

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/321706338>

# Silicate Minerals : An Overview

Article · January 2006

CITATIONS

0

READS

1,323

1 author:



**Christopher Duffin**

Natural History Museum, London

203 PUBLICATIONS 1,487 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



History of Medicine [View project](#)



Fossil Chondrichthyans [View project](#)

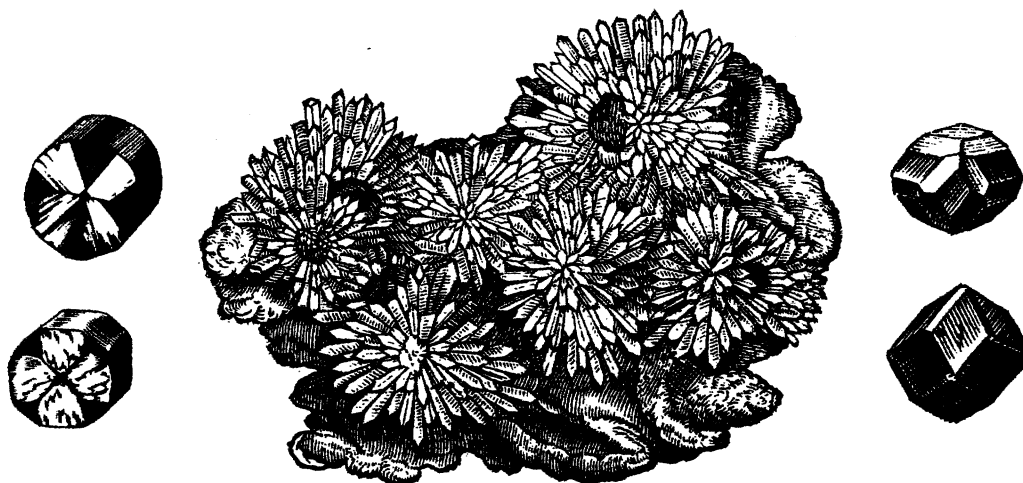
BMS Occasional Papers are written for amateur mineralogists. They are intended to be useful and concise. Your comments, suggestions and questions on this, or any other paper, would be welcomed by the authors, or any member of the editorial board.

**General Editor**

David Green

**Editorial Board**

Shirley Adrian, John Pearce, Roy Starkey, Max Wirth



**Andalusite**

**Quartz**

**Garnet**

**Silicate minerals from the cabinets of the Italian collectors Michel Mercati (1541-1593) and Ferrante Imperato (1550-1625)**

**Bibliographic Data**

**Author: Duffin, Christopher**

**Title: Silicate Minerals: An Overview**

**BMS Occasional Paper No. 21, published 2006 by the British Micromount Society**

The views and opinions expressed in this paper are not necessarily those of the BMS or the editorial board. The author and publisher accept no liability for injury, loss or damage incurred as a result of information given in this publication. Chemicals and experimental procedures are potentially hazardous; the reader should obtain expert advice if in any doubt as to the appropriate safety measures or precautions prior to the commencement of work.

Unless otherwise stated, copyright remains with the author, whose permission should be sought before copying any part of this publication.

## CONTENTS

Examples of the different classes of silicates	3
Introduction	5
1. Nesosilicates	9
2. Sorosilicates	15
3. Inosilicates	17
4. Cyclosilicates	21
5. Phyllosilicates	25
6. Tectosilicates	29
References	37
List of other BMS Occasional Papers	39

## ACKNOWLEDGEMENTS

I would like to thank John Pearce and Austin Woodbridge, who, after I gave talks on Silicates to the Russell Society S.E. branch and Sussex Mineral & Lapidary Society, persuaded me to write this paper. They provided me with much useful information as the various sections were being written. Shirley Adrian, Roy Starkey and Richard Tayler made a range of useful comments and corrections on the first full draft, while John Hall provided the specimens, and photographed the minerals which exemplify the 6 classes of silicates (see page 3).

I should also like to acknowledge my thanks to John Wiley for granting permission to reproduce figures 7, 9 and 13 from Klein, C. and Hurlburt, C.S. Manual of Mineralogy after J.D. Dana.

Chris Duffin  
September 2006

# SILICATE MINERALS : An Overview

Christopher J. Duffin

146, Church Hill Road, Sutton, Surrey SM3 8NF

*Silicates are the most common rock-forming minerals. Their hierarchical structural arrangement gives rise to considerable diversity; over 25% of all known minerals are silicates. Their varied chemical and physical properties mean that they have been exploited in many ways, including the use of some as gemstones. This paper is aimed at the amateur mineralogist and explains the classification of silicate minerals.*

## INTRODUCTION

Silicon (chemical symbol Si) is a Group 4 element in the Periodic Table and is estimated to be the second most abundant terrestrial element (behind oxygen), comprising around 25.7 % by weight of the earth's crust. By contrast, it is the element which is sixth in terms of relative abundance in the universe as a whole, behind hydrogen, helium, oxygen, neon and nitrogen. It was first identified by Antoine Lavoisier in 1787, but was not properly isolated in an amorphous state until the work of Gay Lussac in 1811. The name derives from the Latin *silex*, which means flint. Classified as a metalloid, it has characteristics intermediate between metals and non-metals (particularly in being a semiconductor rather than a conductor).

Group 4 elements have a valency or combining power of 4 and silicon atoms commonly form four covalent bonds. Unlike the closely related Group 4 element carbon, silicon does not occur in the free state. However, both elements can be involved in giant three-dimensional lattices, for example diamond in the case of carbon with its strong carbon to carbon bonds, and quartz ( $\text{SiO}_2$ ), which involves strong silicon to oxygen bonds. As a result of these strong bonds, carbon atoms bond preferentially with other carbon atoms and also with elements such as hydrogen and oxygen to form the enormous diversity of organic molecules exploited in life processes, but they only give rise to simple carbonates as rock-forming minerals. In contrast, silicon combines preferentially with oxygen resulting in a wide range of silicate rock-forming minerals. Silicates are by far the most abundant group of minerals in the earth's crust, contributing around 90% of its total. If a mineral's chemical formula includes silicon and oxygen in any proportions, it is a **silicate**.

Silica ( $\text{SiO}_2$ ) is the only oxide of silicon, occurring mainly as quartz, chalcedony, agate and flint. All of the other silicate minerals have various metallic cations, and sometimes some anions, accommodated within their crystal lattice. They are built up from a basic  $\text{SiO}_4$  tetrahedron, with the silicon atom central to this structure. The silicon atom is surrounded by four divalent oxygen atoms at the corners of the tetrahedron. The central silicon atom shares one of its four electrons with each of the adjacent oxygen atoms. This helps to anchor the oxygen atoms in place with strong, directional covalent bonds (bonds based upon shared electrons). Further background to the chemical principles discussed here can be found in Pearce & Woodbridge (1999).

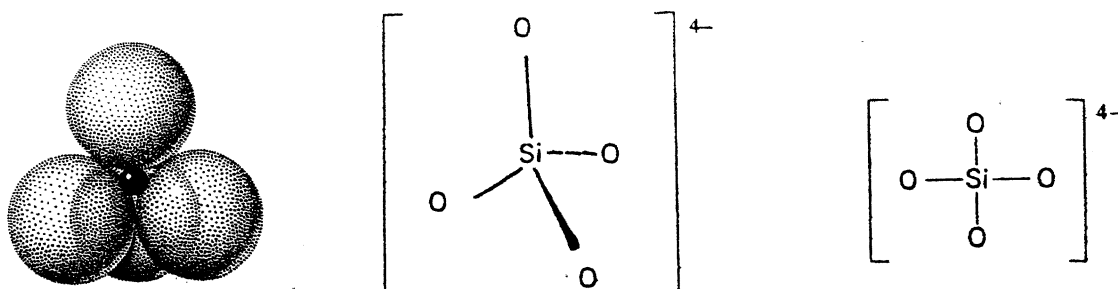


Figure 1. Some representations of the  $\text{SiO}_4$  unit

The  $\text{SiO}_4$  units are sometimes represented by solid tetrahedra. A silicon atom is assumed to be in the centre of the tetrahedron and the oxygen atoms at its corners. Figure 2 shows such a chain of tetrahedra linked through two of their corners (i.e. each tetrahedron sharing two oxygen atoms) as in an inosilicate pyroxene, e.g. augite.

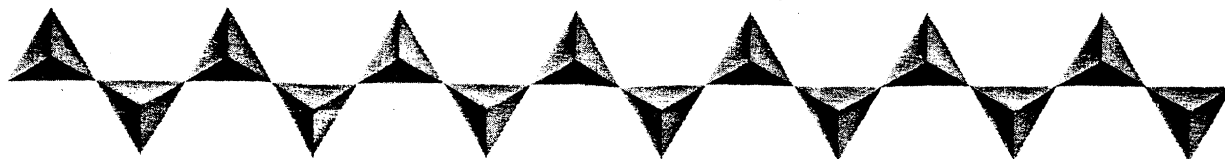


Figure 2. Representation of the single silicate chain in augite

There is an overall charge of 4- on a  $\text{SiO}_4$  tetrahedron unit (Si with a 4+ charge and oxygen atoms each with a 2- charge i.e.  $+4 - 8 = -4$ ), so the basic silicate unit of  $[\text{SiO}_4]^{4-}$  is an anion with four negative charges. These negative charges are balanced by various metal cations such as sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ) and ferric iron ( $\text{Fe}^{3+}$ ).

The basic silicate unit  $[\text{SiO}_4]$  can exist in isolation (Fig. 3), with its accompanying cations, but 1, 2, 3 or 4 of the oxygen atoms in a basic  $[\text{SiO}_4]$  unit can be shared with other silicate units (Figs 4 and 5):

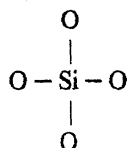


Figure 3. An isolated  $[\text{SiO}_4]$  unit where no oxygen atoms are shared with other  $[\text{SiO}_4]$  units

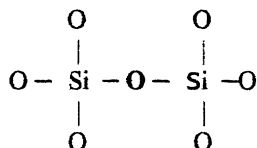


Figure 4. A couplet where one oxygen atom is shared between 2  $[\text{SiO}_4]$  units.

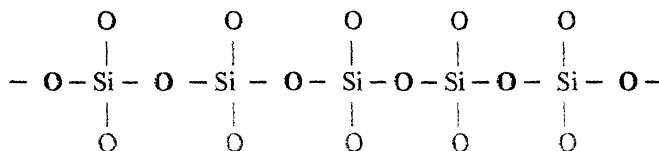


Figure 5. A chain where many  $[\text{SiO}_4]$  units share two oxygen atoms.

In 2D sheet silicate and 3D framework silicate structures, three and four oxygen atoms in the  $\text{SiO}_4$  unit are shared with other  $\text{SiO}_4$  units.

Thus basic silicate structures of islands, couplets, chains, rings, sheets or three-dimensional frameworks can form and this is the structural basis on which silicates are classified. These different silicate classes are summarised in Table 1 and illustrated in Figure 6.

Class	Common name	General formula	Si:O ratio	Examples
<i>Nesosilicates</i>	Island silicates	$\text{SiO}_4$	1:4	Olivine; garnets
<i>Sorosilicates</i>	Couplet silicates	$\text{Si}_2\text{O}_7$	1:3.5	Epidote group
<i>Inosilicates</i>	Chain silicates	$\text{SiO}_3$ or $\text{Si}_8\text{O}_{22}$	1:3 or 4:11	Pyroxenes; amphiboles
<i>Cyclosilicates</i>	Ring silicates	$\text{Si}_6\text{O}_{18}$	1:3	Beryl; tourmalines
<i>Phyllosilicates</i>	Sheet silicates	Complex and variable	1:2.5	Micas; clay minerals
<i>Tectosilicates</i>	Framework silicates	Complex and variable	1:2	Feldspars; feldspathoids; zeolites; quartz

Table 1. An outline classification of the silicate minerals

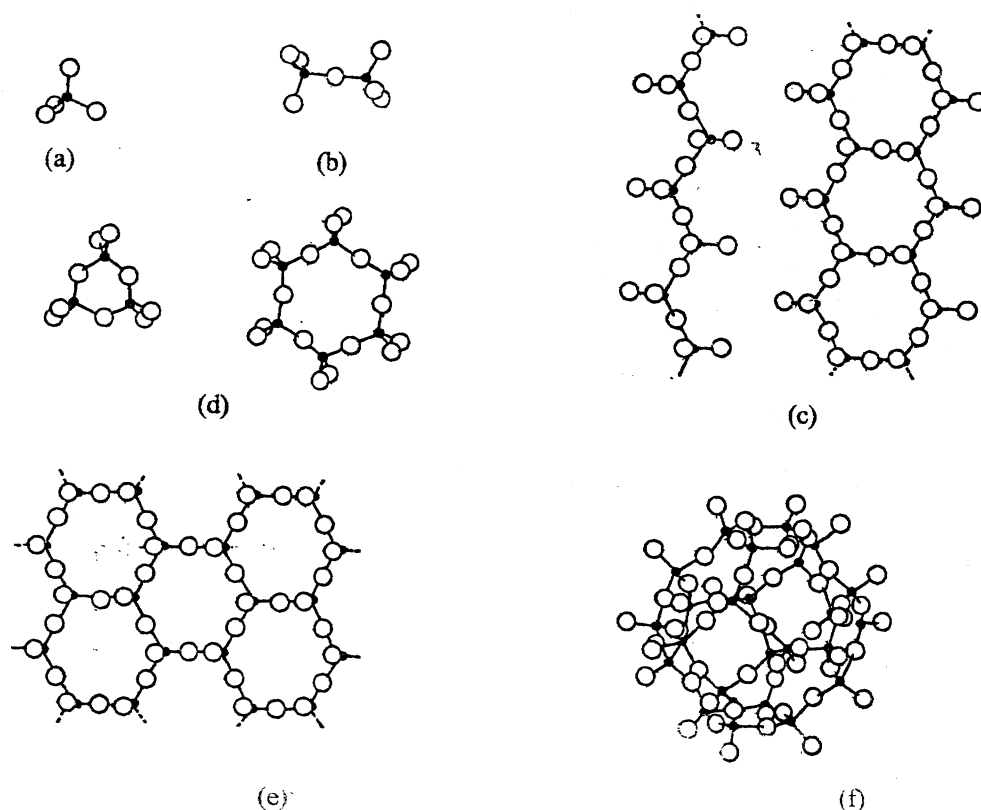


Figure 6. Illustration of the different silicate classes: (a) isolated  $\text{SiO}_4$  unit, (b) couplets, (c) single and double chains, (d) 6 and 12 membered rings, (e) sheet and (f) framework silicates

As the number of shared oxygen atoms in a basic  $[\text{SiO}_4]$  unit increases, so the ratio of Si : O will decrease and this can be seen in Table 1.

Aluminium, next to silicon and oxygen, is the third most abundant element in the earth's crust (8 %) and it plays a very important dual role in silicate crystal chemistry. Not only can the  $\text{Al}^{3+}$  function as a cation, alongside the  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$  cations, balancing the charge on silicate tetrahedra, but the aluminium can also replace some of the silicon atoms in the basic  $\text{SiO}_4$  tetrahedron resulting in the grouping  $[\text{AlO}_4]^{5-}$ .

When an aluminium ion is surrounded by 4 oxygen atoms (a co-ordination of 4) at the corners of a regular tetrahedron  $(\text{AlO}_4)^{5-}$ , it occupies a very similar space to  $(\text{SiO}_4)^{4-}$ . Note the different overall charge on the  $(\text{AlO}_4)^{5-}$  compared to the  $(\text{SiO}_4)^{4-}$  resulting from the different charges of  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$ . An extra  $\text{M}^+$  charge (a metallic cation) is therefore required to balance each  $(\text{AlO}_4)^{5-}$  unit present.

This special role of aluminium can be explained by looking at the ionic radii of various cations commonly found in silicates (see Table 2).

Co-ordination	Ion	Ionic radius (Å)
4	Si <sup>4+</sup>	0.26
4	Al <sup>3+</sup>	0.39
6	Al <sup>3+</sup>	0.54
6	Ti <sup>4+</sup>	0.61
6	Fe <sup>3+</sup>	0.65
6	Mg <sup>2+</sup>	0.72
6	Fe <sup>2+</sup>	0.78
6	Mn <sup>2+</sup>	0.83
8	Ca <sup>2+</sup>	1.12
8	Na <sup>+</sup>	1.18
8 - 12	Ba <sup>2+</sup>	1.42 - 1.61
8 - 12	K <sup>+</sup>	1.51 - 1.64
8 - 12	Rb <sup>+</sup>	1.61 - 1.72

Table 2. Co-ordination numbers and ionic radii of various cations  
(ionic radii from Shannon, 1976)

Table 2 shows that co-ordination is determined by the relative size of the cations. Ionic substitution in silicates is common between elements which lie between the bold horizontal lines drawn in the table above. i.e. between cations which, because of their size, have the same co-ordination in relation to oxygen, e.g. between Si<sup>4+</sup> and Al<sup>3+</sup>, and also between Al<sup>3+</sup>, Ti<sup>4+</sup>, Fe<sup>3+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup> and Mn<sup>2+</sup>.

