American Mineralogist, Volume 81, pages 1021–1035, 1996

REVIEW

Effects of pressure on order-disorder reactions

ROBERT M. HAZEN[1] **AND ALEXANDRA NAVROTSKY**[2]

[1]Geophysical Laboratory and Center for High Pressure Research, Carnegie Institution of Washington,
5251 Broad Branch Road NW, Washington, DC 20015-1305, U.S.A.
[2]Department of Geological and Geophysical Sciences and Center for High Pressure Research,
Princeton University, Princeton, New Jersey 08544, U.S.A.

ABSTRACT

Order-disorder phenomena, which play a key role in the energetics, crystal chemistry, and physical properties of numerous solids, may be strongly affected by pressure. The effect of pressure on the state of cation order depends fundamentally on the volume of disordering, $\Delta V_{\mathrm{dis}} = V_{\mathrm{disordered}} - V_{\mathrm{ordered}}$. Although ΔV_{dis} may be positive or negative, it is usually positive for cation ordering in rock-forming minerals; pressure, therefore, tends to increase order in geological systems. Three structural mechanisms that contribute to ΔV_{dis} are (1) positive ΔV_{dis} (typically $\leq 1\%$) associated with ordering of similar cations over two or more similar sites, (2) variable ΔV_{dis} ($-1\% \leq \Delta V_{\mathrm{dis}} \leq 1\%$) associated with Al-Si tetrahedral ordering in framework minerals, and (3) large ΔV_{dis} (up to 5%) associated with cation ordering involving mixed valence, mixed coordination, or both. Pressure alters order-disorder reaction rates by restricting cation motions or changing cation diffusion mechanisms. Influences of pressure on ordering in olivines, orthopyroxenes, high-pressure ferromagnesian silicates, spinels, garnets, perovskites, and rhombohedral carbonates are discussed. Several experiments are proposed to elucidate the phenomenon of high-pressure ordering in systems of mineralogical interest.

INTRODUCTION

Order-disorder phenomena play a key role in the energetics and crystal chemistry of numerous solids, including alloys, ferroelectric materials, fullerenes, high-temperature superconductors, and rock-forming minerals. Variations in degree of ordering result in changes in free energy and, therefore, affect phase stability. Transitions between disordered and ordered states, furthermore, can alter crystal symmetry and cause significant changes in physical properties, including thermal and electrical conductivity, vibrational spectra, and elastic moduli.

Order-disorder behavior has traditionally been considered in terms of its temperature and compositional dependence. Recent studies, however, suggest that ordering in many crystals is strongly affected by pressure as well. High-pressure synthetic crystals of olivine (Aikawa et al. 1985), wadsleyite (Finger et al. 1993), garnets (Hazen et al. 1994), and anhydrous phase B (Hazen et al. 1992), for example, display cation ordering to an extent that is not generally observed in analogous low-pressure phases. Other materials, including binary metal alloys (Owen and Liu 1947), spinels (O'Neill and Navrotsky 1983), framework silicates (Smith and Brown 1988), orthopyroxenes (Domeneghetti et al. 1995), and carbonates (Capobianco et al. 1987), experience significant variations in molar volume with changes in the state of order, behavior that implies an important role for pressure in ordering phenomena.

Pressure-induced ordering has implications for studies in materials science, geophysics, and solid-state physics. In materials science, an understanding of pressure-induced ordering could lead to new techniques for tuning the properties of synthetic materials such as ferroelectrics and cuprate superconductors. In geophysics, recognition of high-pressure ordered states in the oxides, silicates, and metal alloys that form much of the Earth's deep interior is essential for developing realistic models of the transport properties and dynamic behavior of our planet. In solid-state physics, high-pressure order-disorder behavior may provide a sensitive indicator of relative changes in the nature of interatomic potentials. The objective of this review is to examine structural and thermochemical aspects of high-pressure ordering, to summarize existing high-pressure data on order-disorder reactions, and to suggest needs and opportunities for future research.

Types of crystallographic order-disorder transitions

Each atom in an ideally ordered crystal occurs in a specific position and chemical environment—a crystallographic site that repeats identically, essentially to infinity. From a crystallographic point of view, four kinds of

0003–004X/96/0910–1021$05.00

disorder phenomena that may affect the regularity of a stoichiometric crystal are commonly cited in the literature: positional disorder, rotational disorder, distortional disorder, and substitutional disorder. Note, however, that the distinctions between these phenomena in many cases may be somewhat arbitrary.

(1) Positional disorder: All atoms experience some dynamic positional disorder as a result of thermal vibrations. In addition, static positional disorder occurs in some crystals when an atom occupies slightly different mean positions in different unit cells. In the alkali feldspar albite, $NaAlSi_3O_8$, for example, Na atoms adopt four distinct positions, depending on the local arrangement of Al and Si (Winter et al. 1977).

(2) Rotational disorder: The closely related phenomenon of rotational disorder occurs in molecular crystals such as high-pressure H_2 (Mao and Hemley 1994) and C_{60} (Fischer and Heiney 1993), in which the molecules have no fixed orientation but rotate more or less freely, increasing the entropy of the phase. Rotational disorder may also occur about a specific axis, as observed for CO_3 groups in some rhombohedral carbonates (Ferrario et al. 1994).

(3) Distortional disorder: Distortional disorder, which is also closely related to thermal disorder, may occur in structures like α-SiO_2, quartz, that can distort in more than one equivalent way from a high-symmetry form (Kihara 1990). High-symmetry structures may thus represent a dynamic or static distortionally disordered averaging of unit cells that are, locally, in the low-symmetry configuration. This type of disorder abounds in perovskite-type structures.

(4) Substitutional disorder: Substitutional disorder, which is the primary focus of this study, results from the interchange of different atoms over two or more sites. These sites are crystallographically distinct in the ordered phase but may be either distinct or equivalent (on the average) in the disordered phase. In the classic example of Cu-Au alloys (see, e.g., Hume-Rothery et al. 1969; Rahman 1994), the disordered structure features a random distribution of Cu and Au on a single symmetrically distinct site. Ordered forms, such as CuAu and Cu_3Au, on the other hand, possess a lower symmetry, with at least two crystallographically distinct sites. Numerous rock-forming minerals, including ferromagnesian silicates, spinels, feldspars, and carbonates, exhibit this type of disorder, as discussed below.

Any change in the degree of substitutional disorder requires atoms to move from one site to another in the structure, generally a distance of several angstroms. This situation contrasts with changes in positional and distortional disorder, in which only a very small shift in atomic coordinates is required (generally <0.5 Å). As a result, an energy barrier must be overcome for intracrystalline diffusion to occur and substitutional order to change. Consequently, order-disorder transitions of this kind are often sluggish.

Substitutional disorder also occurs in nonstoichiometric crystals, which are defect structures with partial disorder. Defects in these structures may occur as missing atoms (vacancies), as in the case of wüstite $Fe_{1-x}O$ (Hazen and Jeanloz 1984) and the oxide superconductor $YBa_2Cu_3O_{7-x}$ (Hazen 1990). Alternatively, interstitial atoms may occur, as observed in the excess O of La_2NaO_{4+x} (e.g., Chaillout et al. 1989).

Other types of order-disorder transitions

Structural order-disorder reactions may also occur in materials that are not strictly crystalline, including quasicrystals, liquid crystals, plastics, and amorphous phases (Venkataraman et al. 1989). In most cases these transitions are analogous to those in more regular crystals.

Of special interest are recently documented examples of molecular compounds in which pressure stabilizes highly ordered crystalline arrangements of dissimilar atoms or molecules—mixtures that form fluids at room temperature and lower pressures. Examples include van der Waals compounds such as $He(N_2)_{11}$ (Vos et al. 1992), $Xe(He)_2$ (Barrat and Vos 1992), $Ne(He)_2$ (Loubeyre et al. 1993), and $Ar(H_2)_2$ (Loubeyre et al. 1994), high-pressure clathrates such as those in the systems He-H_2O (Londono et al. 1988) and H_2-H_2O (Vos et al. 1993), and molecular compounds such as $(O_2)_3(H_2)_4$ (Loubeyre and LeToullec 1995) and phases in the H_2-CH_4 system (Somayazulu et al. 1996).

In addition to structural order-disorder, which involves the positions of atoms, a variety of electronic and magnetic order-disorder effects are known. Indeed, these phenomena, which include the Verwey transition in Fe_3O_4 and related spinels (see, for example, Kakol et al. 1992), electron delocalization (for example, the insulator-to-metal transition in VO_2; Pintchovski et al. 1978), and spin unpairing, as in Co_3O_4 and $CaFeO_3$ (O'Neill 1985; Takano et al. 1991; Mocala et al. 1992), provide the focus for most condensed matter research on ordering. Electronic and magnetic transitions have usually been studied as a function of temperature, though there have been some high-pressure investigations (see, for example, Skelton et al. 1994; Harada et al. 1994; Kelso and Banerjee 1995). Because the change in electronic state involves a volume change, metallization and spin-pairing reactions may become favorable at high pressure when ΔV of ordering is positive (see below).

