

# Toward Understanding the Thermodynamic Viability of Zeolites and Related Frameworks through a Simple Topological Model

Martijn A. Zwijnenburg,<sup>†</sup> Stefan T. Bromley,<sup>\*,†</sup> Martin D. Foster,<sup>‡,||</sup>  
Robert G. Bell,<sup>‡</sup> Olaf Delgado-Friedrichs,<sup>§</sup> Jacobus C. Jansen,<sup>†</sup> and  
Thomas Maschmeyer<sup>†,⊥</sup>

Ceramic Membrane Centre "The Pore", Delft University of Technology, Julianalaan 136,  
2628 BL Delft, The Netherlands, The Davy Faraday Research Laboratory, The Royal  
Institution of Great Britain, 21 Albemarle Street, London, W1S 4BS, U.K., and Wilhelm  
Schickard Institute for Computer Science, University of Tübingen,  
Sand 14, 72072 Tübingen, Germany

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Framework materials (e.g., zeolites, metallophosphates, chalcogenides, and metal organic frameworks) are widely used as catalysts, adsorbents, and ion exchangers. Although many different frameworks have been synthesized (or found in nature), numerous applications still call for frameworks with larger pores, lower framework densities, and/or higher specific absorption volumes than currently available. Thus, research into synthesizing novel framework materials with one or more of the desired properties has been extensively pursued in recent years, often however with no prior knowledge regarding their synthetic viability. In this study, we show how the decomposition of an archetypal class of framework materials (zeolites) into polyhedral tiles and the analysis of the face-size distribution obtained (using topological descriptors and periodic atomistic calculations on both synthesized and hypothetical frameworks) can lead to definite predictions regarding the thermodynamic viability of their synthesis. Moreover, it is demonstrated that pore size and framework density cannot be varied freely, but that they, at least for frameworks corresponding to simple tilings, are intimately connected to the thermodynamic viability of the framework's synthesis through its topology. These new insights allow us not only to rationalize the thermodynamic viability of a range of desirable (but as yet unmade) frameworks but also to begin to understand the physical and topological boundaries which inherently limit attempts to synthesize frameworks with ever-larger pores and lower framework densities. Although the methodology is validated for all-silica frameworks, the mode of investigation, due to its generality and nonreliance on specific geometric/chemical details, should be applicable to framework materials in general.

## Introduction

Framework materials such as zeolites, metallophosphates, chalcogenides,<sup>1–3</sup> mixed coordination silicates,<sup>4,5</sup> sodium niobates,<sup>6,7</sup> cyanometalates,<sup>8</sup> organic-substituted

zeotypes,<sup>9,10</sup> and metal organic frameworks<sup>11–13</sup> constitute a scientifically interesting and industrially important class of materials having significant applications as catalysts, adsorbents, and ion exchangers<sup>14–17</sup> and technological potential in the fields of solid-state electrolytes,<sup>18</sup> membranes,<sup>19</sup> hydrogen storage,<sup>20–22</sup> and

\* To whom correspondence should be addressed. E-mail: S.T.Bromley@tnw.tudelft.nl.

<sup>†</sup> Delft University of Technology.

<sup>‡</sup> The Royal Institution of Great Britain.

<sup>§</sup> Universität Tübingen.

<sup>||</sup> Current address: Department of Physics and Astronomy, Arizona State University, Tempe, AZ 85287-1504.

<sup>⊥</sup> Current address: Centre for Molecular Catalysis, School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia.

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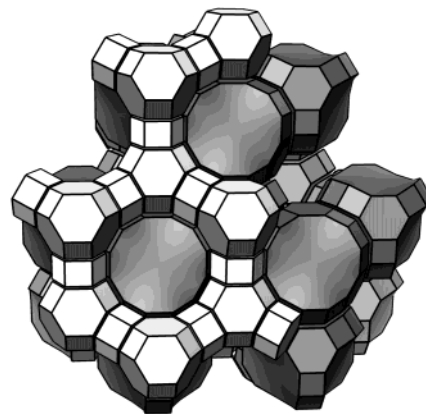
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magnetic materials.<sup>23,24</sup> While very wide ranging in terms of chemical composition, all these materials consist of three-dimensional periodic networks of vertex atoms (usually metal atoms) linked by either nonmetal atoms (e.g., O, S) or ligands (e.g., 1,4-benzenedicarboxylate). Key to their utility is the regular, nanosized channels, threading through their structure, allowing molecules to adsorb into and diffuse through the material. The wide scope of their use originates from the fact that they span a uniquely large spectrum of easily synthesized structures, differing in pore size, framework density (the number of T-atom per 1000 Å<sup>3</sup>), and absorption volume, making it possible to select a structure that most ideally suits the desired application.

While, in principle, once a possible framework structure has been postulated one can calculate any of its specific properties using a range of atomistic and electronic modeling methods, such calculations do not provide general insight into how the framework thermodynamic viability depends on its global structural characteristics nor the physical and topological constraints delimiting the range of viable framework materials. To rationalize synthetic progress and to understand structural trends, it would therefore be very advantageous if one could predict and understand the properties of framework materials based only on their underlying topology. Recently, we developed a general methodology to predict the energetics of polyhedral cages based only on their face-size distribution<sup>25</sup> (i.e., no reference is made to the precise chemical constitution or geometry of the cages) and successfully applied it to rationalize trends in polyhedral silica-cage energetics. Building on this result, we now for the first time demonstrate that decomposing framework materials into a space-filling set of face-sharing polyhedral cages (henceforth referred to as polyhedral tiles), and analyzing the face-size distribution obtained, leads to powerful insights into the dependence of the thermodynamic viability of framework material synthesis upon changes in structural properties such as pore size and framework density. [The face-size distribution is defined as  $x_3^a x_4^b \dots x_n^z$  (with  $x_n$  a face of  $n$  T-atoms and  $z$  its occurrence, e.g., 4<sup>6</sup> for a cube). The face-size distribution of a framework is the sum of the face-size distribution of its constituent space-filling polyhedra (i.e., polyhedral tiles).] In this we use the fact that formally and intuitively regular periodic frameworks can be described as tilings of Euclidian space with the polyhedra as tiles.<sup>26–30</sup> In this way, for example, the zeolite framework FAU can be described as a 1:1:2 space-filling packing of faujasite



**Figure 1.** Part of the FAU framework, clearly showing its constituting polyhedral tiles.

(4<sup>18</sup>6<sup>4</sup>12<sup>4</sup>), sodalite (4<sup>6</sup>6<sup>8</sup>), and “double 6-ring” (4<sup>6</sup>6<sup>2</sup>) polyhedral tiles (see Figure 1).

In this paper we focus on an archetypal class of framework materials, the zeolites, because of their wide industrial importance<sup>15–17</sup> and the availability of well-tested theoretical methods to describe them. It is emphasized, however, that the general methodology described should be applicable to framework materials in general. Although more than 140 different zeolite frameworks have been synthesized (or found in nature [throughout we use “synthesized” in a general sense to include also “naturally synthesized” zeolites]),<sup>31</sup> many applications still call for zeolites with larger pores, lower framework densities, and/or higher specific absorption volumes than found in the currently available frameworks.<sup>32–34</sup> In recent years much work has focused on the generation of hypothetical frameworks<sup>29,30,35–41</sup> and the evaluation of their energetic and structural properties,<sup>42–45</sup> demonstrating that the zeolite structural diversity is much richer than might be expected from a simple assessment of the already available frameworks.

