ZSE Manuscript Outline

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Introduction

- Zeolites can naturally be represented using graph theory, where atoms are nodes, and bonds are edges.
  - Sometimes in the literature, oxygen atoms are used as bridges instead of nodes, since they only connect to two T-sites
- Topology of zeolite frameworks and associated tetrahedral sites (T-sites) are commonly characterized by their associated rings
- Rings are defined as a close cycle traversing the T-site and oxygen atoms of the framework, and cannot be decomposed into smaller cycles by a shortcut.[1]
- 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.
- 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.

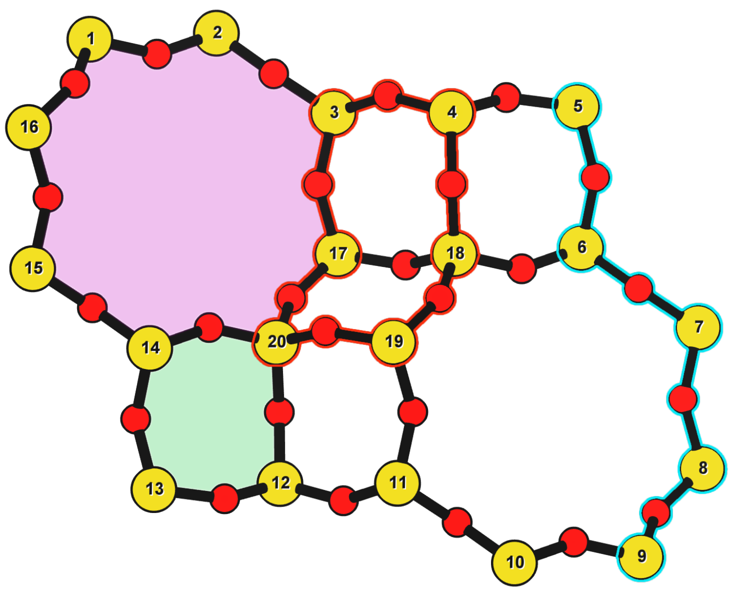

Figure 1: Cutout of the Chabazite framework showing a path from node 3 to node 9 outlined in teal, a cycle (3-4-18-19-20-17) outlined in red, an 8-MR in pink, and a 4-MR in green. Yellow atoms are Si (T-sites), and red atoms are oxygen.

Table 1: Matrix showing relationship between frameoworks, nodes, paths, cycles, and various ring types.

	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 from at least one set of O-T-O on the cycle	A smaller subset of the rings above	All shortest path rings that pass through T-site	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	

- Rings have been used to identify feasible zeolite topologies,[2] to descirbe the similarity and differences between zeolites,[3] to identify sites or voids of catalytic relevance,[4,5] and as machine learning finger prints [will get citations for this]
- Different methods exist to count rings present in a zeolite
- These methods return different sets of rings
- Vertex symbols are the set of shortest paths connecting the 6 oxygen-oxygen pairs around a T-site[6]
- Shortest path rings count all the vertex symbol rings that pass through a T-site or an oxygen atom[7]
- Or we can count all the rings that do not have a short cut[1]

- 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.
- 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 [1] for finding rings in arbitrary frameworks.
- We compare the results of a number of common and new ring definitions applied to a large number of common zeolite frameworks. [4]

Software Description

- All of the frameworks listed on the IZA Database of zeolite structures [8] are included in a database with ZSE
- These structures are Atomic Simulation Environment Atoms objects, [9] 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
- ZSE has 3 previously published rules for ring finding implemented
  - All cycles with out a shortcut [1]
  - All shortest path cycles [7]
  - Cycles that compose the vertex symbol for a T-site [6]
- We have also implemented a new rule that finds all rings with out a shortcut, but excludes rings that are made by traversing a stacked set of rings.
  - 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

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 NetworkX [10] 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 base on the algorithm presented by Goetzke and Klein [1]
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 indicies that compose each ring, Atoms objects for each ring that can be further analyzed or visualized by the user

Results

- Ring counts frequency plots

– 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 ring rules, and shows that results will vary depending on rule.

