

MINERAL CLASSIFICATION IN THE MINERAL POWDER DIFFRACTION FILE

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ABSTRACT

The concept of the mineral classification in the Mineral Powder Diffraction File (MPDF) is somewhat different from that used in classical mineralogical references. The goal of the classification is to exploit the crystal chemistry characteristics to the fullest to assist in the identification of mineral phases. The primary criterion is the similarity of the diffraction **pattern**, which results from the isostructural nature of the group members. One example is the halite, NaCl-type, halide compounds being included in the same group as the periclase, MgO-type, oxide compounds and the galena, PbS-type, sulfides. All the phases in this group are face-centered cubic, and the diffraction patterns differ in the position of the diffraction peaks and somewhat in intensity but not in the sequence. *Subgroups* are defined on the basis of chemistry or other structural characteristic.

Derivative structure types, which follow group-subgroup symmetry relationships, such as dolomite from calcite or nepheline from tridymite, are also the basis for many subgroupings. Such situations lead to similar patterns with extra weak peaks for the lower symmetry phases. Where the derivative structure results in major changes of symmetry and lattice distortions, subgroups of *related structures* are recognized.

A scheme for writing structure-type formulas using a consistent nomenclature for site symbols has also been developed for representing the mineral group general structure formula. The 12 letters of the Roman alphabetic which are not used for element symbols (**A, D, E, G, J, L, M, Q, R, T, X, and Z**), are used to represent structure sites with specific characteristics such as element size and coordination. The ability to write a general structural formula and recognize minerals which fit the formula and crystallography leads to the groupings which are the most useful to users of X-ray powder diffraction.

Group name nomenclature is based on the mineral in the group, which has been recognized for the longest time, *i.e.*, the rule of historical priority. For example, corundum predates hematite and halite predates either periclase or galena, which defines the proper mineral group name. Subgroup names follow the same rule. Over 170 groups are recognized in the MPDF with some groups having as many as seven subgroups.

INTRODUCTION

The Group Data Book of the Mineral Powder Diffraction File, MPDF, has been a successful product of the International Centre for Diffraction Data since 1983 (Bayliss et al., 1983). This product is now being reviewed and updated for future use.

The goal for classifying the diffraction data for minerals is to assist in the identification of minerals which are isostructural or otherwise similar in their X-ray powder diffraction patterns. Phases such as halite (NaCl), periclase (MgO), and galena (PbS) usually are not classified together in crystal chemical classifications because of the different anion, but all are isostructural and produce very similar diffraction patterns. In the MPDF, these minerals are considered one group and subgrouped by the anion chemistry. The result is to bring the diffraction data for all face-centered cubic phases together in one group for easy comparison.

In addition to isostructural groups and subgroups, there are other criteria used for collecting diffraction patterns into a grouping. Mineral families, subfamilies, super groups, and related structures are also recognized. This presentation will describe the several categories, which have been used and illustrate with examples.

MINERAL CLASSIFICATIONS

Within the geological sciences, there are three potential classifications for minerals: chemical, genetic, and crystallographic. Each has value for specific applications. The chemical classification, commonly considered the Hey classification, is based on the chemical formula only. It groups and subgroup minerals based primarily on the anion or anion complex. The Dana classification is also based primarily on chemistry with subdivisions based on crystallographically-related properties. The genetic classification is based on the method of formation of the mineral, such as igneous, sedimentary, metamorphic, hydrothermal, etc. The crystallographic classification is based on the geometrical characteristics of the crystal structure of the mineral. Most modern textbooks in mineralogy still use the chemical-crystallographic classification as the basis for presentation of the minerals with the structure as a secondary level for organization. A diffraction pattern classification must emphasize the geometric structural characteristics and use the chemical properties for further subdivisions.

A guide to classification schemes may be found by examining the scheme for classification in biology that consists of the hierarchical categories implying evolutionary relationships: kingdom, phylum, class, order, family, group, species, and individual. This scheme is only crudely applicable to minerals where the hierarchy is based on physical and chemical principles not evolutionary. The most definable entity in minerals is the species and any classification should be built up and down from the species level. Species may be organized for diffraction applications based on properties where the main property is the crystal structure followed by the chemical composition without regard to method of formation.

Mineral species are based on three specific requirements including: natural inorganic occurrence, crystallinity and definable composition. Organic minerals are acceptable if they are formed by inorganic reactions. All new mineral proposals now require approval by the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA). CNMMN is also responsible for approving suggested changes to old mineral species.

MINERAL CLASSIFICATION FOR THE MPDF

For the MPDF, the group level is based on collections of three or more species that are isostructural but may have considerable chemical variability. Other categories are defined based on relations to the groups. Examples of each category follow.

