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CHEMICAL CHARACTERIZATION OF CLAY MINERALS ASSOCIATED WITH ZEOLITIZATION OF PERLITES (BOROVITZA, EASTERN RHODOPES, BULGARIA)

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Abstract: The clay minerals associated with zeolitization of perlites in endogenous domes in the eastern part of the Borovitza caldera are: illite-1Md formed by the alteration of the glass in the perlite-trachyrhyolite transition zone, and illite/smectite mixed-layers in zeolitized perlites from the dome periphery. The illite is ferriferous (0.94 - 1.05 Fe^{3+}) and has a high K content (0.69 - 0.76) characteristic of intermediate interlayer charge. It is associated mainly with K-mordenite, quartz and adularia. The I/S has from 90 to 10 smectite layers (estimation from chemical analyses) which are montmorillonitic and only rarely beidellitic. They are associated with clinoptilolite, opal-cristobalite, adularia and mordenite. This mineralogical zonation is related to decreasing temperature and increasing alkalinity of the solutions from the transition zone to the peripheral perlitic one. The chemical reactions established from microprobe analyses give evidence that the hydrothermal alteration of perlites is not isochemical, and that Fe, Mg and Ca have to be imported while alkali cations, mainly Na are lost.

Key words: perlites, illite, illite/smectite, clinoptilolite, mordenite, microprobe analyses, chemical balance.

Introduction

Many works have been devoted to the zeolitization of volcanic glasses and mostly to those in vitroclastic tuffs since the pioneering studies of Hay (1963, 1966). On the other hand, little is known concerning the associated clay minerals, especially in alteration zones containing quartz and adularia. Knowledge of the chemical compositions of clay minerals allows a better understanding of the chemical behaviour of elements during zeolitization, and physico-chemical parameters may be derived from these clay minerals compositions.

A mineralogical characterization of clay minerals crystallized during hydrothermal alteration of perlites from the Eastern Rhodopes has been performed by XRD on many samples originating from different endogenous domes in the eastern part of the Borovitza caldera (Stefanov & Yanev 1982). The present work is devoted to the chemical characterization of the clay minerals, originating from the most studied dome in the same area, in relation to their distribution relative to the alteration zones.

Geological setting and materials studied

The Borovitza caldera (30 x 15km), where zeolitized perlites are encountered, is located in the northeastern part of the Eastern Rhodopes, Bulgaria. This caldera is filled with acid volcanic rocks, dated to the Oligocene

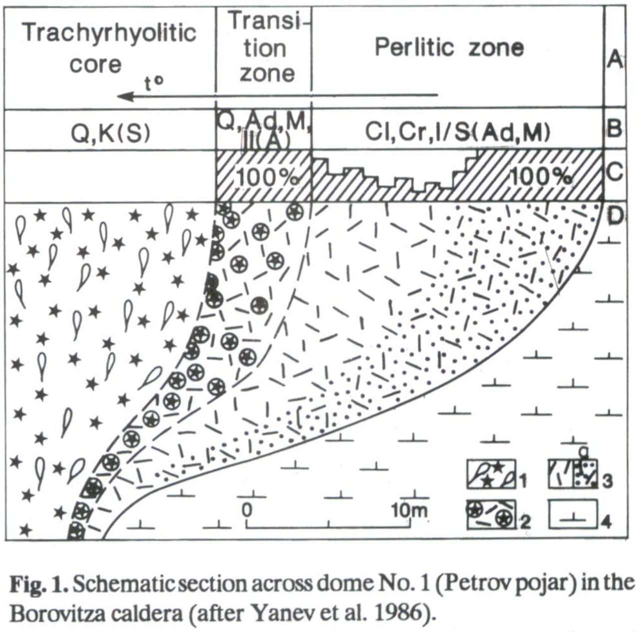


Fig. 1. Schematic section across dome No. 1 (Petrov pojar) in the Borovitza caldera (after Yanev et al. 1986).
A - dome zonation with the supposed temperature gradient of the hydrothermal solutions; **B** - main and minor (between brackets) hydrothermal minerals: quartz Q, opal-cristobalite Cr, adularia Ad, albite A, illite Il, illite/smectite I/S, kaolinite K, mordenite M, clinoptilolite Cl, "sericite" S; **C** - degree of perlite alteration; **D** - geological section across the dome. 1 - vesicular spherulitic trachyrhyolites, 2 - transitional zone (trachyrhyolitic spherulites in perlitic matrix), 3 - perlitic zone (a- fully zeolitized), 4 - acid tuffs.

(30 - 34 MA, Lilov et al. 1987). Perlites studied are linked to the last volcanic phase when several trachyrhyolitic domes intruded into pumice tuffs in the eastern part of the caldera. Perlites constitute the rims of these domes, a transition zone being located between them and trachyrhyolitic cores (Yanev 1987). This transition zone consists of trachyrhyolitic spherulites cemented by glass, these two components being in variable proportions. A zonation is thus observed (Fig. 1), induced by the cooling conditions of the lava: crystallized volcanic rocks (often with spherulitic structure) in the centre of the dome, trachyrhyolitic spherulites with perlites in the transition zone, and perlites in the rims.

The domes have been altered by hydrothermes of fumarole type (Naboko 1978) and this alteration also presents a zonation (Fig. 1): the core of the dome is altered into quartz, adularia, kaolinite and rare "sericite"; while glass from the transition zone is transformed into quartz, adularia and K-mordenite (quartz-adularia zone in the following text), associated with clay minerals and sometimes albite. Perlites are partially or fully altered (at the near contact with the surrounding rocks) into Ca-clinoptilolite associated with opal-cristobalite, clay minerals, and small amounts of mordenite and adularia. In some domes, erionite or calcite or albite have been identified (Yanev et al. 1986). The homogenization temperatures of fluid inclusions in quartz veinlets from the altered core of the dome indicated alteration temperature of 160 - 180 °C (A. Krasteva, personal communication).

