U3A
The geology of copper (1)

Introduction

- Copper is a metallic mineral with the chemical symbol Cu
- characterised by colour, ductility, malleability and high thermal and electrical conductivity
- plays a very important role in our everyday life*
- the most widely used metal after iron and aluminium
  → e.g. electrical wiring, plumbing
- first smelted from Cu ores ~4500BCE
- became very important at beginning of bronze age ~3300BCE*

Properties of Copper

Chemical symbol:	Cu
Atomic no.:	29
Atomic wt.:	63.546
S.G.:	8.96
Melting temp.:	1085°C
Av. Crustal conc.:	50ppm
Valence states:	+1 (cuprous), +2 (cupric)

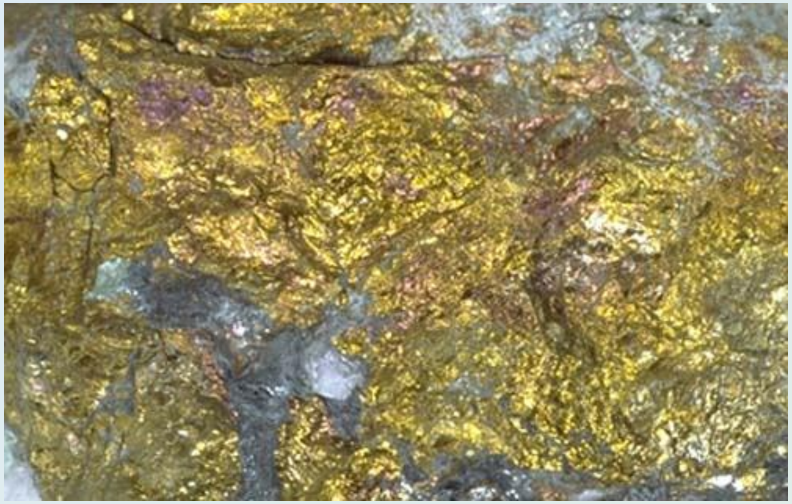
Uses: coins, electrical wiring, plumbing, heat conductors (e.g. car radiators), production of brass and bronze

Cu minerals

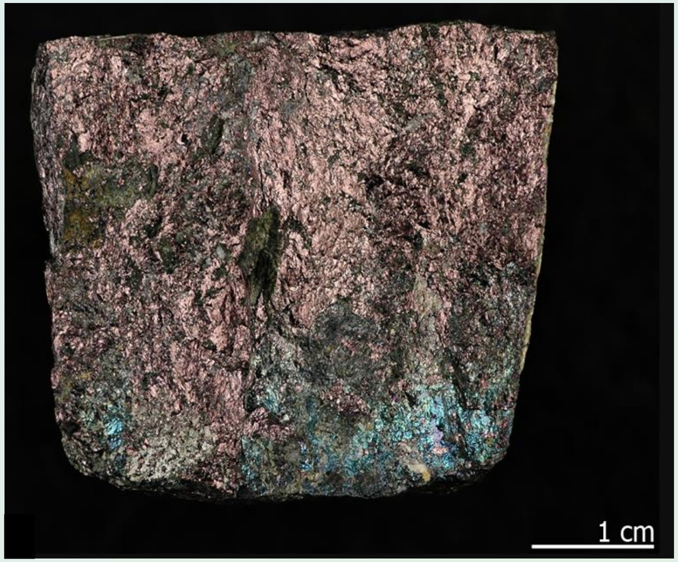
There are >500 Cu minerals → only 20 or so are common

Sulphides:	chalcopyrite	$CuFeS_2$	bornite	Cu_5FeS_4
	chalcocite	Cu_2S	digenite	Cu_9S_5
	covellite	CuS		
Sulphosalts:	enargite	Cu_3AsS_4	tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$
	tennantite	$(Cu,Fe)_{12}As_4S_{13}$		
Sulphates:	chalcanthite	$CuSO_4.5H_2O$		
Carbonates:	malachite	$Cu_2CO_3(OH)_2$		
	azurite	$Cu_2(CO_3)_2(OH)_2$		
Oxides:	cuprite	Cu_2O	tenorite	CuO
Native metal:	native copper	Cu		
Silicates:	chrysocolla	$(Cu,Al)_2H_2Si_2O_5(OH)_4.nH_2O$		

Cu sulphide minerals



chalcopyrite $CuFeS_2$



bornite Cu_5FeS_4

chalcocite Cu_2S

covellite CuS

Cu content of principal Cu ore minerals

chalcopyrite	$CuFeS_2$	34.62% Cu
bornite	Cu_5FeS_4	63.32% Cu
chalcocite	Cu_2S	79.86% Cu
covellite	CuS	66.47% Cu
cuprite	Cu_2O	88.82%

Cu oxide minerals

- Cu oxide polymorphs cuprite and tenorite occur in the oxidised zones of Cu ore bodies
- cuprite is a reddish coloured sub-metallic mineral, tenorite is dark-grey to black

cuprite Cu_2O

tenorite CuO

Cu carbonate minerals

- Malachite is the most common carbonate mineral and is green in colour, azurite is blue

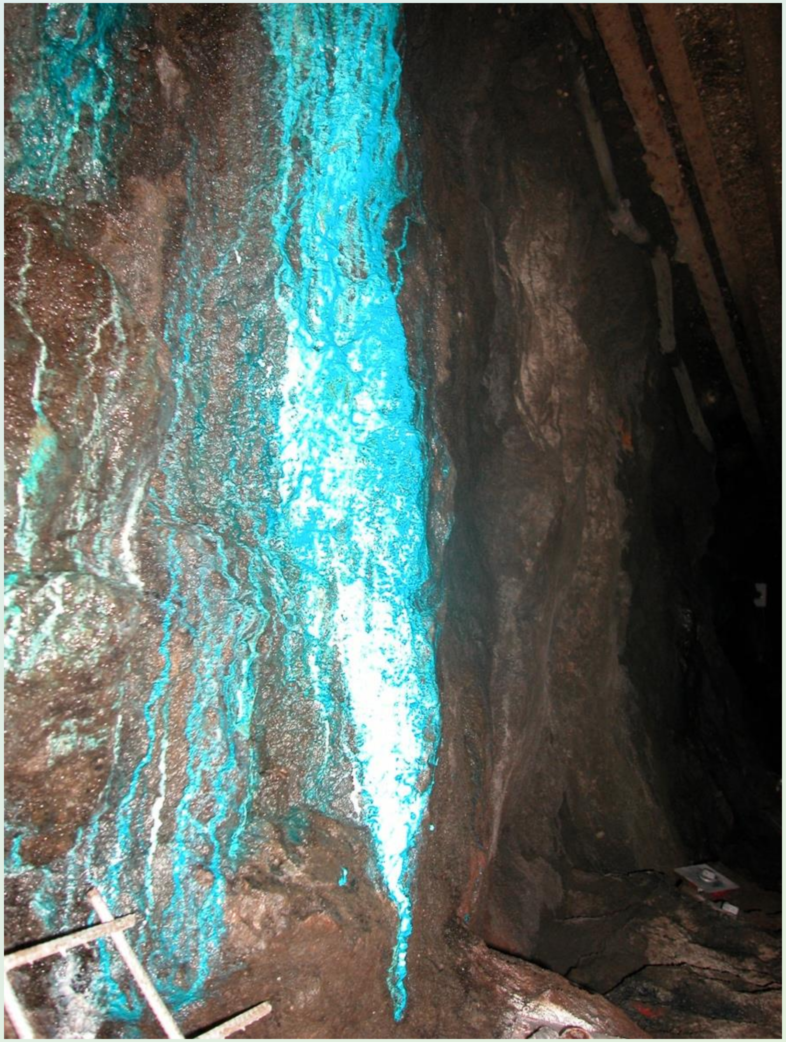
malachite $Cu_2CO_3(OH)_2$

azurite $Cu_3(CO_3)_2(OH)_2$

Native copper

Cu silicate (chrysocolla)

chrysocolla $(Cu,Al)_2H_2Si_2O_5(OH)_4.nH_2O$



chrysocolla, Temperino, Italy

Cu deposits

Types of deposits

(1) Porphyry Cu

(2) Stratiform sediment-hosted Cu

(3) Volcanic-hosted massive sulphide (VMS)

(4) Iron oxide-Cu-Au (IOCG)

