

ZSE Manuscript Outline

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1 Abstract

The topology of zeolite frameworks and of associated tetrahedral sites (T-sites) are commonly characterized by their associated rings, typically defined as some set of closed paths or cycles through a framework that cannot be decomposed into shorter cycles. These ring descriptors have been used to identify feasible zeolite topologies, to describe the similarity and differences between zeolites, to identify sites or voids of catalytic relevance, and as machine learning fingerprints. Numerous definitions and algorithms for finding zeolite rings have been proposed and applied throughout the literature. Here we report an analysis of rings and T-sites in a large number of zeolite frameworks using Zeolite Simulation Environment, a Python package that implements an efficient algorithm presented by Goetzke and Klein for finding rings in arbitrary frameworks. We compare the result of a number of common and new ring definitions applied to a large number of common zeolite frameworks. We discover previously unrecognized rings in a number of frameworks. We show that the vertex symbol, a common approach used to characterize T-sites, misses important parts of the stereochemistry around a T-site, and propose an alternative definition. This tool provides an effective platform for characterizing zeolite and T-site structures useful for building models and doing machine learning.

2 Highlights

What is the main point of the paper? What problem is it addressing? What are the main insights?

1. Zeolite framework and nodes commonly classified in terms of rings
2. Various conventions for associating some subsets of rings with either a framework, the T-sites of a framework, or the oxygens of a framework.
3. PROBLEM TO ADDRESS: The convention used will provide different ring counts
4. SOLUTION: We provide a Python package that has the ability to identify and classify these rings based on previously published and new conventions
5. This software tool uses a node-based search procedure that takes advantage of algorithms developed for general nets
6. We compute and compare conventions across all known frameworks, highlighting differences in which rings get counted by which convention
7. Some features treated by convention as rings are not rings in a topological sense but are rather defined by the void space they create.
8. We show that the common method of describing a T-site by its vertex symbol does not incorporate important information about the stereochemistry of the rings, and provide a new method for listing vertex symbol rings that compensates for that deficiency

3 Introduction

Paragraph 1: background on uses for zeolite rings

- Zeolites are microporous and crystalline, natural to characterize by the sizes of the features present in the crystal. Rings are one common type of feature widely reported and used, both to characterize a zeolite crystal and as descriptors of the individual tetrahedral sites of the zeolite.

- Rings have been used to identify feasible zeolite topologies,¹ to describe the similarity and differences between zeolites,² to identify sites or voids of catalytic relevance,^{3,4} and as machine learning finger prints [will get citations for this]

Paragraph 2: Explain features of graph representing zeolites

- Zeolites can naturally be represented using graph theory, where atoms are nodes, and bonds are edges. **REFS**
 - Sometimes in the literature, oxygen atoms are used as bridges instead of nodes, since they only connect to two T-sites
- Table 1 summarizes the various topological features based on connectivity that can be used to describe a framework, T-site, or oxygen atom
- A path is a series of connected nodes from some source node to some target node
- A cycle is a path that starts and ends at the same node, and doesn't repeat any other nodes

Paragraph 3: Explain the various ring counting methodologies we intend to cover

- Rings in zeolites are defined as a cycle traversing the T-site and oxygen atoms (nodes) of the framework, and cannot be decomposed into smaller cycles by a shortcut.^{5,6}
- A shortcut is defined as a path connecting two nodes of a cycle that is shorter than both the paths connecting those nodes along the cycle^{5,6}
- Shortest path ring is a ring that is the shortest ring for at least one set of O-T-O on the cycle,⁷ this ring will be contained in the vertex symbol for at least one of the T-sites within the framework
- See Figure 1 for example of rings
 - The pink highlighted cycle (1-2-3-17-20-14-15-16) is a 8-membered ring (8-MR)
 - The green highlighted cycle (14-20-12-13) is a 4-MR
 - The red outlined cycle following 3-4-18-19-20-17 is not an 6-MR because there is a shortcut connecting nodes 17 and 18.
 - Nodes 5-6-7-8-9 outlined in teal represent a path through the framework.

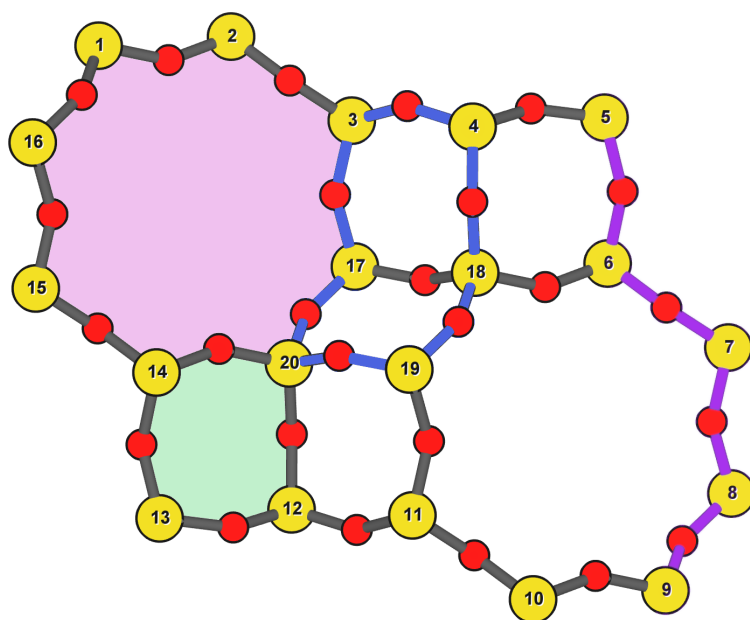


Figure 1: Cutout of the Chabazite framework showing a path (5-6-7-8-9) highlighted with purple bonds, a cycle (3-4-18-19-20-17) highlighted with blue bonds, an 8-MR filled in with pink, and a 4-MR filled in with green. Yellow atoms are Si (T-sites), and red atoms are oxygen.