In this paper, we are presenting the results obtained from one altered dome (No.1 - Petrov pojar) and more specifically from two samples originating from the quartz-adularia zone and from the zeolitized perlites zone.

Methods

Petrographic study has been performed on thin sections, using an optical microscope and on rock fragments by Scanning Electron Microscope (SEM Philips, Université Paris-Sud) in order to get information on the alteration of the morphology of minerals. In this paper, we present in situ microprobe analyses of clay minerals, glass and zeolites performed by using a Camebax operating at 15 Kev, 5 nA (Université Paris VI). For glass and zeolites, the beam was defocused (20 μm). For zeolites, we selected only analyses with E <10% [E = 100 x (Al+Fe-Na-K-2Mg-2Ca-2Sr-2Ba)/(Na+K+2Mg+2Ca+2Sr+2Ba)] (Gottardi & Galli 1985).

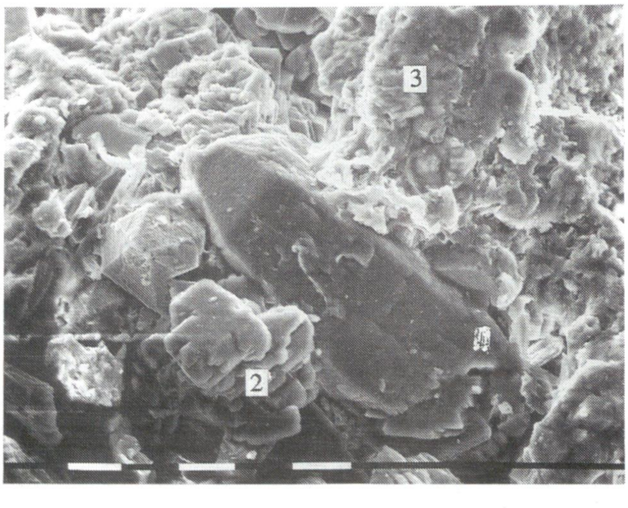


Fig. 2. Products of the glass alteration in the transition zone: 1 - quartz, 2 - adularia and 3 - illite. SEM scale bar = 10μm.

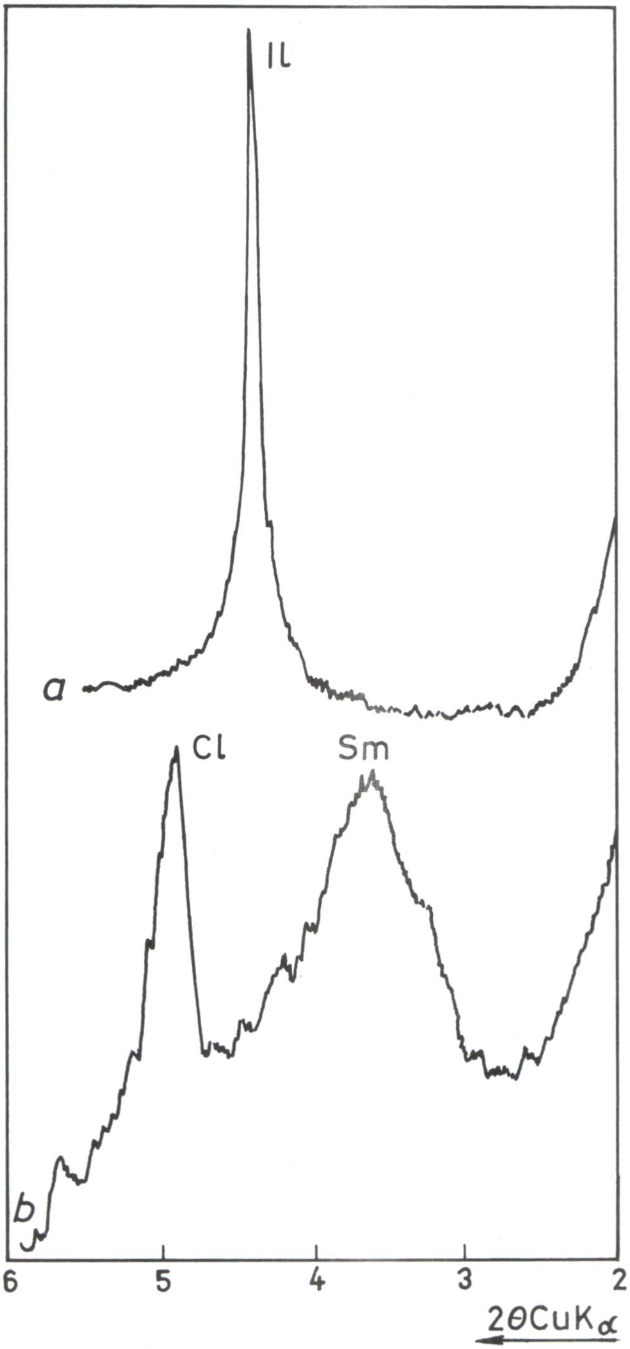


Fig. 3. X-ray powder diffractograms of illite (Il) from quartz-adularia zone (**a**) and of smectites (Sm) and clinoptilolite (Cl) from zeolitized perlites zone (**b**).

