

Chapter 4

Crystallography

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4.1 CRYSTALLINE SUBSTANCES

Crystallography emphasizes the long-range order or crystal structure of crystalline substances. It focuses on the symmetry of crystalline materials and on the ways in which their long-range order is related to the three-dimensional repetition of fundamental units of pattern during crystal growth. In minerals, the fundamental units of pattern are molecular clusters of coordination polyhedra or stacking sequences (Chapter 2). The ways in which these basic units can be repeated to produce crystal structures with long-range order are called symmetry operations. In addition, crystallography focuses on the description and significance of planar features in crystals including planes of atoms, cleavage planes, crystal faces and the forms of crystals. Crystallography is also concerned with crystal defects, local imperfections in the long-range order of crystals. Given the broad scope of

this text, a more detailed treatment of crystallography cannot be provided.

4.1.1 Crystals and crystal faces

Mineral crystals are one of nature's most beautiful creations. Many crystals are enclosed by flat surfaces called crystal faces. **Crystal faces** are formed when mineral crystals grow, and enclose crystalline solids when they stop growing. Perfectly formed crystals are notable for their remarkable symmetry (Figure 4.1). The external symmetry expressed by crystal faces permits us to infer the geometric patterns of the atoms in mineral crystal structures as well. These patterns inferred from external symmetry have been confirmed by advanced analytical techniques such as X-ray diffraction (XRD) and atomic force microscopy (AFM).

Mineralogists have developed language to describe the symmetry of crystals and the crystal faces that enclose them. Familiarizing students with the concepts and terminology of crystal symmetry and crystal faces is one of the primary goals of this chapter. A second

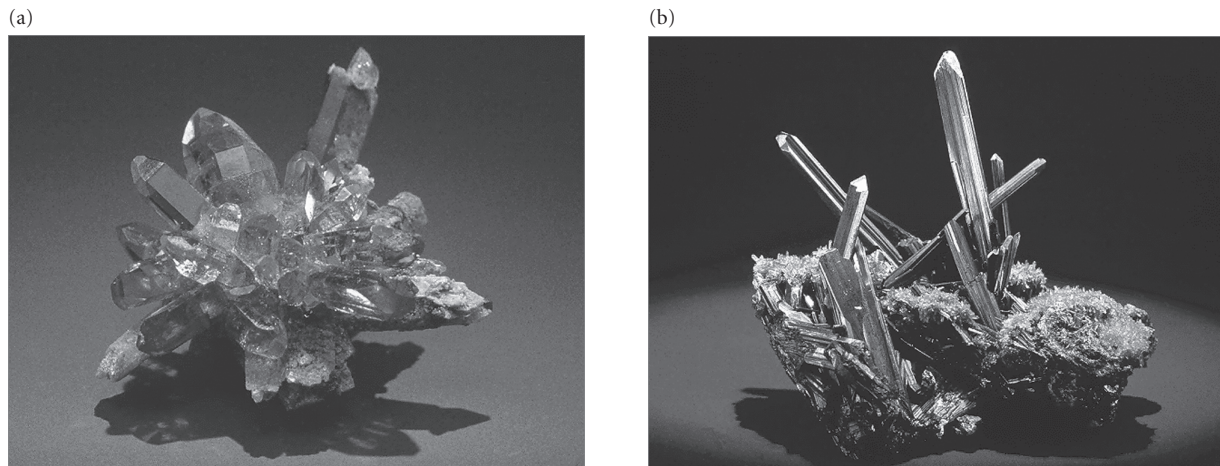


Figure 4.1 Representative mineral crystals: (a) pyrite; (b) tourmaline. (Photos courtesy of the Smithsonian Institute.) (For color version, see Plate 4.1, between pp. 248 and 249.)

goal of this chapter is to build connections between crystal chemistry (Chapters 2 and 3) and crystallography by explaining the relationships between chemical composition and coordination polyhedra and the form, symmetry and crystal faces that develop as crystals grow.

4.1.2 Motifs and nodes

When minerals begin to form, atoms or ions bond together, so that partial or complete coordination polyhedra develop (Chapter 2). Because the ions on the edges and corners of coordination polyhedra have unsatisfied electrostatic charges, they tend to bond to additional ions available in the environment as the mineral grows. Eventually, a small cluster of coordination polyhedra is formed that contains all the coordination polyhedra characteristic of the mineral and its chemical composition. In any mineral, we can recognize a small cluster of coordination polyhedra that contains the mineral's fundamental composition and unit of pattern or motif. As the mineral continues to grow, additional clusters of the same pattern of coordination polyhedra are added to form a mineral crystal with a three-dimensional geometric pattern – a long-range, three-dimensional crystal structure. Clusters of coordination polyhedra are added, one atom or ion at a time, as (1) the crystal nucleates, (2) it becomes a microscopic crystal, and, if growth continues, (3) it becomes a

macroscopic crystal. Growth continues in this manner until the environmental conditions that promote growth change and growth ceases.

Long-range, geometric arrangements of atoms and/or ions in crystals are produced when a fundamental array of atoms, a unit of pattern or motif, is repeated in three dimensions to produce the crystal structure. A **motif** is the smallest unit of pattern that, when repeated by a set of symmetry operations, will generate the long-range pattern characteristic of the crystal. In minerals, the motif is composed of one or more coordination polyhedra. In wallpaper, it is a basic set of design elements that are repeated to produce a two-dimensional pattern, whereas in a brick wall the fundamental motif is that of a single brick that is repeated in space to form the three-dimensional structure. The repetition of these fundamental units of pattern by a set of rules called **symmetry operations** can produce a two- or three-dimensional pattern with long-range order. When several different motifs could be repeated by a similar set of symmetry operations, we may wish to emphasize the general rules by which different motifs may be repeated to produce a particular type of long-range order. In such cases it is useful to represent motifs by using a point. A point used to represent any motif is called a **node**. The pattern or array of atoms about every node must be the same throughout the pattern the nodes represent.

4.2 SYMMETRY OPERATIONS

4.2.1 Simple symmetry operations

Symmetry operations may be simple or compound. **Simple symmetry operations** produce repetition of a unit of pattern or motif using a single type of operation. Compound symmetry operations produce repetition of a unit of pattern or motif using a combination of two types of symmetry operation. Simple symmetry operations include (1) translation, by specific distances in specified directions, (2) rotation, about a specified set of axes, (3) reflection, across a mirror plane, and (4) inversion, through a point called a center. These operations are discussed below and provide useful insights into the geometry of crystal structures and the three-dimensional properties of such crystals.

Translation

The symmetry operation called **translation** involves the periodic repetition of nodes or motifs by systematic linear displacement. One-dimensional translation of basic design elements generates a row of similar elements (Figure 4.2a). The translation is defined by the **unit translation vector** (t), a specific length and direction of systematic displacement by which the pattern is repeated. Motifs other than commas could be translated by the same unit translation vector to produce a one-dimensional pattern. In minerals, the motifs are clusters of atoms or coordination polyhedra that are repeated by translation.

Two-dimensional translations are defined by **two unit translation vectors** (t_a and t_b or t_1 and t_2 , respectively). The translation in one direction is represented by the length and direction of t_a or t_1 ; translation in the second direction is represented by the length and direction of t_b or t_2 . The pattern generated depends on the length of the two unit translation vectors and the angles between their directions. The result of any two-dimensional translation is a **plane lattice** or **plane mesh**. A plane lattice is a two-dimensional array of motifs or nodes in which every node has an environment similar to every other node in the array (Figure 4.2a,b).

Three-dimensional translations are defined by **three unit translation vectors** (t_a , t_b and t_c

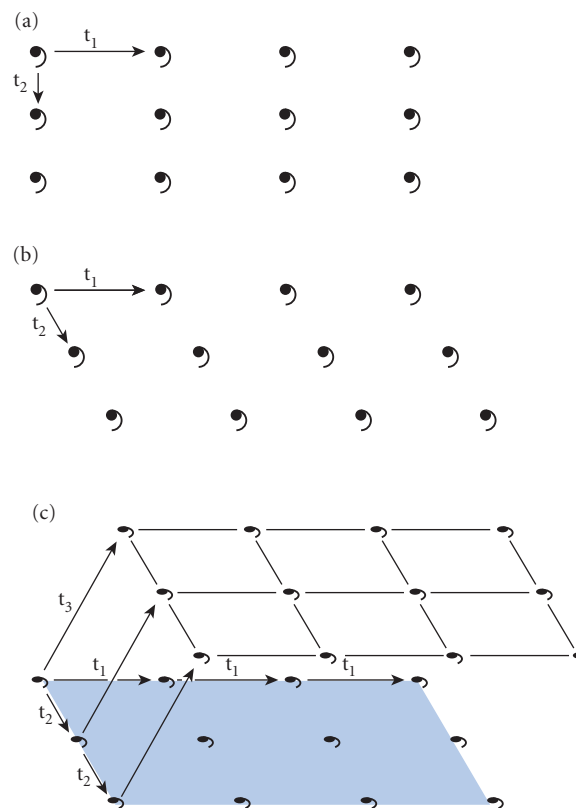


Figure 4.2 (a) Two-dimensional translation at right angles (t_1 and t_2) to generate a two-dimensional mesh of motifs or nodes. (b) Two-dimensional translation (t_1 and t_2) not at right angles to generate a two-dimensional mesh or lattice. (c) Three-dimensional translation (t_1 , t_2 and t_3) to generate a three-dimensional space lattice. (From Klein and Hurlbut, 1985; with permission of John Wiley & Sons.)

or t_1 , t_2 and t_3 , respectively). The translation in one direction is represented by the length and direction of t_a or t_1 , the translation in the second direction is represented by t_b or t_2 and the translation in the third direction is represented by t_c or t_3 . The result of any three-dimensional translation is a **space lattice**. A space lattice is a three-dimensional array of motifs or nodes in which every node has an environment similar to every other node in the array. Since crystalline substances such as minerals have long-range, three-dimensional order and since they may be thought of as motifs repeated in three dimensions, the resulting array of motifs is a **crystal lattice**. Figure 4.2c illustrates a space lattice produced

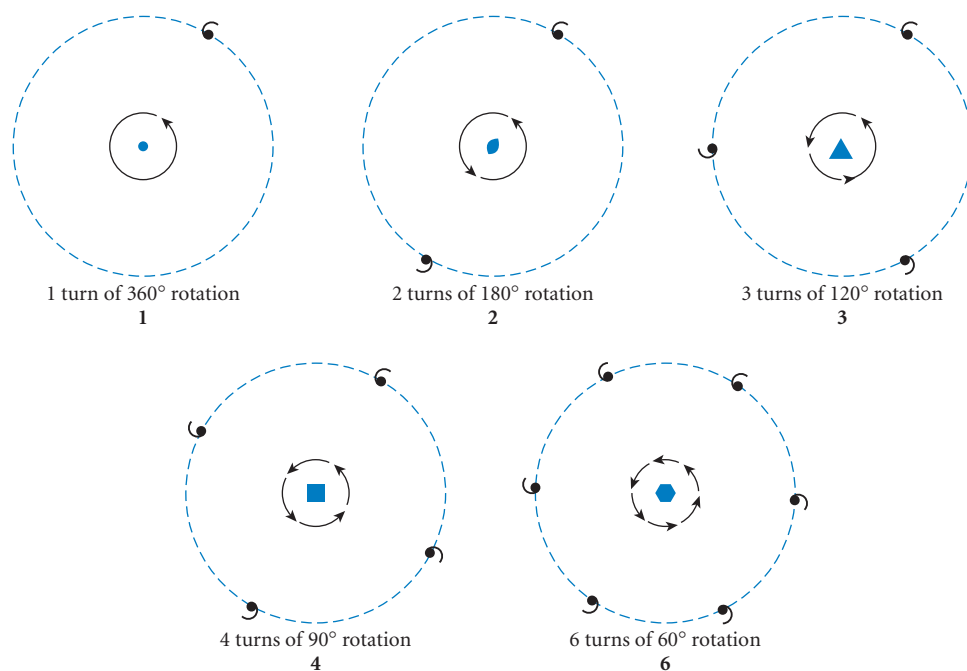


Figure 4.3 Examples of the major types of rotational symmetry ($n = 1, 2, 3, 4$ or 6) that occur in minerals. (From Klein and Hurlbut, 1985; with permission of John Wiley & Sons.)

by a three-dimensional translation of nodes or motifs.

Rotation

Motifs can also be repeated by non-translational symmetry operations. Many patterns can be repeated by rotation (n). **Rotation (n)** is a symmetry operation that involves the rotation of a pattern about an imaginary line or axis, called an **axis of rotation**, in such a way that every component of the pattern is perfectly repeated one or more times during a complete 360° rotation. The symbol “ n ” denotes the number of repetitions that occur during a complete rotation. Figure 4.3 uses comma motifs to depict the major types of rotational symmetry (n) that occur in minerals and other inorganic crystals. The axis of rotation for each motif is perpendicular to the page. Table 4.1 summarizes the major types of rotational symmetry.

Reflection

Reflection is as familiar to us as our own reflections in a mirror or that of a tree in a

Table 4.1 Five common axes of rotational symmetry in minerals.

Type	Symbolic notation	Description
One-fold axis of rotation	(1 or A_1)	Any axis of rotation about which the motif is repeated only once during a 360° rotation (Figure 4.3, (1))
Two-fold axis of rotation	(2 or A_2)	Motifs repeated every 180° or twice during a 360° rotation (Figure 4.3 (2))
Three-fold axis of rotation	(3 or A_3)	Motifs repeated every 120° or three times during a complete rotation (Figure 4.3 (3))
Four-fold axis of rotation	(4 or A_4)	Motifs repeated every 90° or four times during a complete rotation (Figure 4.3 (4))
Six-fold axis of rotation	(6 or A_6)	Motifs repeated every 60° or six times during a complete rotation (Figure 4.3 (5))

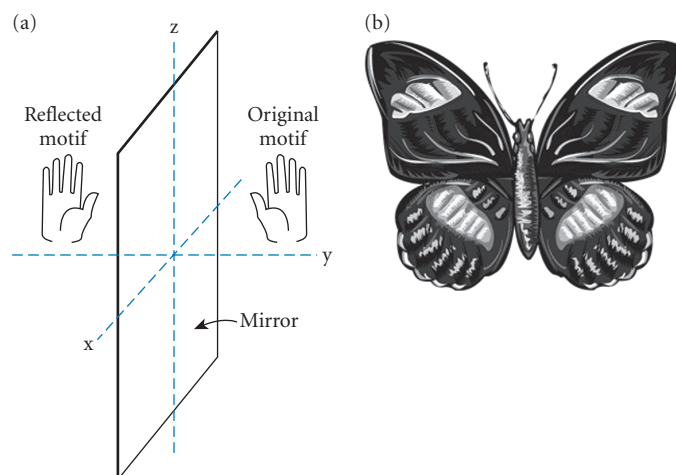


Figure 4.4 Two- and three-dimensional motifs that illustrate the concept of reflection across a plane of mirror symmetry (m). (a) Mirror image of a hand. (From Klein and Hurlbut, 1985; with permission of John Wiley & Sons.) (b) Bilateral symmetry of a butterfly; the two halves are nearly, but not quite, perfect mirror images of each other. (Image from butterflywebsite.com.)

still body of water. It is also the basis for the concept of bilateral symmetry that characterizes many organisms (Figure 4.4). Yet it is a symmetry operation that is somewhat more difficult for most people to visualize than rotation. **Reflection (m)** is a symmetry operation in which every component of a pattern is repeated by reflection across a plane called a **mirror plane** (m). Reflection occurs when each component is repeated by equidistant projection perpendicular to the mirror plane. Reflection retains all the components of the original motif but changes its “handedness”; the new motifs produced by reflection across a mirror plane are mirror images of each other (Figure 4.4). Symmetry operations that change the handedness of motifs are called **enantiomorphic operations**.

One test for the existence of a mirror plane of symmetry is that all components of the motifs on one side of the plane are repeated at equal distances on the other side of the plane along projection lines perpendicular to the plane. If this is not true, the plane is not a plane of mirror symmetry.

Inversion

Inversion is perhaps the most difficult of the simple symmetry operations to visualize. **Inversion** involves the repetition of motifs by

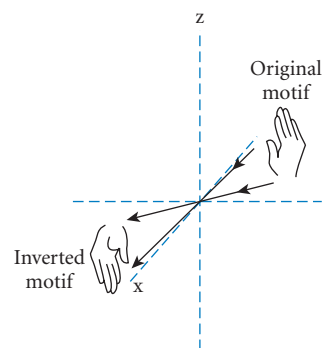


Figure 4.5 Inversion through a center of symmetry (i) illustrated by a hand repeated by inversion through a center (inversion point). (From Klein and Hurlbut, 1985; with permission of John Wiley & Sons.)

inversion through a point called a **center of inversion** (i). Inversion occurs when every component of a pattern is repeated by equidistant projection through a common point or center of inversion. The two hands in Figure 4.5 illustrate the enantiomorphic symmetry operation called inversion and show the center through which inversion occurs. In some symbolic notations centers are symbolized by (c) rather than (i) .

One test for the existence of a center of symmetry is that all the components of a

pattern are repeated along lines that pass through a common center and are repeated at equal distances from that center. If this is not the case, the motif does not possess a center of symmetry.

4.2.2 Compound symmetry operations

Three other symmetry operations exist but, unlike those discussed so far, they are **compound symmetry operations** that combine two simple symmetry operations. **Glide reflection** (g) is a symmetry operation that combines translation (t) or (c) parallel to a mirror plane (m) with reflection across the mirror plane to produce a glide plane (Figure 4.6).