Table 1: Matrix showing relationship between frameworks, nodes, paths, cycles, and various ring types. **Vertex symbol doesn't belong in the first column. It isn't a topological feature.**

	Description	Framework	Node (T-Sites)	Node (Oxygen)
Nodes	T-sites and oxygen atoms	Contains some set of symmetry distinct T-sites and oxygen atoms		
Paths	Collection of connected nodes from source to target	Periodic cell contains an infinite number of paths		
Cycles	Path that starts and ends at the same node	Periodic cell contains an infinite number of cycles		
Rings	Cycle that contains no shortcuts	Contains a finite number of unique rings	All rings that pass through particular T-site	All rings that pass through particular oxygen atom
Unstacked Rings	Ring that does not traverse two stacked rings	A subset of the Rings above	All unstacked rings that pass through T-site	All unstacked rings that pass through oxygen atom
Shortest Path Rings	Ring that is the shortest ring for at least one set of O-T-O on the cycle	A smaller subset of the rings above	All shortest path rings starting from a T-site (Vertex)	All shortest path rings that pass through oxygen atom
Vertex Symbol	Way to classify the rings around a T-site, shortest ring (and its multiplicity) for each O-O pair around a T-site	Collection of vertex symbols for all symmetry distinct T-sites in framework	Vertex symbol for particular T-site	
Geometric rings	A cycle that may contain a shortcut, but has similar geometric/chemical properties to a ring without a shortcut	Contains a finite number of geometric rings	Can be described by the geometric rings that pass through	Can be described by the geometric rings that pass through

Paragraph 4: Problem to address

- Different conventions exist that can reduce the set of rings to more strictly defined properties

- These methods return different sets of rings
- We can use rings to characterize oxygen atoms, T-sites, and entire frameworks
- T-sites:
 - Vertex symbols are the set of shortest paths connecting the 6 oxygen-oxygen pairs around a T-site⁸
 - Shortest path rings count all the vertex symbol rings that pass through a T-site or an oxygen atom⁷
 - Or we can count all the rings that do not have a short cut⁵
- Oxygen atoms:
 - Shortest path rings
 - All rings with out a shortcut
- Framework
 - Vertex symbol rings
 - Shortest path rings
 - All rings with out a shortcut
- Differences in ring counts leads to differences in how we describe the topology of zeolites. Therefore, when discussing the rings in a zeolite it is important to also state which method of ring counting is used.

Paragraph 5: Our solution to the problem

- Here we present Zeolite Simulation Environment (ZSE), a Python package that implements the ring finding algorithm presented by Goetzke and Klein⁵ to find rings up to a user defined cutoff size, and can implement the previously published ring set reduction conventions.
- We use ZSE to provide an analysis of rings using each of these conventions on the entire set of IZA zeolite frameworks to compare how they result in different characterizations

Using ZSE we show the differences in framework, T-site, and oxygen ring descriptors when using the various ring counting conventions. We highlight rings that are found by these conventions but not typically discussed for a number of frameworks. We also show that the vertex symbol, a common approach used to characterize T-sites misses important parts of the stereochemistry around a T-site.

4 Software Description

Paragraph 1: Basics of ZSE tooles

- All of the frameworks listed on the IZA Database of zeolite structures⁹ are included in a database with ZSE
- These structures are Atomic Simulation Environment Atoms objects,¹⁰ and can be used with any of the functions in ZSE
- ZSE also includes CIF tools to read structure files for frameworks not listed in the IZA website, such as hypothetical zeolites, and return an Atoms object that can be used with ZSE

Paragraph 2: Implementation of ring counting methodologies

- ZSE has 3 previously published rules for ring finding implemented
 - All cycles without a shortcut⁵
 - All shortest path cycles⁷
 - Cycles that compose the vertex symbol for a T-site⁸
- We have also implemented a new rule that finds all rings without a shortcut, but excludes rings that are made by traversing a stacked set of rings. **Have to define stacked ring.**
 - Figure showing example of 8-MR in the d6r of CHA and 14-MR in AFI
- Each of the rules: shortest path, vertex symbols, and our new rule are a subset of the no shortcuts rule

Paragraph 3: Process to find rings

Process to find rings:

1. To find rings in a zeolite, ZSE makes a custom connectivity matrix for the Si and O atoms in the framework
2. We use NetworkX¹¹ to build a shortest path matrix for every atom pair in the zeolite framework
3. We then find all the rings up to some cutoff size based on the algorithm presented by Goetzke and Klein⁵
4. Depending on the rule chosen by the user, ZSE then removes rings from this list that don't meet the qualifications of the rule
5. ZSE returns a list of the rings found, a list of the atom indices that compose each ring, Atom objects for each ring that can be further analyzed or visualized by the user

5 Results

Paragraph 1: IZA doesn't list all rings in a framework

- IZA is a common reference used to identify all the rings in a zeolite framework
- It only lists the rings that define a channel (ex: 12-MR in AFI), or rings associated with the vertex symbol of a T-site
- These rings have been called tabulated rings in previous literature²
- In some frameworks, other rings (cycles not containing shortcuts) exist that are not included in the tabulated rings
- These rings still may provide important information about the topology of a zeolite framework, or the local void environment around a T-site
- Fig. 2 shows counts of frameworks containing each size ring from 3- to 18-MR using the Goetzke algorithm and the listed rings on the IZA database
- At larger sized rings (>8-MR) we see the two counts diverge