In order to establish chemical reactions, we used the average composition of each compound analysed. Structural formulae of the glass and zeolites were calculated on a 12 oxygens basis as proposed by Noh & Boles (1989) to avoid misfit in the chemical balance of elements. Adularia (analyses from Rainov & Yanev 1991) and quartz are calculated on an 8 oxygens basis. Mordenite and albite from the zeolitized perlites zone have not been analysed and are expressed from theoretical compositions. In all the chemical reactions presented, Al is considered to be an inert component (for quartz-adularia zone after Zaraisky et al. 1981; for zeolitized perlites zone - after Noh & Boles 1989), which has also been confirmed by the chemical balance calculations performed on bulk altered rocks. The proportions of hydrothermal minerals in these reactions have been fixed according to their amounts in the altered rocks, determined by microscopic study and XRD analyses.

Chemical characterization of clay minerals in the altered dome

Quartz-adularia zone

Glass is altered as irregular clayey aggregates (10 μm in diameter) between quartz and adularia crystals (Fig. 2). XRD analyses indicated that these clayey volumes are composed of illite-1Md (Stefanov & Yanev 1982) - Fig. 3. Microprobe analyses identified an iron-rich clay mineral (Fe^{3+} = 0.84 - 1.05) with mainly K as an interlayer cation (0.69 - 0.76), and an interlayer charge of 0.79 - 0.84 (Tab. 1).

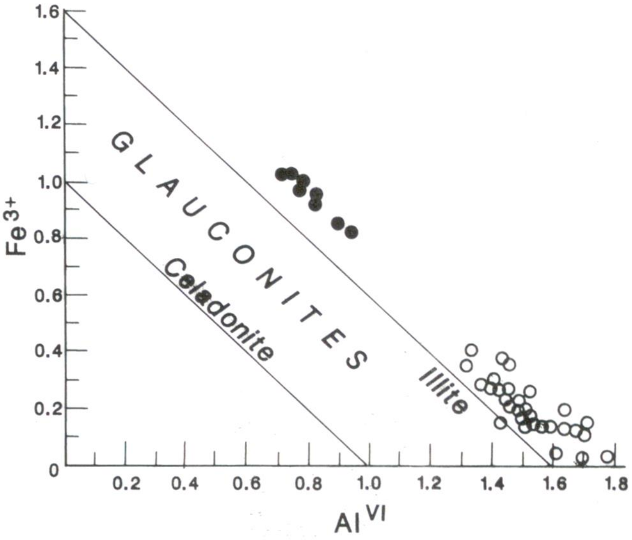


Fig. 4. Chemical composition of clay minerals analysedin the Fe^{3+} - Al^{VI} diagram (Velde 1985). Filled circles: clay minerals in the quartz-adularia zone, open circles: clay minerals in the zeolitized perlites zone.

The Fe^{3+}/Al ratio is quite constant (Fig. 4) which indicates that iron substitutes for Al in the clay structure and is not present as iron oxide impurities. The sum of the octahedral cations is always > 2 (2.03 - 2.05) which could be due to the high substitution rate of Al by Fe as in glauconites (Thompson & Hower 1975). In the Yoder & Eugster diagram (1955), all chemical analyses plot in the illite field (Fig. 5), and in the M^+-4Si-R^{2+} diagram (Meunier & Velde 1989)

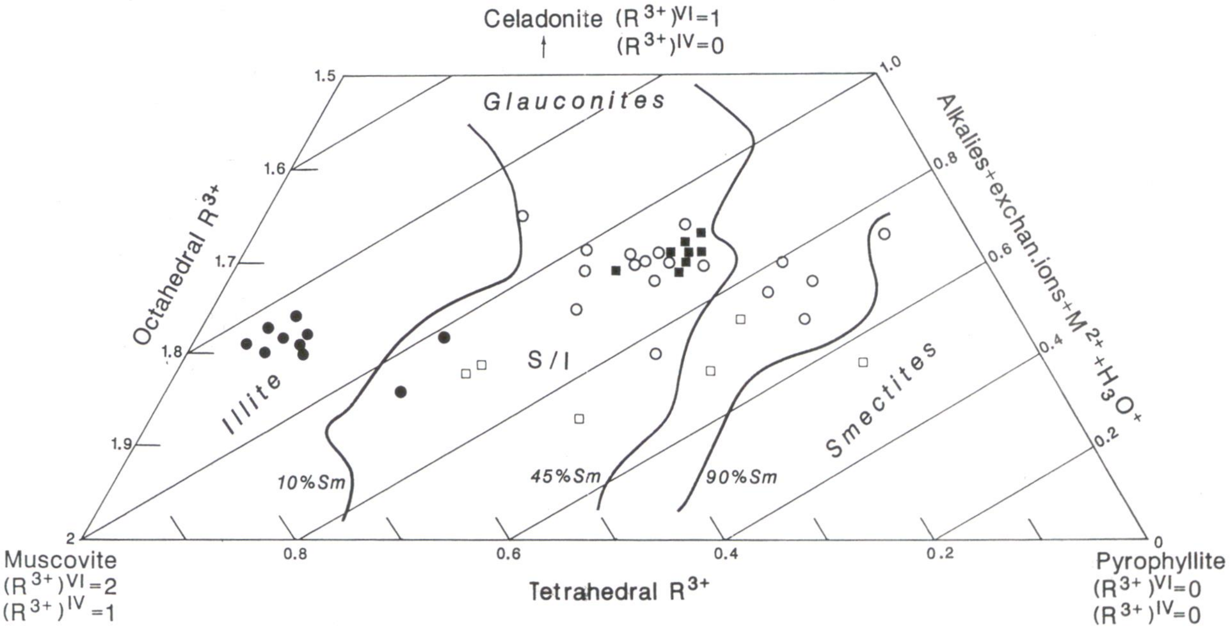


Fig. 5. Chemical composition of clay minerals analysed in the Yoder & Eugster magic diagram (1955) (composition fields for illite, glouconite, I/S and smectite established after Srodon & Eberl 1984).
Filled circles: clay minerals in the quartz-adularia zone; filled squares: clay minerals in perlitic cracks (beginning of alteration) of the zeolitized perlites zone; open circles (I/S with montmorillonitic layers), and open squares (I/S with beidellitic layers): clay minerals in the zeolitized perlites zone.

