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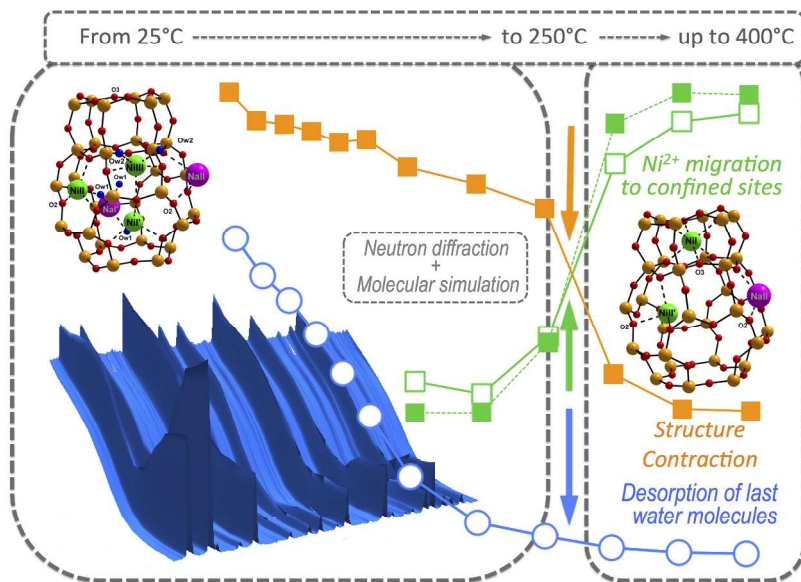
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Graphical Abstract

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Cation Migration and Structural Deformations upon Dehydration of Nickel-Exchanged NaY Zeolite: A Combined Neutron Diffraction and Monte Carlo Study

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Abstract

Combining neutron diffraction and classical molecular simulations, we describe the cations migration and associated structural changes taking place in a Ni-exchanged NaY faujasite zeolite upon stepwise dehydration from room temperature up to 400°C. The cation redistribution between sites and the associated framework deformations taking place upon water removal are identified and quantified. Neutron diffraction allows monitoring the zeolite structure, the average cation location and the water content, while molecular modeling provides insights into the correlations between the positions of cations and water molecules. Importantly, we demonstrate that the migration of Ni²⁺ toward highly confined sites upon dehydration is the driving force behind deformation of the hexagonal prisms. The present work illustrates the relevance of combining these two experimental and theoretical approaches to clarify the complex interplay between cation hydration, cation location and framework deformation. It also underlines the importance to capture the flexibility of the framework in molecular simulation of hydrated zeolite in particular when multivalent ions are involved.

Keywords: Faujasite zeolite, Nickel, Cation migration, Dehydration, Monte Carlo simulations, Neutron diffraction, Neutron scattering, Rietveld refinement

1) INTRODUCTION

Zeolites are crystalline aluminosilicates well known for their unique organized networks of nanopores and their adsorption and cation exchange properties. Their three-dimensional frameworks (231 known topologies¹) consist of ordered assemblies of building units made of tetrahedral T atoms (commonly Si and Al) bridged by oxygen ones. Each type of TO₂ zeolite framework defines specific cages and channels (void volume) whose organization (regular) and sizes (4-20 Å, similar to those of many molecules) are at the origin of the wide use of zeolites in domains such as adsorption, separation or shape-selective catalysis. Besides porosity, an important feature of zeolites lies in the tetrahedral aluminum atoms present as Al³⁺ in their TO₂ lattice, which generates framework negative charges (one per framework Al atom) that are neutralized by charge compensating cations (alkali, protons, transition metal ions...) located in their proximity, in the pores. These cations are easily exchangeable, especially in aqueous solution, a property widely used in processes where removal of undesired ions is needed (additives in laundry detergents, water softener, purification of metal polluted soils or of effluents). The exchange capacity of zeolites also allows the easy tuning of their cationic composition, which is at the basis of their extensive applications as metals supports in heterogeneous catalysis,² as selective gas adsorbents or separators³ or as tunable materials in the photovoltaic, medicine or sensors fields.⁴

To achieve proper control of the zeolite performances, many parameters must be understood, including structural, morphological and chemical properties. Amongst them, not only (i) the nature of the exchanged cations and their content in the solid but also (ii) their location and distribution amongst the cationic sites as well as (iii) their interaction with the surrounding framework and molecules adsorbed in the pores are important. Hence, many studies have been dedicated to the understanding of alkali cation features in these solids, from the pioneering works of Barrer⁵ and Breck and Flanigen⁶ on synthetic zeolites, to the numerous subsequent works as reviewed in the late 90s.⁷ Similarly, the identification of the location and environment of metal cations, including transition ones, in partially exchanged metal zeolites used as catalysts⁸ in DeNO_x,⁹⁻¹² methanol conversion¹³ or methane activation¹⁴ has prompted a tremendous number of works. For these reactions that take place in the gas phase, combined experimental (often spectroscopic) and theoretical (Density Functional Theory, DFT) studies are frequently performed to provide a proper description, at a local scale, of the metal site configuration and of its environment.¹⁵⁻¹⁷ From these works, it is now well established that many parameters such as the structure type, the framework composition or the nature of the

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3 co-cations (ensuring solid neutrality) strongly influence the transition metal cation
4 configuration.¹⁸⁻²³ In addition, the propensity of cations to move from one particular site to
5 another (possibly in a distinct cage) upon addition of molecules, for instance adsorbed water
6 or a reactant, has been largely demonstrated.²⁴⁻²⁶
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10 Nevertheless, due to the entailed computational cost of DFT, accurate theoretical descriptions
11 are currently limited to clusters containing only up to a few 10-100 atoms. For zeolites, in
12 which unit cells usually contain more than 100 TO₂ tetrahedra (i.e. more than 300 framework
13 atoms), this means that only small portions of the overall lattice can be considered. Therefore,
14 DFT alone is not sufficient to describe larger systems such as those involving the migration of
15 a cation from one cage to another, or the adsorption of many molecules, as occurs in cation
16 exchange in aqueous solution. A way to overcome such limitation consists in performing
17 classical molecular simulation (molecular dynamics or Monte Carlo methods), which allows
18 taking into account a much larger (compared to DFT) part of the framework, at the price of
19 using simpler models of interactions between atoms.²⁷ Such force fields are now quite well
20 established for porous aluminosilicates containing light exchangeable cations (e.g. in
21 zeolites²⁸⁻²⁹ and in clays³⁰⁻³³), but not yet in presence of heavy ones as the noble or transition
22 metals involved in catalysts or the heavy elements trapped in adsorbents after nuclear
23 effluents purification. Despite a few recent successes of molecular simulation (e.g. water
24 adsorption in partially exchanged Co-NaX faujasite³⁴), the question of adsorption-induced re-
25 distribution of multivalent cations amongst the possible sites and its coupling to the
26 framework deformations remains largely open. A reason for that is the challenge posed by the
27 simultaneous experimental determination of the framework structure and of the cations and
28 water molecules locations.
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42 In the context of understanding the migration of multivalent cations upon water adsorption (or
43 desorption), we recently demonstrated the power of neutron diffraction. Compared to X-ray
44 absorption spectroscopy (XAS) that gives an average picture of the Ni²⁺ ions environment
45 (coordination, nature, number and distances of neighbouring atoms),^{25,35} neutron diffraction
46 can provide simultaneously (i) structural information (precise identification of framework
47 sites and of average cationic sites occupancies) and (ii) quantitative measurement of the
48 residual water content (thanks to the incoherent signal resulting from neutron scattering by the
49 ¹H hydrogen atoms of water molecules).³⁶ However, the localization of water still remains
50 difficult, especially when different locations and therefore different environments coexist.
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3 In the present work, we combine this neutron scattering approach to classical molecular
4 simulations in order to analyze in detail the redistribution of cations in Ni-exchanged NaY
5 faujasite (7%wt Ni) upon dehydration and its coupling to the deformation of the zeolite
6 framework. Thus, we apply neutron diffraction to monitor both in real time and quantitatively
7 the simultaneous water removal and structural changes upon stepwise heating from 25 to
8 400°C. Then, we perform Monte Carlo simulations of the same system, using the
9 experimental structure and water content identified at each temperature, following our
10 recently introduced method allowing to localize cations from their local environment instead
11 of the crystallographic coordinates of the sites.³⁷ We validate the simulation results by
12 comparing the experimental and calculated Na⁺ and Ni²⁺ distributions among cationic sites
13 (and their evolution with water content). Finally, we discuss the coupling between framework
14 deformation and water and cation locations. Materials and methods are described in Section 2,
15 while results are presented in Section 3.