Herein, we will concentrate on frameworks constituted of only silicon and oxygen atoms so as not to complicate thermodynamic comparisons between dif-

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ferent phases (i.e., no disproportionation is allowed). Although we are focusing on a particular chemical framework representation, this does not limit our choice of framework topology upon which our methodology is based. The structural diversity and abundance of framework topologies is considerably richer when we do not limit ourselves to synthesized frameworks only; hence, in this paper we analyze a selection of both synthesized and hypothetical zeolite frameworks. Of this large set of frameworks we mainly focus on zeolites that can be decomposed solely into three-connected polyhedral tiles (i.e., every T-atom maps onto a polyhedral-tile vertex that is connected to three edges). As these frameworks can be derived from the Simple Tilings,<sup>29</sup> we will subsequently refer to them as ST-frameworks. Such frameworks constitute a significant fraction of all thus far synthesized zeolite frameworks, including SOD, LTA, FAU, RHO, KFI, CHA, AST, MEI, TSC, and DOH. Also discussed are zeolite frameworks that are decomposable solely into sets of polyhedral tiles in which some tiles have a number of two-connected vertexes (so-called  $\lambda \neq 0$  polyhedra tiles<sup>25</sup>), such as MFI, VFI, GIS, and MOR. Of the set of hypothetical frameworks (as enumerated by Delgado et al.<sup>29,30</sup> and containing all mathematically possible ST-frameworks with up to three symmetrically independent T-atoms) we consider a large representative sample, including all frameworks with pores circumscribed by 14 or more T-atoms.

### Methodology

The thermodynamics of zeolite synthesis are still surrounded by uncertainties, especially due to the limited amount of data present for such complex systems. However, recent calorimetric data<sup>46–48</sup> suggests that zeolites can be the thermodynamically preferred synthesis product in the presence of a structure-directing agent (SDA), even though the thermodynamic driving forces involved appear to be very small. Solution calorimetry experiments<sup>47</sup> have shown the interaction enthalpy between framework and organic SDA to be small and to span only a narrow range of values, suggesting that SDAs cannot significantly stabilize an otherwise thermodynamically unstable framework. Furthermore, independent of whether the zeolites formed are metastable or stable under the hydrothermal synthesis conditions, one can assume that the probability of synthesizing zeolites in general decreases rapidly with increasing thermodynamic instability. The thermodynamic viability of synthesizing a framework in the form of a zeolite is, therefore, strongly related to its thermodynamic stability compared to the most thermodynamically stable phase for its chemical composition (i.e.,  $\alpha$ -quartz for  $\text{SiO}_2$ ), often approximated by the transition enthalpy.<sup>49,50</sup> Ideally, one would like to use experimentally determined transition enthalpy values for the different zeolites. However, only limited thermodynamic data is available (i.e., for about 15 out of more than 140 synthesized zeolite frameworks<sup>50</sup>). Therefore, we rather employ the results of accurate atomistic calculations of the lattice enthalpy of zeolite frameworks.

In the atomistic calculations, the interaction between silicon and oxygen ions was described by the Sanders force field,<sup>51,52</sup>

consisting of a Coulomb, Buckingham, and a harmonic three-body term. The oxygen ions were modeled using the shell model of Dick and Overhauser,<sup>53</sup> allowing for the effective polarizability of each oxygen ion to vary as a function of its environment. All initial structures of synthesized frameworks were taken from the Zeolite Atlas of the International Zeolite Association<sup>31</sup> and were made all-siliceous where needed, while the structures of the hypothetical frameworks were taken from the library of structures enumerated through dualization of tetrahedral tilings by Delgado et al.<sup>29,30</sup> and prepared for evaluation as described by Foster et al.<sup>42</sup> The lattice enthalpy of 33 synthesized and 90 hypothetical frameworks was then minimized without symmetry constraints using a constant pressure optimization algorithm as implemented in the program GULP<sup>54</sup> (i.e., both atom positions and cell volume were optimized). All energies quoted for zeolites are relative energies compared to quartz, normalized to the number of T-atoms per unit cell.

To verify the applicability of the Sanders force field for calculating accurate values of the lattice enthalpies, we compared the calculated relative energies for eight silica polymorphs with experimentally measured values by Piccione et al.<sup>50</sup> Like Henson et al.,<sup>55</sup> who compared the Sanders potential to more limited measurements (i.e., data available for less structures) by Petrovic et al.,<sup>49</sup> we observe a good quantitative agreement between calculated relative energies and experimental transition enthalpies ( $r^2 = 0.84$ , see Supporting Information). However, due to the experimental error in the calorimetry ( $\pm 1$  kJ/mol) and inherent small scattering, structures differing by less than 1 kJ/mol become difficult to distinguish and can even be misplaced relative to each other. Frameworks containing three rings were excluded from our analysis as the accuracy of the lattice enthalpies for these materials could not be verified with experimental results.

The synthesized frameworks were decomposed into sets of three-connected polyhedral tiles (the smallest set of polyhedral tiles that fills space by translation only) by means of visual inspection and verified where possible by the results of enumeration.<sup>30</sup> The decomposition of the hypothetical frameworks results inherently from the dualization of the tetrahedral tilings used in their enumeration. Structure comparison was performed by calculating the coordination sequence of a framework<sup>31</sup> until the 13th shell by means of the ZeoTsites package.<sup>56</sup>

Following on from our previous work,<sup>25</sup> we employ the first two cumulants of the face-size distribution obtained, that is, the average and variance, as a descriptor of the framework topology. The use of such a topological descriptor as compared to more conventional geometric descriptors (framework density, nonbonded distances, mean T–X–T angle) has two distinct advantages. First, one does not require accurate crystal data but merely the framework topology to predict properties of frameworks. Second, topologically independent concepts, such as framework density, are often not very intuitive when comparing and/or characterizing (novel) frameworks. For instance, LOV and MTN frameworks have comparable FDs (LOV FD = 18.3, MTN FD = 18.7) but completely different structures.<sup>31</sup> Furthermore, although we do not explicitly incorporate specific geometric details into our model, by considering the higher level concept of framework topology (or connectivity) together with the bonding characteristics of the framework atoms, we implicitly define and take into account the geometry of the framework.

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**Table 1. Polyhedral Decomposition Result, Face-Size Distribution, Average Face-Size, and the Variance of the Face-Size Distribution for a Selection of the Various Synthesized ST-Frameworks**

zeolite framework	polyhedral decomposition	face-size distribution	$\langle x \rangle$	Var( $x$ )
AFS	$(4^6 6^3)^2 (4^{12} 6^6 12^2)^1 (4^{18} 6^6 12^2)^1$	$4^{21} 6^6 8^3 12^2$	5.25	4.688
AST	$(4^6)^1 (4^6 6^{12})^1$	$4^6 6^{12}$	5.00	1.000
BPH	$(4^6 6^3)^2 (4^{12} 6^6 12^2)^1 (4^{18} 6^6 12^2)^1$	$4^{21} 6^6 8^3 12^2$	5.25	4.688
CHA	$(4^{12} 6^2 8^6)^1 (4^6 6^2)^1$	$4^6 6^2 8^3$	5.14	2.694
FAU	$(4^{18} 6^4 12^4)^1 (4^6 6^8)^1 (4^6 6^2)^2$	$4^6 6^4 12^1$	5.14	4.408
KFI	$(4^{12} 6^8 8^6)^1 (4^{12} 8^6)^3 (4^6 6^2)^4$	$4^6 6^2 8^3$	5.14	2.694
MEP	$(5^{12})^1 (5^{12} 6^2)^3$	$5^6 6^1$	5.11	0.099
MTN	$(5^{12})^2 (5^{12} 6^4)^1$	$5^6 6^1$	5.10	0.090
SOD	$(4^6 6^8)^1$	$4^3 6^4$	5.14	0.980
TSC	$(4^6 6^2)^8 (4^6 6^8)^2 (4^8 8^2)^6 (4^{12} 6^8 8^6)^1 (4^{24} 6^8 8^{18})^1$	$4^{12} 6^4 8^3$	5.05	2.260

## Results

The decomposition results and the associated face-size distribution for a selection of the synthesized zeolite frameworks are given in Table 1 (and for all frameworks studied in the Supporting Information). An intriguing first observation is that a major fraction of the synthesized frameworks (19 out of 33) has an average face size of 5.14, while 12 frameworks have a lower and 2 a higher average face size. Second, it is noteworthy that several sets of face isomers (i.e., frameworks with identical face-size distribution) and one set of tile isomers (i.e., frameworks that can be constructed from identical sets of tiles) AFS/BPH are present.

