

U3A Geology

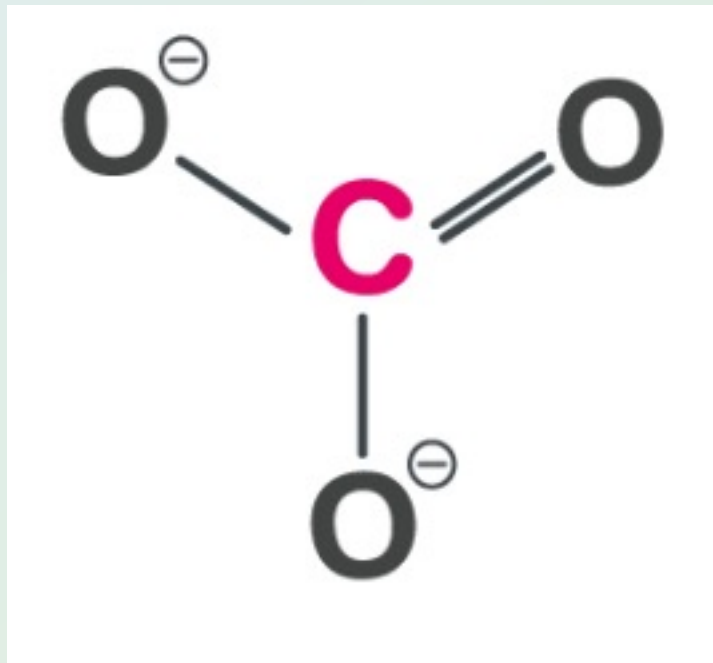
Mineralogy of carbonates

Carbonates

- Carbonates are a group of minerals in which the essential unit is the $(\text{CO}_3)^{2-}$ ion
- there are nearly 150 carbonate minerals, many of them relatively rare
- some are hydrated containing hydroxyl (OH^-) or halogen ions or are compound with sulphate, phosphate or silicate radicals
- common rock-forming carbonate minerals may be grouped structurally into calcite, aragonite or dolomite groups

Carbonate ion structure

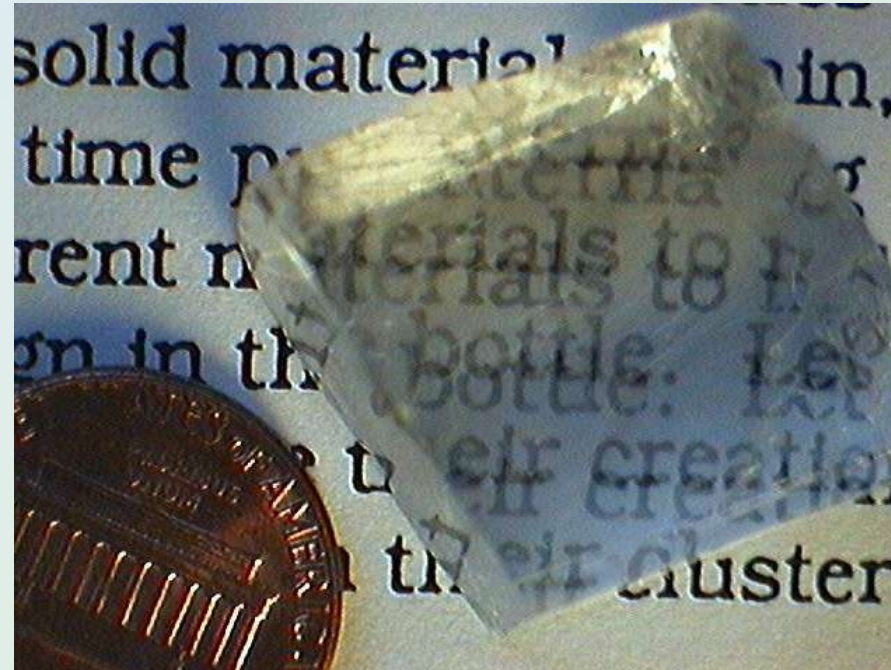
- The carbonate ion consists of a carbon atom surrounded by three oxygen ions in a trigonal planar arrangement
- carbonate bond has two single bonds to oxygen anions and a double bond to the neutral oxygen atom
- resultant overall charge is -2



