A COMPARISON OF CRYSTALLINE AND MOLTEN STRUCTURES OF
ZIRCONOLITE (CaZrTi$_2$O$_7$), A POTENTIAL PLUTONIUM
WASTEFORM MEDIUM, BY MOLECULAR DYNAMICS SIMULATION
AND TOPOLOGICAL ANALYSIS

by

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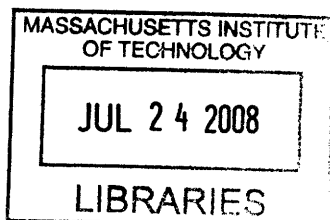
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1

Abstract

Molecular dynamics simulations of the ceramic compound zirconolite ($CaZrTi_2O_7$), a potential crystalline wasteform host for plutonium, were carried out for ideal and experimental crystalline forms and a simulated molten state, and the connectivities of the resulting structures were compared. Local primitive-ring topological clusters were determined for individual atoms, and averages of ring counts were calculated for atom types within each form of zirconolite. The ideal crystalline structure and the best experimental structure, deduced by Rossell from neutron diffraction data, proved very similar, though the Rossell local clusters contained small variations from the ideal. Molten zirconolite appeared very different; it exhibited much larger ring counts and local clusters, together with a tendency for Ca and Ti (but not Zr) cation clustering. The technique of looking at ring counts for individual atoms was found to be very sensitive to small changes in the structure, though more suited to comparison of the two crystalline structures because of their uniformity. Significant connectivity differences and heterogeneity in the molten structure were best compared by considering the average local cluster. The structure of metamict zirconolite, amorphized by α-recoil of incorporated waste actinides, is conjectured to exhibit some characteristics of both crystalline and molten forms, likely stabilized by polymerization of cation coordination units signaled by the observed clustering of like Ca and Ti cations observed in the molten state.

Acknowledgements

Table of Contents

List of Tables

List of Figures

Introduction

Nuclear waste in crystalline ceramics

The large scale use of nuclear power over the last several decades has created an engineering challenge of disposing safely of the waste left behind. The currently prevailing method is to store the spent fuel intact inside layers of physical barriers. A method proposed for more widespread use in the future is to reprocess the waste, separating component materials that can still be used and dividing the shorter-lived waste from the long-lived waste, thereby reducing the amount of material that needs to be stored for centuries. In order to protect the environment from the high level waste, the latter can be incorporated into a ceramic material. In the 1980s, one such material suggested was SYNROC, a synthetic ceramic, of which zirconolite ($CaZrTi_2O_7$) was a component [1]. Samples have been made which replace the Ca or the Zr in the ceramic with plutonium. Chemically, this material is predominantly ionically bonded and very stable; the challenge arises when one considers the damage done to the structure by the alpha decay of Pu-239 [2,3].

Zirconolite

Zirconolite, as it is found naturally, contains some cesium in the place of calcium, and iron, niobium and aluminum all take the place of titanium at times [4]. For the purposes of SYNROC, these other elements are not included, and about 10% of the zirconium is replaced by plutonium. In the ideal structure of zirconolite, calcium occupies the M1 cation site, zirconium the M2 site, and titanium sites M3, M4 and M5. Oxygen ions occupy seven crystallographically distinct sites, five of which are topologically equivalent and two (O2, O3) topologically distinguishable from each other and from the other five. A more realistic structure, deduced experimentally from neutron diffraction data by Rossell [1] and exhibiting partial cation disorder, has Ti atoms randomly occupying 7% of the M2 sites and Zr atoms correspondingly 14% of the M4 sites.

Radiation effects in zirconolite

The incorporation of an alpha emitter such as Pu into zirconolite has a variety of effects on the material. When the nuclide decays, the recoil atom causes extensive local damage in the crystal by displacing several thousand of its neighboring atoms from their crystal sites as it loses kinetic energy. In addition, the alpha particle released picks up electrons and becomes a neutral He atom, which is then trapped in the zirconolite. The effects of alpha emitters on polycrystalline zirconolite ceramic have been studied by substituting Pu-238 for Pu-239 because of its much shorter half-life. The substitution allows experiments to be completed in a 1-2 year time span that achieve an end product similar to the state of the waste medium thousands of years in the future.

The dense collision cascades effected by the recoiling alpha emitters comprise areas of disordered ions that have been knocked out of place by either the recoil atom or the atoms that it hit. Some of the displaced atoms will return to their original places, while others will not. The largest determining factor in how many do is the temperature of the ceramic during or after irradiation. The higher the temperature, the more likely the atom will find its way back to an appropriate crystalline location [2].

The disordered zones left by recoil atoms are mostly responsible for swelling observed in the material. When the Pu-238-doped zirconolite is kept at 350 K (the

6

closest to room temperature possible, since the decays heat the material), the swelling is about 5.4% by volume at saturation. After enough time has passed that the collision cascades start to overlap, the swelling ceases, as the crystal becomes uniformly disordered. This limit of swelling is different at different temperatures, though. For a sample kept at 575 K, the swelling leveled off at 4.3%. When another sample was kept at 575K until it has reached its maximum volume, then kept at a lowered temperature of 350K, the swelling began again and continued until it had reached the same magnitude as if the crystal had been wholly irradiated at that temperature. The swelling saturated when the crystal was rendered metamict (amorphized), but there was a clear difference between the metamict structures at 575K and 350K, as evidenced by their different densities [2].

The change in volume due to irradiation poses structural problems for the ceramic. A larger piece is likely to develop microcracks from the stresses caused by internal swelling [2,3]. In addition to stress imposed from any non-uniform swelling of the material internally or externally imposed volume constraints, there is also concern about stresses arising from the build up of He in material. The helium comes from the alpha particle picking up electrons as it moves through the zirconolite. The amount of He trapped in the material is proportional to the amount of damage the ceramic has sustained [5]. If the temperature of zirconolite becomes high enough to allow for annealing, the helium is released, which may stress the secondary containment for the material.

Topology and Connectivity

In order to better understand what will happen to the waste storage material in the long term, detailed information about the metamict state it approaches is required. Unfortunately, the structures of metamict and highly radiation-damaged materials are not as easily deduced as crystalline ones because of their lack of long-range order. However, by looking at the connectivity of the material rather than the exact positions of the atoms, comparisons can be made more easily. Often, two different materials will have the same connections (*e.g.* atom A connected to two atoms B, which are in turn connected to three A atoms, *etc.*) but different bond angles, resulting in very different looking structures that are nevertheless topologically identical or closely related. Also, this *local* approach more closely reflects how these materials alter, since the atoms themselves connect to each other based on what is close by and what bond angles or coordinations are favored, and not on whether the connection matches a long-range pattern [6].

This sort of information is not attainable by experimental methods, which are usually sensitive only to the presence of the first few neighbor atoms and cannot distinguish the third or fourth atom down the connectivity chain. This leaves simulations as the best way to compare radiation-damaged material to its crystalline precursor. A molecular dynamics (MD) simulation can be run to determine the positioning of the atoms given their environment, and the results can be analyzed for connections and patterns. Simulations have their own disadvantages, in that their spatial extent is seriously limited by computing power. There is a size restraint on how big the simulated systems can be and still be manageable [7]. The present MD simulations involved just over 5,600 atoms.

When considered from a topological point of view, atoms must arrange themselves into closed circuits (*rings*) along their coordination "bonds," in order to keep density under control [6]. Rings for zirconolite always have even-numbered counts (4-rings, 6-rings, *etc.*) because the cations do not bond to each other, and neither do the anions, requiring an alternating anion-cation pattern along the ring. A *primitive ring* can

be defined as one that doesn't contain links across it made by other atoms, dividing it into two or more rings, all of which are smaller than the original ring. All the atoms in the primitive rings for a particular starting atom, grouped together, are considered to be the *local cluster* for that atom. In an ideal crystalline material, the local clusters are identical for the same type of atom [6].

Molecular Dynamics Simulations

Molecular dynamics simulations were carried out using the DL_POLY_3 code [7], a third-generation MD simulation program written by William Smith of Daresbury Laboratory in the UK. The potential used was designed by Prof. Robin Grimes of Imperial College, London as a pairwise ionic formulation incorporating three-body terms and a splined short-range repulsive term.

The topological analyses in this work were carried out using Yi Zhang's ring analysis codes for zircon ($ZrSiO_4$) [8], appropriately modified for zirconolite. Zhang's code requires a file containing the positions of the atoms and the maximum bond length allowed between atoms to consider them still "connected." In the present case, a bond length was assumed to be 0.32 nm or less. The code provides information about a single local cluster – the group of atoms included in all the primitive rings passing through a single center atom, including the number and types of rings that pass through the center atoms and the numbers of atoms that make up the cluster. It also enumerates all the atoms of a particular type and provides the average ring counts for that group. The atom position file was outputted from DL_POLY_3 and inputted into the ring-finding code.

For all three simulations run (ideal, Rossell and melt structures), a 4x4x4 box of 256 unit cells (5632 atoms, 512 for each formula unit) was used with periodic boundaries implemented. The simulation was allowed to run for 100,000 steps with a time step of 0.001 picoseconds, enough to ensure that all adjustments to the original positions had been made. To obtain a topologically disordered zirconolite configuration, more characteristic of a melt-like state that might occur within a collision cascade before cooling or being quenched to the metamict state, the Rossell structure was melted by running the simulation at a simulation temperature of 2500 K for 100,000 steps, with a time step of 0.001 picoseconds.

Images were generated using Atomeye [9], a visualization code designed by Ju Li when he was at MIT, from the local cluster files calculated with Zhang's ring-finding code.

Results

Rossell vs. Ideal Structure Ring Counts
The local clusters of the Rossell zirconolite structure differ in only small ways from the local clusters of the ideal structure. **Table 1** below lists the average ring sizes of the local clusters for each atom type and site, for both the ideal and Rossell structures.

The averages for the ideal structure were determined by looking at a single local cluster. All the local clusters are identical because of the perfect crystalline nature of the ideal version. The averages for the Rossell zirconolite are indeed averages. The substitutions made were randomly scattered about the crystal, and so some local clusters were more affected than others. The column designated "atoms avged" lists the number of local clusters that were averaged together for that atom type. The entry varies because

of the different percentages of that atom type in the crystal. For example, only a few atoms were averaged together for the M2 Ti site because only 7% of the atoms on that site were titanium, the rest being zirconium. The average ring size for each type of cluster was determined by taking the average of the 4-, 6-, 8- and 10-rings, including the 12-rings where applicable.

Table 1 – Number of rings and atoms in all the local clusters averaged together for both Rossell-structure zirconolite (in white) and ideal structure zirconolite (in gray).

atom (position)	avg ring size	avg # of 4 rings	avg # of 6 rings	avg # of 8 rings	avg # of 10 rings	avg # of 12 rings	atoms avged	atoms in avg cluster
Ca (M1)	6.444	12	18	24	0	0	-	45
Ca (M1)	6.495	11.915	16.508	25.158	0.011	0	177	46.6
Zr (M2)	6.625	9	15	24	0	0	-	47
Zr (M2)	7.056	8.241	12.982	20.553	0.024	3.924	170	47.8
Ti (M2)	6.502	8.9	14.4	19.7	0	0	10	44.8
Ti(M3)	6.857	6	12	24	0	0	-	49
Ti (M3)	6.940	5.4	12.181	25.781	0	0	155	49.4
Ti (M4)	6.444	12	18	24	0	0	-	45
Ti (M4)	7.423	8.972	15.423	17.239	0.338	9.141	71	43.8
Zr (M4)	6.458	11.643	17.643	23.643	0.071	0	14	45
Ti (M5)	6.857	6	12	24	0	0	-	49
Ti (M5)	7.004	5.275	12.05	28.012	0.012	0	80	49.4

For the most part, the averages for the Rossell structure ring counts are very close to those of the ideal structure. There are a couple of exceptions. The average number of 4-rings for Ti (M4) local clusters is twelve for the ideal structure, but less than nine for the Rossell structure. What is interesting is that this is not the case for Zr (M4) local clusters, even though the zirconium is taking the place of the titanium. This is also the case for the number of 6- and 8-rings for those two kinds of local clusters. The average Ti (M4) Rossell local cluster has almost seven fewer 8-rings than the ideal, while the Zr (M4) average is nearly the same as the ideal, indicating some local rearrangement in the Rossell substitutions.

Another large difference in the averages is found in the number of 8-rings for the Ti (M5) local clusters, where the average Rossell one has four more than the ideal. It is also important to point out that, for the most part, the number of atoms in the local clusters is the same despite the type of zirconolite, except in the case of Ti (M4), where there is one atom fewer, and Ti (M2), an out-of-place atom, where there are two fewer atoms in the local cluster.

Since the values for the Rossell structure zirconolite are averages, it is of interest to look at some individual, randomly chosen local clusters. **Table 2** lists the ring sizes for local clusters of five different atoms for each atom type and site.

Table 2 – Number of rings and atoms in five different local clusters for each type of cation and cation site in Rossell-structure zirconolite

atom (position)	atom #	4-rings	6-rings	8-rings	10-rings	atoms in cluster
Ca (M1)	14	12	17	25		45
	213	12	17	24		45
	321	12	16	26		45
	335	11	24	27	1	53
	458	12	18	24		45
Zr (M2)	595	8	13	24		49
	685	8	15	22		47
	727	9	15	22		47
	824	8	13	27		47
	951	8	13	26		49
Ti (M2)	998	9	13	20		45
	1001	9	15	20		44
	1010	9	15	20		44
	1012	9	14	17		45
	1019	9	14	20		46
Ti (M3)	1060	6	12	23		49
	1168	5	12	28		51
	1266	6	12	22		49
	1366	6	12	23		49
	1424	5	10	36		49
Ti (M4)	1560	7	12	19		39
	1621	9	17	16		45
	1686	9	17	16		45
	1707	9	17	16		45
	1782	12	18	24		45
Zr (M4)	1762	12	18	24		45
	1768	12	18	24		45
	1774	12	18	24		45
	1776	12	18	24		45
	1787	12	18	24		45
Ti (M5)	1820	5	10	37		49
	1880	5	13	25		49
	1917	5	13	25		49
	1965	5	12	29		51
	1973	5	10	37		49

The ring counts listed in Table 2 do not show much variation in the 4- and 6-rings, nor in the number of atoms in the cluster. This is to be expected, since the Rossell-structure zirconolite is still a crystal, despite the switching of some of the atom locations. One interesting feature of this list is the appearance of a 10-ring. The ideal crystal does not have any rings larger than 8-rings. The averages reflect the presence of a very few 10- and 12-rings for the Rossell-structure zirconolite, therefore among the 35 atoms listed in Table 2 there is but one example of a local cluster with an unusual size ring. Another

feature to note is the uniformity of the Zr (M4) ring counts, which are identical for at least the five atom clusters chosen at random from fourteen possible ones.
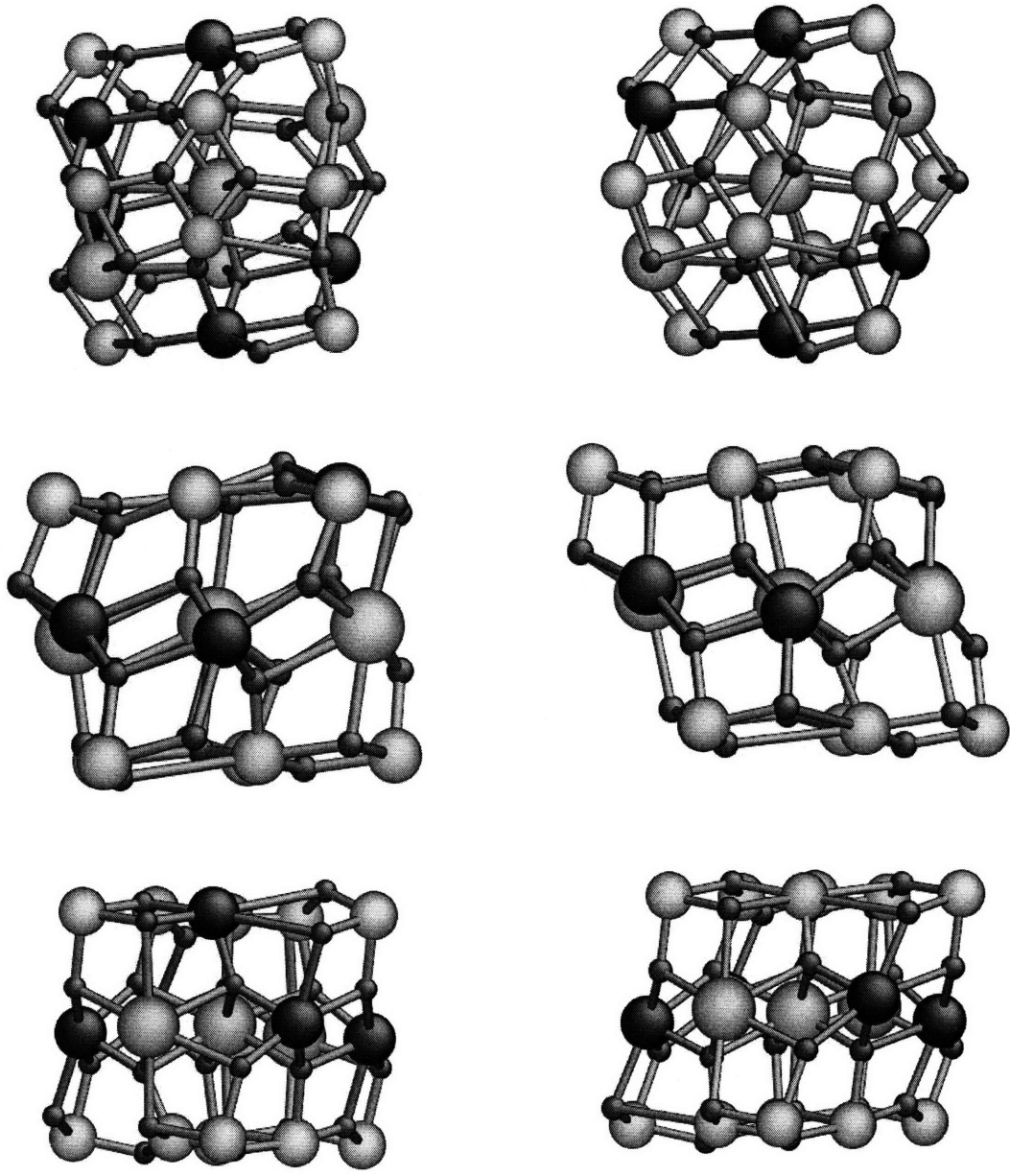
Rossell vs. Ideal Structure

Only so much information can be determined from the number of rings and atoms in a local cluster. To get a better understanding of the variations in the local clusters for the Rossell structure, up to three of each type of local cluster were modeled in Atomeye; the resulting images are shown here side by side with the corresponding ideal structure local cluster. From these images one can see the differences in bonding that lead to the changes in ring counts, and where atoms go missing or get added. It is also easy to see if any of the titanium or zirconium atoms in the local clusters are in the substituted locations.

Three of the five local clusters for Ca (M1) are pictured here in **Figures 1, 2** and **3**. The first two, #213 and #321, were chosen because of their similarity to the other local clusters, and because both vary slightly from the ideal structure. The number of rings and number of atoms in the cluster are very close to the average values determined for the entire sample. For #213, a change in connectivity can be seen in the lower left hand corner of the bottom view, where a titanium atom is skewed out of position just enough to be too far to be considered as bonded to the oxygen atom next to it. A similar change in connectivity can be seen in #321, this time in the upper left hand corner of the bottom view.

The local cluster for atom #335 is especially interesting because it shows a 10-ring, while the ideal clusters show only rings of up to 8 atoms. The cluster includes several extra atoms in the 10-ring, giving the cluster eight more atoms than usual. The overall structure is not changed that much from the original; some bonds are missing in places because of atoms being pulled out of position, but overall the same general pattern is reproduced, even among the extra atoms.

