

1 **Synthesis, characterization, and thermodynamic study of selected Na-based zeolites**

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31 **Abstract**

32 Zeolites are crystalline aluminosilicates with three-dimensional framework structures that can  
33 form in alkali-activated cements, Roman cements, and the interaction zone of cements and  
34 clays. However, their stability domains are uncertain due to their high structural variability  
35 and the lack of experimental solubility data. Thermodynamic data were here determined for  
36 selected Na-based zeolites built from six different secondary building units that could possi-  
37 bly form in the interaction zones of cement/clay. The zeolites were synthesized by hydrother-  
38 mal methods and full-scale characterized with respect to framework structures, extra-frame-  
39 work cations, Si/Al ratios, and water contents. Their thermodynamic properties were  
40 determined based on the experimental solubility products at different temperatures using  
41 GEMS. Predominance diagrams of zeolite-clay/mica-SiO<sub>2</sub>/Al(OH)<sub>3</sub> minerals in the chemical  
42 sub-systems of Na<sub>2</sub>O-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O were successfully established using PHREEQC-  
43 PhreePlot code. The experimentally derived thermodynamic data provide insights on the early  
44 stage of the zeolite ageing and predicting zeolite stability domains during cementitious mate-  
45 rial hydration.

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48 **Keywords**

49 Zeolite; Solubility product; Thermodynamic data; Degraded cement/clay interface; Cemdata;  
50 Stability domain; Nuclear waste disposal.

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## 56 **1. Introduction**

57 Zeolites have three-dimensional framework structures. Typically, their frameworks are nega-  
58 tively charged due to the partial (half in maximum) substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$ , and the nega-  
59 tive charge is balanced by exchangeable cations (e.g.,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$ ) in the cages. The  
60 microporous structures and the exchangeable cations enable zeolites to have diverse applica-  
61 tions in different areas, such as petrochemical industry, catalysis, agriculture, heat storage,  
62 and cement industry [1]. In cement industry, zeolites can be used as supplementary cementi-  
63 tious materials, which can reduce  $\text{CO}_2$  emission by partially replacing cement clinkers [2]; the  
64 high content of alkalis generally present in zeolites accelerates the reaction of cement clink-  
65 ers. Zeolites can also potentially form in alkali-activated cements [3, 4], have been observed  
66 in Roman cements [5] or possibly precipitate instead of expansive alkali silica reaction (ASR)  
67 products if sufficient aluminum is available [6].

68 Zeolites can also form as secondary mineral phases at the interaction zone of degraded ce-  
69 ments and clays [7, 8], e.g. in underground concrete structures or cementitious nuclear waste  
70 repositories. Zeolitic precipitates, such as nitrate-sodalite, nitrate-cancrinite, and faujasite,  
71 could form from clays (e.g., illite, vermiculite, or montmorillonite) subjected to weathering in  
72 high-level radioactive tank waste leachate [9], such that cements, zeolites and clays can be ex-  
73 pected to co-exist in long-term underground constructions [10, 11].

74 Although zeolites are used in diverse areas and are present in different cementitious systems,  
75 their stability and the conditions of formation or dissolution are still uncertain, as the compo-  
76 sitions and structures of zeolites are quite variable and little experimental solubility data are  
77 available. The solubility products for different zeolites are typically determined from meas-  
78 ured or calculated enthalpy and heat capacity data, which leads, due to the uncertainty associ-  
79 ated with the measurements of enthalpy data, to significant errors on the solubility product.  
80 Due to the lack of experimental data, researchers tried developing "critical and systematic"

81 estimation strategies of thermodynamic data of zeolites [11, 12]. The standard Gibbs free en-  
82 ergies of formation ( $\Delta G_f^0$ ) and standard enthalpies of formation ( $\Delta H_f^0$ ) has been calculated by  
83 the polymer model [13, 14], polyhedral model [15], exchange models [16], and phase relation  
84 methods [17]. The calculation of the standard entropy ( $S^0$ ) and heat capacity ( $C_p^0$ ) has been  
85 made typically using additivity methods [17-19]. However, unclear kinetics of mineralogical  
86 equilibrium/transformation and limited mineralogical and chemical compositions, makes this  
87 difficult and the resulting stability fields might not agree with experimental observation as  
88 discussed in Blanc et al. [11]. Problems arise with the completeness of the thermodynamic da-  
89 taset, e.g., with  $\Delta H^0$  and  $S^0$  measured on minerals displaying slightly different compositions.  
90 Mineralogical determinations of zeolites are hard to be precise based on X-ray diffraction  
91 (XRD) alone. One way to verify the estimation models was to process solution experiments  
92 using well-defined zeolite structures. This underlines the need for systematic experimental de-  
93 termination of the solubility for different zeolites.

94 The internal consistency of thermodynamic data can be ensured considering the coexistence  
95 of cements, zeolites, and clays. Currently, the thermodynamic database of Cemdata'18 [20]  
96 mainly contains the data of cement phases but lacks the data for zeolites and clays. By com-  
97 plementing Cemdata'18 with the clay data from ThermoChimie [21] and determining the ex-  
98 perimental data for zeolites (including Na-, K-, Ca-, and Mg-based forms), the global con-  
99 sistency in the framework of Cemdata'18 database could be verified in future. The objective  
100 of current study is to investigate the thermodynamic properties of Na-based zeolites that could  
101 possibly form in the cementitious system; data for zeolites containing Ca are discussed in  
102 [22]. High purity Na-based zeolites were synthesized by hydrothermal method and character-  
103 ized. Their solubility products as a function of temperature were determined via dissolution  
104 experiments and further employed to generate the corresponding thermodynamic data (except  
105 for  $C_p^0$ ) using GEMS. The currently generated data were compared with the relevant values in  
106 literatures. Thermodynamic modelling was conducted to predict the stable zeolite phases in a

107 degraded PC/rock system, and to verify the consistency between the newly generated data and  
108 the available databases as a function of  $\text{Na}^+/\text{H}^+$  ratios and activities of  $\text{SiO}_2(\text{aq})$  and  $\text{AlO}_2^-$ .  
109 The experimentally derived thermodynamic data will allow us to predict zeolite stability do-  
110 mains in systems where zeolites could potentially exist.

## 111 **2. Materials and methods**

### 112 **2.1. Materials**

113 Sodium hydroxide pellets ( $\text{NaOH}$ , >99% purity, Emsure), potassium hydroxide pellets  
114 ( $\text{KOH}$ , >85%  $\text{KOH}$  basis, Sigma-Aldrich), and various aluminum and silica sources were  
115 used as the principal raw materials for the hydrothermal synthesis of zeolites. The aluminum  
116 sources used included sodium aluminate ( $\text{NaAlO}_2$ , technical grade, Sigma-Aldrich), alumin-  
117 ium hydroxide gel (50 wt.%  $\text{Al}_2\text{O}_3$ , Geloxal 10), and  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (chemical grade,  
118 Merck). Five kinds of silica sources were used, including aqueous colloidal silica (40 wt.%  
119 suspension in  $\text{H}_2\text{O}$ , Ludox HS-40 and AS-40), fumed silica ( $\text{SiO}_2$ , chemical grade, Aerosil  
120 200), sodium metasilicate ( $\text{Na}_2\text{SiO}_3$ , reagent-grade, Aldrich), and sodium silicate solution (re-  
121 agent-grade, Sigma-Aldrich). Where necessary in the synthesis, tetramethylammonium hy-  
122 droxide pentahydrate (97%  $(\text{CH}_3)_4\text{N}(\text{OH}) \cdot 5\text{H}_2\text{O}$ , Sigma) and triethanolamine (98%  
123  $\text{N}(\text{C}_2\text{H}_4\text{OH})_3$ , Sigma-Aldrich) were introduced as structure-directing agents (SDAs).  $\text{NaCl}$   
124 ( $\geq 99.5\%$ , puriss p.a.) was bought from Sigma-Aldrich and used for cation exchange. Fresh  
125 Milli-Q water ( $18.2 \text{ M}\Omega \cdot \text{cm}$ ) was used for all solutions and suspensions.

126 Natural and commercial zeolites were collected for seeding during zeolite synthesis and for  
127 the determination of their thermodynamic properties. Scolecite (New Malden, U.K.) and mor-  
128 denite (Alfa Aesar) were collected and used for seeding the synthesis of natrolite and mor-  
129 denite, respectively. The commercial molecular sieve of zeolite  $4\text{\AA}$  purchased from Sigma-  
130 Aldrich was investigated as well in this study. All the natural and commercial zeolites were

131 crushed, picked, ground by an agate mortar, and passed through a 63- $\mu$ m pore size stainless  
132 sieve.

## 133 **2.2. Zeolite synthesis**

134 Hydrothermal methods were used for the zeolite synthesis. Different alkali concentrations,  
135 Si/Al ratios, Al and Si sources, SDAs/seeds, and crystallization temperatures and durations  
136 were explored to obtain different types of pure zeolites (Table 1). Typically, the silica, alumi-  
137 num and cation sources were mixed together in a highly basic medium. If needed, SDAs or  
138 seeds would be added as well in this mixing stage. The aqueous reaction mixtures were heated  
139 in temperature-controlled ovens from 80 to 200 °C. Teflon vessels were used as reactors at  
140 crystallization temperatures below 110 °C. When higher hydrothermal temperatures were re-  
141 quired, Teflon-lined stainless steel autoclaves were employed. The hydrothermal synthesis of  
142 natrolite [23], low-silica gismondine P [24-26], and chabazite [27, 28], were modified based  
143 on the corresponding literature, while those of other zeolites were done according to Robson  
144 [29]. Regarding the selection of raw materials, priorities were given to commonly commercial  
145 chemicals, in order to facilitate successful synthesis repetitions by other researchers. The nec-  
146 essary modifications of recipes were explored, due to the different reactivity of the raw mate-  
147 rials with those of the materials used in the literature. After crystallizing for different times  
148 (Table 1), the obtained solids were recovered by, in sequence, vacuum filtration, Milli-Q wa-  
149 ter washing (until the filtrate pH was  $\sim$ 10 to confirm the removal of excess Na without dis-  
150 solving the zeolite), and drying in an oven at 80 °C (to remove excess water without causing  
151 thermal damage to the samples). Finally, the dried zeolites were equilibrated in a desiccator,  
152 with saturated CaCl<sub>2</sub> solution and CO<sub>2</sub> trap placed inside to maintain a constant 35% relative  
153 humidity and low CO<sub>2</sub> level, respectively. It was observed, that the formation of hydrosodalite  
154 was strongly preferred under highly alkaline synthesis conditions (at H<sub>2</sub>O/Na<sub>2</sub>O molar ratio <  
155 38, see Figure A1), while an increase of the amount of water (the molar ratio of raw materials

156 used was  $3\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 152\text{H}_2\text{O}$ ) resulted in low-silica gismondine P(Na) with the least  
 157 amount of impurities. For the synthesis of analcime different molar ratios of raw materials  
 158 were explored to obtain the pure phase, as the alkali, Si, and Al sources used were different  
 159 from those in literature [29] and had different reactivity. Hydroxycancrinite  
 160 ( $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2\cdot 2\text{H}_2\text{O}$ ) often existed in the solid products [30], as confirmed by XRD  
 161 (Figure A2). Finally, the molar ratio of  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  was adjusted to 5.2.

162 **Table 1.** Experimental conditions for the hydrothermal synthesis of zeolites.

Zeolite	$\text{Na}_2\text{O}(\text{+K}_2\text{O})/\text{Al}_2\text{O}_3$	$\text{SiO}_2/\text{Al}_2\text{O}_3$	Al and Si sources	Seeding	SDA/ $\text{Al}_2\text{O}_3$	$\text{H}_2\text{O}/\text{Al}_2\text{O}_3$	time <sup>a</sup> / h	<i>t</i> <sup>b</sup> / °C
Analcime: ANA	6.5	5.2	$\text{NaAlO}_2$ $\text{Na}_2\text{SiO}_3$	No	6.1 TEOA <sup>c</sup>	380	24	200
Low-silica P-Na: LS-P(Na) <sup>d</sup>	3	2	$\text{NaAlO}_2$ SSS <sup>e</sup>	No	No	152	192	100
Phillipsite-NaK: PHI(NaK)	1.53 (+0.44)	5	$\text{NaAlO}_2$ Fumed $\text{SiO}_2$	No	No	82.7	168	100
Phillipsite-Na: PHI(Na)			Na <sup>+</sup> exchanged product from PHI(NaK)					
Linda type A: LTA <sup>f</sup>	8.12	2.5	$\text{NaAlO}_2$ SSS <sup>e</sup>	No	No	190	2	100
Molecular sieve 4Å: 4 Å			Commercial zeolite from Sigma Aldrich					
Hydrosodalite: SOD(OH)	4	2.0	$\text{NaAlO}_2$ SSS <sup>e</sup>	No	No	76	192	100
Sodalite: SOD(Cl) <sup>g</sup>	8.12	2.5	$\text{NaAlO}_2$ SSS <sup>e</sup>	No	No	190	2	100
Cancrinite- $\text{NO}_3$ : CAN( $\text{NO}_3$ ) <sup>h</sup>	8.12	2.5	$\text{NaAlO}_2$ SSS <sup>e</sup>	No	No	190	2	100
Chabazite-Na: CHA(Na)	2.67 (+0.89)	7	Fresh $\text{Al}(\text{OH})_3$ HS-40 <sup>i</sup>	No	0.04 TMA- OH <sup>j</sup>	110	168	95
Faujasite-X: FAU-X	16	8	$\text{NaAlO}_2$ SSS <sup>e</sup>	No	No	650	20	90
Faujasite-Y: FAU-Y	4	8.1	$\text{NaAlO}_2$ HS-40 <sup>i</sup>	No	No	120	60	80
Natrolite: NAT	8	10	Geloxal10 AS-40 <sup>k</sup>	10% SCO <sup>l</sup>	No	150	120	150
Mordenite-Na: MOR(Na)	6	30	$\text{NaAlO}_2$ Fumed $\text{SiO}_2$	5% MOR	No	780	24	170

163 <sup>a</sup> Crystallization time; <sup>b</sup> Crystallization temperature; <sup>c</sup> triethanolamine; <sup>d</sup> Mixing the raw ma-  
 164 terials at 60 °C [25]; <sup>e</sup> sodium silicate solution; <sup>f</sup> Incubation for 3 h at 70 °C without stirring

165 before crystallization at 100 °C; <sup>g</sup> Additionally introducing 3 molar proportions of NaCl; <sup>h</sup> Ad-  
166 ditionally introducing 3 molar proportions of NaNO<sub>3</sub>; <sup>i</sup> aqueous colloidal silica HS-40; <sup>j</sup> tetra-  
167 methylammonium hydroxide pentahydrate; <sup>k</sup> aqueous colloidal silica AS-40; <sup>l</sup> scolecite.

