

Chapter 9

HIGH-PRESSURE CRYSTAL CHEMISTRY

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INTRODUCTION

The response of earth materials to increasing pressures and temperatures is an area of research that is of interest to many investigators in geochemistry and geophysics. There have been many scientific pioneers including Bernal, Goldschmidt, Bridgman, Birch, and Ringwood, who made essential contributions to understanding how earth materials combine, disassociate, and transform as environmental conditions change. However, it is only in the past 10-20 years that we have had access to the experimental and theoretical tools that allow us to confirm or dispute the ideas of the pioneers and to make a priori predictions of what will happen when a particular mineral composition is subjected to specific conditions of temperature, pressure, or stress. These developments include new instrumentation for x-ray diffraction and spectroscopy, particularly synchrotron sources, but also new laboratory-based systems with improved x-ray optics and detectors. Neutron scattering sources are built and maintained by national governments, but made available to a wide community of scientists, including earth scientists. Raman, infrared, Brillouin, and Mössbauer spectroscopic techniques have improved substantially, techniques for quantitative chemical and isotopic analysis are accurate and reliable, and powerful digital computers with sophisticated software are available almost everywhere. Thus, we have an astounding array of scientific facilities available to us for, we hope, making astounding discoveries.

The most abundant elements in the Earth are O, Si, Fe, and Mg, and consequently, the most abundant minerals in the Earth contain these elements as major components. As a result, much current research at high pressure involves these elements, the phases they form, and the transitions that take place as we simulate Earth's interior in laboratory apparatus or in computers. The phases of magnesium-iron silicates serve as model systems for studies of high-pressure structures, phase transitions, vibrational dynamics, and chemical bonding. In view of the wide-ranging importance of the high-pressure behavior of oxides, silicates, and sulfides, the literature on this subject is extensive and growing, but far from complete. Recent discoveries include new phases, electronic and magnetic transitions, contrasting results from hydrostatic or differential stress, insight to the role of hydrogen, and how specific phases respond to changing conditions. Thus, there is much new interest in the high-pressure behavior of minerals, with important implications for geology, planetary science, materials science, and fundamental physics. The goal of this chapter is to explore the crystal chemical constraints imposed by the high temperatures and high pressures within the Earth and to provide an overview of the dominant phases

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resulting from mixtures of the major elements under these conditions. We will also discuss the methods used to study crystal structures of minerals under extreme conditions.

An Appendix is included at the end of this chapter that provides the cell parameters, space groups, and atom coordinates for the principal mineral phases of the mantle and core. Although these are parameters derived at ambient conditions, it is felt that they will be useful to those who want to explore the structures more thoroughly using one of the excellent programs now available for displaying and manipulating crystal structures on personal computers.

HIGH-PRESSURE EFFECTS ON BONDING AND COORDINATION NUMBER

Most physical properties of crystalline materials can be understood by examining their crystal structures and the nature of the bonding, i.e. its crystal chemistry. In order to simplify the chemistry and physics involved in high-pressure crystal chemistry we have assembled a set of high-pressure crystal chemical rules of thumb to guide our understanding. Perhaps the starting point for such a set are the rules put forward by Linus Pauling, known as Pauling's Rules. It is assumed that the reader is familiar with these because they are summarized and discussed in most introductory mineralogy texts (see, for example, *Crystallography and Crystal Chemistry*—Bloss 1994).

Rules of thumb

1. *A structure usually compresses by displaying the greatest distortion between atoms separated by the weakest bonds.* Imagine that a crystal structure is composed of spheres separated by springs, each with a given strength, or force constant. In general it is sufficient to assume that the springs exist between nearest neighbors and next-nearest neighbors. For example, within SiO_4 groups in quartz, the nearest neighbor springs are between Si and O and next-nearest neighbor springs are between the six pairs of O atoms. These next nearest neighbor interactions can often be thought of in terms of bond bending. So the O-O springs in SiO_4 tetrahedra are associated with O-Si-O angle bending. A structure usually compresses by displaying the greatest distortion between atoms separated by the softest force constants. In quartz, the force constants can be ranked as stiffest for the SiO bond, then the O-Si-O angle, and weakest for the Si-O-Si angle. Therefore the greatest change in the structure with application of pressure will be the Si-O-Si angles.

