## A SCHEME FOR THE CLASSIFICATION OF MICACEOUS MINERALS

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#### ABSTRACT

The classification scheme for micaceous minerals is described. According to the size of mineral particles micas are divided into macrocrystalli ne compounds and microcrystalline clay micas. Macrocrystalline micas are differentiated into (a) Mg-Fe-Al micas, (b) Li-micas, (c) micas with other cations. Vertical boundary in the suggested scheme divides micas into trioctahedral and dioctahedral members. Additional subdivision is carried out on the basis of the extent of Si substitution in tetrahedral positions of their crystal lattice. Microcrystalline ( $<4 \mu m$ ) micas are subordinate to the crystallochemical scheme for macrocrystalline micas. List of mica species together with their varieties and synonyms is in Table 2.

KEYWORDS: macrocrystalline micas, clay micas, IS ordered structures, ISII ordered structures, fundamental particles

#### INTRODUCTION

Micaceous minerals or micas are one of the most frequent components of the earth's crust. They form ~ 4 % of igneous rocks, an even greater proportion of metamorphic rocks and ~ 50 % or more of sedimentary rocks. The micaceous minerals are characterised by a layer lattice consisting of two sheets of silica tetrahedra held together by an octahedral sheet. This imparts their characteristic perfect cleavage. Chemically micaceous minerals are varied. There is an extensive literature on their crystal structure, chemistry, properties and stability. The most recent compendium on this group of minerals is by Fleet (2003) in the second edition of Rock-Forming Minerals (Sheet Silicates) of Deer, Howie & Zussman and extends to over 700 pages. The purpose of my brief overview of the classification of micaceous minerals is to give students and scientists an introduction to these widely occuring rock-and sediment-forming minerals.

# GENERAL CRYSTAL STRUCTURE CHARACTERISTICS

Micas are hydrated silicates with layer crystal lattice – a group of minerals with the extremely variable chemical composition of general crystallochemical formula:

 $(K,Na) (Al,Fe,Mg)_{2-3} [(Si,Al)_4 O_{10}] (OH,F)_2$ 

Their crystal structure is composed of negatively charged 2:1 layers consisting of two tetrahedral Si-O sheets separated by an octahedral Al,MgFe-OH sheet, which are connected with large interlayer cations (most commonly K,Na,Ca). In the case of true micas these interlayer cations are usually univalent, whereas in brittle micas they are divalent. The layer charge (x) is ideally (-1) per a half unit cell in the true micas; this results from:

- (a) the substitution of  $R^{3+}(Al,Fe^{3+})$  for  $Si^{4+}$  in tetrahedral positions
- (b) the substitution of  $R^{1+}$  or  $R^{2+}$  for  $R^{2+}$  or  $R^{3+}$  in octahedral positions
- (c) the presence of vacancies in octahedral positions.

The layer charge of individual varieties of mica can originate either in the tetrahedral sheet itself or in the octahedral sheet. In some cases both sheets are involved. Tetrahedral positions in the crystal structure of micas are usually occupied by Si;  $Al^{3+}$  is the commonest cation to replace Si<sup>4+</sup>. Less frequent tetrahedral cations are Fe<sup>3+</sup>, Ti<sup>4+</sup> or Ge<sup>4+</sup> (synthetic micas). The commonest octahedral cations are Al, Mg,  $Fe^{2+}$  and  $Fe^{3+}$ ;  $Mn^{2+}$ ,  $Mn^{3+}$ ,  $Cr^{3+}$ ,  $Ti^{4+}$ ,  $Li^{1+}$ ,  $V^{3+}$ may also occur. Hydroxyl (OH)<sup>1-</sup> group can be replaced by  $F^-$  in the crystal structure of some micas.  $K^{I+}$  or Na<sup>I+</sup> are most frequent interlayer cations. In case of clay micas (illites) the interlayer space is partly occupied by hydronium ions  $(H_3O)^+$ , according to Brown, Norrish (1952) and White, Burns (1963).  $Rb^+$  and  $Cs^+$  were recorded less frequently as interlayer cations. When trivalent cations replace a considerable proportion of Si in the tetrahedral layers, interlayer cations of higher valency (e.g.  $Ca^{2+}$ ) are accepted into the crystal structure to achieve its electroneutrality. This is realized in brittle micas.