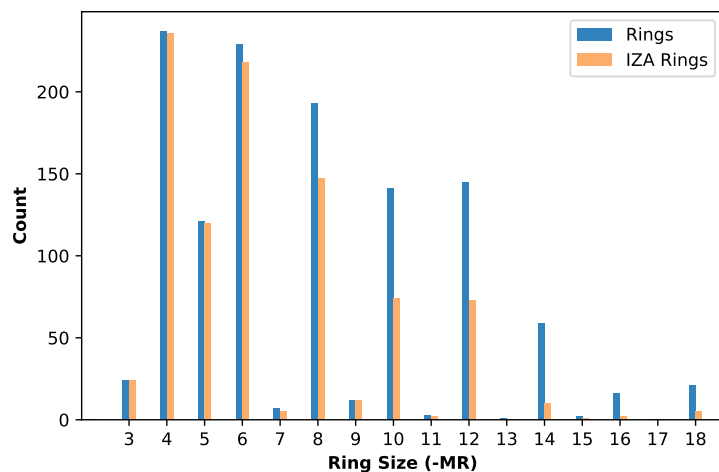


Figure 2: Counts of frameworks containing each size rings between 3 and 18-MR using the Goetzke algorithm and the tabulated rings on the IZA database.

Paragraph 2: Example of untabulated rings in CHA shows 12-MR belt on cage, and 8-MRs in the D6R

- Taking a closer look at some of these untabulated rings, highlights rings not typically but listed for some frameworks, but still relevant to describing their topology
- Here we show an example of untabulated rings in the Chabazite framework
- Show the cage belts results for CHA, AFT, etc... and discuss how those rings don't show up in previous literature, Figure 3
 - Looking at results for CHA in Table 2 we see the Goetzke method finds $4_3 \bullet 6_1 \bullet 8_6 \bullet 12_1$
 - This is different from the results in the Sastre paper,⁷ in that they only show 2 8-MRs and no 12-MRs
 - The extra 8-MRs result from cycles traversing nodes in both 6-MRs of the d6r
 - The 12-MR is a cycle that circumferences the CHA cage

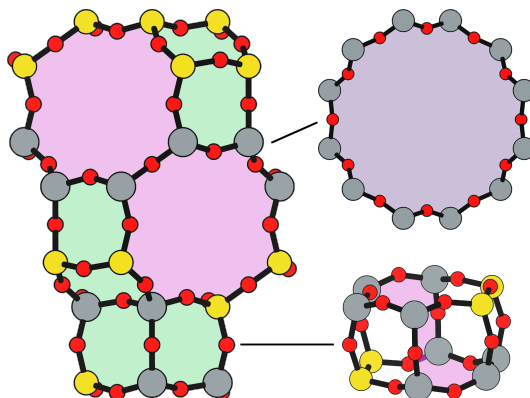


Figure 3: Chabazite cage and d6r with highlighted rings: 4-MR in green, 8-MR in pink, and 12-MR in purple. The 8-MR in the d6r and the 12-MR are rings not typically discussed in literature, Si atoms have been replaced with Al atoms to help identify those rings in the overall cage structure.

Paragraph 3: Untabulated rings in AFI also reveals rings traversing a pair of stacked rings

- AFI has one unique T-site
- According to the IZA it contains 4, 6, and 12-MRs
- When we search using the Goetzke algorithm, we also find that it contains 14-MRs that traverses two stacked 12-MRs shown in Fig. 4
- These types of rings may not be of interest depending on what you want to describe
- Using the method outlined in section X.Y we can remove these types of rings from the Goetzke ring counts

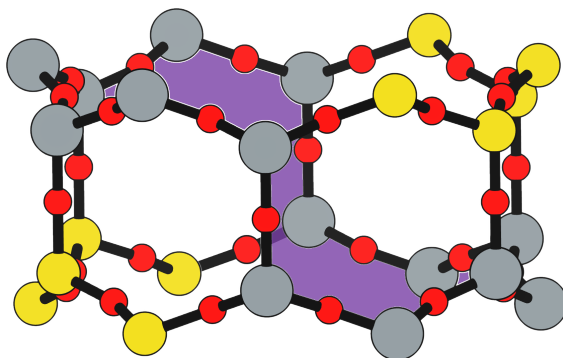


Figure 4: 12-MR channel in AFI with a 14-MR traversing 7 T-sites of each 12-MR highlighted in purple.

Paragraph 4: Comparing all 4 ringing finding conventions and IZA listed rings by counting the number of frameworks containing each size ring

- Plot showing how many frameworks on the IZA contain each size ring found using the various ring counting methods
- This highlights the differences in the conventions, and shows that results will vary depending on method used.
- In general a hierarchy of rings sizes found by each method is rings>this work>shortest path rings>vertex symbol rings
- While the IZA lists all vertex symbol rings, and a selection of general rings

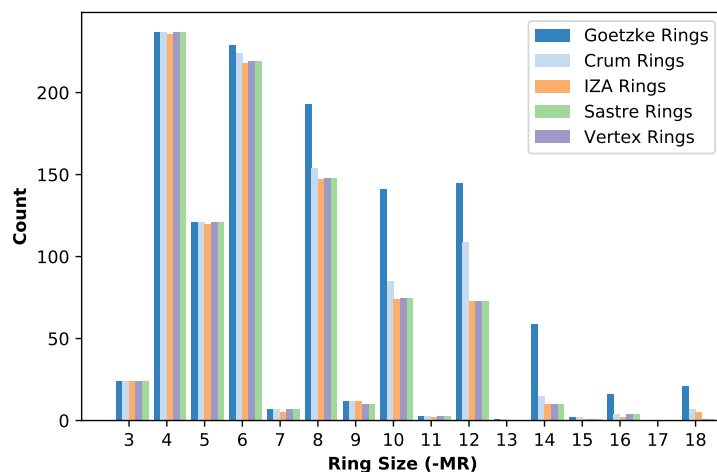


Figure 5: Number of IZA frameworks containing each size ring, using the various ring counting rules. [This will be updated with the Sastre method, vertex method, and the rings listed on the IZA website. Currently the IZA does not show any ring data for the SVY framework, providing one less framework to count.]