SIGNIFICANCE AND STRUCTURAL ORIGINS OF ΔV_{dis}

The effect of pressure on the state of order depends fundamentally on the volume of disordering, ΔV_{dis}, which may be defined as

$$\Delta V_{\text{dis}} = V_{\text{disordered}} - V_{\text{ordered}}. \tag{1}$$

Combining the first and second laws of thermodynamics,

$$\delta G = -S\delta T + V\delta P. \tag{2}$$

It follows that

TABLE 1. Volumes of disordering, ΔV_{dis}, for various minerals

Structure	Formula	Sites	Ions	V_{dis} (cm³/mol)*	ΔV_{dis} (cm³/mol)*	% change*	References
Cu-Au alloy	Cu_3Au	12-fold	Cu,Au	31.64	0.13	0.4	Owen and Liu (1947)
	CuAu	12-fold	Cu,Au	17.4	0.15	0.8	Johansson and Linde (1936) and JCPDS card 25-1220
Olivine	$(MgFe)SiO_4$	oct	Mg,Fe	44.9	0.24	0.5	Akamatsu et al. (1993)
	$(MgMn)SiO_4$	oct	Mg,Mn	46.2	−0.6	−1.3	Akamatsu et al. (1988)
	$(MgNi)SiO_4$	oct	Mg,Ni	43.1	0.4	0.9	Ottonello et al. (1989)
Orthopyroxene	$(MgFe)Si_2O_6$	oct	Mg,Fe	64.4	0.3	0.5	Domeneghetti et al. (1995)
Spinel**	$ZnAl_2O_4$	oct and tet	Zn,Al	40.2	0.40	1.0	O'Neill and Dollase (1994)
	$NiAl_2O_4$	oct and tet	Ni,Al	39.1	0.36	0.9	O'Neill et al. (1991)
	$MgFe_2O_4$	oct and tet	Mg,Fe	44.7	0.54	1.2	O'Neill and Navrotsky (1983) and O'Neill et al. (1992)
	Mg_2SiO_4	oct and tet	Mg,Si	39.5	slightly +	0.1	Smith and Brown (1988)
Pseudobrookite	$MgTi_2O_5$	oct	Mg,Ti	55.0	0.3	0.5	Brown and Navrotsky (1989)
	$(Mg,Fe)Ti_2O_5$	oct	(Mg,Fe),Ti	55.4	0.4	0.6	Brown and Navrotsky (1989)
Carbonates	$(CdMg)(CO_3)_2$	oct	Cd,Mg	61.9	0.03	0.05	Capobianco et al. (1987)
	$(CaFe)(CO_3)_2$	oct	Ca,Fe	64.3	−0.3	−0.5	Davidson et al. (1993) and Chai and Navrotsky (1996)
	$(CaMg)(CO_3)_2$	oct	Ca,Mg	65.6	0.15	0.2	Reeder and Wenk (1983)
Feldspar	$NaAlSi_3O_8$	tet	Si,Al	100.5	0.5	0.5	Downs et al. (1994) and Winter et al. (1979)
	$KAlSi_3O_8$	tet	Si,Al	108.8	0.0	0.0	Smith and Brown (1988)
	$RbAlSi_3O_8$	tet	Si,Al	112.0	−0.3	−0.3	Pentinghaus and Henderson (1979) and Viswanathan (1971)
Pentlandite	M_9S_8	oct and tet	Ni,Fe	157.0	7.0	4.5	Tsukimura et al. (1992)

* Estimated errors for molar volumes are typically <0.1%. Errors for ΔV_{dis} are generally unknown, but they range from about 0.1% of molar volume for compounds in which end-member molar volumes for ordered and disordered states are well known (i.e., albite), to >0.5% of molar volume for samples in which end-member volumes are extrapolated from intermediate states. Consequently, errors in percent change are large, in several cases as large as the estimated change itself.

** For both inverse and normal spinels, $\Delta V_{dis} = V_{dis} - V_{ord}$, where V_{dis} corresponds to a spinel order parameter of $x = 0.67$.

$$\left(\frac{\delta \Delta G_{dis}}{\delta P}\right)_T = \Delta V_{dis}. \tag{3}$$

Values for ΔV_{dis} have been determined from X-ray diffraction studies for a number of alloys, minerals, and other materials (see Table 1). These volumes were obtained from differently ordered samples quenched to ambient conditions, with the exception of the Cu-Au alloys, which were examined as a function of temperature. In some instances, as in the case of orthopyroxenes and carbonates, the volume differences between fully ordered and disordered states were obtained by extrapolation from states of intermediate order. The relationship between molar volume and degree of disorder is not constrained to be linear, and few data are available to test linearity. In the exhaustively studied case of alkali feldspars, however, near-linear behavior is observed (Kroll and Ribbe 1987; Smith and Brown 1988).

As evident from Table 1, ΔV_{dis} may be positive (i.e., the ordered form may be denser than the disordered form) or negative. A closer inspection of the materials involved reveals three structural trends that may be used to rationalize the sign of ΔV_{dis} in most of these examples.

Ordering of two metal atoms between two similar close-packed sites

The easiest ΔV_{dis} behavior to rationalize involves ordering of metal atoms of different sizes between two similar sites in a close-packed structure. Examples in Table 1 include the 12-fold coordinated atoms in Cu-Au alloys and the pairs of octahedrally coordinated cations such as Mg, Fe, and Mn in olivines, orthopyroxenes, and carbonates. In these cases, ΔV_{dis} is generally small and positive.

Cu-Au alloys provide a useful example of the volume effects that may accompany ordering of two similar atoms on two similar sites. All these Cu-Au alloy structures possess a cubic close-packed (CCP) arrangement of metal atoms, in which every Cu and Au is surrounded by 12 neighbors. Owen and Liu (1947) documented the unit-cell volumes of ordered and disordered Cu_3Au, with molar volumes at room conditions, of 31.51 and 31.64 cm³/mol (extrapolated from a partially ordered state), respectively. This change represents a density increase with ordering of 0.4%. The disordered structure (space group *Fm*3*m*) has only one symmetrically distinct atom position (see Fig. 1A), whereas ordered Cu_3Au adopts a primitive cubic structure (space group *Pm*3*m*), in which Au is located at the origin and Cu occupies face-centered sites (½,½,0; see Fig. 1B).

The situation for CuAu is similar. Disordered CuAu ($V \approx$ 17.45 cm³/mol; Johansson and Linde 1936), for example, has the same *Fm*3*m* structure as disordered Cu_3Au (see Fig. 2A), whereas ordered CuAu (V = 17.3 cm³/mol; JCPDS card 25-1220) features alternating close-packed layers of smaller Cu and larger Au atoms in a tetragonal structure (space group *P*4/*mmm*; see Fig. 2B). The 0.8% density increase with ordering of CuAu can be understood in terms of the packing of spheres. In the ordered form, thicker layers of Au atoms alternate with thinner layers of Cu atoms. The resulting molar volume

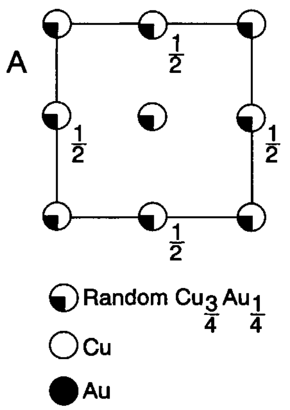

Figure 1. The structure of Cu_3Au: (**A**) disordered form, space group *Fm*3*m*; (**B**) ordered form, space group *P*4/*mmm*. The fully ordered form is approximately 0.4% denser than the fully disordered form.

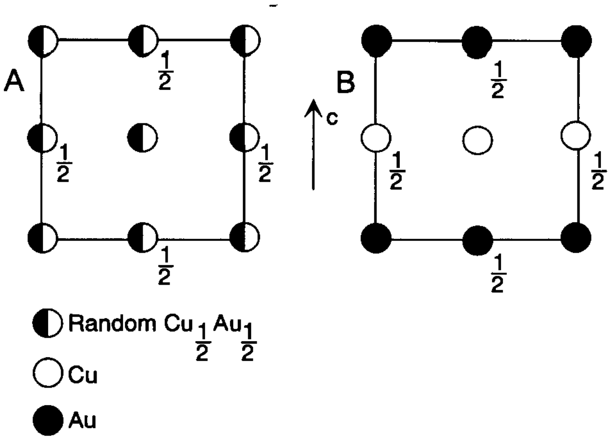

Figure 2. The structure of CuAu: (**A**) disordered form, space group *Fm*3*m*; (**B**) ordered form, space group *Pm*3*m*. The fully ordered form is approximately 0.8% denser than the fully disordered form.

is identical to the sum of the molar volumes of pure copper (CCP; V = 7.1 cm^3/mol) and pure gold (CCP; V = 10.2 cm^3/mol). In the disordered phase of CuAu, however, larger Au atoms are randomly interspersed with smaller Cu atoms in a less efficiently packed arrangement. Some Cu atoms occupy sites that are larger than in pure copper because of relatively long Au-Au contacts. Consequently, the disordered forms of these alloys have slightly greater molar volumes.

