

TOPOTACTIC TRANSFORMATIONS OF ZEOLITES IN THE TEMPERATURE RANGE (300-500 °C)

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Abstract. Rarely occurring cases are considered when zeolites, during the gradual increase in temperature and bypassing the amorphization stage, recrystallize into densely packed framework phases. Examples of transformations include: gismondine → anorthite, laumontite-wairakite, low-silica Na- and Ca-chabazites → phases with a sodalite framework. It is shown that these transformations occur due to the inversion of the vertices of part of the framework tetrahedra to the opposite side, i.e., through the "swing transfer" mechanism, which determines the presence of common structural elements in the original and newly formed phases. The role of the stoichiometric factor and the presence of water molecules in the frameworks at the moment of recrystallization is examined. Based on the developed concepts, the possibility of recrystallization of the Na, Ca form of synthetic zeolite type P (Si/Al=1.8) into a feldspar phase of the andesine type is predicted and experimentally confirmed.

Keywords: crystal structure, topotactic transformations, structural fragments, solid solutions

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Introduction

The thermal transformations of alkali and alkaline-earth forms of zeolites usually proceed according to the following scheme: initial zeolite → partially or fully dehydrated zeolite → amorphous product → crystallization product (framework anhydrous phases) [1]. Crystallization of the amorphous phase typically occurs at temperatures above 800°C. In the literature, only 4 cases are described where zeolite, when heated at a rate of 3-10°C/min, bypasses the amorphization stage and recrystallizes at 300-500°C into a feldspar or feldspathoid-type phase. The study of the crystal-chemical mechanism of these transformations is of both theoretical and practical interest.

DISCUSSION AND CONCLUSIONS

According to the literature, the following zeolites, when heated in the range of 300-500°C, bypass the amorphization stage and recrystallize into a new phase. For instance, gismondine -

$[\text{CaAl}_2\text{Si}_2\text{O}_8]\cdot 4\text{H}_2\text{O}$ transforms into anorthite - $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ [2], laumontite - $\text{Ca}[\text{Al}_2\text{Si}_3\text{O}_2]\cdot n\text{H}_2\text{O}$ into wairakite - $\text{Ca}[\text{Al}_2\text{Si}_4\text{O}_{12}]\cdot 6\text{H}_2\text{O}$ [9], low-silica Na and Ca chabazites - $\text{Ca}[\text{Al}_2\text{Si}_4\text{O}_{12}]\cdot 6\text{H}_2\text{O}$ into sodalite [6] - $\text{Na}_8[\text{AlSiO}_4]_6$ [4], and edingtonite - $\text{Ba}[\text{Al}_2\text{Si}_3\text{O}_{10}]\cdot 3\text{H}_2\text{O}$ into a zeolite-like phase - $\text{Ba}[\text{Al}_2\text{Si}_2\text{O}_8]$ [5].

Figure 1 shows fragments of the frameworks of the original and newly formed phases. The construction was based on data presented in the following works: feldspar, gismondine, chabazite, sodalite: wairakite (analcime) - [7]; laumontite - and edingtonite (Figure 1).

It should be noted that the transformations under consideration are accompanied by a significant compression of the frameworks, which causes corresponding deformation of the structural elements that make up the frameworks (chains, rings, ribbons, nets). As a result, the data presented in Figure 1 are simplified into idealized schemes to enhance clarity, reflecting various ways of combining these idealized elements rather than their true configuration. According to the presented structural schemes, the transformation of one phase into another is formally reduced to the reorientation of the vertices of some of the tetrahedra that make up the framework to the opposite side.

In the case of transformations such as laumontite \rightarrow wairakite (Figures 1 a and b) and gismondine \rightarrow anorthite (Figures 1 c and d), the main structural fragments that clearly demonstrate the common features of the original and newly formed phases are preserved: chains made of alternating 4- and 8-membered rings in the first case, and those composed of alternating 4- and 6-membered rings in the second. The inversion of the tetrahedron vertices only leads to changes in how these structural fragments are connected to each other. In the case of the transition from chabazite \rightarrow sodalite, the configuration of the chains oriented along the threefold axis changes (Figures 1 d and e); however, the manner of their spatial orientation (joining at an angle of 120° to each other) is preserved. As a result, 6-membered rings oriented perpendicular to the threefold axis emerge.

