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THERMAL BEHAVIOR OF NATURAL AND CATION-EXCHANGED CLINOPTILOLITE FROM SARDINIA (ITALY)

ALESSIO LANGELLA[1,*], MICHELE PANSINI[2], GUIDO CERRI[3], PIERGIULIO CAPPELLETTI[4]
AND MAURIZIO DE'GENNARO[4]

[1] Dipartimento di Studi Geologici ed Ambientali, Via Port'Arsa 11, 82100, Benevento, Italy
[2] Laboratorio Materiali del Dipartimento di Meccanica, Strutture, Ambiente e Territorio dell'Università di Cassino, Via Di Biasio 43, 03043 Cassino (FR), Italy
[3] Istituto di Scienze Geologico-Mineralogiche dell'Università di Sassari, Corso Angioj 10, 07100 Sassari, Italy
[4] Dipartimento di Scienze della Terra dell'Università Federico II, Via Mezzocannone 8, 80134 Naples, Italy

Abstract—The thermal behavior of two clinoptilolites from an epiclastic and a pyroclastic deposit of central-northern Sardinia and of their exchanged forms (Li, Na, K, Cs, Mg, Ca, Sr and ammonium) were investigated by differential thermal analysis and thermogravimetry up to 1000°C. Their thermal stability was studied by evaluating the residual crystallinity (expressed as rehydration capacity) after 2 h thermal treatments at 450, 600 and 900°C. The water loss at 1000°C was linearly related to the radius (r) and the charge (z) of the exchangeable cations by the equations r^2/z or r^3/z, which are proportional to the inverse of the charge density over the surface or to the charge density over the volume of the cations.

The cation composition plays a crucial role in determining the thermal behavior of clinoptilolite. The presence of cations such as Cs or K, which have low surface or volume charge densities, was found to increase the thermal resistance. In particular, the crystallinity of Cs- and K-exchanged forms of both clinoptilolites was not affected by thermal treatment at 450°C and was only slightly reduced by thermal treatment at 600°C.

Predicting the thermal behavior of natural and cation-exchanged forms of these clinoptilolites can provide useful information for possible applications in catalysis, in the case of high thermal stability, or for thermal transformation into ceramics or lightweight aggregates.

Key Words—Clinoptilolite, Ionic Potential, Rehydration Capacity, Thermal Stability, Sardinia, Italy.

INTRODUCTION

Research over the past six years on Tertiary heulandite/clinoptilolite-rich volcaniclastic rocks from Sardinia has demonstrated the potential of these natural resources in industrial applications. Most of the studies were aimed at investigating the mineralogy and the distribution of zeolitized areas (de' Gennaro *et al.*, 1995; Ghiara *et al.*, 1995, 1999; Cappelletti *et al.*, 1999; Langella *et al.*, 1999; Cerri and Oggiano, 2002), whereas a few studies focused on the zeolitization processes (Cerri *et al.*, 2001). Other research investigated possible applications of these materials (Cappelletti *et al.*, 2000; Langella *et al.*, 2000; Cerri *et al.*, 2002), including those that exploit the cation and water adsorption properties of the minerals.

The thermal behavior of heulandite/clinoptilolite zeolites was investigated extensively by Alietti (1972), Boles (1972), Alietti *et al.* (1977) and Koyama and Takeuchi (1977); their results were summarized by Gottardi and Galli (1985). Three possible types of thermal behavior were described.

Type I – reversible dehydration with small contraction of the framework upon heating up to ~230°C. Irreversible structural changes, which hinder rehydration, occur in the temperature range 230–260°C. Heating at temperatures >450°C results in the thermally induced collapse of the structure.

Type II – reversible dehydration with small contraction of the framework upon heating up to ~280°C. Irreversible structural changes, which hinder rehydration, occur in the temperature range 280–400°C. Heating to temperatures >550°C results in the collapse of the structure.

Type III – continuous reversible dehydration with only a very small structural contraction; the framework is not destroyed by heating up to 750°C.

Gottardi and Galli (1985), based on the results of Shepard and Starkey (1964) and Alietti *et al.* (1974), showed that the thermal behavior of clinoptilolite is mainly dependent on the extraframework cation contents of the zeolite and, to a lesser extent, on its Si/Al ratio. High Al and alkaline-earth contents give rise to type-I thermal behavior, whereas an increase in Si and/or alkaline-earth cations leads to a progressive change in the thermal behavior, following the sequence type I → type II → type III. Armbruster (1993) also discussed the relationship between the dehydration mechanism of heulandite/clinoptilolite and the positions occupied by Al and cations in the structure. Thermodilatometric curves of Na, K, Ca and NH_4 forms of a clinoptilolite-bearing sample from Pentalofos (Thrace, Northeastern

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* E-mail address of corresponding author:
langella@unisannio.it
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Greece; Dell'Agli *et al.* 1999) substantially confirm the previously reported thermal behavior.