168  
169 The Na<sup>+</sup>-endmembers of the as-synthesized phillipsite and chabazite, which contained mixed  
170 extra-framework cations (i.e., Na<sup>+</sup> and K<sup>+</sup>), were prepared by hydrothermal cation exchange  
171 method [31], using 3.0 M NaCl solution as the exchange solution. Typically, a solid-to-liquid  
172 (S/L) ratio of 50 g L<sup>-1</sup> was used. The suspensions were sealed in a Teflon vessel and placed in  
173 an oven at 80 °C for 24 h. After the exchange reaction, the suspensions were centrifuged and  
174 the remaining solids were washed with Milli-Q water one time. In order to obtain a pure  
175 enough Na<sup>+</sup>-endmember (further confirmed by energy-dispersive X-ray spectroscopy (EDS)  
176 results in Section 3.1.2), this process was repeated 3 times. In the last cycle, the solid product  
177 was collected by vacuum filtration and washed by Milli-Q water for 4 times to remove the re-  
178 sidual NaCl. The drying and storage methods were then the same as described above. By  
179 these methods, 12 types of Na-based zeolites were synthesized, belonging to six different sec-  
180 ondary building units (SBUs) groups.

### 181 **2.3. Solid phase characterization**

182 The framework structures of zeolites were identified by XRD. XRD and Fourier transformed  
183 infrared (FT-IR) were also used to confirm the identity of the zeolite, while the bulk element  
184 compositions were determined by scanning electron microscopy (SEM) and EDS, partially  
185 combined with acid digestion. The water contents of zeolites were obtained from the weight  
186 loss observed by TGA-DTA.

187 The zeolites were ground and passed through a 63 μm sieve before XRD measurements to  
188 check their purities and any possible competing crystalline phase. XRD patterns were col-  
189 lected with a PANalytical X'Pert Pro diffractometer in a  $\theta$ -2 $\theta$  configuration. The step size,  
190 scan speed, and range were 0.017° 2 $\theta$ , 0.54 s, and 5-90° 2 $\theta$ , respectively. Oriented mounts  
191 were prepared and Co K $\alpha$  radiation at 1.789 Å used.



192 TGA was performed with a Mettler Toledo TGA/SDTA 851e on ~40 mg of sample using a  
193 heating rate of 20 °C min<sup>-1</sup> from 30 to 980 °C and N<sub>2</sub> as protective gas. Prior to performing  
194 TGA, samples were equilibrated in a CO<sub>2</sub>- controlled desiccator at 35% relative humidity (us-  
195 ing a CaCl<sub>2</sub> solution) for at least one week, in order to unify the adsorbed water content on all  
196 the zeolites.

197 FT-IR spectra were collected in the mid-region (3996 to 339 cm<sup>-1</sup>) on a Bruker Tensor 27 FT-  
198 IR spectrometer using the attenuated total reflection (ATR) technique on small amounts (~5  
199 mg) of powdered sample. Spectra were corrected with background subtraction and normalized  
200 by the maximum absorbance of asymmetrical stretch of Si-O(Si/Al) bands.

201 The morphology and elemental fraction of zeolites were characterized by SEM and EDS anal-  
202 yses, respectively, which were carried out with a Philips ESEM FEG XL 30. Powder samples  
203 were used to characterize the morphology, while pressed zeolite pellets, with relatively flat  
204 surfaces were used for the analysis of elemental fraction. In both cases, samples were placed  
205 on carbon discs. A beam voltage of 15 kV and the carbon coating were chosen for EDS analy-  
206 sis. The composition of selected zeolites (ANA, PHI(NaK), LTA, FAU-X, and NAT) was  
207 also obtained from chemical analysis of the samples digested in concentrated HCl, which  
208 agreed well with the SEM/EDS composition verifying both the accuracy of the EDS method  
209 and the high quality of the synthesized target zeolites (Table A1).

#### 210 **2.4. Batch dissolution experiments**

211 First, the dissolution kinetics of several selected zeolites (FAU-X, FAU-Y, ANA, and LS-  
212 P(Na)) were studied at 20 °C by sampling after 30, 72, and 138 days of dissolution. Each type  
213 of zeolite was dispersed into ultrapure water with an identical S/L ratio of 50 g L<sup>-1</sup>. Once the  
214 equilibrium time was confirmed, batch dissolution experiments were conducted at 20, 50, 60,  
215 and 80 °C, in order to obtain solution composition data from which the solubility products  
216 ( $K_{sp}$ ) were calculated for all zeolites at different temperatures. The suspension was passed

217 through 0.22  $\mu\text{m}$  syringe Nylon filters after equilibrating for 30 days. The same day, a small  
218 aliquot of the filtrate for each reactor was extracted and was measured at laboratory tempera-  
219 ture using a Knick pH meter (pH-Meter 766) and a Knick SE100 electrode. Another portion  
220 of the filtrate was diluted with Milli-Q water as necessary and the total aqueous concentra-  
221 tions of Na, K, Ca, Al, Si, Cl and N were analyzed by ion chromatography (IC, Dionex DP  
222 series ICS-3000) on the same day. The experimental detection limit of the IC was estimated to  
223 be 0.025  $\text{mg L}^{-1}$  for all elements and the IC measurement error 5-10%.

## 224 **2.5. Thermodynamic modelling**

225 Thermodynamic modelling was carried out using the Gibbs free energy minimization program  
226 GEM-Selektor v3.3 [32], a powerful geochemical modelling code that computes the equilib-  
227 rium speciation and the amount of both aqueous and solid phase in a complex chemical sys-  
228 tem using Gibbs free energy minimization algorithms. General thermodynamic data for aque-  
229 ous, solid, and gaseous species were taken from the PSI-GEMS thermodynamic database [33].  
230 The cement database Cemdata'18 [20], and the C-N-A-S-H model from [34], was used for ce-  
231 ment minerals. Data for albite were taken from the SUPCRT database [17].

232 In order to draw the predominance diagrams for the cement-zeolite-clay system, the  
233 PHREEQC (Version 3) [35] and PhreePlot codes (Version 1) [36], coupled to the PHREEQC  
234 database version of Cemdata'18, the thermodynamic data for clay minerals in the THERMO-  
235 CHIMIE database [37], and the generated thermodynamic data for zeolites, were employed.  
236 Note that the thermodynamic data in Cemdata18 and in THERMOCHIMIE are not fully con-  
237 sistent; to minimize inconsistencies, the  $\log K_{\text{sp}}$  as given in THERMOCHIMIE were used. The  
238 "hunt and track" algorithm (i.e., ht1) was used for finding field boundaries of most abundant  
239 minerals.

240 The activity of a species  $i$ ,  $\{i\}$ , was calculated using GEMS from the measured concentrations  
 241 using  $\{i\} = \gamma_i \cdot m_i$ , where  $\gamma_i$  is the activity coefficient and  $m_i$  is the concentration in mol kg<sup>-1</sup>  
 242 H<sub>2</sub>O. Values of  $\gamma_i$  were computed with the built-in extended Debye-Hückel equation:

$$243 \quad \log \gamma_i = \frac{-A_y z_i^2 \sqrt{I}}{1 + B_y a_i \sqrt{I}} + b_y I \quad (1)$$

244 where the ion size parameter  $a_i = 3.31 \text{ \AA}$  is assigned a common value for all charged ions and  
 245  $b_y = 0.098$  in NaOH solutions at 25 °C,  $z_i$  denotes the charge of species  $i$ ,  $I$  is the effective mo-  
 246 lar ionic strength (M), and  $A_y$  and  $B_y$  are P,T-dependent coefficients. This activity correction  
 247 is thought to be applicable up to  $\sim 1$  M ionic strength [38]. For neutral species,  $z = 0$  and  
 248 Equation (1) simplifies to the Setschenow equation [39]:  $\log \gamma_i = b_y I$ . The activity of water is  
 249 in GEMS directly calculated from its mole fraction:  $\log \gamma_{\text{H}_2\text{O}} = \log (x_{\text{H}_2\text{O},w} / X_w)$ , where  $X_w$  is  
 250 the total mole quantity of the aqueous phase (including water-solvent).

251 The activities of aqueous species  $\{\text{Na}^+\}$ ,  $\{\text{K}^+\}$ ,  $\{\text{Ca}^{2+}\}$ ,  $\{\text{AlO}_2^-\}$ ,  $\{\text{SiO}_2^0\}$ ,  $\{\text{Cl}^-\}$ ,  $\{\text{NO}_3^-\}$ ,  
 252  $\{\text{OH}^-\}$ , and  $\{\text{H}_2\text{O}\}$ , were used to calculate the solubility products,  $K_{\text{sp}}$ , for zeolites at 20, 50,  
 253 60, and 80 °C according to the corresponding stoichiometric composition of the different zeo-  
 254 lites. The Gibbs free energy of reaction,  $\Delta_r G^0$  (J/mol), to describe the dissolution reaction of a  
 255 zeolite can be calculated from  $K_{\text{sp}}$ :

$$256 \quad \Delta_r G^0 = -RT \ln K_{\text{sp}} = \sum_i \nu_i \Delta_f G_i^0 \quad (2)$$

257 where  $R = 8.31451 \text{ J/mol/K}$  and  $T$  is absolute temperature in K. The Gibbs free energy of for-  
 258 mation,  $\Delta_f G^0$  (J/mol) of a zeolite can then be calculated from Equation 2.  $\nu_i$  is the stoichio-  
 259 metric reaction coefficient and  $\Delta_f G_i^0$  (J/mol) refers to  $\Delta_f G^0$  (J/mol) of the species used in the  
 260 dissolution reaction.

261 The apparent Gibbs free energy of formation,  $\Delta_a G^0$  (J/mol), can be calculated at the tempera-  
 262 ture of interest using:

263 
$$\Delta_a G_T^0 = \Delta_f G_{T_0}^0 - S_{T_0}^0 (T - T_0) + \int_{T_0}^T C_p^0 dT - \int_{T_0}^T \frac{C_p^0}{T} dT \quad (3)$$

264 where  $T_0$  is equal to 298.15 K,  $S^0$  the standard entropy in J/mol K, and  $C_p^0$  the standard heat  
 265 capacity in J/mol/K. Assuming that  $C_p^0$  [40] is a constant over the narrow temperature interval  
 266 studied (20 – 80 °C), the integral terms in Equation (3) can be solved to give:

267 
$$\Delta_a G_T^0 = \Delta_f G_{T_0}^0 - S_{T_0}^0 (T - T_0) - C_p^0 \left( T \ln \frac{T}{T_0} - T + T_0 \right) \quad (4)$$

268 A more detailed description of the derivation of the dependence of the Gibbs free energy on  
 269 temperature is given in [19] and [41].

270  $C_p^0$  values for the zeolites were selected from experimentally measured  $C_p^0$  values in the liter-  
 271 ature when their frameworks and compositions were nearly identical; if not available, they  
 272 were estimated using the additivity method [17-19] based on a reported experimental  $C_p^0$   
 273 value of zeolite having the same framework and/or on the elementary (hydro)oxide compo-  
 274 nents assuming  $\Delta C_{p,r} = 0$ . Also the entropy values were taken if possible from the literature or  
 275 calculated from structurally similar zeolites according to the procedure outlined in [17].

276  $S^0$  of the target zeolite was calculated from the entropy of the elementary (hydro)oxide com-  
 277 ponents and of the zeolite with the same framework assuming  $\Delta S_r^0 = 0$  considering the molar  
 278 volume ( $V^0$ , in cm<sup>3</sup>/mol) according to Eq. 62 in [17]:

279 
$$S^0 = \frac{\sum v_i S_i^0 (\sum v_i V_i^0 + V^0)}{2 \sum v_i V_i^0} \quad (5)$$

280 Where  $v_i$  represents the stoichiometric number of the  $i$ th elementary component in the chemi-  
 281 cal formula of the target zeolite;  $S_i^0$  and  $V_i^0$  are the standard entropy and molar volume, re-  
 282 spectively, of the  $i$ th elementary component. Only the  $S^0$  value of LS-P(Na) that was deter-  
 283 mined independently by fitting the log  $K_{sp}$  data as a function of temperature with the  
 284 assistance of the GEMS-Selektor code. The polymer model described by [13] was also tried  
 285 but the resulting  $S^0$  values had larger difference with our experimental solubility products

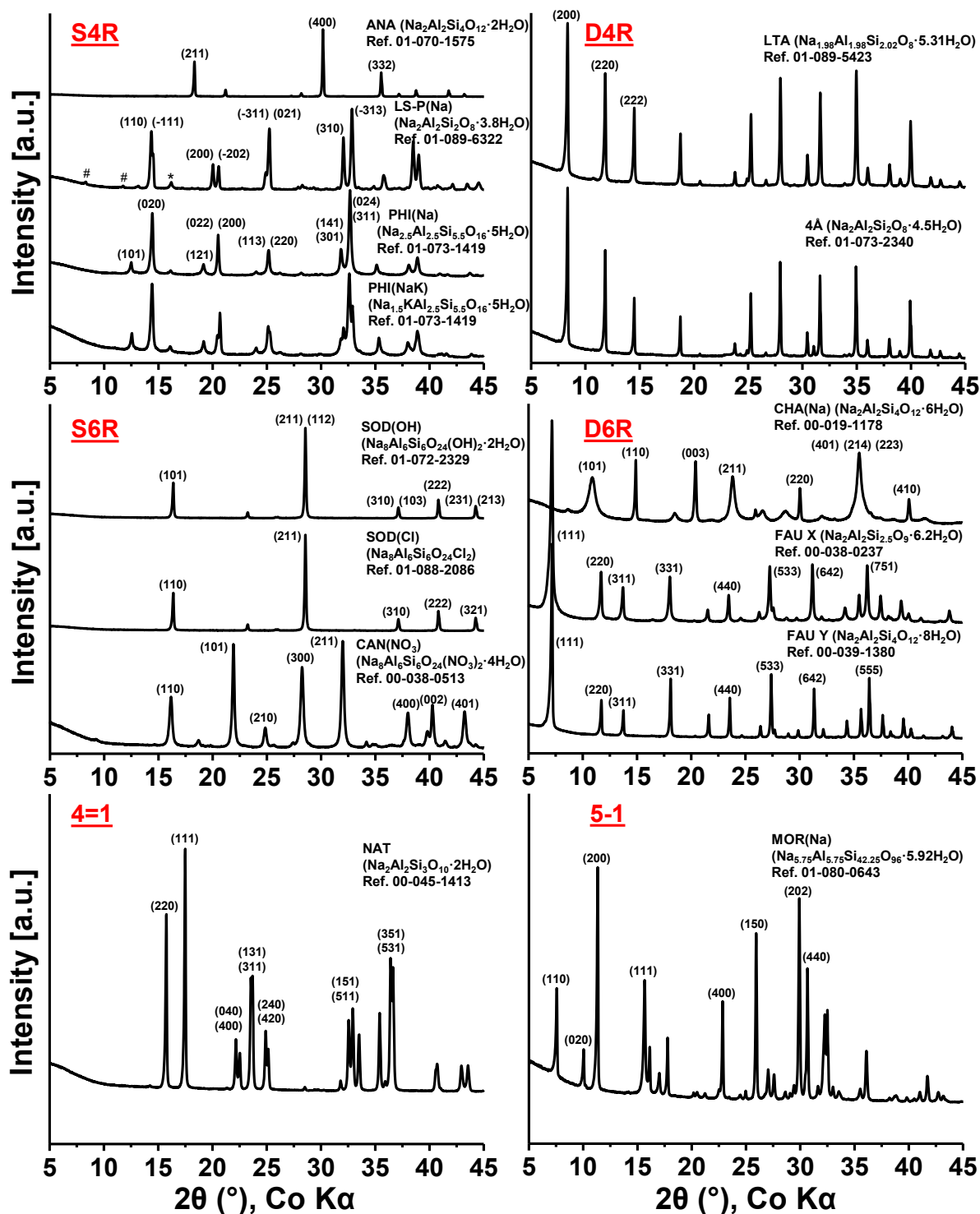
286 compared to that with the additivity method. For the additivity method, the thermodynamic  
287 data of the elementary (hydro)oxide components (i.e., NaOH, Ca(OH)<sub>2</sub>, KOH, Al(OH)<sub>3</sub>, SiO<sub>2</sub>,  
288 NaCl, NaNO<sub>3</sub>, and Na<sub>2</sub>CO<sub>3</sub>) was extracted from [42, 43] and summarized in Table A2. In-  
289 stead of free H<sub>2</sub>O, zeolitic H<sub>2</sub>O was adopted in the calculation, with S<sup>0</sup> and C<sub>p</sub><sup>0</sup> values of 59.0  
290 and 47.7 J/mol/K, respectively [17]. The V<sup>0</sup> values of zeolites were calculated from the in-  
291 dexed PDF cards that matched well with our experimental XRD data. Slight differences in  
292 composition and the effect this may have on V<sup>0</sup> values were ignored.