The table shows in more detail how aluminium has this very special role in silicate crystal chemistry. Al<sup>3+</sup> is small and similar in size to Si<sup>4+</sup>, and both have a co-ordination of 4 with oxygen i.e. they form a basic tetrahedral unit of [AlO<sub>4</sub>]<sup>5-</sup> and [SiO<sub>4</sub>]<sup>4-</sup> respectively. The size of the Al<sup>3+</sup> cation is such that it can also have a co-ordination number of 6 with oxygen, with the aluminium in the centre of an octahedron and 6 oxygens at its corners. In this case it has a somewhat larger ionic radius, as can be seen in the table, and behaves like Ti<sup>4+</sup>, Fe<sup>3+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup> and Mn<sup>2+</sup>.

Aluminium can therefore assume a dual role in silicate crystals; it can form basic tetrahedral units with the Al effectively replacing some of the Si, and/or it can assume an octahedral arrangement bonding with oxygens in neighbouring tetrahedra. Examples of this dual role of aluminium will be seen in later sections.

Details of each of the silicate classes are expanded below and examples of silicates from each class are given with an indication of some of their chemical and physical properties. However, in a paper of this length, examples can only be given to illustrate the different classes of silicates and a more comprehensive coverage can be found, for example, in *An Introduction to the Rock-Forming Minerals* by Deer, Howie and Zussman, (1992).

## 1. NESOSILICATES

The nesosilicates or “island silicates” are based upon isolated, individual  $\text{SiO}_4$  tetrahedra. They are also sometimes known as orthosilicates. Because each  $\text{SiO}_4$  tetrahedron has an overall charge of 4-, as explained previously, positively charged, metallic cations are used to balance these charges. The size of the atom (atomic radius) is one factor determining which metals can be incorporated into the structure. The arrangement of the  $\text{SiO}_4$  tetrahedra and intervening cations is very close packed, generally leading to strong bonds, higher density and higher hardness than the minerals in other silicate classes. These properties also mean that nesosilicates incorporate a considerable number of gemstones.

### The Olivine Group

An illustration of the structure of olivine  $(\text{Mg,Fe})_2\text{SiO}_4$  is shown in Figure 7. Like most silicates its structure is complex, but in Figure 7 one can see the tetrahedra corresponding to the  $(\text{SiO}_4)^{4-}$  units and the octahedra corresponding to the metal ions  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$ , each linked to 6 oxygen atoms at its corners.

Note: The octahedral sites M1 and M2 differ. M2 is a regular octahedron, while M1 is a larger distorted octahedron. The  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  ions show no preference, but in the mineral monticellite,  $\text{CaMgSiO}_4$ , the larger  $\text{Ca}^{2+}$  occupies the M2 sites and the  $\text{Mg}^{2+}$  the M1 sites.

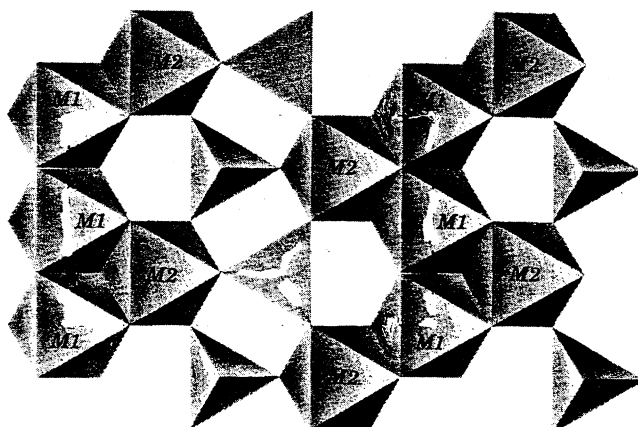


Figure 7. Idealised illustration of the structure of olivine projected on (100) (Klein and Hurlburt, 1993)

Iron and magnesium are both relatively abundant components of the earth's crust, have fairly similar ionic radii ( $0.72 \text{ \AA}$  for  $\text{Mg}^{2+}$  and  $0.78 \text{ \AA}$  for  $\text{Fe}^{2+}$ ), and are easily accommodated into the lattice. If every  $\text{SiO}_4$  tetrahedron has  $\text{Mg}^{2+}$  associated with it, the chemical formula will be  $\text{Mg}_2\text{SiO}_4$  (the mineral forsterite). On the other hand, the mineral might contain all  $\text{Fe}^{2+}$  and therefore have the formula  $\text{Fe}_2\text{SiO}_4$  (the mineral fayalite). These two minerals are the most common, and end members, of the olivine group.

Because  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  have similar ionic radii, it is possible for one ion to substitute directly for the other in the crystal lattice. This is known as solid solution or isomorphism and the range of minerals formed is called a solid solution series. The minerals intermediate between forsterite (often abbreviated to Fo) and fayalite (Fa) - (Table 3) are defined by their Mg/Fe proportions, which are reflected in the optical properties of the mineral in thin section. Continuous substitution of one ion for another also has implications for the crystallisation sequence of these minerals from magma.

% $\text{Mg}^{2+}$	100-90	90-70	70-50	50-30	30-10	10-0
Mineral	Forsterite	Chrysolite	Hyalosiderite	Hortonolite	Ferro-hortonolite	Fayalite
% $\text{Fe}^{2+}$	0-10	10-30	30-50	50-70	70-90	90-100

Table 3. Solid solution of iron and magnesium minerals in the olivine series



Manganese (ionic radius 0.83Å) can also substitute for iron and there is a solid solution series between fayalite and tephroite ( $\text{Mn}_2\text{SiO}_4$ ). Similarly calcium can substitute for iron, magnesium or manganese, giving rise to the mineral species monticellite ( $\text{CaMgSiO}_4$ ), glaucophroite ( $\text{CaMnSiO}_4$ ) and kirschsteinite ( $\text{CaFeSiO}_4$ ). All of these minerals belong to the olivine group, and share orthorhombic symmetry.

The olivine group minerals are most commonly associated with igneous rocks. Since the Si : O ratio in the olivines is relatively low (1:4), they are characteristic of ultrabasic and basic rocks, which contain less than 45% and 45-52% silica by weight respectively. Dunite is a monomineralic rock consisting only of olivine ( $\text{Fo}_{92}$ ), while olivine occurs with pyroxenes in peridotite rocks such as lherzolite, wehrlite and harzburgite. It is often a phenocryst (a relatively large, early-formed crystal) in basic rocks such as basalt, dolerite and gabbro.

The olivines are relatively high temperature minerals. Being formed in conditions of high thermal energy, they tend to be more easily broken down by weathering processes at normal temperatures and pressures than other silicate minerals. For this reason, whilst olivine may occur in sediments, it readily degrades to a range of clay minerals and serpentine.

The thermal metamorphism of impure limestones sees the reaction of dolomite with quartz to produce forsterite, which may appear as green streaks in certain marbles. Fayalite is more commonly produced in regionally metamorphosed iron-rich sediments.

Olivines are also known from stony nickel-iron meteorites called pallasites, to which they may contribute over 50% by volume. In addition, olivine has been discovered in the Nili Fossae region of Mars by means of Thermal Emission Spectrometry (TES). This technique relies on measuring the infra red energy emitted by surface materials as part of the Mars Global Surveyor Program (Hoefen et. al. 2003).

The distinctively green-yellow gem variety of olivine is called peridot. This usually has a high Fo content (it is generally reckoned that the best colours are achieved with less than 15% Fa in the crystal - fayalite crystals are generally darker in colour). The old German term chrysolite (not to be confused with chrysotile asbestos) is still occasionally used for light yellowish-green olivine gemstones.

The olivine group minerals vary in colour from light, through olive green to almost black. Crystallising in the orthorhombic system, they have a white streak, a hardness of 6.5-7.0, vitreous lustre, conchoidal fracture, and poor cleavage in two directions. The specific gravity varies with the dominant cation; forsterite's is 3.2 while fayalite's is 4.3.

## The Garnet Group

Garnets are also based upon the  $\text{SiO}_4$  structural unit. In the case of this mineral group, however, some trivalent ions are introduced into the crystal lattice. The  $\text{SiO}_4$  tetrahedra are still independent of each other, but they link to trivalent ions which are arranged in an octahedral pattern. Divalent ions are also present in the lattice, but they are located in the interstices in the network, each one being surrounded by 8 oxygen atoms. This means that the general chemical formula is written as  $\text{A}^{2+}_3\text{B}^{3+}_2[\text{SiO}_4]_3$ . Here, A represents divalent ions such as calcium  $\text{Ca}^{2+}$ , magnesium  $\text{Mg}^{2+}$ , iron  $\text{Fe}^{2+}$  and manganese  $\text{Mn}^{2+}$ , while B represents trivalent ions such as iron,  $\text{Fe}^{3+}$ , aluminium  $\text{Al}^{3+}$  or chromium  $\text{Cr}^{3+}$ . This diversity of metallic cations obviously increases the number of possible combinations and therefore mineral species.

The most common members of the garnet group are :

Grossular :	Ca-Al garnet	( $\text{Ca}_3\text{Al}_2[\text{SiO}_4]_3$ )
Pyrope :	Mg-Al garnet	( $\text{Mg}_3\text{Al}_2[\text{SiO}_4]_3$ )
Almandine :	Fe-Al garnet	( $\text{Fe}_3\text{Al}_2[\text{SiO}_4]_3$ )
Spessartine :	Mn-Al garnet	( $\text{Mn}_3\text{Al}_2[\text{SiO}_4]_3$ )
Andradite :	Ca-Fe garnet	( $\text{Ca}_3\text{Fe}_2[\text{SiO}_4]_3$ )
Uvarovite :	Ca-Cr garnet	( $\text{Ca}_3\text{Cr}_2[\text{SiO}_4]_3$ )

Notice that in almandine, iron is the divalent ion whilst in andradite it is the trivalent ion. This variable valency is a property found in Transition Elements such as iron and chromium, for example. Iron exists in two forms, referred to as ferrous iron ( $\text{Fe}^{2+}$ ) and ferric iron ( $\text{Fe}^{3+}$ ) respectively.

In garnets  $\text{A}_3\text{B}_2(\text{SiO}_4)_3$  where A and B refer to 8 and 6 coordinated cationic sites (see Table 2), the A sites are occupied by large divalent cations, while the B sites house smaller trivalent cations. Because  $\text{Ca}^{2+}$  is a relatively

large divalent cation, garnets can be divided into those containing  $\text{Ca}^{2+}$  [ugrandite where  $\text{A}=\text{Ca}$ ] and those with easily interchangeable divalent ions such as  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  and with calcium absent - pyralspite

PYRALSPITE		UGRANDITE	
Pyrope	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	Uvarovite	$\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$
Almandine	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	Grossular	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
Spessartine	$\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	Andradite	$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$

Table 4. Pyralspite and Ugrandite Garnets

The names PYRALSPITE and UGRANDITE serve as excellent mnemonic aids for the names of these garnets!

Solid solution exists between the magnesium (pyrope), iron (almandine) and manganese (spessartite) end members. By contrast, the ugrandite garnets with calcium in the A site, have limited solid solution between the chromium (uvarovite), aluminium (grossular) and iron (andradite) rich end members.

Garnets occur most frequently in metamorphic rocks. They are typical of high grade regional metamorphic rocks such as schists, gneisses and eclogites, which have formed under conditions of high temperature and pressure. Within these rocks they grow as new minerals or porphyroblasts. Calcium-rich varieties, especially grossular, may occur in thermally metamorphosed limestones (marble). Pyrope may be found in ultrabasic igneous rocks such as the olivine-containing peridotite, dunite and kimberlite. Garnets are relatively stable under conditions of chemical weathering and may be found in clastic sediments (gem gravels) as isolated heavy mineral grains. Under the right circumstances they may be concentrated in environments such as the insides of meander bends in mature river systems, forming placers.

A summary of the distinguishing features of the Garnet Group minerals is given in Table 5. All garnets belong in the isometric class as cube-based crystals, are hard (7 to 7.5 on Moh's scale) and have a vitreous lustre. The fracture is conchoidal (poor to good). The variations included in the table are most clearly reflected in the specific gravity and colour of the mineral; the chromium, magnesium and iron contents are most significant in this respect.

Mineral	Composition	Common form	Typical Colour	Specific Gravity
Grossular	$\text{Ca}_3\text{Al}_2[\text{SiO}_4]_3$	Rhombdodecahedron	Olive green, orange or colourless	3.5
Pyrope	$\text{Mg}_3\text{Al}_2[\text{SiO}_4]_3$	Rarely crystallised	Dark red to ruby red	3.6
Almandine	$\text{Fe}_3\text{Al}_2[\text{SiO}_4]_3$	Trapezohedron & Rhombdodecahedron	Deep red through reddish brown to brown	4.3
Spessartine	$\text{Mn}_3\text{Al}_2[\text{SiO}_4]_3$	Rhombdodecahedron	Orange, brown or pink	4.2
Andradite	$\text{Ca}_3\text{Fe}_2[\text{SiO}_4]_3$	Trapezohedron & Rhombdodecahedron	Black, brownish or yellowish green	3.8
Uvarovite	$\text{Ca}_3\text{Cr}_2[\text{SiO}_4]_3$	Rhombdodecahedron	Emerald green	3.8

Table 5. Distinguishing features of the more common garnet group minerals.

Rare members of the garnet group include (in alphabetical order) calderite, goldmanite, henritermierite, hibschite, katoite, kimzeyite, knorringite, majorite, morimotoite and schorlomite, which is a titanium-rich variety.

The hardness of garnets, their transparency, lack of cleavage, high refractive index, colour variety and durability make them good candidates for gemstones.

## Titanite

Titanite is a titanium-rich nesosilicate which is also known as sphene. The  $\text{SiO}_4$  tetrahedra in this case share their oxygen atoms to form  $\text{CaO}_7$  and  $\text{TiO}_6$  groupings within the crystal lattice, such that the chemical formula becomes  $\text{Ca}_2\text{TiO}(\text{SiO}_4)_2$ . The calcium may be partially replaced by strontium, barium (e.g. benitoite  $\text{BaTiSi}_3\text{O}_9$ ) or the rare earth elements which have higher valencies (often 3 or 4). In these cases, the charges are counterbalanced by means of trivalent iron and aluminium entering the position occupied by titanium. This

gives rise to considerable variety with, for example, keilhauite, also called yttrotitanite, containing significant amounts of yttrium and cerium.

With a name derived from the Greek for 'wedge', sphene has a distinctively wedge-shaped, tabular crystal habit, especially when seen in thin section. Ranging from green through yellow and white to brown or black in colour, its transparent to translucent monoclinic crystals have adamantine lustre, white streak, conchoidal fracture, a specific gravity of 3.5 and a hardness of around 5.

Sphene is widespread as an accessory mineral in igneous rocks, particularly coarse-grained acid and intermediate rocks such as granites and syenites, where it is often the main titanium-bearing mineral. It may occur in hydrothermal veins and is found in high grade metamorphic rocks such as schists and gneisses, as well as in marbles. It survives as detrital grains in clastic sedimentary rocks.

## Zircon

In zircon,  $\text{ZrSiO}_4$ , the  $\text{SiO}_4$  tetrahedra have interspersed zirconium cations such that each is surrounded by four oxygen atoms. The zirconium is often partially replaced (generally up to 3%) by the transition metal hafnium (Hf); indeed zircons are the main source not only of zirconium, but also of commercial hafnium. Uranium and thorium are radioactive contaminants which, as a consequence of their decay, cause the crystal structure of some zircons (variety cyrtolite) to deteriorate (the process of metamiction).

The replacement of zirconium by other metals in the crystal lattice gives rise to a variation in several properties of the mineral, including its hardness (range 6.5 to 7.5). Crystallising in the tetragonal system, it has a colourless streak, specific gravity of around 4.7 and an adamantine lustre.

As with garnets, the combination of hardness, diaphaneity (the degree of translucence), lustre, fire (ability to disperse white light) and colour range make zircon a good gemstone: hyacinth or jacinth is a yellow to reddish-brown variety, while jargon (also known as jargoon) is colourless to pale grey or yellow, starlite is blue and matarua is the colourless variety used to resemble diamond. Zircons are sometimes heat treated in a variety of ways in order to intensify or bring out their colours.