The thermal behavior of various homocationic forms of heulandite/clinoptilolite was studied by Alietti *et al.* (1974, 1975) and Bish (1984, 1988), who reported thermal analyses of Na-, K-, Li-, Cs-, Rb-, Mg-, Ca-, Sr- and Ba-clinoptilolite. Those studies carefully investigated the dehydration of various cation forms of clinoptilolite upon heating but provided few data about their thermal stability.

The main goal of this study is a characterization of the thermal behavior of two natural clinoptilolites representative of the volcaniclastic and epiclastic units of the Logudoro Region, Northern Sardinia (Italy), and of their exchanged forms, to verify the role played by the exchangeable cations.

Data concerning the thermal stability of natural and cation-exchanged forms of these clinoptilolites are useful for applications in catalysis, in the case of high thermal stability (Kalló, 1988), or for thermal transformation into ceramics or lightweight aggregates (Dell'Agli *et al.*, 2000; de Gennaro *et al.*, 2001a, 2001b; Ferone *et al.*, 2002). These results are also germane to gas adsorption applications.

MATERIALS AND METHODS

Clinoptilolite-bearing samples were selected from an ignimbritic unit (sample 80) and an epiclastic layer (sample LacBen) of Northern Sardinia (Cerri *et al.*, 2001). These two samples were purified using the method of de'Gennaro and Franco (1979) to increase the zeolite content and to eliminate other non-zeolitic phases capable of cation exchange, namely clay minerals. Clinoptilolites were separated from other crystalline phases using a mixture of heavy liquids (bromoform/acetone) at selected densities. Whenever interfering phases were detected by X-ray diffraction (XRD), the treatment was repeated with lower-density solutions and by centrifugation (5000 rpm, Hettich Rotina 32). Table 1 reports the mineralogical composition of enriched samples determined by XRD, using the reference intensity ratio (RIR) method (Chipera and Bish, 1995) with 20 wt.% corundum (α-Al_2O_3) as an internal standard. Data were collected with a Philips PW1730/3710 instrument, using CuKα radiation, at 40 kV and 30 mA, and a curved graphite diffracted-beam monochromator, 3–80° scanning interval, step size = 0.020°2θ, and counting time of 10 s per step. The RIR standards (feldspars, clinoptilolite) were separated, whenever possible, from the same bulk rocks analyzed. Errors for each single phase are based on the standard deviation of the RIR values.

A batch exchange method (BEM) was used to prepare zeolites in nearly homocationic forms (Cerri *et al.*, 2002). This method consists of contacting a 0.5 g sample with aliquots of 35 cm^3 of solutions containing 0.5 mol./dm^3 of a selected cation in 45 cm^3 Pyrex test tubes. The exchange solutions were prepared using Na, K, Li, Ca, Mg, Sr and NH_4 nitrates (Carlo Erba reagent grade) and Cs chloride (ACROS reagent grade). The exchange reaction was enhanced by placing the tubes on a vibrating and heating device to supply continuous stirring and uniform temperature between 60 and 70°C. After 2 h of contact, the solution was separated from the solid through centrifugation and the concentration of the cations (Na, K, Ca, Mg) released by the clinoptilolite-bearing material was determined by atomic absorption spectrophotometry (AAS, Perkin Elmer 2100). This treatment was repeated a number of times (generally ten) sufficient to bring the concentration of released cations in solution below 0.5 mg/dm^3. The BEM was proven to be effective in attaining as complete as possible cation exchange of clinoptilolite-bearing materials (Cerri *et al.*, 2002). Table 2 reports chemical formulae of the natural zeolites (Cerri *et al.*, 2001) determined by electron microprobe analysis (EMPA) and the composition of extraframework cations of the exchanged samples, calculated by subtracting from the natural composition the atoms released during exchange (determined by AAS analyses) and substituting them with the ingoing cation. Although these compositions are not homocationic, we found, as others have discovered, that higher levels of exchange are very difficult to attain.

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) of natural and homocationic forms of the two samples were performed in air up to 1000°C using a Netzsch STA 409 multiple thermoanalyzer at 10°C/min heating rate. Thermal resistance was evaluated using the following procedure: samples were subjected to 2 h thermal treatments at 450 (all cation forms), 600 (all cation forms), 900 (all cation forms) and 1000°C (only Cs and K forms). Samples were subsequently cooled to room temperature (20°C), stored at room temperature in a desiccator over a saturated $Ca(NO_3)_2$ aqueous solution (relative humidity (RH) near 50%), and kept in these conditions for 24 h. The latter equilibration proved to be sufficient for attaining

Table 1. Mineral content (wt.%) of enriched samples determined by XRD (RIR).

