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Zeolite reactions in the Smrekovec volcanics, Northern Slovenia

Reakcije zeolitov v vulkanskih kamninah s Smrekovca

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Ključne besede: hidrotermalni zeoliti, laumontit, heulandit, analcim, Slovenija

Abstract

Upper Oligocene Smrekovec volcanics are characterised by the occurrence of zeolites, developed under hydrothermal conditions in the vicinity of the main crater and shallow intrusive bodies. Zeolitisation is the most pronounced in coarse-grained volcaniclastic rocks. The most widespread zeolite is laumontite, which occurs as a replacement of the primary constituents, volcanic glass and plagioclases, as interstitial filling and vein mineral. Sometimes, laumontite replaces prehnite, which developed at higher temperatures and became unstable when the chemistry and temperature of hydrothermal fluids changed. Locally, laumontite is replaced by analcime, mordenite, clinoptilolite and heulandite. The zeolite reactions are related primarily to the changes in chemical composition of reacting fluids, particularly to increased activities of SiO_2, and the H^+ and Na^+ ions.

Kratka vsebina

Za zgornjeoligocenske Smrekovške predornine je značilen pojav zeolitov, ki so nastali v bližini glavnega kraterja in plitvih intruzivov zaradi hidrotermalnih procesov. Zeolitizacija je najmočnejša v debelozrnatih vulkanoklastičnih kamninah. Najbolj razširjen zeolit je laumontit, ki nadomešča prvotne sestavine predornin - predvsem vulkansko steklo in plagioklaze, ter zapolnjuje pore in razpoke v kamnini. Mestoma je laumontit nadomeščen s prehnitom, ki je nastal pri višjih temperaturah in je postal nestabilen, ko sta se spremenili temperatura in kemična sestava hidrotermalnih raztopin. Ponekod je laumontit nadomeščen z analcimom, mordenitom, klinoptilolitom ali heulanditom. Te reakcije zeolitov kažejo, da so posledica menjajoče se kemične sestave hidrotermalnih raztopin, predvsem povišanih aktivnosti kremenice ter vodikovih in natrijevih ionov.

Introduction

Coherent volcanics and volcaniclastic deposits in the Smrekovec volcanic complex, Northern Slovenia, were changed under hydrothermal/geothermal conditions, generated in the vicinity of the main crater and shallow intrusive bodies by heating of pore fluids and the entrapped marine water (Kovič, 1988). The most common authigenic minerals are albite, laumontite, mixed layered filosilicate chlorite/montmorillonite (the most common ratio of chlorite/montmorillonite is 80/20), quartz and sphene. Locally, traces of prehnite, epidote, pumpellyite and amphiboles are encountered and indicate somewhat higher, probably contact metamorphic conditions during the emplacement of high-level intrusive bodies into water-saturated volcaniclastic sediments.

Circulation of hydrothermal fluids was intensive through coarse-graind volcaniclastics, which are more altered than poorly permeable fine-grained tuffs. The latter were zeolitised only in the latest stage of volcanic activity, when they were consolidated enough to became fractured.

Hydrothermally active environment is characterised by rapid changes in temperature and chemical conditions in reacting fluids. For this reason, some early developed zeolites may become unstable and react to form more stable zeolite species. In the Smrekovec volcanics, some uncommon zeolite reactions have been found, and they will be described in the present paper.

Geological setting of the Smrekovec volcanics

The Smrekovec mountains are the most extensive volcanic complex in Slovenia (Fig. 1), composed of coherent volcanics, pyroclastic, autoclastic and resedimented volcaniclastic deposits of the Upper Oligocene age. The complex encompasses an area of about 15 sq. km and includes three major peaks Komen, Krnes and Smrekovec, reaching 1684 m, 1613 m and 1577 m respectively. The complex is underlain by marine marls and silts, which contain Upper Oligocene foraminifera fauna (Mioč, 1983).

Among coherent volcanics, shallow intrusive bodies predominate. Magma composition varied in time. Early volcanic products were submarine lavas of basaltic composition. Later, andesites predominated, and although both, basic and acid varieties occur, acid andesites seem to be more common. The latest magmas were dacitic in composition. The style of volcanism also changed and became dominated by volcanic explosions which produced pumice lapilli and vitric tuffs (Kralj, 1996).