Family: Families are composed of minerals related by partial structural similarities such as framework (e.g. feldspars), sheet (e.g. micas), double chain (e.g. amphiboles), single chain (e.g. pyroxenes), multiple tetrahedra (e.g. melillite), and single tetrahedra (e.g. olivine) structure units. Zeolite minerals are considered as one family and subfamilies are organized according to the classification schemes of the International Zeolite Association based on structure building units.

Subfamily: Subfamilies are collections within families based on specific similarities. In addition to zeolites, other examples of subfamilies are homologous series and homeotypes. Homologous series are composed of two structural units interlayered in different proportions. An example is humite, $Mg_2SiO_4 \cdot nMg(OH)_2$. Homeotypes are derivative structures based on a master structure. An example is the many structures based on ideal perovskite, $CaTiO_3$.

Supergroup: Supergroups are recognized for the highest symmetry phases where the structure arrangement remains unchanged but where chemical substitution and/or ordering modifies the symmetry. An example of a supergroup, group, subgroup relationship based on crystallography is diamond (C), sphalerite (ZnS), and chalcopyrite ($CuFeS_2$) where the bonding topology is identical but the ordering of the element substitutions modifies the symmetry from cF8 (Fd3m) to cF8 (F-43m) to tI16 (I-42d).

Group: A group is composed of isostructural phases. An important large group includes all phases with the cF8 NaCl structure regardless of the chemistry. Derivative structure types based on stuffing or omissions within a group are considered part of the group if the structure retains the same cell as the host structure and as a "related structure" if the cell is distorted. Examples of same-cell stuffed derivatives based on tridymite (SiO_2) are kalsilite ($KAlSiO_4$) and nepheline ($KNa_3Al_4Si_4O_{16}$).

Subgroup: Subgroups are subsets of groups based on chemistry. Phases with the cF8 NaCl structure are subgrouped by the anion chemistry such as halides, oxides, and sulfides.

Related structures: Related structures are based on structural distortions from the group structure. Bunsenite (NiO) with the hR8 structure is a distortion of the cF8 NaCl structure caused by a slight lengthening of one of the threefold axes. There are also minerals with non-hexagonal (monoclinic) related structures based on the apatite topology with very slight deviation of the β angle from 120° .

STRUCTURE-TYPE FORMULAS

It is possible to write formulas for every level of category using a scheme reported by Smith et al. (1998) using a few simple rules and the letters of the Roman alphabet not used for element symbols. This scheme is in addition to the nomenclature recommended by a subcommittee of the International Union on Crystallography (Lima-di-Faria et al., 1990). A summary of the scheme is presented here.

Table 1 Use of symbols for structure sites in mineral and group formulas

<u>Symbol</u>	<u>Usage</u>
A	Reserved for general formulas where it represents either all cations or all cations not in the structural unit.
D	Structure sites with 9-fold coordination or greater
E	Structure sites with 8- or 7-fold coordination
G	Structure sites with 6-fold coordination
J	Structure sites with 5-fold coordination
L	Cations with lone electron pairs and distorted coordinations
M	Neutral molecular units
Q	Structure sites with 4-fold planar coordination or 2-fold linear coordination
R	Structure sites with 3-fold coordination
T	Structure sites with 4-fold tetrahedral coordination
X	Monatomic anions which may be uni-, di-, tri-, or quadrivalent
Z	Polyatomic anions such as $(\text{SO}_4)^{-2}$, $(\text{CO}_3)^{-2}$, etc.

The following letters are not used for element symbols: **A, D, E, G, J, L, M, Q, R, T, X, and Z**. It is possible to use these 12 letters in a scheme for writing structure-type formulas where the use of each letter has a specific assignment and does not lead to any confusion with element symbols. For additional clarity, it is recommended to use a different font when these letters are used, but it is not required. This scheme is in addition to recommendations for structure symbols by the Committee on Nomenclature

of the International Union of Crystallography. Although this scheme has been developed for minerals, it is applicable to all inorganic crystal structures. Table 1 shows the usage of symbols. Table 2 lists symbols that represent structural details. Table 3 lists several mineral groups recognized in the MPDF and the corresponding structure-type formulas.