In our previous paper we demonstrated, by using Eulers equation, that the average face size of a three-connected polyhedral cage is a simple function of its number of vertexes.<sup>25</sup> For a space-filling packing of polyhedral tiles a similar analysis<sup>27</sup> shows that its average face size can be calculated from the total number of faces in a repeat set of tiles (the smallest set of polyhedral tiles that fills space by only applying translations), via (eq A3.15 in ref 27)

$$\langle X \rangle = 6 - \frac{6N_{P,p}}{N_{F,p}} \quad (1)$$

Here,  $N_{P,p}$  and  $N_{F,p}$  are respectively the number of polyhedra and the total number of faces present in the repeat set. In a four-connected framework every face is shared by two polyhedral tiles and  $N_{F,p}$  can be written as the sum

$$N_{F,p} = \frac{1}{2} \sum_{j=1}^{N_{P,p}} N_{F,j} \quad (2)$$

Here,  $N_{F,j}$  is the number of faces of polyhedral tile  $j$ . Assuming that the polyhedral tile is three-connected,  $N_{F,j}$  can be expressed in terms of the number of vertexes (T-atoms) of the polyhedral tile ( $N_{V,j}$ ) via (eq 3b in ref 25)

$$N_{F,j} = 2 + \frac{1}{2} N_{V,j} \quad (3)$$

Using the latter two results, the average face size of a space-filling packing of three-connected polyhedral tiles can be expressed as

$$\langle X \rangle = 6 - \frac{6N_{P,p}}{N_{P,p} + \frac{1}{4} \sum_{j=1}^{N_{P,p}} N_{V,j}} \quad (4)$$

which can finally be simplified into

$$\langle X \rangle = 6 - \frac{6}{1 + \frac{1}{4N_{P,p}} \sum_{j=1}^{N_{P,p}} N_{V,j}} \quad (5)$$

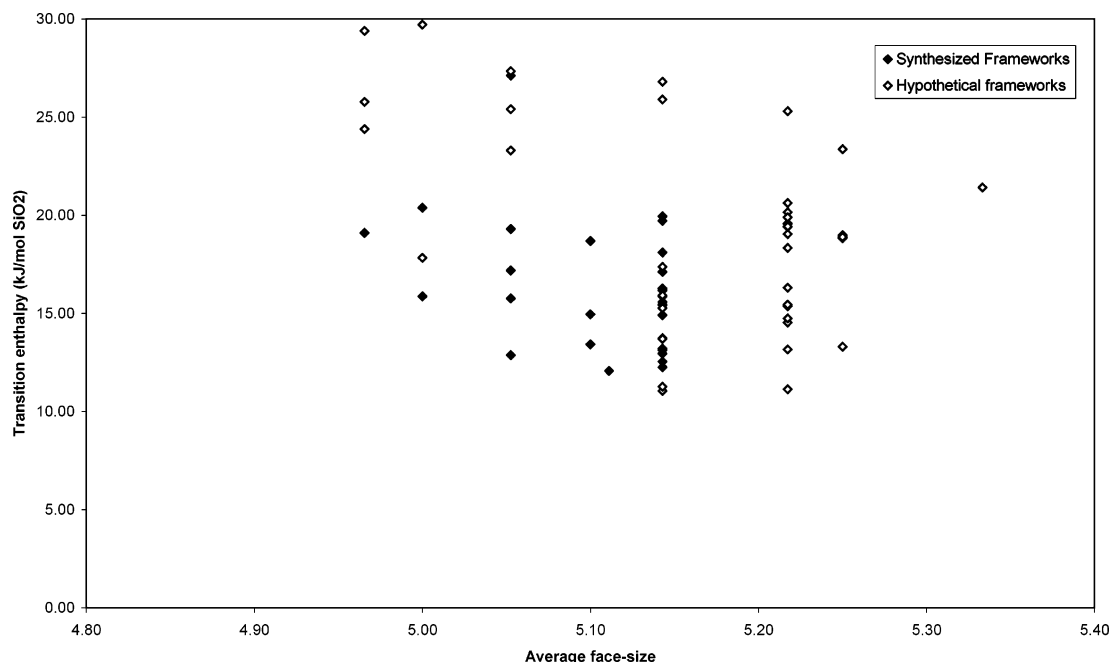
The average face size of a space-filling packing of three-connected polyhedral tiles, thus, only depends on the average polyhedron size (in vertexes) and is, hence, equal for all frameworks with the same ratio between the number of vertexes (sum  $N_{V,j}$ ) and polyhedra ( $N_{P,p}$ ) in the repeat set. This important result demonstrates, just as previously established by us for isolated polyhedral cages,<sup>25</sup> that the average face size of a ST-framework has a limit of six T-atoms. Any ST-framework with faces larger than five T-atoms should, therefore, always have faces smaller than six T-atoms to compensate. The pore size of a ST-framework can consequently not be freely varied, as any pore (by definition larger than a six T-atoms) requires small faces for compensation.

Figure 2 shows how the relative energies of both the synthesized and the hypothetical zeolite frameworks vary with the average face size. Just as previously observed for individual polyhedra tiles,<sup>25</sup> the graph clearly shows that for each average face size there are a multitude of frameworks with differing energetics, while on the other hand it also displays a correlation between the lowest energy framework for each average face size and the average face size. The individual polyhedra and frameworks, however, seem to differ in limiting behavior, while, for the lowest energy polyhedral tiles, the binding energy seems to decrease monotonically and to have a horizontal asymptote, the relative energy for the lowest energy frameworks appears to increase again for average face sizes larger than 5.14.

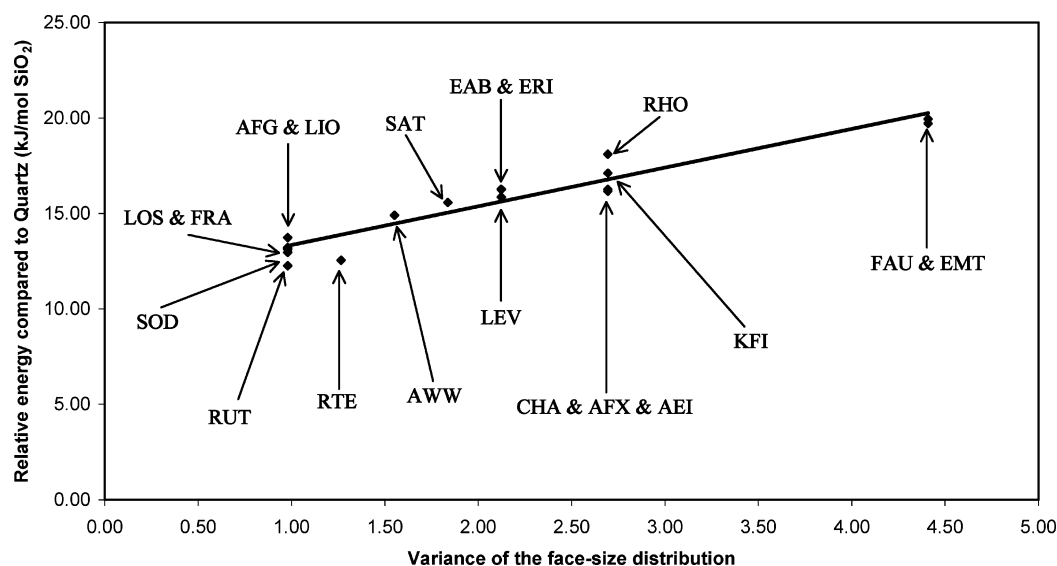
The other parameter of our descriptor, the second cumulant (variance), cannot be calculated from the face-size distribution of the constituting polyhedral tiles, but can be calculated from the face-size distribution of the framework via

$$\sigma_X^2 = \frac{\sum_{i=1}^{N_f} (X_i - \langle X \rangle)^2}{N_f} \quad (6)$$

Figure 3 shows how the relative energy of the synthesized frameworks with an average face size of 5.14 changes with their associated variance. One observes a strong correlation ( $r^2 = 0.92$ ) between relative



**Figure 2.** Calculated relative energies (normalized to number of T-atoms) versus the average face size (view delimited to 30 kJ/mol SiO<sub>2</sub>).