In all three of these clusters, one can see the zirconium atoms substituted where a titanium atom should be, though in none of these examples does the substitution occur the other way around. The changes in atom location do not have such a strong effect that their influence extends more than locally, but they are certainly present.
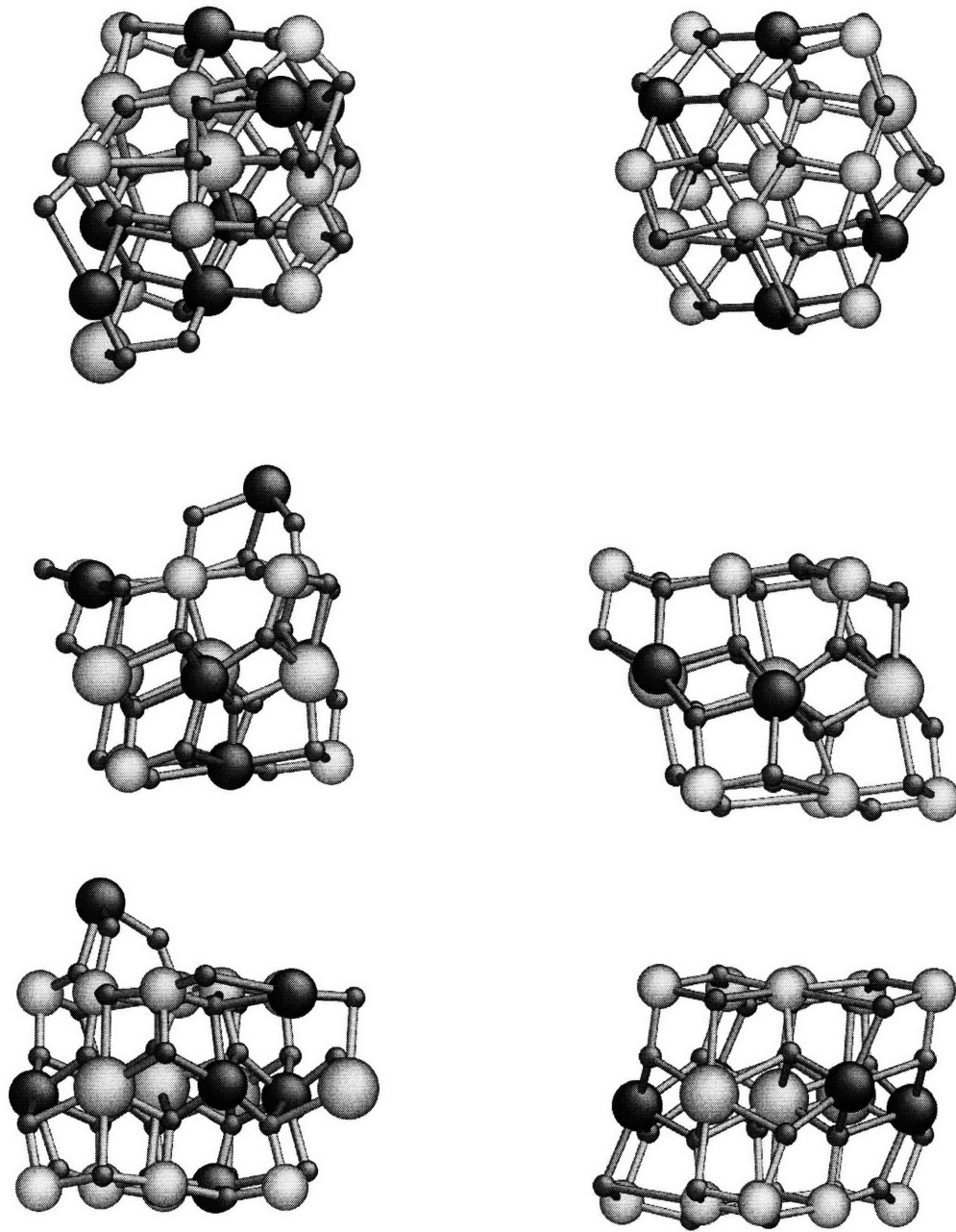
Figure 1 – On the left is a local cluster for Ca (M1) site in Rossell-structure zirconolite, atom #213. The local cluster consists of 12 4-rings, 17 6-rings and 24 8-rings, with a total of 45 atoms. On the right is the Ca (M1) local cluster for ideal zirconolite, which consists of 12 4-rings, 18 6-rings, and 24 8-rings, with a total of 45 atoms.
Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray
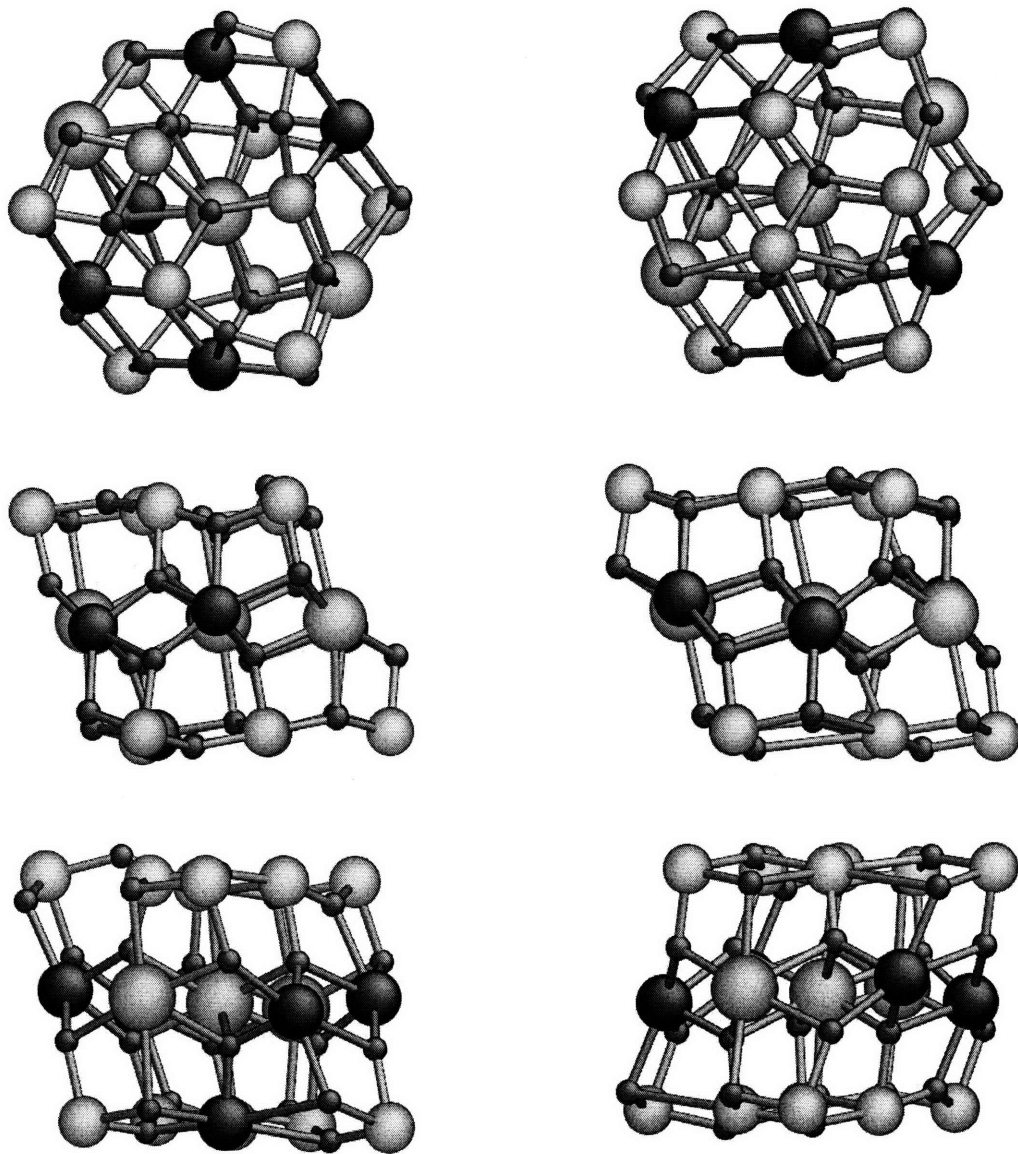
Figure 2 – On the left is a local cluster for Ca (M1) site in Rossell-structure zirconolite, atom #321. The local cluster consists of 12 4-rings, 16 6-rings and 26 8-rings, with a total of 45 atoms. On the right is the Ca (M1) local cluster for ideal zirconolite, which consists of 12 4-rings, 18 6-rings, and 24 8-rings, with a total of 45 atoms.

Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray

Figure 3 – On the left is a local cluster for Ca (M1) site in Rossell-structure zirconolite, atom #335. The local cluster consists of 11 4-rings, 24 6-rings, 27 8-rings and one 10-ring, with a total of 53 atoms. On the right is the Ca (M1) local cluster for ideal zirconolite, which consists of 12 4-rings, 18 6-rings, and 24 8-rings, with a total of 45 atoms.

Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray

Three Zr (M2) clusters were chosen to be reproduced in **Figures 4, 5** and **6**. The first one, #595, is shown for similar reasons as applied earlier to the cluster for Ca #335. This local cluster also has additional atoms, though it is still made up of only 4-, 6- and 8-rings. While this cluster has two more atoms than the ideal cluster, it actually has three extra atoms and one missing one. The oxygen in front of the topmost zirconium atom in the top view is the missing one. The extra three atoms are allowed in because of some broken bonds visible in the top view in the middle. No switched atoms are in this cluster.

The second Zr (M2) cluster, #727, shown is interesting in opposite ways from the first. Here there is a zirconium atom substituted in place of a titanium atom and *vice versa*. Despite that, the connectivity is the same as in the ideal structure. The atoms are not in exactly the same positions, but they are close enough that the identical bond connectivity still occurs.

The third cluster shown, #824, is much more interesting than would appear from the number of rings or atoms in the cluster, which are not that far off from the averages. The pictures clearly show that there are two missing oxygen atoms and a missing titanium atom from the peak of the top view, and an additional calcium atom and two adjoining oxygen atoms on the opposite side of the cluster. The added atoms are the result of a neighboring titanium that is shifted far enough out of position that it does not bond to all of the oxygen atoms it should. In the case of the missing atoms, there are no additional bonds formed; it is likely that the three were shifted too far to be included within the bond cutoff. Again, despite the other changes, there are no Ti/Zr atoms that have switched places.

Three corresponding Ti (M2) clusters are shown in **Figures 7, 8** and **9**. In the ideal structure, only Zr atoms occupy the M2 sites, so the clusters are compared to the ideal structure Zr (M2) clusters. All three are missing some atoms compared to the ideal local cluster; this proved the case for all five of the Ti (M2) clusters considered. The first atom pictured, #998, has fewer rings and several fewer atoms in its local cluster than in the ideal structure. Two oxygen atoms are missing: the one that belongs in front of the left-most Ca atom in the top view, and the one that belongs in front of the upper Zr atom in the top view. The missing atoms account for the reduced ring numbers, since the atoms they bond to in the ideal structure have not bonded to any other atoms as a replacement.

The next cluster shown, #1001, is also missing atoms, this time it is the topmost titanium atom in the top view, along with its neighboring oxygen atoms. This same trio of atoms was missing in one of the Zr (M2) clusters shown as well (#824). For the third cluster, #1019, the only missing atom is the oxygen atom that belongs in front of the uppermost Zr atom in the top view.
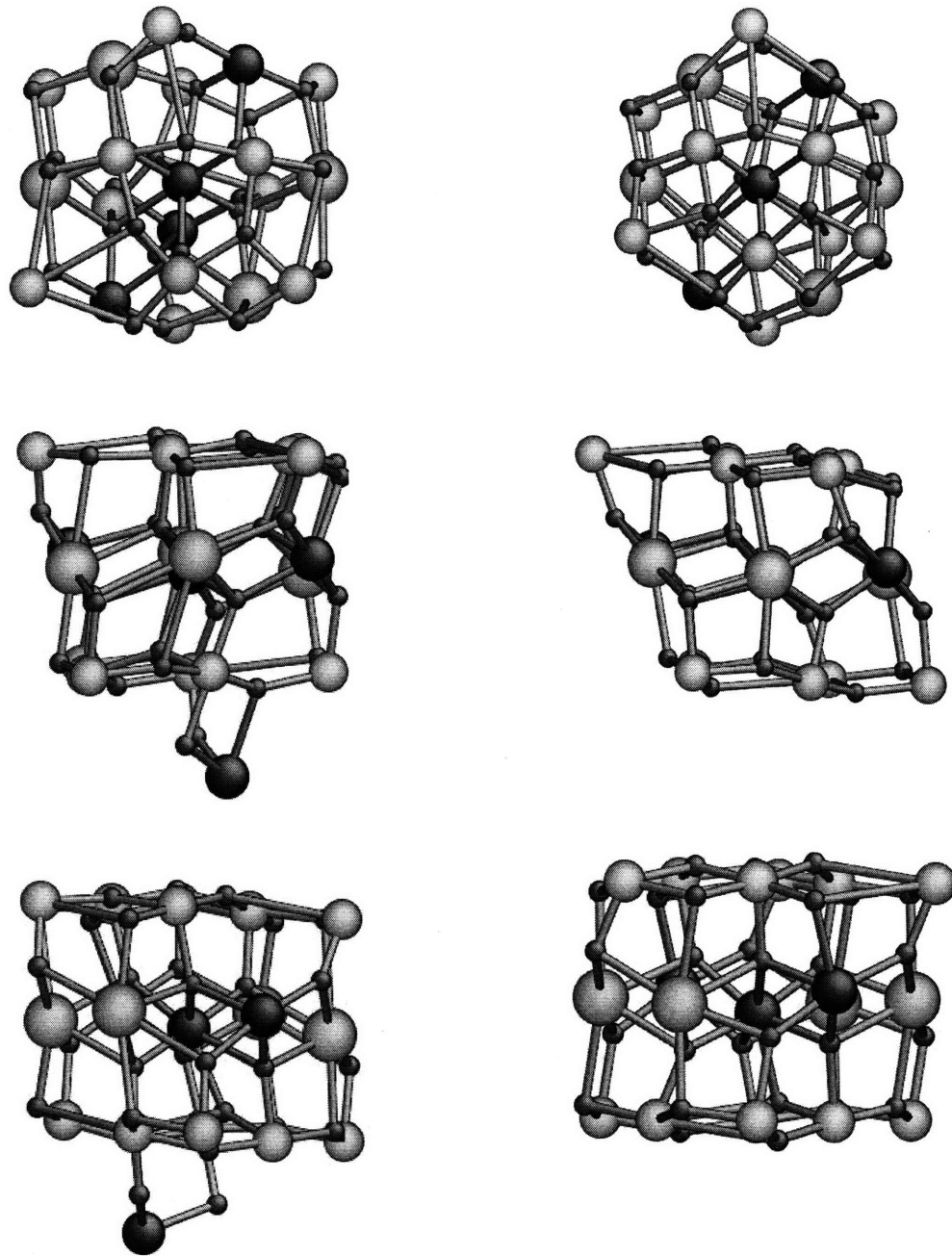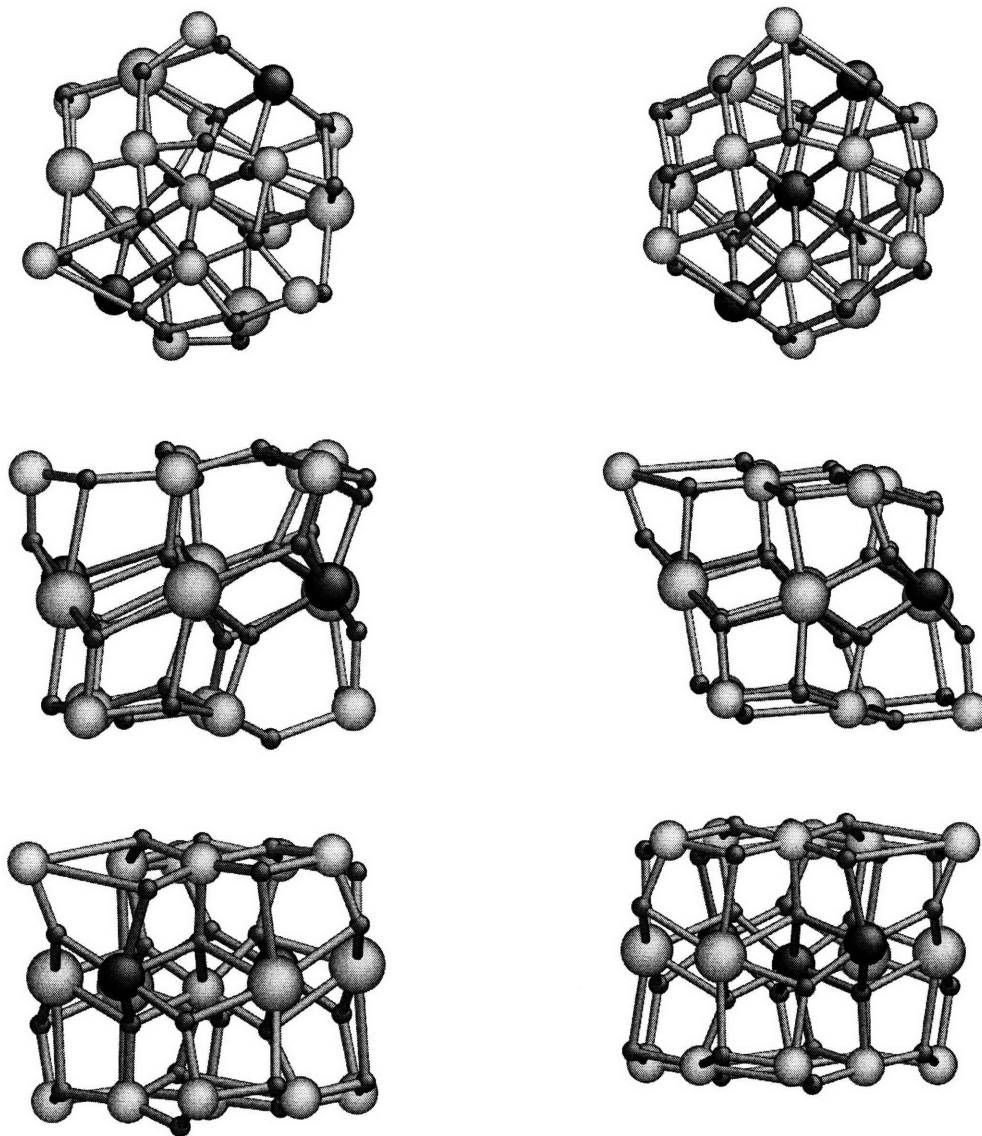
Figure 4 – On the left is a local cluster for Zr (M2) site in Rossell-structure zirconolite, atom #595. The local cluster consists of 8 4-rings, 13 6-rings and 24 8-rings, with a total of 49 atoms. On the right is the Zr (M2) local cluster for ideal zirconolite, which consists of 9 4-rings, 15 6-rings, and 24 8-rings, with a total of 47 atoms.

