TITLE: THERMAL BEHAVIOR OF NATURAL ZEOLITES

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SUBMITTED TO: Proceedings of Zeolite '93 Conference

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THERMAL BEHAVIOR OF NATURAL ZEOLITES

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ABSTRACT

The thermal behavior of natural zeolites impacts topics ranging from their application to their identification and varies significantly from zeolite to zeolite. It is well known that zeolites evolve H₂O upon heating, but recent data show that distinct "types" of water (e.g., loosely bound or tightly bound zeolitic water) do not exist. Rather water is bound, primarily to extra-framework cations, with a continuum of energies, giving rise to a pseudocontinuous loss of water accompanied by a dynamic interaction between remaining H₂O molecules and extra-framework cations. These interactions in the channels of zeolites give rise to dehydration behavior that is very dependent on the nature of the extra-framework cation, in addition to temperature and water vapor pressure. The nature of the dehydration reaction, and thus the type of extra-framework cation, also affect the thermal expansion/contraction behavior. Most zeolites undergo dehydration-induced reductions in volume that may be anisotropic, although minor thermal expansion can be seen with some zeolites. Such volume reductions can be partially or completely irreversible if they involve modifications of the tetrahedral framework and/or if rehydration is sluggish.

Thermally induced structural modifications are also driven initially by dehydration and the concomitant contraction and migration of extra-framework cations. Contraction is accommodated by rotations of the fundamental structural units, and tetrahedral cation-oxygen linkages may break if rotations are large enough and if strong interactions exist between extra-framework cations and framework oxygen atoms. Thermal reactions that involve breaking of tetrahedral cation-oxygen bonds may be markedly irreversible and may be kinetically limited, producing large differences between the results of short- and long-term heating.

INTRODUCTION

The response to heating is an important aspect of natural zeolites, and the details of their thermal behavior bear on topics ranging from industrial applications to their identification. For example, numerous zeolites are used in gas adsorption, as selective catalysts, and as molecular sieves, and a detailed understanding of their short-term (e.g., overnight) thermal behavior and appropriate activation temperatures is crucial. Short-term thermal behavior has also been suggested as a means to distinguish between similar zeolites, such as clinoptilolite and heulandite (Mumpton, 1960) and barrerite from stellerite (Passaglia, 1980). In contrast, other applications (e.g., the performance of clinoptilolite in a high-level radioactive waste repository) require that the long-term (multi-year) behavior of these minerals under elevated-temperature conditions be understood. Because most thermal reactions of interest are at least partially kinetically limited, effects that may not be important during short-term heating can become increasingly important during long-term heating. In some instances, long-term heating experiments show results very different from those of shorter duration (e.g., Bish, 1990).

It is clear from the variety of studies on zeolite thermal stability that a number of factors are important in determining the macroscopically observable thermal effects (e.g., evolution of H_2O , decrease in volume, and structural breakdown or modification). These factors include the amount and type of extra-framework cation (i.e., its ionic potential), the Al/Si ratio, the connectivity of the structure (e.g., "flexibility"), the presence or absence of H_2O , and the time, temperature, and rate of heating. Some "robust" zeolites can be heated to high temperatures and can be completely dehydrated while maintaining their original structure, but many zeolites undergo complex structural transformations upon heating and dehydration, often leading to the destruction of the original structure.

EVOLUTION OF H₂O

Most earlier analyses of natural zeolites by thermogravimetric and calorimetric methods suggested that several specific "types" of H₂O exist in the structural cavities, although as early as 1937, Milligan and Weiser concluded that the term "zeolitic water" was not a useful descriptor. They instead suggested that many zeolites, including scolecite and natrolite, are "definite hydrates," that is the water is contained in well-defined and structurally controlled sites. They further stated that water in stilbite, heulandite, thomsonite, analcime, and chabazite is bound only by adsorption forces in the structural cavities, although we now know that water in all of these zeolites interacts to various degrees with the framework and extra-framework cations. Van Reeuwijk (1974) classified water in zeolites into three categories based on calorimetrically measured heats of dehydration: loosely held water, zeolitic water, and crystal water, with denser zeolites containing primarily crystal water and more open zeolites containing zeolitic water. Knowlton *et al.* (1981) classified water in clinoptilolite as externally adsorbed, loosely bound zeolitic water, and tightly bound zeolitic water. Van Reeuwijk anticipated recent studies by concluding that low-entropy ("crystal") water is associated with cations occupying fixed positions in structural channels and high-entropy ("zeolitic") water is associated with cations "that cannot be located at specific fixed positions." "Zeolitic" water is typically used to describe H₂O molecules that can move freely in and out of the structure without disrupting it.

