kristalna zrna laumontita poleg kalcija tudi manjše količine kalija (sl. 2).

Laumontit lahko nadomešča tudi vulkansko steklo; tedaj nastajata poleg laumontita še albit in kremen. Nadomeščanja vulkanskega stekla po laumontitu, albitu in kremenu so manj pogosta in so vezana na bližino plitvo ležečih intruzivov, kjer je bila temperatura dovolj visoka. Spremembe je mogoče opazovati v robnih, avtoklastičnih delih intruzivov, kjer nadomestimo avtoklaste andezita z različno stopnjo spremenjenosti steklaste osnovne mase.



Med heulanditom in klinoptilolitom obstaja cel niz trdnih raztopin (Gottardi & Galli, 1985). Ime heulandit se najpogosteje nanaša na celotno skupino, sicer pa oba končna člena niza trdnih raztopin ni mogoče ločiti samo z rentgensko difrakcijsko metodo, temveč je treba vpeljati vsaj termični test - po Mumptonu (1960). Po segrevanju vzorca na 600°C se struktura heulandita poruši, klinoptilolit pa ostane kot nespremenjena kristalna faza tudi po toplotni obdelavi.

V vzorcih vulkanoklastitov smrekovskega podgorja smo našli heulandit in trdno raztopino heulandita in klinoptilolita (sl. 3a, 3b). Toplotno obdelane vzorce je analiziral M. Mišič iz Inštituta za geologijo, geotehniko in geofiziko v Ljubljani. Heulandit in trdna raztopina heulandita in klinoptilolita se pojavljata v presedimentiranih hialoklastitih, kjer nadomeščata vulkansko steklo in zapolnjujeta prazne prostore v kamnini. Spremljajoča avtigena minerala sta montmorillonit in kristobalit (ponekod tudi mikrokristalni kremen). Plagioklazi so sorazmerno sveži. Zanimivo je, da se v istem tipu kamnine pod vrhom Komna, kjer izdanja andezit, pojavljajo kot avtigeni minerali laumontit, albit, kremen in glineni minerali z zmesno strukturo vrste klorit/montmorillonit. Ti dve združbi avtigenih mineralov bi torej lahko predstavljali progradni reakcijski niz oziroma dve zoni zeolitov.



Poleg manjših količin analcima, ki spremlja zeolitizirane presedimentirane hialoklastite, izdanjajo na severnem pobočju Smrekovca tudi kamnine, ki vsebujejo do 60 mas.% analcima (tabla 1, sl. 2). Pojav analcima v teh kamninah je zelo nenavaden, kajti analcim nadomešča predhodno nastali laumontit, tu in tam pa tudi albitizirane plagioklaze (sl. 4; tabla 5, sl. 1, 2). Obseg z analcimom bogatih kamnin je prostorsko zelo omejen. Pojav analcima je vezan na kasnejšo intruzijo kislega andezita - verje-

tno dovodnega dyka v že spremenjeno kamnino. Glede na nadomeščanja kalcijskega zeolita laumontita z natrijskim zeolitom analcimom so morale biti delujoče raztopine bogate z natrijem. Eksperimentalno delo na vzorcih s smrekovškega podgorja, ki smo ga opravili s sodelavci Tehniške visoke šole v Gradcu (Barth-Wirsching, osebna komunikacija), je te domneve potrdilo. Analcim je nastajal iz laumontita v odprtem in zaprtem sistemu pri temperaturah, višjih od 150°C.

Kemična sestava preiskanih vzorcev analcima (tabela 6) je pokazala, da pripadajo nizkosilicijskemu kalcijскому tipu kubične strukture. Tako je izključena možnost, da bi analcim predstavljal trdno raztopino analcima in wairakita.

Stilbit $\text{NaCa}_4(\text{Al}_9\text{Si}_{27}\text{O}_{72}) \cdot 30\text{H}_2\text{O}$ in yugawaralit $\text{Ca}_2\text{Al}_2\text{Si}_{12}\text{O}_{32} \cdot 8\text{H}_2\text{O}$

Yugawaralit in stilbit sta značina hidrotermalna zeolita, četudi se stilbit lahko pojavlja tudi v okolju diagenese tonjenja (B o l e s & C o o m b s, 1975). Nastanek stilbita je navadno vezan na temperature, ki so nižje kakor za laumontit (I i j i m a, 1984; L i o u, 1971 a). Yugawaralit pa nastaja pri temperaturah, ki so višje kakor za laumontit; glede na wairakit kristalizira pri nižjih tlakih (L i o u, 1971 b).