Sample	Clinoptilolite	Feldspar	Quartz	Opal-CT	Total
LacBen	[1]85±6	3±1	3±1	6±1	97±8
80	81±6	10±2	4±1	7±1	102±8

[1] Errors = $\sqrt{(\sigma_1^2(RIR) + \sigma_2^2(RIR) + ...)}$ (Chipera and Bish, 1995)

Table 2. Compositions of natural and exchanged clinoptilolites.

Sample		Chemical formulae of clinoptilolite
LacBen	Natural form	$(Na_{0.50}K_{0.86}Ca_{1.57}Mg_{0.70})(Si_{29.73}Al_{6.31}O_{72})$ 22.14H_2O
	exchanged with	Composition of extraframework atoms after exchange
LacBen	K	$K_{4.38}Ca_{0.51}Mg_{0.26}$
LacBen	Na	$Na_{4.27}K_{0.19}Ca_{0.54}Mg_{0.19}$
LacBen	Li	$K_{0.19}$ $Li_{4.30}Ca_{0.71}$
LacBen	Cs	$Cs_{5.19}Ca_{0.16}Mg_{0.20}$
LacBen	NH_4	$K_{0.03}(NH_4)_{5.53}Ca_{0.17}$
LacBen	Ca	$K_{0.21}Ca_{2.46}Mg_{0.39}$
LacBen	Mg	$K_{0.48}Ca_{1.42}Mg_{1.29}$
LacBen	Sr	$Ca_{1.18}Mg_{0.59}Sr_{1.18}$
Sample		Chemical formulae of clinoptilolite
80	Natural form	$(Na_{0.81}K_{1.35}Ca_{1.10}Mg_{0.88})(Si_{29.61}Al_{6.43}O_{72})$ 21.19H_2O
	exchanged with	Composition of extraframework atoms after exchange
80	K	$Na_{0.11}K_{5.20}Mg_{0.40}$
80	Na	$Na_{5.17}Mg_{0.47}$
80	Li	$Na_{0.03}K_{0.27}Li_{3.92}Ca_{0.28}Mg_{0.65}$
80	Cs	$Na_{0.11}Cs_{4.96}Mg_{0.52}$
80	NH_4	$Na_{0.27}K_{0.11}(NH_4)_{5.12}Mg_{0.29}$
80	Ca	$Na_{0.16}K_{0.48}Ca_{1.94}Mg_{0.79}$
80	Mg	$K_{0.80}Ca_{0.83}Mg_{1.82}$
80	Sr	$Na_{0.40}K_{0.45}Ca_{0.89}Mg_{0.79}Sr_{0.93}$

complete rehydration. As there are no hydrous phases in these samples other than clinoptilolite (see Table 1), evaluation of the rehydration capacity (RC) after the heating cycles provides a reasonably accurate picture of the overall structural integrity of the clinoptilolite itself and was therefore used as an indicator of residual crystallinity. It can be defined by

$$RC = 100 - \left[\frac{W_{re} - W_{Trehy}}{W_{re} - W_{calc}} \times 100\right] \qquad (1)$$

where W_{re} is the original weight of the sample, namely the weight of the thermally untreated sample after it was stored for 24 h in a desiccator at 20°C and 50% RH; W_{Trehy} is the weight of the same sample thermally treated at a given temperature, T, for 2 h, cooled to room temperature (20°C), stored at room temperature in a desiccator over a saturated $Ca(NO_3)_2$ aqueous solution (relative humidity near 50%) and kept in these conditions for 24 h. Use of RC ignores the fact that, for some compositions, the clinoptilolite structure may partially collapse at higher temperatures, with associated movement of exchangeable cations, giving rise to a material that will not rehydrate as well, even though the structure may be largely intact. But RC is, nevertheless, a good indicator of the rehydration ability and residual crystallinity of heated clinoptilolite.

RESULTS AND DISCUSSION

Figure 1 shows DTA curves of natural and exchanged forms of samples LacBen and 80. Among the same homocationic forms of the two samples, slight differences were noted in the shapes of the DTA curves although peak temperatures were similar. Results of thermal analyses are in agreement with literature data (Alietti *et al.*, 1974; Bish, 1988), and the following observations can be drawn:

(1) The DTA curves for unexchanged samples of LacBen and 80 were quite similar.

