minerals

Review

Ion Exchange in Natural Clinoptilolite: Aspects Related to Its Structure and Applications

Inocente Rodríguez-Iznaga [1] [iD], **Marina G. Shelyapina** [2,*] [iD] **and Vitalii Petranovskii** [3] [iD]

1 Instituto de Ciencia y Tecnología de Materiales (IMRE), Universidad de La Habana, Zapata y G, La Habana 10400, Cuba

2 Department of Nuclear Physics Research Methods, Saint Petersburg State University, 7/9 Universitetskaya nab., 199034 Saint Petersburg, Russia

3 Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada 22800, Baja California, Mexico

* Correspondence: marina.shelyapina@spbu.ru

Abstract: Clinoptilolite is one of the most common, widespread and abundant zeolites in nature. Its availability, low cost, and outstanding ion exchange properties make clinoptilolite an excellent candidate for both direct use and various modifications to create new low-cost functional materials for sustainable development. Specific applications in which clinoptilolite is already being used include water treatment and heavy metal ion removal, agricultural purposes, storage and conversion of unwanted gaseous emissions into the atmosphere, production of catalysts and photocatalysts, bioactive materials, and a number of others. Unlike some other zeolites, clinoptilolite is difficult to synthesize, which is why most publications refer to this zeolite in its natural form, either directly from the deposit or after applying various processes to this mineral to improve its properties. Among the modification methods used, ion exchange stands out. This review is devoted to the study of ion exchange processes in natural clinoptilolite with two goals: first, as its strategic property for use in processes in which cation exchange is fundamentally necessary; second, as a way to modify it to create composite materials with predetermined desired properties.

Keywords: clinoptilolite; heulandite; ion exchange

1. Introduction

An important factor in understanding why the use of zeolites is on the rise is that they are harmless to humans, which is recognized by various organizations. This circumstance makes it possible to develop new technological processes without much precaution and without increasing risk. Zeolites are classified as "Safe Substances for Food and Feed Additives" by the European Food Safety Authorities [1,2] and are "Generally Recognized as Safe" (GRAS) [3] by the United States Food and Drug Administration [4–6]. The International Agency for Research on Cancer (IARC) [7] also endorses zeolites as "non-toxic materials". IARC has devised a system of categories to evaluate the carcinogenicity of an agent to humans [8]. An agent is classified based on scientific evidence derived from human and experimental animal studies and from mechanistic and other relevant data [9]. According to the IARC classification, zeolites belong to the most safe Group 3 (cannot be classified as carcinogenic to humans). The Expert Panel for Cosmetic Ingredient Safety accredited that the use of zeolites has no hazardous effects [10]. The Cuban health authorities have entered into the Sanitary Register the approval of the use of different zeolite-based products, such as Enterex (antidiarrheal agent) [11], Neutacid (neutralizes stomach acidity) [12,13] and ZZ® (microbicidal drinking water purifier) [14], among others, by humans and animals. All of these materials are prepared from Cuban natural zeolites and are available on the market. A review of the properties of natural zeolites showed an extensive range of activities of these

minerals in biomedicine and veterinary science, which is connected with their particular nature and exceptional properties [15].

In the case of natural zeolites, the interest in them is constantly growing not only because of their non-toxic nature, but also because of their availability in large quantities that determines their low cost (naturel zeolite deposits are on the surface and can be mined in an open way), and most importantly, due to their outstanding physical and chemical properties. Among all the properties of zeolites, their relatively high thermal and chemical stability stands out, and especially their ability to ionic exchange, which leads to both their multiple uses and regeneration. On the one hand, this property makes it possible to use zeolites as cation exchangers in removal processes of undesirable impurities for environmental protection, or for recovery of valuable metals from the aqueous phase, as well as for an important number of other applications [16,17]. On the other hand, the ability to ionic exchange allows for purposeful modification of the cationic composition of the starting zeolite, which can lead to the creation of different species on its surface or in accessible voids [18–20], or deliberately alter some of its qualities, such as acidity, thermal stability and effective porosity size. These changes are the basis for the development of new zeolitic materials for different uses such as catalysts, adsorbents, biocides, platforms to support active components in medicine and pharmacy, etc. [21–25].

Clinoptilolite is one of the most common zeolites in nature and is among the few that have commercial applications [26,27]. There are a number of reports both on the studies of ion exchange properties of natural clinoptilolites and on applications proposed based on the results obtained. A large number of reports include an analysis of the influence of certain factors on ion exchange processes, involving nature and the concentration of ions in solution, pH and temperature of solutions. However, from our point of view, insufficient attention has been paid to the study of these processes, taking into account the initial composition of the clinoptilolite used. Moreover, aspects associated with its structure, the presence of extra-framework exchange sites, their location in the clinoptilolite structure voids, the possibility of diffusion access of exchangeable cations to these sites from the outside—all of these steric factors, which play a key role in the final results—have been given very little consideration.

This review highlights the state of the art in the field of ion exchange in natural clinoptilolites, from two perspectives. First, this strategic property allows for using the natural mineral directly in the processes of purification of industrial and domestic wastewater from heavy metal ions, for conditioning of agricultural land contaminated with metals, or for creating permeable reactive barriers for emergency groundwater protection from the consequences of manmade disasters such as Chernobyl, Three Mile Island, or Fukushima [28–32]. Second, by intentionally modifying this mineral in cation exchange processes with a set of specific cations, it is possible to create composite materials with desired properties for specific applications such as storage and conversion of unwanted exhaust gas emissions into the atmosphere, production of catalysts and photocatalysts, bioactive materials, etc. Special attention is paid to the relationship between the changes of composition in the structure charge compensation cations located in extra-framework positions, the observed modification of structural features, and the target properties of the obtained ion exchange clinoptilolites and composites based on them.

2. Clinoptilolite–Heulandite Series: Classification and Composition Relation

Starting this review, the authors should explain what material we will discuss. When it is reported that "clinoptilolite" will be investigated, it is usually explained that this is a "zeolite with a heulandite structure". In mineralogy, attempts are made to explain the complex relationship between minerals from different regions of the world with the same crystal structure according to the X-ray analysis but, at the same time, with the inherent variability of these samples over a wide range of their chemical composition.

For reliable orientation among the multitude of zeolite structures (specifically, the 248 structures known as of November 2022), the International Zeolite Association (IZA)

adopted a system of their three-letter coding [33]. Paradoxically, the name "clinoptilolite" is only a trivial everyday synonym for crystalline zeolite materials with heulandite topology. Their X-ray patterns are compatible, and the topology of their crystal frameworks is therefore designated as HEU in the IZA coding system. A separate code for the mineral "clinoptilolite" is not provided, although geologists and mineralogists continue to distinguish these two minerals (with the same crystal structure but different composition and physicochemical properties) separately.

Furthermore, *heulandite* and *clinoptilolite* are recognized in mineralogy as two distinct, independent mineral species, for which abbreviations have been adopted that differ from those in the IZA. Over the past half century, serious efforts have been made in the study of common rocks, their composition and structure have been refined, new varieties of rock-forming minerals have been discovered, and there is therefore a need to systematize the data obtained and agree on a single standard at the international level. The International Mineralogical Association (IMA) Commission on New Minerals, Nomenclature and Classification (CNMNC) approved a collection of 5744 abbreviations for mineral names [34] based on the Kretz symbol approach [35]. This list is the first systematic catalog of abbreviations for groups and types of minerals. The adoption of symbols approved by the IMA-CNMNC is considered a necessary step in the standardization of names used in geology and mineralogy. The IMA symbols for clinoptilolite and heulandite in this notation system are Cpt and Hul, respectively.

Nevertheless, in the study of zeolite properties and applications, it is now recognized that clinoptilolite is a member of the heulandite (HEU) structural group of zeolites, although there is still some disagreement about the differences between these closely related zeolites, and their physical and chemical properties may be strikingly different, despite the identity of the crystal structure. Clinoptilolite is clearly distinguishable from heulandite by the difference in thermal stability. When studying heulandite, it was found that its crystal structure is stable up to a temperature of 280 °C, and clinoptilolite is defined as that kind of zeolite that has a structure similar to heulandite, but is stable up to 700 °C [36]. Most specialists agree that clinoptilolite is a silicon- and alkali-rich member of the group. Early discussions, and references to original articles from the 1930s to the 1960s can be found in Ref. [37]. In this review, to underline the difference between these two zeolites, we will use the IZA acronym HEU for heulandite and widespread but "unofficial" acronym CLI for clinoptilolite.

2.1. Main Deposits, Stratification, Impurities

Natural zeolites, which have useful properties that allow them to be widely used [38,39], are an important mineral resource in the geological aspect. The main uses of natural zeolites around the world that have become traditional are water treatment (e.g., drinking water, wastewater, gray water), building materials and agricultural applications. As early as 2000 years ago, the Maya made drinking water filters using zeolites [40]. In recent decades, however, intensive research has uncovered more and more new applications—the development of medications based on them as an example [11–15,41–43]—however, this will be discussed in more detail in the section on clinoptilolite applications.

Georesources are the most important development factor in the world, focused on their rational use to improve the quality of life. Work should be carried out aimed at overviewing the main areas of the use of georesources, their inventory, assessment and analysis. As a result, locations of georesources in various regions of the world will be obtained. Such a research work would create the basis for the formation of natural resource rent—an additional income received through the discovery, exploration and production of natural resources [44], with the best mining and geological characteristics, and the properties of the extracted raw materials studied in detail.

Until 1997, heulandite was recognized as a single mineral species, one of the tectosilicate minerals of the zeolite group. In 1997, IMA reclassified and changed it to a serial name, while individual mineral species were named: Heulandite-Ca, Heulandite-Na,

Heulandite-K, and Heulandite-Sr; in 2002 Heulandite-Ba was added to this family [34]. Apparently, monocationic forms are possible only if an additional ion exchange procedure is carried out to remove impurity cations.

In each of the countries, there is a more or less a complete summary of the availability of mineral resources, including deposits of heulandite and clinoptilolite. For example, a book has been published in Mexico [45] describing the natural zeolites found thus far in the country. A review of European clinoptilolite-bearing deposits was made in [46]. It discusses the mineralogical and structural characteristics of clinoptilolite powders. The scope of research included the determination of the mineral composition of tuffs, the structural analysis of clinoptilolite crystals, as well as the textural and physical properties of powders obtained from the mineral processing of tuffs. In addition, the authors conducted a comparative study of the most significant deposits of zeolites in the world. A comparative analysis of clinoptilolites from various deposits in Mexico and Cuba is presented in works [47,48]. On a global scale, one of the attempts to organize an open database of minerals, rocks, and their places of origin belongs to the non-profit Hudson Institute of Mineralogy [49]. This site provides worldwide maps of localities for heulandite, Figure 1a ([50]), and clinoptilolite, Figure 1b ([51]), including lists of localities in alphabetical order, from Angola, Antarctica and Argentina to Uzbekistan, Vietnam, Yemen and Zimbabwe. As the authors themselves indicate, the maps show only those fields for which the longitude and latitude coordinates are known.
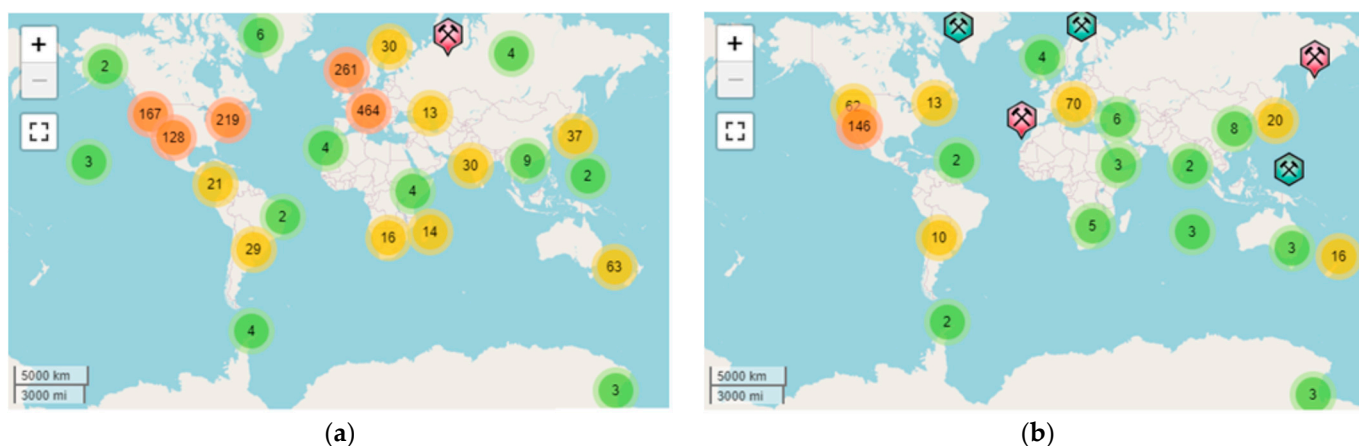

(**a**)   (**b**)

Figure 1. Worldwide map of localities for heulandite (**a**) [50] and clinoptilolite (**b**) [51] zeolite deposits. The numbers in circles correspond to the number of different deposits nearby, the color of the circles consistent with the number of deposits (from smaller to larger: green < yellow < orange). Compliments of Hudson Institute of Mineralogy dba Mindat.org.

Depending on the geological settings and conditions at the time of mineral formation, natural zeolite deposits are usually a heterogeneous mixture of zeolite minerals, one or more, together with various amounts of gangue minerals. Clinoptilolite is associated with each of the other zeolites and with one or more of the following authigenic silicate minerals: clay minerals, potassium feldspar, opal, and quartz [37]. These parameters vary from one deposit to another; especially important are the differences in the cationic composition of zeolites from each deposit; sometimes they differ even for different strata of the same deposit. This makes it difficult to extend the methods of preparation of raw materials tested on minerals from a particular field to similar zeolites from other fields. Consequently, thorough mineralogical knowledge and detailed characterization of natural zeolites in any practical application is necessary when preparing a deposit for exploitation to unlock the full potential of natural zeolites. However, this is rarely conducted because detailed mineralogical analyses are complex and are often ignored in favor of simplified general chemical analyses. An overview of typical technical applications of natural zeolites, as well as a list of requirements for their use, is summarized in [52]. As an example, the authors chose to use the natural zeolite

for ammonium exchange process and developed an analytical protocol to characterize their suitability in detail, consisting of a combination of a number of mineralogical and chemical methods.