A common accessory mineral formed early in the crystallisation sequence of coarse-grained igneous rocks, granites and pegmatites, zircon is quite resistant to weathering and may be present as detrital grains in clastic sedimentary rocks.

## Topaz

Aluminium is the trivalent metallic cation found in topaz, which also contains fluoride ( $\text{F}^-$ ) and hydroxyl ( $\text{OH}^-$ ) ions. Its chemical formula is  $\text{Al}_2\text{SiO}_4(\text{OH},\text{F})_2$ .

Topaz crystallises in the orthorhombic system, usually with prismatic or tabular habit. With a hardness of 8, colourless streak, vitreous lustre and colours ranging from colourless to white, yellow, orange, brown, pink, blues and greens, it is a popular gemstone. Like zircon, topaz is often heat treated in order to enhance or change its colour. It has a strong basal cleavage which is helpful in identifying broken pieces.

Topaz is most commonly found in acid igneous rocks (granites and their allies) and associated pneumatolysis (where magmatic gases react with the surrounding country rock). Quite resistant to weathering, they may be found as sedimentary clasts.

## Staurolite

Staurolite,  $(\text{Fe},\text{Mg},\text{Zn})_{3-4}(\text{Al},\text{Fe})_{18}(\text{Si},\text{Al})_8\text{O}_{48}\text{H}_{2-4}$ , is a metamorphic mineral with a complex chemistry – it is an iron aluminium hydroxide silicate. Named from stauros, the Greek for cross (Lockwood, 2004), staurolite commonly occurs as penetration twins at  $60^\circ$ , and less commonly at  $90^\circ$  to each other. Brown to black in colour, the monoclinic crystals have a white streak, hardness around 7.2, specific gravity of 3.8 and a vitreous lustre. Staurolite is most common in the schists that represent medium grade regional metamorphism of pelitic sediments (which contain an appreciable amount of aluminium as clay minerals).

## Aluminium silicates

A group of three aluminium silicates all have the same chemical formula –  $\text{Al}_2\text{SiO}_5$ , sometimes written  $\text{Al}_2\text{O}(\text{SiO}_4)$ . However, differences in the arrangements of the atoms in the crystal lattice lead to crystallisation in different crystal systems. This means that the three minerals, andalusite, kyanite and sillimanite, are polymorphs; andalusite and sillimanite are orthorhombic, while kyanite is triclinic.

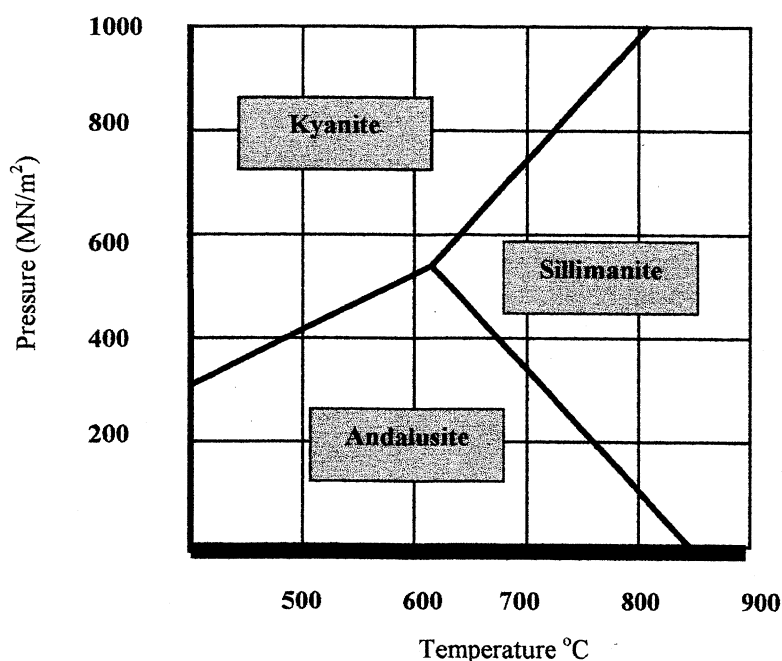


Figure 8. Pressure and temperature stability fields for the  $\text{Al}_2\text{SiO}_5$  polymorphs kyanite, andalusite and sillimanite (after Bell, P.M. 1963)

All three are metamorphic minerals but are stable in different temperature and pressure regimes (Figure 8). Andalusite is most common in thermally metamorphosed rocks such as hornfels, but may also occur in low grade regional metamorphic rocks. Kyanite and sillimanite are more typical of high pressure regional metamorphic rocks such as gneisses, with sillimanite replacing kyanite as the temperature increases.

The fact that some metamorphic minerals are stable only in fairly narrow pressure and temperature regimes has been useful in defining metamorphic facies. Each facies is defined and recognised by a distinctive association of minerals. As long ago as 1893, George Barrow noticed that kyanite gave way to sillimanite with increasing grade of metamorphism in his mapping of the Dalradian rocks of the Scottish Highlands. Later, in the area around Buchan, slightly to the north of Barrow's research area, it was noted that sillimanite was derived from earlier andalusite crystals rather than kyanite.

The crystal structures of these polymorphs are interesting in that they show aluminium in its dual role (see Table 2), both as a cation,  $\text{Al}^{3+}$  surrounded by 6 oxygen atoms, in an octahedral arrangement, and replacing silicon at the centre of a tetrahedron as  $(\text{AlO}_4)^{5-}$ . Figure 9 shows a somewhat idealised projection of sillimanite, illustrating zigzag chains of edge-sharing octahedra parallel to the c axis (on the left) and the presence of  $\text{AlO}_4$  tetrahedra between the  $\text{SiO}_4$  tetrahedra (on the right).

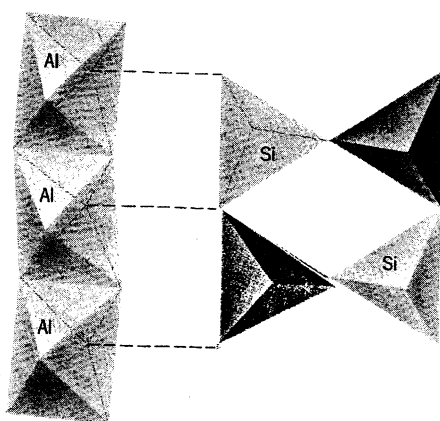


Figure 9. Idealised projection of the crystal structure of sillimanite with aluminium present both as a cation and replacing silicon in some tetrahedra. (Burnham, 1963)

One distinctive variety of andalusite is the mineral chialtolite. This has cross-shaped patterns developed in the mineral's cross-section. These patterns are due to the presence of carbonaceous or clay mineral inclusions becoming arranged symmetrically within the body of the crystal.

Kyanite has the peculiar property of variable hardness. When scratched parallel to the long axis of the crystal the hardness is around 4.5, but when scratched at 90° to the long axis the hardness is 6.5.

The distinguishing features of the aluminium silicates are given in Table 6.

Mineral	Colour	Streak	Lustre	Hardness	Specific gravity
<i>Andalusite</i>	White, red, brown	White	Vitreous	7.5	3.15
<i>Kyanite</i>	Blue, grey, green	White	Vitreous	4.5-6.5	3.58
<i>Sillimanite</i>	White, brown, green	White	Vitreous	7.5	3.20

Table 6. Distinguishing features of the aluminium silicate minerals.

### Other Nesosilicates

The more common nesosilicates are dealt with above, but there is a large number of additional mineral species belonging to this class. Some of the more interesting examples are tabulated below (Table 7) with brief indications of their composition and formation.

Mineral	Contained elements	Comments
<i>Chloritoid</i>	Fe, Mg, Mn, Al, OH	Regional metamorphic mineral
<i>Datolite</i>	Ca, B, OH	Pneumatolytic mineral
<i>Euclase</i>	Be, Al, OH	Granites and pegmatites
<i>Gadolinite</i>	Y, Fe, Be	Granites
<i>Howlite</i>	Ca, B, OH	Sometimes classed as a borate
<i>Humite</i>	Mg, Fe, F	Metamorphic and hydrothermal
<i>Phenakite</i>	Be	Hydrothermal
<i>Thorite</i>	Th, U	Pegmatites, metamorphic, hydrothermal
<i>Uranophane</i>	Ca, U	Oxidation of uranium minerals
<i>Willemite</i>	Zn	Hydrothermal

Table 7. Features of selected nesosilicate minerals.

## 2. SOROSILICATES

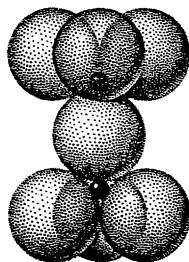


Figure 10. Close-packed representation of the  $\text{Si}_2\text{O}_7$  group

Also known as "couplet silicates" the sorosilicates are based upon pairs of  $\text{SiO}_4$  tetrahedra which are joined together by sharing one oxygen atom. This changes the structure of the basic unit from  $\text{SiO}_4$  to  $\text{Si}_2\text{O}_7$ , which means in turn that the Si:O ratio decreases from 1:4 to 1:3.5. Since the shared oxygen now has both of its negative charges fully satisfied by sharing electrons with two silicon atoms, the overall charge of the unit is reduced to 6-. This means that the equivalent of three divalent cations are now required to balance the charge. This is mostly accomplished using cations of the elements; Fe, Mg, Mn, Al, Ca or Ce. Aluminium is sometimes substituted for silicon. Relatively few minerals are sorosilicates.

### Hemimorphite

Hemimorphite,  $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ , normally occurs as thin tabular crystals, but it can be massive, granular, fibrous, mamillated or banded. Crystals are commonly white, but they can be yellowish-brown, greenish or blue. It occurs in the oxidised portions of zinc deposits associated with galena, smithsonite, sphalerite, cerussite and anglesite. Hemimorphite is named from the Greek prefix *hemi-*, meaning "half", and *morphe*, "form" literally "half-form" in allusion to the differences in crystal forms displayed on opposite ends of the c axis. Hemimorphite was known formerly in USA as calamine, while calamine was formerly used in Britain as a name for smithsonite, zinc carbonate.

### The Epidote Group

Epidote,  $\text{Ca}_2(\text{Fe}^{3+}, \text{Al})\text{Al}_2\text{O}(\text{SiO}_4)(\text{Si}_2\text{O}_7)(\text{OH})$ , is a complex mineral containing both isolated  $\text{SiO}_4$  tetrahedra and  $\text{Si}_2\text{O}_7$  units. These, and the ionic groups connect together parallel chains of  $\text{AlO}_6$  and  $\text{AlO}_4(\text{OH})_2$  octahedra. Epidote minerals crystallise in two crystal systems: orthorhombic and monoclinic. The monoclinic species shows the greater chemical diversity.

Epidote is generally found in high grade regionally metamorphosed rocks belonging to the eclogite-amphibolite facies. It is produced as a consequence of the reaction between chlorite, calcite and quartz. The salient features of the main epidote group minerals are summarised in Table 8.

Mineral	Ions	Crystal system	Colour	Hardness	Specific Gravity
<i>Zoisite</i>	Ca, Al	Orthorhombic	White, grey, green	6-6.5	3.2-3.4
<i>Clinozoisite</i>	Ca, Al	Monoclinic	Grey	6-7	3.2-3.4
<i>Epidote</i>	Ca, Al, Fe	Monoclinic	Shades of green	6-7	3.2-3.5
<i>Allanite</i>	Ca, Al, Fe, Ce, La, Y	Monoclinic	Black to brown	5.5	3.0-4.2

Table 8. Selected characteristics of the main epidote group minerals

Some of the less common epidote group minerals accommodate unusual elements, including rare earths, in their crystal lattices. For example, dissakisite contains lanthanum, androsite may contain niobium, mukhinite contains vanadium and hancockite contains strontium. Allanite, also known as orthite, often contains small amounts of thorium and uranium making the mineral radioactive. Thulite is a pink manganzoisite found in Norway.

Although only discovered by Masai herdsmen in the Usambara Mountains of northern Tanzania in 1967, tanzanite, a gem quality calcium- and aluminium-rich orthorhombic variety of zoisite, has become popular with collectors. Still known only from a single relatively small area, tanzanite is often heat treated to bring out the deep blue and lavender colouring which is caused by traces of vanadium. One recently collected crystal weighs over 3 kg (Anon., New Scientist, 2005).

### The Melilite Group

The melilite group of minerals consists of  $\text{Si}_2\text{O}_7$  units together with  $\text{AlO}_4$  and  $\text{MgO}_4$  tetrahedra arranged in sheet-like patterns bonded together by Ca-O linkages. Calcium is present in each of the main members of the group, but may be replaced by sodium in melilite itself. Melilite and akermanite both contain magnesium, while gehlenite possesses some aluminium in the crystal lattice.

Melilite's chemical formula,  $(\text{Ca},\text{Na})_2(\text{Al},\text{Mg})(\text{Si},\text{Al})_2\text{O}_7$ , is interesting. The  $(\text{Si},\text{Al})_2\text{O}_7$  indicates the replacement of some silicon atoms by aluminium atoms in the basic  $\text{Si}_2\text{O}_7$  sorosilicate structure. The  $(\text{Ca},\text{Na})_2(\text{Al},\text{Mg})$  indicates that the overall negative charge of the silicate anion is balanced by a combination of  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  cations, with substitution of the larger  $\text{Ca}^{2+}$  cation by  $\text{Na}^+$  and the smaller  $\text{Al}^{3+}$  cation by  $\text{Mg}^{2+}$  (see Table 2). The presence here of  $\text{Al}^{3+}$ , and its replacement of some Si atoms within the  $\text{Si}_2\text{O}_7$  structure, is another example of the dual role that aluminium has in silicate structures.

Melilite is relatively common where basic magmas react with carbonate rocks, while the other members of the group occur in thermally metamorphosed siliceous limestones and dolomites.

### Other metamorphic sorosilicate minerals

Lawsonite,  $\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ , is a hydrated calcium aluminium sorosilicate, bluish in colour, which is found in high pressure, low temperature burial metamorphic rocks of the glaucophane schist facies. Pumpellyite, an index mineral for the low temperature, low pressure prehnite-pumpellyite metamorphic facies, is named after the famous American geologist, Raphael Pumpelly (1837-1923). It is a hydrated sorosilicate containing calcium and aluminium and is most common in basalts which have been subjected to burial metamorphism.

Vesuvianite,  $\text{Ca}_{19}(\text{Al},\text{Mg},\text{Fe})_{13}\text{Si}_{18}\text{O}_{68}(\text{O},\text{OH},\text{F})_{10}$ , or idocrase (named from Vesuvius, where it was first discovered) is rather peculiar in that it contains both  $\text{SiO}_4$  tetrahedra and  $\text{Si}_2\text{O}_7$  units. Because of the latter, it is usually classified with the sorosilicates rather than the nesosilicates, the higher level of organisation being taken as significant. It is produced by the thermal metamorphism of impure limestones and includes a massive green gem variety called californite. Other metamorphic sorosilicates include the calcium-containing rankinite and tilleyite.

### 3. INOSILICATES

The easiest way to imagine forming an inosilicate or chain silicate is to link the tetrahedra in a straight line. In this way, each  $\text{SiO}_4$  tetrahedron shares two oxygen atoms with its neighbours. The apices of the tetrahedra in these chains all point in the same direction and the excess charges are balanced by cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . These two ions bind the chains together, the calcium being surrounded by eight oxygen atoms and the magnesium by six. In terms of chemical formula, this type of single chain silicate consists of multiple  $\text{Si}_2\text{O}_6$  units running parallel to the c-axis, and includes the pyroxenes.

Double chain silicates include the amphiboles and consist of two identically oriented adjacent chains, linked by shared oxygens. This sharing of oxygen atoms at regular intervals along the length of the chain results in a structure whose most simple unit is  $\text{Si}_4\text{O}_{11}$ . Adjacent paired chains are bonded together by means of a range of ions including  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Hydroxyl groups are also present in the structure and may be replaced by fluorine. Also, aluminium may substitute for silicon.

#### The Pyroxenes

This mineral group consists of linked  $\text{SiO}_4$  tetrahedra such that they describe an alternating pattern, one tetrahedron pointing left and then the next pointing right, along the length of the chain. Pyroxenes have the general formula  $\text{XY}(\text{Si,Al})_2\text{O}_6$ . Here, X consists of ions of Ca, Na, Fe and Mg, and occasionally of Zn, Mn and Li. Ions of generally smaller radius are represented at Y. These include ions of Cr, Al, Fe, Sc, Ti and V. The large number of potential combinations of these elements gives rise to considerable diversity in the group.