Paragraph 5: Some cycles behave like rings while not be considered rings by connectivity rules

- On the other end of the spectrum, there are cycles that would not be classified as a rings by the connectivity rules previously outlined, but display properties similar to rings
- The trade-off to using well defined connectivity based ring definitions leaves out these particular void environments that may still be of interest
- These shortcut containing cycles can display chemical and/or geometric properties consistent with rings, and are of interest to catalysis researchers even though they are not considered rings by connectivity rules
- One example is the 6-membered cycle referred to as the α -6-MR in literature (Figure 6) and is present in a number of frameworks including but not limited to MOR, FER, MFI, and BEA, ^{12,13} which is a potential location for Co^{2+} uptake when two Al atoms are 3rd nearest neighbor in the cycle. Similar to Co^{2+} uptake in 3NN Al atoms in 6-MRs in other frameworks such as CHA and AEL.
- This 6-membered cycle would not be considered a ring by any of the connectivity rules outlined here due to the shortcut splitting the cycle into two 5-MRs

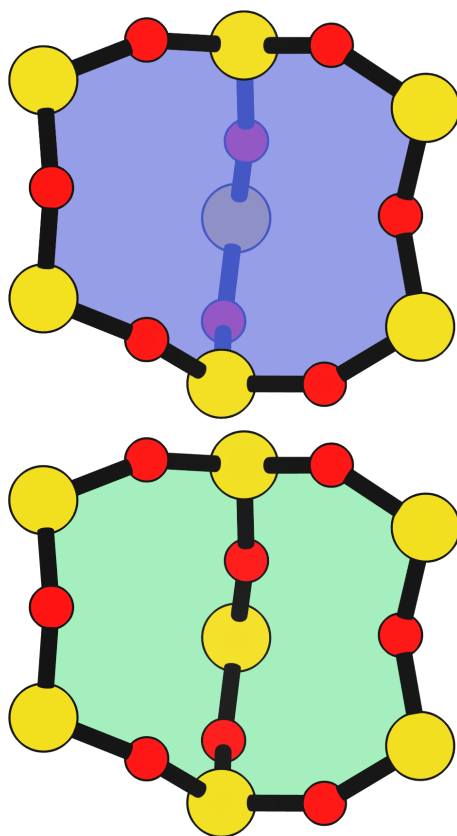


Figure 6: Cutout of MFI framework showing the structure referred to as an α -6-MR in blue, and the two 5-MRs that compose it in green. The 6-membered cycle would not be found as a ring by any of the connectivity ring rules (Goetzke, Crum, Sastre, or vertex symbol).

Paragraph 6: We can describe T-sites of a framework by the rings of that framework that pass through it AFI Example

- Take for example the AFI framework, made of 4, 6, 12, and 14-MRs and containing one

symmetry distinct T-site

- We can describe that T-site by counting how many rings of each size pass through it
- We can prune this list of rings using other definitions, such as the shortest path rings presented by Sastre et al.,⁷ by counting only the vertex symbol rings,⁸ or by our new algorithm that removes any ring that traverses a stacked set of rings
- Listing these rings by using a ring index (size_{count} from smallest to largest rings)⁷ shows the differences in counts by each method
 - Rings: $4 \bullet 6_{13} \bullet 12 \bullet 14_7$
 - This work: $4 \bullet 6_{13} \bullet 12$
 - Shortest Path Rings: $4 \bullet 6_{13}$
 - Vertex Symbol Rings: $4 \bullet 6_{11}$
- Each method returns a different count, this is highlighted in figure...

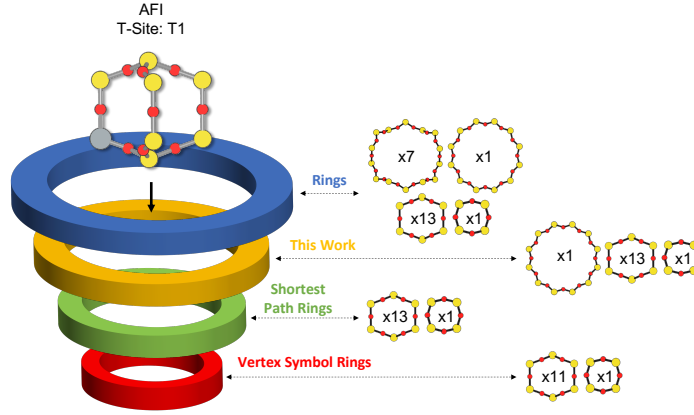


Figure 7: Diagram showing the ring counts of each size ring that pass through the single symmetry distinct T-site in AFI for each of the various ring finding conventions.

Paragraph 7: Comparison to previously published results by Sastre

Table 2: Comparison of Ring Indices for the T-sites in Various Uninodal Zeolite Frameworks

