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Local environments of boron heteroatoms in non-crystalline layered borosilicates†

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Boron heteroatom distributions are shown to be significantly different in two closely related layered borosilicates synthesized with subtly different alkylammonium surfactant species. The complicated order and disorder near framework boron sites in both borosilicates were characterized at the molecular level by using a combination of multi-dimensional solid-state nuclear magnetic resonance (NMR) spectroscopy techniques and first-principles calculations. Specifically, two-dimensional (2D) solid-state J-mediated (through-bond) ¹¹B(²⁹Si) NMR analyses provide direct and local information on framework boron sites that are covalently bonded to silicon sites through bridging oxygen atoms. The resolution and identification of correlated signals from distinct ¹¹B-O-²⁹Si site pairs reveal distinct distributions of boron heteroatoms in layered borosilicate frameworks synthesized with the different C₁₆H₃₃N⁺Me₃ and C₁₆H₃₃N⁺Me₂Et structuredirecting surfactant species. The analyses establish that boron atoms are distributed non-selectively among different types of silicon sites in the layered $C_{16}H_{33}N^+Me_3$ -directed borosilicate framework, whereas boron atoms are preferentially incorporated into incompletely condensed Q³-type sites in the C₁₆H₃₃N⁺Me₂Etdirected borosilicate material. Interestingly, framework boron species appear to induce framework condensation of their next-nearest-neighbor silicon sites in the $C_{16}H_{33}N^+Me_3$ -directed borosilicate. By comparison, the incorporation of boron atoms is found to preserve the topology of the $C_{16}H_{33}N^+Me_2Et$ -directed borosilicate frameworks. The differences in boron site distributions and local boron-induced structural transformations for the two surfactant-directed borosilicates appear to be due to different extents of cross-linking of the siliceous frameworks. The molecular-level insights are supported by density functional theory (DFT) calculations, which show the distinct influences of boron atoms on the $C_{16}H_{33}N^+Me_3$ - and $C_{16}H_{33}N^+Me_2Et$ directed borosilicate frameworks, consistent with the experimental observations.

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1. Introduction

Porous materials, such as silica and zeolites, have attracted significant attention over the past decades, because of their diverse properties that have been exploited in numerous industrial applications, including as ion exchangers,¹⁻³ adsorbents,⁴⁻⁶ separation membranes,^{7,8} or heterogeneous catalysts.^{9–11} These applications substantially rely on properties that are often attributed to the presence of heteroatoms (e.g., Al, B, Ga) in silica- or silicate frameworks. Consequently, understanding the influences of the type, quantity, and distributions of heteroatoms in siliceous frameworks is expected to aid improvements in the properties of such materials.¹²⁻¹⁴ This has been a major challenge, in part because characterization of heteroatoms siting is difficult. Even in porous materials with well-ordered structures, such as zeolites, it is challenging to identify the locations of heteroatoms in their frameworks, as diffraction methods tend to provide predominantly average long-range order, except for some types of heavy heteroatoms (e.g., Fe or Ti).^{15–17} Diffraction data of sufficiently good quality (typically using synchrotron

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[†] Electronic supplementary information (ESI) available: Two-dimensional through-bond-mediated ²⁹Si-²⁹Si correlation spectra (Fig. S1). Estimations of the range of the perturbation induced by B incorporation (Table S1). Transverse dephasing time measurements (Fig. S2). Model borosilicate structures using surfactant-mimicking alkylammonium molecules for the charge balance (Fig. S3). Comparisons between experimental and calculated ²⁹Si chemical shifts (Fig. S4). Summary of ¹¹B chemical shift calculations conducted for models of the C₁₆H₃₃N⁺Me₃and C16H33N*Me2Et-directed borosilicates with surfactant-mimicking molecules (Tables S2 and S3, respectively). DFT-optimized models of the reference C16H33N+Me2Etdirected silicate material and corresponding calculations of ²⁹Si chemical shifts (Fig. S5). Illustration of the procedure used to build a borosilicate model with two additional Si-O-Si connectivities (Fig. S6). Description of pseudo-potentials used in DFT calculations (Table S4). Calculated shielding and experimental chemical shifts of reference compounds of known crystal structure (Table S5). Correlation plots between experimental chemical shifts and calculated shielding (¹¹B and ²⁹Si) of known structure (Fig. S7). See DOI: 10.1039/c5cp03448e

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X-rays and/or neutrons on highly-crystalline powders or on single crystals) may provide average mixed compositions for all crystallographic sites in the favorable cases where structure factors between the heteroatom and Si are different (*e.g.*, Fe¹⁸ or Ga,^{19,20} but not for Al²¹). Although this is typically true for boron, the degree of crystallinity and/or the amount of incorporated heteroatoms is in many cases nevertheless insufficient to obtain a reliable refinement of mixed site compositions, especially in the case of layered materials with stacking disorder. And even when the overall siting can be obtained with a good accuracy, this only corresponds to a long-range average that provides no information on the short-range ordering and the local structural distortions that can result from the presence of these heteroatoms in the framework.^{22,23}

Solid-state nuclear magnetic resonance (NMR) spectroscopy is sensitive to the local environments of heteroatoms and their distributions in heteroatom-containing silicates, although the limited resolution of one-dimensional (1D) NMR spectra has often led to ambiguous results.^{24,25} Previous investigations have suggested near-random¹⁹ or relatively unselective distributions of heteroatoms in zeolite frameworks.^{12,25-29} Zeolites with threedimensional (3D) structures are composed of four-coordinate Si or heteroatom sites (abbreviated as T-sites for tetrahedral) that are bonded to four other T-sites via bridging oxygen atoms, which lead to solid-state ²⁹Si NMR signals that are designated as Q^{4} ²⁹Si species. (The Q^{n} notation describes bonding configurations of T-sites, where n refers to the number of connected T-sites for a given T-site.) Incompletely condensed Q³ ²⁹Si sites are in general only present in zeolites in the form of defects, with the exception of a few zeolites where ordered (intrinsic) vacancies have recently been revealed.^{30,31} In siliceous zeolites with 3D crystalline order, subtle differences in Si-O-Si bond angles and lengths lead to ²⁹Si signals that can be resolved from crystallographically distinct T-site environments. However, heteroatoms inserted into these Q4 29Si sites appear to result in 29Si NMR signals that are difficult to resolve, making it challenging to determine the locations of heteroatoms in the frameworks. In rare cases, heteroatoms are incorporated into specific framework sites (e.g., B in the borosilicate zeolite MCM-70³² and layered borosilicate RUB-39,³³ Al^{21,34} or Ga³⁵ in natrolite-type zeolites), leading to resolved ²⁹Si NMR signals. However, heteroatoms are more typically incorporated into silicate frameworks without detectable extents of long-range order, leading to broad signals that provide little information on the distinct local heteroatom environments or their distributions.

In contrast to most zeolites, the ordered 2D frameworks of layered silicates contain incompletely condensed Q³ ²⁹Si framework moieties that are generally intrinsic to their structure, in addition to fully condensed Q⁴ sites.^{36–45} Such Q³ and Q⁴ ²⁹Si species yield ²⁹Si NMR signals over different frequency ranges: *ca.* –92 to –103 ppm and *ca.* –105 to –120 ppm, respectively. Among different types of layered silicates, surfactant-directed layered silicates^{46,47} provide several different types of Q³ and Q⁴ ²⁹Si framework sites into which heteroatoms can be incorporated and potentially distinguished. Here, we focus on surfactantdirected layered silicates that are synthesized in the presence of cationic alkylammonium surfactants CH₃(CH₂)₁₅N⁺Me₃ or $CH_3(CH_2)_{15}N^+Me_2Et$, where $Me = -CH_3$ and $Et = -C_2H_5$;⁴⁶ these different surfactant head groups lead to siliceous frameworks with different structures containing one Q³ site and one Q^{4 29}Si site or two Q³ and three Q^{4 29}Si species, respectively. Furthermore, solidstate ²⁹Si NMR signals for these two layered silicate materials are well resolved and expected to facilitate characterization of distributions of heteroatoms incorporated into their frameworks. Al heteroatoms have previously been incorporated in the $C_{16}H_{33}N^{+}Me_{3}$ – directed layered silicate material, which led to the creation within the framework of acidic sites whose location could not be clearly established from standard 1D NMR measurements.^{48,49} In this work we investigate the intercalation of B heteroatoms into both CH₃(CH₂)₁₅N⁺Me₃ or CH₃(CH₂)₁₅N⁺Me₂Etdirected borosilicate. The weaker acidity of incorporated B as compared to Al heteroatoms opens the way to a modulation of the acid catalytic properties for reactions requiring mild acidic solid catalysts.^{50,51} In addition, borosilicate zeolites are post-synthetically modified by isomorphic substitution of B by other heteroatoms to prepare zeolites that are difficult to synthesize directly.^{52,53}

Among the main strengths of NMR spectroscopy is the ability to unambiguously establish the existence of chemical bonds, which are probed through indirect spin-spin couplings between nuclei, also referred to as *I* couplings. Reviews on the methods to probe and use these couplings in solids have been published.^{54,55} They have been used for many years in zeolites, layered and other types of silica(tes) materials to probe Si-O-Si46,47,56-59 or Si-O-Al60-62 connectivities in the form of through-bond mediated twodimensional correlation experiments or spin-counting experiments.⁶¹ In addition to shedding light on local framework topologies, this is extremely valuable information, particularly when combined with molecular modeling (at the density functional level of theory, DFT), to assist structure determination or refinement,^{63–65} or even describe T–O–T bond angle distributions in the presence of geometrical disorder.⁶⁶ These methodologies furthermore offer the opportunity to identify and/or spectrally resolve otherwise overlapping local environments based on their connectivities, to then distinguish between such variations in the local bonding geometry (geometric disorder) and disorder of chemical origins, such as atomic substitutions.^{23,67,68}

Here, B atom site distributions in $C_{16}H_{33}N^+Me_{3^-}$ and $C_{16}H_{33}N^+Me_{2^-}$ directed layered borosilicates are established and shown to be significantly different. Specifically, the complicated order and disorder near B sites were probed using a combination of solid-state multi-dimensional NMR techniques and DFT calculations. Importantly, our results reveal significantly different B site distributions in the two surfactant-directed borosilicates synthesized under otherwise identical compositions and conditions.

Results and discussion

2.a. Average long-range structures from diffraction and elemental analyses

The locations of boron atoms in surfactant-directed layered silicates are exceedingly difficult to elucidate, because they

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Fig. 1 (a and c) Small- and (b and d) wide-angle powder X-ray diffraction patterns of as-synthesized (a and b) $C_{16}H_{33}N^+Me_2Et$ - (Si/B \sim 52) and (c and d) $C_{16}H_{33}N^+Me_3$ -directed layered borosilicates (Si/B \sim 142) with natural ²⁹Si abundance.

exhibit less extents of long-range order than crystalline structures. Such characteristics make diffraction-based analyses, which are sensitive to long-range framework order, less suitable for this task. For example, powder X-ray diffraction (XRD) patterns of as-synthesized C₁₆H₃₃N⁺Me₃- and C₁₆H₃₃N⁺Me₂Et-directed borosilicates (with natural ²⁹Si abundance) show small- (Fig. 1a and c) and high-angle reflections (Fig. 1b and d) in both borosilicate materials, indicating a high degree of mesoscopic lamellar order and long-range framework order, respectively. The mesoscopic lamellar ordering was visually confirmed elsewhere by high resolution transmission electron microscopy for the siliceous analog of the C₁₆H₃₃N⁺Me₂Et-directed borosilicate material studied here,⁶⁴ which also yields identical XRD and ²⁹Si NMR (see below) signatures.⁴⁷ The XRD pattern of the $C_{16}H_{33}N^+Me_3$ -borosilicate is also similar to the one obtained for the siliceous analog.⁴⁶ The basal distances of *ca.* 3.7 and 3.2 nm extracted from the low-angle reflections for the C₁₆H₃₃N⁺Me₂Etand C₁₆H₃₃N⁺Me₃-borosilicate materials, respectively, indicate similarly high extents of vertical alignment (i.e., perpendicular to the layers) of the surfactant hydrophobic tails. In contrast to these reference silicate materials, however, bulk elemental analyses summarized in Table 1 reveal the presence of boron in the two materials whose XRD patterns are shown in Fig. 1. The C₁₆H₃₃N⁺Me₃- and C₁₆H₃₃N⁺Me₂Et-directed borosilicate materials are shown to have Si/B ratios of 142 and 52, respectively. Based on the XRD and elemental analyses, B incorporation does not appear to induce substantial changes of long-range order in $C_{16}H_{33}N^{+}Me_{3}$ - and $C_{16}H_{33}N^{+}Me_{2}Et$ -directed layered borosilicates, as compared to their siliceous counterparts. However, it is not possible to establish the locations of B atoms in the two borosilicate frameworks by using XRD analyses alone. Consequently, distributions of B sites, as well as their interactions with structure-directing surfactant species and silicon framework sites have still remained elusive.