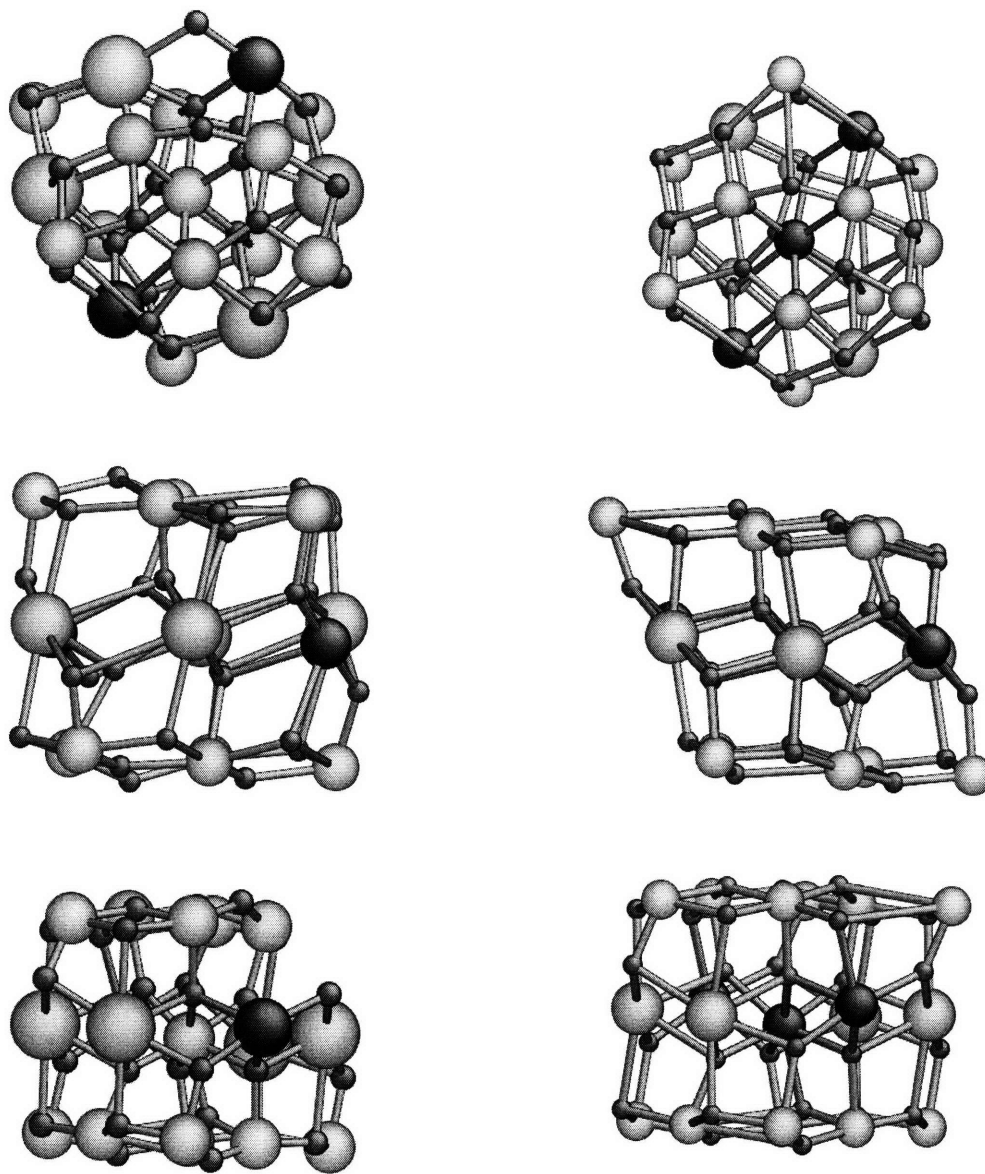Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray
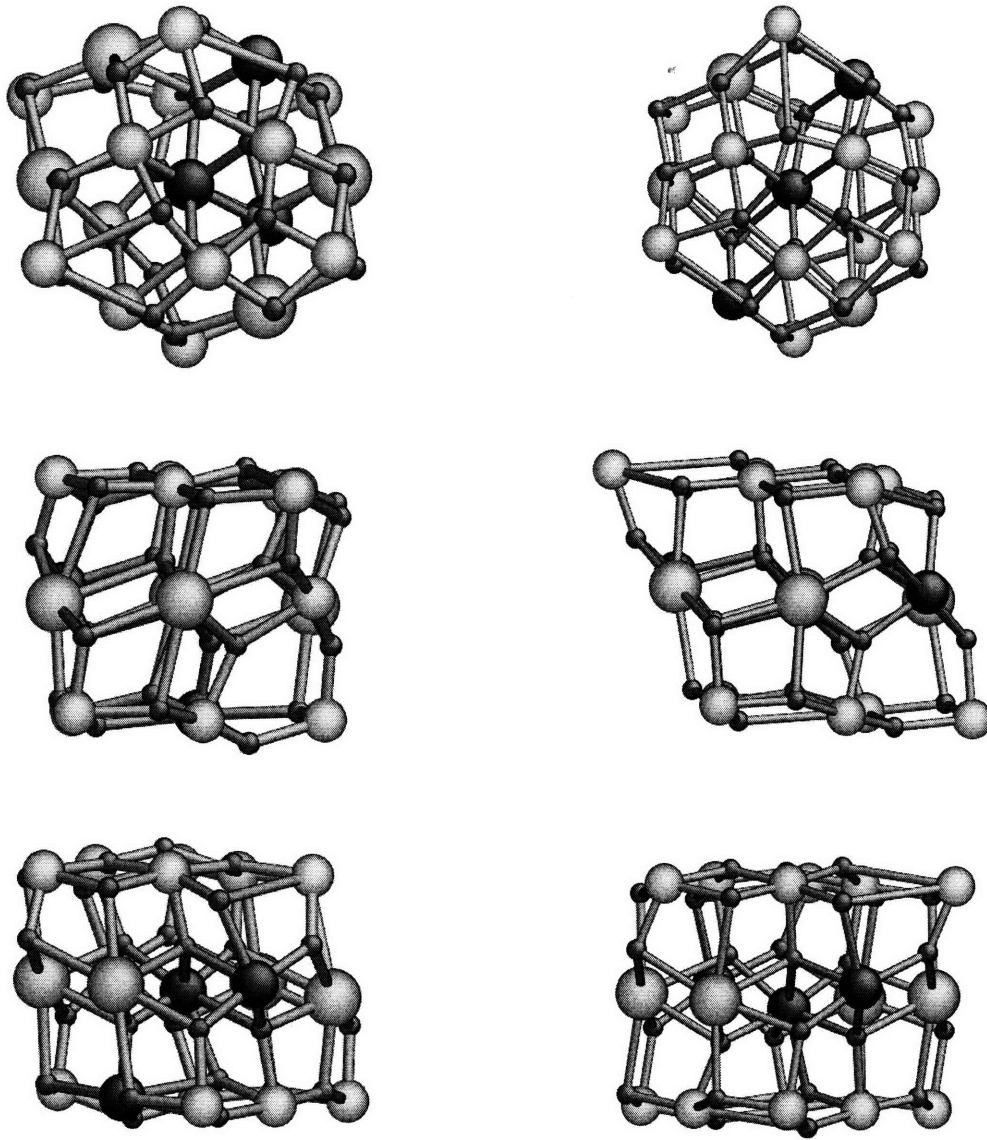
Figure 5 – On the left is a local cluster for Zr (M2) site in Rossell-structure zirconolite, atom #727. The local cluster consists of 9 4-rings, 15 6-rings and 24 8-rings, with a total of 47 atoms. On the right is the Zr (M2) local cluster for ideal zirconolite, which consists of 9 4-rings, 15 6-rings, and 24 8-rings, with a total of 47 atoms.
Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray
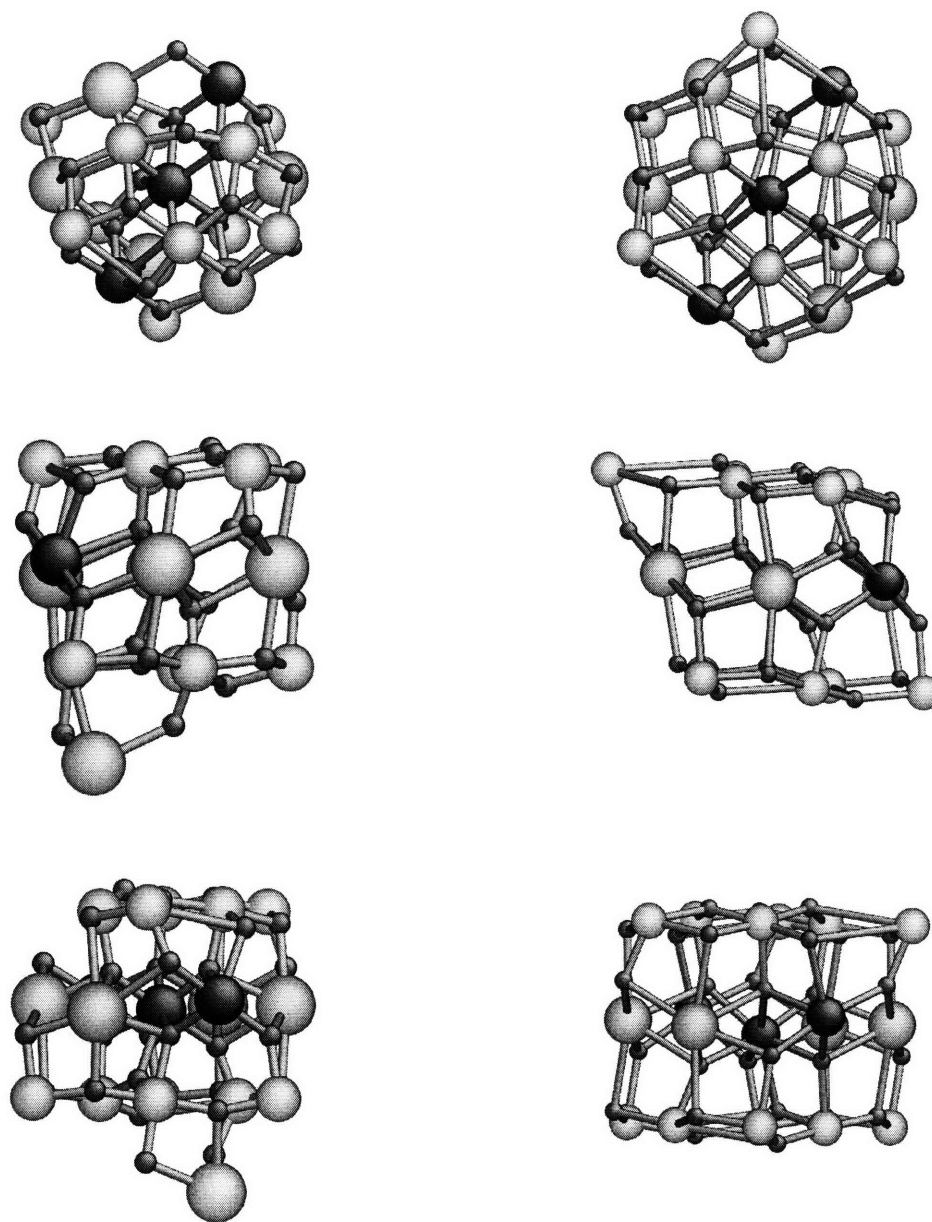
Figure 6 – On the left is a local cluster for Zr (M2) site in Rossell-structure zirconolite, atom #824. The local cluster consists of 8 4-rings, 13 6-rings and 27 8-rings, with a total of 47 atoms. On the right is the Zr (M2) local cluster for ideal zirconolite, which consists of 9 4-rings, 15 6-rings, and 24 8-rings, with a total of 47 atoms.
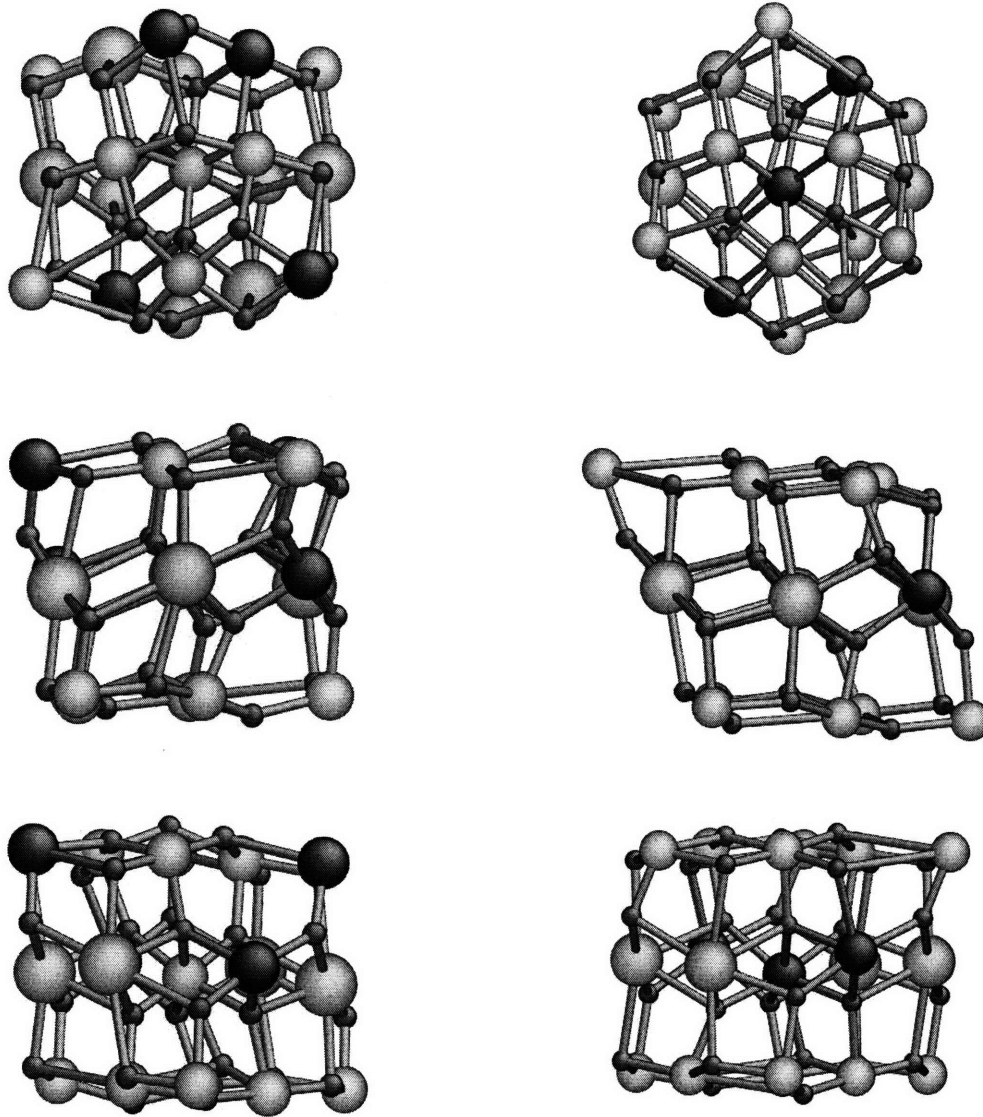Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray

Figure 7 – On the left is a local cluster for Ti (M2) site in Rossell-structure zirconolite, atom #998. The local cluster consists of 9 4-rings, 13 6-rings and 20 8-rings, with a total of 45 atoms. On the right is the Zr (M2) local cluster for ideal zirconolite, which consists of 9 4-rings, 15 6-rings, and 24 8-rings, with a total of 47 atoms.
Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray

Figure 8 – On the left is a local cluster for Ti (M2) site in Rossell-structure zirconolite, atom #1001. The local cluster consists of 9 4-rings, 15 6-rings and 20 8-rings, with a total of 44 atoms. On the right is the Zr (M2) local cluster for ideal zirconolite, which consists of 9 4-rings, 15 6-rings, and 24 8-rings, with a total of 47 atoms.
Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray
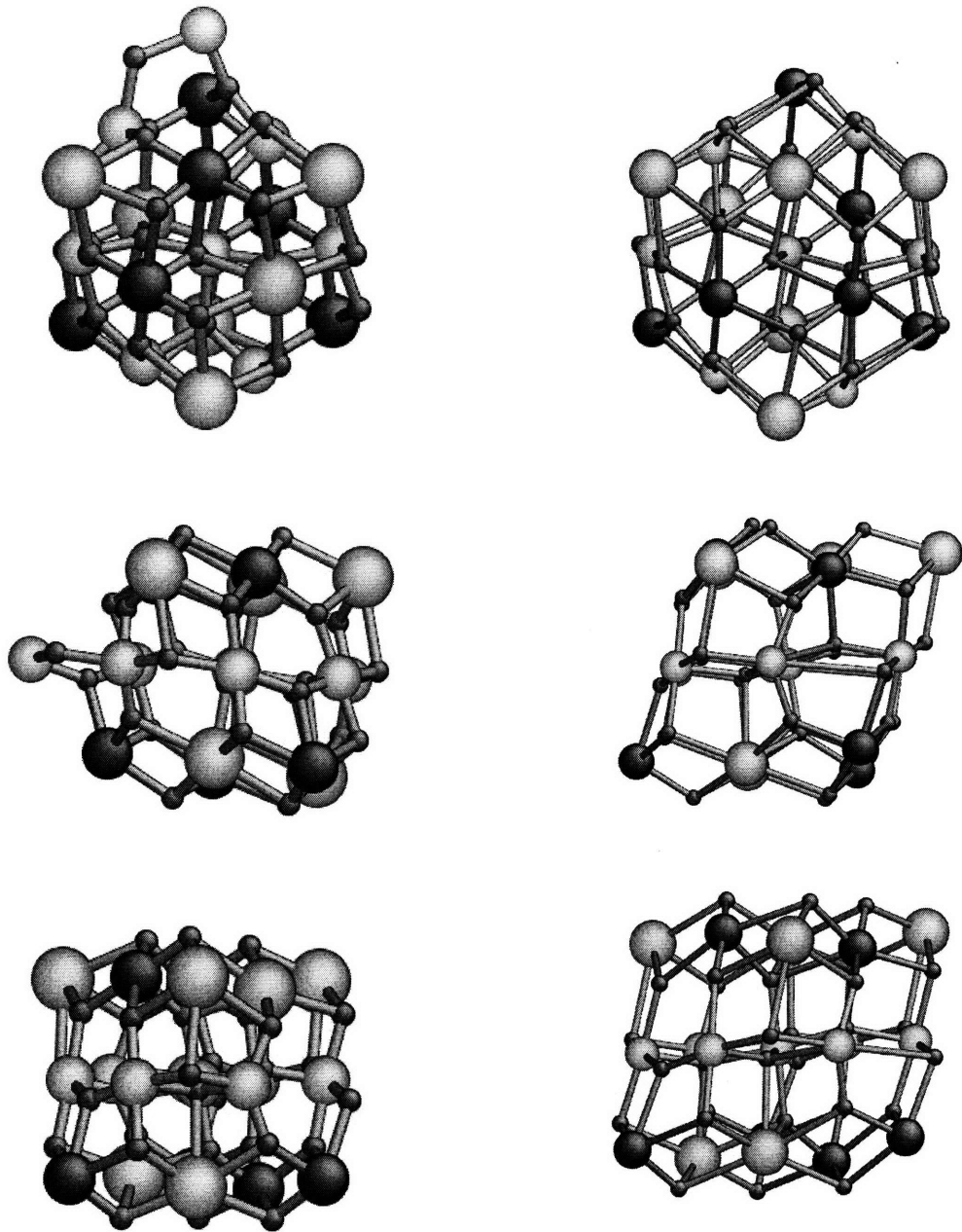
Figure 9 – On the left is a local cluster for Ti (M2) site in Rossell-structure zirconolite, atom #1019. The local cluster consists of 9 4-rings, 14 6-rings and 20 8-rings, with a total of 46 atoms. On the right is the Zr (M2) local cluster for ideal zirconolite, which consists of 9 4-rings, 15 6-rings, and 24 8-rings, with a total of 47 atoms.
Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray

The three Ti (M3) local clusters pictured in **Figures 10, 11** and **12** show a range of variations from the ideal. The first, #1168, includes two extra atoms because of missing bonds in the region, the result of a titanium atom that is skewed away from the center atom. The second local cluster shown, #1266, is nearly identical to the ideal structure cluster. The only difference is that it has two fewer 8-rings, due to a single missing bond. Otherwise the two are identical; not even the titanium and zirconium atoms have been swapped. The third, #1424, has several atoms that are slightly out of position. The titanium atom to the left of center in the bottom view is pulled far enough to the left that it does not bond to either of the oxygen atoms in the middle, as it would in the ideal structure. This is why it has fewer 4- and 6-rings, but more 8-rings.

Three Ti (M5) local clusters are shown in **Figures 13, 14** and **15**. The local cluster for atom #1820 differs from the ideal crystal local cluster by one bond between a titanium atom and an oxygen atom. The bond would in the ideal structure connect the oxygen atom closest to the center on the middle view and the titanium atom on the far left. This one missing bond is the reason why this cluster has so many 8-rings, thirteen more than the ideal structure.

The second Ti (M5) cluster shown, #1917, has two missing bonds in it, between the oxygen atoms in the center and the titanium atom to the right in the bottom view. One can clearly see that the atoms are displaced out of position away from each other, and so they are not able to bond. Otherwise, the structure matches that of the ideal crystal and does not contain any Ti/Zr atom swaps.