(5) Cu skarn

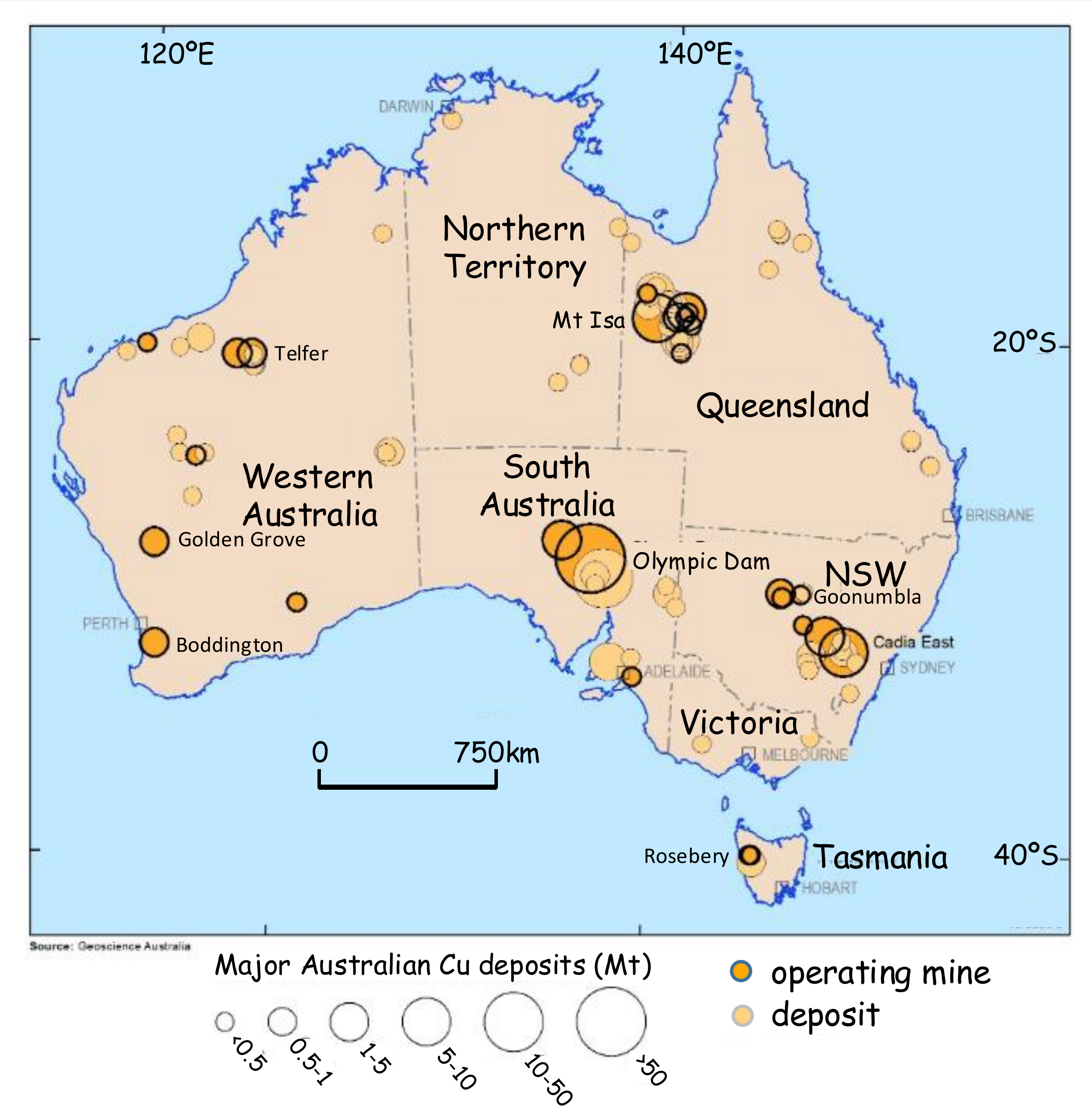
(6) Lake Superior Cu

There are two distinct types of Cu ore:

(1) sulphide Cu ore

(2) oxide Cu ore

Australian Cu deposits



Porphyry Cu deposits

- Large, low grade stockwork/disseminated Cu deposits (minor Mo, Au)
- form in areas of shallow magmatism along linear, calc-alkaline volcano-plutonic arcs related to subduction e.g. Pacific rim
- generally associated with multiple intrusions of porphyritic, intermediate to acid intrusive rocks (diorite to quartz monzonite)
- associated with intrusives emplaced at shallow depths → 1-6km with vertical thickness 2km*
- provide >50% of world's Cu (reserves 170,000,000,000t)
- world's largest deposits occur in the Andes
- most deposits are Mesozoic to Cenozoic in age (also Palaeozoic)

Characteristics of porphyry-type deposits

- Mineralisation occurs as disseminations and in stockwork-forming hairline fractures and quartz veins
- host rocks are highly fractured with pervasive wallrock alteration
- breccia zones and pipes are common in many deposits and may be mineralised
- Cu values typically 0.2 - 2%
- large (commonly 50 - 500 Mt), but may exceed 1000Mt
- ores can be mined at low grade because of size of ore-bodies*
- host intrusion typically zoned, cylindrical with porphyritic core enclosed by a shell of medium equigranular rock

Vein stockwork

Generalised porphyry Cu model
(Sillitoe 1973)

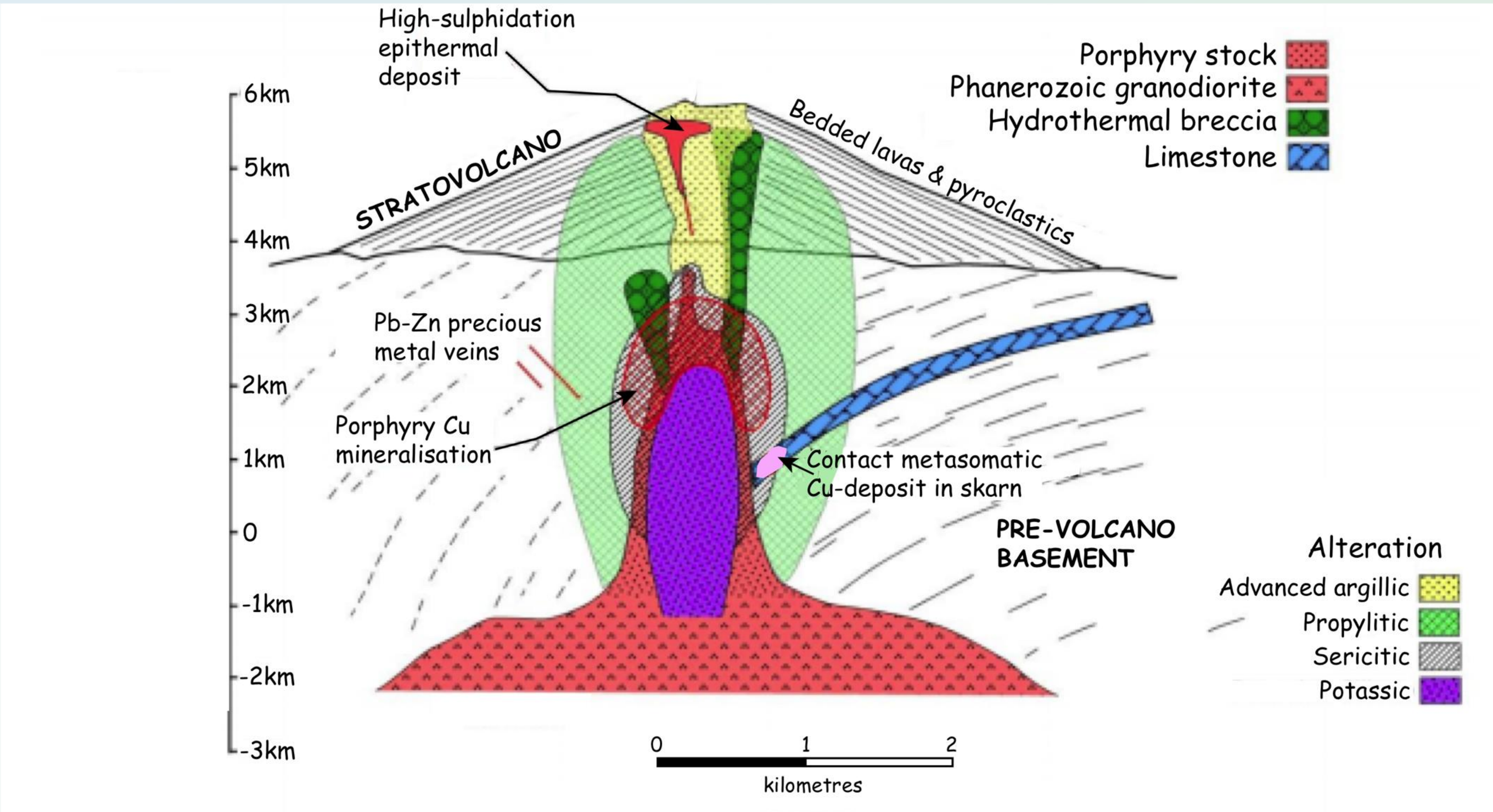
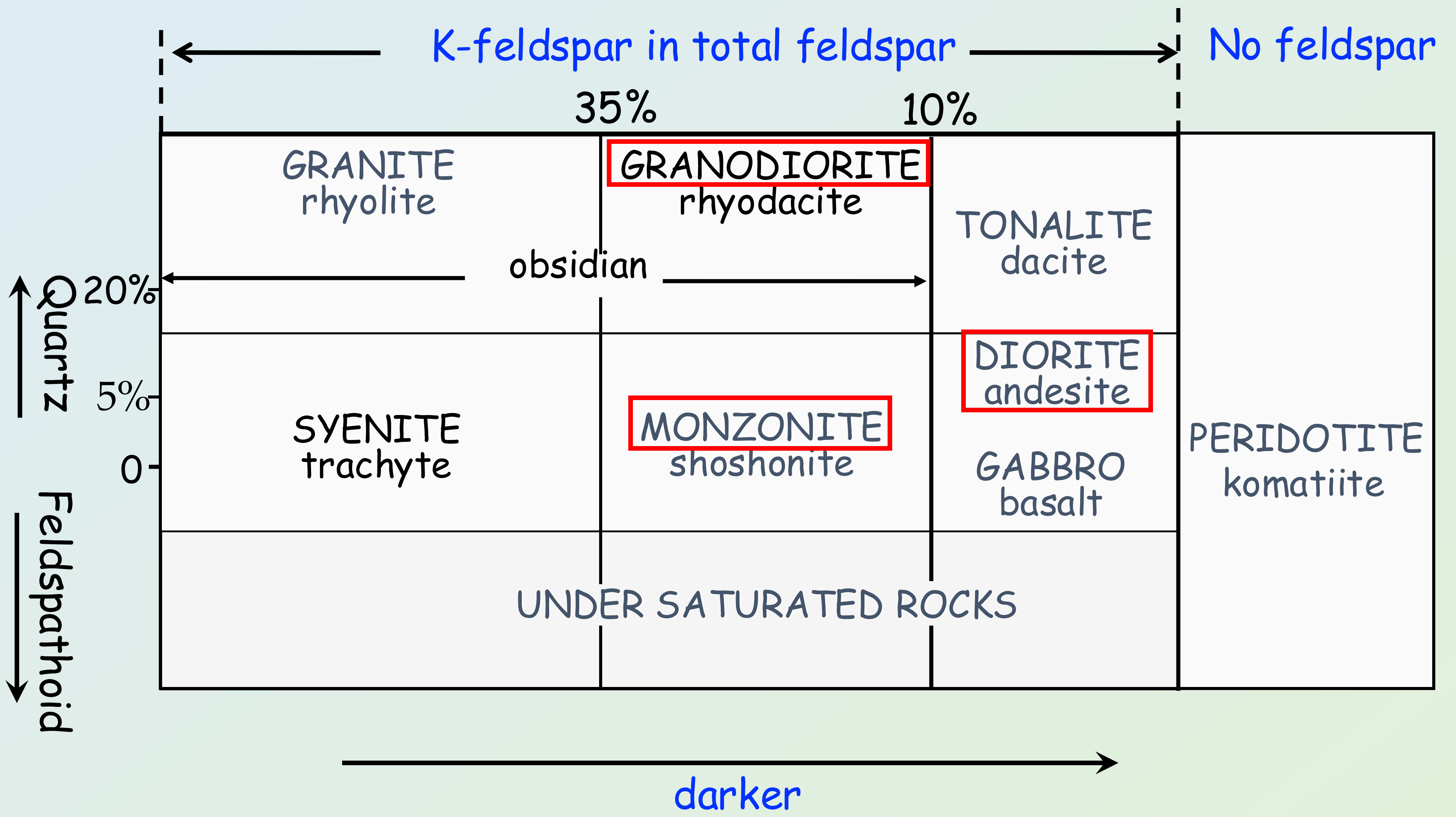