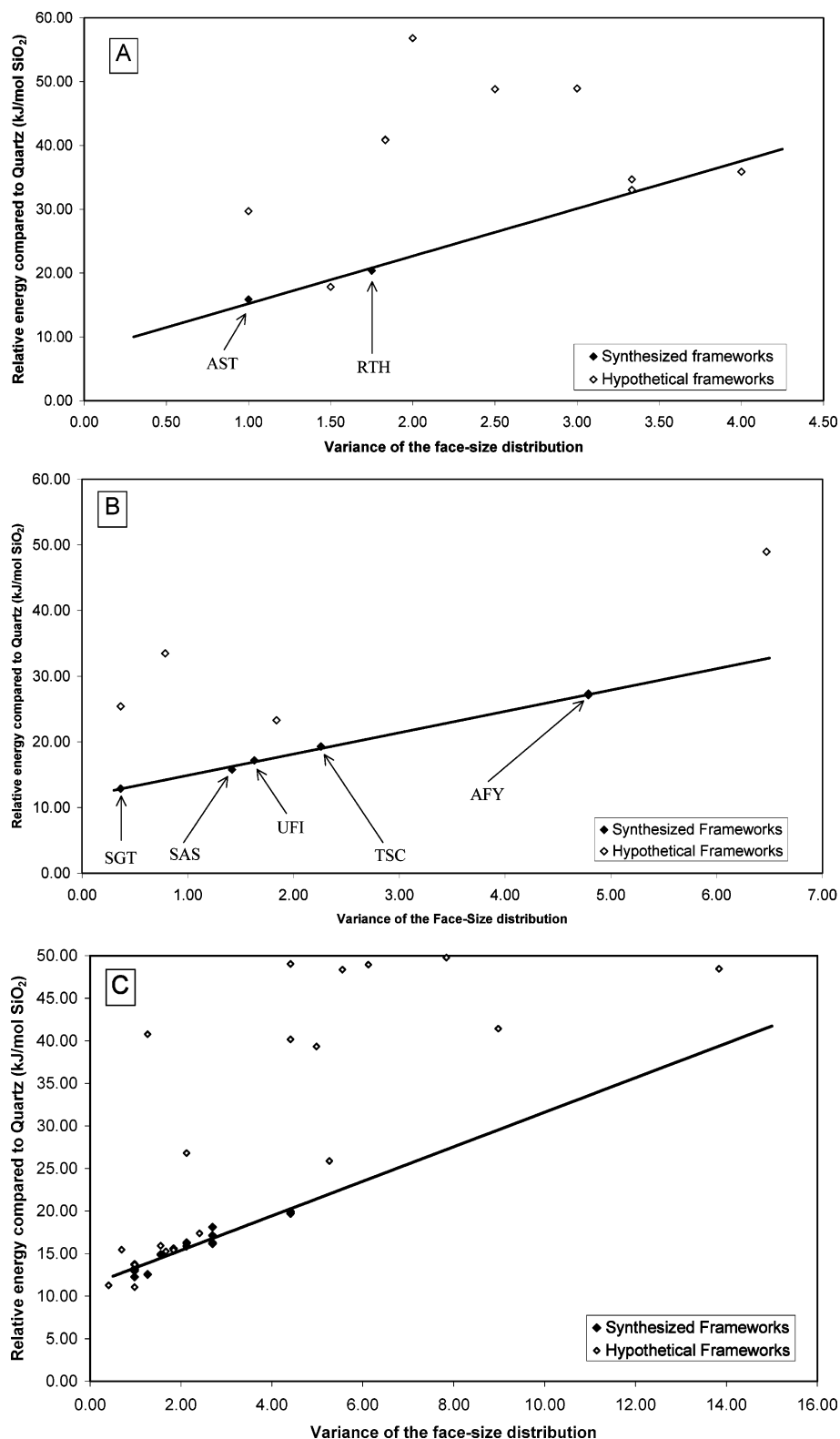


**Figure 3.** Calculated relative energies of the synthesized ST-frameworks with an average face size of 5.14 versus the variance of their face-size distribution. The line shown is the best linear least-squares fit to the data points.

energy and variance of the face-size distribution, demonstrating that the energetics of these synthesized all-silica zeolites can be predicted based on only their topology (i.e., no specific geometric information is required). Furthermore, one can clearly see the face isomers (which by definition have equal variance), forming narrow bands of points of maximum 2 kJ/mol width, comparable in magnitude to the uncertainty in the relative energy. It thus appears that the energetics of these frameworks with equal average face size is well-described by the variance. Finally, it is interesting to note that the tile isomers (by definition also face isomers) have near identical energies (18.83 and 18.98 kJ/mol SiO<sub>2</sub> for AFS/BPH).

Figure 4A–C shows how the relative energy changes with the variance for four sets of frameworks (both synthesized and hypothetical) with different average

face sizes, respectively 5.00, 5.05, and 5.14. We again observe a strong correlation ( $r^2 > 0.9$ ) between the relative energy and variance of the face-size distribution for all synthesized, and for a large part of the hypothetical, frameworks. However, a significant percentage of the hypothetical frameworks lie considerably higher in relative energy than simply expected from their variance alone. Visual inspection of the topology of these higher energy frameworks reveals that many contain certain combinations of polyhedral tiles known to be energetically disadvantageous (e.g., chains of 2 or 3 double 6-rings, see Figure 5, or large 2D rosettes, see A and D of Figure 4 in ref 29). Furthermore, hypothetical frameworks can be found that are tile isomers of known synthesized frameworks, but lie significantly higher in relative energy. An example of such a set of tile isomers are the four frameworks: dt3\_717 (50.63 kJ/mol),

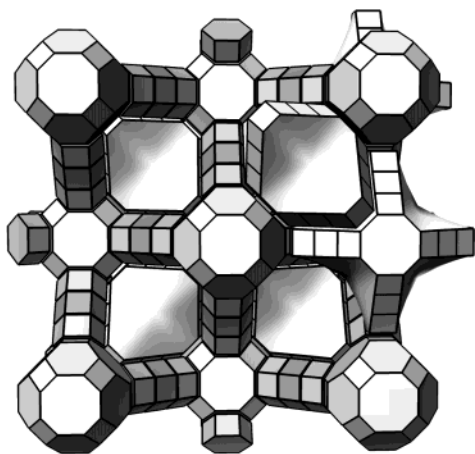


**Figure 4.** Calculated relative energy versus the variance of the face-size distribution for frameworks with an average face size of 5.00 (A), 5.05 (B), and 5.14 (C). The lines shown correspond to the best linear least-squares fit to the synthesized framework data points. Please note that the synthesized frameworks points for Figure 4C (5.14) correspond to the points in Figure 3.

dt3\_718 (50.67 kJ/mol), AFS (18.83 kJ/mol), and BPH (18.98 kJ/mol), the former two higher energy frameworks being hypothetical and the latter two lower energy frameworks being synthesized. These four tile isomers can all be decomposed into the same set of polyhedral tiles, but correspond to different packings,

as can be verified by the fact that all four frameworks have different coordination sequences.

It thus appears that, just as for polyhedral silica cages, the energetics of zeolite frameworks can be described as a function of the average and variance of the face-size distribution, while for some of the hypo-



**Figure 5.** Part of the hypothetical extra-large-pore ST-framework dt2\_32, showing the 16 pore windows and the D6R chains.

thetical frameworks an additional positive energy contribution due to packing is present. The relative energy (derived from the average and variance of the face-size distribution) appears to predict the minimum framework energy, which is expected to increase with variance and be minimal around an average face size of 5.14. Although the framework energy, as has been noted, can be increased above this lower limit via energetically unfavorable tile packing, it is important to note that for all synthesized frameworks our method predicts the correct relative energy ordering, indicating that for such frameworks the effect of tile packing is negligible.