The third Ti (M5) cluster, #1965, includes two extra atoms, visible at the bottom of the top view. The oxygen at the bottom of the cluster and the titanium next to it have been displaced away from each other and so did not bond. As a result, two extra atoms are included in the local cluster. Aside from this addition, the cluster structure is the same as that in the ideal crystal.
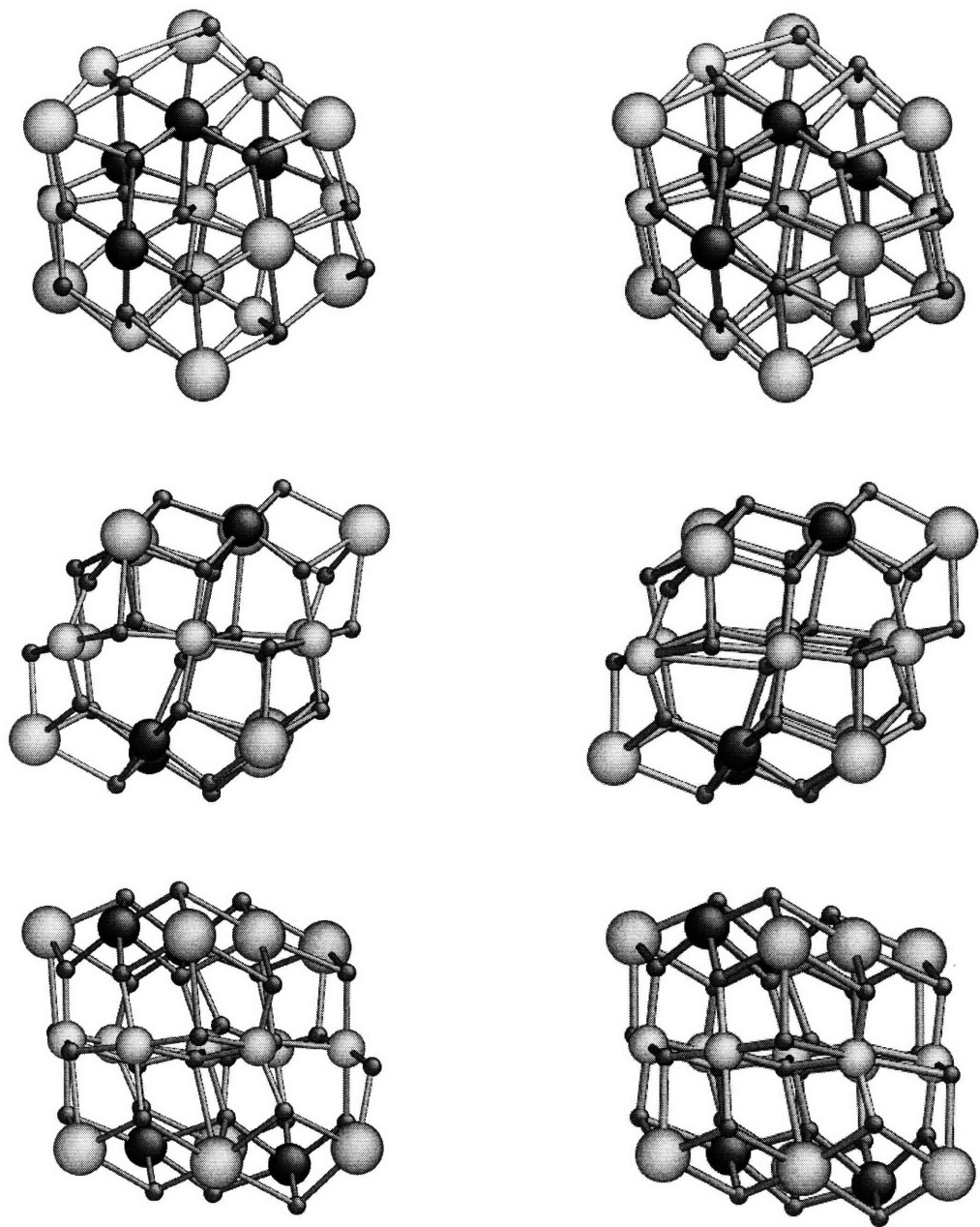
Figure 10 – On the left is a local cluster for Ti (M3) site in Rossell-structure zirconolite, atom #1168. The local cluster consists of 5 4-rings, 12 6-rings and 28 8-rings, with a total of 51 atoms. On the right is the Ti (M3) local cluster for ideal zirconolite, which consists of 6 4-rings, 12 6-rings, and 24 8-rings, with a total of 49 atoms.
Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray
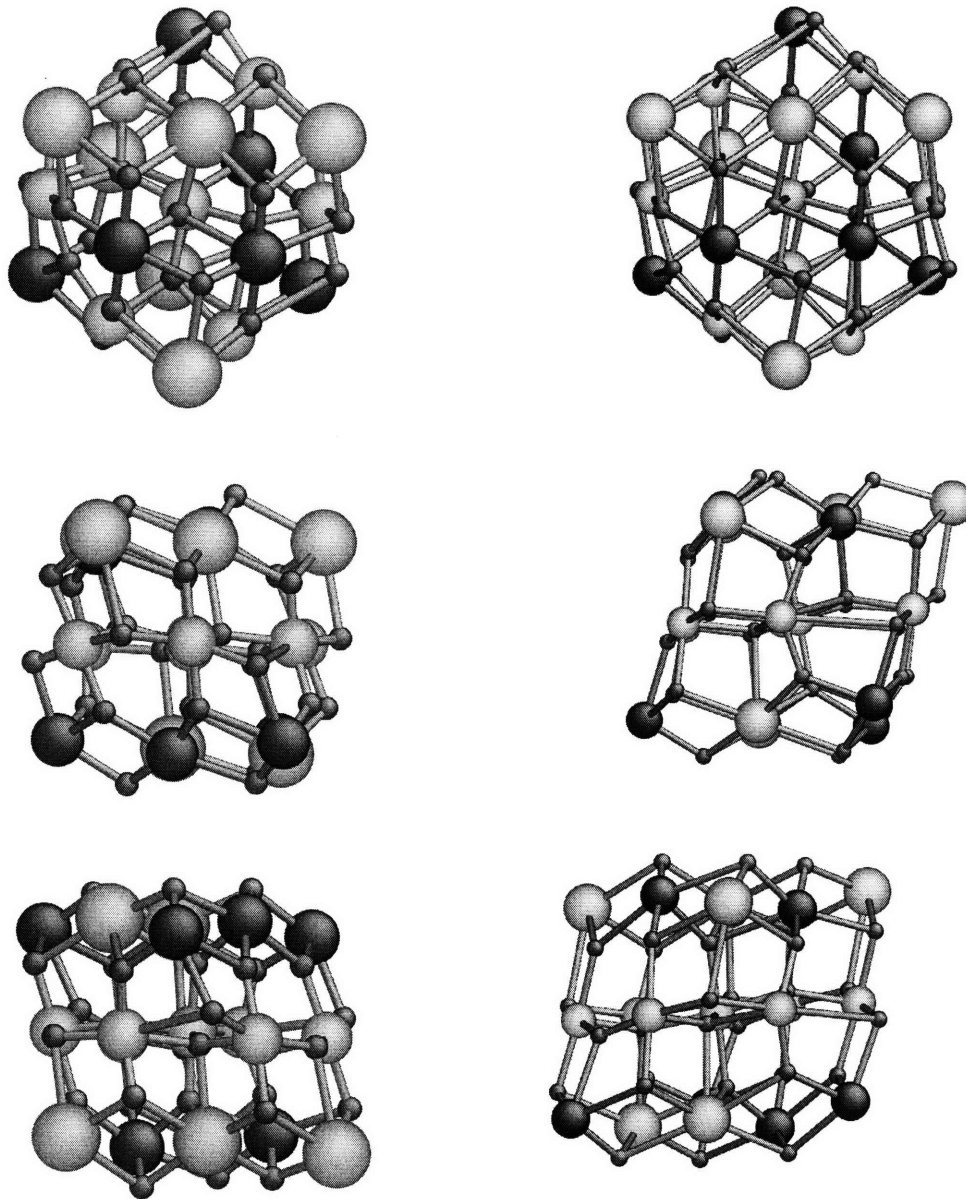
Figure 11– On the left is a local cluster for Ti (M3) site in Rossell-structure zirconolite, atom #1266. The local cluster consists of 6 4-rings, 12 6-rings and 22 8-rings, with a total of 49 atoms. On the right is the Ti (M3) local cluster for ideal zirconolite, which consists of 6 4-rings, 12 6-rings, and 24 8-rings, with a total of 49 atoms.
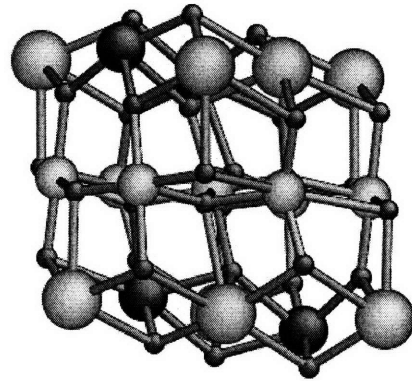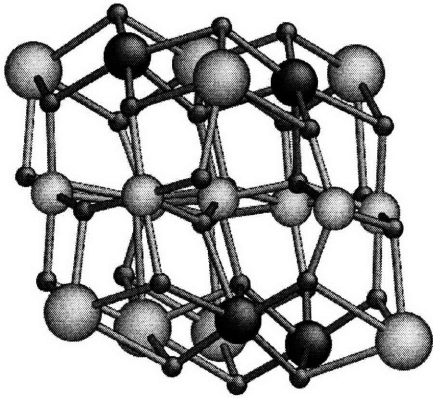Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray
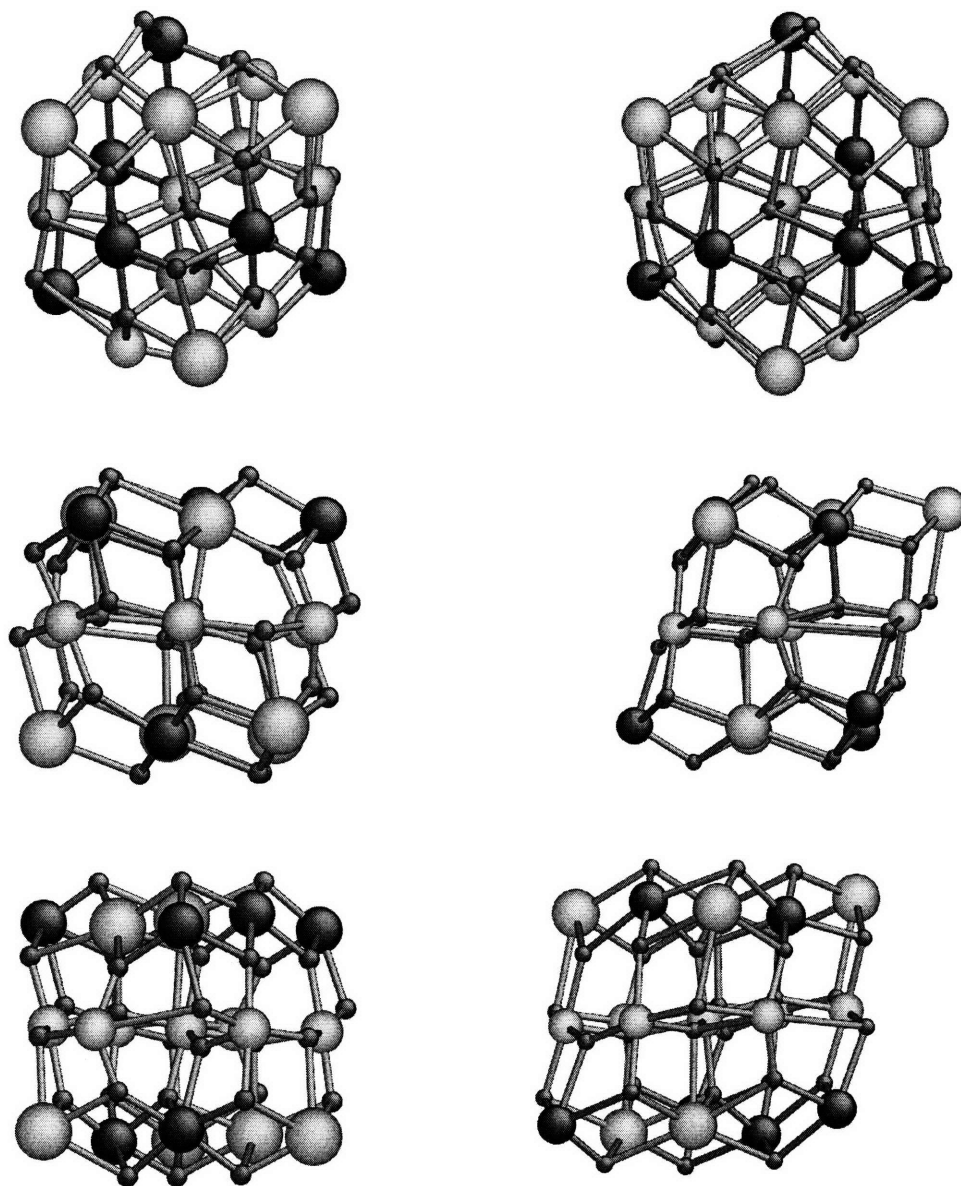
Figure 12 – On the left is a local cluster for Ti (M3) site in Rossell-structure zirconolite, atom #1424. The local cluster consists of 5 4-rings, 10 6-rings and 36 8-rings, with a total of 49 atoms. On the right is the Ti (M3) local cluster for ideal zirconolite, which consists of 6 4-rings, 12 6-rings, and 24 8-rings, with a total of 49 atoms.
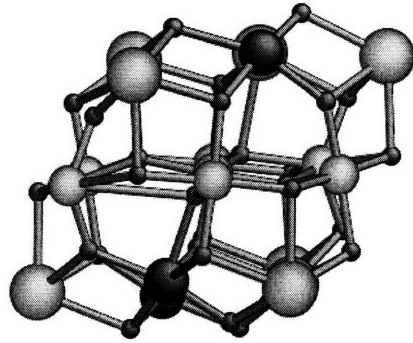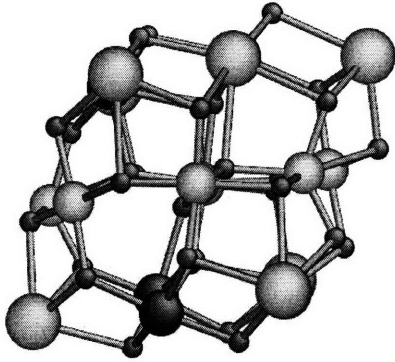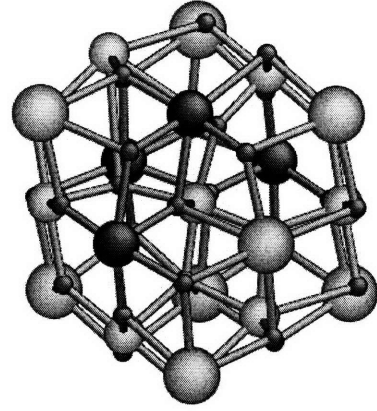Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray
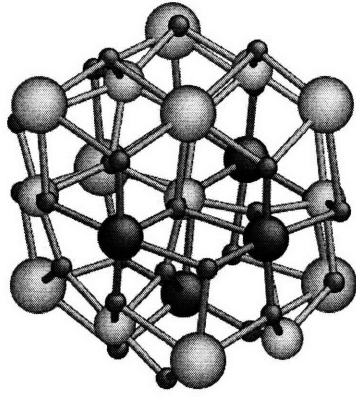
Figure 13 – On the left is a local cluster for Ti (M5) site in Rossell-structure zirconolite, atom #1820. The local cluster consists of 5 4-rings, 10 6-rings and 37 8-rings, with a total of 49 atoms. On the right is the Ti (M5) local cluster for ideal zirconolite, which consists of 6 4-rings, 12 6-rings, and 24 8-rings, with a total of 49 atoms.
Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray

Figure 15 – On the left is a local cluster for Ti (M5) site in Rossell-structure zirconolite, atom #1965. The local cluster consists of 5 4-rings, 12 6-rings and 29 8-rings, with a total of 51 atoms. On the right is the Ti (M5) local cluster for ideal zirconolite, which consists of 6 4-rings, 12 6-rings, and 24 8-rings, with a total of 49 atoms.
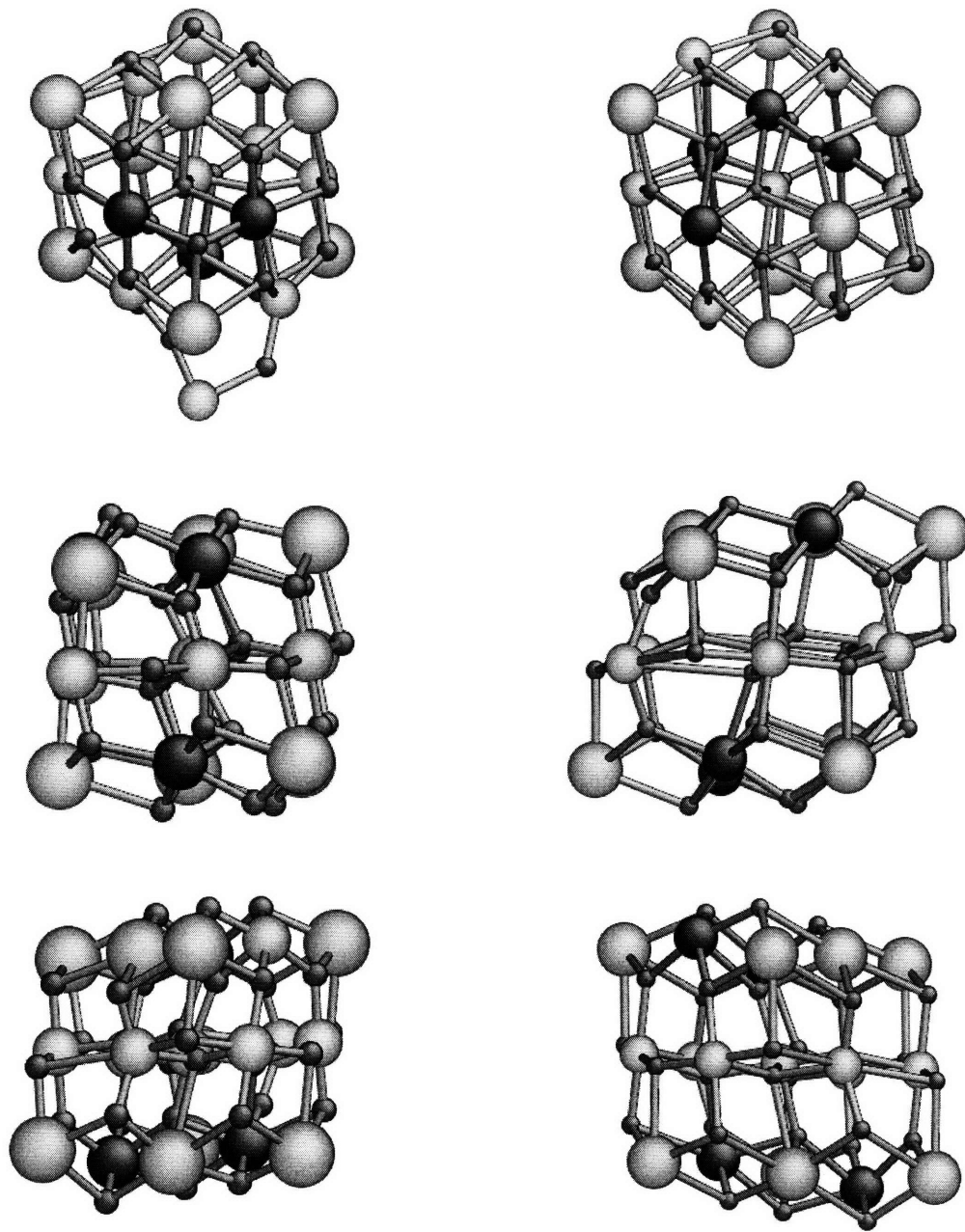Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray

Two local clusters for Ti (M4) are pictured in **Figures 16** and **17**. The first, #1560, is missing six atoms, two zirconium atoms and the two oxygen atoms attached to each. The first is missing from the upper left hand corner of the topmost view, and the second is missing from the bottom center of the same view.

The second cluster has all the atoms present, except that the center atom, #1707, is sitting just to the left of center in the top view. It is far enough displaced that it doesn't bond with one of its neighboring oxygen atoms, resulting in the lower number of rings. The number of rings in this cluster is actually quite close to the average values for the Rossell structure, so it seems likely that many of the clusters have just one middle bond missing, resulting in very different numbers of rings.