V vulkanoklastitih smrekovškega podgorja dobimo stilbit in yugawaralit navadno v žilicah skupaj z laumontitom (sl. 5a, 5b). Blizu izdankov z analcimom bogatih kamnin so tudi žilice, kjer najdemo ob prikamnini yugawaralit z laumontitom nad njim še analcim in nato laumontit. Zaporedje mineralov v teh žilicah kaže na to, da so bili procesi zeolitizacije zelo zapleteni.

Nastanek zeolitov v vulkanoklastitih smrekovškega podgorja

Pojav zeolitov v vulkanoklastitih smrekovškega podgorja kaže, da je njihov izvor predvsem hidrotermalen. Hidrotermalne razmere so ustvarile intruzije andezitne mame v še nekonsolidirane, z vodo prepojene sedimente. Najmočnejše so kamnine spremenjene prav v bližini takšnih intruzivnih teles, kjer laumontit, skupaj z albitom in kremenom, nadomešča tudi vulkansko steklo in drobnozrnato tufsko osnovo. Ti intruzivi so nastali v sklopu vulkanskega delovanja, s katerim je nastal kompleks stratovulkana pa so bili ali premajhni ali tudi preplitvo ležeči, da bi lahko povzročili kontaktno metamorfne spremembe večjih, kilometrskih razsežnosti.

Kremen, albit in glineni minerali z zmesno strukturo vrste klorit/montmorillonit so močno razširjeni v vseh kamninah smrekovškega vulkanskega kompleksa ne glede na njihovo bolj ali manj debelozrnato strukturo, lego ali vsebnost zeolitov. Zato je verjetno, da so vsaj deloma nastali med zgodnjo diagenozo tonjenja.

Zahvala

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Plate 1 - Tabla 1

Fig. 1. A laumontite veinlet system in andesite from Vranji Vrh

Sl. 1. Sistem žilic laumontita v andezitu z Vranjega Vrha

Fig. 2. Analcime (A) replacing laumontite and a plagioclase feldspar grain (F). Crossed nicols, magnification 66 ×

Sl. 2. Analcim (A), ki nadomešča laumontit in zrno plagioklaza (F). Pogled med navzkrižnimi nikoli, povečano 66 ×

Fig. 3. Laumontite (L) and prehnite (P) as cementing minerals in a coarse-grained volcanoclastic rock. Plane polarised light, magnification 53 ×

Sl. 3. Laumontit (L) in prehnit (P) kot cement v debelo-zrnati vulkanoklastični kamenini. Presečna polarizirana svetloba, povečano 53 ×

Fig. 4. The same as in the previous photo, under crossed nicols

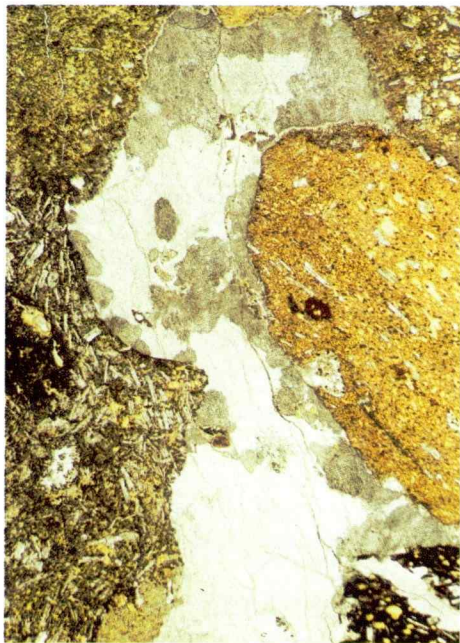
Sl. 4. Enako kot na prejšnji sliki, med navzkrižnimi nikoli



1



2



3



4

Plate 2 - Tabla 2

Fig. 1. Laumontite infilling a vesicle (larger one) in a lithic fragment. Plane polarised light, magnification 66 ×

Sl. 1. Laumontit, ki zapolnjuje votlinico plinskega mehurčka v litičnem drobcu. Presevna polarizirana svetloba, povečano 66 ×

