Packing and the structural transformations in liquid and amorphous oxides from ambient to extreme conditions

Anita Zeidler*a,1, Philip Stephen Salmonb,1, and Lawrie Basil Skinnet,c,d

*Department of Physics, University of Bath, Bath BA2 7AY, United Kingdom; bMineral Physics Institute, State University of New York, Stony Brook, NY 11794-2100; cAdvanced Photon Source, Argonne National Laboratory, Argonne, IL 60439; and dMaterials Development, Inc., Arlington Heights, IL 60004

Edited* by J. C. Phillips, Rutgers University, Summit, NJ, and approved June 3, 2014 (received for review April 1, 2014)

Liquid and glassy oxide materials play a vital role in multiple scientific and technological disciplines, but little is known about the part played by oxygen–oxygen interactions in the structural transformations that change their physical properties. Here we show that the coordination number of network-forming structural motifs, which play a key role in defining the topological ordering, can be rationalized in terms of the oxygen-packing fraction over an extensive pressure and temperature range. The result is a structural map for predicting the likely regimes of topological change for a range of oxide materials. This information can be used to forecast when changes may occur to the transport properties and compressibility of, e.g., fluids in planetary interiors, and is a prerequisite for the preparation of new materials following the principles of rational design.

network structures | oxygen packing | oxide ion radius | high pressure | high temperature

Network-forming structural motifs such as AO₃ triangular units and AO₄ tetrahedra, where A denotes an electropositive chemical species such as B, Si, or Ge, govern topological ordering in liquid and amorphous oxide materials and therefore have a profound effect on their physical properties (1, 2). Examples range from the dependence of network connectivity on the transport properties (e.g., viscosity) of glass-forming and/or magma-related oxide melts (3–7) to the role played by atomic packing in determining the elastic behavior of glass (8–10). In the case of open glass-forming structures, the network connectivity often follows from Zachariasen’s rules (11), but there is no reliable guide for predicting the conditions under which transformations occur in the character of network-forming motifs, e.g., from AO₃ to AO₄ or from AO₄ to AO₆ polyhedra.

With increasing density, oxygen–oxygen interactions are expected to manifest themselves in the structural transformations that occur (12), but the nature of this role is unknown. For example, the oxygen atom number density ρ₀ will depend on the type of network-forming motifs, can be altered by adding network modifiers, and will increase with density. Nevertheless, a plot of ρ₀ Versus the measured mean A–O coordination number Nₐ for network-forming structural motifs does not offer a basis for generalization (Fig. 1). It will be shown, however, that if the data are scaled by the volume occupied by an oxide ion V₀, and an adjustment is made for the volume occupied by any network-modifying atoms (i.e., atoms other than oxygen that are not at the centers of network-forming motifs), then the resultant oxygen-packing fraction η₀ offers a means for rationalizing the structural transformations that occur. An important proviso is that a constant oxide ion size cannot be assumed. Instead, the oxide ion environment has a profound influence as evidenced by the instability of these ions in the gas phase but their omnipresence in condensed matter (13, 14). This variability was recognized in the construction of well-known tables of ionic radii (15, 16), although a constant size was assumed for a given oxide ion coordination number. The variability of the oxide ion size is also a key theme in the development of transferable aspherical ion models which have been successful in accounting for many of the structure-related properties of oxide materials (13, 14). In the following we use an empirical approach to tackle this oxygen size issue which leads, for example, to accurate packing fractions for the rutile-type structures of SiO₂ and GeO₂ (SI Text, section 2).