### 293 **3. Results and discussion**

#### 294 **3.1. Characterizations of zeolites**

##### 295 **3.1.1. Zeolite SBUs and frameworks**

296 The XRD patterns of the investigated zeolites are summarized in Figure 1, where they were  
297 plotted according to their SBU groups. The primary building block of the zeolite structure is a  
298 tetrahedron of four oxygen atoms surrounding a central Si atom (SiO<sub>4</sub>), which are connected  
299 through shared oxygen atoms to form a wide range of small SBUs. Different combinations of  
300 the same SBU may give numerous distinctive structural polyhedra formed from smaller ring  
301 units and zeolites are often classified based on SBUs contained in the structure. In the present  
302 study zeolites with a singly connected 4-ring structure (S4R: ANA, LS-P(Na), PHI(Na), and  
303 PHI(NaK)), with a doubly connected 4-ring structure (D4R: LTA and 4Å), with a singly con-  
304 nected 6-ring structure (S6R: SOD(OH), SOD(Cl), and CAN(NO<sub>3</sub>)), with a doubly connected  
305 6-ring structure (D6R: CHA(Na), FAU-X, and FAU-Y), with a 4=1 structure (NAT), and with  
306 a 5-1 structure (MOR(Na)) were synthesized and studied. Most of the zeolites were pure and  
307 no impurities were observed except for LS-P (Na). In LS-P (Na), in addition to LS-P (Na) a  
308 very small amount of SOD(OH) and LTA were detected, which have the same Si/Al molar  
309 ratio.



310  
 311 **Figure 1.** Powder XRD patterns of the synthesized Na-based zeolites. For each pattern, the  
 312 identified phase component with PDF reference card number is attached on the top right. Only  
 313 the diffraction peaks of impurities are marked with #: LTA and \*: hydrosodalite, while all the  
 314 other peaks are attributed to the pure zeolite phases.

315  
 316 Zeolites having the same SBU often show a certain similarity on their XRD patterns, e.g., LS-  
 317 P and PHI in the S4R group, indicating that the short-range ordering strongly affected the

318 long-range ordering. The comparison of the XRD patterns of PHI, where only Na is present,  
319 with PHI(NaK), where both K and Na are present, shows that the structure symmetry in-  
320 creased when the cavity was occupied by Na<sup>+</sup> only as indicated by the absence of peak splits  
321 at ~20.5, 25.2, and 32.0 ° 2θ.

322 In D4R group, the commercial molecular sieve of zeolite 4Å had almost the same XRD pat-  
323 tern as LTA. SOD(OH), SOD(Cl), and CAN(NO<sub>3</sub>) are built with the same SBU (i.e., S6R),  
324 resulting in very similar XRD patterns as well. In the D6R group, FAU-X and FAU-Y have  
325 the same framework structure and thus nearly indistinguishable patterns, with almost the same  
326 2θ angle positions but slightly different ratios of peaks intensity. According to their Si/Al mo-  
327 lar ratio, FAU zeolites are generally classified into X type (having a ratio between 1 and 1.5)  
328 and Y type (above 1.5) [44]. CHA(Na) showed quite different patterns although it also be-  
329 longs to the D6R group.

330 The synthesized natrolite, classified in the 4=1 group, shows a high phase purity. As reported  
331 by [23], Natrolite has ordered Si and Al T-sites distribution in orthorhombic symmetry, and  
332 can form at longer crystallization times from tetranatrolite, which has completely disordered  
333 T-sites in tetragonal symmetry. The transformation of tetranatrolite to natrolite can be verified  
334 by the split of XRD peaks at ~22.3, 23.5, 25.0, 32.5, and 36.5° 2θ. The almost complete peak  
335 splits in our work indicated a well ordered T-sites distribution in the highly crystalline NAT  
336 structure. Besides, highly pure Na-based mordenite, belonging to 5-1 SBU group, was synthe-  
337 sized successfully, showing the strongest diffraction peak from its crystal face of (200). Sec-  
338 ondary electron images of the zeolites, shown in Figure A3, showed the typical 3-D structures  
339 of the zeolites and confirmed the absence of other phases. The framework types of zeolites  
340 can be easily identified by XRD as shown above. However, zeolites with the same framework  
341 type may have different contents of Si, Al, and extra-framework cations, and can still result in  
342 very similar diffraction patterns.

### 343 3.1.2. Elemental composition

344 The bulk element compositions of Na, Al and Si in the synthesized zeolites were determined  
345 by SEM-EDS on flattened samples. The atomic percentages of the heavier elements ( $Z \geq 11$ )  
346 are listed in Table 2. The molar ratio of the positive extra-framework charge number to the  
347 aluminum substitution, represented by Cat/Al, should be equal to one in a perfect aluminosili-  
348 cate zeolite structure. As shown in Table 2, most of the Cat/Al values were approximately  
349 equal to 1, except for SOD(Cl) and zeolite 4Å.

350 For SOD(OH) and CAN(NO<sub>3</sub>), it was assumed that the respective extra-framework OH<sup>-</sup> and  
351 NO<sub>3</sub><sup>-</sup>, which are too light to be analyzed reliably by EDS, were equal to one-quarter of Na in  
352 mole according to the XRD analysis. Considering the estimated molar fraction of OH<sup>-</sup> and  
353 NO<sub>3</sub><sup>-</sup>, the Cat/Al ratios of SOD(OH) and CAN(NO<sub>3</sub>) were calculated to be 1.03 and 1.04, re-  
354 spectively, which were reasonable for the zeolite structure. The Cat/Al ratio of SOD(Cl) was  
355 0.17 more than 1.00, indicating the existence of ~1.61 atomic percentage (at.%) of OH<sup>-</sup>. The  
356 OH<sup>-</sup> partly coupled with Na<sup>+</sup> and partly acted as the extra-framework anion for charge balance  
357 of zeolite structure.

358 The commercially available zeolite 4Å, characterized as a Type A zeolite  
359 (Na<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>·4.5H<sub>2</sub>O) by XRD, had Si/Al ratios of ~1.3, which was larger than expected for  
360 Type A zeolite. This could be explained by the possible existence of non-framework Si such  
361 as amorphous silica and by the possible substitution of Si<sup>4+</sup> by non-Al<sup>3+</sup> cations such as Fe<sup>3+</sup>;  
362 if all the cations in zeolite 4Å were counted as the charged extra-framework ions, the whole  
363 zeolite structures would be positively charged (Cat/Al ratios of zeolite 4Å were 1.31). The  
364 TGA data (Figure 2) indicate that surplus of cations are probably present as carbonates. The  
365 composition of the zeolite 4Å phase is here taken as Na<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>·4.5H<sub>2</sub>O; the presence of  
366 amorphous SiO<sub>2</sub> and carbonates contributes to the relatively low water content of 18.3% ob-  
367 served by TGA (Table 3) instead of the theoretical 19.9%.



368 The EDS results indicated that PHI(Na), the cation exchanged zeolite, still contained a small  
 369 fraction of the previous host cation (i.e., K<sup>+</sup>), suggesting that complete cation exchange was  
 370 not reached. Thus, a chemical formula of PHI(Na) was calculated to be  
 371 Na<sub>2.3</sub>K<sub>0.2</sub>Al<sub>2.5</sub>Si<sub>5.5</sub>O<sub>16</sub>·5H<sub>2</sub>O. The Si/Al ratio of MOR(Na) was determined to be 7.43, which  
 372 was very close to the value (i.e., 7.35) obtained from XRD characterization. Overall, the ele-  
 373 mental fractions obtained from EDS analysis agreed well with the XRD results, confirming  
 374 the expected chemical compositions of the various zeolites.

375 **Table 2.** Atomic percentages of selected elements of zeolites. The ratio of positive extra-  
 376 framework charge number to negative framework charge number (Cat/Al) was calculated and  
 377 the molar ratio of Si to Al listed as well.

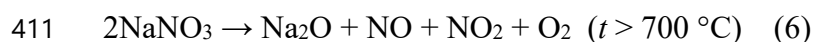
Zeolite	Na at.%	Al at.%	Si at.%	K at.%	Ca at.%	Fe at.%	Mg at.%	Cl at.%	Cat/Al	Si/Al
ANA	7.50	7.95	15.21						0.94	1.91
LS-P(Na)	10.31	10.26	10.54						1.00	1.03
PHI(Na)	6.62	7.06	14.75	0.58					1.02	2.09
PHI(NaK)	3.99	6.29	12.91	2.54					1.04	2.05
LTA	10.20	10.69	11.06						0.95	1.03
4Å	8.09	8.48	11.47	0.05	0.20	0.27	1.06		1.31	1.35
SOD(OH)	13.21	9.53	9.67						1.03	1.01
SOD(Cl)	13.49	9.47	9.92					2.38	1.17	1.05
CAN(NO <sub>3</sub> )	12.92	9.31	9.96						1.04	1.07
CHA(Na)	6.33	6.47	12.65						0.98	1.96
FAU-X	8.82	9.35	12.12						0.94	1.30
FAU-Y	7.67	7.65	14.49						1.00	1.89
NAT	8.16	7.91	11.57						1.03	1.46
MOR(Na)	3.15	3.06	22.70						1.03	7.43

378  
 379 **3.1.3. Water content**  
 380 All the zeolite powder was characterized by TGA-DTG analysis, in order to quantify the wa-  
 381 ter content and to check possible contaminations and carbonation during the synthesis. As  
 382 shown in Figure 2, the TGA-DTG curves of the zeolites were also grouped based on the SBU  
 383 group. All zeolites, with the exception of natrolite, analcime, cancrinite and sodalite, lost most  
 384 water at relatively low temperatures, between 100 and 300°C, consistent with the presence of

385 water within the cavities of the zeolites. Zeolites with the same framework type showed in  
386 many cases a similar water loss pattern. Zeolite 4Å has an LTA framework and has thus a  
387 very similar water loss pattern. However, less relative weight loss was obtained for 4Å proba-  
388 bly due to the presence of some amorphous silica as deduced from the EDS results. FAU-X  
389 and FAU-Y, which were synthesized at 80 and 90 °C, showed both similar dehydration tem-  
390 peratures and approximately equal weight losses (Table 3). In general, it was found that the  
391 temperatures for the main dehydration peaks increased with the crystallization and thus syn-  
392 thesis temperatures of the synthesized zeolites. The temperatures of the main dehydration  
393 peaks are in the order of LTA = PHI (Na) = PHI (NaK) (all the three were synthesized at  
394 100 °C) < NAT (synthesized at 150 °C) < ANA (synthesized at 200 °C). MOR(Na), whose  
395 dehydration peak located at around 100°C, was the exception, indicating that the zeolite dehy-  
396 dration temperature is related to both the crystallization temperature as well as to the size of  
397 the channels within the zeolitic structure.

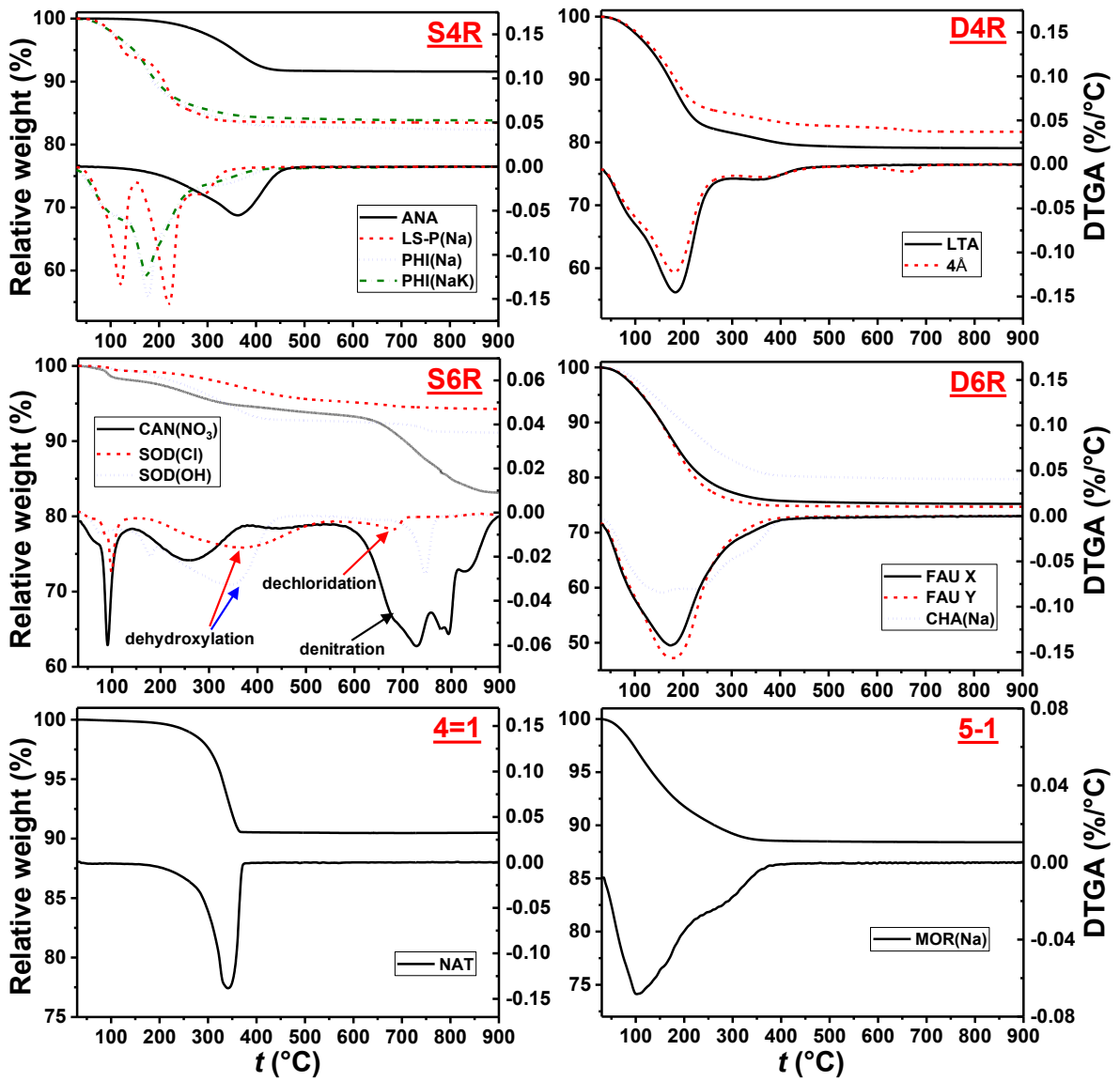
398 LS-P (Na), the gismondine (GIS) type zeolite, shows at least three DTGA peaks of dehydra-  
399 tion in the region of 120-350 °C (Table 3), in good agreement with previous reports [45, 46].  
400 Natural gismondine often has quite complex thermal behavior and several types of ex-  
401 traframework cations, whose water molecules are distributed on six sites in their structural re-  
402 finement [47]. Compared to the natural gismondine, our synthesized GIS type zeolites have  
403 smaller sizes, only one type of cation, more simplified water distribution environment, and  
404 thus less dehydration steps. Similar phenomenon was observed for PHI (Na) and PHI (NaK).  
405 PHI(Na), having a single type of cation (Na<sup>+</sup>), exhibited fewer dehydration steps than  
406 PHI(NaK), which has both Na<sup>+</sup> and K<sup>+</sup> in cages. Na<sup>+</sup> is more hydrophilic than K<sup>+</sup> and can at-  
407 tract more water molecules, leading to slightly more water loss for PHI(Na) than for  
408 PHI(NaK).

