

Chapter 2

Order–Disorder in Clay Mineral Structures

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1. INTRODUCTION

CHAPTER 1 has reviewed the regular or ordered structures of layer silicates determined mainly by single crystal, X-ray diffraction methods. The present chapter and the two following chapters are concerned with irregular and disordered structures mainly in the 0.1–10 μm particle size range. X-ray powder diffraction methods are commonly used in studying these clay-grade materials, but single crystal, electron diffraction analysis furnishes additional important information (see Gard, 1971; Zvyagin, 1967).

Structural disorder is so prevalent in clay minerals that its recognition and evaluation are important aspects of the identification process. Some acquaintance with the fundamental concepts of diffraction by disordered systems is very helpful in understanding the phenomena involved. A full treatment would go far beyond what can be given in the present monograph, but from the simple treatment presented it is hoped that the main features of powder patterns from disordered layer structures will be more clearly recognized and interpreted than would be possible from a purely descriptive treatment.

The theoretical discussion is presented in Sections 3, 4, 5 and 6 and its application is given in Sections 7 and 8. Inevitably there will be some overlap between the theoretical sections and their application to different mineral groups.

It may be remarked that macro-crystalline minerals are not devoid of structural disorders, but in single crystal methods of structure analysis the investigator can usually select "good" crystals with a minimum of disorder. In studying clay minerals it is usually necessary to study them as formed in Nature and without the option of selecting "good" materials.

2. TYPES OF DISORDER IN CLAY MINERALS

Structural disorders in layer silicates, particularly in clay minerals, are of many kinds.

2.1 Thermal disorder

Disorder due to thermal motion of atoms is present in all materials and generally is not isotropic. It reduces the intensities of X-ray reflections and the reduction increases with the angle of diffraction and with the temperature. The thermal movements of the atoms in a crystal are

coupled and can be considered as thermo-elastic waves within a structure. Normally their effects outside the range of Bragg reflections are negligible but highly exposed diffraction patterns of single crystals reveal scattering effects between the Bragg reflections.

2.2 Disorder in the distribution of cations

Disorder of this type is common in silicate minerals and is mentioned frequently in Chapter 1. When Al replaces Si in tetrahedral sites, and Mg, Fe(II), Al, Fe(III), and other ions occupy octahedral sites, ordered or disordered arrangements may occur. Usually order-disorder of this kind is studied by meticulous single crystal, diffraction analysis and therefore falls outside the domain of clay mineralogy except in so far as electron diffraction by single crystals of clay size can be used. Other methods, such as infrared analysis, may be applicable. The results of single crystal, X-ray analysis (as discussed in Chapter 1) are applicable in so far as we can assume that macro-crystalline and micro-crystalline minerals are structurally similar.

2.3 Long-range and short-range order

Short-range order is compatible with long-range disorder. Silica glass is an extreme example; every Si atom is surrounded by a tetrahedral group of four O atoms, but little or no order occurs over a long range. Cation replacements in crystals may possibly be ordered within small domains, but may change from one domain to another so that over a crystal composed of many domains there is apparent disorder. A crystal as small as $1\ \mu\text{m}$ is also as large as $10^4\ \text{\AA}$, and therefore could contain many domains of 10^2 – $10^3\ \text{\AA}$ size; if the size of a unit cell is of the order of $10\ \text{\AA}$ many unit cells will occur within a domain. Therefore even in clay mineral crystals short-range order, long-range disorder may occur. An important example is the case of muscovite where tetrahedral cations per formula unit are near (Si_3Al) . As discussed in Chapter 1, Section 4.5.4, refined structure analyses indicate a random distribution of these cations. From observations of diffuse scattering by single crystals outside normal Bragg reflections Gatineau (1964) concluded that the Al ions tend to lie in linear bands parallel to a and $\pm 120^\circ$ to a in small domains, with different directions in different domains so that the resultant long-range effect is equivalent to a random distribution. Experiments of this kind require single crystals and in the case of clay minerals are possible only by electron diffraction.