## Discussion

**1. Understanding the Framework Energetics.** To rationalize the observed trends between average and variance of the face-size distribution of a framework and the energy of the corresponding all-silica zeolite, one requires a theoretical model linking framework topology and energetics. In our previous work, we successfully demonstrated that a simple physical model based on the energies attributed to faces<sup>25</sup> explains the observed correlations for isolated polyhedral tiles. Such a model predicts correctly that the polyhedral tiles become more stable with increasing average face size and with decreasing variance. As we do not expect any changes in the basic physical rationale underlying this model, we would expect the model to hold for (zeolite) frameworks also. While indeed the overall observed trends for the reported frameworks fit with the predictions of the physical model developed for isolated tiles, we also observe two minor additional effects: (i) an energetic packing penalty for a significant portion of the hypothetical frameworks and (ii) the relative energy minimum around an average face size of 5.14.

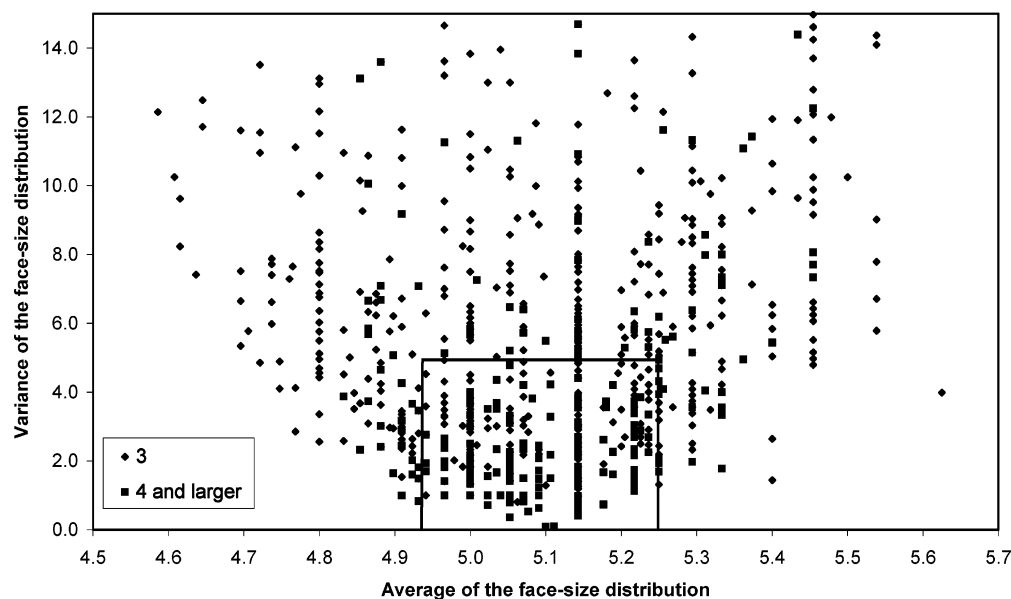
The first effect, the packing penalty, is due to the fact that we approximate the topology of the framework by a set of distinct polyhedral tiles and make no reference to the way these tiles are packed together, although this can lead to strain and an associated energetic destabilization. We have shown that for freely relaxed polyhedral silica cages (i.e., geometry optimized without any constraints) the energetics are well-described by our model; thus, we expect that, for frameworks which can be constructed with minimal geometrical distortion of

the constituting polyhedral tiles, the energetics would be equally well-predicted. This hypothesis is verified by fact that all synthesized, and a large fraction of the hypothetical, frameworks show no obvious extra energetic destabilization, while many of the frameworks with a notable energetic destabilization contain packing motifs known to be particularly energetically disadvantageous (e.g., double 4-ring and double 6-ring chains). Further evidence for packing as origin of the extra destabilization is given by those tile isomers that consist of the same polyhedral tiles but differ in packing and relative energy (differences of the order 10–40 kJ/mol are observed, comparable in magnitude to the energetic destabilization attributed to packing effects). To fully take into account this energetic packing penalty on the relative energy, a more elaborate descriptor would be required that additionally does take into account the tile arrangement (e.g., the Delaney symbol<sup>29,57,58</sup>). However, as such descriptors are inherently more complex, insight is traded for precision. Finally, the lack of an obvious extra energetic destabilization for most frameworks implies that the face-size distribution is the principal factor determining their energetics (see Figures 3 and 4A–C).

The second effect, the apparent relative energy minimum around an average face size of 5.14, is not so much a deviation from the model but, rather, seems to result from topological limitations inherent to four-connected frameworks. For distinct polyhedral cages the lowest energy isomers are easily shown to be the “principal” polyhedra, i.e., those consisting of only one size of face (if the average face size is integral) or those solely consisting of the two types of faces closest to the average face size.<sup>25</sup> More importantly, for almost all even numbers of vertexes there seems to exist such a principal polyhedron. However, the same is not necessarily true for ST-frameworks (including the full collection of hypothetical frameworks) for which we only find “principal” frameworks (defined in a similar way as for “principal” polyhedra above) with average face sizes 5.10 (MTN, 5<sup>96</sup>1) and 5.11 (MEP, 5<sup>86</sup>1). Furthermore, Figure 6 shows not only that principal frameworks are rare but also that the minimal variance of a framework increases dramatically while lowering or increasing the average face size away from 5.1–5.11. The lowest energy frameworks are thus, with the two exceptions noted above, not the principal frameworks, but rather the frameworks with the lowest topologically realizable variance. It should be noted that although our collection of frameworks used for Figure 6 is not complete, over 1000 different frameworks and all classes of enumerated ST-frameworks (uninodal, binodal, and trinodal) contained therein show the same behavior. The shape of the line connecting the lowest points of Figure 2 is, thus, not determined by the average face size, as for polyhedra, but rather by the apparent topological restrictions of the four-connected framework. Furthermore, it appears that if we assume that the quality of packing can be judged by the variance of its associated face-size distribution, then the best possible space-filling packing of three-connected polyhedral tiles has an average face-size around 5.10–5.11, the latter region

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**Figure 6.** Variance of the face-size distribution for all the hypothetical ST-frameworks versus their corresponding average face size. View delimited to a variance of 15; style of the symbol signifies size of smallest face present and box shows ranges for synthesized frameworks.

**Table 2.** Pore Systems Present among the Synthesized ST-Frameworks with an Average Face Size of 5.14 and the Associated Variance and Relative Energy (Values in kJ/mol SiO<sub>2</sub>) Windows

pore system	variance window	relative energy window	frameworks
clathrasils	0.980	12.25–13.73	AFG, FRA, LIO, LOS, RUT, SOD
8*	1.265–1.551	12.55–14.90	AWW, RTE
8**	2.122	15.86–16.27	EAB, LEV
8***	1.837–2.694	15.58–18.10	AEI, AFX, CHA, ERI, KFI, RHO, SAT
12***	4.408	19.71–19.95	FAU, EMT

lying very close to the “centre of gravity” (the average “average face size”) for all synthesized ST-frameworks (5.12).

Based on the above, it is clear that the embedding of the polyhedral tiles in a space-filling packing results in additional topological constraints not present for isolated tiles. More specifically, these constraints appear to lead to a minimum in the energy difference compared to quartz (around average face size of 5.14) instead of the inverse proportional behavior found for isolated tiles, and an additional positive packing contribution to the energy. As the latter energetic packing penalty is negligible for all 34 considered synthesized ST-frameworks (irrespective from the fact if they were ever synthesized in an all-siliceous form), we propose that a minimal packing penalty is critical in order for a framework to be synthesized.

