RESPONSE OF OXYGEN-BASED STRUCTURES TO CHANGES IN
PRESSURE, TEMPERATURE AND COMPOSITION

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ABSTRACT
The results obtained from investigations of crystal structures at high temperature and at high pressure are reviewed. Compression and thermal expansion of each type of cation-anion coordination polyhedron are independent of structure type. Empirical relationships have been proposed for variations in cation-anion distance with temperature and pressure as a function of ionic bonding parameters. These relationships may lead to predictions of structural variation with pressure, temperature and composition.

INTRODUCTION
For many years, crystallographers of different disciplines have studied the structural topology and crystal chemistry of materials. Mineralogical crystallographers are interested in understanding the interrelationships of bulk chemistry, conditions of formation, thermal and pressure history, and other geologic parameters with the phase equilibria and crystal chemistry of natural inorganic solids. The role of the mineralogical crystallographer has been changing rapidly during the past two decades because of developments in automated diffractometry and computations. It is now possible to perform studies that are too complex or too time-consuming to have been attempted without the modern equipment. This report describes recent efforts to characterize changes in crystal structure that occur as a result of variations in pressure, temperature, and composition. High-pressure studies are emphasized because recent investigations at the Geophysical Laboratory are not widely known.

HIGH-TEMPERATURE STUDIES
Several instrumental developments have had a major impact on studies of the systems of crystal structures as a function of pressure, temperature, or composition. In addition to the all-important development of computer-controlled diffractometers and the general availability of computational facilities for structure solution and refinement, there have been other developments of importance. One of these is a single-crystal heater used on an X-ray diffractometer. A summary of early devices was provided by Buerger. Recent designs that utilize resistance heaters to reach temperatures of 1000-1200°C have been reported with a temperature stability of a few degrees Celsius. Temperatures as high as 2000°C can be reached if a flame heater is used, although thermal stability is

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reduced. These devices have been used to study the thermal expansion, crystal structures, and phase transitions at high temperature for many minerals.\textsuperscript{4-41}

At high temperature increased thermal diffuse scattering may introduce systematic bias to the observed intensities. These effects may be corrected if elastic constants are known.\textsuperscript{42} Recent advances in measurement of Brillouin scattering from small crystals\textsuperscript{43} are greatly increasing the number of materials for which elastic constants are available.

In spite of the number of structures that have been measured at temperature, there have been few attempts to summarize the results of lattice or cation polyhedral expansion. Megaw\textsuperscript{44} (see also Deganello\textsuperscript{45}) examined the theoretical basis for lattice expansion, and Lager\textsuperscript{46} considered aspects of cation polyhedral expansion. In the most extensive compilation of high-temperature structure data to date, Hazen and Frewitt\textsuperscript{47} summarized the bond expansions that were available for simple compounds as well as the few complex structures that had been determined at high temperature. They plotted the thermal expansion coefficient to 1000°C against a bond strength obtained by dividing the formal cation charge by the number of coordinating anions (Fig. 1). The agreement between the data points and the regression line is reasonably acceptable. Small, highly charged cations have smaller expansion coefficients than large monovalent or divalent cations. A significant difficulty

with this model is that polyhedra with a charge-to-coordination ratio greater than 0.75 are predicted to have a negative expansion, whereas these cation polyhedra (such as silicon in tetrahedral coordination) are observed to have zero expansion. Another problem with the interpretation of this simple model is that all cations of a given charge and coordination (e.g., all divalent cation octahedra) are predicted to have an identical coefficient of thermal expansion. Obviously there are factors significantly affecting the expansion of metal-oxygen bonds that are not included in this simple relationship.
HIGH-PRESSURE STUDIES

The majority of studies of crystal-structure variation with pressure have been conducted with the opposed-anvil, diamond cell. The opposed-diamond configuration was first used by Wier et al., 48 and has been incorporated in a variety of cell designs by Merrill and Bassett, 49 Keller and Holzapfel, 50 Schiferl et al., 51 Finger and King, 52 and Hazen and Finger, 53 and others.