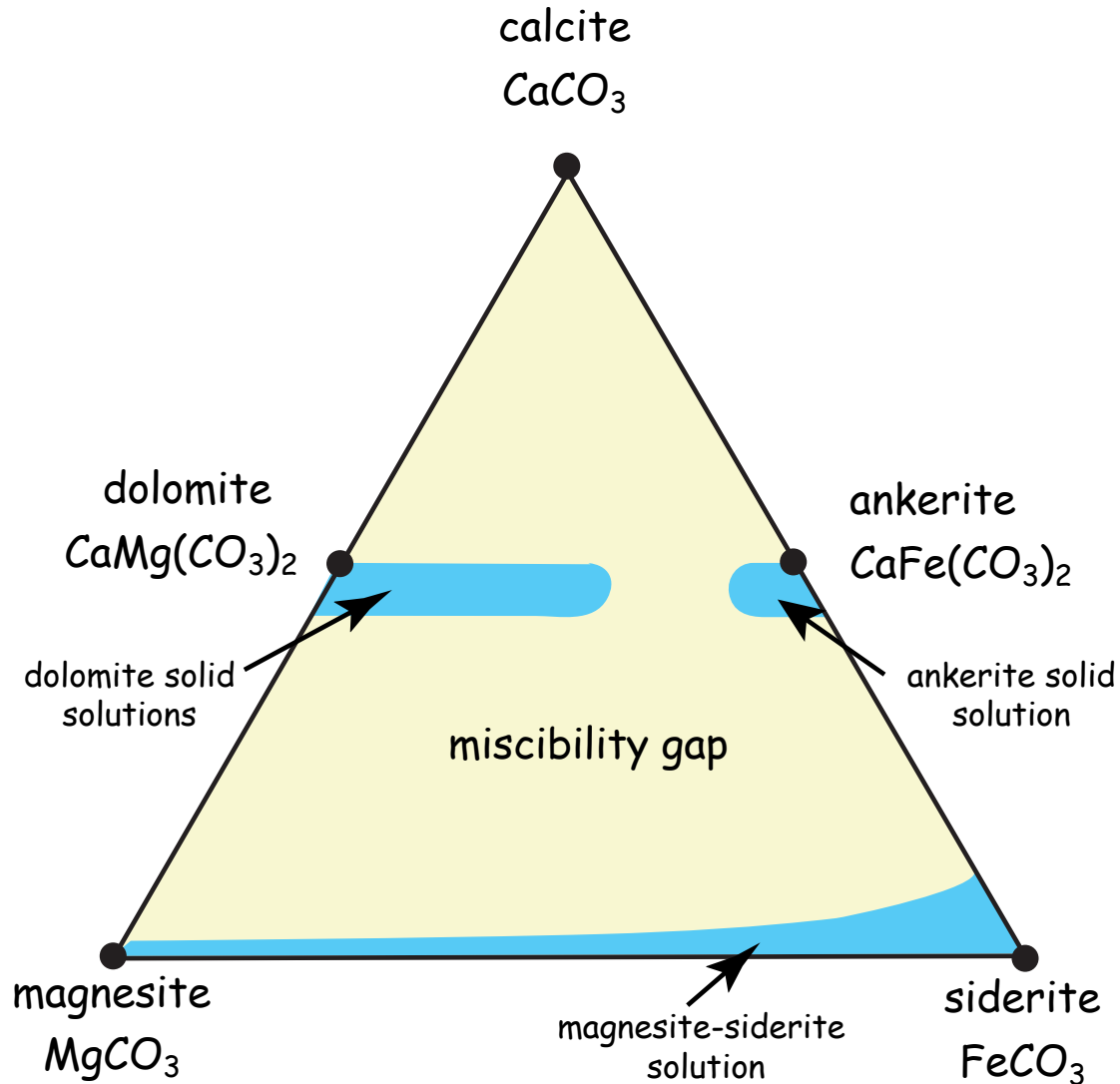
Calcite group

- Most common members of the calcite group are calcite (CaCO_3), magnesite (MgCO_3), siderite (FeCO_3), rhodochrosite (MnCO_3) and smithsonite (ZnCO_3)
- otavite (CdCO_3) and gaspeite (NiCO_3) are rare calcite-type carbonate minerals
- all members of the calcite group crystallise in the trigonal crystal system have perfect cleavage and exhibit strong refraction in transparent crystals

