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# Cationic hydration impact on zeolite formation and properties: A review and discussion

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**Abstract.** The ion hydration is crucial in many natural and technological processes. In this work some aspects of the modern theory of aqueous solutions were used to clarify the formation and properties of zeolites: the influence of hydrated cations as templats in the formation of nanoporous aluminum silicate frameworks; the importance of ion hydration on the ion exchange selectivity and action mechanism of two-temperature and gradient exchange systems; the effect of ion hydration on the processes of dehydration and rehydration of zeolites; the characteristics of the zeolite couple laumontite–"leonhardite" and their genetic significance.

*Key words*: zeolites, cation hydration, ion-exchange, hydration-dehydration

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**Георги Киров, Людмила Филизова. Катийонна хидратация, образуване и свойства на зеолитите: обзор и обсъждане**

**Абстракт**. Йонната хидратация има определящо значение в множество природни и технологични процеси. В тази работа някои аспекти на съвременната теория на водните разтвори се използват за изясняване на проблеми на образуването и свойствата на зеолитите: влиянието на хидратираните катиони като темплейти при образуването на нано-порести алумосиликатни скелети; значението на йонната хидратация за йонообменната селективност и механизма на действие на двутемпературните и градиентни обменни системи; влияние на йонната хидратация върху процесите на дехидратация и рехидратация на зеолитите; особеностите на двойката зеолити ломонтит-"леонхардит" и тяхното генетично значение.

Natural zeolites form a large group of minerals – water aluminium-silicates of alkali and alkaline earth cations with the general formula $M^{n}_{x/n}$ $(Al_xSi_yO_{2(x+y)}).pH_2O$, where M = Ca, Na, K, Mg, Ba, y/x = 1 to 6 and p/x = 1 to 4 (Breck 1974; Tsitsishwili et al., 1985, 1992; Gottardi & Galli 1985). In their crystal structure $Si^{4+}$ and $Al^{3+}$ are tetrahedrically coordinated by oxygen atoms and form strongly linked framework pierced by channels and pores. The framework has a negative charge created substitution of $Si^{4+}$ by $Al^{3+}$. The charge is compensated by alkali and/or alkaline earth cations, which together with water molecules fill framework channels. The latter are relatively weakly linked with the framework

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and can be subject of cation exchange and reversible dehydration. Thus, in every zeolite structure can be obtained three relatively independent components: a silica-alumina framework, exchangeable cations and water molecules, which interact both in the formation of the crystals and in every subsequent change in the environment. The cationic exchange causes changes in the number and arrangement of the water molecules, while the dehydration causes change of the cation positions. Both processes influence the aluminium-silicate framework, leading to its deformation or even destruction. Zeolites are formed only in aqueous solutions and the ion exchange reactions occur most commonly in aqueous solutions and the reactions of dehydration and rehydration are also highly dependent on the cation-water interactions.

By reason of that, herein we focus on the important role, which cation hydratation plays in the creation of particular zeolite structures and for the ion exchange, thermal and other processes in zeolite crystals, as we have faced for years.

## Cations and water molecules in aqueous solutions and in zeolite channels

*In water solutions,* an ion hydrates by orienting the water dipoles and in this way forming hydration shells. The bonding strength and the thickness of these hydration shells depend mainly on the ionic radius and charge. The monovalent cations have one-layer shells and the larger ones have very loosely linked hydration shells. In case of ions with higher-charge the shells can be bi- and three-layer, strongly linked to the cation. The cation hydration influences the structure and properties of the solution. For example, strongly hydrating cations increase the solution viscosity, whereas the non-hydrated ones reduce viscosity below that of pure water. The state of the cations in the solution predetermines their behavior in various processes and reactions, such as ion transport through biological membranes or zeolite channels, formation and dissolution of crystals and many others. Thus the ion hydration concerns many scientific fields: physical-chemistry of solutions, biology, medicine, meteorology, geochemistry etc. and each of them uses a given aspect of the phenomenon.

Information on the nature of water solutions and the ion hydrations can be obtained through investigation of various solution properties and by various techniques: diffusion, transference, electromotive force, infrared spectroscopy, isotopic exchange, sound velocity-spectroscopy, effective volume, dielectric properties, X-ray, neutron and electron diffraction, NMR, thermodynamic calculations etc. As a result, depending on the choice of method, for one single ion there can be obtained widely differing hydrate numbers. For instance, for Li diffraction methods usually give hydration number from 4 to 6; while according to transference measurements – 25. The diffraction methods determine the number of closest neighbors, i.e. the coordination number of the ion. Transference measurements determine bigger hydration shell including loosely bonded water molecules from second and third layer.

For our purposes, most useful is the interpretation of Zavitsas (2001, 2005, 2010) according to whom the thermodynamic hydration number ($H_T$) is "the average number of water molecules that are bound sufficiently strongly to ions to be removed from the solvent and become part of the solute. Strong bounding is estimated as a binding energy of approximately 13.3 Kcal $mol^{-1}$ or grater" (Zavitsas 2001). In contrast to the classic theory, which is applicable only for very diluted solutions ("ideal solutions"), the used method proves that relevant results are achieved with solutions with relatively high concentrations. Usually, there are used properties such as freezing point depression, vapor pressure lowering and boiling point elevation, which are well studied, but have not been applied for the determination of hydration of ions. By reason of that, initially the notion of solution concentrations should be changed. The conventional calculation of mole

fraction of solute ($x$) is performed by eq. 1:

$x$ = (mol of solute particles) / (mol of $H_2O$ + mol of solute particles) (1)

If part of water molecules are binding sufficiently strongly and become part of solute, this decrease the number of water molecules constituting "bulk" water, but do not change the number of solute particles. Mole fraction of solute then must be calculated by eq. 2, where the value $H_T$ is the number of water molecules removed from the bulk solvent by strong bonding with cations:

$x$ = (mol of solute particles) / [(mol of solute particles) + (mol of $H_2O$) – ($H_T$ x mol of cation)](2)

Both situations are graphically presented on Fig. 1. Plots of experimental measurements using eq. 1 show large curvatures, commonly described as indicating deviation from ideal behavior (Fig. 2). The linear part of the curve is in the very low concentrations range of the so called ideal solutions. If the mole fraction of the solute is corrected according to eq.2 at relevant choice of $H_T$, there is no deviation from the ideal behavior over wide concentration range and the linear part of the curve is extended to the high concentrations. In this way there are estimated identical hydration numbers from different colligative properties that are also in good agreement with values obtained by other methods. In Table 1 are given the hydration numbers of some important cations for the zeolite systems. Certain dependencies between the hydration number ($H_T$) and the ion potentials of the cations and between the $H_T$ and heat of hydration ($H_h$) are given on the Fig.3.

