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REVISION 1

The Incompressibility of Atoms at High Pressures

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Abstract

The structures of the silica polymorphs α-quartz and stishovite have been geometry optimized at high simulated, isotropic pressure within the framework of Density Functional Theory. The atoms of the high pressure polymorph stishovite are virtually incompressible with the bonded radii for Si and O atoms decreasing by only 0.04 Å and 0.08 Å, respectively, at 100 GPa. In compensating for the increase in the effective interatomic potential associated with the compression of the Si-O bonded interactions, the electron density at the bond critical point between the bonded pair increases from 0.69 e/Å^3 to 0.89 e/Å^3. The bonded radii of the Si and O atoms for α-quartz decrease by 0.006 Å and 0.008 Å, respectively, between 1 bar and 26.4 GPa. The impact of simulated, isotropic pressure on the bonded radii of the atoms for three perovskites $YAlO_3$, $LaAlO_3$ and $CaSnO_3$ was also examined at high pressure. For the $YAlO_3$ perovskite, the bonded radii for Y and Al decrease by 0.06 Å and 0.05 Å, respectively, at 80 GPa while the electron density between the bonded atoms increases by 0.12 e/Å^3 and 0.15 e/Å^3, on average. The calculations also show that the coordination number of the Y atom increases from 9 to 10 while the coordination number of the O1 atom increases concomitantly in the structure from 5 to 6 at 20 GPa. Hence pressure not only promotes an increase in the coordination number of the metal atoms but also a necessary concomitant increase in the coordination number of the O

atoms. The bonded radii, determined at a lower pressure between 0.0 and 15 GPa for $LaAlO_3$ and $CaSnO_3$, decrease a smaller amount with the radii for the La and Ca atoms decreasing by 0.03 Å and 0.04 Å, respectively, while the radii for the smaller Al and Sn atoms decrease by 0.01 Å and 0.02 Å, respectively. In general, O atoms are more compressible than the metal atoms but overall, the calculations demonstrate that the bonded radii for the atoms in crystals are virtually incompressible when subjected to high pressure. The reason that the bonded radii change little when subjected to high pressure is ascribed to the changes in the effective interatomic potentials that result in increased repulsion when the atoms are squeezed together.

Keywords: High pressure, bonded radii, silica polymorphs, perovskites

Introduction

To appreciate the impact of pressure on the structure and crystal chemistry of an oxide crystal, it is important, as argued by Prewitt and Downs (1998), that we understand the impact of pressure on the oxide anions, the bonded cations and the cation containing coordination polyhedra. They also argued that coordinated polyhedra, containing large cations with small valences can be expected to be more compressible than those containing smaller cations with larger valences. Based on an examination of several experimental electron density maps determined by Sasaki et al. (1980), they also suggested that the atomic nuclei of the individual ions of an oxide crystal are shrouded by incompressible spherical cores of electron density that in turn are enclosed by more compressible, low lying shells. On the basis of this suggestion, they argued that the outer shells of the ions are ideal regions where the compressibility of a crystal may be accommodated. These arguments, combined with results of density functional theory (DFT) calculations for the silica polymorphs (Nicoll et al., 1994) and force constants estimated for the bonded interactions for a number of oxide molecules (Hill et al., 1994), Prewitt and Downs (1998) developed guidelines as to how the sizes of the ions, the bond lengths and the coordination numbers of the atoms of a material may be expected to respond to pressure. These guidelines include: (1) Longer bonded interactions are more likely to decrease than shorter stronger ones; (2) The shared character of a bonded interaction increases with decreasing bond length, (3) The coordination number of a cation increases upon compression and (4) Oxygen anions are more compressible than metal cations. Grochala et al. (2007) have since examined the rules for a variety of materials, ranging from molecules to metals, with atoms that they considered to be in ‘very tight places’, that is, at pressures ranging up to that at the center of the Earth, 380 GPa. Despite the relative simplicity of

the rules, they observed that the Prewitt and Downs (1998) rules are quite correct and serve as useful constructs for understanding how the structures and bonded interactions for a variety of materials respond to high pressure.

In this study, we have determined the impact of pressure on the sizes of the bonded radii of the atoms and the polarization of the electron density distributions for two polymorphs of SiO_2 with different structures and coordination numbers and three metal-oxide perovskites with similar structures but different compositions. We used the approach of Bader and his colleagues (Bader, 1985; Runtz et al., 1977) who examined the electron density distribution for a number of molecules in a search for a feature that may serve and qualify as a bonded interaction. In the search, they discovered that adjacent atoms that were possibly bonded were connected by well-defined continuous pathways of maximum electron density. Furthermore, the value of the electron density along the paths was found to decrease systematically from the nucleus of each pair to a local minimum in the electron density along the path where the gradient of the electron density is zero. The pathway of maximum electron density that connects the nuclei of the pair was denoted the bond path of the interaction and the point along the path where the electron density adopts a minimum value was denoted the bond critical point, $\mathbf{r}_c$. Later, based on the topological properties of the electron density, Bader (2009) concluded that two atoms, M and O, are necessarily bonded only if the pair is connected by a bond path. In addition, he asserted that 'One may define the bond path operator as a Dirac observable, making the bond path a measurable expectation value of a quantum mechanical operator.' The distances between the nuclei of the pair and the point along the path where the electron density adopts a minimum value, define the bonded radii for the pair of bonded atoms, M and O, denoted $r_b(M)$ and $r_b(O)$. It