In contrast to the Ti (M4) clusters, the Zr (M4) ones are identical to the ideal Ti (M4) clusters. Zr (M4) is one of the substitutions, but it seems to behave exactly the same as the Ti (M4) atom in the ideal crystal. Both clusters shown have exactly the same connectivity as the ideal Ti (M4) cluster. The first cluster, #1768, in **Figure 18**, does not have any switched Ti/Zr atoms except for the center one, while the second cluster, #1776 in **Figure 19**, has two titanium atoms taking the place of zirconium atoms. The surroundings of the two do not look any different because of the substitution.
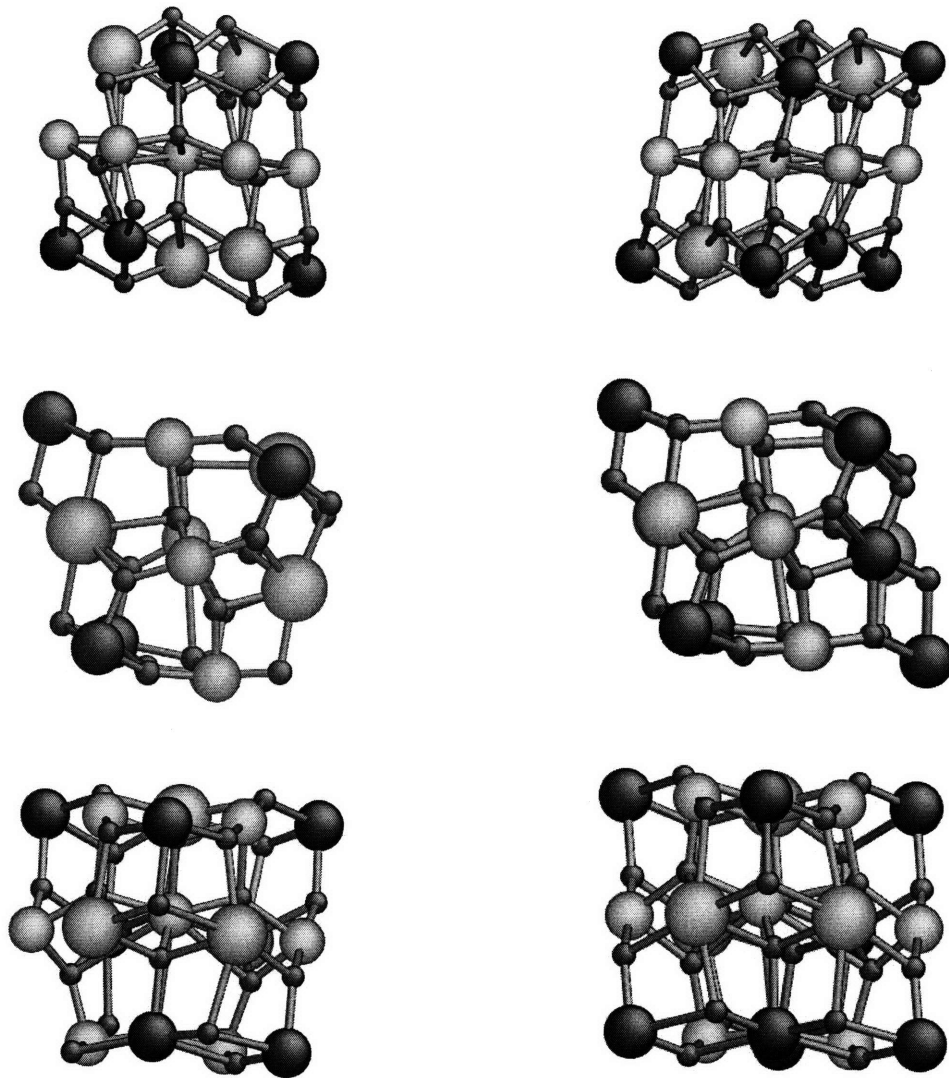
Figure 16– On the left is a local cluster for Ti (M4) site in Rossell-structure zirconolite, atom #1560. The local cluster consists of 7 4-rings, 12 6-rings and 19 8-rings, with a total of 39 atoms. On the right is the Ti (M4) local cluster for ideal zirconolite, which consists of 12 4-rings, 18 6-rings, and 24 8-rings, with a total of 45 atoms. Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray
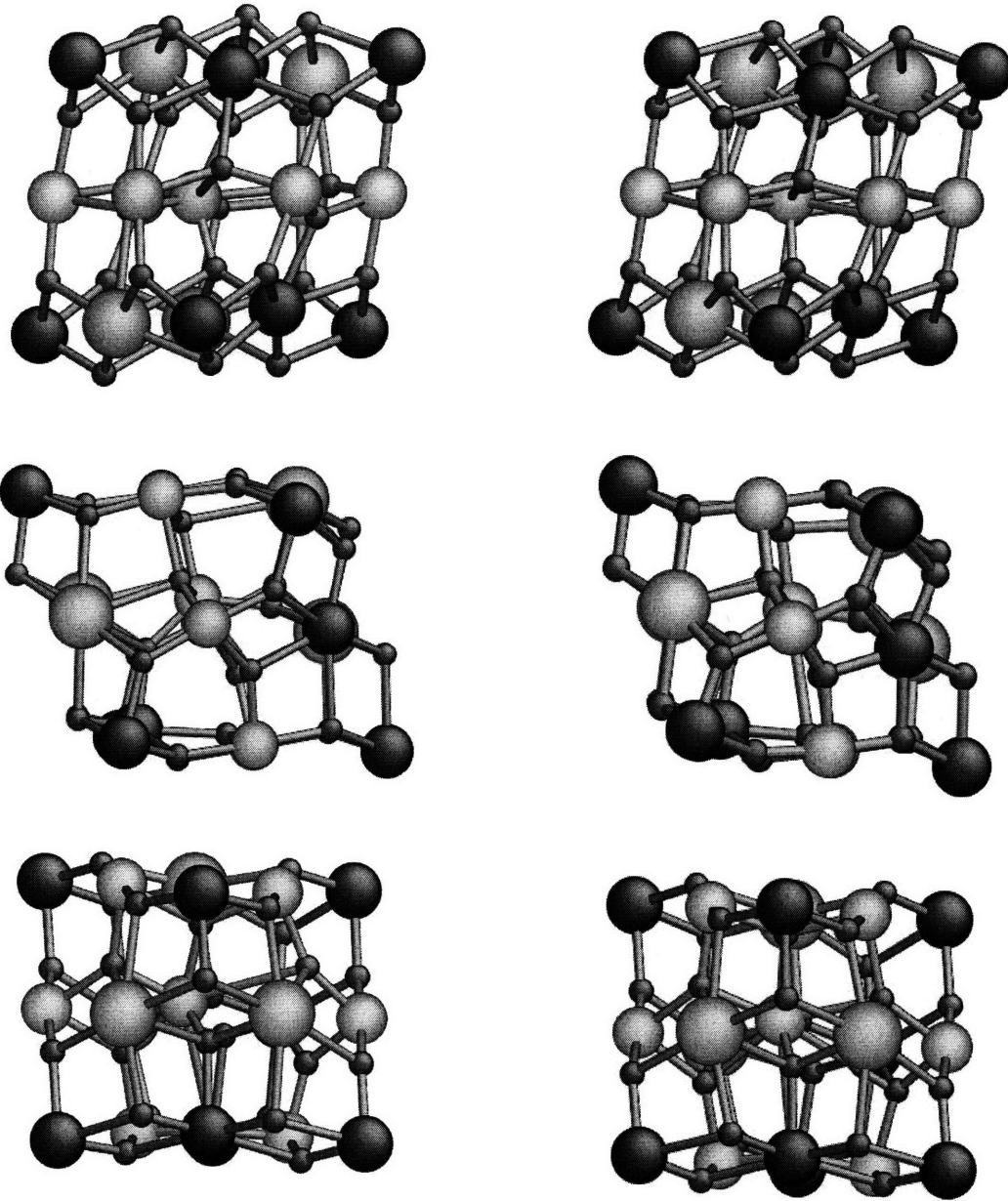
Figure 17 – On the left is a local cluster for Ti (M4) site in Rossell-structure zirconolite, atom #1707. The local cluster consists of 9 4-rings, 17 6-rings and 16 8-rings, with a total of 45 atoms. On the right is the Ti (M4) local cluster for ideal zirconolite, which consists of 12 4-rings, 18 6-rings, and 24 8-rings, with a total of 45 atoms.
Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray
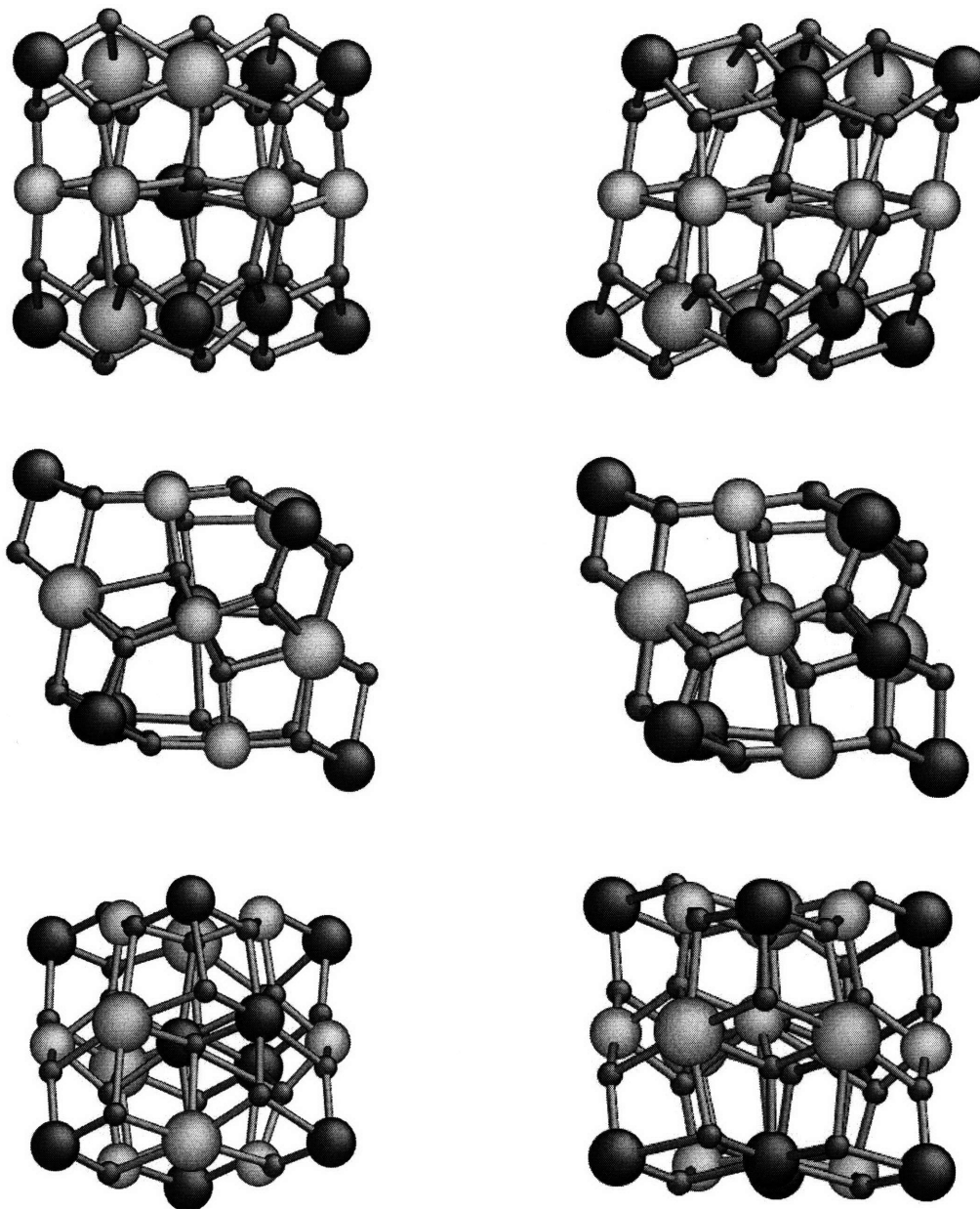
Figure 18 – On the left is a local cluster for Zr (M4) site in Rossell-structure zirconolite, atom #1768. The local cluster consists of 12 4-rings, 18 6-rings and 24 8-rings, with a total of 45 atoms. On the right is the Ti (M4) local cluster for ideal zirconolite, which consists of 12 4-rings, 18 6-rings, and 24 8-rings, with a total of 45 atoms.
Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray

Figure 19 – On the left is a local cluster for Zr (M4) site in Rossell-structure zirconolite, atom #1776. The local cluster consists of 12 4-rings, 18 6-rings and 24 8-rings, with a total of 45 atoms. On the right is the Ti (M4) local cluster for ideal zirconolite, which consists of 12 4-rings, 18 6-rings, and 24 8-rings, with a total of 45 atoms. Color scheme: Ca-large gray, Zr-medium black, Ti-medium white, O-small gray
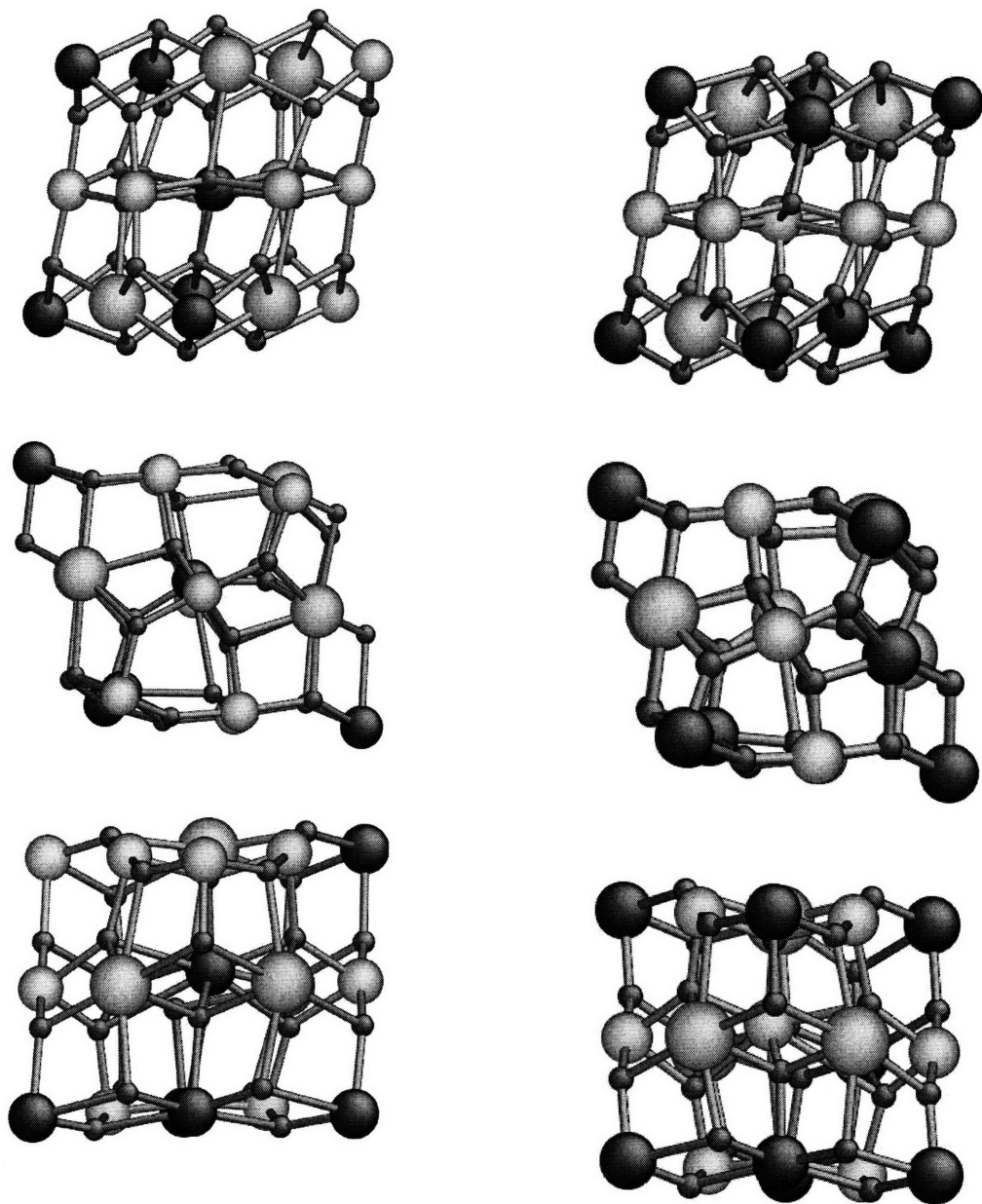
Molten Zirconolite

The structure of the molten zirconolite obtained by MD simulation is completely different from that of the crystal. By definition, the melt structure does not repeat itself at long range, so the average ring counts cannot be expected to be identical to the individual ring counts. Nevertheless, they serve to summarize the differences between the crystalline and the molten material. **Table 3** lists the average ring counts for the three metal atoms in zirconolite. Here they are not separated by site because those designations are meaningless in the topologically disordered melt. Again, there are about twice as many titanium atoms averaged as the other cations, because titanium is the largest cation component of the material.

Table 3 - Number of rings and atoms in all the local clusters averaged together for molten zirconolite

atom	avg ring size	avg # of 4 rings	avg # of 6 rings	avg # of 8 rings	avg # of 10 rings	avg # of 12 rings	atoms avged	atoms in avg cluster
Ca	7.090	15.203	32.349	36.977	16.698	3.523	172	63
Zr	7.104	15.656	35.039	35.733	19.065	2.305	154	74.2
Ti	6.882	17.355	33.797	32.541	13.945	2.387	346	70.2

The local clusters of the molten structure are much larger than those of the crystalline structure. There are almost half again as many atoms in the clusters, the number of rings is higher for all sizes, and the clusters include plenty of 10- and 12-rings. The 4- and 6-ring counts for the three different types of atoms are closer to each other than to the ring counts for the different types of atoms in crystalline zirconolite.

The averages for the three types of atoms may be similar, but the individual local clusters vary widely. Several different local clusters were chosen for each atom type. Their ring counts and number of atoms in the cluster are listed in **Table 4**.

Table 4 - Number of rings and atoms in several different local clusters for each type of cation in molten zirconolite

atom type	atom #	4-rings	6-rings	8-rings	10-rings	12-rings	atoms in cluster
Ca	201	8	16	27	4		56
	306	7	21	30	17	2	79
	501	10	19	45	40		54
Zr	590	8	17	36	25		69
	677	14	52	12	88		70
	1770	4	13	39	45		91
	1775	10	25	54	35		77
	1788	20	32	33	2		64
Ti	1009	21	46	38	6		65
	1015	18	25	31	4	6	79
	1161	22	51	28	5		71
	1226	20	50	31	1		57
	1554	13	38	7	8		56
	1639	17	38	20	2		86
	1648	21	47	27	6	1	81
	1883	24	38	47	5		74
	1949	16	47	33	3		63

The most striking feature of the ring counts in the local clusters is their range. This MD sample has clusters with between 13 and 56 6-rings and between 1 and 88 10-rings, to enumerate the more striking examples. Only a few of the clusters contained 12-rings, which is not that surprising, given that the average values were around three 12-rings per cluster. It is also interesting to note that the number of atoms in the cluster does not scale with the number of rings.

Molten Zirconolite Structure

In order to take a closer look at the structure of the molten zirconolite, the local clusters are displayed side-by-side with a Rossell-structure example for a local cluster for that same atom. The designations of M2 and M3 no longer signify specific environments in the molten structure, so they have been omitted. There are several local clusters for each atom type pictured, because each cluster is different, since the structure is no longer crystalline and long-range ordered. The local clusters for the melt are much larger than those for the crystal. All of them include some 10-rings, and a few have 12-rings. These have been included in the images, since they are a part of the local cluster and, if the Rossell-structure local clusters had included up to 12-rings, they would have been displayed (the one crystalline local cluster containing a 10-ring did have it included in **Figure 3**).