Framework	Rings	This Work	Shortest Path Rings ⁷	Vertex Symbol Rings ⁹
ABW	$4_2 \bullet 6_3 \bullet 8_4$	$4_2 \bullet 6_3 \bullet 8_4$	$4_2 \bullet 6_3 \bullet 8_4$	$4_2 \bullet 6_3 \bullet 8_2$
ACO	$4_3 \bullet 6_3 \bullet 8_6 \bullet 10_{15}$	$4_3 \bullet 8_6$	$4_3 \bullet 8_6$	$4_3 \bullet 8_6$
AFI	$4_1 \bullet 6_{13} \bullet 12_1 \bullet 14_7$	$4_1 \bullet 6_{13} \bullet 12_1$	$4_1 \bullet 6_{13}$	$4_1 \bullet 6_{11}$
ANA	$4_2 \bullet 6_2 \bullet 8_{16}$	$4_2 \bullet 6_2 \bullet 8_{16}$	$4_2 \bullet 6_2 \bullet 8_{16}$	$4_2 \bullet 6_2 \bullet 8_8$
ATO	$4_1 \bullet 6_9 \bullet 8_8 \bullet 12_{20}$	$4_1 \bullet 6_9 \bullet 12_{20}$	$4_1 \bullet 6_9$	$4_1 \bullet 6_9$
BCT	$4_1 \bullet 6_6 \bullet 8_{20}$	$4_1 \bullet 6_6 \bullet 8_{12}$	$4_1 \bullet 6_6$	$4_1 \bullet 6_6$
CHA	$4_3 \bullet 6_1 \bullet 8_6 \bullet 12_1$	$4_3 \bullet 6_1 \bullet 8_2 \bullet 12_1$	$4_3 \bullet 6_1 \bullet 8_2$	$4_3 \bullet 6_1 \bullet 8_2$
DFT	$4_2 \bullet 6_6 \bullet 8_{10} \bullet 10_{10}$	$4_2 \bullet 6_6 \bullet 8_{10}$	$4_2 \bullet 6_6 \bullet 8_{10}$	$4_2 \bullet 6_4 \bullet 8_6$
GIS	$4_3 \bullet 8_4$	$4_3 \bullet 8_4$	$4_3 \bullet 8_4$	$4_3 \bullet 8_4$
GME	$4_3 \bullet 6_1 \bullet 8_6 \bullet 12_7$	$4_3 \bullet 6_1 \bullet 8_2 \bullet 12_1$	$4_3 \bullet 6_1 \bullet 8_2$	$4_3 \bullet 6_1 \bullet 8_2$
MER	$4_3 \bullet 8_4 \bullet 10_{10} \bullet 14_{14}$	$4_3 \bullet 8_4$	$4_3 \bullet 8_4$	$4_3 \bullet 8_4$
MON	$4_1 \bullet 5_5 \bullet 8_6$	$4_1 \bullet 5_5 \bullet 8_6$	$4_1 \bullet 5_5 \bullet 8_6$	$4_1 \bullet 5_4 \bullet 8_4$
NPO	$3_1 \bullet 6_6 \bullet 12_{40}$	$3_1 \bullet 6_6 \bullet 12_{40}$	$3_1 \bullet 6_6$	$3_1 \bullet 6_6$

- Reproduce the results from Sastre paper, show ring counts with the other rules, Table 2
 - Results in the Sastre column were found using ZSE but agree directly with the results shown by Sastre and Corma⁷
 - Results in the Vertex symbol rings column were also found with ZSE but agree directly with the vertex symbols listed on the IZA website
 - * These vertex symbols have been compressed into a ring index to compare with the other methods
 - This provides an in depth look at some of the frameworks and the differences in rings found by each rule.
 - Leads into the next section discussing the specific rings of CHA and pentasil that do or don't get counted by each rule.

Paragraph 8: Example of T-site ring counts for 6 symmetry distinct T-sites in MOZ shows limitations of shortest path and vertex symbol rings

- MOZ framework is made of 4, 6, 8, 10, 12, 14, and 18-MRs, and contains 6 symmetry distinct T-sites
- Table 3 shows the ring index for each T-site using each ring finding method

Table 3: Ring indices for each distinct T-site in the MOZ framework using each ring counting convention.

T-Site	Rings	This Work	Shortest Path Rings	Vertex Symbol Rings
T1	$4_3 \bullet 6_2 \bullet 8_7 \bullet 10_7 \bullet 18_5$	$4_3 \bullet 6_2 \bullet 8_3$	$4_3 \bullet 6_2 \bullet 8_3$	$4_3 \bullet 6_2 \bullet 8$
T2	$4_3 \bullet 6_2 \bullet 8_7 \bullet 10_7 \bullet 14_5$	$4_3 \bullet 6_2 \bullet 8_3$	$4_3 \bullet 6_2 \bullet 8_3$	$4_3 \bullet 6_2 \bullet 8$
T3	$4_3 \bullet 6_2 \bullet 8_5 \bullet 10_4 \bullet 12_4 \bullet 14_5$	$4_3 \bullet 6_2 \bullet 8 \bullet 12_4$	$4_3 \bullet 6_2 \bullet 8$	$4_3 \bullet 6_2 \bullet 8$
T4	$4_2 \bullet 6 \bullet 8_6 \bullet 10_6 \bullet 12 \bullet 18_{26}$	$4_2 \bullet 6 \bullet 8_6 \bullet 12$	$4_2 \bullet 6 \bullet 8_6 \bullet 12$	$4_2 \bullet 6 \bullet 8_6 \bullet 12$
T5	$4_2 \bullet 6 \bullet 8_7 \bullet 10_6 \bullet 14_{18}$	$4_2 \bullet 6 \bullet 8_7$	$4_2 \bullet 6 \bullet 8_7$	$4_2 \bullet 6 \bullet 8_7$
T6	$4_2 \bullet 6 \bullet 8_3 \bullet 10_2 \bullet 12_8 \bullet 14_{18}$	$4_2 \bullet 6 \bullet 8_3 \bullet 12_8$	$4_2 \bullet 6 \bullet 8_3$	$4_2 \bullet 6 \bullet 8_3$

- Fig. 8 shows the T-site locations inside the framework
- If you were interested in which T-sites have access to the 12-MR channels, the shortest path rings and vertex symbol rings would only say T3
- However general rings, and this work would tell you T4 and T6 also have access to the 12-MR channels as highlighted in Figure ..