The *c*-dimension of the mica structure unit is ~10 Å, while lateral dimensions *a*, *b* fluctuate in the range of ~5.2-5.4 Å and ~9.0-9.3 Å respectively.

In case of some naturally occuring true micas (polylithionite, tainiolite and celadonite) Si<sup>4+</sup> practically fills completely the tetrahedral positions, while in the majority of common mica species

(muscovite, phlogopite)  $Al^{3+}$  replaces  $Si^{4+}$  in the ratio 1:3. Some true micas (ephesite, preiswerkite) exhibit the substitution of  $Al^{3+}$  for  $Si^{4+}$  in the proportion 1:1. Trioctahedral brittle mica, clintonite, has unusually high content of  $Al^{3+}$  with Al:Si = 3:1. In ferriphlogopite and anandite (brittle mica)  $Fe^{3+}$  replaces  $Si^{4+}$  in tetrahedra in the ratio Fe:Si ~1:3. The rare presence of  $B^{3+}$  in the tetrahedral sheets occurs in boromuscovite and  $Be^{2+}$  in brittle mica – bityite.

#### SUBDIVISION OF MICAS

Micas can be divided from several points of view. One of these subdivisions is based on the occupancy of the interlayer space. We can distinguish between true micas and brittle micas.

In *true micas* univalent cations occupy the interlayer space. Interlayer charge, x, is -1 per a half unit cell. In *brittle micas* divalent cations occur in the interlayer positions, the interlayer charge, x, is -2.

Micas are differentiated according to their crystal size. They can occur in the *macrocrystalline* form or as *microcrystalline* particles. The latter are termed *clay micas* – with the size fraction of their platy particles below 4 $\mu$ m. The crystallochemical formula of clay micas exhibits an interlayer deficit of cations: 0.85-0.60 positive interlayer charges per a half unit cell. In special cases (e.g. wonesite) the interlayer charge may be lower than 0.6 provided the material does not have swelling or expanding capabilities (Rieder et al., 1999).

According to the occupancy of octahedral positions micas are divided into trioctahedral and dioctahedral subgroup. In *trioctahedral micas* all octahedra are filled with divalent cations, while in *dioctahedral micas* only two thirds are filled with trivalent cations, leaving one third of the octahedra sites vacant. The 060 X-ray diffraction line specifies the trioctahedral or dioctahedral character of mica.

Micas occur in various polymorphs and polytypic forms\*, that are designated by Ramsdell indicative symbols. This is based on the number of layers in the repeating unit along *c*-direction: 1, 2, 3, ....... and by letters indicating the lattice symmetry: M (monoclinic), T (trigonal), H (hexagonal), Or (orthorhombic). For example, Ramsdell symbol 3T means that the mica has a 3-layer trigonal structure.

The mica structure consists of 2:1 layers (two Si-O tetrahedral sheets with one octahedral sheet between them) that are held together by large interlayer cations, which results in adjacent 2:1 layers being located directly above each other. The situation

is different within the 2:1 layer; the Si-O tetrahedral sheets are displaced relative to each other by a/3 in the positive or negative direction of X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>. Depending on the type of displacement these arrangements are termed I or II. It is possible to convert the arrangement I into the arrangement II. Polytypism describes the sequence of types I and II within the mica structure.

To identify a polytype the sequences of selected non-basal X-ray diffractions are necessary. The intensity distributions of non-basal diffractions  $20\ell$ ,  $13\ell$  and  $02\ell$ ,  $11\ell$  identify a polytype using *unoriented preparations*. Basal *c*-spacing, determined from  $00\ell$ diffractions by using preferentially *oriented preparations*, characterizes micas as a group.