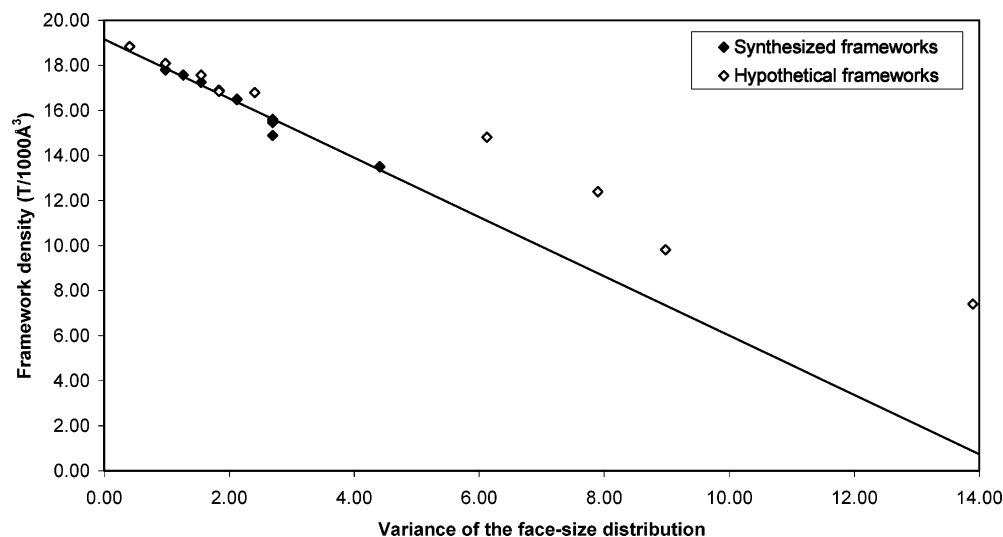
**2. Understanding Structural Trends.** On the basis of our results and the discussion above, one can now link structural properties of zeolite frameworks (e.g., pore size and framework density) with the thermodynamic viability of their synthesis.

*a. Pore Size.* We have previously successfully demonstrated that topological considerations (i.e., Euler’s formula) dictate that large pores in ST-frameworks require small faces as compensation.<sup>27</sup> Furthermore, we showed that this compensation by small faces leads to a rise in variance and a decrease in the energetic stability of a polyhedral tile with an increasing number and size of the large faces associated with pores. On the basis of these findings, we predicted that the energetic stability of a zeolite framework would decrease with

increasing pore size and pore-system dimensionality<sup>25</sup> (i.e., through how many pores the cage can be entered and left). All these predictions were, however, based on energy calculations for isolated polyhedral tiles. As we have demonstrated above, that a similar compensation mechanism holds for frameworks corresponding to space-filling packings of polyhedral tiles, these predictions were now tested against our data for the synthesized ST-frameworks. Table 2 shows which pore systems can be found among the synthesized frameworks with an average face size of 5.14 and the associated relative energy and variance windows. It is clear, despite some overlap, that both the relative energy and the variance increase with both pore size and pore-system dimensionality as clathrasils > 8\* > 8\*\* > 8\*\*\* > 12\*\*\* (asterisks indicating pore-system dimensionality), verifying our earlier prediction. Based on the relative energy, we would, therefore, expect that the thermodynamic viability of synthesizing ST-frameworks decreases with both increasing pore size and pore-system dimensionality.

For all the extra-large pore zeolite frameworks (zeolites with pores circumscribed by 14 or more T-atoms) in the collection of hypothetical ST-frameworks, a considerable packing penalty (10–40 kJ/mol) is observed that is induced by the associated packing motifs (e.g., chains of double 6-rings, chains of double 4-rings, and rosettes of small tiles). The origin of this packing penalty is the fact that extra-large pores require large polyhedral tiles ( $N_v > 48$ ) to be accommodated<sup>25</sup> and that such tiles need to be compensated for by smaller tiles in order to reach an average face size close to the best possible





**Figure 7.** Framework density of ST-frameworks with an average face size of 5.14 versus the variance of their face-size distribution.

**Table 3. Three Extra-Large-Pore ST-Frameworks with an Average Face Size of 5.14 and Their Pore System, Variance, Relative Energy (in kJ/mol SiO<sub>2</sub>), Extrapolated Relative Energy without Packing (kJ/mol SiO<sub>2</sub>), and the Actual Packing Motif of Chains of Three Double 6-Rings**

framework	polyhedral decomposition	pore system	variance	relative energy	extrapolated relative energy
dt2_31	(4 <sup>6</sup> 6 <sup>2</sup> ) <sup>6</sup> (4 <sup>6</sup> 6 <sup>8</sup> ) <sup>1</sup> (4 <sup>4</sup> 26 <sup>4</sup> 244) <sup>1</sup>	24**	13.837	48.46	39
dt2_32	(4 <sup>6</sup> 6 <sup>2</sup> ) <sup>12</sup> (4 <sup>12</sup> 6 <sup>8</sup> 8 <sup>6</sup> ) <sup>1</sup> (4 <sup>2</sup> 8 <sup>2</sup> 16 <sup>2</sup> ) <sup>3</sup>	16*	7.837	49.77	27
dt2_33	(4 <sup>6</sup> 6 <sup>2</sup> ) <sup>3</sup> (4 <sup>2</sup> 46 <sup>2</sup> 12 <sup>6</sup> ) <sup>1</sup>	12***	6.122	48.94	24

packing. Note, furthermore, that even for  $\langle X \rangle = 5.45$ , the largest  $\langle X \rangle$  in the collection of hypothetical ST-frameworks used,  $N_v$  equals 40 and is thus still smaller than 48. Taking, for example, a framework that is decomposable into three different polyhedral tiles (large tiles, tiles equal to the average face size, and small tiles), one can calculate the ratio between small tiles and large tiles needed to obtain an average face size  $\langle X \rangle$  via

$$R = \frac{N_{vl} - N_{va}}{N_{va} - N_{vs}} \quad (7)$$

where  $N_{vl}$  is the number of vertexes of the large tile,  $N_{vs}$  the number of vertexes of the small tile, and  $N_{va}$  the analogous number for a tile corresponding to the average face size  $\langle X \rangle$ . A large polyhedral tile of size  $N_{vl}$ , thus, requires  $R$  small polyhedral tiles of size  $N_{vs}$  for compensation, where  $R$  rises rapidly with increasing  $N_{vs}$ , irrespective of the actual feasibility of the space-filling packing. For a large polyhedral tile of 96 vertexes one needs, for instance, either 18 tiles of 20 vertexes or 6 tiles of 12 vertexes to reach an average face size of 5.14. Extra large-pore ST-frameworks, thus, have either very large repeat units (e.g., 456 T-atoms for  $N_{vs} = 20$  in the example above) or a relatively large number of small tiles. In which case the relatively large number of small tiles, in the latter option, significantly increases the chance of energetically unfavorable packing motifs such as double 6-ring chains. Table 3 gives data for three extra-large pore zeolite frameworks with an average face-size of 5.14 and clearly shows that without the packing penalty two out of the three frameworks would have quite reasonable relative energies (judged from the relative energies extrapolated along the correlation found for synthesized frameworks). Based on the above, it seems unlikely that one could synthesize extra-large pore ST-frameworks.