Use of the high-pressure cell is complicated by variable absorption of the primary and diffracted beams due to diamond and other cell components. Furthermore, a portion of the diffracted region is obscured by metal supports and gaskets in most cells. Santoro et al., 54 Hazen, 26 Finger and King, 52 and Denner et al. 55 have corrected measured intensities for absorption by the pressure cell. The last two studies also presented methods for maximizing the region of reciprocal space that could be observed by suitable operation of four-circle diffractometers.

Merrill and Bassett 49 have shown by calculation that approximately 30% of the limiting sphere is available when optimum conditions are obtained in their miniature diamond cell. In addition, the increased absorption from the diamonds and other parts of the cell reduces the signal-to-noise ratio and obscures many of the weaker diffracted intensities. These two factors result in decreased precision for refined parameters, particularly for atoms with low atomic number. Derived quantities, such as interatomic distances and angles, have relatively large uncertainties, even though residuals are quite small. Several high-pressure data sets for spinel of nickel silicate composition, for example, have been refined to a weighted $R$ of 2.4% or less; however, the precision of the results is not adequate for the calculation of a significant slope for the variation of the silicon-oxygen bond distance with pressure. Other bonds are more compressible, and meaningful compressibility relationships may be obtained.

Within recent years the number of crystal structures that have been refined from intensity data measured at high pressure has increased dramatically. One major reason for this increase in activity is the development of secondary pressure calibration based on the ruby fluorescence technique 56-58 calibrated against the Decker equation of state 59 for NaCl. With this method the pressure may be determined quickly with a precision of a few tenths of a kilobar by measurement of the wavelength shift of the $R_1$ line in ruby. Previous X-ray methods used to measure the lattice constant of a material such as NaCl could require many hours to determine the pressure. Piermarini et al. 60 used the non-hydrostatic broadening of the ruby fluorescence line to determine the "glass transition" for several fluids and found that a 4:1 mixture of methanol-ethanol had the highest pressure of this transition for any of the substances studied. Although this liquid has relatively high viscosity at pressure 61 and a finite relaxation time to
changes in stress, it has become the standard pressure-transmitting fluid for most single-crystal experiments, which must be conducted under hydrostatic conditions.

The earliest studies of the structures of single crystals at high pressure were performed on bromine\(^{62}\) and benzene.\(^{63}\) The first studies of mineral structures at pressure were for calcite\(^{64}\) and gillespite.\(^{65,66}\) More recent studies of the structures of minerals or mineral-like phases include periclase,\(^{26}\) forsterite,\(^{27}\) fayalite,\(^{31}\) pyroxene,\(^{67}\) layer minerals,\(^{68,69}\) garnet,\(^{70}\) NaCl,\(^{52}\) ruby,\(^{71,72}\) quartz,\(^{73,74}\) zircon,\(^{75}\) and nickel-silicate spinel.\(^{40}\) Studies of other materials such as FeS,\(^{76}\) coesite, pyrope and diopside,\(^{77}\) hematite, esquelaite and karelianite,\(^{78}\) rutile, cassiterite, and the rutile analogs of germanium and ruthenium dioxide\(^{79}\) are in progress.

Several groups have studied samples in a diamond-anvil cell at elevated temperature using laser heating.\(^{80,81}\) This technique is not particularly useful for single-crystal studies that require temperature stability of a few degrees over time periods of the order of days. A modification of the Merrill and Bassett pressure cell\(^{49}\) with a miniature wire-wound resistance furnace is in use at the Geophysical Laboratory,\(^{82}\) and another cell is being developed by Piermarini and Block\(^{83}\) at the National Bureau of Standards. The Geophysical Laboratory design has a range in excess of 700\(^\circ\)C at 50 kbar. When heated cells such as these are in routine usage, studies of both lattice and structural equations of state will be possible for many materials.