The methodology includes mineralogical studies using X-ray diffraction (XRD) and electron microprobe analysis (EPMA) to obtain data on the composition of minerals and in situ chemical analysis (Si/Al ratio, cation content). In parallel, volumetric chemical analysis (XRF) and thermoanalytical studies (TG/DSC) are carried out. Finally, ammonium ion exchange experiments are carried out to determine the ion exchange capacity of zeolite samples, and the dependence of this parameter on concentration is determined (Figure 2). The individual results of this set of analyses provide comprehensive information about the entire sample and a detailed view of the crosslinking parameters (e.g., Si/Al ratio, ion exchange capacity and exchange cations presented in mineral), which can be helpful to evaluate the raw materials from other deposits.
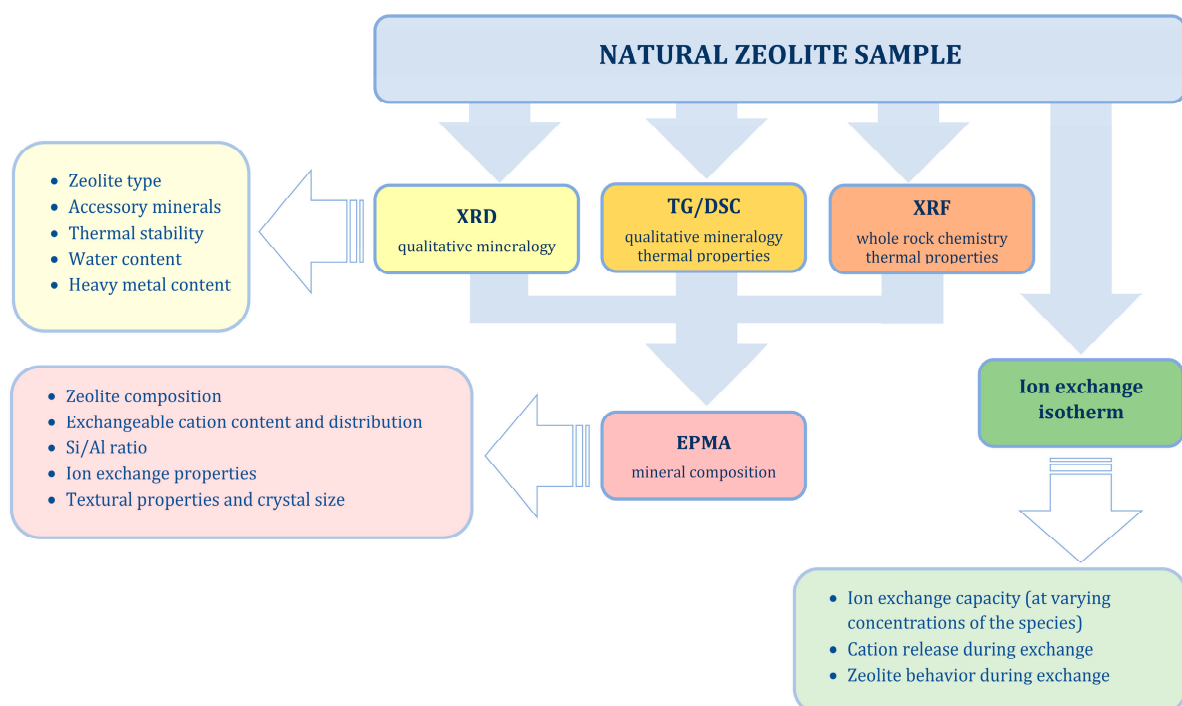

Figure 2. An example of an analytical protocol for determining the suitability of mineral raw materials for a given task. Adapted with permission from Stoker, K. et al. *BHM*; published by Springer Nature, Cham, Switzerland AG, CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/, accessed on 18 November 2022), 2017 [52].

The purpose of the study conducted in [52] was to develop an analytical procedure to characterize samples of natural zeolite in detail and to propose standards for evaluating its suitability for use in specific technical processes. Other technological processes may require additional measurements, and thus, sound recommendations can be made on the use of zeolites from each particular deposit.

Thus, zeolites are crystalline aluminosilicates of alkali and alkaline earth metals with a variable composition. They have many desirable features—high ion exchange capacity, molecular sieve action, and catalytic properties—that make them valuable minerals. During the last 70 years, zeolites have become widely used in commercial processes. Ironically, research into the properties of natural zeolites created the synthetic zeolite industry. When the commercial use of natural zeolites, hitherto considered a mineralogical curiosity, was discovered, from the end of the 1940s, emphasis was placed on the commercial production of their synthetic counterparts. Then, in turn, the useful properties found in synthetic zeolites stimulated the search for much cheaper natural materials. Natural zeolites began

to be used for industrial purposes, not as a replacement for synthetic zeolites, but in areas where the use of synthetic zeolites would be unprofitable. Taking into account the fundamental variability of the composition of natural minerals, an important motive for the study of natural zeolites was their detailed classification, which makes it possible to determine in advance possible areas of application depending on the physicochemical properties of the original minerals.

Extensive exploration for natural zeolites began in the 1950s when, following the success of the first patents for synthetic zeolites, the search for minable quantities of natural zeolites was initiated. Describing the start of this project, Mumpton reports [53] that the experts did not believe that exploitable zeolite deposits would be found. However, several hundred new manifestations of zeolites in volcaniclastic sedimentary rocks were quickly discovered. The deposits contained up to 80%–85% clinoptilolite and demonstrated that near-mono-mineral deposits of natural zeolites could be found in recoverable quantities. Zeolites have not previously been identified in these rocks due to their extremely fine grained nature (from 0.1 to a few micrometers, typically <10 μm). Unlike previously known examples of hydrothermal-derived zeolites, which were characterized by beautiful, very pure centimeter-sized euhedral crystals, new zeolite minerals embedded in volcaniclastic rocks and of sedimentary origin were usually formed at lower temperatures and in slower processes. They were often co-crystallized with other types of zeolites, and were constantly accompanied by noticeable amounts of impurities, usually a couple of tens of percent.

Further discussion opens up about the mechanisms of zeolite formation in some hydrothermal manifestations, or as a result of alteration of volcanic glasses or weakly crystalline silicate minerals. The most common raw materials are volcanic glass, clays, montmorillonite, plagioclase, nepheline, biogenic silica and quartz, and so on. The temperature, pressure, chemical composition and activity of the ionic species, and the partial pressure of the water affect which types of zeolite are formed [54,55]. In this way, it is possible to determine exactly how numerous members of the zeolite family with heulandite topology were formed, but such a discussion is beyond the scope of our manuscript. Those interested in these questions can refer to the relevant literature, but we will return to the problems of the ion exchange properties of clinoptilolite.

2.2. Composition, Properties, Si/Al, Cationic Pool, Relationship with HEU/CLI Recognition

As already mentioned, clinoptilolite and heulandite are isostructural zeolites and belong to the HEU crystal structure type [33]. It has a two-dimensional channel system, Figure 3a,b, containing water molecules and cations [56–58]. To compensate for the negative charge of the zeolite structure, cations are located inside the channels in certain extra-framework positions. These cations can move freely and undergo substitution, entering into ion exchange processes with other cations from another phase, usually from a solution in which the crystals are immersed.
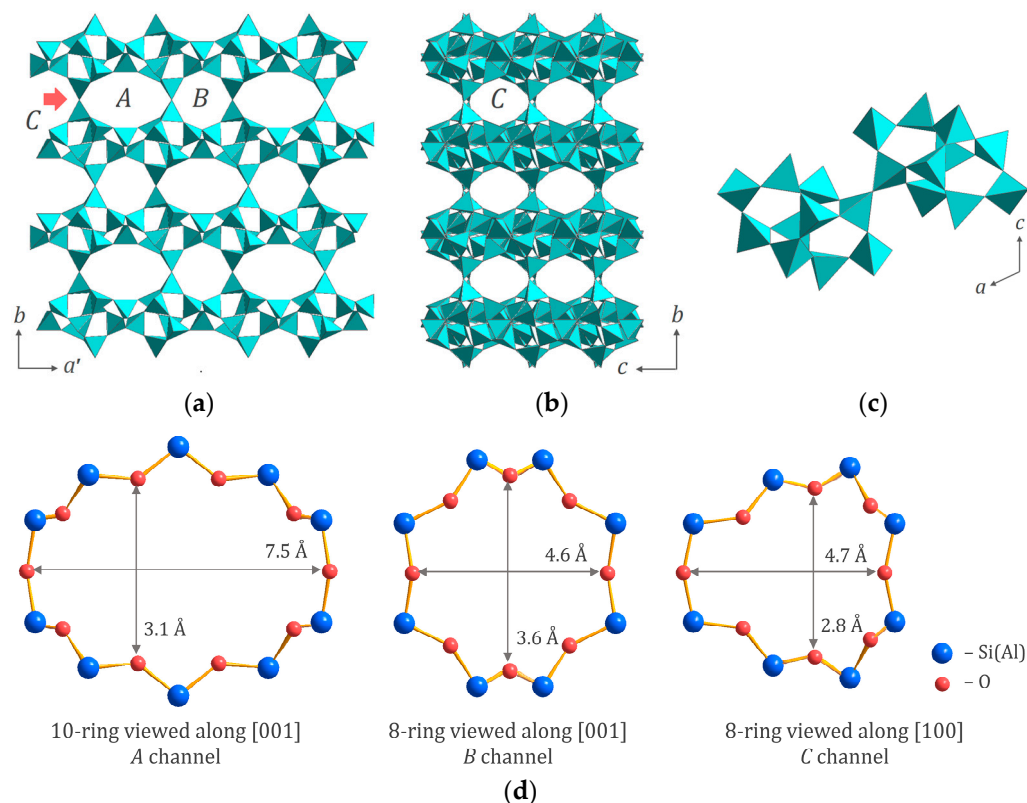
Figure 3. Schematic representation of different sections of HEU zeolite framework type viewed along [001] (a′ = a sinβ) (a), [100] (b) and [010] (c) directions; A, B, C channels (a,b) and two corner-sharing T10O20 units (c) as well as 10- and 8-membered rings (d) of the HEU structure are shown.

In both clinoptilolites and heulandites, the chemical composition varies greatly. Two relatively independent variables are essential: the Si/Al ratio of their crystal structure, which determines the total amount of necessary positive charges and the content of various alkali and alkaline Earth cations included in their composition. Minerals are known with a predominance of Ca, Na, and K; in some cases, they may contain a significant amount of Sr, Ba, and Mg. Equally, the Si/Al ratio and the set of cations in the structure depend on the relative availability of ingredients at the growth site of these zeolites, and their mutual relations give the formed crystal with the heulandite topology one or another certain well-defined property; ultimately, this allows the resulting mineral to be attributed to one of the cationic subspecies of heulandite or clinoptilolite.

Clinoptilolite and heulandite form a continuous compositional series sometimes referred to as the heulandite group zeolites [59,60]. Zeolites having the same topologically distinct tetrahedral structure constitute a series when they exhibit a substantial range of composition in which the various extra-framework cations can be at the highest concentration among others in atomic proportions. These cations can occupy various positions. Such series consist of two or more species that differ in the dominant extra-framework cation.

Such ambiguity leads to the fact that even the data on the crystal structure of clinoptilolite and heulandite turn out to be dependent on the provenance of the samples. The average HEU zeolite in the IZA database [33] is described as monoclinic, with space group $C2/m$, with $a = 17.5230$ Å, $b = 17.6440$ Å, $c = 7.4010$ Å, $\alpha = 90°$, $\beta = 116.104°$ and $\gamma = 90°$, although lower symmetries such as Cm and $C\bar{1}$ have also been reported. However, in the same database [33], other values are given for the reference HEU zeolite with a formula $Ca_4[Al_8Si_{28}O_{72}]\cdot24(H_2O)$: $a = 17.7180$ Å, $b = 17.8970$ Å, $c = 7.4280$ Å, $\alpha = 90°$, $\beta = 116.420°$ and $\gamma = 90°$.

The HEU framework is built from silica and alumina tetrahedra interconnected to form secondary building units $T_{10}O_{20}$; Figure 3c. These units are connected in long chains

along (102) that are linked laterally, forming dense silicate layers (010). Parallel layers are connected into a three-dimensional framework containing three sets of intersecting channels all located in the (010) plane (Figure 3a,b). Two of the channels are parallel to the *c*-axis: the *A* channels are formed by strongly compressed ten-membered rings (aperture 3.1 × 7.5 Å), and *B* channels are confined by eight-membered rings (aperture 3.6 × 4.6 Å). *C* channels are parallel to the *a*-axis, or direction (102), and are formed by eight-membered rings (aperture 2.8 × 4.7 Å); see Figure 3d [33]. Note that these channels are not perpendicular to channels *A* and *B*, but make an angle β with them. The Si/Al distribution in the tetrahedral framework is strongly disordered [56,57]. In the literature, there are values of the apertures of these windows in zeolites with the HEU topology, which differ by several tenths in one direction or another. There is nothing surprising in this, considering that the authors worked with crystals originating from different deposits, and, consequently, with different Si/Al, and a different pool of cations in the channels. As is observed, the substitution of monovalent cations for divalent ones leads to elastic deformations of the zeolite framework; for Cu-mordenites in comparison with Na-, H- and NH_4-mordenites, this was discussed in detail in Refs. [61,62]. As a reference HEU zeolite, the IZA database recognizes a material with a chemical formula: $Ca_4[Al_8Si_{28}O_{72}]\cdot 24(H_2O)$ that corresponds to a Si/Al ratio of 3.5. For natural materials, the IZA Commission on Natural Zeolites provides idealized compositions, which are presented in Figure 4. One can redefine clinoptilolite as a member of the high silica heulandite structural group, usually containing monovalent rather than divalent cations. Separate species in a series of zeolite minerals with different extra-framework cations are designated by attaching a suffix to the name of the structure, indicating the chemical symbol of the extra-framework element that dominates the atomic ratios, for example, clinoptilolite-Ca. However, it must be understood that the content of each of the cations varies widely, and the division of zeolites with HEU topology into series is rather arbitrary. A more unambiguous division into clinoptilolite and heulandite is given by the Si/Al ratio.