26 2) MATERIALS AND METHODS

27 2.1) *Ni-NaY faujasite*

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29 Hydrated Ni-NaY faujasite was taken as a representative zeolite system to conduct the study
30 for four reasons. Firstly, this new work is positioned in the continuation of our previous
31 studies on dehydrated Ni²⁺-exchanged NaX faujasite^{35,38} in which we discussed the effect of
32 framework basicity³⁹⁻⁴⁰ on Ni²⁺ configuration. Secondly, faujasite is commonly obtained in
33 the form of octahedral crystal habits of few microns in size, having high crystallinity and few
34 structural defects, being therefore one of the best zeolite candidate to obtain "artifact free"
35 experimental data that can be compared to modeling ones. Thirdly, the faujasite structure
36 (FAU type)¹ has been the most widely studied amongst zeolites and distinction between its
37 several crystallographic cationic sites is now well established (especially for Na⁺-exchanged
38 faujasite);⁷ this should facilitate sites identification even if their exact position and occupancy
39 can vary depending on the cations nature and content, as it has been recently demonstrated for
40 K-FAU,⁴¹ amongst other examples. Fourthly, the FAU structure contains three distinct types
41 of cages (known as supercages, sodalites and hexagonal prisms) between which transition
42 metal ions tend to migrate depending on the hydration state,⁴² which is well suited for a study
43 of cations rearrangement. For nickel, it is currently assumed that its location in hydrated
44 samples is in supercages that are big enough (pore diameters of the order of 13 Å)¹ to
45 accommodate the hexahydrate Ni²⁺ cluster, whereas after dehydration Ni²⁺ is preferentially
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3 found in more confined environments (inside the double 6-membered-rings) where it can
4 optimize its coordination by interacting with the framework oxygen atoms.⁴³⁻⁴⁴
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7 8 **2.2) Sample preparation**

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10 The parent NaY zeolite was a Linde SK-40 zeolite from Union Carbide Corporation with
11 framework unit cell composition $\text{Na}_{58}\text{Al}_{58}\text{Si}_{134}\text{O}_{384}$ (Si/Al ratio = 2.3). Introduction of the Ni^{2+}
12 cations was done by exchange in solution as follows: 1g of hydrated NaY (approx. 0.75g of
13 dry solid) was suspended in 35 mL of distilled water under stirring, then the pH of the
14 suspension (initially at 10.1) was adjusted to 7.5 by adding 5 drops of a 0.5 M HNO_3 solution.
15 Next, 16 mL of a 0.2 M $\text{Ni}(\text{NO}_3)_2$ solution were added drop by drop and the suspension was
16 let under stirring at RT for 5 h. At the end of the ion-exchange process, the pH was 7,
17 preventing protonation of the zeolite.⁴⁵⁻⁴⁶ The solid was recovered by centrifugation and the
18 exchange procedure was repeated 3 times. After the fourth exchange, the solid was washed
19 three times in distilled water (recovered each time by centrifugation) and dried overnight at
20 60°C in static in an oven. The green (hydrated sample) and pink (dried sample) color of the
21 sample attested the Ni^{2+} -exchange process. Before analyses, the sample was let to rehydrate in
22 room atmosphere for several weeks (full ambient rehydration). Its framework unit cell
23 composition was $\text{Ni}_{18}\text{Na}_{22}\text{Si}_{134}\text{Al}_{58}\text{O}_{384}$ as determined by elemental analysis (wavelength
24 dispersive X-ray fluorescence spectroscopy, PHILIPS MagiX apparatus), hence the sample
25 will be hereafter named $\text{Ni}_{18}\text{Na}_{22}\text{Y}$. An important point to notice is the number of nickel
26 atoms per unit cell (18), close to the number of hexagonal prisms per unit cell (16). Note also
27 that this composition corresponds to 7.7 wt% nickel in the dehydrated material (slightly below
28 the nickel content in the exchange solution - 96 mg for 1 g of dry zeolite - due to some nickel
29 loss during centrifugation and washing steps).
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44 45 **2.3) Thermogravimetric analyses**

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47 The water content in the sample at the start of the neutron diffraction experiments was
48 estimated from thermogravimetric analyses (TGA) performed under distinct evacuation
49 conditions. In the first measurement, the hydrated sample (previously kept at room
50 temperature and pressure) was placed in a STD Q600 thermobalance (TA Instrument) and the
51 weight loss was measured while heating from 20°C up to 900°C in flowing air ($20\text{ mL}\cdot\text{min}^{-1}$,
52 1013 mbar). In the second measurement, the hydrated sample was evacuated at 20°C under
53 1.33×10^{-2} mbar during 4 h to reach equilibrium, then TGA was performed up to 800°C on a
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3 TG Mettler Toledo STARe apparatus in flowing air ($100 \text{ mL}\cdot\text{min}^{-1}$). The third experiment
4 was conducted in a Hiden Isochema IGA-001 gas sorption microbalance: the hydrated sample
5 was evacuated at 4×10^{-6} mbar at 20°C overnight to ensure weight stabilization, then the
6 weight loss was measured while increasing the temperature up to 450°C . Note that this
7 maximum temperature was lower than above because being sufficient to ensure full
8 dehydration under high vacuum conditions.
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13 14 **2.4) Neutron Diffraction**

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16 Neutron powder diffraction patterns were recorded on the two-axis powder diffractometer
17 G4-1 of the LLB-Orphée facility at CEA/Saclay (France). This diffractometer is equipped
18 with a vertically focusing 200 pyrolytic graphite monochromator (nominal wavelength of
19 2.4226 \AA) and with an 800-cell multi-detector covering an 80° range in 2θ ($\Delta\theta=0.1^\circ$ between
20 two detectors). The sample (about 300 mg) was introduced in an open vanadium can and
21 loaded in a vacuum furnace ($P\sim 10^{-6}$ mbar) to avoid any parasitic signal arising from the
22 interaction of neutrons with air (notably moisture). A first diffractogram was recorded after a
23 2 hours pumping at room temperature. Then, vacuum was maintained and the temperature
24 was raised stepwise up to 400°C ($2^\circ\text{C}\cdot\text{min}^{-1}$) with intermediate steps lasting at least 60 min at
25 constant temperatures to ensure stable intermediate hydration states (partially hydrated
26 sample). Series of 5 diffractograms in the 2θ -range $8\text{-}88^\circ$ were continuously recorded (15
27 min exposure each), both during heating (1 diffractogram) and steady temperature steps (4
28 diffractograms). After the last step at 400°C , the sample was cooled down to room
29 temperature (still under vacuum) and a last powder pattern was collected (dehydrated sample).
30 In order to analyse the continuous ^1H incoherent signal, the patterns analysed were subtracted
31 from the sample holder signal. Rietveld refinements were performed with the GSAS
32 package⁴⁷ on the complete pattern via the EXPGUI interface.⁴⁸ Moreover, the pressure in the
33 evacuation chamber was continuously monitored to further inform on the water removal
34 process. Additional details on the crystal structure investigation and on Rietveld plots
35 analyses at steady temperatures can be obtained from Fachinformationszentrum Karlsruhe,
36 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crystaldata@fiz-
37 karlsruhe.de) under depository numbers CSD-431352 (150°C), CSD-431353 (200°C), CSD-
38 431354 (250°C), CSD-431355 (300°C), CSD-431356 (350°C), CSD-431357 (400°C) and
39 CSD-431358 (dehydrated back to 20°C).
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2.5) Monte Carlo Simulations

The Monte Carlo (MC) simulations were done following an approach detailed recently.³⁷ They were performed using a simple force field, whereby all interactions between framework atoms, cations and water molecules are described by pairwise additive potentials of the Coulomb (electrostatic interactions) and Lennard-Jones (repulsion and dispersion) forms. The parameters were taken from Jaramillo *et al.*⁴⁹ for the zeolite framework (in particular, Si and Al atoms are described as "T atoms" carrying identical charges), from Dang⁵⁰ for Na⁺ cations and from Jeffroy *et al.*³⁴ for Ni²⁺ cations, together with the TIP4P water model of water.⁵¹ This force field was successfully used in previous studies of water adsorption in Y and X zeolites.⁵²

Periodic boundary conditions were used, electrostatic interactions were computed using Ewald summation and a cut-off equal to half the box length was used to compute Lennard-Jones interactions. At each temperature, the simulation was carried out (i) by considering the experimental framework measured at that temperature (a choice that is further justified in section 3.3) and (ii) by taking this framework as rigid in the force field. Thus, the framework deformations, if any, are correctly taken into account (since established from experiments) while the force field plays no role on the crystalline structure. The corresponding box size was equal to the lattice spacing a deduced from experiments that are listed in [Table 1](#) together with the number of water molecules used for the simulations (N_{w-sim} , see section 3.2 for more details). The numbers of framework atoms and extra-framework cations correspond to one unit cell, namely: Ni₁₈Na₂₂Al₅₈Si₁₃₄O₃₈₄. The convergence of the MC simulations was ensured by carefully avoiding metastable states.³⁷ For cations localization, we used the new approach which defines the type of site for each cation based on its local environment (coordination by different oxygen types).³⁷ This method can be applied regardless of the local structure of the crystalline framework.

