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Crystal structure of natural and NH4-exchanged Sasbach faujasite: preliminary test for dealumination of natural faujasite in large crystals

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Abstract:	The interest for the environmental, industrial and technological applications of Si-rich zeolites is very high. Among the large pore zeolites, faujasite is one of the most exploited. This paper reports the results of a study aimed at testing the feasibility of the dealumination of large crystals of a natural faujasite sample (from Sasbach - Kaiserstuhl, Germany), needed for single crystal X-ray diffraction experiments. Single-crystal X-ray diffraction structural refinements of both natural and NH4-exchanged samples are reported and discussed. In the natural faujasite, the localization of almost all the extraframework species -never obtained before - was successful. The ammonium and water molecules sites were localized in NH4-exchanged sample. Ammonium cations occupies only two of the three sites present in the original mineral. The dealumination procedure, based on a hydrothermal process using fluorosilicate salt solution, was adapted for the application to large crystals. Despite this, the treatment induced the amorphization of the faujasite crystals, suggesting that milder conditions are needed.
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Cover letter

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Dear Editor,

Please find attached the manuscript entitled: “Crystal structure of natural and NH4-exchanged Sasbach faujasite: preliminary test for dealumination of natural faujasite in large crystals” by Riccardo Fantini, Rossella Arletti, Linda Pastero, Simona Quartieri, Francesco Di Renzo, Fernando Cámara , Giovanna Vezzalini, that we intend to submit for publication in the special issue of European Journal of Mineralogy dedicated to Professors Stefano Merlino and Giovanni Ferraris

We shall be glad to give you any additional information you would need.

With very best regards, yours sincerely,

Rossella ARLETTI

On behalf of the co-authors

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Crystal structure of natural and NH_4-exchanged Sasbach faujasite: preliminary test for dealumination of natural faujasite in large crystals

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Abstract

The interest for the environmental, industrial and technological applications of Si-rich zeolites is very high. Among the large pore zeolites, faujasite is one of the most exploited. This paper reports the results of a study aimed at testing the feasibility of the dealumination of large crystals of a natural faujasite sample (from Sasbach – Kaiserstuhl, Germany), needed for single crystal X-ray diffraction experiments. Single-crystal X-ray diffraction structural refinements of both natural and NH_4–exchanged samples are reported and discussed. In the natural faujasite, the localization of almost all the extraframework species –never obtained before - was successful. The ammonium and water molecules sites were localized in NH_4-exchanged sample. Ammonium cations occupies only two of the three sites present in the original mineral. The dealumination procedure, based on a hydrothermal process using fluorosilicate salt solution, was adapted for the application to large crystals. Despite this, the treatment induced the amorphization of the faujasite crystals, suggesting that milder conditions are needed.

Keywords: Natural faujasite; crystal structure; single crystal X-ray diffraction; NH_4 exchange; dealumination.

1. Introduction

Zeolites are natural and synthetic microporous materials that, thanks to unique physicochemical properties derived from their structural peculiarities, can be exploited for several purposes, spanning from low-added value agricultural and ion exchange applications to high-added value specialty industrial applications. Beyond their traditional applications as shape-selective catalysts and selective sorbents (Bish & Carey, 2001; Corma, 1977), zeolites can be exploited in several new fields, e.g. gas sensors (Baehtz *et al.*, 2000) and biomedical devices (Lulf *et al.*, 2013). Fine-tuned zeolites with controlled pore architectures and chemistry have improved their performances for technological applications and represent a formidable challenge in material sciences (Corma, 2003; Davis, 2002; Calzaferri *et al.*, 2000; Gigli *et al.*, 2014).

High-silica (HS) zeolites - with high SiO_2/Al_2O_3 ratios - are organophilic materials with strong selectivity towards non-polar organic species (see e.g. Damjanovic *et al.*, 2010; Martucci *et al.*, 2013; Datt *et al.*, 2012). The effectiveness of HS zeolites as selective sorbents for the remediation of wastewater from organic pollutants, such as antibiotics (Braschi *et al.* 2016; Martucci *et al.*, 2014) and hydrocarbons (Arletti *et al.*, 2012; Martucci *et al.*, 2012), has been recently demonstrated. HS zeolites are effective also in other technological applications, such as in energetics. It has been found that, depending on external moderate pressure, non-wetting fluids (e.g. water or water and salt solutions) can intrude into the nanopores of hydrophobic nanoporous materials (Washburn, 1921). During this forced penetration, the mechanical energy is converted into “stored” interfacial energy. Depending on various properties of the porous material (i.e. chemistry and structure), when the pressure is released the system is able to restore, dissipate or absorb the supplied mechanical energy (Arletti *et al.*, 2016). It has been demonstrated that the intrusion of highly concentrated electrolyte solutions (e.g. LiCl, MgCl, etc.) in HS zeolites can change the behavior of the system (Ryzhikov *et al.*, 2015). In these cases, understanding the nature of the intruded specie (water molecules? ions? water + ions?) is of primary importance to tune the system.

One of the most powerful tool to unravel the nature and the amounts of the intruded/adsorbed species and their interaction with the framework is X-ray diffraction. In both the cited fields (i.e. pollutants adsorption and energetics) the experiments are in general performed on powders, firstly because the adsorption and diffusion dynamic is faster when the particle dimensions are small, and secondly because of the larger availability of synthetic HS zeolites in form of micrometric crystal powder. However, X-ray powder diffraction experiments on such complex systems are very challenging, because of the low amount of the guest molecules and for the need of detecting light elements. Even if the technological applications require the tests to be performed on powdered zeolites, from the structural point of view the availability of large crystals would allow single crystal diffraction experiments and, as a consequence, an easier location and quantification of the guests.

The direct synthesis of silicon-rich zeolites depends on two basic requirements: a low alkalinity of the system (needed to increase the silicon incorporation) (Di Renzo, 1998; Zhdanov, 1968) and, in most cases, the presence of organic templates with low charge density, like large tetra-alkylammonium cations (Jacobs & Martens, 1987) or, quite seldom, oxygenated templates (Giordano *et al.,* 1994). Most zeolites can be obtained in a quite wide range of Si/Al ratio. However, several zeolitic structures are unstable at high Si/Al ratio. The metastability of zeolites has prompted the elaboration of specific synthesis conditions for each structure. For instance, among the zeolites with medium pores (pores defined by rings of ten SiO_4 tetrahedra, with openings between 0.4 and 0.5 nanometers), the zeolite ZSM-5 and its all-silica analogue silicalite-1 can be realized with an “easy” protocol of synthesis of millimetric crystals with low aluminum content (Kida *et al.,* 2004).

Among the large pore zeolites (pores with diameter larger than 0.6 nm defined by rings of 12 tetrahedra), zeolite Y (FAU framework type (Baerlocher *et al.,* 2007) is usually synthesized as micrometric crystals with Si/Al = 2.5. The use of organic templates allows the formation of this zeolite with a lower aluminum content (Delprato *et al.,* 1990; He *et al.,* 2016) and crystals size has slightly been increased (Berger *et al.,* 2005) It can be pointed out that natural faujasite occurs in millimetric crystals with the same Si/Al ratio as that of zeolite Y. Hence, large crystals of Si-rich faujasite (Si-FAU) could be obtained by dealumination of a natural sample. The main goal of this work is to test the feasibility of the dealumination of large crystals of the natural faujasite from Sasbach – Kaiserstuhl, by means of a procedure that passes through the NH_4-exchanged form. Moreover, the detailed structure of both natural and NH_4-exchanged faujasite are reported and discussed.

2. Faujasite

Faujasite framework (Figure 1) is obtained when cuboctahedral sodalite cages (or β-cages) are connected to double hexagonal rings (D6Rs) through four of their eight 6-ring windows. The resulting structure is characterized by a tridimensional 12-membered channel system and by large cavities referred to as ‘‘supercages’’ or “α cages”, with a diameter of approximately 12 Å, interconnected via 12 membered-ring (12 MR) windows (7.4 Å free diameter) to four other supercages. The topological symmetry, corresponding to a fully disordered Si/Al distribution, is cubic *Fd-3m*.

A detailed description of the exchangeable cations, which balance the negative charge of the faujasite framework both in X and Y forms, was given by Frising & Leflaive (2008). The relative sites are labeled with Roman numerals in Figure 1. The cation site positions depend on the distribution of the surrounding Al atoms and on the distortion of the zeolite framework. Position and fractional occupancies of the cationic sites change with the Si/Al ratio of the zeolite.