Recent work (Bischke *et al.*, 1988; Bish, 1988; Armbruster, 1993) has shown that H₂O molecules are held with a pseudocontinuous range of energies, and furthermore, this range of energies is a function of temperature. As some H₂O molecules evolve at lower temperatures, remaining H₂O molecules are attracted more strongly to extra-framework cations. Thus, H₂O evolution occurs in a pseudocontinuous but stepwise manner, with H₂O evolving from specific sites, often with concomitant migration of extra-framework cations and subsequent structural relaxation (*e.g.*, Armbruster and Gunter, 1991; Armbruster,

1993). Although the so-called externally adsorbed water in zeolites is held loosely, it does not appear to be held in the same manner as water adsorbed on the surfaces of materials, i.e., that associated with structural discontinuities ("broken bonds"). Because much of the H_2O in structural cavities is associated with extra-framework cations, the nature of zeolite dehydration (and the total amount of H_2O) is strongly dependent on the extra-framework cations, in particular their hydration energy. Zeolites containing high hydration-energy cations, such as Ca^{2+} , contain significantly more H_2O than those containing low hydration-energy cations, such as K^{1+} , and those with high hydration-energy cations also generally retain their H_2O to higher temperatures (e.g., Bish, 1988).

Zeolite dehydration reactions are also very dependent on the partial pressure of H_2O , and dehydration reactions can be produced simply by lowering the relative humidity. Simonot-Grange et al. (1968) showed that heulandite transforms to heulandite-B near $300^{\circ}C$ at elevated $P(H_2O)$, but at low $P(H_2O)$, it undergoes this transformation close to $200^{\circ}C$. Similarly, Van Reeuwijk (1974) illustrated that the transformation of natrolite to α -metanatrolite occurs below $300^{\circ}C$ at low pressures but is elevated to $>450^{\circ}C$ at pressures as low as 5 bar. Van Reeuwijk presented similar data for a variety of zeolites in terms of the Clausius-Clapeyron equation which all illustrate the dependence on $P(H_2O)$.

In general, unless very fast heating rates are used, dehydration approaches an equilibrium process, with rates depending on crystallite size, packing density, the partial pressure of H_2O , and, to a lesser extent, the size of the structural cavities. However, rehydration can be kinetically limited by the size of the structural apertures as well as by the other factors listed for dehydration. Chipera and Bish (1991) showed that analcime, with relatively small apertures, rehydrates very sluggishly in contrast with clinoptilolite, erionite, or mordenite which have relatively large apertures and rehydrate quickly. Figure 1 shows a plot of the degree of rehydration of a dehydrated analcime as a function of rehydration time and temperature. Clearly, the rehydration of analcime is very sluggish and would take ~4000 days in

liquid H₂O at 23°C to reach the original degree of hydration. Contrast this behavior with the results shown in Figures 2 and 3 for clinoptilolite and mordenite, showing that they both regain their original volume within 30 min after being returned to room conditions.

VOLUMETRIC AND STRUCTURAL CHANGES ON DEHYDRATION

Alberti and Vezzalini (1984) summarized the volume and structural effects of heating into three categories: 1) reversible dehydration accompanied by rearrangement of the extra-framework cations and water molecules, with little or no modification of the framework or volume; 2) reversible dehydration with a large distortion of the framework and a significant decrease in cell volume; and 3) partially reversible dehydration accompanied by changes in the framework due to breaking of T-O-T bonds. The type of behavior occurring in a particular zeolite is dependent on the nature of the tetrahedral framework, the charge on the framework, and the amount and type of extra-framework cations.