3) RESULTS AND DISCUSSION

3.1) Water quantification during stepwise dehydration of Ni₁₈Na₂₂Y

The water content measured by TGA in hydrated Ni₁₈Na₂₂Y (ambient atmosphere) was 27.2 wt%. This corresponds to about 270 water molecules per unit cell. Part of them are expected to be sensitive to evacuation under secondary vacuum at room temperature (conditions applied at the start of the experiments, see Section 2.2), hence it was necessary to evaluate the

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3 effect of pumping and to determine the effective water content in $\text{Ni}_{18}\text{Na}_{22}\text{Y}$ when starting the
4 heating phase for neutron diffraction analyses. To this end, the hydrated sample was
5 submitted to two additional TGA done after an evacuation at either 1.33×10^{-2} mbar or 4×10^{-6}
6 mbar (19.5 and 6.8 wt% losses, respectively). From these sets of three weight loss
7 measurements and knowing the pressure in the evacuated analysis chamber (estimated at
8 5.5×10^{-5} mbar after stabilization in presence of the sample), the initial water content in
9 $\text{Ni}_{18}\text{Na}_{22}\text{Y}$ in the conditions of patterns recording was found to be 11.3 wt% (corresponding to
10 92 water molecules per unit cell).
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17 As soon as heating started and at each subsequent heating step (**Figure 1A**), water desorption
18 from the zeolite was attested by a pressure increase in the chamber (**Figure 1B**), a
19 phenomenon that was fruitfully used as preliminary "real time" monitoring of water removal,
20 even if only qualitative (no quantification of desorbed water). Below 200°C, the pressure
21 profile is quite similar at each step, independently of the temperature range, with a sharp
22 pressure increase when the temperature starts to raise, then a pressure drop followed by a
23 stabilization around 6×10^{-5} mbar when the steady temperature is reached. The water removal
24 process thus appears to be regular between room temperature and 200°C, with no evidence of
25 a temperature at which dehydration would occur predominantly. Moreover, significant
26 dehydration is already seen below 100°C, it is far to be completed at 120°C and is even
27 accentuated at 150°C, and it continues up to 200°C. This demonstrates (i) the existence of
28 distinct water adsorption states characterized by distinct adsorption strengths (as further
29 discussed in Section 3.4) and (ii) the presence of strong adsorption sites where some water
30 molecules are still retained at 200°C even under vacuum. Above 200°C, only few water
31 molecules continue to be desorbed (low pressure values compared to previous ones and rapid
32 stabilization at pressures of the order of 10^{-6} mbar as expected in the chamber in the absence
33 of any desorption process).
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46 In view of the above-described pressure evolution, neutron diffractograms were recorded
47 during both heating (unstable hydration state) and steady temperature phases (pressure
48 stabilization steps). **Figure 2** shows a typical evolution of patterns during heating, taking the
49 20-40°C temperature step as representative example. In this figure, the effect of initial
50 evacuation is also represented. All Bragg peaks in the diffractograms are typical of the FAU
51 structure¹ and their high intensity and small width indicate high crystallinity. These peaks are
52 superimposed on a background arising from the incoherent scattering on the neutron beam by
53 ¹H hydrogen nuclei. From our previous work, these hydrogen atoms in our sample are fully
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3 attributable to those of the water molecules adsorbed in the zeolite.³⁶⁻³⁷ Accordingly, the
4 incoherent signal significantly decreases upon evacuation (compare curves a and b in **Figure**
5 **2**) and the decrease is accentuated with heating (curve c in **Figure 2**). Nevertheless, the
6 background level no longer varies as soon as heating stops and it remains stable during the
7 steady temperature step (curves d to g in **Figure 2**). As already suggested by pressure
8 evolutions, the hydration level thus rapidly reaches a stable state, which brings two important
9 conclusions: (i) each diffractograms recorded at a steady temperature is properly
10 representative of a given (and stable) hydration state and (ii) the decrease of the incoherent
11 signal intensity from one temperature step to another and its overall evolution along heating
12 steps are directly correlated to water removal, giving thus access in real time to residual water
13 quantification depending on temperature.
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21 Such a decrease is illustrated in **Figure 3** that shows the evolution of the patterns with steady
22 temperatures. For better signal/noise ratio, all patterns correspond to the average of four
23 (stable) patterns recorded at the given temperature. In **Figure 3A**, the patterns are reported in
24 a restricted 2θ range ($58-78^\circ$) where the intensity of the diffraction peaks is low enough to
25 allow easy visualization of the concomitant background level variations; in **Figure 3B**, they
26 are shown on a larger 2θ region, in a 3D representation mode. In accordance with pressure
27 evolutions, the incoherent signal decreases regularly between 20 and 200°C , confirming the
28 continuous dehydration of $\text{Ni}_{18}\text{Na}_{22}\text{Y}$ below 200°C . Then the process slows sharply and it is
29 completed at 350°C , with no further change of background intensity at 400°C , neither after
30 cooling to room temperature under vacuum which confirms that the $\text{Ni}_{18}\text{Na}_{22}\text{Y}$ sample
31 remains dehydrated. Knowing the initial water content in the sample before heating (see
32 above), the intensity of the incoherent signal was used to estimate the residual water contents
33 at all steady temperatures ($N_{\text{w-Inco}}$ in **Table 1**).
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44 **3.2) Ni^{2+} and Na^+ cations locations**

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46 Simultaneous to water content, neutron diffraction informs on structural features, particularly
47 on lattice parameters and cations locations. Whatever the temperature, the diffraction peaks in
48 the patterns are typical of FAU (as in **Figure 2**) but their positions (**Figures 3A**) and
49 intensities (**Figure 3B**) vary with heating, revealing framework distortions and changes in
50 cationic sites occupancies as commonly expected in zeolites. Interestingly, the temperature
51 range between 250 and 300°C seems to be critical (associated with drastic changes), while
52 much fewer variations (in peak positions and peak intensities) are seen below 250°C and
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3 above 300°C, respectively. Hence, the predominant (and regular) dehydration occurring
4 below 200°C (as deduced above from pressure and incoherent signal evolutions) has only a
5 very limited impact on the zeolite structure and the major modifications rather take place
6 above 250°C, when the last few water molecules are removed. Another important point to
7 note is the identical peak positions and intensities at 400°C and after cooling down to room
8 temperature (still under vacuum, to avoid rehydration), which reveals that temperature itself
9 has no effect on the structure.
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15 The structures were determined by Rietveld analysis of the patterns at all steady temperatures.
16 **Figure 4A** shows a representative part of the FAU unit cell where the well-established cationic
17 positions are also represented, identified as site I (at the center of hexagonal prisms), sites I' and
18 II' (inside the sodalite cages) and sites II and III (inside the supercages). From this figure, it is
19 clear that clusters consisting of one sodalite cage and one hexagonal prism allow representing
20 all types of cationic sites. Hence, such type of configuration was chosen to illustrate the
21 framework evolutions and cations migrations identified experimentally along the successive
22 dehydration steps (**Figure 4B**). On these images, the cations are positioned at sites potentially
23 occupied, as determined by refinement, but without taking into account the distributions
24 between sites (that are detailed in **Table 1** together with water contents $N_{w-Rietv.}$ estimated from
25 refinements). Note also that only the 150-400°C temperature range is considered because the
26 amount of adsorbed water below 150°C is too large to allow proper Rietveld analysis.
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36 From these data, the most remarkable observation is the migration of Ni^{2+} from sites II and III
37 (in supercages) to more confined sites (I' and II'), with simultaneous exclusion of Na^+ cations
38 from sodalite cages and hexagonal prisms (all in sites II after heating up to 400°C and back to
39 RT). Even if previously suggested,⁵³⁻⁵⁴ this statement is here unambiguously demonstrated on
40 an experimental basis. In addition, the few water molecules still remaining at low temperature
41 (represented as Ow1 and Ow2 in **Figure 4B**, 150 and 250°C) are no longer present at 350°C, a
42 temperature at which almost all Ni^{2+} ions have reached confined sites I (**Table 1**) while Na^+
43 cations have been simultaneously excluded from confined sites I'. This highlights the close
44 relationship between desorption of the last water molecules and cation migration. Nevertheless,
45 a few Ni^{2+} ions are still found in sites II' after full dehydration (clusters 350°C and Back to RT
46 in **Figure 3B** and data in **Table 1**) due to the fact that all sites I are already populated (only 16
47 sites I per unit cell for 18 Ni^{2+}).
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3 **Figure 5** compares, as a function of temperature, the evolution of the numbers of Na⁺ (**Figure**
4 **5A**) and Ni²⁺ (**Figure 5B**) cations in each type of FAU cationic crystallographic sites as
5 estimated from experiments (full lines) and from Monte Carlo simulations (dotted lines). While
6 experiments provide mean values on observables, modeling can give more precise molecular
7 descriptions. As explained in Section 2, the model used in the simulations considers the
8 framework as rigid, hence the deformation occurring upon (de)hydration had to be taken into
9 account. To this end, we used at each studied temperature the framework coordinates (for more
10 details, see CIF files with depository numbers referenced in Section 2.4) and a water content
11 value N_{w-Sim} similar to that deduced from refinement ($N_{w-Rietv}$ values in **Table 1** that also agree
12 with N_{w-Inco} values at all temperatures).