To obtain faujasite dealumination, minimizing the framework destabilization and the consequent structure collapse expected upon Al cations migration (Breck & Skeels, 1985), a sample of faujasite from Sasbach – Kaiserstuhl (Germany) with high SiO_2/Al_2O_3 (3.22 as determined by Rinaldi *et al.,* 1975) was chosen. This locality has been known since 1842 as the principal faujasite occurrence site. The crystal structure of faujasite from Sasbach was determined by Bergerhoff *et al.,* (1958) and by Baur (1964), but in both cases it was impossible to determine the positions of all the cations and water molecules. Baur (1964) located only 43 water molecules out of 260 and 17 cations out of approximately 43 p.u.c.. Up to now, a detailed structure of natural faujasite still lacks.

3. Methods

3.1 Scanning Electron Microscopy

Both natural and NH_4-exchanged crystals were observed by an ESEM Quanta-200 (Fei Company, Oxford Instruments) sited at the “CIGS-Centro Interdipartimentale Grandi Strumenti” of University of Modena and Reggio Emilia. The dealuminated samples were investigated by a JEOL JSM IT300LV (High Vacuum – Low Vacuum 10/650 Pa - 0.3-30kV) Scanning Electron Microscope, equipped with EDS Oxford INCA Energy 200 with INCA X-act SDD thin window detector at the Department of Earth Sciences of University of Torino. All the images and the chemical analyses were obtained in low-vacum operating condition (≤ 1,5Torr) to avoid the sample metallization at 15KV.

EDS semi-quantitative chemical analyses were carried out on natural faujasite (from now on FAU), NH_4-exchanged (from now on FAU-NH_4) and dealuminated crystals to verify the treatment effects. The rarity of Sasbach faujasite hindered performing thermal analyses, hence the water content reported by Rinaldi *et al.* (1975) was assumed (243.44 water molecules p.u.c.).

3.2 NH_4 exchange and de-alumination procedure

The industrial dealumination of zeolite Y is still based on the original hydrothermal steam treatment devised by Kerr (1969). This method, albeit providing the stability and the acid strength required for catalytical applications, generates a high amount of lattice interruptions and leads to partial amorphization of the solid (Engelhardt *et al.,* 1982). Obtaining HS products with less defective structure was attempted by adopting treatments with fluorosilicate reagents, able to introduce Si in the formed Al vacancies (Breck & Skeels, 1985). The dealumination procedure adopted in this work is based on the Skeels (1991) patent, that improved previous methods by introducing a stepwise procedure aimed to obtain more homogeneous HS organophilic zeolites in powders. Since the substitution of Si for Al involves the formation of Al salts - usually called extraframework aluminium species (EFAL) - it is necessary that these salts be water-soluble to facilitate their removal from the product. Since ammonium cations form the most soluble salts, a preliminary NH_4-exchange of the faujasite crystals is necessary.

The cation exchange was performed at high temperature in batch condition using the “static” run mode. Ten faujasite crystals were placed in a Pt crucible along with a 2M NH_4Cl solution prepared with extra-pure distilled water. The Pt crucible was placed in a Teflon autoclave and kept at 80°C for 15 days, the solution was renewed every 3 days. At the end of the exchange procedure the crystals were cleaned with extra-pure distilled water and then dried at room temperature.

To obtain sample dealumination, few crystals were placed in a 15ml PVC test tube and contacted with 10ml of $(NH_4)_2SiF_6$ 2M solution. The test tube was immersed in a hot silicon oil bath heated at 60°C. A stirring heater and a thermocouple were employed to keep the temperature as stable as possible. The solution was renewed four times, every hour. The resulting crystals were washed with NH_4Cl 2M and then with ultrapure water.

3.3 Single crystal X-ray diffraction of natural faujasite

The single crystal X-ray data collection of FAU was performed on a crystal of $0.5 \times 0.2 \times 0.2$ mm^3 on a Bruker-Nonius X8APEX diffractometer equipped with Mo-Kα generator and area detector sited at the “CIGS-Centro Interdipartimentale Grandi Strumenti” of University of Modena and Reggio Emilia. Data collection and reduction were carried out using APEX2 and SAINT (Bruker AXS, 2008) software, respectively, while absorption correction was applied with SADABS (Bruker AXS, 2008). The structure was refined on F_o^2 by standard methods, using SHELXL-2014/7 (Sheldrick, 2015) program implemented in the WINGX v2014.1 suite (Farrugia, 2012).

Least-squares refinement of the peak positions lead to the following cell parameters: a = 24.6906(2) Å, and V = 15052.03 (2) $Å^3$. The hkl reflections were always found to be absent for h+k, h+l, k+l = 2n+1, confirming the F centered lattice and therefore the space group *Fd-3m* found by Baur (1964). Least-squares refinement was carried out in this space group starting from the framework atomic coordinates reported by Baur (1964). The inspection of the Difference Fourier map allowed the location of three cation and nine water molecule sites, all partially occupied. Neutral atoms scattering curves were used for all atoms. The crystal structure was refined using anisotropic displacement parameters for framework atoms, Na and W2 sites. Because of the high number and closeness of partially occupied sites, the displacement parameters of Mg, W1, W4-W11 sites were initially refined – in different refinement cycles respect the s.o.f. – and successively fixed to 0.09 for Mg and 0.12 for the water sites.

Details on the structure refinements are reported in Table 1. Atomic coordinates and displacement parameters are in Table 2 and framework and extraframework coordination distances in Table 3. CIF file is provided as supplementary material linked to this article.

3.4 Single crystal X-ray diffraction of NH_4-exchanged sample

Single-crystal X-ray studies on FAU-NH_4 were carried out on a crystal of 0.42 × 0.32 × 0.28 mm^3 using an Oxford Xcalibur Sapphire2 diffractometer equipped with a CCD area detector at the Dipartimento di Scienze della Terra “A. Desio” (University of Milan, Italy) with graphite-monochromatized Mo*K*α radiation (λ= 0.71073Å). The sample-to-detector distance was 8.1 cm. A total of 2322 exposures (step = 1°, time/step = 30 s), covering a full reciprocal sphere with a redundancy of about 15 were used. Data were integrated and corrected for Lorentz and polarization background effects, using the package CrysAlisPro, Agilent Technologies, Version 1.171.37.31 (release 15-10-2015 CrysAlis171.38.41). Refinement of the unit-cell parameters was based on 13692 measured reflections, and gave the following lattice parameters: a = 24.7567(2) Å, V = 15173.2(2) Å^3. The data were corrected for absorption using the multi-scan method (SCALE3 ABSPACK) with a $d_{\min}$ of 0.60 Å.

The structure was refined with the SHELXL-2013 program (Sheldrick, 2013) in the cubic space group *Fd*-3*m*, starting from the atom coordinates of FAU sample (this work). Neutral atoms scattering curves were used for all atoms. Framework atoms were refined with anisotropic displacement parameters. The location of NH_4^+ groups was modelled at the cation positions observed for Na and K in the natural model. The water molecules were located by the Fourier difference maps.

Details on the structure refinements are reported in Table 1, atomic coordinates and displacement parameters in Table 2 and framework and extraframework coordination distances in Table 3. CIF file is provided as supplementary material linked to this article.

4. **Results and Discussion**

4.1 Morphology and chemical composition

Faujasite crystals employed for this work appears as well shaped octahedra, some of which twinned on (111) (Figure 2). The ESEM-EDS chemical analysis, resulting from the average of four point analyses on three different crystals, gave the following formula: $Na_{12.1}K_{10.8}Mg_{11.0}Ca_{0.8}(Al_{51.7}Si_{141.6})O_{384}\bullet 243.4\ H_2O$. Comparing this composition with that reported by Rinaldi (1975), the Si/Al ratios result very similar, while the extraframework cation content is rather different. In fact, our sample shows high amounts of Na, K and Mg and a very low Ca content, while the sample analyzed by Rinaldi is poor in K and reach in Mg, Ca and Na, corresponding to the following formula: $Na_{12.79}K_{1.83}Mg_{8.79}Ca_{10.74}(Al_{52.72}Si_{139.08})\ )O_{384}\bullet\ 243.4\ H_2O$.

4.2 Structure of the natural sample FAU

In Sasbach faujasite here studied, 26.1 cations and 199.8 water molecules were found against 34.7 and 243.4, respectively, found from the chemical analysis (Table 2, Figure 3). This discrepancy could be due to the presence of additional low occupancy sites exhibiting an electronic density too low to be located from the Fourier map. The three partially occupied extraframework sites are labeled Na, K and Mg, respectively (Table 2), the water molecules are labeled from W1 to W10 according to Olson (1970), while W11 is a new site. The attribution of the cation sites to the three more abundant extraframework atomic species present in the natural phase was based on the distances from the framework oxygen atoms and the water molecules (Table 3).