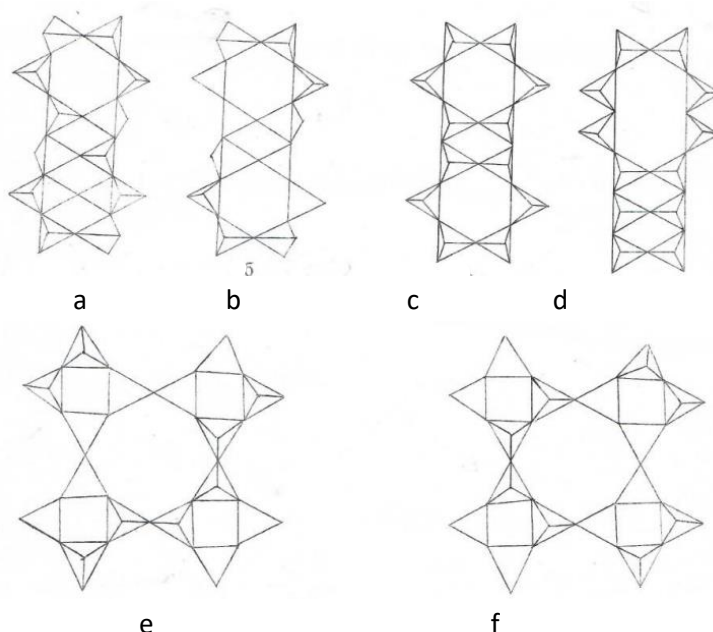


Figure 1. Fragments of zeolite frameworks (a, b, c) and the products of their recrystallization (d, e, f).

A more complex case is the transition from edingtonite to celsian (Ba-feldspar) [3]. However, it can still be shown that by pairwise inverting the vertices of the side tetrahedra of the chains $(\text{T}_5\text{O}_{10})_n$, located respectively to the right and left of the central tetrahedron, infinite double zigzag chains, so-

called "batisite chains," can be formed, which consist of corrugated ribbons of 4-membered rings. These ribbons, when connected together, form the frameworks of feldspar and celsian.

At the same time, an analysis of the behavior of zeolites upon heating allows us to identify other features characteristic of transformations of the type zeolite → feldspar (feldspathoid) phase.

Unlike zeolites, which can exist over a more or less wide range of Si/Al ratios, the products of their recrystallization are stable at relatively constant values of this parameter. For instance, Si/Al = 1 for anorthite, sodalite, and celsian, and Si/Al = 2 for wairakite. Recrystallization occurs only when the original and newly formed phases are close in stoichiometry. Thus, Na- and Ca-chabazites with Si/Al ratios greater than 1.5 do not recrystallize into sodalite, while the isostructural gismondine zeolite Ca-P (Si/Al = 1.8) does not recrystallize into anorthite.

It should be noted that in all four cases discussed above, recrystallization occurred under conditions where the zeolite had not yet lost all of its water. Moreover, attempts to accelerate the dehydration process led to a sharp slowdown in the rate of phase transformation. For instance, heating laumontite in a vacuum significantly reduces the rate of its transformation into wairakite, and when heated edingtonite is purged with dried nitrogen, the exopeak corresponding to its transformation into celsian is not detected on the thermogram. Both facts indicate the involvement of water molecules in the processes under consideration.

This characteristic feature, combined with the aforementioned structural feature (the possibility of phase transformation through the reorientation of the vertices of some of the tetrahedra that make up the framework), suggests that the phase transformations of zeolites occur through a "swing transfer" mechanism of Si(Al) atoms from occupied tetrahedra to vacant ones formed with the participation of water molecules. A similar mechanism has previously been established for phase transformations occurring during the dehydration of calcium aluminosilicate and other silicates and aluminates [1].