Fig. 2. The same as in the previous photo, under crossed nicols

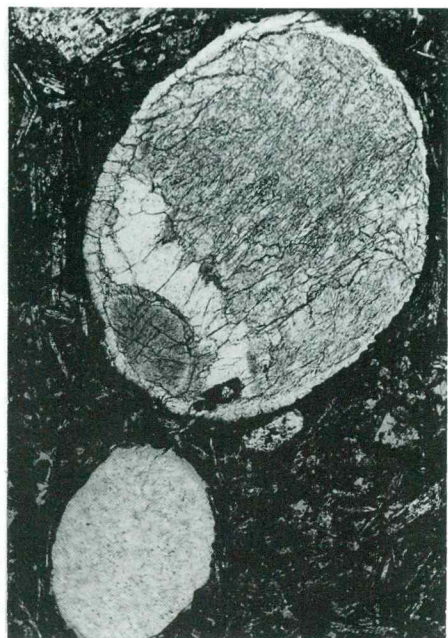
Sl. 2. Enako kot na prejšnji sliki, med navzkrižnimi nikoli

Fig. 3. Laumontite (L) and prehnite (P) as interstitial filling. Crossed nicols, magnification 66 ×

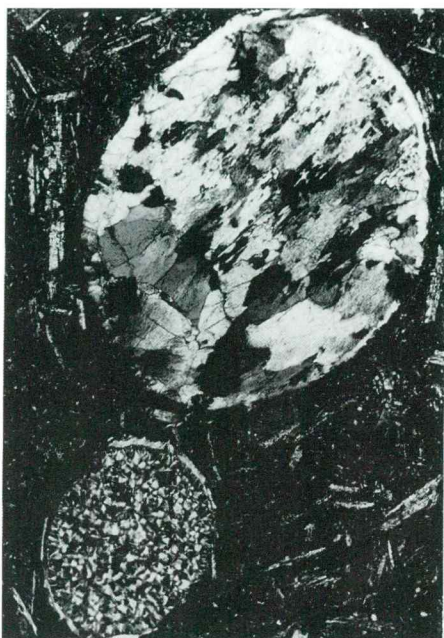
Sl. 3. Laumontit (L) in prehnit (P) kot zapolnitev medzrnskega prostora. Pogled med navzkrižnimi nikoli, povečano 66 ×

Fig. 4. Laumontite (L) and albite (F) replacing a plagioclase feldspar grain. Crossed nicols, magnification 53 ×

Sl. 4. Laumontit (L) in albit (F), ki nadomeščata zrno plagioklaza. Pogled med navzkrižnimi nikoli, povečano 53 ×



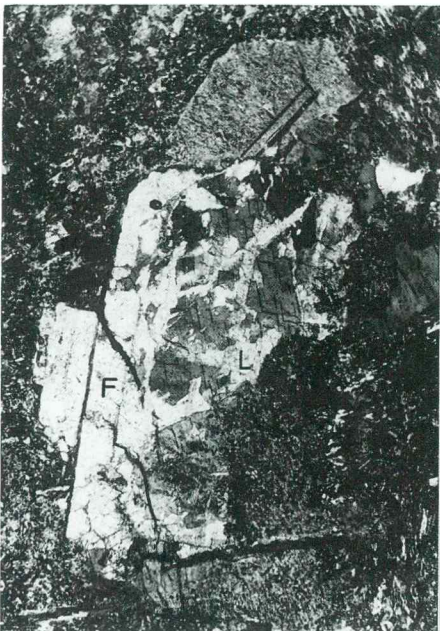
1



2



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4

Plate 3 - Tabla 3

Fig. 1. Laumontite (L) replacing volcanic glass in a lithic fragment with perlitic texture. Plane polarised light, magnification $53\times$

Sl. 1. Laumontit (L), ki nadomešča vulkansko steklo v litičnem drobcu s perlitsko strukturo. Presevna polarizirana svetloba, povečano $53\times$

Fig. 2. The same as in the previous photo, under crossed nicols

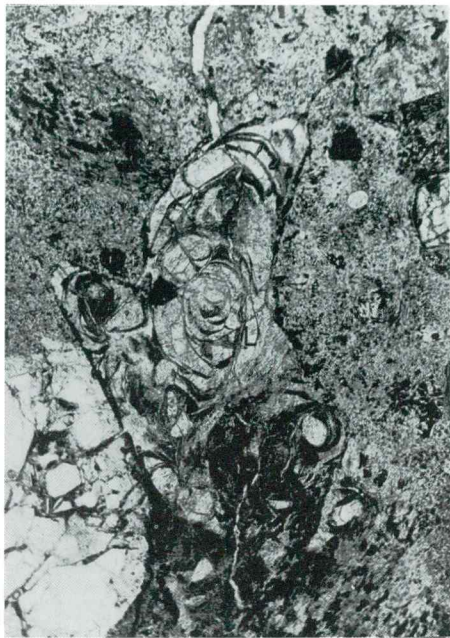
Sl. 2. Enako kot na prejšnji sliki, med navzkrižnimi nikoli

