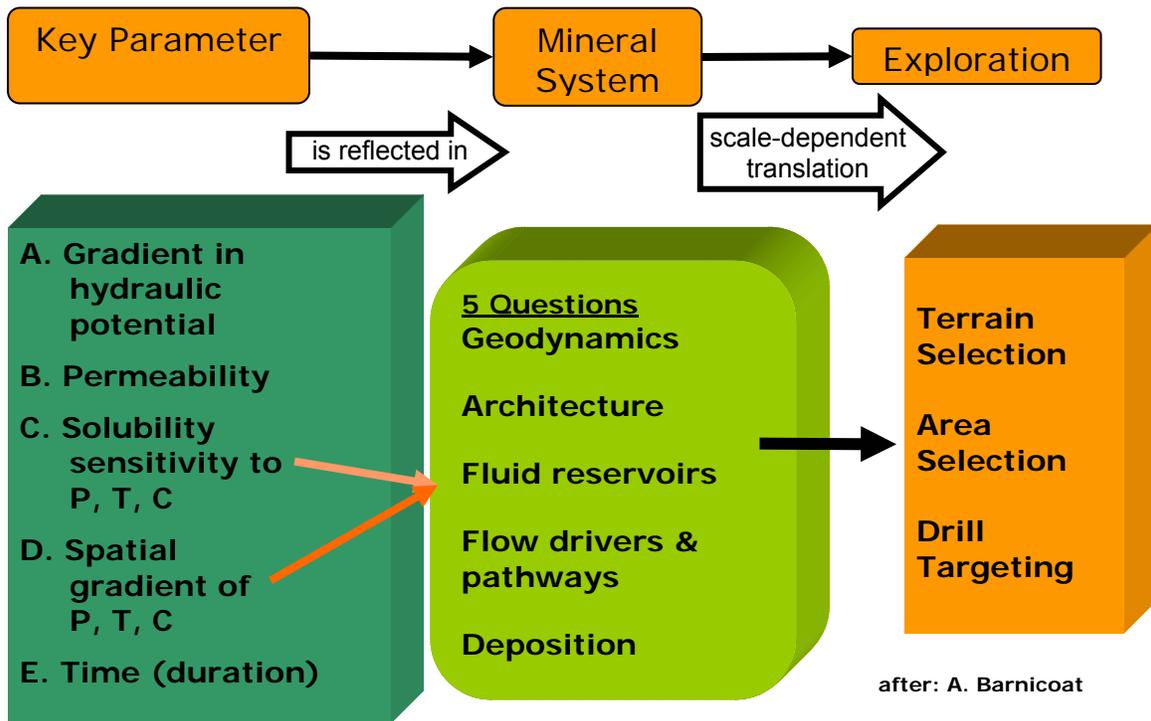


Lecture MS_4

Fluid Reservoirs



Meteoric fluids

Meteoric waters show a remarkably wide range of chemistries. While the anions in basinal fluids are dominated by chloride, the dominant anion in dilute fluids may be sulphate, bicarbonate, chloride or acetate (Hanor, 1994; Kharaka & Hanor, 2003). Sulphate is typically the most important in shallow groundwaters with bicarbonate levels increasing with depth. Acetate may dominate in groundwaters at temperatures around those of oil generation (80-120°C).

The flux of meteoric water through sediments depends on the rainfall, the percentage of infiltration into the groundwater, the ground water head, and on the permeability of aquifers, their distribution and lateral continuity. Meteoric water flow in sedimentary basins will be highest in the shallowest parts (< 1km) and

may be several orders of magnitude higher than for compaction-driven flow (Bjørlykke 1994).