Rotoinversion (\bar{n}) is an operation that combines rotation about an axis with inversion through a center to produce an axis of rotoinversion. Figure 4.7b illustrates an axis of four-fold rotoinversion ($\bar{4}$) in which the motif is repeated after 90° rotation followed by inversion through a center so that it is repeated four times by rotoinversion during a 360° rotation. Axes of two-fold rotoinversion ($\bar{2}$) are unique symmetry operations, whereas axes of three-fold rotoinversion ($\bar{3}$) are equivalent to a three-fold axis of rotation and

a center of inversion ($3i$), and axes of six-fold rotoinversion ($\bar{6}$) are equivalent to a three-fold axis of rotation perpendicular to a mirror plane ($3/m$). **Screw rotation** (n_a) is a symmetry operation that combines translation parallel

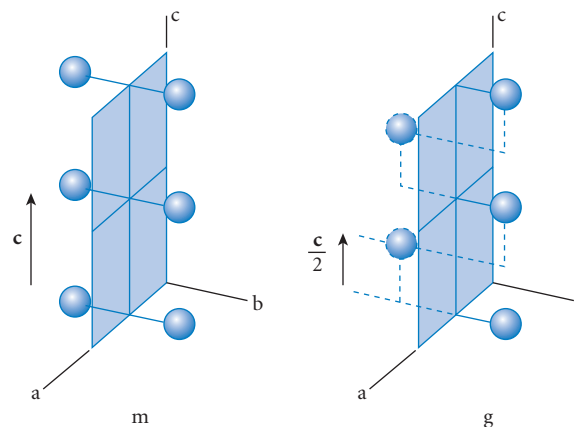


Figure 4.6 Mirror plane (m) with the translation vector (c) on the left, contrasted with a glide plane (g) with the translation vector ($c/2$) combined with mirror reflection on the right. (From Wenk and Bulakh, 2004; with permission of Oxford University Press.)

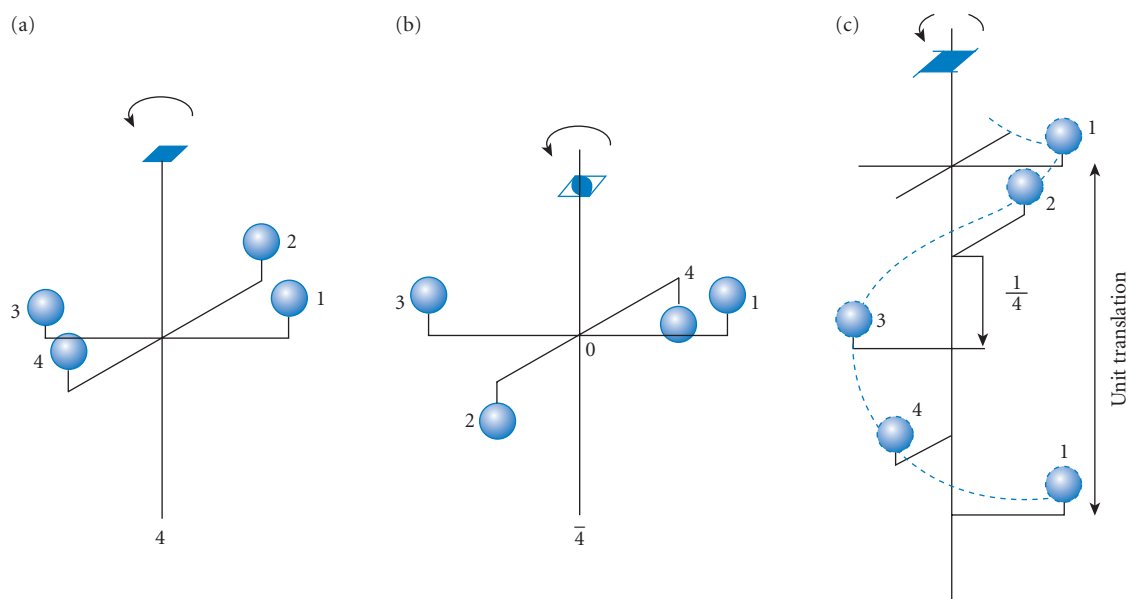


Figure 4.7 (a) An axis of four-fold rotation (4). This contrasts with (b) an axis of four-fold rotoinversion ($\bar{4}$) that combines rotation with inversion every 90° , and (c) a four-fold screw axis (4_1) that combines translation with 90° rotations every one-fourth translation. (From Wenk and Bulakh, 2004; with permission of Oxford University Press.)

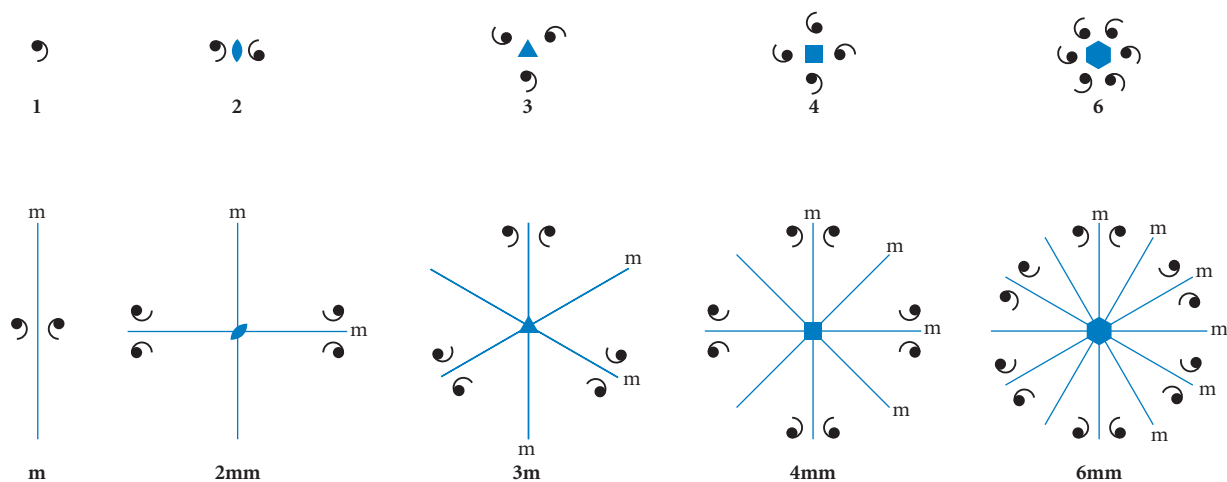


Figure 4.8 The ten plane point groups defined by rotational and reflection symmetry. (From Klein and Hurlbut, 1985; with permission of John Wiley & Sons.)

to an axis with rotation about the axis (Figure 4.7c).

Readers interested in more detailed treatments of the various types of compound symmetry operations should refer to Klein and Dutrow (2007), Wenk and Bulakh (2004) or Nesse (2000).

4.3 TWO-DIMENSIONAL MOTIFS AND LATTICES (MESHES)

The symmetry of three-dimensional crystals can be quite complex. Understanding symmetry in two dimensions provides an excellent basis for understanding the higher levels of complexity that characterize three-dimensional symmetries. It also provides a basis for learning to visualize planes of constituents within three-dimensional crystals. Being able to visualize and reference lattice planes is of the utmost importance in describing cleavage and crystal faces and in the identification of minerals by X-ray diffraction methods.

4.3.1 Plane point groups

Any fundamental unit of two-dimensional pattern, or motif, can be repeated by various symmetry operations to produce a larger two-dimensional pattern. All two-dimensional motifs that are consistent with the generation of long-range two-dimensional arrays can be assigned to one of **ten plane point groups**

based on their unique plane point group symmetry (Figure 4.8). Using the symbolic language discussed in the previous section on symmetry, the ten plane point groups are **1, 2, 3, 4, 6, m, 2mm, 3m, 4mm and 6mm**. The numbers refer to axes of rotation that are perpendicular to the plane (or page); the *m* refers to mirror planes perpendicular to the page. The first *m* refers to a set of mirror planes that is repeated by the rotational symmetry and the second *m* to a set of mirror planes that bisects the first set. Note that the total number of mirror planes is the same as the number associated with its rotational axis (e.g., 3*m* has three mirror planes and 6*mm* has six mirror planes).

4.3.2 Plane lattices and unit meshes

Any motif can be represented by a point called a node. Points or nodes can be translated in one direction by a unit translation vector t_a or t_1 to produce a line of nodes or motifs. Nodes can also be translated in two directions t_a and t_b or t_1 and t_2 to produce a two-dimensional array of points called a plane mesh or **plane net**. Simple translation of nodes in two directions produces five basic types of two-dimensional patterns (Figure 4.9). The smallest units of such meshes, which contain at least one node and the unit translation vectors, are called **unit meshes (unit nets)** and contain all the information necessary to produce the

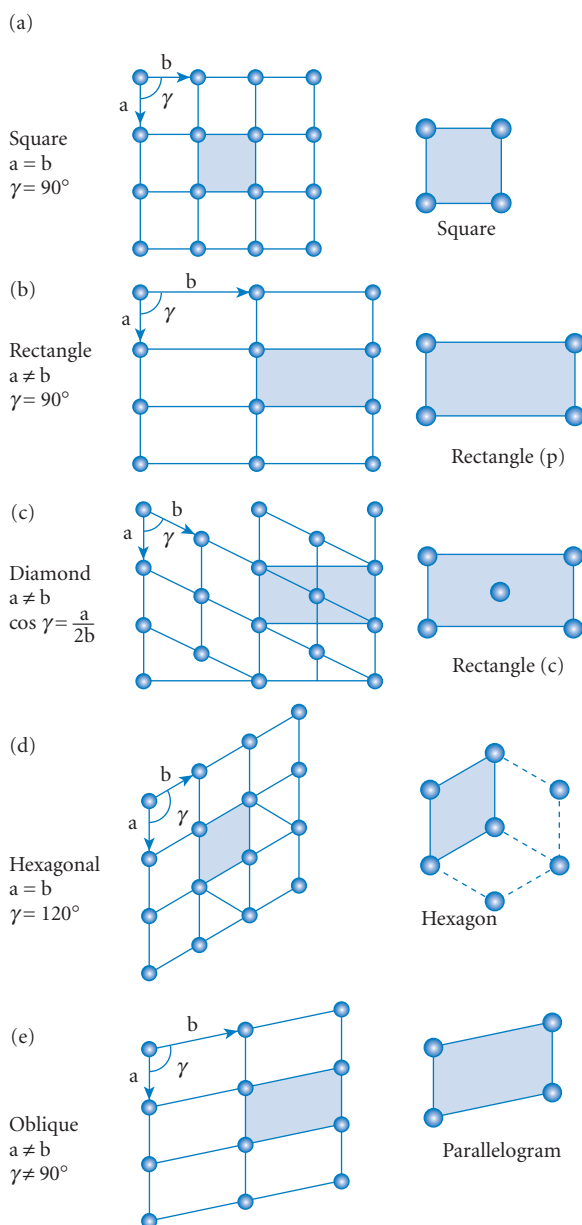


Figure 4.9 The five principal types of meshes or nets and their unit meshes (shaded gray): (a) square, (b) primitive rectangle, (c) diamond or centered rectangle, (d) hexagonal, (e) oblique. (From Nesse, 2000, with permission of Oxford University Press.)

larger two-dimensional pattern. The unit meshes contain only translation symmetry information. The five basic types of unit mesh are classified on the basis of the unit translation vector lengths (equal or unequal), the angles between them (90° , 60° and 120° or none of these) and whether they have nodes

only at the corners (primitive = p) or have an additional node in the center (c) of the mesh.

Square unit meshes (Figure 4.9a) are primitive and have equal unit translation vectors at 90° angles to each other (p , $t_a = t_b$, $\gamma = 90^\circ$). **Primitive rectangular unit meshes** (Figure 4.9b) differ in that, although the unit translation vectors intersect at right angles, they are of unequal lengths (p , $t_a \neq t_b$, $\gamma = 90^\circ$). **Diamond unit meshes** have equal unit translation vectors that intersect at angles other than 60° , 90° or 120° . Diamond lattices can be produced and represented by **primitive diamond unit meshes** (p , $t_a = t_b$, $\gamma \neq 60^\circ$, 90° or 120°). They can also be produced by the translation of **centered rectangular unit meshes** (Figure 4.9c) in which the two unit mesh sides are unequal, the angle between them is 90° and there is a second node in the center of the mesh (c , $t_a \neq t_b$, $\gamma = 90^\circ$). In a centered rectangular mesh there is a total content of two nodes = two motifs. If one looks closely, one may see evidence for glide reflection in the centered rectangular mesh and/or the larger diamond lattice. The **hexagonal unit mesh** (Figure 4.9d) is a special form of the primitive diamond mesh because, although the unit translation vectors are equal, the angles between them are 60° and 120° (p , $t_a = t_b$, $\gamma = 120^\circ$). Three such unit meshes combine to produce a larger pattern with hexagonal symmetry. **Oblique unit meshes** (Figure 4.9e) are primitive and are characterized by unequal unit translation vectors that intersect at angles that are not 90° , 60° or 120° (p , $t_a \neq t_b$, $\gamma \neq 90^\circ$, 60° or 120°) and produce the least regular, least symmetrical two-dimensional lattices. The arrays of nodes on planes within minerals always correspond to one of these basic patterns.

4.3.3 Plane lattice groups

When the ten plane point groups are combined with the five unit meshes in all ways that are compatible, a total of **17 plane lattice groups** are recognized on the basis of the total symmetry of their plane lattices. Note that these symmetries involve translation-free symmetry operations including rotation and reflection, translation and compound symmetry operations such as glide reflection. Table 4.2 summarizes the 17 plane lattice groups and their symmetries. Primitive lattices are

Table 4.2 The 17 plane lattice groups and the unique combination of point group and unit mesh that characterizes each.

Lattice	Point group	Plane group
Oblique (P)	1	P1
	2	P2
Rectangular (P and C)	m	Pm
		Pg
		Cm
	2mm	P2mm
		P2mg
	P2gg	
	C2mm	
Square (P)	4	P4
	4mm	P4mm
		P4gm
Hexagonal (P) (rhombohedral)	3	P3
	3m	P3m1
		P31m
Hexagonal (P) (hexagonal)	6	P6
	6mm	P6mm

denoted by “P” and centered lattices by “C”. Axes of rotation for the entire pattern perpendicular to the plane are noted by 1, 2, 3, 4 and 6. Mirror planes perpendicular to the plane are denoted by “m”; glide planes perpendicular to the plane are denoted by “g”.

The details of plane lattice groups are well documented, but beyond the scope of this text.

4.4 THREE-DIMENSIONAL MOTIFS AND LATTICES

Minerals are three-dimensional Earth materials with three-dimensional crystal lattices. The fundamental units of pattern in any three-dimensional lattice are **three-dimensional motifs** that can be classified according to their translation-free symmetries. These three-dimensional equivalents of the two-dimensional plane point groups are called **space point groups**.

Space point groups can be represented by nodes. These nodes can be translated to produce three-dimensional patterns of points called **space lattices**. Space lattices are the three-dimensional equivalents of plane nets or meshes. By analogy with unit meshes or

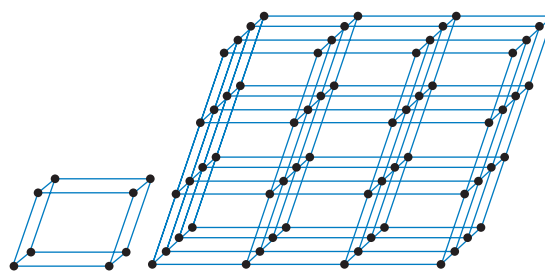


Figure 4.10 A primitive unit cell and a long-range space point lattice that results from its repetition by symmetry operations in three dimensions.

nets, we can recognize the smallest three-dimensional units, called unit cells, which contain all the information necessary to produce the three-dimensional space lattices. In this section, we will briefly describe the space point groups, after which we will detail Bravais lattices, unit cells and their relationship to the six major crystal systems to which minerals belong.

4.4.1 Space point groups

In minerals, the fundamental motifs are parts of clusters of three-dimensional coordination polyhedra sufficient to establish the composition of the mineral. When these are repeated in three dimensions during mineral growth, they produce the long-range order characteristic of crystalline substances (Figure 4.10). Like all fundamental units of pattern, these three-dimensional motifs can be classified on the basis of their translation-free symmetries.

Only 32 different three-dimensional motif symmetries exist. These define 32 space point groups, each with unique space point group symmetry. In minerals, the 32 **crystal classes** – to one of which all minerals belong – correspond to the 32 space point group symmetries of the mineral’s motif. That the crystal classes were originally defined on the basis of the external symmetry of mineral crystals is another example of the fact that the external symmetry of minerals reflects the internal symmetry of their constituents. The 32 crystal classes belong to six (or seven) crystal systems, each with its own characteristic symmetry.

Table 4.3 The six crystal systems and 32 crystal classes, with their characteristic symmetry and crystal forms.