Fig. 3. Laumontit from a veinlet. Plane polarised light, magnification $66\times$

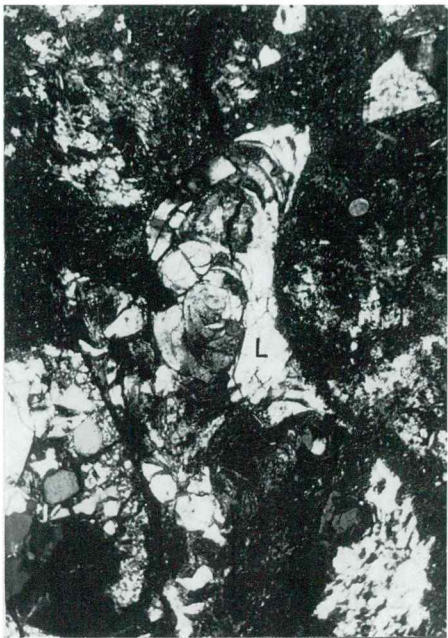
Fig. 3. Laumontit v žilici. Presevna polarizirana svetloba, povečano $66\times$

Fig. 4. The same as in the previous photo, under crossed nicols. Analcime (A) replaces laumontite

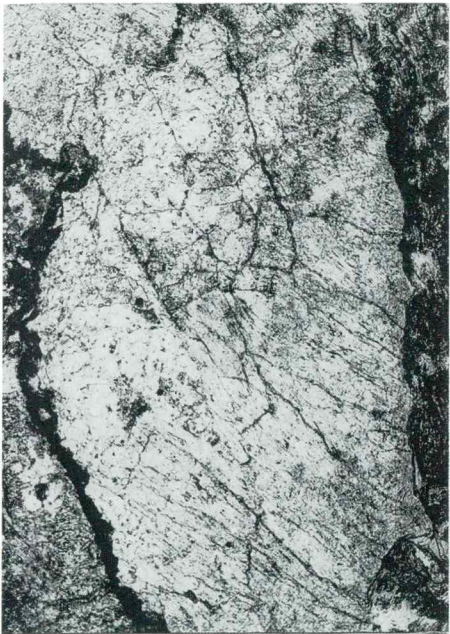
Sl. 4. Enako kot na prejšnji sliki, med navzkrižnimi nikoli. Analcim (A) nadomešča laumontit



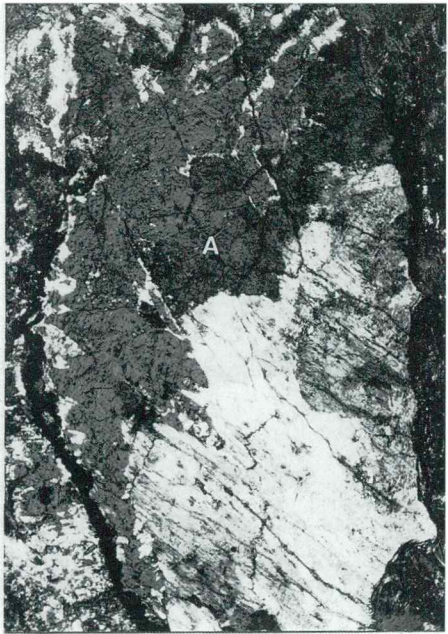
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Plate 4 - Tabla 4

Fig. 1. Heulandite (H) infilling vesicle in a pumice lapillus and replacing volcanic glass. Dark-coloured spherical aggregates are composed of montmorillonite. Plane polarised light, magnification 53 ×

Sl. 1. Heulandit (H), ki zapolnjuje votlinice plinskih mehurčkov in nadomešča vulkansko steklo. Temni kroglasti skupki sestojijo iz montmorillonita. Presevna polarizirana svetloba, povečano 53 ×

Fig. 2. Heulandite (H) replacing laumontite (L) in a glassy fragment. Crossed nicols, magnification 85 ×