Pyroxenes typically possess cleavages which intersect at around  $90^\circ$  ( $87^\circ$  and  $93^\circ$ ) and crystallise in the orthorhombic and monoclinic crystal systems.

##### (i) Orthopyroxenes

The orthorhombic pyroxenes consist essentially of a solid solution series with  $\text{Mg}_2\text{Si}_2\text{O}_6$  and  $\text{Fe}_2\text{Si}_2\text{O}_6$  as end members, corresponding to the minerals enstatite and ferrosilite respectively. Older texts refer to the iron-rich orthopyroxenes as hypersthene. Technically, this name has been abandoned in favour of ferrosilite, but some authors tend to use the terms interchangeably, or to use hypersthene for minerals with a composition intermediate between enstatite and ferrosilite. The picture of orthopyroxene diversity is complicated a little by polymorphic changes that take place with changing temperatures. For example, ferrosilite changes to a monoclinic polymorph called pigeonite at high temperatures, and enstatite changes to clinoenstatite.

Enstatite is typically white in colour, ranging to pale greys, browns and greens, with a pearly lustre on the cleavage surfaces. Iron-rich (about 5-14%) varieties alter under weathering; the iron begins to separate into fine oxide and hydroxide films on the cleavage planes, giving them a metallic sheen. This process is called schillerisation, and the metallic sheen is referred to as a schiller structure. The product of this process is bronzite, a green or brown mineral found in basic and ultrabasic rocks such as gabbros and peridotites. Further alteration by hydration may give rise to bastite or schiller spar which is usually associated with serpentinites. Enstatite itself is a common component of ultrabasic rocks like pyroxenites, harzburgites and picrites. As an early formed mineral in basic magmas, it may be concentrated as cumulate deposits in larger layered igneous intrusions such as the Bushveld and Skaergaard Complexes. Enstatite is also known from stony and iron meteorites, where it usually occurs with olivine in small spherical units called chondrules. In one class of meteorites, the Enstatite Chondrites, magnesium-rich enstatite is by far the main silicate mineral, leading some authorities to suggest that they formed near the orbit of Mercury. One emerald green variety of enstatite, chrome-enstatite, is exploited as a gemstone.

With increasing iron content, the orthopyroxenes tend to become progressively more green and brown in colour. In addition to their occurrence in basic and ultrabasic igneous rocks and meteorites, they are typical of high grade regional metamorphic rocks of the granulite facies.

##### (ii) Clinopyroxenes

Most (90%) of the monoclinic pyroxenes are part of a group that is most easily considered in terms of a triple ion solid solution series; Fe can substitute progressively for Mg, as we have seen several times before, but both ions can



be replaced by Ca, up to a value of 50%. This gives rise to the  $\text{CaMgSi}_2\text{O}_6$  -  $\text{CaFeSi}_2\text{O}_6$  -  $\text{Mg}_2\text{Si}_2\text{O}_6$  -  $\text{Fe}_2\text{Si}_2\text{O}_6$  system. The range of mineral species so produced is best illustrated on a triangular composition diagram. This is effectively a graph with three axes but displayed two-dimensionally in the form of a triangle. The vertices of the triangle are represented by 100%  $\text{Mg}_2\text{Si}_2\text{O}_6$  (clinoenstatite), 100%  $\text{Fe}_2\text{Si}_2\text{O}_6$  (clinoferrosilite)\*\* and 100%  $\text{CaSiO}_3$  (wollastonite) respectively. The larger ionic radius of Ca means that continuous substitution of Mg and Fe by Ca in the 50-100% Ca range does not take place, effectively cutting off the top of the triangle. The clinopyroxene field therefore falls within the basal trapezium of the triangle (Figure 11). If a pyroxene (\*) was analysed and found to have a Mg:Fe ratio of 3:2 (i.e. 60:40) and an identical Mg:Ca ratio it would plot out within the box labelled augite in Figure 11.

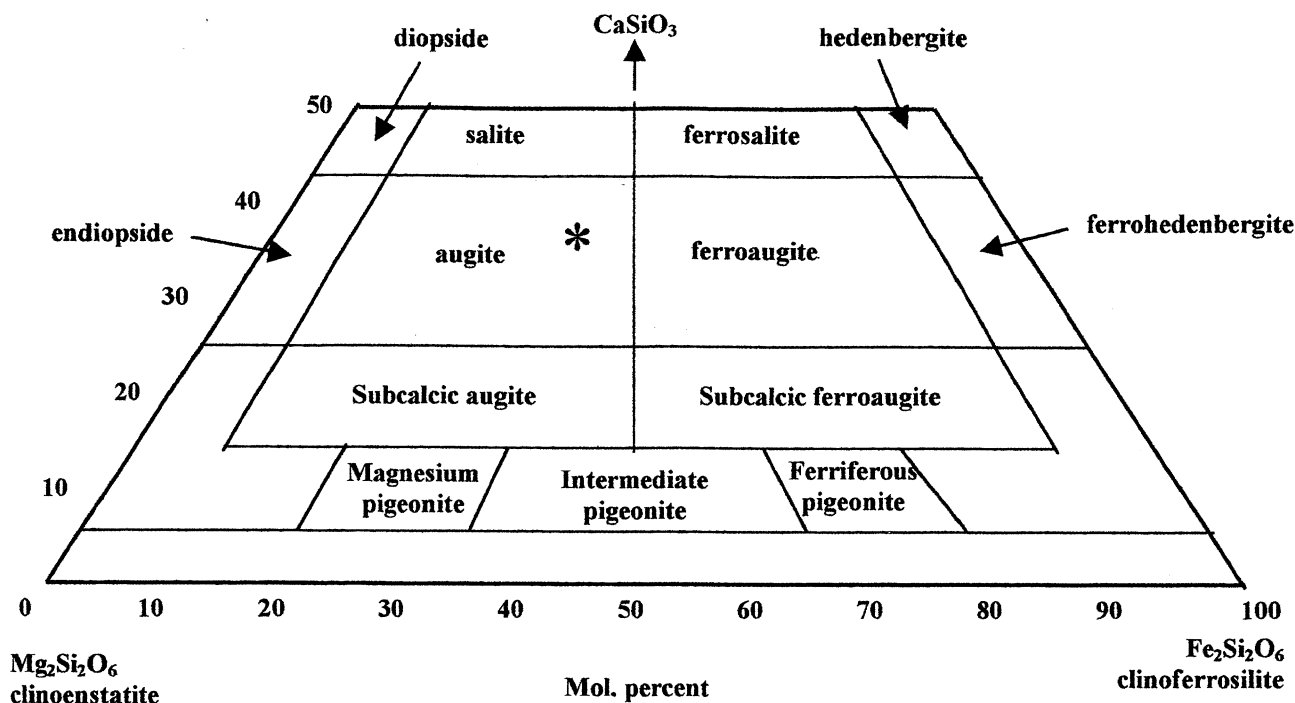


Figure 11. Nomenclature and chemical composition of the main clinopyroxenes (after Paldervart and Hess, 1951)

Augite ranges from dark green through brown to black in colour with a greenish white streak, uneven fracture and a hardness of 5 to 6. In addition to Ca, Mg and Fe it commonly contains Na and significant replacement of Si by Al. An essential mineral in basic rocks like basalts, dolerites and gabbros, it is also found in some metamorphic rocks. The small amounts of Ti found in augite are increased up to around 5% in titanaugite, whilst aegirine (acmite) is a variety of augite enriched in Na and found in highly alkaline igneous rocks such as syenites and alkali granites.

Spodumene may be found in association with other Li-rich minerals in igneous rocks such as granite pegmatites. Its chemical composition is  $\text{LiAlSi}_2\text{O}_6$  and some enormous (12m long) crystals have been reported. Two gem varieties of spodumene are known. Kunzite (Conklin 1987), named after the famous mineralogist George Frederick Kunz (1856-1932), self taught gem expert for Tiffany & Co. and prolific author, is transparent and distinctively pink to lilac in colour. Hiddenite, a much rarer mineral, is green in colour and strongly pleochroic (when viewed from different directions, the crystal shows colour intensity variation), presenting specific problems for gem cutters.

Jadeite,  $\text{Na}(\text{Al}, \text{Fe}^{3+})\text{Si}_2\text{O}_6$ , is the least common of the two minerals that are included in jade (the other is nephrite). Usually green in colour, it has a white streak and hardness of 6.5. A highly ornamental stone with deep cultural significance, it is most famously known from China and Central America (e.g. Laufer 1912; Levy and Scott-Clark 2001). Crystallising in temperatures ranging from 600°C to 1200°C and pressures of between 1000 and 2500 MN/m<sup>2</sup> it occurs in conditions of low grade metamorphism in the blue schist facies.

\*\*However, clinoferrosilite is best thought of as  $(\text{Fe}^{2+}, \text{Mg})_2\text{Si}_2\text{O}_6$  with an iron content of 90-100%.

**Omphacite**,  $(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe}, \text{Al})\text{Si}_2\text{O}_6$ , is a high pressure green clinopyroxene with greenish white streak and vitreous to silky lustre found in eclogites, kimberlites and some blue schists.

Rarer and more unusual clinopyroxenes include johannsenite and kanoite, both of which contain Mn, kosmochlor (containing Cr), jervisite (containing Sc) and the vanadium-containing natalyite.

### The Pyroxenoids

This is a group of triclinic minerals which share a general chemical formula of  $\text{XSiO}_3$  and are often classed together (although some texts include them in the pyroxenes). Whereas the linked tetrahedra in the pyroxene chains always repeat their pattern of orientation every 3 units, repeat patterns are found every three, five or seven units in pyroxenoids, depending on the individual mineral.

**Wollastonite** ( $\text{CaSiO}_3$ ), named for William H. Wollaston (1766-1828), namesake of the Geological Society's Wollaston Medal, is both the most famous and most abundant pyroxenoid. It is formed through the solid state reaction of calcite with quartz (with the evolution of carbon dioxide) in the metamorphism of impure limestones, or where limestones have been contaminated with magmatic Si during metasomatism. Typically white in colour with a colourless streak and a hardness of 5 to 5.5, it breaks with a splintery to uneven fracture and may fluoresce. There is also a rare high temperature polymorph called parawollastonite.

"Larimar", the trade name given to a translucent sky blue rock from the Bahamas and Dominican Republic, is mostly composed of the pyroxenoid pectolite. Here, single and double tetrahedra alternate along the length of the chain. Calcium atoms are each co-ordinated with eight oxygens (as in wollastonite), but Na also enters into the lattice, giving a chemical formula of  $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$ . Pectolite may crystallise from intermediate magmas, occasionally being found in nepheline-syenites, but is more typically found as a hydrothermal mineral in cavities within basic igneous rocks.

There are three Mn-containing pyroxenoids, all found in metasomatic or metamorphic manganese ore bodies. Rhodonite,  $\text{CaMn}_4\text{Si}_5\text{O}_{15}$ , has a distinctive rose pink colour, after which it is named. It is generally distinguished from bustamite and pyroxmangite on the basis of optical properties.

### The Amphiboles

Linking of two adjacent chains of  $\text{SiO}_4$  tetrahedra gives rise to a double chain whose repeating unit is  $\text{Si}_4\text{O}_{11}$ . Adjacent double chains are bonded laterally to each other by means of a wide range of possible ions. The general formula for the group can be written as  $\text{XY}_2\text{Z}_5(\text{Si}, \text{Al}, \text{Ti})_8\text{O}_{22}(\text{OH}, \text{F})_2$ . You can see from this that the Si can be replaced by Al or even Ti in some circumstances, and that hydroxyl (OH) ions enter consistently into the crystal lattice. Larger ions such as  $\text{Ca}^{2+}$  and  $\text{Na}^+$  are usually represented by X, while Y may be represented by ions of the elements Na, Ca, Fe, Li, Mn, Al, Ti and occasionally even Zn, Ni or Co. A wide range of ions can also be represented at Z, including  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Ti}^{4+}$  and  $\text{Cr}^{3+}$ ,  $\text{Li}^+$ , and  $\text{Al}^{3+}$ . Since X, Y and Z can be represented by ions of varying charge, it follows that substitution of one ion by another may require coupled secondary substitutions in order to maintain the overall charge balance within the lattice. This means that the amphiboles show an enormous diversity of chemical composition. Like pyroxenes, they can be subdivided by crystal system into orthorhombic, monoclinic and triclinic groups, onto which can be superimposed aspects of chemical composition.

Amphiboles, like pyroxenes have a typical cleavage. In this case the two cleavages intersect at around  $55^\circ$  and this can sometimes be used to differentiate them from pyroxenes. Nomenclature of the group has been defined by the IMA Subcommittee on Amphiboles (Leake et al. 2004)

#### (i) Orthorhombic amphiboles

These are the Fe- and Mg-rich minerals of the anthophyllite group. Some species, such as ferroholmquistite, may even contain Li. Anthophyllite,  $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ , which forms a series with ferro-anthophyllite,  $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ , and the closely related gedrite (with Al substituted for some of the Si) are metamorphic and metasomatic minerals. Anthophyllite may form by retrograde metamorphism (metamorphism taking place under conditions of lower temperatures and pressures than the original phase of metamorphism) of earlier thermally metamorphosed rocks, or by metamorphism of Mg-rich dolomitic limestones or basic igneous rocks to schists and gneisses. It is brown in colour with a grey streak and hardness 5.5 to 6. It may crystallise into long radiating fibres which can be used as asbestos in refractory cements.

## (ii) Monoclinic amphiboles

### (a) Cummingtonite series

Cummingtonite is a dark grey to green/brown mineral with white streak, silky to vitreous lustre and a hardness of 5 to 6. It is commonly found in amphibolites, high grade regional metamorphic rocks produced by alteration of basic igneous rocks. This mineral has the formula,  $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$  and is the orthorhombic dimorph of anthophyllite. Cummingtonite forms a series with the iron rich grunerite  $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ , which is the monoclinic dimorph of ferroanthophyllite. Small amounts of Mn can replace some of the Fe and Mg in the crystal lattice giving rise to Mn-rich varieties such as tiroidite.

### (b) Tremolite series

Minerals in this series conform to the formula  $\text{Ca}_2(\text{Mg}, \text{Fe}^{2+})_5(\text{Si}_8\text{O}_{22})(\text{OH}, \text{F})_2$ , where the relative quantities of Fe and Mg vary considerably. If Mg predominates the mineral is tremolite, whereas in ferroactinolite the Fe is dominant. Actinolite is the intermediate form. Increasing the Fe content darkens the colour of the mineral and increases the specific gravity. These minerals are found in thermally and regionally metamorphosed rocks, particularly hornfelsed impure limestones and the greenschists produced from basic and ultrabasic igneous rocks. The solid state reaction between dolomite, quartz and water yields tremolite, calcite and carbon dioxide.

Tremolite may crystallise as fine fibres forming asbestos. Some forms, often called Mountain Cork, Mountain Leather and Mountain Wood have a felt-like appearance. Nephrite, one of the two minerals combining to form jade, is a variety of actinolite.

### (c) Hornblende series

Hornblende is known in both igneous and metamorphic rocks. It is a common constituent of intermediate rocks such as diorites and syenites, but can also be found as an accessory mineral in granites and basic rocks like basalts and dolerites. Metamorphism of igneous rocks may give rise to hornblende gneisses, schists and amphibolites. Hornblende shows considerable colour variation (from black, through various greens to brown), forming prismatic, translucent to opaque crystals which break with an uneven fracture.

Hornblende has the rather complex formula  $(\text{Na}, \text{K})_{0-1}\text{Ca}_2(\text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al})_5(\text{Si}_{6-7}\text{Al}_{2-1}\text{O}_{22})(\text{OH}, \text{F})_2$ . This clearly indicates that a wide compositional diversity exists. Indeed, hornblende is now largely a useful field identification term as analysis of mineral chemical composition reveals a suite of closely related minerals which are distinguished largely on the basis of optical properties. Deer, Howie and Zussman (1992) have shown that the series can be conveniently considered as being derived from tremolite. Thus, introduction of Na and replacement of one Si by Al gives rise to edenite and ferroedenite, whilst the replacement of both Mg and some Si by Al results in tschermakite. Pargasite and ferrohastingsite are Mg- and Fe-rich members respectively of the hornblende series. Kaersutite is a Ti-rich mineral closely related chemically to hornblende and found in alkaline igneous rocks such as trachytes, trachyandesites and nepheline-syenites.