114 was also observed that when the bonded radius sum of the bonded pair, r_b (M)+ r_b (O), matches
115 the length of the bonded interaction, denoted, R(M-O), then the M-O bonded interaction is
116 assumed to be a stable and strain free interaction (Bader, 1990; Bader and Matta, 2004).
117
118 In a recent study of electron density distributions, Gibbs et al. (2013) calculated the bonded radii
119 for first, second and third row atoms at ambient conditions, for a relatively large number of
120 crystals. At odds with the assumption that the Shannon and Prewitt 1969) crystal radius of the
121 oxide anion shows little or no change when bonded, it was found that the bonded radii for the O
122 atom decrease systematically from 1.40 Å when bonded to an electropositive atom like
123 potassium to 0.60 Å when bonded to a more electronegative atom like nitrogen. Further, the
124 bonded radii for the more electropositive metal atoms agree with the crystal radii where the
125 electron density distribution of the O atom is largely unpolarized. But the bonded radii for the
126 more electronegative metal atoms are progressively larger than the crystal radii as the electron
127 density is progressively contracted along bond paths of the bonded interactions. This study
128 prompted further scrutiny of the effect of pressure on the oxide anion, the bonded cations and the
129 cation containing coordination polyhedra for different structures.
130
131 With this approach, the impact of simulated isotropic pressures as high as 100 GPa and its effect
132 on the electron density distributions of the silica polymorphs α-quartz (Gibbs et al., 1999) and
133 stishovite and three perovskites of $LaAlO_3$, $CaSnO_3$ and $YAlO_3$ composition (Gibbs et al., 2012;
134 Wang, 2012) were examined. The calculations were completed within the framework of density
135 functional theory, followed by a determination of the electron density distributions, the bond
136 paths and the bond critical points properties for the bonded interactions (Bader, 2009). In short,

rather than examining how the crystal radii of the atoms are impacted for a range of pressures, we describe how the bonded radii are impacted by pressure as it would be very time consuming task to determine how the crystal radii for a variety of crystal structures respond to high pressure. We also examined the extent to which the Prewitt-Downs rules hold in terms of how the bond lengths, and the compressibilities, χ, of the bonded atoms respond to pressure.

The impact of isotropic pressure on the bonded radii of the atoms of α-quartz and stishovite

The structure of the silica polymorph α-quartz consists of a 3D array of corner sharing SiO_4 silicate tetrahedral oxyanions such that each O atom is bonded to two Si atoms and each Si atom is bonded to four O atoms. The number of bond paths and resulting coordination number of the O atoms is 6 thus the complete structural formula is $^{iv}Si^{ii}O_2$ and Hosler's Rule holds as 4*1 = 2*2. On the other hand, the structure of the high pressure polymorph, stishovite, consists of a 3D array of corner- and edge-sharing SiO_6 octahedral oxyanions such that each O atom is bonded to three Si atoms and each Si atom is bonded to six O atoms. Thus the complete structural formula for stishovite is $^{vi}S^{iii}O_2$ and Hosler's Rule holds as 6*1 = 2*3. As the ^{vi}Si and ^{iii}O atoms for stishovite are six and three coordinated, respectively, and the ^{iv}Si and ^{ii}O in quartz are four and two coordinated, respectively, the ^{vi}Si -^{iii}O bond length in stishovite is necessarily longer, 1.75 Å, than the ^{iv}Si-^{ii}O bond length, 1.61 Å, recorded at ambient conditions. The bonded radii for the Si and O atoms, r_b(Si) and r_b(O), respectively, for both α-quartz and stishovite are displayed in Figure 1, as determined within the framework of DFT as a function of isotropic pressure (Gibbs et al., 1999). The observation that the sum of the bonded radii, r_b(Si) + r_b(O), for both silica polymorphs, equals the corresponding Si-O bond lengths at pressure, satisfies the constraint that the Si-O bonded interactions are stable and strain free.

The compression mechanism in α-quartz differs substantially from that of stishovite. In α-quartz, the volume reduction at high pressure is achieved by the bending of the compliant Si-O-Si angles that connect the rigid SiO_4 tetrahedra (Hazen et al., 1989). In stishovite, the major compression mechanism involves reduction of the relatively stiff Si-O bonded interactions, especially the longer Si-O apical bonds in the structure (Ross et al., 1990). The difference in compression mechanisms is reflected in the differing in their bulk modulus. Quartz has a relatively small bulk modulus of 37 GPa (Angel et al., 1997) while stishovite has a substantially greater bulk modulus of 306 GPa (Ross et al., 1990).

As evinced by Figure 1, the O atoms are more compressible, χ, than the Si atoms, in agreement the Prewitt-Downs (1998) rule that O atoms are more compressible than metal atoms. In the case of α-quartz, the value of r_b(Si) decreasing $\chi \approx -1.95 \times 10^{-4}$ Å/GPa with increasing pressure with r_b(O) decreasing, $\chi \approx -3.40 \times 10^{-4}$ Å/GPa, whereas in the case of stishovite, r_b(Si) decreases more, $\chi \approx -3.9 \times 10^{-4}$ Å /GPa, while r_b(O) decreases even more, $\chi \approx -8.4 \times 10^{-4}$ Å /GPa, assuming that the radii for both silica polymorphs decreasing roughly linearly with increasing pressure. As such, the bonded radius for the larger O atom in stishovite decreasing ~2.5 times more than the smaller O atom in α-quartz, upon being compressed, whereas the larger Si atom in stishovite decreases twice as much as the smaller Si atom in α-quartz. As expected, the Si-O bonded interaction, ~1.60 Å, for α-quartz decreases less than the longer and weaker Si-O bond length optimized for stishovite, ~1.75 Å. Overall, the relatively small decrease in the bonded radii for the Si and O atoms, particularly encountered in the case of stishovite at 100 GPa, is ascribed to a change in the effective interatomic potential between the Si and O atoms upon compression. As discussed

in detail by Prencipe and Nestola (2006), the effective interatomic potential is the sum of the Coulomb potential and the kinetic energy of the electrons. The latter increases strongly when the electrons are confined in increasingly smaller volumes with the result that there is an increase of the effective potential as the atoms are squeezed together that increases, in turn, the repulsions between them. In addition, Grochala et al. (2007) asserted that the electron density between a pair of bonded atoms when subjected to pressure, must necessarily be modified upon being compressed. It does so for the silica polymorphs with a migration of electron density into the internuclear region between the compressed bonded atoms, shielding the nuclei of the atoms. In the case of stishovite, this is borne out with a concomitant and progressive increase in the accumulation of the electron density, $\rho(\mathbf{r}_c)$, at the bond critical point, $\mathbf{r}_c$, between the bonded Si and O atoms. The $\rho(\mathbf{r}_c)$-values for the Si-O bonded interactions for α-quartz likewise increase with increasing pressure with the Si-O bonds for both α-quartz and stishovite becoming more shared in character with increasing pressure, in agreement with Prewitt and Downs (1998) rule that the shared character of a bonded interaction increases when a bonded interaction is compressed. These results suggest that a metal atom coordinated by a larger number of O atoms is more compressible than an atom coordinated by a smaller number of O atoms. It also suggests the coordinating O atoms are likewise more compressible than the smaller Si atoms