Chart for igneous rock classification



Igneous rocks associated with porphyry-Cu deposits

- Igneous systems are complex and consist of a number of rock types formed during separate intrusive/extrusive events

- show a variation between island arc settings and continental margins

Island arc settings e.g. Indonesian, New Guinean deposits

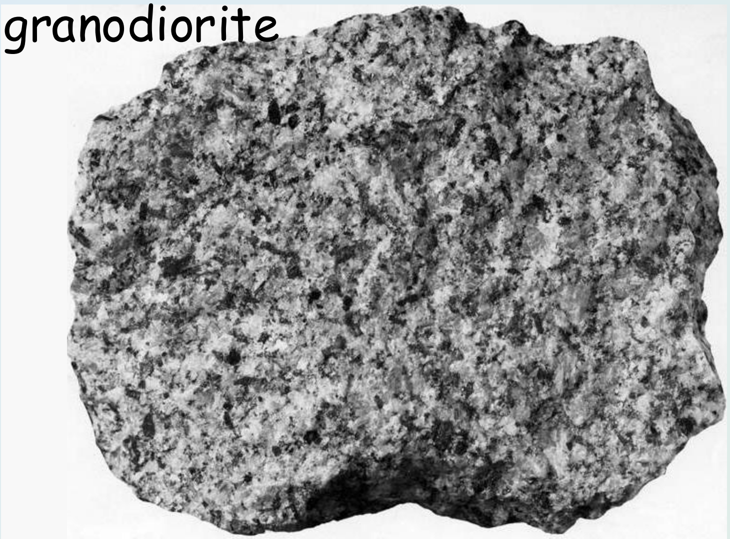
- Calc-alkalic, hornblende diorite and quartz diorites

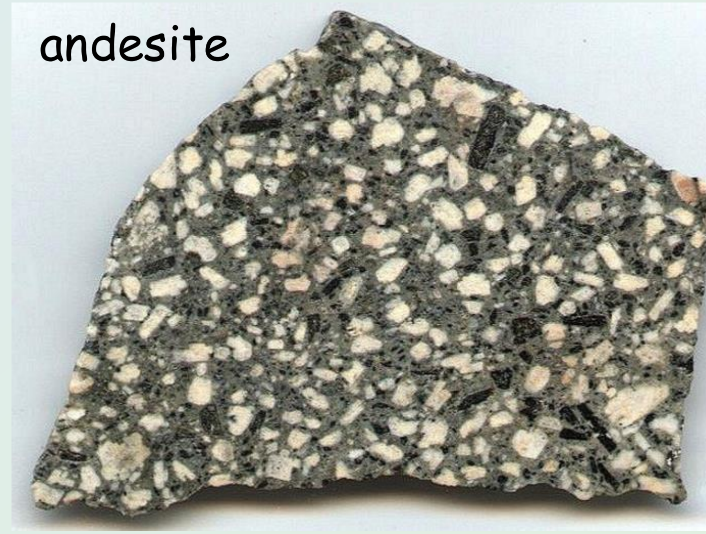
Continental margins e.g. Andean deposits, Nth American Cordillera

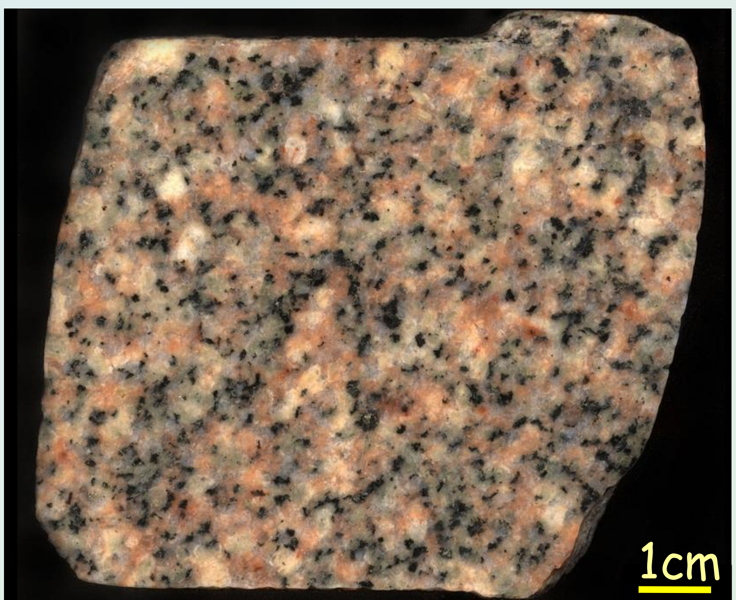
- Granodiorites and quartz monzonites

- Wide range of country rocks host intrusions including coeval volcanics, clastic sedimentary and crystalline basement rocks

Igneous rocks associated with porphyry Cu deposits





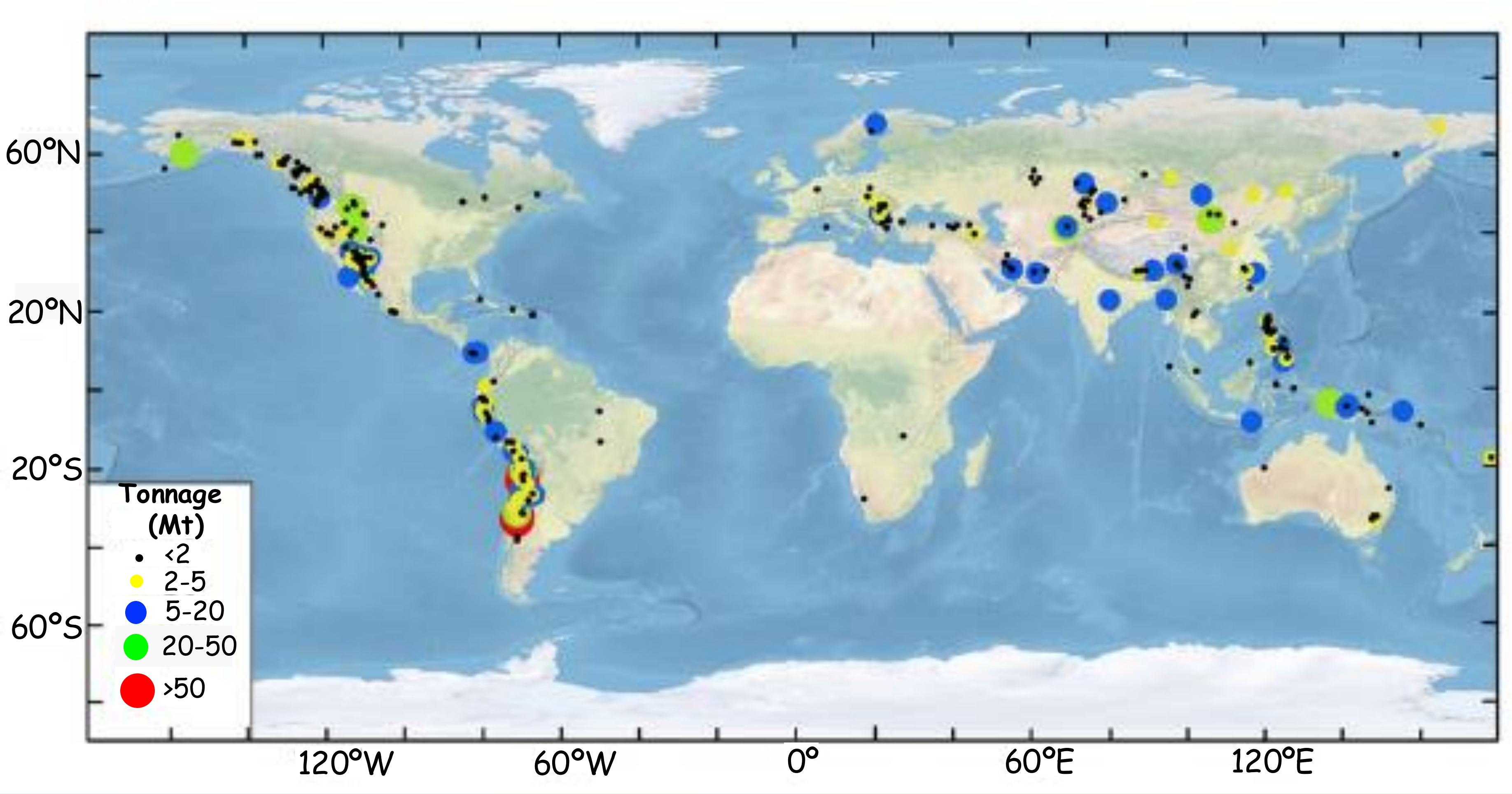


Quartz monzonite

Environments of porphyry-Cu deposits

- Form in areas of shallow magmatism within subduction related environments
- many occur along volcano-plutonic arcs related to subduction
- along N. American cordillera, porphyry-Cu deposits formed 74-48Ma in Western Pacific Miocene to Pleistocene in age (21-2Mya)
- there are also deposits that are of Palaeozoic age
- Late Ordovician to Early Silurian deposits occur in the Parkes and Orange districts in NSW
- Cadia-Ridgeway porphyry system, NSW dated at 438Ma