409 Cancrite and sodalite showed weight losses also at higher temperatures. For CAN(NO<sub>3</sub>) the  
410 weight loss above 700°C was attributed to denitration according to equation (6)



412 as previously reported [48]. The nitrate content of 10.4% obtained from the weight loss at  
413 above 700°C was in agreement with the theoretical value of 9.9%. In SOD(Cl) the anionic  
414 sites should be mainly occupied by Cl<sup>-</sup>, as confirmed by the dechloridation peak at 680 °C in  
415 the DTGA, and was supported by XRD and EDS results. In the DTGA curve of SOD(Cl), a  
416 broad peak attributed to the dehydroxylation was observed at 370 °C, indicating the existence  
417 of some OH<sup>-</sup> in the extra-framework. The small portion of OH<sup>-</sup> was likely structurally intro-  
418 duced during the hydrothermal synthesis under the high pH conditions used during hydrother-  
419 mal synthesis. For SOD(OH), the total relative weight loss (7.3%) from both dehydration and  
420 dehydroxylation was well matched with the corresponding theoretical value (7.2%); some car-  
421 bonation was detected at 750 °C, promoted by the high alkalinity of the synthesis gel of  
422 SOD(OH). The commercial 4Å was also slightly carbonated, showing a decarbonation peak at  
423 around 660 °C. As shown in Figure 2, no carbonation was detected for any of the syn-  
424 thesized zeolites.

425 For MOR(Na), 11.46% was adopted: Na<sub>0.72</sub>Al<sub>0.72</sub>Si<sub>5.28</sub>O<sub>12</sub>·2.71H<sub>2</sub>O as the relative weight loss  
426 of water as its theoretical value, ~3.42% based on the XRD analysis, showed a profound dis-  
427 crepancy with the value obtained experimentally from TGA-DTG analysis. Overall, the ex-  
428 perimental relative weight loss of each zeolite was in accordance with the theoretical value  
429 based on the chemical formula indicated in the PDF reference card (Table 3).



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431 **Figure 2.** TGA-DTG curves of the synthesized Na-based zeolites.

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443 **Table 3.** Summary of the theoretical relative weight loss derived from XRD analysis and the  
 444 experimental value obtained from TGA-DTG of each zeolite. Temperatures of the main  
 445 DTGA peaks were listed as well. The weight loss that was not attributed to dehydration is  
 446 plotted in *italic*.

Zeolite	Theoretical relative weight loss	Experimental relative weight loss / DTGA peak position
ANA (Na <sub>2</sub> Al <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> ·2H <sub>2</sub> O)	8.18%	8.29% / 362 °C
LS-P(Na) (Na <sub>2</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ·3.8H <sub>2</sub> O)	19.4%	16.3% / 121, 221, 288 °C
PHI(Na) (Na <sub>2.5</sub> Al <sub>2.5</sub> Si <sub>5.5</sub> O <sub>16</sub> ·4H <sub>2</sub> O)	14.4%	17.1% / 178 °C
PHI(NaK) (Na <sub>1.5</sub> KAl <sub>2.5</sub> Si <sub>5.5</sub> O <sub>16</sub> ·4H <sub>2</sub> O)	14.0%	15.7% / 178 °C
LTA (Na <sub>1.98</sub> Al <sub>1.98</sub> Si <sub>2.02</sub> O <sub>8</sub> ·5.31H <sub>2</sub> O)	25.5%	20.7% / 183, 353 °C
4Å (Na <sub>2</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ·4.5H <sub>2</sub> O)	-	18.3% / 180, 372 °C
SOD(OH) (Na <sub>8</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> (OH) <sub>2</sub> ·2H <sub>2</sub> O)	3.72% 3.51%	7.29% in total / 75.5 and 180 °C 344 °C ( <i>dehydroxylation</i> )
	-	1.19% ( <i>decarbonation</i> )
SOD(Cl) (Na <sub>8</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> Cl <sub>2</sub> )	-	0.69% / 87.1, 98.9 °C (surface water)
	-	4.84% / 373 °C ( <i>dehydroxylation</i> )
	7.32%	5.78% / 682 °C ( <i>dechloridation</i> )
CAN(NO <sub>3</sub> ) (Na <sub>8</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> (NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O)	6.58% 9.87%	6.48% / 91.0, 264, 444 °C 10.4% / <i>above 728 °C (denitration)</i>
CHA(Na) (Na <sub>2</sub> Al <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> ·6H <sub>2</sub> O)	21.1%	20.2% / 158, 224 °C
FAU-X (Na <sub>2</sub> Al <sub>2</sub> Si <sub>2.5</sub> O <sub>9</sub> ·6.2H <sub>2</sub> O)	26.2%	24.5% / 174 °C
FAU-Y (Na <sub>2</sub> Al <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> ·8H <sub>2</sub> O)	26.3%	25.1% / 178 °C
NAT (Na <sub>2</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> ·2H <sub>2</sub> O)	9.48%	9.47% / 341 °C
MOR(Na) (Na <sub>0.72</sub> Al <sub>0.72</sub> Si <sub>5.28</sub> O <sub>12</sub> ·2.71H <sub>2</sub> O)	-	11.5% / 102 °C

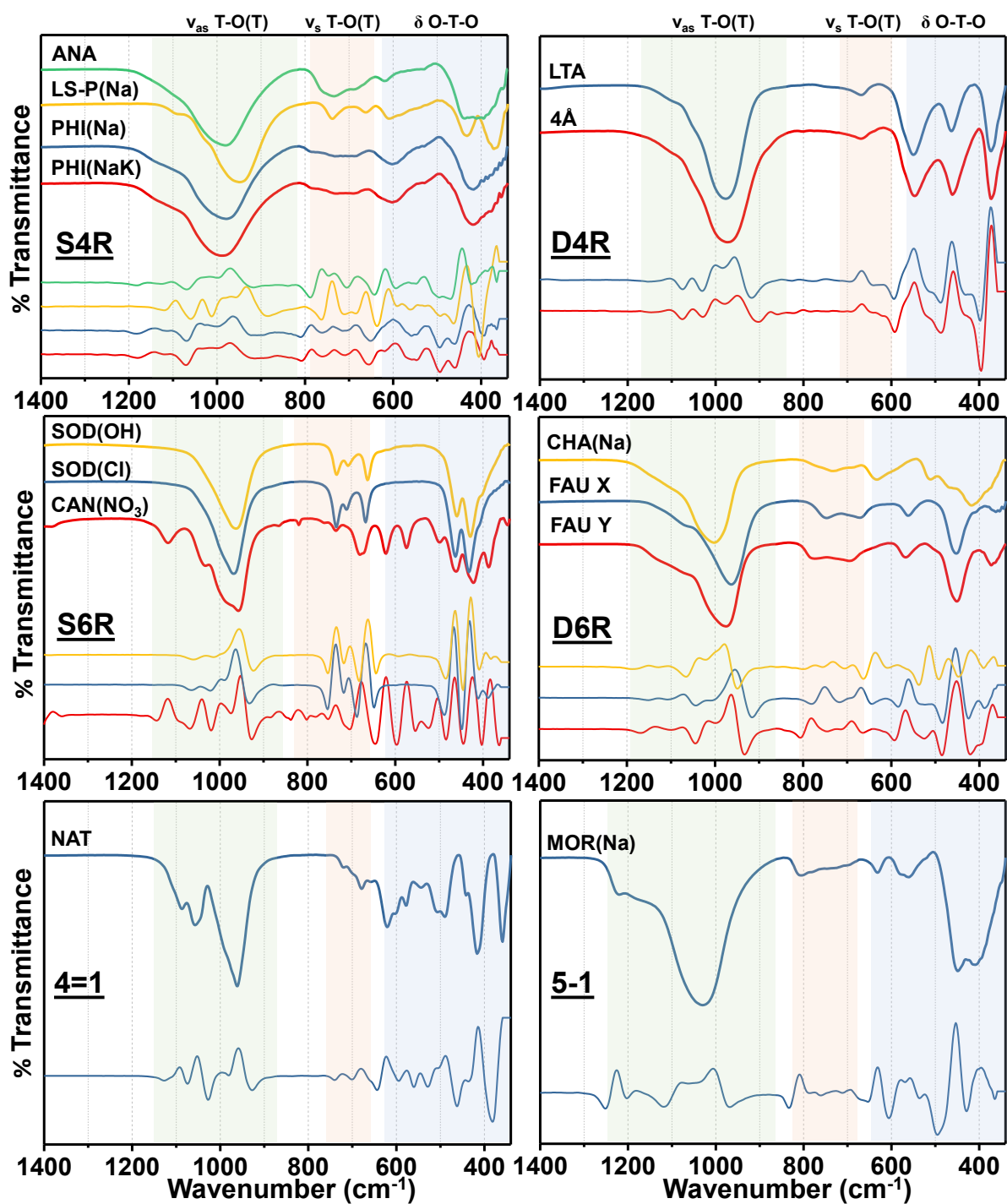
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#### 448 3.1.4. FT-IR analyses

449 FTIR transmittance spectra and the corresponding 2<sup>nd</sup> derivative spectra of the zeolites, with  
 450 wavenumbers ranging from 1400 to 340 cm<sup>-1</sup>, were classified into six subgroups based on the  
 451 SBUs and are shown in Figure 3. The 2<sup>nd</sup> derivative spectra can help identifying the positions

452 of broad vibration peaks more clearly. The vibration features of the aluminosilicate frame-  
453 works of zeolites are mainly visible in the mid and far infrared, especially below  $1400\text{ cm}^{-1}$ .  
454 The spectra in the wavenumber range from  $4000$  to  $1250\text{ cm}^{-1}$  (Figure A4) typically showed  
455 the stretching and bending vibration bands of H-O-H (in  $\text{H}_2\text{O}$ ) at  $\sim 3350$  and  $1630\text{ cm}^{-1}$ , re-  
456 spectively, with the former typically giving a broad peak envelop (except for NAT and  
457 MOR(Na) that showed several stretching vibrations) and the latter a relatively sharp peak. For  
458 CAN( $\text{NO}_3$ ) the strong and sharp peak appearing at  $1427.2\text{ cm}^{-1}$  (less intense signal at  $1379.0$   
459  $\text{cm}^{-1}$ ) belonged to the stretching vibration band of N-O in  $\text{NO}_3^-$ . A summary of the vibration  
460 peak wavenumbers of FTIR spectra is shown in Table 4. The IR transmittance bands can be  
461 generally separated into two groups: 1) internal vibrations of the  $\text{TO}_4$  tetrahedra (i.e.,  $\text{SiO}_4$  or  
462  $\text{AlO}_4$ ), including asymmetrical stretch ( $\nu_{\text{as}}$ ) at  $1250 - 920\text{ cm}^{-1}$ , symmetrical stretch ( $\nu_{\text{s}}$ ) at  $720$   
463  $- 650\text{ cm}^{-1}$ , and T-O bend ( $\delta$ ) at  $500 - 420\text{ cm}^{-1}$ ; 2) external vibrations of linkages, including  
464  $\nu_{\text{as}}$  at  $1150 - 1050\text{ cm}^{-1}$ ,  $\nu_{\text{s}}$  at  $820 - 750\text{ cm}^{-1}$ , ring vibrations at  $650 - 500\text{ cm}^{-1}$ , and pore  
465 opening vibrations at  $420 - 300\text{ cm}^{-1}$  [49].

466 Similar features of IR spectra were observed for zeolites having the same SBU. For instance,  
467 vibration peaks at approximately  $1100, 1030, 740, 670, 600, 430\text{ cm}^{-1}$ , attributed to  $\nu_{\text{as}}$  T-O(T)  
468 - Ex,  $\nu_{\text{as}}$  T-O(T) - In,  $\nu_{\text{s}}$  T-O(T) - Ex,  $\nu_{\text{s}}$  T-O(T) - In, Ring - Ex, and  $\delta$  T-O - In, respectively,  
469 for the zeolites in S4R group. The similarity of IR spectra was also obvious for the other SBU  
470 groups, indicating that the framework vibrations of zeolites can be detected with these IR  
471 bands. The  $\nu_{\text{as}}$  bands of FAU-Y are located at higher wavenumbers than that of FAU-X, as  
472 FAU-Y has a higher Si/Al ratio and the electronegativity of  $\text{Si}^{4+}$  is stronger than that of  $\text{Al}^{3+}$ .  
473 The same tendency of band shift was observed for SOD(OH) and SOD(Cl), resulting from the  
474 electronegativity difference of extra-framework anions. Overall, the wavenumbers of the main  
475 IR bands for each SBU group were in good agreement with the literature values e.g. [50, 51],  
476 indicating that the targeted zeolites were collected successfully.



478

479 **Figure 3.** FTIR transmittance spectra of each SBU group of zeolites, with the corresponding  
 480 2<sup>nd</sup> derivative spectra plotted below.

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487 **Table 4.** Summary of the vibration peak wavenumbers ( $\text{cm}^{-1}$ ) of FTIR spectra for the Na-  
 488 based zeolites<sup>a</sup>.