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20 A very good agreement is globally observed between experimental and simulated cations
21 locations. Two apparent disagreements deserve, however, to be discussed. Firstly, at 150°C,
22 Na⁺ is predominantly found either in sites I' (according to experiments) or in sites I (according
23 to simulations). In fact, as illustrated in **Figure 6**, the site identified by Rietveld analysis is a
24 delocalized one with respect to a "true" site I (expected at the center of the hexagonal prism),
25 and it is close (within 1 Å) to sites classically referred to as sites I' (positioned in proximity of
26 the center of the 6-membered ring widows between the sodalite cage and the prism). We
27 already reported similar delocalization of site I for K⁺ or Ni²⁺ on comparable systems as
28 deduced from EXAFS, X-ray or DFT data.^{35,38,41} Therefore, there is no contradiction between
29 experimental and simulated results in this case. Secondly, as already noted above, some Ni²⁺
30 cations are experimentally found in site II' at 350°C (due to the nickel content slightly higher
31 than that of hexagonal prisms), but the simulation rather assigns these cations to sites II. This
32 discrepancy can be understood by considering sites II' as an intermediate position between sites
33 II (where Ni is positioned at low temperature) and I (after dehydration) during nickel migration
34 towards hexagonal prisms. It is worth adding that the low site II' occupancy is in accordance
35 with a former X-ray single crystal structure study on a dehydrated nickel-exchanged natural Y
36 zeolite of composition Ni₂₇Ca₄Si₁₃₄Al₅₈O₃₈₄ by Olson⁵⁵ and with results from Rietveld
37 refinements on synthetic Y zeolites of compositions Ni₁₄Na₂₃H₅Si₁₃₆Al₅₆O₃₈₄,⁵⁴
38 Ni₂₁Na₁₇Si₁₃₃Al₅₉O₃₈₄,⁵⁶ Ni₃₀Na₇Cl₁₂Si₁₃₇Al₅₅O₃₈₄,⁵⁷ and Ni_{19,8}Na_{19,6}Al₅₅Si₁₃₇O₃₈₄,⁴⁴
39 respectively. The fact that it is an intermediate state could explain the absence of identification
40 of such environment by simulations.

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3 I'), (ii) the migration is predominant between 250°C and 350°C, consisting in the
4 displacement of nickel ions towards more confined sites I (and sites II-II' once sites I are fully
5 populated) and (iii) Na⁺ ions are simultaneously expelled from sites I' (close to sites I)
6 because of steric constraints and of electrostatic repulsion, hence they migrate towards sites
7 II. All these data demonstrate the high affinity of bare divalent nickel ions for sites I.
8 Moreover, this affinity governs not only the location of nickel and its migration upon
9 (de)hydration, but also that of sodium (as further discussed in Section 3.4).
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11 Finally, it is worth adding, with respect to sites III (an expected **location** of the hexahydrate
12 Ni²⁺ clusters in fully hydrated FAU),⁵⁸ that their low occupancy agrees with the fact that
13 many water molecules were already removed at 150°C (about 60% compared to water content
14 after evacuation), nickel ions being therefore no longer in a bulky hexahydrate environment.
15

16 3.3) Crystalline framework deformation

17 Upon temperature changes, the crystalline zeolite structure evolves as well, characterized by
18 an overall framework contraction (lattice parameter decreasing from 24.7 Å at 20°C to 24.4 Å
19 at 400°C, **Figure 7A**) that is concomitant with Ni²⁺ cations displacements from sites II
20 towards more confined sites I (**Figure 7C**). Again, this phenomenon does not take place
21 during the predominant 25-250°C dehydration steps but only at temperatures above 250°C
22 when the last few water molecules are removed (**Figure 7B** and N_{w-Rietv} and N_{w-Inco} values in
23 **Table 1**). Moreover, the contraction of the structure reached at 400°C remains after bringing
24 dehydrated Ni₁₈Na₂₂Y back to room temperature (as already noted in Section 3.2, see also
25 data in **Table 1**). This set of observations demonstrates that the decrease in the lattice
26 parameter is definitively neither due to a temperature effect nor associated to a progressive
27 release of water from the cages; it is rather intimately related to the migration of Ni²⁺ toward
28 sites I (as previously proposed by Gallezot *et al.*⁵³) that occurs in a narrow temperature range
29 and is concomitant to the desorption of the last water molecules.
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31 In addition to the global contraction, we also observe a local distortion of the hexagonal prism
32 (**Figure 8**) which is coupled with the above-mentioned shift of sites I with respect to the centre
33 of the prism. The simple force field used in the present study is not able to capture, by itself, this
34 local deformation induced by cationic sites delocalization. Nevertheless, the importance of
35 taking it into account, and therefore to consider an appropriate structure at each temperature to
36 obtain relevant simulations, can be stressed out. This is demonstrated by the cationic
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3 distributions reported in the last line of **Table 1**: in this simulation, water was not considered
4 (aiming at simulating a dehydrated state) but the framework taken for simulation was the
5 "starting" experimental one (measured at 150°C on a partially hydrated sample). Clearly, the
6 simulation in such case does not correctly reproduce the cations distribution since both Ni^{2+} and
7 Na^+ distributions are quite balanced between sites I and II, in place of positioning Ni^{2+} cations
8 predominantly in sites I and Na^+ cations in sites II as was deduced from both (i) experiments at
9 the dehydrated state and (ii) simulations done by considering the appropriate dehydrated
10 structure (data in line 1 of **Table 1**). This underlines the impact of the framework deformation
11 on the cations locations (and vice versa), both being intimately related to water release or uptake
12 upon (de)-hydration as further discussed below.
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20 For the sake of completion, it can be added that diffraction only provides an average picture of
21 the structure, which reflects all components of the system (including empty cationic sites).
22 Nevertheless, the hexagonal prisms (sites I and I'), which are the most prone to deformation
23 upon migration of nickel cations, are never empty (see Table 1), being either occupied by
24 sodium at low temperature (high water content) or fully occupied by nickel at high temperature
25 (low water content). Therefore the established average structures and the observed deformations
26 give correct representations of the local structure of individual (sodium-filled or nickel-filled)
27 hexagonal prisms. Hence, even if not as accurate as more elaborate force fields or ab initio
28 calculations, the present methodology is able to provide, in a rather simple way, correct
29 description of subtle features of a complex system.
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38 ***3.4) Water and cation localization upon (de)hydration***

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40 Since water molecules are experimentally not easy to localize with high precision, the
41 following analysis is based on the molecular simulations only only. However, the good
42 agreement with experiments for cation localization (including non-trivial features described
43 above) and the water molecules seen at 150°C and 250°C in **Figure 4B** (Ow1 and Ow2)
44 support the relevance of this discussion.
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49 In the presence of water, divalent Ni^{2+} cations tend to hydrate due to strong electrostatic
50 interactions with water. Since water molecules are exclusively found in sodalite cages and
51 supercages (due to steric constraints), these interactions can only take place if the cations are
52 placed in sites compatible with the presence of water molecules. In turn, the location of
53 hydrated Ni^{2+} cations also imposes constraints on the other Ni^{2+} and Na^+ cations due to the
54 strong electrostatic repulsion between them. In the range of experimental water contents
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under study, the radial distribution functions (rdf, not shown) demonstrate that water molecules only coordinate Ni^{2+} cations (Ni-O distance ~ 2.3 Å) whereas Na^+ cations are free of water (Na-O distance ~ 5.3 Å, too long for a coordination state). The integral of the rdfs further provide the coordination numbers with, on average, one water molecule per Ni^{2+} cation for the higher experimental water content (i.e. ~ 17 water molecules at 150°C). The evolution of the number of molecules per unit cell in sodalite cages and supercages as a function of temperature is shown in [Figure 9](#).

At 150°C , the approximately equal numbers of water molecules (8-9) in both types of cages contrast with that of Ni^{2+} cations (13 in supercages and 5 in sodalites). In order to clarify this feature, we analyzed in more detail the joint distributions of cations and water species using two measures. On the one hand, for each *individual* sodalite cage or supercage, we computed the probability $P_{\text{cage}}(N_{\text{Na}}, N_{\text{Ni}}, N_{\text{w}})$ to contain simultaneously N_{Na} sodium cations, N_{Ni} nickel cations and N_{w} water molecules. This led us to the conclusion that a given cage never contains more than one cation. On the other hand, for each type of site occupied by Ni^{2+} cations, we determined the probability $P_{\text{site}}(N^{\text{sod}}, N^{\text{sup}})$ to be coordinated simultaneously by N^{sod} water molecules in sodalite cages (which can accommodate only up to 4 water molecules) and by N^{sup} water molecules in supercages. This allowed us to identify the most probable environments for nickel cations and the associated water molecules ([Figure 10](#)). As a whole, nickel cations are mostly hydrated either in sites I', by a single water molecule in a sodalite cage ($\text{SI}'\text{-W}^{\text{sod}}$), or in sites II, by one molecule in a sodalite cage ($\text{SII}\text{-W}^{\text{sod}}$) or in a supercage ($\text{SII}\text{-W}^{\text{sup}}$). Less frequently, configurations with simultaneous coordination by one molecule in a sodalite cage and another in a supercage are observed ($\text{SII}\text{-W}^{\text{both}}$). Finally, one should note that not all cations in such sites are hydrated ($\text{SI}'\text{-noW}$ and $\text{SII}\text{-noW}$). The number of Ni^{2+} cations per unit cell in such environments is reported as a function of water content in [Table 2](#). Note that many other microscopic arrangements are possible, each contributing only to a minor fraction but adding up to 20-30% of the total configurations. Together with the sodium cation distributions of [Table 1](#), these results provide a consistent picture of the evolution of cations along the dehydration process.