(2) The DTA curves of the Cs, K and Na forms display a single endotherm at temperatures ranging from 140 to 210°C as a result of a single-step dehydration process. Endotherm minima temperatures increase in the sequence Cs-clinoptilolite (140°C) → K-clinoptilolite (150°C) → Na-clinoptilolite (210°C).

(3) The DTA curves of the ammonium forms are characterized by a sharp endotherm at ~150°C and a weak shoulder at 290°C, followed by an exothermic reaction at ~570°C. The two low-temperature endotherms can be ascribed to dehydration and, to a lesser extent, to ammonia evolution, whereas the latter is strictly related to the combustion of the ammonia evolved upon heating. This interpretation is supported by previous thermodilatometric studies (Colantuono *et al.*, 1997) in which the hydrogen forms arising from the deammoniation of ammonium zeolites were found to catalyze the ignition of ammonia evolved upon heating. Moreover the catalytic effect of hydrogen-clinoptilolites arising from the deammoniation of ammonium-clinoptilolites also accounts for the fact that the ignition of ammonium occurs at a lower temperature (570°C) than the temperature of ignition of ammonia in air (650°C).

(4) The DTA curves of Li, Mg, Ca and Sr forms are characterized by three endotherms, related to a three-step dehydration process. The endotherms range between

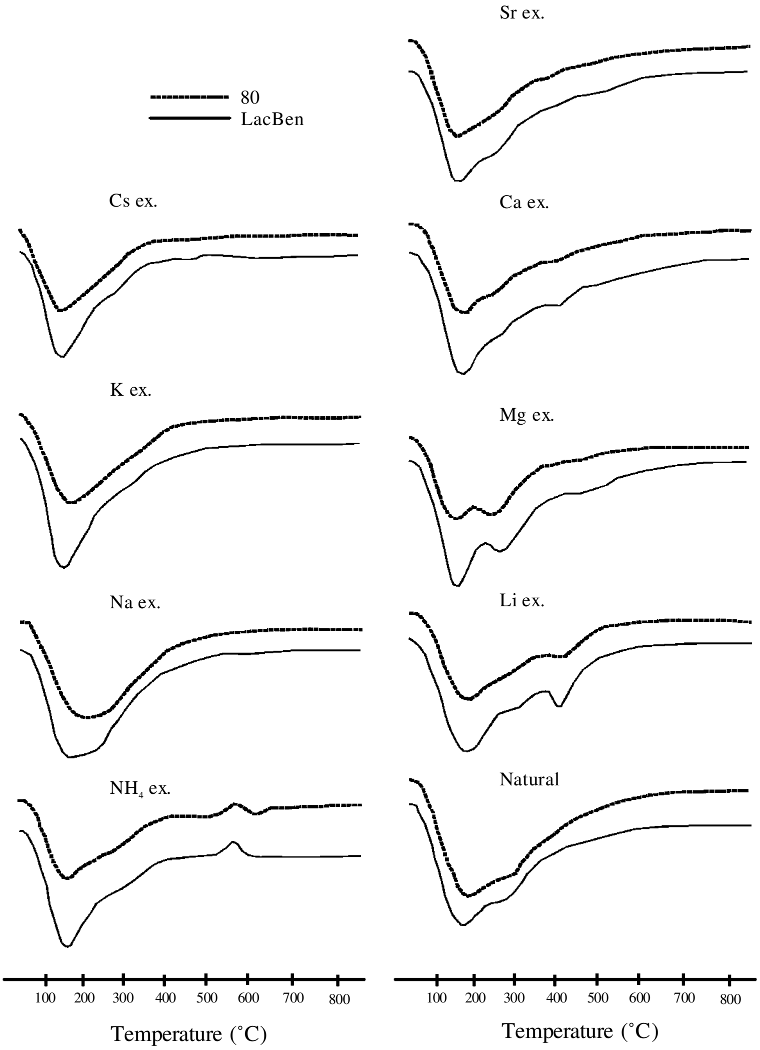

Figure 1. DTA curves of natural and exchanged forms of samples LacBen and 80.

120 and 170°C (first reaction) and between 220 and 330°C (second reaction). Endotherm minima temperatures increase in the sequence: Sr-clinoptilolite → Ca-clinoptilolite → Mg-clinoptilolite → Li-clinoptilolite. The third endotherm, occurring at 400°C (Sr-clinoptilolite), 420°C (Ca-clinoptilolite), 430°C (Li-clinoptilolite), and 450°C (Mg-clinoptilolite), increases in temperature following a different sequence and its magnitude varies depending on the cation, ranging from very evident in the Li form, to obvious in the Ca and Mg forms, and to barely detectable in the Sr form.