Similar reasoning may be applied to edge-sharing octahedral sites in biopyriboles, orthosilicates, carbonates, and many other rock-forming minerals. In these structures two or more divalent cations of similar size may order over two octahedral sites of similar size. Orthopyroxenes, olivines, and carbonates (Table 1), for example, display slightly greater densities, typically <0.5%, with ordering of divalent octahedral cation pairs, including Mg, Ca, Mn, Fe, Ni, and Cd. In each case, segregation of each cation into a distinct crystallographic site results in the most efficient packing of cation polyhedra. High-pressure geological environments, therefore, may favor phases with enhanced cation ordering.

These arguments, that ordered arrangements provide a more efficient volumetric packing of dissimilar units than disordered arrangements, also apply to high-pressure ordered molecular crystals, including van der Waals compounds and clathrates (Vos et al. 1992; Schouten 1995).

Tetrahedral site ordering in framework aluminosilicates

Feldspars and other framework aluminosilicates exhibit a variety of Si-Al tetrahedral ordering patterns. Although Al and Si tetrahedra differ slightly in polyhedral volumes, the molar volumes of framework structures are more closely tied to the magnitude and distribution of T-O-T angles than to individual tetrahedral volumes. Average observed Si-O-Si, Al-O-Si, and Al-O-Al angles are 145, 138, and 133°, respectively (Geisinger et al. 1985). These angles, furthermore, may be significantly affected by the distribution of alkali and alkaline earth cations that commonly occupy framework cavities. Different distributions of Al and Si in a tetrahedral framework, therefore, may result in significantly different molar volumes. In these structures ordered arrangements do not necessarily display smaller molar volumes. Figure 3 presents a two-dimensional analog of this situation. The areas bounded by two 90°- and two 120°-angle segments differ by approximately 1%, depending on the arrangement of the four angles.

The systematics of ΔV_{dis} for framework aluminosilicates must be considered on a case-by-case basis. Consider, for example, the alkali feldspars ($AAlSi_3O_8$; A = Na, K, or Rb). The fully Al-Si–ordered Na end-member, low albite, has a molar volume of 99.98 cm^3/mol (Downs et al. 1994) in comparison with 100.45 cm^3/mol for disordered high albite (Winter et al. 1979). Thus, ordered sodium feldspar is approximately 0.5% denser than the disordered form. This difference may account for anecdotal evidence (H.S. Yoder, personal communication) that although disordered albite may be synthesized at atmospheric pressure, all albite synthesized at high pressure is ordered.

In rubidium feldspar ($RbAlSi_3O_8$), on the other hand, the ordered form (molar volume = 112.3 cm^3/mol; Pentinghaus and Henderson 1979) is 0.3% less dense than the disordered form (molar volume = 112.0 cm^3/mol; Viswanathan 1971). In the case of potassium feldspar ($KAlSi_3O_8$), with an alkali cation intermediate in size between Na and Rb, ordered low microcline and disordered high sanidine have been reported to have almost identical molar volumes (108.8 cm^3/mol; Smith and Brown 1988).

Examples of volume-dependent site ordering are to be expected in other framework aluminosilicates, such as zeolites and feldspathoids, as well as alumino-phosphates and other tetrahedral framework compounds. A similar phenomenon may occur in perovskite-type phases in

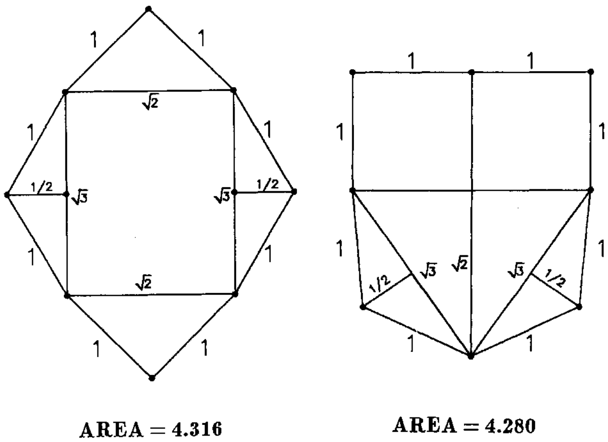

Figure 3. Different distributions of fixed angles in a plane generally result in different enclosed areas. This situation is analogous to the volume dependence of framework aluminosilicates on the distribution of T-O-T angles. The areas (in arbitrary units) of surfaces bounded by two 90°- and two 120°-angle segments, for example, differ by approximately 1% depending on the arrangement of the four angles.

which multiple cations occupy the corner-linked octahedral framework [e.g., Pb(Zr,Ti)O_3, Ca_2CaUO_6, and $Ca_2FeTiO_{5.5}$; Hazen 1988].

Ordering involving mixed valence or mixed coordination

The largest known ΔV_{dis} effects arise in structures in which two cations adopt different valence or coordination states. In the previous two examples, ordering does not drastically change the volume contributions of constituent cation polyhedra or T-O-T angles. Changes in valence or coordination, however, can significantly change the volumes of structural building blocks.

Consider, for example, spinel-type oxides, which have the structural formula $^{[4]}A^{[6]}B_2O_4$. This cubic structure (space group $Fd3m$) has two symmetrically distinct cation sites: A, which is tetrahedrally coordinated at (⅛,⅛,⅛), and B, which is octahedrally coordinated at (½,½,½). The O atom also lies on the unit-cell diagonal, at (u,u,u), where u is approximately ¼. The cubic unit-cell edge a is completely determined by the tetrahedral A-O (R_T) and octahedral B-O (R_O) bond distances:

$$a = \frac{40R_T + 8\sqrt{33R_O^2 - 8R_T^2}}{11\sqrt{3}}. \qquad (4)$$

This variation of cubic a with R_T and R_O is illustrated in Figure 4. Note that of the two sites, the larger octahedron (of which there are 16 per unit cell) plays a significantly greater role than the tetrahedron (eight per unit cell) in determining unit cell a and thus molar volume.

The order-disorder behavior of spinels is discussed at length in a subsequent section, but the unusual spinel $CoFe_2O_4$ provides a dramatic demonstration of the effects of coordination and valence ordering on molar volume. In this binary oxide, both Fe and Co can adopt either +2 or +3 valence states in the octahedral site, whereas Fe^{2+}, Fe^{3+}, and Co^{3+} can adopt tetrahedral coordination. O'Neill and Navrotsky (1983) documented the bond lengths, R_O and R_T, for these spinels, as listed in Table 2 and plotted in Figure 4.

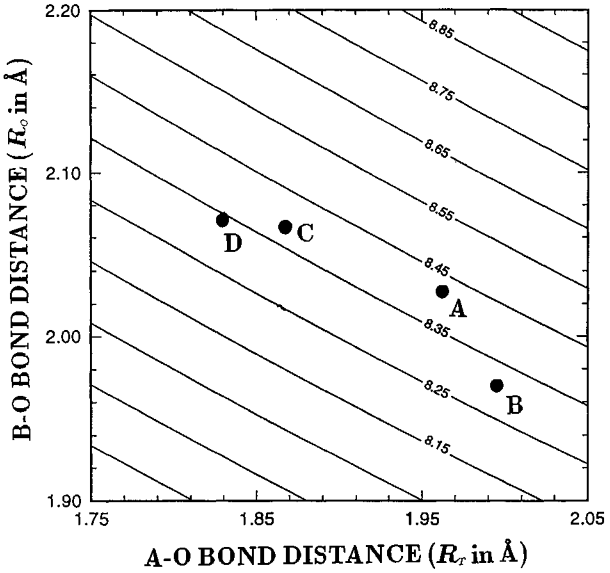

Figure 4. The unit-cell edge a for cubic spinels is a function of the octahedral (R_O) and tetrahedral (R_T) bond distances. Points A, B, C, and D represent four ordered variants of Co_2FeO_4 (see text).