2. *Short bonds are the strongest, and long bonds are the weakest.* The force constants between bonded pairs of atoms often can be quickly estimated by examining their separations. Hill et al. (1994) demonstrated that the magnitudes of the bonding force constants in molecules and crystals of nitrides, oxides and sulfides vary in a systematic fashion, with short bonds displaying the largest force constants and long bonds displaying the smallest. The equation for the force constant F_{MX} between a pair of atoms, M and X, is given as:

$$F_{MX} = 7500 \cdot R(MX)^{-5.4} \text{ N/m,}$$

where the bond length, $R(MX)$, is expressed in Ångströms.

3. *As a given bond compresses it becomes more covalent.* This results from the observation that if the distance between a given pair of atoms decreases then the electron density between the atoms must increase in order to keep the bond stable. Gibbs et al. (1994) have shown that such an increase in the electron density between a bonded pair of

atoms comes laterally from the region normal to the bond, and not from along the bond. This makes sense because it is largely the valence electrons that provide the bonding.

4. Increasing pressure increases coordination number. Above some point the changes in pressure eventually result in changes in the coordination numbers of the atoms. For example, SiO_4 groups transform to SiO_6 groups with sufficient increase in pressure. An increase in coordination number is usually accompanied by a lengthening of the bonds. For example, $R(\text{Si}^{\text{IV}}\text{O}) = 1.62 \text{ \AA}$ in quartz while $R(\text{Si}^{\text{VI}}\text{O}) = 1.78 \text{ \AA}$ in stishovite. However, the O—O separation usually decreases: it is 2.63 \AA in quartz and 2.51 \AA in stishovite. In addition, the change in coordination number is usually accompanied by an increase in the ionic character of the bond.

5. The oxygen atom is more compressible than the cations. Total electron density calculations for coesite and stishovite show that the bonded radius of the oxygen atom decreases by 0.20 \AA while the radius of the Si atoms decreases by 0.02 \AA with the change in coordination from Si^{VI} to Si^{IV} (Nicoll et al. 1994). This is consistent with Pauling's radius ratio rule. For the coordination number of Si to increase from 4 to 6 requires that the ratio of $r(\text{Si})/r(\text{O})$ increase. This can occur only if $r(\text{O})$ decreases relative to $r(\text{Si})$. The reason that oxygen is more compressible than the cations is not related to the size of the atoms but rather to the slope of the electron density in the bonding region. The electron density of oxygen falls off rather rapidly compared to the electron densities around cations, which fall off slowly. Therefore, as a bond is compressed and shortened it appears that the size of the oxygen shrinks relative to the cation.

6. Angle bending is dependent upon coordination. Little is known about angle bending force constant systematics. For example, molecular orbital calculations show that Si-O-Si angles are stiffer than Si-O-Al but weaker than Si-O-B (Nicholas et al. 1992). This observation may be related to the distance between cations as discussed earlier in rule #2. However, we also know that if a bridging oxygen atom is coordinated to yet a third atom then the force constant of the angle increases dramatically (Geisinger et al. 1985). Such effects are observed while compressing framework structures such as the feldspar minerals and may also be related to garnet compressibility systematics.

7. O-O packing interactions are important. Inter-tetrahedral O-O interactions are known to be very important in understanding the compression of silica framework structures. For example, work by Lasaga and Gibbs (1987) and Boisen and Gibbs (1993) using force field calculations could not replicate experimental compression behavior for silica polymorphs unless strong O-O repulsion terms were included in the energy calculations. All first principles and ionic model calculations include the O-O interactions implicitly, but little systematic work has been done to quantify the magnitude of its importance. For instance, olivines are closest-packed structures and yet the compressibility has been studied in terms of the bonding in the octahedral and tetrahedral sites. It may be that its compressibility is determined principally by O-O interactions.

8. High-pressure structures tend to be composed of closest-packed arrays of atoms. Application of pressure on a crystal structure forces the atoms to occupy a smaller volume. Closest-packed structures are the densest arrangement of atoms and therefore high-pressure structures tend to be composed of closest-packed arrays of atoms. For oxide minerals this means that the structures found deep in the Earth are generally closed-packed arrays of oxide atoms, with short-ranged metal-oxygen bonding perturbing the arrangement. Pressure forces the oxygen atoms into more regularly close-packed arrangements, but the cation-oxygen bonds influence how they get there. For example, in their study of kyanite, Yang et al. (1997) found that the arrangement of oxygen atoms became more closest-packed under pressure. They computed a best fitting ideal closest-packed array of oxygen