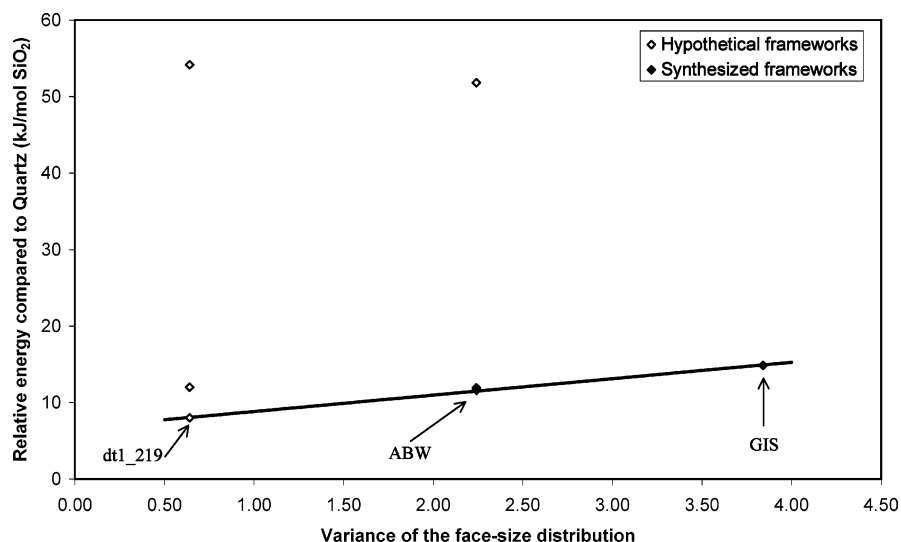
*b. Framework Density.* The framework density of ST-frameworks is strongly related to the volume of the tiles. The volume of a tile should (under the reasonable assumption that the external surface area of a polyhedron is some increasing function of  $N_v$  and that its volume scales as its surface area to the power 2/3) scale as

$$V \propto N_v^{2/3} \quad (8)$$

suggesting that the framework density should scale approximately as

$$FD \propto \frac{\sum_{j=1}^{N_p} N_{v,j}}{\sum_{j=1}^{N_p} N_{v,j}^{2/3}} \quad (9)$$

From the form of eq 9 it is apparent that the framework density of a framework is expected to decrease with the number of large polyhedral tiles present. Moreover, as the number of large polyhedral tiles present tends to increase with the variance, one can propose a simple relationship between variance of the face-size distribution of a framework and its framework density. Figure 7 shows this relationship for frameworks with an average face size of 5.14. It clearly shows the expected negative linear relationship between variance and framework density ( $r^2 > 0.95$ ) for all synthesized, and a large fraction of the hypothetical, frameworks. Some of the hypothetical frameworks lie considerably above the correlation found, and it turns out that these are the same frameworks that show a packing effect in their energetics. The effect of packing on the framework density is most likely of geometric



**Figure 8.** Calculated relative energies of unital frameworks with an average face-size of 5.6 versus the variance of their face-size distribution. The line shown is the best linear fit to the three lowest energy frameworks (dt1\_219, ABW, GIS).

**Table 4. Polyhedral Decomposition, Three-Connected Polyhedron (from Which the  $\lambda \neq 0$  Polyhedron Is Obtained),  $\lambda$ , Pore System, Variance, and Relative Energies (in kJ/mol) for Three NST-Frameworks with an Average Face Size of 5.6**

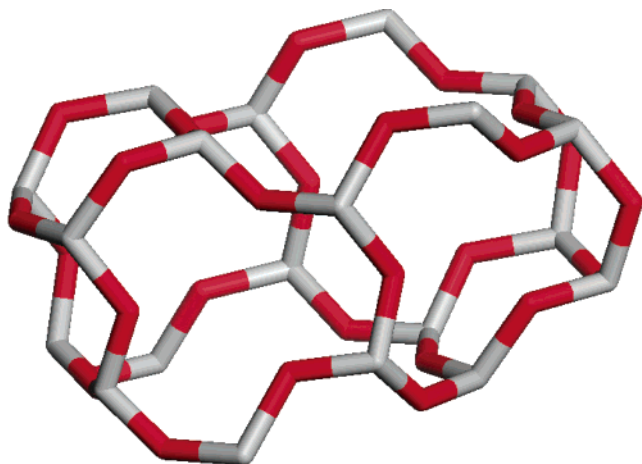
framework	polyhedral decomposition	three-connected polyhedron	$\lambda$	pore system	variance	relative energy
dt1_219	(4 <sup>2</sup> 6 <sup>8</sup> ) <sup>1</sup>	(4 <sup>2</sup> 5 <sup>8</sup> )	0.25	clathrasil	0.640	8.01
ABW	(4 <sup>4</sup> 6 <sup>4</sup> 8 <sup>2</sup> ) <sup>1</sup>	(4 <sup>4</sup> 5 <sup>4</sup> 6 <sup>2</sup> )	0.25	8*	2.240	11.60
GIS	(4 <sup>6</sup> 8 <sup>4</sup> ) <sup>1</sup>	(4 <sup>6</sup> 6 <sup>4</sup> )	0.25	8**	3.840	14.87

origin (i.e., through deformation of the tiles) as those tile isomers that differ in energetics also differ in framework density. The two hypothetical frameworks, dt3\_718 and dt3\_717, have, for instance, a considerably higher framework density than their tile isomers: AFS and BPH (17.50 T/1000 Å<sup>3</sup> instead of 14.84 T/1000 Å<sup>3</sup>). For other average face sizes similar graphs are found. As the variance increases with decreasing framework density and the relative energy increases with increasing variance, the correlation found agrees with the negative trend between framework density and relative energy found by other authors.<sup>42,44,46,50,55</sup> Based on the relative energy, we would expect that the thermodynamic viability of synthesizing ST-frameworks decreases with decreasing framework density. Furthermore, as a low framework density requires large polyhedral tiles, as also needed for extra-large pores, packing effects most probably will limit the lowest attainable framework density for ST-frameworks.

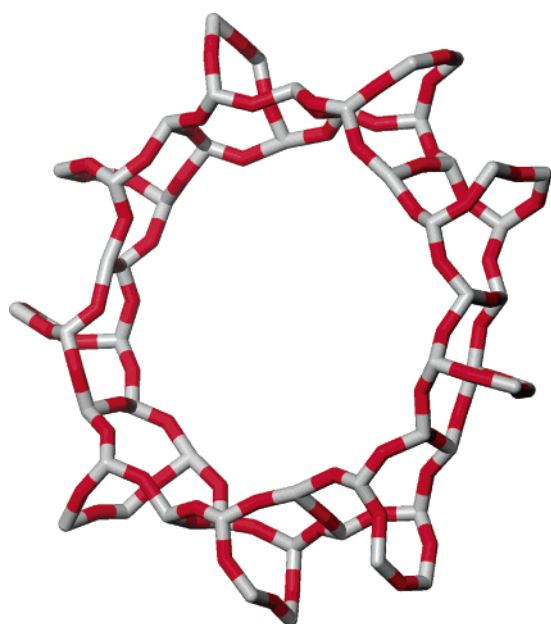
**3. Beyond ST-Frameworks.** As discussed in the Introduction, besides the cage-like ST-frameworks also channel-like frameworks exist that are decomposable into a mixture of  $\lambda = 0$  and  $\lambda \neq 0$  polyhedral tiles ( $\lambda$  equals the ratio between two- and three-connected vertexes in the polyhedral tile<sup>25</sup>). These channel-like frameworks are derivable from Non-Simple Tilings and are subsequently referred to as NST-frameworks. Polyhedral analysis of these NST-frameworks is more complicated than for that for ST-frameworks, as there can be multiple equally valid decompositions into  $\lambda \neq 0$  polyhedral tiles, hindering rapid decomposition. Furthermore, the average face size is not solely a simple function of the polyhedra sizes anymore but, rather, depends also on the number of the three-connected vertexes and  $\lambda$ 's of the polyhedra. The maximum face size that does not need compensation by smaller faces

(5 for ST-frameworks) is now no longer independent of the actual polyhedra it is shared between, as it depends on  $\lambda$  (i.e.,  $5 + 4\lambda$ ).<sup>25</sup> This extra degree of freedom allows tiles of any face-size distribution (e.g., the  $\lambda = 3$  12<sup>6</sup> cage of ITQ-21<sup>59</sup>); however, there might not necessarily be a realizable four-connected framework containing it. For example, while polyhedral tiles with  $\lambda \neq 0$  might have any average face size, the average face size of the uninodal hypothetical NST-frameworks appears to be limited to values between 5.42 and 9.43 (as calculated from the polyhedral decomposition of the uninodal hypothetical frameworks). As the nature of the framework (ST or NST) does not influence the energetics of the faces present (at least for relatively low  $\lambda$ ), despite the complications discussed above, one would still assume that the relative energy of the NST-frameworks could be described in terms of the average and variance of their face-size distribution. Figure 8 shows how the relative energy changes with the variance of the face-size distribution for unital (i.e., decomposable into one tile only) NST-frameworks with an average face size of 5.6 (including the synthesized frameworks ABW (see Figure 9) and GIS (see Figure 5 in ref 27)). We observe again a strong correlation ( $r^2 = 0.999$ ) between the variance and relative energy of the lowest energy frameworks and also again a number of tile isomers with considerable packing penalties (high-energy points in Figure 8). The NST-frameworks, thus, appear to show behavior similar to the ST-frameworks. Table 4 gives the face-size distribution and relative energies for the lowest energy frameworks in Figure 8 (for which the correlation is observed), dt1\_219, ABW, and GIS.