One of the characteristics of the molten structure that is easily visible in the figures is the cluster of cations by type. The ideal crystalline structure groups the atoms into layers, with titanium comprising one layer, and zirconium and calcium making up the other. In the melt, the atoms tend to gather in clusters of three or four. The clustering of calcium atoms is especially visible in **Figures 22, 23, 29** and **32.** The titanium

clustering is harder to discern because titanium ions are more abundant in the material, but the local clusters in **Figures 25, 27** and **29** provide good examples. The zirconium ions do not appear to cluster as much as the other cations, but one can still see a trio of Zr atoms in the local clusters in **Figures 20, 25** and **31.**

Another difference between the crystalline and molten arrangements is the spacing between atoms. In the crystal the spacing is pretty much uniform between the cations, and the oxygen anions are interspersed regularly, if not evenly, between the cations. The middle view of **Figure 24** provides a good example of the uneven spacing in the local clusters; the left side is a relatively dense tangle of bonds, while the right side is spread out with room between clusters. This is not the effect of viewing a three dimensional object in 2-D; the whole cluster is pretty much spherical, so it isn't simply a matter of more overlapping layers on the left side. **Figure 26** also provides a good example of the irregular spacing of the atoms. This is especially evident in the bottom view, where the lower half of the cluster is much more densely packed than the upper half.

While some of the Rossell-structure clusters are asymmetric, with one corner of the regular box cut off or with an extra loop sticking out, some of the molten local clusters are much worse. In both **Figure 25** and **Figure 32,** the main atom of the local cluster is not centered in the cluster. In **Figure 25,** in the middle and bottom depictions, the bulk of the cluster lies above the zirconium atom in question. In the bottom view of the cluster in **Figure 32,** most of the cluster lies to the right of the chosen titanium atom. **Figure 28** provides another example of asymmetry, though in this case the chosen atom is mostly centered, while the local cluster has several loops and lobes, instead of being mainly spherical.

Figures 27, 30 and **31** provide examples of the looping found in the molten zirconolite local clusters. In some patches, the atoms are isolated enough that they only join in spaced-out strings, instead of joining to multiple other atoms. With the exception of the cluster shown in **Figure 27,** titanium #1266, the clusters with the isolated loops do not have large numbers of 12-rings. In fact, the clusters depicted in **Figures 28** and **30,** #1161 and #1639 respectively, do not contain any 12 rings at all.
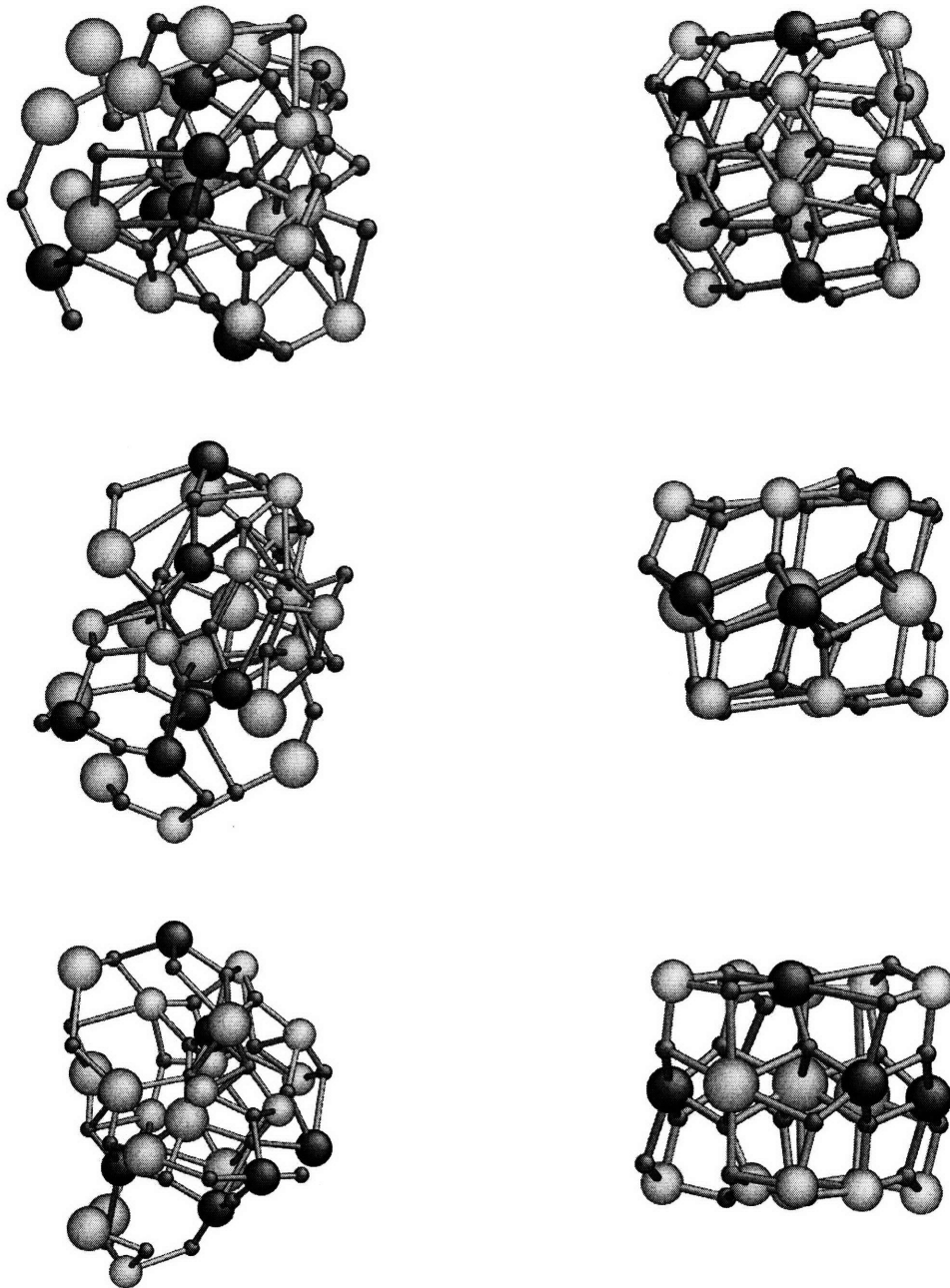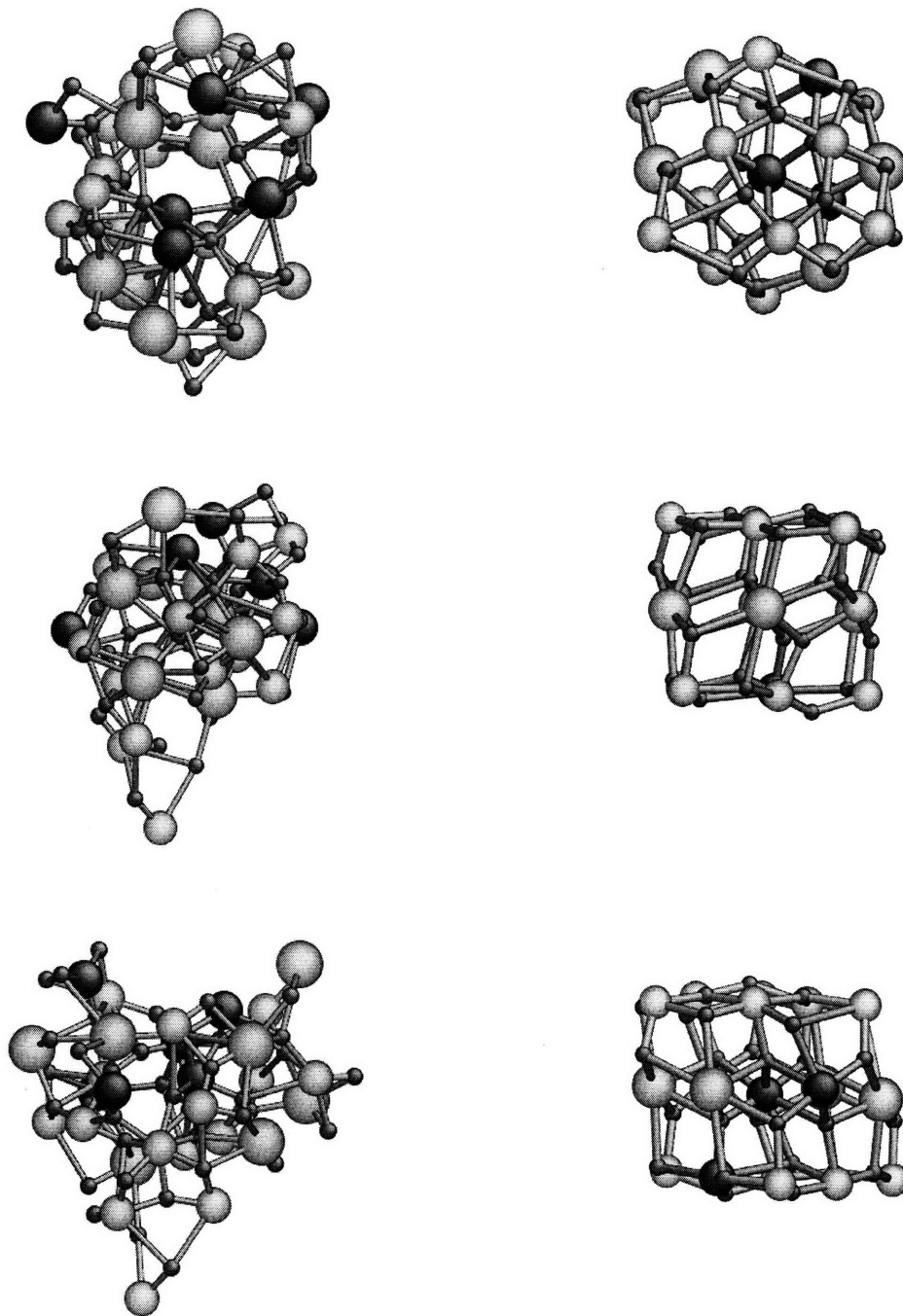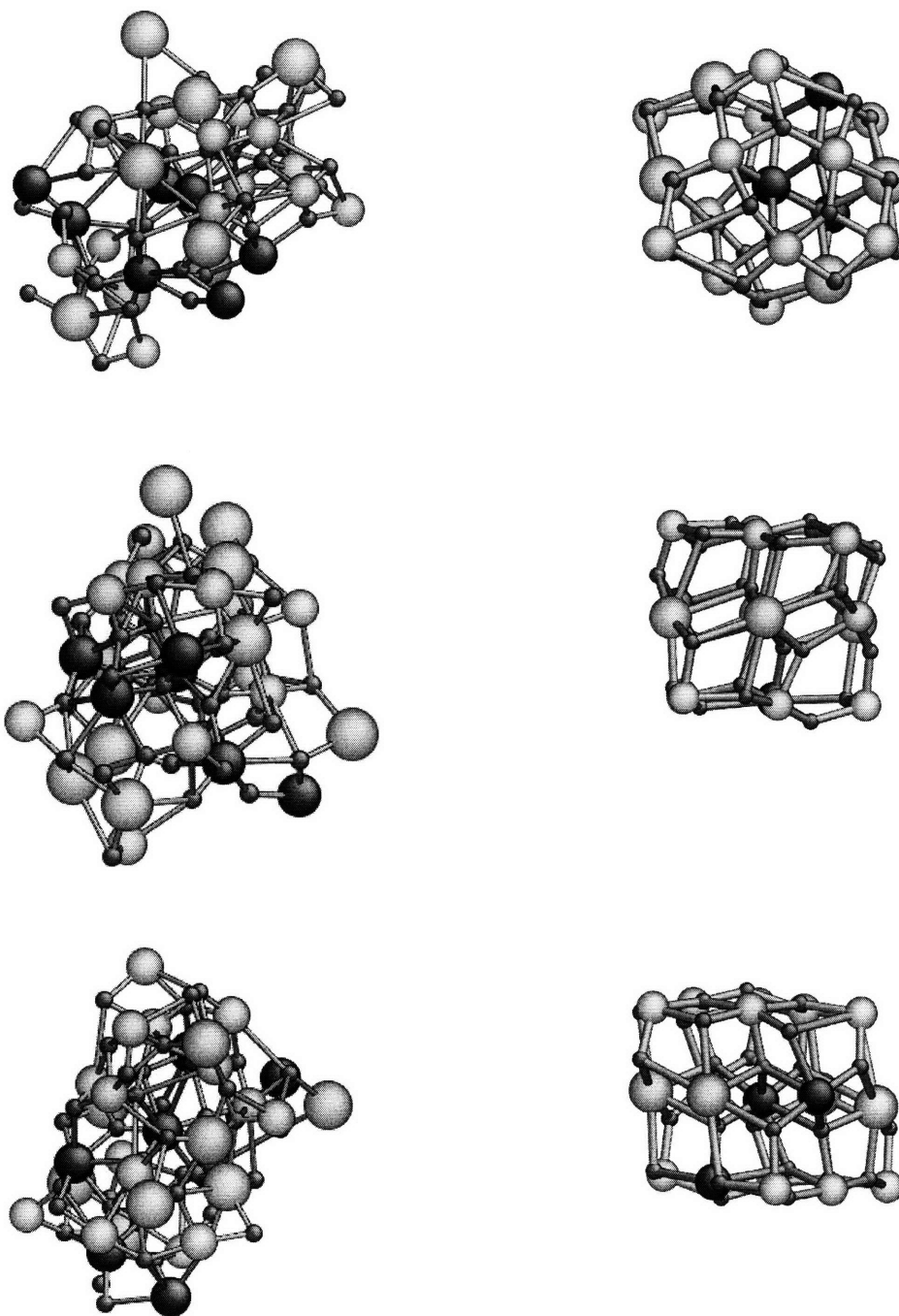
Figure 20 – On the left is a local cluster for a Ca site in melted zirconolite, atom #201. The local cluster consists of 8 4-rings, 16 6-rings, 27 8-rings and 4 10-rings, with a total of 56 atoms. On the right is a Ca (M1) local cluster for Rossell zirconolite (atom #213), which consists of 12 4-rings, 17 6-rings, and 24 8-rings, with a total of 45 atoms.
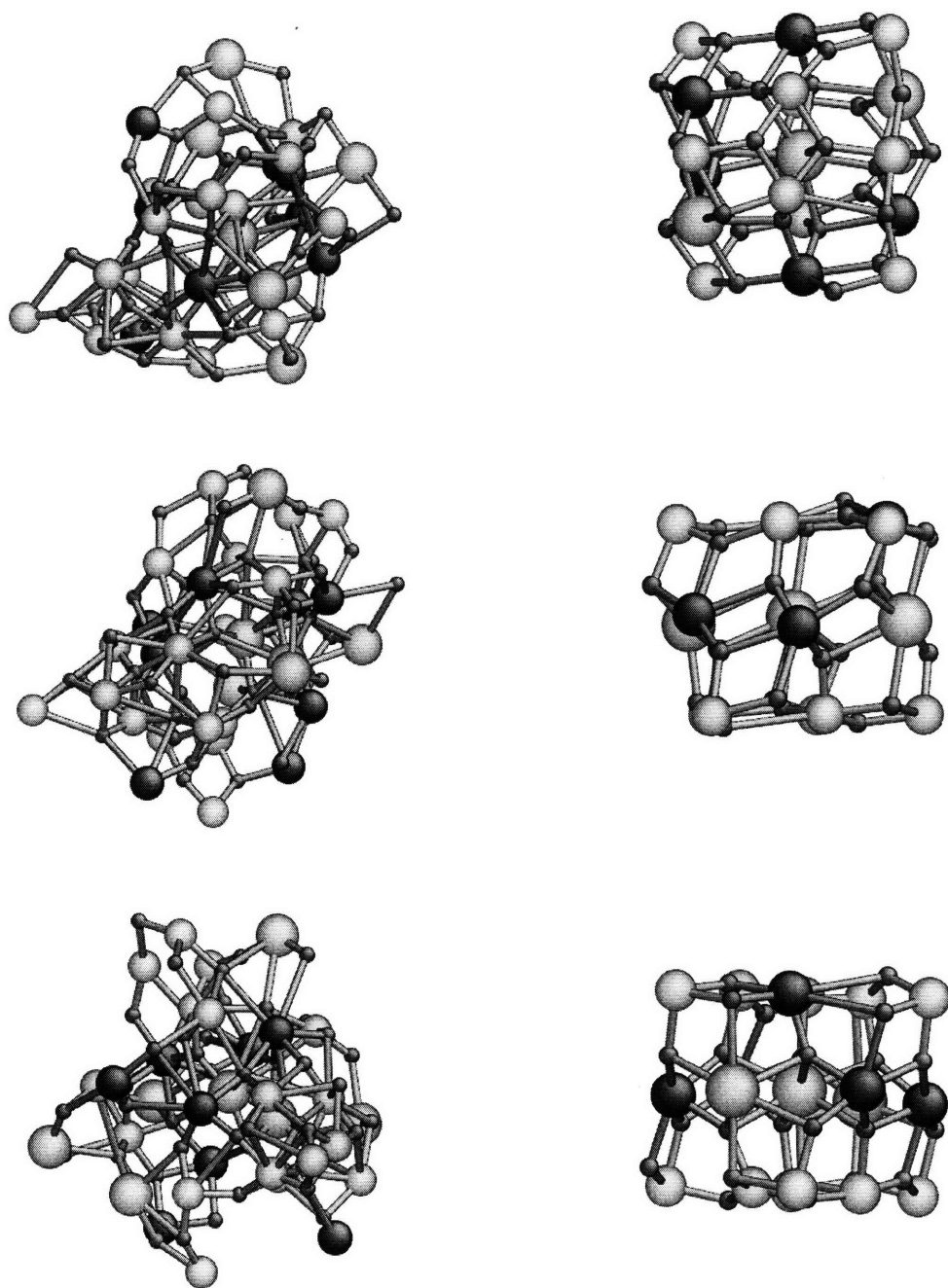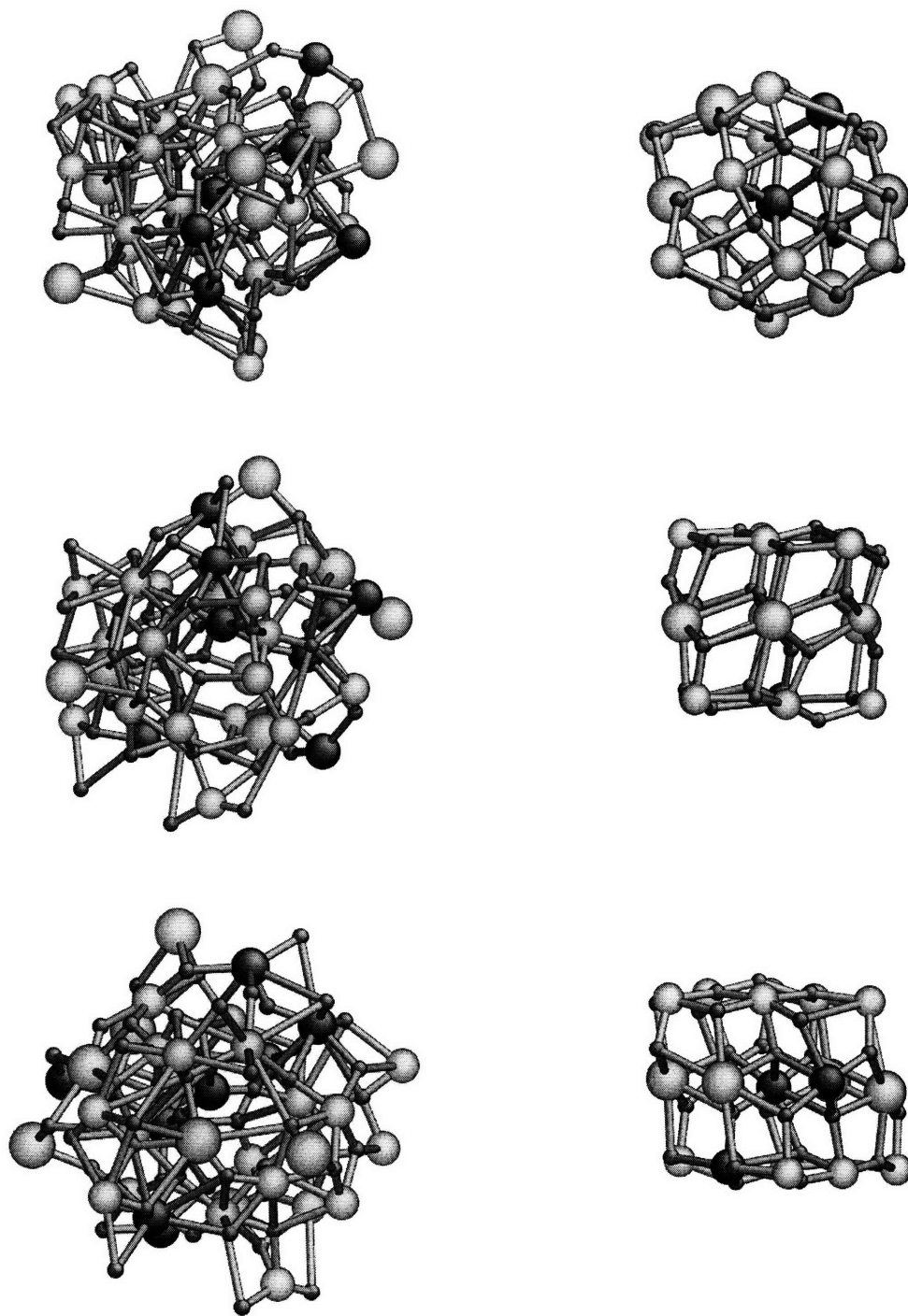
Figure 21 – On the left is a local cluster for a Ca site in melted zirconolite, atom #306. The local cluster consists of 7 4-rings, 21 6-rings, 30 8-rings, 17 10-rings and 2 12-rings, with a total of 79 atoms. On the right is a Ca (M1) local cluster for Rossell zirconolite (atom #213), which consists of 12 4-rings, 17 6-rings, and 24 8-rings, with a total of 45 atoms.
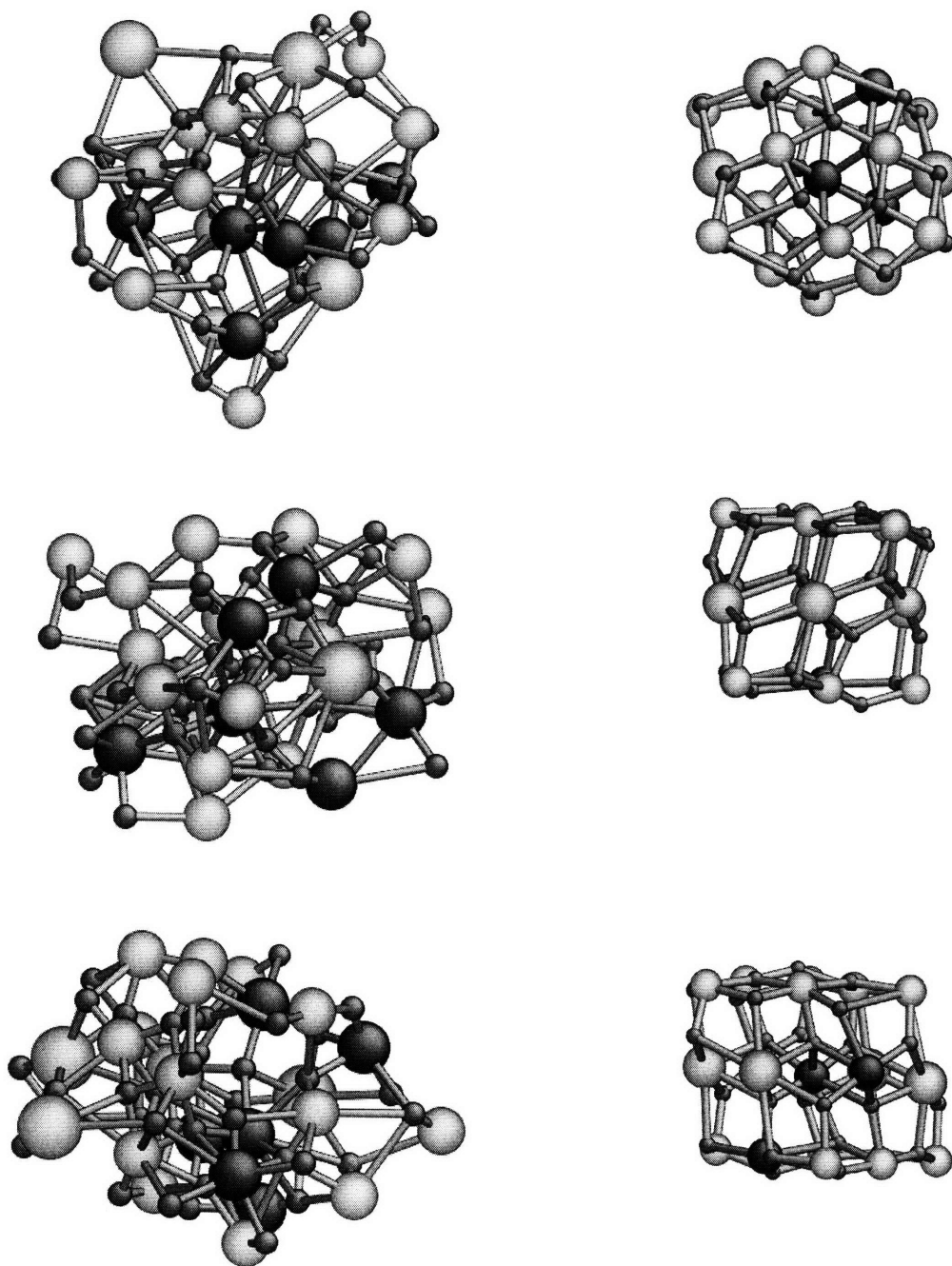
Figure 22 – On the left is a local cluster for a Zr site in melted zirconolite, atom #590. The local cluster consists of 8 4-rings, 17 6-rings, 36 8-rings and 25 10-rings, with a total of 69 atoms. On the right is a Zr (M2) local cluster for Rossell zirconolite (atom #727), which consists of 9 4-rings, 15 6-rings, and 22 8-rings, with a total of 47 atoms.