Heulandite series

Heulandite-Ca	$\lvert(Ca_{0.5},Sr_{0.5},Ba_{0.5},Mg_{0.5},Na,K)_9(H_2O)_{24}\rvert[Al_9\,Si_{27}\,O_{72}]$
Heulandite-Na	$\lvert(Na,Ca_{0.5},Sr_{0.5},Ba_{0.5},Mg_{0.5},K)_9(H_2O)_{24}\rvert[Al_9\,Si_{27}\,O_{72}]$
Heulandite-K	$\lvert(K,Ca_{0.5},Sr_{0.5},Ba_{0.5},Mg_{0.5},Na)_9(H_2O)_{24}\rvert[Al_9\,Si_{27}\,O_{72}]$
Heulandite-Sr	$\lvert(Sr_{0.5},Ca_{0.5},Ba_{0.5},Mg_{0.5},Na,K)_9(H_2O)_{24}\rvert[Al_9\,Si_{27}\,O_{72}]$
Heulandite-Ba	$\lvert(Ba_{0.5},Ca_{0.5},Sr_{0.5}\,,Mg_{0.5},Na,K)_9(H_2O)_{24}\rvert[Al_9\,Si_{27}\,O_{72}]$

Clinoptilolite series

Clinoptilolite-K	$\lvert(K,Na,Ca_{0.5},Sr_{0.5},Ba_{0.5},Mg_{0.5})_6(H_2O)_{20}\rvert[Al_6\,Si_{30}\,O_{72}]$
Clinoptilolite-Na	$\lvert(Na,K,Ca_{0.5},Sr_{0.5},Ba_{0.5},Mg_{0.5})_6(H_2O)_{20}\rvert[Al_6\,Si_{30}\,O_{72}]$
Clinoptilolite-Ca	$\lvert(Ca_{0.5},Na,K,Sr_{0.5},Ba_{0.5},Mg_{0.5})_6(H_2O)_{20}\rvert[Al_6\,Si_{30}\,O_{72}]$

Figure 4. Idealized compositions of heulandite and clinoptilolite series [59,60].

As a rule, the types of zeolite minerals cannot be distinguished only on the basis of the Si/Al atomic ratio in their framework [63]. The exceptions are to distinguish between heulandite and clinoptilolite, once it is identified as a HEU-type zeolite. Heulandite is defined as a series of zeolites having a framework topology characteristic of this mineral and a Si/Al ratio <4.0. Clinoptilolite is defined as a continuation of the same series, with the same framework topology and Si/Al ratio >4.0. Many other zeolites have widely varying Si/Al ratios, but this in itself is not considered to be a sufficient basis for isolating separate species. The exception is based on the established use of the individual names "heulandite" and "clinoptilolite", and their convenience for recognizing an important physicochemical feature. A number of researchers use thermal stability to distinguish clinoptilolite from heulandite. However, this is a derived property offered by [53] as an aid to identification and is not suitable as a basis for definition. The accepted threshold value [64] is arbitrary in a continuous range of compositions, since there are no well-defined compositions of Si, Al

for the extreme members of the series for heulandite and clinoptilolite. Despite the visible regularity in the composition of both the crystal framework and the cationic set, it was shown [64,65] that there is no gap in composition between heulandite and clinoptilolite, and samples with transitional composition exhibit intermediate properties in terms of thermal stability.

In addition to the obvious and easily understood difference in thermal stability between members of the HEU family of zeolites [53], a variety of methods have been proposed to empirically distinguish between the two species [66]. Most of them are based on the exchange cation composition or framework chemistry [67]. Other methods or criteria that can be used for differentiation include optical properties [64], thermogravimetric analysis or differential scanning calorimetry [68], and proton nuclear magnetic resonance spectroscopy [69]. The most interesting observation was made in Ref. [69]: water in heulandite has a long-range order, while water in clinoptilolite does not. This can be caused by a different cation composition, as different cations have different structures of hydrate shells. The sum of all these observations makes the problem of distinguishing between these two isostructural zeolites with very different properties quite interesting.

Moreover, there is another very serious problem. It is not always clear in which phase, clinoptilolite or heulandite, the reported studies and developments were made. In Ref. [70], this uncertainty is formulated implicitly, while criticizing the literature data. They note that some article states: "*the sample was identified as a clinoptilolite because its X-ray pattern matched that given in the literature*". However, heulandite and clinoptilolite are structurally identical and cannot be distinguished by X-ray diffraction. Such results relating to insufficiently confidently defined mineral species are still occasionally uncritically reproduced in the literature.

The same authors [70] suggest the two methods of distinction described earlier, [64] and [65]. Both articles state that there are three (rather than two) minerals: heulandite (I), intermediate varieties (II), and clinoptilolite (III); see Table 1. Two parameters are needed to determine which mineral the sample in question belongs to. These are the Si/Al and $\sum M^{++}/\sum M^{+}$ ratios. Here, $\sum M^{++}$ is the sum of divalent cations, and $\sum M^{+}$ is the sum of monovalent cations.

Table 1. Ranges of composition changes between definitely heulandites, intermediate minerals, and definitely clinoptilolites [64,65]. Adapted with permission from Drebushchak, V.A. et al., *Thermochim Acta*; Elsevier Science B.V., 2000 [70].

Mineral Classification	Ref. [64]		Ref. [65]	
	Si/Al	$\sum M^{++}/\sum M^{+}$	Si/Al	$\sum M^{++}/\sum M^{+}$
Heulandite	2.90 ÷ 3.52	10.31 ÷ 1.61	2.85 ÷ 3.73	3.69 ÷ 0.88
Intermediate	3.57 ÷ 4.31	2.20 ÷ 0.43	3.45 ÷ 4.35	2.06 ÷ 0.73
Clinoptilolite	4.12 ÷ 5.10	0.60 ÷ 0.09	5.10 ÷ 5.20	0.37 ÷ 0.16

Similar ideas in the absence of an unambiguously distinguished transition between the two members of the HEU family naturally lead to attempts to introduce intermediate states between the pronounced representatives of heulandite and clinoptilolite. For example, the thermal behavior of a set of samples was studied in [71]. They were heated at 450 °C for 8 h, and the decrease in intensity and peak area (020) in the X-ray diffraction pattern was measured. The results led to the grouping of HEU-type phases into three different groups: group I, where the main HEU phase is clinoptilolite; group II, representing intermediate characteristics between groups I and III; and group III, where heulandite is the main HEU-type zeolite phase.

These smooth and seemingly continuous ranges of changes in the composition of both the crystalline base and the cation pool (Table 1) actually conceal quite significant changes in the properties of the studied material, and it is variations in the cation composition that are in some cases responsible for the observed effects. Thus, the data on compression

of zeolites of isomorphic series heulandite–clinoptilolite in non-penetrating media [72] indicate that compressibility along coordinate directions differs appreciably from sample to sample, including differences in the direction of the greatest compression, which, as the authors conclude, is obviously related to variations in zeolite composition. Comparison of the available data suggests that the high-pressure behavior of a HEU mineral significantly depends on its composition.

Changes in the cationic composition cause very significant changes in the optical properties of crystals of the zeolite family HEU [73]. The principal refractive indices and optical orientation were measured for heulandite samples (Si/Al = 3.19). The samples were then subjected to exchange with monovalent and divalent cations. In addition to changes in mean refractive indices, corresponding changes in optical orientation from $b||Z$ in the natural sample to $b||Y$ in the monovalent samples and $b||X$ in the divalent samples were observed. In addition, samples exchanged with divalent cations usually have a higher water content in the channel than samples exchanged with monovalent cations.

Assumed trends in optical properties from clinoptilolite to heulandite based on a synthesis of literature data are shown in Figure 5. The replacement of $Ca^{2+} + Al^{3+} + H_2O$ in heulandite by $Na^+ + Si^{4+}$ in clinoptilolite leads to a change in the optical properties of HEU zeolites. Bivalent cations and higher water content in heulandite channels lead to an increase in the average refractive index. The optical orientation changes from $b||Y$ in clinoptilolite to $b||Z$ in heulandite. The refractive index parallel to b increases at a higher rate than the refractive indices in the plane (010). This figure illustrates the ability of channel dwellers to affect the optical properties of heulandites and indicates that induced cation exchange in heulandite can change the optical properties of the mineral.
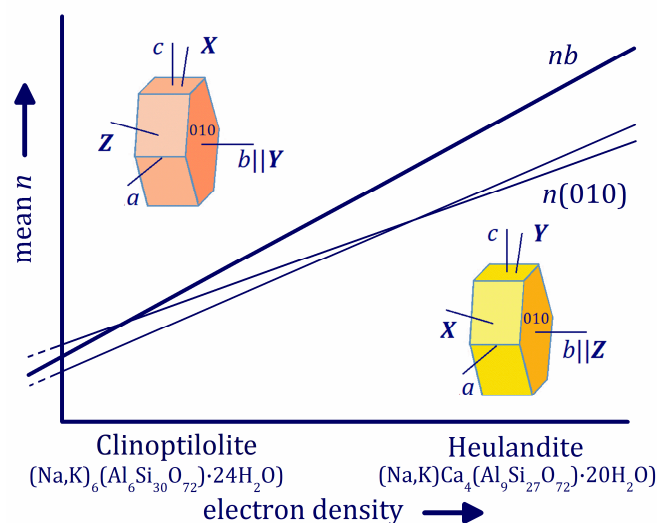
Figure 5. Optical properties of HEU zeolite family. Adapted with permission from Palmer, J.L., Gunter, M.E., *Am Mineral*; Mineralogical Society of America, 2000 [73].

The thermal behavior of natural zeolites affects their application and identification and varies considerably from zeolite to zeolite. The thermal behavior of zeolites is governed by complex interactions between the framework, cations, and water molecules that occur in channel systems. Conceptually, it is useful to divide these effects into (i) modifications of the framework, including changes in the unit cell, structural collapse, and structural failure; (ii) interaction and movement of cations and H_2O in the channel system; and (iii) dehydration behavior. The first two effects are traditionally studied by X-ray or neutron diffraction, and the third by thermal analysis.

The paper [74] describes a convenient way to divide the volumetric and structural effects during heating of zeolites into three categories: (i) reversible dehydration accompanied, in some cases, by rearrangement of extra-framework cations and residual water molecules, with little or no change in framework and/or unit cell volume; (ii) complete or

nearly complete reversible dehydration accompanied by large distortion of framework and significant reduction in unit cell volume; (iii) reversible dehydration at low temperature, usually accompanied by large changes in the framework, followed by irreversible changes due to the breaking of the T-O-T (tetrahedral cation-oxygen-tetrahedral cation, e.g., Al-O-Si) bonds to complete dehydration, see Figure 6. The same structural type of zeolite can occur in several categories depending on the nature of the tetrahedral framework, the charge on the framework, the order/non-order of Al-Si in the framework, and the number and type of extra-framework cations.
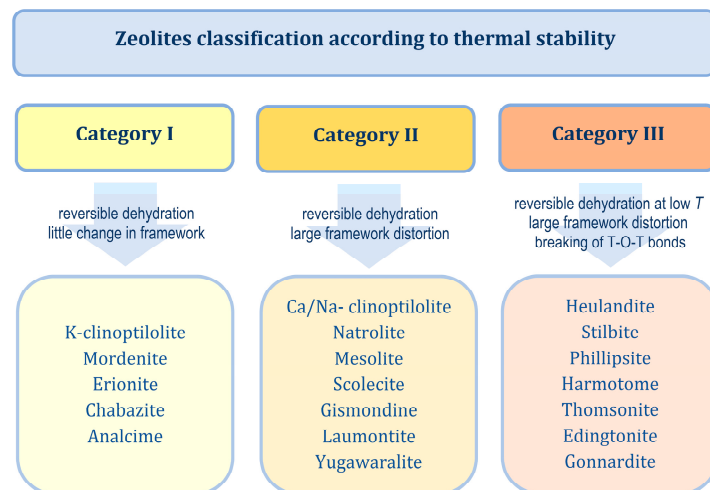

Figure 6. Zeolites classified according to thermal stability [74].

The history of the delineation and definition of the clinoptilolite–heulandite series is rather complicated and still needs additional analysis [66]. As with other mineral groups, numerous ambiguous and overlapping mineral names have been created over the years, eventually leading to the IMA conventions [34,63] governing mineral terminology today. Although the IMA definitions of clinoptilolite and heulandite do not (and should not) account for their compositional variation, minerals whose composition is rich in silica (Si/Al > 4.0) and whose compositional variation consists mainly in the total content of various extra-framework cations are clinoptilolites. Minerals whose composition is aluminous (Si/Al < 4.0) and calcic, and whose variation in composition is mainly due to framework elements (the ratio between Si and Al), are heulandites.

Figure 7 summarizes these trends for two minerals. It shows the assignment of samples (C = clinoptilolite; H = heulandite; I = intermediate) based on their thermal behavior, as well as the formula limits required by the charge balance. The horizontal lines Si/Al = 4 (conditional partition between clinoptilolite and heulandite), and Si/Al = 5.7 (limiting compositions found, compare with Table 1) are plotted. A line showing compositions, in which the amount of divalent and univalent extra-framework cations is the same, is also plotted. The compositions to the right of this line should have more univalent cations than divalent ones. Finally, lines of the "formula limit" are drawn, beyond which zeolite minerals with a given number of charged tetrahedra (Al^{3+} + Fe^{3+}) in their framework cannot go, in order to set boundaries for the HEU compositions containing in the limiting case only divalent cations (left) or only univalent cations (right) [66].
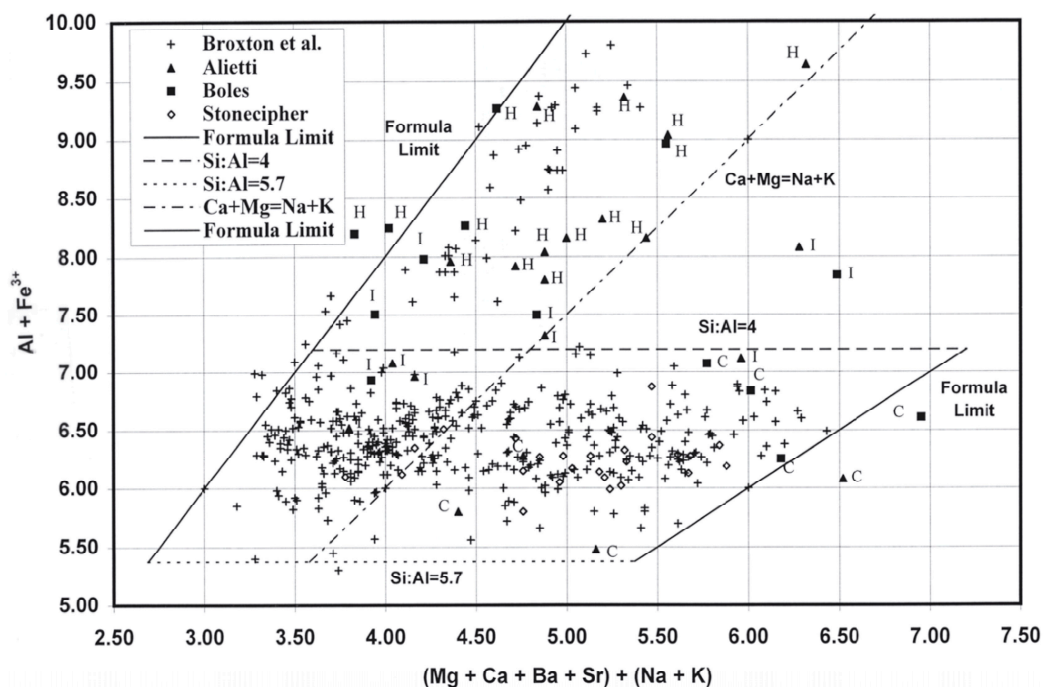
Figure 7. A plot showing the dependence between the composition of the crystal framework (Al^{3+} + Fe^{3+}) (isomorphous substitution of the structural tetrahedron by ions; not only Al^{3+}, but also Fe^{3+} is allowed), and the sum of extra-framework cations for HEU zeolites family. The graph was constructed on the basis of literature data on the analysis of clinoptilolite and heulandite composition. Adapted with permission from Bish, D.L.; Boak, J.M., *Rev Mineral Geochemistry*; Mineralogical Society of America, 2001 [66].