Category-#1 Transformations

The thermal behavior of chabazite and mordenite are examples of category #1 (e.g., Figure 3), showing little decrease in volume up to 300°C in vacuo. The a, b, and, c unit-cell parameters in a natural mordenite from Custer City, Idaho, decreased by only 0.5, 0.3, and 0.2%, respectively, on heating from room temperature to 300°C in vacuo. The bulk of the decrease in a, b, and volume occurred on evacuation at room temperature. Importantly, the unit-cell parameters returned to their pre-heating values within 30 min after exposing to room temperature and humidity (23°C, 25% relative humidity), illustrating that re-expansion and rehydration are not kinetically limited in the same way as they are for analcime. Chabazite from Christmas, Arizona, displays similar thermal behavior, with a decreasing by only 0.5% (volume by 0.9%) on heating from room temperature to 300°C, and chabazite from the Gila River, New Mexico, shows respective decreases of 0.8 and 1.69%. Both samples quickly returned to

their pre-heating unit-cell parameters after re-exposing to room conditions. Erionite from Eastgate, Nevada, is an example of slightly different behavior. On heating to 300°C, the a parameter of this sample decreased by only 0.58%, but the c parameter actually increased by 0.78%. Like mordenite and chabazite, the erionite sample quickly reached its pre-heating unit-cell parameters after returning to room conditions. The type of extra-framework cation in erionite had only a minor effect on the thermal behavior: the a and b unit-cell parameters of the Ca-exchanged sample changed by -0.57% and +0.87%, those for the K-exchanged sample changed by -0.21% and +0.12%, and those for the Na-exchanged sample changed by -0.32% and +1.27%. Erionite is one of the few natural zeolites in which thermal expansion effects are evident below 300°C and are not masked by dehydration-induced decreases in unit-cell parameters.

Structural details can also give rise to variations in the reversibility of the volume-decrease process. Analcime is an example of a zeolite which can be dehydrated with little or no consequent structural effects but for which rehydration and re-expansion are very sluggish due to kinetic constraints. Upon heating to 300°C in vacuo, resulting in almost complete dehydration, analcime decreases in volume by only 0.6-1.0%. Rehydration and associated volume expansion are very slow under room conditions and take ~11 yr in H₂O at room temperature. In this case, the inability to rehydrate readily is not due to thermally induced structural modifications but is instead due to the inability of water to diffuse through the small structural ports in analcime. Rehydration is considerably more rapid at elevated temperatures in liquid water (Chipera and Bish, 1991). Analcime should probably be classified as a category-#1 zeolite as there is little modification of the framework or decrease in unit-cell volume on heating.

Category-#2 Transformations

In category-#2 zeolites, more than for category #1 zeolites, dehydration/rehydration and the amount of H₂O contained in structural cavities affect the zeolite's molar volume, depending on the exact

geometry of the structural cavities. Furthermore, because the manner in which H_2O is lost is often dependent on the extra-framework cation, the volume changes observed on heating are thus often related to the extra-framework cation. For example, whereas K-exchanged clinoptilolite experiences $\sim 1.6\%$ volume decrease upon heating to 300°C , Na-exchanged clinoptilolite undergoes an 8.4% volume decrease (Figure 2; Bish, 1984). The volume observed with category-#1 and -#2 behavior results from a combination of minor thermal expansion and variable dehydration-induced contraction, both of which depend on the three-dimensional connectivity of the structure, which may also give rise to anisotropic behavior upon heating (as seen to a minor extent with category-#1 zeolites). The effects of structure are exemplified by contrasting the thermal behavior of clinoptilolite with that of mordenite shown above. Although mordenite typically undergoes a relatively isotropic volume decrease $< 2\%$, clinoptilolite can experience a large, very anisotropic decrease in unit-cell dimensions (Figure 2, Na-clinoptilolite); the distinction is related to differences in structural "flexibility" and connectivity.

The structural details of the dehydration/volume-decrease process for category-#2 zeolites are typified by clinoptilolite, which has been examined in detail by Armbruster and Gunter (1991) and Armbruster (1993). They examined two different clinoptilolite-heulandite samples at 100K in the hydrated state and several partially hydrated states. Dehydration of Ca-K clinoptilolite leads to an anisotropic decrease in unit-cell dimensions, most pronounced along b , and the structure of the sample with 25, 7, and 5 H_2O molecules per 72 oxygens was determined. They identified a variety of extra-framework cation sites in the hydrated sample, including (Na,K)1 within the ten-membered ring, Ca2 within the eight-membered ring, K3 at the edge of the ten-membered ring, and Mg4 in the center of the ten-membered ring. Mg4 is coordinated by six H_2O molecules, and the remaining cation sites are coordinated by a combination of framework oxygens and H_2O molecules. Sites (Na,K)1, K3, and Mg4 are sufficiently close that they cannot be occupied simultaneously. Armbruster identified only two H_2O sites that are not directly coordinated by cations. Dehydrating the sample to 7 H_2O molecules per 72

