

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

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