Table 1 Elemental analyses of $C_{16}H_{33}N^+Me_2Et$ - and $C_{16}H_{33}Me_3N^+$ -directed layered borosilicates (samples with natural ²⁹Si abundance)

| | Atom content (wt%) | | | | | Surfactort | | |
|--|--------------------|------------|------------|--------------|--------------|------------|-------------------------|--|
| Material | С | Н | N | Si | В | Si/B | per Q ³ unit | |
| $C_{16}H_{33}N^+Me_3$ -borosilicate $C_{16}H_{33}N^+Me_2Et$ -borosilicate | 37.5 42.1 | 7.4 7.4 | 2.5 2.7 | 18.4 17.7 | 0.05 0.13 | 142 52 | 0.64 0.71 | |

2.b. Short-range molecular structures from ²⁹Si NMR data

As the XRD analyses, 1D NMR results show a high degree of similarity between surfactant-directed layered borosilicates and the corresponding siliceous materials. 1D ²⁹Si{¹H} CP-MAS NMR of $C_{16}H_{33}N^+Me_3$ - and $C_{16}H_{33}N^+Me_2Et$ -directed layered borosilicates reveal two and five 29Si species, as shown in Fig. 2a and c, respectively. Interestingly, the 1D ²⁹Si NMR analyses appear to be identical to the associated siliceous counterparts, where C₁₆H₃₃N⁺Me₃- and C₁₆H₃₃N⁺Me₂Et-directed layered silicates have two and five distinct ²⁹Si framework sites, respectively.^{46,47} The results indicate that short-range molecular order of the borosilicate and siliceous frameworks is very similar. Furthermore, the narrow ²⁹Si NMR spectral widths (full-width-at-halfmaximum (FWHM): 0.8 to 1.5 ppm) in Fig. 2a and c show highly uniform local ²⁹Si environments present in both surfactantdirected borosilicates. Specifically, C₁₆H₃₃N⁺Me₃-directed borosilicate has one Q³ and one Q^{4 29}Si species, designated as Si1 and Si2, respectively, with a Q^3/Q^4 ratio of 0.50. By comparison,



Fig. 2 Solid-state 1D (left) ²⁹Si(¹H) CP-MAS and (right) ¹¹B echo-MAS NMR spectra of (a and b) C₁₆H₃₃N⁺Me₃- (Si/B ~ 142) and (c and d) C₁₆H₃₃N⁺Me₂Et-directed layered borosilicates (Si/B ~ 52), respectively. The spectra were all collected at 17.6 T and room temperature. Distinct ²⁹Si and ¹¹B species with their corresponding chemical shifts are described in detail in each MAS NMR spectrum.

two Q³ (Si1 and 2) and three Q⁴ ²⁹Si species (Si3, 4, and 5) are present in the C₁₆H₃₃N⁺*Me*₂*Et*-directed borosilicate with an approximate Q³/Q⁴ ratio of 0.67 (from quantitative ²⁹Si NMR spectra not shown here). Two-dimensional experiments probing the existence of ²⁹Si–O–²⁹Si linkages, which are shown in ESI,[†] Fig. S1 and described in the corresponding captions, also indicate that the topologies (*i.e.* coordination sequences and ring structures) are also identical in the borosilicate and the siliceous analogs. Nevertheless, the ²⁹Si NMR analyses do not provide information that may be directly linked to the possible presence of B species in the frameworks of either of the surfactant-directed borosilicate materials.

2.c. Probing the local structure around boron heteroatoms using ¹¹B NMR spectroscopy

In contrast to XRD and ²⁹Si NMR analyses, ¹¹B NMR spectroscopy provides local information on ¹¹B species in borosilicates. For example, 1D ¹¹B echo-MAS reveals three and one four-coordinate ¹¹B sites in the C₁₆H₃₃N⁺Me₃- and C₁₆H₃₃N⁺Me₂Et-directed layered borosilicates, as evidenced by various ¹¹B NMR signals (FWHM: 0.3 to 0.5 ppm) shown in Fig. 2b and d, respectively. Both $C_{16}H_{33}N^+Me_3$ - and $C_{16}H_{33}N^+Me_2Et$ -directed silicate structures are composed of four-coordinate framework Si sites only. B species (and by extension ¹¹B nuclei) incorporated in the framework, upon substitution of any of these sites, would consequently become four-coordinated as well. In this regard, B incorporation is expected to modify the host inorganic structures, primarily because of different sizes between Si and B atoms, but also because of their different valence states, which will imply a local charge-compensation mechanism around incorporated B atoms. To support such a hypothesis, the elemental analyses (i.e., Si/B ratios) were used to estimate the possible fraction of ²⁹Si NMR signals that result from ²⁹Si sites near ¹¹B species and are therefore expected to differ from the signature of the corresponding reference silicate systems. The detailed description and results are summarized in Table S1 (ESI⁺). Specifically, the results indicate that more than 15% of the ²⁹Si NMR signals would be affected if substantial influences of ¹¹B sites on their neighboring ²⁹Si species exist in the C₁₆H₃₃N⁺Me₂Et-directed borosilicate (assuming for instance a perturbation range of 5 Å or more). However, this estimation is in stark contrast to the 1D ²⁹Si NMR spectrum (Fig. 2c), showing that the $C_{16}H_{33}N^+Me_2Et$ -directed borosilicate has very similar ²⁹Si environments to its siliceous analog. Such facts suggest that framework B species exhibit highly localized influences on their nearby ²⁹Si neighbors (very likely less than 5 Å). The ¹¹B NMR analyses demonstrate a single type of well-defined ¹¹B environment (0.3 ppm fwhm, Fig. 2d) and

suggest that B atoms seem to incorporate into one type of Si sites in the $C_{16}H_{33}N^+Me_2Et$ -directed borosilicate. This is possibly a similar situation to the case of crystalline layered borosilicate RUB-19, of composition $[Si_9O_{18}(OH)][Me_2Pr_2N^+]\cdot xH_2O$,³³ for which the authors concluded that the small amount of B atoms incorporated were preferentially siting in a single T site based on a relatively sharp (*ca.* 1 ppm fwhm) dominant ¹¹B NMR peak and XRD data. Interestingly the single ¹¹B NMR line observed here for the $C_{16}H_{33}N^+Me_2Et$ -directed borosilicate is significantly sharper (0.3 ppm fwhm), further supporting the interpretation of a sitespecific incorporation.

Very different from the case of $C_{16}H_{33}N^+Me_2Et$ -directed borosilicate, 1D ¹¹B NMR analyses provide solid evidence that framework B species induce structural changes in the $C_{16}H_{33}N^+Me_3$ directed borosilicate frameworks. Specifically, three ¹¹B signals at -0.9, -1.9, and -2.5 ppm are identified by 1D ¹¹B NMR (Fig. 2b), all of which correspond to three distinct four-coordinate ¹¹B sites, designated as B1, B2, and B3, respectively. This obviously exceeds the number of distinct framework Si sites (two) available for B incorporation, indicating that structural rearrangements occur in the $C_{16}H_{33}N^+Me_3$ -directed borosilicate frameworks upon ¹¹B incorporation. While distinct ¹¹B species are resolved and identified by 1D ¹¹B NMR, their exact locations and B-induced structural modifications in both surfactant-directed borosilicate materials have still remained elusive.

Molecular interactions that involve ¹¹B species and their neighboring ¹H species were measured to provide insights about B site distributions in both surfactant-directed borosilicate materials. B atoms inserted into Q3 and Q4 29Si sites, designated as Q³ and Q⁴ B species, respectively, are indeed expected to have different extents of influences of ¹H species. Q^{3 11}B sites would typically interact more strongly with ¹H species than Q^{4 11}B sites, due to the fact that Q³ ¹¹B sites bonded to negatively-charged non-bridging O atoms would be charge balanced either by a proton coming from the reaction medium and forming hydroxylated B-O-H species, or by positively-charged headgroups of alkylammonium surfactants. Various spatial proximities between ¹H and ¹¹B species could be distinguished by measuring transverse ¹¹B dephasing times T_2' (*i.e.*, rate of signal loss during a spin echo) in the presence or absence of heteronuclear ¹¹B-¹H decoupling.^{69,70} The results are presented in ESI,† Fig. S2 and summarized in Table 2 for both surfactant-directed borosilicate materials. In the case of the $C_{16}H_{33}N^+Me_3$ -directed borosilicate, ¹¹B sites B1 and B2 show identical T_2' (*i.e.*, 24 ms) in the presence of heteronuclear ¹¹B-¹H decoupling. (Low ¹¹B signal sensitivity and limited spectral resolution for ¹¹B site B3 prevent reliable T_2' measurements.) In contrast, ¹¹B sites B1 and

Table 2 Transverse ¹¹B dephasing times (T_2') measured for $C_{16}H_{33}N^+Me_2Et$ - (Si/B ~ 52) and $C_{16}H_{33}N^+Me_3$ -directed layered borosilicates (Si/B ~ 142) with and without heteronuclear ¹H decoupling during ¹¹B signal acquisition

| | | T_2' (ms) | T_2' (ms) | | |
|--|-------------------------------------|--------------------------------|---|---|--|
| Material | ¹¹ B peak position (ppm) | Decoupling on | Decoupling off | ¹¹ B assignment | |
| $C_{16}H_{33}N^+Me_2Et$ -layered borosilicate $C_{16}H_{33}N^+Me_3$ -layered borosilicate | $-0.4 \\ -0.9 \\ -1.9$ | 35 ± 4 24 ± 1 24 ± 7 | $\begin{array}{c} 3.7 \pm 0.2 \\ 6.7 \pm 0.4 \\ 16 \pm 2 \end{array}$ | Hydroxylated Hydroxylated Fully condensed | |

B2 exhibit significantly different T_2' times, 7.0 and 16 ms, respectively, in the absence of ¹H decoupling, indicating that magicangle-spinning alone is insufficient to remove all the heteronuclear ¹¹B dipole-¹H dipole interactions. Residual ¹H-¹¹B couplings consequently affect T_2' times of the ¹¹B sites B1 and B2, revealing large differences that indicate that the ¹¹B site B1 is under greater influences from ¹H species than ¹¹B site B2. As such, the ¹¹B site B1 can be attributed to B atoms incorporated into Q^{3 29}Si sites, and the ¹¹B site B2 refers to B atoms substituted into Q^{4 29}Si sites. The similar ¹¹B shifts of the ¹¹B sites B2 and B3 suggest that ¹¹B site B3 seems to stem from B atoms incorporated into the Q4 29Si site. Similarly, in the case of the $C_{16}H_{33}N^+Me_2Et$ -directed borosilicate, the ¹¹B signal shows very different T_2' times that are 35 and 4.0 ms measured in the presence and absence of ¹¹B-¹H decoupling, establishing that the associated four-coordinate ¹¹B sites result from the B atoms incorporated into Q³²⁹Si sites.

In addition, 2D dipolar-mediated (through-space) ${}^{11}B{}^{1}H{}$ NMR analyses provide local information on ¹¹B sites that are molecularly proximate to their neighboring ¹H species (<1 nm) in the C₁₆H₃₃N⁺Me₃- and C₁₆H₃₃N⁺Me₂Et-directed layered borosilicates, as shown in Fig. 3a and b, respectively. For example, both 2D ¹¹B{¹H} NMR spectra reveal correlated intensities among all ¹¹B signals and one ¹H signal (at *ca.* 3.5 ppm) that corresponds to ¹H species of surfactant headgroups (*i.e.*, N-CH₃ and/or N-CH₂). Such strong intensity correlations show that the fourcoordinate ¹¹B species are molecularly proximate to surfactant headgroups in both materials, as illustrated in red in the insets of Fig. 3a and b. These spatial proximities are characteristic of the strong electrostatic organic-inorganic interactions that govern the formation of surfactant-directed materials,46 and are consistent with the similar propensity of the surfactant tails in both materials to lie perpendicular to the layers, as inferred from the similarly high basal distances. Interestingly, in the case of the $C_{16}H_{33}N^+Me_3$ -directed borosilicate, the ¹¹B signal at -0.9 ppm (¹¹B site B1) exhibits correlation intensities with the relatively weak ¹H signal at 1.9 ppm associated with the second CH₂ group in the alkyl chain of C₁₆H₃₃N⁺Me₃ surfactant molecules, as shown in blue in Fig. 3a. By comparison, other 11 B signals at -1.9 and -2.5 ppm (¹¹B sites B2 and B3, respectively) do not reveal correlations with such a ¹H signal at 1.9 ppm. These differences demonstrate that the ¹¹B site B1 interacts more strongly with ¹H moieties than ¹¹B sites B2 and B3, consistent with the analyses of T_2' measurements. Similarly, in the case of the C₁₆H₃₃N⁺Me₂Etdirected borosilicate, the ¹¹B signal at -0.4 ppm (¹¹B site B1) is also correlated with the ¹H signal at 1.9 ppm, corresponding to the second CH₂ group in the alkyl chain of $C_{16}H_{33}N^+Me_2Et$ surfactant molecules, and highlighted in blue in Fig. 3b. Furthermore, the ¹¹B signals at -0.9 and -0.4 ppm (in $C_{16}H_{33}N^{+}Me_{3}$ and C₁₆H₃₃N⁺Me₂Et-directed borosilicate respectively) both show correlation intensities with a ¹H signal at *ca.* 1 ppm associated with B-OH or B-(OH)-Si moieties, highlighted in green in Fig. 3a and b, respectively. These correlations indicate that these ¹H species arise from ¹¹B atoms incorporated into Q³ Si sites and consequently represent a small fraction of all the ¹H moieties present in the C₁₆H₃₃N⁺Me₃- and C₁₆H₃₃N⁺Me₂Et-directed layered borosilicates given the low B contents (Si/B ratios of ca. 50 or more).



