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Characterization and Utilization of Natural Zeolites in Technical Applications

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Abstract: Zeolites and zeolite rocks are commonly used in different industrial applications. Natural zeolites present an attractive material for environmental applications because of their high abundance, availability and low costs. Depending on geological settings and conditions during mineral formation, natural zeolite deposits usually represent a heterogeneous mixture of zeolite minerals together with varying amounts of gangue minerals (e. g. quartz, feldspars and phyllosilicates). Hence, profound mineralogical knowledge and a detailed characterization of natural zeolites are essential for tapping their full potential in any practical application. However, this is rarely done as detailed mineralogical characterizations are elaborate and often neglected in favour of bulk chemical analyses (e. g. XRF).

In this paper we describe typical technical applications for natural zeolites as well as the requirements demanded for their use. An analytical protocol has been developed for the detailed characterization of natural zeolites for ammonium exchange consisting of a combination of mineralogical and chemical methods and is exemplarily demonstrated. The methodology comprises mineralogical investigations with X-ray diffraction (XRD) and electron microprobe analyses (EPMA) to provide qualitative data on mineral compositions and in-situ analysis of mineral chemistry (Si/Al-ratio, cation contents). The examinations are accompanied by bulk chemical analysis (XRF) as well as thermoanalytical investigations (TG/DSC) to distinguish between certain zeolite minerals. Finally, ion exchange experiments for ammonium have been carried out to determine the cation exchange capacity (CEC) of zeolite samples for a defined range of concentrations.

The aim of the study is to develop an analytical routine in order to enable the detailed characterization of natural zeolite samples with standardized means of mineralogical/chemical analysis prior to their application in technical processes. This is important for quality assurance and for identifying the best suited zeolites for specific technical processes, especially when the proposed applications are not standardized.

Keywords: Natural zeolites, Clinoptilolite, Ammonium, Ion exchange, Characterization routine

Charakterisierung und Einsatz natürlicher Zeolithe in technischen Prozessen

Zusammenfassung: Zeolithe und zeolithhältige Gesteine werden in verschiedensten industriellen Anwendungen eingesetzt. Natürliche Zeolithe sind besonders attraktive Materialien für den Umwelttechnikbereich, da sie leicht verfügbar und kostengünstig sind. Abhängig von geologischer Stellung und den Bedingungen während der Mineralbildung bestehen Zeolithlagerstätten meist aus einer heterogenen Anreicherung von Zeolithmineralen gemeinsam mit unterschiedlichen Gehalten an Nebengemengteilen wie zum Beispiel Quarz, Feldspat und verschiedenen Phyllosilikaten. Um das vollständige Potential dieser Minerale während des Einsatzes in technischen Prozessen auszuschöpfen, ist es neben der chemischen Analyse der Gesteine notwendig, die mineralogischen und mineralchemischen Eigenschaften verschiedener Zeolithminerale und deren Verhalten genau zu kennen. Dies wird oftmals zu Gunsten von chemischen Gesamtgesteinsanalysen, die alleinstehend jedoch wenig Aussagen über die Minerale selbst zulassen, vernachlässigt.

Der vorliegende Beitrag befasst sich mit der Entwicklung einer Analysenroutine für natürliche Zeolithe zur Ammoniumabtrennung, indem verschiedene mineralogische und physikalisch/chemische Analysemethoden miteinander kombiniert und an einer Probe eines natürlichen Zeoliths exemplarisch dargestellt werden. Die qualitative Mineralidentifikation erfolgte mittels Röntgendiffraktometrie (RDA) gefolgt von einer in-situ-Analytik der Zeolithminerale (qualitative und quantitative Mineralchemie, Si/Al-

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Verhältnis, Kationenbestand) an einer Elektronenstrahl-Mikrosonde (EPMA). Die Gesamtgesteinschemie wurde mittels Röntgenfluoreszenzanalyse (RFA) bestimmt. Durch TG/DSC-Analysen wurde die thermische Stabilität der Zeolithe untersucht. Anhand ihres thermischen Verhaltens können mittels DSC-Analyse auch strukturell ähnliche Zeolithe unterschieden werden. Abschließend wurde die Kationenaustauschkapazität (KAK) für Ammonium durch Bestimmung der Austauschisotherme für einen definierten Konzentrationsbereich gemessen.