The impact of pressure on the bonded radii of the atoms for the perovskites

The ideal perovskite structure with ABO_3 stoichiometry has cubic symmetry (P*m3m*) and consists of corner-sharing BO_6 octahedra with larger A cations filling the cavities within the octahedral framework. Perovskites can attain a variety of symmetries due to tilting of the octahedra that can result in a change of the coordination of the A cation from the ideal 12-fold

coordination with oxygen of the cubic prototype structure (Glazer, 1972; Woodward, 1997). For example, $LaAlO_3$ is rhombohedral (R-3*c*) and bond paths connect each of the La and Al atoms with O atoms. Six bond paths are found to extend between the Al atoms to nearest-neighbor O atoms at 0 GPa verifying its coordination number is six. Twelve bond paths are found to extend between the La atoms and nearest-neighbor oxygen atoms so the coordination of La is determined to be twelve at 0 GPa. The number of bond paths and resulting coordination number of the O atoms is 6 thus the complete structural formula is $^{xii}La^{vi}Al^{vi}O_3$ and Hosler's Rule holds as 12*1 + 6*1 = 6*3. At high pressure, the rotation angle around the threefold axis of the AlO_6 octahedra is determined by the relative compressibilities of the LaO_{12} and AlO_6 sites. Zhao et al. (Zhao et al., 2004)observed that the rotation angle decreases significantly with pressure, ultimately leading to a phase transition from rhombohedral symmetry to cubic symmetry at high pressure.

In contrast to $LaAlO_3$ perovskite, $CaSnO_3$ and $YAlO_3$ are orthorhombic (P*bnm*). Bond paths connect each of the Ca, Sn, Y and Al atoms with O atoms. The Ca-O, Sn-O, Y-O and Al-O linkages for the three perovskites are therefore considered to be necessarily bonded interactions (Bader, 2009). In this study, six bond paths are found to extend between the Sn atoms to nearest-neighbor oxygen atoms in $CaSnO_3$ at 0 GPa verifying its coordination number of 6. Eight bond paths are found to extend between the Ca atoms to nearest-neighbor oxygen atoms so the coordination of Ca is determined to be eight. The bond paths and coordination numbers of the O_1 and O_2 atoms are 4 and 5, respectively, thus the complete structural formula is $^{xiii}Ca^{vi}Sn^{iv}O_1{}^{v}O_2$ and Hosler's Rule holds as 8*1 + 6*1 = 4*1 + 5*2. In $YAlO_3$, six bond paths are found to extend between the Al atoms to nearest-neighbor oxygen atoms at 0 GPa verifying its coordination number is 6. In contrast to $CaSnO_3$, nine bond paths are found to extend between the Y atoms

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and nearest-neighbor oxygen atoms so the coordination of Y is determined to be nine at 0 GPa. The number of bond paths and coordination numbers of the O1 and O2 atoms in $YAlO_3$ are both 5, thus the complete structural formula is $^{ix}Y^{vi}Al^{v}O_1{}^{v}O_2$ and Hosler's Rule holds as 9*1 + 6*1 = 5*1 + 5*2. High-pressure single-crystal X-ray experiments show that the structures of $CaSnO_3$ and $YAlO_3$ undergo a different structural response to pressure. In the II-IV perovskite, $CaSnO_3$, the SnO_6 octahedra are less compressible than the CaO_8 sites with the result that the structure becomes more distorted with pressure (Zhao et al., 2004). In the III-III perovskite, $YAlO_3$, the AlO_6 site is more compressible than the YO_9 site so the structure becomes less distorted with pressure (Ross et al., 2004).

To understand how the bonded radii of the atoms for the three perovskites respond to pressure, we examined the results of high-pressure DFT simulations (Gibbs et al., 2012; Wang, 2012). The structures of $LaAlO_3$ and $CaSnO_3$ were determined at a continuum of simulated isotropic pressures, ranging between 0.0 GPa and 15.0 GPa. On the other hand, the structure of the $YAlO_3$ perovskite was geometry optimized for a wider range of pressures, between 0 GPa and 80 GPa. Below we describe the impact of pressure on the bonded radii for each of the La, Y, Ca, Sn, Al and O atoms in these three perovskites.

Impact of simulated pressure on radii of the atoms in $LaAlO_3$ perovskite

Details of the bonded radii, r_b(La), r_b(Al), and r_b(O), and the electron density at the bond critical point ($\rho(\mathbf{r}_c)$) generated for the nonequivalent atoms for the $LaAlO_3$ perovskite for pressures between 0.0 and 15 GPa are given in Table 1 (see (Gibbs et al., 2012) for the nomenclature of the atoms for the perovskites). In the case of the La–Oi bonded interactions, the bonded radii for both r_b(La) and r_b(Oi) display anomalies: both unexpectedly increasing slightly, 0.003 Å, rather than decreasing with increasing pressure (Fig. 2). The value of $\rho(\mathbf{r}_c)$ of R(La-Oi) shows no

change between 0.0 and 15 GPa (Table1). As R(La - Oi) = r_b(La) + r_b(Oi), the La - Oi bonded interaction is indicated to be stable and free of strain despite the increase in bond length. As such, they are stable bond lengths and bonded radii as they both show a slight increase with increasing pressure. However, as described below, the remaining La-O bonded interactions, La – Oii and La –Oiii, both decrease with increasing pressure (Fig. 2). The Al-O bond lengths in $LaAlO_3$ also decrease with increasing pressure (Table 1).

For the La – Oii bonded interaction, R(La – Oii) = 2.656 Å with r_b(La) = 1.431 Å and r_b(Oii) = 1.225 Å at 0.0 GPa. At 15 GPa, the bonded interaction decreases to 2.600Å with r_b(La) = 1.407 Å and r_b(Oii) = 1.193 Å and $\rho(\mathbf{r}_c)$ increases slightly (Table 1). Similar results are seen for the La – Oiii bonded interaction (Table 1). The compressibilities of the bonded radii are $\chi \approx r_b(La) = -1.6x10^{-3}$ Å /GPa, $\chi(r_b(Oii)) = -2.13x10^{-3}$ Å / GPa for R(La-Oii), and $\chi(r_b(La)) = -3.3x10^{-3}$ Å /GPa and $\chi(r_b(Oii) \approx -4.7x10^{-3}$ Å / GPa for R(La-Oiii). On the basis of the bonded radii for the La atom, the bonded radius of the atom is 1.42 Å and that of the O atom bonded to the La atom is 1.21 Å.