Fig. 3 Solid-state 2D HETCOR ¹¹B{¹H} NMR spectra, acquired at 17.6 T and room temperature, of (a) $C_{16}H_{33}N^+Me_{3}$ - (Si/B ~ 142) and (b) $C_{16}H_{33}N^+Me_{2}Et$ -directed layered borosilicates (Si/B ~ 52), establishing spatial proximities between the four-coordinate ¹¹B and their nearby ¹H species. The corresponding 1D ¹¹B echo-MAS and ¹¹B{¹H} CP-MAS NMR spectra are shown along the top horizontal axis, and the 1D ¹H MAS spectrum is shown along the right vertical axis. The horizontal lines in different colors point to the various ¹H environments of the surfactants, as illustrated as insets.

2D ¹¹B{¹H} NMR analyses provide such molecular-level insights about charge compensation of anionic B sites in the borosilicate frameworks and are helpful for establishing models of the distorted local structures around these ¹¹B sites.

2.d. Modeling approaches to describe possible local structures around incorporated boron heteroatoms

Molecular modeling can yield information about such shortrange order and disorder near B sites in the $C_{16}H_{33}N^+Me_3$ - and $C_{16}H_{33}N^+Me_2Et$ -directed layered borosilicates to support the

Paper

NMR analyses. In particular, calculation of NMR parameters using density functional theory (DFT) is a powerful means to validate structural models. DFT calculations were conducted on representative models of both surfactant-directed borosilicates to examine and evaluate possible order and disorder near framework B species in both surfactant-directed borosilicates, which can be described by (periodic) models that consist of a single 2D borosilicate sheet, because the presence of flexible and mobile surfactants in the inter-layer space of these layered materials results in a high degree of stacking disorder. Our C₁₆H₃₃N⁺Me₃-directed silicate models were based on the octosilicate structure⁷¹ that possesses similar ²⁹Si-NMR signatures to the $C_{16}H_{33}N^+Me_3$ -directed silicate.^{46,72} There are two distinct types of Q⁴ and Q^{3 29}Si sites (labeled as T1 and T2) in the octosilicate corresponding to ²⁹Si sites Si2 and Si1 in the C₁₆H₃₃N⁺Me₃directed layered silicate, respectively. On the other hand, advanced NMR-based structure determination protocols led to the identification of three equally valid candidate framework models of the C₁₆H₃₃N⁺Me₂Et-directed silicate,⁶⁴ all of which were considered in our calculations. This silicate framework was also found to be identical to the individual layers of two newly reported materials HUS-2 of composition (per unit cell) $[Si_{20}O_{40}(OH)_4]^{4-}[HO-(CH_2)_2-N^+Me_3]_4 \cdot 1.03(H_2O)^{73}$ and CLS-1 of composition $[Si_{20}O_{40}(OH)_4]^{4-}[Me_2N-C_5H_4N^+-Et]_4\cdot 7.6(H_2O)_{,65}^{65}$ which exhibit substantially higher extents of long-range interlayer stacking order (albeit incomplete in CLS-1⁶⁵). Elemental analyses (Table 1) indicate that the samples contain between 0.6 and 0.7 surfactant molecules per Q³ groups. This means that, in analogy to the cases of octosilicate, HUS-2, and CLS-1 materials,65,72,73 the rest of the negative charges of nonbridging O atoms is compensated in both borosilicates studied here by protons forming a strong Si-O-H···O-Si hydrogenbonds between two adjacent Q³ Si sites, leading primarily to $[Si_5O_{10}(OH)]^-$ formula units for the framework. These protons, which are characterized by ¹H NMR peaks in the 13-16 ppm range in (at least partly) crystalline layered silicates octosilicate, HUS-2 and CLS-1, have never been clearly observed in the isostructural surfactant-directed silicates. This is probably because they are considerably more mobile in the latter at room temperature and are potentially also exchanging with nearby Si₅O₁₁²⁻ units, which causes their ¹H NMR resonance frequencies to be distributed across a large part of the ¹H frequency range as a result of distributions of H-bond lengths, such that they are hidden at the feet of other ¹H NMR peaks.

The basic idea of our modeling approach is to replace one Si atom by a B atom in supercells made from the reference $C_{16}H_{33}N^+Me_{3^-}$ and $C_{16}H_{33}N^+Me_2Et$ -directed silicate systems to then evaluate these borosilicate models and study the effect of the Si to B substitution on the framework structure. The difficulty here resides in the strategies used for the compensation of the negative charges associated with the non-bridging O atoms (those not compensated by a proton) and the incorporated B atom. Two different approaches were tested to model the alkylammonium surfactant molecules. In the first, unsuccessful, approach described in the ESI† (Fig. S3, S4 and Tables S2, S3), surfactants with relatively short alkyl chains, such as

 $CH_3-(CH_2)_3-N^*Me_3$ or $CH_3-(CH_2)_3-N^*Me_2Et$ molecules, were included in the inter-layer space of all candidate structure models to mimic charge-compensating surfactant molecules. While ¹¹B NMR chemical shifts calculated with this method seem to be reasonably reliable, calculated ²⁹Si chemical shifts are not consistent with the experimental NMR analyses. It has been established before that freezing the surfactant-headgroup motions by decreasing the temperature has a strong impact on ²⁹Si NMR signals.⁷⁴ The frozen states of the surfactantmimicking molecules in our models are therefore not representative of the mobile surfactants and their dynamically-averaged influence on the electronic structure of borosilicate layers at room temperature.

In an alternative approach to model the complicated organic-inorganic interactions and their influence on the ²⁹Si and ¹¹B NMR signatures, the surfactant molecules were omitted and replaced by positive charges homogenously distributed across the entire unit cell. This strong approximation was first validated for the siliceous systems, as illustrated in Fig. S5 (ESI[†]). Best results were obtained with calculations conducted on model unit cells that contain one H atom per pair of nonbridging O atoms, corresponding to reference compositions $[Si_8O_{16}(OH)_2]^{2-}$ in the case of the $C_{16}H_{33}N^+Me_3$ -directed silicate, $[Si_{10}O_{20}(OH)_2]^{2-}$ for the $C_{16}H_{33}N^+Me_2Et$ -directed silicate. Such configurations would lead to borosilicates with 0.5 chargecompensating surfactant molecule per Q³ unit, which is reasonably close to the elemental analyses of both surfactant-directed borosilicates (see Table 1). This modeling strategy appears to substantially improve the agreement between experimental and calculated NMR parameters in the case of C16H33N+Me2Et-directed silicates, as compared to the previously used approximation,⁶⁴ where all non-bridging oxygen atoms were protonated to form silanol groups. Importantly, these calculations further validate the three "equally-valid framework structural models" that were previously established,⁶⁴ two of which (structural models 2 and 4 using the designation of ref. 64) appear to converge to a single structure when only two of their non-bridging oxygen atoms are protonated. Structural models 2 and 3, obtained after optimization with 2H atoms per supercell, were considered as model systems to construct a second series of models of the $C_{16}H_{33}N^{+}Me_{2}Et$ -directed borosilicates. In both series of systems, B atoms were then introduced by replacing one Si atom in a $2 \times 2 \times 1$ supercell, corresponding to models of compositions $[BSi_{39}O_{80}(OH)_8]^{9-}$ for the $C_{16}H_{33}N^+Me_2Et$ -directed borosilicates, and $[BSi_{31}O_{64}(OH)_8]^{9-}$ for the $C_{16}H_{33}N^+Me_3$ -directed borosilicates, as reported in Table 3, and in the first two rows of Table 4, respectively.

2.e. Evaluation of $C_{16}H_{33}N^+Me_2Et$ -directed borosilicate models: calculated NMR data *vs.* advanced experimental correlation NMR data

Calculated NMR parameters obtained from the second modeling approach appear to be more reliable than the first approach. Fig. 4a shows a representative structural model of the $C_{16}H_{33}N^+Me_2Et$ directed borosilicate (viewed from *c*-axis) after DFT geometry optimization. This model was built from the reference silicate

Table 3 Experimental and DFT ¹¹B chemical shift values for $C_{16}H_{33}N^+Me_2Et$ -directed layered borosilicates based on the siliceous counterparts (frameworks 2 and 3), where surfactants have been replaced by homogeneously-distributed positive charges for charge compensation

| | | Calculated $\delta_{iso}(^{11}$ | B) (ppm) | |
|-------------------------------|------------------------|---------------------------------|-------------|--|
| Model composition and charge | B/Si substitution site | Framework 2 | Framework 3 | Experimental ¹¹ B shift (ppm) |
| $[BSi_{39}O_{80}(OH)_8]^{9-}$ | $Si1(Q^3)$ | 0.3 | 0.9 | -0.4 |
| | $Si2(Q^3)$ | -0.8 | 0.5 | |
| | $Si3(Q^4)$ | -2.8 | -2.8 | |
| | $Si4(Q^4)$ | -3.8 | -3.2 | |
| | $Si5(Q^4)$ | -3.9 | -4.1 | |

Table 4 ¹¹B chemical shift values calculated by DFT for the model structures of the $C_{16}H_{33}N^+Me_3$ -layered borosilicate material with surfactants replaced by homogeneously-distributed positive charges and 2 × 2 × 1 supercells

| Model composition and charge | B/Si substitution site | New framework connectivity | BOH/SiOH groups | Calculated $\delta_{iso}(^{11}B)$ (ppm) | Experimental ¹¹ B shift ^a (ppm) |
|--|--|--------------------------------|---------------------|---|--|
| $\begin{array}{l} \left[BSi_{31}O_{64}(OH)_{8}\right]^{9-}\\ \left[BSi_{31}O_{64}(OH)_{8}\right]^{9-}\end{array}$ | ${ Si1(Q^3) as BOH \ Si2(Q^4) }$ | None None | 1BOH/7SiOH 8SiOH | $-0.2 \\ -3.4$ | $-0.9 \\ -2.5$ |
| Models with additional Si- [BSi ₃₁ O ₆₄ (OH) ₇] ^{8–} [BSi ₃₁ O ₆₄ (OH) ₇] ^{8–} | -O-Si or Si-O-B connectiv Si1(Q ³) as BOH Si1(Q ³ = >Q ⁴) | rities. 1Si–O–Si 1Si–O–B | 1BOH/6SiOH 7SiOH | 0.2 N.A. ^b | -0.9 |
| $\begin{bmatrix} BSi_{31}O_{64}(OH)_7 \end{bmatrix}^{8-} \\ \begin{bmatrix} BSi_{31}O_{64}(OH)_6 \end{bmatrix}^{7-} \end{bmatrix}$ | $Si2(Q^4)$ $Si2(Q^4)$ | 1Si–O–Si 2Si–O–Si | 7SiOH 6SiOH | -3.5 -3.0 | -2.5 -1.9 |

^{*a*} The ¹¹B experimental shift corresponds to the position of the experimental peak that gives the best match between all available experimental and calculation constraints. ^{*b*} The additional Si–O–B connectivity formed (manually) on the starting structure broke in the course of the optimization to form a three-coordinated BO₃ environment. No such environment was observed by ¹¹B NMR (Fig. 2b) and this model was consequently discarded.

framework structure 2 (Fig. S5, ESI[†]) in a 2 × 2 × 1 supercell, where one Si site Si1 was replaced by one B atom to form a B–OH unit. The resulting calculated ¹¹B chemical shifts, including the ones with B atoms incorporated into one of the five distinct Si sites in candidate framework structures 2 and 3, are summarized in Table 3. Interestingly, these calculations match well-separated ranges of ¹¹B chemical shifts for B atoms located in Q³ (–0.8 to 0.9 ppm) or Q⁴ sites (–2.8 to –4.1 ppm). More importantly, the range of calculated ¹¹B NMR signals for Q³ ¹¹B sites corresponds well to the experimental ¹¹B signal at –0.4 ppm attributed to a BOH moiety formed by substitution of a Q³ ²⁹Si site in the C₁₆H₃₃N⁺Me₂Et-borosilicates (Fig. 2d).