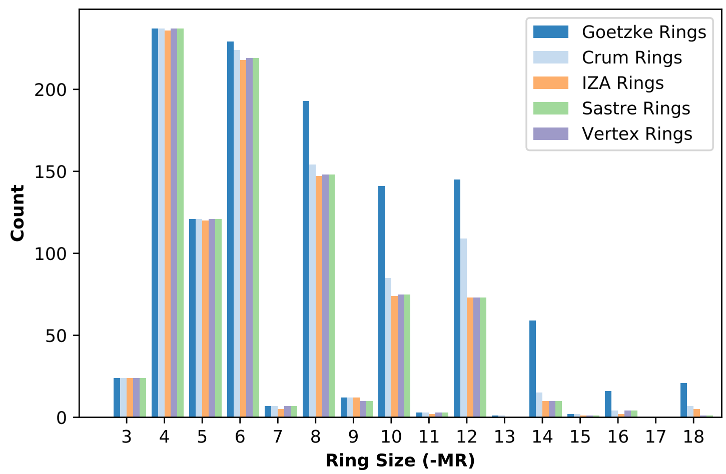

Figure 2: Number of IZA frameworks containing each size ring, using the various ring counting rules. [This will be updated with the Sastre method, vertex method, and the rings listed on the IZA website. Currently the IZA does not show any ring data for the SVY framework, providing one less framework to count.

- 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
  - Sastre did this, and called the list of rings, the ring index
  - If we do this using different rules for ring finding how do the results change?
    - See Figure 3
  - 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 use machine learning to correlate T-site rings to chemical properties, which ring method should you use?

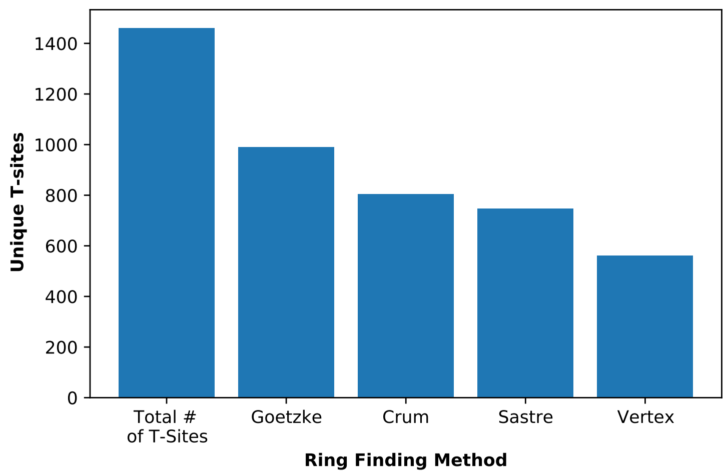

Figure 3: Number of unique T-sites when classified by the rings passing through them using varrious ring finding rules.

- 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 4 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

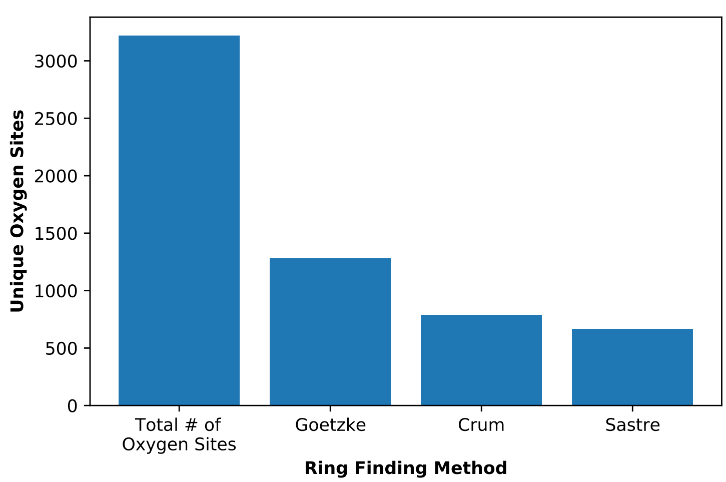

Figure 4: Number of unique oxygen sites when classified by the rings passing through them using varrious ring finding rules. Vertex method not included, since that is a way to classify T-sites only.