SBU group	Zeolite	$\nu$ O-H	$\delta$ O-H	$\nu_{\text{as}}$ T-O(T) - Ex	$\nu_{\text{as}}$ T-O(T) - In	$\nu_{\text{s}}$ T-O(T) - Ex	$\nu_{\text{s}}$ T-O(T) - In	Ring - Ex	$\delta$ T-O - In	Pore - Ex
S4R	ANA	3379	1634	1105	1016, 970	762, 735	681	617, 530	442	
	LS-P(Na)	3330	1639	1094	1034, 934	739	662	611	432	364
	PHI(Na)	3395	1638	1140, 1105	1038, 964	785, 737	685	600, 527	428	
	PHI(NaK)	3416	1638	1142, 1107	1042, 970	785, 733	687	596, 525	428	
D4R	LTA	3379	1649	1105, 1053	999, 957		667	550	463	374
	4Å	3340	1643	1105, 1051	1001, 951		667	548	459	372
S6R	SOD(OH)	3350	1645		1034, 957	735		704, 662		463, 428
	SOD(Cl)	3350	1653		1043, 997, 964	735		706, 667		467, 430
	CAN(NO <sub>3</sub> ) <sup>b</sup>	3350	1628	1119	1040, 997, 953	735	677	621, 575, 503	465, 424	384
D6R	CHA(Na)	3396	1643	1151, 1107	1036, 978	773, 733	689	636, 515	471	418, 368
	FAU-X	3381	1645	1128, 1072	955	750	669	561	453	
	FAU-Y	3398	1641	1136, 1074	1014, 962	781	690	567, 505	451	370
4=1	NAT	3537, 3321, 3219, 3175	1632	1092, 1053	995, 959		723, 681	623, 577, 546, 507	488, 444	415
5-1	MOR(Na)	3620, 3410	1628	1076	1227, 1180, 1007	811		631, 577, 557, 525	453	395

489 <sup>a</sup>  $\nu_{\text{as}}$ , asymmetric stretching vibrations;  $\nu_{\text{s}}$ , symmetric stretching vibrations;  $\delta$ , bending vibra-  
 490 tions; T, Si/Al tetrahedron; Ex, external linkage; In, internal tetrahedra; Ring, ring vibrations;  
 491 Pore, pore opening vibrations. <sup>b</sup> The stretching vibration peaks attributed to N-O were at  
 492 1427.2 and 1379.0  $\text{cm}^{-1}$ .

493

## 494 3.2. Thermodynamic properties of Na-based zeolites

### 495 3.2.1. Solubility products

496 The dissolution kinetics of FAU-X, FAU-Y, ANA, and LS-P(Na) at 20 °C were studied and  
 497 the results are shown in Figure A5. After 30 days of dissolution, the solubility product (log



498  $K_{sp}$ ) of each zeolite was not significantly different from the values after 72 and 138 days, sug-  
499 gesting that the zeolite dissolution is near equilibrium after 30 days.

500 Based on the corresponding dissolution reaction listed in Table A3, the log  $K_{sp}$  values of each  
501 studied zeolite at different equilibrium temperatures were calculated and shown in Table 5,  
502 together with the aqueous concentrations and pH values. Typically, the IC measurement has  
503 errors of 5-10%. The 10% error of the IC measurement will give errors of 0.9-1.5% on the log  
504  $K_{sp}$  values. In order to evaluate the systematic error of the whole dissolution experiment, re-  
505 peated dissolution experiments were performed on five selected types of zeolites (ANA, LS-  
506 P(Na), FAU-X, FAU-Y, and CAN(NO<sub>3</sub>)). The resulting uncertainty percentages ranged from  
507 1.1% to 7.1% (Table A4). In this study, a general error of 3% was applied on the log  $K_{sp}$  val-  
508 ues (Table 5 and 6).

509 For each Na-based zeolite the element concentrations and the resulting log  $K_{sp}$  value in-  
510 creased with temperature generally, indicating a positive enthalpy for the dissolution reaction.  
511 The incompletely Na<sup>+</sup> exchanged phillipsite, i.e., PHI(Na) with a chemical formula of  
512  $Na_{2.3}K_{0.2}Al_{2.5}Si_{5.5}O_{16} \cdot 5H_2O$ , still contained minor amount of K<sup>+</sup> in the cage. The solubility of  
513 a solid with different ions in the cage can be expressed as a solid solution, as a single solid  
514 with both ions present, or as pure end-members containing either Na or K. According to the  
515 three models, the Lippmann's total solubility product ( $\Sigma\Pi$ ) and  $K_{sp}$  values of PHI(Na) were  
516 calculated ([52, 53], see details in Text A1) and plotted in Figure A6. The value for the Na<sup>+</sup>  
517 end member was found to be almost equal to that from the solid solution, while the values  
518 given by single solid approach and for the K<sup>+</sup> end member deviated largely, suggesting that  
519  $Na_{2.3}K_{0.2}Al_{2.5}Si_{5.5}O_{16} \cdot 5H_2O$  can be treated as solid solution. Since the log  $K_{sp}$  values from the  
520 solid solution and the Na<sup>+</sup> end member PHI(Na) were almost equal, the Na<sup>+</sup>-endmember form  
521 was included in the thermodynamic study. Typically, hydrothermal phillipsite displays a wide  
522 range of chemical composition, especially of extraframework cations, making the synthesis

523 with a single cation infeasible. The synthesis of phillipsite is often facilitated in the presence  
524 of  $K^+$  plus  $Na^+$  and/or  $Ca^{2+}$  [46]. This also implies that the natural phillipsite should contain  
525 more than one type of cation in most cases. Therefore, also the thermodynamic property of  
526 PHI(NaK) was investigated individually, in which the amount of  $Na^+$  and  $K^+$  was comparable.  
527 As shown in Table 6, the solubility of PHI(NaK) is slightly lower than that of PHI(Na), indi-  
528 cating that the Na/K solid solution of PHI(NaK) should be more stable thermodynamically  
529 than PHI(Na).

530 **Table 5.** Solution composition and pH of zeolite dissolution experiments at 20, 50, 60, and  
531 80 °C. Experimental  $\log K_{sp}$  values were calculated and listed. <sup>a</sup>

Zeolite	T °C	pH <sup>c</sup>	[Na] <sub>tot</sub> mM	[K] <sub>tot</sub> mM	[Si] <sub>tot</sub> mM	[Al] <sub>tot</sub> mM	[N] <sub>tot</sub> mM	[Cl] <sub>tot</sub> mM	$\log K_{sp}$
ANA	20	10.61	2.128	bdl	0.6916	0.4878	bdl	bdl	-27.87±0.84
	50	9.77	3.455	bdl	1.200	1.005	bdl	bdl	-24.71±0.74
	60	9.58	3.962	bdl	1.287	1.128	bdl	bdl	-24.18±0.72
	80	9.35	5.091	bdl	1.962	1.562	bdl	bdl	-22.86±0.68
LS-P(Na)	20	10.30	1.842	bdl	0.3836	0.5568	bdl	bdl	-20.00±0.60
	50	9.08	2.831	bdl	0.5358	1.347	bdl	bdl	-17.82±0.53
	60	8.70	3.250	bdl	0.6163	1.688	bdl	bdl	-17.25±0.52
	80	8.22	4.775	bdl	0.6112	2.931	bdl	bdl	-16.39±0.49
PHI(Na)	20	11.01	3.441	0.0011	0.3229	0.1534	bdl	bdl	-41.44±1.24
	50	9.91	5.826	0.0037	0.5716	0.2467	bdl	bdl	-36.03±1.08
	60	9.40	6.422	0.0052	0.6027	0.2628	bdl	bdl	-34.28±1.02
	80	8.98	7.295	0.0077	0.8398	0.3510	bdl	bdl	-32.42±0.97
PHI(NaK)	20	10.98	3.213	0.1562	0.4799	0.1341	bdl	bdl	-40.49±1.21
	50	10.24	3.669	0.2340	0.8632	0.2239	bdl	bdl	-37.01±1.11
	60	9.94	3.822	0.2361	0.9825	0.2381	bdl	bdl	-35.72±1.07
	80	9.62	4.307	0.3791	1.312	0.3664	bdl	bdl	-33.86±1.02
LTA	20	11.80	21.27	bdl	1.596	2.565	bdl	bdl	-18.21±0.55
	50	10.74	21.05	bdl	1.358	3.077	bdl	bdl	-17.01±0.51
	60	10.49	20.39	bdl	1.472	2.690	bdl	bdl	-16.83±0.50
	80	10.08	22.01	bdl	1.838	3.486	bdl	bdl	-16.01±0.48

4Å <sup>b</sup>	20	11.06	23.49	bdl	3.240	0.0282	bdl	bdl	-20.10±0.60
	50	9.85	21.80	bdl	3.518	0.0123	bdl	bdl	-19.52±0.58
	60	9.36	20.47	bdl	3.036	0.0133	bdl	bdl	-19.14±0.57
	80	8.48	17.23	bdl	2.424	0.0220	bdl	bdl	-18.52±0.56
SOD(OH)	20	12.28	26.20	bdl	1.285	1.144	bdl	bdl	-67.33±2.02
	50	11.74	54.58	bdl	2.236	2.280	bdl	bdl	-61.20±1.84
	60	11.45	64.06	bdl	2.573	2.714	bdl	bdl	-59.03±1.77
	80	11.17	78.64	bdl	3.169	3.745	bdl	bdl	-57.41±1.72
SOD(Cl)	20	11.12	21.64	bdl	0.6079	0.0529	bdl	3.0514	-72.10±2.16
	50	10.90	31.31	bdl	1.181	0.6574	bdl	4.2416	-64.00±1.92
	60	10.67	36.07	bdl	1.569	1.096	bdl	4.7609	-60.76±1.82
	80	10.62	46.37	bdl	2.212	1.941	bdl	5.5687	-59.10±1.77
CAN(NO <sub>3</sub> )	20	11.28	77.65	bdl	0.4292	1.539	20.24	bdl	-59.95±1.80
	50	10.37	78.55	bdl	0.6696	0.3708	22.89	bdl	-59.93±1.80
	60	10.09	80.40	bdl	0.7774	0.5332	23.05	bdl	-57.61±1.73
	80	9.83	82.06	bdl	1.044	0.9516	27.30	bdl	-55.01±1.65
CHA(Na)	20	8.09	0.8714	bdl	0.1341	0.0026	bdl	bdl	-32.89±0.99
	50	7.17	1.275	bdl	0.2835	0.0507	bdl	bdl	-28.72±0.86
	60	7.07	1.471	bdl	0.3579	0.0911	bdl	bdl	-27.69±0.83
	80	7.10	1.452	bdl	0.5250	0.2452	bdl	bdl	-26.15±0.78
FAU-X	20	10.61	9.678	bdl	0.2569	0.4940	bdl	bdl	-21.83±0.65
	50	9.90	6.725	bdl	0.6106	0.7554	bdl	bdl	-20.28±0.61
	60	9.62	6.874	bdl	0.6407	1.042	bdl	bdl	-19.64±0.59
	80	9.25	7.721	bdl	0.7007	2.076	bdl	bdl	-18.56±0.56
FAU-Y	20	10.11	0.9961	bdl	0.3373	0.0679	bdl	bdl	-29.95±0.90
	50	9.02	1.166	bdl	0.4014	0.2195	bdl	bdl	-27.39±0.82
	60	8.61	1.282	bdl	0.4295	0.2054	bdl	bdl	-27.00±0.81
	80	8.31	1.594	bdl	0.6288	0.4734	bdl	bdl	-25.37±0.76
NAT	20	10.06	1.296	bdl	1.052	0.0065	bdl	bdl	-26.34±0.79
	50	8.54	1.536	bdl	1.074	0.0121	bdl	bdl	-24.61±0.74
	60	8.33	1.544	bdl	1.155	0.0140	bdl	bdl	-24.36±0.73
	80	8.06	1.885	bdl	1.406	0.0259	bdl	bdl	-23.35±0.70
MOR(Na)	20	9.80	0.2219	bdl	0.2847	0.0007	bdl	bdl	-23.12±0.69

50	8.78	0.4855	bdl	0.8051	0.0025	bdl	bdl	-20.64±0.62
60	8.48	0.5534	bdl	1.105	0.0030	bdl	bdl	-19.77±0.59
80	8.00	0.5369	bdl	1.635	0.0077	bdl	bdl	-18.41±0.55

532 <sup>a</sup> bdl: below detection limit that was approximately 0.025 mg/L for each element. <sup>b</sup> The  
533 adopted chemical composition of 4Å is Na<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>·4.5H<sub>2</sub>O and thus [Ca]<sub>tot</sub>, [Mg]<sub>tot</sub>, and  
534 [Fe]<sub>tot</sub> are not shown here. <sup>c</sup> pH measured at laboratory temperature (25°C) and corrected to  
535 20°C, 50, 60 and 80°C. The pH differences caused by temperatures were calculated with  
536 GEMS, i.e., the pH values (all values were measured at laboratory temperature and were  
537 above 8) were corrected +0.16 for 20 °C, -0.74 for 50 °C, -0.98 for 60 °C, and -1.40 for  
538 80 °C.

539

### 540 3.2.2. Thermodynamic data of Na-based zeolites

541 Based on the measured log K<sub>sp</sub> values at different temperatures, the Gibbs free energy, Δ<sub>f</sub>G<sup>0</sup>,  
542 at different temperatures could be calculated. Completing these data with measured or calcu-  
543 lated data for the heat capacity, C<sub>p</sub><sup>0</sup>, and entropy, S<sup>0</sup>, data allowed to compute the solubility  
544 of the zeolites at 25 °C and its changes with temperature based on Eq. (2)-(4) using GEM-Sel-  
545 ektor. The generated standard thermodynamic data of Na-based zeolites based on our experi-  
546 ments are shown in Table 6.

547 Corresponding thermodynamic properties of the selected zeolites in literatures were reviewed  
548 and tabulated in Table 7. As shown in Table 7, quite few solubility products were obtained  
549 experimentally and some of the reported log K<sub>sp</sub> values had several log units difference for the  
550 same zeolites, such as for analcime, natrolite, chabazite, and zeolite P. Diverse reasons can be  
551 responsible for these large discrepancy, such as differences in their derivation (solubility ex-  
552 periments, calorimetric measurements, or phase relations), varying Si/Cat and Si/Al ratios,  
553 different cations in the cages, impure samples and varying crystallinity of the selected zeo-  
554 lites. In Figure 4, the log K<sub>sp</sub> values of several selected zeolites were compared with the avail-  
555 able literature values. Those for other zeolites were shown in Figure 5. The log K<sub>sp</sub> values of

556 each zeolite were fitted well by the modelling curve that was generated based on the thermo-  
557 dynamic data in Table 6.