This modeling approach, where surfactants are omitted, also considerably improves the reliability of ²⁹Si NMR calculations as compared to the models with included surfactant-mimicking molecules. The calculated ²⁹Si chemical shifts for Q^{n} ²⁹Si sites (*i.e.* ²⁹Si sites that are not connected to a B atom), shown in black in Fig. 4c, are all in good agreement with the experimental results (Fig. 4b). The ²⁹Si chemical shifts calculated for ²⁹Si sites neighboring the B atoms, $Q^{n}(1B)$ sites Si2, Si3, and S5, shown in yellow in Fig. 4c, also compare well to experimental data (Fig. 4d) that were obtained from advanced multi-dimensional solid-state NMR techniques, and which will be discussed in further detail below. The structural rearrangements induced by B incorporation may be probed through differences in the ²⁹Si chemical shifts between corresponding ²⁹Si sites calculated in the borosilicate and siliceous framework model, which are plotted in Fig. 4e. The qualitative influences of an isolated B atom on its nearby ²⁹Si sites in terms of proximities are highlighted in grey in Fig. 4e. The shift difference is surprisingly weak for the ²⁹Si sites with a next-nearest neighbor replaced by a B atom (the $O^{3}(1B)$ species within the black ellipse in Fig. 4e), which may be explained by a compensation between the effect due to the difference in electronegativity between Si and B and the local geometrical rearrangements caused by the smaller size of the B atom. T-O bond lengths, T-O-T bond angles and T-O-H-O-T hydrogen bond strengths all influence ²⁹Si chemical shifts³⁷ in ways which appear here to oppose to the expected effect of the change in electronegativity between Si and B (in analogy to the well-known systematic effect of Si to Al substitutions). This structural model with the B atom incorporated in one specific Q^3 Si site appears to match with all the experimental data discussed so far. Similar calculations conducted for the other models, with B atoms incorporated into the ²⁹Si site Si2 and/or using candidate structure no. 3 as the reference silicate framework structure, will be discussed further below, in relation to the identification of the crystallographic site on which the B atom is siting. For this, however, it is first necessary to explain how the experimental ²⁹Si spectrum of Fig. 4d featuring selectively $Q^n(1B)$ species was obtained.

The specific signature ²⁹Si nuclei connected to ¹¹B nuclei through bridging O atoms exploits the unique ability of solidstate NMR spectroscopy to provide two-dimensional (2D) correlation experiments that are mediated through the ${}^{2}J({}^{11}B-O-{}^{29}Si)$ scalar couplings. Fig. 5a shows in red a 2D ${}^{2}J({}^{11}B-O-{}^{29}Si)$ mediated heteronuclear multiple-quantum correlation (HMQC) ${}^{11}B{}^{29}Si$ } NMR spectrum of a $C_{16}H_{33}N^{+}Me_{2}Et$ -directed layered borosilicate material prepared with *ca.* 99% enrichment in ${}^{29}Si$. The 1D ${}^{11}B$ echo-MAS and ${}^{29}Si{}^{1}H$ } CP-MAS spectra of this ${}^{29}Si$ -enriched material are shown along the top horizontal and



Fig. 4 (a) DFT-optimized structural model of C₄H₉N⁺Me₂Et-directed layered borosilicates with one ¹¹B atom inserted into one ²⁹Si site 1 (Q³ ²⁹Si), which was constructed using a 2 × 2 × 1 supercell and has 8 ¹H atoms as well as homogenously distributed positive charges for charge compensation. (b) The 1D ²⁹Si NMR MAS spectrum of C₁₆H₃₃Me₂EtN⁺-directed layered borosilicates (Si/B ~ 52) is compared with (c) the calculated ²⁹Si NMR spectrum (in red) *via* DFT calculation that includes ²⁹Si signals corresponding to distinct types of Qⁿ (in black) and Qⁿ(1B) ²⁹Si species (in orange). (d) The 1D ²⁹Si projection extracted from the 2D *J*-mediated HMQC ¹¹B(²⁹Si) NMR spectrum shows ²⁹Si signals associated with Qⁿ(1B) ²⁹Si sites. (e) A summary plot manifests differences of calculated ²⁹Si chemical shifts between the borosilicate model and the silicate model (*i.e.*, no ¹¹B incorporation) as a function of relative distances of Various ²⁹Si sites with respect to the nearest B atoms. The influences of B atoms on borosilicate frameworks are depicted in grey for visual illustrations.

the right vertical axis of the 2D $^{11}B\{^{29}Si\}$ spectrum. Both are similar to the 1D spectra of the corresponding $C_{16}H_{33}N^+Me_2Et$ -directed layered borosilicate with natural abundance of ^{29}Si

(Fig. 2c and d), except for the presence of a boron-containing impurity (marked with a star in the 1D¹¹B echo-MAS spectrum). Various correlated intensities in this 2D ¹¹B{²⁹Si} NMR spectrum (Fig. 5a, in red) reveal different ²⁹Si sites covalently bonded to ¹¹B atoms via bridging oxygen atoms in the borosilicate framework. It is the ²⁹Si projection of this 2D spectrum, shown in red on the right of Fig. 5a, that was included in Fig. 4d for direct comparison with calculated ²⁹Si chemical shifts corresponding to $O^{n}(1B)$ ²⁹Si environments. Because they lack a ¹¹B–O–²⁹Si connection, ²⁹Si Qⁿ sites are indeed totally filtered out in the 2D correlation spectrum, and thus in its ²⁹Si projection. Details of the 2D spectrum reveal three distinct ²⁹Si signals at -98.4, -100.5 and -113.8 ppm that are correlated with one ¹¹B signal at -0.4 ppm. As mentioned above, the small broadening of this ¹¹B signal suggests a highly uniform single type of ¹¹B environment. Consequently, the three types of ²⁹Si-O-¹¹B correlations indicate that every incorporated B atom is connected to three distinct Si atoms $(Q^3(1B) \text{ or } Q^4(1B))$ via bridging oxygen atoms. Specifically, two of the three $Q^{n}(1B)^{29}Si$ sites revealed in the J-mediated ¹¹B{²⁹Si} correlation NMR spectrum fall within a region of the ²⁹Si spectrum that is compatible with Q³(1B) signatures, consistent with the connectivities established from the siliceous counterpart, where each Q³ ²⁹Si site is connected to another Q³ ²⁹Si site. Such information allows us to confirm that the ¹¹B signal at -0.4 ppm can be attributed to B atoms incorporated into one of the two types of Q^3 Si sites. Additionally, the local topology near B sites in the C₁₆H₃₃N⁺Me₂Et-directed borosilicate does not appear to rearrange during framework crystallization. As will be discussed further below this is in stark contrast to the case of the $C_{16}H_{33}N^{+}Me_{3}$ directed borosilicate material.

While the 2D J-mediated (through-bond) ¹¹B₁²⁹Si} NMR analyses provide specific information on the ¹¹B sites that are covalently bonded to the next-nearest-neighbor ²⁹Si sites, ²⁹Si sites in the first coordination shells may be spatially close to ¹¹B sites in the C₁₆H₃₃N⁺Me₂Et-directed layered borosilicate framework, which can be revealed *via* 2D dipolar-mediated ¹¹B²⁹Si} NMR experiments. Fig. 5a shows in blue a 2D dipolar-mediated HMQC ¹¹B{²⁹Si} NMR spectrum of the *ca.* 99% ²⁹Si-enriched C₁₆H₃₃N⁺Me₂Et-directed layered borosilicate. Intensity correlations that involve the impurity, identified by the ¹¹B signal at ca. 4 ppm in the 1D ¹¹B NMR spectrum, are resolved using this 2D dipolar-mediated ¹¹B{²⁹Si} NMR technique, but they are distinguishable from the NMR signature of the layered borosilicate. The ¹¹B signal at ca. -0.4 ppm exhibits intensity correlations with the ²⁹Si signals at -98.4, -100.5 and -113.8 ppm in the 2D dipolar-mediated ¹¹B{²⁹Si} NMR spectrum (in blue, Fig. 5a), consistent with the 2D J-mediated ${}^{11}B{}^{29}Si$ } NMR spectrum (in red, Fig. 5a), because of the short distances (ca. 3 Å) between the ²⁹Si-O-¹¹B site pairs. More importantly, additional correlated intensities are shown between the ¹¹B signal at -0.4 ppm and the ²⁹Si signals at -111.3 and -108.6 ppm, as well as a shoulder at *ca.* -101.0 ppm, all of which correspond to ²⁹Si sites that are molecularly proximate to (ca. 5 Å or less) yet not connected with the ¹¹B sites. Interestingly, the ²⁹Si signals at -108.6 and -101.0 ppm are very close to the ²⁹Si signals at -108.7 and -100.7 ppm, associated with ²⁹Si sites Si4 and Si2, respectively.



Fig. 5 (a) Solid-state 2D dipolar- (in blue) and *J*-mediated (in red) HMQC ¹¹B(²⁹Si) NMR spectra, acquired at 9.4 T and room temperature, of ²⁹Sienriched $C_{16}H_{33}N^+Me_2Et$ -directed layered borosilicates (Si/B ~ 52 expected), which establish spatial proximities and site connectivities between ²⁹Si and ¹¹B species, respectively. The 1D ¹¹B echo-MAS spectrum is shown along the top horizontal axis. The ²⁹Si(¹H) CP-MAS spectrum (in black) and the ²⁹Si projections, extracted from 2D dipolar- (in blue) and *J*-mediated (in red) ¹¹B(²⁹Si) NMR spectra that focus on the regions associated with $C_{16}H_{33}N^+Me_2Et$ -directed layered borosilicates (*i.e.*, from 1.0 to -2.0 ppm in the ¹¹B dimension), are all shown along with the right vertical axis. (b) A schematic representation illustrates the ¹¹B atom distributions in $C_{16}H_{33}N^+Me_2Et$ -directed layered borosilicates, where the influences of ¹¹B sites on borosilicate frameworks are highlighted in blue.

Both ²⁹Si sites Si4 and Si2 in the $C_{16}H_{33}N^+Me_2Et$ -directed layered borosilicate exhibit similar ²⁹Si signals to the ²⁹Si sites Si4 and Si2 (-109.1 and -101.0 ppm) in the closely related $C_{16}H_{33}N^+Me_2Et$ -directed siliceous framework,⁴⁶ suggesting that the presence of ¹¹B atoms subtly modifies their nearby ²⁹Si environments. Similarly, another correlation that involves the ²⁹Si signal at -111.3 ppm could be attributed to ²⁹Si site 5, whose ²⁹Si chemical shift is more distinctly displaced with respect to the main one at -114.7 ppm due to its proximity to the ¹¹B sites. These 2D NMR analyses indicate that the ¹¹B incorporation would induce subtle influences on the ²⁹Si sites neighboring B atoms, within a small region of less than *ca.* 5 Å radius.

A direct consequence of the preservation of the framework topology and of such minor geometric distortions is a high degree of local molecular order near the B sites, as revealed by the narrow linewidths in both ¹¹B and ²⁹Si dimensions of the 2D ${}^{11}B{}^{29}Si$ NMR spectra of the $C_{16}H_{33}N^+Me_2Et$ -directed borosilicates (Fig. 5a). Specifically, the narrow linewidths of the ¹¹B signals (FWHM: 0.3 ppm) and the ²⁹Si signals (FWHM: 1.0-1.6 ppm) all reveal well-defined local ¹¹B and ²⁹Si environments, respectively, rather than distributions of local bonding geometries. By comparison, typical linewidths of ¹¹B and ²⁹Si signals observed in borosilicate glasses are of the order of 4 ppm for four-coordinate ¹¹B species and 10 ppm for Q³ or Q4²⁹Si environments.⁷⁵ The narrow linewidths as well as 2D ¹¹B²⁹Si} NMR analyses clearly indicate that all ¹¹B nuclei are preferentially inserted into one type of Q³ Si sites (*i.e.*, Si1 or Si2) in the $C_{16}H_{33}N^+Me_2Et$ -directed borosilicate, and lead to very similar and localized influences on their local ²⁹Si environments in this material. Additionally, these B sites can be considered to be well isolated from each other, due to the Si/B molar ratio on the order of 50. Therefore, a substantial fraction of framework sites remain occupied by Si atoms, which suggests that B atoms are distributed in a random manner, rather than

periodically (*e.g.*, every unit cell) in the $C_{16}H_{33}N^+Me_2Et$ -directed borosilicate framework. The ¹¹B site distributions in the proposed structure are depicted schematically in Fig. 5b, where B atoms exhibit poor or no periodicity in their long-range order and yet strong similarity in the subtle influences that they exert locally on the borosilicate frameworks.

The case of the $C_{16}H_{33}N^{\dagger}Me_2Et$ -directed borosilicate is significantly different from the case, for instance, of borosilicate zeolite MCM-70 (crystal code MVY⁷⁶) of composition $[Si_{10}B_2O_{24}]^2 - [K^+]_2$. 2(H₂O) that contains four distinct crystallographic tetrahedral Si sites, three of which are exclusively occupied by Si atoms, whereas the fourth is only occupied by B atoms, as established by X-ray diffraction analyses.³² To our knowledge, there is no evidence that a siliceous MCM-70 structure can be formed, where this crystallographic site would be occupied (even partially) by Si atoms in the average long-range structure. The situation is completely different here, first because the C16H33N+Me2Etdirected borosilicate lacks the 3D (and even long-range 2D) periodicity, while possessing molecular order. Second, the B loadings are small enough so that B sites can be considered to be independent of each other. Based on the understanding of local order and disorder near B sites in the C₁₆H₃₃N⁺Me₂Etdirected borosilicate, we anticipate that the corresponding physico-chemical properties of all B sites in the material should be similar.