- 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 Corma[7]

- 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.

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

Framework	Goetzke	Crum	Sastre[7]
ABW	$4_2 \bullet 6_3 \bullet 8_4$	$4_2 \bullet 6_3 \bullet 8_4$	$4_2 \bullet 6_3 \bullet 8_4$
ACO	$4_3 \bullet 6_3 \bullet 8_6 \bullet 10_{15}$	$4_3 \bullet 8_6$	$4_3 \bullet 8_6$
AFI	$4_1 \bullet 6_{13} \bullet 12_1 \bullet 14_7$	$4_1 \bullet 6_{13} \bullet 12_1$	$4_1 \bullet 6_{13}$
ANA	$4_2 \bullet 6_2 \bullet 8_{16}$	$4_2 \bullet 6_2 \bullet 8_{16}$	$4_2 \bullet 6_2 \bullet 8_{16}$
ATO	$4_1 \bullet 6_9 \bullet 8_8 \bullet 12_{20}$	$4_1 \bullet 6_9 \bullet 12_{20}$	$4_1 \bullet 6_9$
BCT	$4_1 \bullet 6_6 \bullet 8_{20}$	$4_1 \bullet 6_6 \bullet 8_{12}$	$4_1 \bullet 6_6$
CHA	$4_3 \bullet 6_1 \bullet 8_6 \bullet 12_1$	$4_3 \bullet 6_1 \bullet 8_2 \bullet 12_1$	$4_3 \bullet 6_1 \bullet 8_2$
DFT	$4_2 \bullet 6_6 \bullet 8_{10} \bullet 10_{10}$	$4_2 \bullet 6_6 \bullet 8_{10}$	$4_2 \bullet 6_6 \bullet 8_{10}$
GIS	$4_3 \bullet 8_4$	$4_3 \bullet 8_4$	$4_3 \bullet 8_4$
GME	$4_3 \bullet 6_1 \bullet 8_6 \bullet 12_7$	$4_3 \bullet 6_1 \bullet 8_2 \bullet 12_1$	$4_3 \bullet 6_1 \bullet 8_2$
MER	$4_3 \bullet 8_4 \bullet 10_{10} \bullet 14_{14}$	$4_3 \bullet 8_4$	$4_3 \bullet 8_4$
MON	$4_1 \bullet 5_5 \bullet 8_6$	$4_1 \bullet 5_5 \bullet 8_6$	$4_1 \bullet 5_5 \bullet 8_6$
NPO	$3_1 \bullet 6_6 \bullet 12_{40}$	$3_1 \bullet 6_6 \bullet 12_{40}$	$3_1 \bullet 6_6$

- Here we show the most common ring indices for T-sites in the IZA database using each of the ring finding rules
- Table 3 shows the five most common ring indices for T-sites using the Goetzke rule

Table 3: 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 4 shows the five most common ring indices for T-sites using the Crum rule

Table 4: 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 5 shows the five most common ring indices for T-sites using the Sastre rule

Table 5: 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 6 shows the five most common ring indices for T-sites using vertex symbols

Table 6: Five Most Common Ring Indices Using Vertex Symbolscite:bernauer-proton-2016