### (d) Alkali amphiboles

Glaucophane and riebeckite are two closely related minerals, both of which are distinctively blue with a blue to grey streak. Riebeckite is the more Fe-rich of the two with the formula  $\text{Na}_2\text{Fe}_3^{2+}\text{Fe}_2^{3+}(\text{Si}_8\text{O}_{22})(\text{OH})_2$ . A fibrous form of the mineral, crocidolite, is a significant source of commercial "blue" asbestos. Riebeckite occurs in granites and syenites, and is a component of the famous Rubislaw Granite of Aberdeen. Glaucophane,

$\text{Na}_2\text{Mg}_3\text{Al}_2(\text{Si}_8\text{O}_{22})(\text{OH})_2$ , is an index mineral for the glaucophane schist or "blueschist" facies typical of burial metamorphism and retrograde metamorphism of eclogites. Crossite has an intermediate composition between glaucophane and riebeckite, while arfvedsonite is Na-rich.

## (iii) Triclinic amphiboles

Aenigmatite,  $\text{Na}_2\text{Fe}_5^{2+}\text{TiSi}_6\text{O}_{20}$ , has, as its name suggests, been difficult to classify, having been at various times included in the pyroxenes and the amphiboles. Its black triclinic crystals are known from alkaline volcanic rocks such as phonolites and trachytes and their plutonic equivalents, syenites.

## 4. CYCLOSILICATES

Cyclosilicates, or ring silicates, are formed by several tetrahedra being linked together and then closed to form a ring. One subgroup consists of three  $\text{SiO}_4$  tetrahedra linked in such a way that each shares two oxygen atoms with its neighbours, forming a 6-membered ring. This means that the ring structure has the chemical formula  $\text{Si}_3\text{O}_9$  and an overall charge of 6-. Alternatively, rings may be composed of four or six interlinked  $\text{SiO}_4$  tetrahedra. In the latter case a structure whose formula is  $\text{Si}_6\text{O}_{18}$  results with an overall charge of 12-. In each case, the sharing of oxygen atoms by adjacent tetrahedra reduces the Si:O ratio to 1:3. Aluminium may substitute for silicon in each of these arrangements, and the cations which most commonly balance the charges include  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . The more unusual elements beryllium, lithium, boron and fluorine are also present in some cyclosilicates.

### Rings with Three- $\text{SiO}_4$ Tetrahedra

#### Benitoite

This is a barium titanium silicate,  $\text{BaTiSi}_3\text{O}_9$ . The triangular arrangement of the three interlinked  $\text{SiO}_4$  tetrahedra results in trigonal crystals. For some time benitoite was confused with sapphire, with which it shares a distinctive blue colour. Benitoite has no cleavage, a hardness of 6 to 6.5 and is transparent to translucent. This combination of characteristics makes it a good gemstone. It fluoresces pale blue under ultra-violet light.

### Rings with Four- $\text{SiO}_4$ Tetrahedra

#### Axinite

$(\text{Ca}, \text{Fe}^{2+}, \text{Mn})_3\text{Al}_2(\text{BO}_3)(\text{Si}_4\text{O}_{12})(\text{OH})$ . Here, four  $\text{SiO}_4$  tetrahedra link to form an 8-membered  $\text{Si}_4\text{O}_{12}$  ring. Separate rings and adjacent hydrated  $\text{BO}_3$  groups are bound together by means of iron, aluminium, magnesium, manganese and calcium ions. Solid solution series exist with the iron- magnesium- and manganese-rich end members ferro-axinite, magnesio-axinite and manganaxinite respectively. Tinzenite is an intermediate mineral containing manganese and iron. These differences in chemistry are reflected in colour and specific gravity variation. Axinite most commonly occurs in thermally metamorphosed limestones with metasomatic introduction of boron.

### Rings with Six- $\text{SiO}_4$ Tetrahedra

#### Beryl

This is a beryllium aluminium silicate with the chemical formula  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ . Six  $\text{SiO}_4$  tetrahedra link to form a 12-membered  $\text{Si}_6\text{O}_{18}$  ring. Aluminium and beryllium lie between adjacent rings such that the Al is surrounded by six oxygen atoms and the Be with four in such a way as to link adjacent rings both laterally and vertically in the crystal lattice (see Figure 12).

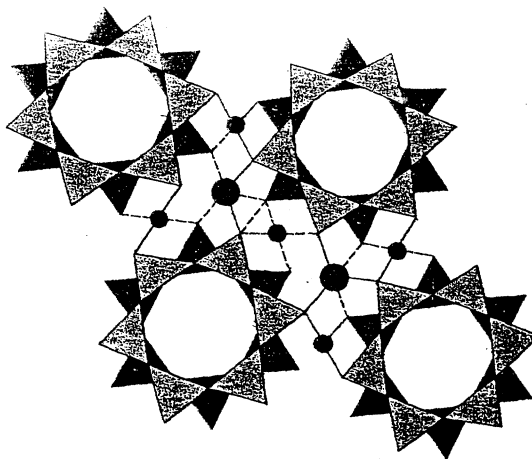


Figure 12. Beryl structure as projected on its pinacoid. (Milovsky & Kononov, 1985)

Four rings of six  $\text{SiO}_4$  tetrahedral units forming rings can be seen, while the large black circle represents the aluminium and the small black circles the beryllium atoms. The whole arrangement resembles a honeycomb structure and results in transparent to translucent hexagonal crystals.

Beryls have a conchoidal fracture, white streak, specific gravity 2.6-2.9 and a hardness of 7.5 to 8. The presence of a wide range of trace elements causes much variation in colour. This factor makes beryl a versatile gemstone, of which the following types are recognised :

<b>Aquamarine :</b>	<b>blue</b>
<b>Emerald :</b>	<b>green</b>
<b>Goshenite :</b>	<b>colourless</b>
<b>Heliodor :</b>	<b>yellow</b>
<b>Morganite :</b>	<b>pink</b>

Beryllium is not easily accommodated into the lattice of other silicates. Beryl and the variety aquamarine are igneous minerals which crystallise from residual magmatic fluids, usually forming in vugs (cavities lined with minerals which are different to those in the immediate surroundings; an old Cornish mining term), druses (cavities lined with minerals which are the same as those in the immediate surroundings) and granite pegmatites. Beryls are also found in metamorphic rocks such as schists and marbles. Emeralds are typically found in biotite schists.

### Cordierite

$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$  : A mineral characteristic of thermally metamorphosed pelites, cordierite is also known from high grade gneisses and even some granites. It survives well as a sedimentary clast. Hexagonal  $\text{Si}_6\text{O}_{18}$  rings are linked via aluminium and magnesium ions. Crystallising in the orthorhombic system, cordierite has a white streak, specific gravity of 2.3 and hardness of 7-7.5. Its vitreous lustre, transparency and single poor cleavage make it a gemstone candidate. Indeed, iolite, the gem variety, occurs in a range of blues and violet.

### The Tourmaline Group

(see Nicholson, 2004, for more details). In this case, a series of  $\text{Si}_6\text{O}_{18}$  rings are stacked on top of each other and interlayered with triplets of triangular  $\text{BO}_3$  units. A string of alternating sodium and hydroxyl ( $\text{OH}^-$ ) ions run up the centre of each stack, flanked by lithium, magnesium and aluminium ions. Iron and manganese ions are located down the outer margins of the stack (see Figure 13). This arrangement gives rise to the rather bewildering formula  $\text{Na}(\text{Mg,Fe,Mn,Li,Al})_3\text{Al}_6[\text{Si}_6\text{O}_{18}](\text{BO}_3)_3(\text{OH,F})_4$ .

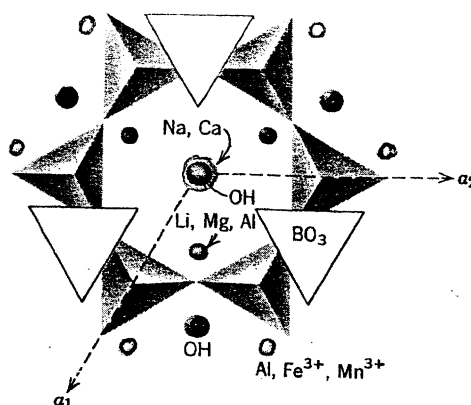


Figure 13. Part of the structure of tourmaline projected onto to (0001)  
(Keine and Hurlburt, 1993)

Tourmalines are piezoelectric. This means that when a crystal is heated or compressed, different electrical charges form at opposite ends of the crystal. Most examples are hemimorphic, which means that in doubly terminated crystals, the top of the crystal has a different shape from the base. Tourmalines are typical of skarn deposits, usually formed when late stage residual magmatic fluids react with adjacent limestone country rocks. They are also found in granite pegmatites. In luxullianite, a striking rock from Cornwall, granite minerals such as biotite and feldspars have been completely or partially replaced by pneumatolytic tourmaline. The salient features of some tourmaline minerals are given in Table 9.

Mineral	Chemistry	Colour	Diaphaneity	Comments
<i>Elbaite</i>	Li, Al	Various	Transparent	Hemimorphic. Named by colour, e.g. <i>Indicolite</i> (blue), <i>Rubellite</i> (red), <i>Verdelite</i> (green)
<i>Schorl</i>	Na, Fe, Al	Black	Opaque	Hemimorphic – top of crystal different shape to bottom
<i>Dravite</i>	Fe, Mg, Al	Brown	Translucent to opaque	Hemimorphic
<i>Uvite</i>	Ca, Mg, Fe	Green to black	Transparent to translucent	Hemimorphic

Table 9. Features of minerals belonging to the tourmaline group.

## 5. PHYLLOSILICATES

These are the "sheet" silicates. You can imagine how a sheet is formed if you visualise several of the double chain structures of the amphiboles laid down adjacent to each other, and then being joined by the sharing of oxygen atoms. In this way, rings of tetrahedra become linked together in a single plane which, when viewed from above, has a tessellated pattern. This means that one of the oxygen atoms in each tetrahedron is free and pointing away from the sheet, while the other three oxygens are shared with adjacent tetrahedra. This reduces the Si:O ratio down to 1:2.5. Adjacent sheets are then bonded to each other by layers of cations together with other ions, elements and molecules which are associated with them. Since relatively weak ionic chemical bonds are used here, the sheets are prone to separation from each other. This often makes the final mineral fairly soft (generally hardness 1 to 3) and gives it a platy appearance with perfect basal cleavage. In spite of this, phyllosilicates are very resilient, and are resistant to chemical weathering and metamorphic changes. This makes them common in igneous, metamorphic and sedimentary environments. Phyllosilicates show enormous diversity and include the commonest silicate minerals, the clay minerals, as well as the micas and serpentine group minerals.

### Micas

The micas consist of sheets of tetrahedra which are joined together in six-sided rings. This gives repeated units of  $(\text{Si,Al})_2\text{O}_5$ . All of the free, unshared oxygen atoms project from the surface of the sheet in the same direction. The immediately adjacent sheet has its unshared oxygen atoms projecting from the opposite surface. As one sheet is laid on top of another, six different superimposition patterns are possible by rotational transformations in  $60^\circ$  increments. As further sheets are added, each again with different possible orientations, a unit cell is constructed with one, two, three or more composite layers. Cells consisting of two layers commonly crystallise in the monoclinic system, while three-layered unit cells result in trigonal crystals. The layers of cations and associated neutral atoms and molecules intervening between the sheets generally contain a wide diversity of ions including  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$  and  $\text{OH}^-$  amongst many others. Each sheet of tetrahedra has a net negative charge which is balanced by the intervening cation layers.

The general formula of micas can be written as  $\text{X}_2\text{Y}_{4-6}\text{Z}_8\text{O}_{20}(\text{OH,F})_4$  where :

X is mainly K, Na or Ca, but could also be Ba, Rb, Cs, etc.

Y is mainly Al, Mg or Fe, but could also be Mn, Cr, Ti, Li, etc.

Z is mainly Si or Al, but could potentially be  $\text{Fe}^{3+}$  or Ti.

If the number of Y ions is 4, then the mica belongs to the di-octahedral class, whereas if Y is 6, the mica is tri-octahedral. The compositions of the most common micas can be summarised as follows (Table 10).

Di-octahedral Mica	X	Y	Z	Colour
Muscovite	$\text{K}_2$	$\text{Al}_4$	$\text{Si}_6\text{Al}_2$	White
Paragonite	$\text{K}_2$	$\text{Al}_4$	$\text{Si}_6\text{Al}_2$	White
Glauconite	$(\text{K, Na})_{1-2}$	$(\text{Fe}^{2+}, \text{Mg, Al})_4$	$\text{Si}_{7-7.6}\text{Al}_{1-0.4}$	Green
Tri-octahedral Mica	X	Y	Z	Colour
Phlogopite	$\text{K}_2$	$(\text{Mg, Fe}^{2+})_6$	$\text{Si}_6\text{Al}_2$	Brown
Biotite	$\text{K}_2$	$(\text{Mg, Fe}^{2+}, \text{Al})_6$	$\text{Si}_{6-8}\text{Al}_{2-3}$	Black
Zinnwaldite	$\text{K}_2$	$(\text{Li, Fe}^{2+}, \text{Al})_6$	$\text{Si}_{6-7}\text{Al}_{2-1}$	Brown
Lepidolite	$\text{K}_2$	$(\text{Li, Al})_6$	$\text{Si}_{6-5}\text{Al}_{2-3}$	Pink

Table 10. Compositions of the more common micas.

Around 40 mica species have been recognised. Muscovite, named from Moscow, the type locality, is usually white in colour, but chromium impurities make it a distinctive green, forming fuchsite. Muscovite is a late stage mineral in magmatic crystallisation, meaning that it is most commonly found in acid igneous rocks such as granites and pegmatites. It is also a common constituent of metamorphic rocks such as schists and gneisses, where it is often responsible for the foliated metamorphic fabric. Like all micas it survives weathering, erosion, transportation and deposition very well. Being platy, micas tend to behave hydrodynamically as much smaller grains than they actually are. They are often the last clasts to settle out of the water column, forming a fine dusting over the top surface of the bed. Their perfect basal cleavages, all aligned together in one plane, mean that the rock will break cleanly along a flat bedding surface. This is why micaceous sandstones make good flagstones.

Biotite can be difficult to distinguish from phlogopite since both are dark brown to black in colour. They are end members of a solid solution series, with biotite being the more Fe-rich. Consequently, biotite is found in acid and intermediate igneous rocks and regional metamorphosed rocks. Phlogopite, on the other hand, is less common, being found in ultramafic igneous rocks such as peridotites and kimberlites, and metamorphosed Mg-rich (dolomitic) limestones.

Glauconite is more or less confined to marine sediments, where it may be a primary mineral, especially of greensands, or diagenetic (related to post-depositional changes) in origin. Glauconite is sometimes classified with the clay minerals.

Lepidolite is the most common Li-bearing mineral, containing between 3.3% and 7%  $\text{Li}_2\text{O}$  in the crystal lattice. It is largely confined to granite pegmatites where it is usually found in association with other Li-rich minerals (e.g. amblygonite, spodumene and zinnwaldite).

Table 10 shows that  $\text{K}^+$  is the most common inter-layer cation. It may, however be replaced to some extent by  $\text{Na}^+$ , giving rise to paragonite, or by  $\text{Ca}^{2+}$  (accompanied by an increase in Al) forming margarite, xanthophyllite or clintonite. The cleavage sheets of these minerals are less elastic than those of regular micas such as muscovite and biotite, often resulting in their being called "brittle micas". All three are generally found in metamorphic rocks such as schists, or metasomatically altered limestones.

Stilpnomelane is a low grade metamorphic mineral which is relatively rich in Fe and Mn. Pyrophyllite consists of two sheets of linked tetrahedra enclosing a central sheet of octahedrally co-ordinated Al. Not all of the available sites are occupied by Al, however – some are empty. This makes the layers electrically neutral so no further cations are needed to restore balance, giving a formula of  $\text{Al}_4(\text{Si}_8\text{O}_{20})(\text{OH})_4$ . Talc is structurally very close to this arrangement, except that Al is replaced by Mg, giving  $\text{Mg}_6(\text{Si}_8\text{O}_{20})(\text{OH})_4$ . This is a low grade metamorphic mineral which is usually white in colour, with dull to pearly lustre, a hardness of 1 and a greasy feel. It commonly pseudomorphs other minerals and is the main constituent of soapstone or steatite, being exploited both as an ornamental stone because of the ease with which it can be carved, and for a wide range of industrial and domestic uses (e.g. talcum powder, filler, thermal and electrical insulator etc.).