Table 1: Chemical analyses of clay minerals in the quartz-adularia zone (analyses calculated on $O_{10}(OH)_2$ basis).

Si	Al^{IV}	Al^{VI}	Ti	Fe^{3+}	Mn	Mg	Ca	Na	K	Tet. charge	Oct. charge	Lay. charge	Oct. charge	Si/Al ratio
3.31	0.69	0.94	0.02	0.84	0.01	0.23	0.04	0.00	0.71	-0.69	-0.10	-0.79	2.04	2.02
3.30	0.70	0.82	0.02	0.96	0.01	0.24	0.05	0.00	0.69	-0.70	-0.08	-0.79	2.05	2.16
3.26	0.74	0.74	0.02	1.05	0.01	0.23	0.04	0.01	0.72	-0.74	-0.08	-0.82	2.05	2.21
3.31	0.69	0.73	0.02	1.05	0.01	0.23	0.04	0.01	0.71	-0.69	-0.12	-0.81	2.04	2.32
3.31	0.69	0.82	0.01	0.97	0.00	0.23	0.05	0.00	0.73	-0.69	-0.14	-0.83	2.03	2.20
3.27	0.73	0.78	0.02	1.02	0.01	0.21	0.04	0.00	0.76	-0.73	-0.10	-0.84	2.03	2.16
3.32	0.68	0.89	0.01	0.87	0.02	0.25	0.04	0.01	0.70	-0.68	-0.11	-0.79	2.05	2.12
3.29	0.71	0.77	0.01	1.00	0.02	0.24	0.04	0.01	0.75	-0.71	-0.12	-0.83	2.04	2.23
3.38	0.62	1.64	0.00	0.20	0.01	0.22	0.09	0.00	0.48	-0.62	-0.03	-0.66	2.06	1.49
3.45	0.55	1.52	0.01	0.26	0.01	0.25	0.06	0.00	0.54	-0.55	-0.12	-0.67	2.04	1.67

they plot near the high charge illite - 0.87 (Fig. 6). When considering the octahedral layers (Fig. 7), the iron-rich character is well expressed and the analyses are in the glauconite field determined by Weaver & Polard (1975). However, this described mineral contains less Si (3.26 - 3.31), less Mg (0.21 - 0.25) and more Al^{VI} (0.73 - 0.94), than ideal glauconites (Odom 1984) which contain 3.62 - 3.69 Si, 0.34 - 0.41 Mg and 0.39 - 0.47 Al.

Different points of view are expressed concerning glauconites and ferriferous illites. According to several authors (e.g. Velde 1985), there exists a continuous composition series between these two minerals, 10 % Fe_2O_3 being an upper limit for illite and glauconite having typically 10 - 25 % Fe_2O_3. Other authors (e.g. Odin & Matter 1982) argue that there is not a solid solution between illite and glauconite and that there exists a chemical gap (between 10 and 15 % Fe_2O_3). Recently, the Nomenclature Committee of the AIPEA (Bailey 1980) defined glauconite as an iron-rich dioctahedral mica, in which Al^{IV} (or Fe^{3+IV}) >0.2, R^{3+VI} > 1.2 and Fe^{3+} >> Al. The clay minerals analysed in this study present Fe^{3+} < Al which characterize ferriferous illites with approximatively 5 % smectite layers according Fig. 5. Similar clay minerals, hydrothermal in origin have been described in uranium ore deposits (Cathelineau 1983).

Moreover, two chemical analyses of clays from the quartz-adularia zone present a different chemical composition (Tab. 1). They are more aluminium rich and have a lower layer charge than previous ferriferous illite and are therefore located in the illite/smectite field (Fig. 5).