Figure 23 – On the left is a local cluster for a Zr site in melted zirconolite, atom #677. The local cluster consists of 14 4-rings, 52 6-rings, 12 8-rings and 88 10-rings, with a total of 70 atoms. On the right is a Zr (M2) local cluster for Rossell zirconolite (atom #727), which consists of 9 4-rings, 15 6-rings, and 22 8-rings, with a total of 47 atoms.

Figure 24 – On the left is a local cluster for a Zr site in melted zirconolite, atom #1770. The local cluster consists of 4 4-rings, 13 6-rings, 39 8-rings and 45 10-rings, with a total of 91 atoms. On the right is a Zr (M2) local cluster for Rossell zirconolite (atom #727), which consists of 9 4-rings, 15 6-rings, and 22 8-rings, with a total of 47 atoms.
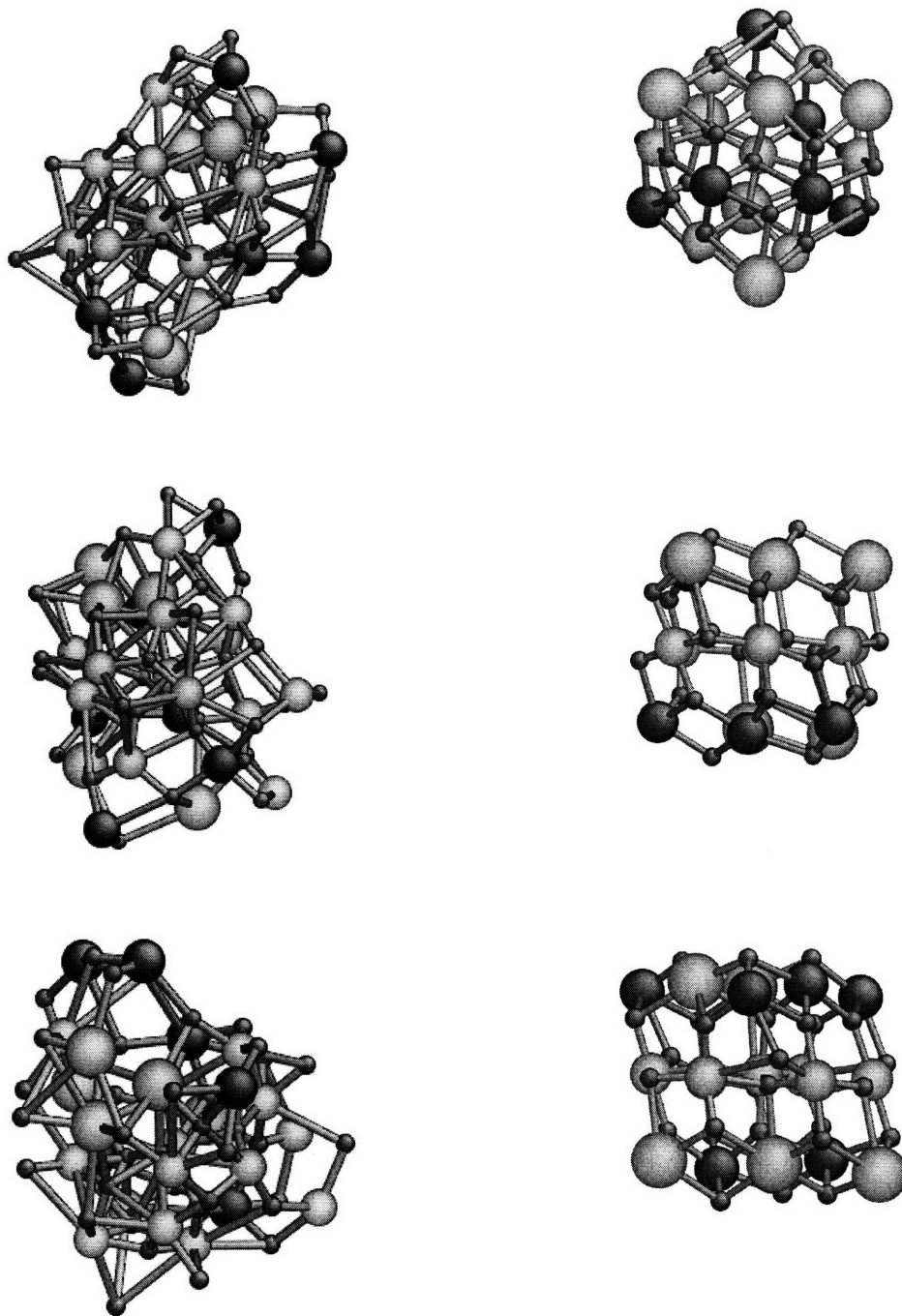
Figure 25 – On the left is a local cluster for a Zr site in melted zirconolite, atom #1788. The local cluster consists of 20 4-rings, 32 6-rings, 33 8-rings and 2 10-rings, with a total of 64 atoms. On the right is a Zr (M2) local cluster for Rossell zirconolite (atom #727), which consists of 9 4-rings, 15 6-rings, and 22 8-rings, with a total of 47 atoms.
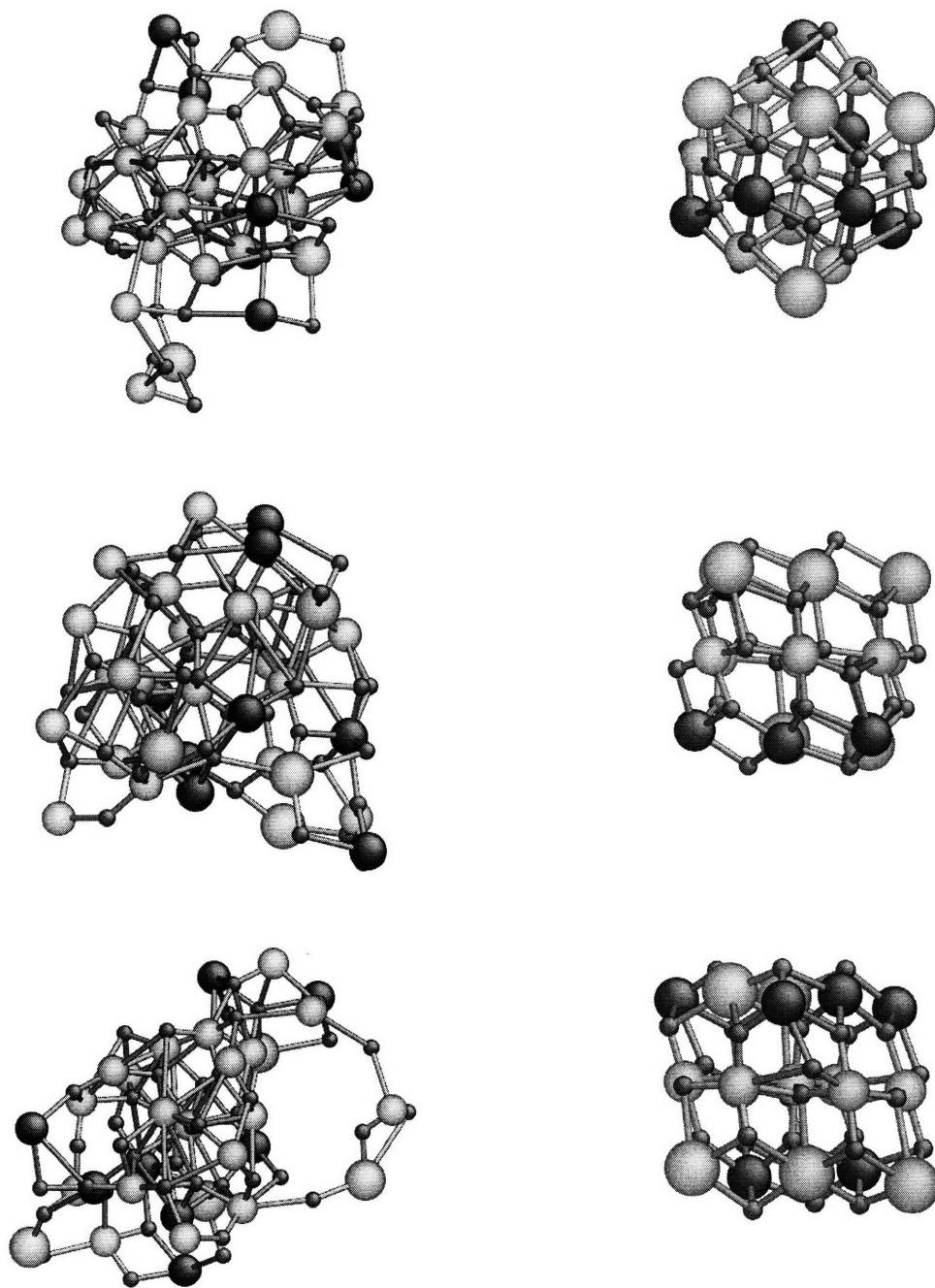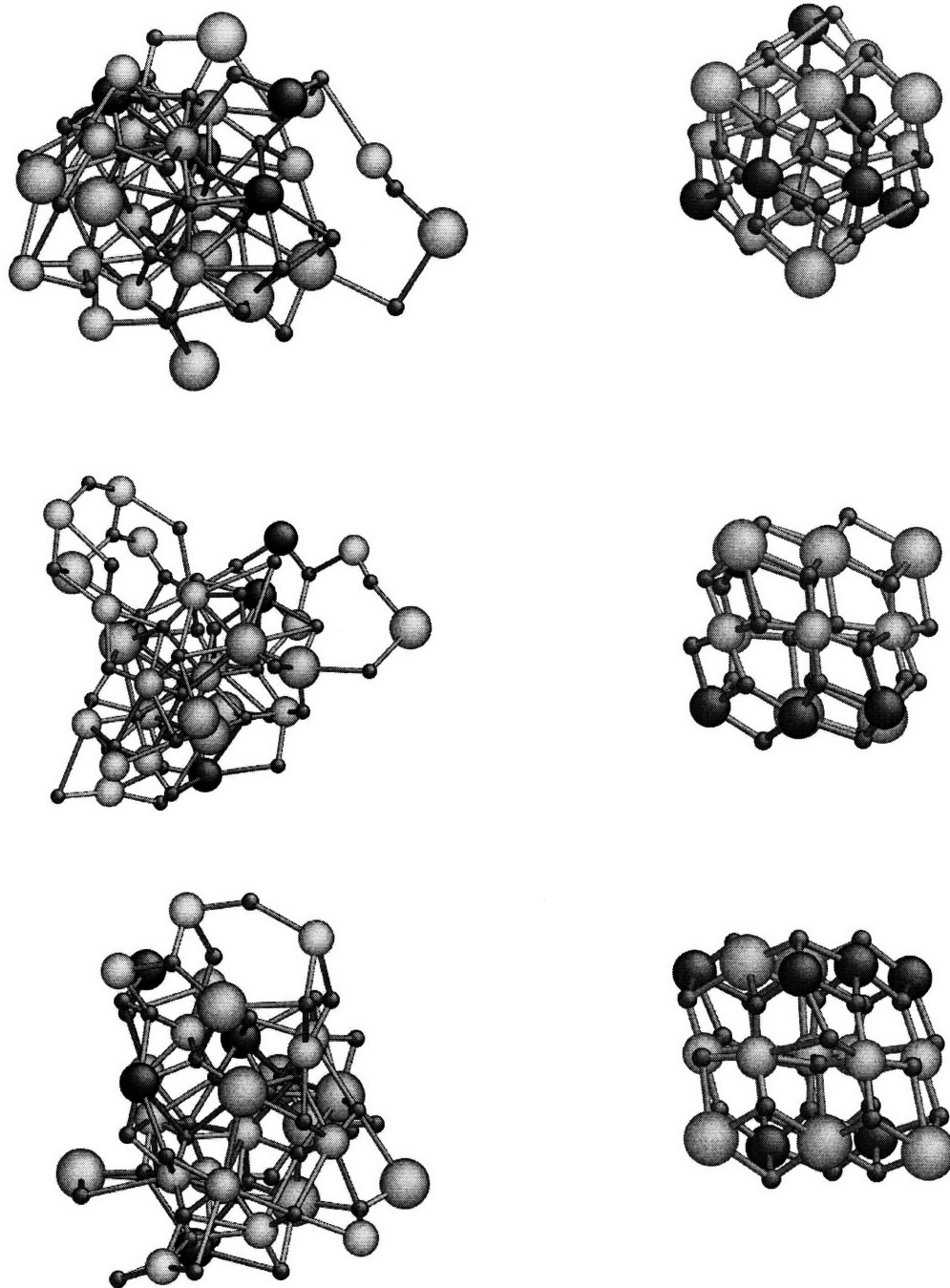
Figure 26 – On the left is a local cluster for a Ti site in melted zirconolite, atom #1009. The local cluster consists of 21 4-rings, 46 6-rings, 38 8-rings and 6 10-rings, with a total of 65 atoms. On the right is a Ti (M3) local cluster for Rossell zirconolite (atom #1266), which consists of 6 4-rings, 12 6-rings, and 22 8-rings, with a total of 49 atoms.
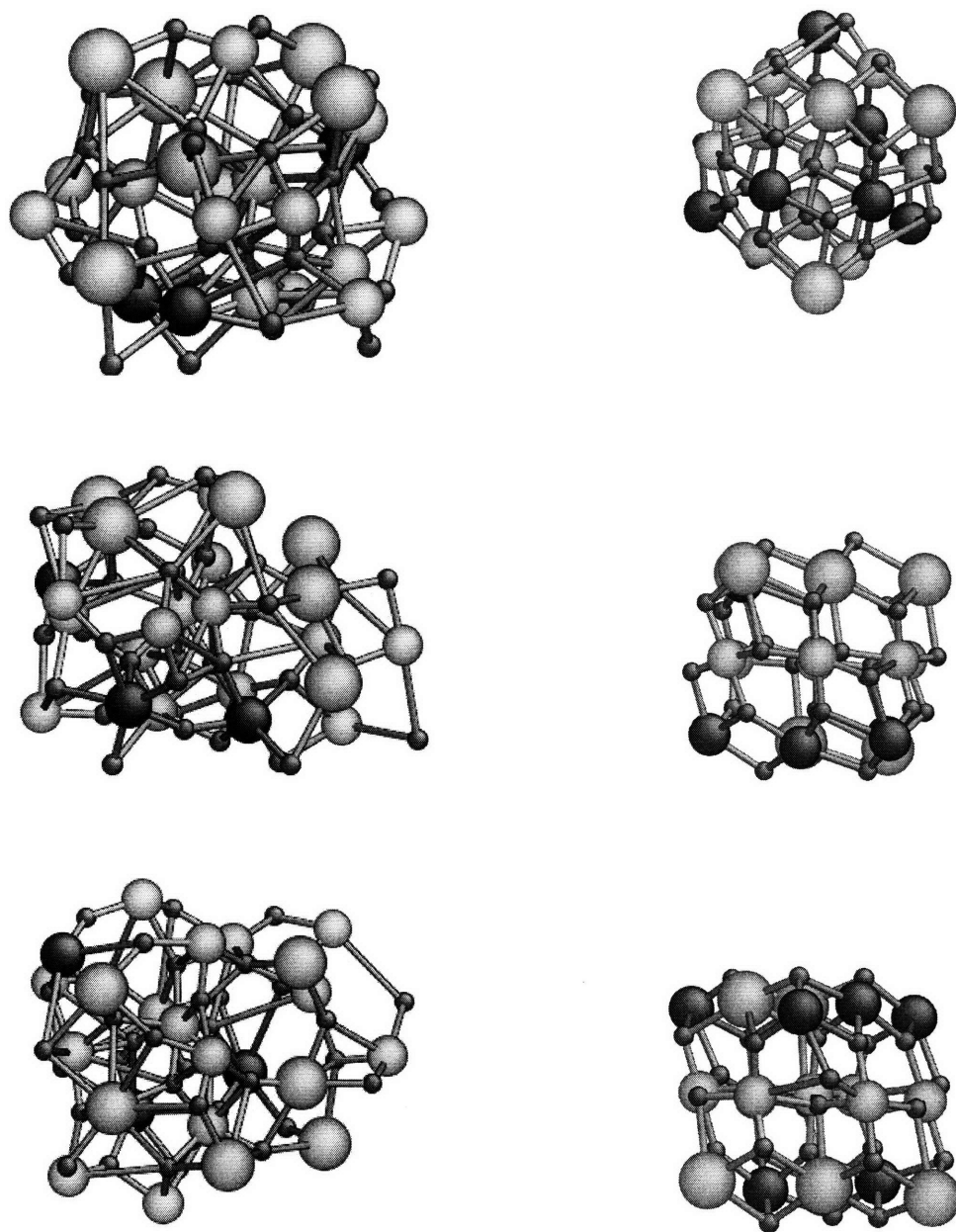
Figure 27 – On the left is a local cluster for a Ti site in melted zirconolite, atom #1015. The local cluster consists of 18 4-rings, 25 6-rings, 31 8-rings, 4 10-rings and 6 12-rings, with a total of 79 atoms. On the right is a Ti (M3) local cluster for Rossell zirconolite (atom #1266), which consists of 6 4-rings, 12 6-rings, and 22 8-rings, with a total of 49 atoms.