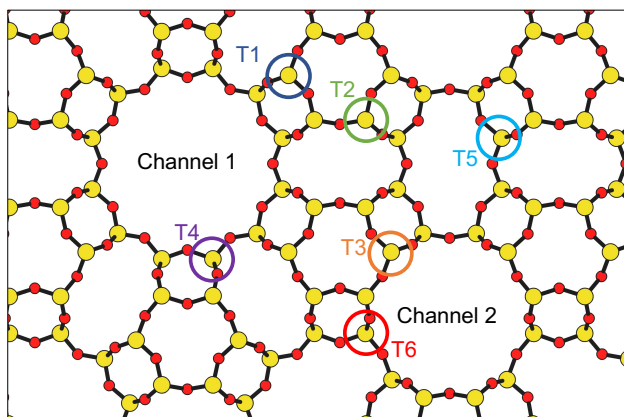


Figure 8: Cutout of the MOZ framework showing two 12-MR channels, with distinct T-sites highlighted. T1: navy, T2: green, T3: orange, T4: purple, T5: blue, T6: red.

Paragraph 9: Comparing ring counts for every T-site across the IZA database highlights differences in conventions

- Number of unique T-sites
 - There are 1460 T-sites through all the frameworks listed on the IZA website.
 - We can characterize those T-sites by the rings that pass through them
 - Most common T-site ring index using Goetzke method is: $5_6 \bullet 10_4$ showing up 23 times through the IZA frameworks.
 - Most common T-site ring index using Crum method is: $4_3 \bullet 8_4$ showing up 31 times through the IZA frameworks.
 - * Next most common T-site with Crum method is $5_6 \bullet 10_4$ showing up 25 times
 - This raises the question, if you want to ascertain chemical or physical properties about a T-site based on it's ring count, the results will depend on the convention used

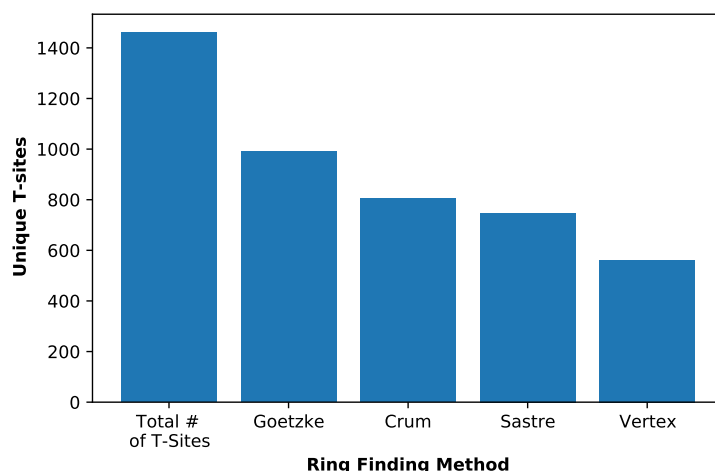


Figure 9: Number of unique T-sites when classified by the rings passing through them using various ring finding rules.

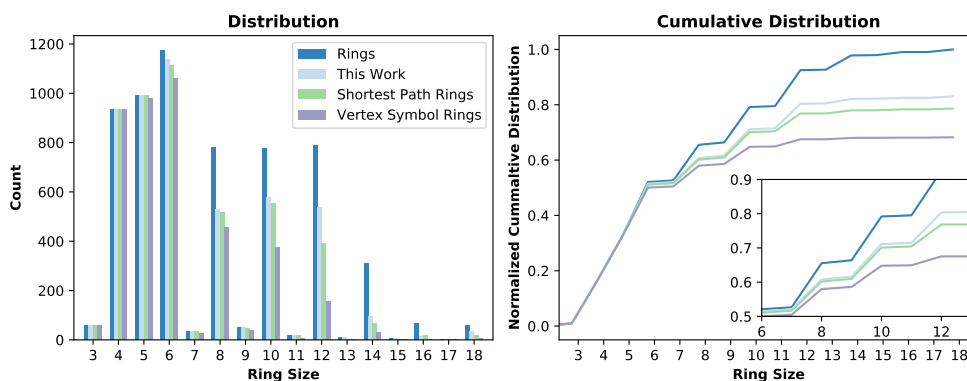


Figure 10: Frequency of T-sites across all IZA frameworks containing ring sizes between 3- and 18-MR (left), and cumulative distribution of T-sites containing each ring size normalized to final rings value (right).

Paragraph 10: Similarity of results returned by each ring finding convention

- Here we use a similarity score to determine how similar or different the rings found by each counting method are to each other

- The similarity score is determined by Eq. (1), where sr is the number of similar rings found by each method, and mr is the max number of rings found by either method.

$$s = \frac{sr}{mr} \quad (1)$$

- We compare each method for every T-site in the IZA database, and average the similarity scores for each method pair
- The results are shown in the following heat map
- We see that down the diagonal is each method compared to itself, and thus has a similarity score of 1
- The remainder of the table follows intuition
- the most restrictive counting method (vertex symbol rings) compared to the least restrictive method (rings) has the lowest similarity score
- The two most similar ring counting methods are this work compared to the shortest path rings

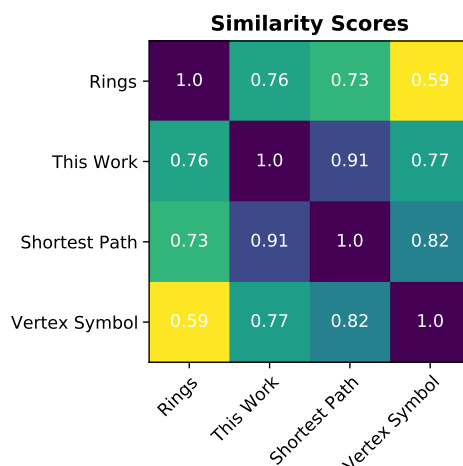


Figure 11: Heat map showing the similarity score for four ring counting methods. Similarity score of 1 means identical, and a similarity score of zero implies no similar rings found.