Results

To address the structural role played by oxide ions, we first consider the transformations associated with cold compression (i.e., pressurization at ambient temperature) of the prototypical network-forming glasses B₂O₃, SiO₂, and GeO₂, where significant changes to their ambient pressure structures have now been characterized by using a variety of in situ experimental methods (17–23). These transformations offer an ideal starting point because O–O interactions are expected to become ever more important with increasing density (12). The oxygen-packing fraction was calculated using η₀ = V₀/ρ₀ = V₀/ρcO, where V₀ = (4/3)πρ₀r₀, r₀ is the oxygen radius as deduced from the type of structural motif and the measured mean nearest-neighbor A–O distance rₐO (Methods), ρ is the measured number density, and cO is the atomic fraction of oxygen. The results for the dependence on η₀ of the measured mean A–O coordination number Nₐ reveal that threefold-coordinated B atoms are stable over the interval 0.32 ≤ η₀ ≤ 0.4, and that fourfold-coordinated Si or Ge atoms are stable over the interval 0.40 ≤ η₀ ≤ 0.56–0.59 (Fig. 2A). If the oxygen volume V₀ was fixed then, because the oxygen-packing fraction for the B₂O₃, SiO₂, and GeO₂ systems is given by η₀ = V₀/ρ₀,

Significance

The structures of liquid and amorphous oxides are difficult to solve because of the complexity of their disordered networks, and the adaptability in size of oxide ions to their coordination environments. Particular difficulty is therefore associated with an identification of generic features associated with structural transformations. This paper adopts an empirical approach to find the oxide ion size, and shows that the network structures of a wide variety of disordered oxides can be categorized in terms of the oxygen-packing fraction over an extensive pressure and temperature range. The packing fraction provides a basis for predicting changes in network structures (e.g., from tetrahedral to octahedral) that will affect material properties such as the compressibility and viscosity.

Author contributions: A.Z., P.S.S., and L.B.S. designed research; A.Z. performed research; A.Z. analyzed data; and P.S.S. wrote the paper.

The authors declare no conflict of interest.

*This Direct Submission article had a prearranged editor.

Freely available online through the PNAS open access option.

1To whom correspondence may be addressed. E-mail: p.s.salmon@bath.ac.uk or a.zeidler@bath.ac.uk.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1405660111/-/DCSupplemental.

The dependence of the mean A–O coordination number $n^A_\Omega$ on the oxygen number density $\rho_O$. Data are given for (i) the network-forming glasses $B_2O_3$ (solid black circles), $SiO_2$ (solid red triangles), and $GeO_2$ (solid blue squares) under cold compression at pressures up to 100 GPa; (ii) liquid $Al_2O_3$ along with a variety of glassy and liquid silicate, aluminate, and aluminosilicate materials (open red circles) with several of them under high-temperature and/or high-pressure conditions, together with molten basalt at pressures up to 60 GPa and temperatures in the range of 2,273 to 3,273 K (7) (black crosses); and (iii) glassy and liquid borate (solid green circles), boroaluminate (open blue down triangles), borosilicate (open black squares), and germanate (solid magenta squares) materials.

Fig. 2A would appear simply as a scaled version of the corresponding data shown in Fig. 1.) At higher packing fractions, $\eta^B_0$ increases from 3 to 4 as planar BO$_3$ triangles make way for BO$_4$ tetrahedra in B$_2$O$_3$, whereas $\eta^A_0$ increases from 4 to 6 as AO$_4$ tetrahedra make way for AO$_6$ octahedra in SiO$_2$ or GeO$_2$. Tetrahedral motifs therefore become increasingly unstable as $\eta_O$ approaches the range of values expected for a random loose packing (RLP) of hard spheres, i.e., $\eta_{RLP} = 0.55$–0.60, and the majority of datasets point to a maximum $\eta_O$ value near to that expected for random close packing (RCP) $\eta_{RCP} = 0.64$ (24–27). For SiO$_2$ and GeO$_2$, chemical bonding assures that all of the oxygen atoms are in AO$_4$ tetrahedra below a packing fraction $\eta_O = 0.56$–0.59. In contrast, the hard spheres in dense disordered packing arrangements are not subject to this constraint, and all of them are not involved in tetrahedral motifs until the packing fraction increases to a value near to the limit $\eta_{RCP} = 0.64$ (28). Although it becomes increasingly difficult to reconcile disorder with higher packing fractions (29), there is also an indication at the highest pressures (21) for octahedral SiO$_2$ glass structures with $\eta_O \approx 0.719$ as for the rutile-type crystalline phase (Fig. 2). The data therefore suggest another stability plateau for sixfold-coordinated Si atoms, although the differences between the densest octahedral glassy and crystalline structures have yet to be established.