For the largest water content (at 150°C), most of the 18 Ni^{2+} cations are hydrated by one water molecule, either in sites II (3 $\text{SII}\text{-W}^{\text{sod}}$, 5 $\text{SII}\text{-W}^{\text{sup}}$, 1 $\text{SII}\text{-W}^{\text{both}}$ and 4 $\text{SII}\text{-noW}$) or in sites I' (3 $\text{SI}'\text{-W}^{\text{sod}}$ and 2 $\text{SI}'\text{-noW}$), while (non hydrated) Na^+ cations occupy mainly sites II (13) and half of the most confined sites, *i.e.* sites I (8). As temperature increases to 200°C , then 250°C , the departure of water (6 water molecules per unit cell at 250°C) is associated with the migration of

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3 Ni^{2+} cations from sites II towards sites I' (the number of hydrated Ni^{2+} cations in both types of
4 sites decreasing, as expected). At that temperature, half of sites I are still occupied by Na^+
5 cations, but the temperature is not yet high enough to allow full water desorption and nickel
6 migration towards non-occupied confined sites I. This significant reorganization only takes
7 places between 250 and 300°C, afterwards sites I are fully populated with (dehydrated) Ni^{2+}
8 cations, which induces, in turn, the full displacement of Na^+ cations toward sites II.
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13 The migration of Ni^{2+} cations toward more accessible sites in the presence of water indicates
14 that the interaction of these ions with water is stronger than with the zeolite framework. To
15 further confirm this tendency, we also performed a simulation considering a water content
16 much larger than the experimental one (114 molecules per unit cell). In this highly hydrated
17 situation, hydrated Ni^{2+} cations lay in the more accessible sites (including 11 Ni^{2+} in site II
18 and 2 Ni^{2+} in site III), while Na^+ cations occupy the remaining available sites (on average 4.5
19 Na^+ in site I, 6.5 Na^+ in site I', 9 Na^+ in site II and 2 Na^+ in site III). In the dry state, the
20 interaction with the framework is maximized not only by shifting toward more confined sites,
21 into the hexagonal prism, but also by deforming it, as already discussed in Section 3.3 and
22 reported in a molecular simulation study of $\text{Na}_{16}\text{Co}_{40}\text{X}$ faujasite.³⁴ Overall, the present study
23 illustrates the complex interplay between cation hydration, cation location and framework
24 deformation, in particular for multivalent ions.
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35 4. CONCLUSION

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38 Upon heating from room temperature up to 400°C, Ni-exchanged NaY faujasite zeolites
39 undergo a series of structural rearrangements involving dehydration, cation redistribution and
40 framework deformation. In the present work, we have characterized the various steps in
41 details by a new approach combining neutron diffraction and classical molecular simulations.
42 On the one hand, the diffraction patterns allow monitoring the zeolite structure and the
43 average cation location depending on the temperature, but also the water content that is
44 quantified in real time from the incoherent signal. On the other hand, molecular simulations
45 provide insights into the correlations between the positions of cations and water molecules.
46 Importantly, the dehydration process is progressive between 20 and 200°C, whereas the
47 migration of Ni^{2+} toward highly confined sites takes place only above 250°C together with the
48 removal of the last few water molecules. Importantly, this cation displacement is closely
49 correlated with a unit cell contraction associated, in turn, with a strong deformation of the
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3 hexagonal prism where the Ni^{2+} cation is hosted. On the contrary, temperature by itself does
4 not play any role in this deformation.
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7 Several strategies can be envisioned to improve the microscopic model used in the present
8 work. In principle, it would be desirable to use DFT calculations to circumvent the use of
9 classical force fields. Despite their own limitations (choice of the functional, basis set, etc),
10 such calculations provide to date the most accurate description of interactions between atoms.
11 Nevertheless, as underlined in Section 2.5, they currently do not allow full unit cell
12 description, in particular in the presence of water. Moreover, they do not allow a proper
13 sampling of relevant configurations at finite temperature, which requires generating enough
14 statistically independent configurations by molecular dynamics or Monte Carlo simulations.
15 Therefore, in the near future, it may be easier to overcome the limitations of the present model
16 by improving classical force fields.
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24 A first obvious step in this direction would be to differentiate Si and Al atoms, which have
25 been treated here as average T atoms. While such a distinction has been shown to play a
26 minor role when only sodium cations are present,⁵⁹ it may be more important in the presence
27 of divalent nickel cations. We are currently investigating this possibility. More importantly,
28 the present work underlines the importance of taking structural changes into consideration.
29 This highlights the need for classical force fields able to estimate the framework flexibility
30 when considering various hydration conditions, in particular in the presence of multivalent
31 ions. The recent developments of a polarizable force field for similar alumino-silicates,
32 namely clay minerals, should benefit the present case of zeolites.⁶⁰⁻⁶¹
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Table 1. Structural characteristics of the $\text{Ni}_{18}\text{Na}_{22}\text{Y}$ faujasite sample at the studied temperatures: (i) lattice parameter (a), (ii) experimental ($N_{\text{w-Inco}}$ and $N_{\text{w-Rietv}}$) and theoretical ($N_{\text{w-Sim}}$) number of water molecules per unit cell and (iii) number of Na^+ and Ni^{2+} cations per unit cell in the different types of cationic crystallographic sites (and total number) as estimated experimentally (Exp) or by Monte Carlo simulations (Sim). The estimated standard deviations are indicated in brackets.

Temperature (°C)	Water content (molecules/u.c.) ^a			a (Å) ^b	Site I				Site I'				Site II				Site III				Total			
	Exp.		Sim.		Na ⁺ -I		Ni ²⁺ -I		Na ⁺ -I'		Ni ²⁺ -I'		Na ⁺ -II		Ni ²⁺ -II		Na ⁺ -III		Ni ²⁺ -III		Total Na ⁺		Total Ni ²⁺	
	$N_{\text{w-Inco}}^b$	$N_{\text{w-Rietv}}$	$N_{\text{w-Sim}}$		Exp.	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.	Sim.
	150	22.6	16.1 (±1.3)		17	24.626 (±0.003)	0	8.9 (±0.9)	1.8	0.3 (±0.5)	12.5	1.3 (±0.9)	4.8	4.7 (±0.7)	7.7	12.6 (±0.3)	6.8	12.9 (±0.1)	0	0	2.2	0	22.2	22.8
200	9.1	6.5 (±0.7)	7	24.611 (±0.001)	0	7.6 (±0.6)	1.2	0.3 (±0.5)	10.5	0	8.6	7.9 (±0.7)	12.2	14.2 (±0.6)	7.3	9.7 (±0.5)	0	0	0	0	22.7	21.8	17.0	17.9
250	5.3	6.1 (±0.9)	6	24.590 (±0.002)	0	7.6 (±0.9)	4.0	3.7 (±1.5)	9.6	0	6.4	4.6 (±1.5)	12.2	14.2 (±0.9)	7.8	9.7 (±1.0)	0	0	0	0	21.8	21.8	16.2	18.0
300	1.9	4.1 (±0.6)	4	24.445 (±0.001)	0	1.5 (±0.5)	12.5	14.5 (±0.5)	6.0	0	0	1.0 (±0.5)	14.7	20.4 (±0.5)	4.4	2.5 (±0.5)	0	0	0	0	20.7	21.9	16.9	18.0
350	0.4	0	0	24.415 (±0.001)	0	0.3 (±0.5)	14.6	16.0 (±0.2)	0	0	0	0	20.4	21.7 (±0.3)	3.2 ^c	2.0 (±0.2)	0	0	0	0	20.4	22.0	17.8	18.0
400	0.0	0	0	24.413 (±0.001)	0	0.3 (±0.5)	15.0	15.9 (±0.2)	0	0	0	0	19.4	21.7 (±0.3)	2.3 ^c	2.0 (±0.2)	2.1	0	0	0	21.5	22.0	17.3	18.0
Back to RT	0.0		-	24.417 (±0.001)	0	-	15.6	-	0	-	0	-	21.4	-	2.0 ^c	-	0	-	0		21.4	-	17.6	-
150 ^d	0.0		0		-	7.5 (±0.7)	-	6.0 (±1.2)	-	0.2 (±0.5)	-	2.0 (±1.2)	-	13.6 (±0.6)	-	9.0 (±0.1)	-	0.3 (±0.5)	-	0	-	21.6	-	17.0

a: Number of water molecules per unit cell estimated from the incoherent signal ($N_{\text{w-Inco}}$), from Rietveld refinements ($N_{\text{w-Rietv}}$) and values used in Monte Carlo simulations ($N_{\text{w-Sim}}$). Note that $N_{\text{w-Inco}}$ was obtained from the mean intensity value of the incoherent signal in the 12-15° 2 θ range (free of diffraction peaks, stable level) for four patterns successively recorded at each steady temperature.

b: At temperatures below 150°C (20, 40, 60, 80, 100 and 120°C, respectively), the unit cell parameter (a , in Å) is 24.692, 24.667, 24.664, 24.658, 24.648, 24.651 and the water content deduced from the incoherent signal ($N_{\text{w-Inco}}$, number per unit cell) is 91.8, 80.9, 73.8, 64.0, 52.7 and 40.1

c: Location in off-centered sites II (appearing as sites II')

d: Cations distributions obtained by Monte Carlo simulations considering the dehydrated framework in place of that experimentally determined at 150°C

Table 2. Distribution of Ni^{2+} cations located in Sites I' and II, in the various water environments described in **Figure 10**. Numbers per unit cell from Monte Carlo calculations are reported as a function of the water content $N_{\text{w-Sim}}$ used for simulations.