The Na site is located on the threefold axis in the sodalite cage, near the six membered ring between sodalite cage and D6R, corresponding to site I’ in the classical nomenclature (Frising & Leflaive, 2008). It coordinates three O1, three O3, three W1 and three W2 water molecules (Figure 4a, Table 3). K site, corresponding to site II, is in the supercage near the six membered ring of the sodalite cage. K coordinates three O3 oxygen atoms and three W8 water molecules, assuming a distorted octahedral coordination (Figure 4b, Table 3). Mg site is in the supercage near the water site W6 of Olson (1970) and is at coordination distances with 21 water molecules, distributed on the sites W7, W8, W9, W10, and W11 (Figure 4c).

Site I, at the center of the D6R - usually occupied in the FAU synthetic phases, also exchanged with various cations (see for example K-faujasite (Lim *et al.*, 2007a,b) and Na-Y (Hai *et al.* 2012)) - is empty in our faujasite. This site is empty also in the natural sample studied by Baur

(1964), in the Ca-exchanged faujasite by Bennet & Smith (1968) and in the Ca-X phase by Smolin *et al.* (1989).

Water molecules W1 and W2 - each other coordinated - are in the sodalite cage and coordinate Na and framework oxygen atoms, as well. All the other water molecules are located in the supercage and coordinate both framework oxygen atoms and water molecules. In addition, the water sites W7, W8, W9, W10, and W11 are also coordinated to Mg (Table 3).

4.3 Cation exchange

The images reported in Figure 5a,b show that the morphology of the crystal is preserved after the cation exchange. The chemical analyses reported in Figure 6 confirm that the exchange procedure lead to an almost complete cation exchange, being the residual amount of the original cations left in the FAU-NH_4 cavities lower than 0.5%.

To test the exchange homogeneity in these large crystals, one of the specimen was cut in three fragments, that were analyzed to test whether the thickness of the crystal could hinder the cation diffusivity (Figure 7a,b). The analyses performed in different points, both in the central part and near the crystal surface, indicate that the NH_4Cl solution contacted the whole crystal and hence the exchange can be assumed as homogeneous.

4.4 Structure of FAU-NH_4

The structural refinement of FAU-NH_4 gave a unit cell volume of 15173 Å^3, to be compared to the volume of 15059 Å^3 determined for the natural FAU. The slight volume increase (0.76%) is compatible with that observed in other NH_4-exchanged natural zeolites, like chabazite (Gualtieri & Passaglia, 2006), phillipsite (Gualtieri, 2000), stilbite (Alberti *et al.*, 1999), barrerite (Martucci et al., 2000). This increase can be due to a very slight framework distortion due to the tetrahedra rotation and the increase of the T-O-T angles (Table 3).

The N atoms were found only in two of the three cation sites (now labeled N1 and N2 in **Figure 8** and Table 2, corresponding to the sites N(I') e N(II) found by Lim *et al.* 2010). These two sites – previously labeled Na (I') and K (II) in natural FAU – have higher s.o.f. with respect to FAU. Mg site is empty in the exchanged sample. Of the nine water sites present in FAU, W1, W2 and W4 are now empty and the others have a lower s.o.f. respect to FAU. As a whole, 68.5 N atoms and 138 water molecules were located. The water content is significantly lower than that found from FAU refinement (200). However, some water molecules could be located in the N sites, being the ammonium content higher than expected on the basis of the aluminium content (68.5 *vs.* 51.7 atoms p.u.c.). Moreover, as observed in other NH_4-exchanged zeolites (Yang & Armbruster, 1998; Alberti *et al.*, 1999; Gualtieri, 2000; Martucci *et al.*, 2000; Gualtieri & Passaglia, 2006), the exchange process reduces the space available for the water molecules.

Site N1, with coordinates slightly different from Na (I') (*x,y,z*=0.0829(2) *vs.* 0.0696(1)) is coordinated to three O1 and three O3 framework oxygen atoms, and three N1 atoms (Table 3). Site N2 coordinates three O3 atoms, three O2 and twelve partially occupied water molecules (in the sites W5, W8 and W9, Table 2). As a whole, considering these partial occupancies, the maximum local coordination is less than 9. Figure 8 shows the distribution of the N1, N2 and water sites. From the distances reported in Table 3 it can be assumed that hydrogen bonds are formed between nitrogen and both framework and water oxygen atoms.

The sites occupied by N atoms are the same reported by Zhen & Seff (1999) for NH_4-X and Lim *et al.* (2007, 2010) for NH_4-Y. However, in NH_4-X another site at (0.42, 0.42, 0.42) fractional coordinates is also occupied, while in NH_4-Y nitrogen is found also in the I site (classical nomenclature). The position refined for N (I') (*x,y,z* = 0.0777(2)) by Lim *et al.* (2010) is half way among that of Na (I') in FAU and N1 in NH_4-FAU of our study, which is more inside the β-cage along [111]. Consequently we observe longer N1-O1 distances (2.937(3) Å *vs.* 2.774(5) Å) and shorter N···N distances (2.95(2) Å *vs.* 3.344(11) Å).

With the exception of W5, all the water molecules are at bond distance from at least one framework oxygen atom and form clusters with other water molecules.

4.5 Dealumination of faujasite crystals

Some FAU-NH_4 crystals were submitted to the dealumination procedure, based on the use of ammonium hexafluorosilicate ($(NH_4)_2SiF_6$, AHFS) as dealuminating agent (Skeels, 1991). AHFS achieves a mild dealumination through the isomorphic substitution of aluminum with silicon (Pál-Borbély & Beyer, 2003), and has the advantage of producing materials virtually free of extra framework aluminum (EFAL) species (Triantifillidis *et al.*, 2001). Literature reports that this dealumination process has limitations when performed in aqueous solution, due to the difficulty of controlling the experimental parameters and the degree of dealumination (Garralón *et al.*, 1988). Solid-state dealumination was first used in 1994 to overcome those limitations (Beyer *et al.*, 1994), however in our study the solid state treatment was not possible due the scarcity of faujasite crystals and the necessity not to grind the samples. Consequently, the protocol proposed by Skeels (1991) was followed. The chemical analyses performed on the crystals after the treatment show that all the aluminum is completely released from the faujasite framework (Figure 9a), but the SEM image (Figure 5c) clearly shows the complete crumbling of the crystal. The X-ray diffraction pattern, collected sticking the fragments on a capillary, confirmed the complete amorphization of the dealuminated faujasite sample (Figure 9b). Probably the applied methodology, while resulted effective and not destructive on powders, is too severe in the case of large crystals. This result proves the necessity of milder conditions to obtain the dealumination of large zeolite crystals, for example a lower AHFS concentration, shorter contact time between zeolite and solution, lower temperature. In this first study, the limited availability of faujasite crystals, did not allow the systematic test of different working conditions, that need to be further explored.

5. Conclusions

Aim of this work was to test the feasibility of the dealumination of large crystals of Sasbach faujasite, necessary to study, in great details, the adsorption of organic molecules and their host/guest and host/host interactions inside this organophilic zeolite. A preliminary single-crystal X-ray diffraction study of the sample was performed because detailed siting of the extraframework cations and water molecules was not present in literature. The structure refinement identified three cation sites partially occupied by Na, K and Mg, respectively. Na is hosted in the sodalite cage and Mg and K in supercage. Mg is completely solvated, while Na and K are coordinated both to framework oxygen atoms and water molecules.

The NH_4-exchange, necessary to proceed to the dealumination, was successfully performed. The adopted procedure demonstrated to be effective, since the complete and homogeneous exchange was verified also in crystals of up to 0.06 mm^3. Ammonium occupies only the original Na and K sites. The lower water amount determined with respect to the natural phase is due to the reduced space left for the water molecules after the NH_4-exchange. The results of the adopted dealumination procedure indicate that milder conditions are necessary to avoid the amorphization phenomenon when large crystals are treated.

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Figure and Table captions

Figure 1. Framework of faujasite viewed along [111].

Figure 2. Macro-photograph of Sasbach faujasite crystals.

Figure 3. Structure of FAU viewed along [111]. Only one of each extraframework cation and water molecule site is shown for sake of clarity. The coordination of Na within the sodalite cage, of K and of Mg are reported in 4 (b), (c) and (d), respectively.

Figure 4. Coordination polyhedra of extraframework cation in FAU.

Figure 5. SEM images of natural (a), NH_4-echanged (b) and dealuminated (c) faujasite crystals.

Figure 6. EDS semi-quantitative analysis of natural and NH4-exchanged faujasites.

Figure 7. SEM image (a) and EDS analyses (b) of NH_4-exhanged faujasite.