**SYSTEMATIC CHANGES IN BOND LENGTH WITH PRESSURE**

Although there are difficulties in the precise determination of bond distances at elevated pressure, there are many structures such as rock salt that have no variable positional parameters. All bond distances and angles are completely specified if the lattice parameters are known. Most of the available bond expansion and compression data come from studies of the lattice variation of simple compounds with temperature and pressure because experiments to determine lattice expansion or compression are more easily performed than the complete structure determination.

Bridgman\(^{84}\) noted in 1923 that the bulk modulus of thirty metals was inversely proportional to the fourth power of the lattice constant. Anderson and Anderson\(^{85}\) examined this relationship for ionic compounds and found that experimental results were more consistent with bulk modulus proportional to the inverse of the molar volume (i.e., the third power of the lattice constant). The Anderson and Anderson results appear to be valid for a series of isostructural ionic compounds; however, the results are not easily applied to complex structures. It may be difficult, therefore, to relate a bulk property such as volume compressibility to properties of individual cation-anion bonds.

Hazen and Prewitt\(^{77}\) tested the Anderson
and Anderson relationship for subunits of a crystal structure by compiling compressibility data and plotting the mean results to 100 kbar versus the inverse of the polyhedral charge density (Fig. 2). The regression line represents the results for divalent cations in octahedral coordination; however, Si\(^{4+}\) and Al\(^{3+}\), which have different charge and coordination, deviate from the line. Additional high-pressure crystal-structure and compressibility data are now available and have led to a modified empirical expression that more successfully models the bond compression in polyhedral units for many types of compounds. This expression, given below, is in the form of a bulk modulus-volume relationship.

Volumes of polyhedral units in oxygen-based structures have been computed from structural and lattice parameters determined at high pressure for complex structures, as well as from the compressibilities of structures with no variable atomic positional parameters. The bulk modulus has been obtained for each polyhedron by fitting a first-order Birch-Murnaghan equation of state to the pressure-volume results. These calculated polyhedral bulk moduli for oxides and silicates, denoted by \(K_p\) rather than \(K_o\), have been plotted.

**Fig. 2.** Mean coefficients of compressibility vs. \(d^{3/2}\). Cations are given in the form described in Fig. 1. This figure is also from ref. 47.

**Fig. 3.** The bulk modulus-volume relationship for polyhedra in oxides and silicates. Triangles represent tetrahedra; crosses, octahedra; and circles, eight or greater coordination.
against \( <d>^3/z_c \) in Fig. 3, where \( <d> \) is the mean bond distance and \( z_c \) is the cation formal charge. Note that \( K_p \) and \( K_o \) are identical for simple structures. Polynuclear bulk moduli, \( K_p \), were first plotted versus polyhedral volumes, \( V_p \). Polyhedral volume, however, was discarded in favor of \( <d>^3 \), an entity with more obvious physical significance, yet with the same functional dependence. Weighted linear regression of all available cation-oxygen bond compression data yields:

\[
\frac{K_p <d>^3}{z_c} = 7.5 \text{ Mbar} \cdot \text{Å}^3.
\]  

(1)

The most significant deviations from the line (Fig. 3) occur for the least compressible bonds, specifically tetravalent cations in four-coordination. Other deviant points include monovalent sodium and potassium cations, which have large uncertainties in the effective coordination number and, consequently, the mean cation-oxygen distance, and trivalent vanadium in \( V_2O_3 \), an anomalous oxide with metallic conduction and metallic luster.

As demonstrated by Anderson and Nafe, bulk modulus-volume relationships may be extended to materials with anions other than oxygen if the anion formal charge, \( Z_a \), and effective "ionicity," \( S^2 \), are taken into account. If all oxides and silicates are assigned an ionicity of 0.5, the value of \( S^2 \) for other anions may be obtained by calculation of formulae similar to equation (1). For the present, ionicity is assumed to be constant for a given anion. With \( S^2 \) defined as 0.5 for oxygen-based compounds, then the value is approximately 0.7 for halides; 0.4 for sulfides, selenides, and tellurides; 0.25 for phosphides, arsenides, and antimonides; and 0.2 for carbides. Figure 4 illustrates the polyhedral bulk modulus-volume relationship:

\[
\frac{K_p <d>^3}{S^2z_c z_a} = 7.5 \text{ Mbar} \cdot \text{Å}^3,
\]  