Ziel ist es, die Charakterisierung natürlicher Zeolithe durch die dargestellte Analysenroutine zu vereinheitlichen und vergleichbar zu machen. Dies ist hinsichtlich der Qualitätssicherung und zur Identifikation des für einen bestimmten technischen Einsatz am besten geeigneten Zeoliths wichtig, besonders wenn es sich dabei um neue, noch nicht etablierte Anwendungen handelt.

Schlagworte: Natürliche Zeolithe, Klinoptilolith, Ammonium, Ionenaustausch, Charakterisierung

1. Introduction

Zeolites are hydrated alumosilicates with exchangeable cations and open channel systems in their lattice. They consist of infinitely extending three dimensional networks of SiO_4^{4-} and AlO_4^{3-} tetrahedra linked by shared oxygen atoms [1–4]. The frameworks form voids or cages and channels in which exchangeable cations can enter. Due to substitution of tetravalent silicon by trivalent aluminium charge deficiency has to be balanced by incorporation of loosely bound monovalent and divalent cations of alkali and alkaline earth elements [5]. Additionally, water can reversibly enter these structures forming partial hydration spheres around the cations where the negative dipole of the water molecules point towards the positively charged monovalent and divalent cations [5]. The more silica is substituted by aluminium, it is expressed by the Si/Al ratio, the higher the ability to incorporate cations which enhance the properties of zeolite minerals as ion exchangers. Beside 232 synthetic zeolites (molecular sieves) 67 different mineral species of natural zeolites subdivided into 28 different framework types [6] are currently known. Among them, clinoptilolite is one of the most abundant zeolites and widely used in various applications [7, 8]. Clinoptilolite belongs to the HEU structure type and forms a continuous solid solution series with heulandite [9]. According to IMA (International Mineralogical Association) nomenclature [10] heulandite has Si/Al <4 and clinoptilolite has Si/Al >4.

The microporous structure of their framework as well as their capability to selectively exchange ions of different size and valence have made zeolites interesting for many industrial applications. Natural zeolites are widely applied in the construction and building materials industry, water and wastewater treatment, environmental remediation as well as agriculture, consumer products and medical applications. Clinoptilolite is the main zeolite used for commercial applications, while chabazite and mordenite are used in smaller quantities [11]. Zeolitic tuffs are used as additives in cement and concrete to neutralize excess lime, but can also be thermally expanded to form light weighed insulation materials [12]. Large-scale cation-exchange processes for water treatment using natural zeolites were described in the early 1970s, e. g. [13]. Natural zeolites have advantages over other cation exchange materials such as commonly used organic resins, because they are cheap, exhibit excellent selectivity for different cations at low temperatures, are compact in size and allow simple and cost-efficient maintenance in full-scale applications [14].

Although synthetic zeolites generally have higher cation-exchange capacities, natural zeolites exhibit a greater selectivity for ammonium [15], what makes them an interesting adsorption reagent for nitrogen removal and recovery [16]. Furthermore, natural zeolites were extensively studied for the removal of heavy metals from municipal, agricultural and industrial waste waters including soil effluents and acid mine drainage [17, 18]. Especially, natural clinoptilolite is a selective ion exchanger for ammonium and this has prompted its use in soil amendment and remediation, swimming pools and fish farming [19]. Further potential uses for clinoptilolite are in energy storage [20] and nitrogen recovery [21, 22].

Natural zeolites commonly form as low-temperature alteration products in a variety of rocks, but the most important deposits are found in volcanoclastic and sedimentary rocks [23]. Depending on the geological setting and physico-chemical conditions during mineral formation, zeolite deposits usually represent a heterogeneous mixture of zeolite minerals together with gangue minerals like quartz, feldspars and phyllosilicates (mica, clay minerals). Hence, geological factors control the stability of zeolite phases (i. e. which zeolites form) as well as the type and amount of gangue minerals present and have a strong influence on the quality and applicability in technical processes. Prior to any technical application a detailed characterization of these materials is therefore necessary in order to understand performance and behaviour within any practical application [14, 24]. The enormous diversity of zeolites and varying experimental setups and characterization methods make it difficult to compare the results especially when proposed applications are not standardized.