The Global Meteoric Water Line states the average relationship between hydrogen ($\delta^{18}\text{O}$) and oxygen (δD) isotope ratios (Figure 1).

$$\delta \text{D} = 8 \delta^{18}\text{O} + 10 \text{‰ SMOW} \text{ (Craig, 1961)}$$

Craig's line is only global in application, and is actually an average of many local or regional meteoric water lines which differ from the global line due to varying climatic and geographic parameters (i.e. temperature, evaporation-precipitation regime). Local lines will differ from the global line in both slope and deuterium intercept. Nonetheless, Craig's global meteoric water line (GMWL) provides a reference for interpreting the provenance of groundwaters. A key observation made by Craig was that isotopically depleted waters are associated with cold regions and enriched waters are found in warm regions (Figure 1).

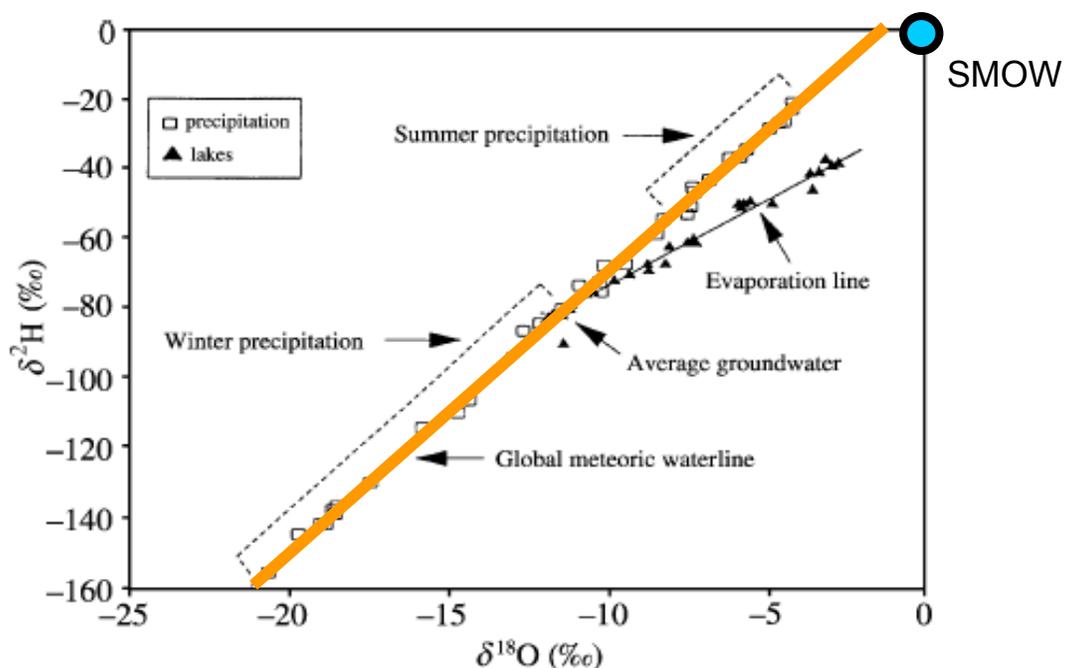


Figure 1:

Basinal fluids

Basinal fluids are frequently considered an essential part of a range of mineral systems, and are thought by many workers to be responsible for MVT-style Pb-Zn deposits, sediment-hosted copper such as the K pferschiefer and many uranium deposits. However, much is poorly understood about basinal fluids by workers on ore deposits. Much of the material presented here is based on an excellent review by Kharaka and Hanor (2003). The water occurring in sedimentary basins has a range of origins. It may be **connate** (trapped in the basin when it formed and subsequently unmodified), or it may be modified meteoric water infiltrated recently or at some time in the geological past and trapped within the sediment pile. The terms **formation water** means water present in pores and fractures immediately prior to drilling. Stable isotope data indicates that a surprisingly large number of basins contain meteoric water and not trapped seawater. Whilst many examples indicate that these groundwaters are recent, others show that old meteoric water may be present. Many basinal waters are, however of mixed origin with marine, meteoric and bittern components recorded in different cases.