Naturally, IMA definition of clinoptilolite and heulandite does not allow for an area of compositional overlap. However, there is an intriguing compositional region characterized by a Si/Al ratio of approximately 4 ± 0.5 (Al^{3+} + Fe^{3+} from 6.5 to 8 in Figure 7), with the amount of divalent extra-framework cations exceeding those of univalent ones. IMA determinations are quite consistent with the observed thermal behavior, although they are in no way based on thermal behavior. The samples with intermediate thermal behavior are in the region noted above, at the junction of the two mineral series.

2.3. Options for Synthetic Clinoptilolite

This review focuses on natural clinoptilolites. The main reason for this concentrated attention is that it is this natural mineral raw material that finds the widest use. Synthetic clinoptilolite is not usually available on the market. Unlike other zeolites, clinoptilolite (and heulandite as well) is difficult to synthesize. Already in [66], some interesting features of this type of zeolite structure were noted. In particular, Figure 7 shows a number of points that go beyond the formula limits, and the authors wonder about the reasons for the existence of such limits. One of the reasons they believe is that other zeolite structures become more thermodynamically stable when the composition goes beyond the delineated limits. Synthetic zeolites with HEU topology further expand the possible limits for the Si/Al ratio. The IZA database for zeolite structures [75] presents only two materials with framework-type HEU [76,77]. Recently, a detailed review of studies related to the synthesis, modification and application of synthetic clinoptilolite was presented in Ref. [78]. The authors indicate that single-phase clinoptilolite can be hydrothermally synthesized within 1–10 days in an autoclave from various sources of silica, alumina, and alkali with an initial Si/Al ratio of 3.0 to 5.0 at temperatures ranging from 120 to 195 °C. The crystallization rate and crystallinity of the resulting clinoptilolite can be improved by seeding, further emphasizing the difficulty of forming this structure. Further analysis of the studies related to the

synthesis of clinoptilolite undoubtedly appears to be a most interesting material, but it goes far beyond the scope of the task at hand—to review the studies in the field of ion exchange of clinoptilolite zeolite having the HEU topology. Only one thing can be asserted with certainty—for synthetic zeolites, the regularities of ionic exchange depending on Si/Al of their framework, cationic composition, temperature, pH and concentration of exchange solution should be the same as for their natural counterparts.

3. The Ion Exchange Property and the Extra-Framework Cations in Natural Clinoptilolites

The ion exchange property is characteristic in crystalline silicate minerals such as zeolites, clay and feldspars, which originates due to the isomorphic substitution of Si atoms from its structure by other atoms, such as Al. Substitution of Si^{4+} with Al^{3+} generates an excess of negative charge of the framework that must be compensated by cations to maintain the electroneutrality of the zeolite structure. Being located in extra-framework sites, these cations are mobile and can experience an ion exchange with other cations. For the framework of natural clinoptilolite, other atoms (such as trivalent Fe) may also isomorphically substitute silicon [79].

There are models that describe the structure of HEU type zeolites [56,80]. Among these, the structural model of the natural clinoptilolite provided by Koyama and Takeuchi [56] is more accepted and used. This model (see Figure 8) considers that natural cations (Ca^{2+}, Na^+, K^+ and Mg^{2+}) are located in four different preferential extra-framework sites (M1, M2, M3 and M4) in three channels (A, B, and C, see Figure 3a,b). The M1 site is located in the A channel, occupied by Ca^{2+} and Na^+, with preference to this last cation. M2 is in the B channel and is also occupied by Ca^{2+} and Na^+ but with preference to this first cation. M3 has absolute preference for K^+; it is located in the C channel, at the entrance to A and very close to M1. The latter does not allow cations to occupy both sites simultaneously. M4 is locate in the center of the A channel, where the Mg^{2+} cation is positioned.
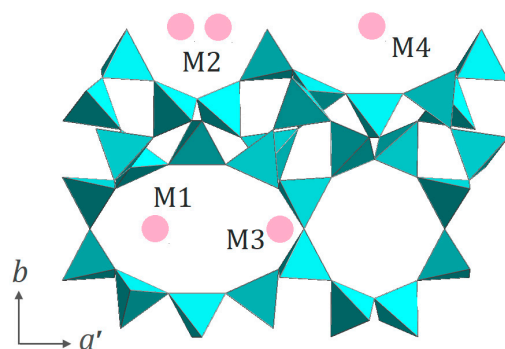
Figure 8. Cations sites M1, M2, M3 and M4 in A and B channels of clinoptilolite according to the Koyama and Takeuchi model [56] viewed along [001] ($a' = a \sin\beta$).

It is well known that the ion exchange process, which commonly involves contact between the zeolite and a liquid phase, is influenced by several factors such as the nature and concentration of cations and anions in solution, used solvent type, zeolite nature, temperature and pH of the medium. The analysis of the influence of these factors must be carried out by interrelating their effects with each other, which is better reflected in four fundamental aspects or qualities: ion exchange capacity, selectivity, ion distribution effect and secondary effects.

3.1. Effect of Initially Present Cations on Ion exchange Properties

Similar to other zeolites, the selectivity of a clinoptilolite is related with its ability to preferentially exchange a given cation from the mixture to the detriment of others. The selectivity depends on the crystalline structure, differences in its exchange sites and a great variety of practical parameters, being necessary to study it in each particular case. It is

recognized that, in a general approach, zeolites with a low Si/Al ratio (high structural charge) prefer small hydrated cations, while zeolites with a high Si/Al ratio (low structural charge) prefer large hydrated cations. The cation exchange capacity (CEC) is one of the most important qualities for a zeolite. A number of works [81–83], reporting on how to define CEC, evidence different viewpoints and technical complexity in its definitions, which are not presented in a single form. This makes it difficult to use, mainly when it comes to natural zeolites and complex ionic exchanges. CEC is a magnitude that gives a measure of the equivalent amounts of a given cation retained by a defined amount of the zeolite exchanger through an ion exchange process. CEC is a function on aluminum amounts from the zeolitic framework and is inversely proportional to the Si/Al ratio. The theoretical CEC maximum (exchangeable equivalent amounts per unit cell mass) cannot always be reached, which could be due to the presence of ion exchange sites inaccessible inside the zeolite. In this sense, the experimental conditions under which the exchange takes place have a marked effect on the accessibility of the cations to the ion exchange sites. As soon as the term CEC has evolved to be used currently as a more effective and industrial term, it is more appropriate to talk about practical or effective CEC. Several studies on ion exchange in clinoptilolites evidence these limitations for some cations in reaching extra-framework cationic positions, which also restricts the zeolite selectivity to a particular cation. Limitations in the cations accessibility to the extra-framework ion exchange sites have been rigorous arguments used to explain the deviations observed for the ion exchange selectivity [16,84,85] in light of the Eisenman–Sherry theory [86,87]. This theory establishes the exchange selectivity by relating the zeolite structural charge density (anionic field strength) with the nature of the competing cations and their properties such as sizes, charge density and hydration free energy.

3.2. Interplay between Nature and Location of the Exchanged Cation, Its Effects on Adsorption, Zeolite Acidity, etc.

On the other hand, the ionic distribution effect refers to the relationship between the zeolite channel sizes and the exchangeable cation dimensions, i.e., steric factors, restrictions due to space limitations that can limit the ion exchange. It is expected that cations smaller than the zeolitic channel sizes are interchangeable, and they can diffuse through these channels. However, it has been observed that ions and molecules with diameters slightly larger than those of the zeolitic pores can diffuse through them, due to thermal vibrations of the zeolitic crystal structure and of the ions and molecules [88]. The secondary effects are associated with several factors, such as temperature, solution composition, pH and others, which influence the ion exchange processes. A detailed study on ion exchange and the reduction of Cu^{2+} cations in natural clinoptilolite from the Caimanes deposit (Cuba) modified for the ammonium form is reported in [18]. The results showed a large value of the practical ion exchange capacity of this clinoptilolite to remove Cu^{2+} from solution at 80 °C in a dynamic column process. The reached capacity (2.7 meq/g) is higher than the expected one (2.2 meq/g). The authors outlined that this high capacity is associated with other parallel processes, such as copper precipitation in the form of a low-solubility oxy-hydroxide, salt adsorption and copper overexchange, which take place joint to the ion exchange. These parallel processes have been reported in other ion exchange processes in natural clinoptilolite [89,90], which could result in an increase in the total amounts of removed cation.

Although these four aforesaid aspects or qualities involve the different factors that influence the ion exchange, an increase in the ion exchange complexity level will limit its analyses in a separate form. This is more critical when it comes to natural zeolite, a mineral that contains other phases and that is used both in raw or purified form. In this case, it will not be wrong to talk of a removal capacity that includes all the factors involved. In this sense, rigorous equilibrium and kinetic studies of ion exchange are key tools to determine the selectivity orders and CEC of a clinoptilolite for different cations [16–18]. A key aspect is to analyze the behavior of the ion exchange property and processes of a zeolitic exchanger,

as the natural clinoptilolite is related with the exchange sites and the exchangeable cations accessibility to these extra-framework sites [16,17,91–93]. This issue has a direct impact on the selectivity and CEC of clinoptilolite, as mentioned above for zeolites in general. However, this topic was not always considered and discussed when studying the process of ion exchange in clinoptilolite; moreover, the number of clinoptilolites (minerals from different deposits) considered from this point of view is small.

Studies on equilibrium and kinetic aspects of Pb^{2+}, Cu^{2+}, Cr^{3+} and Fe^{3+} ion exchange in natural and Na-rich forms of clinoptilolite from a deposit in the northern part of Greece showed changes in the selectivity of this forms by these cations. It was associated with new exchange sites available in the Na-rich form and difficulty in the diffusion of cations to these new sites [94]. Exhaustive kinetic and thermodynamic studies on the NH_4^+, Mn^{2+}, Co^{2+} and Ni^{2+} ion exchange in single and mixed solutions, at 25, 80 and 100 °C, in natural clinoptilolite from Caimanes deposit (Cuba), and their modified forms (NH_4-CLI and metal-CLI) have shown that at 25 °C, the NH_4-CLI form selectively removes Co^{2+} and Mn^{2+} from mixed solutions (Ni^{2+}–Co^{2+}–Mn^{2+}) by ion exchange, being poorly selective to Ni^{2+} [16]. However, NH_4-CLI capacity to remove Ni^{2+} prominently increases when temperature rises. Accordingly, the obtained selectivity order of the metal-CLI forms by NH^{4+} at 25 °C was Mn-CLI > Co-CLI > Ni-CLI. The differences in these ion exchange processes were related to limitations of cations to access ion exchange sites inside the clinoptilolite structure; Furthermore, the divergences in the interaction of cations with their ligands in both solution and into clinoptilolite are also influenced. The authors showed that activation energy (25–100 °C) of NH_4^+ exchange in this clinoptilolite is not very high. This result is very important because it gives a wide temperature range to reach NH_4^+ ion exchange; furthermore, this constitutes an important support for the possibility of using this cation to study CEC of these materials.

Rodríguez-Iznaga et al. [17] also reported the results of a detailed kinetic study of ion exchange of $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$ complex cations in solution, at 25 and 80 °C, in this same natural clinoptilolite modified to ammonium form. The obtained results evidence that CEC of this clinoptilolite to remove the complex cations increases with temperature. This increase was also outstanding for Ni^{2+}, which was associated with increased exchange site accessibility compared with exchanges at low temperature. The authors outlined that due to the complex, cation sizes (hydrated radius around 4 Å [95–97]) are higher than the maximum opening (3.1×7.5 Å) of clinoptilolite channels [57,58]; these exchanges must occur through cations of smaller size. According to this, a diffusive mechanism for the ion exchange was proposed, which includes the following steps: (i) diffusion of the cationic complex from bulk of the solution to the liquid thin layer that surrounds each particle; (ii) diffusion of the cationic complex through this liquid thin layer and into the spaces between the zeolite crystals; (iii) liberation of single metallic cations and/or cationic species of these complexes with a number of ligand molecules smaller than six; (iv) intra-crystalline diffusion of the exchange cationic species. This mechanism is diffusive for ions into both solution and clinoptilolite, and these exchanges are controlled by intracrystalline diffusion (steps (iii) and (iv)) inside the clinoptilolite framework. Step (iii) is affected by increasing the attraction interaction between the central metallic cation (Ni^{2+} and Co^{3+}) and their ligand molecules (H_2O or NH_3).