Therefore, a characterization scheme is proposed for technical applications by combined mineralogical and chemical methods and results are presented exemplarily for one selected zeolite sample (Z-01) from an Austrian supplier.

2. Methodology

The identification of the crystalline phases of the sample was conducted by XRD using a Philips X'Pert System, Goniometer Type PW3050/60, with CuKα radiation (Chair of Petroleum Geology, Montanuniversität Leoben). The sample was manually powdered in an agate mortar to a final grain size <2 µm. The accelerating voltage was 40 kV and the current 40 mA. Scans were run 5 times by a minimum step size of 0.01 [2θ] between 2.5° to 65° [2θ], scan velocity was 0.5 [2θ/min]. The qualitative mineral content was determined on a calculated scan out of all measurements using ICDD-database within the software X'pads. The mineral identification was carried out by at least 2 key peaks allowing a maximum deflection of 0.2 [2θ] for peak matching. R-value (goodness of fitting) of mineral peaks was set below 1.4.

Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) measurements of the sample were conducted using a STA 449 C (Netzsch Gerätebau GmbH) system (Chair of Process Technology and Industrial Environmental Protection, Montanuniversität Leoben). The analysis was carried out on about 20 mg of powdered sample material using open type ceramic crucibles. The sample was heated from room temperature up to 1100 °C with a linear heating rate of 5 °C min^{-1} in nitrogen atmosphere (flow rate 80 ml min^{-1}).

Whole rock chemical composition was determined using a wavelength dispersive X-ray fluorescence spectrometer (WD-XRF AXIOS from PANalytical) at the Chair of General and Analytical Chemistry, Montanuniversität Leoben. Loss on ignition (LOI) was determined gravimetrically by heating about 3 g of material in platinum crucibles to 1000 °C in a muffle furnace for three hours. Fused glass beads were prepared by fusing the ignited sample with $Li_2B_4O_7$ (ratio 1:8).

Zeolite minerals were analysed by electron microprobe (EPMA) using the Superprobe Jeol JXA8200 at the Eugen F. Stumpfl Laboratory (Chair of Resource Mineralogy, Montanuniversität Leoben) using EDS and WDS techniques. Back scattered electron (BSE) images were obtained using the same instrument. For quantitative analysis (WDS mode) an accelerating voltage of 15 KV, a beam current of 10 nA and a beam diameter of about 1 micron was used. The elements Si, Al, Na, K, Ca, Mg, Fe were analysed using the respective Kα lines and the following standards: adularia (Na, K), corundum (Al), quartz (Si), wollastonite (Ca), fluorphlogopite (Mg) and chromite (Fe). Diffracting crystals used were TAP for Na, Mg and Al; PETJ for Si; PETH for K, Ca; LIFH for Fe. The peak and background counting times were 15 and 5 s for Mg, and 20 and 10 s, respectively for Si, Al, Na, K, Ca and Fe. Detection limits were calculated automatically by the JEOL internal software and are (ppm): Si (240), Al (110), Na (150), K (60), Ca (80) and Fe (330).

The cation-exchange capacity (CEC) for ammonium was measured in batch-experiments with ammoniumsulfate-solutions (Chair of Process Technology and Industrial Environmental Protection, Montanuniversität Leoben). 500 ml of $(NH_4)_2SO_4$-solutions (concentration range: 500–5000 mg NH_4^+ l^{-1}) were contacted with 20 g of zeolite in an overhead shaker for 24 h at 20 °C. Liquid samples were taken before and after ion-exchange and filtrated by syringe filters (0.22 µm). Ammonium was analysed via Kjeldahl-method using boric acid and HCl/Tashiro's indicator for titration. The difference in the ammonium concentration of the initial and final solution represents the amount of exchanged NH_4^+ and therefore the CEC for different equilibrium concentrations (exchange isotherm).