atoms to the observed structure as a function of pressure by minimizing the distance between the observed atomic positions and those in the ideal array by varying the radii and orientation of the ideal array. The result produced a value for the radius of oxygen and an isotropic root-mean square displacement parameter that describe the deviation of the structure from ideal. They found that the oxygen atoms became more closest-packed, with $U_{\text{iso}} = 0.0658 \text{ \AA}$ at room pressure and $U_{\text{iso}} = 0.0607 \text{ \AA}$ at 4.5 GPa. Furthermore the radius of the oxygen atom decreases from 1.372 \AA to 1.362 \AA . The compression was anisotropic, with the most compressible direction oriented parallel to the direction of the closest-packed planes that were furthest apart. Another example is quartz, SiO_2 . Quartz traditionally represents the prototype framework structure with its corner-linked SiO_4 groups and is never called a closest-packed structure. Yet as pressure is applied the O atoms tend to arrange themselves in closest packed layers, oriented parallel to (1 20) (Hazen et al. 1989).

9. *Elements behave at high pressures like the elements below them in the periodic table at lower pressures.* For example, at high pressure Si behaves like Ge does at low pressure. Because of this observation, many studies of germanate compounds have been conducted as high-pressure silicate analogues in days past because sufficiently high-pressure experimental conditions were unattainable. The germanates tend to display structures that are similar to silicates and undergo similar phase transformations at more modest pressures. This can also be understood in terms of softer anions with Pauling's radius ratio rule. Upon application of pressure to, say a SiO_4 group we see that the $r(\text{O})$ decrease at a faster rate than the $r(\text{Si})$ and so $r(\text{Si})/r(\text{O})$ increases. However, at ambient conditions $r(\text{Ge}) > r(\text{Si})$ so the ratio of $r(\text{Ge})/r(\text{O})$ is already greater than for Si-O. This rule of thumb may also apply to oxygen and sulfur inasmuch as sulfides at room pressure appear to behave like oxides at high-pressure. For example, it is known that S-S bonding in sulfides is prevalent, e.g. pyrite. Recent work has shown that at high pressures O-O bonding can be found in low quartz (Gibbs et al., submitted).

As with many rules of thumb, ours are not laws of nature because the behavior of crystalline materials can often be quite complicated. These rules are provided as a guide of what first to think about when pressure is applied. Departures from the rules often can indicate the presence of multiple interactions, which are, of course, the most exciting to investigate. For every one of these rules of thumb we could probably find an exception. For example, GeO_2 does not crystallize with the coesite structure. Even though closest packing is the most efficient way to pack atoms, many elemental phases (such as Pb) convert to a body-centered structure at high-pressure. Ideal MgSiO_3 perovskite is cubic and can be regarded as composed of a closest-packed array of O and Mg with Si in the octahedral voids. However, it actually is found to be orthorhombic, with distorted closest packing, which deviates even more with pressure. The reasons are interesting, and can be related to the differences in the force constants between O-O, Si-O and Mg-O.

COMPARATIVE COMPRESSIBILITIES

When analyzing the behavior of a crystal structure with changes in pressure, it is useful to understand how the relative sizes of atoms (ions) change. Measurements of the change of a unit cell as pressure increases can be obtained rather easily. However, it is more difficult to determine the change in individual ions, not only because of experimental difficulties, but also because assumptions have to be made about whether the changes take place in cations or anions, or both. There has been extensive discussion in the scientific literature about how one defines the radius of a cation or anion, ranging from empirical assignments of a specific radius to oxygen ions (Shannon and Prewitt 1968), to relatively sophisticated molecular orbital calculations (Nicoll et al. 1994). Except for structures with no variable atom coordinates (e.g. NaCl), information on compression of interatomic

distances has to be obtained from accurate crystal structure determinations as a function of pressure (and/or temperature).

In general, compressibility of a cation or an anion is proportional to the size of the ion and the coordination number, and inversely proportional to the charge on the ion. Thus, eight-coordinated Na^+ is much more compressible than tetrahedrally-coordinated Si^{4+} . The systematics of ionic compressibility are described in detail by Hazen and Finger (1979, 1982). They give the relation (converted from Mbar to GPa)

$$\frac{K_p d^3}{z_c} = 750 \pm 20 \text{ GPa-}\text{\AA}^3$$

where K_p is the polyhedral bulk modulus in GPa d is the mean cation-anion distance in \AA , and z_c is the integral formal charge on the cation. The polyhedral bulk modulus is obtained by calculating the volume of two coordination polyhedra in a structure at different pressures and using

$$K_p = -\frac{(V_1 + V_2)}{2} \left(\frac{\Delta P}{\Delta V} \right)$$

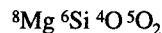
where $(V_1 + V_2)/2$ is the average volume of the two polyhedra being compared. This relation can provide semiquantitative insight into how different cation polyhedra will behave under compression, but it should be noted that the assumption here is that the concept of macroscopic ("continuous") moduli can be transferred to the atomic scale.