Paragraph 11: Stereochemistry concerns when using vertex symbols

- Vertex symbols are common way to identify similar T-sites in zeolite frameworks
- The vertex symbol as defined lists the rings included by finding pairs of opposite edge rings, and listing them from smallest pair to largest pair
- This method does not capture subtle but distinct differences in the orientation of the rings around the T-site that can lead to varying local void environments
- For example: MOR T3, MON T1, and EON T9 all have the same vertex symbol of: $4 \bullet 5_2 \bullet 5 \bullet 8_2 \bullet 5 \bullet 8_2$
 - So each T-site is a member of one 4-MR, four 5-MRs, and four 8-MRs
 - However, the orientation of those rings around each of those T-sites are not identical
 - FIGURE below shows a cutout of each of these frameworks only including the atoms that make up the vertex symbol rings around the specified T-sites

- We can see that MOR T3 and EON T9 have the same ring orientation, and that orientation is different from the rings making up MON T1
- I can make this figure better with more angles, and maybe include a line diagram explaining the differences

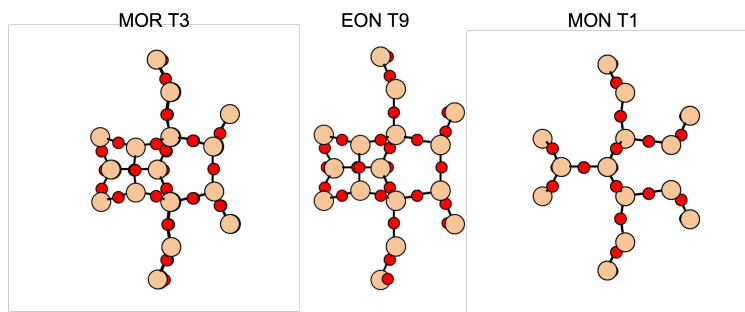


Figure 12: Cutout of MOR, EON, and MON that only shows the rings associated with the vertex symbol of T3, T9, and T1 respectively.

- This has lead us to create a new method for listing the rings in the vertex symbol that takes into account the structural connection of the rings
 - This is accomplished by assigning a weight to each of the oxygen atoms around the T-site in question based on the size of rings that connect to that oxygen
 - need to work out how to describe the method here
 - With this new descriptor MOR T3 and EON T9 would be labeled as: $8_2 \bullet 8_2 \bullet 5_2 \bullet 5 \bullet 4 \bullet 5$ and MON T1 as: $8_2 \bullet 8_2 \bullet 4 \bullet 5 \bullet 5_2 \bullet 5$
 - The difference is subtle, but highlights the distinct structural difference between the two types of T-sites that is not otherwise captured by a vertex symbol
- Here we would include a table of some of the most common vertex symbols, and how many different variations they have with this new descriptor
- Stereochemistry of the rings associated with a T-site could influence the chemical properties we care about, such as deprotonation energy, T-site substitution energy, or catalytic properties
- This would indicate that a vertex symbol is not a complete descriptor, and there is room to define a new descriptor that takes into consideration ring orientation.

Everything below here is not intended to be included in the main text of the paper

Paragraph 3: Differences in O-sites

- Number of unique oxygen sites
 - We can repeat this method for the oxygen atoms in all the frameworks
 - Counting the symmetry distinct oxygen atoms in each framework on the IZA database leads to a total count of 3219
 - We can classify those oxygen atoms based on the rings that pass through them, using the various ring counting rules
 - Figure 13 shows counts based on ring finding rules
 - The percentage of unique oxygen sites is much lower than the percentage of unique T-sites for every ring finding method

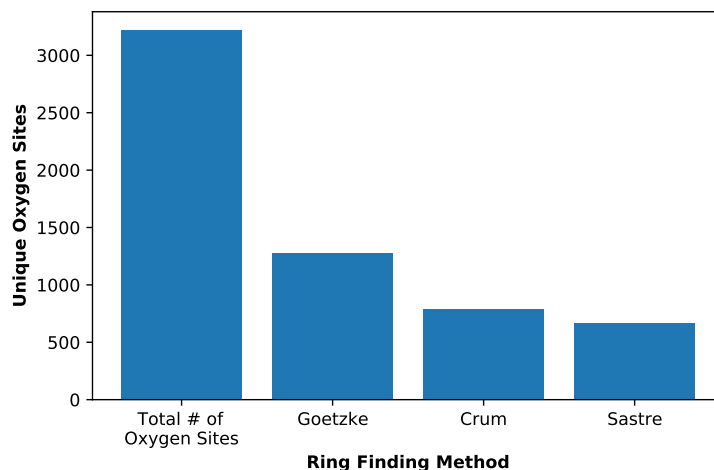


Figure 13: Number of unique oxygen sites when classified by the rings passing through them using varrious ring finding rules. Vertex method not included, since that is a way to classify T-sites only.

Note that in Figure 14 a bar for Vertex rings is not present. This is because the Vertex symbol only defines rings that pass through a specific T-site.

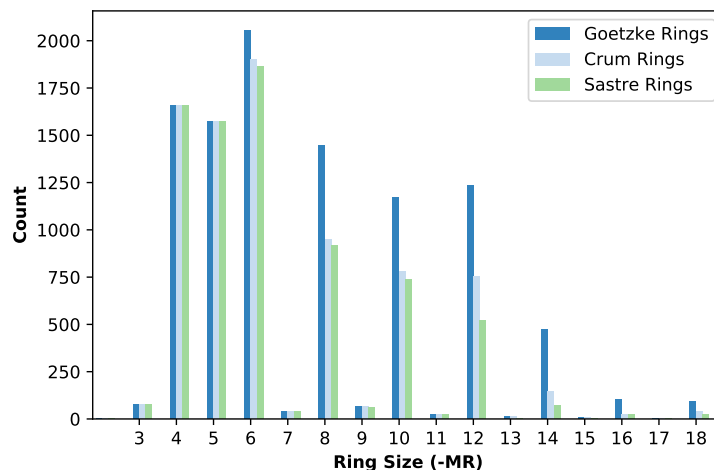


Figure 14: Frequency of O-sites across all IZA frameworks containing ring sizes between 3- and 18-MR.