From the points in Figure 4, it is evident that cubic cell edge a (and thus molar volume) of $CoFe_2O_4$ depends critically on the cation and valence ordering. The ordered end-member ($^{[4]}Co^{2+}$)[$^{[6]}Fe_2^{3+}$]O_4 (point A on Fig. 4), for example, has estimated R_T and R_O bond distances of 1.96 and 2.025 Å, respectively. The resultant molar volume is 44.77 cm^3/mol. The disordered spinel ($^{[4]}Fe^{2+}$) [$^{[6]}Fe^{3+}Co^{3+}$]O_4 (point B on Fig. 4), on the other hand, has expected R_T and R_O bond distances of 1.995 and 1.968 Å, respectively, and the observed molar volume is 43.06 cm^3/mol, approximately 4% denser than the ordered variant. This arrangement, with both Fe^{3+} and Co^{3+} in octahedral coordination, results in the smallest possible octahedral volume for this composition. Intermediate molar volumes are expected for other partially ordered spinels of this composition, including ($^{[4]}Fe^{3+}$)

Table 2. Fe-O and Co-O bond distances in spinels as a function of valence and coordination number (after O'Neill and Navrotsky 1983)

Ion	Octahedral, R_O (Å)	Tetrahedral, R_T (Å)
Fe^{2+}	2.12	1.995
Fe^{3+}	2.025	1.865
Co^{2+}	2.10	1.96
Co^{3+}	1.91	1.83

$[^{[6]}Co^{2+}Fe^{3+}]O_4$ and $(^{[4]}Co^{3+})[^{[6]}Fe^{2+}Fe^{3+}]O_4$ (shown in Fig. 4 as points C and D, respectively).

Several other structures might be expected to display similar volume effects owing to valence and coordination ordering. Pentlandite $[(Ni,Fe)_9S_8]$, with both octahedral and tetrahedral Ni and Fe cations, displays a $\Delta V_{dis} \approx 4.5\%$ (Tsukimura et al. 1992). Other likely candidates include transition-metal binary oxides in the ilmenite ($FeTiO_3$), ferberite ($FeWO_4$), and perovskite ($CaTiO_3$) structures. High-pressure silicates with $^{[6]}Si$, including silicate perovskites ($^{[12]}A^{[6]}BO_3$), silicate garnets ($^{[8]}A_3$-$^{[6]}B_2{}^{[4]}Si_3O_{12}$), and phases related to $^{[6]}A_{15}{}^{[4]}Si_4O_{24}$ (Finger and Hazen 1991), should also display this behavior.

Effects of pressure on ΔV_{dis}

Although few relevant data exist, there is no reason to expect that ordered and disordered variants of a given composition have identical equations of state. In most instances, therefore, ΔV_{dis} is dependent on pressure. In the case of anorthite, for example, Hackwell and Angel (1992) proposed that increasing Al-Si disorder leads to an increase in anorthite compressibility (see also review by Angel 1994). On the other hand, Downs et al. (1994) suggested that disordered high albite should be less compressible than ordered low albite owing to the greater flexibility of Al-O-Si angles in comparison with Si-O-Si angles. In both instances, if ordered and disordered variants have different bulk moduli, then ΔV_{dis} varies with pressure. Additional pressure-volume data for feldspars are required to quantify these effects.

Factors influencing $(\delta\Delta V_{dis}/\delta P)_T$ may be identified by considering the difference in free energy of two compositionally identical phases with different degrees of order:

$$\Delta G_{dis} = \Delta E_{dis} - T\Delta S_{dis} + P\Delta V_{dis}. \qquad (5)$$

Differentiating Equation 5 in pressure at constant temperature gives

$$\left(\frac{\delta\Delta G_{dis}}{\delta P}\right)_T = \left(\frac{\delta\Delta E_{dis}}{\delta P}\right)_T - T\left(\frac{\delta\Delta S_{dis}}{\delta P}\right)_T + P\left(\frac{\delta\Delta V_{dis}}{\delta P}\right)_T + \Delta V_{dis}. \qquad (6)$$

This equation defines the pressure effect of disordering on G. Combining Equations 3 and 6 yields

$$\left(\frac{\delta\Delta E_{dis}}{\delta P}\right)_T - T\left(\frac{\delta\Delta S_{dis}}{\delta P}\right)_T + P\left(\frac{\delta\Delta V_{dis}}{\delta P}\right)_T = 0. \qquad (7)$$

Equation 7 reveals that if the energy and entropy of disordering do not depend on pressure, then neither does the volume of disordering. Conversely, the energy and the entropy of disordering must vary with pressure if the volume of disordering shows a pressure dependence. This more complex behavior is likely if the nature of the chemical bonding changes strongly with pressure, e.g., on the steeply rising portion of a potential energy surface or approaching a change in metallic character, spin state, etc.

If energy and entropy of disorder vary with pressure, then either of two situations may exist. The $(\delta\Delta E_{dis}/\delta P)_T$ and the $(\delta\Delta S_{dis}/\delta P)_T$ terms may fortuitously cancel each other, in which case ΔV_{dis} remains independent of pressure [i.e., $(\delta\Delta V_{dis}/\delta P)_T = 0$]. Alternatively, $(\delta\Delta E_{dis}/\delta P)_T$ and $(\delta\Delta S_{dis}/\delta P)_T$ do not cancel, and ΔV_{dis} is therefore a function of pressure. The point is that ΔE_{dis}, ΔS_{dis}, and ΔV_{dis} cannot vary with pressure in arbitrary and independent ways but are constrained as defined by Equation 7.

As shown in Equations 3 and 6, it is enough to know ΔV_{dis} as a function of pressure to calculate the pressure variation of the free energy of ordering at constant temperature, and therefore the ordering state. In practice, the volume change associated with disordering is known, at best, only at atmospheric pressure for most systems of interest (as summarized in Table 1); no experimental data on the variation of ΔV_{dis} with pressure exist. Consequently, the simplifying (and possibly erroneous) assumption is usually made that ΔV_{dis} is independent of pressure. On the basis of the above analysis, this assumption leads to a linear variation of ΔG_{dis} with pressure, as defined by Equation 3.

Kinetics of order-disorder

It is well known that the rates of order-disorder reactions depend strongly on temperature. At atmospheric pressure, slow rates of divalent cation exchange in silicates and spinels generally preclude equilibration on a laboratory time scale below about 850 K, whereas very rapid equilibration prevents quenching of disordered states from above 1400–1500 K. These rates of equilibration, governed by diffusion rates, have been studied extensively because of their potential applications as geospeedometers. Thus, for example, studies of ordering in Fe-Ni alloys (Scorzelli et al. 1994) and pyroxenes (McCallister et al. 1975; Molin et al. 1991) are useful in documenting the thermal histories of meteorites. Similarly, ordering in $(Na,K)AlSi_3O_8$ alkali feldspars (Megaw 1974; Ribbe 1983) and $(Mg,Fe)SiO_3$ orthopyroxene (Anovitz et al. 1988; Saxena et al. 1989; Domeneghetti and Steffan 1992; Skogby 1992; Tribaudino and Talarico 1992) are widely used in documenting the cooling rates of lunar and terrestrial rocks, even though those cooling events may occur over time scales $>10^5$ yr, whereas laboratory experiments occur in 10^{-4} to 10^{-1} yr.

By contrast, few data exist on the effects of pressure on the kinetics of order-disorder reactions. Pressure confines atoms into a smaller volume and thus affects atomic motions, diffusion, and crystal-growth rates, which are behaviors that can be modeled with a parameter such as the activation volume (Fratello et al. 1980a, 1980b; Lu et al. 1991a). Pressure imposes orientational order in H_2 (Mao and Hemley 1994), C_{60} (Fischer and Heiney 1993), and CH_4 (Prager et al. 1982). Similarly, for a given crystalline phase, intracrystalline diffusion may be expected to become more restricted as interatomic distances decrease at high pressure. (This behavior does not generally result, however, in high-pressure phase transitions involving an increase in coordination number, in which case nearest-neighbor distances between some atoms may increase.) Given the restricted motion of atoms in a compressed phase, it is possible that high-pressure ordered states of many minerals are more slowly achieved, and more readily quenched once achieved, than those at lower pressure.

In spite of this prediction, Goldsmith and Jenkins (1985) observed the opposite effect in albite, in which Al-Si order-disorder reaction rates increase by orders of magnitude between atmospheric pressure and 1.8 GPa. They suggested that at higher pressures a new diffusion mechanism comes into play: Near the transition from albite to jadeite plus quartz, Al experiences transient states of greater than fourfold coordination, during which Al-O bond breaking is facilitated.

Whatever the effects of pressure, it should be remembered that samples recovered at ambient conditions from high-pressure synthesis experiments generally have experienced rapid temperature quenching (a few seconds) at high pressure, followed by slow pressure release (minutes to hours). If the systematics above apply, then one cannot expect to recover the full extent of cation disorder of samples prepared above 1500 K in these studies. We conclude that 1500 K represents an upper temperature limit from which structural states are quenchable. This temperature is also reasonably representative of mantle conditions, under which many of the minerals discussed reach their limits of stability. Thus, below we give some examples with 1500 K as a reference temperature, as illustrated in Figure 5.