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**Figure 9.**  $4^6 4^8^2$  ABW polyhedral tile. Red represents oxygen atoms; gray represents silicon atoms.



**Figure 10.** Extra-large-pore  $6^{18} 18^2$  polyhedral tile of VFI.

Regarding the structural properties of NST-frameworks, it is interesting to note that all three frameworks of Table 4 have lower relative energies than their ST counterparts with similar pore systems (see Table 2). Furthermore, while the extra-large-pore ST-frameworks of Table 3 seem to have inevitably energetically disadvantageous packing motifs, their  $\lambda \neq 0$  analogues CFI and VFI ( $6^{18} 18^2$  polyhedral tile with  $\lambda = 0.5$ , see Figure 10) have much more reasonable relative energies (12.30, 19.11 kJ/mol respectively). Moreover, all currently synthesized extra-large-pore frameworks (AET, CFI, DON, OSO, SFN, and VFI), including the recently reported “18-ring” framework ECR-34<sup>60</sup> (ETR), have  $\lambda \neq 0$  tiles. It, thus, appears that the increased structural versatility of NST-frameworks compared to their ST counterparts allows for much more synthetically viable candidates for extra-large, and by analogy extra-low framework density, frameworks. Even for these frameworks, however, there appear to be limits, the largest average face size in the collection of uninodal frame-

works equals 9.43 (and the largest face size in the same set with a variance below 15 is only 7.76).

**4. Beyond All-Silica Zeolites.** As discussed in the Introduction, the realm of framework materials is broader than the all-silica zeolites on which the bulk of this paper focuses. For tetrahedral frameworks in general the basic results discussed above should hold without limitations, as the origin of the observed constraints is topological rather than chemical in nature. We thus expect these frameworks to follow the same general trends between framework energetics and the average and variance of its face-size distribution as found for their all-silica equivalents. The specific energy values (energy differences between lowest topological realizable variance frameworks, slope of the correlation between energy and variance), however, are expected to change as their values are intimately linked to the strength of the inverse proportionality between face size and face energy (i.e., “ring-strain”), which is known to be dependent on the chemical nature of the T-atoms. This hypothesis is strongly supported by the preliminary results for ST-frameworks with average face size of 5.14 in their  $\text{GeO}_2$  and  $\text{AlPO}_4$  form, as shown in Figure 11.

It is known experimentally that partial substitution of the Si atoms by other metal atoms (Zn, Be)<sup>63–66</sup> can induce the formation of frameworks with smaller faces (e.g., synthesis of zeolites containing faces of 3 T-atoms). Although in our model such faces would increase the variance of the face-size distribution and thus decrease the relative thermodynamic viability of a framework, this effect would be offset by the decrease in the slope of the correlation between energetics and variance induced by the strain-accommodating change in chemical composition of the framework. For nontetrahedral (pentahedral, octahedral) or mixed coordination frameworks, a similar topological analysis to the one presented in this paper should result in comparably rich insights into the topological and physical constraints imposed upon these frameworks.

## Conclusions

A topological analysis method, consisting of decomposing the framework into sets of polyhedral tiles and analyzing the obtained face-size distribution, is shown for the first time to yield powerful insights into the energetics of framework materials and the feasibility of their synthesis. In particular, we have demonstrated for the archetypal all-siliceous zeolites that the relative energies of synthesized frameworks that correspond to Simple-Tilings (ST-frameworks) can be understood in terms of the average and the variance of the face-size distribution (as for isolated polyhedral tiles). Furthermore, we show that to properly describe a part of the studied hypothetical frameworks, an additional packing

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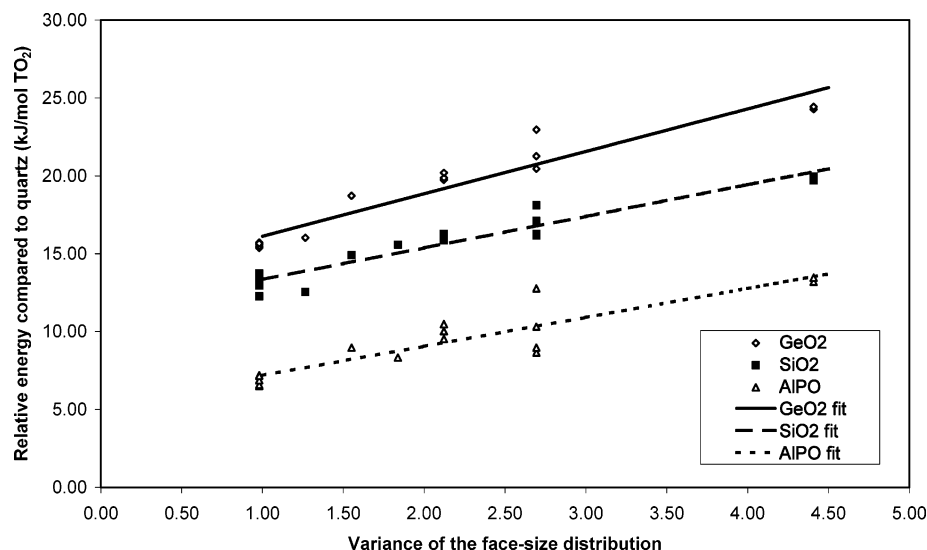
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**Figure 11.** Calculated relative energies of the synthesized ST-frameworks with an average face size of 5.14 (in their GeO<sub>2</sub>, SiO<sub>2</sub>, and AlPO<sub>4</sub> form) versus the variance of their face-size distribution. The GeO<sub>2</sub> data were calculated using the George force field,<sup>61</sup> while the data for the AlPO<sub>4</sub> frameworks were obtained from Dr. A. Simperler<sup>44</sup> (who employed a force field developed by Gale and Henson<sup>62</sup>). All energies are given relative to quartz in the respective chemical composition.

penalty term is required, which is negligible for all synthesized frameworks. We further verify our previous prediction that for these ST-frameworks the relative energy increases (and the thermodynamic viability of their synthesis, thus, decrease) with increasing pore size and pore-system dimensionality. For the same class of frameworks, we show that all extra-large-pore frameworks considered have energetically disadvantageous packing motifs and a considerable associated packing penalty, and we provide an explanatory model linking this to pore size. For frameworks corresponding to Non-Simple Tilings (NST-frameworks) similar trends as for ST-frameworks are found, although NST-frameworks appear to have lower relative energies for comparable pore systems. Furthermore, we show that the structural versatility ( $\lambda$ ) of NST-frameworks opens the possibility of extra-large-pore frameworks without energetically disadvantageous packing motifs, and thus to yield many more synthetically viable candidates than ST-frame-

works for extra-large-pore, and extra low framework density, frameworks. Preliminary calculations on non-siliceous frameworks further confirm our confidence that the proposed methodology is applicable to framework materials in general.

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**Supporting Information Available:** Information on correlation between experimentally measured transition enthalpies and calculated relative energies (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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