For our goals, it is essential that the used colligative properties allow evaluating the influence of the temperature on the hydration numbers of the cations. For $Ca^{2+}$ case the variations are: 12 water molecules per ion at $0^oC$, 6.7 – at water boiling point and 5.0 at $200^oC$. One can observe (Table 1) the lowering of the hydration number of the highly hydrated cations and the reverse tendency for $K^+$, $Rb^+$ and $Cs^+$, whose hydration raises with the temperature.

The water molecules in the hydrate shell of a cation have different binding energy. Thus, the $12^{th}$ water of hydration of the calcium cation is held with a binding energy of 13.3 Kcal $mol^{-1}$, the $10^{th}$ with 14.5, the $8^{th}$ with 17.9, etc. with increasing of the energy for each previous water molecule (Peshke 1998).

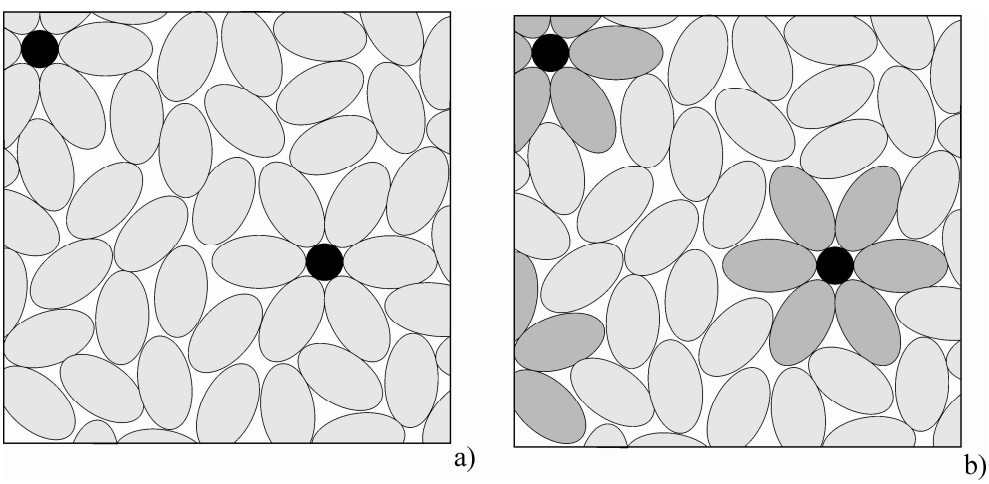


Fig. 1. Water – solute ratio: a) according to equation (1) ($H_2O$ molecules – light grey, cations – black), b) according to equation (2) ($H_2O$ molecules of hydration shell – dark grey, $H_2O$ molecules of free, bulk water - light grey)

Table 1. *Hydration numbers ($H_T$) of some cations at different temperatures (after Zavitsas 2010)*

| Cation | Hydration number | | Cation | Hydration number | | |
|---|---|---|---|---|---|---|
| | 0°C | 100°C | | 0°C | 100°C | 200°C |
| $Li^+$ | 6.7 | 4.5 | $Mg^{2+}$ | 14.0 | 10.0 | – |
| $Na^+$ | 3.4 | 2.5 | $Ca^{2+}$ | 12.0 | 6.7 | 5.0 |
| $K^+$ | 1.2 | 1.9 | $Ba^{2+}$ | 9.5 | 7.0 | – |
| $Rb^+$ | 0.6 | 1.5 | $Fe^{3+}$ | 19.0 | – | – |
| $Cs^+$ | 0 | 1.3 | $Al^{3+}$ | 23.0 | 14.3 | – |

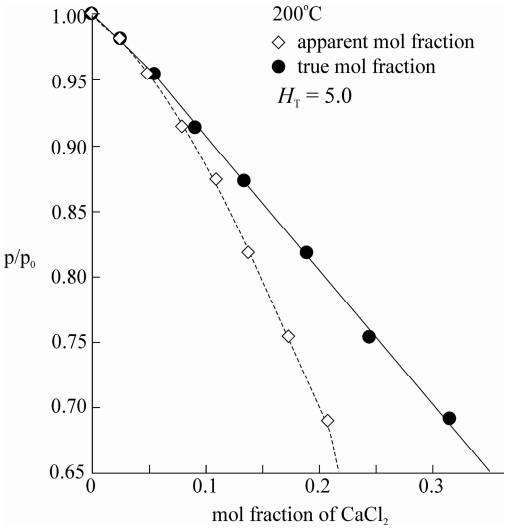


Fig. 2. Plots of vapor pressure lowering measurements for $CaCl_2$ in 4.85 mol of salt per 1L $H_2O$ at 200°C. Open points are calculated by eq. (1). Solid circles are points calculated by eq. (2) with a hydration number ($H_T$) of 5.0. (Zavitsas 2005)

*The water molecules and the cations in the channels and cavities* of the zeolite structures interact in both ways to each other and to oxygen of aluminum silicate framework. There are two major types of water in the zeolite cages: one has strong interaction and may be associated with the hydration of the extra-framework cations, and the other has weak interaction with the zeolite and may simply fill the voids. In most cases, the close surrounding of a cation is composed of framework oxygen atoms and water molecules. As is shown in Table 2 the highly hydrating cations ($Ca^{2+}$, $Mg^{2+}$, $Na^+$) have more water molecules than oxygen atoms in their surrounding, even in many cases they are coordinated only by water molecules. Such cation-water groups are located in the cavities and large channels,

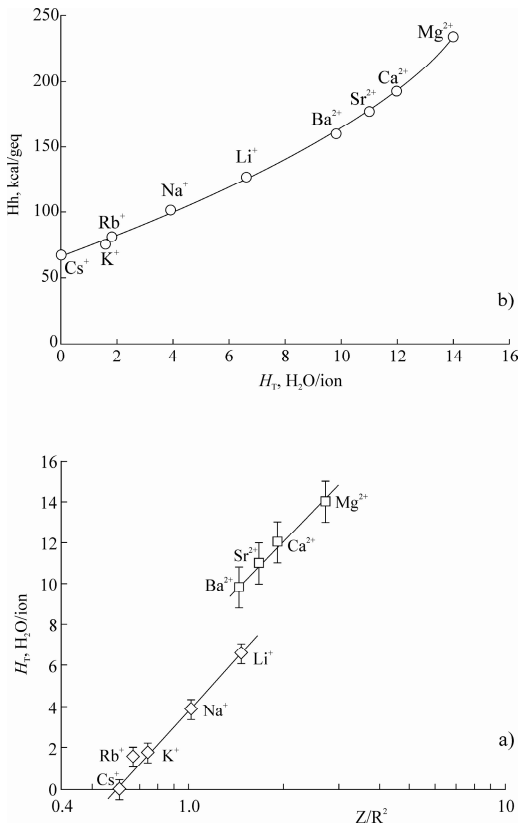


Fig. 3. Relationship between the hydration numbers ($H_T$) of alkaline and alkaline-earth cations and: a) ion potential ($Z/R^2$) and b) hydration heat (Hh). (The used values of Hh are after Mishchenko & Poltorattskii, 1968)