MINERALOGICAL EXAMPLES OF ORDERING AT PRESSURE

Numerous examples of cation ordering have been documented in mineralogical systems. In the following sections we consider specific examples with regard to the possible influence of pressure.

Iron-magnesium silicates: General considerations

Iron-magnesium oxides and silicates have been studied extensively because of their importance in understanding the Earth's deep interior. Fe^{2+} and Mg behave as interchangeable ions in many low-pressure oxides and silicates. Divalent Fe and Mg have similar ionic radii (0.78 vs. 0.72 Å, respectively; Shannon 1976) and electronegativities, and both tend to adopt octahedral environments in oxides and silicates. These similarities have three important consequences: (1) Solid solution: Most common rock-forming minerals, including olivines, pyroxenes, micas, amphiboles, garnets, spinels, and carbonates, display complete solid solution between Fe^{2+} and Mg end-members. (2) Intercrystalline partitioning: Coexisting pairs of ferromagnesian minerals, such as olivine and clinopyroxene in a basalt or amphibole and mica in a granite, commonly possess similar Mg/Fe, indicating no strong tendency for these elements to segregate from each other in the low-pressure environment. (3) Intracrystalline partitioning: In oxides and silicates with more than one crystallographically distinct octahedral Fe^{2+} and Mg site of similar size and distortion, these cations tend to be disordered.

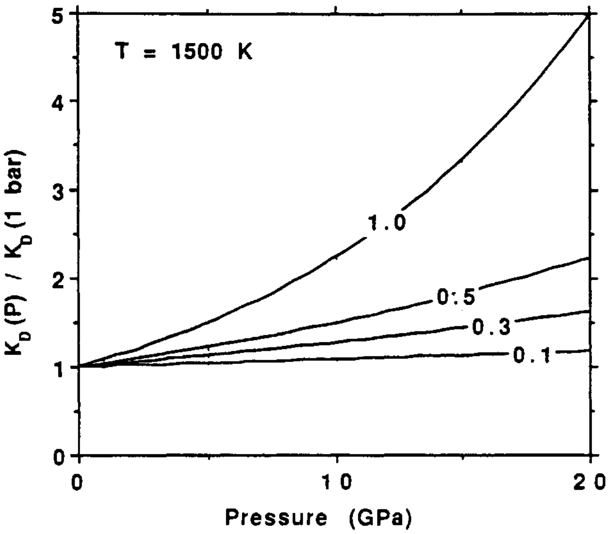

FIGURE 5. Equilibrium constant, K_D, for Fe-Mg distribution in a ferromagnesian silicate varies as a function of pressure for different volumes of disordering (ΔV_{dis} in cubic centimeters per mole), as marked on each curve. Curves were calculated for a temperature of 1500 K. At lower temperatures the effect of pressure on K_D is somewhat larger for a given ΔV_{dis} (see Eq. 10).

Ordering over two sites can be expressed as a distribution coefficient, K_D:

$$K_D = (X^{M2}_{Fe}/X^{M2}_{Mg})/(X^{M1}_{Fe}/X^{M1}_{Mg}). \quad (8)$$

Given this definition, $K_D = 1$ for complete disorder. Most low-pressure ferromagnesian minerals have $K_D < 2$, whereas four recent studies have suggested that the situation at high pressure may be more complex.

Note that, rigorously, the equilibrium constant should be written as an activity ratio, not a concentration ratio:

$$K_D = (a^{M2}_{Fe}/a^{M2}_{Mg})/(a^{M1}_{Fe}/a^{M1}_{Mg}). \quad (9)$$

Because $\Delta G_{dis} = -RT \ln K_D$, the pressure effect on K_D can be written as

$$RT \ln[K_D(P_2)/K_D(P_1)] = (P_2 - P_1)\Delta V_{dis}. \quad (10)$$

Figure 5 shows the pressure effect in K_D by plotting $K_D(P)/K_D$ (1 atm) for various values of ΔV_{dis} at 1500 K. Note that in this figure and in subsequent discussions we assume Fe^{2+}/Fe^{3+} does not change. As noted above, changes in Fe valence generally have a much larger effect on molar volume than changes in Fe-Mg ordering.

Ferromagnesian olivine

Ferromagnesian olivines, α-$(Mg,Fe)_2SiO_4$, at low pressure show little Fe-Mg ordering and generally display $K_D < 1.2$. Aikawa et al. (1985), however, found that pressure enhances Fe-Mg ordering in olivines. Akamatsu et al. (1993) equilibrated ferromagnesian olivines at pressures to 10 GPa and found that K_D increases significantly with pressure. They reported $dK_D/dP \approx 0.02$ GPa^{-1} and estimated that the K_D of olivine may exceed 2.0 in the Earth's mantle. On the basis of these experiments, Akamatsu and Kumazawa (1993) and Akamatsu et al. (1993) demonstrated that above 1273 K, Mg-Fe ordering equilibrates in less than a hundredth of a second. Thus, they concluded, quench experiments from higher temperatures cannot preserve the equilibrium cation distribution.

Akamatsu et al. (1993) presented a fairly complex five-parameter model to account for the dependence of K_D on pressure, temperature, and composition, as well as nonideal mixing on M1 and M2 sites. They noted that in the case of ferromagnesian olivine, because both the deviation from random Fe-Mg distribution and the volume change associated with order-disorder reactions are small, it is difficult to constrain the ΔV_{dis} from crystallographic data alone. Using their thermodynamic model, Akamatsu et al. (1993) obtained $\Delta V_{dis} = 0.24$ cm^3/mol, a value about one-half of that cited in their earlier study (Akamatsu et al. 1988). The cation-distribution equilibrium constant, K_D, increases with pressure, reaching values near 2.2 for olivines near the 400 km discontinuity in the mantle in comparison with values of 0.9–1.2 near the surface. The variation of K_D with pressure contains contributions from nonideality of the solid solutions and from the $P\Delta V$ term, because nonunity activity coefficients must be used to convert the experimental (concentration ratio) K_D to a thermodynamic (activity ratio) equilibrium constant (see, for example, Akamatsu et al. 1993). It should be noted that f_{O_2} may play a significant role in olivine Mg-Fe ordering (Will and Nover 1979, 1980), and these effects have not been taken explicitly into account in the work of Akamatsu et al. (1988, 1993).

Other transition metals, especially Mn, Co, and Ni, also substitute into olivine, and cation distributions have been studied as a function of temperature for Ni- and Mg-containing olivines (Rajamani et al. 1975; Ottonello et al. 1989) and as a function of both temperature and pressure for Mn- and Mg-containing olivines (Akamatsu et al. 1988). Both of these systems show greater ordering than ferromagnesian olivines, with Ni preferring M1 and Mn preferring M2. Although the ferromagnesian and Mg- and Ni-containing olivines show positive volumes of disordering, Akamatsu et al. (1988) reported a significant negative ΔV_{dis} and pressure-induced disordering for Mg- and Mn-containing olivine (see Table 1). No structural reasons for this unusual behavior have been proposed. Significant ordering has also been observed in several other olivines, including those with Co-Mg, Ca-Mg, and Fe-Mn (Ghose and Wan 1974; Brown 1982), but their dependence on pressure and temperature has yet to be studied.

Orthopyroxene

In $(Mg,Fe)_2Si_2O_6$ orthopyroxene Fe orders preferentially into the M2 site, which is both significantly larger and more distorted than M1. Distribution coefficients >50 have been reported for slowly cooled natural orthopyroxenes (Tribaudino and Talarico 1992) and for samples annealed at temperatures near 500 °C, whereas samples equilibrated above 1000 °C and rapidly quenched more typically have K_D between 3 and 4 (Virgo and Hafner 1969). These large K_D values probably reflect strong differences in the degree of distortion of M1 and M2 sites, with Fe^{2+} preferring the more distorted M2 environment.