Vertex Symbol	Count	Frameworks Containing Index
$4 \bullet 4 \bullet 6 \bullet 6 \bullet 6 \bullet 6$	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)
$4 \bullet 4 \bullet 4 \bullet 6 \bullet 8 \bullet 8$	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)
$4 \bullet 4 \bullet 4 \bullet 6 \bullet 6 \bullet 8$	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)
$4 \bullet 4 \bullet 4 \bullet 8 \bullet 8 \bullet 8_2$	30	GIS(1), MER(1), MWF(14), PAU(6), PHI(2), PWN(2), SIV(4)
$5 \bullet 5 \bullet 5 \bullet 5 \bullet 5 \bullet 6$	26	DDR(1), DOH(2), IHW(1), IMF(1), MEL(1), MEP(1), MFI(1), MTN(1), SFS(1), SFV(15), TUN(1)

- These ring finding rules often find rings that are not commonly discussed in literature, and are not listed by the IZA
- These are classified as untabulated rings by Curtis and Deem[3]
- However it is possible that these rings are relevant for describing chemical, catalytic, or topological properties of zeolites
- 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 5
  - 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
    - Crum rule removes these 8-MRs while still finding the 12-MR
    - Sastre rule does not find the 8-MRs in the d6r or the 12-MR
  - The 12-MR is a cycle that circumferences the CHA cage

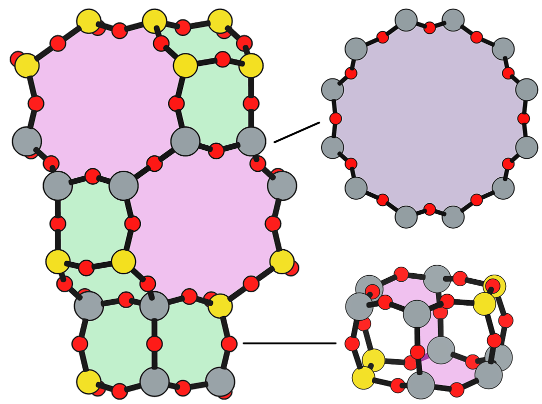

Figure 5: Chabazite framework with highlighted rings: 4-MR in green, 8-MR in pink, and 12-MR in purple. The 8-MR in the d6r and the 12-MR are rings not typically discussed in literature, Si atoms have been replaced with Al atoms to help identify those rings in the overall cage structure..

- On the other end of the spectrum, there are cycles that would not be classified as a rings by the connectivity rules previously outlined that display properties similar to rings
- 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,[11,12] 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 AEI.
- 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

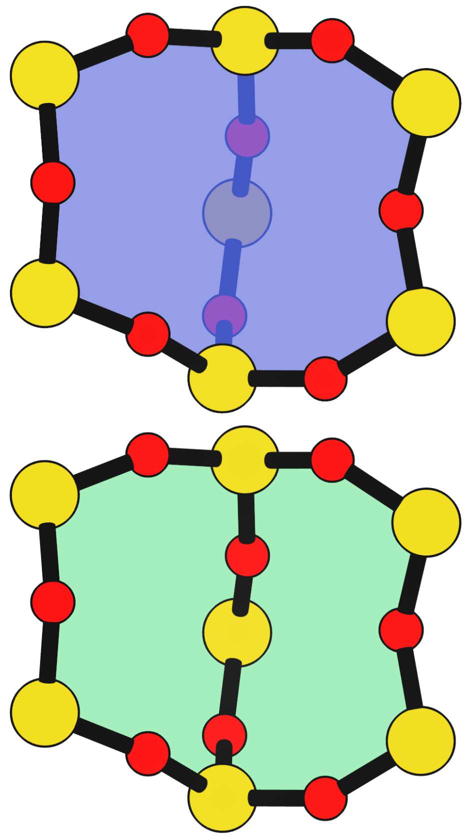

Figure 6: Cutout of MFI framework showing the structure referred to as an α-6-MR in blue, and the two 5-MRs that compose it in green. The 6-membered cycle would not be found as a ring by any of the connectivity ring rules (Goetzke, Crum, Sastre, or vertex symbol).

Conclusions

- The method used to find rings in a zeolite will provide different ring counts
- 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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