Table 3 reports the total weight loss for all cation forms determined by TG analysis, referenced to a 100%-clinoptilolite rock. The weight loss in the NH_4-form is due to the combined effect of water loss and NH_4 evolution as ammonia. These data allow the following observations:

(1) Water content (Table 3) increases in the order: $Cs < K < Na < Li < Sr \cong Ca < Mg$.

The water content of sample LacBen and its exchanged forms is consistently higher than sample 80. These differences (Table 3) range from 1.2 to 2.7% for monovalent cation forms and from 2.0 to 2.6% for divalent cation forms. The higher water content of sample Lac Ben (and of its exchanged forms) than of sample 80 may be related to the different Si/Al ratio of the two samples (Lac Ben: 4.71; 80: 4.60). A higher Si/Al ratio results in a lower cation content, leaving more extra-framework space available for water molecules.

Figure 2 shows the RC of natural and homocationic forms of samples LacBen and 80 after 2 h thermal treatments at 450, 600 and 900°C, and Table 4 reports these same data together with the RC capacity of Cs and K forms of sample Lac Ben and 80 after 2 h thermal treatment at 1000°C. Careful inspection of these data reveals that the same homocationic forms of the two different samples exhibit similar rehydration capacities. As the quantity RC was taken as a measure of the

Table 3. Water content (wt.%) of various cation forms (referred to 100% zeolite content).

Sample	Form								
	Natural	Cs-ex.	K-ex.	Na-ex.	Li-ex.	Sr-ex.	Ca-ex.	Mg-ex.	NH_4-ex.
LacBen	16.2	9.9	14.1	16.2	16.8	16.8	16.9	17.9	18.1
80	13.9	8.7	11.6	14.0	14.1	14.8	14.9	15.3	15.7
Δ	2.3	1.2	2.5	2.2	2.7	2.0	2.0	2.6	*–