MECHANISMS OF PHASE TRANSITIONS

One of the more interesting aspects of crystal chemistry at high pressures and temperatures involves phase transitions that are accompanied by changes in physical and chemical properties of the phases involved. Phase transitions are very important in studies of Earth's interior because they involve changes in elastic properties and densities of minerals that can be detected via the analysis of seismic waves created by earthquakes and thus provide information about the inner structure of the Earth. One goal of mineral physics investigations is to study relevant phase changes in the laboratory and to attempt to understand why they take place under specific conditions of pressure, temperature, and varying composition.

From a crystal structural point of view, phase transitions are generally described as *reconstructive* or *displacive*, and from a thermodynamic perspective as *first-order* or *second-order* (Buerger 1961). The fundamental definition of a reconstructive transition involves breaking of bonds and can range from a relatively subtle change in a structure to a very drastic one. In contrast, a displacive transition is one that does not involve breaking of existing bonds and creation of new ones, but only involves a shifting of the atomic positions, possibly with a symmetry change. It is incorrect to equate reconstructive with first-order and displacive with second-order, because there are examples where differences are subtle and it is not possible to make such comparisons. There are, for example, displacive transitions that are accompanied by discontinuities in lattice parameters, which indicates that they are also first-order transitions. Other descriptions of phase transitions include *martensitic* (one involving a tilt or distortion of the structure and mostly applied to metals and alloys) and *soft mode* (where one or more modes in, say, a Raman spectrum disappear at the transition). A more complete discussion of phase transition theory is not warranted in this chapter, but the reader should be aware that these categories do exist and are discussed extensively in the literature.

A major aspect of high-pressure phase transitions is the increase in cation and anion coordination as a function of increasing pressure. Emphasis is usually placed on changes in cation coordination, but anion coordination must also increase, as described by the formula for magnesium silicate perovskite:



Thus, the total coordination of the cations is $8 + 6 = 14$, and for oxygen is $4*1 + 5*2 = 14$. This relation holds for all phase transitions and it should be noted that in some structures crystallographically-different oxygens or other anions may have different coordination numbers. Shannon and Prewitt (1968) showed that as coordination of an ion increases, the average interatomic distances to that ion also increase, an apparent paradox for a transition where the density of the high-pressure phase is always higher. It works out satisfactorily, however, because the ions in the high-pressure phase must always be packed together more efficiently. Several other examples for MgSiO_3 phases are

Enstatite	${}^6\text{Mg } {}^4\text{Si } {}^3\text{O}_2 \text{ } {}^4\text{O}$	$6*1 + 4*1 = 3*2 + 4*1$
Majorite	${}^8\text{Mg}_3 \text{ } {}^6(\text{MgSi}) \text{ } {}^4\text{Si}_3 \text{ } {}^4\text{O}_{12}$	$8*3 + 6*2 + 4*3 = 4*12$
Ilmenite	${}^6\text{Mg } {}^6\text{Si } {}^4\text{O}_3$	$6*1 + 6*1 = 4*3$

One other feature related to coordination number is the geometrical relation of the coordinating ions to each other. In high-pressure phases the four- and six-coordinating groups almost always form tetrahedra or octahedra. Five-coordinated cations are relatively unusual although one Al site in andalusite can be described as a trigonal bipyramid and Angel et al. (1996) and Kudoh et al. (1998) reported that a phase transition in CaSi_2O_5 at about 0.2 GPa results in five-coordinated Si. In MgSiO_3 perovskite, oxygen is coordinated by three Mg and two Si in a rectangular pyramid with two Mg and two Si forming the base and the other Mg at the apex. The Mg coordination in this structure is sometimes referred to as dodecahedral (Poirier 1991), but it is perhaps better described as a bicapped trigonal prism with the six closest oxygens forming a trigonal prism and the next two closest oxygens positioned outside two of the prism faces. In contrast to the one in perovskite, the polyhedron around Mg in majorite is a slightly distorted triangular dodecahedron with eight vertices and twelve triangular faces. There are, of course, other geometrical arrangements in high-pressure phases, but these are the ones most common in mantle phases.