In the case under consideration, a vacant tetrahedron can be occupied if a water molecule is located at the base of the occupied tetrahedron. The migration of Si(Al) into the vacant tetrahedra, leading to the reorientation of the tetrahedron vertices to the opposite side, will be accompanied by the redistribution of protons and oxygen exchange between the framework and water molecules. Intense oxygen exchange in zeolites has been experimentally established when investigating the catalytic properties of zeolites [8]. However, the presence of oxygen exchange alone cannot trigger the recrystallization of zeolites, as the interaction between water molecules and the framework is only one of the three conditions outlined above under which the recrystallization of the zeolite becomes possible.

Based on the stated conditions and an analysis of the geometric features of zeolite frameworks, it can be shown that the number of zeolites capable of recrystallization in the moderate temperature range may significantly exceed the number of cases described in the literature. This can be demonstrated using the example of the previously mentioned zeolite - P (Si/Al = 1.8). In this case, the main obstacle to the transformation of Ca-P into anorthite (Si/Al=1) or Na-P into albite (Si/Al = 3) is the apparent mismatch in stoichiometry.

However, for the solid solutions anorthite-albite $x\text{CaAl}_2\text{Si}_2\text{O}_8(1-x)\text{NaAlSi}_3\text{O}_8$, the total Si/Al ratio lies within the range of 1-3 and is determined by the following formula derived from the composition of the solid solution:

$$\text{Si/Al} = \frac{2x+3(1-x)}{2x+1-x} = \frac{3x}{x+1}$$

Using this formula, it is possible to calculate at what Na/Ca ratios $(1-x)/x(1-x)/x(1-x)/x$ for a given Si/Al ratio the composition of the zeolite will correspond to the stoichiometry of the anorthite-albite solid solution, meaning that alongside the structural condition, the condition related to stoichiometric requirements will also be fulfilled. For zeolite P (Si/Al = 1.8), this condition is met at a Na/Ca ratio of 0.75. A sample of Na-, Ca-P with a ratio close to this was obtained through ion exchange and heated in a furnace at a rate of 40 °C/min. Analysis of the X-ray diffraction patterns of the samples heated to various temperatures showed that a new phase of andesine type forms in the range of 410-520 °C, whereas the X-ray patterns of the CaP zeolite heated under the same conditions indicated its amorphization during dehydration.

Thus, the experimental data we obtained support the hypotheses formulated above regarding the main factors that determine the possibility of phase transformation processes in zeolites proceeding via a topotactic mechanism.

References

- [1] Breck DW. Zeolite molecular sieves: structure, chemistry and use. New York and London: Wiley and Sons, **1974**, 771 p.
- [2] Ghobarkar H, Schaef O. Synthesis of gismondine-type zeolites by the hydrothermal method. *Materials Res. Bull.*, 34, **1999**, p.517-525.
- [3] Griffen DT, Ribbe P.H. Refinement of the crystal structure of celsian. *American Mineralogist* 61, **1976**, p.414-418.
- [4] Hassan I, Grundy HD. Structure of basic sodalite, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. *Acta Crystallography*, C39, **1983**, p.3-5.
- [5] Mazzi F, Galli E, Gottardi G. Crystal structure refinement of two tetragonal edingtonites. *N. Jb. Miner. Mh.*, **1984**, p.373-382
- [6] Mortier WJ, Pluth JJ, Smith JV. Positions of cations and molecules in zeolites with the chabazite-type framework. III. Dehydrated Na-exchanged chabazite. *Materials Res. Bull.*, 12, **1977**, p.241-250.
- [7] Takeuchi Y, Mazzi F, Haga N, Galli E. The crystal structure of wairakite. *American Mineralog.*, 64, **1979**, p.993-1001
- [8] Jule A. Rabo. Zeolite chemistry and catalysis. American Chemical Society, Washington, **1976**, 506 p.
- [9] Rahimov KG, Bagirova AF, Shirinova AF, Chiragov M.I. Crystallochemical features of laumontite in the Eocene volcanic succession of Talish (Azerbaijan). *Azerbaijan National Academy of Science, Proceedings the Sciences of Earth*, №3-4, **2016**, c.16-21 (in Russian)