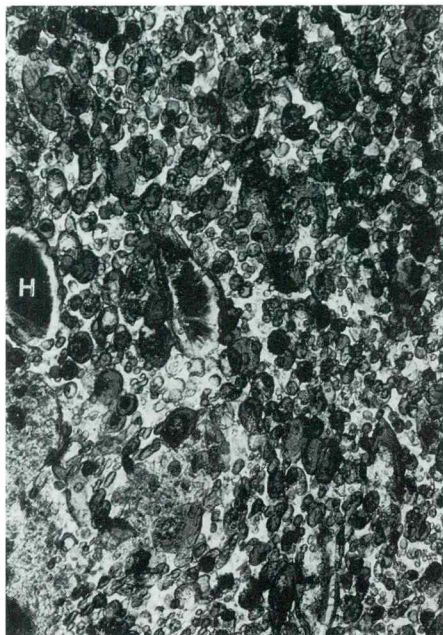
Sl. 2. Heulandit (H), ki nadomešča laumontit (L) v steklastem drobcu. Pogled med navzkrižnimi nikoli, povečano 85 ×

Fig. 3. Heulandite (H) replacing a fine-grained matrix. Plane polarised light, magnification 66 ×

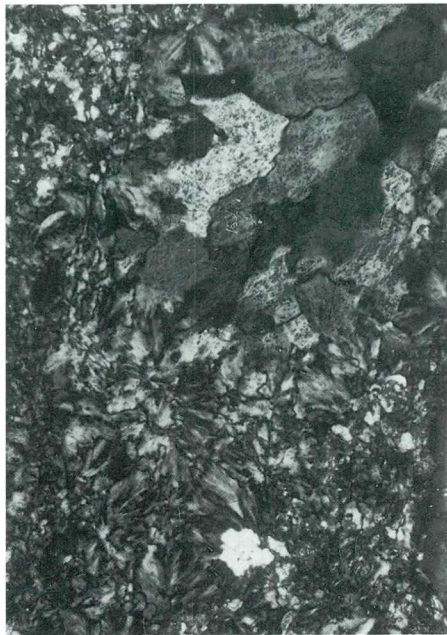
Sl. 3. Heulandit (H), ki nadomešča drobnozrnato osnovo. Presevna polarizirana svetloba, povečano 66 ×

Fig. 4. The same as in the previous photo, under crossed nicols

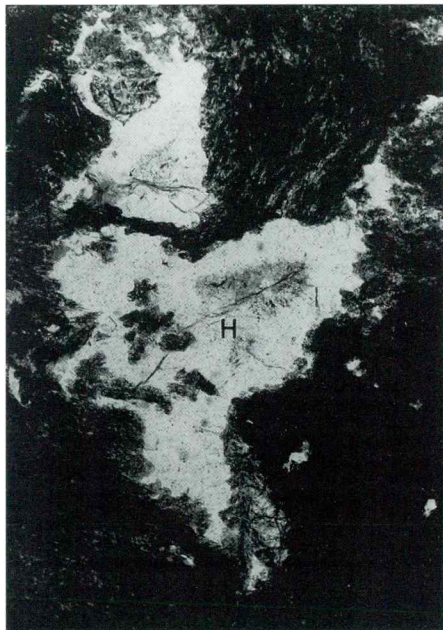
Sl. 4. Enako kot na prejšnji sliki, med navzkrižnimi nikoli



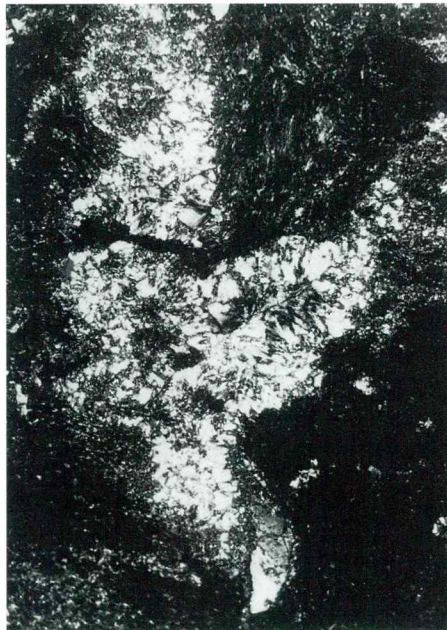
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Plate 5 - Tabla 5

Fig. 1. A plagioclase grain replaced by analcime (A), prehnite (Pr) and pumpellyite (Pu). Plane polarised light, magnification 53 ×

Sl. 1. Zrno plagioklaza, ki ga nadomeščajo analcim (A), prehnit (Pr) in pumpellyit (Pu), povečano 53 ×