EXAMPLE OF A MINERAL GROUP

Apatite as a mineral was recognized as a single mineral species for some time with several varieties recognized. More recently, the varieties were upgraded to species status and the name "apatite" was applied to the group as a whole. The structural formula of the apatite group is $(D/L)_3(D'/L')_2(TO_4,RO_3)_3X$, where **D** = Ca, Sr, Na, Ce, Ln, Ac.....; **L** = Pb.....; **T** = P, As, V, Si, S.....; **R** = C; and **X** = F, OH, Cl. Chemically, there are 5 subgroups of the apatite group based on PO_4^{3-} with (CO_3^{2-}) substitution, VO_4^{3-} , AsO_4^{3-} , SO_4^{2-} , and SiO_4^{4-} (with P, Cr, B and S also in the Si site). There are also minerals with non-hexagonal related structures based on the apatite topology. Some of the minerals in the apatite group and its subgroups are illustrated in Table 4.

Table 2 Use of symbols for structure details in mineral and group formulas

' " "'	For multiple distinct sites in any coordination
()	Indicates the principal radicals involving a single polyhedron or complex
[]	Structural units involving one or more polyhedral unit
↔	Indicates possible change of coordination numbers between the corresponding values and between subscripts to indicate a possible continuous variation between the values
,	Indicates substitution between symbols or subscripts
/	Indicates limited substitution between symbols
*	Indicates chemical substitution within a structure site
h i j l m n p -	
q r s t	Integral subscript or multiplier value
u v w x -	
y z	Non-integral subscript or multiplier
^	Indicates inclusive integers in subscripts and multipliers
v	For the valence of the cation in subscripts
δ	Indicate small deviations from the integer in subscripts such as 1-δ

NOMENCLATURE RULES FOR GROUP NAMES

The titles for each of the groupings are always a matter of considerable debate because some groupings have been labeled by different names within the mineralogical community. Some of the nomenclature derives from historic times when some mineral families and groups were single mineral names. Sometimes the name of the most

common or most easily recognized mineral in the group was used for the group name regardless of any rules for nomenclature.

Table 3 Some examples of mineral groupings and their structure-type formulas

Group	Specific structure-type formula
Amphibole	$A_{0 \leftrightarrow 1}(E \leftrightarrow G)_2 G'_3 G''_2 [T_4 O_{11}]_2 X_2$
Apatite	$(D/L)_3 (D'/L')_2 (TO_4)_3 X$
Aragonite	$(D/L)(RO_3)$
Astrophyllite	$D_3 G_7 G'_2 [T_8 O_{24}] X_{6,7}$
Axinite	$E_2 GAl_2 [B[Si_2 O_7]_2 O](OH)$
Barite	$(D/L)(TX_4)$
Brucite	GX_2
Cancrinite	$D_{6 \leftrightarrow 9} [T_6 T'_6 O_{24}] Z_{1 \sim 4} \bullet 0^{\wedge} 2 H_2 O$
Chlorite	$G_{4 \sim 6} [T_4 O_{10}] X_8$
Crichtonite	$DG_{21} X_{38}$
Epidote	$D_2 G_3 (SiO_4) [Si_2 O_7] X_2$
Feldspar	$D_{2x/v,3} [T_x T'_{4-x} O_8]_2; x=1^{\wedge} 2$
Garnet	$E_3 G_2 [TX_4, X_4]_3$
Humite	$G_{2n+1} (SiO_4)_n X_2; n=1^{\wedge} 4$
Kaolin-serpentine	$G_{2,3} [T_2 O_5] (OH)_4 \bullet 0, 2 H_2 O$
Lazulite	$GG'_2 (PO_4)_2 (OH)_2$
Marcasite	GXX'
Melilite	$E_2 [TT'_2 O_7]$
Mica	$DG_{2,3} [T_4 O_{10}] X_2$
Monazite	$(D/L)(TX_4)$
Olivine	$G_2 (TO_4)$
Pentlandite	$GT_8 S_8$
Perovskite	$(D,E)GX_3$
Pyrite	GXX'
Pyrochlore	$E_{1 \sim 2} G_2 X_6 X'$
Pyroxene	$(E \leftrightarrow G)G' [TO_3]_2$
Scapolite	$D_4 [T_4 O_8]_3 (X,Z)_{2/v}; v=1,2$
Smectite	$D_8 G_{2,3} [T_4 O_{10}] X_2 \bullet 0^{\wedge} 8 H_2 O; \delta \div 0.3$
Sodalite	$D_4 [T_3 T'_3 O_{12}] (X,Z)_{2/v}; v=1,2$
Sphalerite	$T_3 (T'/L) X_4$
Spinel	$G_2 TX_4$
Tetradymite	$L_n X_{n+1}; n=1^{\wedge} 5$
Tetrahedrite	$T_6 T'_6 L_4 X_{12} X'$
Tourmaline	$DG_3 G'_6 (BO_3)_3 [Si_6 O_{18}] X_4$
Zeolite	$D_{n/v} [Al_n Si_p O_{2(n+p)}] \bullet x(H_2 O, M)$

For the MPDF, the following rules have been established for nomenclature of the titles. Family names that are well established, such as feldspar, mica, amphibole, pyroxene, etc. are retained. Where no family or common name is well established, the name of the mineral within the grouping that claims priority in date of discovery, i.e. the mineral that was first recognized. An example of this rule is the corundum group, which may also be titled hematite group. Corundum as a name predates hematite and thus is the correct name to use for this group. Halite predates both periclase and galena to become the correct name for the group with halite also the proper name for the halide subgroup, periclase for the oxide subgroup, and galena for the sulfide subgroup.