Table 2. *Number of water molecules and framework oxygen atoms surrounding $Na^+$, $Ca^{2+}$, $K^+$, $Mg^{2+}$ cations in some zeolite structures*

| Str. type | Mineral | $Na^+$ | | $Ca^{2+}$ | |
|---|---|---|---|---|---|
| | | $H_2O$ | fr. O | $H_2O$ | fr. O |
| ANA | analcime (Na) – wairakite (Ca) | 2 | 4 | 2 | 4 |
| NAT | natrolite (Na) – scolecite (Ca) | 2 | 4 | 3 | 4 |
| LAU | laumontite | – | – | 3 | 4 |
| GIS | amicite | 3 | 3 | 3 | 4 |
| GIS | gismondite | – | – | 4 | 2 |
| HEU | heulandite | 6 | 2 | 5 | 3 |
| STI | stilbite | 3 | 2 | 7 | 0 |
| SHA | chabasite | – | – | 5 | 0 |
| OFF | offretite | – | – | 6 | 0 |
| | | $K^+$ | | $Mg^{2+}$ | |
| HEU | clinoptilolite | 3 (1) | 6 | 6 | 0 |
| OFF | offretite | 0 | 6 | 5 | 0 |
| FER | ferrierite | – | – | 6 | 0 |
| PHI | phillipsite | 4 | 4 | – | – |

where the water molecules distribute the cationic charges to these anionic sites ($AlO_4$-tetrahedrons), which are not directly contacted with the cations, predetermining stability of the large channels. Figure 4 shows the surroundings of exchangeable cations in the clinoptilolite structure. In agreement with the cationic hydration properties in clinoptilolite structure the $K^+$ cation is mostly surrounded by oxygen atoms of an 8-membered tetrahedral ring, the $Ca^{2+}$ and $Na^+$ cations – with water molecules and framework oxygen atoms, and $Mg^{2+}$ cations – only with water molecules.

The number of water molecules in the surrounding of $Ca^{2+}$ and $Na^+$ decreases in the structures of high temperature narrow-porous zeolites, such as analcime, wairakite, natrolite, scolecite, etc. As is shown on Fig. 5 the cations in these structures are in close contact with the anionic sites (aluminum tetrahedra) and directly influence their number and distribution.

The establishment of the actual existence of stable cation-water clusters and in particular of hydration numbers at higher temperatures, conform our previous assumption and enable an adequate interpretation of many observed phenomenon, which are discussed below.

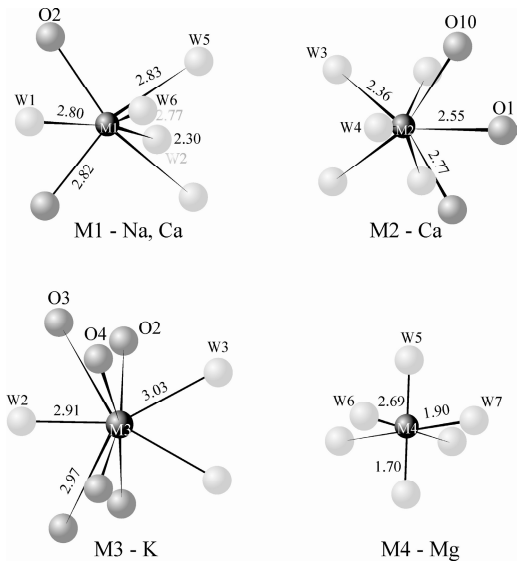


Fig. 4. Cation coordination in the clinoptilolite structure (Distances are given in Å). (Koyama & Takeuchi 1977)

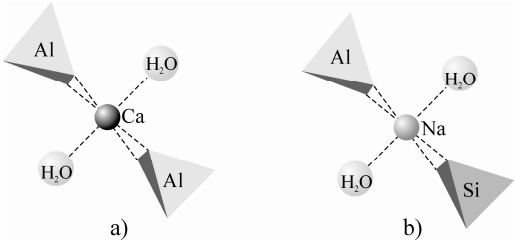


Fig. 5. Coordination of cations, water molecules and Si,Al-tetrahedra in the structure of wairakite (a) and analcime (b). (Takeuchi et al. 1979)

## Template mechanism for natural zeolite formation

The first question is: how are zeolite porous structure formed in both natural and laboratory conditions. In reality, these structures are so densely packed as those of feldspars and silica minerals (Table 3) and become porous after dehydration.

Present day concepts about the mechanism of zeolite crystal growth have been developed for the synthesis of zeolites with participation of large organic cations or molecules, which, as templates determine the porous character of the structure and the type of the zeolite obtained. The formed porous silicate frameworks with channels filled with organic molecules or cations convert into zeolites when organic "guests" are replaced by alkali cations and water molecules by ion exchange or after combustion of organic matter (Flanigen 1973; Cundy & Cox 2005).

In particular cases a template mechanism is supposed for the formation of zeolites without any organic molecules. According to Breck (1964) alumosilicate tetrahedra re-group about hydrated sodium ions to form the basic polyhedral units (24-hedra) of zeolite A. Galli (1974) speculated that $Mg(H_2O)_6$ complexes acts as templates for the formation of gmelinite type cage in the mazzite structure. Much earlier Belov (1961) suggested the idea that clatrate-like groups of water molecules are possible templates forming zeolite A and X. However, in this hypothesis the role of exchangeable cations is ignored.

The starting point of our research (Kirov 1990) was the observation that in natural conditions zeolites with the same framework topology form with different exchangeble cations, but at different temperatures. The zeolites in hydrothermal veins are much more calcium in comparison to the isostructural samples formed in diagenethic conditions. Typical examples are shown on Fig. 6. The working hypothesis to explain these observations was constructed based on the theory of ion hydration: dependence on the number of water molecules in the hydrate shell of a single ion and the strength of their bonding with the surface charge of the ion ($Z/R^2$ , were Z is the charge and R – radius of the ion) and unproven at that time assumption, that the hydration number and the stability of the hydrated complexes decrease with the rise of temperature. Similar water configurations are expected to form around different cations at various temperatures and that they would predeterminate the appearance of zeolite of similar framework topology.