Double refraction in calcite

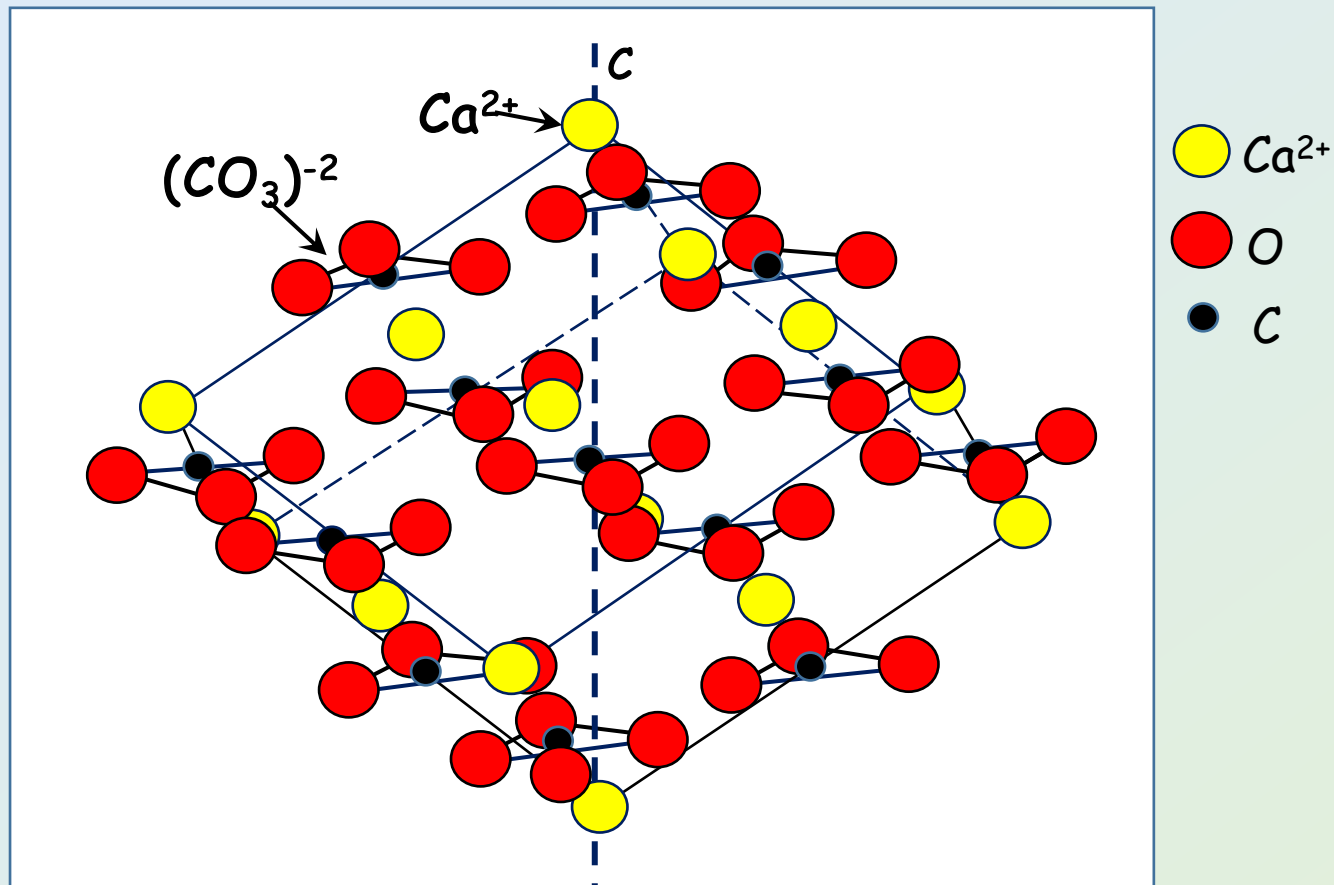


Major calcium group phases



Calcite structure

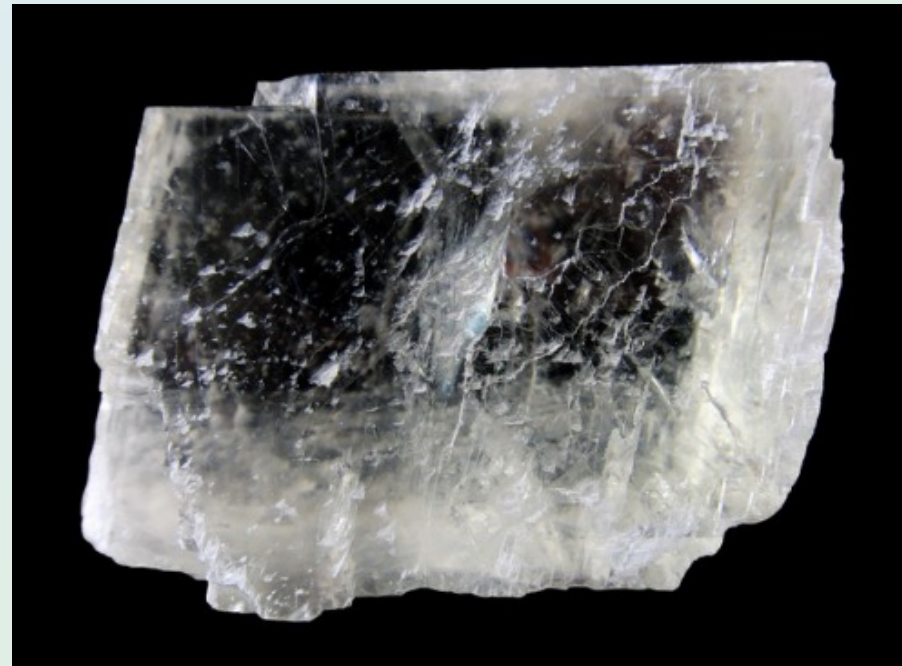
- Rhombohedral unit cell
- equilateral triangular CO_3 group with C atom in centre of triangle
- CO_3 groups have opposite orientations in successive CO_3 layers



Calcite - CaCO_3

- One of the most common and widely distributed of all minerals
- occurs predominantly in marine sedimentary rocks
- essentially the only mineral present in limestone. Present in some sedimentary rocks as skeletal remains of marine organisms
- crystalline metamorphosed limestones are marble
- chalk is fine-grained CaCO_3 → formed by compression of microscopic plankton that settled on the sea floor

Calcite (Iceland spar)

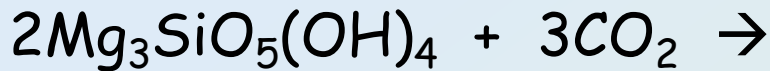


Calcite - CaCO_3

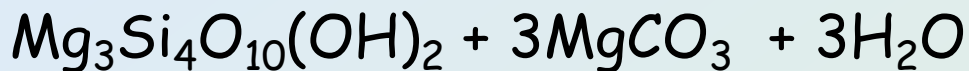
Crystal system:	trigonal
Lustre:	vitreous, pearly
Hardness:	3
Cleavage:	perfect rhombohedral cleavage
S.G.:	low (2.71)
Colour:	normally white to colourless (but other colours also)
Habit:	crystal aggregates, stalactitic
Remarks:	soluble in dilute HCl with effervescence

Magnesite - $MgCO_3$

- Commonly occurs in veins and irregular masses derived from the alteration of Mg-rich ultramafic rocks
- also forms through weathering of dolomite [$CaMg(CO_3)_2$]
- occurs as an accessory in some mafic igneous rocks
- may form through carbonate metasomatism of serpentine



serpentine



talc

magnesite

magnesite nodules



Magnesite - MgCO_3

Crystal system:	trigonal
Lustre:	vitreous, earthy
Hardness:	3.5 - 5
Cleavage:	rhombohedral
S.G.:	low (3.0)
Colour:	white, grey yellow, brown
Habit:	usually massive, finely granular, earthy
Remarks:	effervesces in warm, dilute HCl

Siderite - FeCO_3

- Most commonly found in shallow, bedded sedimentary rocks where it is the chief iron bearing mineral in iron-rich claystones
- may form by replacement of limestone by Fe-rich solutions
- common vein mineral associated with various metal ores containing pyrite, chalcopyrite, tetrahedrite and galena



siderite crystals

Siderite - FeCO_3

Crystal system:	trigonal
Lustre:	vitreous, pearly
Hardness:	3.5 - 4
Cleavage:	perfect rhombohedral
S.G.:	medium-high (3.96)
Colour:	light to dark brown
Habit:	usually rhombohedral crystals
Remarks:	effervesces in warm HCl

Rhodochrosite - MnCO_3

- Comparatively rare mineral → forms a complete solid solution with siderite, magnesite and calcite
- occurs in hydrothermal veins with ores of Ag, Pb, Zn and Cu and in limestone replacement bodies
- also in high-temperature metamorphic deposits with rhodonite, spessartine garnet and Mn oxides
- minor ore of Mn

rhodochrosite crystals (pink)



Rhodochrosite - MnCO_3

Crystal system:	trigonal
Lustre:	vitreous, pearly
Hardness:	3.5 - 4
Cleavage:	rhombohedral
S.G.:	3.5 - 3.7 (medium)
Colour:	pink to rose-red
Habit:	massive, granular, botryoidal
Remarks:	effervesces in warm HCl, alters to black Mn oxides

Smithsonite - ZnCO_3

- Found as a supergene mineral in oxidised Zn deposits mostly from weathering of sphalerite (ZnS)



- commonly found in Zn deposits in limestone and as fracture fillings and botryoidal coatings on rocks
- fine crystals found in Broken Hill mines