Volcaniclastics are abundantly encountered. They are subdivided into autoclastic deposits, pyroclastic deposits and syn-eruptive volcaniclastic deposits. The latter are the most extensive in occurrence; they were settled by volcaniclastic debris and turbidity ash flows. Autoclastic deposits consist of hyaloclastites and hyaloclastic breccias. Peperites and peperitic breccias frequently surround shallow intrusive bodies (Kralj, 1996).

Zeolites and their reactions

Zeolites are the most common in autoclastic deposits. The rocks of andesitic composition contain mainly laumontite, which commonly infills interstitial space and fissures. Hyaloclastites and pyroclastic deposits are dacitic in composition, and they are dominated by clinoptilolite and the clinoptilolite-heulandite solid solution. Prehnite commonly occurs, but in very small amounts. Analcime locally replaces volcanic glass and infills pore space, but the most extraordinary occurrence are replacements of laumontite and pyrogenetic plagioclases.

Prehnite is a hydrous Ca-Al silicate, and in burial settings, it commonly crystallises from the laumontite precursor at higher temperatures and pressures than laumontite (Boles & Coombs, 1975; 1977). Its stability also depends on the activity ratios $a_{Ca^{2+}}/a_{H^+}$ and a_{SiO_2} (Surdam, 1973). Laumontite also alters to prehnite, an aluminous silicate "kaolinite", quartz and water (Coombs et al., 1959; Kisch, 1983), if the molar fraction of water μ_{H_2O} decreases with respect to the molar fraction of carbon dioxide X_{CO_2}.

At higher activities of silica and hydronium ions, prehnite seems to become unstable and reacts to laumontite. In the Smrekovec volcanics, prehnite commonly infilled interstitial space and fissures, but it was almost entirely replaced by laumontite (Plate 1 - Fig. 1).

In burial settings, heulandite usually precedes laumontite (Boles & Coombs, 1975). Sometimes, heulandite persists metastable in the laumontite zone, and reacts directly to prehnite (Boles & Coombs, 1975; 1977). In the Smrekovec volcanics, prehnite and the solid solution clinoptilolite-heulandite coexist and indicate an opposite relationship, so that heulandite-clinoptilolite replaces prehnite. Both minerals occur in hyaloclastites, which were developed by disintegration of dacitic lava. Prehnite probably developed in the disintegrating lava flow as the replacement of volcanic glass, but when the temperature decreased, owing to the rapid cooling and the change in chemical composition of reacting fluids, the reaction ceased very soon, and heulandite-clinoptilolite begun to crystallise instead. The new conditions must have included an increased activity of silica and the Na^+ and H^+ ions. Prehnite poorly persisted under the new conditions and it was almost entirely replaced by heulandite-clinoptilolite (Plate 1 - Fig. 2).

Similar changes in chemical composition of hydrothermal fluids probably caused the reaction from laumontite to clinoptilolite (Plate 1 - Fig. 3). Laumontite is extensively