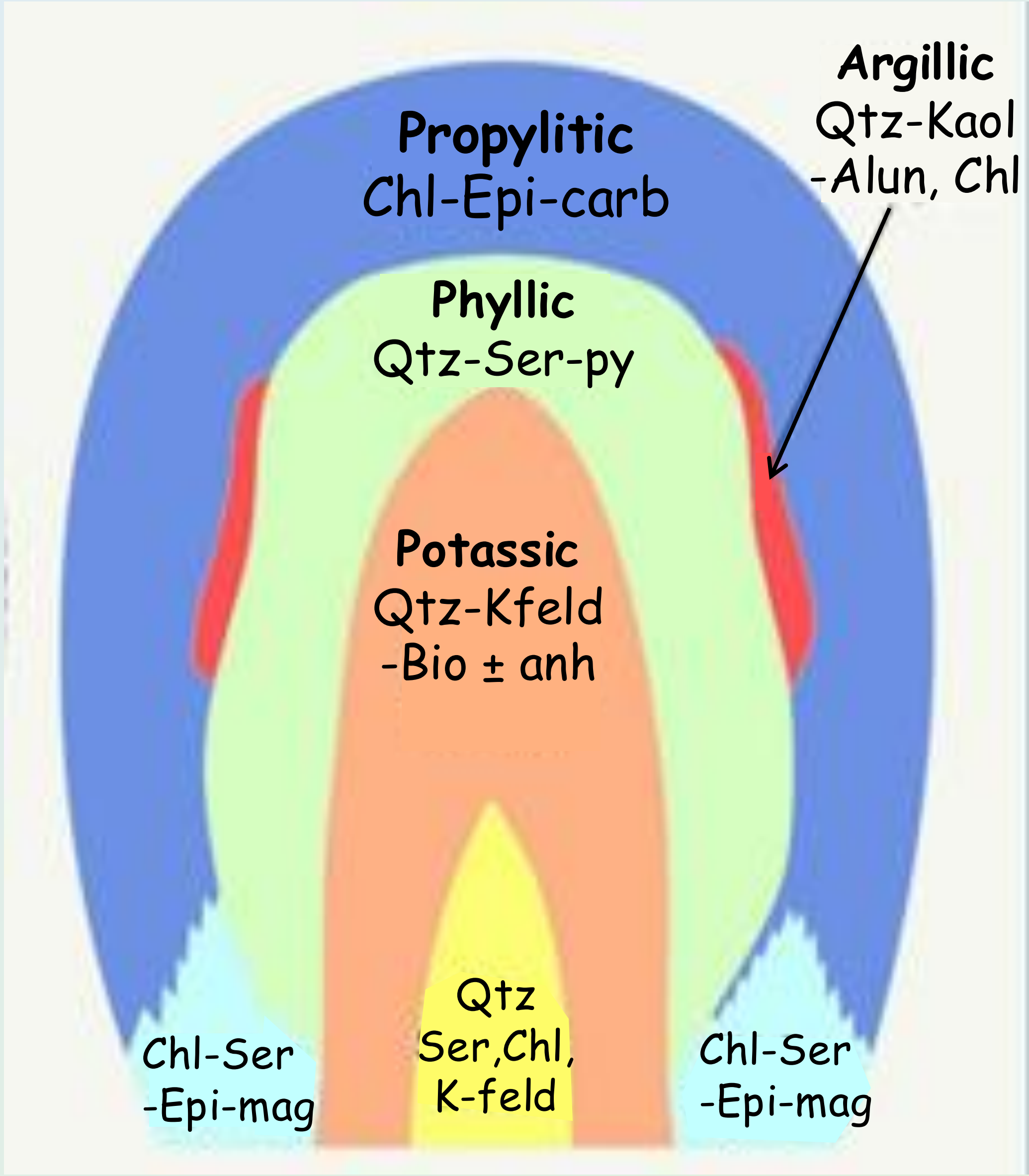
Global distribution of porphyry Cu deposits



Hydrothermal alteration

- Porphyry Cu host rocks → pervasive hydrothermal alteration with partial to complete alteration of primary minerals
- as magma crystallises, it evolves volatiles (e.g. H_2O, CO_2, H_2S) that transport ions (including metals) and permeate into enclosing rocks
- alteration forms concentric zones centred on a porphyry stock
- alteration can extend laterally and vertically for distances ranging from a few hundred metres to several Km
- in late stages of alteration, circulating meteoric waters may interact with magmatic fluids

Generalised alteration zonation



Alteration facies in porphyry-Cu deposits

Four types of hypogene alteration* common:

(1) Potassic alteration - not always present, orthoclase and/or biotite, magnetite, quartz, anhydrite, chalcopyrite

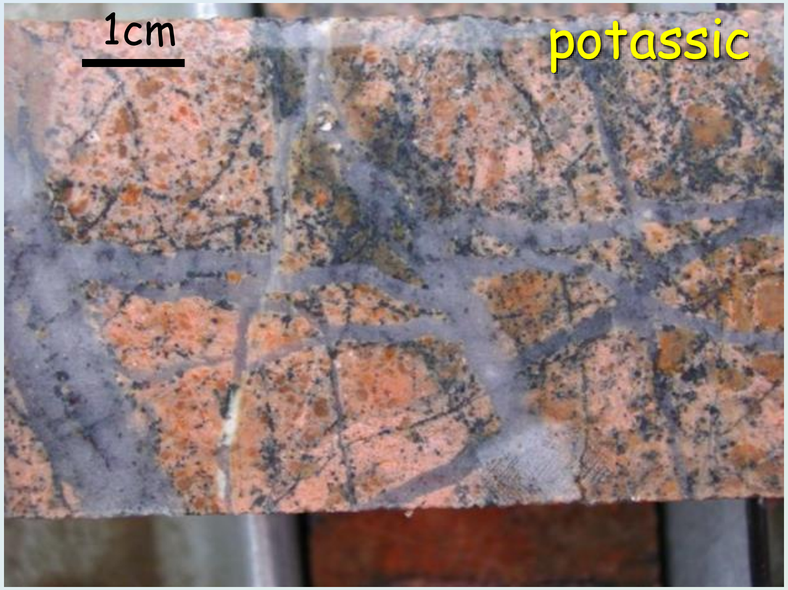
(2) Phyllic (sericitic) alteration - quartz-sericite-pyrite, contains the most developed disseminated and veinlet pyrite

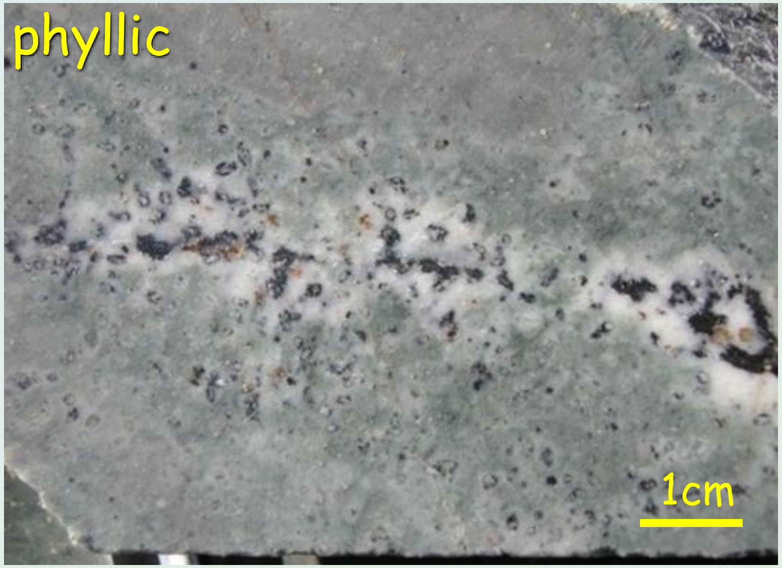
(3) Propylitic alteration - outermost zone always present, chlorite-epidote-carbonate-pyrite

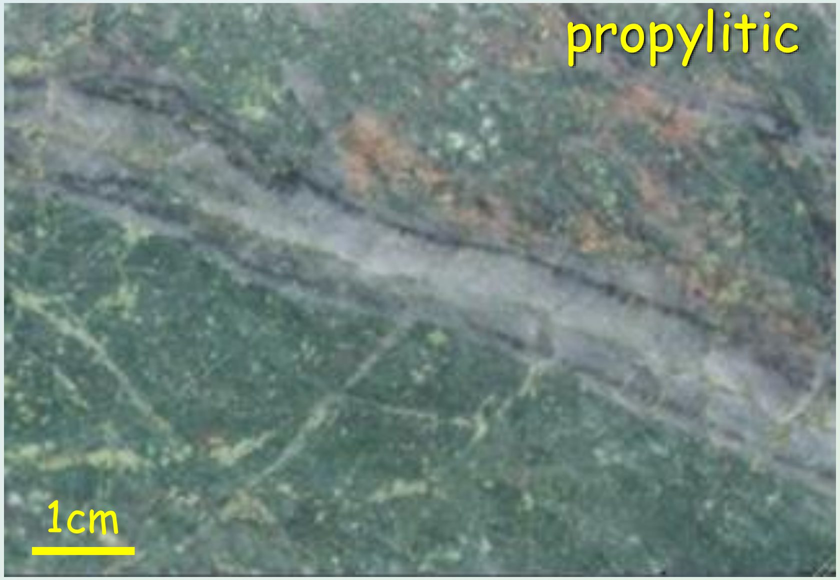
(4a) Intermediate argillic alteration - not always present, sericite, chlorite, kaolinite/illite, pyrite, calcite

(4b) Advanced argillic - alunite, kaolinite, pyrophyllite, quartz, dickite, gibbsite, pyrite, enargite, covellite

Alteration facies





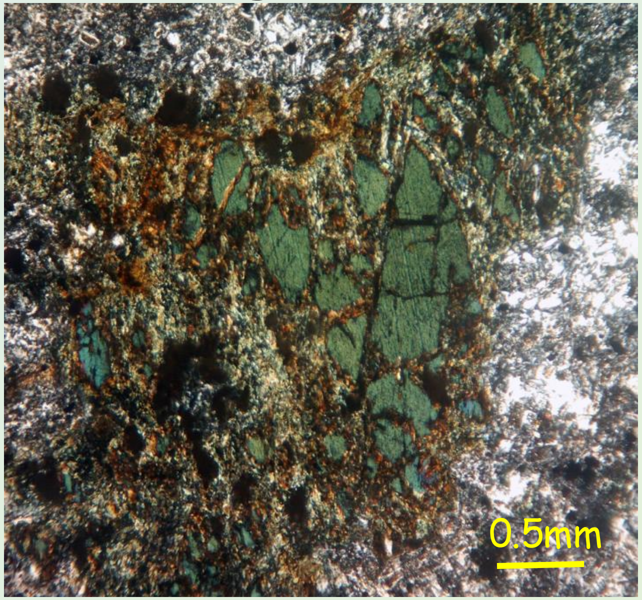


Alteration styles

(1) *Pervasive alteration* - complete replacement of primary minerals by secondary minerals

(2) *Selectively pervasive* - alteration only affects certain mineral phases eg. hornblende phenocrysts

(3) *Vein-veinlet* - refers to alteration assemblages enveloping vein mineralisation.