Chlorite - general formula  $(\text{Mg},\text{Al},\text{Fe})_{12}[(\text{Si},\text{Al})_8\text{O}_{20}](\text{OH})_{16}$  - variously classified with the micas or clay minerals, actually refers to a group of minerals which can be difficult to isolate and distinguish from each other. They are common in low grade regional metamorphic rocks, such as the Dalradian chlorite schists, greenschists, as hydrothermal alteration products of igneous rocks, or associated with clay minerals in sediments. They are often white or green in colour, but the hue varies with composition. Kämmererite, for example, varies from brilliant lavender to deep crimson depending on the Cr content. Chlorite sometimes forms inclusions in quartz crystals. If the chlorite grows as a coating on the crystal surface and then the quartz undergoes a second period of growth, enclosing the film of chlorite, a phantom crystal is formed – one in which an earlier "ghost" crystal outline can be seen. Chamosite, a brown, Fe/Mg-rich mineral is also part of the chlorite group.

## Serpentines

The serpentine group minerals consist of a stack of silicate sheets with intervening layers of  $\text{Mg}(\text{OH})_2$  units. These latter units consist of two sheets of octahedrally co-ordinated hydroxyls, sandwiching a central layer of Mg. The  $\text{Mg}(\text{OH})_2$  has no overall charge. It is an arrangement found in the naturally occurring hydroxide mineral called brucite, a fairly common alteration product of periclase. For this reason, the intervening layers of  $\text{Mg}(\text{OH})_2$  units are usually referred to as brucite layers. The Mg can be replaced to some extent by Fe, giving rise to a suite of minerals, most of which are distinguished by their optical properties. The best known serpentine mineral is chrysotile, which is commonly found in veins crystallising with a silky, fibrous habit.



Chrysotile is an asbestiform mineral. Like most of the serpentines, it shows polymorphism, with some varieties crystallising in the monoclinic system (clinochrysotile) while others are orthorhombic (orthochrysotile). Lizardite, on the other hand, is hexagonal. The Fe-rich serpentine minerals include antigorite, with its orthorhombic polymorph, parachrysotile.

The serpentines most commonly occur as the alteration products of ultrabasic igneous rocks such as dunites and peridotites. The minerals are commonly green, but range through yellow and brown to black. They have a white streak, hardness 3 to 4.5, specific gravity of 2.2 to 2.6, and, depending on the form, silky or waxy lustre.

### Clay minerals

Clays are sedimentary grains of particle size  $<0.002\text{mm}$ . Many of these particles may be clay minerals which are best summarised as hydrous layer aluminosilicates. They are called aluminosilicates because Al commonly substitutes for Si in the tetrahedral structure, and hydrous because OH groups are important interlayering components. Structurally, clay minerals are made up of sheets of tetrahedra and sheets of octahedra linked together to form a layer. The tetrahedra are linked together to form a hexagonal pattern with the vertiginal oxygen directed to the centre of the layer. The octahedral sheet consists of two planes of close-packed oxygen ions with cations such as  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Mg}^{2+}$  occupying the enclosed octahedral co-ordination site.

Clay mineral classification depends on the types of layer involved. A combination of one tetrahedral and one octahedral sheet is known as a 1:1 layer. If an octahedral sheet is sandwiched between two tetrahedral sheets, a 2:1 layer is produced. Further diversity is introduced by differences in the ways in which the sheets are stacked on top of each other, and the nature of the interlayering components. If replacement takes place between ions of a particular charge with those of a different charge anywhere in the layer (e.g. trivalent Al for tetravalent Si, or divalent Mg for trivalent Fe) electrostatic neutrality is lost and the sheet becomes charged. The role of the interlayered chemicals is to balance the charges on the sheets. Interlayered components include cations such as  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{NH}_4^+$ , hydrated cations (usually  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , or  $\text{Na}^+$ ), or single sheets of hydroxide octahedral groups. One of the simplest of these latter components is brucite,  $\text{Mg}(\text{OH})_2$ , as mentioned above, but  $\text{Al}(\text{OH})_3$  (gibbsite) may also be involved. X-ray diffraction analysis is an essential tool in clay mineral identification. Most clay minerals are white to grey in colour, sometimes with other tints. They have a dull lustre, a hardness of 1 to 2 and a specific gravity of between 2 and 3.

Kaolinite, named from Kao-Ling in Jianxi Province, China, has the formula  $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$ . It is the most common of the kaolinite group of clay minerals and is generally formed by the weathering or hydrothermal alteration of feldspars, feldspathoids and certain other silicate minerals. Slightly carbonated waters cause the degradation of, say, orthoclase feldspar as follows: water + carbon dioxide + orthoclase gives rise to kaolinite + silicic acid + potassium carbonate. The massive China Clay deposits of the St Austell region of west Cornwall are believed to have been produced as the result of deep-seated hydrothermal alteration of granite. Kaolinite is an important mineral in the manufacture of porcelain and fine bone china because it retains its white colour on firing. It is also used extensively as a filler and to increase the gloss on paper. Closely related minerals in this group include dickite, nacrite and halloysite.

The smectites are 2:1 layered clay minerals with very low charges on the composite sheets, leading to extensive use of hydrated cations in the interlayers. This gives the minerals the ability to expand and contract as water and some organic molecules are gained or lost from the crystal lattice respectively; they are sometimes referred to as 'exploding' clays. One application of this property is in medicine as a treatment for diarrhoea. Montmorillonite, with the complex formula  $(\text{Ca},\text{Na})_{0.3}(\text{Al},\text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2.n\text{H}_2\text{O}$  is one such mineral, a major constituent of bentonites (the weathering product of volcanic ash), which are important components of the slurry used to cool the drill bit in the oil industry. Other minerals in this group include saponite, beidellite, hectorite and sauconite.

Clay minerals of the illite group show 2:1 layers with non-hydrated cations in the interstices. As a consequence, they have a chemical formula which is closely similar to many of the micas; indeed, they are sometimes referred to as clay-grade muscovite solely on the basis of grain size. Phengite also occurs in this group.

Vermiculite gives its name to a group of clay minerals which are closely related to the smectites. They have 2:1 layering with intervening brucite sheets. Their name, from the Latin for 'to breed worms', refers to their strange ability to exfoliate when rapidly heated. At temperatures above  $870^\circ\text{C}$ , water in the crystal lattice vaporises, causing expansion of the mineral and separation along the cleavage planes; increases in volume of up to 3000% are possible. This gives rise to a very lightweight material with excellent thermal and acoustic insulation.

properties. It is also used to clean up spills of toxic chemicals. Vermiculite is a weathering and hydrothermal alteration product of biotite and other micas.

Sepiolite and palygorskite (sometimes known as attapulgite) are non-swelling clays with a fibrous structure. Prehnite, an index mineral for the prehnite-pumpellyite facies of low grade regional metamorphism, is also known in igneous rocks. It has the chemical formula  $\text{Ca}_2\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ .

Chrysocolla,  $(\text{Cu},\text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4.n\text{H}_2\text{O}$ , a weathering product of copper ore bodies, has a distinctive blue colouration and white to blue-green streak. Amorphous (non-crystalline) in structure, there is some evidence that, at high temperatures, it is composed of  $\text{Si}_4\text{O}_{10}$  sheets.

## 6. TECTOSILICATES

The tectosilicates or framework silicates are characteristically made up of  $\text{SiO}_4^{4-}$  tetrahedra which share each of their oxygen atoms with an adjacent tetrahedral unit. This results in a 3-dimensional framework of interlinked units. In its purest form, this gives rise to an Si:O ratio of 1:2, expressed as the mineral quartz and other forms of silica.  $\text{Al}^{3+}$  is easily substituted for the  $\text{Si}^{4+}$ , however, giving an  $\text{AlO}_4^{5-}$  tetrahedron. The tetrahedral unit now has a charge of 5-, rather than 4- as was the case with the nesosilicates. A range of cations is needed to maintain electrochemical stability, thus giving rise to a diverse group of minerals.

### The Feldspars

The feldspars are the most abundant minerals in the Earth's crust. Common to all igneous rocks except for some ultrabasic and rare alkaline rocks, they are an important tool in igneous rock classification. They are also known from a wide range of metamorphic rocks and, although easily weathered to clay minerals, survive rapid erosion and deposition to become clastic components of mostly arenaceous sedimentary rocks such as arkosic sandstones (e.g. Torridonian sandstone). They may also grow within sediments as new, relatively low temperature diagenetic minerals.

Essentially, the feldspar structure is based upon four interlinked tetrahedra, two of which have their apical O atoms pointing upward, and two are pointing downward. This gives a unit of composition  $\text{AlSi}_3\text{O}_8$ . These units are then linked to form a chain-like arrangement, the individual chains then being linked laterally to form a framework.

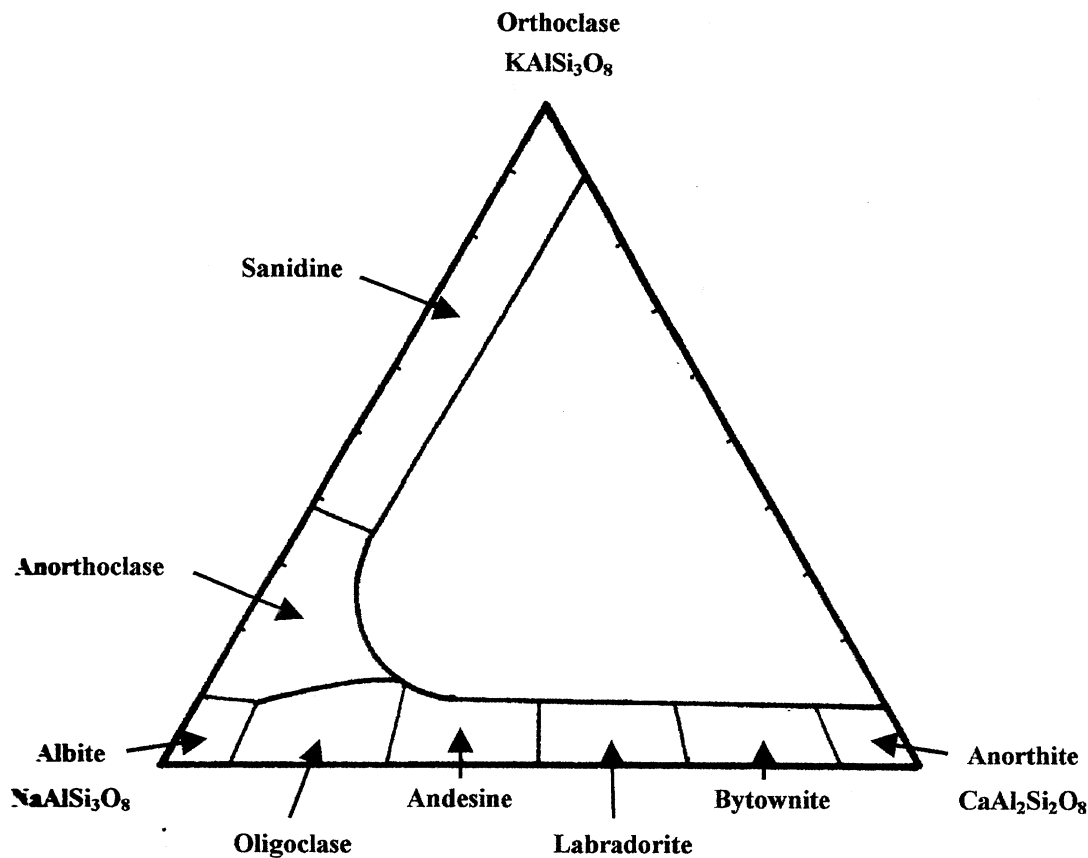


Figure 14. Solid solution in the feldspars. The base line represents variation in the plagioclase feldspars, while the line on the left represents the high temperature alkali feldspars.

The common substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  at the centres of the interlinked tetrahedra means that a range of ions is employed to bring overall electrochemical stability to the unit. One way of writing the general formula for feldspars

is  $\text{XAl}_{(1-2)}\text{Si}_{(3-2)}\text{O}_8$ . This shows that Al may comprise up to 50% of the tetrahedral sites. Since the difference in charge between Al and Si is  $1^+$ , this must be reflected by variation in the accompanying cations (most commonly  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ), signified by X in the general formula. Thus, where two Al and two Si atoms are present,  $\text{Ca}^{2+}$  will be used to balance the unit, whereas either  $\text{Na}^+$  or  $\text{K}^+$  could be used if there were one Al and three Si atoms.

The easiest way to consider the feldspars is as members of two linked solid solution series, also known as a ternary system. As indicated above,  $\text{Na}^+$  or  $\text{K}^+$  can be freely substituted for each other. This gives a solid solution series with  $\text{NaAlSi}_3\text{O}_8$  and  $\text{KAlSi}_3\text{O}_8$  as end members. These are the alkali feldspars. Alternatively, there may be a range of substitutions between  $\text{NaAlSi}_3\text{O}_8$  and  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , giving rise to the plagioclase feldspars. The relationship between these three end-member compositions and their intermediates in the ternary system is illustrated in Figure 14.

### (i) The Plagioclase Feldspars

As can be seen in Figure 14, the plagioclase feldspars range in composition from  $\text{NaAlSi}_3\text{O}_8$  (Albite - Ab) to  $\text{CaAl}_2\text{Si}_2\text{O}_8$  (Anorthite - An) with a range of intermediates. The minerals in this series are usually described in terms of their An molecular percentage. The six constituent minerals are thus albite (0-10% An), oligoclase (10-30%), andesine (30-50%), labradorite (50-70%), bytownite (70-90%) and anorthite itself (90-100%). These gradational changes in composition also give rise to variation in physical properties. All crystallise in the triclinic system, but there are small changes in the angles between the cleavage planes (decreasing from  $86^\circ 24'$  in albite to  $85^\circ 50'$  in anorthite). Similarly, as calcium has a higher atomic mass than sodium (40 compared to 23), the specific gravity of the mineral gradually increases from 2.60 in pure albite to 2.77 in pure anorthite. This is accompanied by changes in the optical properties of the mineral, notably the refractive index. All plagioclase feldspars show a vitreous lustre which dulls with weathering.

Variations in chemistry also affect the melting temperatures of the plagioclase feldspars; anorthite melts at around  $1550^\circ\text{C}$  while albite melts at around  $1100^\circ\text{C}$ . Anorthite, a Ca-rich, high temperature feldspar forms early in the crystallisation history of a magma and is more typical of basic igneous rocks such as basalts and gabbros. The lower temperature, Na-rich albite is a later-stage crystal more typical of acid igneous rocks such as granites and rhyolites. Extraction of calcium by crystallisation of An-rich feldspars enriches the remaining melt in sodium, leading to the formation of progressively more Ab-rich feldspars. If there is insufficient time for the early formed crystals to react with the melt, zoned plagioclase crystals may be formed. These have An-rich cores surrounded by concentric layers, often picked out by tiny inclusions, of progressively more Ab-rich composition. Zoned crystals of this type are quite common in granitic plutons, such as the Dartmoor Granite. Feldspars closer to the centre of the An-Ab compositional range, such as andesine, are typical of intermediate igneous rocks such as andesite and trachyte.

Twinning is common in the feldspars. The plagioclase series all show a type of twinning which is named after albite. Twin laws define the sum of the various components of twinning, notably the amount of rotation needed to bring the two parts of the twinned crystal together and the position of the twin axis in relation to the twin plane. Twinning on the Albite Law typically results in thin (usually much less than 1mm) parallel sheets of the mineral being stacked on top of each other. The mineral sheets or lamellae are all of the same composition, and contact each other along the 010 direction (a side pinacoid). This is an example of repeated, lamellar or polysynthetic twinning. The twinned layers can sometimes be discerned as parallel lines on the surfaces of the mineral faces, as well as the cleavage surfaces.

Plagioclase feldspar crystals are usually white to grey in colour, but often are tinged with blue, red, yellow or green. The hardness ranges from 6 to 6.5 and the fracture is uneven.

Labradorite shows a distinctive iridescence or schiller often referred to as labradorescence. This consists of a play of colours, especially obvious on cut surfaces, as light is diffracted across the cleavage and twin planes within the crystal. The colours involved are violets, blues, greens, gold, yellows, orange and occasionally reds. Spectrolite is the trade name given to a variety of labradorite with a particularly vibrant play of colours. It was discovered in Finland in 1940 during the building of a defence line in World War II. Labradorite itself was first discovered in 1770 by a Moravian missionary on the Isle of Paul, Labrador (part of Newfoundland). It is particularly common in largely monomineralic stratiform masses called anorthosites.

Oligoclase may be sold as a semi-precious stone. Sunstone, also known as aventurine-feldspar, is so-called because inclusions of haematite or sometimes goethite produce flashes of red within the crystal. Varieties of moonstone may also be oligoclase (although it is more commonly a mixture of albite and orthoclase) and is sometimes distinguished as having a property known as adularescence. This closely resembles labradorescence, although purists argue that the play of light moves over the body of the transparent stone in adularescence as a floating, milky sheen, while labradorescence is a surface sheen confined to opaque minerals.