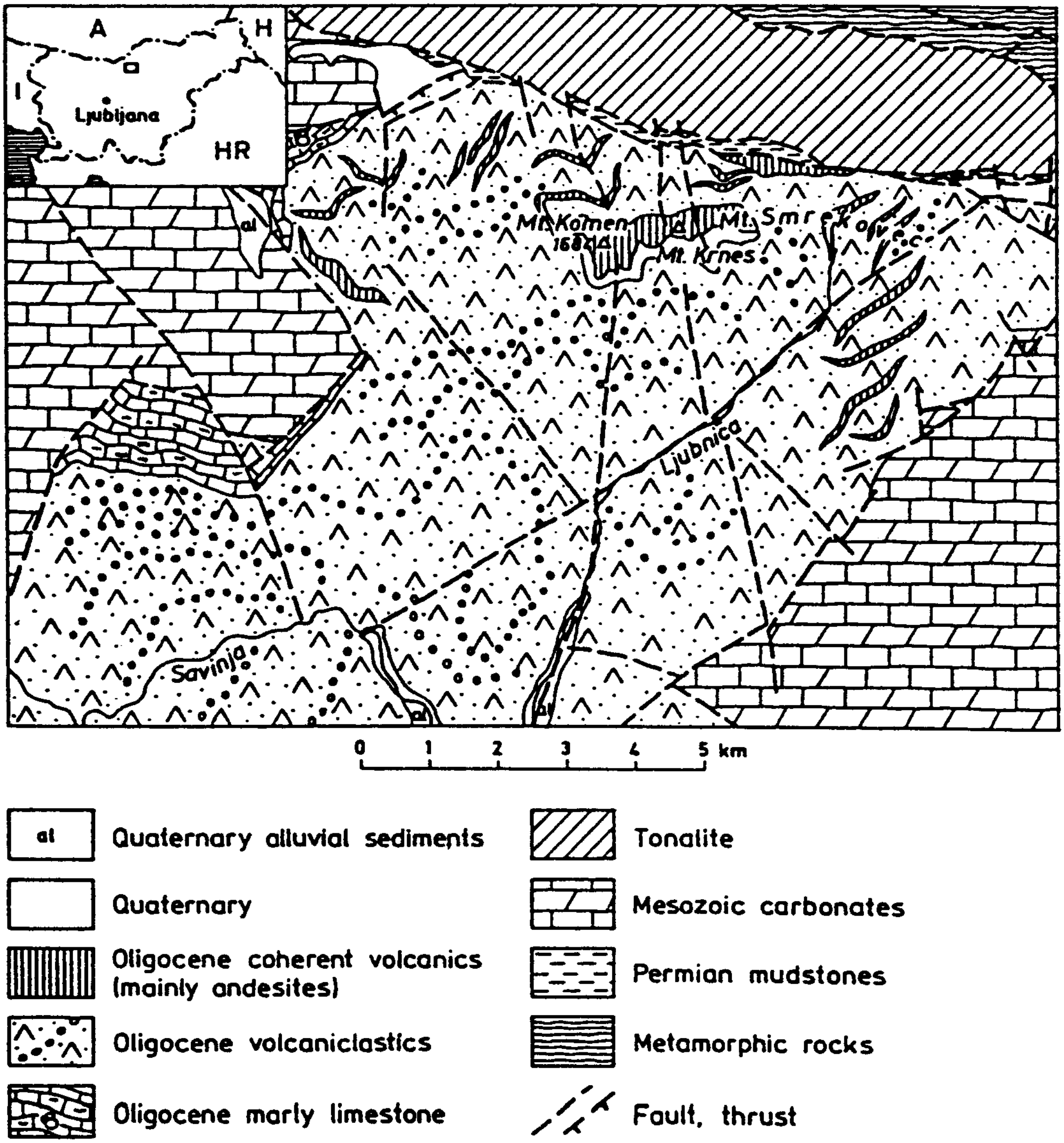


Fig. 1. Geological sketch map of the Smrekovec volcanic complex (after Mioč, 1983)

Sl. 1. Poenostavljena geološka karta smrekovškega vulkanskega kompleksa (prirejeno po Mioču, 1984) altered to smectite, and it could be involved in the reaction as a byproduct or an intermediate phase. Sometimes, moredenite replaced laumontite in the first place, and later, mordenite was replaced by clinoptilolite (Plate 1 - Fig. 4).

The above mentioned reactions can be regarded as retrograde, as the change in chemical composition of hydrothermal fluids probably accompanied the decrease in temperature. In the Smrekovec volcanic complex, the reaction from laumontite to analcime also occurs (Kovič & Krošl-Kuščer, 1986); Kralj, 1998), but it is related to an increased temperature and activity of the Na^+ ions. The reaction from laumontite to analcime has been proven experimentaly (Barth-Wirsching et al., 1994). In the natural environment, it was caused by a shallow intrusion of magma into water-saturated volcaniclastic sediments. The reaction from laumontite to analcime was accompanied by the alteration of chlorite dominated mixed layered clay minerals with the chlorite/montmorillonite ratio of about 80/20 to the minerals with the ratio of 50/50.

Conclusions

Zeolites and related silicate minerals, developed in a hydrothermally active environment of the Smrekovec volcanic complex, were subjected to transformations, caused by the change in chemical composition of reacting fluids and the temperature. The reactions are opposite to those, which are commonly observed in burial diagenetic settings, and in this sense, they can be regarded as retrograde. The reaction from prehnite to laumontite must have involved the increased activities of silica and the H^+ ions, and the reactions from prehnite to heulandite-clinoptilolite, from laumontite to clinoptilolite, from laumontite to mordenite and from mordenite to clinoptilolite also an increased activity of the Na^+ ions. The reaction from laumontite to analcime was related to a higher temperature, generated during the emplacement of a shallow intrusive body into water-saturated volcaniclastic sediments.