Hornblende partially replaced by chlorite

Ore mineralisation

- Ore minerals are disseminated through altered rock matrix and in veinlets
- grain-size is generally in the order of mm but may reach 2cm
- mineralisation may result from hypogene, supergene or oxidation processes
- hypogene fluids are high temperature fluids that ascend from a magmatic source

Hypogene mineralisation

Found in three different locations:

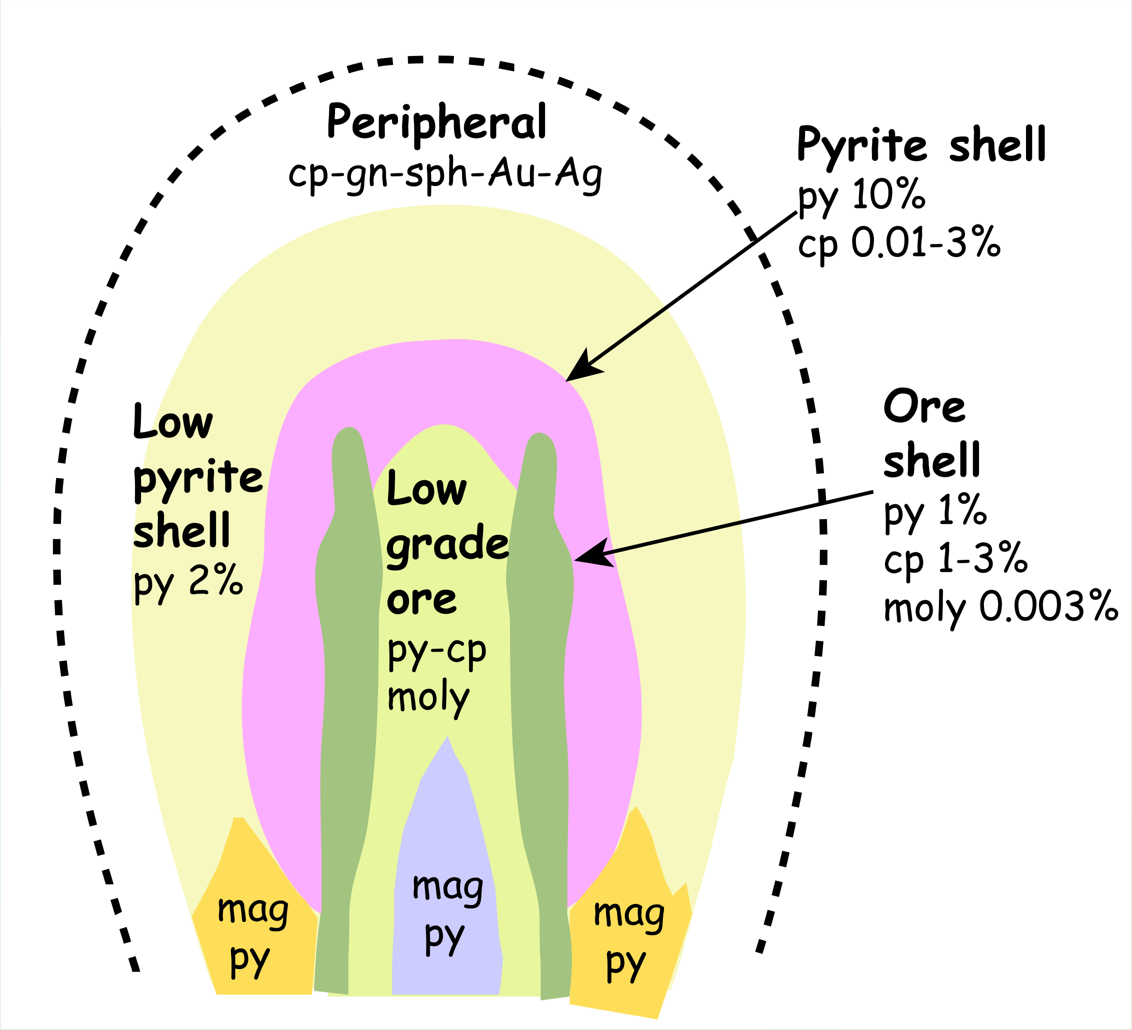
(1) wholly within the igneous host rock

(2) partially within host stock and partially in the country rocks

(3) wholly within the country rocks

- Hypogene ore mineralisation tends to occur in concentric zones with a spatial relationship to wall rock alteration
- stockwork and disseminated mineralisation generally associated with K-silicate alteration
- principal copper ore minerals are chalcopyrite and bornite. Molybdenite may also be present.

Sulphide mineralisation zones for generalised porphyry-Cu model
(after Lowell & Guilbert 1970)



Hypogene mineralisation features

- Ore types: Cu-only; Cu-Au; Cu-Mo; Cu-Au(-Mo); Mo-only
- main ore minerals: chalcopyrite, bornite, gold, molybdenite
- gangue minerals: quartz, orthoclase, anhydrite, magnetite, biotite, sericite and pyrite
- zonation: low pyrite, Cu-rich core (chalcopyrite, bornite); outer pyrite-rich halo
- abundant magnetite with biotite alteration. Anhydrite ($CaSO_4$) present as a vein mineral and in most alteration

Hypogene minerals

Primary (hypogene) ore mineral(s) are predominantly

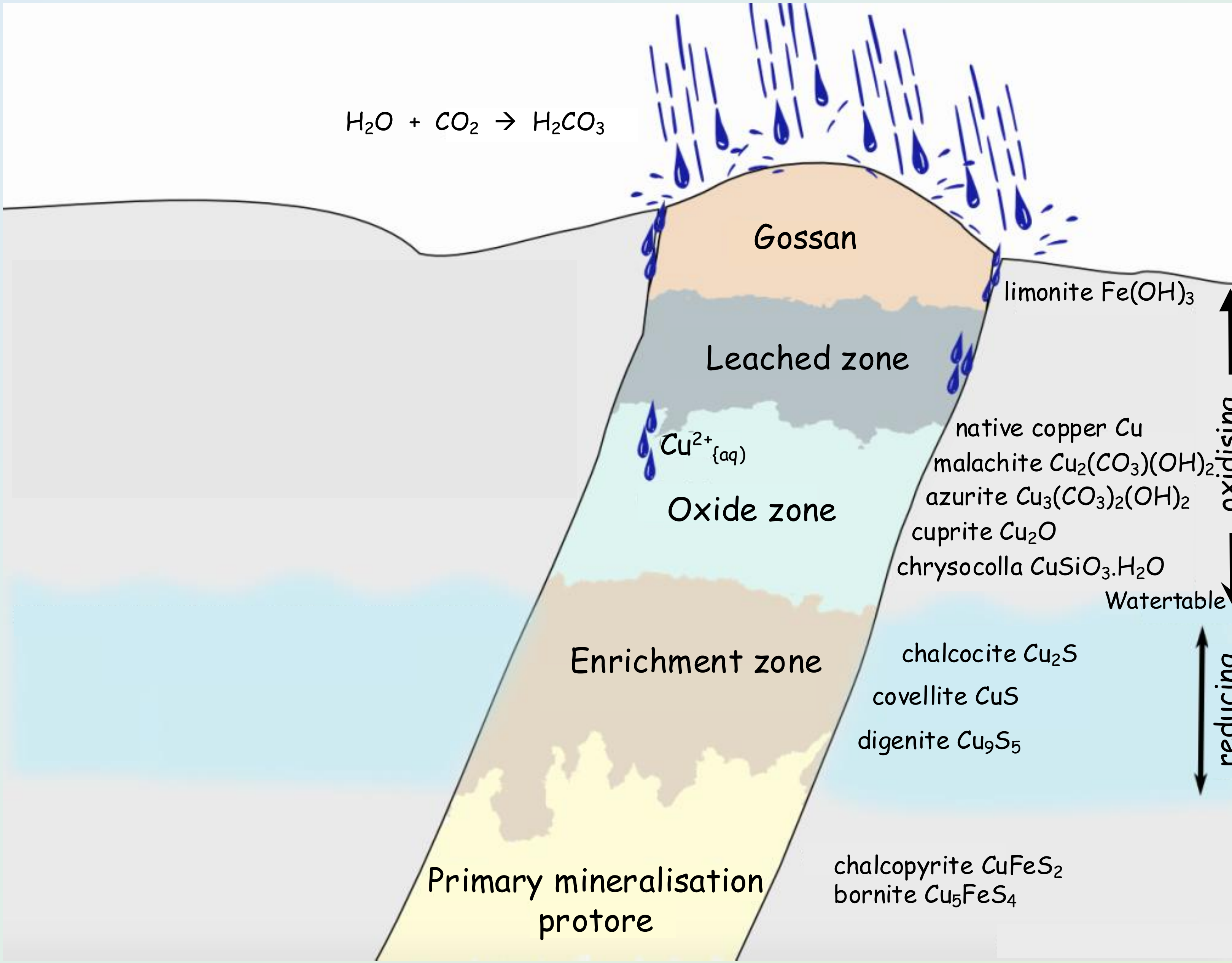
chalcopyrite ± bornite

chalcopyrite and bornite

Oxidation and supergene mineralisation

- When weakly acidic surface water percolates down through upper part of Cu sulphide orebody, sulphides are oxidised → form gossan cap
- resulting solutions may dissolve further minerals forming sulphuric acid
- in underlying leached zone other metals are leached and transported downwards where they may be precipitated as oxides
- in this zone, carbonated waters may form Cu-carbonates
- dissolved metals are reprecipitated in reducing environment below the water table → supergene enrichment
- supergene enrichment is an important process in economic viability of many porphyry Cu deposits