$N_{\text{w-Sim}}$	I'		II			
	SI'-noW	SI'-W ^{sod}	SII-noW	SII-W ^{sod}	SII-W ^{sup}	SII-W ^{both}
17	1.8±1.1	2.9±0.4	3.4±0.3	3.2±0.1	5.2±0.1	1.1±0.1
7	6.6±0.8	1.3±0.1	4.6±0.8	1.1±0.1	4.0±0.2	0
6	3.9±1.7	0.7±0.2	4.7±0.6	0.5±0.1	4.5±0.5	0
4	1.0±0.5	0	0	0.5±0.1	2.0±0.4	0.4±0.1
0	0	0	2.0±0.2	0	0	0

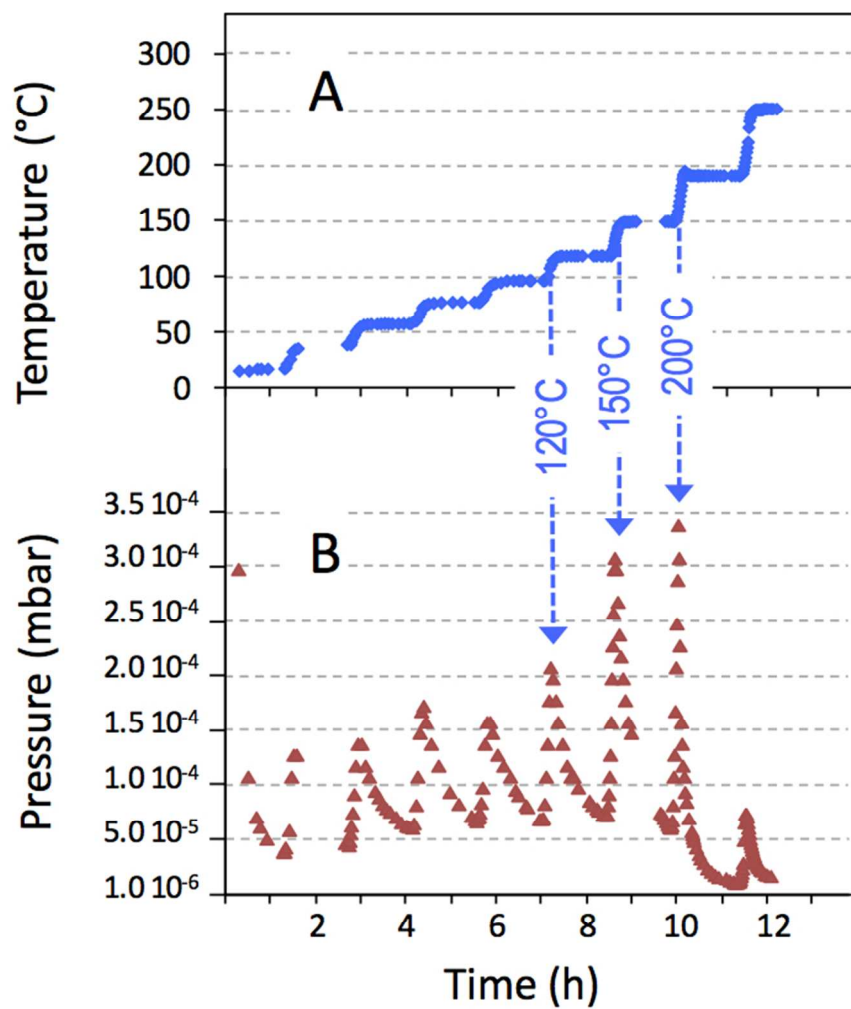


Figure 1: (A) Temperature profile of stepwise heating of Ni₈Na₂₂Y and (B) related evolution of the residual pressure in the vacuum furnace.

137x138mm (150 x 150 DPI)

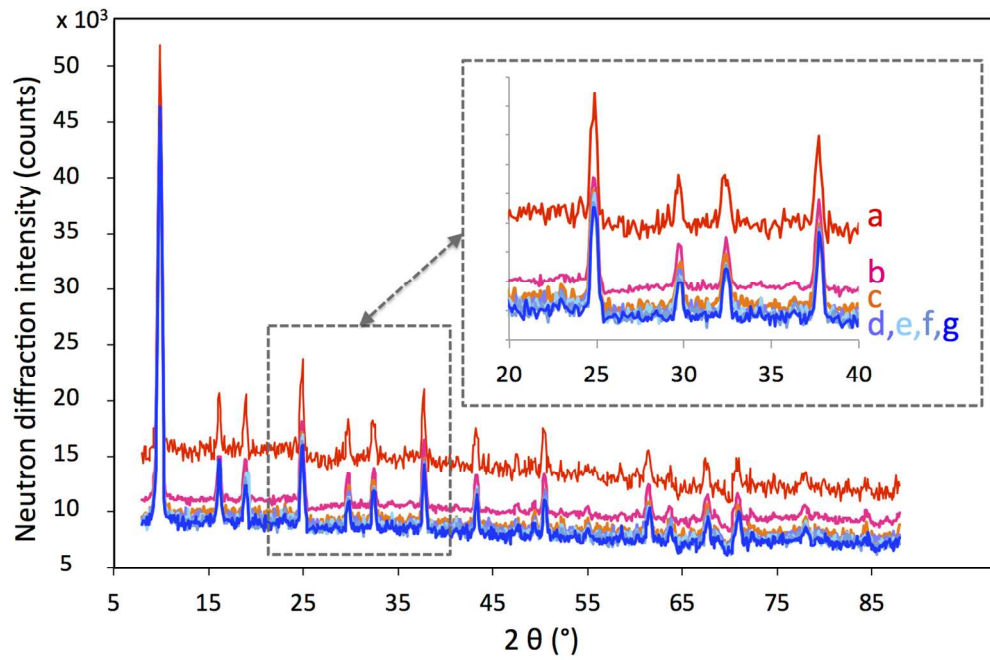


Figure 2: Neutron diffractograms of Ni₁₈Na₂₂Y: (a) before evacuation, (b) after evacuation at 20°C, (c) during heating up to 40°C and (d-g) along the step at steady temperature of 40°C.

254x168mm (150 x 150 DPI)