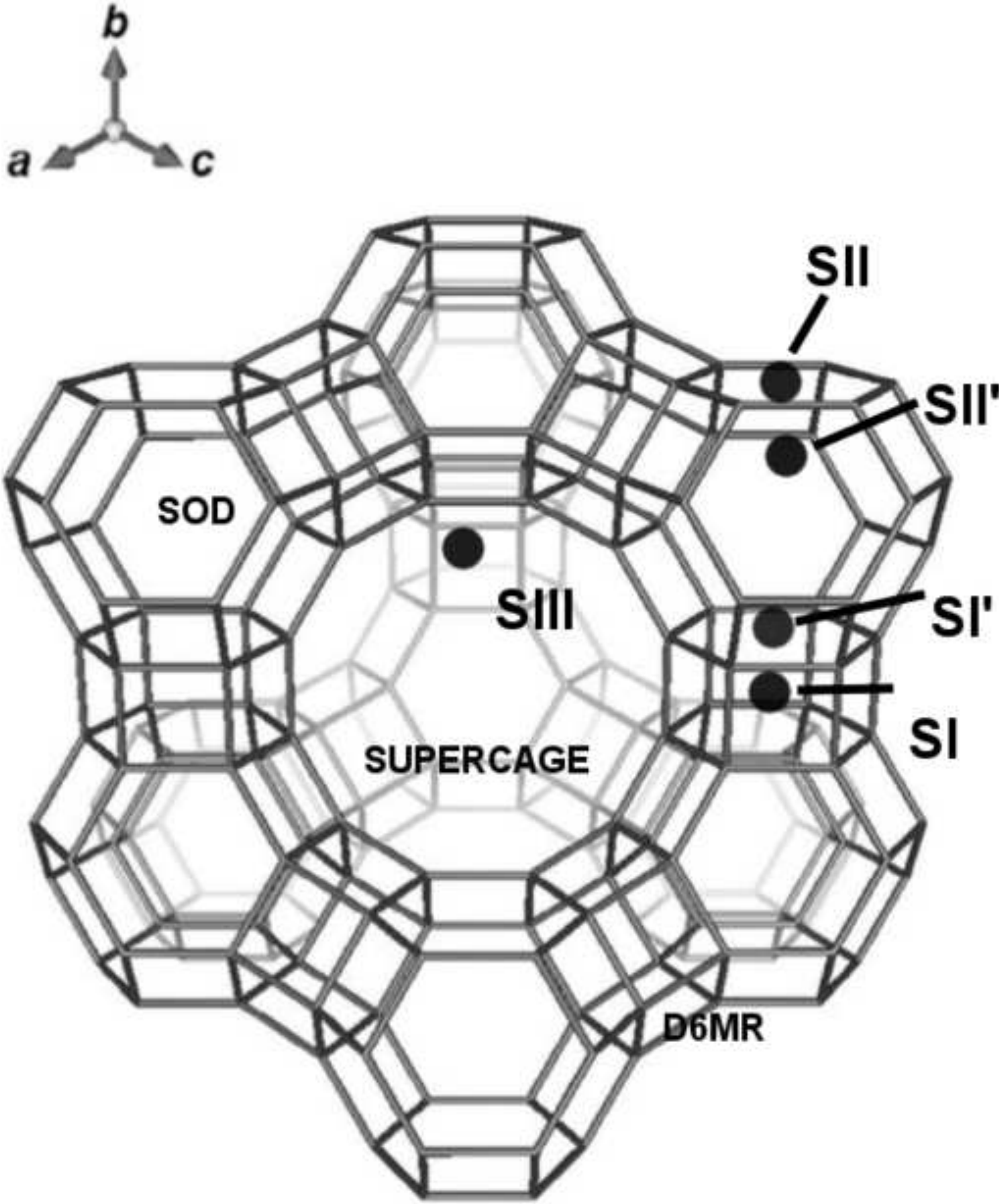
Figure 8. Structure of FAU-NH_4 viewed along [111].

Figure 9. (a) EDS spectrum of dealuminated faujasite; (b) XRD image collected on of dealuminated faujasite.

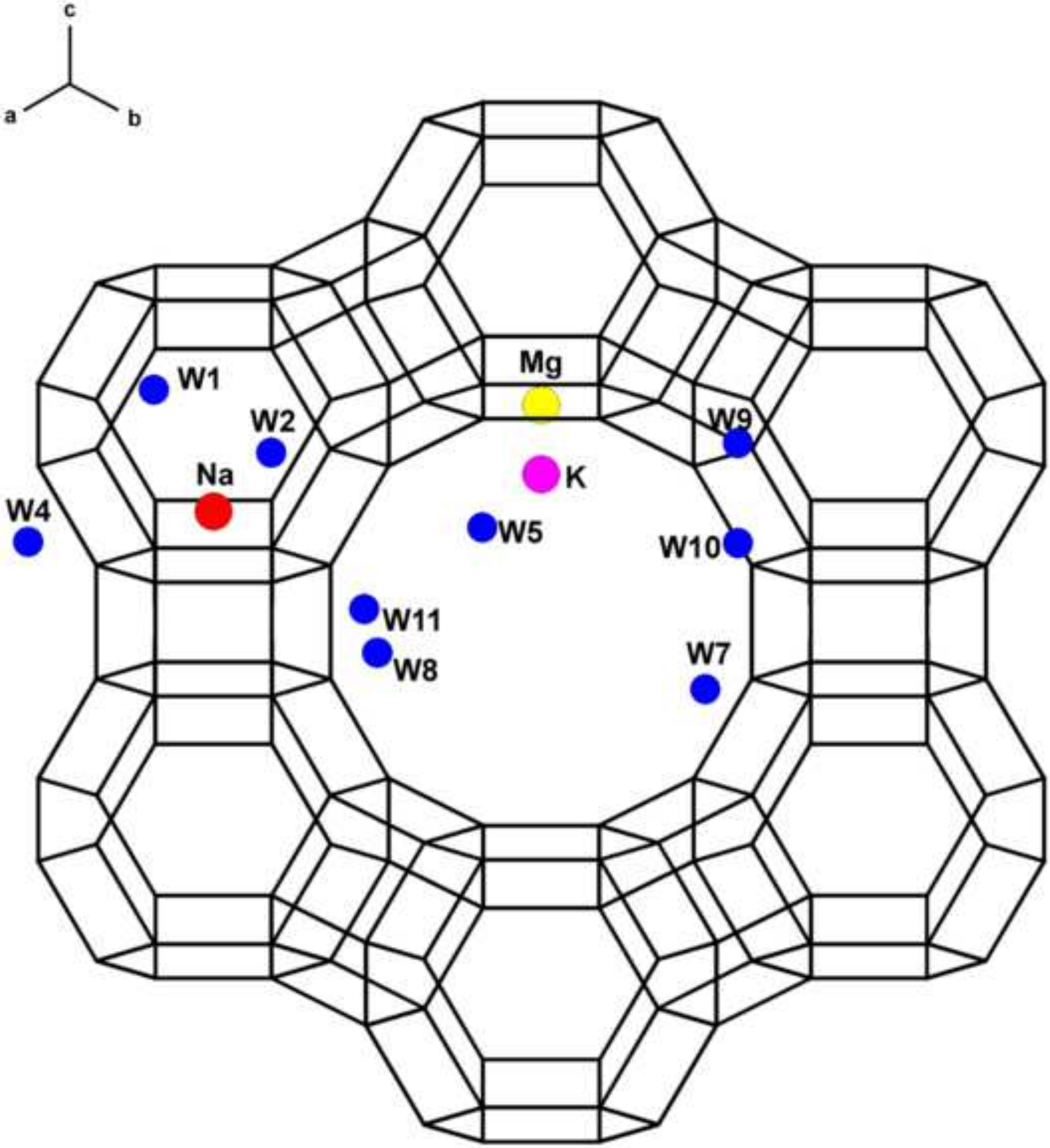
Table 1. Crystallographic and refinement data for FAU and FAU-NH_4.

Table 2. Atomic fractional coordinates and displacement parameters of FAU and FAU-NH_4 (in italic bold).