These last two mentioned reports [16,17] showed that the exchange of Ni^{2+} ions involves ion exchange sites within the clinoptilolite structure, which are relatively poorly accessible at low temperature. Based on the level of exchange (%) and the ion exchange behavior between these cations and the native cations (Ca^{2+}, Na^+, K^+ and Mg^{2+}) on the natural clinoptilolite used, the authors [16,17] found that the M1 and M3 sites, which are defined by the structural model of clinoptilolite presented by Koyama and Takeuchi [56]— see Figure 8—are involved in Ni^{2+} exchange. In this model, the M3 site has an absolute preference for K^+, which firmly coordinated to the clinoptilolite framework through a direct binding to six structural oxygens, while the M1 site has a preference for Na^+, which coordinated to two structural and to an additional five water oxygens. M3 (the *C* channel,

entrance to the *A* channel) is located very close/near to M1 (in the *A* channel), and the simultaneous/concurrent occupation of both sites is restricted due to steric hindrance/space limitations. Therefore, it should be expected that the Ni^{2+} exchange in clinoptilolite is very limited at low temperature and becomes favorable with increasing temperature due to weakened interactions between the cations (mainly K^+) and the clinoptilolite framework. The authors also pointed out that the exchange of NH_4^+, Mn^{2+} and Co^{2+} cations mainly involves another site, M2 of the clinoptilolite structural model, which in this case is the most favorable position for ion exchange, in contrast to the Ni^{2+} ion, preferentially fixed in M1 and M3. This is consistent with the conclusions made by Traviesó et al. [93] on the possible location of Ni^{2+} in the natural clinoptilolite from the Castilla deposit, Cuba, reported in early studies of the molecular sieve properties of this mineral. Other early studies of the same clinoptilolite from the Castilla deposit, reported by Pozas et al. [98], pointed out that Ni^{2+} tends to occupy all sites, M1, M2 and M3 sites from the Koyama and Takeuchi model [56]. Studies of Ni^{2+} selectivity to various ionic Na^+, K^+ and Ca^{2+} forms of natural clinoptilolite from the KwaZulu-Natal deposit, South Africa, also showed that the highest nickel exchange levels correspond to the K^+- and Na^+-clinoptilolite forms, which showed that Ni^{2+} tends to exchange with native cations located primarily at the M3 sites (K^+ in the *C* channel) and the M1 sites (Na^+ in the *A* channel) [99]. However, this conclusion about the localization of ions at all these sites was made based on the analysis of the ion exchange processes between these cations and the native cations of natural clinoptilolite, during which they should participate in the exchange, and at least be transiently occupied by these cations (Ni^{2+}, Co^{2+}, Mn^{2+}, NH_4^+).

Some refined structural studies on extra-framework cation positions into clinoptilolite are available in the literature, where it is common to apply to natural zeolites an a priori purification process that in some cases can be invasive. Armbruster et al. [100] reported detailed structure refinement studies for different copper–heulandite forms obtained from natural heulandite single crystals from Nasik, India, which were pre-modified for complete homoionic Na-heulandite form before obtaining the copper forms by two ways: one by treatment with 0.36 M Cu^{2+}-acetate solution (pH = 6) and another by treatment with 1 M NH_3 solution (pH = 11) containing 0.025 M Cu^{2+} (cuprammine solution). The authors reported that the main copper sites in both samples have no bonds to framework oxygen, which are located in both the *A* and *B* channels from the Koyama and Takeuchi model [56]. In the samples obtained using acetate solution, 45% of copper is located in the center of the *A* channel, forming a disordered $[Cu(H_2O)_6]^{2+}$ complex, and 43% of copper is in the *B* channel in a form of an approximately square planar aqua-complex. In the samples obtained using cuprammine solution, 49% of copper is in the center of the *A* channel forming a disordered square planar $[Cu(NH_3)_4]^{2+}$ complex with two additional H_2O molecules, completing the Cu coordination to a strongly elongated octahedron, while its location in the *B* channel is very similar to the samples obtained using acetate solution. Thus, the differences in ligand nature led to the coordination of Cu^{2+} as in heulandite, a zeolite that is isostructural to the clinoptilolite.

A thorough X-ray diffraction analysis also provides valuable information about ion exchange. Petrov [101] observed important changes in intensities of (020) and (200) diffraction peaks of exchanged natural clinoptilolite, which was explained from crystal chemical calculations. It was found that the structure factor of these peaks changes in line with different cation compositions in this zeolite (modeling the content of Li^+, Na^+, Ca^{2+}, K^+, Ba^{2+}, Cs^+, and Tl^+ cations in the plane of symmetry of the structure). These observations and arguments reported by Petrov [101] stimulated new structural studies on location of exchangeable cations in clinoptilolite. A structural study on ion exchange and location of Cd^{2+} cations in natural clinoptilolite using powder XRD and helped by Rietveld refinement [102] revealed that this cation occupies two principal positions, one sited where magnesium was positioned natively (M4 in the *A* channel in [56]; see Figure 8) and another very near to calcium position M2 (the *B* channel [56]). The authors pointed out that only magnesium and sodium leave extra-framework positions at higher temperature (90 °C) and

longer time (22 days) while potassium partially leaves its extra-structural site. In addition, H_2O experiences diffusion in line with the motions of cations (Cd^{2+} and remaining native cations), and some cations migrate to unusual positions.

Dimova et al. reported on the results of XPD studies of natural clinoptilolite from the Beli Plast deposit, Bulgaria, ion exchanged with Tl^+ [103], Ba^{2+} [104], Ag^+ [105] and Zn^{2+} [106]. Using powder RXD Rietveld refinement, they found that Tl^+ cations are located in the three clinoptilolite channels (*A*, *B* and *C* channels in [56]) positioned in three sites: one in the B channel center, another in the *C* channel near to the original potassium position (M3 in [56]) and the third in the *A* channel shifted toward the center in comparison with the native Na^+ position (M1 in [56]). For clinoptilolite exchanged for Ba^{2+}- (at room temperature and 90 °C), they found that the maximum of Ba atoms per unit cell of clinoptilolite for the longest exchange time (22 days) at 90 °C was 3.04 atoms, whereas at room temperature it did not exceed only 1.64 atoms. The M3 position in the *C* channel was found the main position for the Ba^{2+} cation, in the same place where the native K^+ position was before the exchange. This position of Ba^{2+} (near M3) may explain the lower level of ion exchange of this cation at room temperature due to the fact that this position was initially occupied by K^+, a cation coordinated very strongly with the clinoptilolite structure, and as a consequence, it undergoes limited ion exchange at low temperatures. The study of the fully Ag^+-exchanged clinoptilolite [105] (the full exchange was reached by applying a complex procedure that involved crushing, sieving, sedimentation processes, heavy liquid separation and treatment with NaOH solution) revealed that silver is located in three independent extra-framework sites, one per each channel (*A*, *B* and *C* channels in [56]). The most populated is that sited in the *B* channel. The site in *A* is in the center of this channel, and the site in *C* is close to M3 (native K^+ position); these two last sites are far enough from one another, of which they can be simultaneously occupied. XPD and positron annihilation lifetime spectroscopy (PALS) studies of Zn^{2+}-exchanged clinoptilolite [106] proposed that Zn^{2+} is located in three sites; one site is in the B channel, in a similar position to M2 (native Ca^{2+} position, mainly), coordinating with two water molecules and two framework oxygens. The other two are in the *A* channel, one in the center coordinating with six water molecules in an octahedral arrangement (same to Mg in M4) and another in a proximity that does not allow both sites to be simultaneously occupied. The most populated is that sited in the *A* channel center, followed by that located in the *B* channel.

Garcia-Basabe et al. [91] have developed a methodology based on laboratory X-ray powder diffraction and the use of reciprocal and real space methods, assisted by atomistic computer simulations. This technique was applied to samples of natural clinoptilolite from a Caimanes deposit (Cuba) enriched in Ni^{2+} and Co^{2+}. The obtained results were validated by EXAFS and XANES studies. The authors found two different positions for both cations: the majority occupy the *A* channel, while the rest are in the window of the B channel from the Koyama and Takeuchi model [56]. Furthermore, they found the native Ca^{2+}, Na^+, and K^+ cations located in the M2, M1 and M3 sites, respectively, in line with that reported by Koyama and Takeuchi [56] for the natural clinoptilolite. Garcia-Basabe et al. [92] also reported on the location of Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} in this same clinoptilolite, which was previously subjected to a chemical treatment to eliminate the native cations (mainly Ca^{2+}, Na^+, Mg^{2+} and K^+) and a partial dealumination. In line with early studies [91], the authors found all these cations located in two different sites in the *A* and *B* channels. They concluded that geometrical factors (framework and metal radii) are the main ways to determine the studied cation location in the clinoptilolite framework.

Natural clinoptilolite from Vranjska Banja deposit, Serbia, as well as their modified Ca-clinoptilolite and Na-clinoptilolite forms were used to obtain Zn-clinoptilolite forms, which were once more exchanged with Na^+ solution to extract the initially retained zinc. The samples were subjects of structural studies helped by XRD, SEM, EDXS, XPS, XAS and EXAFS [107]. The authors found that Zn^{2+} in zinc form obtained directly from untreated clinoptilolite is bonded to four oxygens with a distorted tetrahedral coordination, while in the zinc forms obtained from both Ca-clinoptilolite and Na-clinoptilolite, it is located at

sites with distorted octahedral symmetry. Thus, the applied may affect the coordination and location of Zn^{2+} in clinoptilolite.

The aforesaid reports showed important differences in the extra-framework ion exchange sites that cations occupy in clinoptilolite. Consequently, it should be expected that the cations tend to be exchanged in those positions that are more stable or of minimum energy, in which their coordination number is satisfied to a greater degree. The concept of minimum energy considers the tendency to reach optimal values of cation–structural oxygen, cation–water molecule and water molecule–structural oxygen distances as well as minimum repulsion between neighboring ions. Such an arrangement must provide stability both for extra-framework cations and the zeolite structure for all systems. In addition to this, there are some differences among the reported extra-framework sites where the exchanged cations are preferentially situated. Divergences in the amount and composition of the natural cations in the starting natural clinoptilolite could also influence the location of the co-cation incorporated into the zeolite from another non-zeolite phase (solution). However, this starting cation amount and composition are not always reported or considered, which does not help to interpret the results and to compare with other reports. Furthermore, it was observed that if the native potassium position (M3 in the *C* channel from natural clinoptilolite) is involved, it is difficult to reach the ion exchange, mainly at room temperature [16,17,102,104], as occurs in the case of Ba^{2+} and Ni^{2+}. This is in line with the power coordination of K^+ to the clinoptilolite framework, requiring an increase in temperature to weaken this interaction to improve the ion exchange process.

3.3. Strategies for Ion Exchange Modifications

Ion exchange has been also used to improve other properties of the natural clinoptilolites. Thermal stability of the clinoptilolite from the Beli Plast deposit, Bulgaria, was increased by exchanging with Zn^{2+} cations [108]. The authors reported that continuous displacement of the cations along the a- and c-axis and the transformations of their initial position symmetry during heating are the key factors to hold the integrity of the structure above 600 °C, which is more remarkable for Zn^{2+} due to its smaller size compared with the larger ones of Na^+, K^+ and Ca^{2+} (presented as the majority of native cations).

4. Applications of Natural Clinoptilolites Based on Their Ion Exchange Properties

There are many natural zeolites, of which a small number, including clinoptilolite, chabazite, mordenite, erionite, ferrierite, and phillipsite offer the greatest promise for industrial applications [87]. The publications from the United States Geological Survey and National Minerals Information Center of the USA on Statistics and information on the worldwide supply of, demand for, and flow of minerals and materials essential to the US economy, the national security, and protection of the environment have reported the clinoptilolite, along with chabazite, erionite, mordenite, and phillipsite, among the five natural zeolites that are currently in commercial use [26,27]. It is pertinent to emphasize that such a report could not but take into account the requirements and recommendations of the FDA [5]. The appearance of erionite in this list attracts particular attention. Erionite (ERI) is an intriguing material that has generated many years of multilateral discussion. The fact is that over the past 50 years, hundreds of publications on the carcinogenic effect of erionite have been published. This was mainly due to numerous publications about the unusual coincidence of an epidemic of endemic cancer (particularly mesothelioma) in three small remote Turkish villages located in close proximity to the erionite deposit [109]. The epidemic of mesothelioma is unprecedented in medical history; about 50% of all deaths (including neonatal deaths and traffic fatalities) have been caused by mesothelioma. However, recent data have shown that this phenomenon is associated with a combination of simultaneous exposure to erionite and a rare gene mutation causing sensitization to the development of this cancer [110]. This is a good example of an informal fallacy. The source of the error is related to their content and context. Misconceptions, despite being wrong, usually appear to be right and thus tempt people to accept and use them. Despite

the fact that natural erionite deposits are widespread throughout the world, and in other regions people live quietly in such places, such a truly extraordinary case was mistakenly associated with the presence of the mineral only: post hoc, ergo propter hoc.

This circumstance allows us, without undue fear, to return to the consideration and discussion of the useful properties of this zeolite, among other available materials. It can be expected that after it turns out that erionite is not as hazardous to human health as previously erroneously postulated [110], its use in various industrial processes will develop rapidly. Natural erionite finds application in fuel processing, as well as in the adsorption and separation of gases [111,112]. However, further discussion of this intriguing problem is beyond the scope of the present work. Moreover, we will later discuss published evidence that clinoptilolite has certain anti-cancer properties and can be considered as a new adjuvant in anticancer therapy [113].

Natural clinoptilolites have been the subject for different modifications in order to improve their use potentialities, where the ion exchange property has been a key role for their different applications. This review focuses on those clinoptilolite applications in which its pre-modification using ion exchange is critical. Application of ion exchange to modify clinoptilolites, cation selection, mono- and polycationic exchange to create new functional materials for specific applications are key issues.

4.1. Removal of Cationic Contaminants from Water
4.1.1. Removal of Heavy Metals

As [114] states, "*The world is so polluted with heavy metals, mainly due to human pollution, that it affects the health of so many people*". Therefore, research and engineering work to find a way out of this situation must continue intensively so that we are aware of the effects caused by pollution of the biosphere with these metals, the symptoms observed, and ways to remove at least part of the pollution that we have from all heavy metals.

The depletion of water resources and water scarcity have become one of the greatest threats to society today, plaguing the environment [115]. Due to population growth, the demand for water exceeds the amount of available water resources; thus, wastewater treatment becomes indispensable to reduce water scarcity. Removal of heavy metal ions from industrial and domestic wastewater is of paramount importance for the purity of the environment and human health. The presence of heavy metals in wastewater increases with the growth of industry and human activities, for example, in the electroplating industry, electrolysis, metal washing processes, the production of batteries, pesticides, paper, metal smelting, mining, viscose industry, leather industry, textile industry, etc. Heavy-metal-contaminated wastewater enters the environment, threatening human health and the ecosystem. Heavy metals are not biodegradable; thus, the presence of these metals in water in the wrong amounts can lead to critical health problems for living organisms. Various methods have been devoted to the removal of heavy metal ions from various wastewater sources. These methods can be divided into adsorption, membrane, chemical, electrical, and photocatalytic methods. [116] reviews and discusses these methods in terms of removal efficiency, operating conditions, and the pros and cons of each method. The authors point out that the study of heavy metal removal should focus more on using real wastewater rather than synthetic wastewater.