- (a) Intensities of X-ray diffractions 00l, 20l and 13l depend upon the total amount of Fe, relative to Mg, in the octahedral sites.
- (b) Intensities of X-ray diffractions  $02\ell$  and  $11\ell$  depend upon the distribution of atoms in the octahedral sites.
- (c) Intensities of X-ray diffractions vary also with increasing atomic scattering factor associated with the tetrahedral sites.

In some cases micas display both tetrahedral and octahedral cation ordering. Generally, octahedra with Al<sup>3+</sup>in their central positions are smaller than octahedra containing  $Mg^{2+}$ . Vacant octahedra are the biggest. Central positions of cations in the octahedral network are called M(1), M(2), M(2'). Figure1 shows a schematic sketch of the ditrigonal network of tetrahedra in case of micaceous minerals in the projection on (001) with labelled positions T(1) and T(2) for tetrahedral cations and M(1), M(2), M(3) for octahedral cations. Octahedra M(1) (trans-position) are placed on a symmetry plane, M(2) and M(3)=M(2') (cis-positions) on the right and the left side of this plane. In the octahedral network hydroxyls of trans-octahedra are situated in their opposite apices, whereas hydroxyls in cis-octahedra are shared in the common edge (Fig.2). In dioctahedral micas, M(1) is usually vacant, whereas in trioctahedral micas all three octahedral sites are occupied.

# CLASSIFICATION SCHEME FOR MICACEOUS MINERALS

The main *horizontal boundary* in the scheme (Table 1) divides micaceous minerals into: Macrocrystalline micas and Clay micas. Macrocrystalline micas are subdivided into:

<sup>\*</sup> Stacking sequences of layers with various types of periodicity occur in layer lattice silicates. In connection with their crystal structure this phenomenon is designated as *polytypism*. In the case of mixed layer structures, the layers of various structure units are stacked one upon another. Warshaw and Roy (1961) designate this kind of polytypism as *heteropolytypism*. They recommend the use of the term *homopolytypism* for instances where layers of the same structural type are mutually stacked. There are two possibilities: layers of the same type are randomly displaced – "*disordered structures*" (e.g. pseudomonoclinic kaolinite, metahalloysite) or they are regularly shifted relative to each other – "*ordered structures*". We speak about *layer polymorphism* (e.g. micas, kaolinite, dickite, nacrite).

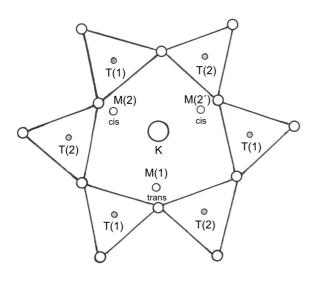


Fig. 1 Schematic sketch of the ditrigonal network of tetrahedra in micaceous minerals. Projection on (001) showing positions T(1) and T(2) for tetrahedral cations and M(1)-trans position, M(2) and M(3)=M(2')-cis positions for octahedral cations.

Mg-Fe-Al micas (increasing Fe content is shown) Li-micas

Micas with other cations.

The main *vertical boundary* divides micas into Trioctahedral and Dioctahedral sections. Each section is subdivided according to the extent of Si substitution in the tetrahedral positions into the following types:

$$Si_4 - (Si_5X)_4 - Si_3X - Si_{2.5}Al_{1.5}$$
 (or  $Si_{3.5}Al_{0.5}$ ) -  $Si_2Al_2$ ,

where X = Al,  $Fe^{3+}$ , B. Increasing amounts of Si are indicated by arrows in both sections. Cations filling interlayer sites together with cations contained in octahedral sheets are marked under the mineral name.

Table 2 lists the names of micaceous minerals together with their varieties and synonyms.

#### CLAY MICAS

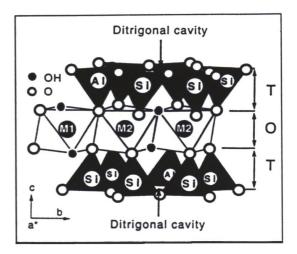
Illite (I) and glauconite (G) very often contain smectite (S) component in various amounts, show some expandability and occur as different types of *interstratifications*. Illite/smectites, according to Srodon (1984), form a continuous sequence of interstratifications:

random – random/IS ordered – IS ordered –

- IS ordered/ISII ordered - ISII ordered.