Figure 28 – On the left is a local cluster for a Ti site in melted zirconolite, atom #1161. The local cluster consists of 22 4-rings, 51 6-rings, 28 8-rings and 5 10-rings, with a total of 71 atoms. On the right is a Ti (M3) local cluster for Rossell zirconolite (atom #1266), which consists of 6 4-rings, 12 6-rings, and 22 8-rings, with a total of 49 atoms.

Figure 29 – On the left is a local cluster for a Ti site in melted zirconolite, atom #1226. The local cluster consists of 20 4-rings, 50 6-rings, 31 8-rings and 1 10-ring, with a total of 57 atoms. On the right is a Ti (M3) local cluster for Rossell zirconolite (atom #1266), which consists of 6 4-rings, 12 6-rings, and 22 8-rings, with a total of 49 atoms.

Figure 30 – On the left is a local cluster for a Ti site in melted zirconolite, atom #1639. The local cluster consists of 17 4-rings, 38 6-rings, 20 8-rings and 2 10-rings, with a total of 86 atoms. On the right is a Ti (M3) local cluster for Rossell zirconolite (atom #1266), which consists of 6 4-rings, 12 6-rings, and 22 8-rings, with a total of 49 atoms.
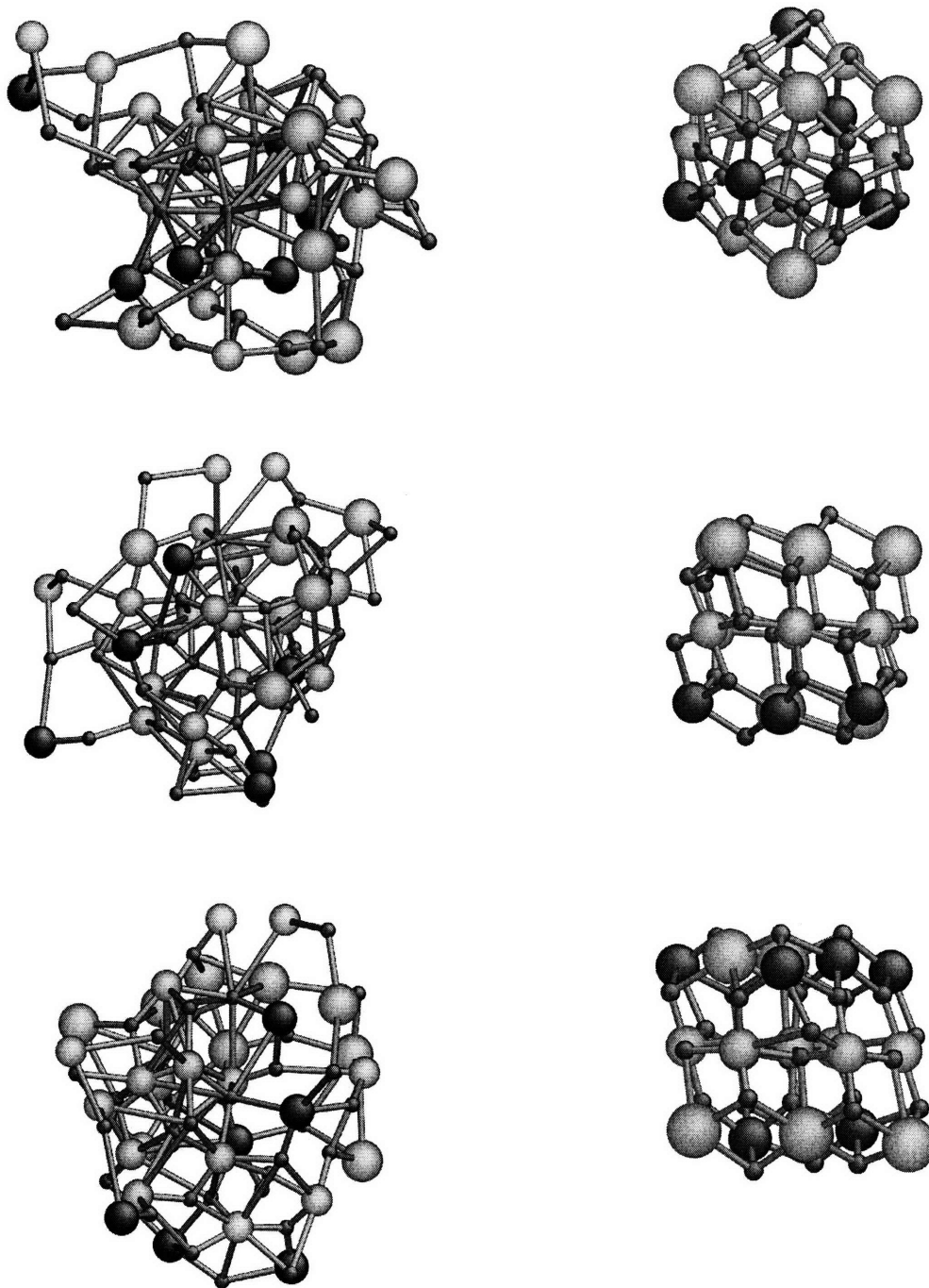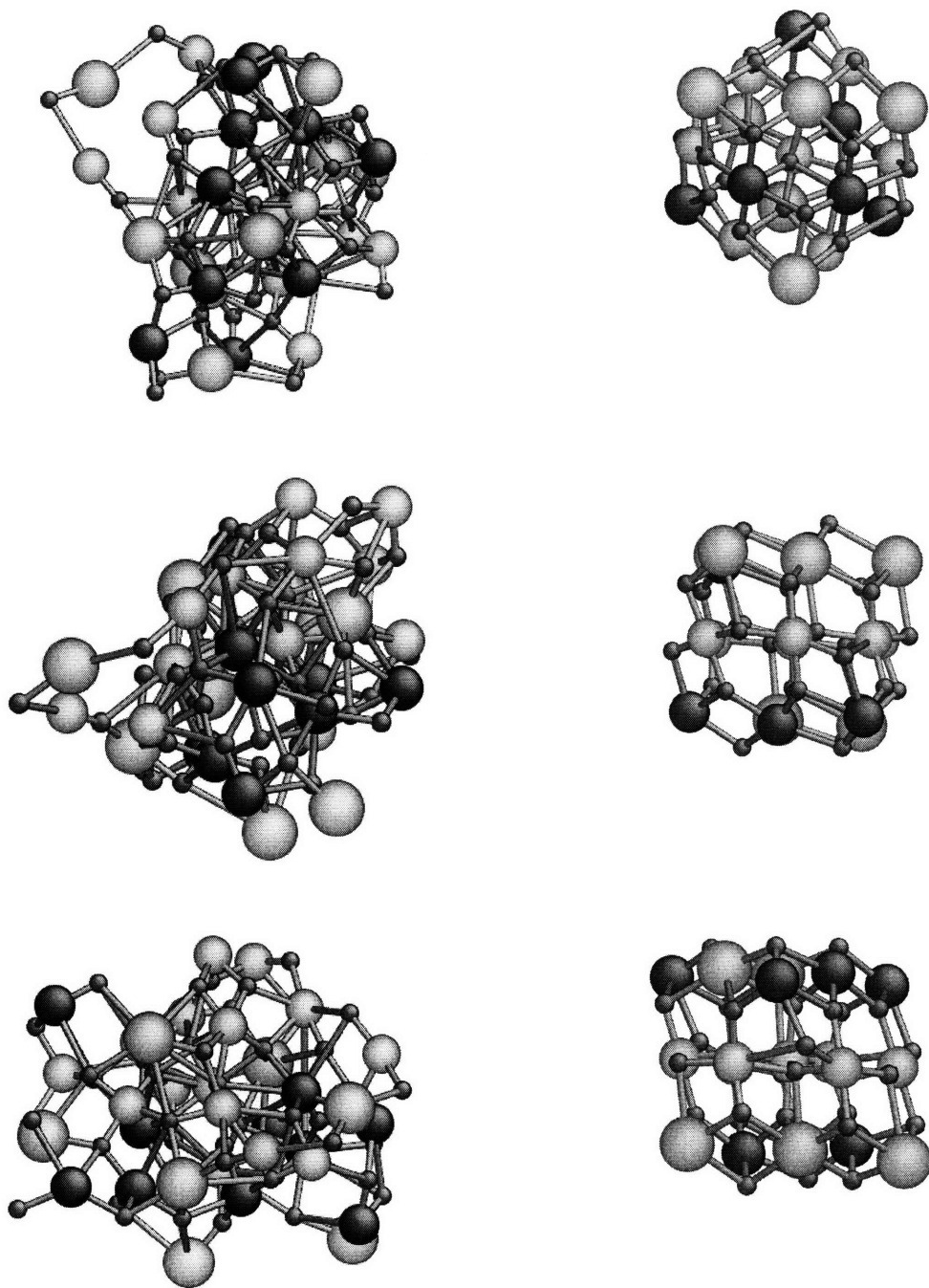
Figure 31 – On the left is a local cluster for a Ti site in melted zirconolite, atom #1648. The local cluster consists of 21 4-rings, 47 6-rings, 27 8-rings, 6 10-rings and 1 12-ring, with a total of 81 atoms. On the right is a Ti (M3) local cluster for Rossell zirconolite (atom #1266), which consists of 6 4-rings, 12 6-rings, and 22 8-rings, with a total of 49 atoms.

Figure 32 – On the left is a local cluster for a Ti site in melted zirconolite, atom #1949. The local cluster consists of 16 4-rings, 47 6-rings, 33 8-rings and 3 10-rings, with a total of 63 atoms. On the right is a Ti (M3) local cluster for Rossell zirconolite (atom #1266), which consists of 6 4-rings, 12 6-rings, and 22 8-rings, with a total of 49 atoms.
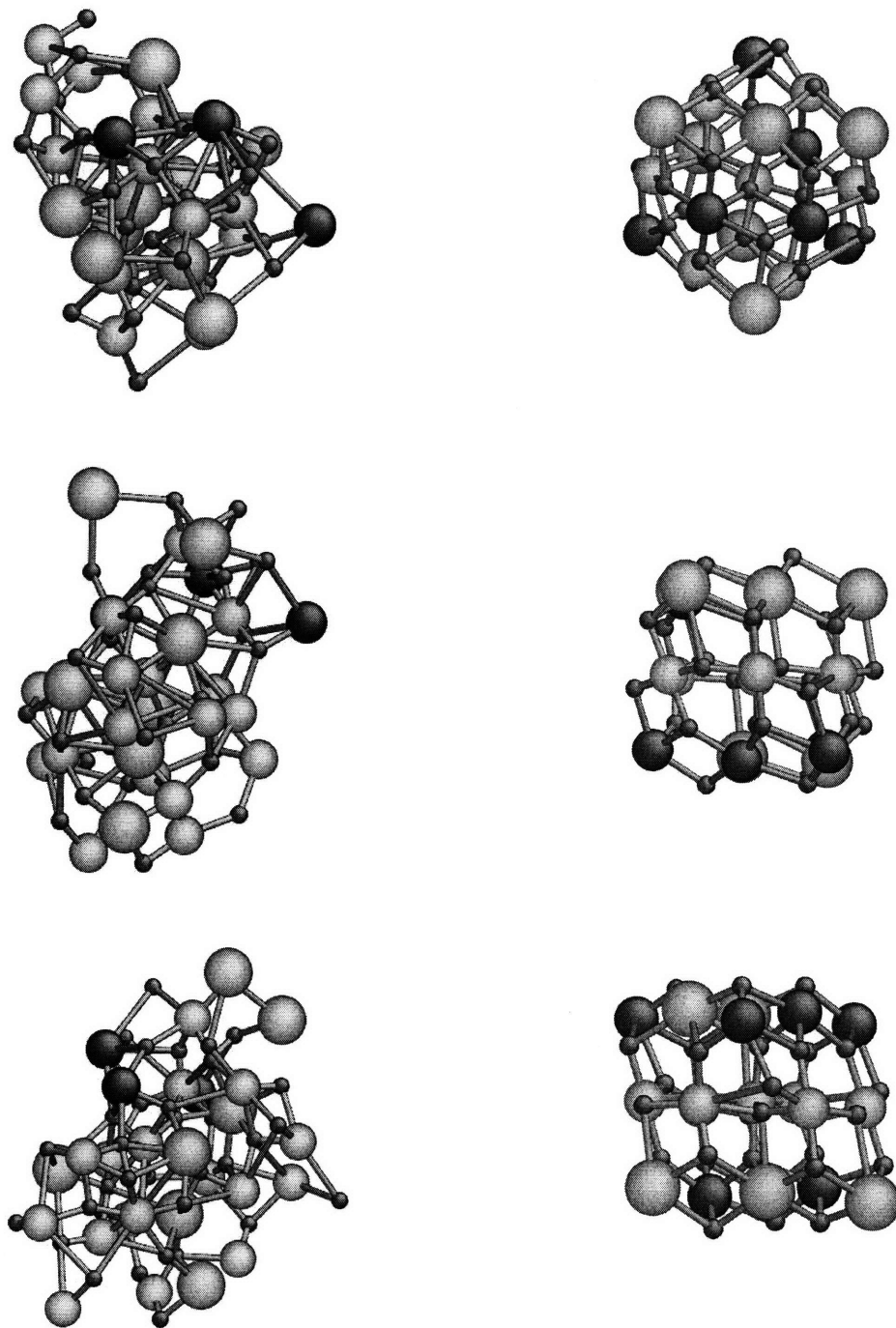
Discussion

Rossell Structure

Some patterns can be seen in the Rossell-structure deviations from the ideal. Looking at two to three clusters per atom site is not enough to make an definite conclusions about the changes to the Rossell structure, but some observations can be safely generalized.

For two of the Ca (M1) local clusters, the only change from the ideal was a missing bond near the edge of the cluster. This seems to fit with the average ring counts calculated; the average number of 4-rings is pretty close to ideal, while the average number of 6-rings is slightly lower and the average number of 8-rings is slightly higher. The local cluster that included a 10-ring (from atom #335, **Figure 3**) was very different from the others. There were many excess atoms in the cluster and quite a few missing bonds that allowed for the inclusion of the extra atoms.

Again, similarities can be found in the M2 clusters. All of them had the upper right-hand oxygen atom missing, with the exception of cluster #727 (**Figure 5**), in which there were no atoms missing. In this case the oxygen atom in question was skewed away from the center of the cluster but still close enough to bond. This is probably why the averages for these clusters are lower for the 8-ring count.

Unlike the clusters around the M2 sites, the M3 and M5 local clusters always have additional atoms. In the ideal structure, the M3 and M5 sites have similar local clusters, and that carries on into the Rossell structure. This shows in the local clusters that were viewed, and also in the average ring counts which are very close for the 4- and 6-rings, and only a few rings different for the 8-ring count. Another inference from the local clusters for the M3 and M5 titanium sites is the lack of dependence between the ring counts and which bonds are missing. In two of the local clusters for Ti (M3), #1168 and #1424, a single bond on the outside of the cluster was missing, but one had 28 8-rings, while the other had 36.

The Zr (M4) sites were surprising in their uniformity: the connectivity was identical to the ideal Ti (M4) site, despite the changes in which atoms were on which sites. One of the Ti (M4) clusters that was calculated fit this model as well, but for the most part the Ti (M4) local clusters seem to be missing a bond right in the center of the cluster, which is why the average ring counts are so much lower for that type.

Melt Structure

The melt structure is easily distinguished from the crystal structure. The cations cluster by atom type, they fail to maintain regular spacing between each other, and they form more bonds with other atoms. The local clusters tend to be asymmetric, with the occasional loop of atoms protruding from an otherwise compact cluster. Not only can the difference be seen looking at the image of the local clusters, but it can be seen simply in the ring counts and cluster sizes. The local clusters contain many more atoms than their crystalline counterparts, and the ring counts are also increased. The number of 4-rings is generally far higher than what is found in the crystalline structure and there are very large numbers of 10-rings. This approach to mapping the connectivity of the atoms clearly distinguishes melt from crystal.

The segregation of cation types observed in the MD-simulated melt is an important finding. Such segregation was observed also by Zhang [8] in both molten and metamict zircon (ZrSiO$_4$). He surmised that the metamict form of zircon, for irradiation below the melting point, was stabilized by intermediate-range polymerization of [SiO$_4$] coordination units, in what could be viewed as a form of incipient phase separation into ZrO$_2$ and SiO$_2$. Notably, little clustering of Zr ions was found, into what might otherwise define a ZrO$_2$ phase, just as in the present case with zirconolite, where little Zr ion clustering was observed, compared to both Ca and Ti clustering. It could be that metamict zirconolite is stabilized by the tendency of clustered [TiO$_6$] octahedra to polymerize, paralleling the limited polymerization of [SiO$_2$] tetrahedra in zircon.

,
Conclusion
In this report, comparisons between the ideal and Rossell-determined structures of zirconolite, and also between the Rossell structure and the structure of molten zirconolite, were made with the help of molecular dynamics simulations and topological analysis of connectivities. The Rossell structure varied in small ways from the ideal structure, and these variations are sometimes repeated and occur frequently. The connectivity analysis reveals very small changes in structure; the topological analysis is a sensitive enough indicator to detect a single missing bond at the edge of a local cluster. However, similar changes in ring counts do not always signify the equivalent change in connectivity within the local cluster.

The molten structure is substantially different from the crystalline structure, and this is shown by the dramatic changes in ring counts and local cluster sizes. Because of the sensitivity of the ring counts to small changes in coordination, the ring counts for the melt structure vary widely. For this purpose, average ring counts were found more useful.

The next step in this study is to carry out a ring analysis for the metamict portion of a collision cascade. By looking at the individual clusters and the average ring counts, one should be able to tell if the metamict structure is better compared to the disordered structure of molten zirconolite, or a less ordered version of Rossell-structure crystalline material. The conjecture that radiation-induced amorphization of zirconolite to one or more metamict states, that differ in density at different irradiation temperatures, may be stabilized by incipient phase separation or [TiO$_6$] polymerization could be tested.

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