In practice, the term "heavy metal" has come to encompass any metal, exposure to which is clinically undesirable and potentially hazardous [117]. The cited review provides a summary of some general concepts of metal toxicology, and several metals of particular importance are discussed in detail. More information on various aspects of metal toxicity can be found in [114,116]. Nevertheless, metal poisonings constitute an important aspect of toxicology because of their widespread use and availability. Some aspects of human exposure to heavy metals are shown in Figure 9.
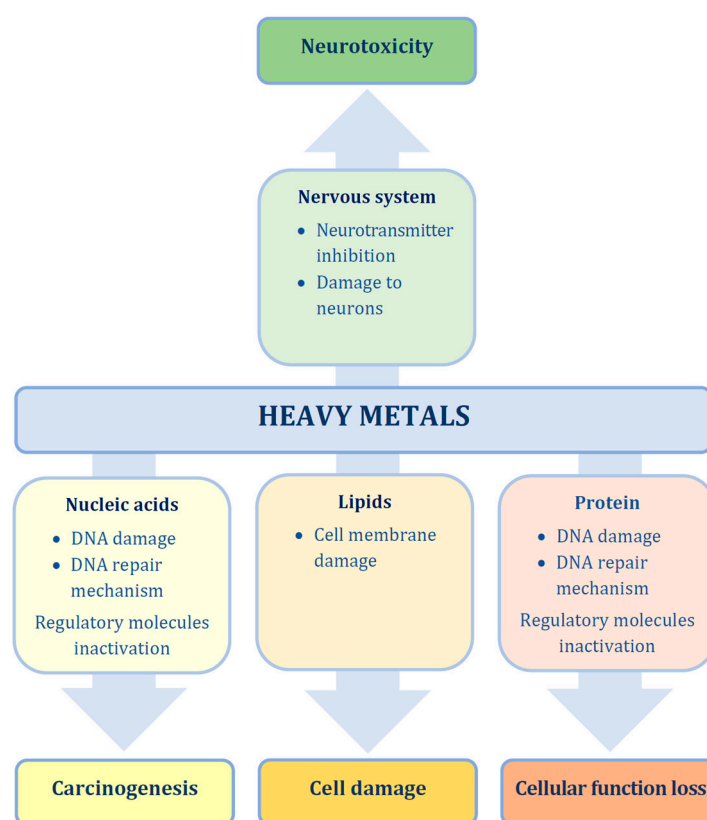
Figure 9. The pathways of heavy metal ions in the human body and their effects. Adapted with permission from Briffa, J. D et al., *Heliyon*; Elsevier Ltd. CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/, 18 November 2022), 2020 [114].

The heavy metals that draw the most attention include V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Sb, Cd, Hg, Pb (and not only), which are arranged in order of their atomic numbers in the above list. Compared to other methods of heavy metal elimination, ion exchange methods for the selective removal of heavy metals are energy efficient and environmentally friendly. In particular, zeolites have been attractive adsorbents for heavy metals since the first attempt to systematically use zeolites for water purification in the 19th century [118]. Many types of zeolites have been tested for the removal of heavy metals, such as zeolites X, Y, A, P (types FAU, LTA, GIS), clinoptilolite, etc. [119]. Recent studies have focused on modifying zeolites with metals or metal oxides to improve their ability to remove heavy metals. For example, iron-coated clinoptilolite showed significantly improved adsorption capacity for heavy metals, especially Pb, compared to uncoated clinoptilolite [120]. This was probably because iron could reduce PbII ions on the clinoptilolite surface to Pb0. Taking advantage of iron's reducing ability, nanoscale zero-valent iron/zeolite composites can be fabricated. Due to the large surface area of iron nanoparticles and the stabilizing effect of zeolites with respect to iron nanoparticles, the absorption of PbII can be greatly improved.

Among the main reports on the use of the natural clinoptilolites as ionic exchanger are industrial wastewater treatment and the pollution removal and industrial wastewater treatments, where special attention is paid to the removal and recovery of heavy metals [16,17,89,121]. Although there are a very large number of reports in the literature devoted to these processes, most of them describe only the removal of impurities to purify the water itself, i.e., without considering the recovery of the valuable metal (by subsequent elution, etc.) and furthermore without any recommendations on how to proceed with the zeolite used.

Rodriguez-Iznaga et al. [89] reported a large-scale study of natural clinoptilolite from the Caimanes deposit, Cuba, modified into its ammonium form by replacing the original mineral cations through ion exchange in a ammonium-concentrate solution (concentrated

NH_4OH) and then using the resulting material as an efficient exchanger in cyclic Ni^{2+} removal–elution processes 20 or more times in a row, without significantly degrading both the crystal framework and the Ni^{2+} and NH_4^+ exchange capacity for this modified clinoptilolite. The authors showed that use of this ammonium-rich solution allows ion exchange processes to be carried out that lead to both the recovery of nickel once retained on zeolite phase during its removal from solution and the regeneration of the ammonium–clinoptilolite form for starting a new cycle. Moreover, the Ni^{2+} removal capacity of this clinoptilolite substantially increased due to the OH^- anions from ammoniac solution are retained (adsorbed, occluded) on zeolite phase, and consequently, a low-soluble nickel hydroxide precipitation process takes place parallel to the ion exchange.

Greek natural clinoptilolite, supplied by S&B Industrial Minerals S.A. Zeolite, was treated with different wasters (synthetic aqueous solutions, secondary effluent from system treating municipal wastewater and primary treated wastewater collected from municipal wastewater treatment plant) containing Zn(II) and Pb(II) [122]. The desorption (elution) of Zn(II) and Pb(II) retained on zeolite was evaluated by using solutions of HNO_3, NaCl, KCl and NH_4Cl in batch processes, which lead to test the clinoptilolite regeneration by conducting successive Pb(II) and Zn(II) removal/elution (adsorption/desorption) cycles. The best results in the clinoptilolite regeneration and metal elution were obtained with KCl solutions (3 M KCl solution for lead and 1 M KCl for zinc). However, after nine and four cycles for lead and zinc, respectively, regeneration–elution efficiency decreased by more than 50%, which showed difficulty desorbing the ions that were easily adsorbed. The authors suggest several issues that could affect the regeneration–elution efficiency, such as impurities (carbonates, sulfates, etc.) mainly in the wastewater, replacement of Ca^{2+}, Na^+, Mg^{2+} (native cations in the zeolite) by K^+ and the formation of chloride–metal complexes. In addition to this, it is necessary to take into account that high coordination K^+ cation can achieve with the clinoptilolite framework. It makes the subsequent K^+ elution and zeolite regeneration difficult, which is in line with the aforesaid in Section 3. The removal of Cd, Cu, Ni, Pb and Zn from solutions on the natural clinoptilolite from Beli Plast deposit, Bulgaria, and then their elution from it by using diethylenetriaminepentaacetic acid (DTPA) solution was studied in [123]. The sequence of the removal selectivity obtained for this clinoptilolite was Pb > Cu > Zn > Cd > Ni, while elution (recovery) of the metals retained by using DTPA followed the order Ni > Cd > Cu > Zn > Pb.

The ion exchange capacity of the Bulgarian natural clinoptilolite to remove Cd^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} from mono- and multi-component solutions was improved after applying a modification pretreatment by Na^+ cation exchange to obtain the exchanged Na-clinoptilolite. However, the reached change had no significant effect on Pb^{2+} removal, which was associated with the fact that Pb^{2+} ion exchange is more related with other cations (Ca^{2+} and K^+) different to Na^{2+} [124]. In the same way, the ammonium removal capacity of the natural clinoptilolite from Beli Plast deposit, Bulgaria, was enhanced after modifying this zeolite to its Na- form [125,126]. The effect of pretreatment of Chilean natural zeolite (composed mainly of clinoptilolite and mordenite) with NaCl, NaOH, Na_2CO_3 and NH_4Cl solutions on its capacity to be removed by Mn^{2+} ion exchange was studied [127]. The results showed that the applied pretreatment type led to an increase in the level of manganese removal. The efficiency depends on the applied treatment in the following way: NaCl ~ NaOH > Na_2CO_3 > NH_4Cl > natural clinoptilolite. The level of Ni^{2+} cation removal on natural clinoptilolite from a Serbian deposit was improved by modifying this zeolite through Na^+ ion exchange to its Na-clinoptilolite form [128]. The authors have also reported a low level of nickel removal at room temperature, which can be improved with temperature increases is in line with other reports [16,17].

The ion exchange property has also been used to improve the natural clinoptilolites capacity in removal processes of water pollution that is unusual, difficult to eliminate or that cannot be removed by direct ion exchange, for example metal oxyanions, such as described in [129]. Natural clinoptilolite from Puebla State, México, was exchanged with 0.1 N HCl solution and then treated with silicon in the presence of peroxide and heptane at

70 °C [130]. This leads to the deposit of silicon nanocrystals on the zeolite surface without affecting its crystalline structure and textural characteristics, which could help to improve its capacity to remove Cs and Sr isotopes from pollutant residues. Material of inexpensive cost with increased capacity to remove Cr(VI) in chromate anion form from waters was prepared using natural clinoptilolite from St. Cloud Mine in Winston, NM, Japan, modified by Fe^{3+} ion exchange and then an adjustment of pH to 9 [131]. The authors report that CrO_4^{2-} oxyanion binds with oxy-hydroxides of iron on the zeolite surface, favoring the removal of this anion. This same natural clinoptilolite from St. Cloud Mine in Winston, NM, Japan, but modified by Fe(II) ion exchange, was used as an efficient material to remove chromium in CrO_4^{2-} anions form from watery solution [132]. The Cr(VI) removal in chromate and dichromate form on natural clinoptilolite from Chihuahua, Mexico, was improved by pre-modifying it through applying Na^+ ion exchange and then treated with hexadecyltrimethylammonium bromide (HDTMA-Br) [133]. The modification by ion exchange led to a light increase in the specific surfaces of this zeolite, which could favor the retention of HDTMA-Br on teh clinoptilolite surface and, consequently, increase its capacity to remove Cr(VI).

Natural clinoptilolite from Metaxades deposit, Greece, was evaluated in the removal of Cu^{2+}, Fe^{3+} and Cr^{3+} from nitrate salt solutions (containing KNO_3 too) in the presence of SO_4^{2-} and HPO_4^{2-} anions (as K_2SO_4 and K_2HPO_4) [134]. The authors report that Cu^{2+} removal is significantly affected by both anions, while this negative effect is less significant for Fe^{3+} and Cr^{3+} in the presence of SO_4^{2-} and HPO_4^{2-}, respectively. This was associated with the formation of a metal–anion complex. In the case of Fe^{3+}, the presence of HPO_4^{2-} provokes the iron precipitation that occurs joint to its ion exchange, which results in a higher removal (complete iron removal). Furthermore, a significant level of anion removal was reached.

In addition to the modification of clinoptilolites with single cations (monocationic exchange), there are other reports on modifications with mixed cations (multicationic exchange) that lead to improving its properties for diverse uses, nanospecies stabilizing on natural clinoptilolite matrix, etc. [19,20].

4.1.2. Removal of Dissolved Ammonia

Dissolved ammonia, the ammonium ion (NH_4^+), is a water pollutant that can enter water bodies continuously and persist for a long time. Natural sources of NH_4^+ in water include decomposition of organic matter, gas exchange with the atmosphere, forest fires, animal and human waste, etc. Another serious cause of ammonium in surface water is anthropogenic activities such as municipal sewage discharge, deposition from the air, and runoff from agricultural land [135]. One of the forms of nitrogen normally presents in aquatic systems at pH below 8.75 [136]; ammonium, however, differs from them in its effects at elevated levels. While high concentrations of other forms of nitrogen can only lead to nutrient overenrichment and indirect effects on hydrobionts, high concentrations of ammonium (particularly ammonium nitrate) have direct toxic effects on aquatic inhabitants [137].

To detect ammonium in aqueous solutions, conductometric sensors have been developed using the intrinsic cation exchange of the natural zeolite clinoptilolite [138]. The sensor recognition element was fabricated with a primary layer of clinoptilolite and a subsequent layer of Nafion on the electrode surface. The protocol for using the sensor included soaking the sensor membrane in 5 mM sodium prior to analysis to ensure optimal conditions for ion exchange in the zeolite. The linear range of the sensor studied for the first time was 0–1.5 mM ammonium. The mechanism of clinoptilolite selectivity to ammonium has been widely studied and is explained by cationic exchange between Na^+ ions, which initially occupy the extra-framework exchange sites of the zeolite, and NH_4^+ from the environment [139]. The optimization data obtained by the authors can be useful for the accurate detection of ammonium by sensors and biosensors based on clinoptilolite. Other features of the optimized ammonium selective sensors described in this work are their low

cost, high stability of operation, and stability during long-term storage, which makes these sensors promising analytical devices for analyzing real samples.

The use of clinoptilolite allows for the development of other conductometric sensors. The ion exchange properties of zeolites can be used to accumulate electroactive cations within zeolite particles located on the electrode surface [140]. This is a key starting point for many electroanalytical applications using zeolite-modified electrodes. Highly sensitive conductometric urea biosensors have been developed by exploiting the successful combination of the ion exchange selectivity of clinoptilolite to ammonium with the unique biorecognition ability of urease. To optimize the performance of urea biosensors based on clinoptilolite, the dependencies of their analytical signals on the pH, buffer capacity, and ionic strength of the phosphate-buffered solution were investigated [141].

Due to its high affinity for the ammonium ion, clinoptilolite can be used not only for its determination, but also for its removal from wastewater. This raises the need for the preparation of engineered zeolites having a high ammonium exchange capacity and at the same time mechanical strength and abrasion resistance. Research [142] was devoted to the production and evaluation of synthetic zeolites and comparison with natural clinoptilolite in a demonstration ion exchange plant treating secondary effluents from municipal wastewater treatment plants. Future work should focus on optimizing the granular zeolite production process (temperature, time, and furnace size during calcination) to produce a spherical engineered zeolite that will reduce possible sharp edges that can affect mechanical strength.

4.1.3. Removal of Contaminants from Organic Solutions

Besides the ion exchange removal processes performed commonly in aqueous solutions, there are other unusual methods such as those where the solvents used are organic. The natural clinoptilolite from the northern part of Greece was used to remove Cu^{2+}, Cr^{3+} and Fe^{3+} cations from nearly pure ethanol and acetone where the cations are in the form of cation–solvent complex [143]. The authors have compared the ion exchange levels in water with respect to those reached in the organic solvents, being observed as satisfactory levels only to Cr^{3+} in ethanol and Cu^{2+} in acetone.

4.2. Storage and Conversion of Undesirable Gas Emissions into the Atmosphere

The unique and exceptional physical and chemical properties of zeolites in general, and of the heulandite–clinoptilolite family of zeolites in particular, favor their use in many applications, including CO_2 post-combustion adsorption [144]. One of these properties is a high adsorption capacity, which is combined with a molecular sieve effect, which makes it possible to selectively absorb certain gases from mixtures. In combination with ion exchange properties that allow one to control the number and size of cations in the channels of clinoptilolite, such adsorption becomes somewhat controllable.