- Here we show the most common ring indices for T-sites in the IZA database using each of the ring finding rules
- Table 4 shows the five most common ring indices for T-sites using the Goetzke rule

Table 4: Most Common Ring Indices Using the Goetzke Rule

Ring Index	Count	Frameworks Containing Index
$5_6 \bullet 10_4$	23	IMF(2), MEL(1), MFI(2), PRO(1), SVR(2), TUN(2), SFV(13)
$4_1 \bullet 5_3 \bullet 6_2 \bullet 10_3 \bullet 12_4$	14	MEL(1), SFV(13)
$4_1 \bullet 5_3 \bullet 6_2 \bullet 8_5 \bullet 10_1$	14	MEL(1), SFV(13)
$5_5 \bullet 6_3 \bullet 10_1 \bullet 12_1$	14	MEL(1), SFV(13)
$5_4 \bullet 6_3 \bullet 8_2 \bullet 10_3$	14	MEL(1), SFV(13)

- Table 5 shows the five most common ring indices for T-sites using the Crum rule

Table 5: Five Most Common Ring Indices Using the Crum Rule

Ring Index	Count	Frameworks Containing Index
$4_3 \bullet 8_4$	31	APC(1), GIS(1), MER(1), MWF(13), PAU(6), PHI(2), PWN(2), SIV(4)
$5_6 \bullet 10_4$	25	IMF(3), MEL(1), MFI(2), RRO(1), SVR(2), TUN(3), SFV(13)
$4_2 \bullet 6_4$	17	FAR(1), FRA(6), GIU(1), LIO(1), LOS(2), LTN(2), MAR(1), SOD(1), TOL(2)
$5_5 \bullet 6_3 \bullet 10_1$	17	IMF(1), MEL(1), MFI(1), TUN(1), SFV(13)
$4_3 \bullet 6_1 \bullet 8_2 \bullet 12_1$	16	AFS(1), AFT(3), AFV(1), AFX(2), AVL(2), BPH(1), CHA(1), GME(1), SBE(1), SFW(3)

- Table 6 shows the five most common ring indices for T-sites using the Sastre rule

Table 6: Five Most Common Ring Indices Using the Sastre Rule

Ring Index	Count	Frameworks Containing Index
$4_2 \bullet 6_4$	39	AFG(3), CAN(1), FAR(4), FRA(6), GIU(5), LIO(4), LOS(2), LTN(2) MAR(4), SOD(1), TOL(7)
$5_6 \bullet 10_4$	33	IMF(3), MEL(2), MFI(2), RRO(1), SVR(2), TUN(2), SFV(21)
$4_3 \bullet 8_4$	30	GIS(1), MER(1), MWF(14), PAU(6), PHI(2), PWN(2), SIV(4)
$4_3 \bullet 6_1 \bullet 8_2$	28	AEI(3), AFT(3), AFV(1), AFX(2), AVL(2), CHA(1), GME(1), KFI(1), LTF(1), MWF(2), PAU(2), PWN(1), RHO(1), SAV(3), SFW(3), TSC(1)
$4_3 \bullet 6_2 \bullet 8_1$	24	AFV(1), AVE(2), AVL(1), CLO(2), EAB(1), ERI(1), IFY(1), IRN(1), LEV(1), LTA(1), LTN(1), MOZ(1), OFF(1), SAT(1), SWY(2), TSC(1), UFI(1), PTT(1), SYT(3)

- Table 7 shows the five most common ring indices for T-sites using vertex symbols

Table 7: Five Most Common Ring Indices Using Vertex Symbolscite:bernauer-proton-2016

Vertex Symbol	Count	Frameworks Containing Index
4•4•6•6•6•6	40	AFG(3), CAN(1), FAR(4), FRA(6), GIU(5), LIO(4), LOS(2), LTN(2), MAR(4), RON(1), SOD(1), TOL(7)
4•4•4•6•8•8	32	AEI(3), AFT(3), AFV(1), AFX(2), ATT(1), AVL(2), CHA(1), ETV(1), GME(1), KFI(1), LTF(1), MRT(2), MWF(2), PAU(2), PWN(1), RHO(1), SAV(3), SFW(3), TSC(1)
4•4•4•6•6•8	30	AFV(1), AVE(2), AVL(1), CGS(1), CLO(2), EAB(1), ERI(1), ETR(1), IFY(1), IRN(1), JSW(1), LEV(1), LTA(1), LTL(1), LTN(1), MOZ(3), OFF(1), PTT(1), SAT(1), SWY(2), SYT(3), TSC(1), UFI(1)
4•4•4•8•8•8 ₂	30	GIS(1), MER(1), MWF(14), PAU(6), PHI(2), PWN(2), SIV(4)
5•5•5•5•5•6	26	DDR(1), DOH(2), IHW(1), IMF(1), MEL(1), MEP(1), MFI(1), MTN(1), SFS(1), SFV(15), TUN(1)

Removed paragraph, because we don't want to describe frameworks using these other ring finding methods. Keeping text in case we want to bring this back. **Paragraph 1: Differences in frameworks**

6 Conclusions

- Rings of graph are well defined; here identify all rings up to XXX in YYY frameworks. Find that commonly reported (IZA) ring sizes miss certain rings.
- The method used to find rings in a zeolite will provide different ring counts unclear
- When discussing rings in a zeolite it is import to disclose by which method those rings were found
- Using ZSE we can find rings based on various methods
- This provides a foundation for using ring fingerprints in machine learning models to correlate chemical properties and topology

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