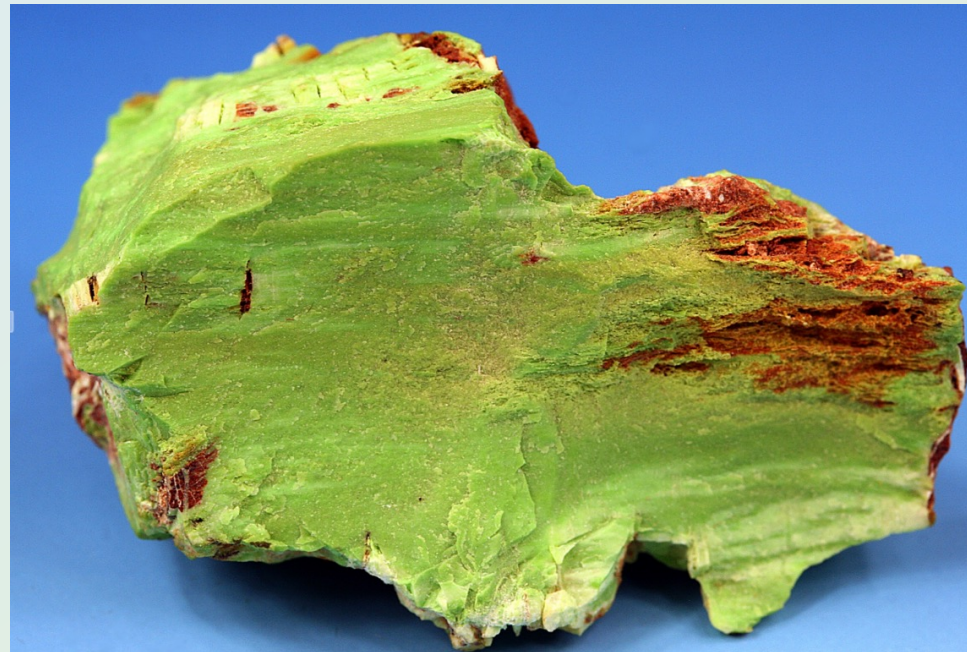
smithsonite

Smithsonite - ZnCO_3

Crystal system:	trigonal
Lustre:	vitreous, pearly
Hardness:	4 - 4.5
Cleavage:	rhombohedral
S.G.:	medium-high (4.4)
Colour:	variable commonly yellowish-green
Habit:	usually botryoidal, encrusting, perfect crystals are rare
Remarks:	effervesces in cold HCl

Gaspeite ((Ni,Fe,Mg)CO₃)

- Very rare Ni carbonate
- forms massive to reniform in fractures, botryoidal, concretions in laterite or fracture fill
- found in regolith as supergene enrichment mineral of hypogene Ni sulphides in environments in which calcareous carbonates occur
- known from handful of localities around the world including Kambalda, WA
- formed from weathering of Ni sulphides to form carbonate



Gaspeite, Kambalda, WA

Gaspeite (Ni,Fe,Mg)CO₃

Crystal system:	trigonal
Lustre:	vitreous to dull
Hardness:	4.5 - 5
Cleavage:	rhombohedral
S.G.:	medium-high (3.7)
Colour:	yellow-green
Habit:	massive, botryoidal,
Remarks:	effervesces in warm HCl

Aragonite group

- When the CO_3 group is combined with large ionic radii divalent cations \rightarrow orthorhombic structures result
- carbonates with large cations (e.g. BaCO_3 , SrCO_3 , and PbCO_3) have aragonite structure stable at room temperature
- carbonates that crystallise with aragonite structure include aragonite (CaCO_3), witherite (BaCO_3), strontianite (SrCO_3) and cerussite (PbCO_3)

Aragonite - CaCO_3

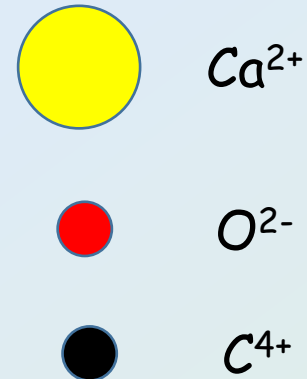
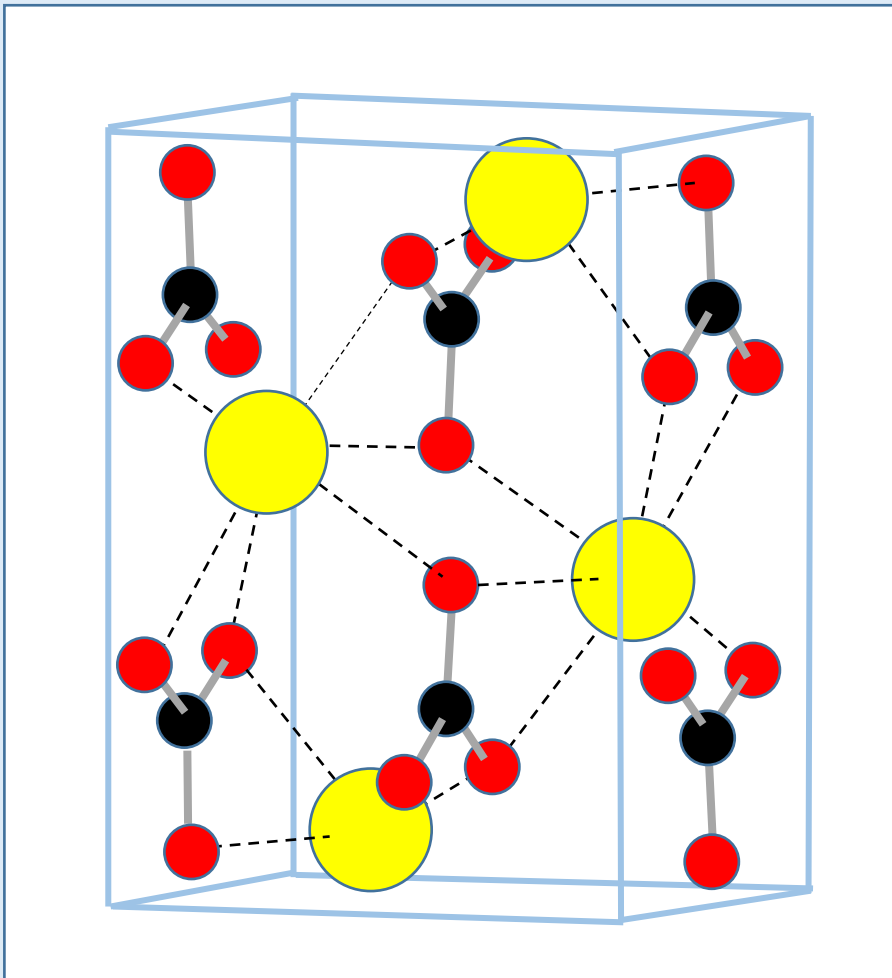
- High pressure polymorph of calcite → less stable than calcite under atmospheric conditions
- many marine skeletal parts are composed of aragonite
- deposited by hot, carbonated springs, found associated with beds of gypsum and iron ore