System	Crystal class	Class symmetry	Total symmetry
Isometric	Hexoctahedral	$4/m\bar{3}2/m$	$3A_4, 4\bar{A}_3, 6A_2, 9m$
	Hextetrahedral	$\bar{4}3m$	$3\bar{A}_4, 4A_3, 6m$
	Gyroidal	432	$3A_4, 4A_3, 6A_2$
	Diploidal	$2/m\bar{3}$	$3A_2, 3m, 4\bar{A}_3$
	Tetaroidal	23	$3A_2, 4A_3$
Tetragonal	Ditetragonal–dipyramidal	$4/m2/m2/m$	$i, 1A_4, 4A_2, 5m$
	Tetragonal–scalenohedral	$\bar{4}2m$	$1\bar{A}_4, 2A_2, 2m$
	Ditetragonal–pyramidal	4mm	$1A_4, 4m$
	Tetragonal–trapezohedral	422	$1A_4, 4A_2$
	Tetragonal–dipyramidal	4/m	$i, 1A_4, 1m$
	Tetragonal–disphenoidal	$\bar{4}$	\bar{A}_4
Hexagonal (hexagonal)	Tetragonal–pyramidal	4	$1A_4$
	Dihexagonal–dipyramidal	$6/m2/m2/m$	$i, 1A_6, 6A_2, 7m$
	Ditrigonal–dipyramidal	6m2	$1A_6, 3A_2, 3m$
	Dihexagonal–pyramidal	6mm	$1A_6, 6m$
	Hexagonal–trapezohedral	622	$1A_6, 6A_2$
	Hexagonal–dipyramidal	6/m	$i, 1A_6, 1m$
	Trigonal–dipyramidal	$\bar{6}$	$1\bar{A}_6$
Hexagonal (rhombohedral or trigonal)	Hexagonal–pyramidal	6	$1A_6$
	Hexagonal–scalenohedral	$\bar{3}2/m$	$1\bar{A}_3, 3A_2, 3m$
	Ditrigonal–pyramidal	3m	$1A_3, 3m$
	Trigonal–trapezohedral	32	$1A_3, 3A_2$
	Rhombohedral	$\bar{3}$	$1\bar{A}_3$
Orthorhombic	Trigonal–pyramidal	3	$1A_3$
	Rhombic–dipyramidal	$2/m2/m2/m$	$i, 3A_2, 3m$
	Rhombic–pyramidal	mm2	$1A_2, 2m$
Monoclinic	Rhombic–disphenoidal	222	$3A_2$
	Prismatic	2/m	$i, 1A_2, 1m$
	Sphenoidal	2	$1A_2$
Triclinic	Domatic	m	1m
	Pinacoidal	$\bar{1}$	i
	Pedial	1	None

Table 4.3 summarizes the six (or seven) crystal systems, the symmetries of the 32 space point groups or classes and their names, which are based on general crystal forms. It is important to remember that a crystal cannot possess more symmetry than that of the motifs of which it is composed, but it can possess less, depending on how the motifs are arranged and how the crystal grew.

4.4.2 Bravais lattices, unit cells and crystal systems

As noted earlier, any motif can be represented by a point called a node. Nodes, and the motifs they represent, can also be translated in three directions (t_a , t_b and t_c) to produce three-dimensional space point lattices and unit cells (see Figure 4.10).

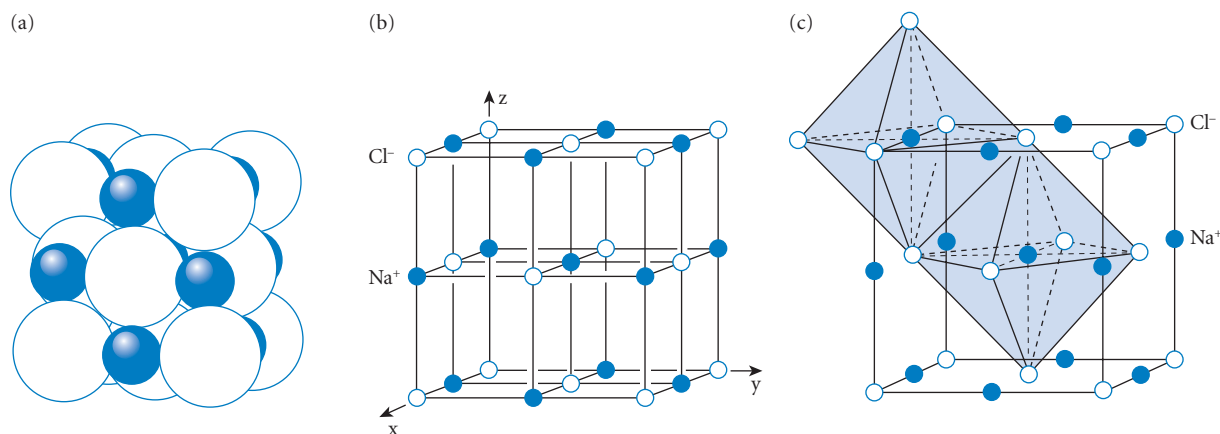


Figure 4.11 Relationship between (a) atomic packing, (b) a unit cell, and (c) octahedral coordination polyhedra in halite (NaCl). (From Wenk and Bulakh, 2004; with permission of Cambridge University Press.)

Unit cells are the three-dimensional analogs of unit meshes. A **unit cell** is a parallelepiped whose edge lengths and volume are defined by the three unit translation vectors (t_a , t_b and t_c). The unit cell is the smallest unit that contains all the information necessary to reproduce the mineral by three-dimensional symmetry operations. Unit cells may be primitive (P), in which case they have nodes only at their corners and a total content of one node (= one motif). Non-primitive cells are multiple because they contain extra nodes in one or more faces (A, B, C or F) or in their centers (I) and possess a total unit cell content of more than one node or motif.

Unit cells bear a systematic relationship to the coordination polyhedra and packing of atoms that characterize mineral structures, as illustrated by Figure 4.11.

Bravais (1850) recognized that only 14 basic types of three-dimensional translational point lattices exist; these are known as the **14 Bravais space point lattices** and define 14 basic types of unit cells. The 14 Bravais lattices are distinguished on the basis of (1) the magnitudes of the three unit translation vectors t_a , t_b and t_c or more simply a , b and c ; (2) the angles (alpha, beta and gamma) between them, where ($\alpha = b \wedge c$; $\beta = c \wedge a$; $\gamma = a \wedge b$); and (3) whether they are primitive lattices or some type of multiple lattice. Figure 4.12 illustrates the 14 Bravais space point lattices.

The translational symmetry of every mineral can be represented by one of the 14 basic types of unit cells. Each unit cell contains one or more nodes that represent motifs and contains all the information necessary to characterize chemical composition. Each unit cell also contains the rules according to which motifs are repeated by translation; the repeat distances, given by $t_a = a$, $t_b = b$, $t_c = c$, and directions, given by angles α , β and γ (where $b \wedge c = \alpha$; $c \wedge a = \beta$; $a \wedge b = \gamma$). The 14 Bravais lattices can be grouped into **six crystal systems** on the basis of the relative dimensions of the unit cell edges (a , b and c) and the angles between them (α , β and γ). These six (or seven) systems in which all minerals crystallize include the **isometric** (cubic), **tetragonal**, **orthorhombic**, **monoclinic**, **triclinic**, **hexagonal** (hexagonal division or system) and **hexagonal** (**trigonal** division or system). Table 4.4 summarizes the characteristics of the Bravais lattices in major crystal systems.

4.5 CRYSTAL SYSTEMS

Imagine yourself in the minerals section of a museum. Large crystals are partially or completely bounded by planar crystal faces that are produced when minerals grow. Many other mineral specimens are partially or completely bounded by flat, planar cleavage faces produced when minerals break along planes of relatively low total bond strength. The

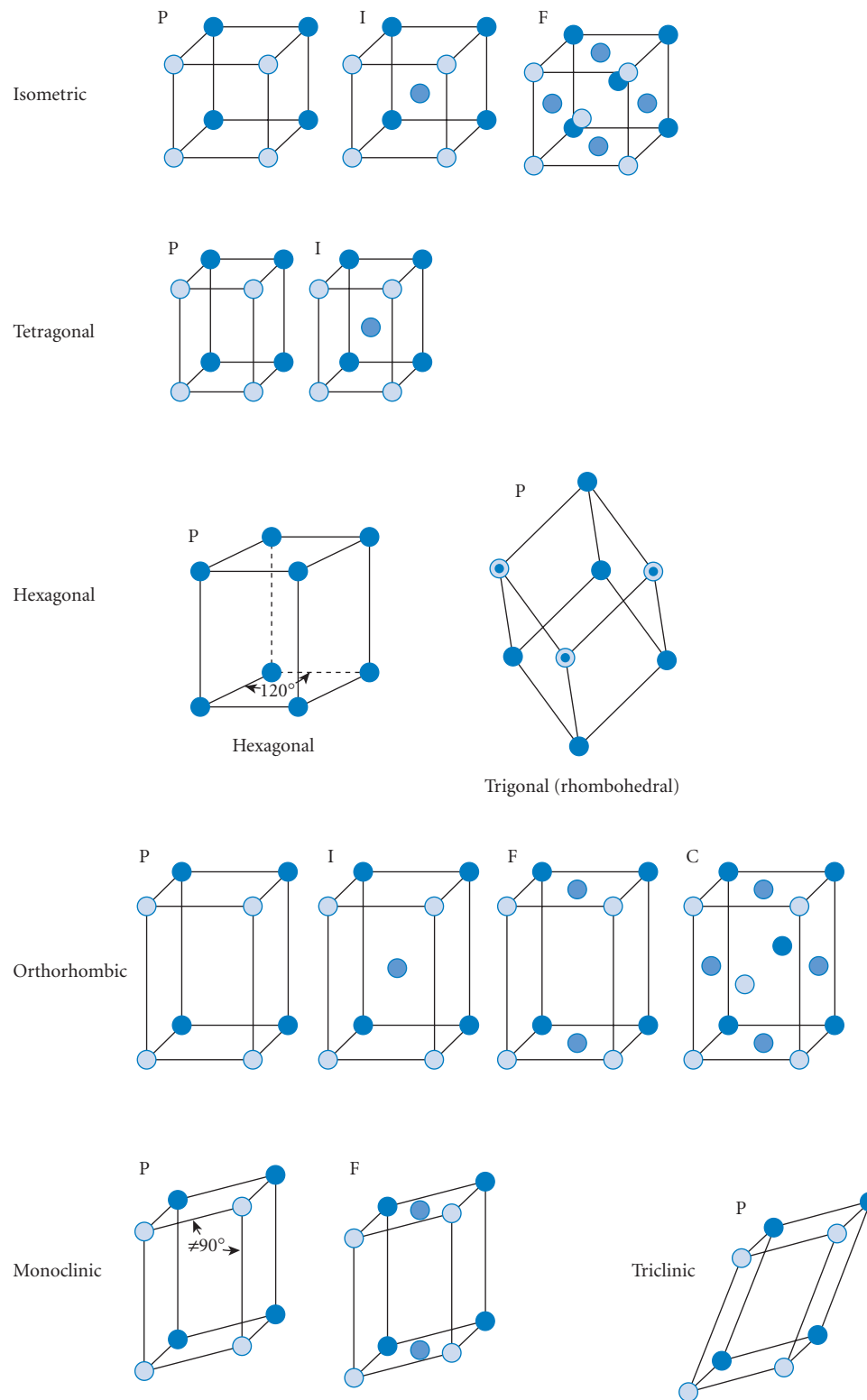


Figure 4.12 The 14 Bravais lattices and the six (or seven) crystal systems they represent. (Courtesy of Steve Dutch.)

Table 4.4 Major characteristics of Bravais lattice cells in the major crystal systems.

Crystal system	Unit cell edge lengths	Unit cell edge intersection angles	Bravais lattice types
Isometric (cubic)	($a = b = c$) Preferred format for edges of equal length is ($a_1 = a_2 = a_3$)	$\alpha = \beta = \gamma = 90^\circ$	Primitive (P) Body centered (I) Face centered (F)
Tetragonal	($a_1 = a_2 \neq a_3$) or $a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Primitive (P) Body centered (I)
Hexagonal (hexagonal)	($a_1 = a_2 \neq a_3$) ($a = b \neq c$)	($\alpha = \beta = 90^\circ \neq \gamma = 120^\circ$)	Primitive (P)
Hexagonal (trigonal or rhombohedral)	($a_1 = a_2 = a_3$)	$\alpha = \beta = \gamma \neq 90^\circ$	Primitive (P)
Orthorhombic	$a \neq b \neq c$	($\alpha = \beta = \gamma = 90^\circ$)	Primitive (P) Body centered (I) End centered (A,B,C) Face centered (F)
Monoclinic	$a \neq b \neq c$	($\alpha = \gamma = 90^\circ \neq \beta$)	Primitive (P) End centered (C)
Triclinic	$a \neq b \neq c$	(α, β and $\gamma \neq 90^\circ$)	Primitive (P)

shapes of the crystals, the number and orientation of the crystal faces and the nature of the cleavage depend on the crystal structure of the mineral. That is, they depend on the basic motif and the symmetry operations that produce the three-dimensional crystal lattice. The nature of the crystal forms and cleavage surfaces depends on the crystal system and crystal class in which the mineral crystallized.

4.5.1 Crystallographic axes

To identify, describe and distinguish between planes in minerals, including cleavage planes, crystal faces and X-ray diffraction planes, a comprehensive terminology has been developed that relates each set of planes to the three **crystallographic axes** (Figure 4.13). For all but the rhombohedral division of the hexagonal system, the three crystallographic axes, designated a , b and c , are generally chosen to correspond to the three unit cell translation vectors (t_a , t_b , and t_c). With the exception noted, the three crystallographic axes have lengths and angular relationships that correspond to those of the three sets of unit cell edges (Table 4.4). The rules for labeling the three crystallographic axes are specific to each system; some systems have

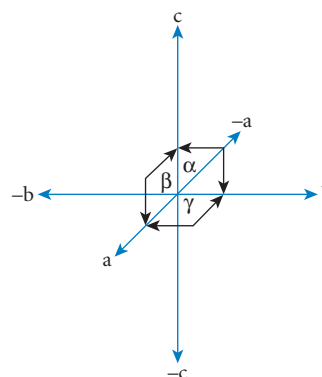


Figure 4.13 Conventional labeling of crystallographic axes, illustrating the positive and negative ends of the three crystallographic axes and the angles between the axes for crystals in the orthorhombic system.

multiple sets of rules. The details are beyond the scope of this text.

When referencing crystallographic planes to the crystallographic axes, a **standard set of orientation rules** is used (Table 4.5). To indicate their similarity, crystallographic axes with the same length are labeled a_1 , a_2 and/or a_3 instead of a , b and c . In the isometric, tetragonal and orthorhombic systems (Figure 4.14), the b -axis (or a_2 -axis) is

Table 4.5 The relationships of crystallographic axes and the rules for orienting crystals in each of the crystal systems. Note that the trigonal system (division) is listed independently of the hexagonal system (division) in this table.

Crystal system	Verbal description	Symbolic description
Isometric (cubic)	Three mutually perpendicular axes (a_1, a_2, a_3) of equal length that intersect at right angles	$(a_1 = a_2 = a_3)$ $(\alpha = \beta = \gamma = 90^\circ)$
Tetragonal	Three mutually perpendicular axes; axes (a_1, a_2) are of equal length; the c axis may be longer or shorter	$(a_1 = a_2 \neq c)$ $(\alpha = \beta = \gamma = 90^\circ)$
Orthorhombic	Three mutually perpendicular axes of different lengths (a, b, c); two axial length ratios have been used to identify the axes: $c > b > a$ (older) or $b > a > c$ (newer)	$(a \neq b \neq c)$ $(\alpha = \beta = \gamma = 90^\circ)$
Monoclinic	Three unequal axes lengths (a, b, c) only two of which are perpendicular. The angle (β) between a and c is not 90° . The a -axis is inclined towards the observer. The b -axis is horizontal and the c -axis is vertical	$(a \neq b \neq c)$ $(\alpha = \gamma = 90^\circ; \beta \neq 90^\circ)$
Triclinic	Three unequal axes, none of which are generally perpendicular. The c axis is vertical and parallel to the prominent zone of crystal faces	$(a \neq b \neq c)$ $(\alpha \neq \beta \neq \gamma \neq 90^\circ)$
Hexagonal	Four crystallographic axes; three equal horizontal axes (a_1, a_2, a_3) intersecting at 120° . One longer or shorter axis (c) perpendicular to the other three. a_1 oriented to front left of observer; a_2 to right; a_3 to back left; c vertical. Six-fold axis of rotation or rotoinversion	$(a_1 = a_2 = a_3 \neq c)$ $(\alpha = 120^\circ; \beta = \gamma = 90^\circ)$
Trigonal (or rhombohedral)	Axes and angles are similar to the hexagonal system; crystal symmetry is different with the c -axis a three-fold axis of rotation or rotoinversion	$(a_1 = a_2 = a_3 \neq c)$ $(\alpha = 120^\circ; \beta = \gamma = 90^\circ)$

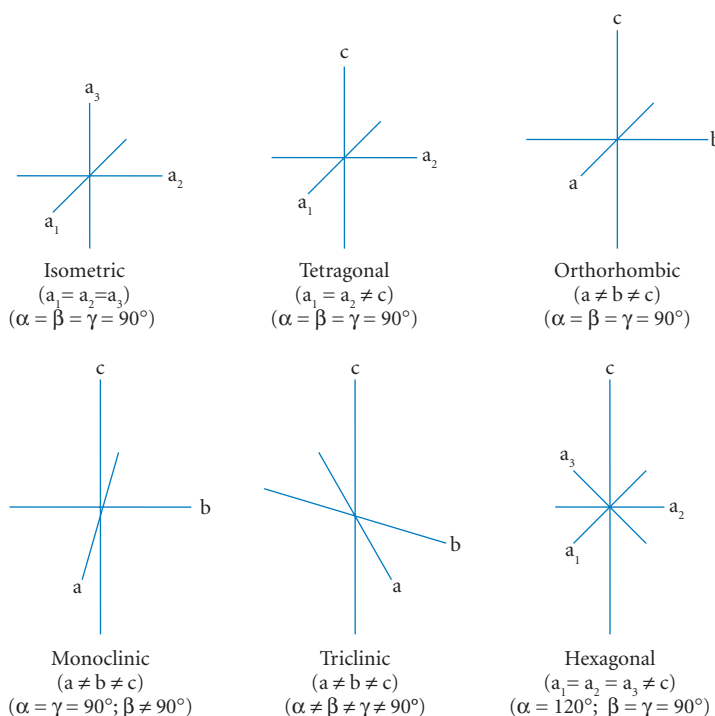


Figure 4.14 Crystallographic axes (positive ends labeled) and intersection angles for the major crystal systems: isometric, tetragonal, orthorhombic, monoclinic, triclinic and hexagonal systems.

oriented from left to right, with the right end designated as the positive end of the axis (b or a_2) and the left end designated as the negative end of the axis (\bar{b} or \bar{a}_2). The a -axis (or a_1 -axis) is oriented so that it trends from back to front toward the observer. The end of the a -axis toward the observer is designated as the positive end of the axis (a) and the end of the a -axis away from the observer is designated as the negative end (\bar{a}). The c -axis is oriented vertically with the top end designated as the positive end of the axis (c) and the bottom end designated as the negative end (\bar{c}). There are small exceptions to these rules in the hexagonal, monoclinic and triclinic systems that result from the fact that unit cell edges are not perpendicular to one another and not all crystallographic axes intersect at right angles. Even in the hexagonal and monoclinic systems, the b -axis is oriented horizontally with the positive end to the right, and in all systems the c -axis is vertical with the positive end toward the top and the negative end toward the bottom. The orientations, lengths and intersection angles between crystallographic axes in each of the major crystal systems are illustrated in Figure 4.14. The characteristics of the crystallographic axes in each system and the standard rules for orienting them are summarized in Table 4.5.