Domeneghetti et al. (1985) investigated the effects of Fe-Mg order on the structure of three orthopyroxenes with different Fe/(Fe + Mg): 0.180, 0.462, and 0.755. In all three samples, increased Fe-Mg disorder (induced by heat treatment) caused an increase in unit-cell volume. In their sample with Fe/(Fe + Mg) = 0.462, for example, a decrease in K_D from 49.2 to 7.3 is accompanied by an increase in unit-cell volume from 851.6 to 852.8 Å^3, or 0.14%. In a subsequent study Domeneghetti et al. (1995) performed multiple linear-regression analysis on composition and structure information on >200 orthopyroxenes. For $(Mg,Fe)_2Si_2O_6$ orthopyroxenes they defined unit-cell volume, V, as a linear function in terms of the fraction of Fe^{2+} in M1 and M2:

$$V = 26.20X_{Fe}^{M1} + 17.67X_{Fe}^{M2} + 832.74 \text{ Å}^3. \quad (11)$$

Equation 11 can be used to predict unit-cell volumes for the extreme cases of complete disorder and complete order with all Fe in M2. For a composition of $(MgFe)Si_2O_6$, volumes for ordered and disordered samples are predicted to be 850.41 and 854.68 Å^3, respectively. Thus, $\Delta V_{dis} = 4.27$ Å^3, or approximately 0.32 cm^3/mol, which suggests that increased pressure favors Fe-Mg order in orthopyroxene. Studies by Virgo and Hafner (1969) on samples annealed at atmospheric pressure and at ~2 GPa, however, did not detect any significant effect of pressure on ordering. Similarly, a synthetic orthopyroxene sample with Fe/(Fe + Mg) = 0.44, quenched from 1873 K at 11 GPa (Hazen et al. 1993a), has $K_D = 3.9$, which is a relatively disordered value that is generally consistent with the low-pressure results of Virgo and Hafner (1969). Taking this last case,

$$\begin{aligned}&\Delta G_{dis}(11 \text{ GPa}) - \Delta G_{dis}(1 \text{ atm})\\ &= 11 \times 10^4 \times 0.32 = 3540 \text{ J}. \quad (12)\end{aligned}$$

Assuming the samples preserved a cation distribution characteristic of 1500 K,

$$RT \ln[K_D(11 \text{ GPa})/K_D(1 \text{ bar})] = 3540$$

or

$$K_D(11 \text{ GPa})/K_D(1 \text{ bar}) = 1.33. \quad (13)$$

Thus, a K_D of 3.9 at 11 GPa would imply a K_D of 2.9 at 1 atm, within the range of the uncertainties for the data of Virgo and Hafner (1969) and subsequent work. Therefore, a fairly small pressure effect on K_D is consistent with both the volume data and the experimental K_D determinations. The above simple illustrative argument does not account for nonideal mixing; however, when comparing samples of the same composition, this effect is minor if the change in cation distribution is small over the range considered.

High-pressure ferromagnesian silicates

Wadsleyite, β-$(Mg,Fe)_2SiO_4$, is a high-pressure polymorph of olivine stable above about 13 GPa. Finger et al. (1993) described the crystal chemistry of a series of Fe-bearing wadsleyite samples that were synthesized at approximately 15 GPa at temperatures >1973 K. These wadsleyite crystals have three symmetrically distinct Fe-Mg octahedra, all of similar size and distortion, yet Fe is significantly depleted in M2 relative to the other two sites, with $K_D \approx 2.7$. Further systematic studies on the effects of annealing and cooling rate on wadsleyite Fe-Mg order are necessary to characterize fully this behavior.

Hazen et al. (1992) described single crystals of Fe-bearing anhydrous phase B, $(Mg_{0.88}Fe_{0.12})_{14}Si_5O_{24}$, that was synthesized at 24 GPa and 2073 K. This complex silicate has six crystallographically distinct Mg-Fe octahedral sites, all of similar size and distortion. Nevertheless, Fe is significantly more concentrated in one of these sites (designated M3) than the other five. Typical values of K_D between M3 and other octahedra range from 7 to 9, which are larger than in any comparable low-pressure phase.

Observed Fe-Mg ordering in wadsleyite and anhydrous phase B is especially striking because the specimens were synthesized at temperatures above 1973 K and rapidly cooled at high pressure. Such extreme annealing temperatures usually produce relatively disordered Fe-Mg distributions in low-pressure silicates. The large K_D values of these materials suggest that pressure could be a controlling factor in Fe-Mg ordering. However, the apparent effect of pressure may result from several mechanisms. The most straightforward mechanism is that a large positive ΔV_{dis} enhances order by the thermodynamic arguments above. If these studies capture distributions on quenching that are characteristic of 1500 K, then changing K_D by about a factor of three implies a change in free energy of 13.7 kJ/mol. If this change is induced by a pressure of about 20 GPa, then $(\delta\Delta G_{dis}/\delta P)_T = 0.65$ kJ/GPa, or from Equation 7, $\Delta V_{dis} = 0.07$ J/bar = 0.7 cm^3/mol. Similarly, an increase by a factor of five would imply a ΔV_{dis} of about 1 cm^3/mol (see also Fig. 5). Such values of ΔV_{dis}, though large, are not physically impossible. Although the structures of these high-pressure phases may also show large K_D values at low pressures (where the phases would be metastable), there are no obvious crystal-chemical reasons for strong Mg-Fe partitioning. The behavior of wadsleyite and anhydrous phase B thus seems to suggest a greater difference in the crystal-chemical behavior of Fe and Mg in high-pressure phases than in low-pressure silicates. A similar conclusion was reached by Hazen (1993) in his study of the compressibilities of high-pressure Fe-Mg silicate spinels.

A cautionary note is in order, because it is extremely difficult to ensure equilibrium states of order in high-pressure synthesis. The wadsleyite sample of composition $(Mg_{1.2}Fe_{0.8})SiO_4$ described by Finger et al. (1993), for example, is clearly a metastable product, because it crystallized well within the silicate spinel field. Even in the synthesis of stable phases, reversals are rarely attempted, much less achieved in high-pressure experiments. Degrees of Mg-Fe order in the above examples, therefore, are not presented as equilibrium states.

Spinels

Oxide spinels encompass a large group of natural and synthetic compounds of the general form AB_2O_4, where A and B are tetrahedrally and octahedrally coordinated cations, respectively. As reviewed above, the cubic spinel structure is fully defined by one O positional parameter and the cubic cell edge. For a fully ordered "normal" spinel, A and B cation charges may be either +2 and +3, or +4 and +2, respectively. If parentheses are used to designate A-site cations and brackets are used to designate B-site cations, then a normal spinel has the structural formula $(A)[B_2]O_4$.

In spite of the apparent simplicity of this structural formula, spinels display complex patterns of disorder (Navrotsky and Kleppa 1967; Lindsley 1976; O'Neill and Navrotsky 1983, 1984). The mineral spinel, $MgAl_2O_4$, was the first stoichiometric compound found to incorporate a disordered site (Barth and Posnjak 1931). The cation distribution has been found to vary from normal to about 30% inverse (Navrotsky and Kleppa 1967; Schmocker and Waldner 1976; Wood et al. 1986; Peterson et al. 1991), depending on temperature.

In $MgAl_2O_4$ and many other spinels, the range 800–1400 K is accessible for equilibration and quenching experiments on cation distribution. A review of thermodynamic models for the temperature dependence of cation distribution is given by Navrotsky (1994). The most disordered state for a spinel is the random cation distribution $(A_{1/3}B_{2/3})[A_{2/3}B_{4/3}]$, which both normal and inverse spinels tend to approach at high temperature. For spinels of the 2-3 charge type (e.g., $MgAl_2O_4$, $MgFe_2O_4$), the inverse distribution generally has a smaller volume than the normal (see Table 1). Thus, 2-3 spinels tend to become more inverse with increasing pressure at constant temperature. Spinels that tend toward normal (e.g., $MgAl_2O_4$) at low temperature would become more disordered with increasing pressure, whereas those that approach the inverse distribution (e.g., $MgFe_2O_4$) at low temperature would become more ordered with increasing pressure.

For spinels of the 2-4 charge type (e.g., Mg_2TiO_4,

γ-Mg_2SiO_4), the situation is less clear. Both O'Neill and Navrotsky (1983) and Hazen et al. (1993b) suggested a small positive volume of disordering for the normal spinel Mg_2SiO_4. The effect of temperature probably outweighs that of pressure, and a small degree of disorder (about 4%) has been suggested for Mg_2SiO_4 spinel quenched from 20 GPa and 1673 K but not for Fe-bearing silicate spinels (Hazen et al. 1993b).

In spinels containing two or more cations of variable valence (e.g., in the case of Co_2FeO_4 discussed above), considerable volume differences have been predicted from ionic radius arguments (O'Neill and Navrotsky 1983) for different distributions of elements and charges among octahedral and tetrahedral sites. Thus, the site occupancies and charge distributions may change significantly with pressure, with the densest forms being favored at high pressure.

High-pressure garnets

Materials that change symmetry upon ordering can be more complex than the examples considered above. A first-order phase transition may be involved, or a change from second- to first-order behavior (a tricritical point) may occur as a function of temperature, pressure, composition, and ordering state. Symmetry rules dictate whether a transition can be higher order; however, a transition that is allowed by symmetry to be second order can be first order. In many cases, the detailed nature of the transition is poorly understood at atmospheric pressure and totally unknown at high pressure. Nevertheless, several relevant, mostly qualitative, observations have been made. The important cases of alkali feldspars and Cu-Au alloys have been described previously, and additional examples are summarized below.