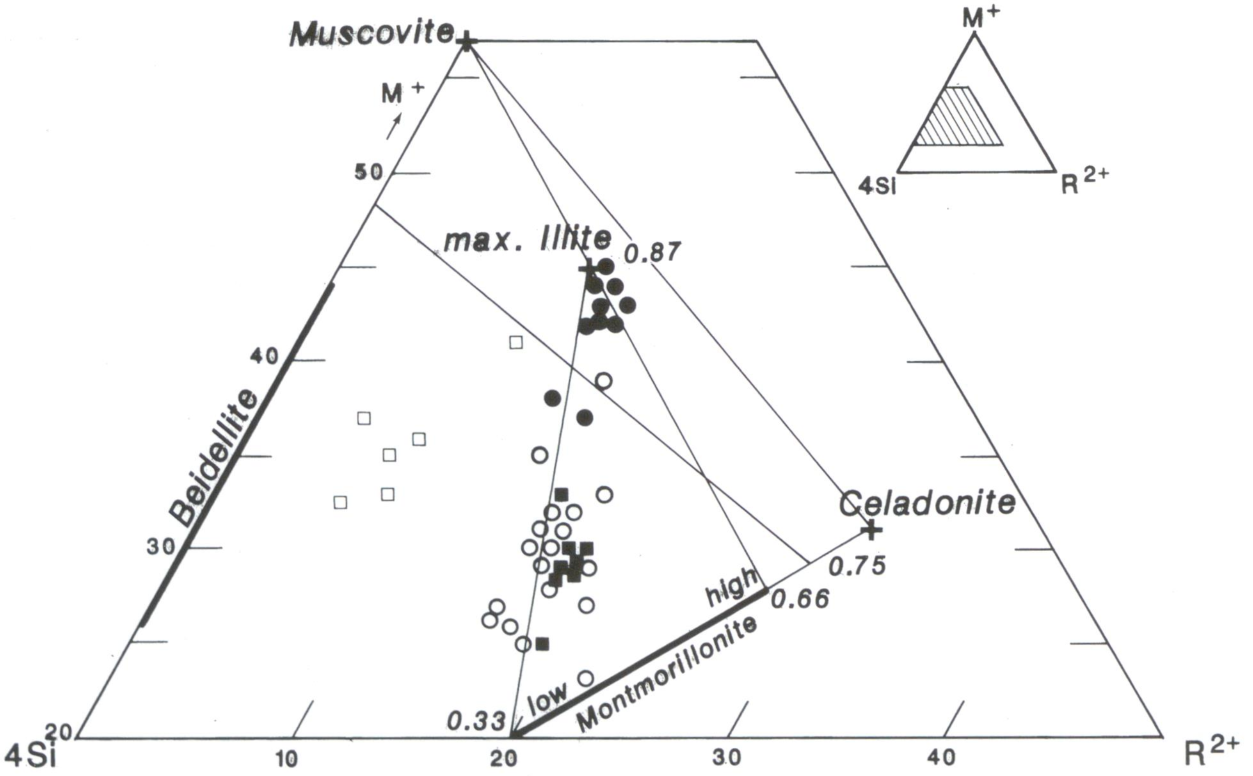


Fig. 6. Chemical composition of clay minerals analysed in the M^+-4Si-R^{2+} diagram (Meunier & Velde 1989). Same symbols as in Fig. 5.

Table 2: Chemical analyses of clay minerals in perlitic cracks in the zeolitized perlites zone (analyses calculated on $O_{10}(OH)_2$ basis).

Si	Al^{IV}	Al^{VI}	Ti	Fe^{3+}	Mn	Mg	Ca	Na	K	Tet. Charge	Oct. Charge	Lay. Charge	Oct. Charge	Si/Al ratio
3.71	0.29	1.47	0.02	0.22	0.02	0.29	0.21	0.01	0.11	-0.29	-0.24	-0.53	2.02	2.10
3.73	0.27	1.50	0.02	0.19	0.02	0.29	0.20	0.01	0.10	-0.27	-0.23	-0.50	2.02	2.11
3.65	0.35	1.42	0.02	0.28	0.02	0.28	0.20	0.02	0.16	-0.35	-0.23	-0.58	2.02	2.06
3.75	0.25	1.51	0.02	0.16	0.04	0.28	0.22	0.01	0.08	-0.25	-0.26	-0.51	2.01	2.13
3.71	0.29	1.58	0.01	0.14	0.03	0.29	0.18	0.00	0.07	-0.29	-0.15	-0.44	2.05	1.98
3.73	0.27	1.53	0.02	0.15	0.04	0.28	0.19	0.03	0.08	-0.27	-0.24	-0.50	2.02	2.07
3.73	0.27	1.53	0.01	0.15	0.03	0.29	0.20	0.01	0.12	-0.27	-0.27	-0.54	2.01	2.07
3.72	0.28	1.56	0.01	0.14	0.04	0.28	0.18	0.01	0.14	-0.28	-0.22	-0.50	2.03	2.03

Zeolitized perlites zone

In partially altered perlites, clay minerals and opal-cristobalite filled perlitic cracks which constitute the beginning of the hydrothermal alteration (Fig. 8). In fully zeolitized perlites, perlitic "bulbs" are replaced by concentric zeolitized bands separated by thin clayey films (Fig. 9). Clay minerals also crystallize between fibrous zeolites. XRD study (Stefanov & Yanev 1982) identified smectite-like minerals (Fig. 3). Microprobe analyses of these clay minerals show that in the first stage of alteration, thin films of clay have relatively constant illite/smectite (I/S) mixed layers compositions (Tab. 2). According to the data of Srodon & Eberl (1984), these chemical compositions characterize an average ratio 50 : 50 for I/S (Fig. 5).

In the zeolitized perlites, the microprobe analyses of clay minerals are much more heterogeneous than in the perlitic cracks (Tab. 3). This heterogeneity is well expressed even in the same sample and indicates variations from a smectite composition to 90 % illite layers, the average composition being 50 : 50 illite/smectite layers (Fig. 5). These mixed layers are more iron-rich than the clay minerals in thin perlitic cracks (Fig. 7). In the M^+-4Si-R^{2+} diagram (Meunier & Velde 1989), these clay minerals compositions are plotted along a line corresponding to low charge illite/montmorillonite mixed-layers (Fig. 6). Some analyses, with Mg $\ll Al^{IV}$, charakterize beidellitic layers (Fig. 6) and are also well distinguished when considering their octahedral layers (Fig. 7).

Formation conditions of clay minerals and zeolites: thermal and geochemical gradients

As previous studies have shown this hydrothermal alteration of perlites is due to Cl-Na solutions of fumarole type (Naboko 1978). The volcanic neck and fractured surrounding rocks constituted solution paths towards the surface, while the volcanic dome itself represented the discharge zone of the hydrothermal system (Yanev et al. 1986; Stefanov & Yanev 1982). The observed mineralogical zonation was controlled by decreasing temperature and increasing alkalinity of alteration solutions circulating from the centre of the dome (with vesicular texture) to its perlitic periphery. The decrease of temperature in this direction, according to the Oswald step rule (Dibble & Tiller 1981), is expressed by the replacement of stable phases (quartz, illite, adularia, mordenite) crystallized in the transition zone, by metastable ones (clinoptilolite, opal, I/S mixed layers) formed from perlites at the rim of the dome.