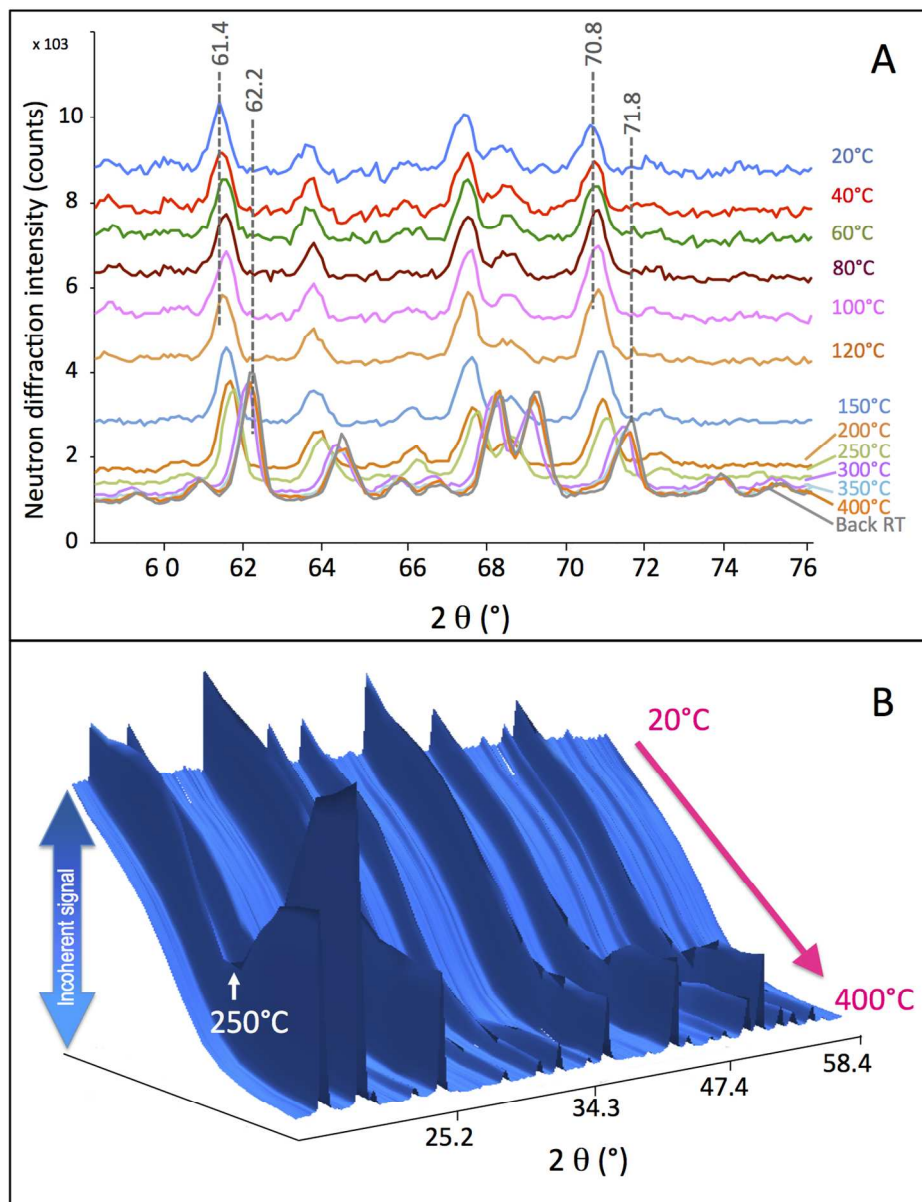


Figure 3: Evolution of the neutron diffraction patterns during heating of Ni₁₈Na₂₂Y previously evacuated at 5.5×10^{-5} mbar at 20°C for 20 min: (A) patterns in the 58-78° (2θ) region showing the progressive decrease of the incoherent signal and the related shifts of diffraction peaks and (B) 3D representation in the 58-78° (2θ) region highlighting the overall loss of incoherent signal together with changes in the relative intensities of the diffraction peaks. The reported diffractograms are the average of four patterns as systematically recorded at each steady temperature.

235x304mm (150 x 150 DPI)

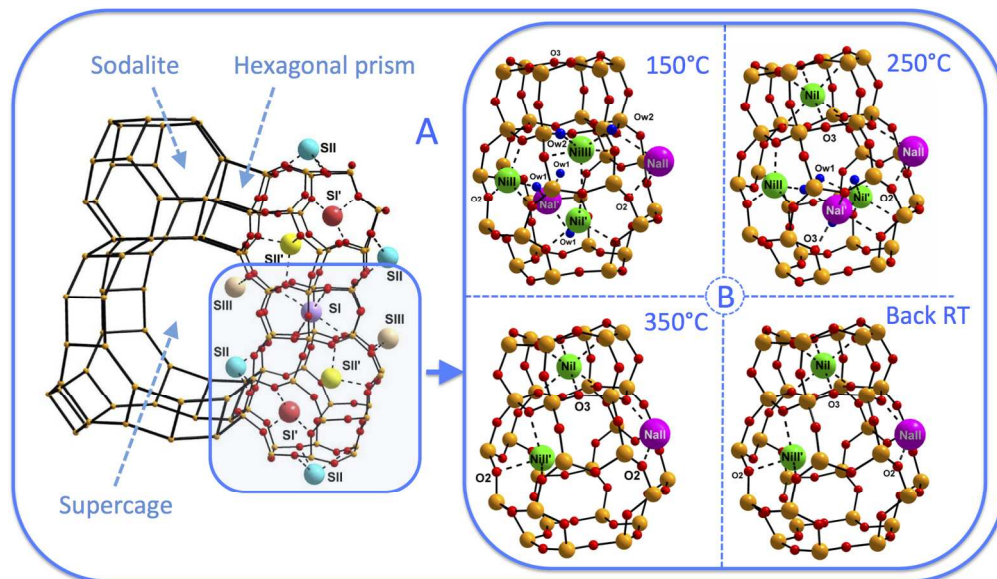


Figure 4: (A) Schematic representation of the FAU structure together with its constitutive cages and known position of crystallographic cationic sites I, I', II, II' and III (their total number per unit cell is 16, 32, 32, 32 and 48, respectively). (B) Experimental structures (clusters limited to a sodalite and a hexagonal prism) obtained from Rietveld refinement of the neutrons diffractograms of $\text{Ni}_{18}\text{Na}_{22}\text{Y}$ after heating at varying temperatures under vacuum; the green (Na^+) and pink (Ni^{2+}) balls show the identified cation positions without taking into account their distribution (which is detailed in Table 1).

315x183mm (150 x 150 DPI)

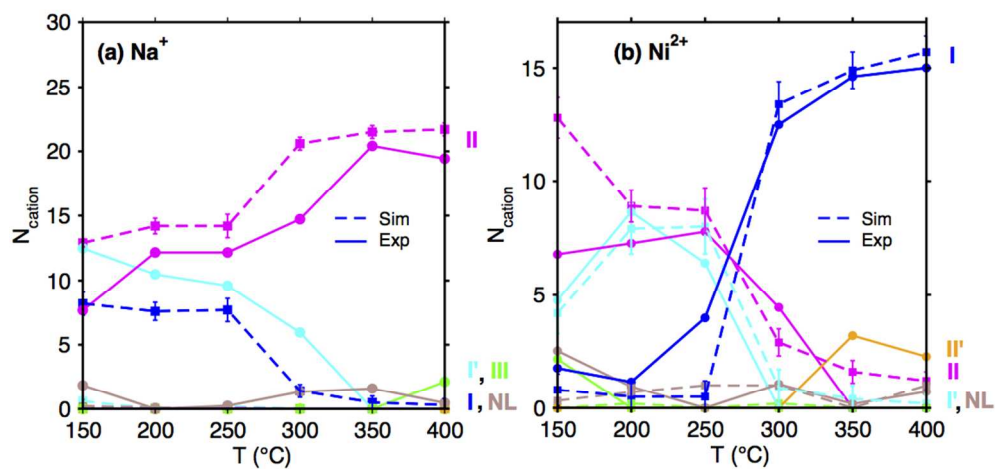


Figure 5: Evolution with temperature of the number per unit cell of (a) Na^+ and (b) Ni^{2+} cations in each type of site (I, I', II, II' and III) as obtained from experiments (full lines) and from Monte Carlo simulation (dotted lines). NL refers to not located cations.

195x98mm (150 x 150 DPI)

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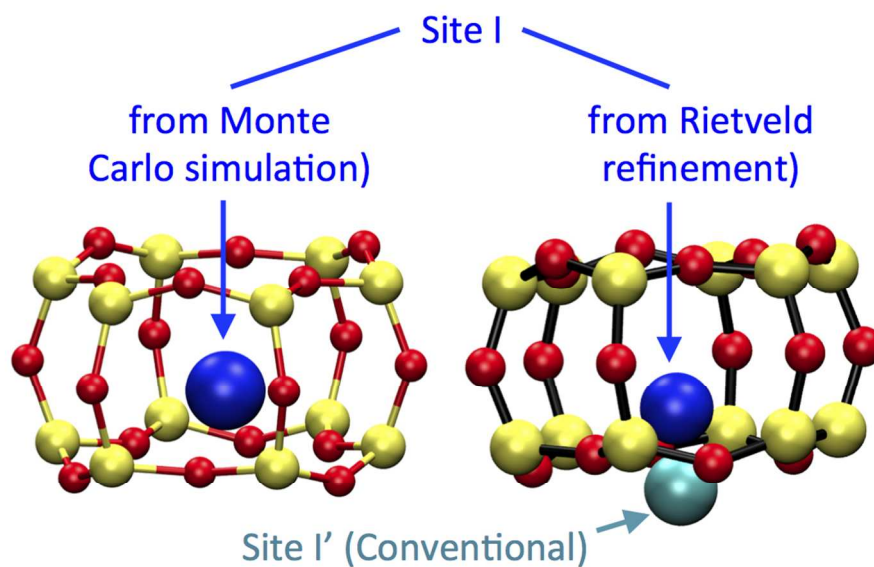


Figure 6: Structures showing the delocalization of site I (Na^+ cations) with respect to the center of the hexagonal prism: delocalized site I from Monte-Carlo simulations for structures at a limited temperature (left structure) and comparison with site I identified as I' in $\text{Ni}_{18}\text{Na}_{22}\text{Y}$ by Rietveld refinement (right structure).