Supergene enrichment (after Asmus 2013)



Oxidised zone

- Oxidation occurs above the water table producing a leached cap on the deposit

- several types of capping are recognised in the oxidised zone:

  (1) goethite [$FeO(OH)$]

  (2) jarosite $(K,H)Fe_3(SO_4)_2$

  (3) hematite (Fe_2O_3)

  (4) chrysocolla $(Cu,Al)_2H_2Si_2O_5(OH)_4.nH_2O$

  (5) malachite [$Cu_2CO_3(OH)_2$] and azurite [$Cu_2(CO_3)_2(OH_2$]

  (6) cuprite (Cu_2O)

Genesis of porphyry Cu deposits

Magma emplaced in crust*

↓

equigranular crystallisation in outer parts of the intrusion

↓

fractionation → magma enriched in volatiles → fluid saturation of magma

↓

exolved aqueous phase → forms foam between crystal mush and carapace

↓

vapour pressure exceeds confining pressure

↓

fracturing of carapace

↓

decrease in pressure → boiling → vapour expansion

↓

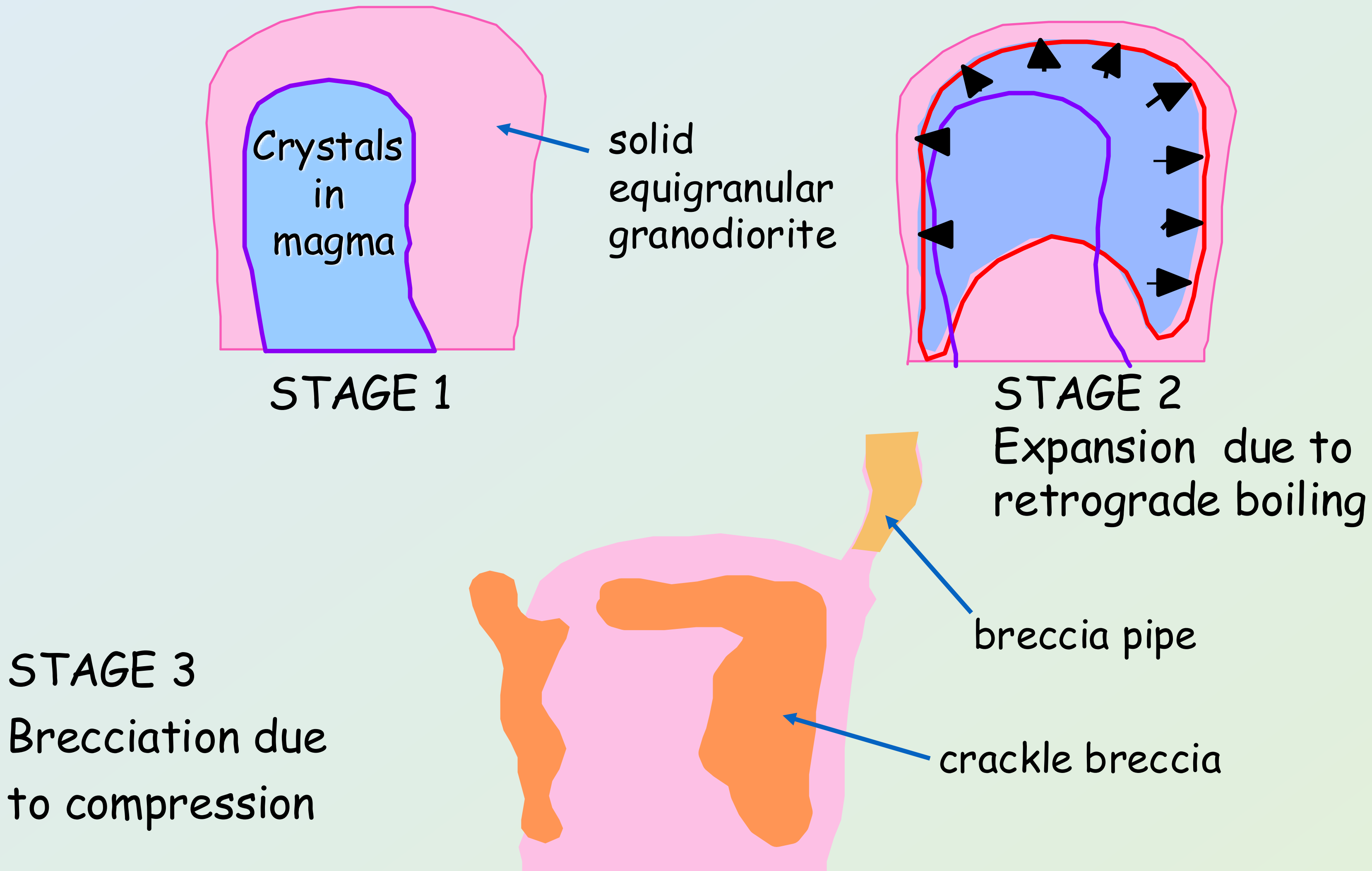
hydraulic fracturing (several events)

Origin of crackle breccia

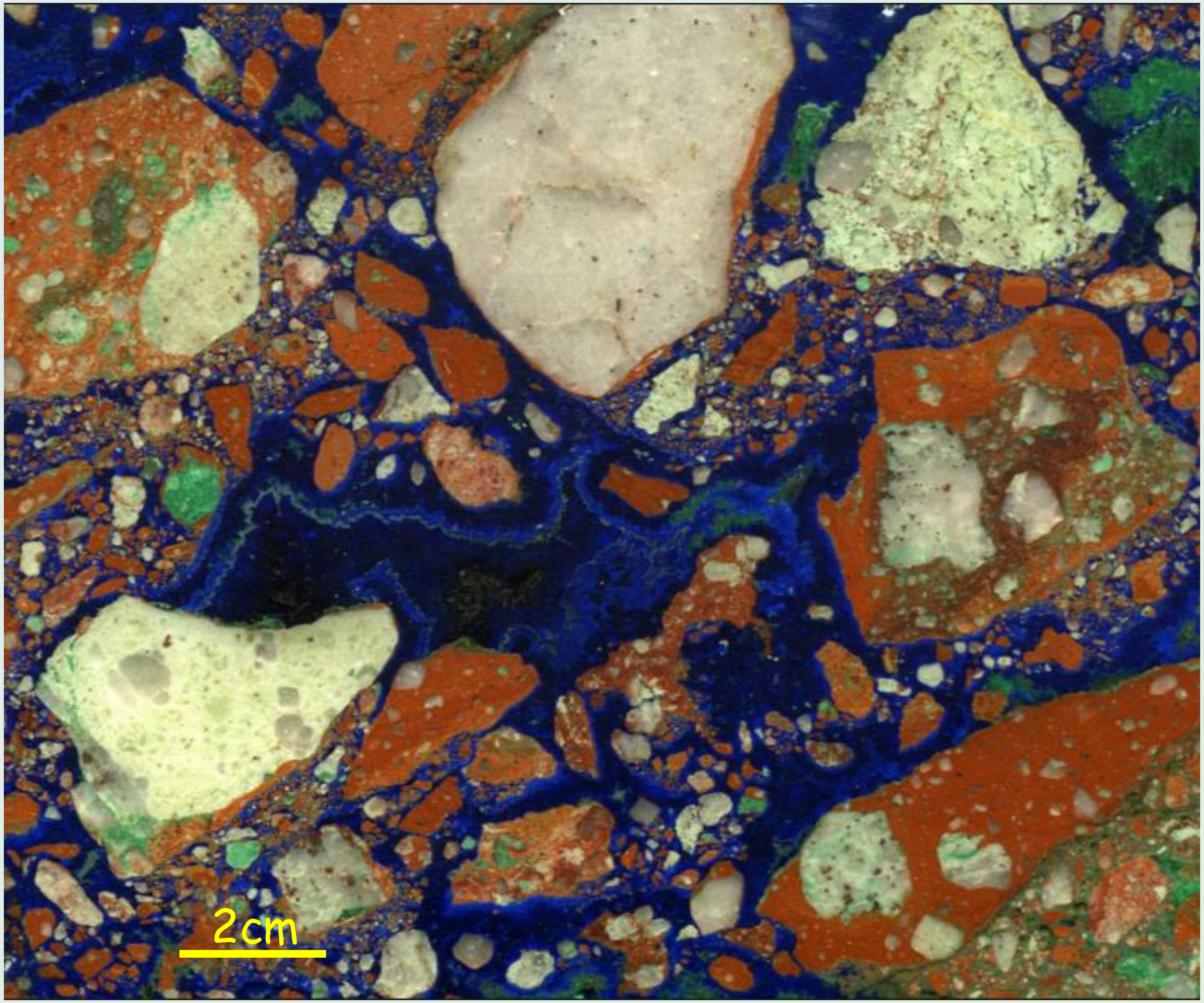
- Crackle breccia → healed fractures forming stockwork
- zone of crackle breccia → usually circular → surrounds the core, diminishes in intensity towards propylitic zone
- brecciation forms in response to release of volatiles from magma

Crackle breccia, El Salvador deposit, Chile

Stages in the development of crackle breccia
(after Phillips 1973)