558 The log  $K_{sp}$  values of FAU-X obtained currently agree well with literature values obtained  
559 from undersaturation experiments of Sefcik and McCormick [54], while the data calculated  
560 from the dissolution study by Cizmek et al. [55] were somewhat lower, which is likely related  
561 to the very short equilibration time of only 3 hours used in those experiments. The log  $K_{sp}$  ob-  
562 tained from oversaturation [56] and [7] are above the curve obtained from undersaturation in-  
563 dicating a gap between the solubility reached from over and undersaturation. The same ten-  
564 dency was discovered in the case of FAU-Y, a higher solubility for the experiments from  
565 oversaturation (even after an equilibration time of 3 years) [7], than those measured here from  
566 undersaturation indicating again a gap between the solubility reached from over- and from un-  
567 dersaturation. Thus, either the solubility experiment or the precipitation experiment did not  
568 reach equilibrium.

569 For CAN(NO<sub>3</sub>) the solubility increases as a function of temperature, with the exception of the  
570 data point at 20 °C, due to a higher aluminum concentration measured in that sample due to  
571 reasons unknown. Similar dissolution results were obtained in the repeated dissolution experi-  
572 ment for CAN(NO<sub>3</sub>) (Table A4). The experimental  $S^0$  value of CAN(NO<sub>3</sub>) estimated from the  
573 log  $K_{sp}$  curve was 1128 J/mol/K, close to the value of 1149 J/mol/K obtained from the experi-  
574 mental  $S^0$  value of CAN(CO<sub>3</sub>) [57] using the additivity method. Accordingly, the  $C_p^0$  value of  
575 CAN(NO<sub>3</sub>) was calculated from the measured  $C_p^0$  value of CAN(CO<sub>3</sub>) [57]. As reported by  
576 Bickmore et al. [58], the experimental log  $K_{sp}$  values of CAN(NO<sub>3</sub>) at 89 °C were -59.33 and  
577 -53.53, respectively, at pH ~12.4 and ~11.3. The value of -53.53 at pH ~11.3 was closer to the  
578 pH values in the CAN(NO<sub>3</sub>) dissolution experiments (Table 6) and corresponded precisely to  
579 the log  $K_{sp}$  curve in the present work. Sodalites, together with cancrinites, are some of the few  
580 zeolites, which possess anionic sites in the extraframeworks. However, no solubility study is

581 available for sodalities such that their stability can only be estimated from available enthalpy  
582 measurements [59, 60], and entropy data estimated from structurally related zeolites as done  
583 in Myers et al. [18].

584 The thermodynamic data of NAT determined in the present study agreed well with the values  
585 based on a critical review from Blanc et al. [11], but were clearly less negative than those de-  
586 termined in the presence of albite [7]. This might be due to the slow dissolution of albite in  
587 these experiments, which led to non-equilibrium conditions; in fact re-measurement of these  
588 data after longer equilibration times (6 years) resulted in similar values as reported here [22].

589 In this study, ANA, FAU-Y and CHA(Na) have the same chemical formula (except for the  
590 hydrate numbers) but different frameworks. It can be expected the framework largely deter-  
591 mines the zeolite solubility. In the investigated temperature range of 20 to 80 °C, ANA was  
592 more soluble than FAU-Y and CHA(Na). The ANA framework formed under higher tempera-  
593 ture (200 °C) than FAU/CHA (~90 °C) framework, and could be thus expected to be less sol-  
594 uble around 200 °C. Assuming that  $C_p^0$  variations with temperature are similar for ANA,  
595 FAU-Y and CHA(Na), the extrapolated  $\log K_{sp}$  curves of the three zeolites (Figure A7) veri-  
596 fied that analcime was more stable than FAU-Y and CHA(Na) at 200 °C.

597 In addition, the measured  $\log K_{sp}$  values for ANA were considerably larger than those re-  
598 ported for natural analcime in literatures [11, 13, 61, 62]. As shown in Figure 4e, all the data  
599 points and curves were corresponding to an identical chemical composition of  
600  $\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12}\cdot 2\text{H}_2\text{O}$ , except for the one from Blanc et al. [11] with a chemical formula of  
601  $\text{Na}_{1.98}\text{Al}_{1.98}\text{Si}_{4.02}\text{O}_{12}\cdot 2\text{H}_2\text{O}$ . Note that a difference of 0.03 cation per formula unit can result in  
602 2 log units difference in the solubility products expressed as  $\log K_{sp}$  as shown in [11]. The ex-  
603 periments for ANA and FAU-Y were repeated and confirmed this observation (Table A4).  
604 The solubility data recalculated from the measured concentration in Wilkin and Barnes [62]  
605 from natural samples, resulted in roughly 4 log units lower solubility products than those

606 measured in the present work from synthetic samples as shown in Figure 4e. This large differ-  
607 ence could be related to either a strongly stabilizing effect of minor elements by an as yet un-  
608 determined mechanism on the natural analcime investigated by Wilkin and Barnes [62] or an  
609 effect of the synthesis method. In the current work, ANA was synthesized with an assistance  
610 of organic template, which could lead to more structural defects and possible organic residues  
611 in the synthesized ANA.

612 No experimental solubility data is available in literature for MOR(Na) with the same Si/Al ra-  
613 tio and as Na<sup>+</sup>-endmember. After normalizing to the same total number of TO<sub>4</sub>, the calculated  
614 log K<sub>sp</sub> values from Blanc et al. [11] were plotted in Figure 4f to compare with our experi-  
615 mental data. The significant discrepancy was probably due to the different Si/Al ratios and  
616 due to the presence of Ca<sup>2+</sup> as extraframework cation, although the high Si/Al ratio of the  
617 mordenite should suppress the effect of extraframework cations as there are little cationic sites  
618 in such an aluminosilicate framework [63]. Therefore, the large difference on the solubility  
619 behavior should be mainly resulted from the different Si/Al ratios.

620 From a kinetic point of view, the cases of LTA and LS-P(Na) are of specific interest. Both  
621 LTA and LS-P(Na) were synthesized at 100 °C with the former phase lasting for 2 h and the  
622 latter for 192 h (Table 1). As shown in Figure 5, the log K<sub>sp</sub> value of LTA is larger than that  
623 of LS-P(Na) at 25 °C, indicating that LTA is less stable than LS-P(Na). The log K<sub>sp</sub> curves of  
624 both phases are overlapping between 80 and 100 °C, suggesting that LTA could be more sta-  
625 ble at higher temperature and that in the temperature range the equilibration time could be of  
626 large importance.

627 In general, the zeolites synthesized in this study have a higher solubility than natural zeolites.  
628 Such differences between natural and synthetic zeolites could be related to the presence of mi-  
629 nor elements that can stabilize the natural zeolites, to different crystallinity of the zeolites,  
630 and/or to smaller crystal sizes of synthetic zeolites. Blanc et al. [11], for instance, derives a 3

631 log units lower solubility for the natural zeolite gismondine than for the synthetic zeolite  
632 P(Ca), with the same nominal composition. The solubility discrepancy was especially obvious  
633 for analcime. Murphy et al. [64] and Wilkin and Barnes [62] used natural analcime, which  
634 could be more stable due to the higher crystallinity than the phase precipitated here and due to  
635 the presence of minor phases. Although high crystallization temperature (e.g., 200 °C for  
636 ANA) was applied during synthesis and the zeolites showed sharp peaks (i.e., good crystallin-  
637 ity) in the XRD patterns, their crystallinity degrees could be still lower and more structural  
638 defects that increase solubility could exist compared to the natural ones. On the other hand, the  
639 equilibration time could also affect the results (Figure A5), which could lead to somewhat  
640 higher solubility here. For analcime for example, Benning et al. [63] and Murphy et al. [64]  
641 used equilibration times up to two years at 25 °C in order to achieve equilibrium from dissolu-  
642 tion and precipitation, although the differences in dissolution experiments were small after 3  
643 months and longer. In addition, the presence of minor elements in the natural zeolites could  
644 stabilize them, compared to the relatively pure synthesized zeolites, which is however, diffi-  
645 cult to assess based on the limited amount of experimental data available. Differences in mi-  
646 nor elements and/or variation in the composition could also explain the relatively large differ-  
647 ence in experimentally determined solubility data for analcime as shown in Figure 4.

648 In contrast, the log  $K_{sp}$  values of natrolite determined in the present study compare favorably  
649 (Figure 4) with the values derived in Blanc et al. [11] generated from calorimetric measure-  
650 ments [65] as well as with recent data of a long-term (6 years) solubility study [22]. In con-  
651 trast, the solubility values determined by Lothenbach et al. [7] after 1 and 3 years of equilibra-  
652 tion (within the same experimental series as [22]) were considerably lower, indicating that  
653 those experiments containing calcium and slowly reacting albite had not been in equilibrium.

654 In the current study, the precipitation/crystallization and dissolution processes investigated  
655 can be considered as "young" synthetic Na-based zeolites. Such "immature" zeolites could



656 evolve to more stable states with time and/or temperature, but as they are synthetic they are  
657 also less influenced by the presence of minor elements. The data selected in the present study  
658 seem thus well suited to model the precipitation of zeolites over relatively short periods (e.g.,  
659 during cementitious material hydration or ageing).

660 **Table 6.** Standard thermodynamic data of Na-based zeolites at 25 °C, derived in the current  
661 study.

SBU group	Zeolite	log K <sub>sp</sub>	Δ <sub>f</sub> G <sup>0</sup> (kJ/mol)	Δ <sub>f</sub> H <sup>0</sup> (kJ/mol)	S <sup>0</sup> (J/mol/K)	C <sub>p</sub> <sup>0</sup> (J/mol/K)	V <sup>0</sup> (cm <sup>3</sup> /mol)
S4R	ANA (Na <sub>2</sub> Al <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> ·2H <sub>2</sub> O)	-26.8±0.8	-6139.70	-6575.84	469 <sup>a</sup>	425 <sup>b</sup>	194.84
	LS-P(Na) (Na <sub>2</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ·3.8H <sub>2</sub> O)	-19.6±0.6	-4858.72	-5314.82	374	384 <sup>c</sup>	153.49
	PHI(Na) (Na <sub>2.5</sub> Al <sub>2.5</sub> Si <sub>5.5</sub> O <sub>16</sub> ·5H <sub>2</sub> O)	-39.4±1.2	-8717.83	-9438.72	692 <sup>d</sup>	620 <sup>d</sup>	304.74
	PHI(NaK) (Na <sub>1.5</sub> KAl <sub>2.5</sub> Si <sub>5.5</sub> O <sub>16</sub> ·5H <sub>2</sub> O)	-39.9±1.2	-8741.26	-9461.67	707 <sup>d</sup>	626 <sup>d</sup>	304.74
	LTA (Na <sub>1.98</sub> Al <sub>1.98</sub> Si <sub>2.02</sub> O <sub>8</sub> ·5.31H <sub>2</sub> O)	-18.2±0.6	-5203.75	-5701.89	584 <sup>e</sup>	513 <sup>e</sup>	186.95
D4R	4Å (Na <sub>2</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ·4.5H <sub>2</sub> O)	-20.5±0.6	-5029.88	-5486.36	536 <sup>e</sup>	475 <sup>e</sup>	187.00
	SOD(OH) (Na <sub>8</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> (OH) <sub>2</sub> ·2H <sub>2</sub> O)	-65.2±2.0	-13221.4	-14120.1	943 <sup>f</sup>	895 <sup>f</sup>	424.74
S6R	SOD(Cl) (Na <sub>8</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> Cl <sub>2</sub> )	-69.4±2.1	-12719.1	-13473.4	848 <sup>g</sup>	812 <sup>g</sup>	421.53
	CAN(NO <sub>3</sub> ) (Na <sub>8</sub> Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> (NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O)	-64.8±1.9	-13600.8	-14717.6	1149 <sup>h</sup>	1119 <sup>h</sup>	435.96
D6R	CHA(Na) (Na <sub>2</sub> Al <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> ·6H <sub>2</sub> O)	-31.9±1.0	-7117.55	-7808.31	548 <sup>c</sup>	578 <sup>c</sup>	249.95
	FAU-X (Na <sub>2</sub> Al <sub>2</sub> Si <sub>2.5</sub> O <sub>9</sub> ·6.2H <sub>2</sub> O)	-21.9±0.7	-5857.79	-6456.94	566 <sup>i</sup>	586 <sup>i</sup>	195.80
	FAU-Y (Na <sub>2</sub> Al <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> ·8H <sub>2</sub> O)	-29.5±0.9	-7578.22	-8352.62	734 <sup>i</sup>	739 <sup>i</sup>	282.94
4=1	NAT (Na <sub>2</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> ·2H <sub>2</sub> O)	-26.6±0.8	-5305.15	-5707.02	360 <sup>j</sup>	359 <sup>j</sup>	169.36
5-1	MOR(Na) (Na <sub>0.72</sub> Al <sub>0.72</sub> Si <sub>5.28</sub> O <sub>12</sub> ·2.71H <sub>2</sub> O)	-22.5±0.7	-5955.95	-6442.40	388 <sup>c</sup>	405 <sup>c</sup>	210.59

662 All values shown were obtained in the current study except where indicated <sup>a</sup> Measured by  
663 [17]; <sup>b</sup> Measured by [61]; <sup>c</sup> Calculated using additivity method based on the elementary (hy-  
664 dro)oxide components; <sup>d</sup> Calculated by additivity method starting from zeolites with the PHI  
665 framework [11]; <sup>e</sup> Calculated starting from the LTA framework [66]; <sup>f</sup> Measured by [67]; <sup>g</sup>  
666 Measured by [68]; <sup>h</sup> Calculated starting from the CAN framework[57]; <sup>i</sup> Indicated by [7]; <sup>j</sup>  
667 Measured by [65]; log K<sub>sp</sub> was calculated with respect to the species of AlO<sub>2</sub><sup>-</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>,  
668 SiO<sub>2</sub><sup>0</sup>, Cl<sup>-</sup>, OH<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and H<sub>2</sub>O. For the additivity method, the thermodynamic data of the ele-  
669 mentary (hydro)oxide components (i.e., zeolitic H<sub>2</sub>O, NaOH, Ca(OH)<sub>2</sub>, KOH, Al(OH)<sub>3</sub>, SiO<sub>2</sub>,  
670 NaCl, NaNO<sub>3</sub>, and Na<sub>2</sub>CO<sub>3</sub>) was summarized in Table A2 and the reference reactions shown  
671 in Table A5.