Table 3. Framework interatomic distances and extraframework coordination polyhedra (< 3.20 Å) of FAU and FAU-NH4. Too short cation-water and water-water distances (acceptable thanks to the not simultaneous presence of the two extraframework species, as testified by the low s.o.f.) are not reported for sake of clarity.


b
a
c
SII
SII'
SOD
SIII
SI'
SI
SUPERCAGE
D6MR


0.2 mm


c
a
b
Mg
W1
W2
W9
K
Na
W4
W5
W10
W11
W8
W7

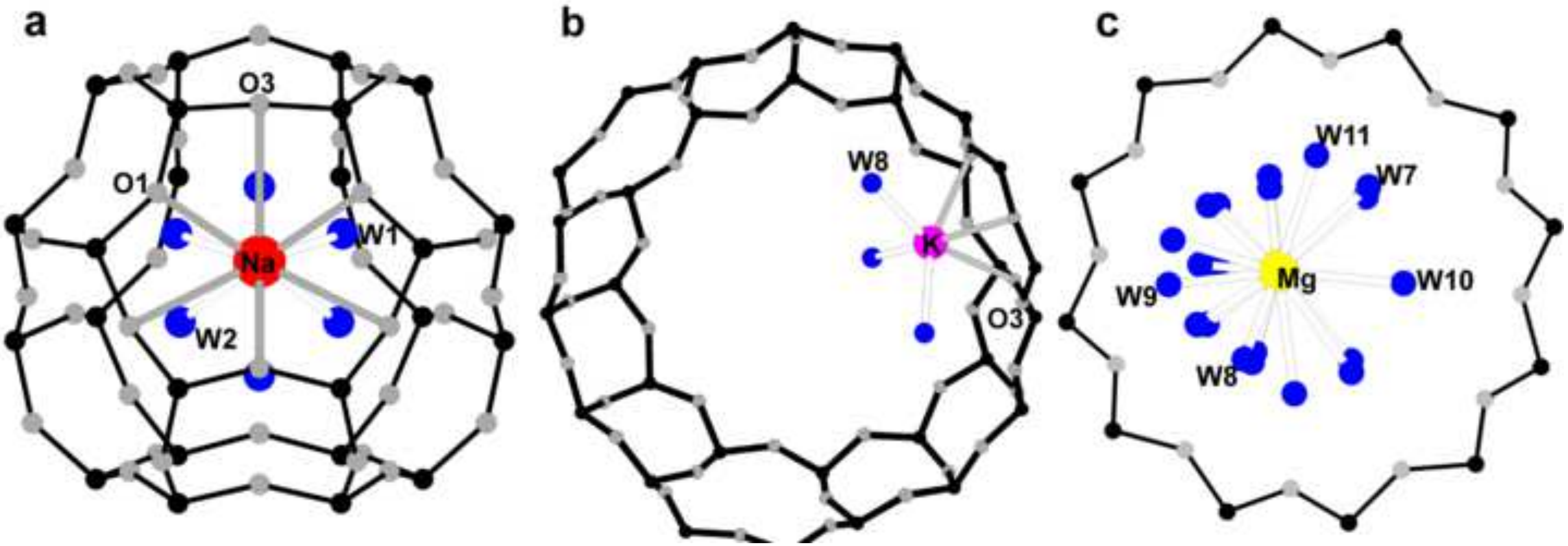