There are many natural zeolites, a number of which, including clinoptilolite, chabazite, mordenite, erionite, ferrierite and phillipsite, are widely available and are the most promising for gas separation. The results [111] show that these natural zeolites are particularly well suited for the removal of gaseous impurities. Clinoptilolite and chabazite are considered the most versatile.

Separation of mixtures is always necessary in modern industry, especially in the fine chemical, petrochemical, and pharmaceutical industries. The problem of the separation process is usually associated with small molecules with very similar physical and chemical properties. The widely used high-pressure cryogenic distillation process is energy intensive. The adsorptive separation process based on zeolite sorbents is a promising low-energy alternative; however, the efficiency in this case directly depends on the zeolitic material. Review [145] considers separation mechanisms based on steric, equilibrium, kinetic, and other effects and summarizes recent advances in adsorption separation using zeolites, including the separation of CO_2, light olefins, C-8 aromatics, and hydrogen isotopes.

It has been found [146] that in Na- and Ca-clinoptilolites, the diffusion rate of N_2 is much higher than the diffusion rate of CH_4, resulting in excellent separation performance.

The separation kinetics for an N_2/CH_4 mixture depend on the cationic composition; in clinoptilolites with Li^+, Mg^{2+}, and Ca^{2+}, N_2 diffuses much faster than CH_4. In addition, a mixed ion exchanged clinoptilolite such as Mg/Na (50/50) exhibits even better kinetic selectivity for N_2/CH_4 separation.

A serious problem is the processing of organic waste. Composting is a promising technology that makes it possible to obtain a humus-like high-quality compost substance that can be used as an organic fertilizer. However, both greenhouse gases (N_2O, CO_2, CH_4) and odorous emissions (H_2S, NH_3) are emitted, which is a serious concern. These secondary pollutants have adverse effects on the environment and human health. It is known that in the process of composting, an important role for the quality of the resulting fertilizer is played by the nitrogen cycle. In review [147], the authors summarized the basics of the nitrogen composting cycle; examined the impact of operating parameters, microbial activity, enzyme functions influencing the nitrogen cycle; and discussed strategies to mitigate nitrogen losses. Operating parameters such as humidity, oxygen content, temperature, C/N ratio and pH play an important role in the nitrogen cycle, and adjusting them is the simplest method to reduce nitrogen losses. Furthermore, the addition of biochar, and especially clinoptilolite, helps control nitrogen losses, which has a beneficial effect on the quality of the compost and controls air pollution.

An even more serious problem is the food waste digestate (FDP), which is high in NH_4^+-N and difficult to compost due to higher NH_3 emissions (and loss of nitrogen from the resulting fertilizer). The study [148] used clinoptilolite as a physical additive for ammonia retention. The results showed that the addition of zeolite had a positive effect, since at dosages of additives of 5%–10%, nitrogen losses decreased by 34%–39%. At the same time, the addition of zeolite increased the decomposition rate by 30%–32%.

4.3. Production of Catalysts and Photocatalysts

All people and animals need access to clean water in their daily lives. Unfortunately, we face water shortages all over the world. At the same time, however, we inevitably pollute water in various ways. Population growth, globalization and industrialization are generating more and more wastewater that contains pollutants such as organic substances, metal salts, agrochemicals, herbicides, pesticides, antibiotics, dyes, radioactive pollutants, etc. This whole range of pollutants can cause various diseases in humans and animals, as well as damage to the environment. In addition to existing contaminants, a number of new pollutants are now being produced by developing industries. To solve this problem, we need new effective tools and materials to remove impurities from wastewater. Earlier in this review, we have already discussed techniques to use zeolites for the efficient removal of cationic pollutants due to their exceptional ion exchange properties. Photocatalysis can often be very effective for the removal of complex organic substances, especially under the influence of natural sunlight. However, zeolite itself shows little photocatalytic efficiency; thus, zeolites, using their ion exchange potential, are enriched with various photoactive materials to increase their photocatalytic efficiency. The production of such zeolite-based composites is developing.

Natural clinoptilolite can be used as support for immobilization of TiO_2 nanoparticles [149–151]. Moreover, it was found that the efficiency of this composite for photocatalytic degradation of organics under sunlight irradiation was significantly improved [149]. TiO_2 supported on alkaline clinoptilolite followed by NH_4NO_3 treatment exhibited its effectiveness in hydrogen production by photocatalytic water splitting [151]. The results obtained suggest that the ion exchange alkaline treatment of clinoptilolite along with providing strong basic sites creates mesoporosity; altogether, this improves the photocatalytic activity of TiO_2/clinoptilolite composites for hydrogen evolution.

The photocatalytic activity of CuS in the composition of clinoptilolite during the bleaching of a mixture of methyl orange and bromocresol green under sunlight irradiation was investigated in [152]. The degree of discoloration was estimated from the residual concentration spectrophotometrically and was confirmed by the reduction in chemical oxygen

demand (COD). The formation of catalytically active copper and nickel nanoparticles on natural zeolites for the complete oxidation of hydrocarbons was studied in [153,154]. A combination of green chemistry and nano-engineering is needed to produce minimal waste, using simpler and safer products, and new technologies. Dyes have a complex structure, an intractable/recalcitrant nature and a greater number of intermediates. Various attempts to degrade dyes in textile wastewater using various advanced oxidation processes are being made everywhere. Treatment technology can be improved by advanced oxidation processes [155]. These processes are efficient, inexpensive, and environmentally friendly methods of decomposing toxic pollutants. Advanced oxidation processes (AOPs) are broadly defined as a set of chemical treatment procedures designed to remove organic pollutants. AOPs are classified as non-photochemical and photochemical processes. Various technologies such as ozonation, Fenton oxidation, wet-air oxidation, electrochemical oxidation, and photocatalytic oxidation can be included. The production of highly reactive free radicals is the main goal of the AOP process. The production of free radicals is increased by a combination of two or more AOP processes, resulting in higher oxidation rates.

The review [156] highlights the types and mechanisms of synthesis of zeolite-based materials for wastewater treatment and analyzes the gaps in current research, which gives a qualitative background of world research on this topic.

In [157], Aguiñaga et al. reported that natural mixed clinoptilolite–mordenite tuff is an effective photocatalyst. Pretreatment of the sample consisted of acid etching. The rock was crushed and sieved to obtain grains with sizes of 2.38 and 3.36 mm. The particles were treated in 1 M aqueous hydrochloric acid for 8 h at 60 °C, thus obtaining protonated zeolite. The results obtained were compared with those for titanium dioxide particles, and it was found that under similar conditions, both zeolite and TiO_2 require the same time to completely degrade caffeine. On the basis of spectroscopic analysis of UV–Vis spectra of the materials obtained in this work, it was found that the absorption bands in the range of 200–500 nm refer to different states of iron, and in natural zeolites, the presence of iron is common.

In the case of clinoptilolites, it is iron that often becomes the active centers in photocatalysis and catalysis. For example, in [158], the natural form of clinoptilolite was similarly protonated. Both the initial and H-forms were then subjected to mechanochemical treatment in water and air. XRD, FTIR, SEM, XPS and UV–Vis spectroscopy were used to examine both the initial and milled samples. The authors showed that dry milling leads to destruction of the crystal structure, whereas milling in water partially preserves the crystal structure; however, a meso-macroporous structure is formed in both cases. The surface of these materials was enriched with oxygen-containing particles of iron compounds that served as photocatalytic centers. These samples exhibit increased photocatalytic activity in the degradation of rhodamine B under the action of visible light [158].

Natural zeolite with a crystalline framework of heulandite type was modified with iron and tested as a catalyst for selective catalytic reduction of nitrogen oxides by ammonia (NH_3-SCR) in the temperature range of 150–450 °C [159]. The activity of the catalyst was tested under industry conditions using tail gases from a pilot nitric acid plant. The effect of temperature, catalyst loading, and amount of reducing agent (ammonia) on the NOx reduction process was investigated. The results of the catalytic tests showed that Fe-clinoptilolite showed about 58% NO conversion at 450 °C. In addition, it was noted that the ratio of N_2O concentrations after and before the catalytic bed was below 1, indicating that the catalyst exhibited activity in both the de-NOx and de-N_2O processes.

The authors [160] prepared protonated clinoptilolite as a catalyst carrier and then subjected it to ion exchange with salts of Fe, Cu, and Co. Their experimental protocol included repeated ultrasound treatment at various stages of preparation. The zeolite catalysts obtained were used for biomass conversion. The following organic acids were obtained during conversion: lactic acid, formic acid, pyruvic acid, acetic acid, and levulinic acid. The highest yield of lactic acid (66.2%) was achieved with Co-clinoptilolite, formic acid (93.6%) with Cu-clinoptilolite, and acetic acid (87.4%) with Fe-clinoptilolite.

The property of ion exchange has found wide application in the preparation of catalysts. Transition metals, their oxides and ionic compounds are known to be very effective catalysts. Their use applied to zeolites creates interesting opportunities for nanoengineering solutions when cations are distributed over the carrier surface. The use of natural clinoptilolite as a support matrix modified by ion exchange with cations such as Fe^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Zn^{2+}, etc. led to the development of low-cost NO_x reduction catalysts [159,161–163]. The authors call attention to the substance (e.g., salts) used as a precursor of the cation active in the catalytic reaction and complete removal of its residue on the zeolite support after ion exchange, which can affect the activity of the developed catalyst. A review of studies on samples of HEU-type zeolites, both pure and modified with transition elements of d- and f-blocks and Pb, is given in [164]. The interest in such modified zeolites is mainly due to their use for pollution control and their potential catalytic properties. Detailed information on the crystal structure of HEU-type crystals fully subjected to cation exchange shows that the ions mainly occupy two out-of-frame positions: one in the center of the ten-membered ring, octahedrally coordinated with six H_2O molecules, and one in the eight-membered ring, coordinated with framework oxygen and additional H_2O (see Figure 3). Additional microscopic, spectroscopic, and thermal data for heulandite and clinoptilolite interacting with these ions showed non-homoionic and non-stoichiometric metal loading. Excessive accumulation on the crystal surface due to adsorption and deposition phenomena on the surface was usually observed. Only a very low incorporation of trivalent lanthanide/rare Earth element ions into the clinoptilolite channel system was experimentally achieved.

Despite the fact that the use of natural raw materials as catalysts causes a number of problems related to their non-homogeneous composition, the efforts to create such materials continue. This is due to the fact that synthesis of zeolites generates rather large volumes of aggressive high-alkali wastes, and synthetic zeolites themselves due to prices for raw materials and energy turn out to be rather expensive. Modernization processes in the chemical industry over the past few years have increased concerns about the sustainable use of natural resources and the introduction of solvent-free and toxic synthesis processes. In addition, the development of new catalysts capable of minimizing or even eliminating harmful substances commonly used in the chemical industry is receiving increasing attention in academia and the industry in the context of "green chemistry," based on the search for products and processes that can reduce or even eliminate the use of hazardous substances. Review [123] describes the main classes of green catalysts, their main characteristics, and various synthesis methods.

4.4. Bioactive Materials

Reviews on medical and veterinary applications of different natural clinoptilolite-based materials as well as their safety can be found in [15,42]. Modification of natural clinoptilolite by ion exchange with certain cations known for their oligodynamic activity, such as Zn^{2+}, Cu^{2+}, Ag^+, etc., makes it possible to obtain materials and products with biocide activity for different interest fields [14,15,165]. In [166], the authors reviewed the bioactive properties of exchanged natural Ag-clinoptilolites, its activity mechanism, antimicrobial agent and biomedical applications. Studies of Mexican natural clinoptilolite from Etla, Oaxaca, showed that *Escherichia coli* and *Salmonella typhi* bacteria experience a rapid reproduction on this zeolite [167]. However, when this clinoptilolite is modified by using it first with Na^+ ion exchange, followed by Ag^+ exchange and finally thermal reduction, it is transformed into a material efficient enough to eliminate both bacteria.

The natural clinoptilolite from Sardinia, Italy, was modified by ion exchange with Zn^+ cations and erythromycin, resulting in a patented product [168] with the potential for biomedical application in the topical treatment of acne, where the combination of zinc and erythromycin is effective against resistant strains of *Propionibacterium* [165]. The antibacterial activity against *Escherichia coli* (Gram-negative bacteria) and *Staphylococcus aureus* (Gram-positive bacteria) of the natural clinoptilolite from Zlatokop, Serbia, modified with Cu^{2+}, Zn^{2+} and Ni^{2+}, was tested in different liquid media (namely Luria Bertani,

synthetic wastewater and real effluent water from the secondary stage of the biological wastewater treatment plant) [167]. The only Cu- and Zn-clinoptilolite forms showed important activity against these pathogens, which reduced the bacterial numbers for six orders of magnitude in effluent water. Ni-clinoptilolite showed weak antibacterial activity, which was associated with a high leaching of Ni^{2+} from the zeolite phase to solution. Chilean natural clinoptilolite supplied by Minera Formas, Chile, was subjected for several size reduction processes to obtain it in nanoparticle form with an average diameter of 37.2 ± 15.8 nm, which then was chemically treated with HCl solution and finally modified to its copper form by using Cu^{2+} ion exchange [169]. This Cu-nanozeolite showed antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*, primary pathogens that are present in food and that are resistant to multiple drugs. In addition, the authors have outlined that its nanometric size increase the available surface area and leads to its applicability in different matrices. Exchanged Ag-, Zn- and Cu-clinoptilolite were the obtained forms of natural clinoptilolite from Vranjska Banja deposit (Serbia) by using ion exchange, first with Na^+ ions and then with Ag^+, Zn^{2+} and Cu^{2+} cations, respectively, and they were tested as antibacterial agents for wastewater treatment in a batch and bead filter system [24]. Ag-clinoptilolite showed higher antibacterial activity, which was outstanding in the bead filter system against hospital pathogenic bacterium *Acinetobacter baumannii,* completely removing the pathogenic carbapenem-resistant bacteria from real effluent wastewater.

Based on Cuban natural clinoptilolite modified by Zn^{2+} ion exchange, a zeolitic product ZZ@ was developed, which has microbicidal properties against bacteria, yeasts, and protozoa [14]. ZZ@ has been used in different drinking water purification systems (domestic and collective) and preparation of other microbicidal products. Its microbicidal action consists in the controlled release of Zn^{2+} cations into contacting media (for example, water), which have a wide spectrum of bactericidal effects on pathogenic microorganisms, suppressing their infectious effect on humans. The levels of zinc achieved in this way in water are below those recommended by the Guidelines for Drinking Water Quality (<5 ppm) [170]. Furthermore, zinc is an essential element for human and animal life. This element, sometimes referred to as the spark of life, is effective against a wide variety of pathogens, mostly those living in water that commonly cause gastrointestinal, lung, and skin infections in humans.