Fig. 2B shows the measured $\eta^A_\Omega$ versus $\eta_O$ dependence for liquid $Al_2O_3$ and for a variety of glassy and liquid silicate (M–Si–O), aluminate (M–Al–O), and aluminosilicate (Al–Si–O and M–Al–Si–O) systems where M denotes a network-modifying atom, many of which have geophysical relevance (30). For the modified materials, the oxygen-packing fraction was calculated by first removing the volume occupied by M atoms because this space is not available to oxygen, i.e.,

$$\eta_O = V_{O}/\rho_O \left[1 - \sum_{M} V_{M/PM}\right], \tag{1}$$

where $V_{M/PM}$ is the atomic fraction of M atoms of volume $V_M = (4/3)\pi r_M^3$, and $r_M$ is the radius of an M atom. As for the data shown in Fig. 2A, the network-forming A atoms are assumed to fit into the interstitial spaces between oxygen atoms. In general, the Al atoms in the investigated materials are four- or fivefold-coordinated and were both treated as network formers such that $\eta^A_\Omega$ represents either the Si–O or Al–O coordination number, or an average of both. The assignment of a network-forming role to fivefold-coordinated Al follows from the existence of pure aluminate glasses, in which networks are found with both four- and fivefold-coordinated Al atoms (SI Text, section 3.3), and from work on aluminosilicates (31). The exception is molten basalt (another aluminosilicate) under deep mantle conditions, where $\eta^A_\Omega = 6$ at pressures up to 60 GPa and temperatures in the range of 2,273 to 3,273 K (7). In this case both the Al and M atoms were treated as network modifiers such that $\eta^A_\Omega$ represents the Si–O coordination number alone. For the investigated silicate and aluminosilicate materials over the interval 0.35 ≤ $\eta_O ≤ 0.56$, the Si–O coordination number $\eta^A_\Omega = 4$ such that larger $\eta^A_\Omega$ values arise primarily from fivefold-coordinated Al atoms.
At higher packing fractions, the Si–O coordination number then increases rapidly to \( n_{\text{tet}} \approx 6 \) as \( \eta_{0} \) approaches \( \eta_{\text{RCP}} \).

The measured \( \eta_{\text{tet}} \)-versus-\( \eta_{0} \) dependence for a variety of glassy and liquid borate (M–B–O), borosilicate (M–B–Si–O), boronate (M–B–Al–O), and germanate (M–Ge–O) materials is shown in Fig. 2C. The M atoms were treated as network modifiers and the oxygen-packing fraction was calculated by using Eq. 1. Groups of different materials can again be identified, although they do not follow the same \( \eta_{0} \)-dependences as for the network structures shown in Fig. 2A and B. This difference in behavior presumably originates from the electronic structure which leads to a predisposition for B and Ge atoms to take coordination numbers other than \( n_{\text{tet}} = 3 \) and \( n_{\text{tet}} = 4 \) in modified materials, even at ambient conditions. A mean coordination number \( n_{\text{tet}} \approx 3 \) is usual in borates owing to the formation of BO\(_{4}\) tetrahedra (32), and a mean coordination number \( n_{\text{tet}} \approx 4 \) is often found in germanates owing to the formation of GeO\(_{4}\) or GeO\(_{6}\) polyhedra (33). In comparison, Si atoms prefer to retain a coordination number \( n_{\text{tet}} > 3 \) in silicates (5), and \( n_{\text{tet}} \approx 4 \) for the majority of Al atoms in the materials shown in Fig. 2. Accordingly, Fig. 2C shows a coordination number \( n_{\text{tet}} \approx 3.3 \) over the interval \( 0.29 \leq \eta_{0} \leq 0.41 \) for borates and boronates, and an increase in \( n_{\text{tet}} \) from \( 3.2 \) to \( 3.9 \) over the interval \( 0.32 \leq \eta_{0} \leq 0.44 \) as the Si content increases in borosilicates. In the case of germanates, the Ge–O coordination number is in the range of 4 to 4.4 over the interval \( 0.43 \leq \eta_{0} \leq 0.54 \).