3. Results and Discussion

The X-ray diffraction pattern shows HEU-type zeolite as the main phase (Fig. 1). Minor phases present include potassium-rich phyllosilicates, plagioclase (dominantly albite), alkalifeldspar and quartz. Due to the structural similarity it is not possible to accurately distinguish heulandite and clinoptilolite on the basis of XRD data [25].

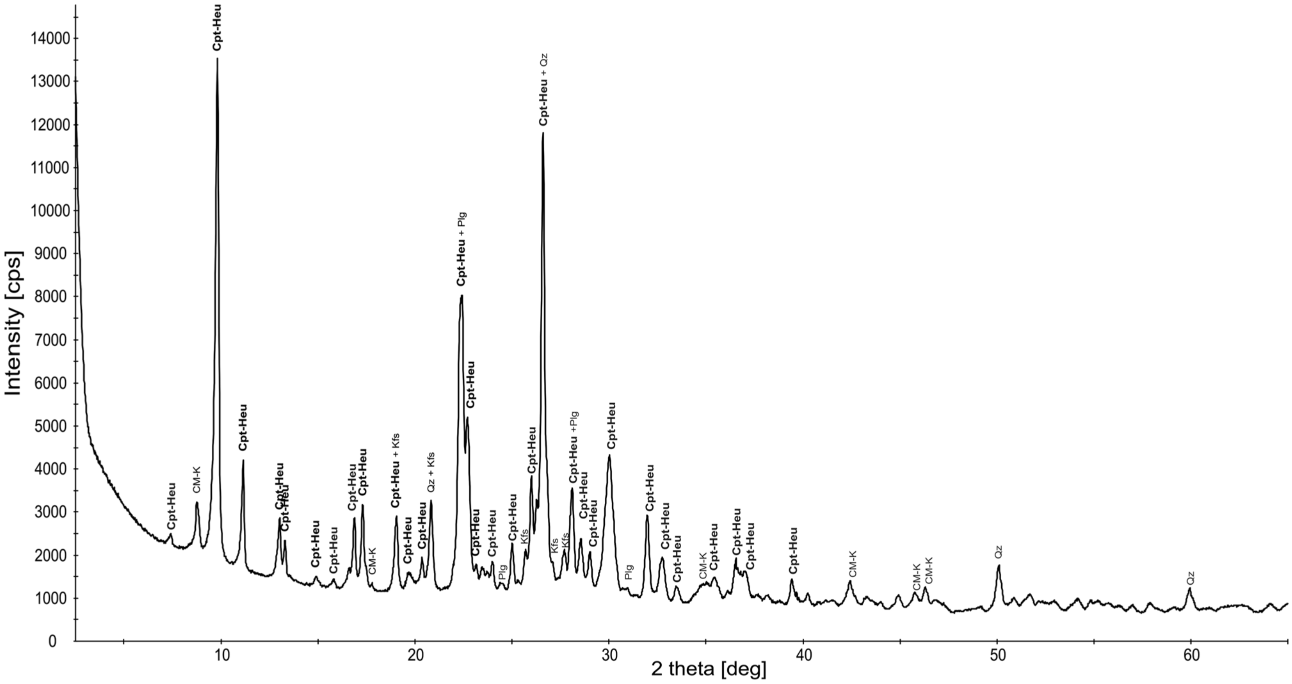


Fig. 1: XRD pattern of the sample Z-01 compiled from 5 individual measurements; *Cpt-Heu* heulandite-type zeolite, *CM-K* potassium-rich phyllosilicate, *Kfs* alkalifeldspar, *Plg* plagioclase (albite), *Qz* quartz

Fig. 2: TG-DSC curves of zeolite sample Z-01 compared to DSC-curves of clinoptilolite and heulandite [2]