2.f. Boron siting in the $C_{16}H_{33}N^+Me_2Et$ -directed borosilicate material

Understanding the incorporation of boron atoms into Q^{3} ²⁹Si sites in the C₁₆H₃₃N⁺*Me*₂*Et*-directed borosilicate framework is important for rational zeolite synthesis with controlled heteroatom siting, which has received considerable attention for many years. Such preferential B incorporation is supported by the DFT analyses, as summarized in Fig. 6, which shows comparisons of experimental and calculated NMR data for different models of





Fig. 6 Comparisons between experimental and calculated ²⁹Si chemical shifts for 4 distinct DFT-optimized models of the $C_{16}H_{33}N^+Me_2Et$ -directed borosilicate material. All structures were obtained from pure-silicate structures # 2 and 3 (see Fig. S5, ESI†), by considering a 2 × 2 × 1 supercell and replacing one Q³ Si atom (site Si1 or Si2) by a B atom. Surfactants are omitted in these models and simply replaced by positive charges homogeneously distributed across the entire supercell. Black circles and red squares correspond to the ²⁹Si chemical shifts of Qⁿ and Qⁿ(1B) sites, respectively. Experimental ²⁹Si chemical shift values for Qⁿ(1B) sites are obtained from the projection of the *J*-mediated ¹¹B-²⁹Si correlation NMR spectrum (shown in red above the plots), which selectively reveals ²⁹Si sites connected (*via* a bridging O atom) to a B atom. The positions of the red squares are derived from the assignment giving the best agreement between experimental and calculated ²⁹Si chemical shifts for these sites.

the C₁₆H₃₃N⁺Me₂Et-directed borosilicate material, using reference candidate structures 2 (in a and b) and 3 (c and d), both shown in ESI,† Fig. S5, and B atoms siting in site Si1 (a and c) or Si2 (b and d). Data points corresponding to ²⁹Si Qⁿ sites are shown as open black circles in Fig. 6, where they should be compared to the standard ²⁹Si 1D spectrum collected for this material, shown in black on top of the figure. $Q^{n}(1B)^{29}Si$ sites, represented as filled red squares, should be compared to the projection of the J-mediated HMQC spectrum, shown in red on top. Fig. 6a is no more than a different representation of the data shown in Fig. 4a-d, with B incorporated in the Q³ Si site Si1 within reference silicate framework structure 2 (see Fig. S5, ESI[†]), which shows in particular a very good agreement between experimental and calculated data for $Q^{n}(1B)$ sites (red squares). A reasonably good agreement is also observed for $Q^{n}(1B)$ in Fig. 6c, when B is incorporated also in the Q^3 Si site Si1, but within reference structure 3 instead of 2. By comparison, the models where the B is in substitution of the Q^3 Si site Si2, as shown in Fig. 6b and d, yield much poorer agreement between experiments and calculations. These results thus seem to establish that the preferential substitution site of the ¹¹B atoms in the C16H33N⁺Me2Et-directed layered borosilicate is the Q^{3 29}Si site Si1.

2.g. Evaluations of $C_{16}H_{33}N^+Me_3$ -directed borosilicate models: calculated NMR data *vs.* advanced experimental correlation NMR

The situation is remarkably different in the case of the $C_{16}H_{33}N^{+}Me_{3}$ -directed borosilicate, where the incorporation of B atoms induces profound structural modifications of the silicate framework near B atoms, as was first evidenced by the three ¹¹B NMR signals (Fig. 2b) that over specify the number of distinct ²⁹Si sites (only two in this case). To understand the local disorder near B species in the C₁₆H₃₃N⁺Me₃-directed borosilicate materials, the same DFT-modeling approach using homogeneously-distributed positive charges instead of surfactant molecules was applied to calculate the ²⁹Si and ¹¹B NMR chemical shifts. Fig. 7 shows two DFT-optimized models with the chemical composition [BSi₃₁O₆₄(OH)₈]⁹⁻ that were obtained by substituting one B atom in Q^3 Si site Si1 (Fig. 7a) or in Q^4 Si site Si2 (Fig. 7d) in a $2 \times 2 \times 1$ supercell. The main characteristics of these models are summarized in Table 4. The calculated NMR parameters based on these models are shown as vertical bars in the plots of Fig. 7b, c, e and f. Calculated ²⁹Si chemical shifts are in reasonable agreement with the experimental data (black spectrum on top of Fig. 7b and e) for both



Fig. 7 DFT-optimized structural models of $C_{16}H_{33}N^+Me_3$ -directed layered borosilicates viewed from the *c*-axis, where B atoms are manually inserted into the Si site (a) Si1 or (d) Si2. For each structural model, 8 H atoms per unit cell and other homogeneously distributed positive charges are included for charge compensation. Calculated isotropic chemical shifts for distinct ²⁹Si and ¹¹B species in the models (a) and (b) are shown in plots (b and c) and (e and f), respectively, where the ²⁹Si chemical shifts in blue reveal the ²⁹Si species connected to one B atom only. Experimental ²⁹Si and ¹¹B MAS NMR spectra are shown along the top axis accordingly for reference.

Q³ and Q^{4 29}Si sites (black lines). Interestingly, the calculated ²⁹Si chemical shifts for $Q^{n}(1B)$ ²⁹Si environments (blue lines in Fig. 7b and e) exhibit small and non-systematic shift differences between Q3(0B) and Q3(1B) 29Si or between Q4(0B) and $Q^4(1B)^{29}$ Si sites. These DFT analyses suggest that, as in the case of the $C_{16}H_{33}N^+Me_2Et$ -directed layered borosilicate, such $Q^n(1B)$ ²⁹Si sites could be very hard to distinguish experimentally from Q^{n} ²⁹Si sites. As for ¹¹B chemical shifts, calculated values are significantly different for ¹¹B species inserted into a Q³ or a Q⁴ ²⁹Si site, as shown in Fig. 7c and f, respectively, suggesting that the ¹¹B site B1 (at -0.9 ppm) is very likely to correspond to the B species incorporated into the Q³ Si site Si1 as a BOH moiety (Fig. 7c). By comparison, ¹¹B signals at -1.9 and -2.5 ppm (labeled as ¹¹B sites B2 and B3, respectively) should be associated with the B atoms incorporated into the Q⁴ Si site Si2 (Fig. 7f). Nevertheless, these results do not explain the presence of two distinct four-coordinate ¹¹B sites B2 and B3, both of which are attributed to the B atoms in Q⁴ environments in the $C_{16}H_{33}N^+Me_3$ -directed borosilicate.

The challenges of understanding such complicated shortrange disorder near ¹¹B species in borosilicate frameworks were again overcome by 2D *J*-mediated ¹¹B{²⁹Si} NMR techniques probing ¹¹B-O-²⁹Si site connectivities. Fig. 8a shows the 2D ²*J*(¹¹B-O-²⁹Si)-mediated HMQC ¹¹B{²⁹Si} NMR spectrum of *ca.* 99% ²⁹Si-enriched C₁₆H₃₃N⁺Me₃-directed layered borosilicate materials, whose 1D ²⁹Si and ¹¹B NMR spectra are shown in black on the right vertical and top horizontal axis of the 2D spectrum, respectively. The ²⁹Si projection shown in red on the right again selectively reflects a fraction of $Q^n(1B)^{29}Si$ environments that are not possible to identify *via* 1D ²⁹Si NMR analyses, because their ²⁹Si signals are obscured by the much larger fraction of ²⁹Si signals contributed by $Q^{n-29}Si$ environments. This ²⁹Si projection is included (in blue) in Fig. 7b and e for direct comparison with calculated ²⁹Si chemical shifts corresponding to $Q^n(1B)^{29}Si$ environments, which reveal good agreement between the calculated and experimental results. Both experimental and theoretical NMR analyses indicate that framework B species have limited influences on their next-nearest-neighboring ²⁹Si sites.

Specifically, the ¹¹B signal at -2.5 ppm associated with the ¹¹B site B3 exhibits in Fig. 8a correlated intensities with the ²⁹Si signals at -111 and -101 ppm, corresponding to Q⁴ and Q³ ²⁹Si sites, respectively, establishing that the ¹¹B site B3 is bonded to the Q³ and Q⁴ ²⁹Si sites through bridging oxygen atoms. This is in agreement with the assignment of the ¹¹B site B3 inserted into Q⁴ framework sites, because every Q⁴ Si site is connected to two Q³ and two Q⁴ Si sites, as described using the DFT-optimized model shown in Fig. 7a. In contrast, ¹¹B signals B1 and B2 at -0.9 and -1.9 ppm, assigned to the B atoms incorporated into Q³ and Q⁴ Si environments, respectively, both show correlation intensities with the ²⁹Si signals corresponding to Q⁴ Si sites but no correlation with any ²⁹Si signals



Fig. 8 (a) Solid-state 2D *J*-mediated HMQC ¹¹B{²⁹Si} NMR spectrum, acquired at 9.4 T and room temperature, of ²⁹Si-enriched C₁₆H₃₃N⁺*M*e₃-directed layered borosilicates (Si/B ~ 142 expected), establishing ²⁹Si-O-¹¹B site connectivities between the ¹¹B species and their next-nearest-neighboring ²⁹Si sites through bridging oxygen atoms. The 1D ¹¹B echo-MAS NMR spectrum (in black) and the ¹¹B projection (in red) are shown along the top horizontal axis. The 1D ²⁹Si{¹H} CP-MAS spectrum (in black) and the ²⁹Si projection (in red) are shown along the top horizontal axis. The 1D ²⁹Si{¹H} CP-MAS spectrum (in black) and the ²⁹Si projection (in red) are shown along the right vertical axis. (b) The structural model of C₁₆H₃₃N⁺*M*e₃-directed borosilicates for DFT optimization was constructed using multiple unit cells. (c) An example is selected to illustrate local structural changes in the DFT-optimized model of C₁₆H₃₃N⁺*M*e₃-directed borosilicates per supercell, where one ¹¹B atom is inserted into a Q³ site, inducing framework condensations between next-nearest-neighboring Q^{3 29}Si sites.

corresponding to Q^3 Si species. This is inconsistent with the site connectivities of either Q^3 or $Q^{4\ 29}$ Si sites established from the $C_{16}H_{33}N^+Me_3$ -directed silicate framework⁷¹ and confirmed

for the borosilicate (see ESI,† Fig. S1a). Indeed B atoms incorporated into Q^3 or Q^4 Si sites are expected to be bonded to one or two Q^3 Si atoms, respectively, which would lead to correlation intensities in the Q^3 ²⁹Si region (highlighted in Fig. 8a). This analysis establishes that the local Si structure around B sites B1 and B2 is modified to have these B sites connected with Q^4 Si sites exclusively, reflecting a locally-increased degree of framework condensation with respect to the siliceous counterparts.

Such local structural rearrangements near B atoms in the $C_{16}H_{33}N^+Me_3$ -directed borosilicate material are supported via DFT calculations. For example, Fig. 8b and c illustrates how a DFT-optimized borosilicate model (Fig. 8c) may be built using a supercell (in this case made of $1 \times 3 \times 1$ cells of the reference pure-silicate structure, Fig. 8b), where one Q^3 Si site was manually substituted by one B atom with the addition of a H to form a B-OH environment for charge compensation. The Q³ Si atom bonded to the B site was manually connected with its next-nearest-neighbor Q³ Si atom by replacing the two nonbridging oxygen atoms of these two Si atoms by a single bridging oxygen atom placed at their center of mass. In the example model shown here, the decreased framework charge caused by replacing two oxygen atoms with one oxygen atom was compensated by removal of two surfactant-mimicking $C_4H_9N^+Me_3$ molecules, leading to a chemical composition $(BSi_{23}O_{53}H)^{10-}$. $10(C_4H_9N^+Me_3)$. Interestingly, this model appears to deform during the geometry optimization (Fig. 8c) to accommodate the additional cross-linking between silicate units. This is a consequence of the local structural rearrangements necessary for SiO₄ and BO₄ units to retrieve appropriate tetrahedral geometries. The configurations of the B atoms inserted into Q³ sites and their connected Si neighbors (Q⁴(1B) only) in this model are consistent with all the experimental NMR data of the ¹¹B site B1. The ¹¹B chemical shift calculated via this model is 0.1 ppm, which is in reasonable agreement with the experimental ¹¹B shift of the ¹¹B site B1 (-0.9 ppm). Similar results were obtained for other models describing the same situation yet with different supercell sizes or strategies for the compensation of framework negative charges, as summarized in Table S3 (ESI[†]). Collectively, they all yielded calculated ¹¹B shifts between 0.1 and -0.4 ppm, in similarly good agreement with the experimental ¹¹B peak at -0.9 ppm. As has been discussed above, however, the approach including surfactantmimicking yields calculated ²⁹Si NMR data that are considerably more scattered than the experimental distributions of ²⁹Si chemical shifts.