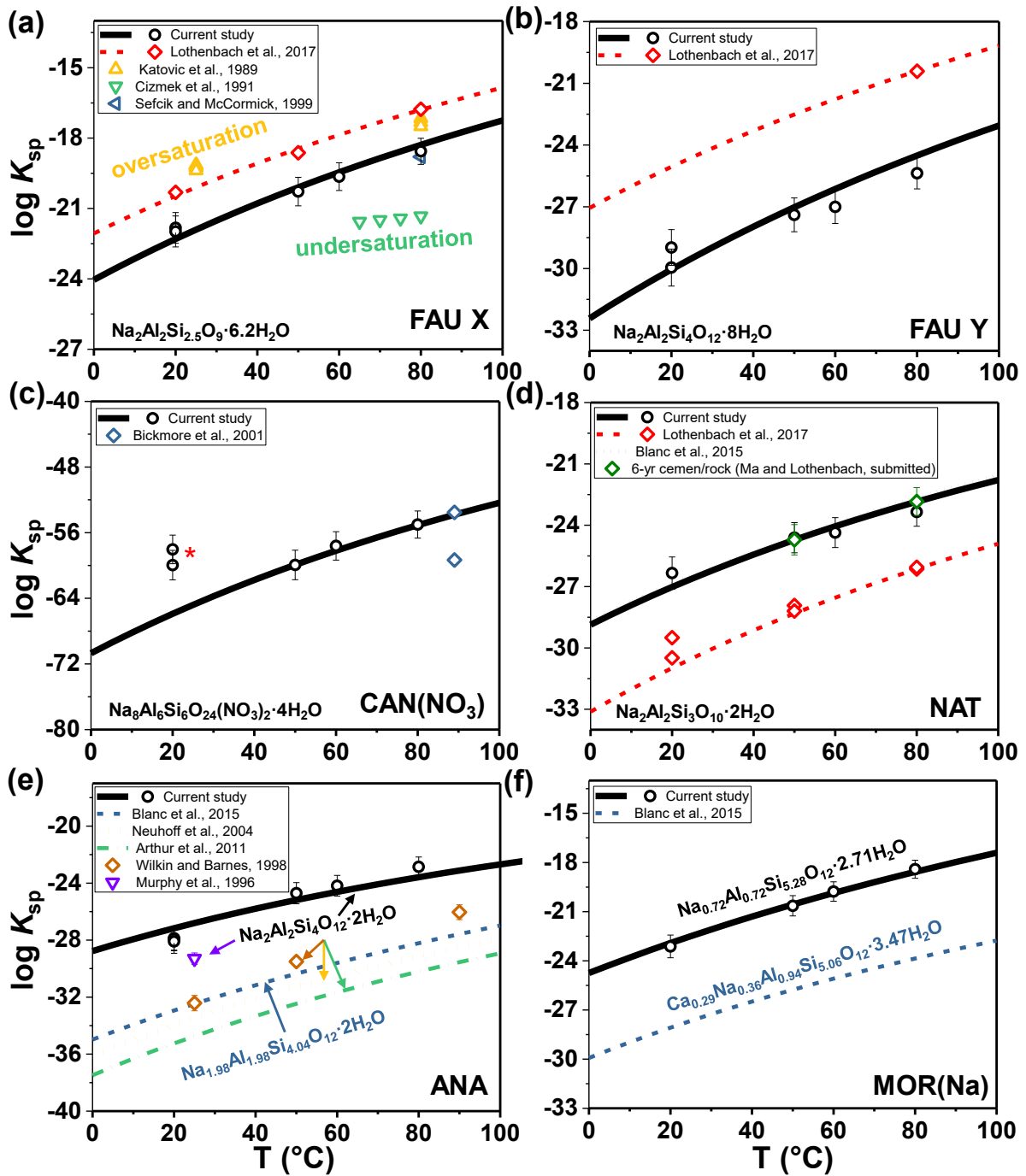
672

673 **Table 7.** Thermodynamic properties of zeolites reported in the literature. Experimental values  
 674 (e.g., derived from solubility experiments and calorimetric measurement) were marked in  
 675 bold.

Zeolite	Formula	$\log K_{sp}$ (298.15 K)	$\Delta G_f^\circ$ kJ/mol	$\Delta H_f^\circ$ kJ/mol	$S^\circ$ J/mol K	$C_p$ J/mol K	Ref
Analcime	$\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$	-33.47	-6177.8	-6616.9	459	425	[7] <sup>a</sup>
	$\text{Na}_{1.98}\text{Al}_{1.98}\text{Si}_{4.02}\text{O}_{12} \cdot 2\text{H}_2\text{O}$	-32.00	-6178.1	<b>-6616.0</b>	<b>462</b>	<b>425</b>	[61]
	$\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$	-33.23	-6176.4	-6613.4	469	424	[17]
	$\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$	-34.74	-6192.6	-6624.0			[13]
	$\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$	<b>-32.12</b>	<b>-6178.4</b>				[62]
	$\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 2\text{H}_2\text{O}$	<b>-29.30</b> <b>± 0.4</b>	<b>-6160.2</b>				[64]
Natrolite	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$	-26.43	-5316.7	<b>-5718.6</b>	<b>360</b>	<b>359</b>	[65]
	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot \text{H}_2\text{O}$				<b>425</b>	<b>380</b>	[17]
	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$	<b>-30.20</b>	<b>-5325.7</b>	<b>-5728.0</b>	<b>360</b>	359	[7]
Gismondine	$\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4.5\text{H}_2\text{O}^b$	-26.25	-5102.4	-5589.9	371	435	[11]
Zeolite P	$\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4.5\text{H}_2\text{O}^b$	-23.17	-5084.8	-5564.6	397	459	[11]
	$\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4.5\text{H}_2\text{O}^b$	<b>-20.30</b>	<b>-5057.8</b>	<b>-5424.0</b>	<b>779</b>	753	[7]
Phillipsite	$\text{Na}_2\text{Al}_2\text{Si}_6\text{O}_{16} \cdot 6\text{H}_2\text{O}$	-42.84	-8863.7	-9623.3	<b>764</b>	<b>662</b>	[11]
	$\text{K}_2\text{Al}_2\text{Si}_6\text{O}_{16} \cdot 6\text{H}_2\text{O}^b$	-45.66	-8920.9	-9683.7	<b>780</b>	<b>702</b>	[11]
	$\text{CaAl}_2\text{Si}_6\text{O}_{16} \cdot 6\text{H}_2\text{O}^b$	-41.10	-8882.7	-9648.0	<b>684</b>	<b>644</b>	[11]
	$\text{Na}_{1.08}\text{K}_{0.80}\text{Al}_{1.88}\text{Si}_{6.12}\text{O}_{16} \cdot 6\text{H}_2\text{O}^b$				<b>771.9</b> <b>± 2.4</b>	<b>786.2</b>	[70]
	$\text{CaAl}_2\text{Si}_6\text{O}_{16} \cdot 6\text{H}_2\text{O}^b$				<b>697</b>	<b>586</b>	[17]
Zeolite A	$\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$		-3899.2	<b>-4121.7</b>	<b>271</b>	<b>260</b>	[66]
	$\text{Na}_2\text{Al}_2\text{Si}_{2.12}\text{O}_{8.24}$	-23.24 <sup>c</sup>	-4078.4				[16]
	$\text{Na}_{2.0}\text{Al}_{2.0}\text{Si}_{2.0}\text{O}_{8.0} \cdot 4.36\text{H}_2\text{O}$			<b>-5454.8</b>			[13]
Cancrinite	$\text{Na}_{8.28}\text{Al}_{5.93}\text{Si}_{6.07}\text{O}_{24}(\text{CO}_3)_{0.93}(\text{OH})_{0.49} \cdot 3 \cdot 64\text{H}_2\text{O}$		-13690.0 ± 51	<b>-14684.0</b> ± 50	<b>1057</b> ± 35	<b>1047</b> ± 30	[57]
	$\text{Na}_{7.282}\text{Al}_{5.854}\text{Si}_{6.146}\text{O}_{24}(\text{NO}_3)_{1.336}(\text{CO}_3)_{0.046} \cdot 3.365\text{H}_2\text{O}$			<b>-14258.3</b> ± 17.3			[60]
Sodalite-Cl	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$		-12703.7	<b>-13457.9</b>	<b>848</b>	<b>812</b>	[68]
Hydrosodalite	$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$		-13384.2	<b>-14283.0</b>	<b>943</b>	<b>895</b>	[67]
	$\text{Na}_{7.26}\text{Al}_6\text{Si}_{6.21}\text{O}_{24.03}(\text{OH})_{1.68} \cdot 2.91\text{H}_2\text{O}$	-60.34 <sup>d</sup>					[71]
Chabazite	$\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}^b$	-34.22	-7173.6	<b>-7824.4</b>	<b>614</b>	<b>643</b>	[11]
	$\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}^b$				<b>640</b>	<b>589</b>	[61]
	$\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}^b$	<b>-25.80</b>	<b>-7111.8</b>	<b>-7774.0</b>	581 <sup>e</sup>	617 <sup>e</sup>	[7]
Faujasite(X)	$\text{Na}_2\text{Al}_2\text{Si}_2.5\text{O}_9 \cdot 6.2\text{H}_2\text{O}$	<b>-20.10</b>	<b>-5847.5</b>	<b>-6447.0</b>	<b>566</b>	586	[7]
Faujasite(Y)	$\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 8\text{H}_2\text{O}$	<b>-25.00</b>	<b>-7552.5</b>	<b>-8327.0</b>	<b>734</b>	739	[7]
Mordenite	$\text{Ca}_{0.25}\text{K}_{0.15}\text{Na}_{0.35}\text{AlSi}_5\text{O}_{12} \cdot 3.667\text{H}_2\text{O}$		-6294.6	-6807.6			[13]
	$\text{Ca}_{0.289}\text{Na}_{0.361}\text{Al}_{0.940}\text{Si}_{5.060}\text{O}_{12} \cdot 3.468\text{H}_2\text{O}$		-6229.89	-6738.44	486.54	484.45	[11]
	$\text{Ca}_{0.289}\text{Na}_{0.361}\text{Al}_{0.940}\text{Si}_{5.060}\text{O}_{12} \cdot 3.468\text{H}_2\text{O}$		-6247.6 ± 4.5	<b>-6756.2</b> ± 4.5	<b>486.54</b> ± 0.97	<b>484.33</b> ± 0.97	[72]
	$\text{Ca}_{0.29}\text{Na}_{0.36}\text{Al}_{0.94}\text{Si}_{5.06}\text{O}_{12} \cdot 3.47\text{H}_2\text{O}$		-6227.9	-6736.7	486.5		[17]

676 <sup>a</sup> Derived from [61]; <sup>b</sup> Data of Ca and K endmembers are shown for comparison; <sup>c</sup> Estimated  
 677 from [73]; <sup>d</sup>  $\log K_{sp}$  is extrapolated value based on [74, 75]; <sup>e</sup> Recalculated for  
 678  $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$  from the values measured by [76] for natural chabazite.

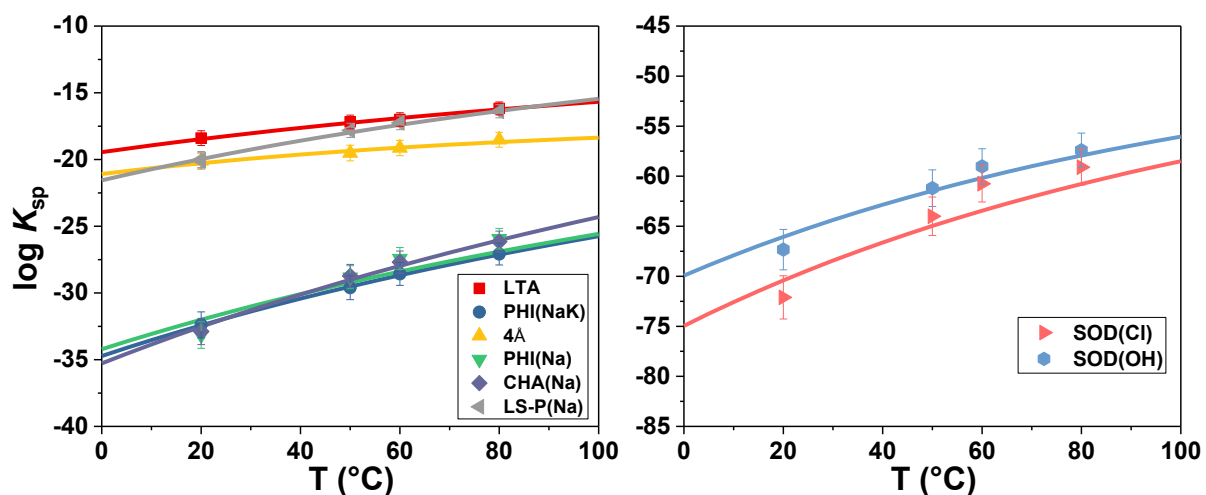
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680

681 **Figure 4.** Log solubility products,  $K_{sp}$  for (a) FAU-X, (b) FAU-Y, (c) CAN( $\text{NO}_3$ ), (d) NAT,  
 682 (e) ANA, and (f) MOR(Na). Values derived from current study are indicated by the black hol-  
 683 low dots and bold lines. For comparison, solubility products and the relevant curves with tem-  
 684 perature [7, 11, 13, 22, 54-56, 58, 61, 62, 64, 77] were also plotted. \* Data points excluded in  
 685 the fits.

686



687  
 688 **Figure 5.** Experimental  $\log K_{sp}$  values of different zeolites at 20, 50, 60, and 80 °C. The solid  
 689 lines were generated with the GEMS code using the thermodynamic data and the chemical  
 690 compositions compiled in Table 6.

691

### 692 3.3. Predominance diagrams in the chemical sub-systems of $\text{Na}_2\text{O-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$

693 As the newly generated thermodynamic data of Na-based zeolites are devised as an addition  
 694 to the Cemdata database, the consistency between thermodynamic data of zeolites, clays/mi-  
 695 cas, and  $\text{SiO}_2/\text{Al}(\text{OH})_3$  was examined by establishing their predominance diagrams for the  
 696  $\text{Na}_2\text{O-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$  system at 25 and 80°C. The data shown in Figure 6 and 7, exhibit in  
 697 general a similar sequence of predominance as reported in Blanc et al. [11], indicating a good  
 698 compatibility of the derived zeolite data with the stability of  $\text{Al}(\text{OH})_3$  and with clays. How-  
 699 ever, the stable zeolites predicted show some clear differences, in the present study in addition  
 700 to natrolite, also Na-chabazite and Na-mordenite were calculated to be stable.

701 For the  $\text{Al}(\text{OH})_3$ -saturated chemical system, the presence of microcrystalline  $\text{Al}(\text{OH})_3$  (Figure  
 702 6a) and gibbsite (Figure 6b) were considered at 25 °C as  $\text{Al}(\text{OH})_3$  with poor crystallinity  
 703 could be thermodynamically favored at room temperature. Compared to the diagrams with  
 704 gibbsite, microcrystalline  $\text{Al}(\text{OH})_3$  had as expected a more limited predominance area, while  
 705 the stability domains of its neighbor phases expanded. In addition of the neighboring miner-  
 706 als, paragonite and kaolinite, two clay minerals, beidellite(Na) and pyrophyllite, were pre-  
 707 dicted to predominate the corresponding regions in agreement with Blanc et al. [11]. Besides,

708 the domains characterized by either high [Si] or high alkalinity were predominated by three  
709 types of zeolite, i.e., NAT, CHA(Na), and MOR(Na). At 25 °C, the stability domains of zeo-  
710 lites were mainly occupied by CHA(Na) and MOR(Na) under low and high [Si], respectively.  
711 With increasing temperature, the stability domains of NAT expanded, resulting in a decrease  
712 of the stability region of CHA(Na).