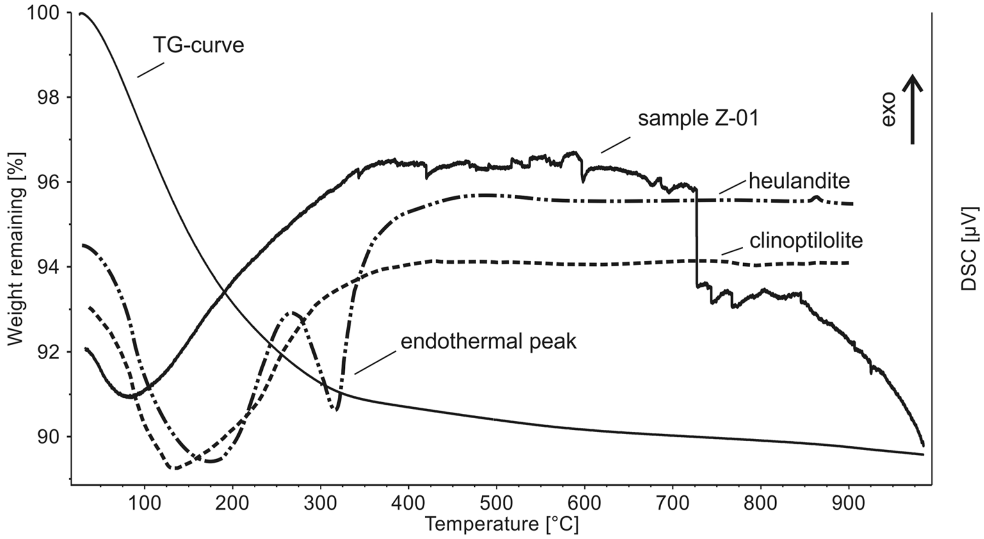


TABLE 1

Results of XRF analysis and mean mineral composition of clinoptilolite determined by EPMA for sample Z-01 (in mass % oxides)

	XRF	EPMA
#	1	42
SiO_2	67.25	63.44 (0.03)
Al_2O_3	11.91	11.68 (0.22)
Fe_2O_3	1.43	0.02 (0.01)
MgO	1.01	0.89 (0.14)
CaO	2.68	3.68 (0.20)
Na_2O	0.76	0.07 (0.03)
K_2O	2.83	1.46 (0.16)
LOI/H_2O	10.74	11.00
Cations based on 72 O		
Si		29.69
Al		6.44
Fe^{3+}		0.01
Mg		0.62
Ca		1.84
Na		0.07
K		0.87
Si/Al	4.99_{tot}	4.61_{fr}
D/M		*2.66*

number of analysed points, single standard deviation in brackets; *LOI/H₂O* loss on ignition for XRF, H_2O from DTA for EPMA; total Fe as Fe_2O_3; cations calculated based on 72 oxygens; *D/M* ratio of divalent to monovalent cations

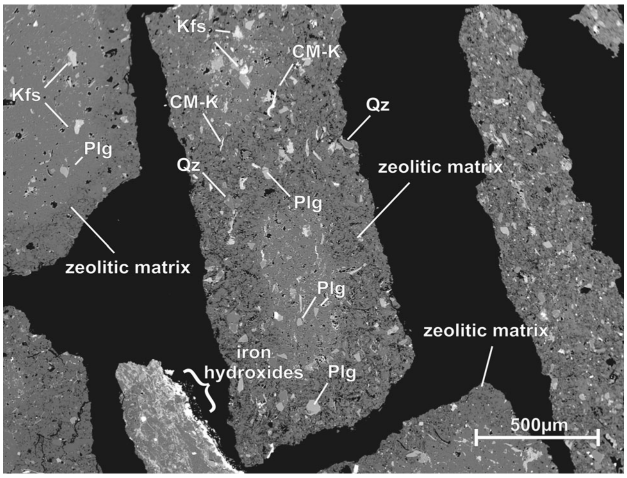


Fig. 3: Backscattered electron image of sample Z-01 (detail); *CM-K* potassium-rich phyllosilicate, *Kfs* alkalifeldspar, *Plg* plagioclase (albite), *Qz* quartz