Similar conclusions can be drawn for ¹¹B chemical shifts calculated with the alternative approach, where homogeneously distributed positive charges rather than surfactant molecules were applied for charge compensation in the surfactantdirected borosilicates, which are summarized in Table 4. For example, the DFT-optimized model with the chemical composition $[BSi_{31}O_{64}(OH)_7]^{8-}$ (Fig. 9a) depicts a similar BOH environment in a 2 × 2 × 1 supercell with one ¹H atom per pair of non-bridging oxygen atoms. With this model, the calculated ¹¹B shift (0.2 ppm, see Fig. 9c or Table 4) is very close to the



Fig. 9 DFT-optimized structural models of $C_{16}H_{33}N^+Me_3$ -directed layered borosilicates viewed from the *c*-axis, where ¹¹B atoms are manually inserted into the ²⁹Si site (a) Si 1 or (d and g) Si2. For each structural model, 8 H atoms per unit cell and other homogeneously distributed positive charges are included for charge compensation. Specifically, B incorporation induces framework condensations between nearby Q³ Si sites to form (a and d) one or (g) two new Si–O–Si site connectivities. Calculated isotropic chemical shifts for distinct ²⁹Si and ¹¹B species in the models (a), (d) and (g) are shown in plots (b, e and h) and (c, f and i), respectively, where the ²⁹Si chemical shifts in blue reveal the ²⁹Si species connected to one B atom only. The calculated ²⁹Si chemical shifts in orange refer to newly formed Q⁴ ²⁹Si species *via* framework condensations. Experimental ²⁹Si and ¹¹B MAS NMR spectra are shown along the top horizontal axis accordingly for reference.

calculated value using the surfactant-included models and in reasonable agreement with the ¹¹B signal associated with the ¹¹B site B1. Calculations of ²⁹Si chemical shifts conducted under such conditions (Fig. 9b) predict Q⁴(1B) ²⁹Si signatures close to the region of the ²⁹Si spectrum correlated with the B1 frequency (Fig. 8a), which is obscured by the dominant Q⁴ ²⁹Si signal. In summary, all models that describe one ¹¹B atom inserted into the Q³ ²⁹Si site Si1 to form a B–OH and a new Si–O–Si connectivity involving its Q³(1B) neighbour are compatible with the ¹¹B shift of the ¹¹B site B1.

Similar calculations were conducted on various models that describe local structures of the ¹¹B site B2 (*i.e.* one B atom incorporates into one Q^4 Si site), as well as its connectivities with other Q^4 Si sites. Such local Si and B environments may be

obtained by generating two additional framework condensations that involve the two Q³ Si sites adjacent to the B atom, which become Q⁴(1B) Si sites in the optimized structure. This procedure is illustrated in Fig. S6 (ESI†) for the model of chemical composition ($BSi_{31}O_{70}H_6$)^{7–} whose DFT-optimized structure is shown in Fig. 9g. A very similar situation may alternatively be obtained by incorporating B in a Q³ Si site and transforming this B site to a Q⁴ by creating a new B–O–Si connectivity with an adjacent Q³ Si atom (thereby changed to a Q⁴ Si). This and other models that describe the same type of Si and B environments, but with different initial locations of B atoms and charge-balance strategies (see Table 4), lead to ¹¹B chemical shifts between -3 and -4 ppm, which is not too far from the experimental ¹¹B shift of ¹¹B site B2 (–1.9 ppm). In combination with 2D NMR data, these calculations thus shed light on the possible rearrangements of the framework topology (*i.e.*, the coordination sequences and ring structures) that may take place upon B incorporation into the $C_{16}H_{33}N^+Me_3$ -directed layered borosilicate material during framework ordering. Such B incorporation appears to promote or to be facilitated by the condensation of originally incompletely-condensed Si atoms around the incorporated B site.

2.h. Understanding the differences between $C_{16}H_{33}N^+Me_2Et$ and $C_{16}H_{33}N^+Me_3$ -directed borosilicate materials

When B atoms are incorporated into the two surfactant-directed silicate frameworks with very similar lamellar morphologies (see Section 2.a), prepared under identical synthesis conditions with very similar structure-directing alkylammonium molecules, profound differences appear between them. XRD and ${}^{11}B{}^{1}H{}$ correlation NMR data (Section 2.c), along with ²⁹Si{¹H} correlation NMR data published previously for the siliceous analogs,⁴⁶ suggest that the orientations of the surfactant molecules and their interactions with silicate layers are similar in both materials. (In fact the latter appear to primarily depend on the nature $(Q^3 \text{ or } Q^4)$ of the site in which the boron is incorporated.) We consequently believe that the origin(s) of the different boron siting and distributions between these materials must be sought instead in the molecular structures of their layered frameworks. The presence of B atoms of smaller size as compared with Si atoms in a silicate framework with otherwise unchanged topology is expected to create a certain amount of stress, which causes a relaxation of the bonding geometry to attain a stable conformation. This mechanism particularly depends on the availability of sufficient degrees of freedom, and the subtle differences between the molecular structures of the layered frameworks in the corresponding reference materials are important in this respect. For example, the $C_{16}H_{33}N^+Me_2Et$ -directed silicates are slightly more condensed than the $C_{16}H_{33}N^+Me_3$ -directed silicates, with 40% of Q^3 Si sites as compared to 50% for the other. This difference somehow contributes to imposing that the B atoms are located in a single T site that can accommodate such structural distortions more easily than others. The slightly more condensed $C_{16}H_{33}N^{+}Me_{2}Et$ -directed frameworks, in particular, do not seem to allow for (or to necessitate) the additional cross-linking that occurs in some cases for the other borosilicate material. Another possible reason for such differences, which may also have impacts on the available degrees of freedom of the frameworks, is the different ways in the linear chains formed by the Q³ sites and their mutually H-bonded non-bridging oxygen atoms are arranged in the two different framework structures. These chains are aligned in the same direction above and below the plane in the $C_{16}H_{33}N^+Me_2Et$ -directed materials, whereas the chains of Q^3 sites located on the top of a given layer are perpendicular to the ones located at the bottom in the $C_{16}H_{33}N^+Me_3$ -directed materials. Possibly as a result of this difference, the lamellar structure of the C₁₆H₃₃N⁺Me₂Et-directed material is less likely to deform such as to accommodate for new ²⁹Si-O-²⁹Si connectivities that appear to facilitate the incorporation of ¹¹B atoms into the framework of the C₁₆H₃₃N⁺Me₃-directed materials.

It should be possible to relate these considerations to the differences in the amount of boron that can be incorporated into the two materials under identical synthesis conditions. All of our syntheses lead to a final amount of B (Si/B $\sim ca.$ 50 to 140) that is considerably lower than that used for the synthesis (Si/B = 2.5). And yet this final amount of B is generally higher for the C₁₆H₃₃N⁺Me₂Et-directed materials, where the Si/B substitution can take place in a Q^3 Si site (a situation seemingly more favorable than in a Q⁴ Si site) without local topological rearrangements of the framework. For the $C_{16}H_{33}N^+Me_3$ directed materials, one among the three distinct types of B sites that could be distinguished is still a Q³ Si site, but we showed that its local Si environment is profoundly modified as compared to the Q³ Si sites without covalently-bonded B atoms, with additional Si-O-Si connectivities involving the next-nearest neighbors of the boron. The topological rearrangements that promote (or are driven by) the B/Si substitution probably represent a relatively high energy barrier that makes this situation kinetically unfavorable. Another possible reason for the lower amount of boron incorporated into the $C_{16}H_{33}N^+Me_3$ -directed materials is the shorter synthesis time (2 days) as compared to the $C_{16}H_{33}N^{+}Me_{2}Et$ -directed material (7 days). These synthesis durations were kept to the minimum time needed to achieve a complete extent of molecular order in the reference silicate materials.⁴⁶ It is possible that longer crystallization times could lead to increased boron contents in the C₁₆H₃₃N⁺Me₃-material, as previously reported by Zones and Hwang for borosilicate zeolite B-SSZ-42,⁷⁷ but this has not been extensively tested.

The astounding selectivity of B incorporation into a single type of Q³ Si sites in the $C_{16}H_{33}N^{+}Me_{2}Et$ -directed borosilicates cannot be explained by obvious thermodynamic criteria. As shown in Table 5, for a given framework (2 and 3 using the labeling of ref. 64) the energies calculated for models with B incorporated into site Si1 and Si2 are indeed very similar to each other (0.17 and 0.02 eV difference for frameworks 2 and 3, respectively). The accessibility to both Q³ sites being seemingly the same (both correspond to the most easily-accessed parts on the top and bottom of each layer, as shown in Fig. S5, ESI⁺), one can therefore think of reasons related to differences in the local structure around these sites. For example, analyses of the average T-O-T angles around Si sites Si1 and Si2 in the reference frameworks without B incorporation (Table 5) indicate significantly lower angle values around site Si1 as compared to Si2. In addition, the average B-O-Si angle appears to be systematically lower than the corresponding average Si-O-Si angle of the considered substitution Si site in the reference silicate model, as expressed in Table 5 by the negative values of their difference ⊿. This suggests that the smaller average T-O-T angle around Si1 might correspond to a lower energy barrier for the incorporation of B in this site as compared to the other Q³ Si site Si2 because the structural rearrangements required to accommodate the B atom are less pronounced in substitution of a site Si1. This explanation is compatible with the low amount of B that can be incorporated into the C₁₆H₃₃N⁺Me₂Et-directed silicate framework (albeit higher than

Table 5 Local structure analyzes around (potential) B incorporation site in the reference silicate and borosilicate framework models of the $C_{16}H_{33}N^+Me_2Et$ -directed material

| | Reference framework | B incorporation site | Energy (eV) | Average T–O–T angle | | |
|---|---------------------|----------------------|-------------|---------------------|-----------|---------------------|
| Model composition | | | | Name | Value (°) | \varDelta^{a} (°) |
| $\frac{\left[{\rm Si}_{10}{\rm O}_{20}({\rm OH})_{2}\right]^{2-}}{3}$ | 2 | | -11436.09 | Si1-O-Si | 143.5 | |
| | | | | Si2-O-Si | 151.8 | |
| | 3 | | -11435.99 | Si1-O-Si | 144.6 | |
| | | | | Si2-O-Si | 151.8 | |
| $[BSi_{39}O_{80}(OH)_8]^{8-}$ 2 3 | 2 | Si1 | -45652.59 | B-O-Si | 138.8 | -4.7 |
| | | Si2 | -45652.46 | B-O-Si | 150.1 | -1.7 |
| | 3 | Si1 | -45652.10 | B-O-Si | 138.8 | -5.8 |
| | | Si2 | -45652.08 | B-O-Si | 140.7 | -11.0 |
| | | | | | | |

 a Δ is the difference between the average B–O–Si angle and the corresponding average Si–O–Si angle in the reference structure (without B incorporation).

in the $C_{16}H_{33}N^+Me_3$ -directed framework), which indicates a relatively high energy barrier during the synthesis, and thus a kinetically-limited process.

3. Conclusions

We have established the B site distributions in the two chemically and structurally related C₁₆H₃₃N⁺Me₃- and C₁₆H₃₃N⁺Me₂Etdirected layered borosilicates by using advanced solid-state NMR techniques, in conjunction with DFT calculations. The results and analyses reveal that B atoms are incorporated into different types of framework sites in the C₁₆H₃₃N⁺Me₃-directed borosilicates, and induce in some cases local topological rearrangements of nearby Si sites that tend to be more polymerized than in the reference silicate framework. In C₁₆H₃₃N⁺Me₂Et-directed borosilicates, in contrast, B atoms are shown to be selectively incorporated into one type of Q3 29Si sites without topological modifications of the framework. Furthermore, the distorted local environments near B sites in C16H33N*Me2Et-directed borosilicates appear to be similar throughout the framework, resulting in a degree of molecular order that approaches that of crystalline structures, though without long-range periodicity. The ability of NMR combined with DFT calculations to distinguish between topological and subtle geometrical disorder resulting from a chemical disorder in otherwise molecularly-ordered solids may be a key to understand the origins of many advanced materials properties.²³ In particular, the types and distributions of order and disorder near framework B sites in the borosilicate frameworks studied here might well be correlated with the reaction and other material properties of borosilicates, as is now wellestablished for aluminosilicate zeolites.¹² While there is little evidence that this is also true for borosilicates, which have received less attention, some studies nevertheless revealed different conversion rates and selectivities for borosilicate zeolites depending on the Si/B ratios,78 which may be interpreted as changes in the B siting among the different framework sites as the B content changes. The molecular-level insights into B site distributions in the two surfactant-directed borosilicates are expected to guide rational syntheses of borosilicate zeolite catalysts with controlled B site distributions.