713 For the SiO<sub>2</sub>-saturated chemical system, again the presence of either amorphous SiO<sub>2</sub> or  
714 quartz was considered at 25 °C (Figure 7a and 7b). Due to the high solubility of amorphous  
715 SiO<sub>2</sub>, the stability domain of am-SiO<sub>2</sub> was much smaller than that of quartz. Both quartz and  
716 gibbsite showed larger stability domain areas at higher temperature (i.e., 80 °C), indicating  
717 that these crystalline phases were more stable thermodynamically at higher temperatures. In  
718 the chemical system saturated with amorphous SiO<sub>2</sub>, the resulting higher [Si] compared to the  
719 case of quartz stabilized the most siliceous zeolite [10], i.e., MOR(Na), at relatively low alu-  
720 minum concentrations. In addition of the three zeolites observed in the Al(OH)<sub>3</sub>-saturated sys-  
721 tem, LS-P(Na) with a very low Si/Al ratio of 1 appeared at the top right part of the diagram,  
722 suggesting that LS-P(Na) can be stabilized by high Al and Na concentrations. The Si/Al ratios  
723 of MOR(Na), CHA(Na), NAT, and LS-P(Na) are 7.35, 2.00, 1.50, and 1.00, respectively. As  
724 can be seen, the four zeolites predominate in sequence as [Al] increases, in good accordance  
725 with their Si/Al ratios. For 80°C, a similar predominance diagram was calculated, the main  
726 difference is that the stability field of CHA(Na) was clearly smaller.

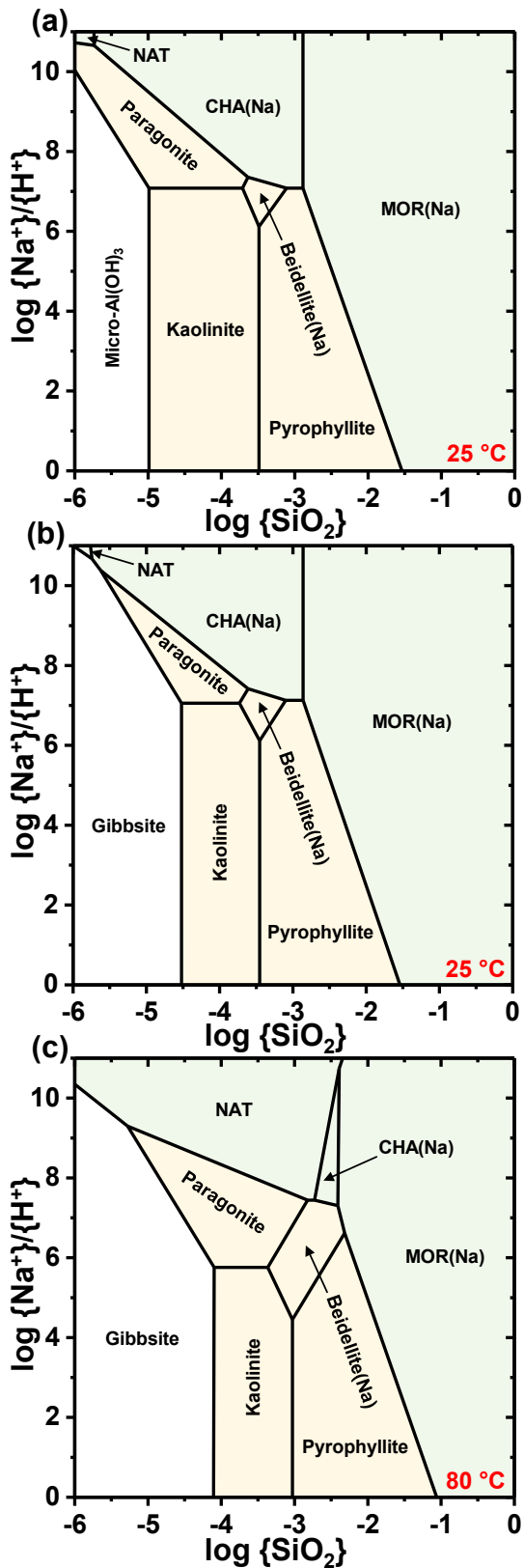
727 For the system saturated by quartz at 25 °C, the resulting higher [Si] destabilized MOR(Na)  
728 and the CHA(Na) region was also reduced. A significant change of the stability domain of  
729 NAT and CHA(Na) with temperature was observed similar to the Al(OH)<sub>3</sub>-saturated system.  
730 CHA(Na) was predicted to be destabilized at 80°C with respect to NAT indicates that NAT is  
731 stabilized at higher temperature.

732 The zeolites of the S6R group (sodalites and cancrinite) were not included during the calcula-  
733 tion of predominance diagrams as no  $\text{Cl}^-$  or  $\text{NO}_3^-$  are present in the cement-zeolite-clay sys-  
734 tem. In the investigated chemical system, LTA, FAU, PHI, and ANA were undersaturated  
735 compared to NAT, CHA(Na), MOR(Na) and LS-P(Na). As discussed above, LTA and FAU  
736 might be the intermediate phases regarding the more stable phases of LS-P(Na) and  
737 CHA(Na), respectively. However, analcime was not predicted in the temperature range of 25  
738 to 80 °C although it is one of the most common zeolites at the earth's surface. Its composi-  
739 tional ratio range is quite small with the number of Si atoms ranging from 1.8 to 2.3 for six  
740 oxygen atoms [61]. Analcime was commonly observed to form in the alteration process of  
741 clays (e.g., smectite and bentonite) under hyperalkaline ( $\text{pH} > 13.5$ ) conditions from 90 °C to  
742 200 °C [78]. Higher reaction temperatures and higher Na concentrations promoted the for-  
743 mation of analcime. Besides, the stability domain of analcime calculated by Blanc et al. [11]  
744 at 25°C was very narrow, indicating that its formation at lower temperature was not favored.  
745 In the current work, the absence of analcime in predominance diagrams at 25 and 80°C is due  
746 to its relatively higher solubility determined here for synthetic samples compared to the litera-  
747 ture values on natural samples; extrapolation of the solubility to higher temperature indicated  
748 the stabilization of analcime with respect to FAU-Y and CHA(Na) from 110 °C and from  
749 150 °C, respectively (Figure A7).

750 Phillipsite (mostly K-based phillipsite) and chabazite were also commonly observed in ce-  
751 ment/clay interaction systems as reported in the review by Gaucher and Blanc [78]. However,  
752 Na-phillipsite was missing in the calculated predominance diagrams, where CHA(Na) was  
753 predicted to be more stable than PHI(Na), as the Si/Al ratio (2.2) of PHI(Na)  
754 ( $\text{Na}_{2.5}\text{Al}_{2.5}\text{Si}_{5.5}\text{O}_{16} \cdot 4\text{H}_2\text{O}$ ) is quite close to that (2.0) of CHA(Na) ( $\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$ ). It  
755 seems quite unlikely that phillipsite could be an intermediate phase. Typically, phillipsite pre-  
756 fers to accommodate different types of extraframework cations together, e.g.,  $\text{K}^+$  plus  $\text{Na}^+$

757 and/or  $\text{Ca}^{2+}$  [46]. K-prevailing phillipsite with other cations doped is the most common in na-  
758 ture and thus the most stable in thermodynamics. The phillipsite currently investigated is  
759 purely Na-based and thus less stable than K-containing phillipsites [11], such that it can be  
760 expected that in systems containing Ca, K and Na phillipsite would be stable. In addition, the  
761 Si/Al ratio (2.2) of PHI(Na) ( $\text{Na}_{2.5}\text{Al}_{2.5}\text{Si}_{5.5}\text{O}_{16}\cdot 4\text{H}_2\text{O}$ ) was quite close to 2.0, the ratio of  
762 CHA(Na) ( $\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12}\cdot 6\text{H}_2\text{O}$ ). In the predominance diagrams, CHA(Na) was predicted  
763 more stable than PHI(Na) and thus covered up PHI(Na) in stability domain. These could ex-  
764 plain the reported frequent occurrence of phillipsite [78] although it is not predicted in a pure  
765 Na-system.

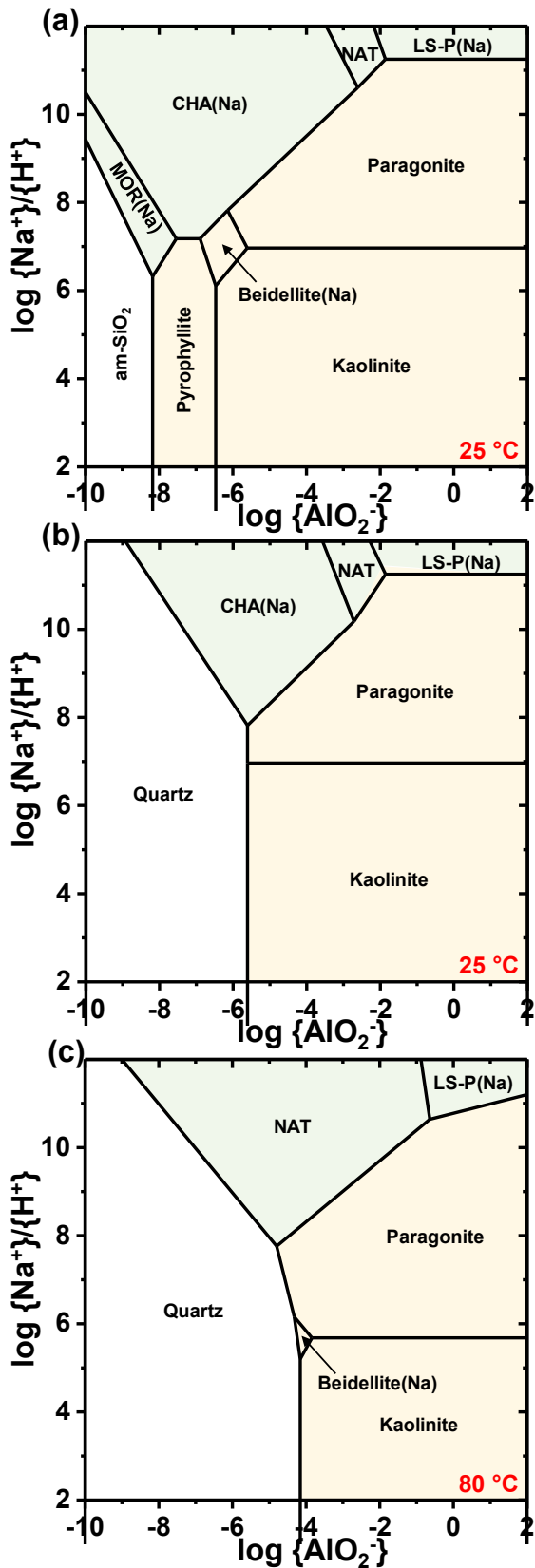
766 In contrast, mordenite is rarely reported in clay/cement experiments except by [78], but pre-  
767 dicted here to occur. Mordenite is a high-silica zeolite with Si/Al ratios ranging from 4.0 to  
768 6.1. The Al content available in many clay/cement experiments could be too high to facilitate  
769 the formation of mordenite. In the predominance diagrams in the current study all the investi-  
770 gated Na-based zeolites were enabled to precipitate. Therefore, the predominance results only  
771 obeyed the extent of oversaturation but might not agree exactly with the natural abundance or  
772 previous mineral observations where no such zeolite was formed.



773

774 **Figure 6.** Predominance diagrams in  $Na_2O-SiO_2-Al_2O_3-H_2O$  chemical systems for zeolite  
 775 (light green), clay and mica (light yellow), and  $Al(OH)_3$  (colorless) phases. (a) saturated with  
 776 respect to microcrystalline  $Al(OH)_3$  (micro- $Al(OH)_3$ ) at 25 °C; saturated with respect to  
 777 gibbsite (b) at 25 °C and (c) at 80 °C.





778

779 **Figure 7.** Predominance diagrams in  $Na_2O-SiO_2-Al_2O_3-H_2O$  chemical systems for zeolite  
 780 (light green), clay and mica (light yellow), and  $SiO_2$  (colorless) phases. (a) saturated with re-  
 781 spect to amorphous  $SiO_2$  (am- $SiO_2$ ) at 25 °C; saturated with respect to quartz (b) at 25 °C and  
 782 (c) at 80 °C.

783

#### 784 **4. Conclusions**

785 In this study, Na-based zeolites of six different secondary building units (i.e., S4R, D4R, S6R,  
786 D6R, 4=1, and 5-1) were synthesized via hydrothermal methods in a temperature range of 80  
787 to 200 °C. In addition, a typical molecular sieve 4Å (LTA type) was also investigated. The  
788 framework structures, the ratios between extra-framework cations, Si, and Al, and the water  
789 contents of these different zeolites were determined by XRD, SEM-EDS, and TGA, respec-  
790 tively. The low-frequency bonding vibrations of zeolite structures were characterized by FT-  
791 IR, showing that zeolites having the same secondary building units always have similar IR  
792 band features. The solid characterization results indicated that the targeted zeolites were syn-  
793 thesized successfully with high purity. The precise element composition and framework struc-  
794 ture type (i.e., ANA, GIS, PHI, LTA, SOD, CAN, CHA, FAU, NAT, or MOR) of each zeolite  
795 were thus identified.

796 The solubility of these zeolites was investigated from under-saturation at 20, 50, 60, and  
797 80 °C and compared where possible with literature values. Based on these solubility measure-  
798 ments  $\log K_{sp}$  and  $\Delta_f G^0$  values at different temperatures' could be calculated. Completing these  
799 data with measured or calculated data for the heat capacity,  $C_p^0$ , and entropy,  $S^0$ , data allowed  
800 to compute the solubility of the zeolites at 25 °C and its changes with temperature using  
801 GEM-Selektor. Differences in  $\log K_{sp}$  values were observed between the data measured in  
802 this paper and the literature values, especially for analcime, in which case the synthetic ANA  
803 resulted in roughly 4 log units larger solubility product than previously reported for natural  
804 analcime [62] but showed comparable results to another natural analcime [64].

805 Predominance diagrams in the chemical sub-systems of  $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  were estab-  
806 lished successfully and compared with literature. The derived database for Na-based zeolites  
807 is compatible with the Cemdata18 database and the thermodynamic data of the selected Na-  
808 based clays and micas in the literature. The experimentally derived thermodynamic data partly

809 reflect the early stage of the zeolite ageing, which could provide insights on the zeolite for-  
810 mation process not only in the context of radioactive waste disposal but also in environments  
811 where zeolites could exist (such as the cementitious material hydration system). In future, fur-  
812 ther careful data collations and verifications (e.g., the  $S^0$  value derived from limited solubility  
813 data points, the larger  $\log K_{sp}$  value of ANA probably caused by poorer crystallinity, etc.) re-  
814 quire further consideration.

815 This database for Na-containing zeolites is freely downloadable at  
816 <http://www.empa.ch/cemdata> in formats supporting the computer programs GEM-Selektor  
817 [32, 79] and in PHREEQC format.

818

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828

## 829 **Appendix**

830 Supplementary data to this article can be found online.

831

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