Thermoanalytical techniques can be used to understand interactions between zeolite minerals and adsorbed water molecules as well as thermal behaviour of zeolites. Additionally, it can be used to distinguish between the structural similar endmembers of the HEU-type group heulandite and clinoptilolite, e. g. [26]. Clinoptilolite, in contrast to heulandite, does not undergo a phase transition at about 300 °C und is stable up to around 650 °C [27]. Fig. 2 shows TG-DSC curves of sample Z-01 compared to curves of natural clinoptilolite and calcian heulandite; the latter showing a distinct sharp endothermal peak between 280 and 400 °C [2]. The investigated sample shows a single-step dehydration (8.5%) from 50 to 300 °C, i. e. a steeper slope of the TG curve in this temperature range, which goes on at a lower rate above 400 °C (in total 11%). The DSC curve of sample Z-01 has a broad endothermal peak at 50–120 °C due to continuous water loss. The typical heulandite endothermal peak at around 300 °C is missing, which identifies the zeolite mineral as a clinoptilolite. The sample does not show major structural changes up to 720 °C; there a dramatic change of the DSC curve is observed (while the mass loss curve remains unchanged) indicating the structural decay of the zeolite.

The bulk chemical composition was obtained by XRF and is listed in Table 1. The mean chemical composition (EMPA) of clinoptilolite ($n = 42$) and the cations per formula unit (based on 72 oxygens) are also shown in Table 1. The clinoptilolite is characterized by higher calcium, potassium

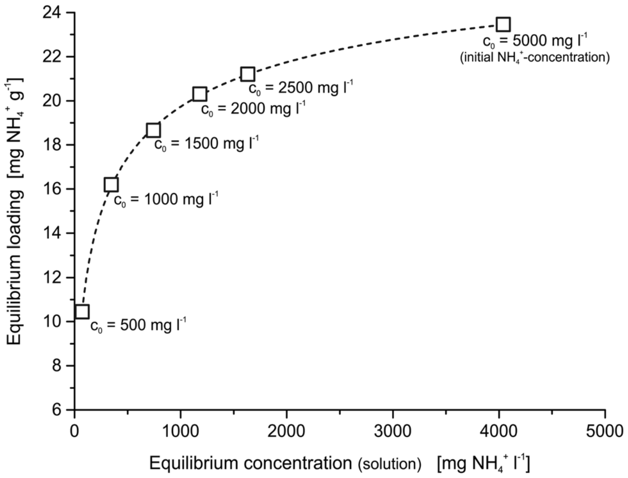


Fig. 4: Ion exchange isotherm for ammonium on sample Z-01

and magnesium and low sodium and iron contents. The framework Si/Al-ratio is 4.61 compared to 4.99 for the bulk rock. Small differences can be noted between the whole rock and mineral chemical data: XRF data show higher values of silica and alkalis indicating the presence of quartz, feldspars and K-rich phyllosilicates in addition to clinoptilolite. The feldspars are Na-plagioclase (albite) and alkalifeldspar (orthoclase); i. e. Ca is mostly hosted in clinoptilolite and not in plagioclase. Fe_2O_3 as reported by XRF is hosted by accessory iron hydroxides (goethite?). Because these phases are X-ray amorphous they were not detectable by XRD but they were qualitatively confirmed by EPMA. Iron hydroxides occur as thin layers at the rim of some zeolite grains due to weathering. Angular fragments of plagioclase, quartz and alkalifeldspar (approx. 10–50 µm in size) are surrounded by a finer grained zeolite matrix (Fig. 3).