4.5.2 Crystal forms

Each of the crystal systems has an associated set of common crystal forms. **Crystal forms** consist of a three-dimensional set of one or more crystal faces that possess similar relationships to the crystallographic axes. Some natural crystals possess only one crystal form; others possess multiple or combined crystal forms. Crystal forms can be subdivided into two major groups: closed forms and open forms.

Closed crystal forms have the potential to completely enclose a mineral specimen and therefore to exist alone in perfectly formed (euhedral) crystals. Common closed forms include all the forms in the isometric system and many forms in the tetragonal, hexagonal, trigonal and orthorhombic systems. The pyritohedron (Figure 4.15) is a typical closed form, common in the mineral pyrite. Each closed form possesses a different shape that is related to the number and shape of faces in

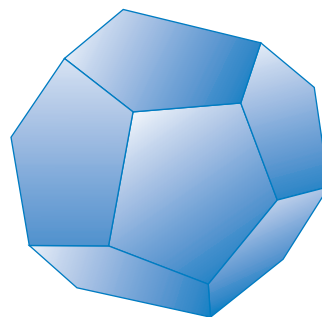


Figure 4.15 A pyritohedron, a closed form in which all faces have the same general relationship to the crystallographic axes.

the form and their angular relationships to the crystallographic axes. Figure 4.16 illustrates common dipyrmaid closed forms in the trigonal, tetragonal and hexagonal systems.

Open crystal forms (Figure 4.17) do not have the potential to completely enclose a mineral specimen and so must occur in combination with other open or closed crystal forms. Common open forms include: (1) **pedions**, which consist of a single face, (2) **pinacoids**, a pair of parallel faces, (3) **prisms**, three or more faces parallel to an axis, (4) **pyramids**, three or more faces that intersect an axis, (5) **domes**, a pair of faces symmetrical about mirror plane, and (6) **sphenoids**, a pair of faces symmetrical about an axis of rotation. Figure 4.17b illustrates the kinds of prisms that occur in the trigonal, tetragonal and hexagonal crystal systems.

The most common crystal forms in each system are discussed later in this chapter, after we have presented the language used to describe them. More detailed discussions are available in Klein and Dutrow (2007) and Nesse (2000).

4.6 INDEXING CRYSTALLOGRAPHIC PLANES

4.6.1 Axial ratios

Whatever their respective lengths, the proportional lengths or **axial ratios** of the three crystallographic axes ($a:b:c$) can be calculated. The standard method for expressing axial ratios is to express their lengths relative to the length of the b -axis (or a_2 -axis) which is taken to be unity so that the ratio is expressed as

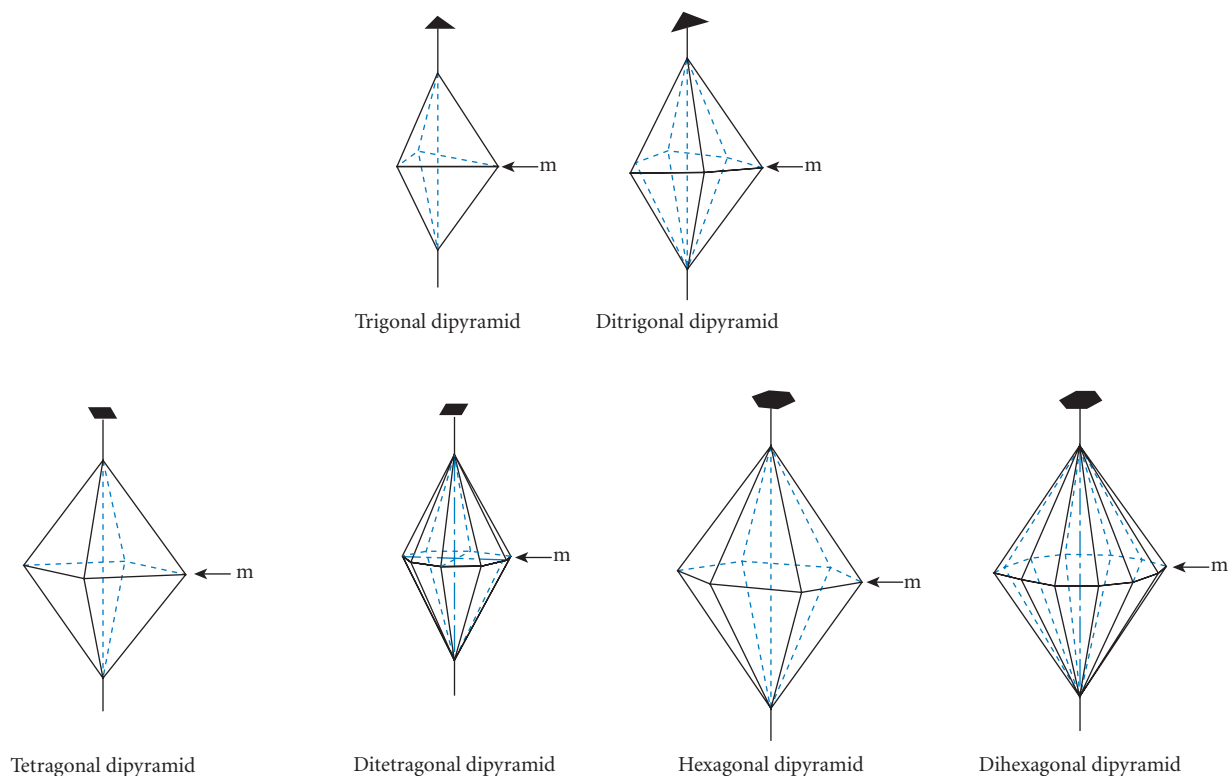


Figure 4.16 Different types of dipyramid forms in the trigonal, tetragonal and hexagonal systems. (From Klein and Hurlbut, 1985; with permission of John Wiley & Sons.)

$a:b:c$; $b = 1$. This is accomplished by dividing the lengths of all three axes by the length of the b -axis ($a/b:b/b:c/b$). An example from the monoclinic system, the pseudo-orthorhombic mineral staurolite, will illustrate how axial ratios are calculated. In staurolite, the unit cell edges have average dimensions expressed in angstrom (\AA) units of: $a = 7.87 \text{\AA}$, $b = 16.58 \text{\AA}$ and $c = 5.64 \text{\AA}$. The axial ratios are calculated from $a/b:b/b:c/b = 7.87/16.58 \text{\AA} : 16.58/16.58 \text{\AA} : 5.64/16.58 \text{\AA}$. The average axial ratios of staurolite are $0.47:1.00:0.34$.

Axial ratios are essential to understanding how crystallographic planes and crystal forms are described by reference to the crystallographic axes as discussed in the section that follows.

4.6.2 Crystal planes and crystallographic axes

Crystalline substances such as minerals have characteristic planar features that include: (1)

crystal faces that develop during growth, (2) cleavage surfaces that develop during breakage, and (3) crystal lattice planes that reflect X-rays and other types of electromagnetic radiation. All these types of planes possess a number of shared properties.

Each type of plane is a representative of large sets of parallel lattice planes. As a mineral with a particular crystal form grows freely it may be bounded by a sequence of planar faces. When it stops growing, it is bounded by crystal faces that are parallel to many other lattice planes that bounded the mineral as it grew over time. When a mineral cleaves, it breaks along a specific set of parallel planes of relative weakness, but these cleavage planes are parallel to large numbers of planes of weakness or potential cleavage surfaces in the mineral structure along which the mineral did not happen to rupture. When X-rays are reflected from a reflecting plane, they are reflected simultaneously from all the planes in the crystal that are parallel to one

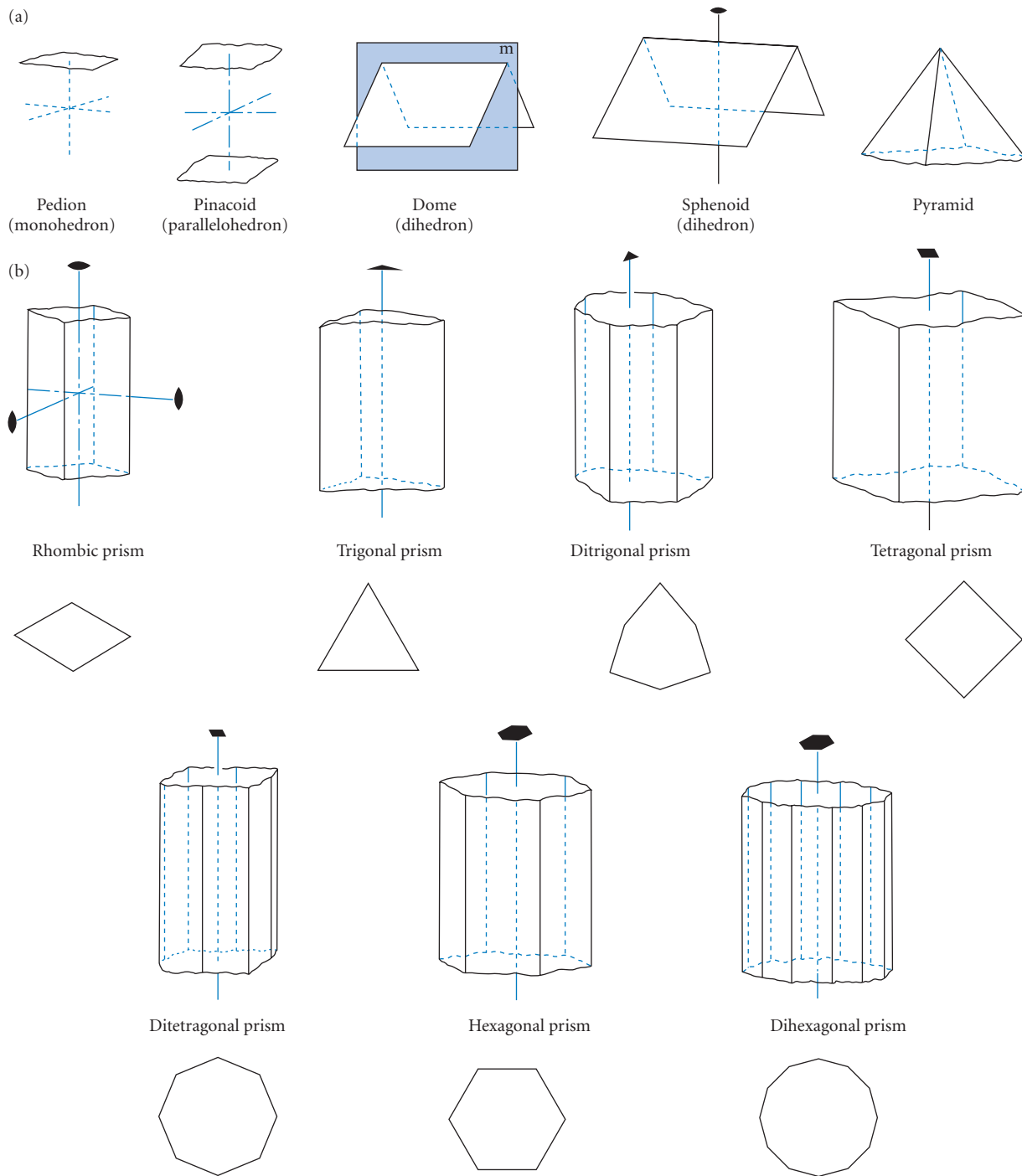


Figure 4.17 (a) Common open forms: pedions, pinacoids, domes, sphenoids and pyramids. (b) Different types of prisms that characterize the trigonal, tetragonal and hexagonal systems. The illustrated prisms are bounded by pinacoids at the top and bottom. (From Hurlbut and Klein, 1985; with permission of John Wiley & Sons.)

another to produce a “reflection peak” that is characteristic of the mineral and can be used to identify it. In addition, any set of parallel planes in a crystal is characterized by a particular molecular content; all the parallel planes in the set possess the same molecular units, spacing and arrangement. A molecular image of one of these planes is sufficient to depict the molecular content of all the planes that are parallel to it. Third, all the planes in a set of parallel planes have the same general spatial relationship to the three crystallographic axes. This means that they can be collectively identified in terms of their spatial relationship to the three crystallographic axes. This is true for crystal faces, for cleavage surfaces, for X-ray reflecting planes or for any set of crystallographic planes that we wish to identify. A universally utilized language has evolved that uses the relationship between the planar features in minerals and the crystallographic axes to identify different sets of planes. A discussion of this language and its use follows.

Figure 4.18 depicts several representative crystal planes with different relationships to the three crystallographic axes. Some crystal planes, or sets of parallel planes, intersect one crystallographic axis and are parallel to the other two (Figure 4.18a, b). Alternatively, a set of crystal planes may intersect two crystallographic axes and be parallel to the third (Figure 4.18c, d). Still other sets of planes

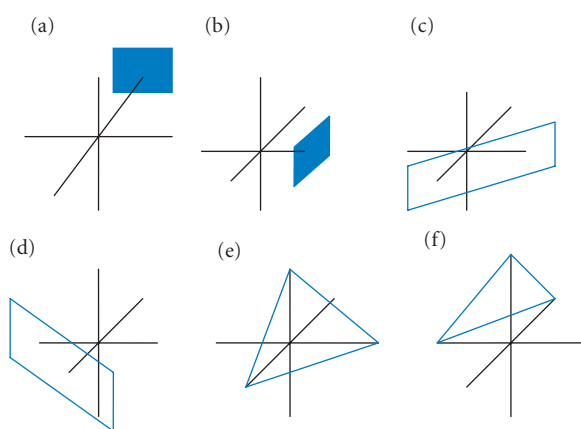


Figure 4.18 Representative crystal faces that cut one, two or three crystallographic axes. See text for further discussion of parts (a) to (f).

intersect all three crystallographic axes (Figure 4.18e, f). No other possibilities exist in Euclidean space; sets of planes in crystalline substances must intersect one, two or three axes and be parallel to those they do not intersect.

Of course, some sets of planes or their projections intersect the positive ends of crystallographic axes (Figure 4.18b, c, e). Others, with different orientations with respect to the axes, intersect the negative ends of crystallographic axes (Figure 4.18a). Still others, with yet different orientations, intersect the positive ends of one or more axes and the negative ends of the other crystallographic axes (Figure 4.18d, f). Given the myriad possibilities, a simple language is needed that allows one to visualize and communicate to others the relationship and orientation of any set of crystal planes to the crystallographic axes. The language for identifying and describing crystallographic planes involves the use of symbols called Miller indices, which has been employed since the 1830s and is explained in the following sections.

4.6.3 Unit faces and planes

In any crystal, the three crystallographic axes have a characteristic axial ratio, typically grounded in the cell edge lengths of the unit cell. No matter how large the mineral becomes during growth, even if it experiences preferred growth in a particular direction or inhibited growth in another, the axial ratio remains constant and corresponds to the axial ratio implied by the properties of the unit cell.

In the growth of any mineral one can imagine the development of a crystal face, one of many potential crystal faces, that intersects the positive ends of all three axes at lengths that correspond to the axial ratio of the mineral (Figure 4.19). For crystals with a center (i), such faces would intersect each axis at a distance from the center of the crystal that corresponds to the axial ratio. For the monoclinic (pseudo-orthorhombic) mineral staurolite discussed in the previous section, such a face could cut the *a*-axis at 0.47 mm, the *b*-axis at 1.00 mm and the *c*-axis at 0.34 mm from the center, or, for a larger crystal, it could cut the three axes at 0.47, 1.00 and 0.34 cm from the center. Any face or plane that intersects all three axes at

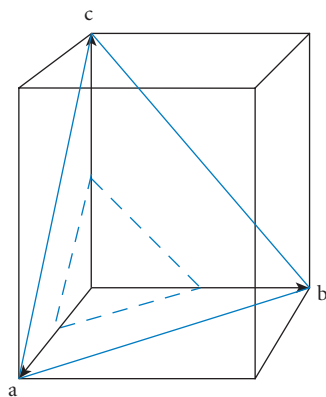


Figure 4.19 Unit face (outlined in solid blue) in an orthorhombic crystal with three unequal unit cell edges and crystallographic axes that intersect at right angles. All parallel faces (e.g., outlined in dotted blue) will have the same general relationship to the crystallographic axes and the same atomic content and properties.

distances from the center that correspond to the axial ratio of the mineral is a **unit face** or **unit plane**. It is part of a set of parallel planes all of which are unit planes because they intersect the three crystallographic axes at lengths that correspond to the axial ratios.