aragonite

Aragonite structure

CO_3 groups lie perpendicular to the c-axis but in two structural planes with triangular groups of one plane pointing in the opposite direction to those of the other

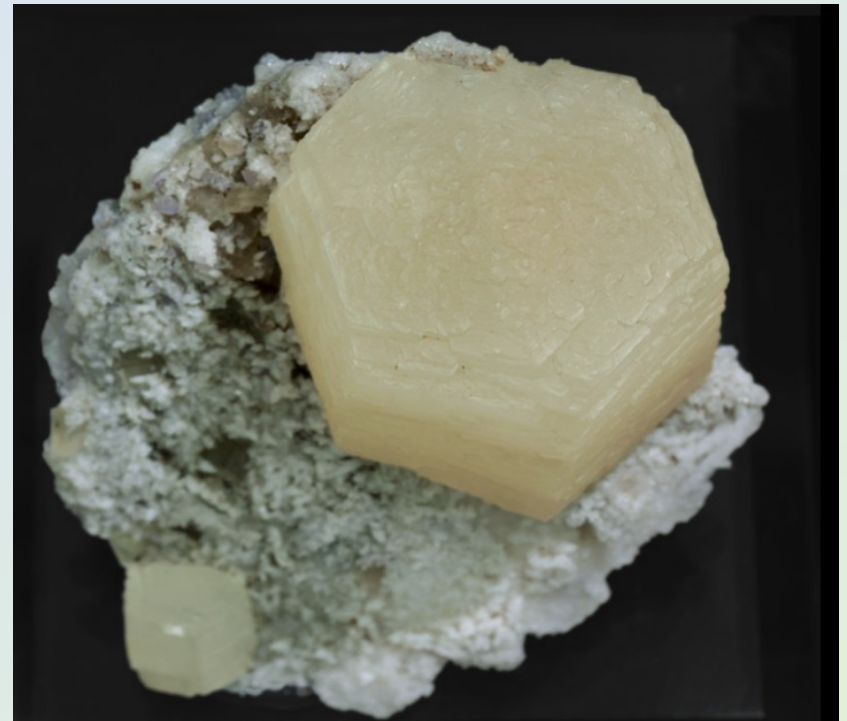


Aragonite - CaCO_3

Crystal system:	orthorhombic
Lustre:	vitreous
Hardness:	3.5 - 4
Cleavage:	1 good 1 poor
S.G.:	low (2.94)
Colour:	colourless, white, pink, pale yellow
Habit:	radiating crystals, pseudo-hexagonal prisms

Witherite - BaCO_3

- Comparatively rare Ba carbonate mineral
- forms in low temperature hydrothermal environments commonly associated with fluorite, celestite (SrSO_4), galena, barite and calcite
- most commonly found in hydrothermal veins with galena
- alters to more common barium mineral, barite (BaSO_4)
- minor source of barium
- poisonous, used as rat poison



Witherite, Illinois, USA

Witherite - BaCO₃

Crystal system:	orthorhombic
Lustre:	vitreous
Hardness:	3.5
Cleavage:	1 good 1 poor
S.G.:	medium-high (4.31)
Colour:	colourless, white, grey
Habit:	pseudo-hexagonal dipyramids

Strontianite - SrCO_3

- Uncommon low-temperature hydrothermal mineral associated with barite, celestite and calcite in veins in limestone and marl
- less frequently in sulphide veins and igneous rocks
- Ca can substitute for up to 27% of Sr cations and Ba up to 3.3%
- under appropriate conditions \rightarrow alters to celestite (SrSO_4)
- found in association with barite and calcite
- source of strontium

Strontianite, Styria, Austria



Strontianite - SrCO_3

Crystal system:	orthorhombic
Lustre:	vitreous
Hardness:	3.5 - 4
Cleavage:	1 good
S.G.:	medium (3.78)
Colour:	white, grey, yellow, green
Habit:	usually radiating acicular

Cerussite - PbCO_3

- Important supergene Pb-ore mineral formed by the action of carbonated waters on galena
- associated with galena, sphalerite, anglesite, smithsonite and other secondary ores of Pb, Zn and Cu
- occurs in oxidised zone in Pb sulphide deposits
- important ore of Pb



cerussite

Cerussite - PbCO_3

Crystal system:	orthorhombic
Lustre:	adamantine
Hardness:	3 - 3.5
Cleavage:	1 good
S.G.:	high (6.58)
Colour:	colourless, white, grey
Habit:	often tabular
Remarks:	dissolves in dilute HCl striated crystals

Dolomite Group

- The dolomite group includes :

