#45

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 systematics 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.[1] Recent designs that utilize resistance heaters to reach temperatures of 1000-1200°C have been reported[2] with a temperature stability of a few degrees Celsius. Temperatures as high as 2000°C can be reached if a flame heater is used[3], although thermal stability is

reduced. These devices have been used to study the thermal expansion, crystal structures, and phase transitions at high temperature for many minerals.[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.[42] Recent advances in measurement of Brillouin scattering from small crystals[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[44] (see also Deganello[45]) examined the theoretical basis for lattice expansion, and Lager[46] considered aspects of cation polyhedral expansion. In the most extensive compilation of high-temperature structure data to date, Hazen and Prewitt[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 $1000^\circ C$ 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
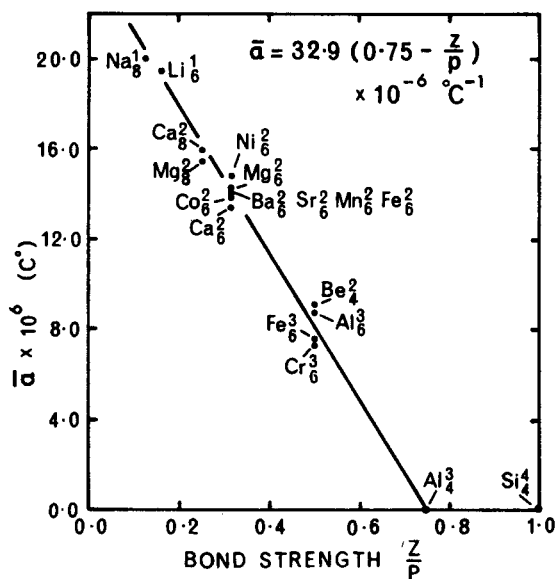

Fig. 1. Mean coefficients of thermal expansion vs. bond strength (z/p). Cations are given in the form PR_z, where $\underline{z}$ is the cation charge, and $\underline{p}$ is the coordination number (from ref. 47).

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;[40] 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, escolaite 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[47] 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 com-
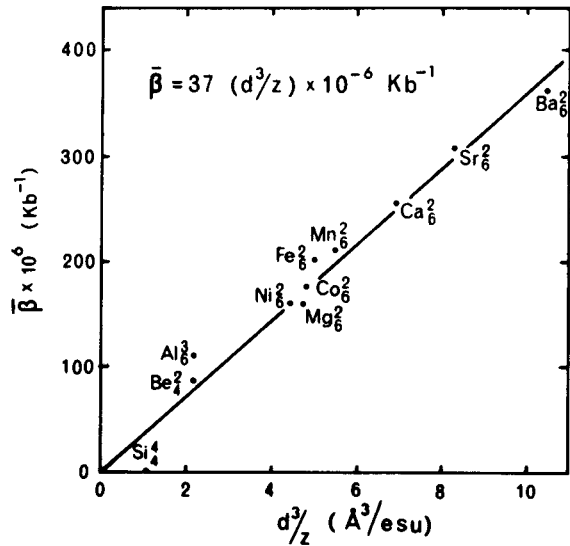

Fig. 2. Mean coefficients of compressibility vs. d ^{3}/z. Cations are given in the form described in Fig. 1. This figure is also from ref. 47.

pounds. 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_0, have been plotted
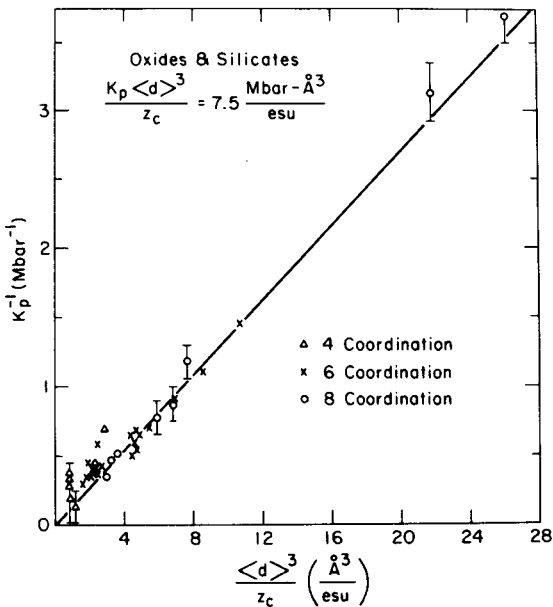

Fig. 3. The bulk modulus-volume relationship for polyhedra in oxides and silicates. Triangles represent tetrahedra; crosses, octahedra; and circles, eight or greater coordination.

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_0 are identical for simple structures. Polyhedral 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:

$$\frac{K_p<d>^3}{z_c} = 7.5 \text{ Mbar-Å}^3. \qquad (1)$$

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[86] and metallic luster.

As demonstrated by Anderson and Nafe[87] and Anderson,[88] 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:

$$\frac{K_p<d>^3}{S^2 z_c z_a} = 7.5 \text{ Mbar-Å}^3, \qquad (2)$$

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:

$$K_p \equiv \frac{1}{3\beta\underline{\ell}} \qquad (3)$$

where $<\beta\underline{\ell}>$ 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
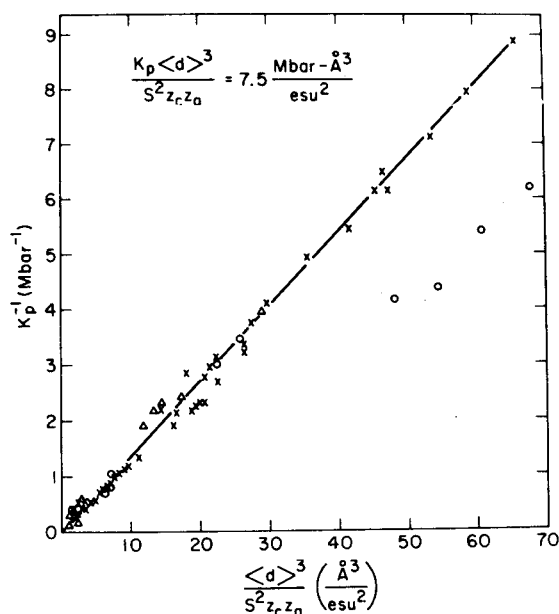
Fig. 4. The bulk modulus-volume relationship for polyhedra in a variety of materials. Triangles, crosses, and circles indicate coordination as in Fig. 3.

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

<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.[89] 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.[73,74] 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.[90] 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.[91,92]

   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!

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DISCUSSION

Q: (C. W. Burnham, Harvard University)
You didn't talk at all about thermal ex-
pansion 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 mis-
taken, 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 correc-
tions of this sort? Can we ignore these
corrections?

A: In all the structures that I've seen,
the bond distance remains essentially con-
stant. 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 tempera-
ture factors that one finds for Si and
oxygen to $1000^\circ C$, I don't think a correc-
tion is that important. Thus for the mo-
ment we can safely ignore it.

Q: (S. Deganello, University of Chicago)
How is absorption corrected for during
high-pressure experiments, and can cor-
rections 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 mea-
suring the data on the four-circle dif-
fractometer. 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 vol-
ume 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.