4.6.4 Weiss parameters

Weiss parameters provide a method for describing the relationships between sets of crystal faces or planes and the crystallographic axes. They are always expressed in the sequence $a:b:c$, where a represents the relationship of the planes to the a -axis (or a_1 -axis), b represents the relationship between the planes and the b -axis (or a_2 -axis) and c depicts the relationship between the planes and the c -axis (or a_3 -axis). A unit face or plane that cuts all three crystallographic axes at ratios corresponding to their axial ratios has the Weiss parameters $(1:1:1)$. Mathematically, if we divide the actual lengths at which the face or plane intercepts the three axes by the corresponding axial lengths, the three intercepts have the resulting ratio $1:1:1$, or unity, which is why such planes are called unit planes. Again, using the pseudo-orthorhombic mineral staurolite as an

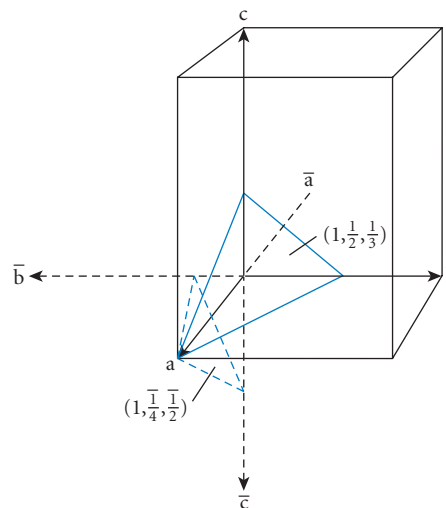


Figure 4.20 Faces with different Weiss parameters on an orthorhombic crystal.

example, if we divide the actual intercept distances by the axial lengths, the resulting ratios are $0.47/0.47: 1.00/1.00: 0.34/0.34 = 1:1:1$. Even if we utilize the magnitudes of the dimensions, the three resulting numbers have the same dimensional magnitude, and so their ratio reduces to $1:1:1$.

As discussed in the section on unit faces and planes, many planes intersect all three crystallographic axes. Unit faces or planes $(1:1:1)$, such as those in Figure 4.19, intersect all three axes at lengths that correspond to their axial ratios. Other sets of planes, however, intersect one or more axes at lengths that do not correspond to their axial ratios. A face or plane that intersects all three crystallographic axes at different lengths relative to their axial ratios is called a **general face**. The Weiss parameters of such a face or plane will be three rational numbers that describe the fact that each axis is intersected at a different proportion of its axial ratio. There are many sets of general planes. For example, a general plane with the Weiss parameters $(1:1/2:1/3)$, shown in Figure 4.20, would be a plane that intersects the c -axis at one-third the corresponding length of the c -axis and the b -axis at one-half the corresponding length of the b -axis. Since many general faces are possible, for example $(1:1/2:1/3)$ or $(1/2:1:1/4)$, it is possible to write a general notation for all the faces that intersect the three crystallographic

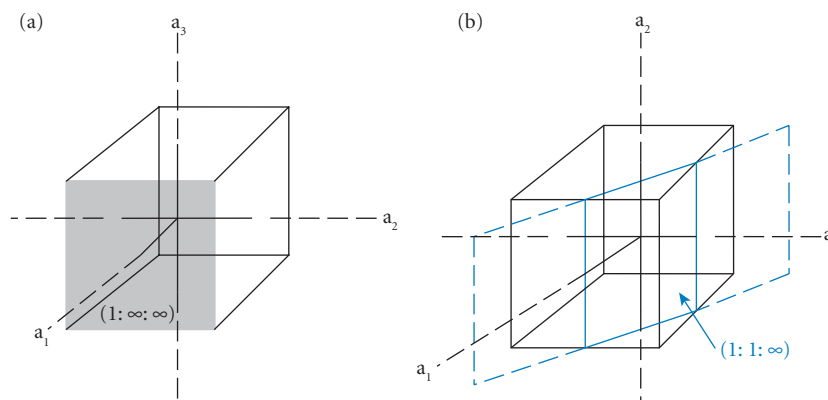


Figure 4.21 (a) The darkened front crystal face possesses the Weiss parameters: $(1:\infty:\infty)$. (b) The face outlined in blue possesses the Weiss parameters $(1:1:\infty)$.

axes as $(h:k:l)$ where h , k and l are intercepts with a , b and c .

Many crystal planes intersect the negative ends of one or more crystallographic axes. The location and/or orientation of these planes are not the same as those of planes that intersect the positive ends of the same axes. Planes that intersect the negative ends of one or more crystallographic axes are indicated by placing a bar over their Weiss parameters. For example, the dashed plane in Figure 4.20 has the Weiss parameters $(1:\bar{1}/4:\bar{1}/2)$.

Mineral planes may be parallel to one or two crystallographic axes. How do we determine the Weiss parameters for such faces and planes? The Weiss parameters of any face or plane that is parallel to a crystallographic axis are infinity (∞) because the plane never intersects the axis in question. If a set of planes is parallel to two crystallographic axes and intersects the third, it is assumed to intersect that axis at unity. Planes that are parallel to the a - and b -axes and intersect the c -axis have the Weiss parameters $(\infty:\infty:1)$. Planes parallel to the b - and c -axes that intersect the a -axis have the Weiss parameters $(\infty:1:\infty)$. Planes that cut the b -axis and are parallel to the a - and c -axes (Figure 4.21a) have the Weiss parameters $(1:\infty:\infty)$. Each set of planes, with its unique relationship to the crystallographic axes possesses its own unique Weiss parameters. If a set of planes intersects two axes and is parallel to the third, only one of the Weiss parameters will be infinity. The other two will be one if, and only if, the two axes are intersected at lengths corresponding to their axial

ratios. Therefore, the Weiss parameters $(1:\infty:1)$ represent planes that parallel the b -axis and intersect the a - and c -axes at unit lengths. Similarly the Weiss parameters $(1:1:\infty)$ are those of planes that cut the a - and b -axes at unit lengths and are parallel to the c -axis (Figure 4.21b).

Having begun to master the concepts of how Weiss parameters can be used to represent different sets of crystal planes with different sets of relationships to the crystallographic axes, students are generally thrilled to find that crystal planes are commonly referenced, not by Weiss parameters, but instead by Miller indices.

4.6.5 Miller indices

The **Miller indices** of any face or set of planes are the **reciprocals of its Weiss parameters**. They are calculated by inverting the Weiss parameters and multiplying by the lowest common denominator. Because of this reciprocal relationship, large Weiss parameters become small Miller indices. For planes parallel to a crystallographic axis, the Miller index is zero. This is because when the large Weiss parameter infinity (∞) is inverted it becomes the Miller index $1/\infty \rightarrow 0$.

The Miller index of any face or set of planes is, with a few rather esoteric exceptions, expressed as three integers **hkl** in a set of parentheses **(hkl)** that represent the reciprocal intercepts of the face or planes with the three crystallographic axes (a , b and c) respectively.

We can use the example of the general face cited in the previous section (see Figure 4.20), where a set of parallel planes cuts the a -axis at unity, cuts the b -axis at half unity and cuts the c -axis at one-third unity. The Weiss parameters of such a set of parallel planes are $1:1/2:1/3$. If we invert these parameters they become $1/1, 2/1$ and $3/1$. The lowest common denominator is one. Multiplying by the lowest common denominator yields 1, 2 and 3. The Miller indices of such a face are (123) . These reciprocal indices should be read as representing all planes that intersect the a -axis at unity (1) and the b -axis at one-half unity (reciprocal is 2), and then intercept the c -axis at one-third unity (reciprocal is 3) relative to their respective axial ratios. Every parallel plane in this set of planes has the same Miller indices.

As is the case with Weiss parameters, the Miller indices of planes that intersect the negative ends of one or more crystallographic axes are denoted by the use of a bar placed over the indices in question. We can use the example from the previous section in which a set of planes intersect the positive end of the a -axis at unity, the negative end of the b -axis at twice unity and the negative end of the c -axis at three times unity. If the Weiss parameters of each plane in the set are $\frac{1}{1}, \frac{2}{3}$ and $\frac{1}{2}$, inversion yields $1/1, \frac{3}{2}$ and $2/1$. Multiplication by two, the lowest common denominator, yields $2/1, \frac{6}{2}$ and $4/1$ so that the Miller indices are $(2\bar{3}4)$. These indices can be read as indicating that the planes intersect the positive end of the a -axis and the negative ends of the b - and c - crystallographic axes with the a -intercept at unity and the b -intercept at two-thirds unity and the c -intercept at one-half unity relative to their respective axial ratios.

A simpler example is the cubic crystal shown in Figure 4.22. Each face of the cube intersects one crystallographic axis and is parallel to the other two. The axis intersected is indicated by the Miller index "1" and the axes to which it is parallel are indicated by the Miller index "0". Therefore the six faces of the cube have the Miller indices (100) , $(\bar{1}00)$, (010) , $(0\bar{1}0)$, (001) and $(00\bar{1})$.

Miller indices are a symbolic language that allows us to represent the relationship of any crystal or cleavage face or crystallographic plane with respect to the crystallographic axes.

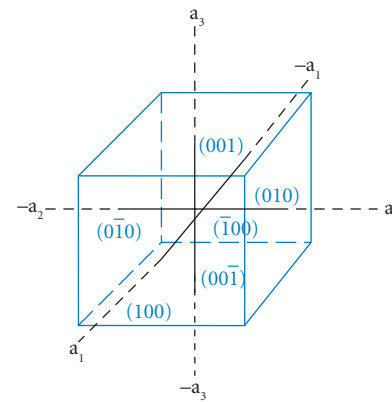


Figure 4.22 Miller indices of various crystal faces on a cube depend on their relationship to the crystallographic axes.

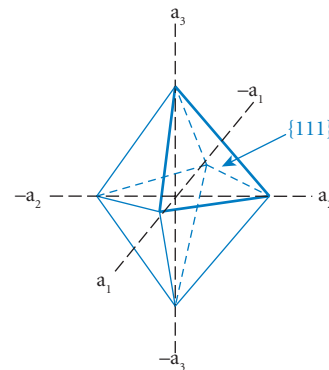


Figure 4.23 An isometric octahedron outlined in red possesses eight faces; the form face $\{111\}$ is outlined in bold blue.

4.6.6 Form indices

Every face in a form has the same general relationship to the crystallographic axes and therefore the same general Miller index, yet every face in a form has a different specific relationship to the crystallographic axes and therefore has a different Miller index. These statements can be clarified by using an example. Figure 4.23 shows the common eight-faced isometric form called the octahedron.

Each face in the octahedron has the same general relationship to the three crystallographic axes in that each intersects the three crystallographic axes at unity. The Miller

indices of each face are some form of (111) . However, only the top, right front face intersects the positive ends of all three axes. The bottom, left back face intersects the negative ends of all three axes, and the other six faces intersect some combination of positive and negative ends of the three crystallographic axes. None of the faces are parallel to one another; each belongs to a different set of parallel planes within the crystal. The Miller indices of these eight faces and the set of planes to which each belongs are (111) , $(\bar{1}\bar{1}\bar{1})$, $(11\bar{1})$, $(1\bar{1}\bar{1})$, $(\bar{1}\bar{1}1)$, $(\bar{1}1\bar{1})$, $(1\bar{1}1)$ and $(11\bar{1})$. Their unique Miller indices allow us to distinguish between the eight faces and the sets of planes to which they belong. But they are all parts of the same form because they all have the same general relationship to the crystallographic axes. It is cumbersome to have to recite the indices of every face within it. To represent the general relationship of the form to the crystallographic axes, the indices of a single face, called the form face, are chosen and placed in brackets to indicate that they refer to the form indices. The rule for choosing the **form face** is generally to select the top face if there is one, or the top right face if there is one, or the top right front face if there is one. In the case of the octahedron, the top right front face is the face that intersects the positive ends of the a_1 -axis (front), the a_2 -axis (right) and the a_3 -axis (top) and has the Miller indices (111) . The form indices for all octahedral crystals are the Miller indices of the form face placed between curly brackets, $\{111\}$. Similarly the form indices for the cube (see Figure 4.22), in which the faces intersect one axis and are parallel to the other two are $\{001\}$, the Miller indices of the top face, whereas the form indices for the dodecahedron, in which each face intersects two axes

at unity and is parallel to the third is $\{011\}$, the indices for the top, right face.

Many other forms exist. Every crystal form has a form index, which is the Miller index of the form face placed in brackets. Each form consists of one or (generally) more faces and each face possesses a Miller index different from that of every other face in the form. Every crystal system has a characteristic suite of forms that reflect the unique characteristics of the crystal lattice of the system, especially the relative lengths of the three crystallographic axes that directly or indirectly reflect the lengths of the unit cell edges. The forms characteristic of each class (space point group) in each crystal system are beyond the scope of this text. A brief review of some common forms in each crystal system follows.

4.6.7 Common crystal forms in crystal systems

Isometric (cubic) system forms

All forms in the isometric system are closed forms. Common crystal forms in the isometric system include the cube, octahedron, dodecahedron, tetrahedron and pyritohedron (Figure 4.24), all closed forms. These forms often occur in combination with each other. Common isometric minerals, their crystal forms and form indices are summarized in Table 4.6.

These form indices are also used to describe cleavage in isometric minerals such as halite and galena, which possess cubic cleavage $\{001\}$ with three orientations of cleavage at right angles; fluorite, which possesses octahedral cleavage $\{111\}$ with four orientations; and sphalerite, which possesses dodecahedral cleavage $\{011\}$ with six orientations of cleavage.

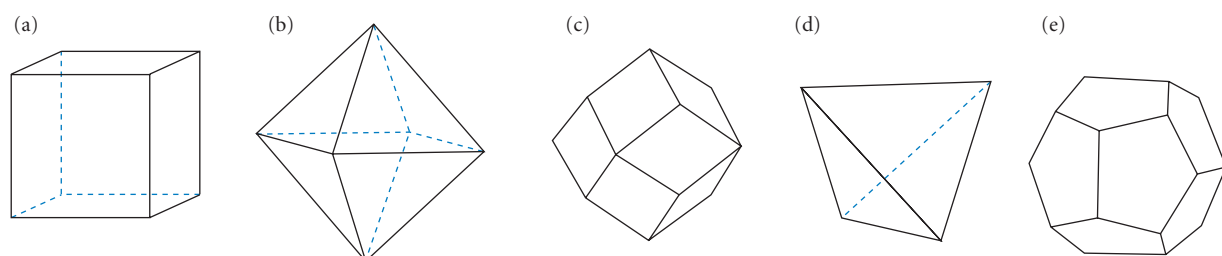
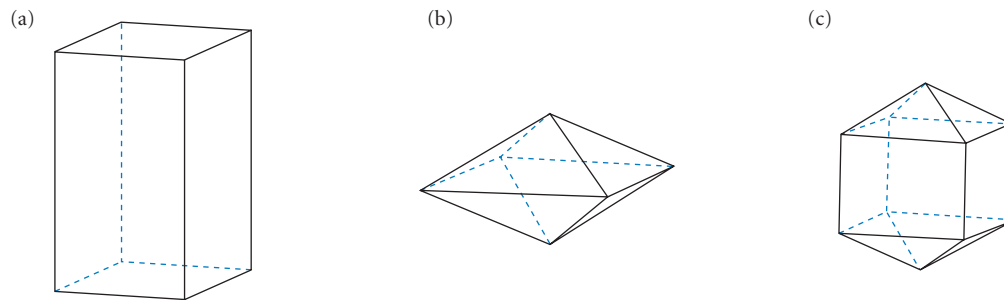


Figure 4.24 Five common forms in the isometric system: (a) cube, (b) octahedron, (c) dodecahedron, (d) tetrahedron, (e) pyritohedron.

Table 4.6 Common isometric crystal forms, form indices, form descriptions and minerals.

Crystal form	Form indices	Form description	Minerals that commonly exhibit crystal form
Cube	{001}	Six square faces	Halite, galena, pyrite, fluorite, cuprite, perovskite, analcite
Octahedron	{111}	Eight triangular faces	Spinel, magnetite, chromite, cuprite, galena, diamond, gold, perovskite
Dodecahedron	{011}	12 diamond-shaped faces	Garnet, sphalerite, sodalite, cuprite
Tetrahedron	{ $\bar{1}\bar{1}\bar{1}$ }	Four triangular faces	Tetrahedrite, sphalerite
Pyritohedron	{h0l}	12 pentagonal faces	Pyrite

**Figure 4.25** Common crystal forms in the tetragonal crystal system: (a) tetragonal prism in combination with a pinacoid, (b) tetragonal dipyrmaid, (c) tetragonal dipyrmaid in combination with a tetragonal prism.**Table 4.7** Common tetragonal crystal forms, form indices, form descriptions and minerals.