**Discussion**

Strikingly, the data in Fig. 2 show that the adaptability of oxide ions to their coordination environment (13, 14) leads to a sensitivity that can be exploited to categorize \( \eta_{\text{tet}} \) in terms of \( \eta_{0} \). For instance, the limit of stability for tetrahedral units in SiO\(_{2}\) or GeO\(_{2}\) glass corresponds to the packing fraction found for an RLP of hard spheres, with the majority of datasets pointing to a maximum packing fraction that is comparable to the RCP limit (24–27). This structural map (34–36), in which \( \eta_{\text{tet}} \) is classified in terms of \( \eta_{0} \), allows for several properties of disordered oxides to be rationalized, and leads to predictive power for estimating the likely regimes of topological change.

For example, Fig. 2A and B indicates why it is so difficult to recover silicate glasses from high-pressure and temperature conditions with Si-O-Si coordination higher than \( \approx 4 \). On releasing an applied load, the oxygen-packing fraction will generally decrease but the gradient \( d\eta_{\text{tet}}/d\eta_{0} \) is steep and there is no stability plateau associated with \( n_{\text{tet}} = 5 \), i.e., there is no special reason to expect a trapping of higher coordinated motifs. Also, for liquids such as magmas under experimentally challenging high-pressure and temperature conditions, the equation of state is usually unknown. It follows from Eq. 1, however, that if an increase in \( \eta_{\text{tet}} \) above 4 can be measured at a given state point from, e.g., spectroscopic experiments, then the upper bound of \( \eta_{0} \approx 0.59 \) gives a lower bound for the density \( \rho \).

Another example is provided by constraint-counting theory, where an enumeration of the number of bonding constraints per atom versus the number of degrees of freedom can be used to predict the topology of network-forming materials, and related properties such as the composition dependence of glass-forming tendency and network rigidity (1, 2). More recently, temperature-dependent constraint theory has been used to calculate other macroscopic network properties such as the composition dependence of the glass transition temperature and liquid fragility (37–39). Fig. 2 gives a means for predicting \( \rho_{0}^{*} \) for a given \( \eta_{0} \), thus providing one of the prerequisites for counting the number of constraints. The results are therefore pertinent for understanding the properties of high-density liquids to aid, e.g., in the design of glasses with new network topologies (8, 38–40). They are also relevant to magma-related melts because the onset of higher coordinated modifying species changes the network polymerization (i.e., the ratio of bridging versus nonbridging oxygen atoms), thereby affecting the transport properties (e.g., viscosity) and compressibility (3–7).

We note that a tetrahedral-packing fraction (TPF) defined by TPF \( = V_{0}^{\text{tet}}/V_{\text{PMH}} \) was recently introduced by Wang et al. (41) for M–A–O materials, where \( V_{0}^{\text{tet}} \) is the packing fraction of oxygen atoms in regular AO\(_{4}\) tetrahedra. The TPF is therefore equivalent to the oxygen-packing fraction \( \eta_{0} \) calculated in the present work for modified tetrahedral networks such that the observation of an increase in \( \eta_{\text{tet}} \) above 4 when TPF \( \approx 0.6 \) (41) is in accord with the present work. As defined, the TPF values for unmodified networks do not, however, have clear physical meaning when \( n_{\text{tet}}>4 \), and TPF \( \neq \eta_{0} \) for modified networks because the volume occupied by M atoms is not removed as per the definition of \( \eta_{0} \) given by Eq. 1.