In the case of the Al atom, R(Al-O) decreases from 1.886 Å to 1.842 Å, r_b(Al) decreases by 0.014 Å between 0.0 and 15 GPa resulting in a smaller compressibility, $\chi(r_b(Al) \approx -9.3x10^{-4}$ Å /GPa. The bonded radius of the O bonded to the Al atom, r_b(O) decreases 0.029 Å with $\chi(r_b(O) \approx -1.9x10^{-3}$ Å /GPa. Thus the compressibility of the Al atom is substantially less than the O atom bonded to the Al.

The values of r_b(Al) and rb(O) determined at P = 0.0, 0.791 Å and 1.095 Å, respectively, match those determined earlier (0.80 Å and 1.12 Å, respectively by (Gibbs et al., 2012). At P = 0.0 GPa, the value of r_b(O) ranges between 1.13 Å and 1.33 Å with an average value of 1.23 Å whereas the value of $r_b(^{i}La)$ ranges between 1.35 Å and 1.51 Å with an average value of 1.43 Å.

As r_b(Al) +rb(O) = 1.886 Å, the (Al-O) bonded interactions is considered to be stable. The geometry optimized bond lengths, R(M-O), determined for the geometry optimized structures, plotted in Figure 3 in terms of r_b(M) + r_b(O) for the La and Al atoms, scatter along a line, as anticipated for stable bonded interactions (Fig. 3). The average compressibilities for the larger La atoms is less than that for the O atoms but substantially greater than that for the smaller Al atom, demonstrating that larger metals atom are more compressible than smaller ones.

Impact of isotropic pressure on the bonded radii of the atoms for $CaSnO_3$ perovskite

Details of the nonequivalent bonded radii for the Ca, Sn, O_1 and O_2 atoms for $CaSnO_3$ perovskite and the values of $\rho(\mathbf{r}_c)$ for pressures that range between 0.0 GPa and 15.0 GPa are given in Table 2. As shown in Figure 4, the Ca - O1 and Ca- O2 bond lengths and the bonded radii decrease with increasing pressure. The bonded radii of the Ca atom, r_b (Ca), at P = 0.0, range between 1.147 and 1.360 Å with an average value of 1.22 Å, taken as an estimate of the bonded radius of the Ca atom, compared with 1.25 Å determined by Gibbs et al. (2013). The bonded radii of the O1 and O2 atoms at 0.0 GPa range between 1.13 Å and 1.44 Å, with an averaged value of 1.24 Å, compared with 1.26Å, the value determined for the O atom bonded to Ca (Gibbs et al., 2013). For all of the Ca-O bonded interactions, $\rho(\mathbf{r}_c)$ increase with pressure. The compressibilities of the Ca atom, range roughly between $\chi \approx -1.73 \times 10^{--3}$ Å /GPa and-2.27×10^{-3} Å /GPa with an average value of -1.99x1 0^{-3} Å /GPa, smaller than that determined for the O atoms bonded to the Ca atom that range between $\chi \approx -2.7 \times 10^{-3}$ Å/GPa and $\chi \approx -3.8 \times 10^{-3}$ Å / GPa with an average compressibility value of $\chi \approx -2.94 \times 10^{-3}$ Å /GPa (Table 2).

The two nonequivalent Sn-O bond lengths and the bonded radii for the Sn and O1 and O2 atoms likewise decrease with the increasing pressure (Table 2). The three nonequivalent Sn-O bond

lengths, R(Sn -O1) = 2.068 Å, R(Sn -O2i) =2.068 Å, R(Sn -O2ii) = 2.064 Å are virtually identical at P= 0 GPa, with an average bonded radii of r_b(Sn) = 1.07 Å and rb(O) = 1.01 Å. The values of $\rho(\mathbf{r}_c)$ for all of the Sn-O bonded interactions increase slightly with pressure. The compressibilities of the Sn atoms range between -1.20x10^{-3} Å/GPa and -1.4x10^{-3} Å/GPa while those of the O atoms bonded to the Sn atoms rare larger and range between -1.4x10^{-3} Å/GPa and -1.67x10^{-3}Å /GPa. The bonded interactions for $CaSnO_3$ are considered to be stable, as evinced by Figure 5 which shows that the sum of the bonded radii matches the bond length for the bonded pair.

Impact of simulated isotropic pressure on the radii of the atoms for the $YAlO_3$ perovskite

The bonded radii for the Y, Al, O_1 and O_2 atoms for $YAlO_3$ perovskite and the values of $\rho(\mathbf{r}_c)$ bonded radii for the atoms of the $YAlO_3$ perovskite, calculated for a larger continuum of pressures between P = 0.0 GPa and 80 GPa are given in Table 3. As described below, the coordination number of the Y atom in the $YAlO_3$ perovskite increases at 20 GPa from 9 to 10 in agreement with the Prewitt and Down's (1998) observation that high pressure favors structures with larger metal coordination numbers. It also suggests, however, that the coordination number of the larger cations in a structure are more susceptible to increase than the smaller ones. In addition, the coordination number of the O1 oxygen atom increases concomitantly from five to six.