Crystal forms	Form indices	Form description	Minerals that commonly exhibit crystal form
Tetragonal dipyrmaid	{111} {hh1} {011} {0kl} and variations	Eight triangular faces; top four separated from bottom four by mirror plane	Zircon, rutile, cassiterite, scheelite, wulfenite, vesuvianite, scapolite
Tetragonal prism	{010} {110} and variations	Four rectangular faces parallel to c-axis	Zircon, scheelite, vesuvianite, rutile, malachite, azurite, cassiterite, scapolite
Tetragonal disphenoid	{0kl}	Four triangular faces; alternating pairs symmetrical about c-axis	Chalcopyrite
Basal pinacoid	{001}	Pair of faces perpendicular to c-axis	Vesuvianite, wulfenite

Tetragonal system forms

Tetragonal crystals can possess either closed or open forms, often in combination. Common closed crystal forms in the tetragonal crystal system include different eight-sided dipyrmaids. Common open forms include four-sided prisms and pyramids, as well as pinacoids and pedions. Typical crystal forms and associated minerals in the tetragonal crystal system are shown in Figure 4.25 and Table 4.7.

Hexagonal system (hexagonal division) forms

Common crystal forms in the hexagonal system include 6–12-sided prisms, dipyrmaids and pyramids. Pinacoids and pedions are also common. Some selected examples of common crystal forms and minerals in the hexagonal system are illustrated in Figure 4.26 and Table 4.8.

Trigonal system (hexagonal system, trigonal division) forms

Common crystal forms in the trigonal system include the six-sided rhombohedron, the 12-sided scalenohedron, six-sided trigonal dipyramids and three-sided trigonal pyramids.

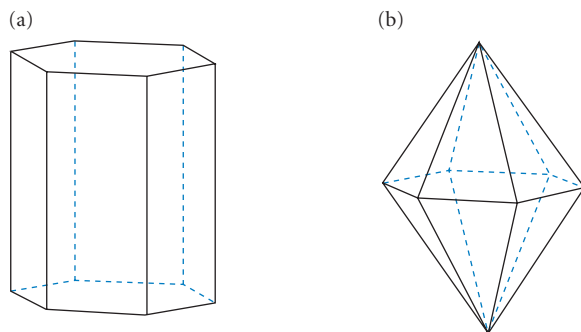


Figure 4.26 Common crystal forms in the hexagonal crystal system (hexagonal division): (a) hexagonal prism with pinacoids, (b) hexagonal dipyramid.

Pinacoids and pedions are also common. Many forms common in the hexagonal division also occur in trigonal crystals, but not vice versa. Common crystal forms and representative minerals in the trigonal crystal system are summarized in Figure 4.27 and Table 4.9.

Orthorhombic crystal system

Common crystal forms in the orthorhombic system include four-sided rhombic prisms, dipyramids and pyramids. Pinacoids are the dominant form and pedions are also common. Common crystal forms and associated minerals in the orthorhombic crystal system are indicated in Figure 4.28 and Table 4.10.

Monoclinic crystal system

Because of its lower symmetry, the only crystal forms in the monoclinic crystal system are four-sided prisms, two-sided domes, sphenoids and pinacoids, and pedions. More

Table 4.8 Common hexagonal crystal forms and associated hexagonal and trigonal minerals.

Crystal forms	Common form indices	Form description	Minerals that commonly exhibit crystal form
Hexagonal dipyramid	$\{11\bar{2}1\}$ and variations	12 triangular faces inclined to c-axis; top six separated from bottom six by mirror plane	Apatite, zincite
Hexagonal prism	$\{11\bar{2}0\}$ and variations	Six rectangular faces parallel to c-axis	Apatite, beryl, quartz, nepheline, corundum, tourmaline
Basal pinacoid	$\{0001\}$	Pair of faces perpendicular to c-axis	Apatite, beryl, corundum

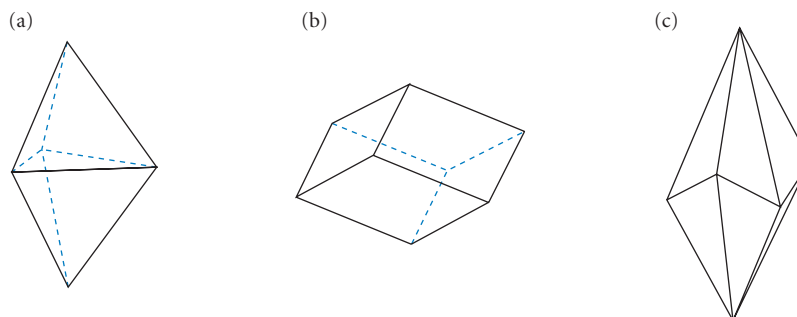
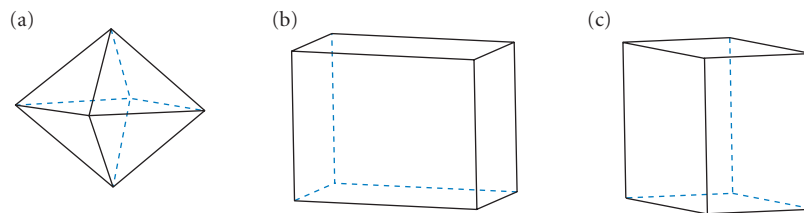


Figure 4.27 Common crystal forms in the trigonal system: (a) trigonal dipyramid, (b) rhombohedron, (c) scalenohedron.

Table 4.9 Common trigonal crystal forms and associated minerals.

Crystal forms	Form indices	Form description	Minerals that commonly exhibit crystal form
Rhombohedron	$\{10\bar{1}1\}$ $\{h0\bar{h}l\}$	Six parallelogram faces inclined to c-axis	Dolomite, calcite, siderite, rhodochrosite, quartz, tourmaline; chabazite
Trigonal Scalenohedron	$\{hk\bar{l}\}$ and variations	12 scalene triangle faces inclined to c-axis	Calcite
Trigonal prism	$\{hk\bar{l}0\}$ and variations	Three rectangular faces parallel to c-axis	Tourmaline, calcite, quartz
Trigonal dipyramid	$\{hk\bar{l}\}$ and variations	Six triangular faces; top three separated from bottom three by a mirror plane	Tourmaline

**Figure 4.28** Common crystal forms in the orthorhombic crystal system: (a) rhombic dipyramid, (b) front, side and basal pinacoids, (c) rhombic prism with a pinacoid.**Table 4.10** Common crystal forms, form indices and minerals in the orthorhombic system.

Crystal forms	Form indices	Form description	Minerals that commonly exhibit crystal form
Rhombic dipyramids	$\{111\}$ $\{hkl\}$ and variations	Eight triangular faces; top four separated from bottom four by a mirror plane	Topaz, aragonite, witherite, olivine
Rhombic prisms; first, second and third order	$\{011\}$ $\{0kl\}$ $\{101\}$ $\{h0l\}$ $\{011\}$ $\{0kl\}$	Four rectangular faces parallel to a single crystallographic axis	Stibnite, aragonite, barite, celestite, topaz, enstatite, andalusite, cordierite, epidote, olivine
Pinacoids; front, side and basal	$\{001\}$ $\{010\}$ $\{001\}$	Two parallel faces perpendicular to a-, b- or c-axis	Barite, celestite, olivine, andalusite, topaz, hemimorphite

complex forms cannot exist in systems with low symmetry in which crystallographic axes do not all intersect at right angles. Common crystal forms and associated minerals in the monoclinic crystal system are indicated in Figure 4.29 and Table 4.11.

Triclinic crystal system

The only crystal forms in the triclinic system, with its extremely low symmetry, are pinacoids and pedions. Common forms and minerals in the triclinic system are illustrated in Figure 4.30 and listed in Table 4.12.

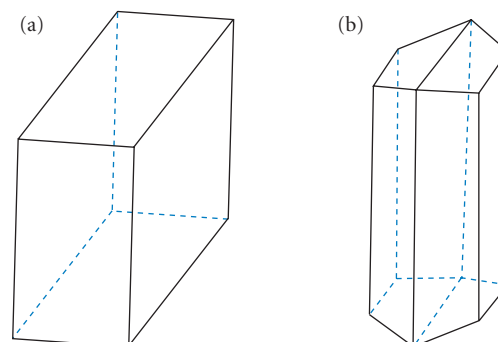
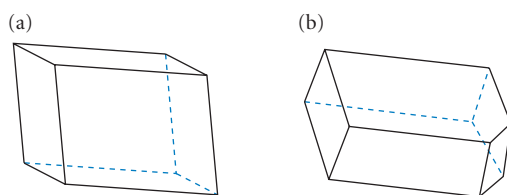
**Figure 4.29** Monoclinic crystal forms: (a) front, side and basal pinacoids, (b) two monoclinic prisms and a side pinacoid.

Table 4.11 Common crystal forms, form indices, and minerals in the monoclinic system.

Crystal form	Form indices	Form description	Minerals that commonly exhibit crystal form
Monoclinic prisms; first, third and fourth order	{011} {0kl} {110} {hk0} {hkl}	Four rectangular faces	Gypsum, staurolite, clinopyroxenes, amphiboles, orthoclase, sanidine, sphene (titanite), borax
Pinacoids; front, side and basal	{001} {010} {001}	Pair of rectangular faces perpendicular to a-, b- or c-axis	Gypsum, staurolite, sphene (titanite), epidote, micas, clinopyroxenes, amphiboles

Table 4.12 Common crystal forms, form indices and minerals in the triclinic system.

Crystal forms	Form indices	Form description	Minerals that commonly exhibit crystal form
Pinacoids	{001}{010}{001} {0k1} {hk1} and variations	Two parallel faces	Kyanite, plagioclase, microcline, amblygonite, rhodonite, wollastonite
Pedions	{hk1}	Single face	Similar

**Figure 4.30** Triclinic crystal forms: (a) front, side and basal pinacoids, (b) various pinacoids and a pedion to the lower right.

4.7 TWINNED CRYSTALS

Many crystals are **twinned crystals** that contain two or more parts called twins. **Twins** have the following characteristics: (1) they possess different crystallographic orientations, (2) they share a common surface or plane, and (3) they are related by a symmetry operation such as reflection, rotation or inversion (Figure 4.31). Because twins are related by a symmetry operation, twinned crystals are not random intergrowths.

The symmetry operation that relates twins in twinned crystals is called a twin law. A **twin law** describes the symmetry operation that produces the twins and the plane (hkl) or axis involved in the operation. For example, swallowtail twins in gypsum (Figure 4.31a) are related by reflection across a plane (001),

which is not a mirror plane in single gypsum crystals. Carlsbad twins in potassium feldspar (Figure 4.31f) are related by a two-fold axis of rotation that is parallel to the c-axis (001), which is not a rotational axis in single potassium feldspar crystals.

The surfaces along which twins are joined are called **composition surfaces**. If the surfaces are planar, they are called **composition planes**, which may or may not be equivalent to twin planes. Other composition surfaces are irregular. Twins joined along composition planes are called **contact twins** and do not appear to penetrate one another. Good examples of contact twins are shown in Figure 4.31a and b. Twins joined along irregular composition surfaces are usually related by rotation and are called **penetration twins** because they appear to penetrate one another. Good examples of penetration twins are shown in Figure 4.31c–f.

Twinned crystals that contain only two twins are called **simple twins**, whereas **multiple twins** are twinned crystals that contain more than two twins. If multiple twins are repeated across multiple parallel composition planes, the twins are called **polysynthetic twins**. Polysynthetic albite twins (Figure 4.31b) are repeated by the albite twin law, reflection across (010), and are very common in plagioclase. They produce small ridges and troughs on the cleavage surfaces of

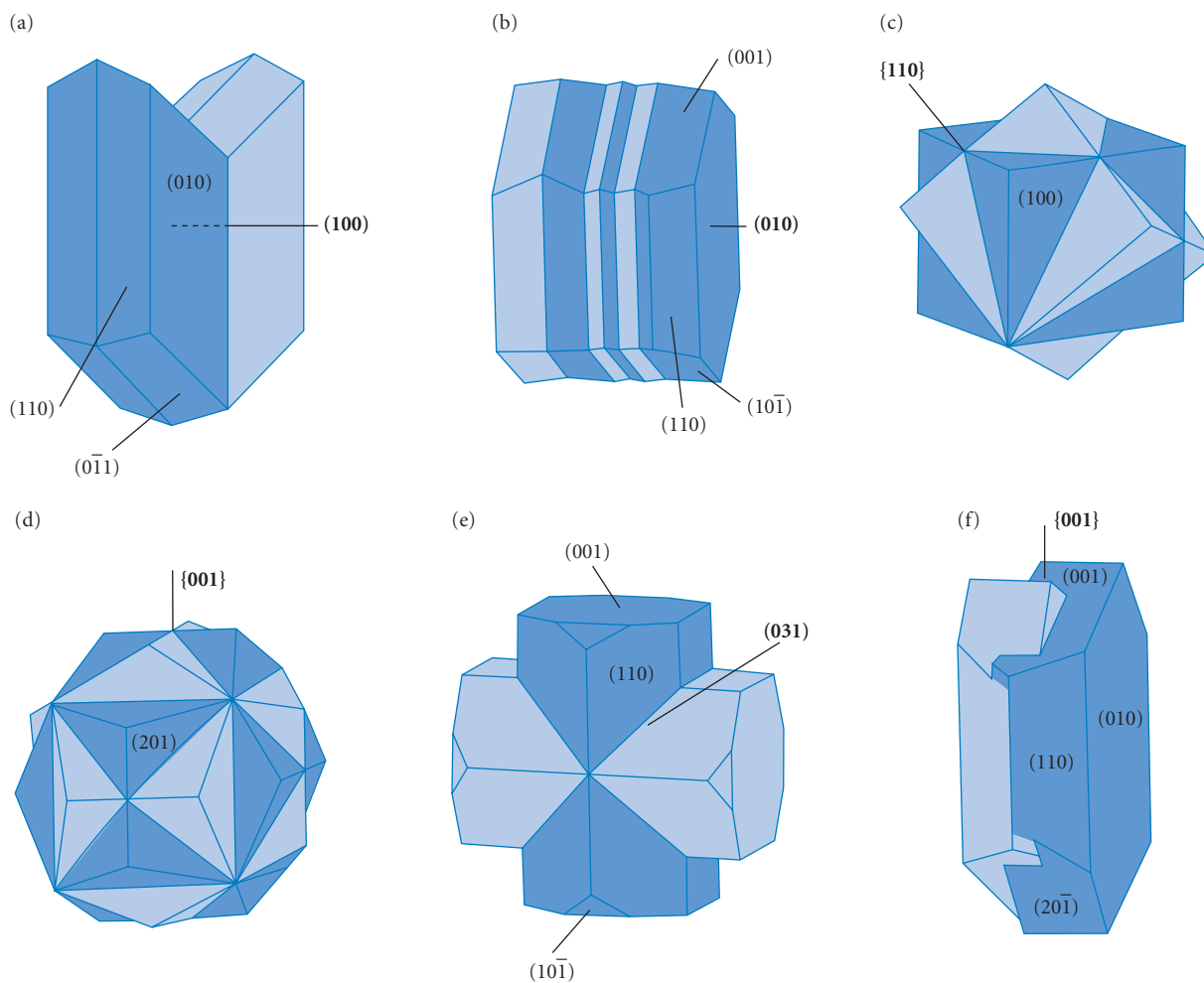


Figure 4.31 Examples of twinned crystals: (a) swallowtail twins in gypsum; (b) polysynthetic albite twins in plagioclase; (c) penetration twins in Galena; (d) penetration twins in pyrite; (e) penetration twins in staurolite; (f) Carlsbad twins in potassium feldspar. (From Wenk and Bulakh, 2004; with permission of Cambridge University Press.)

plagioclase, which the eye detects as striations—a key to hand-specimen identification of plagioclase.

Most twins are **growth twins** that form during mineral crystallization. Less commonly, twins result from displacive mineral transformations or from deformation. Deformation twins are called **mechanical twins**. The common mineral calcite typically develops mechanical twins (102) during deformation, and their development can play a significant role in the deformation of marbles and other metamorphic rocks, especially at low temperatures.

4.8 CRYSTAL DEFECTS

Ideally, crystals are perfectly formed with no defects in their lattice structures (Figure 4.32a). However, nearly all crystals contain small-scale impurities or imperfections that cause mineral composition and/or structure to vary from the ideal. These local-scale inhomogeneities are called **crystal defects**. Crystal defects have some profound effects on the properties of crystalline material that belie their small scale (Box 4.1). A convenient way to classify crystal defects is in terms of their dimensions.

Box 4.1 Frenkel and Schottky defects

Frenkel defects (Figure B4.1a) are formed when the ions in question move to an interstitial site, leaving unoccupied structural sites or holes behind. Frenkel defects combine omission and interstitial defects. Because the ion has simply moved to another location, the overall charge balance of the crystal is maintained, but local lattice distortions occur in the vicinities of both the holes and the extra ions. **Schottky defects** (Figure B4.1b) either are formed when the ions migrate out of the crystal structure or were never there. Schottky defects create a charge imbalance in the crystal lattice. Such charge imbalances may be balanced by the creation of a second hole in the crystal structure; for example, an anion omission may be created to balance a cation omission. They may also be balanced by the substitution of ions of appropriate charge difference elsewhere in the structure. The highly magnetic mineral **pyrrhotite** (Fe_{1-x}S) provides a good example. When a ferrous iron (Fe^{+2}) ion is omitted from a cation site in the crystal structure, leaving a charge deficit of 2, two ferric iron (Fe^{+3}) ions can substitute for ferrous iron (Fe^{+2}) ions to increase the charge by 2 and produce an electrically neutral lattice (Figure B4.1b). The formula for pyrrhotite reflects the fact that there are fewer iron (total Fe^{+2} and Fe^{+3}) ions than sulfur (S^{-2}) ions in the crystal structure due to the existence of a substantial number of such Schottky omission defects.