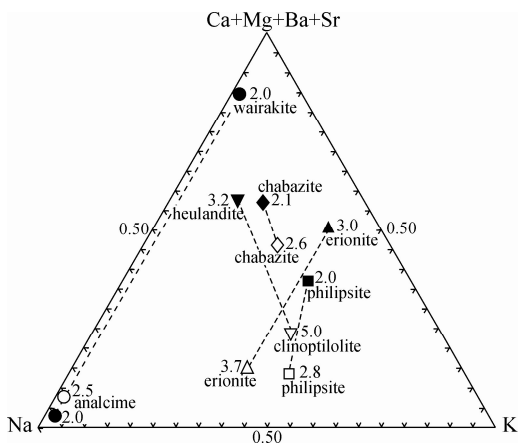


Fig. 6. Average chemical compositions of zeolites from hydrothermal veins (full symbols) and zeolitized volcanic tuffs (empty symbols). The Si/Al ratio is given by figures

Table 3. *Packing index of some zeolite and non-zeolite minerals*

| Mineral | | Packing index, % | |
|---|---|---|---|
| | | hydrated | dehydrated |
| Faujasite | $(Na_2,Ca,Mg)_{29}Al_{58}Si_{134}O_{384}.240H_2O$ | 46.9 | 28.9 |
| Chabasite | $(Ca,Na_2,K_2)_2Al_4Si_8O_{24}.12H_2O$ | 49.2 | 32.6 |
| Mordenite | $(Na_2,Ca)_4Al_8Si_{40}O_{96}.28H_2O$ | 49.0 | 38.0 |
| Laumontite | $Ca_4Al_8Si_{16}O_{48}.16H_2O$ | 49.1 | 38.6 |
| Natrolite | $Na_{16}Al_{16}Si_{24}O_{80}.16H_2O$ | 49.9 | 42.4 |
| Cristobalite | $SiO_2$ | 47.1 | |
| Trydimite | $SiO_2$ | 49.1 | |
| Orthoclase | $KAlSi_3O_8$ | 51.0 | |
| Quartz | $SiO_2$ | 56.7 | |

The results from experimental tests based on the proposed hypothesis are given on Fig. 7. To ensure identical conditions for the tetrahedral section of the system the initial glasses were prepared from mono-cationic forms (Ca, Na and K) of heulandite with Si/Al ratio of 2.96, amorphized by heating at 850°C for 5 hours.

Each glass was treated in a solution of the corresponding hydroxide at temperatures ranging from 70 to 400°C. Several experiments are carried out with mixed solutions and glasses. Three fields were outlined: of unchanged glasses, of zeolites and of feldspars. The glass – zeolite and zeolite – feldspar transition occurred at different temperatures in different cation systems. No crystallization was observed up to 150°C in the calcium system, and the zeolite – feldspar transitions took place at highest temperatures. Zeolites in the potassium system were formed only at low temperature, and potassium feldspar is the main phase already at 150°C. In each cation system the crystallization is subjected to the Cornue's rule: with the increase of temperature less hydrated minerals are formed. However, at the same time, the materials synthesized at the same temperature in various systems have different water content. For example, at 200°C the water molecules per 100 framework oxigens are: 0 for formed potassium feldspar in potassium system; 16.7 for analcime formed in sodium system and 33.3 for heulandite formed in calcium system. Thus, the identical framework topologies can be formed at different temperatures using different cations – the calcium varieties are stable at temperatures 50–150° higher than the temperatures at which sodium ones are obtained.

All these observations can be explained with the action of cation-water clusters as templates during the formations of zeolite structures. If this is a sodium ion with its hydration shell in alkaline alumino-silicate solution, at a certain moment some of the

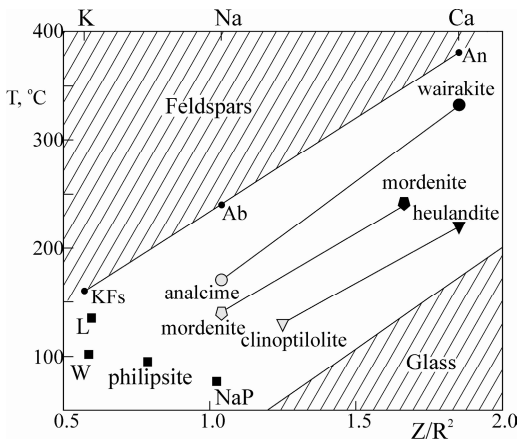


Fig. 7. Temperatures of synthesis of pear iso-structural zeolites and feldspars from artificial glasses as a function of the ion potential of the exchangeable cations in the system glass-solution

water molecules from the shell are replaced by silicate units and a zeolite structure motif is built. By the repetition of this "*in-situ*" construction operation, a nanoporous structure is obtained. In identical conditions, a bi-valence cation is not suitable for being a template, because its hydrate shell is too large and screens the cation charge; however, at higher temperature, it may offer the same configuration and conditions for obtaining the same structural motif. The only difference is that it will integrated two alumina tetrahedra instead of one, for the monovalent cation. Thus, we observe the same framework topology with different /extraframework/ chemical composition. Also, the type of the formed zeolite is influenced by the other factors - Si/Al relation of initial glass, the presence of impurities or seeds, etc.

The presence of a second cation stabilizes a second system of channels in the structure. In clinoptilolite, potassium stabilizes the 8 member cannel C. In heulandite structure such role plays the "unpacked" at high temperature sodium cation.The philipsite is also bi-cationic, etc. Cations with very big and stable hydration shell (like $Mg^{2+}$), as well as non-hydrated or very weakly hydrated cations ($Rb^{+}$, $Cs^{+}$) cannot act as templates and cannot form on their own zeolite minerals.

As is shown, the nature of cation-water clusters in zeolite-forming solutions plays a key role for the type of the resultant zeolite framework. Moreover, in poly-cationic large porous zeolites the size, charge and placing of the original extraframework cations determine the Si, Al ordering in the framework. The divalent cations grouped pairs of closely spaced aluminum tetrahedra, whereas monovalent cations disperse Al-tetrahedra more evenly within the framework. This creates conditions for the formation of frameworks with different Si-Al ordering, but with identical Si/Al ratio and the same framework topology. The differences of Si/Al ordering exert influence on some properties of the samples such as ion exchange selectivity (Tarasevich et al. 1997).

The variability of cation-water templates under slight alterations of conditions determine the considerable diversity of structural types, appearing in the chemically uniform zeolite system in relatively narrow range of formation conditions of these minerals.

## Ion exchange

The ability of zeolites to substitute extraframework cations with other cations in aqueous solutions or salt melts is important for some natural processes and the practical application of zeolites. The ion exchange properties of a zeolite are described by its ion-sieve properties, ion exchange capacity and ion selectivity.