As shown in in Figure 6, six of the seven nonequivalent Y-O bond lengths and associated bonded radii for the of Y and O atoms decrease as the pressure is increases from 0.0 GPa to 80 GPa. R(Y-O1i), for example, decreases from 2.2213 Å to 2.0975 Å, with r_b(Y) decreasing from 1.165 Å to 1.107 Å. $\chi \approx$ - 7.3x10^{-4}Å/GPa; r_b(O1i) decreases from 1.056 Å to 0.991 Å, $\chi \approx$ - 8.1x10^{-4}Å/GPa. Similar results are observed for R(Y-O1ii) with $\chi \approx$ -1.9x10-^{4}Å/GPa and $\chi \approx$ -2.4x10^{-}

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323 ^{4}Å/GPa for rb(Y) and rb(O1ii), respectively. For R(Y-O1iii), $\chi \approx$ -1.11 x 10^{-3}Å/GPa and $\chi \approx$ -1.21
324 x 10^{-3}Å/GPa for rb(Y) and rb(O1iii) (Table 3). For R(Y-O2i), $\chi \approx$ -7.5 x 10^{-4}Å/GPa for rb(Y)
325 and $\chi \approx$ -8.8 x 10^{-4}Å/GPa for rb(O2i). For R(Y-O2ii) $\chi \approx$ - 6.8x10^{-4}Å/GPa for rb(Y) and χ = -
326 8.8x10^{-4}Å/GPa for r_b(O2ii). For R(Y-O2iii), $\chi \approx$ -8.1 x 10^{-4}Å/GPa for rb(Y) and $\chi \approx$ -1.12 x 10^{-}
327 ^{3}Å/GPa for rb(O2iii). At 20 GPa, the number of bonded interactions from Y to O changes from 6
328 to 7 (Fig. 6). The seventh nonequivalent Y-O bond length, R(Y-O1iv), that forms at 20 GPa, is
329 substantially longer than the others and exists up to 80 GPa. From P = 20.0 to 80.0 GPa, R(Y-
330 O1iv) decreases from 2.947 Å to 2.604 Å; r_b(Y), 1.485 to 1.334 Å, $\chi \approx$ - 2.5x10^{-4}Å/GPa; r_b(O2iv)
331 , 1.478 Å to 1.334 Å with $\chi \approx$ - 2.4x10^{-3}Å/GPa.

332 The three nonequivalent Al-O bond lengths are substantially shorter than the Y-O bond lengths
333 and decrease substantially less with increasing pressure from 0.0 to 80 GPa (Table 3). R($^{[}$Al -
334 O1), for example, decreases from 1.886 Å to 1.736 Å with r_b(^{vi}Al) decreasing from 0.790 to
335 0.742 Å, (χ = -6.0x10^{-4}Å/GPa) and r_b(O1) decreasing from 1.096 Å to 0.994 Å ($\chi \approx$ - 1.3x10^{-3}
336 Å/GPa). For R(Al-O2i) $\chi \approx$ - 6.2x10^{-4}Å/GPa for r_b(^{vi}Al) and $\chi \approx$ - 1.3x10^{-3}Å/GPa for r_b(O2i).
337 Lastly, for R(Al-O2ii) r_b(Al) $\chi \approx$ - 6.9x10^{-4}Å/GPa for rb(Al) and $\chi \approx$ - 1.5x10^{-3}Å/GPa for r_b(O2)
338 (Table 3).

339 The average bonded radius adopted by the Y atom, $\langle r_b(Y) \rangle$ = 1.21 Å, at P = 80.0 is 0.06 Å, is
340 smaller than that, 1.27 Å, adopted at P = 0.0. The average bonded radius for the O1 and O2
341 atoms bonded to the Y atoms, r_b(O1) and rb(O2), is also smaller at P=80 GPa, 1.11 Å than that,
342 1.21 Å, adopted at P= 0.0 GPa. Clearly, both atoms are relatively rigid, with the radii decreasing
343 little with increasing pressure with the O atoms being more compressible than the Y atom. The
344 average bonded radius of the Al atoms decreases, on average, from 0.79 Å to 0.74 Å while the
345 average radius for the O1 and O2 atoms bonded to the Al decreases from 1.10 Å to 0.99 Å as the

346 pressure increases from P = 0.0 GPa to 80 GPa. The average bonded radius for the Al atom at
347 P=0.0, 0.79 Å, is slightly smaller than the value, 0.80 Å, determined by Gibbs et al. (Gibbs et al.,
348 2013), but equal to the radius of the Al atom in the $LaAlO_3$ perovskite. As evinced by Figure 7,
349 the radius sum of bonded radii $r_b(Al)+ r_b(O)$ and $r_b(Y) + r_b(O)$ correlate linearly with R(Al-O)
350 and R(Y-O), demonstrating that the Al-O and Y-O bond interactions are stable over the range of
351 pressures studied.

352 **Implications**

353 On the basis of bonded radii determined for the silica polymorphs coesite (Gibbs et al., 2003),
354 Prewitt and Downs (1998) reported that the structure of a crystal typically compresses by
355 displaying the largest distortions for the atoms associated with the weakest bonded interactions.
356 They also asserted that the coordination numbers of atoms at high pressure tend to increase with
357 increasing pressure. These rules of thumb are borne out by the observation that the bonded radii
358 of the atoms for stishovite, with the longer Si-O bonded interactions, contract more upon
359 compression, than the bonded radii for the shorter Si-O bonded interactions observed for α-α-
360 quartz. Also the Si atoms are 6-coordinated and the O are 3-coordinated in the high pressure
361 silica polymorph stishovite while the Si and O atoms are 4- and 2-coordinated in α-quartz, well
362 known evidence that high pressure favors the higher coordination numbers for both atoms. It is
363 noteworthy, that an increase in the coordination number of the Y atom of the $YAlO_3$ perovskite
364 necessarily means that the coordination number of one of the O atoms must necessarily increase
365 as well. It is also clear that that O atoms are more compressible than metal atoms based on the
366 above result that shows the bonded radius of the O atom of stishovite decreases about twice as
367 much, ~0.08 Å, as the Si atom while the bonded radius of the Si atom only decreases ~0.04 Å for
368 an corresponding increase of pressure of 100 GPa. In addition, the bonded radius for the larger$_r$