Each type is related to the specific range of expandability.

Two crystallite models have been suggested for the transformation smectite into illite, with that we



**Fig. 2** In the octahedral network hydroxyls of transoctahedra are situated in their opposite apices, whereas hydroxyls in cis-octahedra are shared in the common edge. Projection perpendicular to *a*-axis. (After Manceau et al., 2000).

usually meet in nature. There is the Mac Ewan crystallite model (1956) of interstratified illitesmectite particle and the fundamental particle model put forward by Nadeau and his co-workers (Nadeau et al., 1984). In the Mac Ewan crystallite model illite and smectite layers are intimately epitaxially connected, stacked either randomly or regularly. This sequence, acting as a coherent unit, scatters X-rays. In the model put forward by Nadeau there is an illite (K-unit) and a smectite unit. If the particle is 10 Å thick, it is a fundamental smectite particle. It can adsorb water or organic molecules to its surface. Illite particles are at least 20 Å thick and they are composed of two smectite units held together by interlayer K. It is not possible mechanically to disaggregate this particle. If two smectite particles are joined by (Mg,Fe)hydroxide sheet in the interlayer space, they become a chlorite particle with a thickness of about 24 Å. The idealized transformation of smectite through random illite-smectite into ordered IS and ISII types is shown in Figure 3. Ordered IS is 20 Å thick and it has 50% expandability. ISII particle is  $\sim 40$  Å thick and it has 20 % expandability.

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# Table 1 Classification scheme for micaceous minerals.

				Trioctahedral micas					Dioctahedral micas			
			Si <sub>4</sub>	(Si,X) <sub>4</sub>	Si <sub>3</sub> X	Si <sub>2,5</sub> Al <sub>1,5</sub>	Si <sub>2</sub> Al <sub>2</sub>	Si <sub>3</sub> X	(Si,X) <sub>4</sub>	Si3,5 Al0,5	Si <sub>4</sub>	
				← Increasing amounts of Si					Increasing amounts of Si $\rightarrow$			
Macrocrystalline micas	Mg-Fe-Al micas	Increasing amount of Fe $\leftarrow$			Phlogopite K-Mg Aspidolite Na-Mg	Eastonite K-Mg,Al	Preiswerkite Na-Mg,Al	Muscovite K-Al Boromuscovite K-Al	Nanpingite Cs-Al			
					Biotite K- Mg,Fe <sup>2+</sup> ,Al,Fe <sup>3+</sup>	Siderophyllite K-Fe <sup>2+</sup> ,Al Mg <10 %		Paragonite Na-Al		Phengite K-Al,Mg, Fe <sup>2+</sup>	Aluminoceladonite K-Al,Fe <sup>3+</sup> ,Mg,Fe <sup>2+</sup>	
					Wonesite Na,K-Mg,Fe,Al			Tobelite NH4,K-Al				
					Annite K-F $e^{2+}$ Ferriannite (F $e^{3+}$ ) K-F $e^{2+}$	Lepidomelane K-Fe <sup>2+</sup> ,Fe <sup>3+</sup> Mg <10 %					Celadonite K-Fe <sup>3+</sup> ,Al,Mg,Fe <sup>2+</sup>	
	Li - micas		Tainiolite K-Mg,Li									
			Polylithionite K-Li,Al	Lepidolite K-Li,Al			Ephesite Na-Li,Al					
			Sokolovaite Cs-Li,Al Norrishite	Zinnwaldite K-Fe <sup>2+</sup> ,Li,Al Masutomilite								
			K-Mn <sup>3+</sup> ,Li	K-Mn <sup>2+</sup> ,Li,Al								
	other		Montdorite K- Fe <sup>2+</sup> ,Mn,Mg	Wodanite	Manganophyllite K-Mg,Mn <sup>2+</sup>			Oellacherite K,Ba-Al,Mg				
	Micas with other		Shirokshinite	K-Mg,Fe <sup>2+</sup> ,Fe <sup>3+</sup> ,Ti <sup>3+</sup>	Shirozulite K-Mn <sup>2+</sup>			Chromphyllite K,Ba-Cr,Al				
	Mic		K-Mg,Na		Hendricksite K-Zn,Mn <sup>2+</sup>			Roscoelite K-V <sup>3+</sup> ,Al,Mg				
Clay micas		Increasing amount of Fe ←		Ledikite K,H <sub>3</sub> O-Mg,Fe <sup>2+</sup> ,Fe <sup>3+</sup> ,Al					Illite K,H <sub>3</sub> O-Al Brammallite Na,H <sub>3</sub> O-Al			
Cla		Increas							Glauconite K- Fe <sup>3+</sup> ,Al,Fe <sup>2+</sup> ,Mg			