The garnet structure, first identified in common rock-forming silicates, has been synthesized in a wide range of oxides and fluorides that incorporate at least 50 elements. This compositional flexibility has led to a wide range of applications for garnet, including abrasives, lasers, waveguide components for microwave communications, low-conductivity magnetic bubble-domain devices, and semiprecious colored gemstones. Silicate garnets, furthermore, are a major rock-forming mineral, and they may account for as much as one-half of the volume of the Earth's transition zone between about 500 and 670 km in depth (Ita and Stixrude 1991).

At crustal pressure most natural garnets have cubic symmetry with the general formula $A^{2+}_3B^{3+}_2Si_3O_{12}$, where eightfold coordinated A is usually Mg, Fe, Mn, or Ca, and sixfold coordinated B is Al, Fe, or Cr. In spite of their compositional complexity, low-pressure garnets usually display complete disorder on A and B sites. It is noteworthy, however, that in these garnets all the substituents on A sites are divalent, all those on B sites are trivalent, and the ions on each site are similar in size.

At high-pressure, the substitution $2M^{3+} = M^{2+} + Si^{4+}$ (or Ge^{4+}) occurs on the octahedral site, and garnets such as $Mn_3(MnSi)Si_3O_{12}$ (equivalent to $MnSiO_3$; Ringwood and Major 1971; Fujino et al. 1986), $Ca_3(CaGe)Ge_3O_{12}$ (Ringwood and Major 1967; Prewitt and Sleight 1969), and $Mg_3(MgSi)Si_3O_{12}$ (Smith and Mason 1970; Angel et al. 1989) have been synthesized. These garnets generally have tetragonal symmetry, and the divalent and tetravalent ions are ordered on two symmetrically distinct octahedral sites. Such ordering may be more a consequence of size and charge than of pressure, as borne out by the existence of tetragonal ordered garnets at atmospheric pressure for compositions $Y_3(AlY)Al_3O_{12}$ (YAG) and $Y_3(FeY)Fe_3O_{12}$ (YIG), with Y and Al or Fe^{3+}, which are trivalent cations of quite different size, sharing octahedral sites. Nevertheless, for silicate and germanate garnets, the salient points are that pressure stabilizes garnets with mixed octahedral occupancies and that these high-pressure phases are ordered.

Hazen et al. (1994) characterized single crystals of a garnet with composition $(Ca_{0.49}Mg_{2.51})(MgSi)Si_3O_{12}$ synthesized at 18.2 GPa and 2323 K. This sample is the first silicate garnet to display ordering on both octahedral and dodecahedral sites. This behavior may increase garnet's compositional flexibility, affect element partitioning at high pressure, and stabilize the garnet structure in the transition zone and upper portion of the lower mantle. Ca is concentrated in the D2 site, which has a refined composition of $Ca_{0.32}Mg_{0.68}$, in comparison with $Ca_{0.08}Mg_{0.92}$ for D1. These site compositions may be expressed as a distribution coefficient:

$$K_D = (X^{D2}_{Ca}/X^{D2}_{Mg})/(X^{D1}_{Ca}/X^{D1}_{Mg}) = 5.4. \tag{14}$$

The reason for this unexpected degree of Ca-Mg ordering in calcic majorite garnet is not obvious. The two dodecahedral sites are not appreciably different in size or distortion. One possibly significant difference between D1 and D2 is the distribution of second-nearest-neighbor cations. Distances between adjacent D1 sites and between D1 and D2 are relatively short: approximately 3.5 Å. Distances between closest D2 sites, on the other hand, are more than 5.7 Å. Ordering of larger Ca atoms onto D2 minimizes Ca-Ca repulsion, which may in turn increase ΔV_{dis}. Whether the observed ordering is characteristic of synthesis temperature or of an effective quench some 1000 K lower, is not known.

Perovskite-type compounds

Perovskites include a wide range of compounds of the general formula ABX_3—a flexible structure that can incorporate more than 70 elements (Hazen 1988). Perovskites display a remarkable variety of properties, including a full range from insulator to metal-type conductivity, ferroelectric effects, superionic conduction, and superconductivity. Furthermore, perovskites of the general formula $(Mg,Fe)SiO_3$, are now thought to be the dominant mineral in the Earth's deep mantle and thus possibly our planet's most abundant mineral (Liu 1975).

Ideal perovskites have cubic symmetry, with a corner-linked array of octahedrally coordinated B cations that define large 12-fold coordinated A sites. Many variants of the ideal structure involve tilting of the octahedral array and consequent lowering of symmetry. The perovskite form of $MgSiO_3$, for example, has orthorhombic symmetry with distorted, ninefold-coordinated A sites (Yagi et al. 1978; Ross and Hazen 1990).

Most perovskites formed at low pressure display complete disorder among cations on A sites and B sites. In the case of two very different B cations, such as Ca and U in $Ca_2(CaU)O_6$, ordering of B cations has been well documented (Rietveld 1966). Variable degrees of ordering of B sites are also observed in ferroelectric perovskites such as $Pb(Fe_{1/2}Nb_{1/2})O_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$, $Pb(Fe_{2/3}W_{1/3})O_3$, and $Pb(Yb_{1/2}Nb_{1/2})O_3$ (Drazic et al. 1993; Bokov et al. 1993). Both ordered and disordered forms of $Pb(Yb_{0.5}Nb_{0.5})O_3$ perovskite occur (Wang and Schultz 1990). The powder patterns are consistent with very similar molar volumes, but lattice parameters were not given. Additional insight was provided by Burton and Cohen (1994, 1995), who used the nonempirical potential-induced-breathing method to calculate significant differences in structural parameters and total energy for ten B-site ordered variants of perovskite-type $Pb(Sc_{0.5}Ta_{0.5})O_3$. They estimated $\Delta V_{dis} \approx 0.1\%$ for this phase.

Under most circumstances ordering of the larger A cations in perovskite would not be expected. Leinenweber and Parise (1995), however, produced a high-pressure perovskite, $CaFeTi_2O_6$, that displays complex ordering of A-site cations Ca and Fe. This ordering results in three symmetrically different A sites and a reduction of topological symmetry from cubic to tetragonal. This high-pressure ordered phase thus parallels the behavior of the Ca-bearing majorite garnet described above. Leinenweber et al. (1995) also produced an ordered high-pressure perovskite with composition $CaFe_3Ti_4O_{12}$, a cubic perovskite in which Ca and Fe are fully ordered into two symmetrically distinct sites. Another example of A-site ordering is in perovskites $KLaTi_2O_6$, $NaLaTi_2O_6$, $NaYTi_2O_6$, $NaBiTi_2O_6$, and $LiLaTi_2O_6$, prepared at atmospheric pressure (Kaleveld et al. 1973). Thus, a large difference in size or charge of both A-site cations and B-site cations can favor ordered structures. The volume differences between ordered and disordered structures are not known, and more work is warranted.

Most high-temperature cuprate superconductors have perovskite-related structures with fewer than three O atoms per two cations (for a review, see Hazen 1990). In many of these compounds, such as $YBa_2Cu_3O_{6+\delta}$ and the series $Tl_2Ba_2Ca_{n+1}Cu_nO_{2n+4+\delta}$, O atoms and O vacancies occur on perovskite-like anion sites. These O atoms may display differing degrees of order. This behavior may significantly affect the superconducting transition temperature, T_c. Crystal symmetry may change (e.g., tetragonal or orthorhombic) as a function of O content. In one such instance, Sieburger and Schilling (1991) documented a strong dependence of T_c for $Tl_2Ba_2CuO_{6+\delta}$ as a function of synthesis pressure. They attributed this phenomenon to pressure-induced ordering of excess O (Takahashi et al. 1993). Thus, it appears that pressure may induce both cation and anion ordering in the perovskite structure.

Rhombohedral carbonates

Carbonates, the most abundant crustal nonsilicates, display significant volume-dependent cation ordering. Calcite, $CaCO_3$, has a structure that features planar CO_3 groups and a single sixfold-coordinated Ca site. Dolomite, $CaMg(CO_3)_2$, has a structure that is topologically identical to that of calcite but with an ordering of Mg and Ca into two symmetrically distinct sites. This ordering reduces the space group symmetry from $R\overline{3}c$ to $R\overline{3}$ (Reeder 1983).

Although virtually all natural dolomites have close to complete Mg-Ca order, Reeder and Wenk (1983) succeeded in partially disordering a dolomite by rapid quenching from high temperature (at pressures sufficient to prevent calcination). They observed a small but significant increase in the *c* unit-cell edge with increased disorder and estimated a 0.15 cm^3/mol ($\sim 0.2\%$) volume change for a (hypothetical) fully disordered end-member. Pressure, therefore, slightly favors the ordered form, though the effect is small.