oxygens results first in loss of the two H₂O molecules not coordinated to cations and a significant decrease in the population of the other H₂O molecules. Accompanying dehydration is a migration of (Na,K)1, Ca2, and Mg4 towards K3 near the cavity wall. The 5-H₂O sample showed further migration of (Na,K)1 and Ca2 to K3 and significant changes in T-O-T angles, producing large compression of the channel system (Figure 4). Although the amount of H₂O and the nature of the dehydration reaction appear to be controlled largely by the hydration energy of extra-framework cations, the structural responses to dehydration are related both to loss of H₂O molecules and to movement of extra-framework cations and their subsequent interactions with the framework oxygen atoms. Hambley and Taylor (1984) and Armbruster (1993) showed that thermal stability of clinoptilolite and heulandite is related both to extra-framework cation and Al-Si substitutions. The T2 tetrahedron in all clinoptilolite-heulandites is enriched in Al, compared with the other tetrahedra, and the underbonded O1 atom is bonded both to T2 and Ca2. Thus, the Ca-O1 interaction will be dependent on the Al population of T2. Armbruster suggested that in high-Al samples (heulandites), the Ca-O1 interaction will be strong and Ca will remain localized around O1, even after dehydration (Armbruster and Gunter, 1991). However, in low-Al samples (clinoptilolites), the Ca-O1 interaction is much weaker and Ca may easily diffuse to other channel positions such as K3 during dehydration. Koyama and Takéuchi (1977) suggested that large cations such as K¹⁺ on K3 prevent the structure from collapsing whereas smaller cations such as Ca²⁺ and Na¹⁺ are too small to keep the channels expanded. The difference in thermal behavior between Na- and Ca-exchanged forms is related to the much stronger interaction between Ca and O1, resulting in statistical breakage of the T-O-T oxygen bridge in heulandite (e.g., Alberti and Vezzalini, 1983). It also appears that the shift of O1 and breakage of the T-O-T oxygen bridge is related to the extra-framework cation content of the zeolite, which is a function of the total Al-for-Si substitution.

Natrolite also undergoes similar anisotropic heating-induced changes, transforming to so-called metanatrolite at ~300°C. Heating from room temperature to 350°C, the a, b, and c unit-cell parameters

decrease abruptly by 12.5, 10.2, and 2.9%, respectively. Alberti and Vezzalini (1983) showed that the large decreases in the a and b unit-cell parameters result from $\sim 11^\circ$ rotations of the tetrahedral chains, and the smaller decrease in c is due to twisting of the chains. This transformation in natrolite is accompanied by movement of the extra-framework Na atoms in metanatrolite to positions originally occupied by H₂O in natrolite. In spite of the large volumetric changes accompanying dehydration, rehydration and re-expansion remain possible in natrolite up to the temperature at which the structure breaks down, $\sim 775^\circ\text{C}$ (Van Reeuwijk, 1974). Interestingly, the only major water-loss event in natrolite occurs at $\sim 330^\circ\text{C}$, illustrating that H₂O molecules are held very tightly in natrolite, comparable to the situation in analcime.

Category-#3 Transformations

Volume expansion, and sometimes rehydration, are typically partially irreversible (i.e., category #3) if dehydration also involves modification of the tetrahedral framework. For example, heulandite, barrerite, stilbite, stellerite, and natrolite exhibit structural transformations below 400°C , involving migration of extra-framework cations and rotations of fundamental structural units. The transformation in heulandite has been studied extensively and is a good example of the types of modifications occurring in category-#3 zeolites. As shown above, the large Ca content and greater substitution of Al-for-Si in heulandite than in clinoptilolite can result in migration of extra-framework cations, structural relaxation, and subsequent strong Ca-O1 interactions. On heating, heulandite typically undergoes rotation of its fundamental polyhedral unit composed of four- and five-membered rings, with a consequent shift in tetrahedral oxygen positions and considerable change in the shape of the two major channels in the structure. Both the eight- and ten-membered ring channels become much more elliptical in shape and the free minimum diameters are reduced considerably (e.g., Figure 4). Although Alberti (1973) distinguished no evidence for statistical breakage of T-O-T bridges in heulandite from the Faroe Islands, Alberti and Vezzalini (1983) documented the breakage of T-O-T bridges, both in the Faroe

Island and Nadap, Hungary, heulandites, due to a large shift in the position of O1. It is the breakage of T-O-T bridges that is the precursor to thermal breakdown and yields a partially or non-reversible transformation with heating.