4. Materials and methods

Syntheses of materials

Cetyltrimethylammonium bromide ($C_{16}H_{33}Me_3NBr$, $\geq 96.0\%$, Sigma-Aldrich), cetyldimethylethylammonium bromide (C16H33- Me_2EtNBr , $\geq 98\%$, Sigma-Aldrich), tetramethylammonium hydroxide (TMAOH, 25 wt% in water, Sigma-Aldrich), boric acid (Sigma-Aldrich), hydrofluoric acid (HF, 48 wt% in water, Sigma-Aldrich), nitric acid (HNO3, ACS reagent and 70%), amorphous silica (SiO₂, CAB-O-SIL M5 scintillation grade, ACROS ORGANICS) and methanol (ACS grade, VWR[®]) were purchased and directly used without any further purification. 99% ²⁹Si-enriched SiO₂ was purchased from CortecNet (France). Syntheses of layered surfactant-directed borosilicates follow the molar composition of 1.0SiO₂: 0.2B₂O₃: 0.7TMAOH: 113.4H₂O: 9.9CH₃OH: 0.7 surfactants (either C16H33Me3NBr or C16H33Me2EtNBr). Surfactants were dissolved in deionized water. TMAOH and CH₃OH were subsequently added and the solution stirred for 30 min, after which silica precursors (either SiO_2 or recondensed ²⁹SiO₂) were added, and the reaction media stirred for a week. Boric acid was then added for 2 h to obtain synthesis gels, which were transferred into a Teflon[™]-lined Parr[™] 4745 stainless-steel reactor, well-sealed and heated at 135 °C under static conditions for 2 ($C_{16}H_{33}N^{\dagger}Me_{3}$ -directed borosilicates) and 7 days ($C_{16}H_{33}N^{\dagger}Me_{2}Et$ directed borosilicates). These crystallization times correspond to the minimal duration needed to obtain complete extents of molecular order for the corresponding reference silicate structures of both materials.⁴⁶ After the hydrothermal treatment, the as-synthesized layered surfactant-directed borosilicates were collected using vacuum filtration and washed with deionized water. The products were dried at 90 °C overnight before characterization.

Recondensed ²⁹SiO₂ was prepared by dissolving ²⁹Si-enriched SiO₂ in 1 M TMAOH solution (pH ~ 14) under reflux at 95 °C and stirring conditions for 19 days. The ²⁹Si-enriched silica was subsequently recovered by adding a concentrated HBr acid solution to obtain precipitated gels (pH of 7–8), which were subsequently collected by vacuum filtration. The precipitated gels were purified by deionized water, high-speed centrifugation, and removal of excess water. The purified silica source (designated as recondensed ²⁹SiO₂) was dried at 90 °C for several days prior to syntheses of borosilicates.

Elemental analyses

Bulk Si/B ratios were obtained using inductively coupled plasma (ICP) analysis (Thermo iCAP 6300 model). Before ICP analysis, the as-synthesized layered materials were calcined at 550 $^{\circ}$ C for 12 h to remove organic surfactants, and the resulting calcined materials were dissolved with 2 wt% HF and 3 wt% HNO₃ acid solution under vigorous stirring conditions for several days. The CHN results were provided by the analytical lab in the Marine Science Institute (MSI), UCSB, using the CEC440HA model from Exeter Analytical, Inc.

Solid-state NMR

Solid-state one-dimensional (1D) ¹¹B, ²⁹Si and two-dimensional (2D) ¹¹B{¹H} HETCOR NMR experiments were performed on a Bruker Avance (III) 750 and 400 NMR spectrometers operating at 17.6 (¹H, ¹¹B, and ²⁹Si Larmor frequencies of 750.12, 240.66, and 149.01 MHz, respectively) and 9.4 T (¹H, ¹¹B, and ²⁹Si frequencies of 400.17, 128.38, and 79.49 MHz, respectively). The 1D ²⁹Si{¹H} CP-MAS experiments were collected at room temperature, at 17.6 T and at 10 kHz under conditions of magic angle spinning (MAS) using a 4 mm probe head, with a crosspolarization (CP) contact time of 8 ms and a recycle delay of 2 s, with 4k transients for the natural abundance sample and 128 scans for the ²⁹Si enriched sample. ¹¹B echo-MAS experiments were performed at 17.6 T, at a MAS frequency of 14 kHz using a recycling delay of 2 s, with a double frequency sweep (DFS)⁷⁹ preparation sequence to increase the signal. Heteronuclear ¹H decoupling at a nutation frequency of 50 kHz using SPINAL64⁸⁰ was utilized during acquisition for both ²⁹Si and ¹¹B NMR experiments. Transverse dephasing time measurements were performed with 7 increments to obtain a series of half-echo delays between 0 and 12 ms, each collected with 1024 scans. Heteronuclear ¹H decoupling (SPINAL64) at a nutation frequency of 60 kHz was alternatively turned on and off during the echo (and kept on during the acquisition).

Two-dimensional (2D) ¹¹B{¹H} HETCOR NMR spectra were collected at room temperature at 17.6 T and under MAS conditions of 14 kHz using a 4 mm probe head. The magnetization was transferred from ¹H to ¹¹B by using adiabatic passage through Hartmann–Hahn condition.⁸¹ CP contact times of 1 and 0.1 ms were used for the $C_{16}H_{33}N^+Me_3$ - and $C_{16}H_{33}N^+Me_2$ Etdirected layered borosilicates, respectively. The signal in the 2D ¹H dimension was accumulated over 96 increments with 176 transients each for the $C_{16}H_{33}N^+Me_3$ -directed material and 128 increments with 64 transients each for the $C_{16}H_{33}N^+Me_2$ Etdirected material. Heteronuclear ¹H decoupling at a nutation frequency of 70 kHz was applied during acquisition. Both spectra were collected using a repetition delay of 2 s.

Two-dimensional ¹¹B{²⁹Si} dipolar- and *J*-mediated HMQC spectra were collected at 9.4 T on materials synthesized with ²⁹Si enrichment, at a MAS frequency of 10 kHz (using 3.2 mm triple-resonance probe head). The heteronuclear dipolar couplings between ¹¹B and ²⁹Si species were reintroduced in dipolar-mediated ¹¹B{²⁹Si} HMQC by means of a $R4^{2}_{1}$ symmetry-based dipolar recoupling^{82–85} scheme at a ²⁹Si nutation frequency of

20 kHz $(2\nu_R)$. The recoupling durations were set to 6 ms (10 symmetry cycles of 6 rotor periods each) before and after the evolution period. The second ²⁹Si dimension was collected with 96 increments, with 1024 transients each, and a repetition delay of 2.17 s (total experimental duration of 61 hours). The half-echo delay before and after the evolution period in the ¹¹B₁²⁹Si} J-mediated HMQC⁸⁶ experiments was optimized experimentally to 10 and 12.5 ms for the $C_{16}H_{33}N^{\dagger}Me_3$ - and $C_{16}H_{33}N^{\dagger}Me_2Et$ directed layered borosilicates, respectively. The indirect dimensions were collected with 32 increments (2304 scans each) for the former material and 96 increments for the latter (768 transients each). Recycling delays of 3 second for both materials led to experimental durations of 62 and 63 hours, respectively. Heteronuclear ¹H decoupling with the SPINAL64 sequence at a nutation frequency of *ca.* 60 kHz was applied during the whole sequence. NMR ²⁹Si and ¹¹B chemical shifts were referenced to tetra methyl silane (TMS) and BF₃OEt₂, respectively.

Error calculations for the transverse dephasing time measurements were conducted using a Monte Carlo approach, by repeating the same fit on 512 sets of data points generated by adding random noise to the experimental data set. The standard deviation of the added random noise was fixed to the standard deviation between the experimental points and the best fit. The reported errors correspond to the standard deviation of the fitted data over the 512 fits.

X-ray diffraction

The mesostructures and local periodic orderings were characterized using small-angle (SAXS) and wide-angle (WAXS) X-ray diffractions. SAXS patterns were collected using a Rigaku SMART lab diffractometer and Cu K α radiation ($\lambda = 1.5405$ Å) generated at 44 kV and 40 mA. The scanning angle range of a SAXS pattern was from 0.5 to 10° 2 θ and the step size was set to 0.5° min⁻¹. WAXS patterns were collected using a Philips XPERT Pro diffractometer and Cu K α radiation ($\lambda = 1.5405$ Å) generated at 45 kV and 40 mA. The materials were scanned at a step size of 4° min⁻¹ between 2 θ angle ranges from 10 to 45°.

DFT calculations

DFT calculations were conducted using CASTEP,⁸⁷ a code based on Density Functional Theory that uses a plane-wave approach and periodic boundary conditions. Geometry optimizations were conducted using PBE as an exchange correlation functional,⁸⁸ a cut-off energy of 650 eV, and the default "on-the-fly" "ultrasoft" pseudopotentials⁸⁹ of Materials Studio (see pseudopotential details in ESI,† Table S4) with convergence thresholds of 10^{-5} eV per atom for the total energy, 3×10^{-2} eV Å⁻¹ for the maximum ionic force, and 10^{-3} Å for the maximum ionic displacement. During the geometry optimization, unit cells were kept frozen, while all the atoms inside were allowed to relax in order to minimize both the forces on the atoms and on the unit cell. Depending on the model size, different Monkhorst-Pack⁹⁰ (MP) grids were used to sample the Brillouin zone so as to give a k-spacing less than 0.04 $Å^{-1}$ in the a, b, c directions. For example, a $4 \times 4 \times 1$ MP grid is used when calculation was made on one unit cell (10 or 8 Si atoms depending on the material),

whereas MP grids of size $4 \times 2 \times 1$, $2 \times 4 \times 1$, $2 \times 2 \times 1$, and $3 \times 1 \times 1$ were used for the $1 \times 2 \times 1$, $2 \times 1 \times 1$, $2 \times 2 \times 1$, and $1 \times 3 \times 1$ supercells, respectively.

Calculations of NMR shielding values were performed using the Gauge Including Projector Augmented Wave approach⁹¹ (GIPAW) method implemented in CASTEP using the same conditions for cut-off energy and MP grid as for geometry optimizations. Reliable absolute chemical shift values may be obtained from correlation plots between experimental isotropic chemical shifts and calculated isotropic chemical shielding for an appropriate series of reference compounds in order to cover a large domain of chemical shifts for each type of nuclei. Here, we used for ²⁹Si and ¹¹B chemical shift calculations the compounds listed in Table S3 (ESI†), which gave rise to the correlation plots shown in Fig. S7 (ESI†). The correlation equations were: $\delta_{iso}(ppm) = -0.920 \sigma_{iso} +$ 288.45 for ²⁹Si, and $\delta_{iso}(ppm) = -1.004 \sigma_{iso} + 95.31$ for ¹¹B.

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References

- 1 K. Tanabe and W. F. Holderich, *Appl. Catal., A*, 1999, **181**, 399–434.
- 2 M. Borja and P. K. Dutta, Nature, 1993, 362, 43-45.
- 3 M. Iwamoto, H. Yahiro, N. Mizuno, W. X. Zhang, Y. Mine, H. Furukawa and S. Kagawa, *J. Phys. Chem.*, 1992, 96, 9360–9366.
- 4 D. Barthomeuf, Catal. Rev.: Sci. Eng., 1996, 38, 521-612.
- 5 S. M. Kuznicki, V. A. Bell, S. Nair, H. W. Hillhouse, R. M. Jacubinas, C. M. Braunbarth, B. H. Toby and M. Tsapatsis, *Nature*, 2001, 412, 720–724.
- 6 S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki and R. Ryoo, *Nature*, 2001, **412**, 169–172.
- 7 J. Choi, H.-K. Jeong, M. A. Snyder, J. A. Stoeger, R. I. Masel and M. Tsapatsis, *Science*, 2009, **325**, 590–593.
- 8 K. Varoon, X. Zhang, B. Elyassi, D. D. Brewer, M. Gettel, S. Kumar, J. A. Lee, S. Maheshwari, A. Mittal, C.-Y. Sung, M. Cococcioni, L. F. Francis, A. V. McCormick, K. A. Mkhoyan and M. Tsapatsis, *Science*, 2011, 333, 72–75.
- 9 R. Bermejo-Deval, R. S. Assary, E. Nikolla, M. Moliner, Y. Roman-Leshkov, S. J. Hwang, A. Palsdottir, D. Silverman, R. F. Lobo, L. A. Curtiss and M. E. Davis, *Proc. Natl. Acad. Sci.* U. S. A., 2012, **109**, 9727–9732.