Point defects can occur on still smaller scales. In some cases electrons are missing from a quantum level, which produces an electron hole in the crystal structure. In others, an electron substitutes for an anion in the crystal structure. As with other point defects, the existence of electron holes plays an important role in the properties of the crystalline materials in which they occur. In most minerals, as temperature increases, the number of omission defects tends to increase. This allows minerals to deform more readily in a plastic manner at higher temperatures.

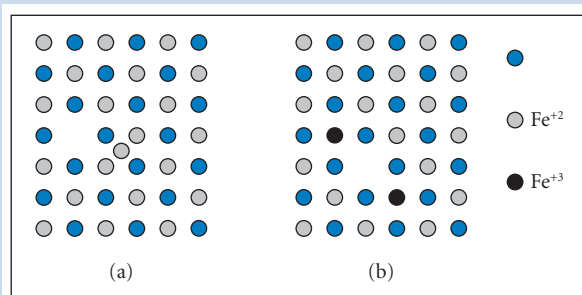


Figure B4.1 (a) Frenkel defect, with a vacancy due to an ion displaced to the interstitial site. (b) Schottky defect in pyrrhotite (Fe_{1-x}S) where a vacancy (absent Fe^{+2}) is balanced by the substitution of Fe^{+3} for Fe^{+2} in two lattice sites.

4.8.1 Point defects

Point defects involve individual atoms and therefore do not have longer range extent; they are considered to be **zero-dimensional defects**. Many types of point defects exist, and they are important in explaining the properties of minerals as well as other materials such as steel, cement and glass products:

- 1 **Substitution defects** (Figure 4.32b) occur when anomalous ions of inappropriate size and/or charge substitute for ions of appropriate size and/or charge in a structural site. These anomalous ions tend to distort the crystal lattice locally and to be somewhat randomly distributed within the crystal lattice.

- 2 **Interstitial defects** (Figure 4.32c) occur when anomalous ions occupy the spaces between structural sites. Such “extra” ions are trapped in the interstices between the “normal” locations of ions in the crystal lattice.

- 3 **Omission defects** (Figure 4.32d) occur when structural sites that should contain ions are unoccupied. In such cases, ions that should occur within the ideal crystal structure are omitted from the crystal lattice leaving a “hole” in the ideal crystal structure.

4.8.2 Line defects

Line defects are called **dislocations**. Like lines, they possess extent in one direction and are

therefore **one-dimensional defects**. Dislocations commonly result from shearing stresses produced in crystals during deformation that cause atomic planes to shift position,

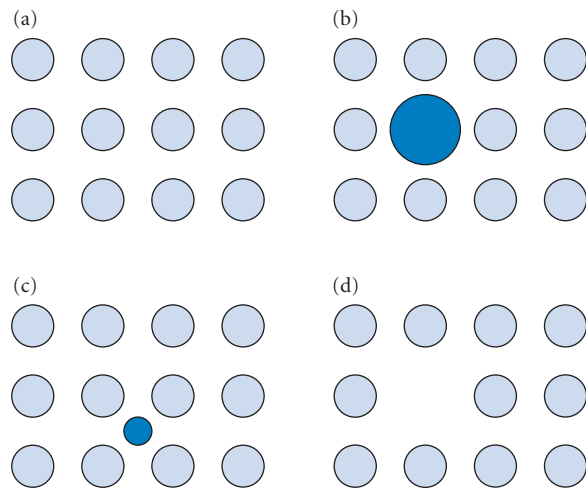


Figure 4.32 (a) Perfect crystal lattice; (b) substitution defect; (c) interstitial defect; (d) omission defect.

producing distortions in the crystal lattice that can be represented by a line called a **dislocation line**. Two major types of dislocations are recognized: **edge dislocations** (Figure 4.33a) and **screw dislocation** (Figure 4.33b).

Dislocations are extremely important in the plastic deformation of crystalline materials that leads to changes in rock shape and volume without macroscopic fracturing. Dislocations permit rocks to flow plastically at very slow rates over long periods of time. Detailed discussions are available in many books on mineralogy (e.g., Wenk and Bulakh, 2004) and structural geology (e.g., Davis and Reynolds, 1996; van der Pluijm and Marshak, 2003). Figure 4.34 shows how an edge dislocation can migrate through a crystal by breaking a single bond at a time. The result of dislocation migration is a change in the shape of the crystal that has been accomplished without rupture. Changes in shape during deformation that do not involve rupture are called plastic deformation, and dislocations are critical to its occurrence (Chapter 16).

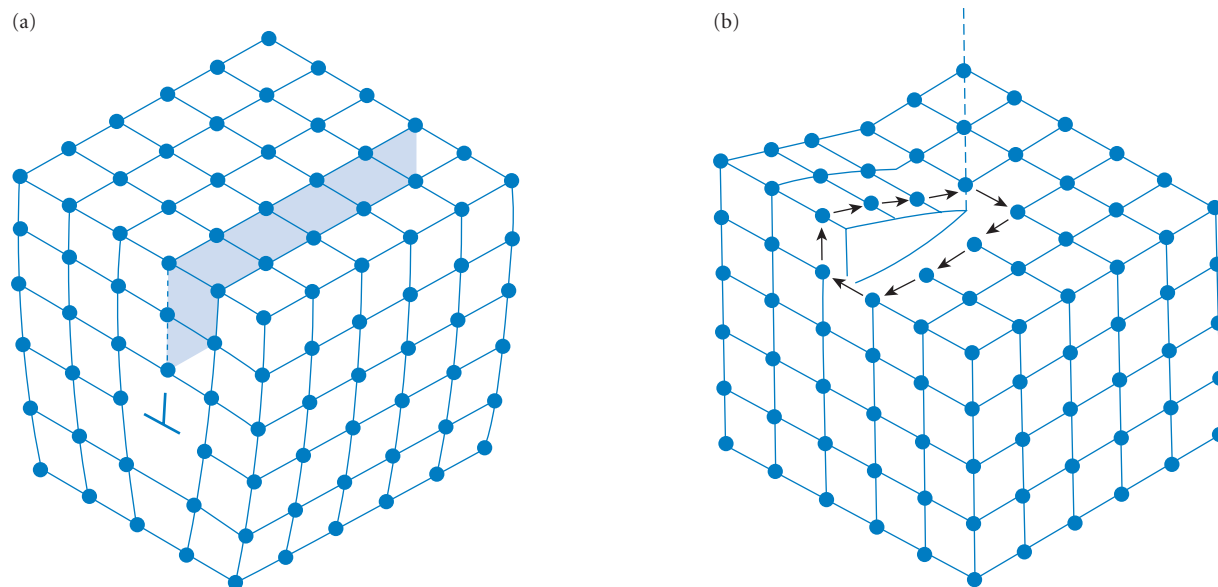


Figure 4.33 (a) Edge dislocation with an extra half plane of atoms; this is a line defect because the base of the half plane can be represented by a dislocation line (\perp). (b) Screw dislocation, where a plane of atoms has been rotated relative to the adjacent plane. (After Klein and Hurlbut, 1985; with permission of John Wiley & Sons.)

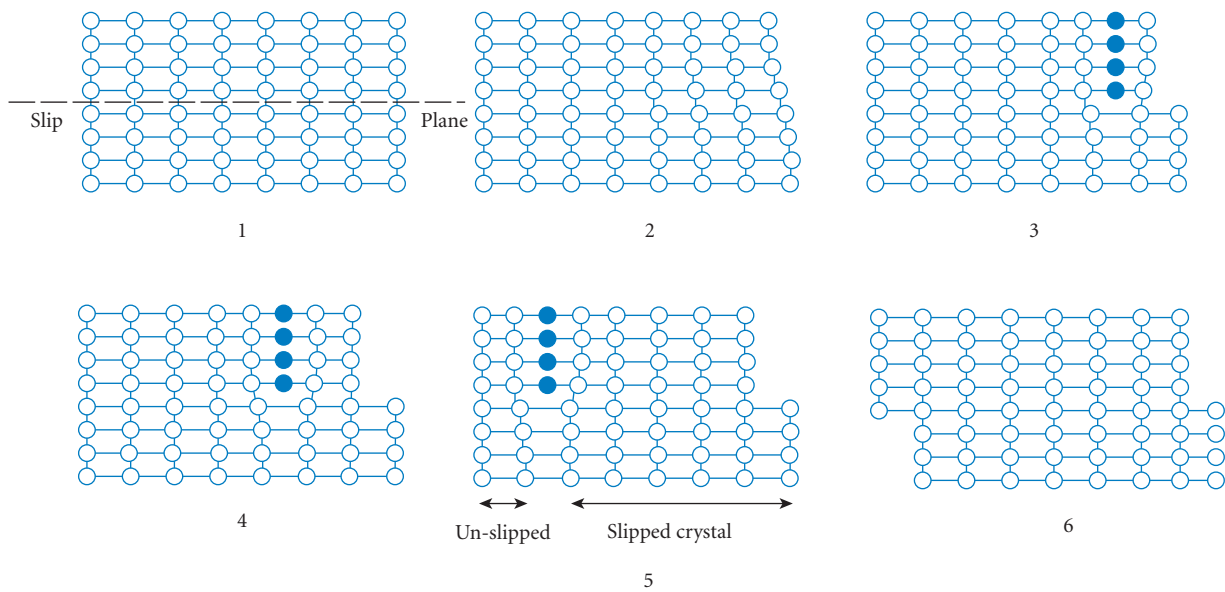


Figure 4.34 Two-dimensional depiction of how an edge dislocation created by slip due to shear can migrate through a crystal by breaking one bond at a time, so that no fractures develop as the crystal changes shape during deformation (steps 1 to 6). (After Hobbs et al., 1976.)

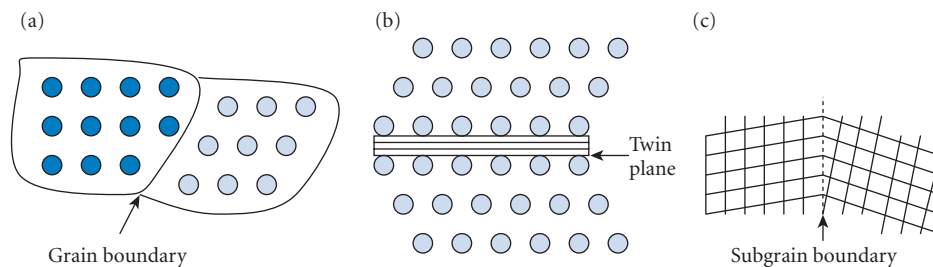


Figure 4.35 Three types of planar defect (shown in two dimensions): (a) intergranular grain boundary between two different crystals; (b) intragranular mechanical twin boundary resulting from mechanical slip; (c) intragranular subgrain boundary within a crystal, separated by a wall of dislocations. Imagine each extending in a second dimension perpendicular to the page and note how (b) and (c) accommodate changes in crystal shape.

4.8.3 Planar defects

Planar defects (Figure 4.35) extend in two dimensions and are therefore called **two-dimensional defects**. They are places within a crystal where the crystal structure changes across a distinct planar boundary. Examples include: (1) the boundaries between exsolution lamellae, for example between albite and

potassium feldspar in perthites; (2) the subgrain boundaries between twins in twinned crystals; (3) the subgrain boundaries within crystals between out-of-phase crystal structures generated during ordering transformations; (4) grain boundaries between different crystals; and (5) extra atomic planes or missing planes called stacking faults.

Point defects, line defects and planar defects are critically important in the study of deformed rocks, particularly in the elastic and plastic deformation processes discussed in Chapter 16 (Box 4.2).

4.9 POLYMORPHS AND PSEUDOMORPHS

4.9.1 Polymorphs

As noted in the opening chapter, different minerals can have the same chemical

Box 4.2 Defects and plastic deformation in crystals

You may recall from earlier courses in which folds, faults and metamorphic foliations were discussed that when stresses are applied to rocks, they experience changes in shape and/or volume. These changes in shape and/or volume that occur in response to stress are called strains. They are analogous to the strains that occur in bones and muscles when they change shape in response to stress. Non-elastic strains are subdivided into those in which rocks break along fractures such as faults or joints and those in which shape changes are accomplished without fracturing. Irreversible strains that involve fracturing are called rupture; those that do not are called plastic strains and accommodate plastic deformation. Rupture is favored by rapid strain rates (think how fast the bone changes shape as it fractures), low confining pressures and low temperatures. On the other hand, plastic strain is favored by very low strain rates, high confining pressures and high temperatures (Figure B4.2a). Under such conditions, deep below the surface, rocks respond very slowly to stress in a manner more like Playdough® or modeling clay than like the rigid rocks we see at Earth's surface. How can rocks undergo significant strain without rupturing? A major key lies in the large number of defects that the minerals in rocks contain.

Plastic deformation at high temperatures and low strain rates largely results from two significant types of diffusion creep (Figure B4.2a) that are dependent on the existence of omission defects in minerals: (1) Coble (grain boundary diffusion) creep, and (2) Herring–Nabarro (volume diffusion) creep. Elevated temperatures are associated with elevated molecular vibration in an expanded crystal lattice. Such vibrations lower bond strength and increase the number of omission defects (also called holes or vacancies) in the crystal structure. As holes are created, adjacent atoms can migrate into the vacancy by breaking only one weak bond at a time. The movement of the ions in one direction causes the holes or vacancies to migrate in the opposite direction (Figure B4.2b).

Under conditions of differential stress, ions tend to be forced toward the direction of least compressive stress (σ_3), which tends to lengthen the crystal in that direction. Simultaneously, holes tend to migrate toward the direction of maximum compressive stress (σ_1) until they reach the surface of the crystal where they disappear, causing the crystal to shorten in this direction (Figure B4.2b). In Coble creep, the vacancies and ions migrate near grain boundaries to achieve the strain, whereas in Herring–Nabarro creep, the vacancies and ions migrate through the interior of the crystals. Since thousands of omission defects are created over long periods of time even in small crystals, the long-term summative effects of plastic strain as each crystal changes shape by diffusion creep can be very large indeed.

At higher strain rates related to higher differential stresses, dislocation creep processes become dominant (Figure B4.1). In these environments edge dislocations and screw dislocations migrate through the crystal structure, once again breaking only one bond at a time, while producing plastic changes in shape. Because such dislocations result from strain, large numbers are produced in response to stress, and their migration accommodates large amount of plastic strain. Imagining the summative plastic changes in shape that can be accomplished by the migration of thousands of diffusing vacancies and/or migrating dislocations in a small crystal or 10^{20} dislocations migrating through the many crystals in a large mass of rock offers insight into the power of crystal defects to accommodate plastic deformation on scales that range from microcrystals to regionally metamorphosed mountain ranges.

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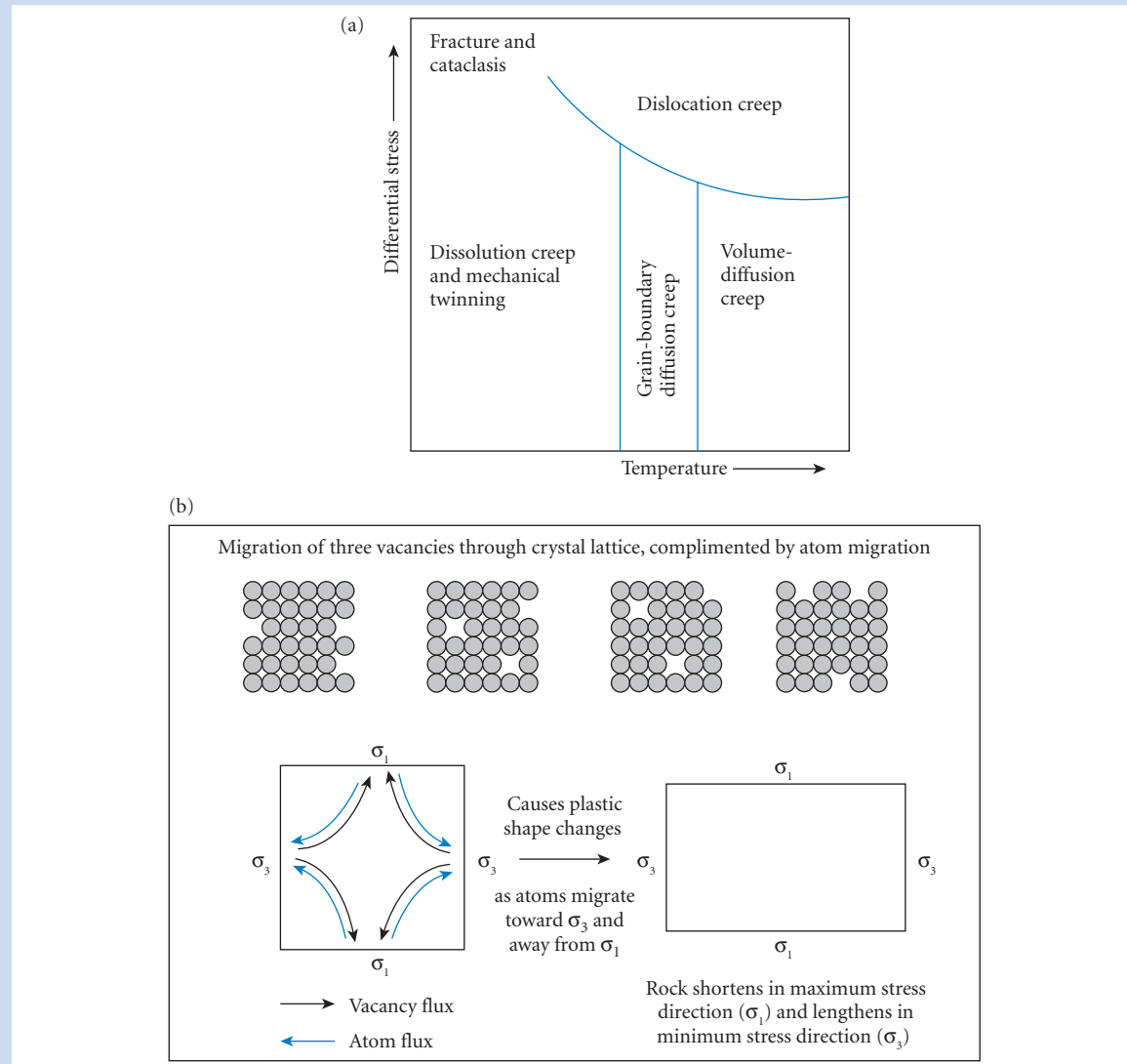
Box 4.2 *Continued*

Figure B4.2 (a) Deformation map showing the significant role of omission defects and dislocations in the high temperature plastic deformation of crystals. (From Davis and Reynolds, 1996; with permission of John Wiley & Sons.) (b) Diagrams showing how the existence of omission defects permits adjacent ions to move into their former locations, effectively causing the omission or hole to migrate in one direction as the ions migrate in the other. The flux of atoms (blue arrows) toward regions of least compressive stress (σ_3) and of vacancies (black arrows) toward areas of maximum compressive stress (σ_1) cause crystals to change shape.

composition, but different crystal structures. This ability for a specific chemical composition to occur in multiple crystal structures is called **polymorphism**. The resulting minerals with the same chemical compositions but different crystal structures are called **polymorphs**. In most cases, the crystal structure or form taken by the mineral is strongly influenced by

the environment in which it forms. Polymorphs therefore record important information concerning the environments that produced them. Many polymorphs belong to very common or economically significant mineral groups, such as the examples summarized in Table 4.13.