Basinal fluids display an exceptionally large range in total dissolved solids from a few ppm up to over 40 wt%. While solutes are often regarded as essentially just NaCl, at higher levels of dissolved solids calcium and/or magnesium are frequently important. In general, salinities increase with depth in basins, although there is much variability in the rate both within and between basins. In some cases, however, densities decrease in the deeper parts of basins. This may be an effect of local sources of salinity. When salinities are higher than seawater, dissolution of evaporites within the sequence and inputs from subaerial evaporation of seawater are the most important sources. The chemistry of basinal fluids is rather variable, although major cations Na, K, Ca and Mg increase in general with increasing salinity (total dissolved solids). The concentration of many cations is controlled by reaction with mineral phases (see also Yardley, 2005) including carbonates, feldspar, illite and chlorite. SiO₂ is controlled by equilibration with metastable silica polymorphs such as opal at low

temperatures, and with quartz at temperatures above about 80°C. pH increases with increasing salinity, a function of fluid rock interaction as exemplified by the reaction



Chloride is the dominant anion in waters of seawater salinity and above. Sulphate concentration is normally less than 1000 mg l⁻¹ (~10⁻² m) even though sea water has nearly 3 times this level. Sulphate levels are controlled largely by equilibrium with anhydrite, and also display an inverse correlation with barium contents, driven by barite solubility. The redox state of formation waters may be rather variable, and equilibrium between species is frequently not attained, especially in cooler waters. Carbon and sulphur species are the main carriers of redox signals, and they are likely to maintain independent, disequilibrium ratios until about 150°C for sulphate-sulphide equilibrium and much higher temperatures for CO₂-CH₄ (Ohmoto & Goldhaber, 1997).

Metamorphic fluids

Metamorphic fluids have been appealed to as a source of ore system fluid by man workers, in particular those studying gold deposits called variously lode gold, mesothermal gold and orogenic gold. Fluids generated by devolatilisation reactions in a range of crustal rock types will be a mixture of H₂O and CO₂, matching the commonly observed approximately 10mol% CO₂ seen in relatively low salinity (5-10 wt% NaCl) fluid inclusions recorded from many gold deposits. While the idea has appeal, a number of issues have been raised that cast doubt on the general applicability of metamorphic fluids as a significant contributor to such gold systems. It has been recognised for some time that gold deposits in the Yilgarn post-date the main metamorphism seen at the current level of exposure, and so the concept of 'deeper later' metamorphism was introduced, backed by. This is important, as there is evidence that fluid is present in

metamorphic rocks only when it is being actively produced, and even slight reduction in temperature from peak values leads to the resorption of any residual fluid due to very minor amounts of retrogression (Yardley & Valley, 1997). Gold systems in eastern Asia, however, that fit all the criteria required for these styles of deposit, are hosted by Archaean to Palaeoproterozoic rocks but formed in the Mesozoic. Any metamorphic fluids must have dissipated long before the deposits formed, and once metamorphosed, basement rocks retain too little water to create ore systems (Goldfarb et al., 2007). The chlorine content of the fluids seen in gold systems, while relatively low, is still significant and devolatilisation of common rock-forming minerals will provide little or no Cl. Yardley & Graham (2002), in a review of the salinity of metamorphic fluids, show convincingly that the geological setting of rocks plays a critical role in controlling the salinity of fluid inclusions in higher-grade rocks. Materials deposited in oceanic or accretionary prism settings retain salinities equivalent to or less than that of seawater, while those rocks originating in continental or shallow marine environments may have salinities up to halite saturation levels. Smith & Yardley (1999) show that in accretionary sediments in New Zealand, detrital igneous apatites that contain up to 1.4 wt% Cl, and that these could add significant Cl to pore fluid during recrystallisation as long as the porosity was <5%. Cl-rich apatite could thus supply Cl into metamorphic fluids, but they are rather rare, with fluorapatite the dominant form in most granitic rocks and Cl-bearing apatites only found in some mafic-ultramafic rocks.