Barrerite exhibits slightly different thermal effects than the related minerals stilbite and stellerite and undergoes several different thermal transformations, involving large volume decreases, only partial reversibility, and, at the highest temperatures, statistical breaking of oxygen bridges. Rotation of the fundamental structural units in barrerite gives rise to the large volume decrease and results in a very different channel geometry than exists in the unheated material (Alberti and Vezzalini, 1978). Interestingly, Alberti and Vezzalini demonstrated the presence of hydroxyl groups in the barrerite structure at elevated temperatures. They speculated that all zeolites exhibiting "water" losses $\geq 500^{\circ}\text{C}$ contain hydroxyl ions that probably form through reaction of intracrystalline H_2O molecules with the tetrahedral framework. Although the frameworks of stellerite and stilbite are identical to that in barrerite, they exhibit significantly different thermal behaviors. Passaglia (1980) showed that the differences in thermal behavior are due to the large influence of the extra-framework cations in these three minerals. Na-exchanged forms of these zeolites (e.g., barrerite) were stable to significantly higher temperatures than Ca-exchanged forms (e.g., stellerite). K- and Rb-exchanged forms of these minerals remained nearly unaffected up to temperatures as high as 900°C , whereas Mg and Ca forms exhibited a progressive contraction with destruction of the structure as low as 350°C . The driving forces for contraction and structural destruction thus include the interactions between dehydrated extra-framework cations and framework oxygen atoms.

Fewer data exist on the structural effects of heating phillipsite and harmotome, but both dehydrate in multiple steps, apparently as a consequence of the variety of discrete water sites in their structures. Rykl and Pechar (1991) suggested that phillipsite transforms to wairakite + quartz at $\sim 200^{\circ}\text{C}$ but did not

comment on the reversibility of the transformation. Garcia *et al.* (1992) showed that dehydration of phillipsite was accompanied by a migration of Al toward the surfaces of crystallites at temperatures as low as 400°C, a phenomenon that may be important in many zeolites upon dehydration. There are few detailed structural data as a function of temperature for mesolite, thomsonite, edingtonite, and gonnardite, although Van Reeuwijk (1974) has documented changes in X-ray powder diffraction patterns accompanying dehydration. Mesolite appears to undergo transformations of category #3 at temperatures as low as 300°C, as rehydration after heating to this temperature is not possible (Van Reeuwijk, 1974). Thomsonite exhibits only minor volume contraction upon heating to <300°C, but it undergoes significant structural rearrangement above 320°C (Van Reeuwijk, 1974). Gonnardite exhibits a significant dehydration event <100°C, accompanied by a marked decrease in the *a* and *b* unit-cell parameters, and the structure is destroyed at temperatures >300°C (Van Reeuwijk, 1974). Dehydration of edingtonite causes reversible decreases in the *a* and *b* axes and expansion along the *c* axis before destruction at ~400°C. The driving forces for these category-#3 transformations appear to be dehydration-induced contraction and the shifts of extra-framework cations and H₂O. As with category-#1 and #2 transformations, the structural transformations are also correlated with extra-framework cation and the three-dimensional connectivity of the structure, as well as the Al/Si ratio. It appears that the presence of H₂O or hydroxyl may be necessary for the occurrence of these transformations.