The polymorphs of carbon can be used to illustrate how environmental conditions

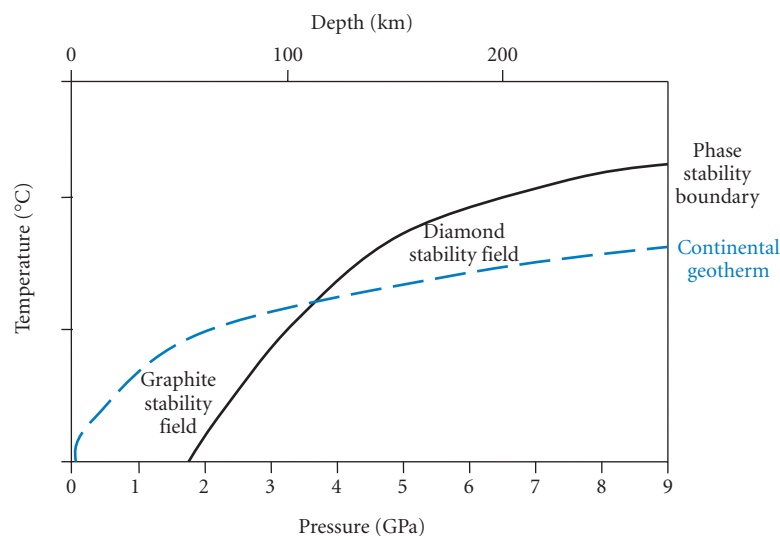


Figure 4.36 Phase stability diagram showing the conditions under which graphite, the low pressure polymorph of carbon, and diamond, the high pressure polymorph of carbon, are stable beneath continental lithosphere.

Table 4.13 Important rock-forming mineral polymorphs.

Chemical composition	Common polymorphs
Calcium carbonate (CaCO ₃)	Calcite and aragonite
Carbon (C)	Diamond and graphite
Silica (SiO ₂)	α-quartz, β-quartz, tridymite, cristobalite, coesite, stishovite
Aluminum silicate (AlAlOSiO ₄)	Andalusite, kyanite, sillimanite
Potassium aluminum silicate (KAlSi ₃ O ₈)	Orthoclase, microcline, sanidine
Iron sulfide (FeS ₂)	Pyrite, marcasite

during growth determine which crystal structure a chemical compound possesses. Figure 4.36 is a phase stability diagram for systems composed of pure carbon. This phase stability diagram clearly indicates that diamond is the high pressure polymorph of carbon, whereas graphite is the low pressure polymorph. If we add **geotherms**, lines showing the average temperature of Earth at any depth, to this diagram, we can infer that diamonds are the stable polymorph of carbon at pressures of more than 3.5 GPa, corresponding to depths of more than 100 km below the surface of old continental shields, whereas graphite is the

stable polymorph of carbon at all shallower depths. Inferences must be tempered by the fact that Earth's interior is not pure carbon and temperature distributions with depth are not constant, but it is widely believed that most natural diamonds originate at high pressures far below Earth's surface. If graphite is the stable polymorph of carbon at low pressures, why do diamonds occur in deposits at Earth's surface where pressures are low? Obviously, as diamonds rise toward Earth's surface into regions of substantially lower pressure, something keeps the carbon atoms from rearranging into the graphite structure. What keeps the transformation from unstable diamond to stable graphite from occurring?

Reconstructive transformations

Reconstructive transformations involve the conversion of one polymorph into another through bond breakage so that a significant change in structure occurs. Such transformations require large amounts of energy, and this requirement tends to slow or inhibit their occurrence. In the transformation of diamond to graphite, a large amount of energy is required to break the strong bonds that hold carbon atoms together in the isometric diamond structure, so that they can rearrange into the more open, hexagonal structure of

graphite. This inhibits the transformation of diamonds into graphite as diamonds find themselves in lower pressure and lower temperature environments near Earth's surface. Minerals that exist under conditions where they are not stable, such as diamond near Earth's surface, are said to be **metastable**. All polymorphs that require reconstructive transformations have the potential to exist outside their normal stability ranges as metastable minerals. This allows them to preserve important information about the conditions under which they, and the rocks in which they occur, were formed and, in the case of diamonds, to grace the necks and fingers of people all over the world.

Displacive transformations

Some polymorphs are characterized by structures that, while different, are similar enough that the conversion of one into the other requires only a rotation of the constituent atoms into slightly different arrangements without breaking any bonds. Transformations between polymorphs that do not require bonds to be broken and involve only small rotations of atoms into the new structural arrangement are called **displacive transformations** and tend to occur very rapidly under the conditions predicted by laboratory experiments and theory. Polymorphs involved in displacive transformations rarely occur as metastable minerals far outside their normal stability ranges and so may preserve less information about the conditions under which they and the rocks in which they occur originally formed.

Alpha quartz (low quartz) is generally stable at lower temperatures than beta quartz (high quartz). Although α - and β -quartz have different structures, the structures are so similar (Figure 4.37) that the conversion of one to the other is a displacive transformation. It is not at all unusual, especially in volcanic rocks, to see quartz crystals with the external crystal form of β -quartz but the internal structure of α -quartz. These quartz crystals are interpreted to have crystallized at the elevated temperatures at which β -quartz is stable and to have been displacively transformed into the α -quartz structure as they cooled, while retaining their original external crystal forms.

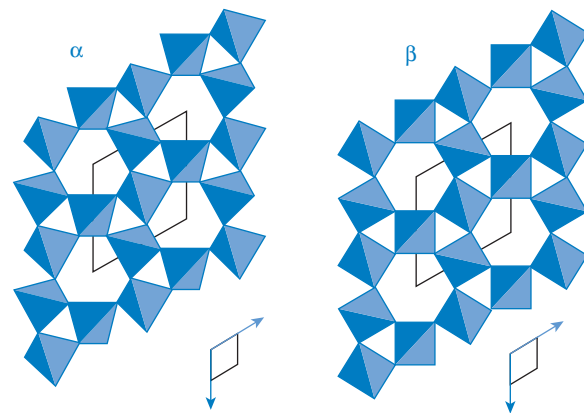


Figure 4.37 The closely similar structures of α - and β -quartz. (Courtesy of Bill Hames.)

Other transformations between silica polymorphs are reconstructive. For example, the transformations between the high pressure minerals stishovite and coesite and between coesite and quartz are reconstructive. Therefore, both stishovite and coesite can be expected to exist as metastable phases at much lower pressures than those under which they are formed. Their preservation in rocks at low pressures allows them to be used to infer high pressure conditions, such as meteorite impacts, long after such conditions have ceased to exist.

Order–disorder transformations

Many polymorphs differ from one another in terms of the degree of regularity in the distribution of certain ions within their respective crystal structures. Their structures can range from perfectly ordered to a random distribution of ions within structural sites (Figure 4.38). The potassium feldspar minerals (KAlSi_3O_8) provide many examples of such variation in regularity or order in the distribution of aluminum ions within the structure. In the feldspar structure, one in every four tetrahedral sites is occupied by aluminum (Al^{+3}), whereas the other three are occupied by silicon (Si^{+4}). In the potassium feldspar **high sanidine**, the distribution of aluminum cations is completely random; the probability of finding an aluminum cation in any one of the four sites is equal. Crystal structures with such random distributions of cations are highly disordered

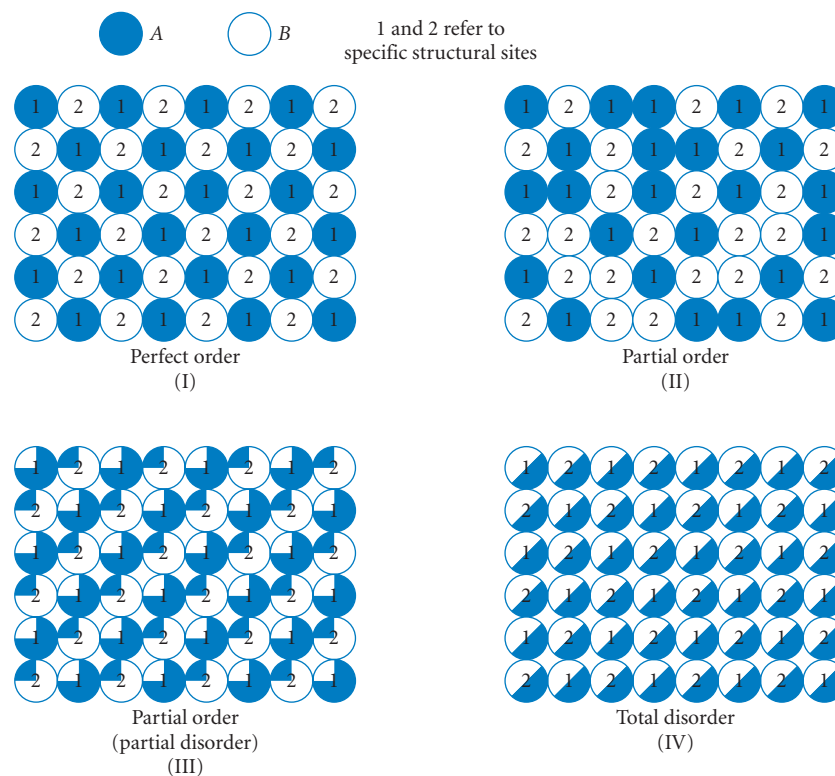


Figure 4.38 Variations in the order of minerals. (From Klein and Hurlbut, 1985; with permission of John Wiley & Sons.)

and are favored by high temperatures and low pressures of formation. On the other hand, in the potassium feldspar **low microcline**, the distribution of aluminum cations is highly ordered, with the aluminum distributed regularly in every fourth tetrahedral site. The probability of finding an aluminum cation in these sites is 100%, and the probability of finding one in the other three sites is zero. Crystal structures with such regular distributions of cations possess very low disorder, and their formation is favored by low temperatures and high pressures of formation. Intermediate degrees of order exist within the potassium feldspar group. Sanidine, with its high degree of disorder, crystallizes in the monoclinic system and is common in volcanic rocks formed at high temperatures and low near surface pressures, whereas microcline, with its low degree of disorder, crystallizes in the triclinic system and is common in rocks formed at higher pressures, and in some cases lower temperatures, below the surface.

4.9.2 Pseudomorphs

Minerals that take the crystal form of another, pre-existing mineral are called **pseudomorphs** and are said to be pseudomorphic after the earlier mineral (Figure 4.39). Pseudomorphs can be produced in many ways. All require that the original crystal possessed a significant number of crystal faces (was euhedral or subhedral) at the time it formed. Some pseudomorphs are produced by **replacement** in which the atoms in a pre-existing mineral are replaced by the atoms of a new mineral that retains the external crystal form of the original crystal. A common example is the replacement of pyrite (FeS_2) crystals by goethite (FeOOH) to produce goethite pseudomorphs after pyrite. Another common example is quartz (SiO_2) pseudomorphs after fluorite (CaF_2). Some pseudomorphs are **casts** produced by dissolution of the old mineral followed by precipitation of the pseudomorph to fill the cavity left behind. Other pseudomorphs

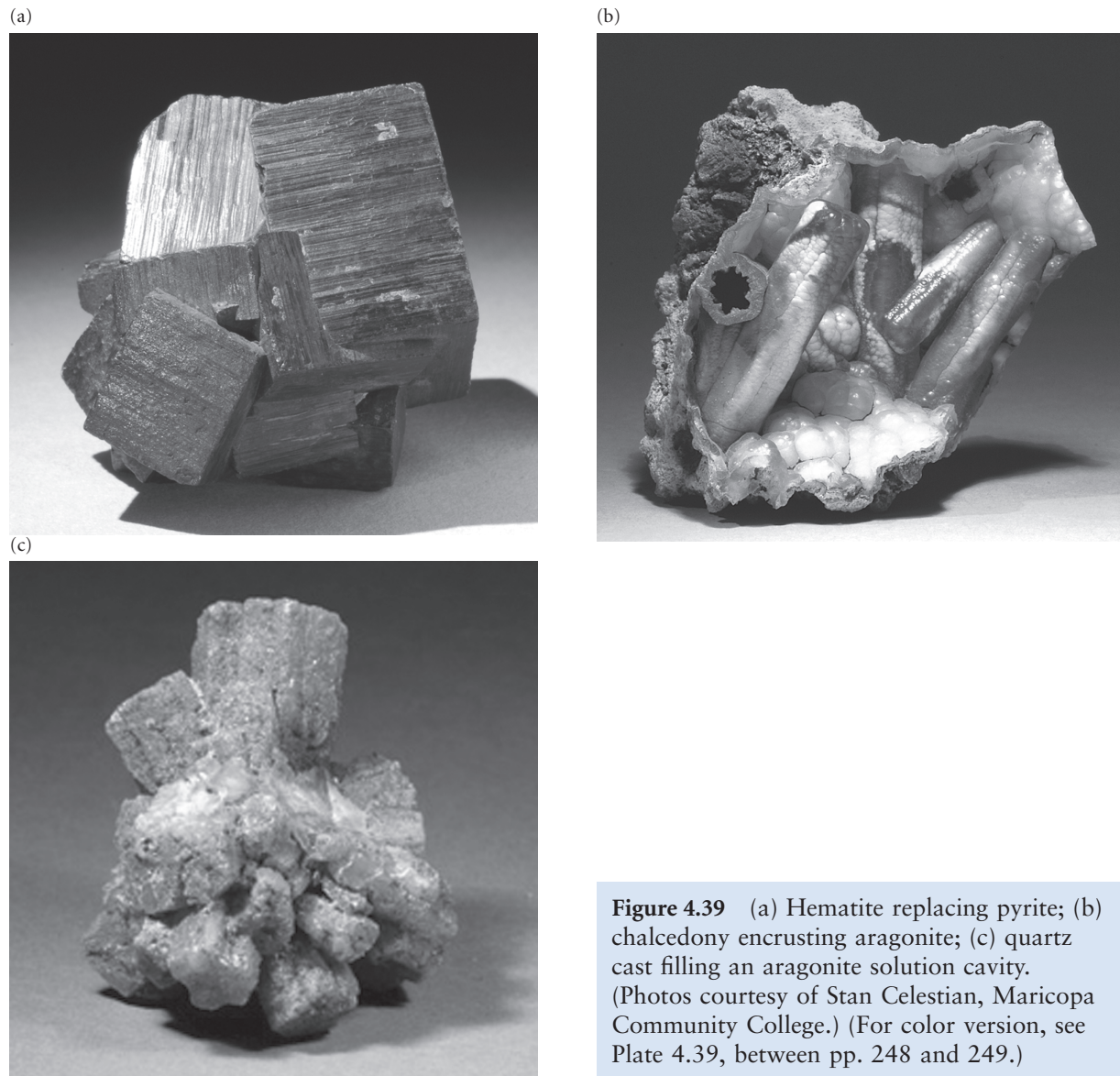


Figure 4.39 (a) Hematite replacing pyrite; (b) chalcedony encrusting aragonite; (c) quartz cast filling an aragonite solution cavity. (Photos courtesy of Stan Celestian, Maricopa Community College.) (For color version, see Plate 4.39, between pp. 248 and 249.)

are produced by the **loss of a constituent** from the original crystals. For example, the dissolution of carbonate ion from crystals of the copper carbonate mineral azurite $[\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2]$ can produce native copper (Cu) pseudomorphs after azurite. Still other pseudomorphs are produced when the new mineral forms a thin layer or crust over the original crystal. Still others form by inversion as when β quartz crystals are transformed

into α quartz. The **encrustation** of the original mineral by the new mineral allows the new mineral to mimic the crystal form of the original mineral.

The properties of minerals and other crystalline materials are strongly influenced by their crystal structures and chemical compositions. These properties and the minerals that possess them are the subjects of Chapter 5.