The rate of fluid production during a metamorphic event depends on the variation in volatile content of the relevant lithologies with pressure and temperature. Water and CO₂ are the primary volatile phases that are released during metamorphism, with the relative proportions of these components being determined by mineralogy and P-T conditions.

The amount of fluid released during metamorphism depends also on the P-T history of the rock; a rock that has been previously metamorphosed is unlikely to be fully hydrated at the start of a subsequent metamorphic event, unless sufficient fluid was available during cooling to permit complete retrogression and

the reactions were sufficiently fast to reach equilibrium before the onset of a subsequent metamorphic event. The models presented below assume that the rock is fully hydrated at the onset of metamorphism so the fluid production rates predicted by these models should be regarded as an upper limit.

These models show that the fluid flux due to regional metamorphism is relatively small (maximum $\sim 10^{-12}$ to 10^{-11} $\text{m}^3/\text{m}^2/\text{s}$, representing a fluid velocity of up to ~ 0.03 m/year) and short-lived (the flux decays by a factor of 10 within ~ 5 Myr for the 40 km crust models, or within ~ 0.5 Myr for the 15 km models with a cooling heat source). Hence the timing of metamorphism relative to mineralisation is critical in determining the role of metamorphic fluids in mineralisation. These fluids will be lost from the crust within a few Myr of the start of a thermal event, and thus will not be available to be involved in mineralisation, unless some other mechanism permits storage of fluids within the crust. The significance of the metamorphic fluid flux for gold mineralisation can be evaluated by considering the total amount of gold that could be deposited by such a fluid. The gold grade, G (g/tonne), is given by:

$$G = \frac{\Delta C \rho_f Q}{L \rho_r}$$

where ΔC (ppm) is the change in gold concentration in the metamorphic fluid (ppm) over distance L (m), ρ_f and ρ_r are the densities of the fluid and rock (kg/m^3), and Q is the time integrated fluid flux (m^3/m^2). The gradient in gold solubility, $\Delta C/L$, could be due to changes in pressure, temperature, or bulk rock composition along the fluid flow path, or due to mixing with fluid from another source (e.g. a magmatic fluid).

Groves and Phillips (1987) emphasised the importance of fluid focusing for generating gold deposits from metamorphic fluids. The analysis presented above (Table 1) shows that the fluid flux due to regional metamorphism is insufficient to generate an economic gold deposit unless it is focused through narrow permeable pathways such as faults or shear zones.

ΔC (ppm)	L (m)	$\Delta C/L$ (ppm/m)	Gold grade (g/tonne)	
			$Q = 160 \text{ m}^3/\text{m}^2$	$Q = 250 \text{ m}^3/\text{m}^2$
0.001	100	0.00001	5.33×10^{-4}	8.33×10^{-4}
0.01	100	0.0001	5.33×10^{-3}	8.33×10^{-3}
0.1	100	0.001	5.33×10^{-2}	8.33×10^{-2}

Table 1: Estimate of gold grade (g/tonne) arising from the metamorphic fluid flux

Magmatic-hydrothermal deposits

A diverse range of ore deposits are thought to have been formed from magmatic-hydrothermal fluids, including:

- Porphyry Cu, Au and Mo deposits
- High-sulphidation epithermal deposits associated with porphyrys
- Intrusion-related gold and other metal deposits, linked to reduced intrusions
- Iron oxide – copper –gold (IOCG) deposits

A range of other ores, including Carlin-type sediment hosted, disseminated gold deposits various vein type ores and even orogenic/mesothermal gold systems have also been linked to magmatic systems.

In the list above of different magmatic-hydrothermal systems, each is associated with a substantial diversity of apparently co-genetic magmatic rocks.

- Porphyrys: gold deposits associated with magnetite series low-K diorite, tonalite & quartz diorite; high-K quartz monzonite, monzonite & syenite; more alkaline and more mafic rocks implicated as well in some sites (Sillitoe, 2000; Jensen & Barton, 2000).