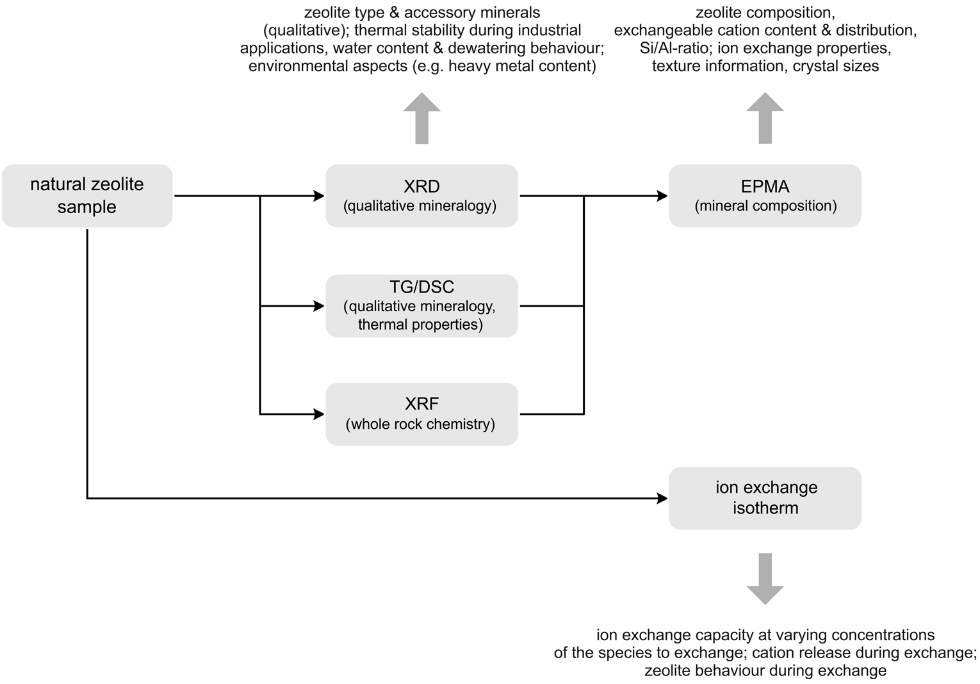
The Si/Al value derived from whole rock data is 4.99 and significantly higher than the Si/Al value determined by in situ-measurement of clinoptilolite by EPMA (4.66). The latter excludes quartz and feldspars and represents the correct Si/Al-ratio for clinoptilolite minerals in the investigated sample. Because Si/Al is one of the chemical key parameters influencing the technical applications of zeolites it is important to use this correct ratio from mineral analyses and not that of the bulk sample.

The exchange isotherm (Fig. 4) shows a steep increase in the ammonium uptake for initial solution concentrations from 500 to 1500 mg l^{-1} with a gradual flattening at higher concentrations. The maximum NH_4^+-loading of 23 mg g^{-1} (1.28 meq g^{-1}) was obtained at 5000 mg l^{-1} initial solution concentration. This value is in good accordance to literature data for clinoptilolite rich zeolites [7], although it is difficult to compare CEC-results for different zeolite samples published in literature as the applied methods are not standardized [28]. Given a CEC for pure clinoptilolite of 1.75 meq g^{-1} [29], the clinoptilolite content of the sample was estimated to be around 73%. Nevertheless, ammonium uptake did not obtain constant values even at the highest initial concentrations as a result of single batch equilibration [28]. Therefore maximum CEC of the sample was not reached and the proposed value of 73% represented the lower limit of clinoptilolite content in the investigated sample.

4. Conclusions

Detailed characterization of natural zeolites for technical applications requires a combination of mineralogical and

Fig. 5: Proposed analytical protocol for the characterisation of natural zeolites



physical/chemical methods, many of which are not standardized. For the characterization of natural zeolites we propose the following scheme of analysis (Fig. 5), which comprises XRD, TG/DSC and XRF in a first step for a simple qualitative identification of the mineral content, thermal properties and chemical composition. More elaborate analytical techniques for the detailed characterization include EPMA measurements to determine zeolite mineral composition, Si/Al-ratio and exchangeable cation content as well as ion-exchange studies to obtain the concentration dependent cation exchange capacity. Individual results of this set of analysis provide comprehensive information about the whole sample and enable a detailed review of cross-linked parameters (e. g. Si/Al-ratio, CEC and exchangeable cations). On the whole, the proposed analytical scheme allows for a detailed characterization of natural zeolites prior to their use in various technical applications and it is a powerful combination of methods for quality assurance and materials testing.

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