$\Delta = (H_2O_{\text{sample LacBen}} - H_2O_{\text{sample 80}})$

* Not for NH_4 form; see text for explanation

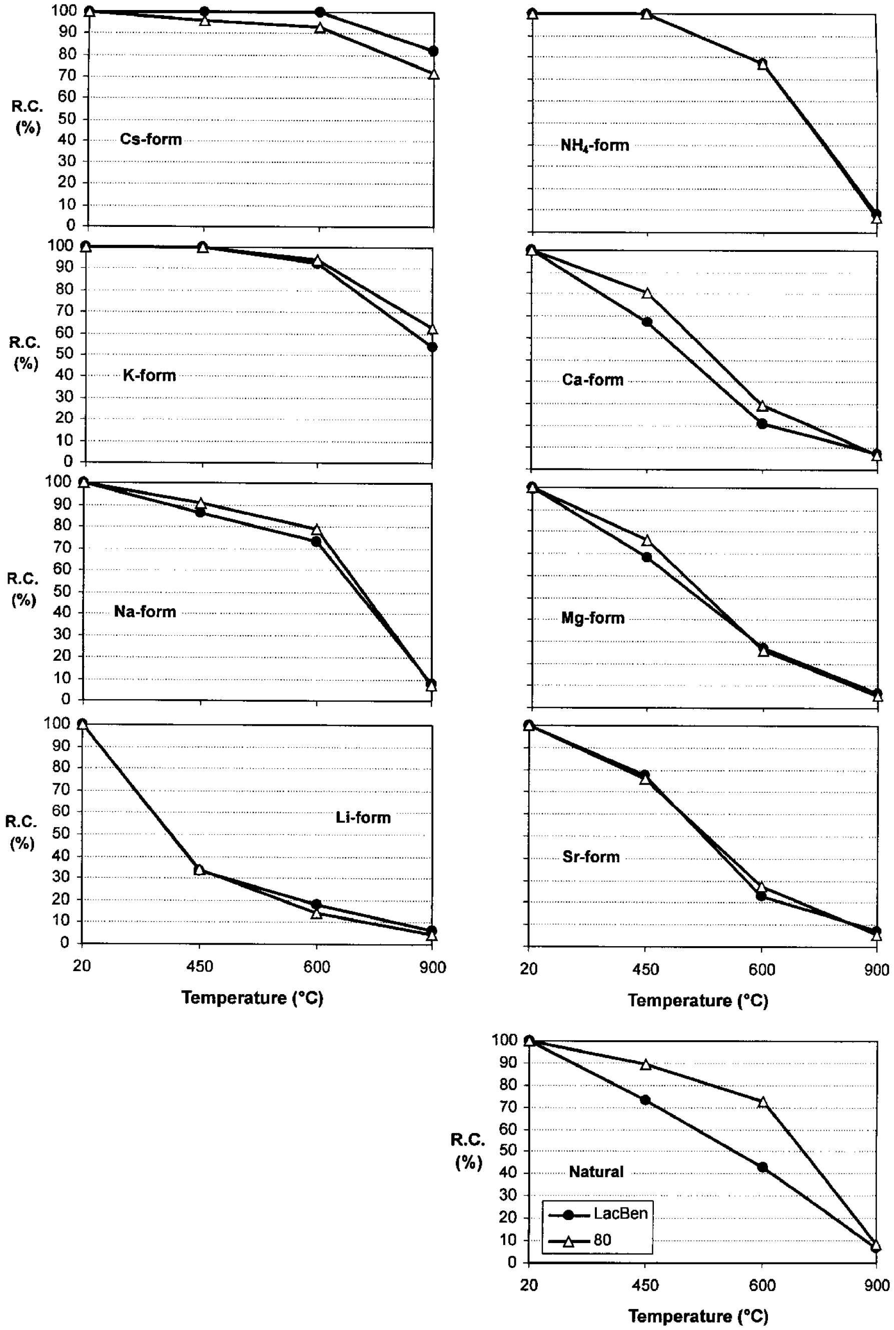

Figure 2. Rehydration capacity (RC) plotted against thermal treatment temperature for natural and cation-exchanged forms of clinoptilolite. Symbols as in the diagrams for the natural forms.

Table 4. Residue crystallinity calculated as rehydration capacity (RC) according to equation 1.

Sample Form	LacBen 20°C	LacBen 450°C	LacBen 600°C	LacBen 900°C	LacBen 1000°C	80 20°C	80 450°C	80 600°C	80 900°C	80 1000°C
Cs-ex.	100	100.0	100.0	82.1	17.9	100	95.8	92.9	71.8	40.7
K-ex.	100	100.0	92.3	53.8	7.7	100	100.0	94.4	62.5	12.5
Na-ex.	100	86.5	72.9	8.3		100	90.6	78.6	7.7	
Li-ex.	100	33.8	17.9	6.2		100	34.3	14.3	4.7	
NH_4-ex.	100	100.0	77.3	8.7		100	100.0	77.4	6.8	
Sr-ex.	100	77.6	23.1	7.5		100	75.6	27.6	5.5	
Ca-ex.	100	67.1	20.7	7.2		100	80.6	29.2	6.9	
Mg-ex.	100	68.2	27.2	7.0		100	76.2	26.2	5.4	
Natural	100	73.3	43.0	6.9		100	89.4	72.5	8.5	

residual crystallinity of the clinoptilolite framework, these data were used to formulate the following sequence of thermal stability of homocationic forms of clinoptilolite, which appears valid for both samples: Cs ≅ K > NH_4 > Na > Sr ≅ Ca ≅ Mg > Li. In particular, the rehydration capacity and, thus, the residual crystallinity of the Cs and K forms are almost unaffected up to 600°C. Moreover, Cs and K forms retain a high rehydration capacity and, thus, high residual crystallinity (ranging between 71.8 and 82.1% for Cs and between 53.8 and 62.5% for K) at 900°C, whereas, at this temperature, thermal collapse of the zeolitic structure is almost totally complete for the other six cation forms (RC usually <10%). It is difficult to explain the residual rehydration capacity of these exchanged forms. However, surface adsorption onto a very fine-grained, almost totally amorphous material, could be invoked.

For the two most resistant forms (namely Cs- and K-exchanged forms), a further 2 h thermal treatment at 1000°C was conducted. It is noteworthy that the Cs-exchanged form of sample 80 still retained high residual crystallinity at 1000°C (Table 4).

As far as the thermal resistance of samples LacBen and 80 in their original composition is concerned, the latter exhibits greater rehydration capacity than sample LacBen at 450 and 600°C, whereas at 900°C the thermal collapse of the zeolitic structure is almost complete for both samples (residual crystallinity <10%).