Fig. 2. The same as in the previous photo, under crossed nicols

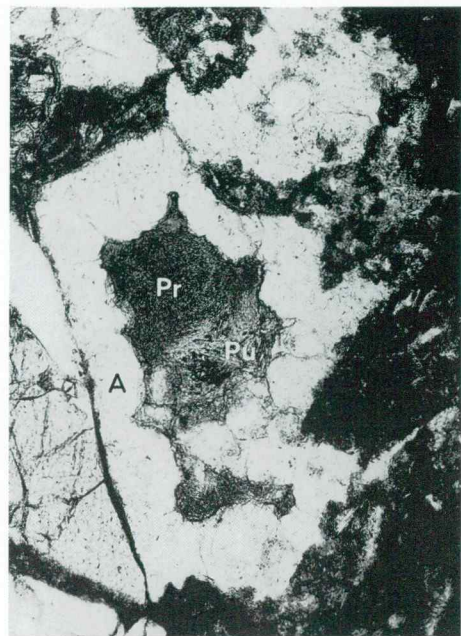
Sl. 2. Enako kot na prejšnji sliki, med navzkrižnimi nikoli

Fig. 3. Alkali feldspars (Kf) and analcime (A) replacing laumontite. Plane polarised light, magnification 66 ×

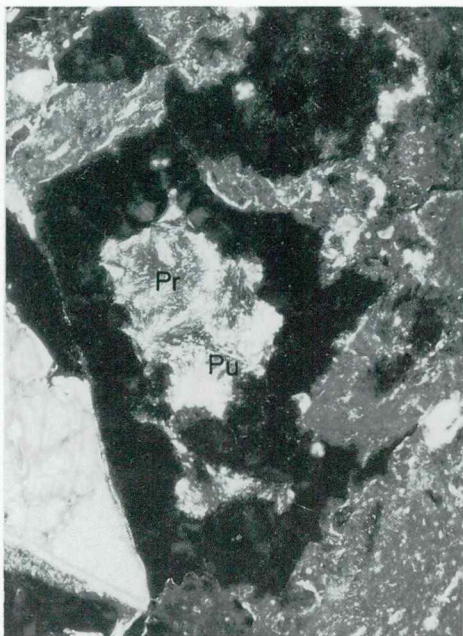
Sl. 3. Alkalni glinenec (Kf) in analcim (A), ki nadomeščata laumontit. Presevna polarizirana svetloba, povečano 66 ×

Fig. 4. Needles of pumpellyite as a vesicle filling. Plane polarised light, magnification 66 ×

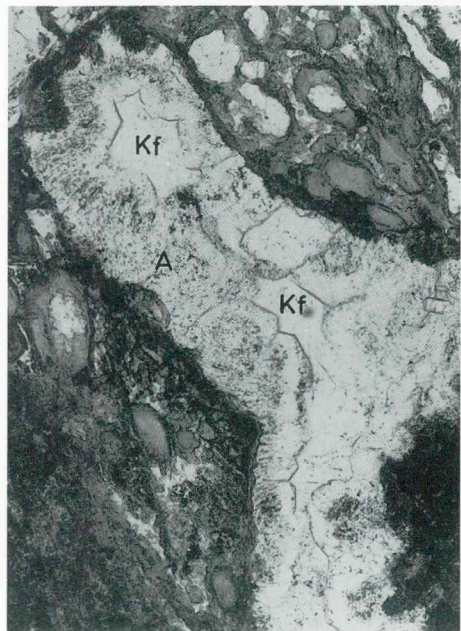
Sl. 4. Igličast pumpellyit, ki zapolnjuje votlinice plinskih mehurčkov. Presevna polarizirana svetloba, povečano 66 ×



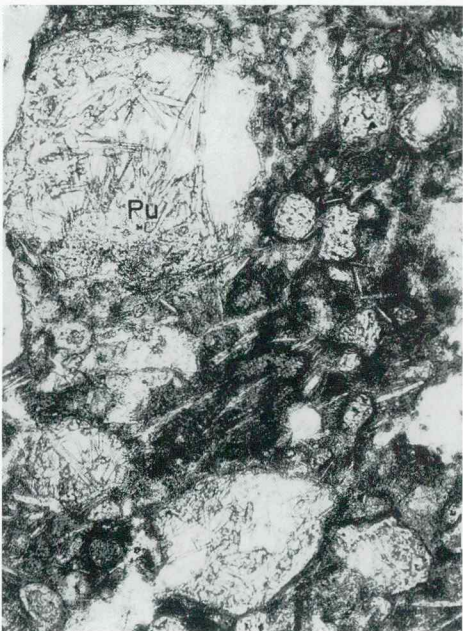
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