In summary, we have found that the pressure dependence of \( \eta_{\text{tet}} \) in the prototypical network-forming glasses B\(_{2}\)O\(_{3}\), SiO\(_{2}\), and GeO\(_{2}\) can be rationalized in terms of the oxygen-packing fraction \( \eta_{0} \). Two plateau regions are found for which three- or fourfold-coordinated A atoms are stable over a broad packing-fraction interval, with an upper limit for the stability of AO\(_{4}\) tetrahedra \( \eta_{0} \approx 0.56–0.59 \) that falls within the range of values expected for an RLP of hard spheres (24–26). It is found that \( \eta_{0} \) also allows for a benchmarking of the coordination number for network-forming motifs in a wide variety of other liquid and glassy oxides over an extensive pressure and temperature range. In the case of molten basalt under deep mantle conditions (7), the results offer an account as to whether and how the transition from four- to sixfold-coordinated Si atoms occurs: The upper limit of stability for fourfold coordination is \( \eta_{0} \approx 0.56 \) and the transformation to sixfold coordination occurs rapidly as \( \eta_{0} \) approaches \( \eta_{\text{RCP}} \approx 0.64 \). The packing arguments that have been introduced should encompass other disordered oxides, and may also extend to other classes of noncrystalline materials.

**Methods**

The experimental results presented in Figs. 1 and 2 were taken from papers in which sufficient information on the structure and density was given to enable the calculation of both \( \eta_{\text{tet}} \) and \( \rho_{0}^{*} \) (SI Text, sections 1–4 and Tables S1–S4). Oftentimes, information on coordination numbers is available from, e.g., nuclear magnetic resonance experiments, but densities are not reported. To calculate \( \eta_{0} \) from Eq. 1, it is necessary to know the oxygen radius \( r_{0} \) and the modifying atom radius \( r_{\text{M}} \) in addition to the number density \( \rho \).

For materials in which the network-forming motifs are three-, four- or sixfold-coordinated, regular polyhedra were assumed such that \( r_{0} = (\sqrt{3}/2) r_{\text{M}} \) for planar AO\(_{3}\) triangles, \( r_{0} = (\sqrt{2}/3) r_{\text{M}} \) for AO\(_{4}\) tetrahedra, and \( r_{0} = r_{\text{M}}/\sqrt{2} \) for AO\(_{6}\) octahedra, where \( r_{\text{M}} \) is the mean nearest-neighbor A–O distance. The \( r_{0} \) values for AlO\(_{4}\) and GeO\(_{4}\) units are given in SI Text, sections 3.2 and 4.3, respectively. In the pressure regime corresponding to the transformation from AO\(_{3}\) to AO\(_{4}\) polyhedra in the case of B\(_{2}\)O\(_{3}\) or from AO\(_{4}\) to AO\(_{6}\) polyhedra in the cases of SiO\(_{2}\) and GeO\(_{2}\), a linear dependence for \( r_{0} \) was assumed, a hypothesis that is supported by the available information (SI Text, section 1.5). This method for estimating \( r_{0} \) was also applied to the data for molten basalt under deep mantle conditions (7).

For modified materials, the mean M–O coordination number \( n_{\text{tet}}^{M} \) for a given composition and temperature/pressure was taken from the measured datasets or was estimated from related structures (SI Text, sections 3 and 4 and Tables S3 and S4), and the corresponding \( r_{0} \) value was then taken from ref. 16. These radii should provide reasonable estimates for materials under pressure because the M atoms are expected to be much less compressible than oxygen (12, 13). Nevertheless, the effect on \( \eta_{0} \) of an uncertainty on \( r_{0} \) was investigated by making a systematic variation of \( r_{0} \) corresponding to \( 1 \sigma \) change in \( r_{0} \) of \( \approx 1 \) for \( r_{0} \) values that is comparable to the size of the horizontal error bars shown in Figs. 2B and C (SI Text, sections 3.7 and 4.4).

**Acknowledgments.** We thank Mark Wilson for helpful discussions on oxide ions and Paddy Royall for comments on the manuscript. A.Z. and P.S.S. were supported by the Engineering and Physical Sciences Research Council, United Kingdom (Grant EP/J009741/1). Manuscript preparation was supported by US Department of Energy Award DE-FG02-09ER46650 (to L.B.S.).