Figure 3 shows different ways of relating the total water content of the various exchanged forms of the two clinoptilolites (determined as water loss at 1000°C) to the two quantities that appear to affect the water content, namely the charge (z) and the dimension (radius, r) of the extraframework cations. The water contents of the various exchanged forms of the two clinoptilolites are reported as a function of r/z, r^2/z and r^3/z. The first quantity is proportional to the inverse of ionic potential (z/r). The second quantity (r^2/z) is proportional to the inverse of the electrical charge density over the surface of the cation (d_s) which may be expressed as follows:

$$d_s = (e^+z)/4\pi r^2$$

where d_s is the electrical charge density over the surface of the cation, e^+ is the charge of the proton (namely 1.6×10^{-19} coulombs), z is the charge of the cation, and $4\pi r^2$ is the surface of a sphere of radius r (the constant of proportionality is $e^+/4\pi$). The third quantity (r^3/z) is proportional to the inverse of the electrical charge density over the volume of the cation (d_v), which may be expressed as follows:

$$d_v = (e^+z)/(4/3)\pi r^3$$

where d_v is the electrical charge density over the volume of the cation, e^+ is the charge of the proton, z is the charge of the cation, and $(4/3)\pi r^3$ is the volume of a sphere of radius r (the constant of proportionality is

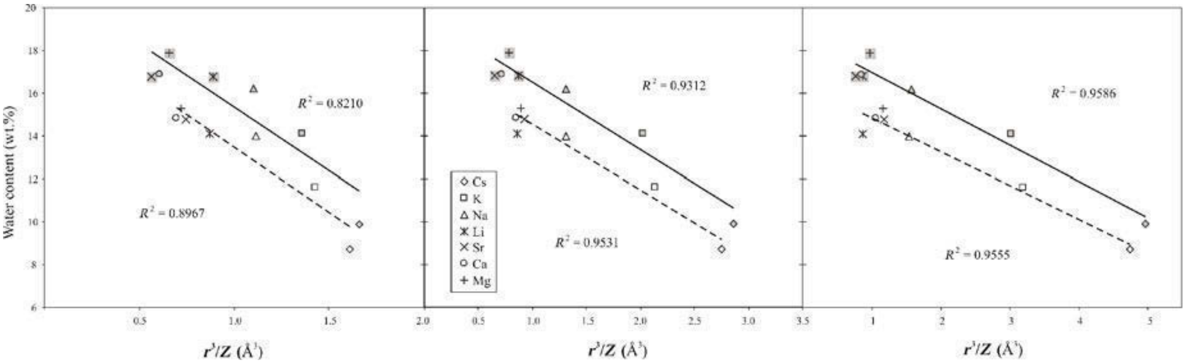

Figure 3. Water content of the various homocationic forms reported as a function of r/z, r^2/z and r^3/z for the LacBen (solid line) and 80 (dashed line) samples.

$e^+/(4/3)\pi$). Cation radii from Shannon (1976) were used in these correlations, and it is important to note that all correlations used cation radii weighted in accordance with the true exchangeable cation composition.

The correlation of the water content of the various homocationic forms of the two clinoptilolites to r^2/z and r^3/z gives rise to several experimental observations: (1) such correlations explain the DTA curves of the Li-exchanged forms of the two clinoptilolites which appear more like those of divalent cations than monovalent forms (the quantities r^2/z and r^3/z for Li lie close to Ca and Sr); (2) the water content of the various homocationic forms of the two clinoptilolites decreases linearly with an increase in r^2/z and r^3/z, namely with increasing the inverse of the electrical charge density over the surface or the inverse of the electrical charge density over the volume of the cation.

The most important conclusion to be gained from Figure 3 is that the water content of the various homocationic forms of the two clinoptilolites decreases linearly with an increase in the inverse of the electrical charge density over the surface or the inverse of the electrical charge density over the volume of the cation. This finding is probably related to the fact that different volume- or surface-charge distributions undoubtedly affect the nature of cation-water interactions in the clinoptilolite extraframework sites. This correlation and the related interpretation could be further investigated using quantum calculations but can also be further evaluated using literature data on water contents of various homocationic forms of clinoptilolite.

It is interesting to relate the relationships depicted in Figure 3 with the cation selectivity sequences (Cs > K > Na > Li and Sr > Ca > Mg) proposed by Ames (1961). Clinoptilolite is selective for monovalent over divalent cations (Eisenmann, 1962; Sherry, 1969; Colella, 1996; Cerri *et al.*, 2002) and, among cations of the same valence, clinoptilolite is selective for cations with decreasing hydration energy of the cation and, thus, with increasing cation radius. Literature data on selectivity may be explained by considering the high Si/Al ratio of clinoptilolite and the weak electric field of the framework (Eisenmann, 1962; Sherry, 1969; Colella, 1996). Thus, interactions between the cations and the weak electric field of the clinoptilolite framework play a secondary role compared with the energy of hydration, which, in practice, determines the selectivity of clinoptilolite for a given cation. It is noteworthy that the sequence in which the water content of the various homocationic forms of the two samples decreases as a function of r^2/z or r^3/z (Figure 3) coincides with the sequence in which the selectivity of clinoptilolite for the various cations increases. This coincidence is due to the fact that both the water content of clinoptilolite and its cation selectivity are strongly affected by the energy of hydration of cations, which increases with increasing electrical charge density.