 Table 2 List of micaceous minerals, their varieties and synonyms.

PHLOGOPITE Varieties: Aspidolite (Na-phlogopite), Ba-phlogopite, Barytbiotite, Ferriphlogopite (Fe <sup>3+</sup> in tetrahedra), Fluor-phlogopite, Pholidolite (phlogopite without F, poor in Al), Hydrophlogopite, Hydroxyl- phlogopite (phlogopite without F), Mg-mica
EASTONITE
PREISWERKITE
BIOTITE
Varieties: Anhydrobiotite, Anomite (2M <sub>1</sub> ), Buldymite (hydrobiotite?), Cs-biotite, Dudleyite (smectite?), Euchlorite, Fluor-biotite, Fluor-meroxene, Haughtonite (high amounts of Fe <sup>2+</sup> and Fe <sup>3+</sup> ), Heterophyllite, Hydroxyl-biotite (biotite without F), Hydroxyl-meroxene, Chrombiotite, Calciobiotite, Meroxene (1M), Natron-biotite, Odenite, Rubellan (altered biotite, redbrown), Tabergite (hydrobiotite - chlorite ?)
WONESITE
SIDEROPHYLLITE Variety: Fluor-siderophyllite
ANNITE
Variety: Fluor-annite
FERRIANNITE
(Fe <sup>3+</sup> in tetrahedra) Synonym: Monrepite (Fe <sup>3+</sup> annite)
LEPIDOMELANE
Varieties: Fluor-lepidomelane, Pterolite Synonyms: Fe-mica, Ferro-muscovite
TAINIOLITE
SHIROKSHINITE
POLYLITHIONITE
SOKOLOVAITE
LEPIDOLITE Varieties: Irvingite, Mn-lepidolite, Paucilithionite, Polyirvingite, Trilithionite Synonyms: Lilalite, Li-mica, Lithionite
EPHESITE Synonyms: Natron-margarite, Soda-margarite
NORRISHITE
ZINNWALDITE
Varieties: Cryophyllite, Protolithionite Synonyms: Lithioneisenglimmer, Rabenglimmer
MASUTOMILITE (Mn-zinnwaldite)
MONTDORITE
WODANITE
Variety: Ferrititanbiotite Synonyms: Ferriwotanite (synonym of ferrititanbiotite), Titanbiotite (synonym of wodanite), Wotanite (synonym of wodanite)
MANGANOPHYLLITE
Synonyms: Manganophyll, Mn-phlogopite, Mn-mica
SHIROZULITE
HENDRICKSITE
LEDIKITE Mainting Paralalita Partanita
Varieties: Bardolite, Bastonite Synonyms: Mg-illidromica, Mg illite-hydromica, Trioctahedral illite