Davidson et al. (1993), by contrast, proposed that disordered $CaFe(CO_3)_2$ has the smaller unit-cell volume, with volume of disordering of about -0.3 cm^3/mol, and they thus concluded that "increasing pressure stabilizes the disordered phase." A negative volume of disordering was also reported for $CaFe(CO_3)_2$ by Chai and Navrotsky (1996). These authors suggested that the enthalpy of disordering of $CaMg(CO_3)_2$ is in the range of 20–30 kJ/mol, whereas that of $CaFe(CO_3)_2$ is about 10 kJ/mol.

Structural and calorimetric studies of order-disorder in $CdMg(CO_3)_2$ (Capobianco et al. 1987) are particularly significant, because they have led to the synthesis of samples with a complete range from fully ordered to fully disordered Cd-Mg distributions. A sample annealed at 873 K and 0.1 GPa has complete Cd-Mg order, whereas one annealed at 1073 K and 1.5 GPa is almost fully disordered. The volume increase of disordering is quite small ($\Delta V_{dis} \approx 0.03$ cm^3/mol). Thus, pressure would have only a minor effect on stabilizing the ordered state.

Peacor et al. (1987) compared two kutnahorite samples near $CaMn(CO_3)_2$ in composition. One from Bold Knob, North Carolina, had an essentially disordered cation distribution, whereas the other from Sterling Hill, New Jersey, had a partially ordered cation distribution. Compositional differences between these two samples preclude direct comparison of their molar volumes to determine δV_{dis}. Nevertheless, because both extremes exist in nature, kutnahorite may provide an excellent candidate for further investigation of pressure-induced ordering in rhombohedral carbonates.

FUTURE STUDIES

The experimental studies and thermochemical systematics outlined above demonstrate that pressure plays a significant role in the order-disorder behavior of a variety of materials. Much additional research is needed, however, to document this phenomenon. Four types of studies—high-pressure synthesis, controlled ordering experiments, comparative compressibility measurements, and theoretical modeling—would enhance our understanding of pressure-induced ordering.

High-pressure synthesis and characterization of ordered states

For compounds with significant ΔV_{dis}, is molar volume a linear function of the degree of order? What is the pressure dependence of the degree of order? Our understanding of pressure-induced ordering is severely limited by the lack of appropriate samples. Although numerous minerals and synthetic compounds display varying degrees of order, it is difficult to find two compositionally identical samples with markedly different ordered states. The most basic experiments required to understand pressure-induced ordering, therefore, are systematic high-pressure synthesis and characterization of samples displaying varying degrees of ordering.

Table 1 reveals several phases for which a range of ordered states are available. Additional investigations of olivine, orthopyroxene, spinels, and feldspars are needed, whereas controlled synthesis studies of pseudobrookite-type $MgTi_2O_5$ and kutnahorite [$CaMn(CO_3)_2$] hold the promise of providing complete suites of ordered intermediates.

Of special interest to the field of mineral physics would be synthesis at several pressures (and the same temperature) of samples of ferromagnesian silicates, including the minerals wadsleyite, anhydrous phase B, and orthopyroxene described above. Multi-anvil devices, which can produce as much as 0.5 mm^3 of sample at 25 GPa, provide an ideal technique for these syntheses. X-ray analysis, Mössbauer spectroscopy, infrared spectroscopy, and other structural probes of the resulting samples would reveal the extent of cation ordering and the corresponding molar volumes, thus providing information on ΔV_{dis} as well. Synthetic specimens could also be examined by vibrational spectroscopy or calorimetry to determine the effect of ordering on heat capacities and to measure directly the energy of disordering. A suite of compositionally identical samples, which differ only in the pressure of synthesis and degree of Fe-Mg ordering, would thus provide unambiguous evidence for the effect of pressure on order. In such a series, control and characterization of oxidation state (ideally all Fe as Fe^{2+}) would also be important. The temperature chosen should be one at which cation distributions can be equilibrated in about an hour but are quenchable when a sample is cooled in seconds, i.e., probably in the range 1073–1173 K or below.

Intracrystalline cation diffusion at high pressure

How quickly do cation distributions equilibrate at high temperature and high pressure? Is it possible to quench states of order from extreme conditions? Does pressure dramatically affect cation mobility and thus the rate of order-disorder reactions? Studies of pressure-induced ordering can provide answers to these kinetic questions.

As noted above, increased pressure tends to confine atoms and restrict their motions, except in unusual circumstances such as proposed by Goldsmith and Jenkins (1985) for albite. Thus, it is possible that high-pressure ordered states are more slowly achieved, and more readily quenched, than those at lower pressure. (Note that experimental protocol in multi-anvil experiments is to reduce temperature while the sample is at pressure.) If pressure tends to increase cation order, then samples quenched while at higher pressure are more likely to retain their equilibrium ordered state than those quenched from the same temperature while at lower pressure.

Until accurate in situ measurements of ordering can be made, these effects can be quantified by studying the cation distribution in a material such as ferromagnesian orthopyroxene, in which the state of order is a sensitive function of temperature (Virgo and Hafner 1969; Yang and Ghose 1994). Several experiments would equilibrate both ordered and disordered samples of the same composition, thus attempting to achieve equilibrium convergence, at a series of pressures and temperatures. In addition, these samples could be quenched at different cooling rates. All samples quenched rapidly from above a certain critical temperature (perhaps ~1500 K) should presumably display identical degrees of disorder. Samples quenched from lower temperatures or at slower rates, however, should produce different degrees of order. Documentation of these ordered states can thus be used to determine minimum rates of intracrystalline cation diffusion, as well as equilibrium ordered states. A series of such studies at different pressures, furthermore, could constrain the effect of pressure on cation diffusion.

Comparative compressibilities of ordered states

If a suite of crystals with varying degrees of order can be obtained, relative compressibilities of these different structural states could be determined by the method of Hazen (1993). In this technique, several crystals are arranged in the same diamond-anvil-cell mount and probed by X-ray diffraction. Small differences in compressibility can be detected because all crystals are at the same pressure. These differences in compressibilities can provide a direct measurement (or place an upper limit) on $\delta\Delta V_{dis}/\delta P$.

First-principles calculations

Experimental studies are complemented by first-principles calculations of the structure and energetics of different ordered states (see, e.g., Ducastelle 1991; Lu et al. 1991b). These calculations may enhance understanding of the relative stabilities of ordered and disordered states and of states that are not attainable experimentally. First-principles methods also facilitate modeling of the properties of known materials at extreme conditions of temperature and pressure. Most previous theoretical work has focused on ordering in alloy systems (see, e.g., Zunger et al. 1988), but investigations of perovskite-type compounds by Burton and Cohen (1994, 1995) demonstrate the applicability of these methods to mineralogical systems and support the proposition that high pressure often stabilizes ordered states relative to disordered states.

CONCLUSIONS

Pressure plays a central role in the structure and energetics of materials in the Earth's deep interior, and it provides a powerful means of probing atomic interactions in solids. In a recurrent historical pattern, however, studies of phenomena at high pressure, which are often technically more difficult, usually follow detailed high-temperature investigations. The high-temperature decarbonation of limestone, for example, was well known to eighteenth-century neptunists, who used room-pressure data in their attempts to disprove the igneous origin of basalt in contact with limestone. Later, Sir James Hall demonstrated that pressure stabilizes carbonate at high temperature and thus supported the plutonist position (Hall, 1806). Almost two centuries later, data on mineral and rock melting, rock mechanical properties, crystal structures, phase transitions, and many other mineral properties are often obtained at high temperatures long before high-pressure studies commence.

The situation is similar for order-disorder phenomena, which have long been viewed as a key to understanding the thermal history of rocks. Detailed studies of the effects of temperature and composition on ordering have been conducted for most rock-forming minerals and for many metal alloys and other synthetic compounds. Thermochemical models and kinetic parameters have been derived and are routinely used to estimate maximum temperatures, cooling rates, and chemical environments of igneous and metamorphic deposits, as well as meteorites. As we attempt to understand the present state and dynamic behavior of our planet, the effects of pressure on order-disorder phenomena deserve closer scrutiny.

ACKNOWLEDGMENTS

We thank Robert Downs, David Mao, and Charles Prewitt for their stimulating discussions and thoughtful reviews during the preparation of this study. We are also indebted to Ross Angel, Benjamin Burton, Raymond Jeanloz, and an anonymous reviewer, who provided detailed and constructive reviews of the manuscript. This research was supported by the NSF Center for High-Pressure Research, by NSF grant EAR-9218845, and by the Carnegie Institution of Washington.

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MANUSCRIPT RECEIVED JUNE 19, 1995
MANUSCRIPT ACCEPTED MAY 6, 1996