(2)

which is derived from structural subunits in more than 100 compounds of approximately 20 different structure types. Several of these materials do not have structures with three-dimensional polyhedra (e.g., planar \( NO_3 \) groups), and an "effective polyhedral bulk modulus" was defined for these materials as:

\[
K_p \equiv \frac{1}{3\langle d \rangle}
\]  

(3)

where \( \langle d \rangle \) is the mean linear compressibility of the cation-anion bonds. The only structure type that deviates systematically from the linear relationship is that of \( CsCl \) in which a cube of anions at the corners of a unit cell is coordinated to a central cation. This structure is unusual in its high degree of face-sharing between polyhedra, which results in cation-cation distances only 15% longer than cation-anion bonds. Cation-cation repulsion in \( CsCl \)-type compounds, therefore, results in significantly greater polyhedral bulk moduli than those predicted by the line in Figure 4, which is valid only for polyhedra...
with weak second-nearest neighbor interactions.

An important consequence of equation (2) is that each polyhedron in a crystal is subjected to the full externally applied pressure. Otherwise, data from polyhedra in simple, constrained structures would not follow the same trends as those in more complex types. Another consequence of equation (2) is that the polyhedral bulk modulus for a given type of polyhedron (e.g., magnesium-oxygen octahedron) is similar in different structures, because

<\textit{d}>is similar in different structures.

An important application of equation (2) is the prediction of cation-anion bond-length variation with pressure. From this equation by itself, however, it is not possible to predict changes in molar volume with pressure. In addition to changes in cation-anion distance, cation-anion-cation bond angles may change with pressure. In structures with extensive corner-linking of polyhedra, as in alpha-quartz, the bulk modulus may be an order of magnitude less than the polyhedral bulk modulus owing to changes in Si-O-Si angles. In other compounds, including oxides, spinels, garnets, and other proposed mantle phases, polyhedra are linked by more rigid edge- or face-sharing. In these materials it may be possible to predict bulk moduli by appropriate linear combinations of moduli of the component polyhedra.

CONCLUSIONS--VARIATION OF STRUCTURE WITH TEMPERATURE, PRESSURE, AND COMPOSITION

High-pressure and high-temperature crystallography are providing important information about the variation of structure with changes in external conditions. High-pressure studies have led to a simple predictive relationship between polyhedral bulk modulus and bonding parameters. A similar empirical relationship for high-temperature bond-distance variation is now being developed.

It has been demonstrated that one effect on a structure of changing temperature and pressure is variation of the absolute, as
well as relative, sizes of component polyhedra. In this sense variations of crystal structure with temperature, pressure, and composition are analogous. This observation supports the simple model of a structure composed of polyhedral units. It appears that each polyhedron in most structures achieves a size based on temperature, pressure, and composition, largely independently of structural linkages. It may be possible, therefore, to predict the P-T-X variation of crystal structures simply by knowing the polyhedral equations of state. Furthermore, if phase stability can be related to geometrical parameters such as the size ratio of polyhedral units, then phase equilibria may be predicted from the known variation of polyhedra.

With the large number of high-temperature and high-pressure structures becoming available, it now seems likely that a coherent picture of the response of structures to temperature, pressure, and composition will soon emerge. The next steps are to systematize high-temperature results and to gain information from simultaneous high-temperature and high-pressure experiments. With such data the mineralogical crystallographer will be in a position to model materials under conditions equivalent to those within the Earth. What an exciting prospect!

REFERENCES


DISCUSSION

Q: (C. W. Burnham, Harvard University)
You didn't talk at all about thermal expansion of bonds, but with respect to the Si-O bond you mentioned that the simple distance between Si and oxygen seems not to expand with temperature. Unless I am mistaken, I believe that once these distances are corrected for thermal motion they do expand some. What are your thoughts about the importance of thermal motion corrections of this sort? Can we ignore these corrections?
A: In all the structures that I've seen, the bond distance remains essentially constant. The one study where the distance decreases with temperature is suspect. The temperature factors are increasing with increasing temperature in these structures, so that any sort of a thermal correction model that might be applied would make the average of the instantaneous bond distances longer. I don't really know what sort of a model should be applied. In answer to your second question, for the kinds of temperature factors that one finds for Si and oxygen to 1000°, I don't think a correction is that important. Thus for the moment we can safely ignore it.