Y atom of $YAlO_3$ perovskite decreases 0.07 Å, on average, while the O atom bonded to the Y atom decreases slightly more, 0.10 Å, for a pressure increase of 80.0 GPa. At 20 GPa, the coordination number of Y increases from 8 to 9 while the coordination of O1 increases from 5 to 6, as observed above. The bonded radius of the smaller Al atom decreases by 0.05 Å while the radius of the O atom bonded to the Al decreases 0.10 Å. In the case of the two remaining $CaSnO_3$ and $LaSnO_3$ perovskites, that were subjected to a much smaller range of pressures between 0 GPa and 15 GPa, the bonded radius of Ca decreases 0.03 Å and radius of Sn decreases 0.02 Å while the bonded radii of the O atoms bonded to the Ca atoms decrease, 0.04 Å with the bonded radius of the O atom to Sn decreases 0.02 Å, on average. For the same pressure range, the bonded radius of the La for $LaAlO_3$, decreases 0.02 Å while the radius of the O atom bonded to the Y atom decreases 0.05 Å. In addition, the bonded radius of Al decreases 0.01 Å while the radius of the O atom bonded to the Al atom decreases 0.02 Å, on average. On the basis of these results, it is apparent the bonded radii of the atoms for the silica polymorphs and the three perovskites, examined in this study compress a relatively small amount when subjected to pressure, indicating that the metal atoms in these materials are relatively rigid and incompressible compared with the somewhat more compressible O atoms. With the exception of the bonded radius for one of the Y atoms, the compressibilities of Al, Sn, Ca and La atoms in the perovskites and the Si atoms in the silica polymorphs are all less than the O atoms to which they are bonded, again demonstrating that anions are more compressible than metal atoms. The results show that the bonded radii of the atoms for the materials are relatively rigid, with the compressibilities of the smaller atoms, in particular, changing relatively little upon being subjected to pressure, supporting the assertion that pressure has little impact on the sizes of atoms (Grochala et al., 2007). Finally, in the course of undertaking VASP/DFT calculations for a

number of molecular, ionic and intrinsically metallic materials, Andreas Hermann and Roald Hoffman (personal communication) have generated a variety of Volume vs. Pressure curves and equations of state, ranging up to pressures of 500 GPa that indicate the atoms like Fe, Au, Ni, W etc. comprising metals and the C atoms in diamond are likewise virtually incompressible and behave as hard sphere atoms at these extremely high pressures. These results and those presented in this report support the argument that high pressure has relatively little impact on the sizes of atoms (Grochala et al., 2007). It is also evident that the small decrease in the bonded radii for atoms at extreme pressures is directly related to changes in the effective interatomic potential with pressure that result in increased repulsion between the nuclei of the bonded atoms as the atoms are squeezed together.

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Figure Captions

Figure 1. Plot of the bonded radii, r_b (Å) of the Si (blue and red circles) and O (blue and red diamonds) atoms in α-quartz between 1 bar and 30 GPa and the Si (red and black solid circles) and O (blue and red squares) atoms in stishovite between 0 and 100 GPa.

Figure 2. Plot of the bonded radii, rb (Å), of the La and O atoms in $LaAlO_3$ between 0 and 15 GPa.

Figure 3. Plot of the La-O and Al-O distances, R(M-O) (Å), in $LaAlO_3$ as a function of the sum of the bonded radii of the metal atoms (La and Al) and oxygen atom, $r_b(M)+r_b(O)$ (Å).

Figure 4. Plot of the bonded radii, rb (Å), of the Ca and O atoms in $CaSnO_3$ between 0 and 15 GPa.

Figure 5. Plot of the Ca-O and Sn-O distances, R(M-O) (Å), in $CaSnO_3$ as a function of the sum of the bonded radii of the metal atoms (Ca and Sn) and oxygen atom, $r_b(M)+r_b(O)$ (Å).

Figure 6. Plot of the bonded radii, rb (Å), of the Y and O atoms in $YAlO_3$ between 0 and 80 GPa.

Figure 7. Plot of the Y-O and Al-O distances, R(M-O) (Å), in $YAlO_3$ as a function of the sum of the bonded radii of the metal atoms (Y and Al) and oxygen atom, $r_b(M)+r_b(O)$ (Å).

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Table 1. Calculated bond lengths (Å), critical bond radii for the La atom, rb(M) (Å), and O atom, rb(O) (Å), and electron density at bond critical points, ρ(Rc) (e/Å^3) for $LaAlO_3$ perovskite between 0 and 15 GPa.

M-O	**P (GPa):**	**0**	**1.18**	**2.78**	**4.63**	**6.81**	**8.62**	**10**	**12**	**15**
La-Oi	R(M-O)	2.4756	2.4750	2.4752	2.4758	2.4761	2.4769	2.4776	2.4785	2.4807
	rb(M)	1.350	1.350	1.350	1.351	1.351	1.351	1.352	1.352	1.353
	rb(O)	1.125	1.125	1.125	1.125	1.125	1.126	1.126	1.126	1.128
	ρ(Rc)	0.3432	0.3438	0.3441	0.3441	0.3444	0.3442	0.3441	0.3440	0.3430
La-Oii	R(M-O)	2.6560	2.6509	2.6443	2.6369	2.6285	2.6219	2.6169	2.6101	2.6001
	rb(M)	1.431	1.429	1.426	1.423	1.419	1.416	1.414	1.411	1.407
	rb(O)	1.225	1.222	1.219	1.214	1.209	1.206	1.203	1.199	1.193
	ρ(Rc)	0.2417	0.2443	0.2484	0.2523	0.2569	0.2605	0.2632	0.2668	0.2725
La-Oiii	R(M-O)	2.8419	2.8324	2.8189	2.8035	2.7863	2.7721	2.7613	2.7465	2.7238
	rb(M)	1.509	1.505	1.499	1.493	1.486	1.480	1.476	1.470	1.460
	rb(O)	1.333	1.328	1.320	1.310	1.300	1.292	1.285	1.277	1.263
	ρ(Rc)	0.1683	0.1716	0.1764	0.1820	0.1887	0.1942	0.1985	0.2044	0.2136
Al-O	R(M-O)	1.8857	1.8818	1.8767	1.8709	1.8644	1.8593	1.8554	1.8501	1.8423
	rb(M)	0.791	0.789	0.788	0.786	0.784	0.782	0.781	0.779	0.777
	rb(O)	1.095	1.092	1.089	1.085	1.081	1.077	1.074	1.071	1.066
	ρ(Rc)	0.4559	0.4598	0.4650	0.4710	0.4780	0.4836	0.4879	0.4938	0.5027

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Table 2. Calculated bond lengths (Å), critical bond radii for the Ca atom, rb(M) (Å), and O atom, rb(O) (Å), and electron density at bond critical points, ρ(Rc) (e/Å^3) for $CaSnO_3$ perovskite between 0 and 15 GPa.