a
O3
O1
Na
W1
W2
b
W8
K
O3
c
W11
W7
W9
Mg
W10
W8

Figure 5

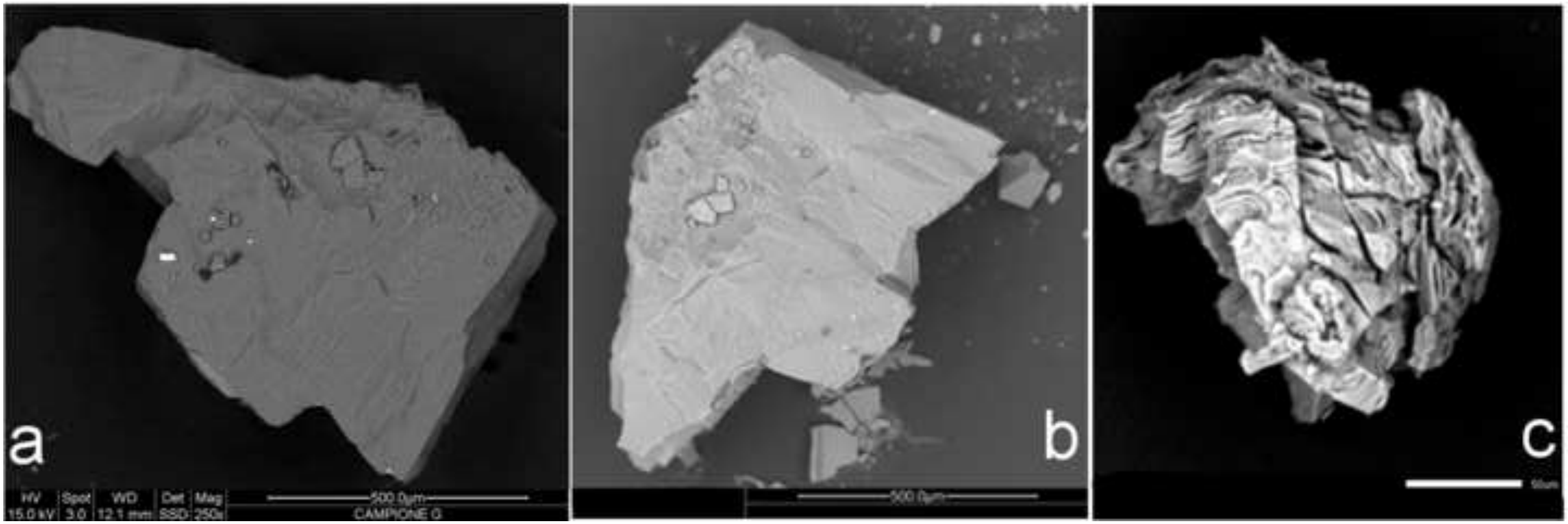
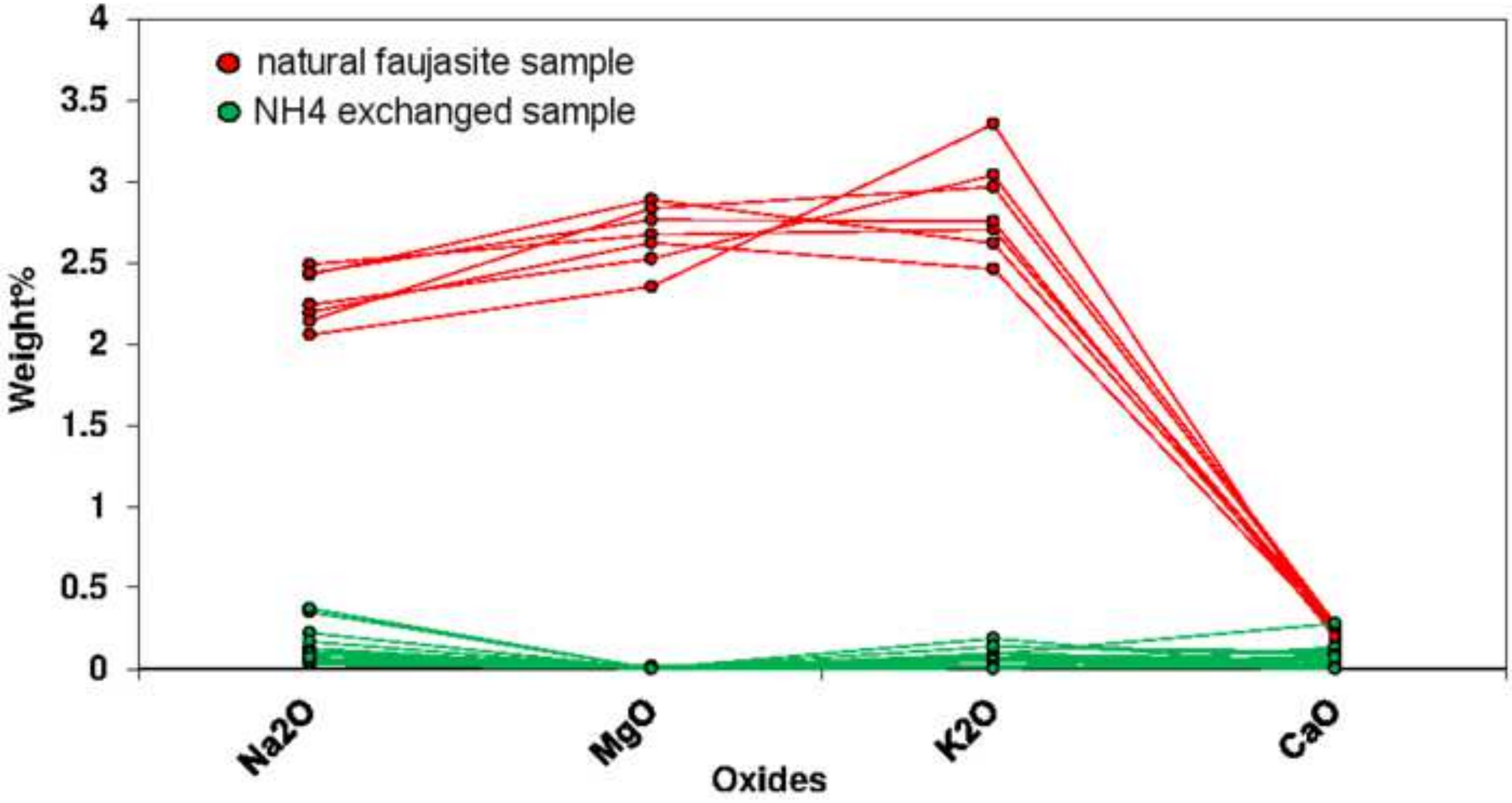
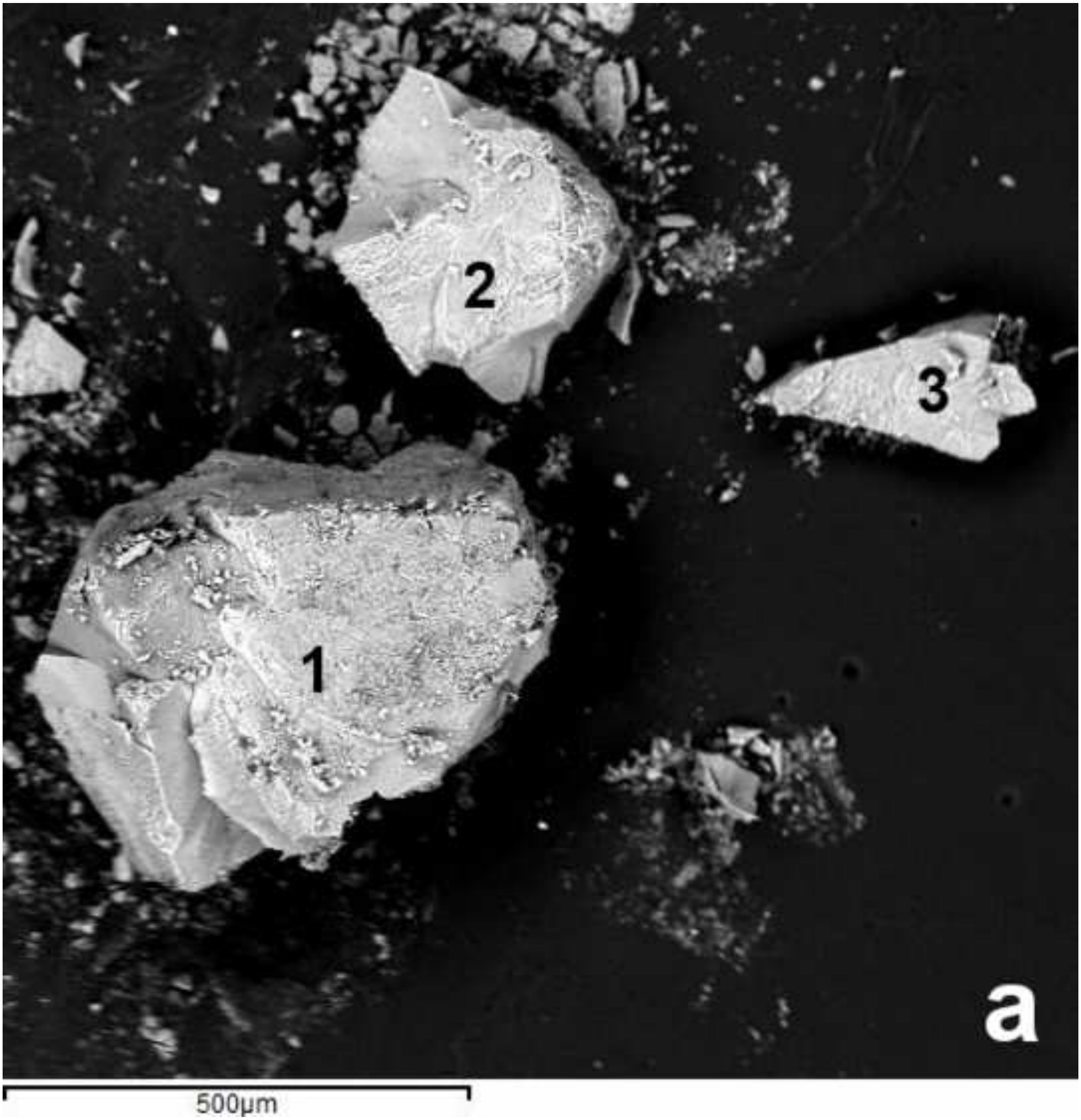
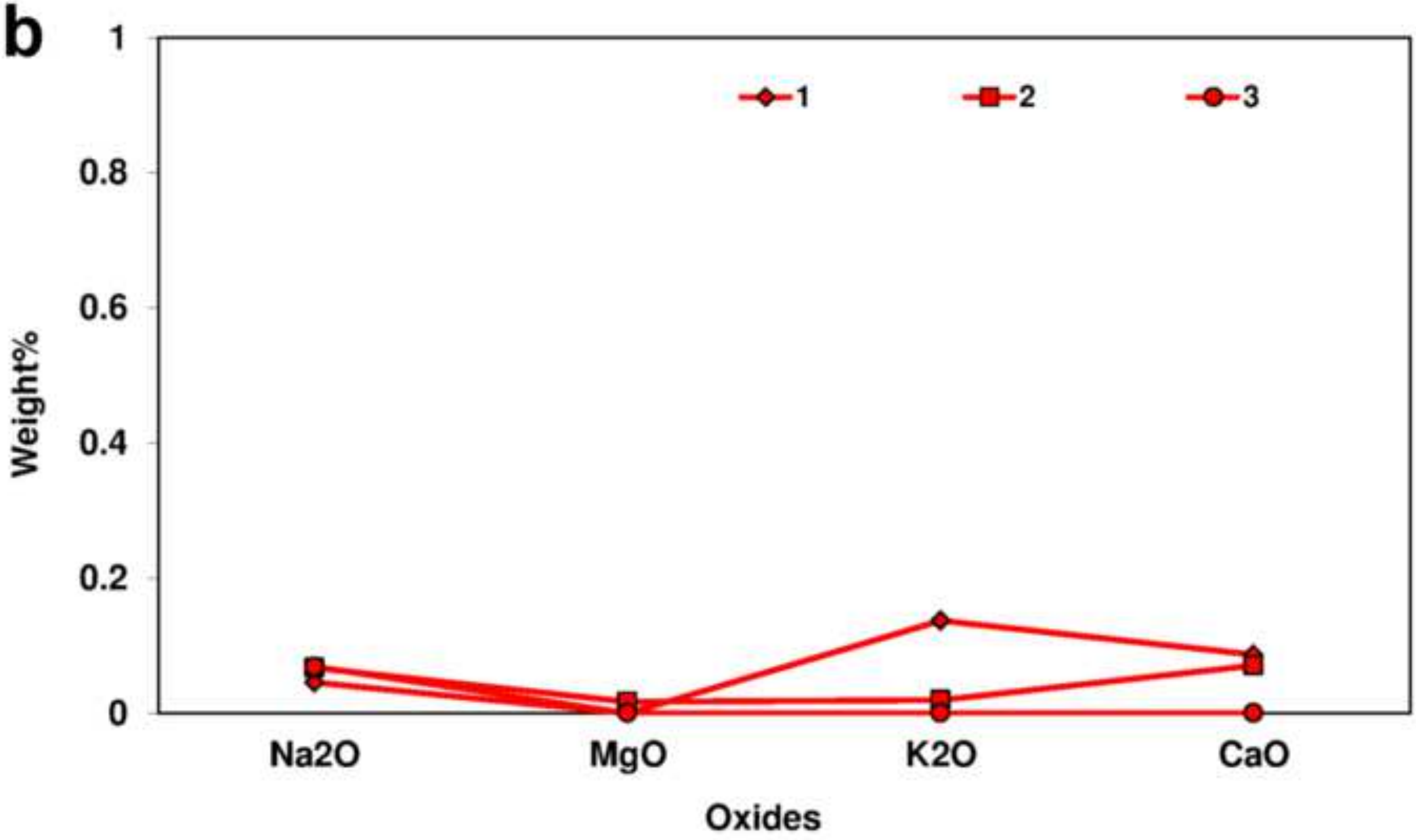

a
HV
15.0 kV
Spot
3.0
WD
12.1 mm
Det
SSD
Mag
250x
500.0µm
CAMPIONE G
b
500.0µm
c
50um

Figure 6



natural faujasite sample
NH4 exchanged sample
4
3.5
3
2.5
2
1.5
1
0.5
0
Weight%
Na2O
MgO
K2O
CaO
Oxides