As mentioned above, the alteration temperatures in the centre of the dome were 160 - 180 °C, according to fluid inclusion data, concerning the latest crystallized quartz (in the centre of the veinlets). In the other zones of the alteration system, secondary minerals may be tentatively used to assess the alteration temperature. For example mordenite is known to crystallize at higher temperature than clinoptilolite (under 230 °C and under 130 °C respectively - Senderov 1980). Variations in the composition and

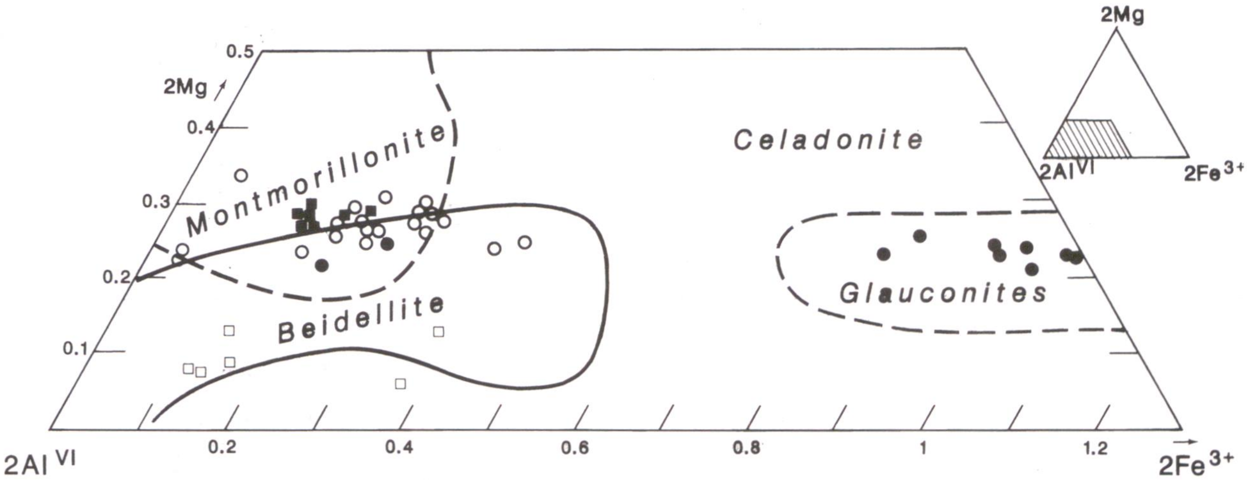


Fig. 7. Chemical composition of clay minerals analysad in the 2Mg - $2Al^{VI}$ - $2Fe^{3+}$ diagram (Güven 1988) (composition fields for celadonite and blauconite after Weaver & Pollard 1977). Same symbols as in Fig. 5.

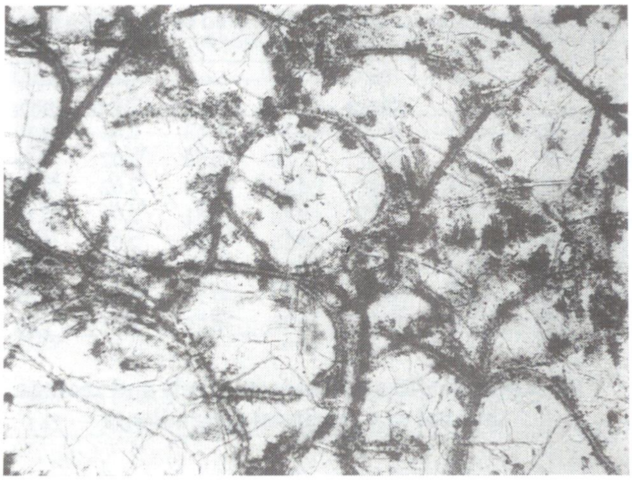


Fig. 8. First stage of perlite alteration. Perlitic cracks field filled with clay minerals (grey) and opal-cristobalite (uncoloured). IIN, x40.

nature of clay minerals are also indicators of the decrease of alteration temperature: medium charge illite (0.79 - 0.83) with 0.72 K crystallize between 200 and 260 °C while smectites indicate a lower alteration temperature, under 150 °C (Velde 1985; Cathelineau & Izquerdo 1989). Clay minerals with I/S compositions could indicate intermediate temperature as mentioned by Buhmann (1992) for I/S with 20 % smectite layers.

In the same direction as temperature decreases (Fig. 1) the pH of the solutions increases: in the centre of the dome the formation of kaolinite and "sericite" is an indication of the acid character of the solutions; quartz and adularia in the transitional zone - of weak acid conditions (Zaraisky et al. 1981), while the formation of zeolites in the perlite rim - of alkaline ones (Hay 1963). This alkalization of the solutions is a result of the dissolution of glass (Naboko 1966; Thomassin & Iiyama 1988). This change of the pH has an effect also on the temperature of conversion of illite into smectite, which is higher in the more alkaline conditions (Sass et al. 1987). However, the activity of potassium is highest in the transitional zone where, among the newly-formed minerals adularia predominates, the clay is also potassic (illite) and they are accompanied by K-mordenite.