- 10 J. Jae, G. A. Tompsett, A. J. Foster, K. D. Hammond, S. M. Auerbach, R. F. Lobo and G. W. Huber, *J. Catal.*, 2011, 279, 257–268.
- T. Willhammar, J. Sun, W. Wan, P. Oleynikov, D. Zhang, X. Zou, M. Moliner, J. Gonzalez, C. Martínez, F. Rey and A. Corma, *Nat. Chem.*, 2012, 4, 188–194.
- J. Dědeček, Z. Sobalík and B. Wichterlová, *Catal. Rev.*, 2012, 54, 135–223.
- 13 Y. Roman-Leshkov, M. Moliner and M. E. Davis, J. Phys. Chem. C, 2011, 115, 1096–1102.
- 14 A. B. Pinar, C. Marquez-Alvarez, M. Grande-Casas and J. Perez-Pariente, *J. Catal.*, 2009, **263**, 258–265.
- 15 C. A. Hijar, R. M. Jacubinas, J. Eckert, N. J. Henson, P. J. Hay and K. C. Ott, *J. Phys. Chem. B*, 2000, 104, 12157–12164.
- 16 C. Lamberti, S. Bordiga, A. Zecchina, G. Artioli, G. Marra and G. Spano, *J. Am. Chem. Soc.*, 2001, **123**, 2204–2212.
- 17 P. F. Henry, M. T. Weller and C. C. Wilson, J. Phys. Chem. B, 2001, 105, 7452–7458.
- 18 M. Milanesio, C. Lamberti, R. Aiello, F. Testa, M. Piana and D. Viterbo, *J. Phys. Chem. B*, 2000, **104**, 9951–9953.
- 19 L. Palin, C. Lamberti, A. Kvick, F. Testa, R. Aiello, M. Milanesio and D. Viterbo, *J. Phys. Chem. B*, 2003, 107, 4034–4042.
- 20 J. Shin, D. S. Bhange, M. A. Camblor, Y. Lee, W. J. Kim, I. S. Nam and S. B. Hong, *J. Am. Chem. Soc.*, 2011, 133, 10587–10598.
- 21 J. A. van Bokhoven, T.-L. Lee, M. Drakopoulos, C. Lamberti, S. Thiesz and J. Zegenhagen, *Nat. Mater.*, 2008, 7, 551–555.
- 22 E. Véron, M. N. Garaga, D. Pelloquin, S. Cadars, M. Suchomel, E. Suard, D. Massiot, V. Montouillout, G. Matzen and M. Allix, *Inorg. Chem.*, 2013, **52**, 4250–4258.
- 23 D. Massiot, R. J. Messinger, S. Cadars, M. Deschamps, V. Montouillout, N. Pellerin, E. Veron, M. Allix, P. Florian and F. Fayon, *Acc. Chem. Res.*, 2013, **46**, 1975–1984.
- 24 C. A. Fyfe, J. L. Bretherton and L. Y. Lam, *J. Am. Chem. Soc.*, 2001, **123**, 5285–5291.
- 25 S. Sklenak, J. Dedecek, C. B. Li, B. Wichterlova, V. Gabova, M. Sierka and J. Sauer, *Angew. Chem., Int. Ed.*, 2007, 46, 7286–7289.
- 26 O. H. Han, C. S. Kim and S. B. Hong, Angew. Chem., Int. Ed., 2002, 41, 469–472.
- 27 J. Dedecek, L. Capek, P. Sazama, Z. Sobalik and B. Wichterlova, *Appl. Catal.*, *A*, 2011, **391**, 244–253.
- 28 J. Dedecek, V. Balgová, V. Pashkova, P. Klein and B. Wichterlová, *Chem. Mater.*, 2012, 24, 3231–3239.
- 29 P. Sazama, J. Dedecek, V. Gabova, B. Wichterlova, G. Spoto and S. Bordiga, *J. Catal.*, 2008, **254**, 180–189.
- 30 C. Baerlocher, D. Xie, L. B. McCusker, S. J. Hwang, I. Y. Chan, K. Ong, A. W. Burton and S. I. Zones, *Nat. Mater.*, 2008, 7, 631–635.
- 31 T. Willhammar, A. W. Burton, Y. Yun, J. Sun, M. Afeworki,
 K. G. Strohmaier, H. Vroman and X. Zou, *J. Am. Chem. Soc.*,
 2014, 136, 13570–13573.
- 32 D. Xie, L. B. McCusker, C. Baerlocher, L. Gibson, A. W. Burton and S. J. Hwang, *J. Phys. Chem. C*, 2009, **113**, 9845–9850.

- 33 A. Grünewald-Lüke, H. Gies, U. Müller, B. Yilmaz, H. Imai, T. Tatsumi, B. Xie, F.-S. Xiao, X. Bao, W. Zhang and D. De Vos, *Microporous Mesoporous Mater.*, 2012, 147, 102–109.
- 34 P. S. Neuhoff, S. Kroeker, L. S. Du, T. Fridriksson and J. F. Stebbins, *Am. Mineral.*, 2002, 87, 1307–1320.
- 35 S. B. Hong, S.-H. Lee, C.-H. Shin, A. J. Woo, L. J. Alvarez, C. M. Zicovich-Wilson and M. A. Camblor, *J. Am. Chem. Soc.*, 2004, **126**, 13742–13751.
- 36 G. Engelhardt and D. Michel, *High-resolution solid-state NMR of silicates and zeolites*, Wiley, 1987.
- 37 K. J. D. Mackenzie and M. E. Smith, *multinuclear solid-state NMR of inorganic materials*, Pergamon Press, Oxford, 2002.
- 38 H. K. Jeong, S. Nair, T. Vogt, L. C. Dickinson and M. Tsapatsis, *Nat. Mater.*, 2003, 2, 53–58.
- 39 T. Ikeda, Y. Akiyama, Y. Oumi, A. Kawai and F. Mizukami, *Angew. Chem., Int. Ed.*, 2004, **43**, 4892–4896.
- 40 T. Ikeda, S. Kayamori and F. Mizukami, *J. Mater. Chem.*, 2009, **19**, 5518–5525.
- 41 L. Palin, G. Croce, D. Viterbo and M. Milanesio, *Chem. Mater.*, 2011, 23, 4900–4909.
- 42 B. Yilmaz, U. Muller, B. Tijsebaert, D. De Vos, B. Xie, F. S. Xiao, H. Gies, W. P. Zhang, X. H. Bao, H. Imai and T. Tatsumi, *Chem. Commun.*, 2011, 47, 1812–1814.
- 43 Z. Li, B. Marler and H. Gies, *Chem. Mater.*, 2008, **20**, 1896–1901.
- 44 B. Marler and H. Gies, Eur. J. Mineral., 2012, 24, 405-428.
- 45 W. J. Roth, P. Nachtigall, R. E. Morris and J. Cejka, *Chem. Rev.*, 2014, **114**, 4807–4837.
- 46 S. C. Christiansen, D. Y. Zhao, M. T. Janicke, C. C. Landry, G. D. Stucky and B. F. Chmelka, *J. Am. Chem. Soc.*, 2001, **123**, 4519–4529.
- 47 N. Hedin, R. Graf, S. C. Christiansen, C. Gervais, R. C. Hayward, J. Eckert and B. F. Chmelka, *J. Am. Chem. Soc.*, 2004, **126**, 9425–9432.
- 48 Y. D. Xia and R. Mokaya, *Microporous Mesoporous Mater.*, 2006, **94**, 295–303.
- 49 Y. D. Xia and R. Mokaya, J. Phys. Chem. B, 2006, 110, 9122-9131.
- 50 G. Coudurier, A. Auroux, J. C. Vedrine, R. D. Farlee, L. Abrams and R. D. Shannon, *J. Catal.*, 1987, **108**, 1–14.
- 51 R. Millini, G. Perego and G. Bellussi, *Top. Catal.*, 1999, **9**, 13–34.
- 52 R. A. Van Nordstrand, D. S. Santilli and S. I. Zones, in *Molcular Sieves*, ed. M. L. Ocelli and H. E. Robson, Synthesis of Microporous Materials, New York, 1992, vol. 1, p. 373.
- 53 S. I. Zones, A. Benin, S.-J. Hwang, D. Xie, S. Elomari and M.-F. Hsieh, J. Am. Chem. Soc., 2014, 136, 1462–1471.
- 54 D. Sakellariou and L. Emsley, in *Encyclopedia of Nuclear Magnetic Resonance*, ed. D. M. Grant and R. K. Harris, Wiley, London, 2002, vol. 9, pp. 196–211.
- 55 D. Massiot, F. Fayon, M. Deschamps, S. Cadars, P. Florian,
 V. Montouillout, N. Pellerin, J. Hiet, A. Rakhmatullin and
 C. Bessada, *C. R. Chim.*, 2010, 13, 117–129.
- 56 C. A. Fyfe, H. Gies, Y. Feng and G. T. Kokotailo, *Nature*, 1989, **341**, 223–225.

- 57 C. A. Fyfe, H. Gies and Y. Feng, J. Chem. Soc., Chem. Commun., 1989, 1240-1242.
- 58 C. A. Fyfe, H. Gies and Y. Feng, J. Am. Chem. Soc., 1989, 111, 7702–7707.
- 59 S. Cadars, D. H. Brouwer and B. F. Chmelka, *Phys. Chem. Chem. Phys.*, 2009, **11**, 1825–1837.
- 60 C. A. Fyfe, K. C. Wongmoon, Y. Huang, H. Grondey and K. T. Mueller, J. Phys. Chem., 1995, 99, 8707–8716.
- 61 M. Deschamps, F. Fayon, J. Hiet, G. Ferru, M. Derieppe, N. Pellerin and D. Massiot, *Phys. Chem. Chem. Phys.*, 2008, 10, 1298–1303.
- 62 P. Florian, E. Veron, T. F. G. Green, J. R. Yates and D. Massiot, *Chem. Mater.*, 2012, 24, 4068–4079.
- 63 C. A. Fyfe, Y. Feng, H. Grondey, G. T. Kokotailo and H. Gies, *Chem. Rev.*, 1991, 91, 1525–1543.
- 64 D. H. Brouwer, S. Cadars, J. Eckert, Z. Liu, O. Terasaki and
 B. F. Chmelka, J. Am. Chem. Soc., 2013, 135, 5641–5655.
- 65 S. Cadars, M. Allix, D. H. Brouwer, R. Shayib, M. Suchomel,
 A. W. Burton, M. N. Garaga, A. I. Rakhmatullin, S. I. Zones,
 D. Massiot and B. F. Chmelka, *Chem. Mater*, 2014, 26, 6994–7008.
- 66 P. Florian, F. Fayon and D. Massiot, J. Phys. Chem. C, 2009, 113, 2562–2572.
- 67 D. Massiot, F. Fayon, V. Montouillout, N. Pellerin, J. Hiet, C. Roiland, P. Florian, J. P. Coutures, L. Cormier and D. R. Neuville, *J. Non-Cryst. Solids*, 2008, **354**, 249–254.
- 68 J. Hiet, M. Deschamps, N. Pellerin, F. Fayon and D. Massiot, *Phys. Chem. Chem. Phys.*, 2009, **11**, 6935–6940.
- 69 G. De Paepe, N. Giraud, A. Lesage, P. Hodgkinson, A. Bockmann and L. Emsley, *J. Am. Chem. Soc.*, 2003, **125**, 13938–13939.
- 70 G. De Paepe, A. Lesage, S. Steuernagel and L. Emsley, *ChemPhysChem*, 2004, 5, 869–875.
- 71 S. Vortmann, J. Rius, S. Siegmann and H. Gies, *J. Phys. Chem. B*, 1997, **101**, 1292–1297.
- 72 I. Wolf, H. Gies and C. A. Fyfe, J. Phys. Chem. B, 1999, 103, 5933-5938.
- 73 N. Tsunoji, T. Ikeda, Y. Ide, M. Sadakane and T. Sano, J. Mater. Chem., 2012, 22, 13682–13690.
- 74 S. Cadars, N. Mifsud, A. Lesage, J. D. Epping, N. Hedin,
 B. F. Chmelka and L. Emsley, *J. Phys. Chem. C*, 2008, 112, 9145–9154.
- 75 L. S. Du and J. F. Stebbins, *J. Non-Cryst. Solids*, 2003, 315, 239–255.
- 76 C. Baerlocher, L. B. McCusker and D. H. Olson, Atlas of Zeolite Framework Types, Elsevier, Amsterdam, 2007.
- 77 S. I. Zones and S. J. Hwang, *Microporous Mesoporous Mater.*, 2003, 58, 263–277.
- 78 A. Boghoz, M. Soltanieh, R. Mondegarian and M. Karbalaee, *Ind. Eng. Chem. Res.*, 1998, 37, 2378–2382.
- 79 D. Iuga and A. P. M. Kentgens, J. Magn. Reson., 2002, 158, 65–72.
- 80 B. M. Fung, A. K. Khitrin and K. Ermolaev, J. Magn. Reson., 2000, 142, 97–101.
- 81 S. Hediger, B. H. Meier, N. D. Kurur, G. Bodenhausen and R. R. Ernst, *Chem. Phys. Lett.*, 1994, 223, 283–288.

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- 82 M. Carravetta, M. Eden, X. Zhao, A. Brinkmann and M. H. Levitt, *Chem. Phys. Lett.*, 2000, **321**, 205–215.
- 83 A. Brinkmann and M. H. Levitt, J. Chem. Phys., 2001, 115, 357–384.
- 84 A. Brinkmann and A. P. M. Kentgens, J. Am. Chem. Soc., 2006, **128**, 14758–14759.
- 85 B. Hu, J. Trebosc and J. P. Amoureux, *J. Magn. Reson.*, 2008, 192, 112–122.
- 86 A. Lesage, D. Sakellariou, S. Steuernagel and L. Emsley, J. Am. Chem. Soc., 1998, 120, 13194–13201.
- 87 S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. J. Probert,
 K. Refson and M. C. Payne, *Z. Kristallogr.*, 2005, 220, 567–570.
- 88 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865–3868.
- 89 D. Vanderbilt, Phys. Rev. B: Condens. Matter Mater. Phys., 1990, 41, 7892-7895.
- 90 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B: Solid State*, 1976, **13**, 5188–5192.
- 91 C. J. Pickard and F. Mauri, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **63**, 245101.