4.5. Agricultural Applications

Among all the zeolites used in agriculture, natural clinoptilolite stands out because it is the most used and contributes to the improvement of some soil properties [38,171–173]. Cuba is among the countries with major natural reserves of zeolites, included clinoptilolite [26,27]. Their deposits are distributed along this Caribbean island [173]; coincidently, its most productive agricultural crop areas are in the vicinity of clinoptilolite deposits. In this sense, it is appropriate to note that silicon, the main component of zeolites, is also considered an important element due to its significant role in the physiology and biochemistry of the crop plants [174–176].

Of all the nitrogen fertilizers commonly used in agriculture, urea is the most widely used in agriculture worldwide, where a high nitrogen content (46%) is of great importance. However, its application in soils is accompanied by high losses and low utilization efficiency (<50%), mainly associated with ammonia volatilization and nitrate leaching. These processes represent severe environmental risks, manifested in the degradation of soil and underground water quality, reduction of biodiversity, increase in the concentration of NO_x, a gas with a powerful greenhouse effect, and contributing to the formation of so-called acid rains, the depletion of the ozone layer and other environmentally unpleasant effects [177]. Thus, it is necessary to develop other alternative fertilizers and technologies that are safer for the environment.

The ion exchange properties of natural clinoptilolites and their affinity for NH_4^+ were used to reduce nitrogen losses by volatilization of ammonia from urea [178–180]. Studies

with urea/natural clinoptilolite mixtures have shown that such a mixture results in a 53% reduction in volatile ammonia [179]. Natural clinoptilolite from Faku County, Liaoning-Chine, was mixed with soil, and then, the ability of this zeolite for retaining and releasing ammonium was tested by contacting the mixture with an NH_4^+ solution [181]. The authors reported that clinoptilolite enhances the nitrogen-retaining capacity of the soil, where ion exchange processes play a key role, and soil quality is improved due to the co-existence of exchangeable K^+ and Na^+ cations, mainly due to the latter. It was reported that the use of natural clinoptilolite in soils significantly reduces the excretion of ammonium and nitrates from urea compared with the use of urea alone [178]. Furthermore, exchangeable NH_4^+ and the retention of total soil nitrogen as well as available nitrate are improved due to the ability of the zeolite to retain NH_4^+ through cation exchange.

The report of the Commission on Natural Zeolites of the International Zeolite Association [I70] on volcanogenic sedimentary zeolite deposits in Cuba overviews different products and technologies of using Cuban natural zeolites in agricultural development that lead to remarkable results. Among these Cuban products, NEREA@ stands out. NEREA@ products are currently available on the market for use as substrates and fertilizers, and technologies for their production and use have been transferred to Cuban and foreign industries [182]. The properties of natural clinoptilolite, including ion exchange, cause its chemical modification with nitrogen, phosphorous, potassium and others (calcium, minor and trace nutrients) in the quantities required by agricultural crops. NEREA@ is an environmentally friendly technology for both industrial production and use. These products facilitate efficient cultivation, saving up to 90% of chemical fertilizers and water, while significantly increasing crop yields and growth speed. The nutrients available to plants are stored in the zeolite, and crop plants receive them directly from the zeolitic particles. NEREA@ products release nutrients in a slow manner, which limits nutrient loss through leaching and volatilization.

In addition, a controlled release fertilizer was prepared starting from Slovak natural clinoptilolite subjected to ion exchanges processes, first with Na^+ and then with NH_4^+ (ammonium chloride) [183]. The authors reported that this fertilizer is an alternative to reduce losses and increase fertilizer efficiency. Studies of soils with the addition of natural clinoptilolite and vermiculite (in combination with urea or manure), and the associated processes of nitrogen mineralization and nitrification, have shown that these materials affect the availability of NH_4^+ and retard the accumulation of NO^{3-} in the soil [184]. Such an effect on NH_4^+ cation can be associated with the ion exchange property of clinoptilolite and its high affinity for this cation.

Review [185] summarizes recent and innovative applications of zeolites in the wine industry and provides a critical discussion of their ability to prevent protein clouding, tartrate instability, or other certain defects. Heavy metal cations at excessively high concentrations in wine can cause metallic off-flavors, unwanted color changes or cloudiness. Cloudiness in wine caused by heavy metals is a major problem in winemaking. It is usually caused by excessively high iron content in wine. Iron is absorbed through the grape roots in relatively small amounts. The most important source is corrosion of winery equipment. Haze due to copper is based on the formation of insoluble copper sulfide. Some transition metals (such as Fe and Cu) can catalyze oxidation reactions of phenols and other compounds in grape wine. Some metals are also undesirable for toxicological reasons. This is why efforts are being made to reduce the heavy metal content of these drinks. The limits below which clarification is not required are 4 ppm for iron and 0.5 ppm for copper.

4.6. Zeolites as a Nature-Forming Factor

Discussion of this range of phenomena leads us to the necessity and possibility to assume that, already by their existence on the surface of our planet, zeolite minerals influence the daily life of mankind. If it is possible to move thousands of tons of natural zeolite to create an artificial barrier on the way of spreading certain ions over the surface and in the hydrosphere, then all the same effects exist for geological times in places where they

are deposited. Consequently, if we compare and analyze some data, it becomes possible to discover some global effects that zeolites have on landscapes in which they occur.

Based on these claims, a new interdisciplinary scientific field has been proposed [186,187]. Medical geology is defined as the science that studies the relationship between geological factors and human, animal, and plant health problems. Medical geology can also be recognized as geomedicine; medical geography is developing in parallel, with a somewhat different meaning associated with the broader field of medical geology. Medical geography looks at the geographic distribution of disease without focusing on the underlying geology; this is why there are universally recognized resort centers where medics send the seriously ill to improve their health. This whole body of evolving knowledge examines the causal relationships between specific diseases and the physical and social environment. As the recent example of the discussion of the properties of erionite (see above) demonstrated, the field of study is complex and requires a serious interdisciplinary approach involving a wide range of specialists, from geologists and geochemists to medical scientists, biologists, and geneticists. The unique and exceptional physical and chemical properties of some minerals favor their use in numerous fields of medicine [188]. On the other hand, it is well known that people selfishly use natural resources to satisfy their needs regardless of what happens to the environment; therefore, nature's "response" and its impact on public health is sometimes unexpected (exposure to toxic levels of trace elements, deficiency of essential trace elements, exposure to mineral dust, radioactivity, industrial disasters, and so on) [186]. Schematically, this complex relationship between the biosphere and the geosphere is shown in Figure 10.
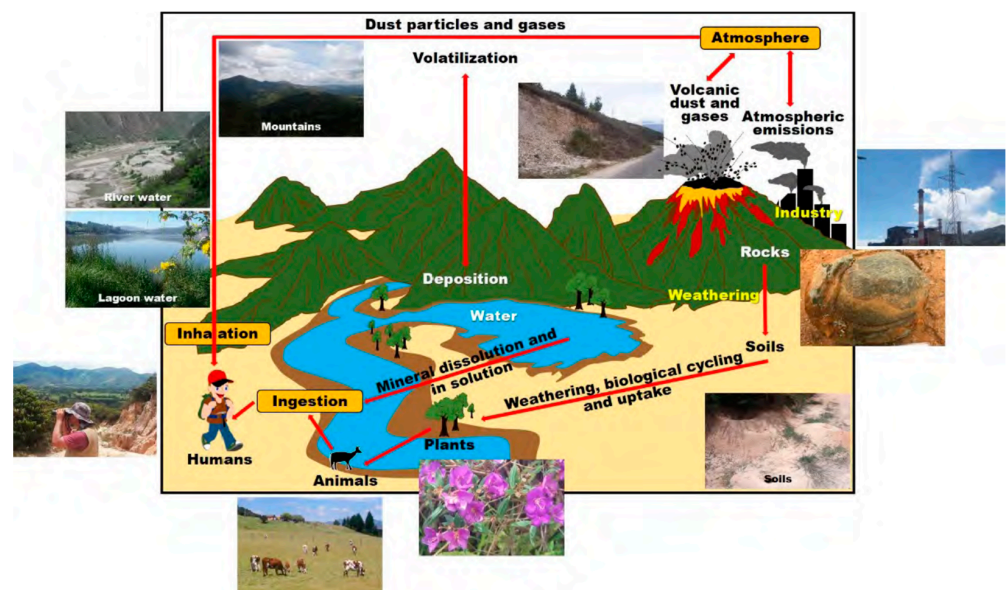

Figure 10. Schematic representation of the relationship between the biosphere and the geosphere. Reproduced with permission from the authors [186].

The relationship between geology and human health is not unexpected news; it was first noted back in antiquity. During the Renaissance, the Swiss alchemist, physician and philosopher Paracelsus proclaimed the principle: "*Everything is poison, everything is medicine; only the dose differentiates a poison and a remedy*". The development of atomic emission spectroscopy made it possible to analyze media with extremely low concentrations of elements. The application of this analytical method made it possible to measure the trace element composition of soils, plants, animal tissues, and other substances, leading to important scientific discoveries. Information about the vital necessity of trace elements and their influence on the condition of living organisms was collected [189].

The use of zeolites in the natural environment is important in terms of monitoring the mobilization of toxic metals and trace elements that affect the food chain, and their defi-

ciency as well as excess determine the quality of plants and human and animal health [190]. In addition, zeolites, having certain physical, physico-chemical and chemical properties, interact with physical, physico-chemical, chemical and biological features of the soil, which can lead to changes in their properties. This exchange depends on many factors; however, when natural zeolites are used, one must remember that they are an ecological material and do not have a harmful effect on humans or animals. People suffering from micronutrient deficiencies usually suffer from cumulative element deficiencies, i.e., their diet lacks several vitamins and minerals at the same time. Quality malnutrition is directly or indirectly responsible for half of the deaths among children under five worldwide. Through deliberate intervention in agro-ecosystems, humans can control their productivity and increase the amount of biomass produced, which can be used as food for humans, feed for animals and raw materials for many industries. Therefore, the future of agriculture must be based on a diversity of plant species from which new, more useful and less processed products are produced. This approach contributes not only to security but also to the food sovereignty of society. Zeolites have proven to be promising binding agents for the mobility of toxic metal ions. In addition, their use alters soil pH values, largely determining the forms in which toxic metals exist in the soil [190].

Future research in medical geology should aim to establish a better understanding of the role of minerals in ecosystems. Among the minerals, zeolites interact easily and most importantly friendly with biological organisms (plants, animals, humans). In order to find new applications, one should determine the characteristics of the samples and their influence with regard to human health. It is necessary to consider minerals in relation to human health, to consider sources of toxic elements and possibilities of their removal. Planet Earth contributes to pollution through volcanic eruptions, radiation, toxic elements, dust, etc.; thus, anthropogenic activities should help to reduce pollution.

5. Challenges and Prospects for Innovation

One of the main and intractable problems of modern technology is the need to produce the maximum amount of useful materials with minimal energy consumption and with a minimized amount of waste. Synthetic zeolites are unsurpassed ion exchange materials, but their production is energy intensive and generates highly alkaline wastewater. In this regard, an intensive search is underway for materials that could perform all, or at least a significant part of the tasks requiring the use of ion exchangers. In addition to purely utilitarian tasks of wastewater treatment from cationic impurities, there are more complex technologies in which ion exchange is just an intermediate step for thee preparation of catalysts or microbicides. Therefore, despite all the difficulties of working with raw materials of variable composition, research work in this direction continues and develops.

The works reviewed here represent data obtained using conventional ion exchange methods, that is, hydrothermal treatment of zeolite at various temperatures with solutions containing cations for exchange. These processes usually take several hours or even days to achieve effective zeolite modification. However, there are other, more advanced methods, such as microwaves [61,62,191,192] and ultrasound [193–195], the use of which leads to a sharp decrease in processing time, down to very few hours or even minutes. Often, such processes are accompanied by increasing the ion exchange level [61,191,193,195]; they do not have a destructive effect on the zeolitic framework [61,191,192]. Furthermore, the use of these auxiliary methods could favor the ion exchange of cations difficult to exchange at room temperature, as it was observed for K^+ cations that are strongly coordinated to five oxygens from the clinoptilolite lattice. However, until now, there are not many reported studies devoted to the use of such methods, and they are mainly limited to the use for zeolite synthesis and modification (ion exchange) of the resultant materials. Moreover, to the best of our knowledge, there are no kinetic studies of the ion exchange processes and their behavior over time using these advanced methods, which would allow them to be carried out more efficiently. The authors hope that the number of such studies will grow rapidly.

Studies of the ion exchange properties of natural clinoptilolites from various deposits of the world indicate a notable influence of the origin of the mineral on its behavior as an ion exchanger. From this point of view, a deeper understanding of the processes of ion exchange in natural clinoptilolite from various deposits, obtained on the basis of complex studies, allows for optimizing the properties of each local material from a particular deposit for specific applications. The development of composite materials based on natural clinoptilolite for topical applications (catalytic or photocatalytic purification of water, air, conversion of by-products into products with high added value), as well as in biomedicine and pharmaceuticals, opens up new prospects for the creation of cheap, environmentally friendly, and scalable technologies for sustainable development.

6. Summary

Clinoptilolite, one of the most common zeolites in nature, has very interesting prospects for wide application in various industries. Its structure is topologically equivalent to that of heulandite, but, at the same time, clinoptilolite exhibits significantly different physico-chemical properties, which is due to its framework and cationic compositions. This review analyzes in detail the relationship between clinoptilolite and heulandite, and the features of these two minerals with very different properties, although having the same structure. Different approaches to the classification of natural zeolites of the same type but from different deposits attempt to unify characterization protocols, established correlations, as well as other systematic studies (including studies of the most recent years), summarized in this review, indicating a growing interest in clinoptilolites, especially in the context of ion exchange. Combined with the availability of this mineral in large quantities, and low cost, ion exchange clinoptilolites have become attractive materials for use in a wide variety of applications. The availability of extra-framework positions in clinoptilolite for exchangeable cations is a key aspect that has a direct impact on its ion exchange capacity and selectivity, two main qualities for the use of clinoptilolites and their derivatives in various fields.

Summing up, we can say that this review examines the studies of the ion exchange properties of natural clinoptilolites from various deposits of the world as well as the ion exchange-based modification strategies proposed by various groups to create new materials with predetermined desired properties.

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