The ion-sieve effect arises by the fact that in ion exchange reactions there can be involved only cations with sizes lesser than the intersection of the channels of the mineral species. The ion hydration causes a change in the radius of the cation-water clusters – the so called hydrated ionic radius. The hydrated radii of large cations such as $K^{+}$, $Rb^{+}$, $Cs^{+}$ appear to be lesser than that of $Na^{+}$ and $Li^{+}$. In the cases of divalent and trivalent cations, the large hydrate shell of magnesium, zinc and similar small cations complicates their exchange in zeolites and trivalent cations do not locate into the channels. The decrease in hydration number of cations at elevated temperature (see Table 1) facilitates obtaining of ion-exchanged zeolite forms with strongly hydrated cations.

The ion exchange capacity depends mainly on the charge of the aluminum silicate framework, i.e. ratio of Si/Al, whereas the exchange selectivity is influenced by the properties of the exchangeable cations, concentration of the solution, presence of other ions, temperature etc, as well as by the charge and the Si/Al distribution in the framework and the characteristics of the channel system therein. The importance of hydration for ion exchange selectivity has been also noted in the early studies in this area (Filizova 1974). The striving of the exchange cations to obtain a comfortable hydrate shell plays a substantial

role in the ion exchange in water solutions. For instance, $Ca^{2+}$ in clinoptilolite has 5 neighbours water molecules, twice less than its hydration number in the solution, while $K^+$ does not change its water surrounding when entering the zeolite. The calcium ion strives to the aqueous solution where it forms full hydrate shell, whereas the potassium cation replaces calcium from zeolite structure becoming surrounded mainly by framework oxygen atoms. By reason of that high selectivity of clinoptilolite to potassium and other large monovalent cations is observed.

The increase of temperature, as shown above, affects to different extent the hydrated shells of the various cations and can cause significant changes of the preferences of zeolites to exchangeable cations. The laboratory experiments confirm, and industrial investigations use the change of selectivity caused by increase of temperature. For example, Figure 8 demonstrates the redistribution of exchangeable cations in clinoptilolite column infused with a 0.1 molar solution of $KNO_3$ and $NaNO_3$ in a 1:1 ratio. The column was situated for a week in thermal gradient autoclave with a gradient of 30 to 220°C (Filizova et al. 1978). The experimental setting was described in the work of Kirov et al. (1979). The typical mineral selectivity for large monovalent cations and the formation of clinoptilolite form with high potassium content were observed at low temperature. The increase in sodium content is less than that of potassium, whereas the most of the calcium cations are expelled from the structure into solution due to their high hydration ability. At high temperatures the cation relationship is quite different. The sodium and calcium contents in clinoptilolite increase, whereas this of potassium decreases. The result relates to the decreasing of the hydration number of the $Na^+$ and $Ca^{2+}$ cations and to increasing of that of the potassium cation with elevating of the temperature. The redistribution of cations occurs through counter diffusion of cations and their concentration varies gradually upon the height of thermal gradient column.

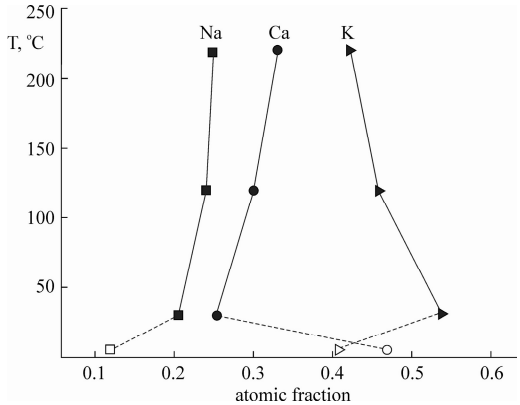


Fig. 8 Distribution of the exchangeable cations of initial clinoptilolite sample (white symbols) and of thermal gradient exchange column (black symbols)

Aleksiev et al. (1997) and Aleksiev & Djourova (1986) explained vertical zonation in distribution of exchangeable cations in clinoptilolite tuffs in Eastern Rhodopes by means of counter diffusion. The authors divided upward zones of sodium, calcium and potassium clinoptilolite. However, the analysis of published data has not confirmed the diffusion hypothesis. On the contrary, variations in the content of the exchangeable cations do not occur gradually, and zones are separated by abrupt boundaries. Furthermore, in the behavior of the exchangeable cations in particular profiles there does not exist a common tendency related to exchangeable selectivity of clinoptilolite. Apparently, there are zonations predetermined by the initial composition of the tuffs.

Khamizov et al. (1994) have described in their patent RU 2006495 a method for obtaining almost complete exchange of potassium in clinoptilolite from seawater despite much higher concentration of sodium – molar ratio K:Na in sea water is about 1:45, and the concentration of potassium is only 0.01 geqiv/l. In this experiment in the first stage at 15°C a large amount of sea water passes trough the clinoptilolite column, which resulted in increasing of potassium content in the zeolite

because of high selectivity to potassium at low temperature. Afterwards, with three volume lesser water at temperature 65-75°C the potassium is replaced by sodium resulting in potassium-rich solution. In a third stage again at 15°C the potassium-rich solution is passed through a column of natural clinoptilolite, which sorbed potassium and produced long-acting potassium fertilizer.

As the heats of hydration (and dehydration) of different ions vary significantly (see Fig. 3a), it should be expected that heat effects of ion exchange reflect in some extent the relationship of hydration heats of exchangeable ions. We have studied calorimetricaly the ion exchange in clinoptilolite and mordenite mono-cationic forms, and the influence of various factors on the thermal effects of the exchange reactions (Kirov et al. 1989; Filizova et al. 1993; Petrova et al. 1997; 2011).

Figure 9 shows the heats of exchange vs. the differences between the hydrated numbers of outgoing and incoming (with respect to zeolite) cations, selected from quoted articles. In the case of ion-exchange of typical for clinoptilolite cation pairs $Ca^{2+}$, $Na^{+}$, and $K^{+}$ (as well as $Rb^{+}$ and $Cs^{+}$) the amendment of heats of exchange are perfectly consistent with the differences between the hydrated numbers of in-going and out-going the zeolite cations and their hydration heats. At high temperature the thermal effects of the reaction change in relation to the change of hydration number of the competing ions: decrease of the small ones and increase of the big ones. The order of the heat values of the exchange is in good agreement with the order of ion selectivity