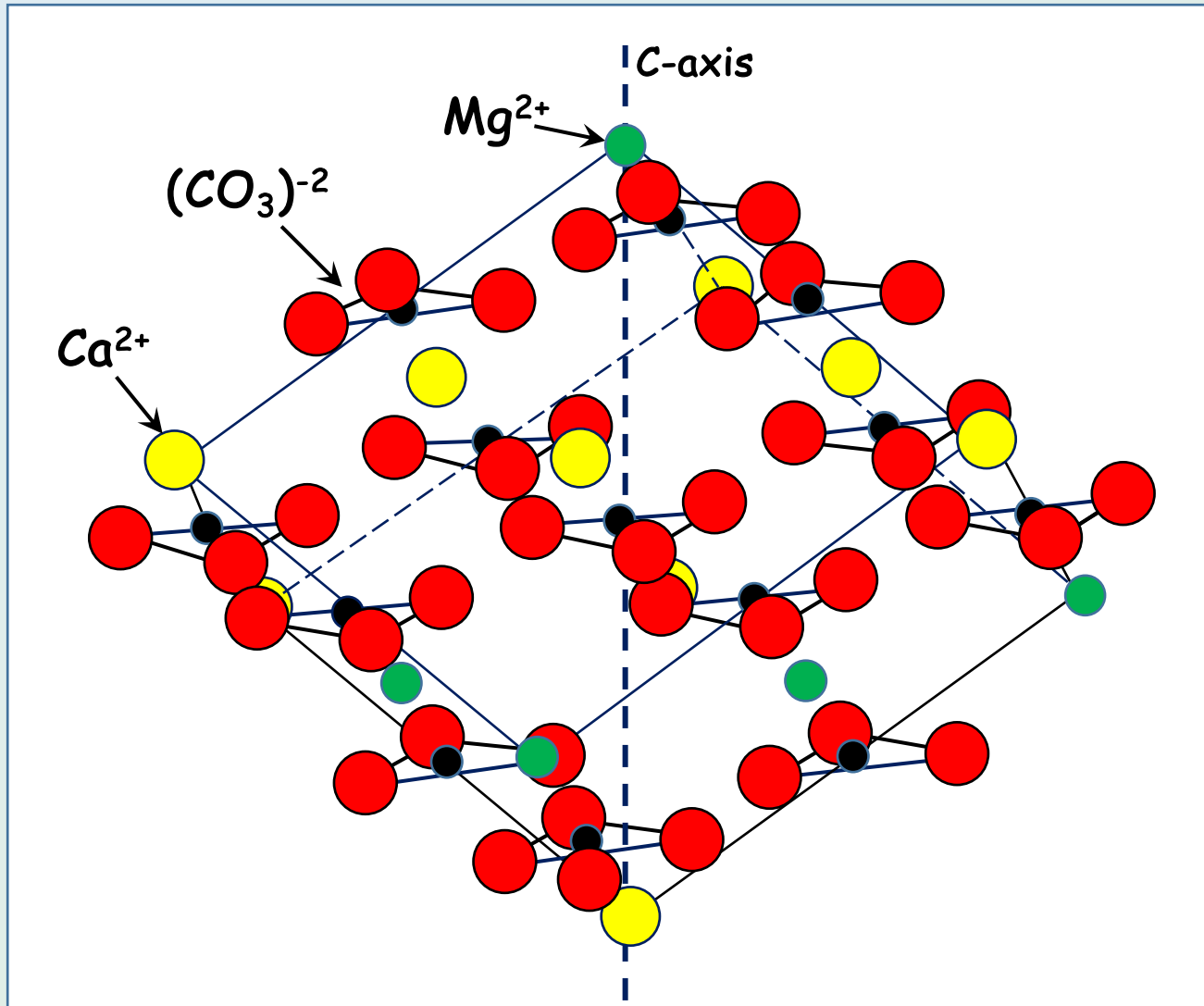
dolomite $\text{CaMg}(\text{CO}_3)_2$

ankerite $\text{Ca}(\text{Fe},\text{Mg},\text{Mn})(\text{CO}_3)_2$

kutnohorite $\text{CaMn}(\text{CO}_3)_2$

- the faces of all three are frequently curved
- the structure of dolomite is similar to calcite but with Ca and Mg alternating along the c-axis

Dolomite structure



Dolomite - $\text{CaMg}(\text{CO}_3)_2$

- Bulk of dolomite in Earth's crust → extensive dolostone formations
- commonly found in association with calcite in hydrothermal veins
- crystal and cleavage faces commonly slightly curved due to large differences in size between Ca^{2+} and Mg^{2+} ions
- may form in saturated saline lagoons e.g. Coorong lakes Sth Aust.
- large deposits present in geological record but rare in modern environments

dolomite



Dolomite - $\text{CaMg}(\text{CO}_3)_2$

Crystal system:	trigonal
Lustre:	vitreous, pearly
Hardness:	3.5 - 4
Cleavage:	rhombohedral
S.G.:	low (2.85)
Colour:	colourless, white, grey, pink
Habit:	fine to coarse-grained aggregates, rhombohedral crystals
Remarks:	does not dissolve in cold dilute HCl slightly curved crystal and cleavage faces

Ankerite - $\text{Ca}(\text{Fe},\text{Mg},\text{Mn})(\text{CO}_3)_2$

- Commonly cream coloured on fresh surfaces that oxidise to a brown colour in a relatively short time
- a common vein mineral and in wallrock alteration in Au deposits
- occurs in some igneous rocks and low-grade, Fe-rich, metamorphic rocks and in BIFs
- white to cream on newly exposed surfaces but oxidises over a very short time to tan colour



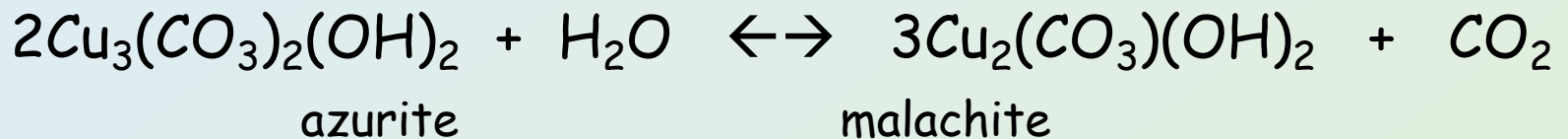
ankerite (brown) in quartz

Ankerite - $\text{Ca}(\text{Fe},\text{Mg},\text{Mn})(\text{CO}_3)_2$

Crystal system:	trigonal
Lustre:	pearly
Hardness:	3.5 - 4
Cleavage:	rhombohedral
S.G.:	low (2.93 - 3.10)
Colour:	cream, yellow, brown
Habit:	rhombohedral crystals, bladed