Porphyry Cu breccia



Porphyry breccia clasts cemented by azurite and malachite, Morenci mine, Arizona

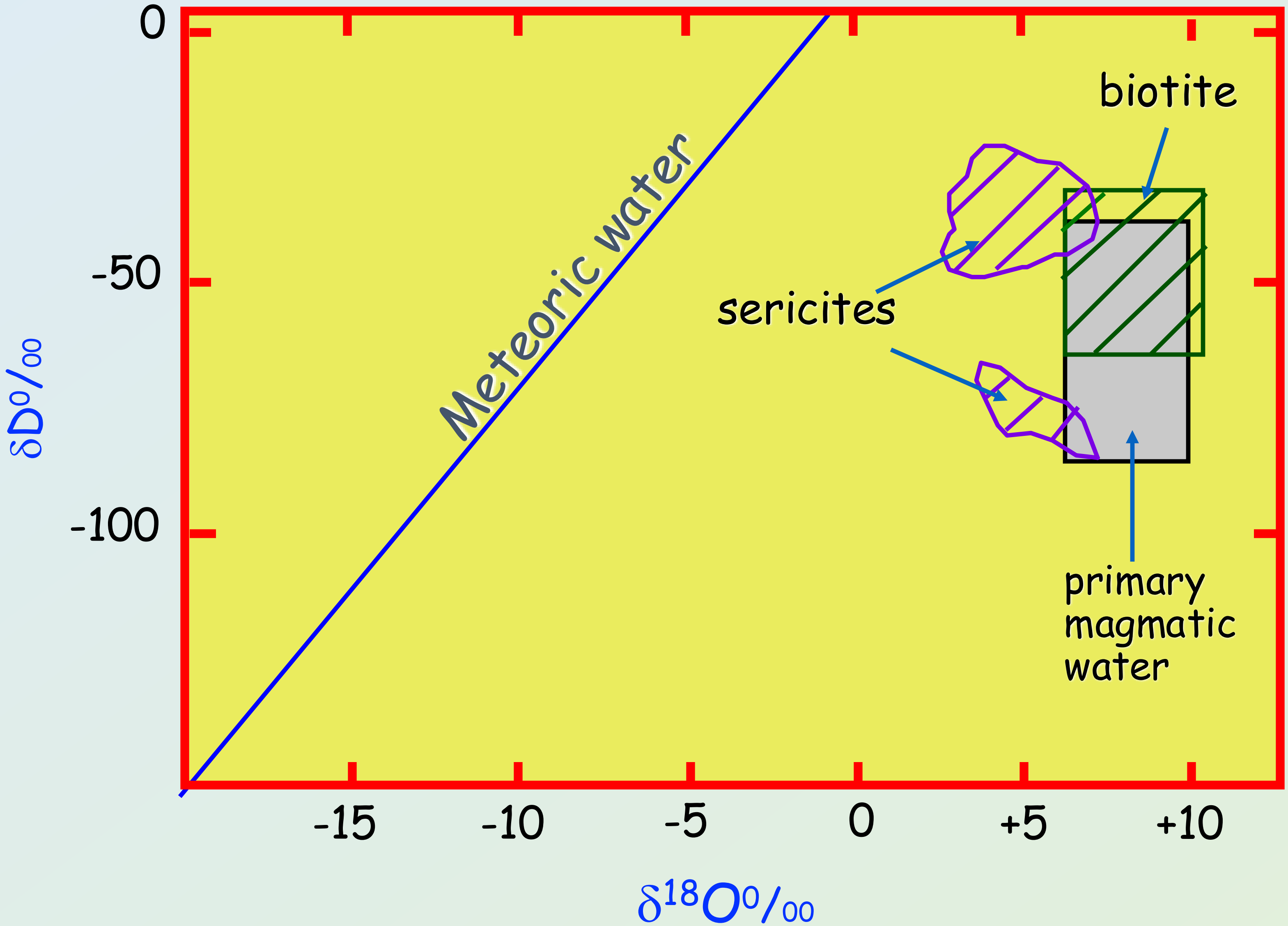
Chemical processes affecting the genesis of porphyry Cu deposits

- Retrograde boiling produces separate volatile and aqueous phases
- retrograde boiling partitions chloride ions into aqueous phase providing transporting medium for metals that also partition into aqueous phase*
- Sulphur can exist in aqueous phase as both H_2S and SO_2
- magmas with high f_{O2} tend to produce sulphur-rich porphyry Cu mineralisation. Low f_{O2} magmas produce tin oxide deposits
- adiabatic expansion → absorbs large amount of heat → increases rate of crystallisation → porphyritic textures

Interaction with meteoric water

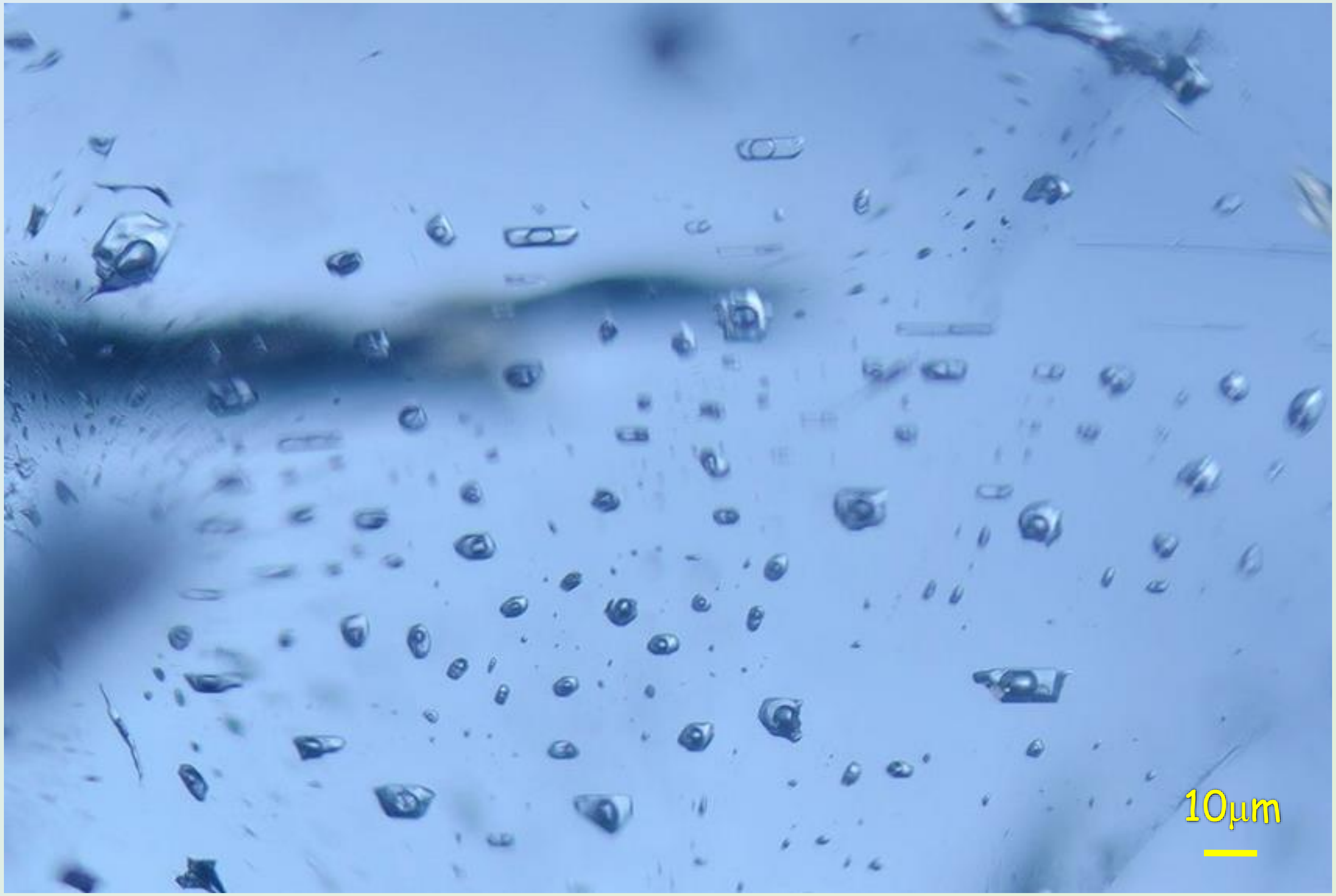
- After the intrusion of magma, crystallisation proceeds and hydrothermal fluid evolves
- magmatic derived fluid reacts with the porphyry forming a central zone potassic alteration
- further out from the intrusion, thermal gradients cause convective circulation of meteoric water → propylitic alteration
- on cooling of intrusion, meteoric waters encroach → mix with waning magmatic system → form lower temperature minerals (sericite, clay)
- Sillitoe (1973) suggests that porphyry systems remain active over 0.5 to 3 million years

Isotopic compositions of alteration minerals from Porphyry copper deposits (after Sheppard 1977)



What are fluid inclusions

Fluid inclusions are small (usually microscopic) volumes of fluid trapped within minerals during their growth and, through the annealing of fractures syn or post mineral growth.



Size and abundance of fluid inclusions

- Most fluid inclusions are less than 30μm across
- inclusions usually trapped as an homogenous liquid or vapour → multiphase at room temperature
- although numerous in many samples → seldom comprise more than a few tenths of a percentage of the total volume
- milky quartz may contain 1 billion inclusions per cm^3. Average size may be only 5μm across → volume of inclusions normally <0.2%

Fluid inclusions in quartz

Clear quartz - igneous → forms from a melt (rare inclusions)

Milky quartz – hydrothermal → forms from enclosed volatiles (abundant inclusions)