Chemical reactions have been calculated for a better understanding of the behaviour of different chemical elements during hydrothermal alteration of perlites. Glass from the transition zone is altered according to the following reaction:

$0.67\,(Si_{4.98}Al_{1.06}Fe_{0.03}Mg_{0.01}Ca_{0.04}Na_{0.30}K_{0.37})O_{12}\,.\,1.71H_2O$
Glass
$+0.38Si^{4+} +0.03Fe^{3+} +0.01Mg^{2+} +0.04Ca^{2+} +0.28K^{+} +0.41O_2$
$=0.05(Si_{3.30}Al_{1.52}Fe_{0.97}Mg_{0.23}Ca_{0.04}Na_{0.01}K_{0.72})O_{10}.(OH)_2\ +$
Fe-Illite
$0.2\,(Si_{4.99}Al_{0.98}Fe_{0.02}Mg_{0.01}Ca_{0.26}Na_{0.12}K_{0.39})0_{12}.3H_2O\ +$
K-mordenite
$0.45(Si_{3.02}Al_{0.97}Ca_{0.02}Na_{0.05}K_{0.93})O_8 + 0.3Si_4O_8 + 0.15Na^{+} + H^{+}$
Adularia Quartz

During zeolitization of perlites, two alteration stages have to be taken into account (Hay 1963, 1966). The first stage is related to the dissolution of the glass and crystallization of opal-cristobalite and clay minerals (I/S mixed layers with constant composition - Fig. 5) in and around perlitic cracks (Noh & Boles 1989), from solution with low alkali/H$^+$ ratio (Hemley 1962). This low ratio may also be related to the higher circulation rate of the solution (Dorfman 1958) in perlitic cracks. According to the Oswald step rule, silica gels and smectites are the first products of the substitution of glass. This alteration reaction liberates most of the alkali cations:

$0.845(Si_{4.98}Al_{1.06}Fe_{0.03}Mg_{0.01}Ca_{0.04}Na_{0.30}K_{0.37})O_{12}.\ 1.71H_2O$
Glass
$+ 0.06\,Fe^{3+} + 0.13\,Mg^{2+} + 0.07\,Ca^{2+} =$
$0.5(Si_{3.72}Al_{1.79}Fe_{0.18}Mg_{0.28}Ca_{0.20}Na_{0.01}K_{0.37})O_{10}(OH)_2\ +$
I/S mixed-layers
$0.585Si_4O_8.nH_20 + 0.25\,Na^{+} + 0.26\,K^{+}$
Opal

In the second alteration stage zeolitic band formed around clay minerals, often associated with adularia. Zeolites, with a high Si/Al ratio, are the next minerals after clays and opal in the decreasing range of the free energy, i.e. in the series of minerals substituting glass. This reaction may be established in this way:

$0.8(Si_{4.98}Al_{1.06}Fe_{0.03}Mg_{0.01}Ca_{0.04}Na_{0.30}K_{0.37})O_{12}.\ 171H_20\ +$
Glass
$0.03\,Mg^{2+} + 0.14\,Ca^{2+} + 0.02\,K^{+} =$
$0.5(Si_{4.9}Al_{1.11}Mg_{0.08}Ca_{0.33}Na_{0.13}K_{0.09})O_{12}.\ 3H_2O\ +$
Clinoptilolite
$0.15Si_4O_8.nH_2O + 0.3(Si_{3.02}Al_{0.97}Ca_{0.02}Na_{0.05}K_{0.93})O_8\ +$
Opal Adularia
$0.02Fe^{3+} + 0.16\,Na^{+}$

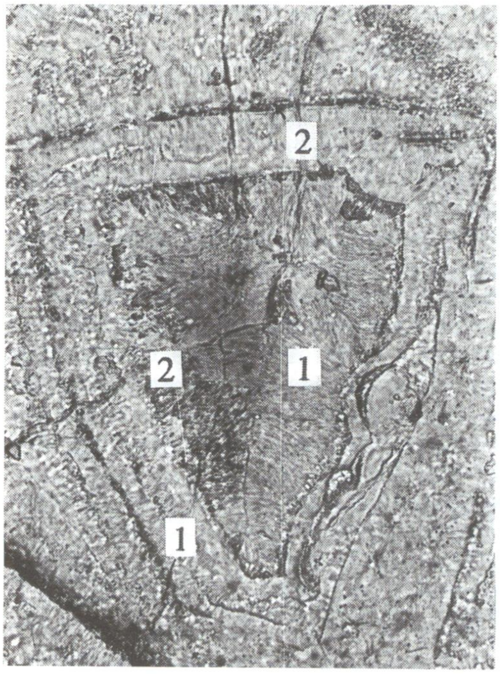
Locally sodic paragenesis has been observed and could be due to an increase of temperature and/or a decrease of the K-activity (Naboko 1966; Senderov & Hitarov 1970). Because of the high activity of Si, albite, and not analcime is formed:

$0.66(Si_{4.98}Al_{1.06}Fe_{0.03}Mg_{0.01}Ca_{0.04}Na_{0.30}K_{0.37})O_{12}.\ nH_2O+$
Glass
$1.21\,Si^{4+} + 0.09\,Ca^{2+} + 0.13\,Na^{+} =$
$0.6(Si_5AlCa_{0.2}Na_{0.4}K_{0.1})O_{12}.3H_2O+0.1(Si_3AlNa_{0.9}K_{0.1})O_8\ +$
Mordenite Albite
$0.3\,Si_4O_8.\ nH_2O + 0.02\,Fe^{3+} + 0.01\,Mg^{2} + 0.18\,K^{+}$
Opal

These chemical reactions give evidence that during the second alteration stage only a few inputs of alkali cations is needed. The loss of alkali cations during the first alteration stage increases the alkali/H$^+$ ratio in solution and promotes zeolites growth (Hay 1963, 1966). Those two stages may by repeated many times and that could lead to the formation of an alternation of clayey and zeolite bands as shown in Fig. 9.

Table 3: Chemical analyses of clay minerals in the zeolitized perlites zone (analyses calculated on $O_{10}(OH)_2$ basis).