ANALYTICAL TECHNIQUES

X-ray diffraction is the most important analytical tool used to gain information on the crystallographic properties of high-pressure phases. The approach used to learn about the crystal chemistry of high-pressure, high-temperature phases depends on the objectives of the investigation and upon the tools available. For example, much information can be derived from examination of quenched high-pressure phases if the material in question retains the high-pressure structure upon quench. However, there are limitations to this approach, including the fact that the unit cell and interatomic distances in a quenched phase are different from the ones in the material before the quench. Furthermore, it is always possible that the symmetry and/or crystal structure undergo significant changes upon quench even though the material remains crystalline—in many examples single crystals remain single through one or more phase transitions as external conditions are varied.

For in situ single-crystal diffraction experiments at high pressures and/or high temperatures, the most common device used to apply pressure is the Merrill-Bassett (Merrill and Bassett 1974) diamond-anvil cell. This cell employs a simple clamping mechanism to push together two brilliant-cut diamonds that are positioned on either side of a hole in a metal gasket that contains the crystal being studied. The crystal is suspended in a pressure

medium that is usually a mixture of ethanol and methanol, although other organic liquids, water, or cryogenic liquids of noble elements such as neon, argon or helium are sometimes used when loading a diamond cell. In order to provide as large an opening for incident and diffracted x-rays as possible a beryllium disk that is relatively transparent to x-rays backs each diamond. One disadvantage of this is that the resulting polycrystalline diffraction pattern and associated diffuse scattering from beryllium must be accounted for in the data analysis. Using this approach pressures up to 10 GPa can be obtained to record good-quality single-crystal intensity data on a routine basis; pressures as high as 33 GPa have been reported (Zhang et al. 1998).

Applying simultaneous elevated pressures and temperatures for a single-crystal experiment is more difficult than for either pressure or temperature alone. Heat is generally applied with resistance wire wrapped around the diamonds and temperatures to about 600°C can be reached. Because beryllium and other metals weaken at high temperatures and because beryllium oxide vapor is poisonous, investigators have generally used other materials for the backing disk. One such material is B₄C, which is a ceramic that transmits x-rays, but is brittle and will crack and break at pressures higher than about 2-4 GPa.

Some of the above limitations may be overcome with the growing use of synchrotron radiation for high-pressure work. There have been relatively few high-pressure single-crystal experiments conducted at synchrotron x-ray sources [examples are by Mao and Hemley (1996) on stishovite at 65 GPa and by Loubeyre et al. (1996) on H₂ crystals at 119 GPa], and even fewer that involved recording of accurate diffraction intensities for structure determinations or refinements. However, the production of shorter x-ray wavelengths at synchrotrons, improvements in beam stability, and increasing availability of area x-ray detectors capable of recording high-energy radiation make such investigations appear feasible. The shorter wavelengths make it possible to collect sufficient diffraction data in a more restricted angular range of incident and diffracted x-ray beams. In the future this may allow the construction of diamond cells that do not require beryllium backing disks. Diamonds can be mounted directly on tungsten carbide plates having conical apertures for the x-rays to enter and leave the cell. Not only will this decrease the background x-ray scattering, it should also permit inclusion of resistance heaters to provide temperatures up to at least 800°C.

Powder x-ray diffraction

In contrast to single-crystal investigations at high pressure, there have been relatively few powder structure determinations at high-pressure using conventional laboratory apparatus. For many years, high-pressure powder diffraction experiments were confined to recording changes in cell parameters and detecting the occurrence of phase transitions because the only available diffraction tools were sealed-tube x-ray generators and film or scintillation detectors that resulted in inefficient recording of diffraction patterns. In the past 10 years however, new developments in x-ray optics, x-ray generators, synchrotron x-ray sources, detectors, computer control, and analytical software have changed the situation drastically. Improved diamond cells and the ability to reduce the amount of sample required (~10 μm) because high-intensity micro x-ray beams can be focused to the same size as the sample result in the ability to obtain good diffraction patterns on polycrystalline samples at pressures in the 1-3 megabar range. Although most of these kinds of experiments are now being done at synchrotron sources, Hasegawa and Badding (1997) showed that it is possible to collect satisfactory data with a laboratory rotating-anode generator, an x-ray monochromator, and x-ray film as a detector. With further developments of focusing optics, x-ray generation, and either imaging plates or CCD (charge-coupled device)