2
3
1
a
500µm


b
1
0.8
0.6
0.4
0.2
0
Weight%
1
2
3
Na2O
MgO
K2O
CaO
Oxides

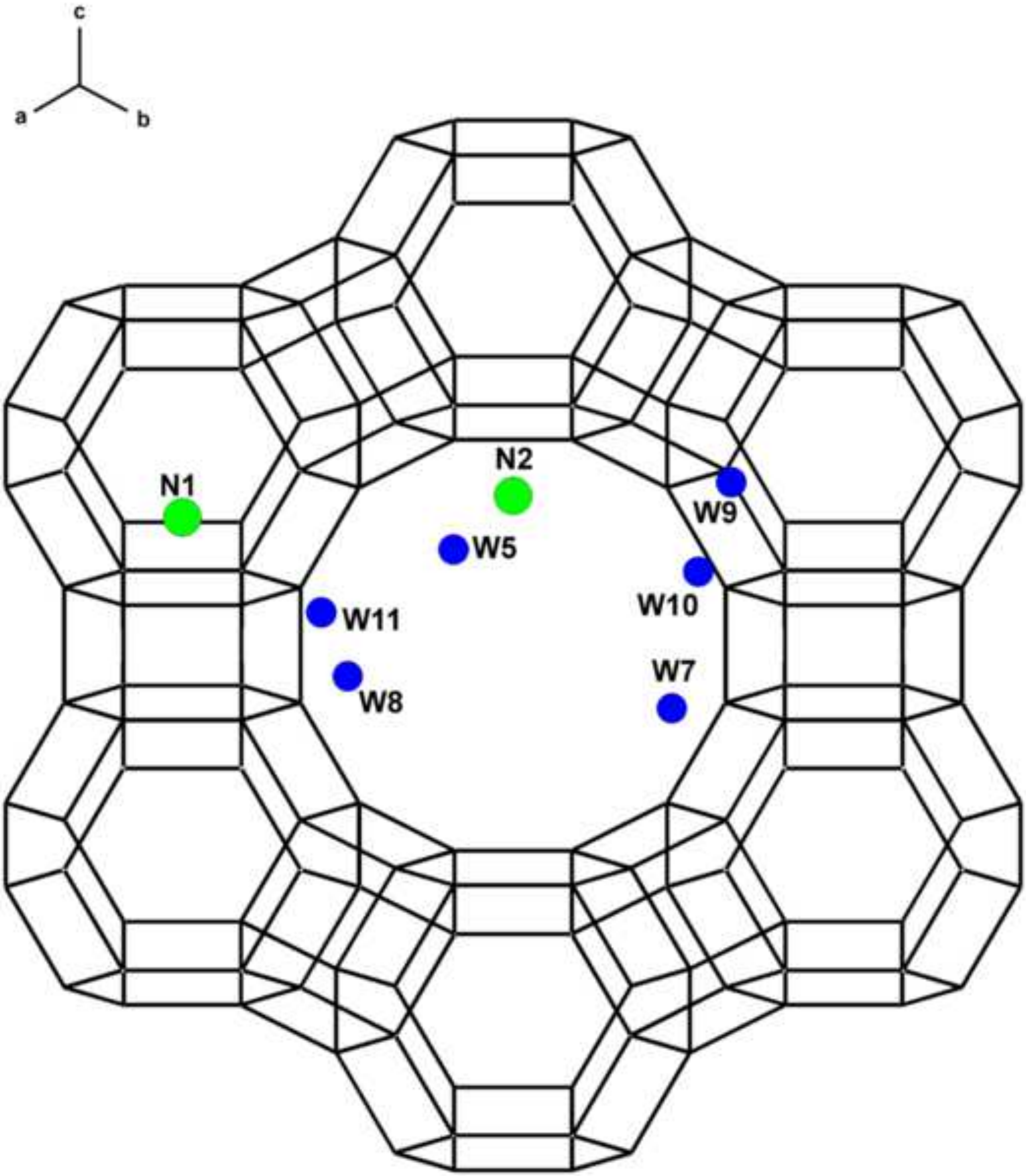
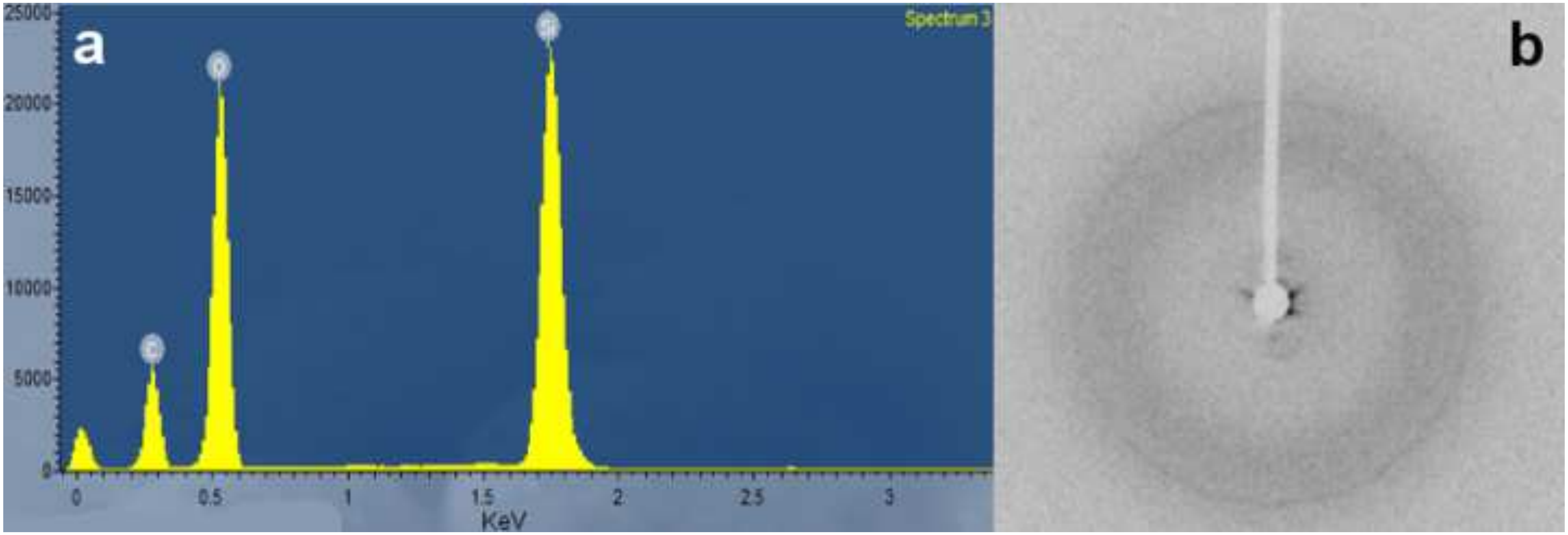

c
a
b
N1
N2
W5
W9
W10
W11
W7
W8

Figure 9


a
b
Spectrum 3
C
O
Si
25000
20000
15000
10000
5000
0
0
0.5
1
1.5
2
2.5
3
KeV

	FAU	**FAU-NH4**
Unit cell parameter (Å)	24.6906(2)	24.7567(2)
Space group	Fd-3m	Fd-3m
h min/max	-35/32	-31/32
k min/max	-38 /20	-40/40
l min/max	-38/13,	-41/40
Unique reflections	1504	1727
Observed reflections I > 4σ(I)	1213	1065
R_{int} (obs)	0.020(9)	0.0893
Number of l.s. parameters	73	67
R_1 (obs)	0.0673	0.0583
R_1 (all)	0.0868	0.1139
wR^2	0.2725	0.1848
GooF	2.001	1.035
Residuals (e^-/Å^3)	+1.26 -1.82	+0.92 -0.49

Table 1. Crystallographic and refinement data for FAU and FAU-NH4.