Malachite and azurite

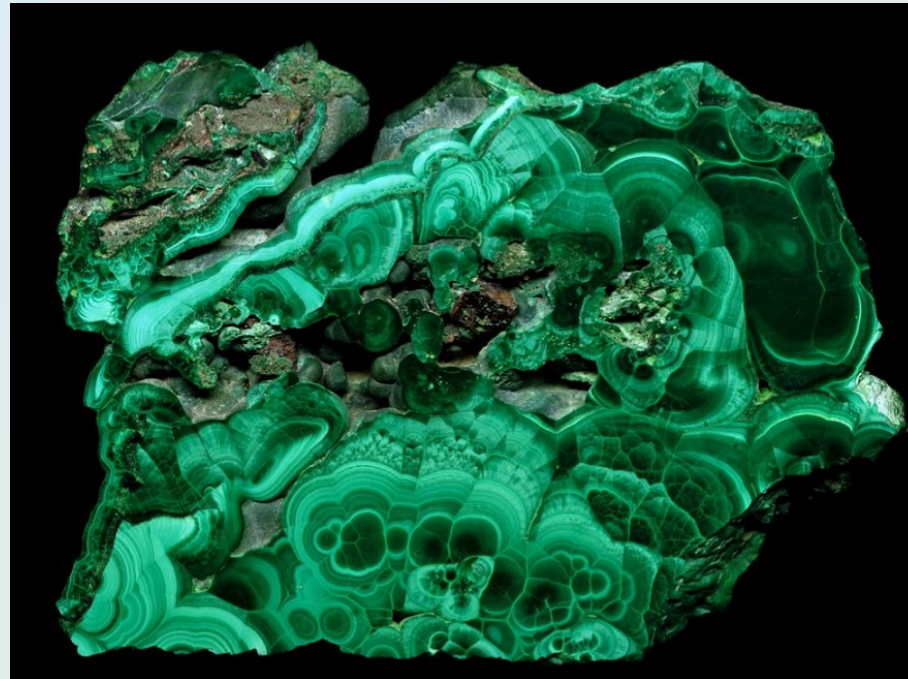
- Malachite and azurite form from the oxidation of primary Cu-sulphide ores
- commonly found with Cu deposits around limestone (source of carbonate) and in weathered zones of Cu sulphide deposits
- malachite is more abundant than azurite and more stable in open air
- the presence of azurite is due to the low partial pressure of CO_2 in the environment of formation



Malachite - $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$

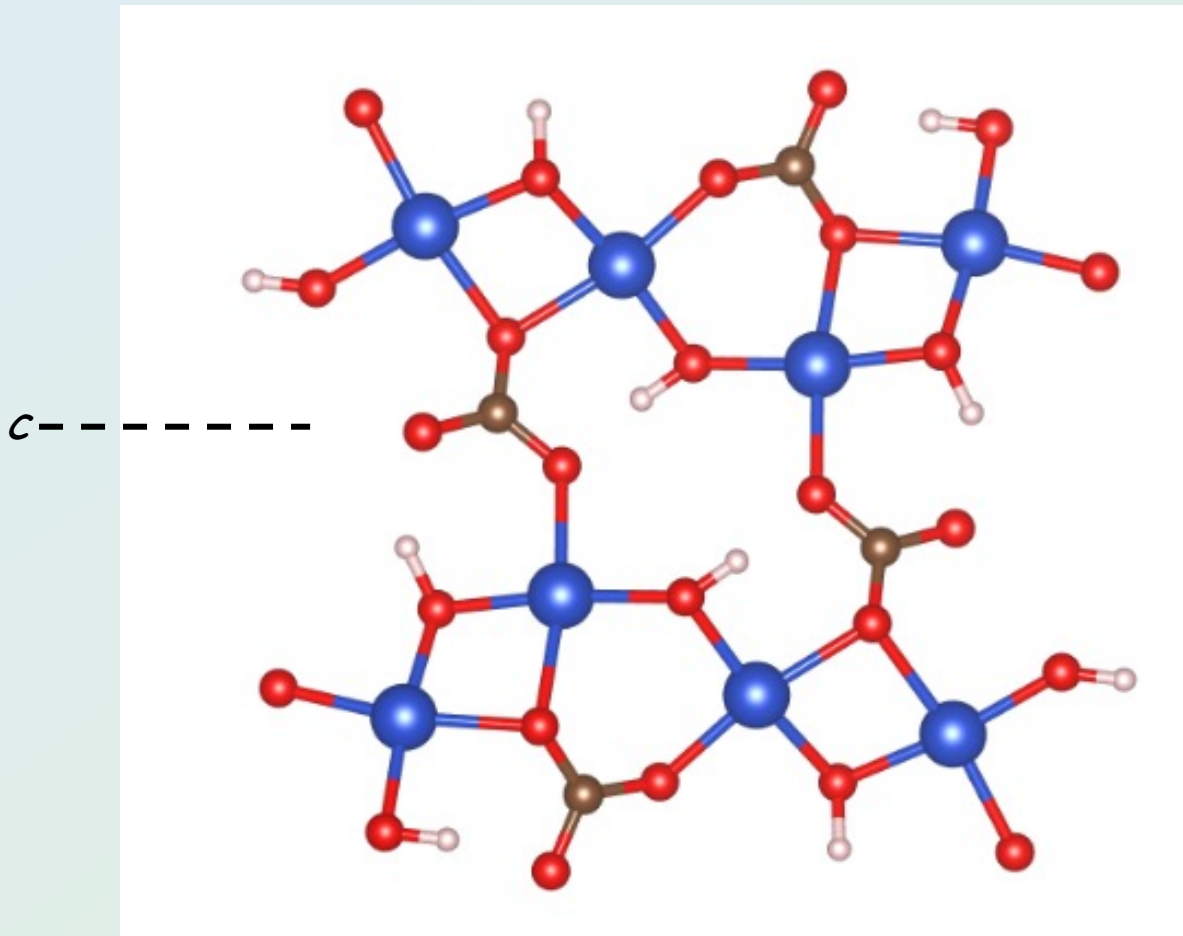
- Widely distributed green supergene copper mineral
- found in upper oxidised zone of Cu deposits
- minor ore of Cu
- used as a pigment in ancient paint
- popular gem mineral (particularly in pendants)

malachite



Malachite structure

$\text{CuO}_4(\text{OH})_2$ octahedra are linked along the edges forming chains that run parallel to the *c*-axis. Chains are cross-linked by triangular $(\text{CO}_3)^{2-}$ groups