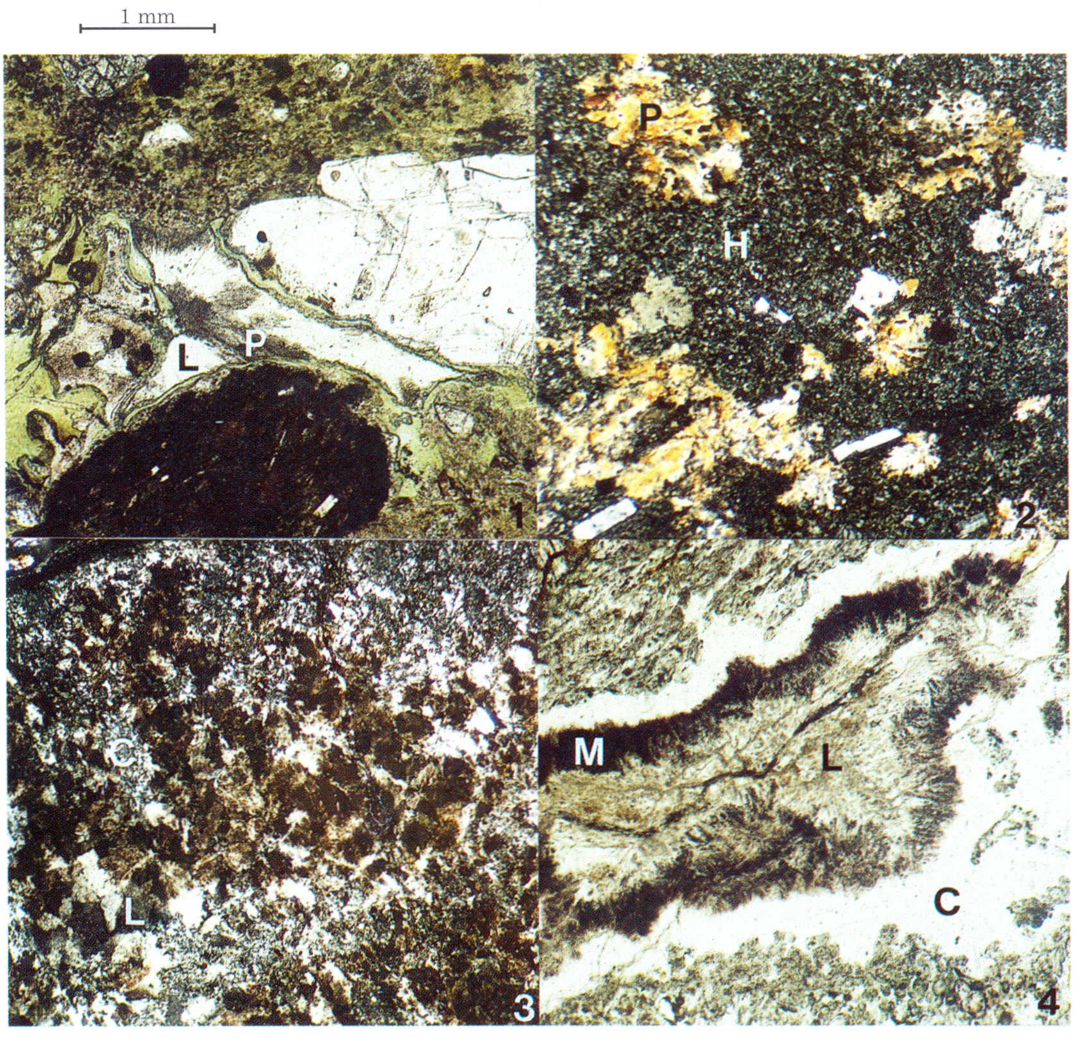
Plate 1 - Tabla 1

Fig. 1. Laumontite (L) replacing prehnite (P)
Sl.1. Laumontit (L), ki nadomešča prehnite (P)

Fig. 2. Solid solution heulandite-clinoptilolite (H) replacing prehnite (P)
Sl. 2. Trdna raztopina heulandita in klinoptilolita (H), ki nadomešča prehnit (P)

Fig. 3. Clinoptilolite (C) replacing laumontite (L)
Sl. 3. Klinoptilolit (C), ki nadomešča laumontit (L)

Fig. 4. Laumontite (L), mordenite (M) and clinoptilolite-heulandite (C) as a reaction suite
Sl.4. Laumontit (L), mordenit (M) in klinoptilolit-heulandit (C), kot reakcijski niz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