206x121mm (150 x 150 DPI)

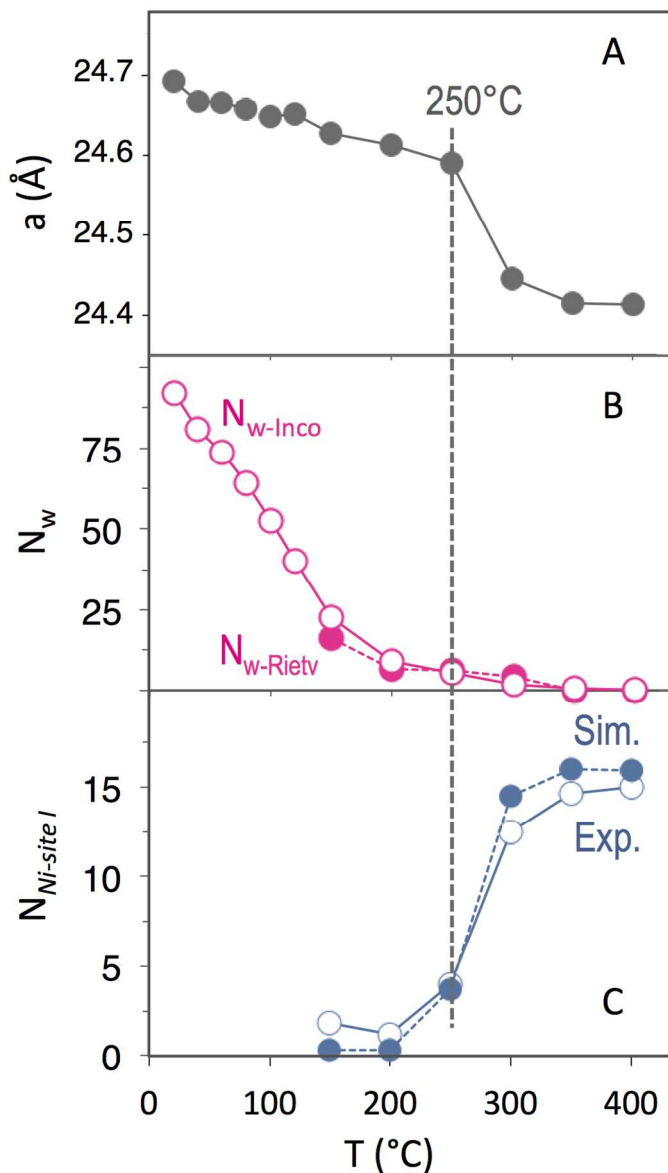


Figure 7: Evolution as a function of temperature of (A) the experimental lattice parameter a , (B) the experimental water content estimated from the incoherent neutron signal intensity ($N_{w\text{-Inco}}$, empty pink circles) and from Rietveld refinement ($N_{w\text{-Rietv}}$, full pink circles) and (C) the number of Ni^{2+} cations in sites I deduced from experiments (empty blue circles) and from simulations (full blue circles). Numbers are given per unit cell. When the fully dehydrated sample at 400°C is brought back to room temperature under vacuum, all the properties remain unchanged (identical to those at 400°C).

238x329mm (150 x 150 DPI)

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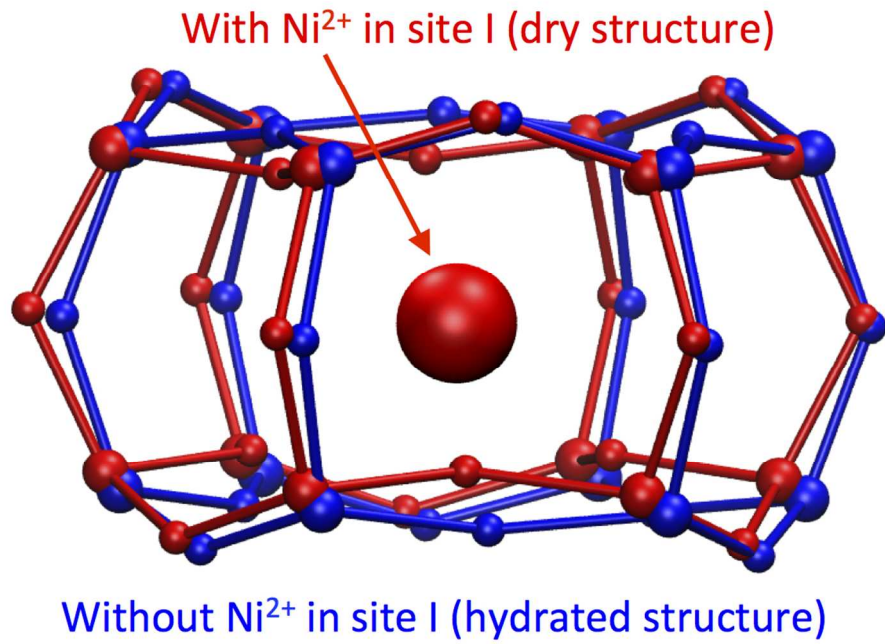


Figure 8: Structural comparison showing the distortion of the hexagonal prisms depending on whether sites I are occupied by Ni²⁺ ions (dry structure obtained at 400°C, in red) or not (hydrated structure at 150°C, in blue).

216x142mm (150 x 150 DPI)

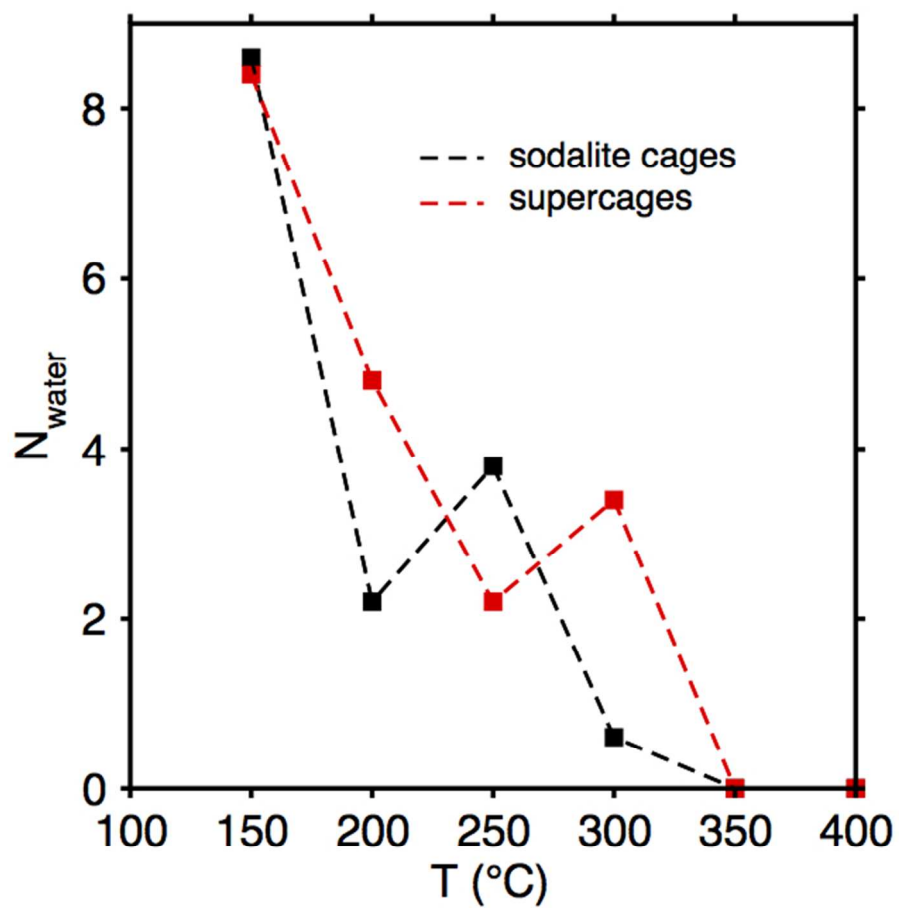


Figure 9: Evolution with temperature of the number per unit cell of water molecules located in sodalite cages and supercages as determined by Monte Carlo simulations.

120x116mm (150 x 150 DPI)

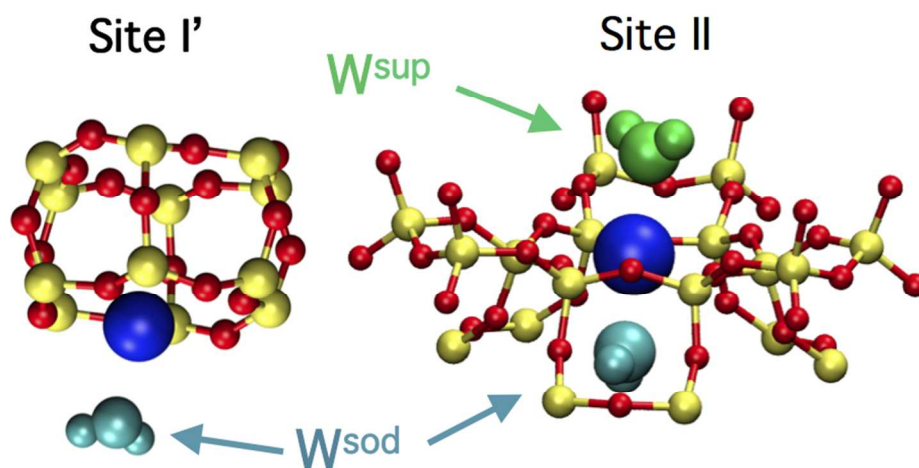


Figure 10: Identification by simulation of the possible hydrated Ni^{2+} environments: Ni^{2+} cations in sites I' can be hydrated by one water molecule in a sodalite cage (SI'-Wsod) whereas Ni^{2+} cations in sites II can be hydrated by one molecule in a sodalite cage (SII-Wsod) or in a supercage (SII-Wsup) or both (SII-Wboth). After full dehydration, Ni^{2+} can be still present in such sites but with no neighbor water molecule (SI'-noW and SII-noW). See Table 2 for the weights of these configurations as a function of water content.

167x82mm (150 x 150 DPI)