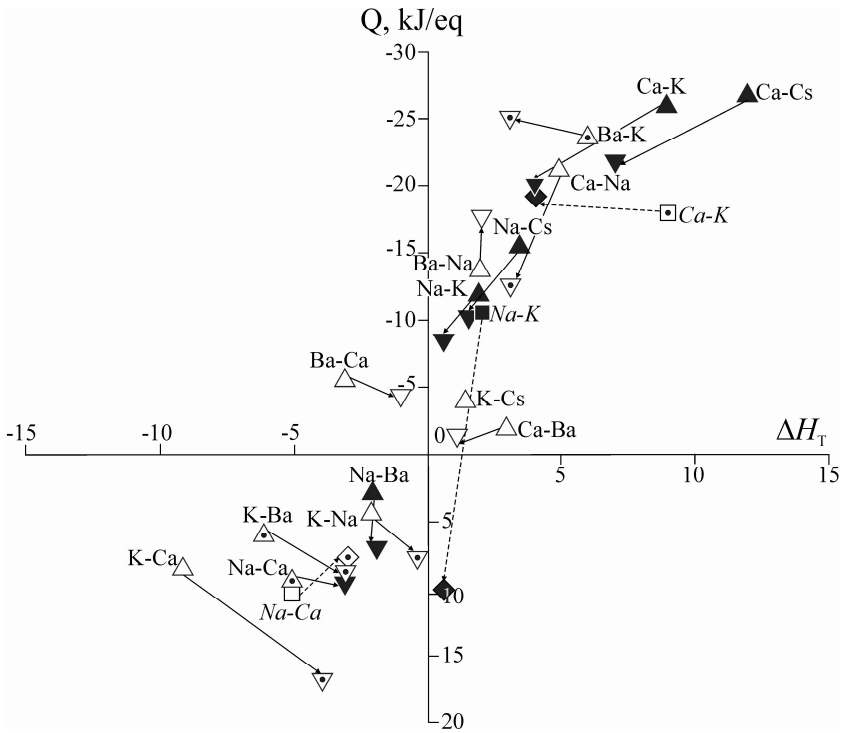


Fig. 9. Ion exchange heat *vs.* difference of hydration number of cations in zeolites and in solutions. Degree of exchange: empty symbols – up to 0.3; empty symbols with dot – 0.3-0.6, full symbols – 0.6-0.9; Temperature: ■, ▲ – 30°C, ◊, ▼– 95°C; ▲ - clinoptilolite, ■, ◊- mordenite

established by other methods (see review in Pabalan & Beretti 2001). Based on these data there has been assumed that, the sign of the reaction (endo- or exothermic) (Roque-Malherbe et al. 1987) or heat of exchange (Kirov et al. 1989) can be used to predict the selectivity of exchange reactions, which is in perfect accordance with the above cases. This idealized picture is distorted, however, when an atypical to the system cation is included in reactions. Such a cation can be barium, which has equal size with potassium, but is with twice bigger charge and 3.5 times bigger mass. While in the reactions whit Na, K and Ca the exchange heat is reduced at 95$^{o}$C, in cases when Ba is outgoing ion, exactly the opposite takes place. Also, the behavior of mordenite samples is different from that of the same cationic couples in clinoptilolite.

It is important to note that the heat of exchange in zeolite is more than ten times lower than the heats of exchange reactions in solutions. Obviously, in all cases, the total heat effect is restricted by the processes in the zeolite part of the system. Tarasevich et al. (1988, 1997) have explained the heat of exchange and the selectivity of ion exchange based mainly on the interaction between the exchangeble cations and the zeolite framework. More recently these authors (Tarasevich et al., 2008) have concluded that the heat of exchange depends predominantly on „the solution part of the system“. The results obtained in our study (Petrova et al., 2011) show that the interpretation of calorimetric data requires consideration both of cation interaction with water molecules in the solution and in the zeolite channels. In the process of ion exchange, both outgoing and ingoing cations change their hydration status. To enter the narrow opening of the channel hydrated ions have to shed some associated water molecules. The energy cost of shedding strongly bond water is greater for small-sized and high charged cations rather than the large-sized and low charged having small hydrated shell. This energy loss is only partially compensated at the secondary hydration of cations in the channels. It should be taken into account either the value of the energy needed to separate the outgoing cations from framework oxygen atoms and the energy for connection of incoming cations to the structure. A prominent energy is required to overcome the resistivity experienced by the cation upon migration throughout channels. During ion-exchange reactions the amount of water molecules non-bonded with cations and the heat of hydration or dehydration were affected by the differences in size and charge of the cations. However, these processes are rather complicated and not well studied yet.

In all cases, the degree of exchange is higher at high temperature. As it is seen on Fig. 9 no correlation is found between the heat effects and the degree of exchange. The strong exothermic reaction Ca-Na has a degree of exchange of only 0.23, whereas the endo-thermic Na-Ca reaction has twice this value. The reaction Na-Ba is also endothermic, with degree of exchange of 0.69 even at 30$^{o}$C. Obviously, the degree of exchange depends mainly on the interactions in the structure, especially on the positional selectivity of competing cations, but to clarify these issues requires more research.

## Reversible dehydration

The *dehydration* is an essential stage in the preparation of zeolites for drying processes or molecular sieving. The rehydration is the basis of thermotechnical applications of zeolites. Both processes depend on ion hydration, and their study yields information on the interaction of the components of the zeolite structure.

The zeolites are dehydrated upon heating and/or vacuum treating whereas the loosely bonded water molecules are expelled in dry air at ambient conditions. The exchangeable cations located in the channels of the zeolite are coordinated with water molecules and framework oxygen atoms (Table 2). The ratio of $H_2O:Ca^{2+}$ varies from 3 in wairakite and scolecite to 6 and 7 in chabazite, stilbite, and the ratio of $H_2O:Na^{+}$ from 1 (natrolite, analcime) to 4 (barrerite etc.). The temperature

of releasing of one water molecule depends mainly on the bonding energy of the cations. The water molecules of small porous zeolites corresponding to the closest and the most strongly bonded molecules from water surrounding the cation release at high temperatures, depending on the ionic potential of the cations. As is shown on Fig. 10a, the expelling of the discrete water molecules surrounding sodium cation in natrolite structure is manifested by a sharp effect at 330°C on the DTA-curve. The thermal curves of the isostructural scolecite (Fig. 10b) display two main water losses at 240 and 420°C, corresponding to two states of water molecules in the structure. One water molecule occupies an empty cationic position and firstly leaves the structure, while the other two water molecules coordinated with calcium ions leave the structure at much higher temperature.

On the thermal curves of large pore zeolites broad peaks were observed due to overlapping of the thermal effects of several water molecules with different binding energy. The peak of Ca-chabasite (Fig. 10c) extends from 40 to 400°C (with a maximum at 200°C) as the low temperature part is due to expelling of water molecules non-bonded with cations. The curve pattern is complicated by the re-distribution of water molecules upon reducing of their number; by relocation in new positions of partially or completely dehydrated cations, as well as by corresponding change in the geometry of the channels. The heulandite DTA-curve (Fig. 10d) is complicated owing to the phase transition at 230°C expressed by narrowing of the channels and redistribution of the remaining cations and water molecules. Together with dehydration, Ca1 moves to the site occupied at room temperature by the water molecule W1 or by the potassium cation K3 being surrounded only by framework oxygen atoms and causing a framework deformation. At the same time the potassium cation leaves the 8-member channel and moves to the center of the narrowed due to phase transformation channel A (Armbruster & Gunter 1991; Khobaer et al. 2008). The complete destruction of heulandite structure occurred at 400°C. In the structure of the iso-structural clinoptilolite the predominant $K^+$ and $Na^+$ cations are not able to deform the framework. By reason of that the water molecules released at wide temperature interval (60 to 280°C with a maximum at 140°C) and the destruction of the structure occurred between 500-800°C, depending on the ratio (K + Na)/Ca in the structure.