Furthermore, the sequence in which the water content of the various homocationic forms of the two samples increases with decreasing r^2/z or r^3/z, (Cs < K < Na < Li $\cong$ Sr $\cong$ Ca < Mg) is almost opposite of the thermal stability sequence (Cs $\cong$ K > Na > Sr $\cong$ Ca $\cong$ Mg > Li), with the exception of Li. Thus, it could be inferred that the thermal stability of clinoptilolite increases with an increase in the inverse of electrical charge density.

The occurrence of a third endothermic peak in the DTA curves for all divalent cation forms and for the Li form in the temperature range 420–530ºC reflects a water loss and associated movements of exchangeable cations that probably result in a partial collapse or modification of the clinoptilolite structure, giving rise to a material that will not rehydrate as well (Figure 2). In particular, the Li form, displaying the sharpest endothermic effect at ~420ºC, has the lowest residual crystallinity after treatment at 450ºC. The RC plots for the three divalent cation forms are similar in form to the plots of water content *vs.* r^2/z or r^3/z, and can be ascribed to the already reported incomplete homocationicity of these forms (Table 2). The low extent to which exchange occurred can easily be related to the low selectivity and slow kinetics of exchange reactions involving divalent cations (Eisenmann, 1962; Sherry, 1969; Colella, 1996; Torracca *et al.*, 1998).

The ammonium-exchanged form exhibits thermal behavior very similar to that of the Na, K and Cs forms except for the presence of an exothermic effect due to ammonia ignition (Figure 1). The rehydration capacity (Figure 2) is also very similar to these monovalent forms, but it should be noted that the calculation of this parameter is based on the ability of the zeolite to regain water molecules, and so it is possibly affected by the evolution of ammonia previously discussed.

The thermal behavior of the NH_4 form reflects deammoniation at ~400ºC, resulting in a hydrogen form (Breck, 1974). Further thermal treatment of the zeolites at 500–600ºC results in the loss of one H_2O molecule from two nearby OH or one H_2O for every two tetrahedral Al atoms. This causes the loss of framework oxygen atoms, producing structural vacancies (Breck, 1974). The fact that the rehydration capacity of NH_4-clinoptilolite is reduced by thermal treatment at 600ºC but is not reduced at all by treatment at 450ºC suggests that deammoniation does not affect the thermal stability of the clinoptilolite framework, whereas dehydroxylation destabilizes the structure (Breck, 1974). The same homocationic forms of the two different samples exhibited the same thermal stability as a consequence of the small difference in Si/Al ratio (4.71 and 4.60 for the Lac Ben and 80 samples, respectively; see Table 2). The greater thermal stability of the natural sample 80 may be related to its higher monovalent cation content; sample 80 exhibits a divalent/monovalent ratio (D/M = 0.92) lower than sample Lac Ben (D/M = 1.67).

In addition to the above results, another consideration regarding heulandite/clinoptilolite classification can be drawn from this paper. Historically, distinctions between heulandite group minerals were based on: (1) chemical parameters such as D/M ratios (Mason and Sand, 1960; Gottardi and Galli, 1985) or Si/Al ratios (Boles, 1972; Coombs *et al.*, 1998); or (2) thermal behavior (Mumpton, 1960; Alietti, 1972; Boles, 1972; Alietti *et al.*, 1977). Data reported herein for natural and variously exchanged samples clearly demonstrate that chemical parameters appear more appropriate for discrimination between heulandite and clinoptilolite, whereas the use of thermal behavior does not always fulfill this goal. This finding supports the conclusions of Bish and Boak (2002), who recently proposed a complete distinctive criterion which considers two chemical parameters: Si/(Al + $^{IV}Fe^{3+}$) and D/M ratio.

CONCLUSIONS

Knowledge of the thermal behavior of zeolites in their natural and cation-exchanged forms allows us to obtain useful information for possible technological applications, *e.g.* catalysis. The results of this study on two clinoptilolites from the Sardinia region confirm the literature data concerning the thermal behavior of this zeolite, with the following additional conclusions:

(1) Interactions between the cations and the weak electric field of the clinoptilolite framework play a secondary role compared with the energy of hydration, which determines the selectivity of clinoptilolite for a given cation.

(2) The thermal stability of clinoptilolite increases with an increase in the inverse of electrical charge density, and thus with increasing r^2/z or r^3/z.

(3) The different thermal behavior of the two natural clinoptilolites is due to the different divalent/monovalent ratio whereas the small differences in Si/Al ratio does not seem to affect this parameter.

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