Long-term transformations

Although many of these transformations are reversible over short times, reactions involving breaking of tetrahedral T-O-T linkages are partially or completely irreversible. Because of the sluggish nature of Al and Si diffusion and the strength of T-O bonds, a number of these transformations are kinetically limited. For example, although clinoptilolite is not affected by short-term heating to 500°C, long-term (>1 yr) heating at 200°C caused irreversible changes to some Na-clinoptilolites (Bish, 1990). Clinoptilolites characterized by low Si/Al ratio, high Na, and low K contents underwent a transformation

to a phase resembling heulandite-B during long-term heating at 200°C. Although Na-clinoptilolite appears to exhibit category-#3 behavior similar to that observed for heulandite during short-term heating, the transformation does not appear to be identical. The Na-clinoptilolites that underwent a long-term transformation at 200°C were unaffected by overnight heating to 480°C, whereas samples that were destroyed by overnight heating to 480°C were unaffected by long-term heating at 200°C. These differences are undoubtedly associated with the greater abundance of univalent Na ions (twice as many required as divalent cations), the inability of the smaller Na¹⁺ ions to maintain expansion of the channels, and the large degree of structural distortion and volume decrease occurring below 100°C for Na-clinoptilolite.

SUMMARY

Several complex interactions exist in the channel systems of zeolites, including: 1) H₂O-extra-framework cation interactions, dominated by the hydration energy of the cation; 2) extra-framework cation-tetrahedral oxygen interactions; 3) extra-framework cation movement and consequent strain on T-O-T bridges; and 4) H attack on T-O-T bridges and consequent breakage. These interactions give rise to dehydration behavior that is very dependent on the nature of the extra-framework cation, in addition to temperature and water vapor pressure. Because the energetics of the interaction between zeolites and water molecules are dominated by interactions with extra-framework cations, water is held with a range of semi-discrete energies. Thus, specific types of water do not exist in zeolites; instead the minerals dehydrate in a pseudocontinuous manner, and the water-cation interactions are dynamic during dehydration.

Volume changes on heating are closely related to the nature of dehydration and thus usually to the type of extra-framework cation. Most zeolites undergo dehydration-induced reductions in volume,

although minor thermal expansion can be seen with certain zeolites having robust, rigid frameworks (e.g., erionite) that do not necessarily collapse when H₂O molecules are removed. Changes in unit-cell parameters are often anisotropic, depending on how the framework collapses. Furthermore, volume reductions can be partially or completely irreversible if they involve modifications of the tetrahedral framework and/or if rehydration is sluggish.

Thermally induced structural modifications are driven initially by loss of H₂O molecules and the concomitant migration of extra-framework cations, both of which often give rise to significant contraction of the framework. Such contraction is accommodated by rotations of the fundamental structural units. Given sufficiently severe compression and accompanying rotations, tetrahedral cation-oxygen linkages may be broken, particularly if strong interactions exist between extra-framework cations and framework oxygen atoms. Breaking of tetrahedral cation-oxygen bonds not only gives rise to a marked irreversibility in the observed thermal transformations, it also explains the sluggish nature of some thermal reactions and the observed differences between the results of short- and long-term heating.

ACKNOWLEDGMENTS

This work was supported by the Yucca Mountain Site Characterization Project Office as part of the Civilian Radioactive Waste Management Program. I am grateful to D. Vaniman and G. Guthrie for constructive reviews.

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FIGURE CAPTIONS.

- Figure 1.** Degree of hydration of a dehydrated analcime as a function of temperature and the log of rehydration time in liquid water. Vertical bars at the bottom of the figure represent the approximate number of days to reach full rehydration at 75, 50, and 23°C, based on extrapolation.
- Figure 2.** Unit-cell parameters of Na-clinoptilolite, showing the significant decrease in volume upon evacuation and increasing temperature and the reversibility of the reaction after re-exposing to room conditions. RT1 represents the sample examined under room conditions before heating, VAC1 represents examination at room temperature under vacuum, points up to 300°C represent examination at-temperature under vacuum, VAC2 represents examination under vacuum at room temperature after heating, and RT2 represents examination under room conditions after heating. Equilibrium time between measurements was 30 min.
- Figure 3.** Unit-cell parameters of mordenite, showing the minor decrease in volume (1.6%) with temperature and the reversibility of the reaction. Conventions as in Figure 2.
- Figure 4.** Projection of the clinoptilolite structure along [001], showing the larger ten-membered ring and the smaller eight-membered ring; a) natural sample; b) heat-collapsed phase. Note that dehydration produces a loss of water and migration of extra-framework cations in addition to a collapse of the rings (modified from Armbruster and Gunter, 1991).

Rehydration of #25608 Analcime

Mordenite, 107119, Idaho

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