2.4 Disorder in layer stacking

This type of disorder is frequent, indeed almost universal, in clay mineral structures and is a major topic of the present chapter.

2.5 Order-disorder in mixed-layer systems

Mixed-layer systems arise in two ways. A major characteristic of many clay mineral structures is their ability to swell by incorporating inorganic and organic material between the layers. Water is the most important of these materials. Generally the swelling (and conversely the shrinking) does not take place equally between all layers at the same time. Consequently situations arise involving mixed spacings and the resulting diffraction phenomena are those of disordered systems. Chapter 3 treats the nature of these systems and their application in clay mineral identification.

Mixed-layer systems arise in a second way. The geometrical similarity of the layer silicate structures, particularly as regards the quasi-hexagonal arrangement of the silicon-oxygen sheets, facilitates the formation of structures containing different kinds of layers. Both ordered and, more generally, disordered sequences of layers of many different kinds are found. Chapter 4

discusses X-ray diffraction by these mixed-layer sequences, particularly in relation to the statistics of order-disorder.

2.6 Finite crystal size as a lattice disorder

From a mathematical standpoint, the finite boundary of a crystal can be regarded as a type of disorder. A crystal lattice is defined as a homogeneous distribution of points, and to be homogeneous the point distribution must be infinite. From a physical standpoint, the distribution of atoms in and near the surface of a crystal will differ from that within the body of a crystal.

When the crystal size is less than about 10^{-6} cm, i.e., 100 Å, the X-ray diffractions are broadened and also may be measurably displaced. Both effects are important in relation to X-ray diffraction by clay minerals.

2.7 Structures with non-planar layers

Layer silicates with markedly polar layer structures, notably chrysotile (Chapter 1, Section 2.4) and halloysite (this chapter, Sections 6 and 7) have layers which curl into rolled and spiral forms. X-ray powder diffraction patterns of these minerals are somewhat similar to those of minerals with disorderly stacked layers. In so far as successive curved layers do not mesh together in the normal crystalline manner, these structures may be regarded as being disordered.

2.8 Mechanically disordered structures

Not all clay minerals occur as finely divided powders. Often they occur in hard, massive form due to some form of cementation. Many shales are of this kind. For X-ray examination the material must be reduced to a fine powder and pestle and mortar grinding is the process most often employed. Prolonged grinding of layer silicates produces marked structural disorder often leading to complete destruction of the diffraction pattern. This mechanically produced disorder is probably different from disorders formed under natural conditions. Mechanical strain in crystals causes broadened X-ray reflections. In the case of very small crystals, strain broadening and small crystal broadening can both contribute to the observed broadening of the X-ray diffractions; in some cases it will be necessary to distinguish the two effects.

2.9 Some general considerations

It is evident that many kinds of structural disorder can occur in clay minerals, and their recognition is an integral part of the process of identification and characterization of clay minerals. Sections 3, 4, 5 and 6 discuss at an elementary level the diffraction of X-rays by systems of small and disordered particles with a view to indicating the nature of the effects which may be observed in powder diffraction diagrams. For further reading the small monograph by Wilson (1949) is recommended; although the mathematical treatment is mainly simple, nevertheless many of the questions raised in this chapter are covered in more detail than is possible here. Among more advanced texts, that of James (1948) may be specially mentioned. A short mathematical discussion of the effect of structural disorders in layered systems on X-ray and electron diffraction processes was given by Gatineau and Tchoubar (1973).

3. DIFFRACTION OF X-RAYS BY SMALL CRYSTALS

3.1 Diffraction by ordered and disordered systems

The theory of X-ray diffraction by crystals treats a crystal as a regular three-dimensional array of identical unit cells, all scattering X-rays with the same amplitude in any particular direction. Fundamentally, X-rays are diffracted (scattered) by the electrons forming the atoms