## Table 2 continued

# MUSCOVITE

- Varieties: Alurgite (variety of muscovite with some amounts of Mn, Mg and Fe<sup>2+</sup>), Anhydromuscovite, Avalite, Cr-muscovite, Damourite, Didymite, Fedorite, Ferriphengite, Ferrimuscovite, Fluormuscovite, Fuchsite (Cr-muscovite), Helvetan, Chacaltaite, Li-muscovite, Mahadevite, Mariposite (variety of Cr-muscovite), Metasericite, Mn-muscovite, Sericite, Shilkinite, Schernikite, Sterlingite
- Synonyms: Adamsite, Agalmatolite (syn. of pinite, pyrophyllite and talc), Amphilogite (syn. of didymite), Astrolite, Cr-mica (syn. of fuchsite), Didrimite (syn. of didymite), Episericite (syn. of sericite), Ferroferrimuscovite (syn. of monrepite), Gaebhardite (syn. of fuchsite), Ivigtite (syn. of gilbertite), Margarodite (syn. of damourite), Pagodite (syn. of agalmatolite), Pycnophyllite (syn. of sericite), Talcite (synonym of damourite), Verdite (impure fuchsite).
- Pseudomorphs of muscovite: Gigantolite (after cordierite), Cataspilite (after cordierite), Pinite (after cordierite); Oncophyllite (after feldspars), Pinitoide (after feldspars); Gieseckite (after nepheline), Liebenerite (after nepheline); Gilbertite (after topas); Killinite (after spodumen); Terenite (after scapolite), Wilsonite (after scapolite). To the pinite group belong: Dysintribite, Gongylite, Hygrophyllite, Iberite (similar to gigantolite), Oncosine, Oösite (similar to oncosine), Parophite (similar to dysintribite), Polyargite, Pyrrholite (pseudomorph after anorthite).

## BOROMUSCOVITE

(B in tetrahedra)

#### PARAGONITE

Varieties: Cossaite, Hallerite (contains Li)

Synonyms: Euphyllite, Na-mica, Pregrattite

# NANPINGITE

TOBELITE

Synonyms: Ammonium hydromica, Ammonium muscovite

#### PHENGITE

Varieties: Alurgite (Mn-phengite), Ferrophengite, Lepidomorphite, Mariposite (Cr-phengite, lower amount of Cr contrary to fuchsite), Picrophengite

## CELADONITE

Varieties: Aluminoceladonite, Svitalskite

Synonyms: Kmaite, Leucophyllite (syn. of aluminoceladonite), Veronite

#### OELLACHERITE

Synonyms: Ba-muscovite, Sandbergite, Ganterite (only Al in octahedra)

#### CHROMPHYLLITE

 $(Cr^{3+} in octahedra)$ 

## ROSCOELITE

Synonyms: Colomite, V-mica

## ILLITE

Varieties: Bravaisite, Gümbellite (fibrous hydromica), Leverrierite, Monothermite, Shilkinite

Synonyms: Al-illhydromica, Al-illidromica, Al illite-hydromica, Andreatite (designation for illidromica), Endothermite (synonym of monothermite), Goeschwitzite, Grundite, Hydromuscovite, Sarospatakite (syn. of bravaisite), Sarospatite (syn. of bravaisite)

## BRAMMALLITE

Synonyms: Hydroparagonite, Na-illite

## GLAUCONITE

Varieties: Marsjatskite (Mn-glauconite), Na-glauconite, Skolite (Al-glauconite) Synonyms: Chlorophanerite, Mn-glauconite (syn. of marsjatskite)

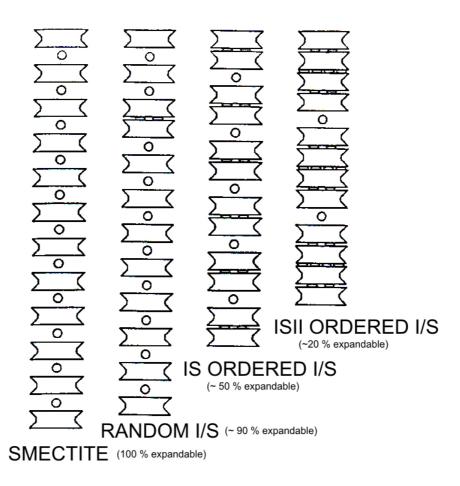


Fig. 3 Idealized transformation of smectite (through random illite-smectite) into ordered IS and ISII types by the formation of illite particles in mixed layer structures. Anvil shapes are negatively charged 2:1 layers. Circles are interlayer cations. Expanded interlayers also contain water. (After Srodon and Eberl in Bailey, 1984).

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