- High-sulphidation epithermals and more alkaline associates including phonolites/phonotephrites etc.
- Intrusion-related deposits - reduced, subalkalic, metaluminous suites comprising granodiorites and granites plus minor alkaline components (Thompson & Newberry, 2000; Lang & Baker, 2001)
- IOCG deposits – predominantly oxidized intrusions (magnetite-bearing quartz monzonite-syenogranite), although in more mafic members commonly contain both ilmenite and magnetite. These intrusions are largely subalkaline, although some of the more mafic end members (called shoshonites) are alkaline. These 'A-type' intrusions can be considered to belong to four groups:
 1. Mafic end member- diorite-monzonite (ilmenite-bearing, $>1000^{\circ}\text{C}$; <52 wt % SiO_2)
 2. Hybrid magmas (a mix between 1 and 3)- magnetite-bearing
 3. Felsic intrusions (66-74 wt. % SiO_2)- magnetite-bearing
 4. Highly fractionated felsic magnetite and hematite-bearing magmas, although hematite is rare.

Hydrothermal fluids

The diversity in igneous rocks associated with magmatic-hydrothermal deposits suggests that the nature of the igneous rocks is not particularly germane to the deposits' formation. Instead, it is likely that the volatiles released by the magmas that play the most fundamental role in controlling the nature of mineralisation, and this is supported by common themes concerning the fluids associated with these mineral systems.

- *Porphyrys*. Low-density water-rich fluids coeval with high-salinity fluids related by the 2-phase region mapped NaCl-H₂O fluids are the most important found in porphyry systems. Note that CO₂ is often not explicitly analysed for and at low levels may be difficult to spot (Hedenquist & Henley, 1985).

- *High-sulphidation epithermals.*
- *Intrusion-related deposits.* Shallow deposits contain immiscible brines and H₂O-CO₂ vapours, whilst deeper systems are characterised by low salinity CO₂-rich aqueous fluids that frequently coexist with an H₂O-rich low-NaCl phase (Lang & Baker 2001; Baker, 2002).
- *IOCG systems.* Extremely saline brines (up to 60 wt% NaCl equiv.) coexist with CO₂-rich fluids. H₂O contents in the latter are not stated but very low.

Porphyries are characterised by CO₂-poor volatiles, and their behaviour is controlled by the behaviours on the NaCl-H₂O binary (summarised in Heinrich, 2005). Phase separation may either be associated with changes in P & T of an initially single fluid phase separated from the magma or two immiscible fluids (a brine and a low-density, H₂O-rich fluid) may form directly from the magma.

Intrusion-related systems contain significant quantities of CO₂, and this leads to behaviours distinctly different to those observed in porphyries. Most notably, deeper intrusion-related systems contain (single phase?) low-salinity, CO₂-rich (?) fluids. IOCG systems record relatively water-poor conditions, with CO₂ and (Na)Cl dominating the volatile budget.

The relationships outlined above thus separate porphyries (low pressure) from intrusion-related and IOCG systems at higher pressures and/or temperatures, a relationship already well established in the literature. What they also do is highlight the difference in composition of the fluid phases in these systems, with porphyries (very) low in CO₂, reduced intrusion systems relatively poor in NaCl and IOCG's very low in H₂O but high in NaCl. There is in fact a clear link between these two observations, as elevated levels of CO₂ and chloride both lead to the early separation of a fluid phase from magmas owing to their relatively low solubilities (Lowenstern, 2000; 2001; Webster, 1999).

Sources of chlorine in magmas are not especially well defined. Kent et al. (2002) suggest four potential factors are likely to influence the Cl level of magmas:

1. Cl concentration in the mantle source
2. Addition of Cl to the mantle wedge from subducted material

3. The melting and fractionation regime
4. (Shallow) assimilation of Cl-enriched material.

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