The use of the above rules results in some differences from other mineral tables such as Fleischer and Mandarino (1995). Several group names are changed and many previously defined groups are now subgroups of different groups. Other group names that are modified include the rozenite group, which becomes the starkeyite group and the whiteite group, which becomes the jahnsite group. The adelite group becomes the calciovolborthite subgroup of the descloisite group, and the ferrotapiolite group becomes the trirutile subgroup of the rutile group. Some groups retain their names but acquire subgroup status such as the arsenic group, which is a subgroup of the tetradymite group. The periclase group and the galena group become subgroups in the halite group. The full list of changes is beyond the scope of this paper. Tables 5A and B list the groups listed in Fleischer and Mandarino (1995) that will have alternate names in the MPDF due to the nomenclature rules. At present, there are over 170 recognized groups in the MPDF and some groups have as many as seven subgroups.

Table 4 Some Examples in The Apatite Group $(D/L)_3(D'/L')_2(TO_4)_3X$

Apatite Subgroup - (PO_4)		
Chlorapatite		$Ca_5(PO_4)_3Cl$
Fluorapatite		$Ca_5(PO_4)_3F$
Pyromorphite		$Pb_5(PO_4)_3Cl$
Strontium apatite		$Sr_5(PO_4)_3(OH)$
Britholite Subgroup - (SiO_4)		
Britholite-(Ce)		$Ca_3Ce_2(SiO_4)_3(OH)$
Fluorellestadite		$Ca_5[(Si,P,S)O_4]_3F$
Cesanite Subgroup - (SO_4)		
Cesanite		$Na_3Ca_2(SO_4)_3(OH)$
Hedyphane Subgroup - (AsO_4)		
Hedyphane		$Pb_3Ca_2(AsO_4)_3Cl$
Mimetite		$Pb_5(AsO_4)_3Cl$
Vanadinite Subgroup - (VO_4)		
Vanadinite		$Pb_5(VO_4)_3Cl$
Related Structures Subgroup		
Hydroxylapatite		$Ca_5(PO_4)_3(OH)$
Samuelsonite		$Ca_9Fe_2Mn_2Al_2(PO_4)_{10}(OH)_2$

Table 5A Groups in Fleischer and Mandarino (1995) that are classified as a group or subgroup under an alternate name in the Mineral Powder Diffraction File.

Fleischer & Mandarino	MPDF Group	MPDF Subgroup
Adelite ⇒	Descloisite	Calciovolborthite
Colusite ⇒	Tetrahedrite	Germanite
Ferrotapiolite ⇒	Rutile	Trirutile
Hematite ⇒	Corundum	
Lovozerite ⇒	Combeite	
Magnetoplumbite ⇒	Hoegbomite	
Manasseite ⇒	Hydrotalcite	Sjogrenite
Rozenite ⇒	Starkeyite	
Schoenfliesite ⇒	Stottite	Soehngeite
Whiteite ⇒	Jahnsite	

Table 5B Groups in Fleischer and Mandarino (1995) that are classified as a subgroup in the Mineral Powder Diffraction File.

Fleischer & Mandarino	MPDF Group	MPDF Subgroup
Arsenic ⇒	Tetradymite	Arsenic
Arsenopyrite ⇒	Marcasite	Arsenopyrite
Beudantite ⇒	Alunite	Beudantite
Cobaltite ⇒	Pyrite	Cobaltite
Crandallite ⇒	Alunite	Crandallite
Dolomite ⇒	Calcite	Dolomite
Hauchecornite ⇒	Chalcopyrite	Hauchecornite
Ilmenite ⇒	Corundum	Ilmenite
Linnaeite ⇒	Spinel	Linnaeite
Loellingite ⇒	Marcasite	Loellingite
Melonite ⇒	Brucite	Melonite
Periclase ⇒	Halite	Periclase
Stannite ⇒	Chalcopyrite	Stannite
Stibiconite ⇒	Pyrochlore	Stibiconite

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