Q: (S. Deganello, University of Chicago)
How is absorption corrected for during high-pressure experiments, and can corrections for thermal diffuse scattering effects be obtained by a systematic survey of high-temperature data that now exist?
A: The cell that we use has a very simple relationship between attenuation by the cell and the angle at which we are measuring the data on the four-circle diffractometer. The cell has an axis of radial symmetry and experimentally we see no violations of this radial attenuation. There are two angles that one needs to know—the angle between the radial axis of the cell and the incident beam, and the angle between the radial axis and the diffracted beam. Those quantities are
easily computed from the diffractometer angles and the attenuation is corrected in the on-line computer. In answer to your second question, I would say that developments in geophysics are making available to us fairly precise elastic constants for a wide variety of materials, so we do have the chance of making thermal diffuse scattering corrections.

Q: (S. Block, National Bureau of Standards) You mentioned combined temperature and pressure equation of state determinations. We did combined T-P work using powder methods on polyethylene a few years ago. You also showed some work on ruby to 40 kbars; are you familiar with the ruby work by the group at Stuttgart?
A: In answer to your question, there is more work that has been done on ruby by the Stuttgart group. Their results are similar to ours but with somewhat larger uncertainties in their parameters.

C: (M. O'Keeffe, Arizona State University) I'd like to make a comment about the silicate tetrahedron. You remarked that the Si-O distance didn't change very much with increasing pressure, and thus the Si-O bond must be very stiff. I think if you look at it from the point of view of Si being compressed, and oxygen having only two neighbors, the oxygen can just move a little bit---change the bond angle if you like---and the bond doesn't know it is being compressed at all.

Q: (G. E. Brown, Jr., Stanford University) The 50 kbar limit that you mentioned as the current upper limit of your diamond cell work gets us down to about 150 km depth into the Earth, which corresponds to the Earth's upper mantle. There are important mineral phases that occur below that depth, and I wonder what ultimate upper limit you foresee for the diamond cell you described that might permit an examination of these higher pressure phases?
A: The fundamental limit that we run into now is the upper limit at which we can have a fluid medium. Anytime we attempt to do crystallography on anything that is in a non-hydrostatic environment we get garbage. The volume of the unit cell that one might determine is correct, so it can be extrapolated with pressure. The only problem is that considerable lattice strain results. If you charge ahead blindly, attempt to measure intensities and try to refine a crystal structure, you get absolute garbage. Therefore we are limited to approximately 100 kbar at present until other liquids are found which remain fluid above the 104 kbar pressure limit of the 4:1 mixture of methanol-ethanol that we are using now. In terms of what can be done within our cell, there are developments at Stony Brook where

*Note added June 26, 1979: H. K. Mao and P. M. Bell, Geophysical Laboratory, have just found no broadening of the ruby line to 650 kbars when solid hydrogen is used as the "fluid." Application of similar techniques to single-crystal experiments should increase the hydrostatic pressure range.
a less pure form of Be seat material that is much stronger is being used. This seat raises routine operation to pressure of at least 80 kbar. We are changing to that style and are, in addition, changing the design of our cell slightly to give us better directional control for the steel backing so the alignment of our diamonds will be improved. We should, therefore, be able to get marginally higher pressures. There is another problem associated with high-pressure apparatus, in that the way you achieve the pressure is to extrude the gasket ever so slightly to compress the liquid so that the pressure is transmitted to the crystal. At high pressures, one has the tendency to thin the gasket to the point that you can't get a significant volume of crystal in the cell without bridging the diamond anvils. I think that routinely one can go to 80 kbar and soon to 100 kbar without much difficulty.