Si	Al^{IV}	Al^{VI}	Ti	Fe^{3+}	Mn	Mg	Ca	Na	K	Tet. Charge	Oct. Charge	Lay. Charge	Oct. Charge	Si/Al ratio
3.78	0.22	1.49	0.01	0.24	0.01	0.25	0.13	0.01	0.18	-0.22	-0.23	-0.45	2.00	2.21
3.53	0.47	1.71	0.02	0.16	0.03	0.09	0.17	0.03	0.13	-0.47	-0.03	-0.50	2.02	1.62
3.74	0.26	1.63	0.03	0.13	0.02	0.12	0.22	0.05	0.12	-0.26	-0.34	-0.60	1.92	1.97
3.62	0.38	1.40	0.02	0.31	0.02	0.28	0.16	0.00	0.23	-0.38	-0.18	-0.56	2.03	2.04
3.73	0.27	1.52	0.01	0.18	0.02	0.28	0.21	0.01	0.09	-0.27	-0.25	-0.52	2.01	2.08
3.68	0.32	1.42	0.02	0.28	0.01	0.29	0.17	0.03	0.18	-0.32	-0.23	-0.55	2.02	2.13
3.67	0.33	1.50	0.02	0.20	0.03	0.30	0.19	0.03	0.11	-0.33	-0.18	-0.51	2.05	2.01
3.64	0.36	1.40	0.02	0.28	0.04	0.30	0.18	0.01	0.23	-0.36	-0.24	-0.60	2.03	2.07
3.68	0.32	1.49	0.02	0.23	0.02	0.27	0.19	0.01	0.10	-0.32	-0.17	-0.49	2.03	2.03
3.70	0.30	1.45	0.02	0.24	0.03	0.27	0.17	0.02	0.19	-0.30	-0.25	-0.55	2.01	2.12
3.71	0.29	1.48	0.02	0.22	0.03	0.28	0.19	0.00	0.12	-0.29	-0.20	-0.49	2.03	2.09
3.67	0.33	1.45	0.02	0.28	0.03	0.25	0.18	0.01	0.14	-0.33	-0.18	-0.51	2.03	2.06
3.68	0.32	1.70	0.02	0.11	0.03	0.08	0.19	0.07	0.12	-0.32	-0.24	-0.57	1.95	1.81
3.83	0.17	1.69	0.01	0.12	0.02	0.08	0.17	0.04	0.11	-0.17	-0.32	-0.49	1.92	2.06
3.45	0.55	1.46	0.09	0.36	0.03	0.06	0.17	0.05	0.18	-0.55	-0.01	-0.56	1.99	1.72
3.71	0.29	1.46	0.02	0.23	0.03	0.31	0.17	0.02	0.09	-0.29	-0.17	-0.46	2.05	2.11
3.59	0.41	1.36	0.03	0.29	0.03	0.26	0.13	0.11	0.40	-0.41	-0.37	-0.77	1.97	2.03
3.63	0.37	1.32	0.05	0.37	0.01	0.23	0.13	0.02	0.33	-0.37	-0.24	-0.61	1.98	2.15
3.73	0.27	1.49	0.02	0.20	0.02	0.26	0.13	0.06	0.24	-0.27	-0.30	-0.56	1.99	2.13
3.59	0.41	1.33	0.01	0.42	0.03	0.25	0.12	0.01	0.28	-0.41	-0.13	-0.53	2.05	2.07
3.92	0.08	1.51	0.02	0.17	0.02	0.24	0.12	0.03	0.20	-0.08	-0.39	-0.47	1.95	2.47
3.83	0.17	1.69	0.00	0.03	0.07	0.22	0.15	0.01	0.12	-0.17	-0.27	-0.44	2.01	2.06
3.47	0.53	1.44	0.02	0.37	0.04	0.13	0.11	0.00	0.48	-0.53	-0.18	-0.71	1.99	1.77
3.64	0.36	1.77	0.00	0.03	0.04	0.24	0.15	0.01	0.08	-0.36	-0.03	-0.39	2.08	1.71



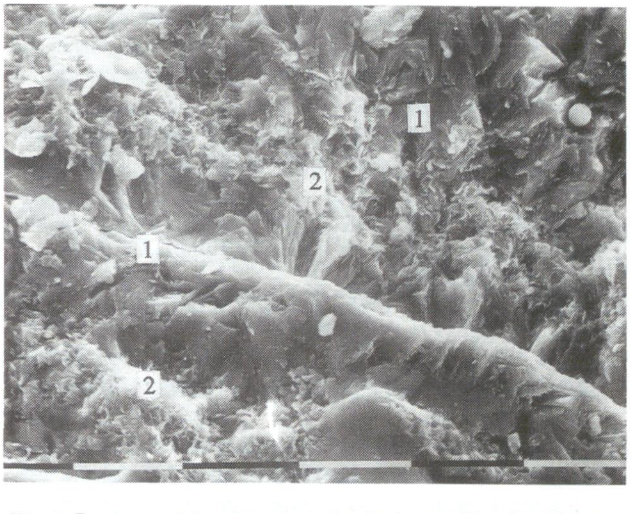


Fig. 9. Products af the glass alteration in the zeolitized perlite zone: **a** - (left): fully altered perlite: perlitic "bulbs" replaced by concentric bands of clinoptilolite (1) and clay minerals (2), IIN, x160; **b** - (right): same alteration feature under SEM, clinoptilolite (1), clay minerals (2). Scale bar = 10 μm.

and promotes zeolites growth (Hay 1963, 1966). Those two stages may by repeated many times and that could lead to the formation of an alternation of clayey and zeolite bands as shown in Fig. 9.

Conclusion

The geochemical study of clay minerals associated with the zeolitization of perlites in the Eastern Rhodopes gives evidence that zeolitization is not an isochemical process as it is often considered (e.g. Noh & Boles 1989). In all alteration zones described above, transformation of the glass to clay minerals and zeolites necessitates an input of Fe and Mg (in clay minerals) and Ca (in zeolites and sometimes calcite). Besides, the alteration of the glass is done with a net loss of alkali cations which are exported out of the alteration system.

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