M-O (Å)	**P (GPa):**	**0**	**0.738**	**1.5**	**2.61**	**3.94**	**5.18**	**5.98**	**6.73**	**10**	**12**	**15**
Ca-O1i	R(M-O)	2.2786	2.2742	2.2697	2.2635	2.2563	2.2497	2.2456	2.2419	2.2263	2.2172	2.2045
	rb(M)	1.147	1.146	1.144	1.141	1.138	1.135	1.134	1.132	1.125	1.121	1.116
	rb(O)	1.131	1.129	1.126	1.122	1.118	1.114	1.112	1.110	1.101	1.096	1.088
	ρ(Rc)	0.3209	0.3239	0.3271	0.3315	0.3368	0.3417	0.3448	0.3476	0.3597	0.3670	0.3774
Ca-O1ii	R(M-O)	2.3548	2.3510	2.3467	2.3414	2.3347	2.3286	2.3249	2.3215	2.3067	2.2981	2.2857
	rb(M)	1.180	1.178	1.176	1.174	1.172	1.169	1.168	1.166	1.160	1.156	1.151
	rb(O)	1.175	1.173	1.170	1.167	1.163	1.160	1.157	1.155	1.147	1.142	1.134
	ρ(Rc)	0.2794	0.2817	0.2843	0.2877	0.2919	0.2959	0.2983	0.3006	0.3107	0.3166	0.3255
Ca-O2i	R(M-O)	2.2994	2.2952	2.2908	2.2852	2.2783	2.2719	2.2682	2.2647	2.2499	2.2414	2.2294
	rb(M)	1.157	1.155	1.153	1.151	1.148	1.145	1.144	1.142	1.136	1.132	1.127
	rb(O)	1.143	1.140	1.138	1.134	1.130	1.127	1.125	1.123	1.114	1.109	1.102
	ρ(Rc)	0.3081	0.3110	0.3140	0.3179	0.3228	0.3273	0.3300	0.3326	0.3436	0.3502	0.3597
Ca-O2ii	R(M-O)	2.5746	2.5702	2.5685	2.5611	2.5557	2.5499	2.5458	2.5424	2.5282	2.5194	2.5073
	rb(M)	1.270	1.268	1.267	1.264	1.262	1.260	1.258	1.257	1.252	1.248	1.244
	rb(O)	1.305	1.302	1.301	1.297	1.293	1.290	1.287	1.285	1.277	1.271	1.264
	ρ(Rc)	0.1728	0.1745	0.1752	0.1780	0.1802	0.1825	0.1841	0.1855	0.1913	0.1951	0.2005
Ca-O2iii	R(M-O)	2.7950	2.7903	2.7834	2.7776	2.7682	2.7601	2.7555	2.7511	2.7315	2.7205	2.7040
	rb(M)	1.360	1.358	1.356	1.353	1.350	1.347	1.345	1.343	1.336	1.332	1.326
	rb(O)	1.436	1.433	1.428	1.425	1.419	1.414	1.411	1.408	1.396	1.389	1.379
	ρ(Rc)	0.1090	0.1101	0.1117	0.1132	0.1154	0.1175	0.1187	0.1198	0.1249	0.1279	0.1325
Sn-O1	R(M-O)	2.0679	2.0651	2.0621	2.0584	2.0538	2.0496	2.0472	2.0448	2.0350	2.0294	2.0214
	rb(M)	1.062	1.061	1.059	1.058	1.055	1.054	1.052	1.051	1.047	1.044	1.041
	rb(O)	1.006	1.004	1.003	1.001	0.998	0.996	0.995	0.994	0.988	0.985	0.981
	ρ(Rc)	0.6087	0.6122	0.6160	0.6209	0.6270	0.6325	0.6359	0.6390	0.6524	0.6603	0.6716
Sn-O2i	R(M-O)	2.0608	2.0583	2.0559	2.0525	2.0486	2.0450	2.0427	2.0407	2.0322	2.0272	2.0204

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	rb(M)	1.059	1.058	1.057	1.055	1.053	1.052	1.051	1.050	1.046	1.043	1.040
	rb(O)	1.002	1.001	0.999	0.998	0.995	0.993	0.992	0.991	0.987	0.984	0.980
	ρ(Rc)	0.6166	0.6199	0.6230	0.6275	0.6326	0.6374	0.6404	0.6431	0.6547	0.6616	0.6713
Sn-O2ii	R(M-O)	2.0642	2.0619	2.0595	2.0565	2.0527	2.0493	2.0472	2.0453	2.0372	2.0326	2.0261
	rb(M)	1.061	1.060	1.058	1.057	1.055	1.054	1.053	1.052	1.048	1.046	1.043
	rb(O)	1.004	1.002	1.001	1.000	0.997	0.996	0.995	0.994	0.989	0.987	0.983
	ρ(Rc)	0.6127	0.6157	0.6188	0.6228	0.6278	0.6324	0.6352	0.6378	0.6489	0.6553	0.6646

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Table 3. Calculated bond lengths (Å), critical bond radii for the Y atom, rb(M) (Å), and O atom, rb(O) (Å), and electron density at bond critical points, ρ(Rc) (e/Å^3) for $YAlO_3$ perovskite between 0 and 80 GPa.