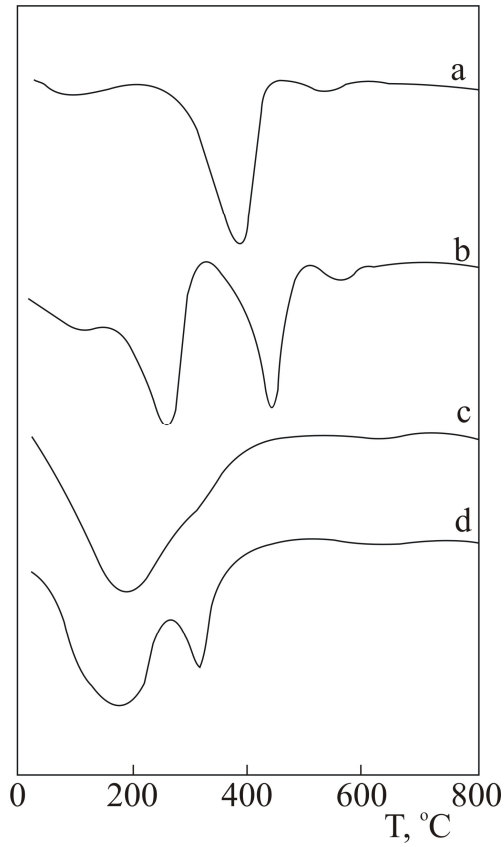


Fig. 10. DTA-curves of natrolite (a), scolecite (b), Ca-chabasite (c) and heulandite (d)

The *rehydration* is possible if the structure has not been irreversibly changed during heating, and water molecules are adsorbed from the air or through moistening. The process is exothermic and the heat

production is mostly determined by the heat of hydration of the exchangeable cations (Barrer & Cram 1971). On Figure 11 there is shown the increase in temperature caused by moistening with water and ethyl alcohol of activated at 300°C almost monocationic ($Ca^{2+}$, $Na^{+}$ and $K^{+}$) forms of chabasite, clinoptilolite, mordenite and phillipsite (Kirov & Gyaurova 1980). The highest heat output caused by moistening with water is observed in the case of calcium forms, followed by the sodium and potassium forms in accordance with the hydration heat of the cations. This trend is disturbed in the case of phillipsite because of the low thermal stability of its calcium form and its partial destruction. The penetration of the larger molecules of alcohol in the channels of zeolites is limited by their cross sections. The channels of clinoptilolite and phillipsite themselves are inaccessible to the molecules of alcohol and do not heat up upon moistening. Some of the exchangeable cations can block the access to a part of the free volume and can cause changes in the order of sorption heats.

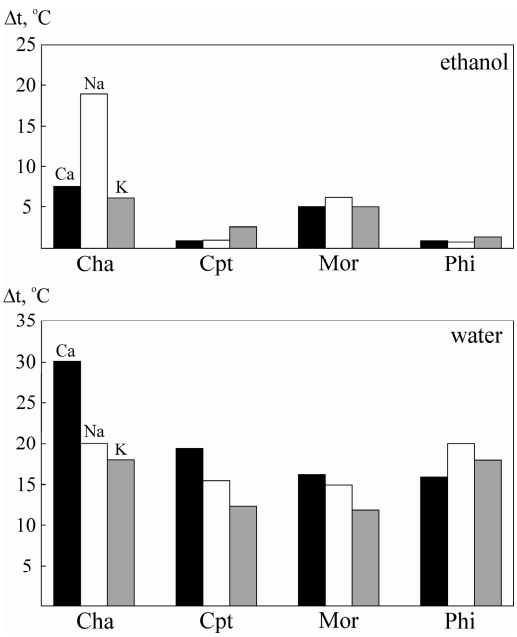


Fig 11. Increasing in temperature of dehydrated at 300°C Ca, Na and K forms of chabasite, clinoptilolite, mordenite and phillipsite after moistening with water and ethyl alcohol (Kirov & Gyaurova 1980)

## The case "laumontite"

The processes of dehydration/rehydration of laumontite deserve attention either because of its attitudes to leonhardite or because of some unique characteristics of this mineral. According to Fersman (1909), laumontite and leonhardite are two separate mineral species. Laumontite is stable on the Earth surface, but easily loses part of the water and converts into leonhardite. Besides this "secondary leonhardite" Fersman described for the first time "primary leonhardite" in which part of calcium is replaced by potassium and sodium. Coombs (1952) established the reversibility of dehydration and its influence both on the optical properties and the unit cell parameters of the two varieties. Pipping (1966) found out an increase of about 50 $A^3$ of the unit cell volume of leonhardite under moistening, while the "primary leonhardite" does not change cell volume under the same conditions. Thus, in the literature leonhardite is referred to be partially dehydrated form of hydrothermal laumontite and for this reason it is even discredited by the IMA Subcommittee on Zeolites as a mineral species (Coombs et al. 1997). Aldthough the name "leonhardite" was discredited it is retained here for simplicity to distinguish the compositional variants – laumontite ($Ca_4Al_8Si_{16}O_{48}.18H_2O$) and leonhardite ($Ca_4Al_8Si_{16}O_{48}.14H_2O$).