Cu - blue

C - brown

O - red

H - pink

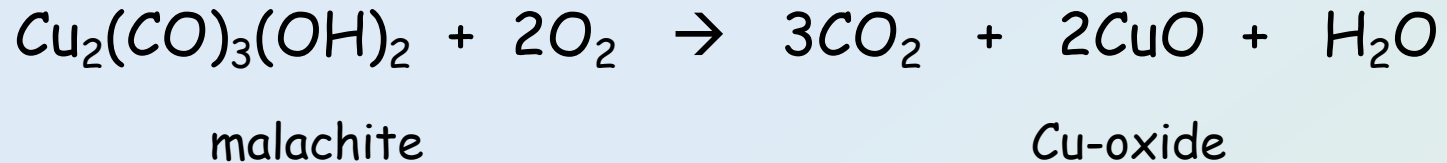
Malachite - $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$

Crystal system:	monoclinic
Lustre:	adamantine to vitreous
Hardness:	3.5 - 4
Cleavage:	1 cleavage
S.G.:	medium (3.6 - 4)
Colour:	bright green
Habit:	massive, encrusting, colloform
Remarks:	effervesces with cold dilute HCl

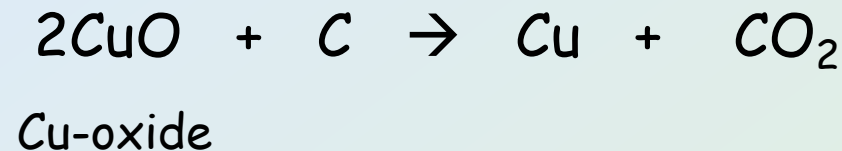
Cu metal from malachite

The Cu-ore extraction from malachite occurs in two stages.

Stage 1 produces Cu-oxide



Stage 2 involves an additional C source (e.g. coal)



Azurite - $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$

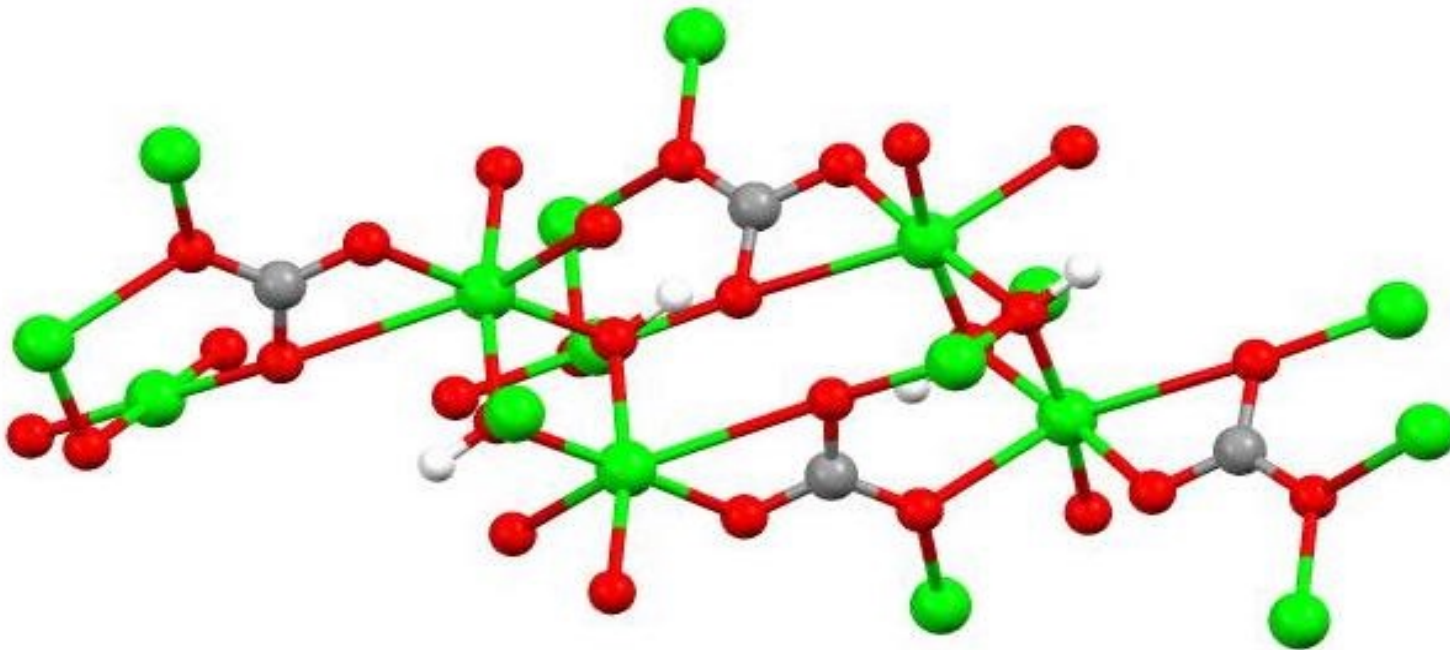
- Deep blue coloured supergene copper mineral formed by the oxidation and carbonisation of Cu oxides and sulphides
- found in upper oxidised zone of Cu deposits e.g. Goonumbla, NSW
- less stable in open air than malachite
- used in ancient Egypt as a pigment
- minor ore of Cu



azurite

Azurite structure

- The structure of azurite contains Cu^{2+} ions in, coplanar groups
- these groups are linked into chains parallel to the b-axis
- Cu cations are linked to two different anions CO_3^{2-} and OH^-



Cu = green

C = grey

O = red

H = white

Azurite - $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$

Crystal system:	monoclinic
Lustre:	vitreous
Hardness:	3.5 - 4
Cleavage:	2 \neq 90°
S.G.:	medium (3.8)
Colour:	light to dark azure blue
Habit:	massive, encrusting, earthy, tabular
Remarks:	effervesces with cold, dilute HCl