M-O	P (GPa):	0	1.05	2.59	3.791	5.09	6.31	7.11	7.94	10	12	15	20	40	60	80
Y-O1i	R(M-O)	2.2213	2.2187	2.2147	2.2118	2.2088	2.2059	2.2042	2.2023	2.1977	2.1935	2.1874	2.1782	2.1462	2.1204	2.0975
	rb(M)	1.165	1.164	1.162	1.161	1.159	1.158	1.157	1.156	1.154	1.152	1.149	1.145	1.130	1.118	1.107
	rb(O)	1.056	1.055	1.053	1.051	1.049	1.048	1.047	1.046	1.044	1.041	1.038	1.033	1.016	1.003	0.991
	ρ(Rc)	0.4652	0.4679	0.4721	0.4751	0.4782	0.4813	0.4832	0.4851	0.4901	0.4947	0.5015	0.5120	0.5505	0.5842	0.6163
Y-O1ii	R(M-O)	2.2839	2.2827	2.2808	2.2793	2.2779	2.2768	2.2758	2.2749	2.2732	2.2712	2.2689	2.2653	2.2565	2.2518	2.2489
	rb(M)	1.195	1.195	1.194	1.193	1.193	1.192	1.192	1.191	1.191	1.190	1.189	1.187	1.183	1.181	1.180
	rb(O)	1.088	1.088	1.087	1.086	1.085	1.085	1.084	1.083	1.083	1.081	1.080	1.078	1.073	1.071	1.069
	ρ(Rc)	0.4110	0.4121	0.4137	0.4150	0.4162	0.4172	0.4181	0.4189	0.4204	0.4220	0.4240	0.4272	0.4353	0.4397	0.4427
Y-O1iii	R(M-O)	2.9720	2.9663	2.9583	2.9522	2.9457	2.9399	2.9361	2.9322	2.9230	2.9143	2.9019	2.8830	2.8232	2.7818	2.7530
	rb(M)	1.487	1.485	1.481	1.479	1.476	1.474	1.472	1.470	1.467	1.463	1.459	1.451	1.428	1.413	1.402
	rb(O)	1.491	1.488	1.482	1.478	1.474	1.470	1.468	1.465	1.459	1.454	1.446	1.434	1.396	1.370	1.352
	ρ(Rc)	0.0990	0.1000	0.1016	0.1028	0.1041	0.1053	0.1061	0.1069	0.1089	0.1108	0.1136	0.1180	0.1337	0.1459	0.1557
Y-O1iv	R(M-O)	Null	Null	Null	Null	Null	Null	Null	Null	Null	Null	Null	2.9466	2.8077	2.6948	2.6038
	rb(M)	Null	Null	Null	Null	Null	Null	Null	Null	Null	Null	Null	1.485	1.418	1.371	1.334
	rb(O)	Null	Null	Null	Null	Null	Null	Null	Null	Null	Null	Null	1.478	1.391	1.324	1.270
	ρ(Rc)	Null	Null	Null	Null	Null	Null	Null	Null	Null	Null	Null	0.1003	0.1314	0.1660	0.2017
Y-O2i	R(M-O)	2.2551	2.2520	2.2477	2.2444	2.2410	2.2379	2.2359	2.2338	2.2287	2.2240	2.2172	2.2068	2.1718	2.1455	2.1256
	rb(M)	1.181	1.180	1.178	1.176	1.175	1.173	1.172	1.171	1.169	1.167	1.164	1.159	1.143	1.131	1.121
	rb(O)	1.074	1.072	1.070	1.068	1.066	1.065	1.064	1.062	1.060	1.057	1.053	1.048	1.029	1.015	1.004
	ρ(Rc)	0.4380	0.4408	0.4449	0.4481	0.4514	0.4545	0.4565	0.4585	0.4636	0.4684	0.4754	0.4863	0.5252	0.5566	0.5820
Y-O2ii	R(M-O)	2.4310	2.4287	2.4253	2.4228	2.4201	2.4176	2.4160	2.4144	2.4106	2.4067	2.4015	2.3931	2.3633	2.3357	2.3067
	rb(M)	1.258	1.257	1.255	1.254	1.253	1.252	1.251	1.251	1.249	1.247	1.245	1.242	1.228	1.216	1.204
	rb(O)	1.173	1.172	1.170	1.169	1.167	1.166	1.165	1.164	1.162	1.159	1.156	1.152	1.135	1.119	1.103
	ρ(Rc)	0.2954	0.2971	0.2992	0.3009	0.3026	0.3043	0.3053	0.3064	0.3087	0.3112	0.3148	0.3205	0.3426	0.3640	0.3881
Y-O2iii	R(M-O)	2.5574	2.5530	2.5469	2.5422	2.5372	2.5329	2.5300	2.5270	2.5202	2.5136	2.5045	2.4907	2.4474	2.4174	2.3977
	rb(M)	1.316	1.314	1.311	1.310	1.308	1.306	1.305	1.303	1.301	1.298	1.295	1.289	1.271	1.259	1.251
	rb(O)	1.241	1.239	1.235	1.233	1.230	1.227	1.225	1.224	1.219	1.215	1.210	1.202	1.176	1.158	1.147
	ρ(Rc)	0.2245	0.2271	0.2301	0.2325	0.2350	0.2372	0.2388	0.2403	0.2437	0.2472	0.2522	0.2600	0.2864	0.3062	0.3205
Al-O1	R(M-O)	1.8855	1.8822	1.8775	1.8739	1.8702	1.8668	1.8646	1.8623	1.8569	1.8518	1.8445	1.8333	1.7948	1.7635	1.7364
	rb(M)	0.790	0.789	0.787	0.786	0.785	0.784	0.783	0.783	0.781	0.779	0.777	0.773	0.761	0.751	0.742

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	rb(O)	1.096	1.093	1.090	1.088	1.085	1.083	1.081	1.080	1.076	1.073	1.068	1.060	1.034	1.012	0.994
	ρ(Rc)	0.4591	0.4624	0.4672	0.4708	0.4747	0.4783	0.4806	0.4830	0.4889	0.4945	0.5027	0.5156	0.5635	0.6073	0.6492
Al-O2i	R(M-O)	1.8949	1.8918	1.8872	1.8838	1.8803	1.8769	1.8747	1.8725	1.8669	1.8617	1.8541	1.8422	1.7999	1.7657	1.7377
	rb(M)	0.793	0.792	0.790	0.789	0.788	0.787	0.786	0.786	0.784	0.782	0.780	0.776	0.763	0.752	0.743
	rb(O)	1.102	1.100	1.097	1.095	1.092	1.090	1.089	1.087	1.083	1.080	1.074	1.066	1.037	1.014	0.995
	ρ(Rc)	0.4522	0.4551	0.4596	0.4630	0.4666	0.4700	0.4723	0.4746	0.4804	0.4860	0.4942	0.5076	0.5591	0.6061	0.6487
Al-O2ii	R(M-O)	1.9095	1.9057	1.9003	1.8962	1.8918	1.8879	1.8853	1.8827	1.8763	1.8704	1.8617	1.8485	1.8029	1.7673	1.7385
	rb(M)	0.798	0.796	0.795	0.793	0.792	0.791	0.790	0.789	0.787	0.785	0.783	0.778	0.764	0.752	0.743
	rb(O)	1.112	1.109	1.106	1.103	1.100	1.097	1.095	1.094	1.089	1.085	1.079	1.070	1.039	1.015	0.995
	ρ(Rc)	0.4339	0.4374	0.4427	0.4467	0.4510	0.4550	0.4576	0.4602	0.4669	0.4732	0.4824	0.4972	0.5528	0.6021	0.6463