However, the X-ray diffraction investigation of laumontite at soft-hydrothermal conditions (95°C, 1 atm pressure) (Kirov & Balkanov 1976) showed that the X-ray diffraction powder pattern of laumontite under these conditions is identical to that of air dry leonhardite (Fig. 12). Hence, under hydrothermal conditions laumontite has the leonhardite parameters. As a result of this study several conclusions were implied:

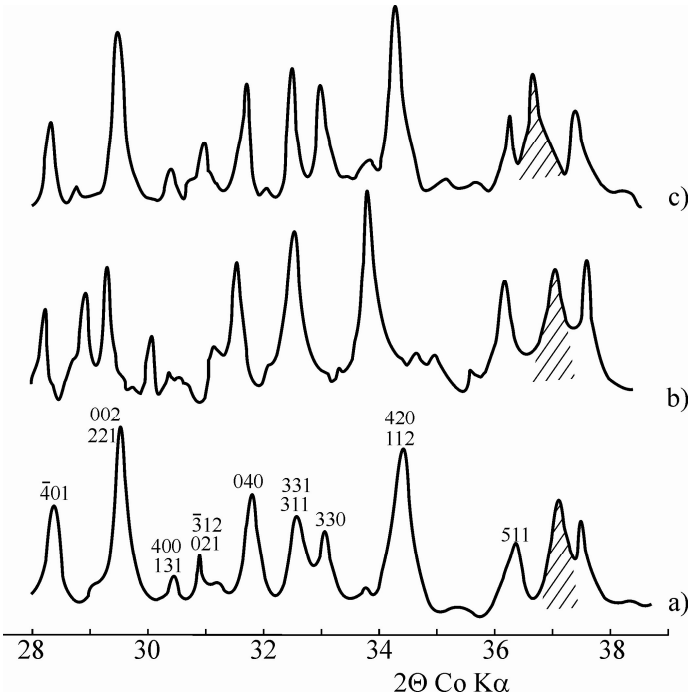


Fig. 12. X-ray diffraction patterns of laumontite: a) air-dry laumontite ("leonhardite"); b) in water at 20°C, 24 h); c) in water at 95°C ("leonhardite"). The hatched reflections belong to Teflon (Kirov & Balkanov 1976)

1. At hydrothermal conditions the stable phase is leonhardite rather than laumontite

2. Laumontite is formed as a result of hydration of leonhardite at decreasing of the temperature. This additional hydration was explained by the striving of the calcium ions to maximal hydration at low temperatures and by unique elasticity of the aluminum silicate framework of this mineral. The lack of additional hydration of the "primary leonhardite" was attributed to the potassium cation, which "as is known (Samoylov 1957) does not form stable hydrated shells." On the other hand, the fact that laumontite structure expels the additional water molecules at low humidity for few hours was explained by the significantly strained framework at thorough hydration.

The interest in these problems has arised 20 years later, producing new results on the crystal chemistry of laumontite and leonhardite. It was firmly establish that fully hydrated laumontite contains 18 water molecules per unit cell (Armbruster & Kohler 1992, Artioli & Stahl 1993) as compared to leonhardite, containing 14 water molecules per unit cell. Also, the positions and occupation of calcium cations and water molecules in completely hydrated and partially dehydrated by heating (Stahl et al., 1996) and at different humidity forms of laumontite have been determined (Fridriksson et al. 2003a, b). The latter authors also proved the unique for zeolites subsequent empting of the water positions in laumontite structure marked by four maximum on the thermal curves: W1 at 40, W5 at 80, W2 at 220 and W8 at 420°C.

Regarding laumontite–leonhardite relationships it is essential to note that Stahl et al. (1996) have observed again dehydration of laumontite in water, as noted: "It is also interesting to note that 90% of W1 is expelled despite the fact that the sample is still submerged in water", but they did not make any genetic assumptions. Based on data from the last paper, and thermodynamic analysis of

the system and geological considerations Neuhoff & Bird (2001) concluded that laumontite forms as leonhardite during metamorphism and diagenesis. They found that consideration of leonhardite, instead of laumontite, in low-grade metamorphic phase relations give calculated entropies of reaction which more correctly reflect the real relationship of the zeolitie in the system. In conclusion, the authors proposed the leonhardite to be considered "as a mineral species diferent from laumontite, at least for the purpose of thermodinamical calculations, in order to beter reflects the composition and stability of this common zeolite in geological systems".

The authors of the mentioned above papers determined two types of water molecules: such bonded with calcium cation (W2 and W8) and hydrogen-bonded water molecules (W1 and W5). Particular attention is given to the water in position W1, which is responsible for the transformation laumontite ↔ leonhardite. However, Fredriksson et al. (2003b) after analyzing the available calorimetric data, concluded that the Ca2 cations in the laumontite channel stabilize water molecules in W1 and W5 sites and accept that the W2 and W8 sites correspond to the first hydration shell of the Ca2 ion, whereas the W1 and W5 sites are equivalent to the second hydration shell. The new data confirm the prominent elasticity of laumontite framework - the changes with de- and rehydration are mainly at the expense of changing the angles T-O-T (Stahl et al. 1996). The introduction of W1 and W5 in the structure causes strain and tension in the framework, and these results in high volatility of the water molecules occupying these sites.

At dry conditions the laumontite crystals are broken into fine powder. This peculiarity has been noticed by the first researchers of the mineral and was reflected in its first name: zeolite efflorescente in French and Mehlzeolith (piebald zeolite) - in German. In 1908 Fersman highlighted the uniqueness of this phenomenon in mineralogy. He stated as analogies both the sputtering of aragonite during its transformation into calcite and the transition of potassium sulphate into polymorphic phase during heating. Fersman pointed out that in these cases the solid modifications converted into modifications having lower density. In the literature, however, sputtering of laumontite has always been explained by expelling of water during transition to leonhardite, i.e. with shrinkage of the cell. In our previous work (Kirov & Balkanov 1976) we considered that the sputtering of laumontite is more correct to be assigned to the extension of the structure caused by the additional hydration. This conclusion is supported by the fact that the "primary leonhardite" can not be additionally hydrated at room temperature and does not sputter in the air.

In conclusion, all data suggest that the diverse and peculiar properties of laumontite can be explained by the tendency of calcium ions to surround with "comfortable" hydrated shell at different environmental conditions.

## Summary

The thermodynamic hydration numbers of aqueous solution of strong electrolytes adequately explain many solution properties in a wide range of concentrations and temperatures and allow predicting the behaviour of ions in different processes (Zavitsas 2010).

The proof of the existence of stable cation complexes in aqueous solutions and variability of hydration numbers with temperature gives strong arguments of supporting the template mechanism of zeolite formation at natural conditions. The observed in natural deposits and the experimental formation of zeolites with same structural type and different exchange cations can be explained by the occurrence of similar templates of different cations at different temperatures.

The cationic hydration is crucial for the ion exchange interactions of zeolites and aqueous solutions (ion-sieve effect, ion exchange selectivity). Also, the topology of the framework and the positions of the cations, the temperatures etc. are of importance.

The opposite behavior of hydrated sodium and potassium ions with change of temperature predicted by the theory explains the effect of the two-temperature exchange method for obtaining of long-acting potassium clinoptilolite fertilizer from seawater.

The vertical zonation of the distribution of exchange cations in clinoptilolite deposits in Eastern Rhodopes, however, can not be explained by cross-diffusion of cations at thermal gradient conditions and clearly can be explained as being a result of the initial composition of the volcanic tuffs.

The thermal effects of dehydration and rehydration of zeolites are determined mainly by the hydration characteristics of the exchangeable cations. The variability and unique properties of the laumontite–leonhardite pair are associated with the hydration of the calcium cation at different conditions.

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