Clear quartz

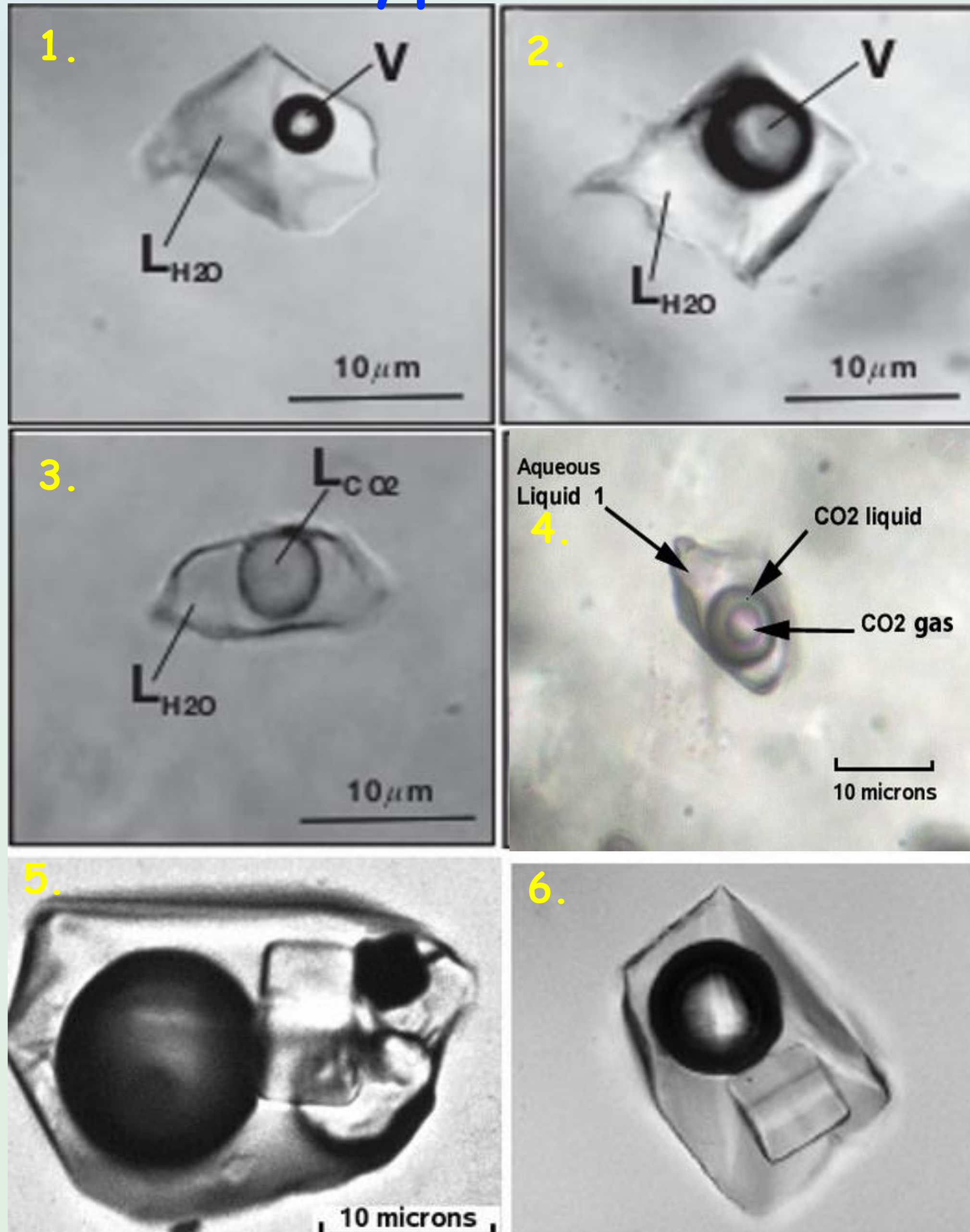
Milky quartz

Fluid inclusion types

Two phase: liquid + vapour

CO_2-rich inclusions with liquid CO_2

Highly saline inclusions NaCl > 26wt% for halite



Why are fluid inclusions useful?

- They provide a trapped sample of the original fluid in which the mineral grew
- provide evidence of the thermochemical environment in which the mineral grew
- can be used to determine the composition and density of ore fluids
- may enable determination of trapping temperature and pressure
- enable determination of hydrothermal history of deposits and minerals

Porphyry Cu fluid inclusion characteristics

Fluid inclusions from porphyry Cu deposits have distinctive characteristics:

(a) High filling temperatures (up to 725°C)

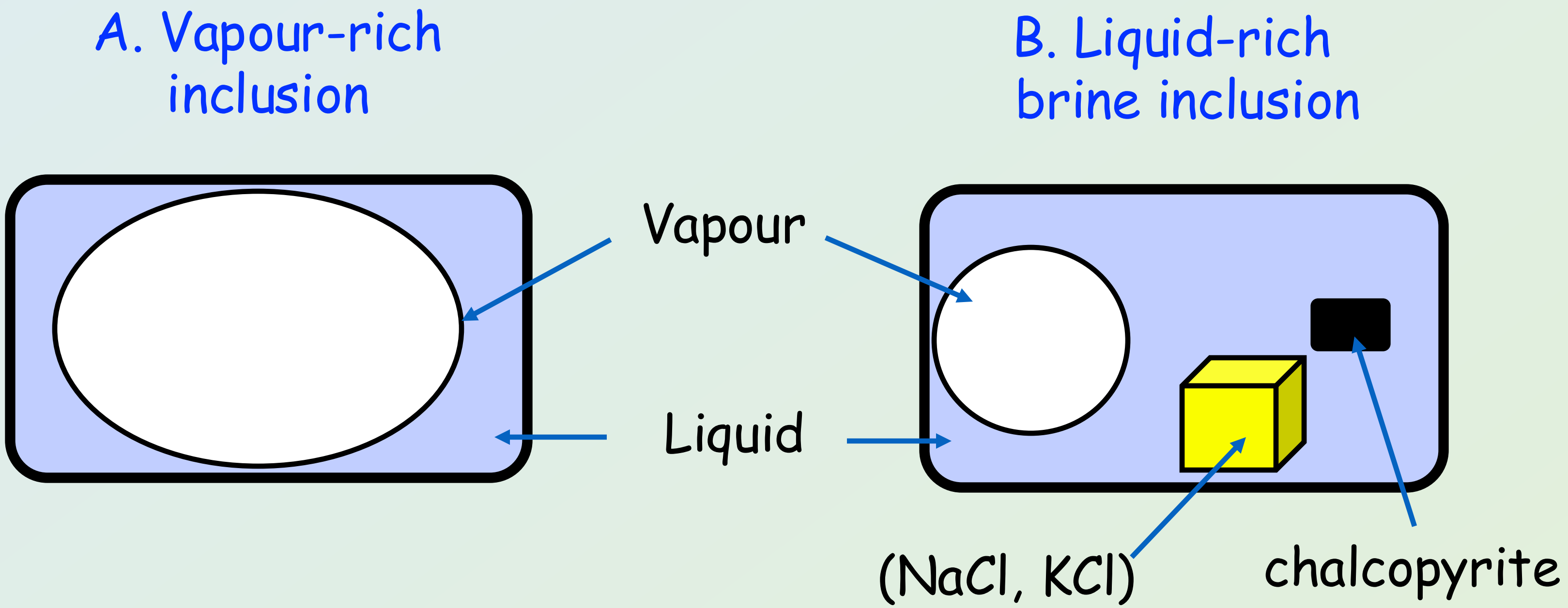
(b) high salinities (up to 60% alkali chlorides)

(c) show evidence of boiling

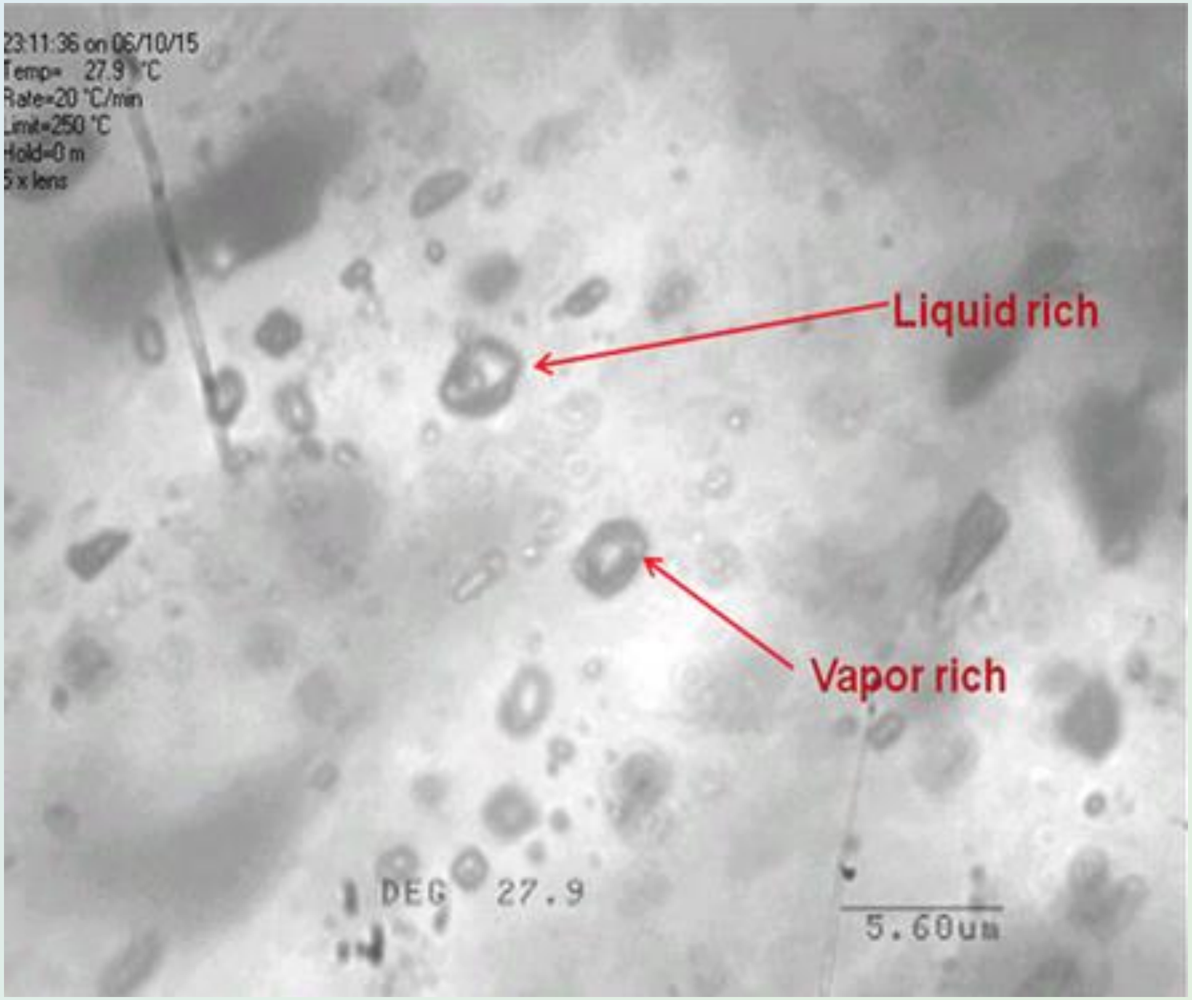
(d) exhibit temporal and compositional variations with decreasing temperatures and salinities away from central core

Fluid inclusion evidence for boiling

- Evidence for boiling is commonly seen in fluid inclusion populations that comprise vapour-rich and liquid-rich inclusions
- hydrothermal fluids derived from melt contain ~5wt.% dissolved salts
- boiling causes separation of brine and vapour → increasing the salinity of the brine



Evidence for boiling in fluid inclusions



Fluid inclusions in porphyry copper minerals

Multi phase fluid inclusions in quartz from a porphyry Cu deposit.