Some feldspars are triboluminescent; on striking one specimen against another, a flash of light is produced. This process is not fully understood, but may be due to the storage of electrons, which have been ejected by the penetrating gamma radiation of  $^{40}\text{K}$  decay, in lattice defects. A small mechanical shock is then sufficient for these electrons to overcome their energy barrier and cascade down to their ground state. Alternatively, asymmetrical crystals may undergo separation of negative and positive charges on fracturing. Charge recombination results in a flash of light as the discharge ionises the surrounding air. The effect was first recorded by Francis Bacon (1605) who noticed that a glow was produced when he chopped up blocks of cane sugar at night.

## (ii) The Alkali Feldspars

Orthoclase is the most common of the alkali feldspars with the chemical formula  $\text{KAlSi}_3\text{O}_8$ . A relatively late-stage mineral in the magmatic crystallisation sequence, it is an essential mineral in acid and intermediate igneous rocks such as granites, granodiorites, syenites and their fine-grained equivalents. It is also common in metamorphic rocks such as gneisses and, like plagioclase feldspar, may be abundant in feldspathic sandstones such as arkoses. Orthoclase and other alkali feldspars can be quite difficult to distinguish from the plagioclases in hand specimens, having a similar hardness (6), colour (white through shades of red and orange to brown), streak (white), diaphaneity (opaque), lustre (vitreous, becoming dull on weathering), specific gravity (around 2.5), habit (commonly tabular crystals), and fracture (conchoidal to uneven). Orthoclase crystallises in the monoclinic system, however, and lacks the striations produced by polysynthetic twinning in plagioclase. Twinning in orthoclase is simple and conforms to the Carlsbad, Manebach and Baveno Laws.

Adularia is a low temperature, orthorhombic form of orthoclase described from the Adula Mountains of Kanton Tessin, Switzerland. A specific variant of this mineral is valencianite, known only from the Valencia Mine in Mexico. Moonstone (a name also given to some varieties of albite, see above) is a semi-precious variety of adularia with a distinctive play of light over the surface (adularescence). Often white to grey in colour, blue varieties, such as those from Sri Lanka are very popular. Murchisonite, a red variety of orthoclase with a distinctive yellowish-golden lustre, was named after the famous Victorian geologist, Sir Roderick Impey Murchison, and originally discovered in Triassic conglomerates near Exeter.

Microcline is a low-temperature triclinic polymorph of orthoclase found in acid igneous rocks such as granites and pegmatites. Varying in colour from greyish white through pink to light red, there is also a highly distinctive deep green variety called amazonite. Microcline very commonly shows repeated twinning on the albite and pericline laws. Sometimes both types of twinning may be present at almost  $90^\circ$  to each other, giving rise to a distinctive cross-matching or "tartan" pattern.

Perthite is a name given to intergrowths of potassium feldspar (orthoclase or microcline) with subsidiary Na-rich plagioclase (usually albite). Colours vary from almost colourless through white, pink, light-brown to a green which is almost as intense as that of amazonite. The name is often modified by the addition of a prefix describing the ease with which the mineral layers can be discerned: in macroperthites they can be seen with the naked eye, in microperthites microscopic examination is required, whilst in cryptoperthites the association can only be inferred from x-ray diffraction studies. If albite is the predominating mineral phase, then the specimen is referred to as an antiperthite.

Sanidine is the high temperature polymorph of orthoclase and is stable above around  $900^\circ\text{C}$  (orthoclase is stable from around  $500^\circ\text{C}$  to  $900^\circ\text{C}$ , while microcline is the stable form below about  $500^\circ\text{C}$ ). The differences between the three polymorphs relate to the degree of randomness in the distribution of Al and Si atoms. With decreasing temperature, the arrangement of these atoms becomes increasingly ordered, leading in turn to the development of lower order crystal symmetry (monoclinic symmetry at high temperatures and triclinic at low temperatures).

Anorthoclase is intermediate in composition between the high temperature end members of a  $\text{NaAlSi}_3\text{O}_8$ - $\text{KAlSi}_3\text{O}_8$  (Albite - Sanidine) solid solution series. It generally contains between 10% and 36% Na and is found, often as phenocrysts, in high temperature Na-rich volcanic rocks.

Larvikite is a rock mainly composed of anorthoclase and exhibits a blue schiller. It is named from the Norwegian town of Larvik on the Skagerrak, about 100km south of Oslo. This rock is well known as a facing stone on British banks and other commercial premises and is often sold under the names Emerald Pearl and Blue Pearl, referring to its darker and lighter forms.

More unusual and uncommon feldspars are sometimes produced by the replacement of K, Na or Ca by other elements. For example, celsian (named after Anders Celsius, 1701-1744, the Swede who developed the Celsius temperature scale) is a barium-rich feldspar ( $\text{BaAl}_2\text{Si}_2\text{O}_8$ ) found in metamorphic aureoles around igneous intrusions, while hyalophane is intermediate in composition between celsian and orthoclase. Rubicline ( $(\text{Rb},\text{K})\text{AlSi}_3\text{O}_8$ ) is a rubidium-rich variety of microcline. Buddingtonite consists of plagioclase feldspar which has been altered by contact with ammonia-rich waters. Kokchetavite is a very high pressure hexagonal polymorph of orthoclase found as microscopic inclusions in garnets and pyroxenes in high grade regional metamorphic rocks in Kazakhstan.

## The Feldspathoids

The feldspathoids are silica-poor in comparison to the feldspars, and are typical of undersaturated igneous rocks - those crystallising from magmas which are rich in alkalis but relatively poor in silica, such that free quartz does not occur (e.g. alkali basalts, phonolites, syenites). The Al component of the mineral is correspondingly high; the Al:Si ratio is commonly up to 1:1 in feldspathoids, whereas it is more usually 1:3 in feldspars.  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra are linked together in rings which are then connected vertically to form a three-dimensional framework. The central cavities of the rings are occupied by a range of monovalent ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ) or divalent ( $\text{Ca}^{2+}$ ) cations, and occasionally anions ( $\text{Cl}^-$ ,  $\text{S}^{2-}$ ,  $\text{SO}_4^{2-}$ ). Alignment of the cavities through the structure gives a much more open framework than is the case with the feldspars, and leads to a lower specific gravity (generally in the range 2.2 to 2.6, as opposed to 2.5 to 2.7 in most feldspars). Feldspathoids are subdivided into three groups, based upon the structure of the rings of tetrahedra and their subsequent interlinking.

### (i) The Nepheline Group

Minerals in this group are characterised by rings made up of six linked tetrahedra, three of which point upwards and three downwards. The interconnected central cavities form channels which run parallel to the c-axis of the crystal. The presence of cations within the cavities distorts the framework, however, much as happens when the high temperature polymorph of tridymite (see below) collapses on cooling. These distortions mean that  $\text{Na}^+$  occupies the larger channels and  $\text{K}^+$  the smaller channels within the structure. A pure  $\text{NaAlSiO}_4$  nepheline can be manufactured artificially and is useful in the ceramic and glass industries. Naturally occurring nephelines have a formula close to  $(\text{Na},\text{K})\text{AlSiO}_4$  and are usually whitish grey to brown with occasional tints of other colours. Nepheline crystallises in the hexagonal system and is slightly softer than the feldspars (hardness 5.5-6, as opposed to 6), although it has a similar white streak and conchoidal fracture. Further points of difference to the feldspars are the possession of poor cleavage, and often a distinctive greasy lustre. Eleolite, from the Greek for oil, is sometimes used to describe massive dark accumulations with a prominent greasy lustre, usually associated with syenites.

### (ii) The Sodalite Group

Minerals in this group have, in addition to hexagonal rings of six interlinked tetrahedra, square four-membered rings. Minerals of the sodalite group have the formula  $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$ , with sodalite, named from its high sodium content, being the most common representative. The channels within the crystal lattice intersect to form very large cavities, accommodating a wider range of ions and reducing the specific gravity to around 2.2. Sodalite itself is commonly dark blue in colour and is often carved as a semi-precious stone. The variety of sodalite called hackmanite fluoresces orange in LW ultraviolet light. The mineral itself also changes to a raspberry colour when exposed to SW UV, a phenomenon known as tenebrescence.

Other closely related minerals in this group include the Na- and Ca-containing hauyne, nosean (which generally lacks Ca) and lazurite. The latter mineral  $(\text{Na},\text{Ca})_8\text{Si}_6\text{Al}_6\text{O}_{24}[(\text{SO}_4),\text{S},\text{Cl},(\text{OH})_2]$ , an important component of the rock known as Lapis Lazuli, has a long pedigree (over 6000 years) as a semi-precious stone used in jewellery. Brilliant blue in colour with splashes of violet and green, it has a dull to greasy lustre, bright blue streak and crystallises in the

cubic system. It is commonly associated with pyrite and calcite crystals in contact metamorphic aureoles around granitic intrusions.

Rather more unusual minerals in this group include the recently discovered (1993) tsaregorodtsevite from the Urals, the Be-containing tugtupite from Greenland, and the Ca-rich bicchulite and kamaishilite, both described from Japan. Cancrinite  $[(Ca,Na)_6(CO_3)_{1-1.7}][Na_2(H_2O)_2](Si_6Al_6O_{24})$  effervesces with hydrochloric acid as a consequence of the carbonate within its lattice; it is found in plutonic igneous intrusions (e.g. nepheline syenites).

## The Zeolites

Axel Frederick Cronstedt (1722-1765), a Swedish mineralogist who famously discovered the chemical element nickel in the mineral niccolite, found in 1756 that, on heating, the mineral stilbite lost water. He used the term 'zeolite', from the Greek for 'boiling stone', to describe this feature.

By contrast to the feldspars, which are made up of interlinked  $SiO_4^{4-}$  and  $AlO_4^{5-}$  tetrahedra arranged in four-fold rings, the zeolites are based upon a wide variety of linked rings of tetrahedra. The rings may contain 4, 6, 8 or 12 tetrahedra, often arranged in various combinations. Analcime contains 4- and 6-fold rings of tetrahedra, for example, while chabazite contains 4-, 6- and 8-fold rings, and gmelinite contains 4-, 6-, 8- and 12-fold rings. These arrangements result in a much more open lattice framework than is true for either the feldspars or the feldspathoids. Stacked 8- and 12-fold rings in the crystal lattice gives rise to open channels and cages of different diameters within the structure. These voids form sites occupied by large balancing cations such as  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$  and  $Ba^{2+}$ , as well as permitting the accommodation of larger groups such as water, or the ions:  $NH_4^+$ ,  $CO_3^{2-}$  and  $NO_3^-$ .

The presence of remarkably uniform channel systems within the crystal lattice gives rise to a number of striking and commercially exploited properties in this mineral group. Water can enter and leave the system repeatedly without changing the volume of the crystal lattice. This contrasts with the situation in certain clay minerals. This is also true of resident ions held within the channels; free movement through, into and out of the lattice is permitted, depending on the electrostatic fields within the channels and interactions with other channel molecules (i.e. pore diameter is not the only constraint on ion mobility). This leads to wide-ranging powers of adsorption and the possibility of exchange of ions between the mineral and surrounding fluids. Furthermore, occupancy of the channels by molecules with specific size ranges opens up the prospect of zeolites being used as highly selective catalysts. These properties have much potential in terms of commercial application and have led to the development of over 150 synthetic zeolites since the first was designed and produced in 1948. As a consequence, natural and synthetic zeolites have been exploited for a wide range of uses including mineral detergents, refrigerants, means of treatment of radioactive wastes, municipal water treatments, water softeners, chemical sieves, catalysts and as pet litters (high water adsorption and odour control).

The zeolites can be divided into a number of groups based upon structure. Minerals in the natrolite group have a chain-like arrangement of four-fold rings of tetrahedra in  $Al_2Si_3O_{10}$  units resulting in the formation of acicular prismatic crystals. Natrolite itself ( $Na_2Al_2Si_3O_{10} \cdot 2H_2O$ ) is Na-rich, while the Na is replaced by Ca in scolecite. Mesolite is virtually intermediate in composition between the two. Natrolite is orthorhombic while scolecite and mesolite are both monoclinic, although all three are colourless to white minerals with a white streak, vitreous lustre, conchoidal fracture and two cleavages. Hardness ranges from 5 to 5.5 (softer than feldspars and feldspathoids), and the specific gravity, as in most zeolites, is reduced to around 2.2 due to the open, somewhat cavernous framework of the crystal lattice. Closely related minerals include thomsonite, gonnardite and the Ba-containing edingtonite.

Chabazite group minerals contain six-fold rings of tetrahedra stacked in pairs which are then arranged in a spiral staircase-like fashion. Crystallising in the trigonal system, chabazite is commonly clear or white in colour, but may be pink, yellow, orange, reddish or even brown. Usually rich in calcium - chabazite-Ca:

$Ca_2(Al_4S_8O_{24}) \cdot 13H_2O$  is known to have Na-, K- and even Sr-rich varieties. Closely related minerals include the Ca-rich willhendersonite, gmelinite, levyne and erionite.

Harmotome,  $Ba_2(Na,K,Ca_{0.5})(Al_5Si_{11}O_{32}) \cdot 12H_2O$ , and related minerals (e.g. phillipsite, gismondine, garronite) are made up of a network of fourfold and eightfold rings of tetrahedra. Harmotome itself is Ba-rich, gismondine and garronite are both rich in Ca, while phillipsite comes in Ca-, Na- and K-rich varieties.

Hollandite-Na,  $(Na,Ca_{0.5},K)_9[Al_9Si_{27}O_{72}] \cdot 24H_2O$ , and its relatives (e.g. stilbite, epistilbite, ferrierite, brewsterite) are composed of sheets of tetrahedra joined together by widely spaced oxygen bridges. The internal channels are too

small to allow much ionic movement, reducing the microporosity of the mineral and making it relatively impermeable. One unusual occurrence of heulandite is as a replacement mineral for apatite in dinosaur bone.

In mordenite,  $(\text{Na}_2, \text{Ca}, \text{K}_2)_4(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \cdot 28\text{H}_2\text{O}$ , five-fold rings of tetrahedra form chains which are laterally interlinked in a number of ways. Larger channels within the structure are bounded by 12-fold rings of tetrahedra, while in the closely related dachiardite they are formed by 10-fold rings.

Zeolites are formed almost exclusively by the alteration of other minerals and rocks. They commonly form at temperatures which are less than  $250^\circ\text{C}$  in aqueous environments within a wide range of geological contexts. The original rock types are usually basic volcanics, such as basalts and tuffs and hyaloclastites, whose constituent minerals are rich both in Si and alkali cations like  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ . Percolating groundwater may react with volcanic glasses forming smectite clay minerals. Now charged with alkaline earth cations, the pore water percolates down to the water table where zeolite crystallisation takes place, either in cavities or replacing glassy material. Thus, zeolites are common occupants of vesicles, often growing inwards from the walls as spectacular crystals, or completely filling the cavity, forming amygdales. Parent rock type appears to have an influence on the species of zeolite formed; phonolitic and tephritic tuffs mostly alter to phillipsite, while rhyolitic rocks result in clinoptilolite, chabazite and mordenite, amongst others. It also appears that a coarse zeolite zonation takes place with increasing depth. Indeed, the "Rule of Cornu" (Cornu, 1908) suggests that zeolites appear in order of increasing degree of hydration with falling temperature of crystallisation.

Zeolites, especially analcime and heulandite, are also known as diagenetic minerals in sedimentary rocks. Bedded zeolite deposits containing clinoptilolite, chabazite, phillipsite and analcime are known from evaporate sequences in playa lakes contaminated by vitric ash from nearby vulcanicity. Phillipsite and clinoptilolite are also known from a wide range of deep sea sediments, probably due to the reaction of sea water with submarine volcanic debris. They are also known from very low grade metamorphism ("zeolite facies"), especially of igneous rocks, as alteration products along fractures and faults in igneous rocks, and as late-stage minerals in the crystallisation of pegmatite veins.

The features of the more important zeolite minerals are summarised below in Table 11.