Table 2

Atom	x	y	z	sof	U11	U22	U33	U23	U13	U12	Ueq
SI1	0.12523(2)	0.94651(2)	0.03619(2)	1	0.0141(3)	0.0152(4)	0.0126(4)	0.0005(2)	-0.0022(2)	-0.0018(2)	0.0140(3)
SI1	***0.12574(3)***	***0.94560(3)***	***0.03597(2)***	***1***	***0.0174(3)***	***0.0198(3)***	***0.0159(3)***	***0.0005(2)***	***-0.0021(2)***	***-0.0018(2)***	***0.0177(2)***
O1	0.17400(7)	0.17400(7)	0.9682(1)	0.5	0.0224(7)	0.0224(7)	0.035(1)	-0.0022(6)	-0.0022(6)	0.0041(8)	0.0264(5)
O1	***0.17274(7)***	***0.17274(7)***	***0.9644(1)***	***0.5***	***0.0247(8)***	***0.0247(8)***	***0.039(1)***	***-0.0009(8)***	***-0.0009(8)***	***0.004 (1)***	***0.0293(6)***
O2	0.17832(7)	0.17832(7)	0.3232(1)	0.5	0.0229(7)	0.0229(7)	0.025(1)	-0.0026(6)	-0.0026(6)	0.0074(8)	0.0237(5)
O2	***0.18014(8)***	***0.18014(8)***	***0.3223(1)***	***0.5***	***0.0250(8)***	***0.0250(8)***	***0.029(1)***	***-0.0018(7)***	***-0.0018(7)***	***0.007(1)***	***0.0264(5)***
O3	0.25277(8)	0.25277(8)	0.1434(1)	0.5	0.0314(8)	0.0314(8)	0.026(1)	0.0054(7)	0.0054(7)	0.013(1)	0.0296(6)
O3	***0.25321(9)***	***0.25321(9)***	***0.1413(1)***	***0.5***	***0.0299(8)***	***0.0299(8)***	***0.030(1)***	***0.0051(8)***	***0.0051(8)***	***0.009(1)***	***0.0300(6)***
O4	0.10624(8)	0.89376(8)	0	0.5	0.0268(8)	0.0268(8)	0.033(1)	-0.0096(7)	-0.0096(7)	-0.0018(9)	0.0290(6)
O4	***0.10712(8)***	***0.89288(8)***	***0***	***0.5***	***0.0293(8)***	***0.0293(8)***	***0.031(1)***	***-0.0069(7)***	***-0.0069(7)***	***-0.006(1)***	***0.0297(6)***
Na	0.0696(1)	0.0696(1)	0.0696(1)	0.098(1)	0.0282(8)	0.0282(8)	0.0282(8)	0.0012(9)	0.0012(9)	0.0012(9)	0.0282(8)
N1	***0.0829(2)***	***0.0829(2)***	***0.0829(2)***	***0.182(4)***	***0.064(2)***	***0.064(2)***	***0.064(2)***	***-0.002(2)***	***-0.002(2)***	***-0.002(2)***	***0.064(2)***
Mg	0.2274(5)	0.2274(5)	0.4843(7)	0.081(3)	0.09						
K	0.266(1)	0.266(1)	0.266(1)	0.019(3)	0.092(7)						
N2	***0.2658(2)***	***0.2658(2)***	***0.2658(2)***	***0.175(8)***	***0.073(3)***	***0.073(3)***	***0.073(3)***	***-0.001(3)***	***-0.001(3)***	***-0.001(3)***	***0.073(3)***
W1	0.060(1)	0.0974(9)	0.0974(9)	0.121(6)	0.12						
W2	0.0817(1)	0.1683(1)	0.0817(1)	0.166(2)	0.040(1)	0.040(1)	0.040(1)	0.001(1)	-0.001(1)	0.001(1)	0.040(1)
W4	0.251(1)	0.282(1)	0.282(1)	0.177(9)	0.12						
W5	0.8203(9)	0.8203(9)	0.227(1)	0.138(8)	0.12						
W5	***0.840(1)***	***0.840(1)***	***0.205(1)***	***0.128(8)***	***0.14(1)***						

W7	0.1856(6)	0.1856(6)	0.4397(8)	0.204(9)	0.12
W7	***0.182(1)***	***0.182(1)***	***0.442(2)***	***0.095(8)***	***0.10(1)***
W8	0.252(1)	0.252(1)	0.386(2)	0.102(9)	0.12
W8	***0.248(1)***	***0.248(1)***	***0.388(2)***	***0.079(6)***	***0.11(1)***
W9	0.8651(9)	0.924(1)	0.1924(9)	0.28(1)	0.12
W9	***0.874(2)***	***0.946(1)***	***0.210(1)***	***0.20(1)***	***0.15(1)***
W10	0.229(1)	0.229(1)	0.421(1)	0.126(8)	0.12
W10	***0.215(2)***	***0.215(2)***	***0.429(3)***	***0.066(8)***	***0.11(2)***
W11	0.785(1)	0.893(1)	0.205(1)	0.20(1)	0.12
W11	***0.773(2)***	***0.924(2)***	***0.197(2)***	***0.15(1)***	***0.14(1)***

Table 2. Atomic fractional coordinates and displacement parameters of FAU and FAU-NH4 (in italic bold).

Table 3

Table 3: Framework bond distances and angles and extraframework coordination polyhedra of FAU and FAU-NH4. Too short cation-water and water-water distances are not reported for sake of clarity. These distances are acceptable when the two extraframework species are not simultaneously present (s.o.f. parameters lower than 0.5)

FAU			**FAU-NH4**		
Si1-	**O1**	1.652(1)		**O1**	1.644(1)
	O2	1.6497(9)		**O2**	1.647(1)
	O3	1.6415(9)		**O3**	1.642(1)
	O4	1.648(1)		**O4**	1.646(1)
Mean		1.648			1.645
Si-O1-Si		140.4(2)	**Si-O1-Si**		145.8(2)
Si-O2-Si		139.2(2)	**Si-O2-Si**		139.5(2)
Si-O3-Si		145.0(2)	**Si-O3-Si**		149.0(2)
Si-O4-Si		138.1(2)	**Si-O4-Si**		137.5(2)
Mean		140.7	**Mean**		143.0
Na-	**O1**	2.513(3) x3	**N1-**	**O1**	2.937(7) x3
	O3	3.115(3) x3		**O3**	3.343(6) x3
	W1	2.91(3) x3		**N1**	2.95(2) x3
	W2	2.474(4) x3			
Mg-	**W7**	1.83(3)			
	W7	2.63(2) x2			
	W7	3.02(2) x2			
	W8	2.37(4) x2			
	W8	2.58(5)			
	W9	2.83(3) x2			
	W10	1.78(3) x2			
	W10	2.68(4) x2			
	W10	2.80(4)			
	W11	2.22(4) x2			
	W11	2.72(4) x2			
	W11	2.94(4) x2			
K-	**O3**	3.04(3) x3	**N2-**	**W5**	3.01(4) x3
	W8	3.01(5) x3		**W8**	3.09(5) x3
				W9	3.20(4) x3
				W9	3.20(4) x3
				O3	3.113(8) x3
				O2	3.308(6) x3
W1-	**W1**	2.83(4) x4			

	W2	2.74(3)			
	O1	2.38(3)			
	O3	3.13(2) x2			
W2-	**W1**	2.74(3) x3			
	W2	3.022(9) x3			
	O3	3.014(4) x3			
W4-	**W8**	2.67(4) x2			
	W9	3.14(4) x2			
	W11	2.95(4) x2			
	O3	2.82(2)			
W5-	**W7**	2.99(2) x2	**W5-**	**W8**	2.78(3)
	W9	2.94(4) x2		**W8**	2.78(3)
	O3	3.11(3)		**W9**	2.75(4)
				W9	2.76(4)
				W11	2.67(4)
				W11	2.67(4)
W7-	**W5**	2.99(2)	**W7-**	**W8**	2.68(6)
	W7	3.19(3) x2		**W10**	2.61(5)
	W8	2.68(5)		**W10**	2.61(5)
	W11	2.78(4) x2		**O2**	2.96(4)
	O2	2.90(2)			
W8-	**W4**	2.67(4) x2	**W8-**	**W5**	2.78(3)
	W7	2.68(5)		**W5**	2.78(3)
	W10	3.11(5) x2		**W7**	2.68(6)
	O2	2.99(4)		**W10**	2.72(6)
				W10	2.72(6)
				W11	3.17(6)
				W11	3.17(6)
				O2	2.90(5)
W9-	**W4**	3.14(4)	**W9-**	**W5**	2.76(4)
	W5	2.94(4)		**W11**	2.75(6)
	W7	3.15(3)		**O4**	2.91(4)
	W10	2.68(3)			
	W10	2.73(4)			
	W11	2.98(5)			
	O2	3.12(2)			
	O4	2.91(2)			
W10-	**W8**	3.09(5) X2	**W10-**	**W7**	2.61(5)

	W9	2.68(3) x2		**W7**	2.61(5)
	W9	2.73(4) x2		**W8**	2.72(6)
	O2	2.98(3)		**W8**	2.72(6)
				W11	3.01(7)
				W11	3.01(7)
				O2	2.92(6)
W11-	**W4**	2.99(4)	**W11-**	**W5**	2.67(4)
	W7	2.76(4)		**W8**	3.17(6)
	W9	2.99(5)		**W9**	2.75(6)
	W11	2.77(6)		**W10**	3.01(7)
	W11	2.79(7)		**W11**	2.61(6)
	O4	2.73(3)		**W11**	2.62(6)
				W11	2.66(9)
				O4	2.84(4)

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