Mineral	Crystal system	Colour	Streak	Lustre	Hardness	Specific gravity
Analcime	Cubic	White/grey/tinted	White	Vitreous	5-5.5	3.2
Chabazite	Trigonal	White/grey/tinted	White	Vitreous	4-5	2.0-2.2
Phillipsite	Monoclinic	White/yellow/red	White	Vitreous	4-4.5	2.2
Heulandite	Monoclinic	White/grey/various	White	Vitreous to pearly	3.5-4.0	2.1-2.3
Laumontite	Monoclinic	Colourless/white	White	Vitreous to dull	<4.0	2.2
Mordenite	Orthorhombic	Colourless/white	White	Vitreous/silky/pearly	4-5	2.1
Natrolite	Orthorhombic	Clear/white/tinted	White	Vitreous to dull	5-5.5	2.2
Stilbite	Monoclinic	Pink/white/tinted	White	Vitreous to pearly	3.5-4.0	2.2
Thomsonite	Orthorhombic	Clear/white/yellow	White	Vitreous	5-5.5	2.2-2.4

Table 11. Salient features of the more important zeolite minerals

Further information on zeolites can be obtained from Wilson, Dyer and Enamy (2003 and 2005) and details of recent changes to the nomenclature of zeolites can be found in the IMA Report (Coombs et al, 1998).

## Forms of Silica ( $\text{SiO}_2$ )

### (i) Crystalline silica

Quartz consists of  $\text{SiO}_4$  tetrahedra linked together such that each of the oxygen atoms is shared by an adjacent tetrahedron, giving an overall chemical formula of  $\text{SiO}_2$ . A three-dimensional framework is constructed consisting of a series of laterally contiguous helices. Each turn of the spiral takes up 4 linked tetrahedra. The helices may be coiled to the right or to the left, giving rise to the property of optical isomerism, as well as the possibility of right- and left-handed crystals. Adjacent helices are linked together in groups of three resulting in the trigonal shape of the quartz crystal. The helical arrangement precludes the development of cleavage planes, restricts the symmetry



ements to those of the trigonal system, and results in a strongly conchoidal fracture. Quartz is almost ubiquitous in terms of its occurrence. It is a late-stage crystallisation product of silica-saturated magmas and so is an essential mineral of acid igneous rock such as granites, microgranites and rhyolites. It may also occur in intermediate igneous rocks such as diorites. Pegmatites and mineral veins commonly contain quartz crystals. Extremely resistant to weathering, it persists as clasts in a wide range of sedimentary environments, and is a fairly common cementing mineral, especially in arenaceous rocks. It is also common in metamorphic rocks. In addition to the properties mentioned above, quartz crystals are transparent to translucent, have a vitreous lustre, white streak, a hardness of 7, a specific gravity of 2.66, and often have striations developed on the prism faces.

Quartz crystals show considerable variation in colour, leading to the recognition of a number of varieties, especially in the jewellery trade. Amethyst is a lilac to purple variety whose colour is due to small amounts of  $\text{Fe}^{3+}$  as an impurity. Yellow/orange citrine is also due to iron impurities. If amethyst is heated to  $550^\circ\text{C}$ , it is converted to citrine, but treatment with radiation will reverse the change. Heat-treated stones can be identified by their reddish hue and are sometimes presented as "Madeira" or "Golden" topaz, a mineral to which it has no relationship at all. Rose quartz has, as its name suggests, a distinctive hue, which may be produced by the presence of traces of titanium. The colour may fade on exposure to light, but is restored by moistening the crystal. Smoky quartz is an  $\text{Al}^{3+}$ -rich variety which has been exposed to radiation of some kind (natural or man induced); in some cases the crystals can become almost black, giving rise to the variant known as morion. If larger crystals of rutile are present within the quartz crystal ("Venus hairs"), the mineral is referred to as rutilated quartz. Aventurine quartz contains fine platy spangles of mica or sometimes haematite or chlorite, giving rise to a green colour. Milky quartz has a cloudy white appearance due to the presence of inclusions of numerous tiny gas bubbles. If the milky appearance is superficial, the crystal may be referred to as quartz "en chemise". The completely clear, transparent, colourless variety of quartz has long been known as rock crystal.

In addition to coloured varieties, quartz also exists in two polymorphic forms: alpha-quartz and beta-quartz. The former, also known as low-quartz, has trigonal symmetry and is stable at normal pressures and temperatures below  $573^\circ\text{C}$  – it is the normal, rock crystal type of quartz described above. Beta-quartz or high-quartz, however, has hexagonal symmetry and is stable between temperatures of  $573^\circ\text{C}$  and  $870^\circ\text{C}$ . The two minerals are interconvertible, accompanied by slight energy changes and twisting of the bonds between adjacent tetrahedra. Two further  $\text{SiO}_2$  polymorphs also have alpha- and beta- varieties. Beta-tridymite consists of a sheet-like, open network of  $\text{SiO}_4$  tetrahedra arranged in six-membered rings (giving rise to hexagonal symmetry), with their apical O atoms pointing alternately upward and downward. Beta-cristobalite has a similar structure to beta-tridymite, except that vertically adjacent sheets of six-membered rings of interlinked tetrahedra are offset from each other by rotation through  $60^\circ$ . Beta-quartz, tridymite and cristobalite are all found in high temperature volcanic rocks. A summary of the salient features of the polymorphs of  $\text{SiO}_2$  is given below (Table 12).

Mineral	Crystal system	Specific gravity
Alpha Quartz	Trigonal	2.65
Beta Quartz	Hexagonal	2.53
Alpha Tridymite	Monoclinic	2.26
Beta Tridymite	Hexagonal	2.22
Alpha Cristobalite	Tetragonal	2.32
Beta Cristobalite	Cubic	2.20
Coesite	Monoclinic	3.01
Stishovite	Tetragonal	4.28
Kesite (synthetic)	Tetragonal	2.50
Seifertite	Orthorhombic	unknown

Table 12. Diagnostic features of the polymorphs of  $\text{SiO}_2$

Coesite is a high pressure polymorph of  $\text{SiO}_2$  which was synthesised in 1953 by the transformation of quartz when subjected to pressures of  $2000 \text{ NM/m}^2$  and temperatures up to  $1700^\circ\text{C}$ . Shortly afterwards (Chao et al., 1960) the mineral was discovered in the sheared Coconino Sandstone of Meteor Crater, Arizona, together with another high pressure polymorph, stishovite (Chao et al., 1962). Coesite has since been identified in kimberlites. It consists of four-membered rings of interlinked tetrahedra bonded into tight chains. Stishovite is a particularly dense, high-temperature form of  $\text{SiO}_2$ .

Seifertite is a high density, high pressure polymorph of  $\text{SiO}_2$  which is shortly to be formally named by the IMA (International Mineral Association) as a valid mineral species. It was originally discovered by x-ray diffraction studies of dense quartz grains in the Martian Shergotty Meteorite of Bihar, India, and has since been identified in further meteorites of Martian origin.

Chatoyant quartzes are those in which light is reflected in fine vertical luminescent bands. For example, tiger's eye is a pseudomorph of quartz and decomposed crocidolite, yellow to brown in colour with a silky lustre. Falcon's eye is a name usually reserved for quartz pseudomorphs of unweathered crocidolite. The absence of weathering gives the stone a bluish to blue-black colour. In cat's eye, amphiboles are pseudomorphed by the quartz, resulting in a greenish-grey colour. Each of these minerals has the same physical properties as quartz itself.

## (ii) Cryptocrystalline silica

Cryptocrystalline materials consist of minute crystallites that can be seen neither with the naked eye, nor easily with the aid of a microscope. Chalcedony is the general name given to the fibrous varieties of cryptocrystalline quartz. Named after the ancient Greek town in Asia Minor, it has a white streak, hardness 6-7, specific gravity of 2.59-2.61, vitreous to greasy, silky or waxy lustre, and uneven, splintery or conchoidal fracture. The colour varies considerably; prase is green due to the presence of actinolite inclusions; chrysoprase, also green, contains Ni as a trace element, carnelian is red to reddish-brown, as is sard, possessing inclusions of haematite; bloodstone, plasma or heliotrope are dark green to greenish-blue in colour (usually due to inclusions of chlorite or amphiboles) with blood red spots (jasper).

Jasper itself is dense and opaque, and coloured red, yellow or brown by the presence of iron oxides. Although not valid as a mineral species, various types of jasper are recognised, largely according to colour, provenance or internal patterning. Creolite, for example, is a red and white banded form, while quetzalitzli is a translucent green coloured form (due to the presence of Cr-rich inclusions of muscovite) from Guatemala, and wilkite is a yellow, pink, purple and green form from Willow Creek in Idaho.

Agate is a generally banded type of chalcedony filling vesicles within basic lavas. The banding is due to concentric centripetal growth of mineral layers into the void from the cavity walls. Again, a wide range of popular, commercial and local names has been developed for different varieties of agate. Onyx consists of alternating black and white bands, whilst in sardonyx the bands are brown and white. Fire agate is iridescent, due to inclusions of goethite and/or limonite. Patterns within the banding of agates give rise to names like moss agate, tree agate, crazy lace agate and landscape agate.

Opal (from the Latin *opalus*, meaning precious stone) is a hydrated form of amorphous silica ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ). The water content usually varies from 5% to 10% but may comprise up to 30% of the mineral in some cases. The water is useful in that it allows the determination of the temperature of formation of the mineral within the host rock. The hardness of the mineral is reduced, usually to around 5.5, by the water content, as is the specific gravity (generally around 2.2 to 2.4). Common opal has the characteristic opalescence (hazy appearance like water to which a few drops of milk have been added), but it is the iridescent play of colours over a white surface which typifies precious opals. This is due to the diffraction of light within uniform, closely-packed, regularly spaced microscopic (25 microns in diameter) silica spheres within the body of the stone. Strangely, common opal shows no such play of colours. Once again, there is a plethora of colloquial and trade names for individual stones based upon the range of colours exhibited and, of course, their provenance. Thus, there are (amongst many others) forcherite (a yellow variety with inclusions of realgar and orpiment), hydrophane (a variety that becomes translucent or even transparent when immersed in water), milk opal, fire opal, and honey opal. Opal is precipitated from Si-rich groundwater and hydrothermal fluids. Colourless opal is a component of hot spring deposits and deep-sea precipitates.

Chert is the name given to dark, usually grey to black chalcedony found as either massive or stratiform bodies in rocks. Flint is a term generally restricted to (usually) grey and darkish brown to black nodular chalcedony found particularly in chalk.

## REFERENCES

- Anon. 2005 Tanzanite. *New Scientist*, 24th September, 52.
- Barrow, G. 1893 On an intrusion of muscovite-biotite gneiss in the south-eastern Highlands of Scotland and its accompanying metamorphism. *Quarterly Journal of the Geological Society of London*, **49**, 330-335.
- Bell, P.M. 1963 Experimentally determined phase diagram for  $\text{Al}_2\text{SiO}_5$ . *Science*, **139**, 1055.
- Burnham, C.W. 1963 Zeitschrift fur Kristallographie, 146.
- Chao, E.C.T., Shoemaker, E.M. and Madsen, B.M. 1960 First natural occurrence of coesite. *Science*, **132**, 220 - 222.
- Chao, E.C.T., Fahey, J.J., Lister, J. and Milton, D.J. 1962 Stishovite,  $\text{SiO}_2$ , a very high pressure new mineral from Meteor crater, Arizona. *Journal of Geophysical Research*, **67**, 419-421.
- Coombs, D.S. et al. 1998 Recommended nomenclature for zeolite minerals: report of the subcommittee on zeolites of the IMA, Commission on New Minerals and Mineral Names. *Mineralogical Magazine*, **22**, 422-437.
- Conklin, L.H. 1987 On Kunz and Kunzite. *Mineralogical Record*, **18**, 369-372.
- Cornu, F. 1908 Über die Paragenese der Minerale, namenliche die der Zeolithe. *Österreichische Zeitschrift für Berg -und Hüttenwesen*, **56**, 1-89.
- Cronstedt, A. 1756 Observation and description of an unknown kind of rock to be named zeolites. *Kungliga Svenska Vetenskaps - Academiens Handlingar* Stockholm, **17**, 120-123. (In Swedish)
- Deer, W.A., Howie, R.A. and Zussman, J. 1992 An Introduction to Rock-Forming Minerals. Longman. 2nd edition, 696 pp.
- Hoefen, T. M. et al. 2003 Discovery of Olivine in the Nili Fossae Region of Mars. *Science*, **302**, 627-630.
- Klein, C. and Hurlbut, C.S. 1993 Manual of Mineralogy after J.D.Dana. 21st edition. Wiley, 681pp.
- Lafer, B. 1912 Jade. A study in Chinese Archaeology and Religion. Field Museum of Natural History (Anthropological series) **10** (Dover Reprint 1974) 370pp.
- Leake, B.E. et al. 2004 Nomenclature of amphiboles: additions and revisions to the International Mineralogical Association's amphibole nomenclature. *European Journal of Mineralogy*, **16**, 191-196.
- Levy, A. and Scott-Clark, C. 2001 The Stone of Heaven. The Secret History of Imperial Green Jade. Weidenfield and Nicolson, London 429pp.

- |                                    |      |  |
|------------------------------------|------|--|
| Lockwood, A.                       | 2004 | The Naming of Minerals with an Appendix on the Naming of the Elements. British Micromount Society (BMS), Occasional Paper, 16, 32 pp.  |
| Milovsky, A.V. and Kononov, O.V.   | 1985 | Mineralogy. Mir Publishers, Moscow, 320pp.   |
| Nicholson, P.                      | 2004 | Tourmaline. British Micromount Society (BMS), Occasional Paper, 17, 31 pp.   |
| Pearce, J. and Woodbridge, A.      | 1999 | Minerals are Chemicals Part 2 : The Periodic Table. British Micromount Society (BMS), Occasional Paper, 13, 31 pp.   |
| Poldervaart, A. and Hess, H.H.     | 1951 | Nomenclature of Clinopyroxenes in the System, $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFeSi}_2\text{O}_6$ - $\text{Mg}_2\text{Si}_2\text{O}_6$ - $\text{Fe}_2\text{Si}_2\text{O}_6$ , <i>Journal of Geology</i> . 59, 472. |
| Shannon, R.D.                      | 1976 | Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halide. <i>Acta Crystallographica</i> , A32, 751-767.   |
| Wilson, O., Dyer, A. and Enamy, H. | 2003 | Zeolites of the British Isles, British Micromount Society (BMS), Occasional Paper, 15, 30 pp.  |
| Wilson, O., Dyer, A. and Enamy, H. | 2005 | Zeolites of the World, British Micromount Society (BMS), Occasional Paper, 19, 27 pp.  |

## BMS OCCASIONAL PAPERS

1. An Introduction to Micromounts	1994	Roy Starkey	£1.00
2. Determining the Optical Properties of Minerals	1994	Max Wirth	£1.50
3. Minerals are Chemicals	1994	John Pearce	£1.50
4. Paper Chromatography	1994	Max Wirth	£1.00
5. Using the Mineralogical Literature	1995	Roy Starkey	£3.00
6. Stereomicroscopes	1995	Mike Edwards	£2.00
7. Photography of Minerals through the Microscope	1995	Elsie Hansford	£1.00
8. A Guide to Micromounting: Part 1, Collecting	1998	Peter Braithwaite	£1.50
9. A Guide to Micromounting: Part 2, Micromounting	1996	Peter Braithwaite	£1.50
10. A Guide to Micromounting: Part 3, Cataloguing	2000	Peter Braithwaite	£1.50
11. Chemical Testing of Mineral Grains	1998	David Green	£2.00
12. A Select and Personal Bibliography from the Mineralogical Magazine	1999	Roy Starkey	£2.00
13. Minerals are Chemicals Part 2: The Periodic Table	1999	John Pearce & Austin Woodbridge	£3.00
14. The Formation of Secondary Minerals	2002	David Alderton	£1.50
15. Zoolites of the British Isles	2003	Oneta Wilson Alan Dyer & Hassan Enamy	£3.00
16. The Naming of Minerals	2004	Austin Lockwood	£2.50
17. Tourmaline Joint publication with Norfolk Mineral & Lapidary Soc.	2004	Paul Nicholson	£3.50
18. Minerals of the Mendips (2nd Edition) Reprint for Russell Soc. Southern Branch	2004	Gary Morse (Ed)	£3.00
19. Zoolites of the World (Excluding the British Isles)	2005	Oneta Wilson Alan Dyer & Hassan Enamy	£3.00
20. A Practical Guide to Producing Combination Photographs of Micro-minerals	2005	David Green	£2.50
21. Silicates: An Overview	2006	Christopher Duffin	£3.00

If you are interested in purchasing any of the above papers, please write to: John Pearce: 7 Condor Way, Burgess Hill, West Sussex RH15 9QB. (or telephone 01444 233958). Cheques payable to BMS please.

Postage and packaging, within the UK, should be added at the following rates:

up to 3 copies	£1.00
up to 10 copies	£2.50
11+ copies	£4.00